University of Stuttgart
Germany

Analytische Qualitätssicherung Baden-Württemberg

Proficiency Test 2/14
TW S3 – alkylphenoles in drinking water

Nonylphenol, Octylphenol, Bisphenol-A

provided by
AQS Baden-Württemberg at
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University of Stuttgart
Bandtäle 2, 70569 Stuttgart-Büsnau, Germany

and
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AQS Baden-Württemberg

IWW

Stuttgart, in April 2014

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General

This PT was provided by AQS Baden-Württemberg in cooperation with IWW Water Center in Mülheim an der Ruhr and with the network “NORMAN” (Network of reference laboratories for monitoring of emerging environmental pollutants). In this round Nonylphenol, Octylphenol and Bisphenol-A were to be determined.

The PT was executed and evaluated according to the requirements of DIN 38402-A45 and ISO/TS 20612.

PT design

Each participant received the following samples:

- 3 samples for the determination of Nonylphenol, Octylphenol and Bisphenol A in 2000-ml-ground bottles.

3 different concentration levels/batches were produced. All participants received the same samples.

Sample preparation

The samples for the determination of the alkylphenoles were based on a real ground water matrix from the northern part of the region Ruhr in North Rhine-Westphalia. The ground water was used without treatment for the sample preparation.

The ground water was spiked with stock solutions and the concentrations covered drinking and ground water relevant ranges.

Sample distribution

The samples were dispatched on 25th February 2014 by express service.

Analytical methods

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

parameter	limit of quantification [µg/l]
Nonylphenol	0,08
Octylphenol	0,02
Bisphenol A	0,02

The participant received more information about the parameters or parameter group with the announcement and sample accompanying letter:

notation long (notation short)	parameter or parameter group	CAS-number of the parameter or parameter group
Nonylphenol (NP)	4-Nonylphenol (branched) / isomeres mixture	84852-15-3
Octylphenol (OP)	4-(1,1′,3,3′-tetramethylbutyl)-phenol	140-66-9
Bisphenol-A (BPA)	Bisphenol-A	80-05-7

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

Submission of results

The deadline for the submission of results was on 17th March 2014.

Evaluation procedure

The statistical evaluation was executed according to DIN 38402-A45 and ISO TS 20612 “Interlaboratory comparisons for proficiency testing of analytical chemistry laboratories”. From the participants’ results a relative standard deviation was calculated for each concentration level and parameter using the Q-method. The reference values (see chapter “Traceable reference values”) were used as assigned values x_a. The standard deviation resulting from the Q-method was used as $\hat{\sigma}$.

$\hat{\sigma}$ was limited as follows:

- lower limit: 5%
- upper limit: 25%

A z-score was calculated for each measurement result derived from the assigned value x_a and the standard deviation for proficiency assessment $\hat{\sigma}$:

$$z-score = \frac{result - x_a}{\hat{\sigma}}$$

The z-score was modified to a z_U-score with a correction factor for proficiency assessment (as described in the standards mentioned above).
The tolerance limit was defined as $|z_U| = 2{,}0$.

Assessment

There was no overall assessment of the proficiency test round, but the single parameters were assessed.
A parameter was assessed as successful, if more than half of the values were correctly determined (2 out of 3 values are within the tolerance limits).

Evaluation

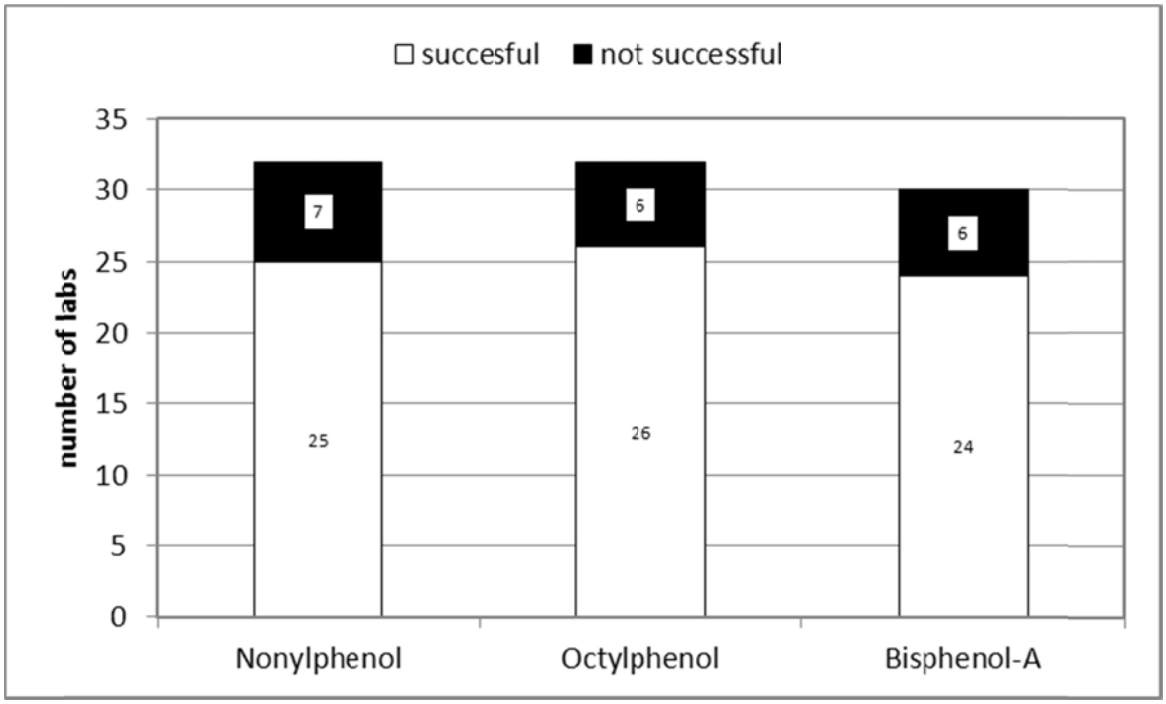
Number of participants: 38

4 laboratories did not report any result.

Number of reported values: 281

Number of accepted values: 221 (78,65%)

In the following figure the successful and not successful laboratories for each parameter are illustrated.



Explanation of Appendix A

Appendix A contains for each parameter

- parameter tables
- a figure of participants' means versus the spiked amounts for the determination of the recovery rate
- a figure of the relative standard deviations versus the concentrations
- a figure of the tolerance limits in the PT versus the concentrations
- the frequency of application of analytical methods
- the method specific evaluation
- a comparison of mean and reference values for each concentration level
- a comparison of the relative standard deviations of the different methods
- the statistical characteristics of the method specific evaluation
- a tabular comparison of the means with the reference values and their uncertainties

Parameter tables

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

- assigned value
- expanded uncertainty of the assigned value according the measurement uncertainty budget of the reference value determination
- standard deviation, calculated using robust statistical method
- standard deviation for proficiency assessment for the calculation of z_U-scores
- rel. standard deviation for proficiency assessment
- tolerance limits above and below
- permitted deviations above and below in %
- number of values in this level
- number of not satisfactory values below and above the assigned value and the percentage of these values in total.

Determination of recovery rate

In the diagrams of the assigned values versus the spiked amount of analyte a linear regression line was calculated using a generalized least square regression which takes into account the uncertainties of the values in both directions. From these values the recovery rate for each parameter was determined (see diagrams). The slope of the line indicates the average recovery rate. The diagrams also contain the expanded uncertainty (k=2) of the concentrations from the spike and the assigned values.

Relative standard deviations and tolerance limits

The diagrams for the relative standard deviation vs. the assigned value show the concentration dependency of the standard deviation and the tolerance limits in percent. The relative standard deviations calculated from participants' data are the stars connected by an interrupted line, the rel. standard deviation (and sometimes limited by the upper or lower limit) are given by squares, connected by a continuous line.

Method specific evaluation

For each parameter the methods used by the participants are shown in a diagram. In a second diagram for each method with a frequency of more than 5 %, values are sorted in 5 categories:

too low	results with z_U-score < -2
low	results with –2 ≤ z_U-score < –1
correct	results with –1 ≤ z_U-score ≤ +1
high	results with +1 < z_U-score ≤ +2
too high	results with z_U-score > +2

Comparison of means and reference values for each concentration level

Finally the mean value calculated from all results, the reference value (see chapter Traceable reference values) are compared with mean values calculated for all methods separately. All mean values were calculated using the Hampel estimator described in ISO/TS 20612. Mean values were calculated only, if more than 8 results were within a z-score-range of ± 2. The means are reported with their expanded uncertainty, calculated according to ISO 13528.
All mean values and their expanded uncertainties are additionally compared with the reference values and their expanded uncertainties.

Explanation of Appendix B

Participants were asked to report expanded uncertainties of their results on a voluntary basis. In this diagram for each parameter the reported uncertainties for all concentration levels with the reproducibility standard deviation (horizontal line) are displayed. Values which deviate from the reproducibility standard deviation with a factor more than 2 are usually not realistic.

Explanation of Appendix C

In the last part of the report, for all concentration levels the results of all participants are illustrated. Confidentiality of participants is ensured by using lab codes. The lab codes were sent to participants with the certificates.
In detail Appendix C contains:

- a table with all data
- figures with
  - all reported results
  - all z_U-scores
  - all reported expanded uncertainties
  - all ζ–scores

Table with all data

The assigned value with the expanded uncertainty and the tolerance limits for the concentration level is illustrated in the table. For each participant the following data are given:

- lab code
- reported result
- measurement uncertainty of the value (if reported)
- ζ-score for this value, calculated with the following formula

$$\zeta = \frac{x - x_a}{\sqrt{u_{lab}^2 + u_{ref}^2}}$$, with

$x - x_a$ = difference from the measured value and the assigned value

- u_{lab} = standard uncertainty of the value, reported by the participant
- u_{ref} = standard uncertainty of the assigned value
- z_U-score for proficiency assessment

- assessment of the value according to its z-score

Meaning of ζ-scores:
The assessment of ζ-scores is similar to that of z_U-scores. If the data are normally distributed and the uncertainties are well estimated, ζ-scores will lie between -2 and +2 with a probability of around 95 %.
ζ-scores are mainly influenced by the measurement uncertainties reported by the laboratory. Therefore ζ-scores are usually not appropriate for the assessment of the reported results, unless the reported measurement uncertainty is checked for fitness-for-purpose.
Therefore we do not use the ζ-scores for the assessment of the laboratories.
Nevertheless ζ-scores are appropriate to check the plausibility of the reported measurement uncertainty:
If the z_U-score of a result is within the tolerance limit and the ζ-score is outside, then the measurement uncertainty is underestimated.
If the z_U-score is outside the tolerance limits and the absolute value of the ζ-score is lower than two, then the requirements of the proficiency test were stronger compared with the reported measurement uncertainty.

Diagrams of uncertainty data
In the first figure for all lab codes the measurement uncertainty (together with the reproducibility standard deviation) is illustrated. The second figure shows the associated ζ-scores.

Measurement uncertainty

12 (35,3%) out of 34 laboratories with valid values reported measurement uncertainties. In total 90 (32%) out of 281 valid values were given with the measurement uncertainty. The following table displays the number of values with measurement uncertainty against the accreditation status.

Accreditation status of the values	Number of values	Number of values with measurement uncertainty
accredited	114	42 (36,8%)
not accredited	123	39 (31,7%)
not specified	44	33 (20,5%)

We would like to put emphasis on the fact that reporting of measurement uncertainties in our PT scheme is absolutely voluntary. The only objective is to help all participants to reasonably handle measurement uncertainties and their estimation.
The diagrams show that the spread of reported uncertainties in some cases is vast, from unrealistic low values up to very high. A plausibility check using reproducibility standard deviations of the PT round could be helpful here.
If measurement uncertainties are underestimated values assessed as “satisfactory” in the PT ($|z_U| \leq 2$), will have a large ζ-score. $|\zeta| > 2$ means that the “own” requirements (defined in terms of estimated uncertainty) are not fulfilled.
27 (41,5%) of the 65 values reported with uncertainties and having a z_U-score $|z_U| \leq 2.0$ had a ζ-score > 2.0. This means that the requirements of the PT scheme have been fulfilled , but not the “own” requirements, the uncertainty is underestimated.

Traceable reference values

Traceability of analytical results to national and international references is of increasing importance in all laboratories. This is not easy to realise for chemical analyses and often can only be done by analysing certified reference materials. But availability of these reference materials in the water sector is very limited. Therefore we try to provide reference values for the proficiency test samples, traceable to national and international references.
Since our PT samples without exception are spiked, real water samples, reference values can be calculated from the sum of matrix content and spiked amount of analyte. For both summands traceable values and their uncertainty have to be determined. Thereby we assume that no unrecognised bias resulting from sample preparation and transport is present and that we recognise all uncertainty components.

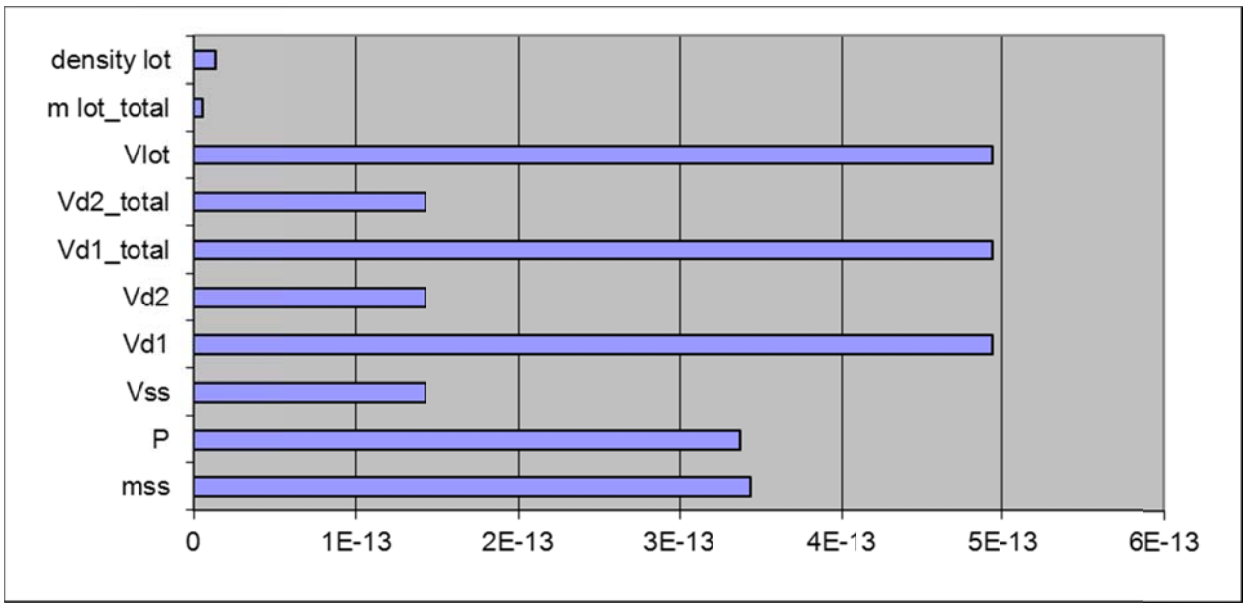
All spiking of samples was controlled gravimetrically and volumetrically. This procedure allows the preparation of a complete uncertainty budget.
The first step is the specification of the measurand with a formula. This shows the links between the result and all influence quantities for the parameter.

$$c_{lot} = \frac{m_{ss} \cdot P \cdot V_{d1} \cdot V_{d2} \cdot V_{lot} \cdot \rho_{lot}}{V_{ss} \cdot V_{d1\_total} \cdot V_{d2\_total} \cdot m_{lot\_total}}$$

with:

c_{lot}	concentration of the analyte in the lot resulting from the spike
m_{ss}	mass of substance added for preparation of the stock solution
V_{d1}	volume of stock solution added into the dilution A
V_{d2}	volume of dilution A added into the dilution B
V_{lot}	volume of dilution B added into the lot
V_{ss}	volume of stock solution
V_{d1_total}	total volume of dilution A
V_{d2_total}	total volume of dilution B
m_{lot_total}	total mass of the lot
ρ_{lot}	density of the lot in g/l
P	purity of the used substance

Based on this formula the uncertainty budget can be prepared and all components can be quantified. The following figure shows a typical distribution of the contributions for Octylphenol. The main contributions result from the purity of the chemical and the pipette steps.



Attention was paid to use a ground water which did not contain any analyte. Therefore no matrix content had to be considered and the reference values could be calculated directly from the spikes.

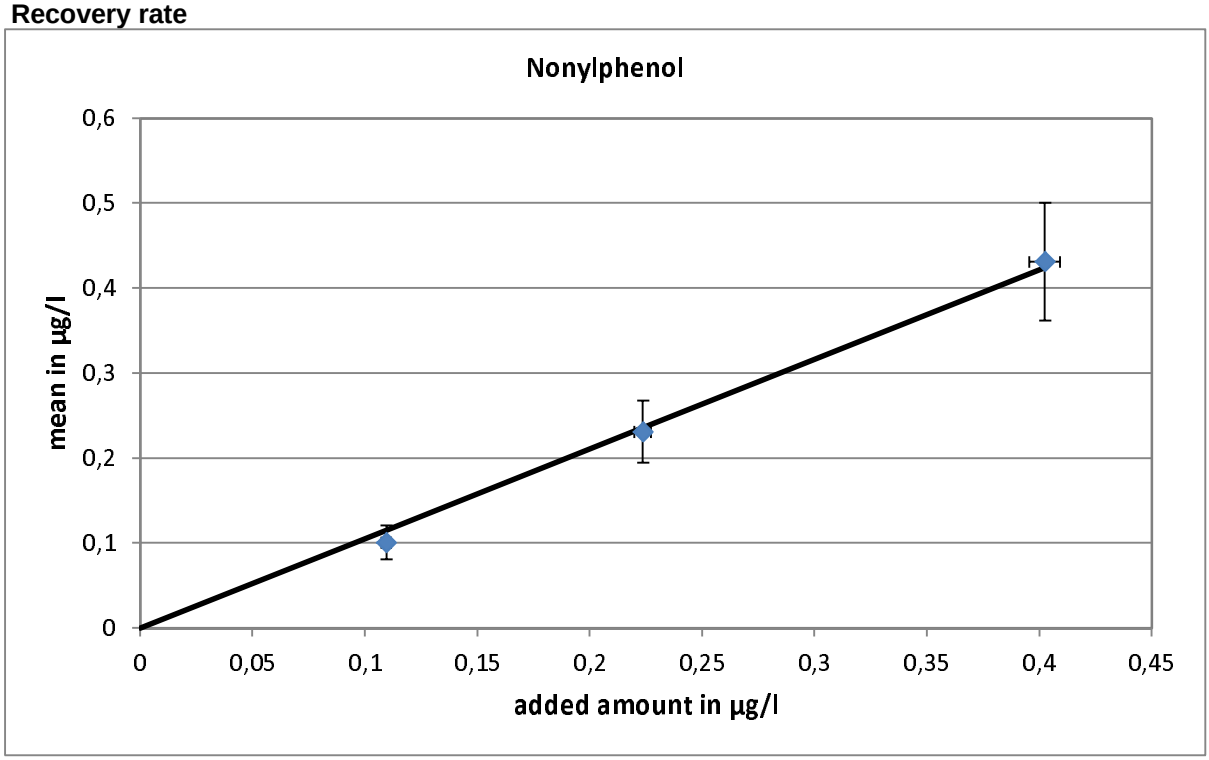
Internet

The report is available on the following webpage: http://www.aqsbw/pdf/report214.pdf

Nonylphenol

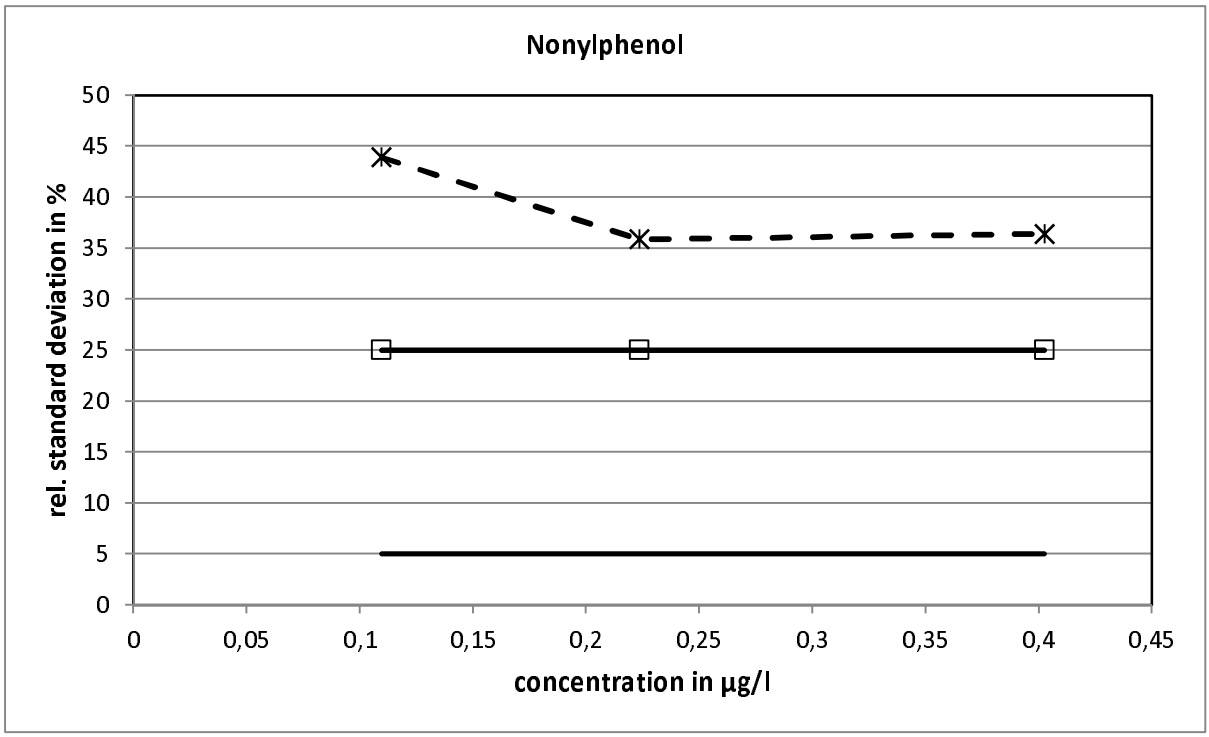
level	assigned value [µg/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [µg/l]	standard deviation for proficiency assessment [µg/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [µg/l]	lower tolerance limit [µg/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,1096	18,98	0,0441	0,0274	25,00	0,1731	0,0601	57,99	-45,19	31	2	7	29,0
2	0,2236	9,41	0,0828	0,0559	25,00	0,3532	0,1226	57,99	-45,19	32	2	7	28,1
3	0,4025	5,41	0,1569	0,1006	25,00	0,6358	0,2206	57,99	-45,19	32	2	6	25,0
									sum	95	6	20	27,4

Recovery rate

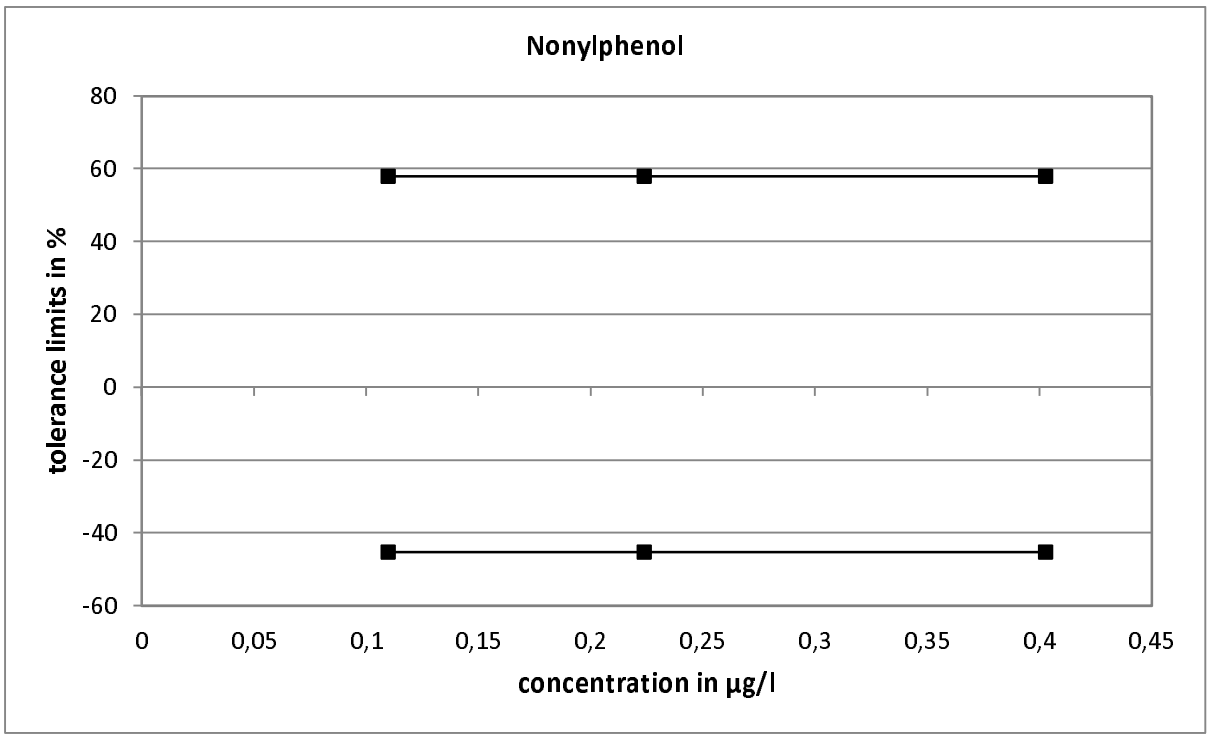


Slope of the regression: 1,054, average recovery rate: 105,4%

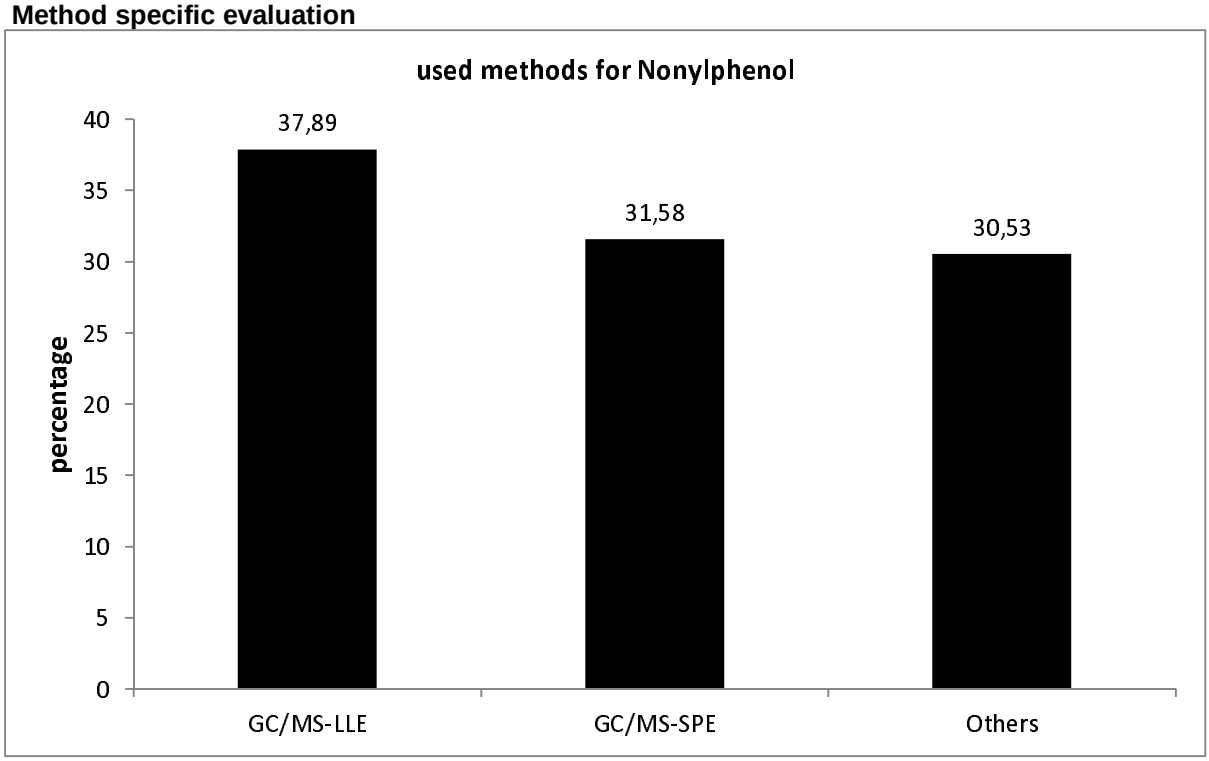
Relative standard deviation and tolerance limits

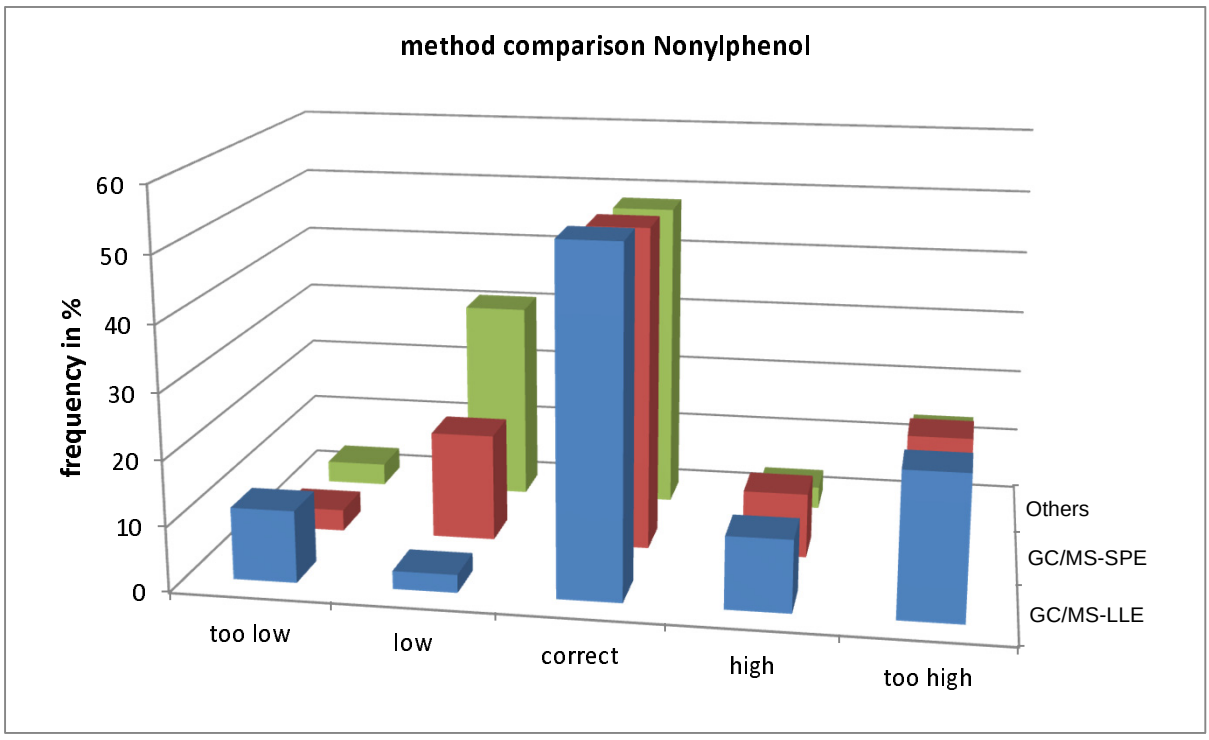


The relative standard deviation, derived from the Q-method, reached with all concentration levels the upper limit.



Method specific evaluation

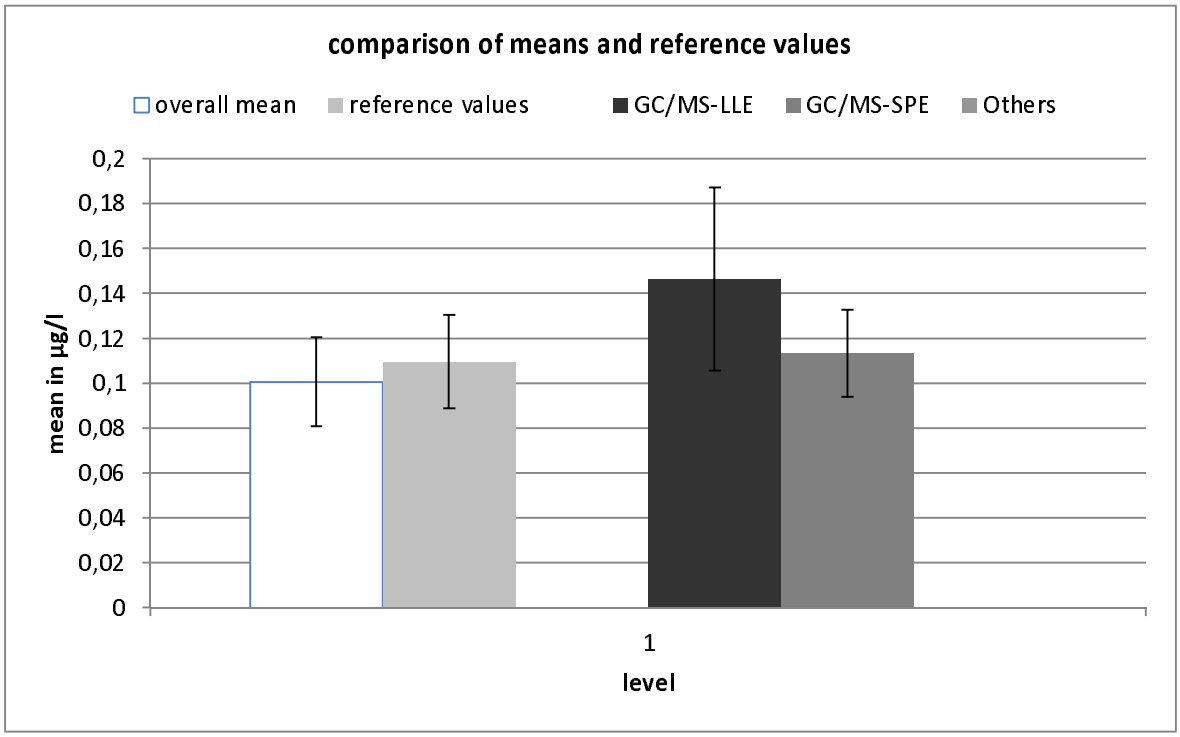


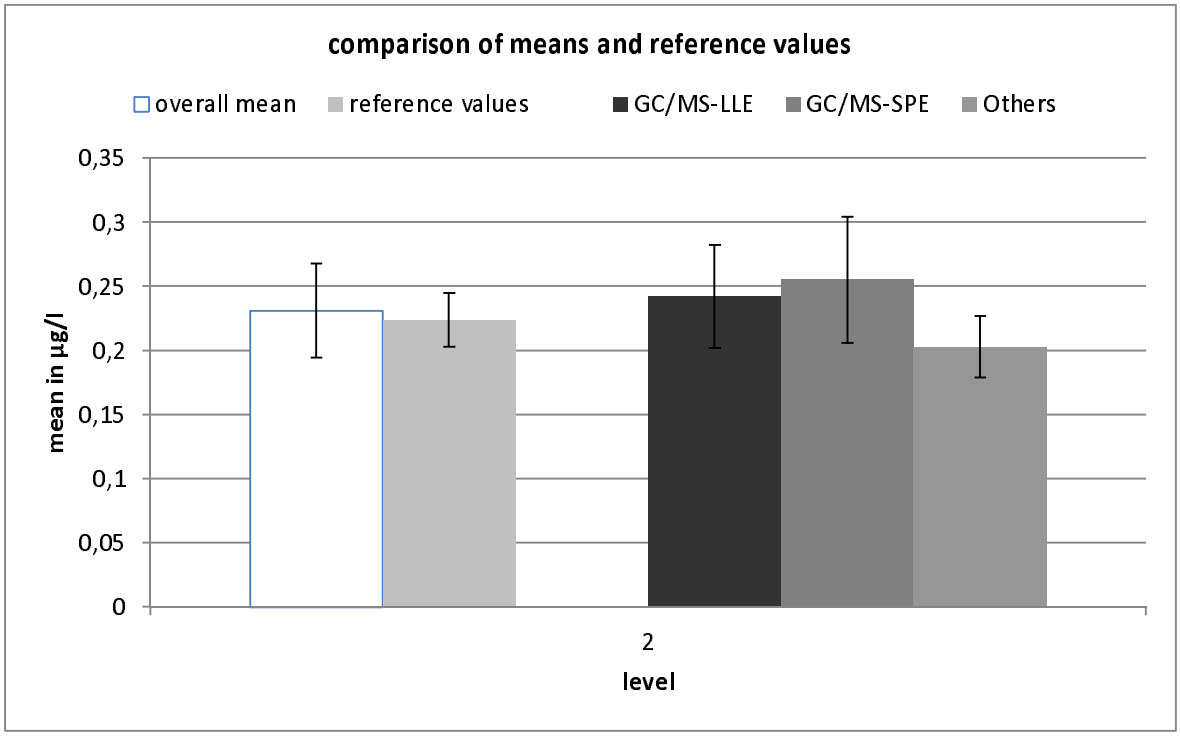


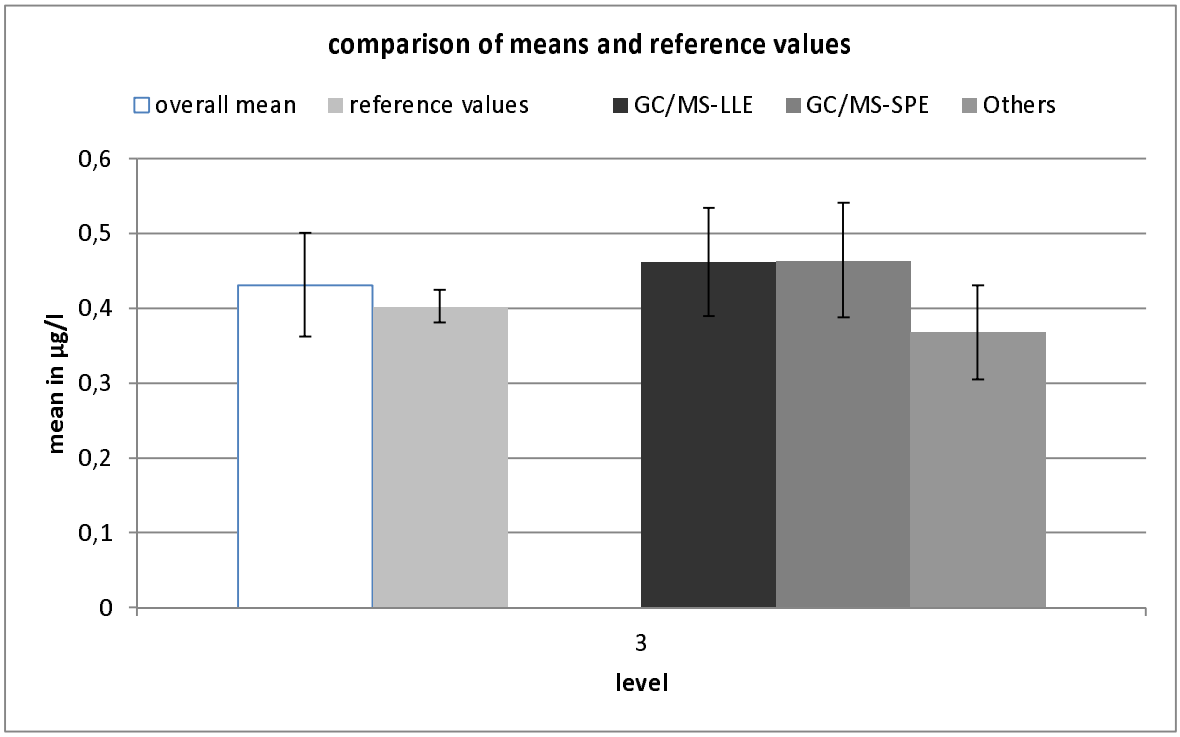
There were no significant differences between the methods.

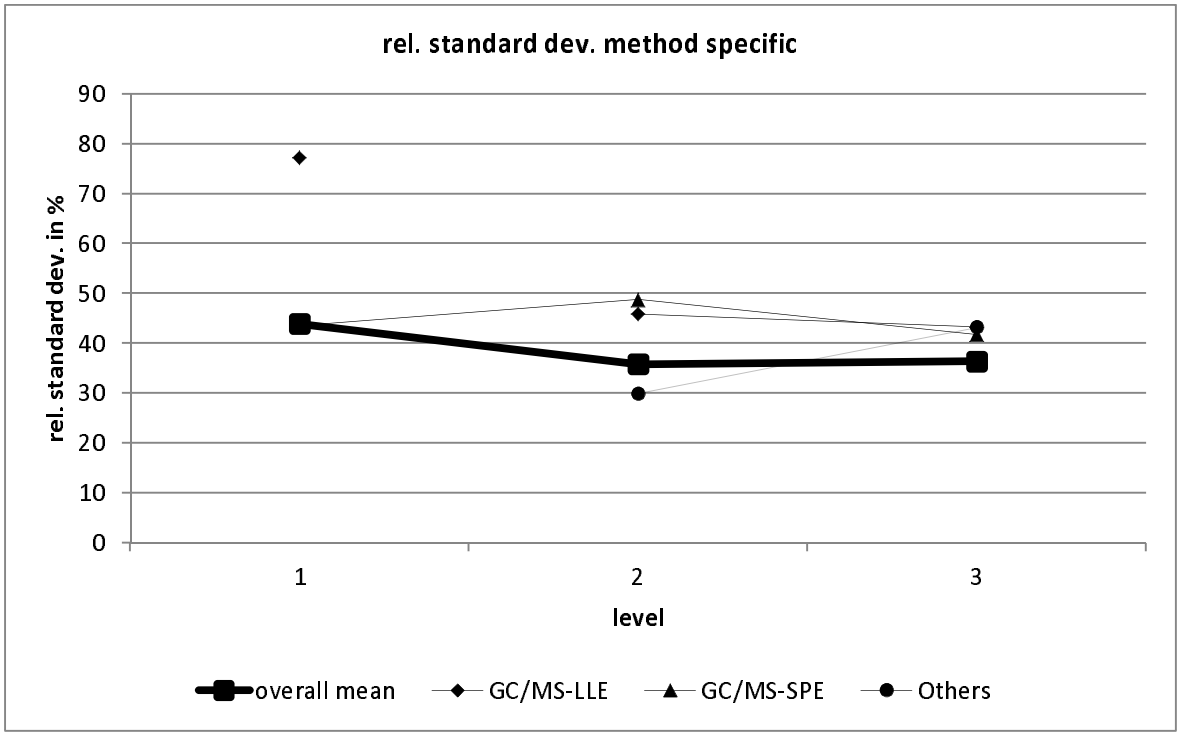
Comparison of means and reference values

level	mean [µg/l]	exp. uncertainty [µg/l]	exp. uncertainty [%]	reference value [µg/l]	exp. uncertainty [µg/l]	exp. uncertainty [%]
1	0,1005	0,0198	19,7	0,1096	0,0208	19,0
2	0,2310	0,0366	15,8	0,2236	0,0210	9,4
3	0,4311	0,0694	16,1	0,4025	0,0218	5,4




comparison of means and reference values
overall mean
reference values
GC/MS-LLE
GC/MS-SPE
Others
mean in µg/l
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
2
level


comparison of means and reference values
overall mean
reference values
GC/MS-LLE
GC/MS-SPE
Others
mean in µg/l
0,6
0,5
0,4
0,3
0,2
0,1
0
3
level



GC/MS-LLE									
level	robust mean [µg/l]	exp. unc. of the mean [µg/l]	exp. unc. of the mean [%]	robust standard deviation [µg/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	0,146	0,041	27,84	0,113	77,15	12	1	1	16,67
2	0,242	0,04	16,55	0,111	45,86	12	1	1	16,67
3	0,462	0,072	15,6	0,2	43,23	12	1	0	8,333

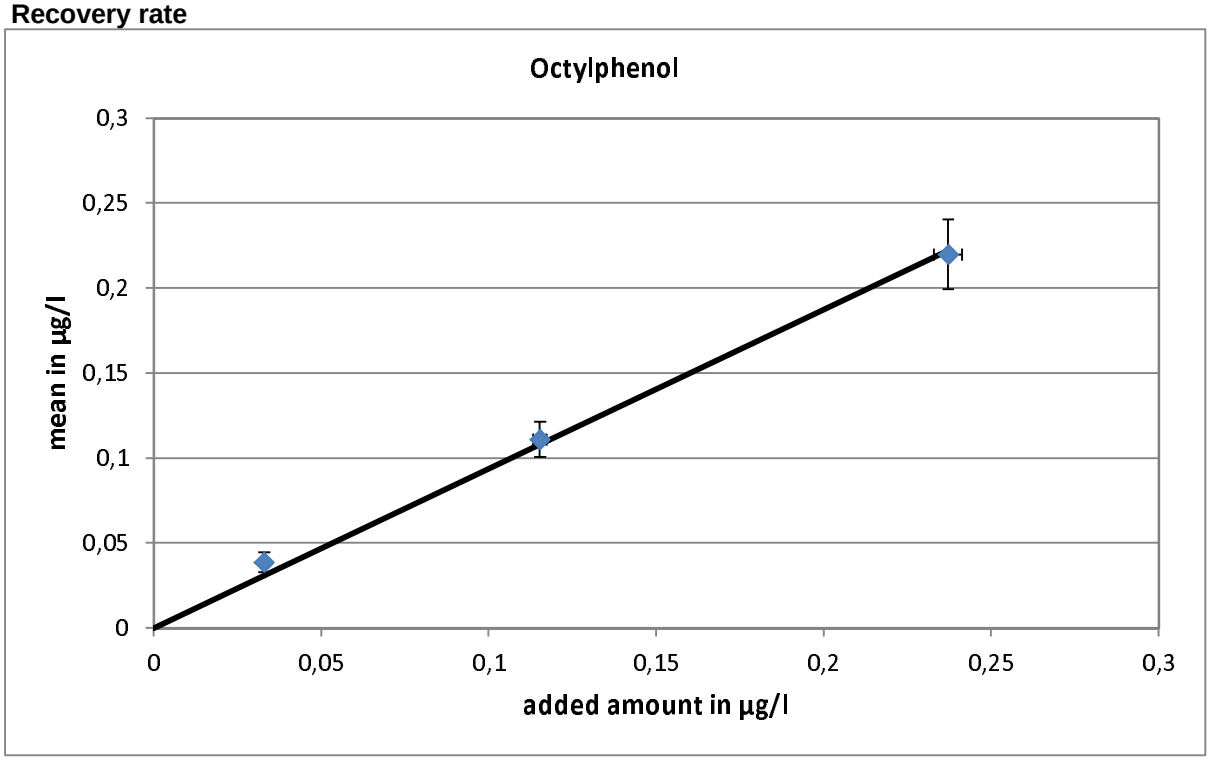
GC/MS-SPE									
level	robust mean [µg/l]	exp. unc. of the mean [µg/l]	exp. unc. of the mean [%]	robust standard deviation [µg/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	0,113	0,019	17,17	0,049	43,44	10	0	2	20
2	0,255	0,049	19,27	0,124	48,74	10	0	0	0
3	0,464	0,077	16,49	0,194	41,71	10	0	0	0

Others									
level	robust mean [µg/l]	exp. unc. of the mean [µg/l]	exp. unc. of the mean [%]	robust standard deviation [µg/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
2	0,203	0,024	11,83	0,061	29,94	10	0	2	20
3	0,368	0,063	17,11	0,159	43,28	10	0	0	0

Octylphenol

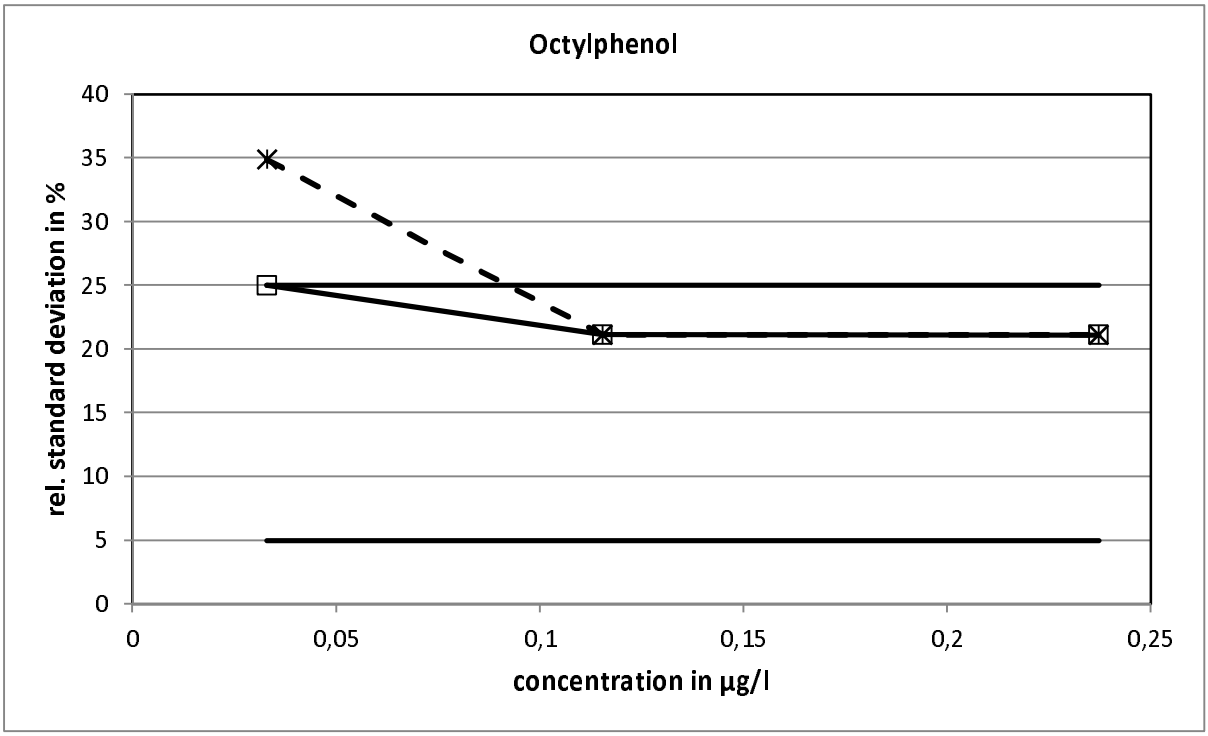
level	assigned value [µg/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [µg/l]	standard deviation for proficiency assessment [µg/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [µg/l]	lower tolerance limit [µg/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,0329	22,00	0,0135	0,0082	25,00	0,0520	0,0181	57,99	-45,19	32	1	9	31,3
2	0,1153	7,77	0,0235	0,0244	21,13	0,1703	0,0707	47,76	-38,69	32	2	3	15,6
3	0,2372	4,21	0,0464	0,0500	21,10	0,3502	0,1455	47,68	-38,64	32	4	1	15,6
									sum	96	7	13	20,8

Recovery rate

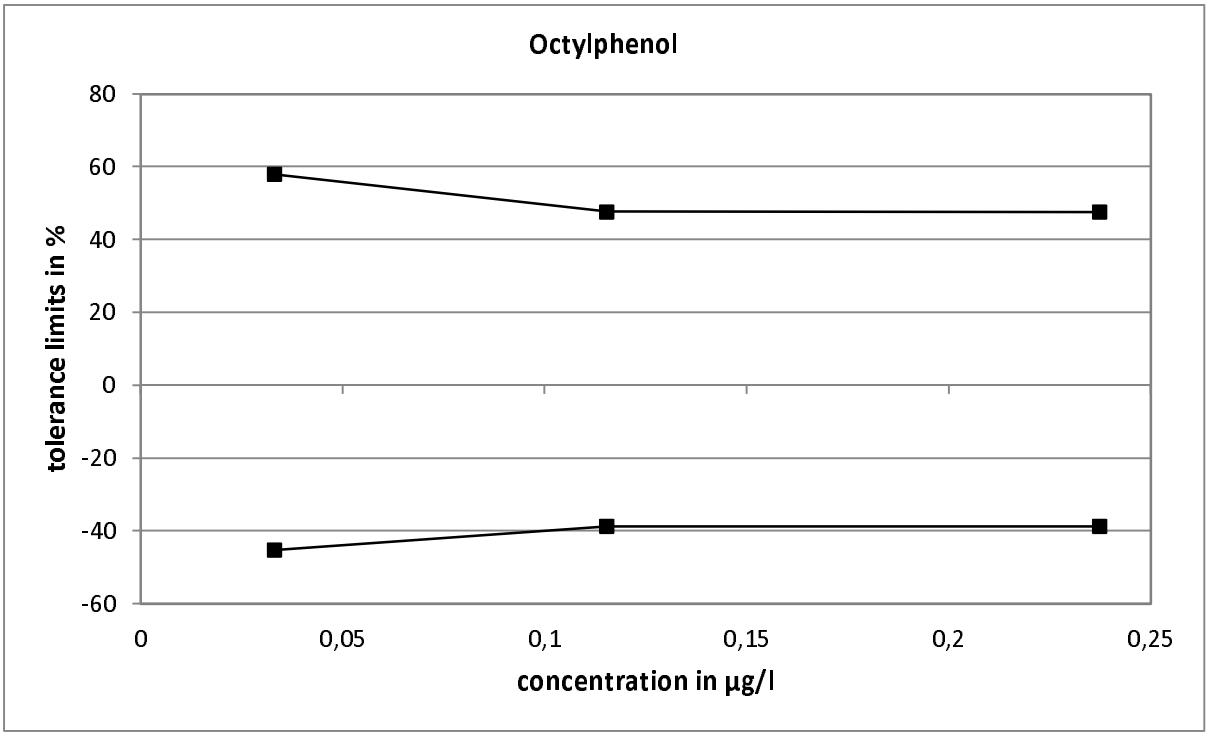


Slope of the regression: 0,937, average recovery rate: 93,7%

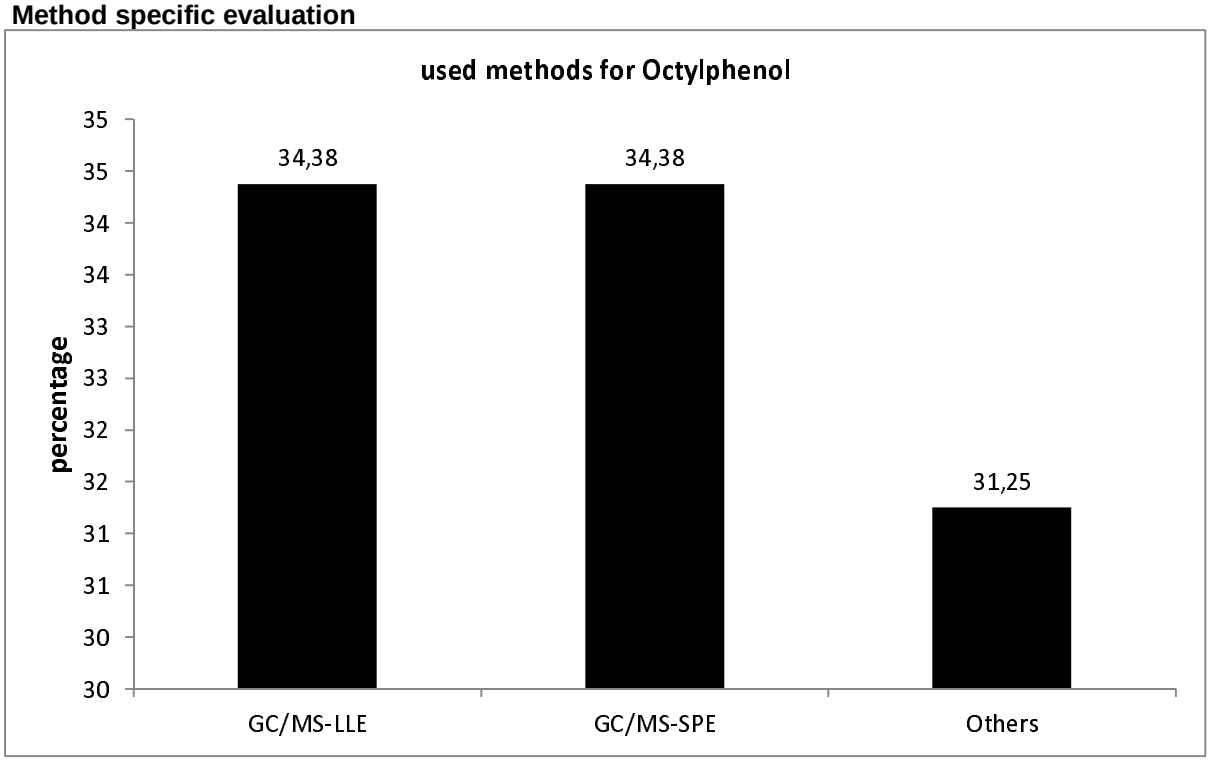
Relative standard deviation and tolerance limits

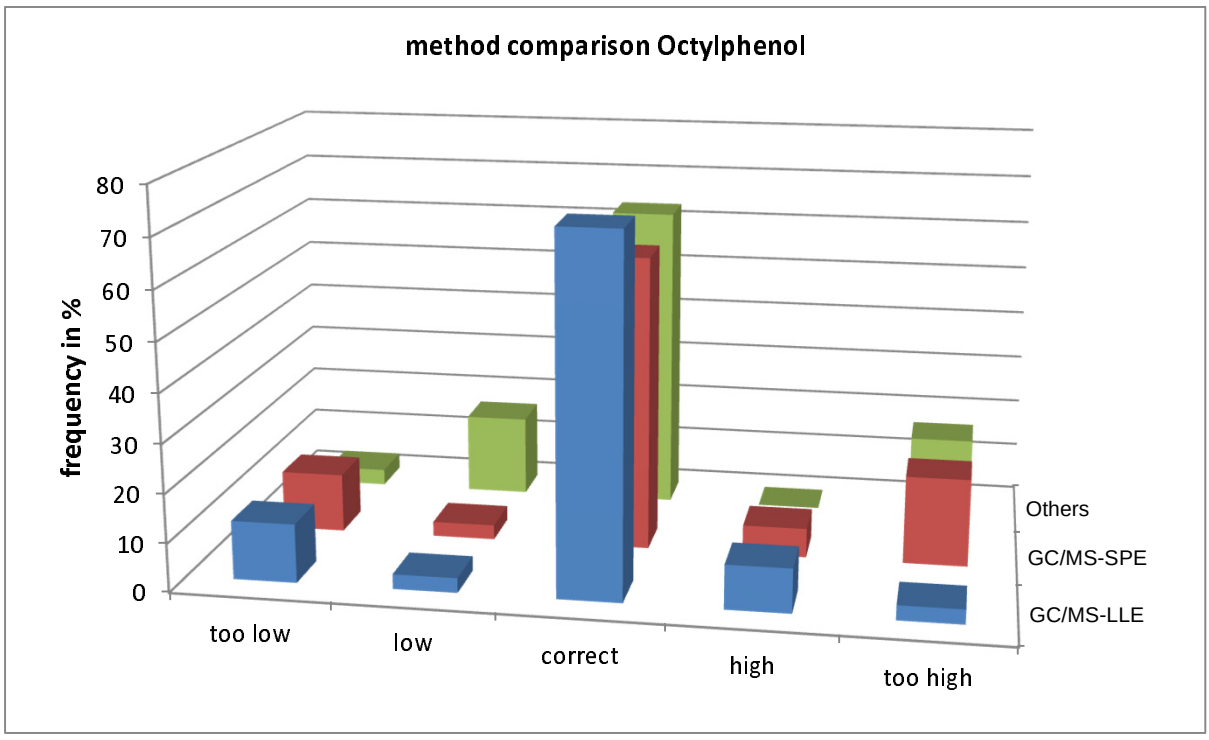


The relative standard deviation, derived from the Q-method, reached with one concentration level the upper limit.



Method specific evaluation

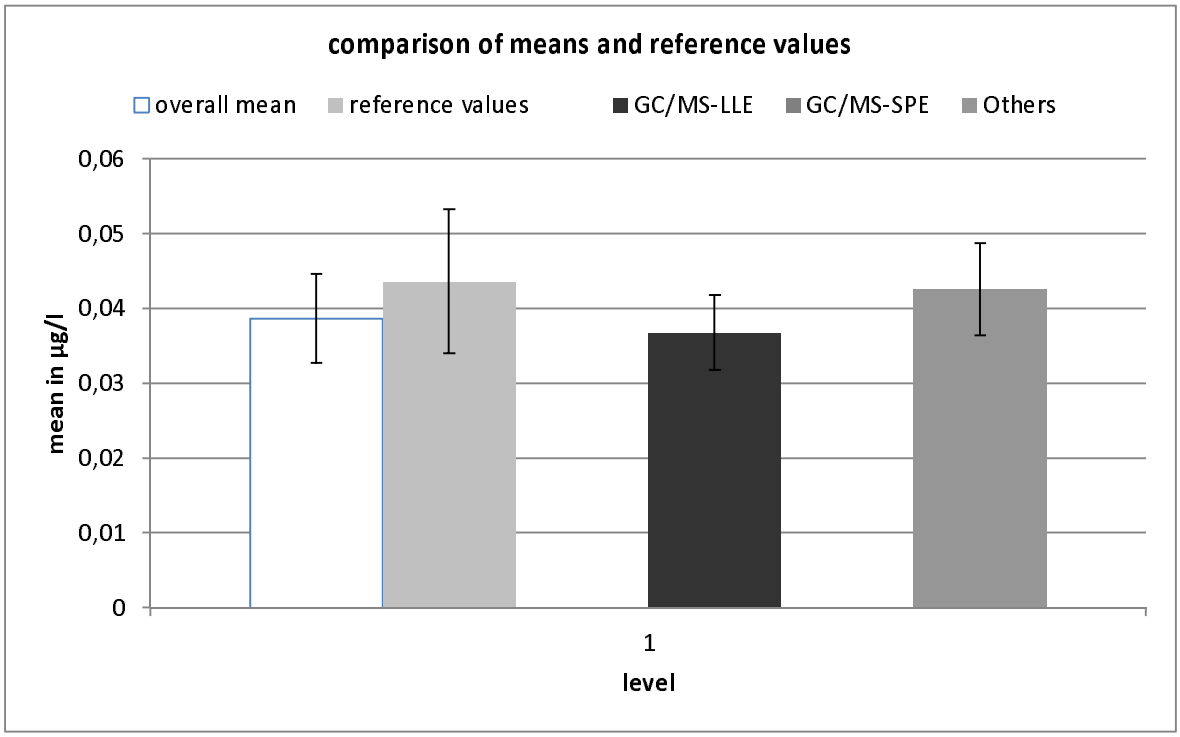


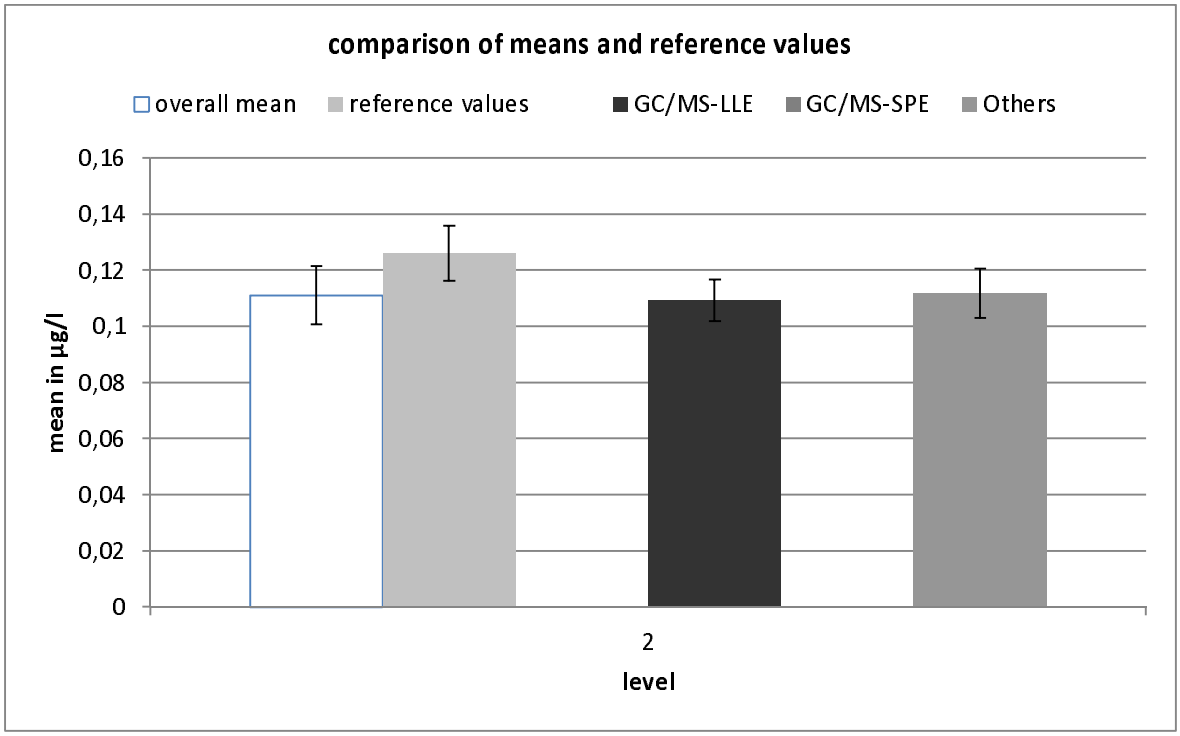


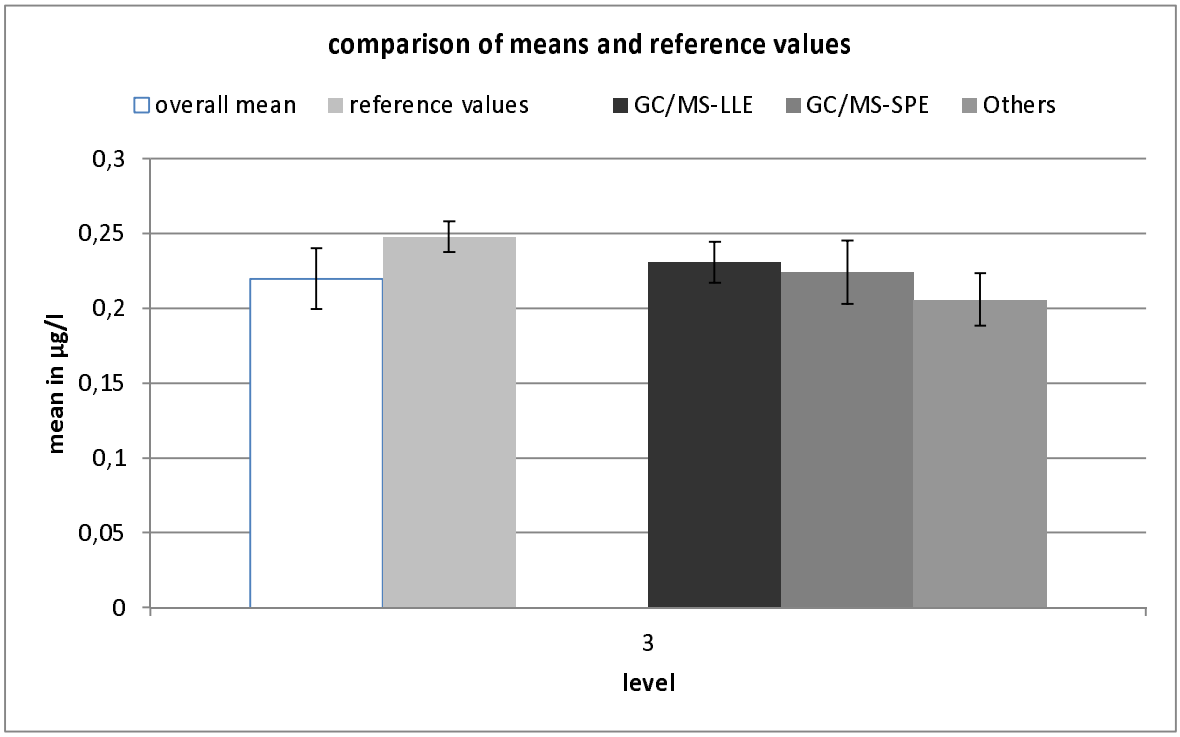
The values determined with GC/MS-LLE showed the closest statistical distribution.

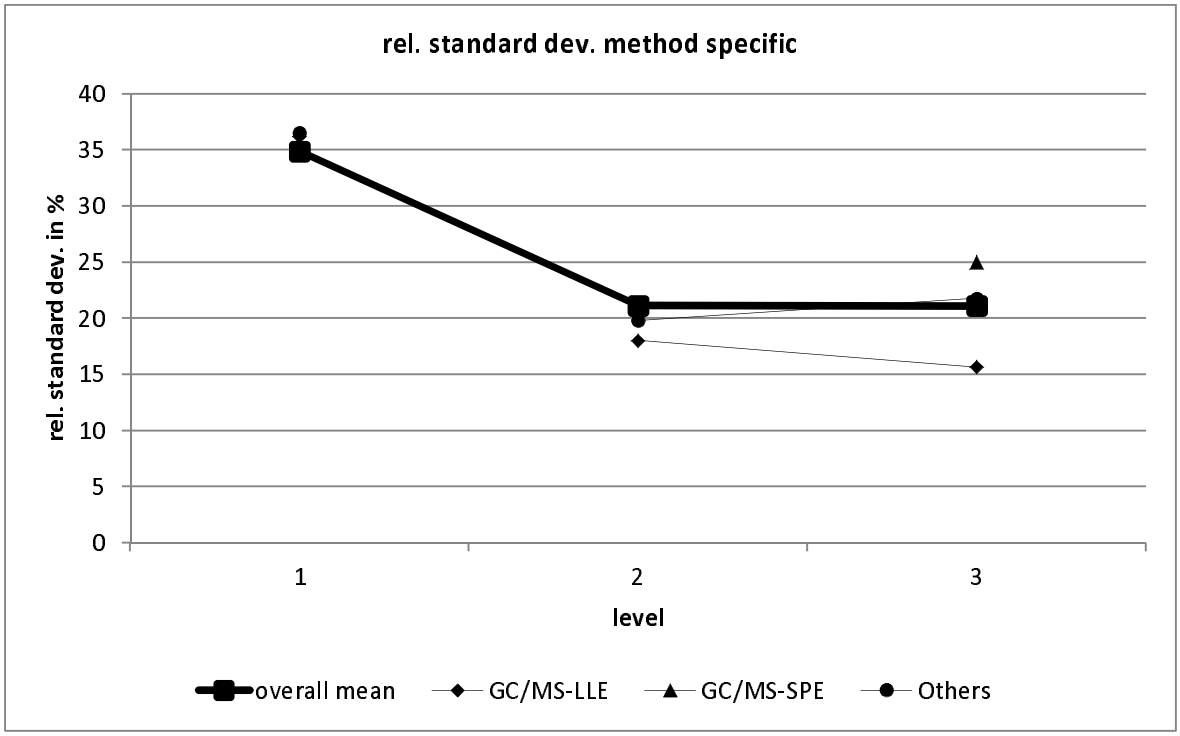
Comparison of means and reference values

level	mean [µg/l]	exp. uncertainty [µg/l]	exp. uncertainty [%]	reference value [µg/l]	exp. uncertainty [µg/l]	exp. uncertainty [%]
1	0,0386	0,0060	15,4	0,0436	0,0096	22,0
2	0,1110	0,0104	9,3	0,1260	0,0098	7,8
3	0,2198	0,0205	9,3	0,2478	0,0104	4,2




comparison of means and reference values
overall mean
reference values
GC/MS-LLE
GC/MS-SPE
Others
0,16
0,14
0,12
0,1
0,08
0,06
0,04
0,02
0
mean in µg/l
2
level


comparison of means and reference values
overall mean
reference values
GC/MS-LLE
GC/MS-SPE
Others
0,3
0,25
0,2
0,15
0,1
0,05
0
mean in µg/l
3
level



GC/MS-LLE									
level	robust mean [µg/l]	exp. unc. of the mean [µg/l]	exp. unc. of the mean [%]	robust standard deviation [µg/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	0,037	0,005	13,65	0,013	36,22	11	0	1	9,091
2	0,109	0,007	6,791	0,02	18,02	11	1	1	18,18
3	0,231	0,014	5,893	0,036	15,64	11	1	1	18,18

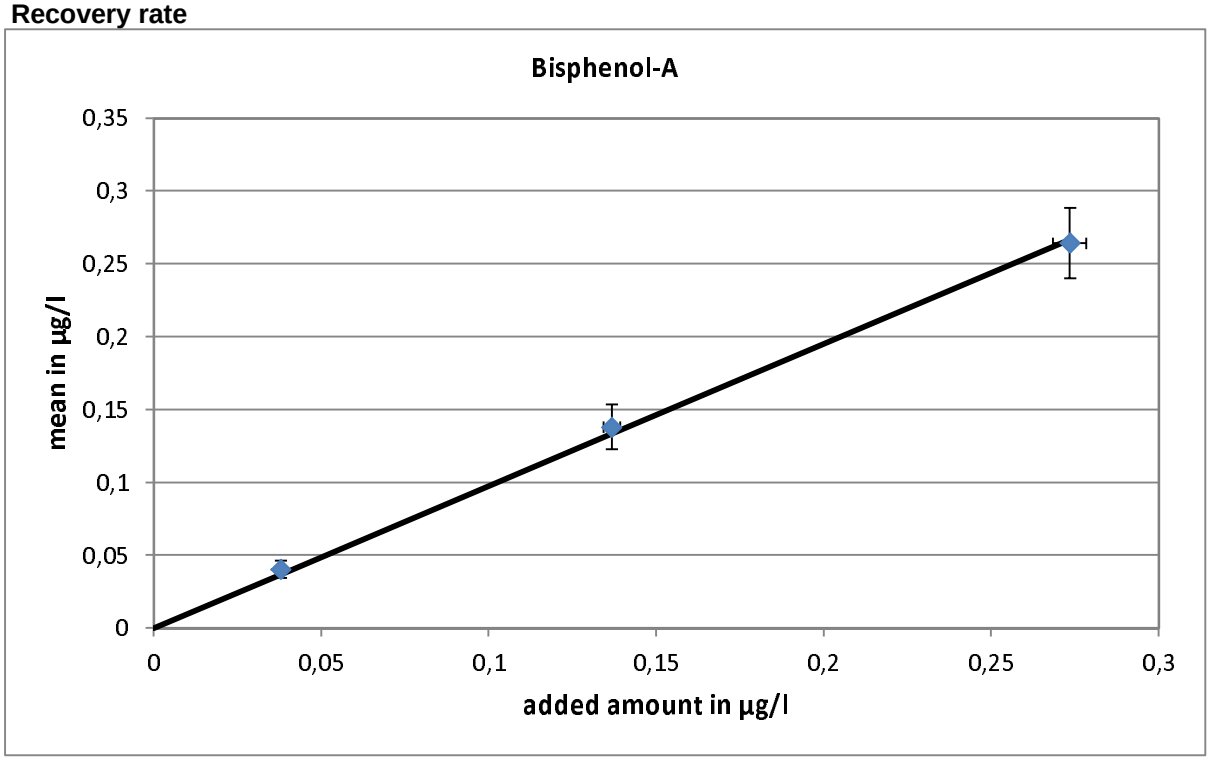
GC/MS-SPE									
level	robust mean [µg/l]	exp. unc. of the mean [µg/l]	exp. unc. of the mean [%]	robust standard deviation [µg/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
3	0,224	0,021	9,424	0,056	25	11	2	1	27,27

Others									
level	robust mean [µg/l]	exp. unc. of the mean [µg/l]	exp. unc. of the mean [%]	robust standard deviation [µg/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	0,043	0,006	14,45	0,016	36,56	10	0	2	20
2	0,112	0,009	7,826	0,022	19,8	10	0	0	0
3	0,206	0,018	8,606	0,045	21,77	10	2	0	20

Bisphenol-A

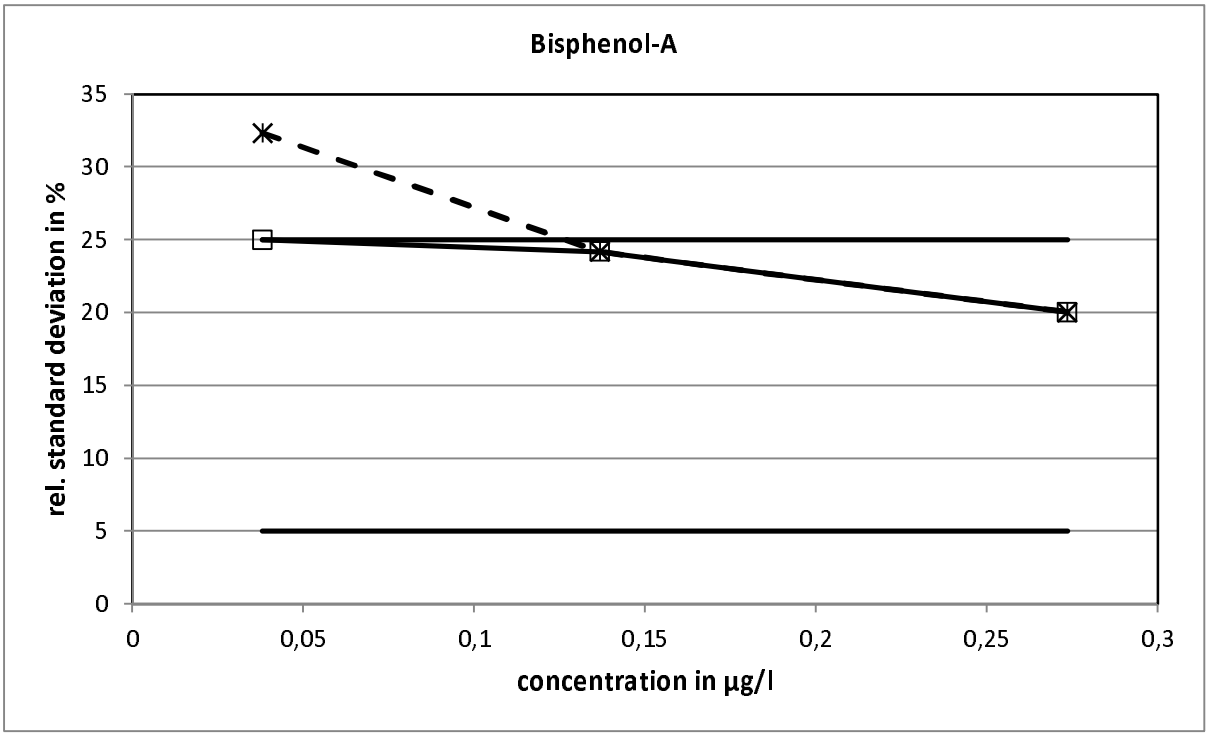
level	assigned value [µg/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [µg/l]	standard deviation for proficiency assessment [µg/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [µg/l]	lower tolerance limit [µg/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,0380	10,34	0,0131	0,0095	25,00	0,0600	0,0208	57,99	-45,19	30	0	5	16,7
2	0,1368	3,54	0,0334	0,0331	24,18	0,2130	0,0768	55,78	-43,82	30	2	4	20,0
3	0,2735	2,38	0,0530	0,0548	20,04	0,3965	0,1728	44,97	-36,83	30	3	4	23,3
									sum	90	5	13	20,0

Recovery rate

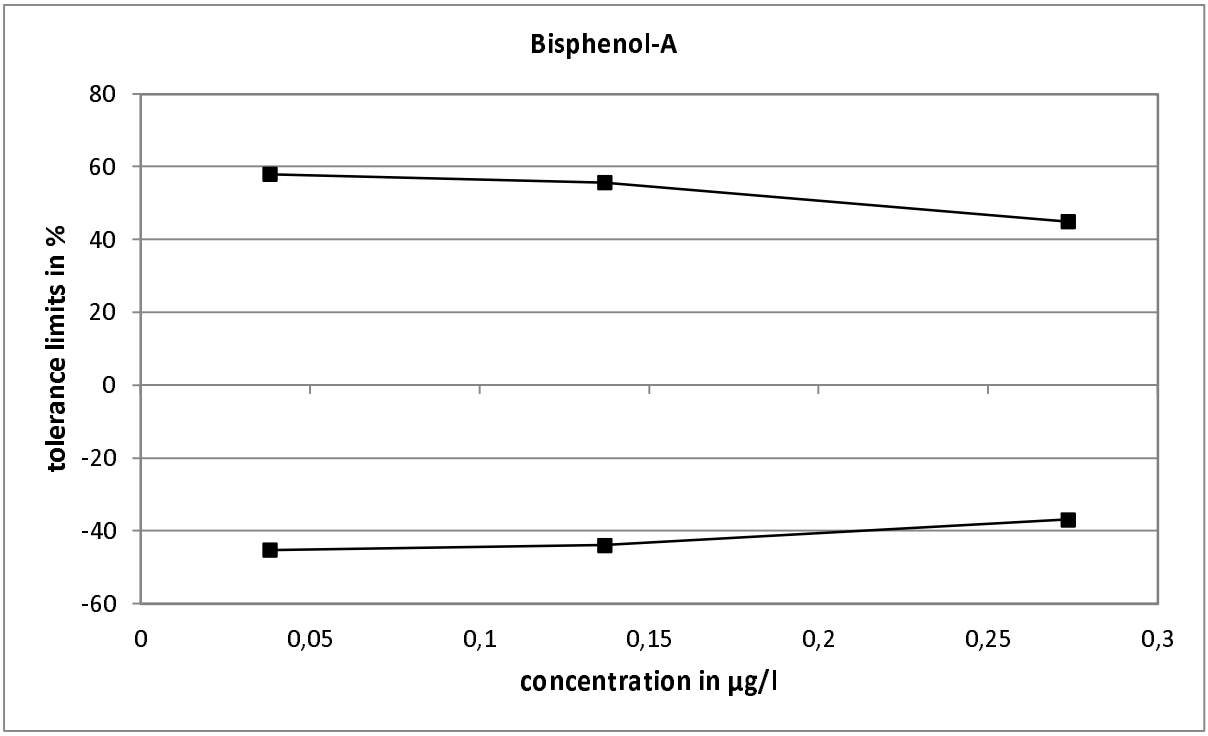


Slope of the regression: 0,976, average recovery rate: 97,6%

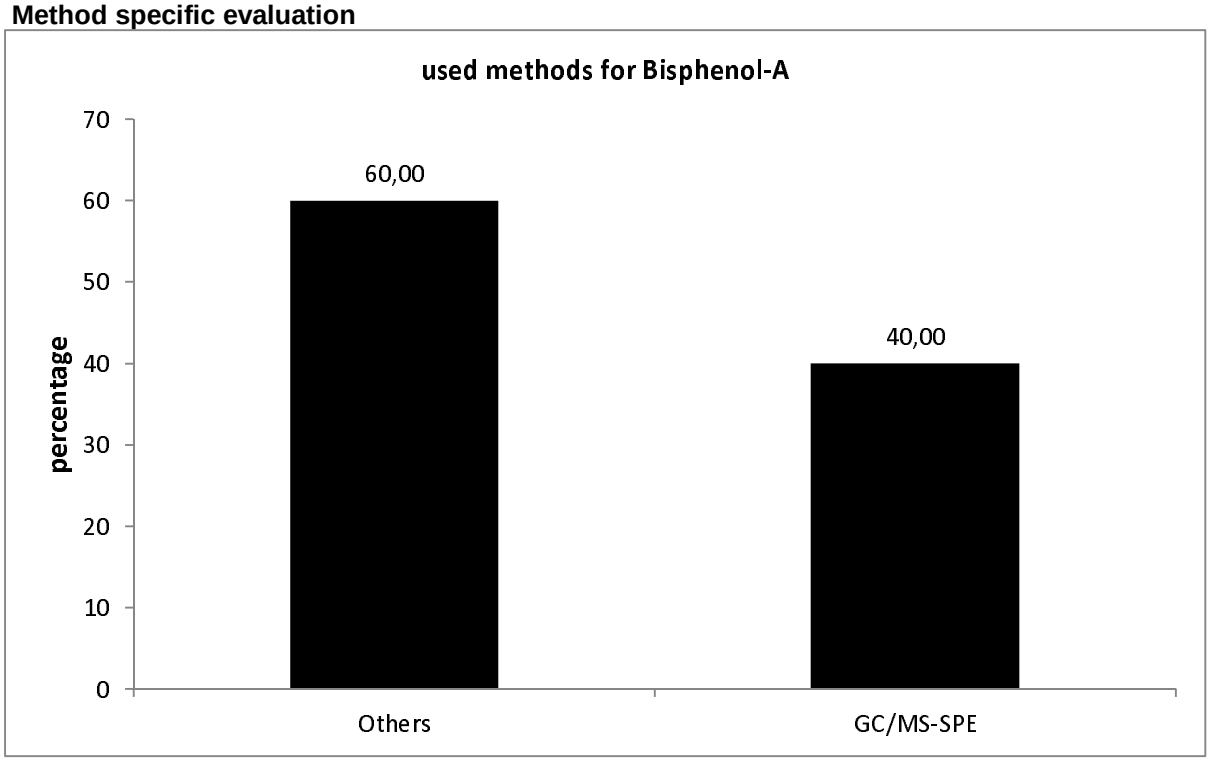
Relative standard deviation and tolerance limits

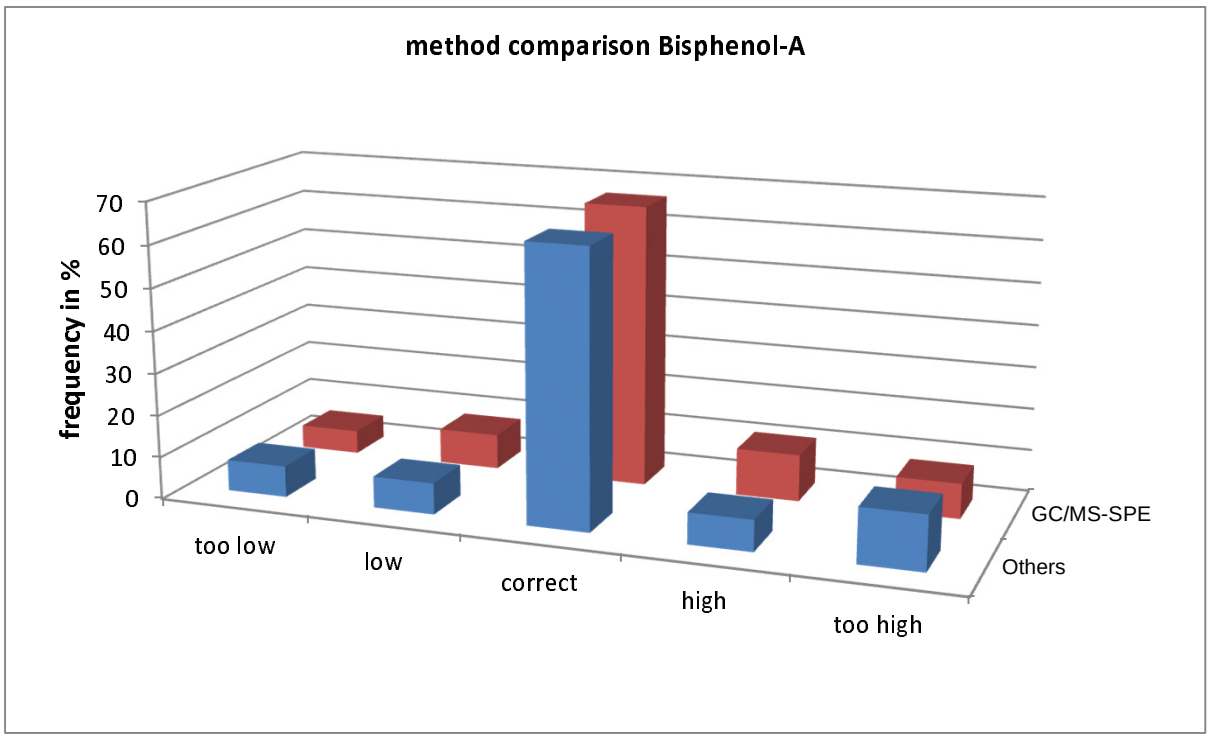


The relative standard deviation, derived from the Q-method, reached with one concentration level the upper limit.



Method specific evaluation

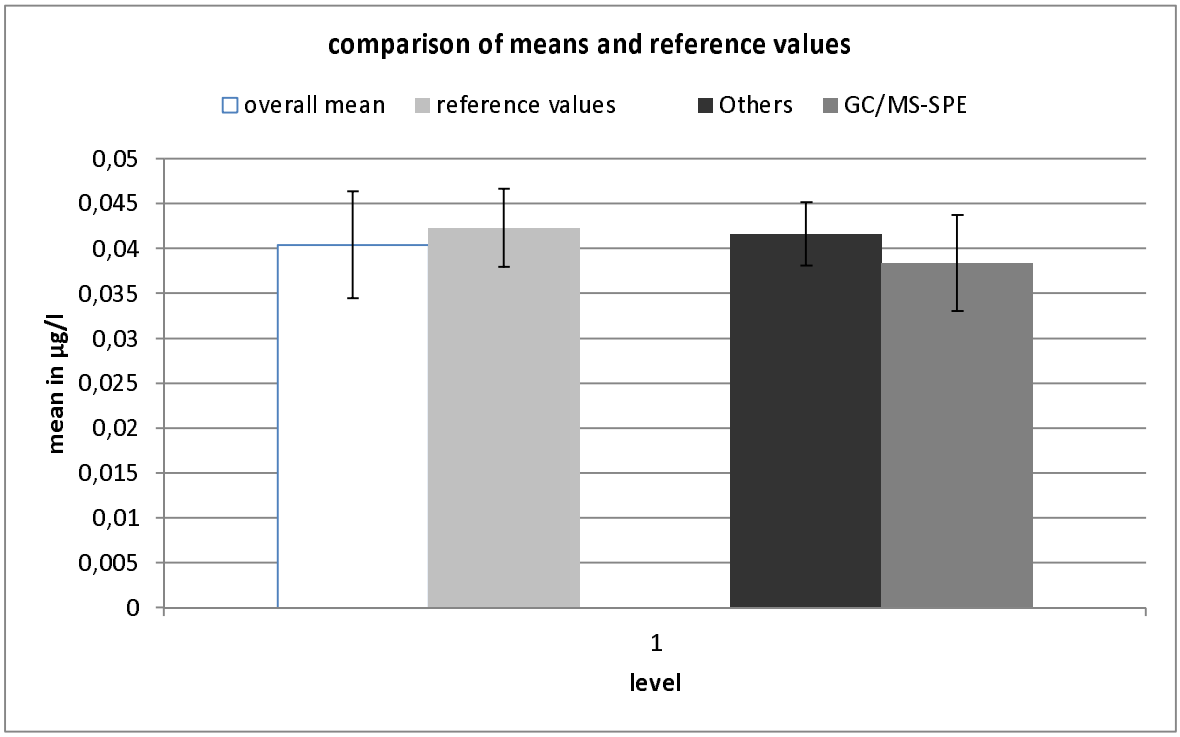


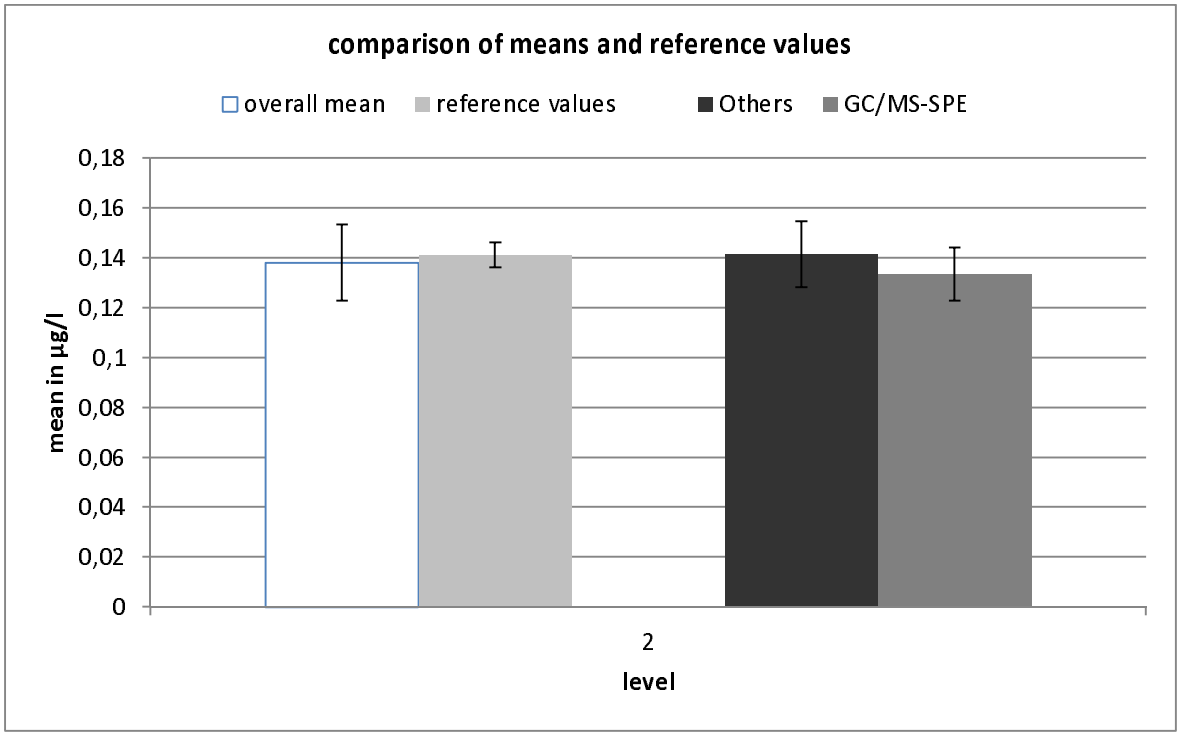


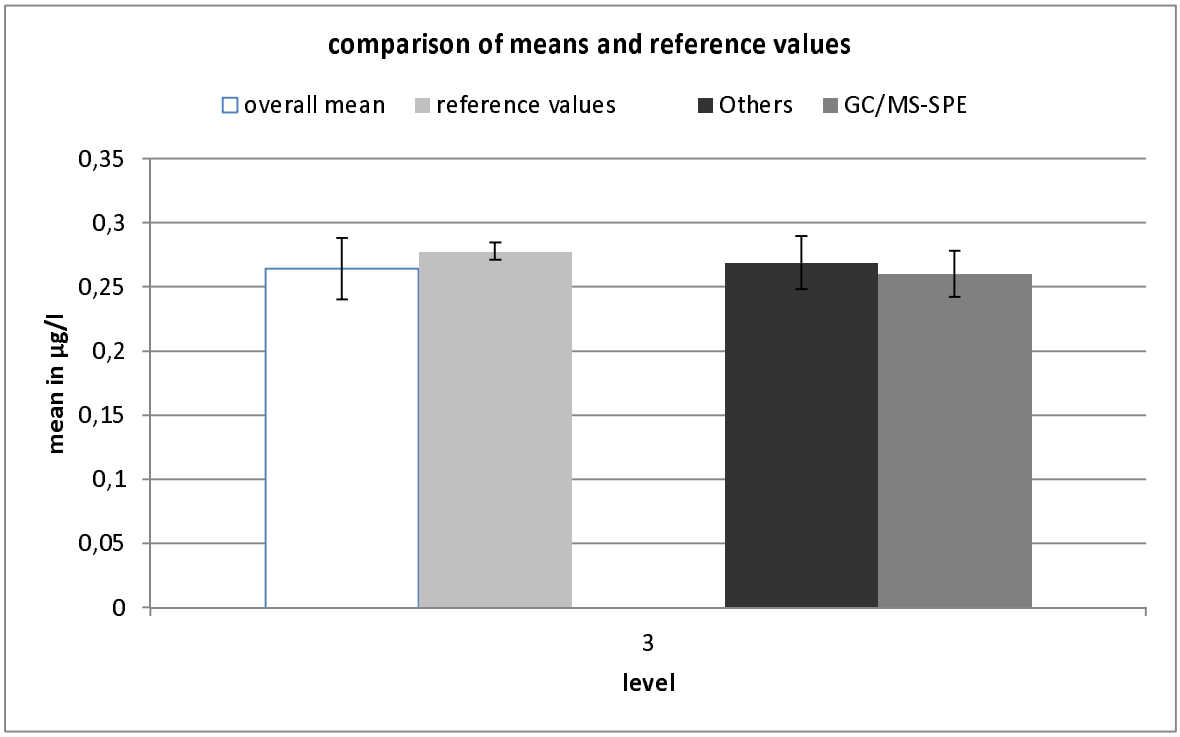
There were no significant differences between the methods.

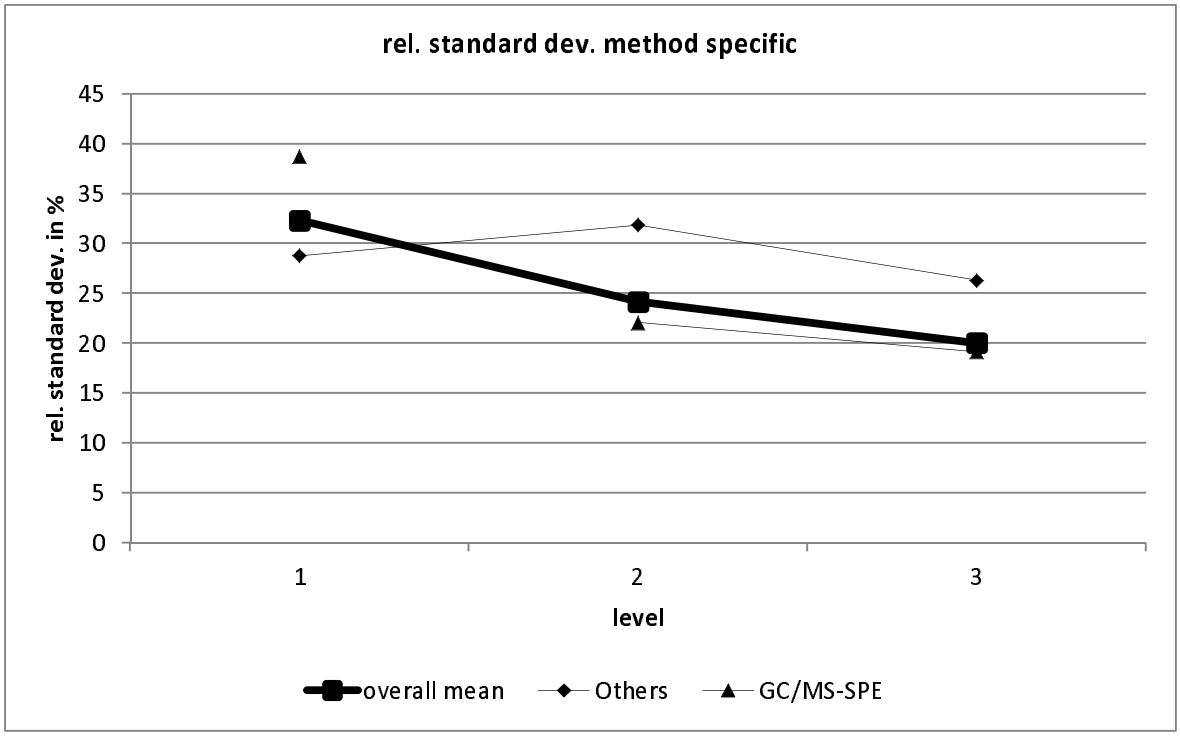
Comparison of means and reference values

level	mean [µg/l]	exp. uncertainty [µg/l]	exp. uncertainty [%]	reference value [µg/l]	exp. uncertainty [µg/l]	exp. uncertainty [%]
1	0,0404	0,0060	14,8	0,0423	0,0044	10,3
2	0,1380	0,0152	11,0	0,1411	0,0050	3,5
3	0,2642	0,0242	9,1	0,2779	0,0066	2,4



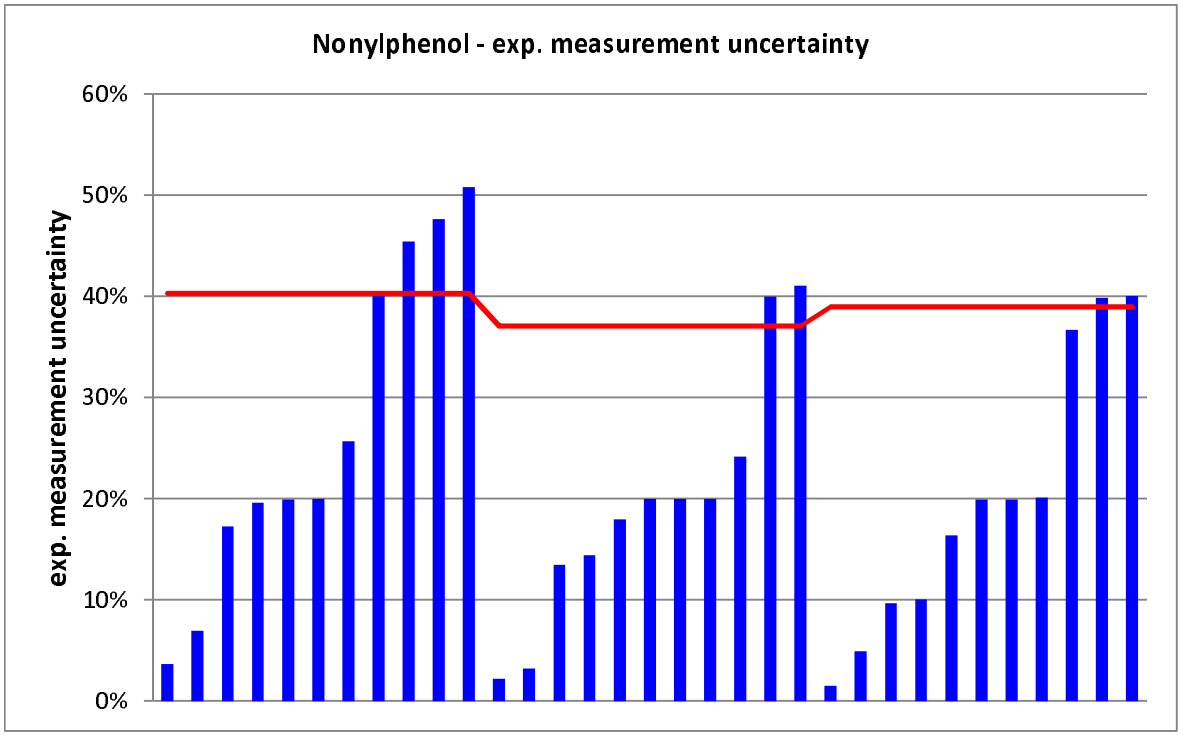

comparison of means and reference values
overall mean
reference values
Others
GC/MS-SPE
0,18
0,16
0,14
0,12
0,1
0,08
0,06
0,04
0,02
0
mean in µg/l
2
level

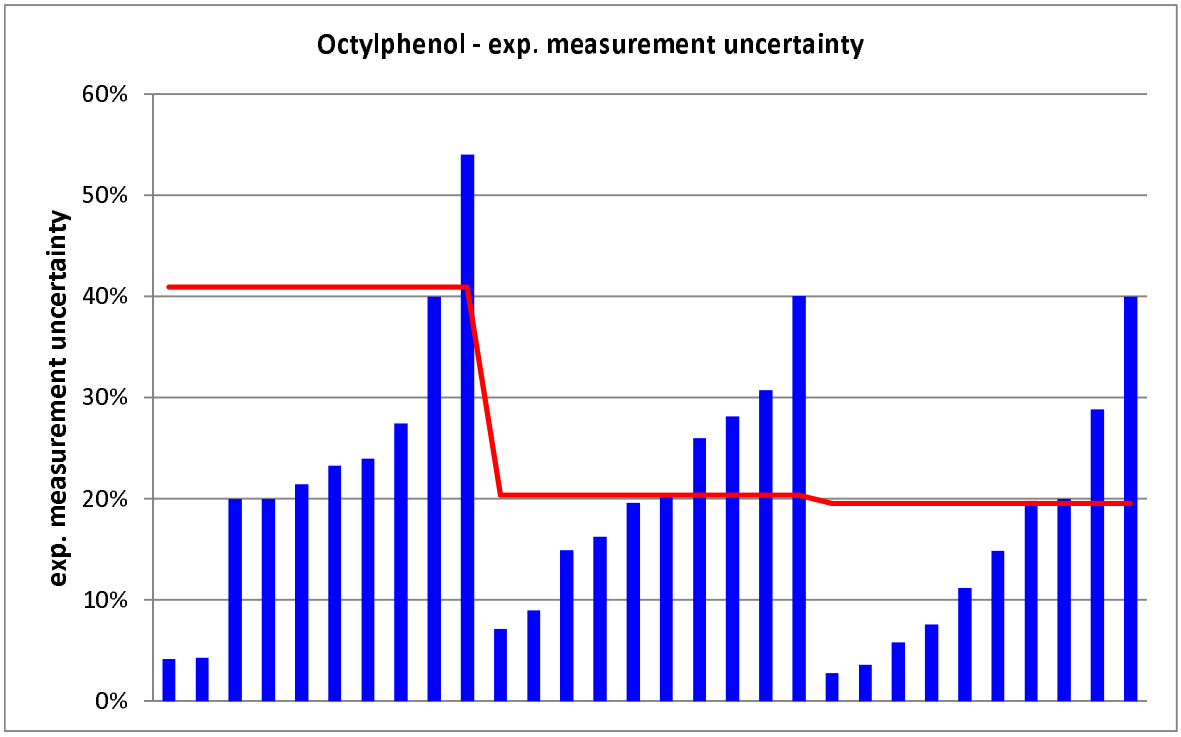

comparison of means and reference values
overall mean
reference values
Others
GC/MS-SPE
0,35
0,3
0,25
0,2
0,15
0,1
0,05
0
mean in µg/l
3
level

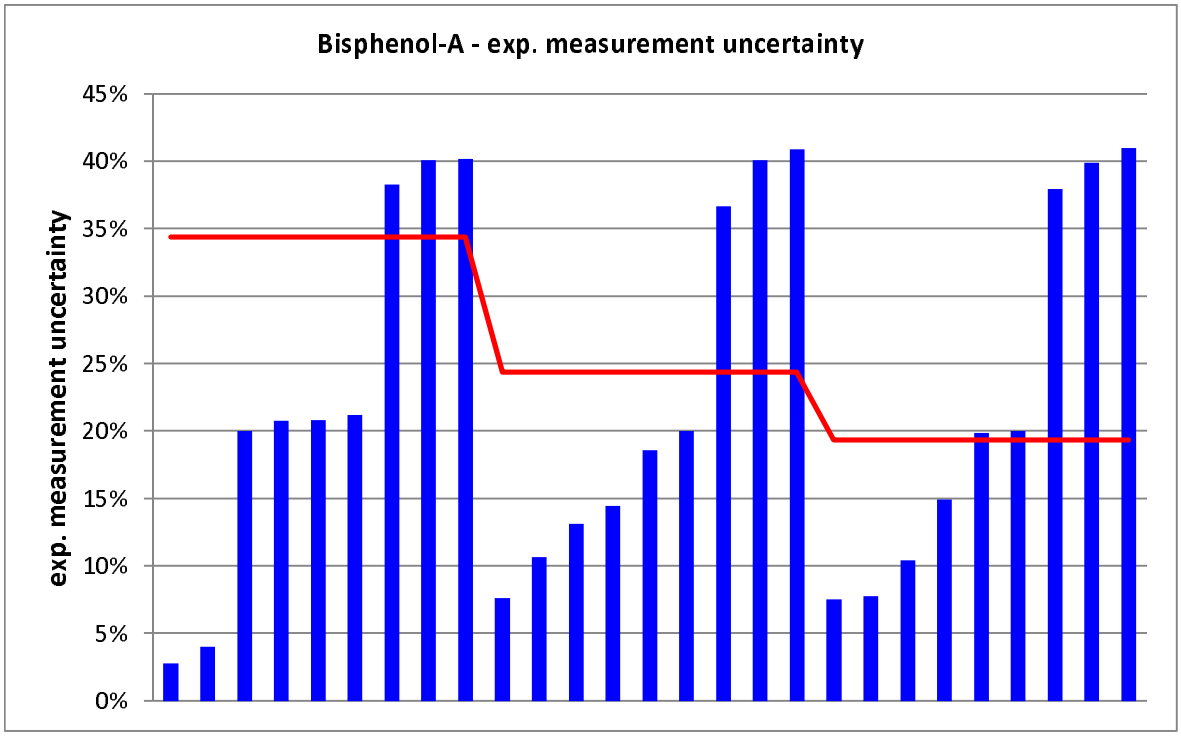


Others									
level	robust mean [µg/l]	exp. unc. of the mean [µg/l]	exp. unc. of the mean [%]	robust standard deviation [µg/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	0,042	0,004	8,477	0,012	28,77	18	1	3	22,22
2	0,141	0,013	9,385	0,045	31,85	18	1	0	5,556
3	0,269	0,021	7,747	0,071	26,29	18	2	1	16,67

GC/MS-SPE									
level	robust mean [µg/l]	exp. unc. of the mean [µg/l]	exp. unc. of the mean [%]	robust standard deviation [µg/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	0,038	0,005	13,98	0,015	38,74	12	0	2	16,67
2	0,133	0,011	7,957	0,029	22,05	12	1	2	25
3	0,26	0,018	6,899	0,05	19,12	12	1	1	16,67

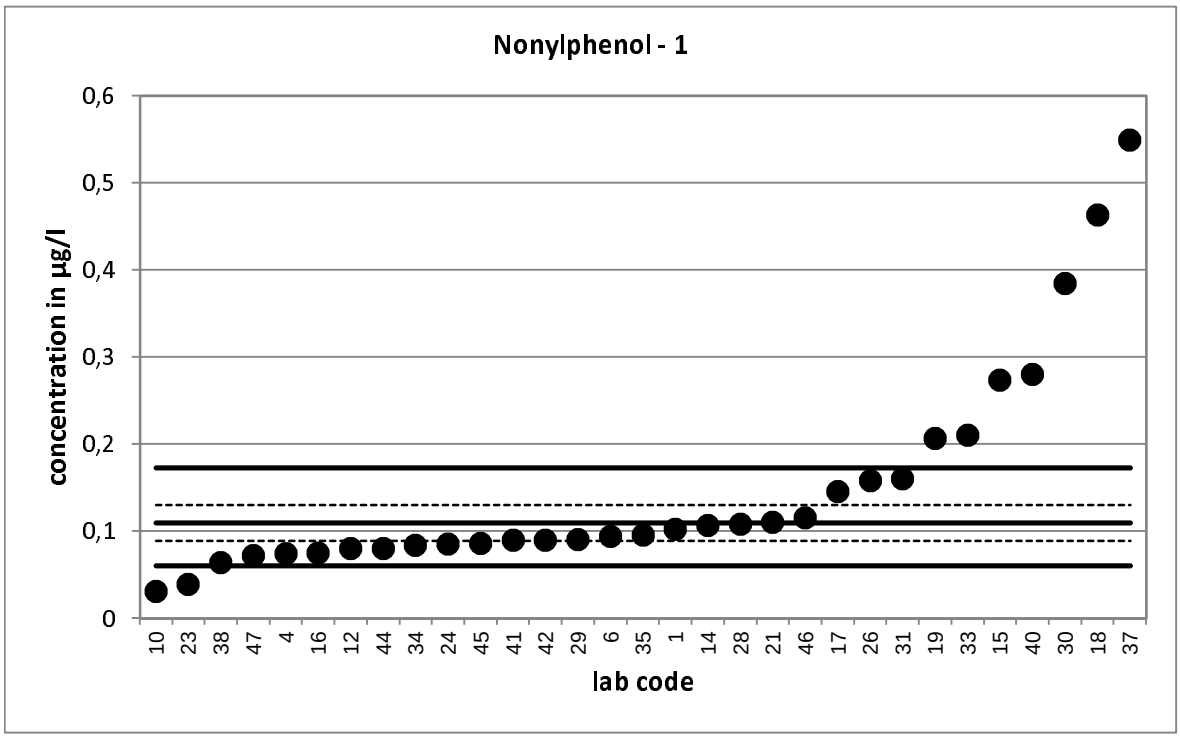

Nonylphenol - exp. measurement uncertainty
exp. measurement uncertainty
60%
50%
40%
30%
20%
10%
0%

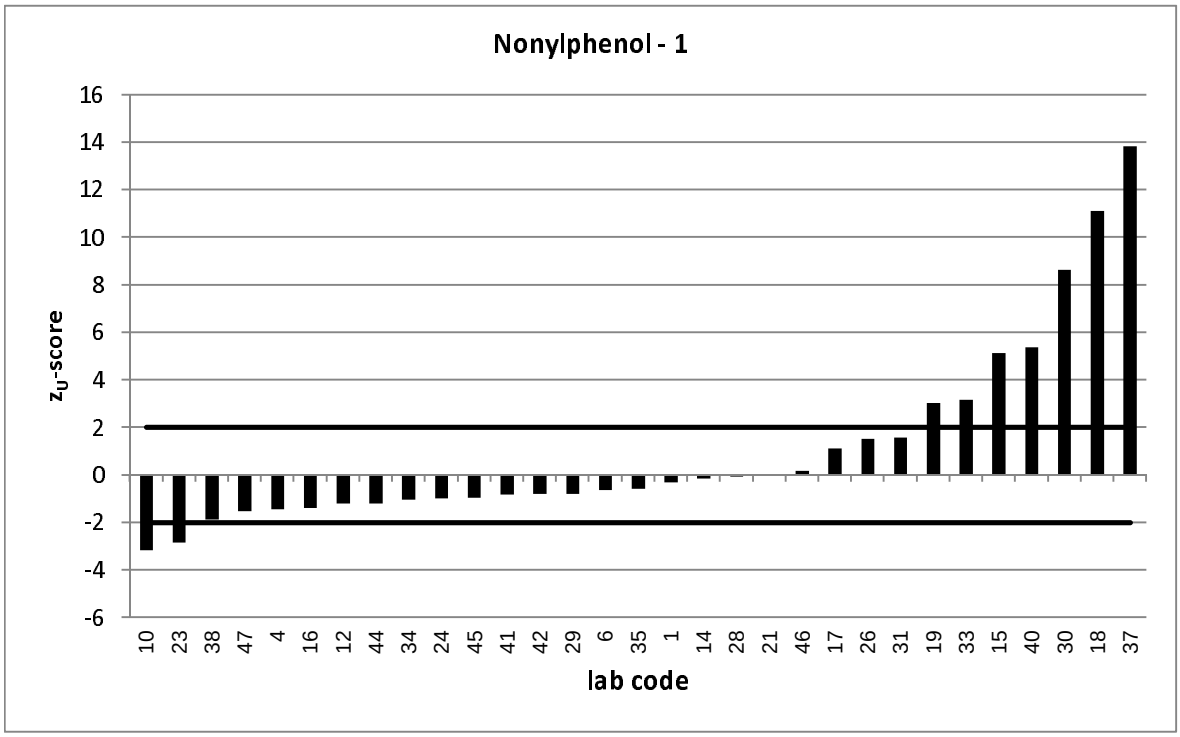

Octylphenol - exp. measurement uncertainty
exp. measurement uncertainty
60%
50%
40%
30%
20%
10%
0%

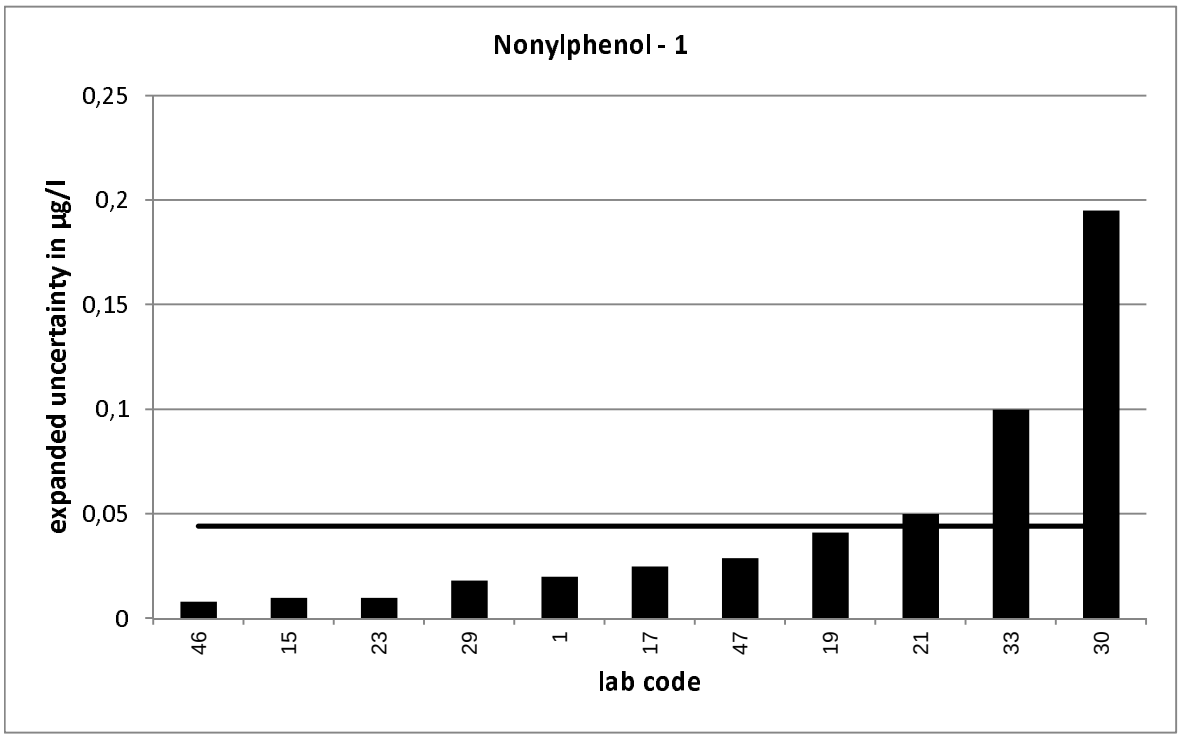

Bisphenol-A - exp. measurement uncertainty
exp. measurement uncertainty
45%
40%
35%
30%
25%
20%
15%
10%
5%
0%

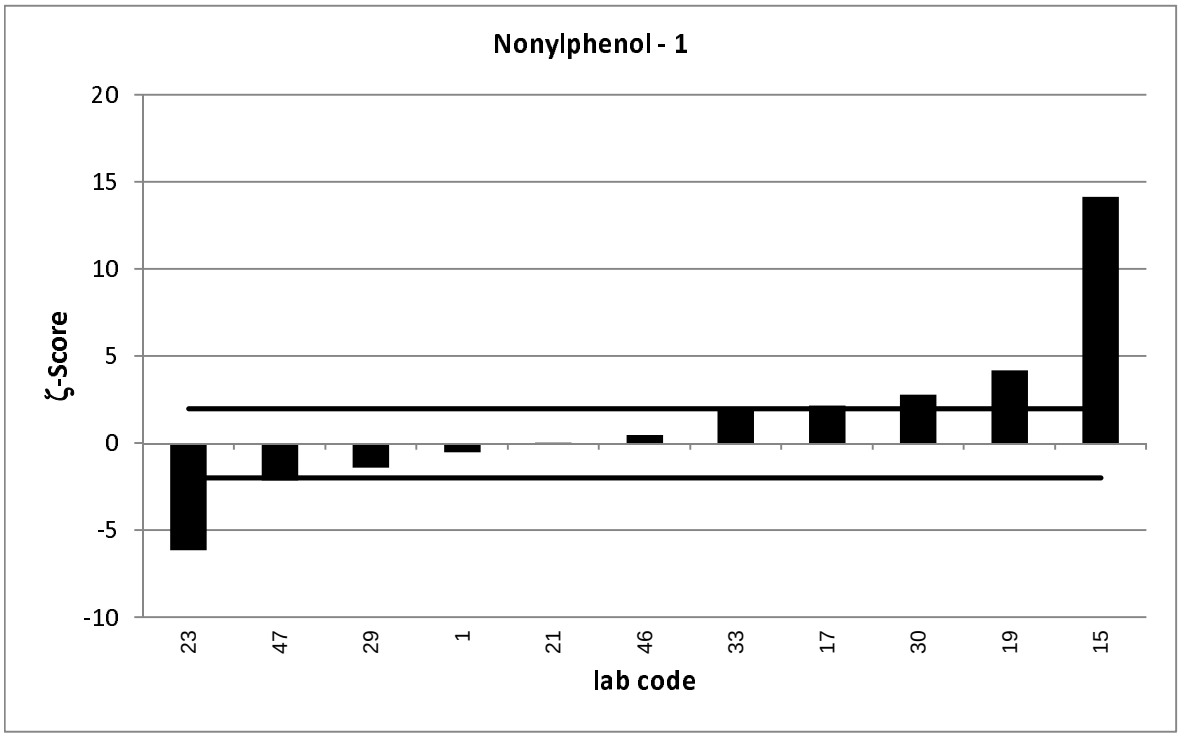
PT 2/14 - TW S3		Nonylphenol - 1			
assigned value [µg/l]*			0,1096	± 0,0208	
upper tolerance limit [µg/l]			0,1731		
lower tolerance limit [µg/l]			0,06005		
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.
1	0,102	0,02	-0,5	-0,3	+
4	0,074			-1,4	+
6	0,0941			-0,6	+
10	0,031			-3,2	-
12	0,08			-1,2	+
14	0,106			-0,1	+
15	0,273	0,01	14,2	5,1	-
16	0,075			-1,4	+
17	0,145	0,025	2,2	1,1	+
18	0,463			11,1	-
19	0,206	0,041	4,2	3,0	-
21	0,11	0,05	0,0	0,0	+
23	0,0389	0,01	-6,1	-2,9	-
24	0,085			-1,0	+
26	0,158			1,5	+
28	0,108			-0,1	+
29	0,0902	0,018	-1,4	-0,8	+
30	0,384	0,195	2,8	8,6	-
31	0,16			1,6	+
33	0,21	0,1	2,0	3,2	-
34	0,0838			-1,0	+
35	0,095			-0,6	+
37	0,549			13,8	-
38	0,0634			-1,9	+
40	0,28			5,4	-
41	0,0895			-0,8	+
42	0,0898			-0,8	+
44	0,08			-1,2	+
45	0,086			-1,0	+
46	0,115	0,008	0,5	0,2	+
47	0,0716	0,029	-2,1	-1,5	+

* 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%


Nonylphenol - 1
concentration in µg/l
0,6
0,5
0,4
0,3
0,2
0,1
0
10 23 38 47 4 16 12 44 34 24 45 41 42 29 6 35 1 14 28 21 46 17 26 31 19 33 15 40 30 18 37
lab code

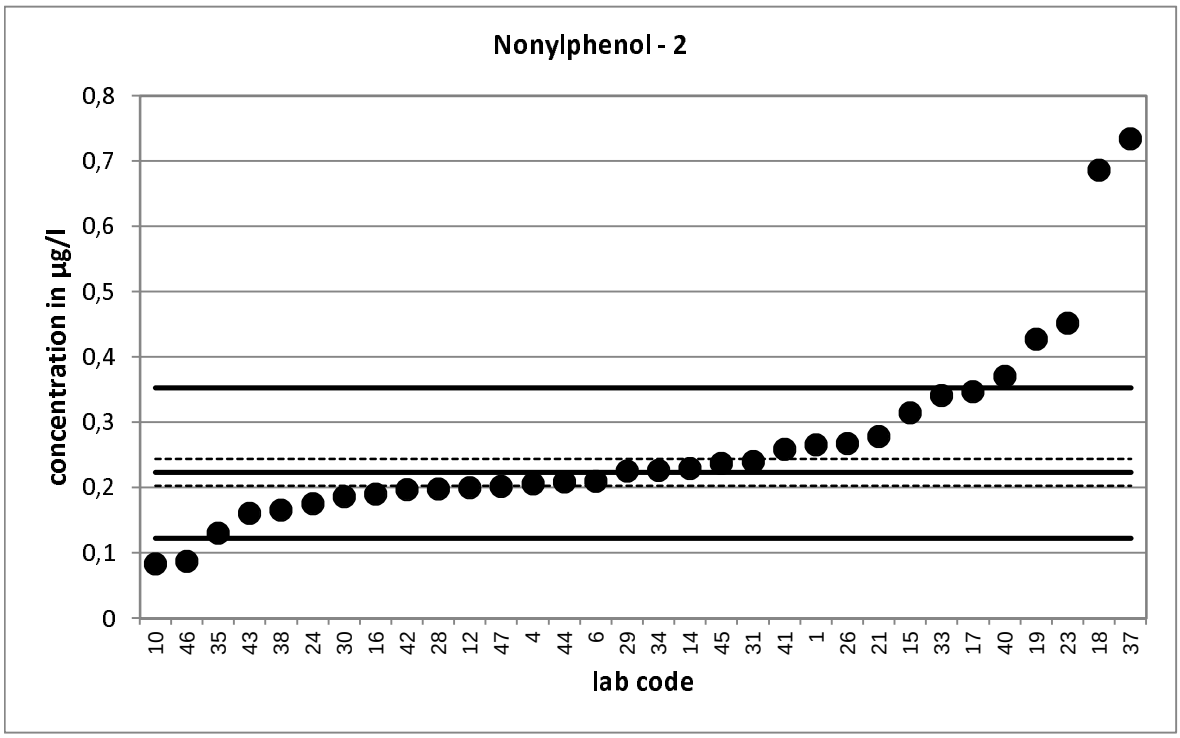

Nonylphenol - 1
z_U-score
16
14
12
10
8
6
4
2
0
-2
-4
-6
10 23 38 47 4 16 12 44 34 24 45 41 42 29 6 35 1 14 28 21 46 17 26 31 19 33 15 40 30 18 37
lab code

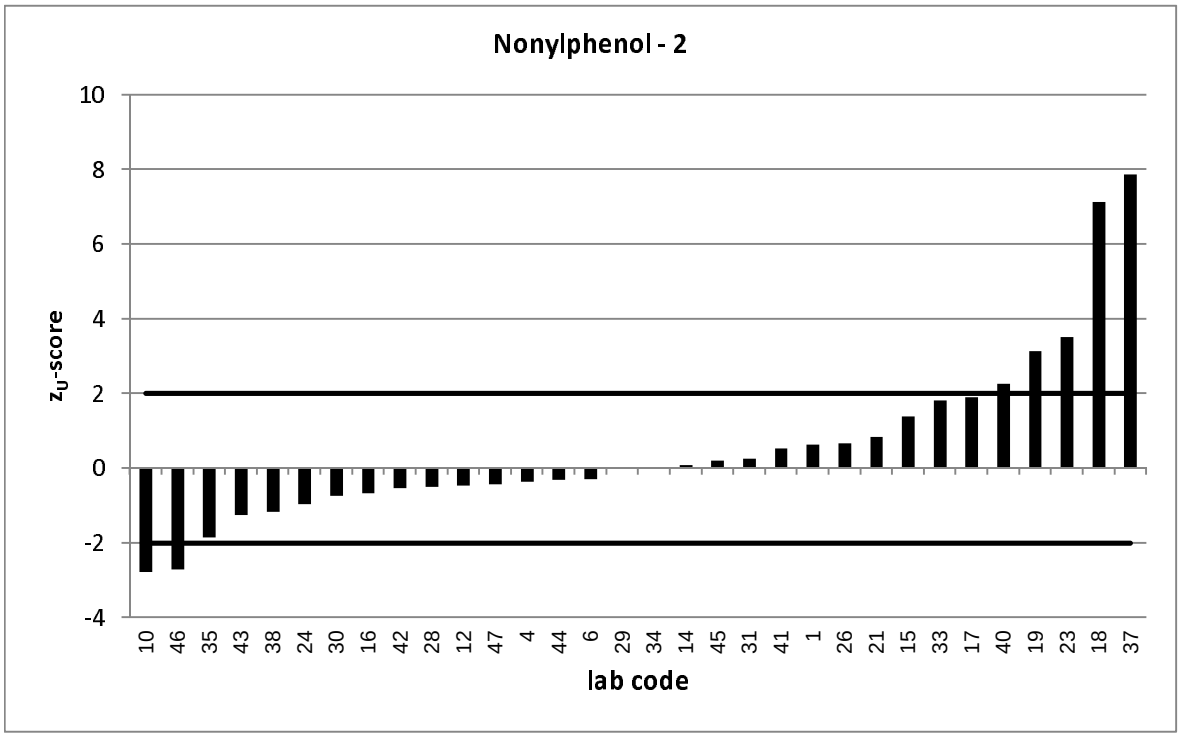

Nonylphenol - 1
expanded uncertainty in µg/l
0,25
0,2
0,15
0,1
0,05
0
46
15
23
29
1
17
47
19
21
33
30
lab code

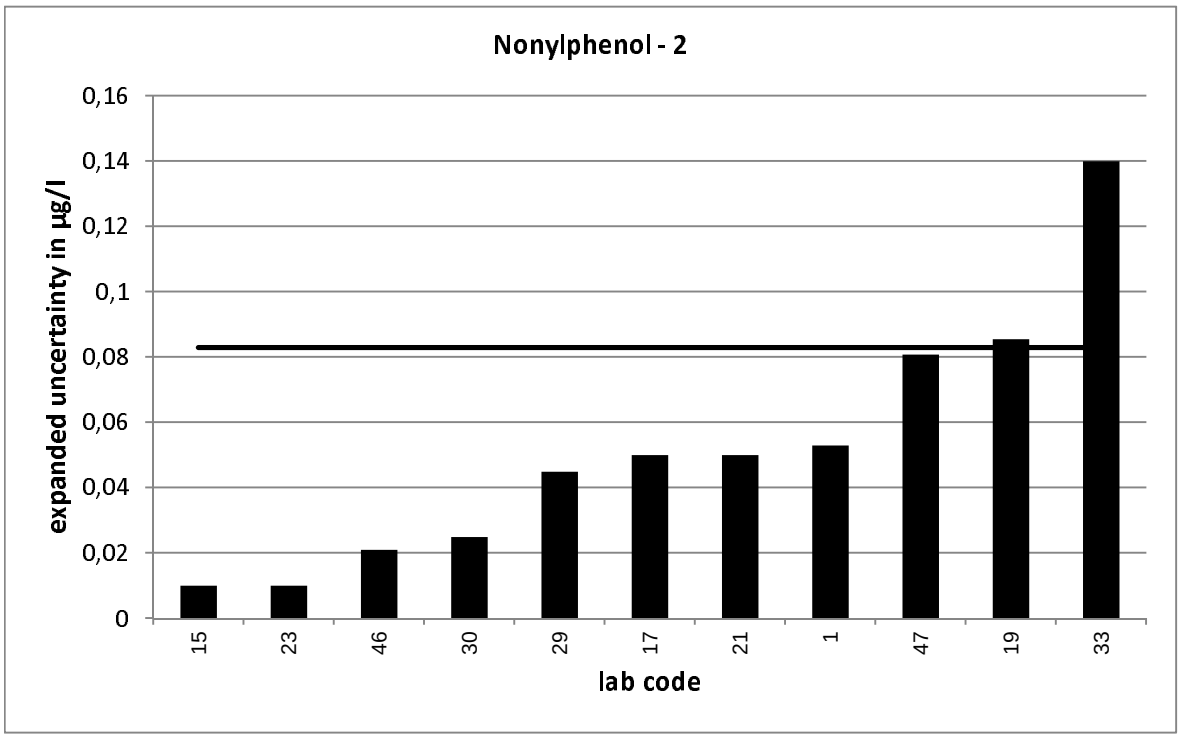

Nonylphenol - 1
ζ-Score
20
15
10
5
0
-5
-10
23
47
29
1
21
46
33
17
30
19
15
lab code

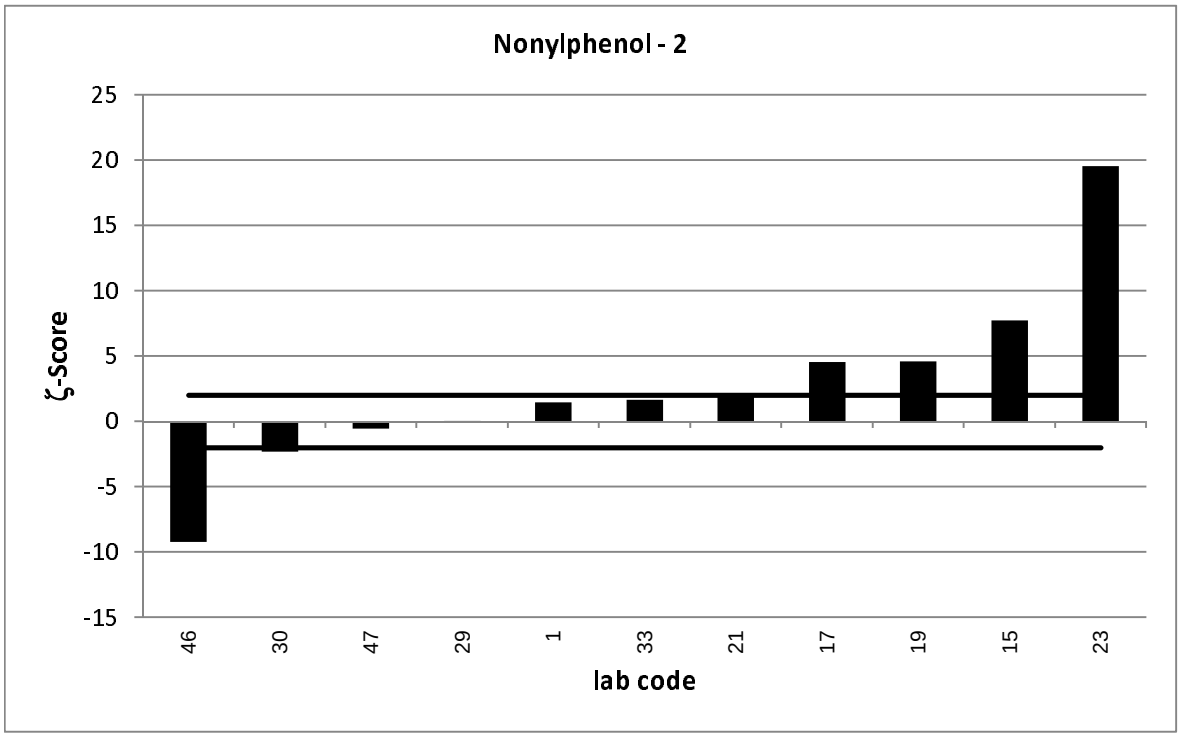
PT 2/14 - TW S3		Nonylphenol - 2			
assigned value [µg/l]*			0,2236	± 0,021	
upper tolerance limit [µg/l]			0,3532		
lower tolerance limit [µg/l]			0,1226		
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.
1	0,265	0,053	1,5	0,6	+
4	0,205			-0,4	+
6	0,209			-0,3	+
10	0,083			-2,8	-
12	0,2			-0,5	+
14	0,229			0,1	+
15	0,314	0,01	7,8	1,4	+
16	0,19			-0,7	+
17	0,347	0,05	4,6	1,9	+
18	0,686			7,1	-
19	0,427	0,085	4,6	3,1	-
21	0,278	0,05	2,0	0,8	+
23	0,451	0,01	19,5	3,5	-
24	0,175			-1,0	+
26	0,267			0,7	+
28	0,198			-0,5	+
29	0,225	0,045	0,1	0,0	+
30	0,186	0,025	-2,3	-0,7	+
31	0,24			0,3	+
33	0,341	0,14	1,7	1,8	+
34	0,226			0,0	+
35	0,13			-1,9	+
37	0,734			7,9	-
38	0,165			-1,2	+
40	0,37			2,3	-
41	0,258			0,5	+
42	0,197			-0,5	+
43	0,16			-1,3	+
44	0,208			-0,3	+
45	0,2367			0,2	+
46	0,087	0,021	-9,2	-2,7	-
47	0,202	0,081	-0,5	-0,4	+

* 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%


Nonylphenol - 2
concentration in µg/l
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
10 46 35 43 38 24 30 16 42 28 12 47 4 44 6 29 34 14 45 31 41 1 26 21 15 33 17 40 19 23 18 37
lab code

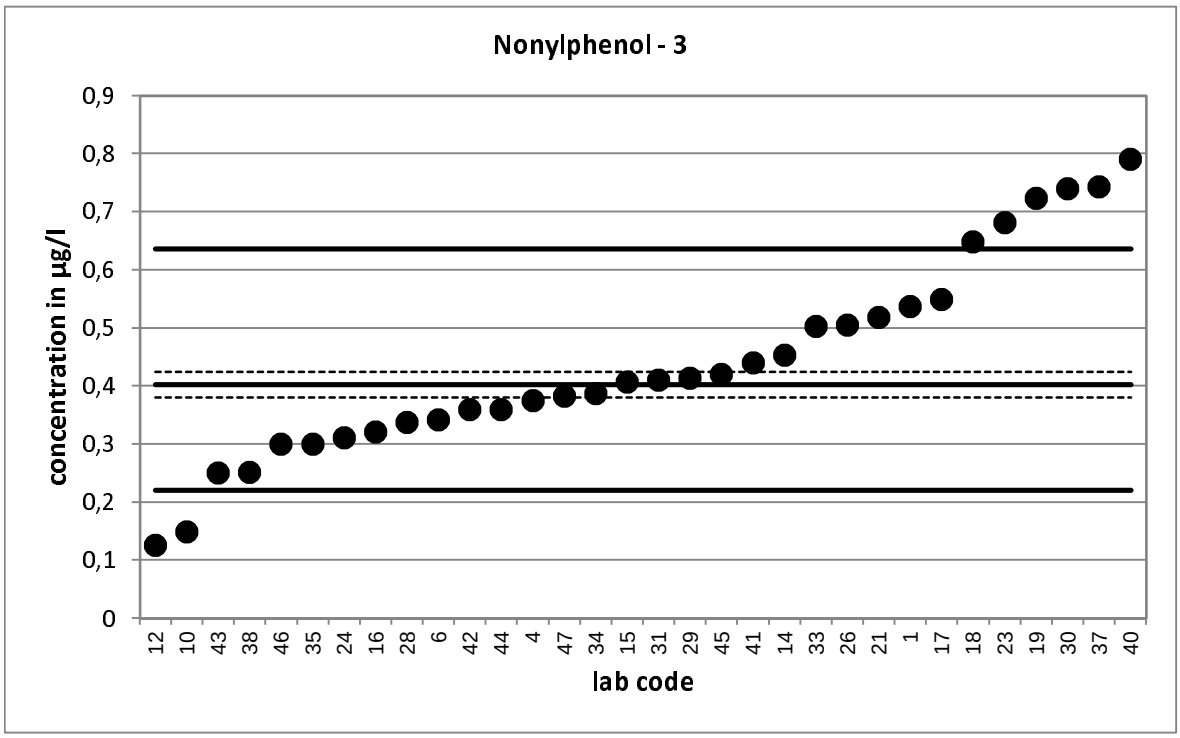

Nonylphenol - 2
z_U-score
10
8
6
4
2
0
-2
-4
10 46 35 43 38 24 30 16 42 28 12 47 4 44 6 29 34 14 45 31 41 1 26 21 15 33 17 40 19 23 18 37
lab code

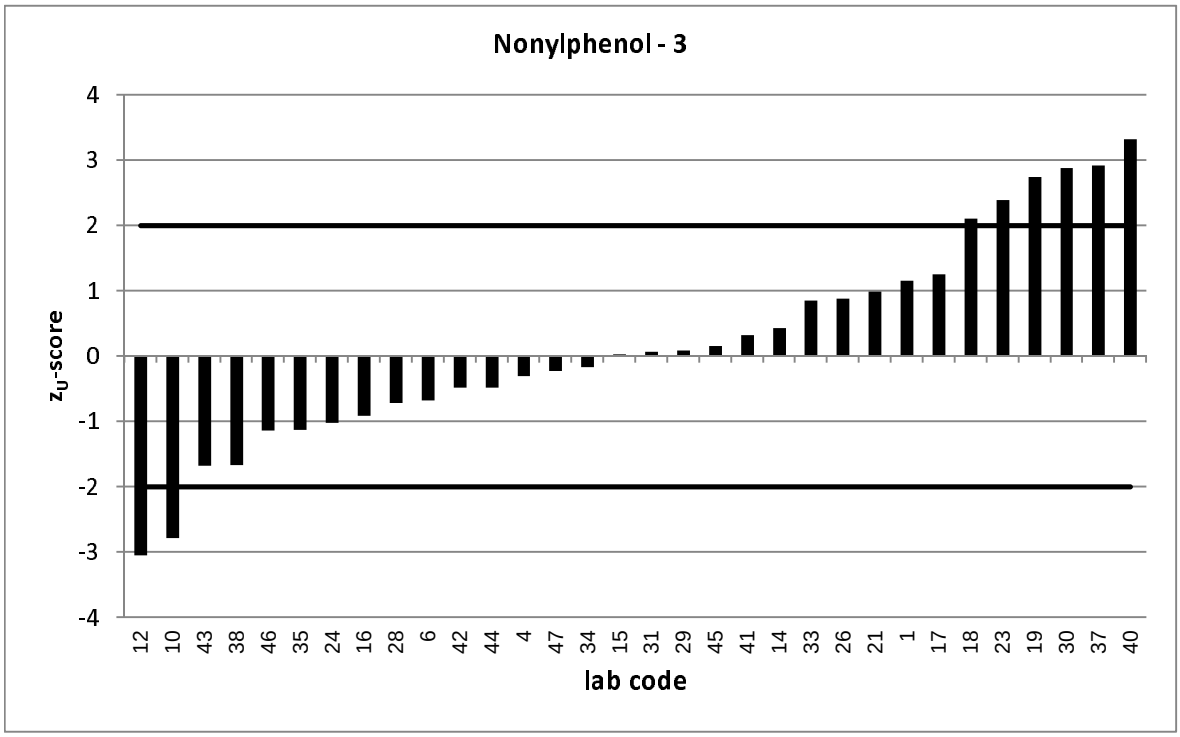

Nonylphenol - 2
expanded uncertainty in µg/l
0,16
0,14
0,12
0,1
0,08
0,06
0,04
0,02
0
15
23
46
30
29
17
21
1
47
19
33
lab code

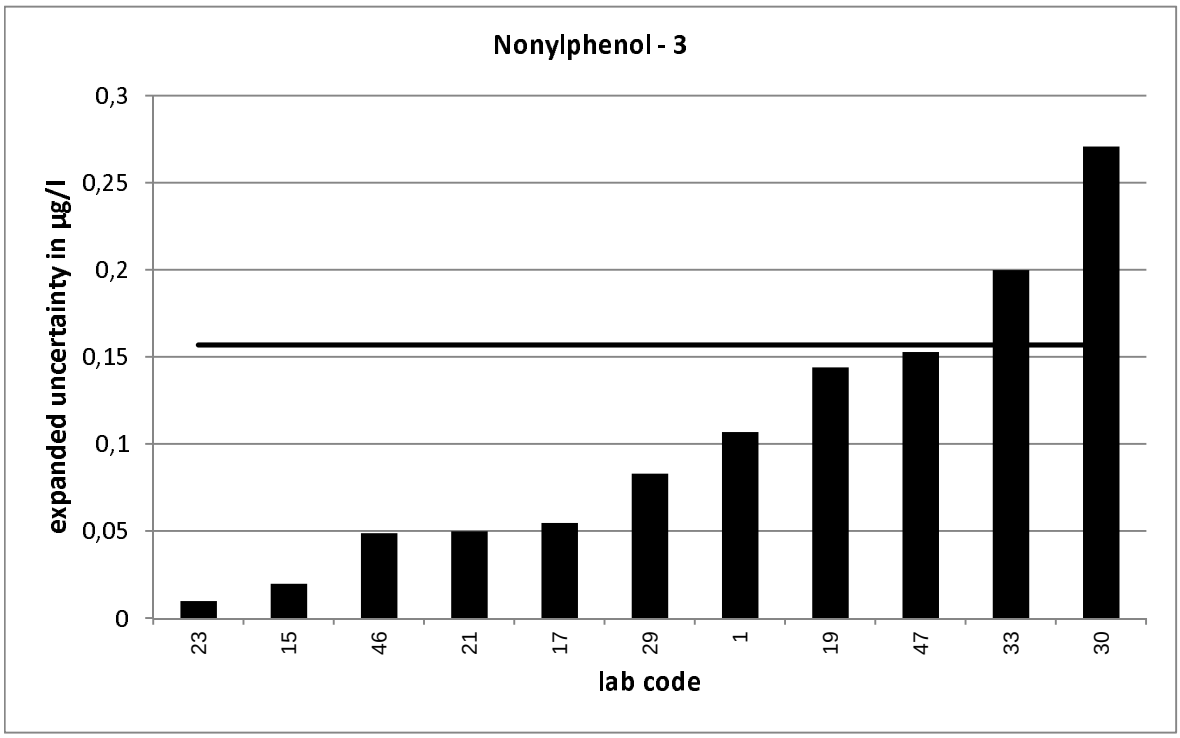

Nonylphenol - 2
ζ-Score
25
20
15
10
5
0
-5
-10
-15
46
30
47
29
1
33
21
17
19
15
23
lab code

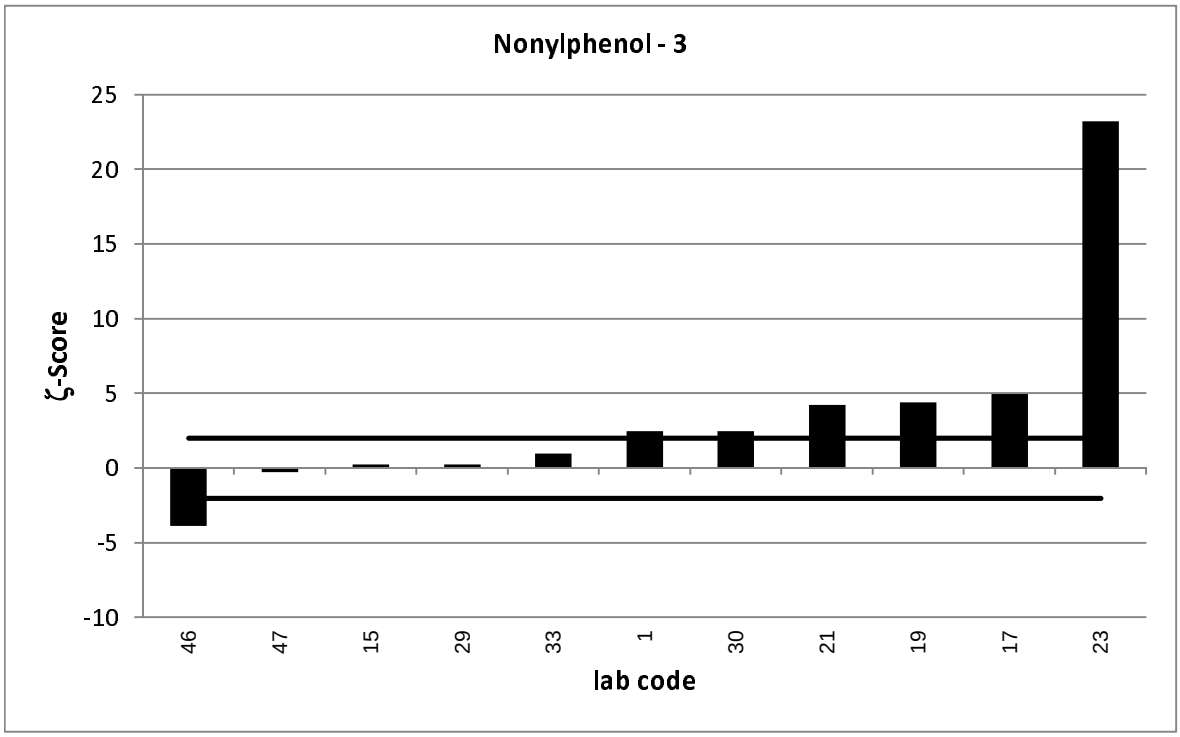
PT 2/14 - TW S3		Nonylphenol - 3			
assigned value [µg/l]*			0,4025	± 0,0218	
upper tolerance limit [µg/l]			0,6358		
lower tolerance limit [µg/l]			0,2206		
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.
1	0,537	0,107	2,5	1,2	+
4	0,375			-0,3	+
6	0,341			-0,7	+
10	0,149			-2,8	-
12	0,125			-3,1	-
14	0,453			0,4	+
15	0,406	0,02	0,2	0,0	+
16	0,32			-0,9	+
17	0,549	0,055	5,0	1,3	+
18	0,648			2,1	-
19	0,723	0,144	4,4	2,7	-
21	0,518	0,05	4,2	1,0	+
23	0,681	0,01	23,2	2,4	-
24	0,31			-1,0	+
26	0,505			0,9	+
28	0,337			-0,7	+
29	0,413	0,083	0,2	0,1	+
30	0,739	0,271	2,5	2,9	-
31	0,41			0,1	+
33	0,502	0,2	1,0	0,9	+
34	0,387			-0,2	+
35	0,3			-1,1	+
37	0,743			2,9	-
38	0,251			-1,7	+
40	0,79			3,3	-
41	0,44			0,3	+
42	0,359			-0,5	+
43	0,25			-1,7	+
44	0,359			-0,5	+
45	0,4202			0,2	+
46	0,299	0,049	-3,9	-1,1	+
47	0,382	0,153	-0,3	-0,2	+

* 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%


Nonylphenol - 3
concentration in µg/l
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
12 10 43 38 46 35 24 16 28 6 42 44 4 47 34 15 31 29 45 41 14 33 26 21 1 17 18 23 19 30 37 40
lab code

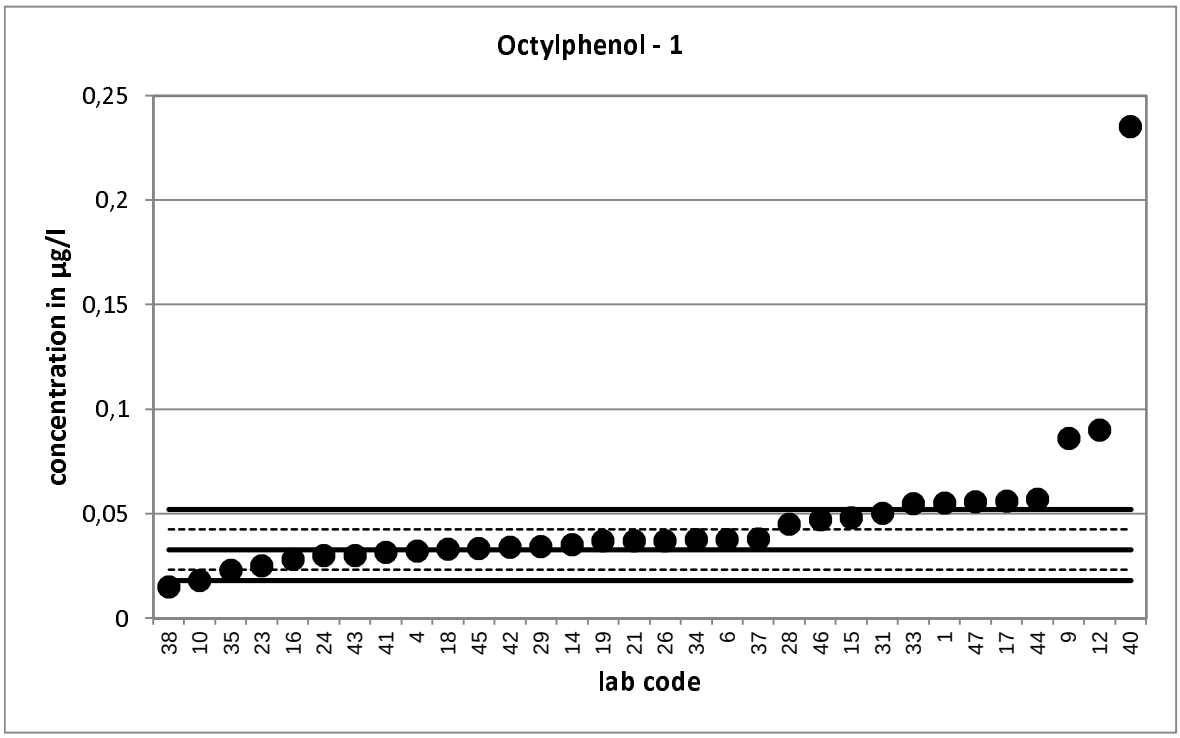

Nonylphenol - 3
z_U-score
4
3
2
1
0
-1
-2
-3
-4
12 10 43 38 46 35 24 16 28 6 42 44 4 47 34 15 31 29 45 41 14 33 26 21 1 17 18 23 19 30 37 40
lab code

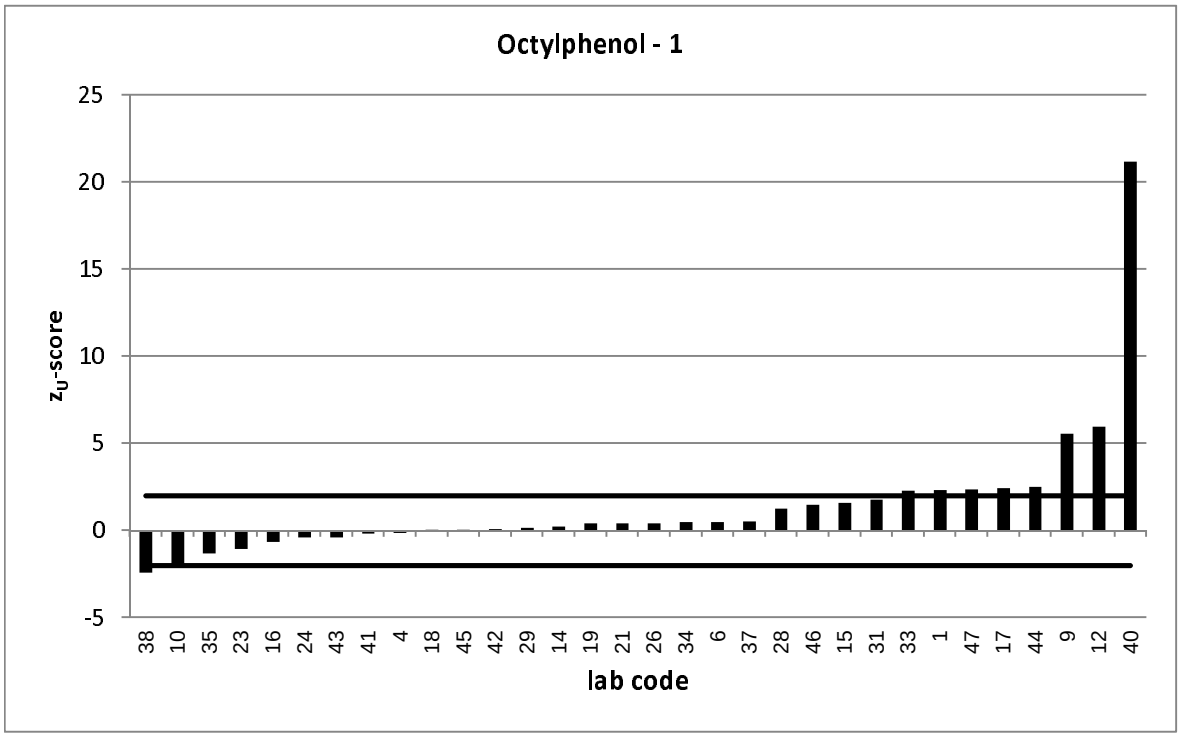

Nonylphenol - 3
expanded uncertainty in µg/l
0,3
0,25
0,2
0,15
0,1
0,05
0
23
15
46
21
17
29
1
19
47
33
30
lab code

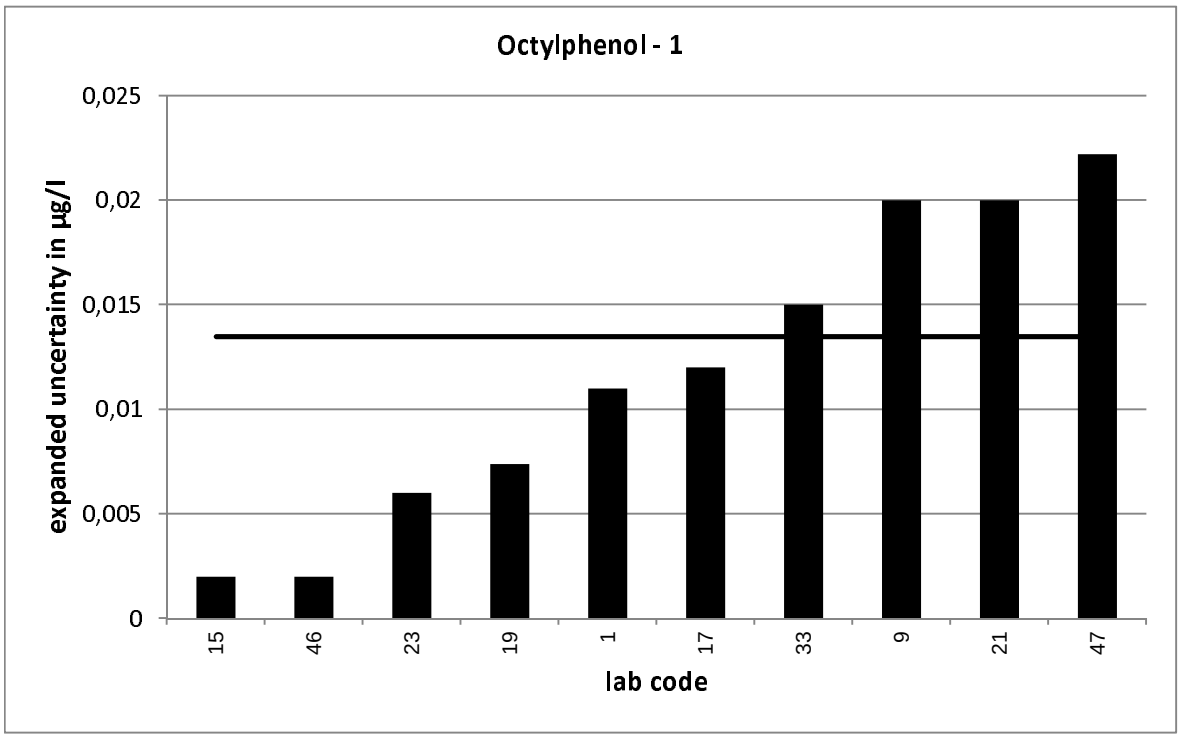

Nonylphenol - 3
ζ-Score
25
20
15
10
5
0
-5
-10
46
47
15
29
33
1
30
21
19
17
23
lab code

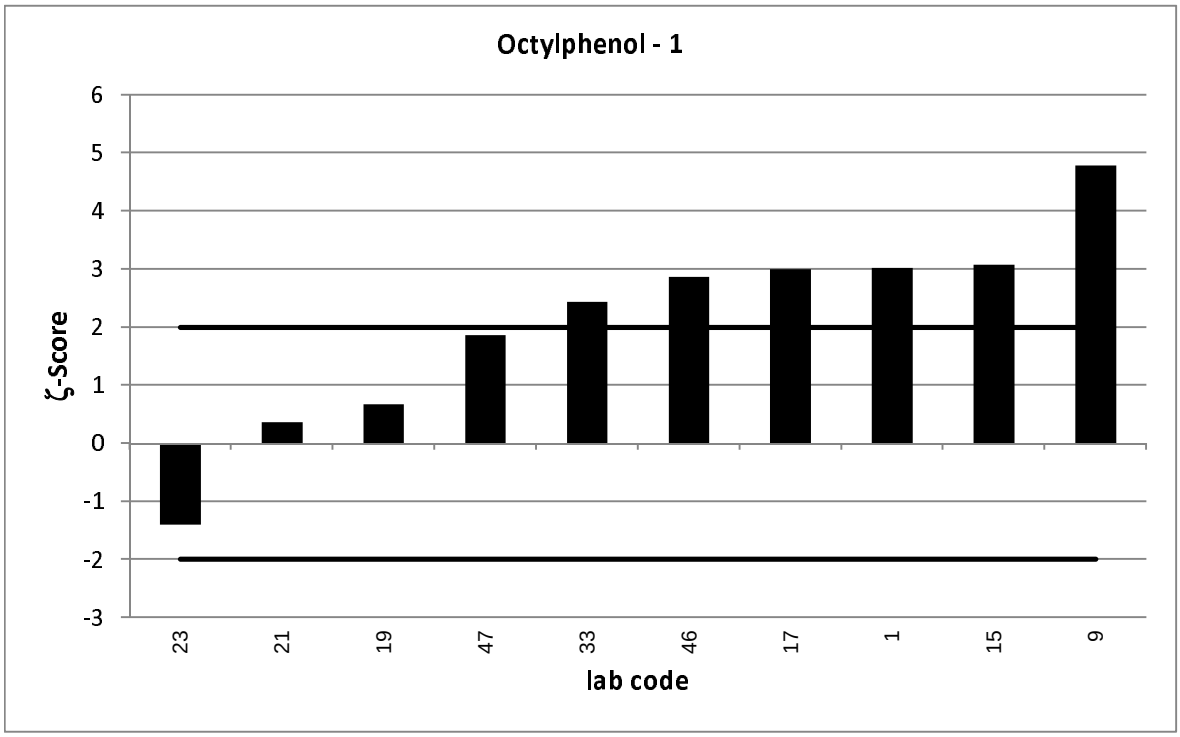
PT 2/14 - TW S3		Octylphenol - 1			
assigned value [µg/l]*			0,03294	± 0,00959	
upper tolerance limit [µg/l]			0,05204		
lower tolerance limit [µg/l]			0,01805		
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.
1	0,055	0,011	3,0	2,3	-
4	0,032			-0,1	+
6	0,0376			0,5	+
9	0,086	0,02	4,8	5,6	-
10	0,018			-2,0	+
12	0,09			6,0	-
14	0,035			0,2	+
15	0,048	0,002	3,1	1,6	+
16	0,028			-0,7	+
17	0,056	0,012	3,0	2,4	-
18	0,033			0,0	+
19	0,037	0,007	0,7	0,4	+
21	0,037	0,02	0,4	0,4	+
23	0,025	0,006	-1,4	-1,1	+
24	0,03			-0,4	+
26	0,037			0,4	+
28	0,045			1,3	+
29	0,0343			0,1	+
31	0,05			1,8	+
33	0,0546	0,015	2,4	2,3	-
34	0,0375			0,5	+
35	0,023			-1,3	+
37	0,038			0,5	+
38	0,015			-2,4	-
40	0,235			21,2	-
41	0,0316			-0,2	+
42	0,0338			0,1	+
43	0,03			-0,4	+
44	0,057			2,5	-
45	0,0332			0,0	+
46	0,047	0,002	2,9	1,5	+
47	0,0555	0,022	1,9	2,4	-

* 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%


Octylphenol - 1
concentration in µg/l
0,25
0,2
0,15
0,1
0,05
0
38 10 35 23 16 24 43 41 4 18 45 42 29 14 19 21 26 34 6 37 28 46 15 31 33 1 47 17 44 9 12 40
lab code

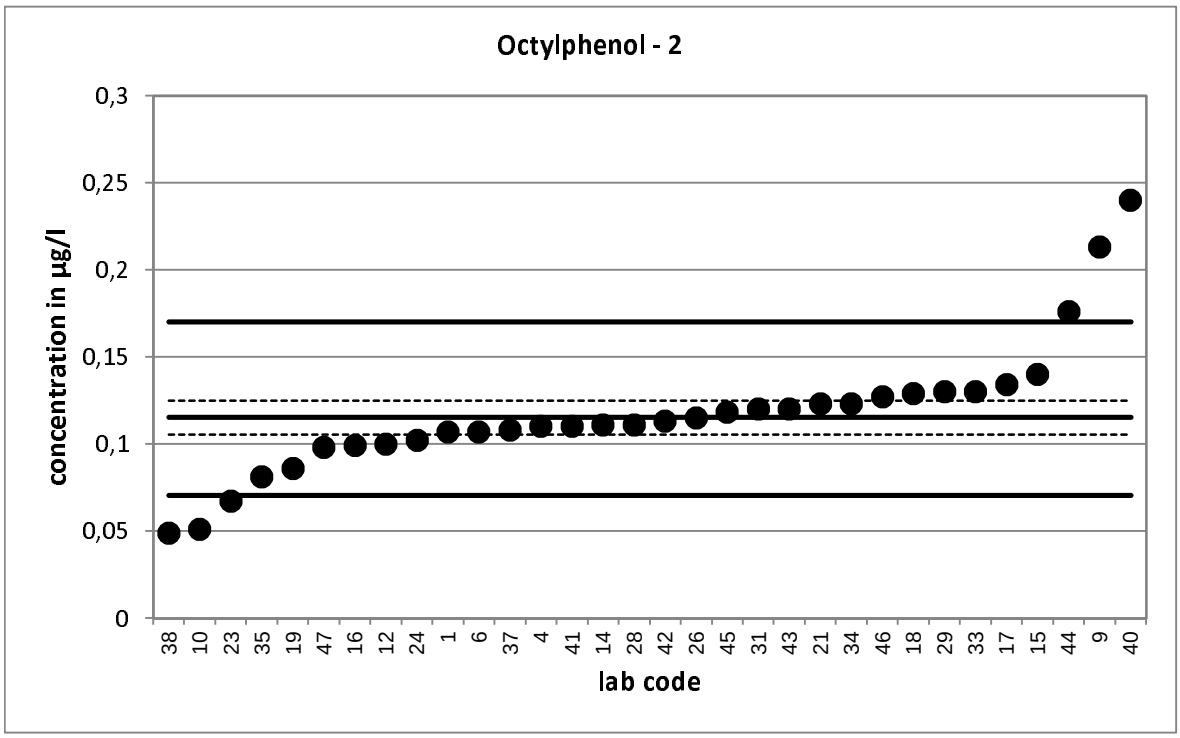

Octylphenol - 1
z_U-score
25
20
15
10
5
0
-5
38 10 35 23 16 24 43 41 4 18 45 42 29 14 19 21 26 34 6 37 28 46 15 31 33 1 47 17 44 9 12 40
lab code

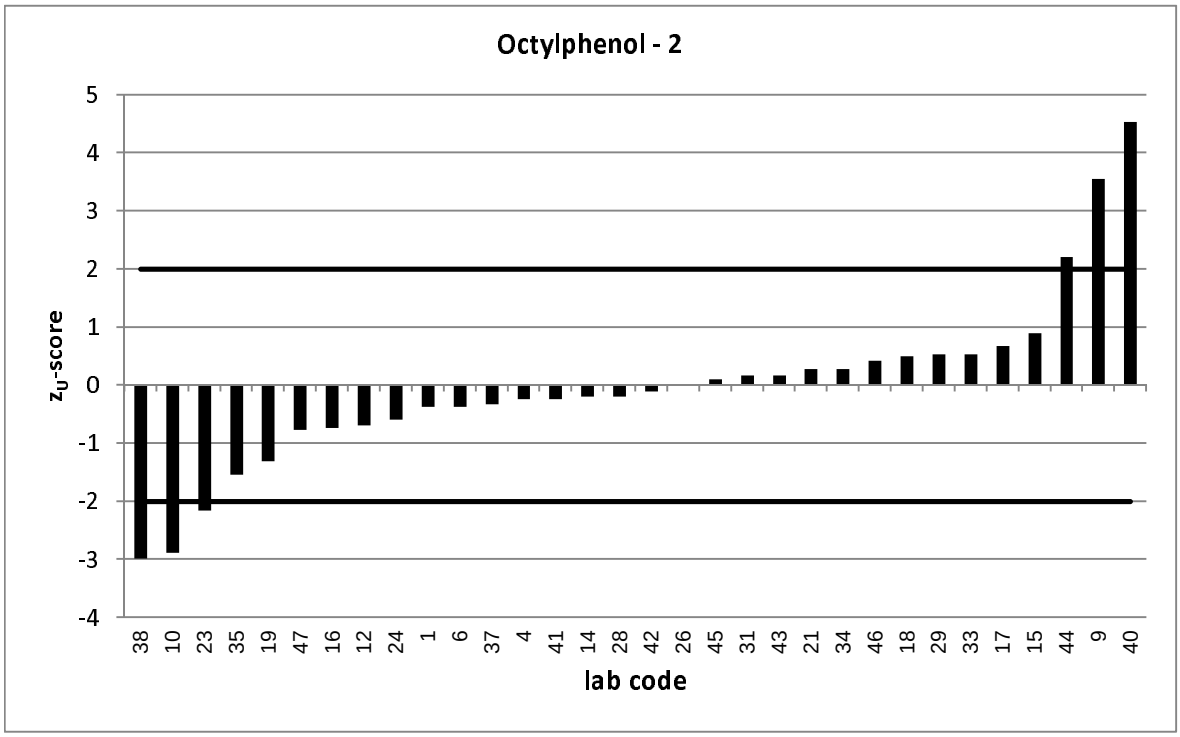

Octylphenol - 1
expanded uncertainty in µg/l
0,025
0,02
0,015
0,01
0,005
0
15
46
23
19
1
17
33
9
21
47
lab code

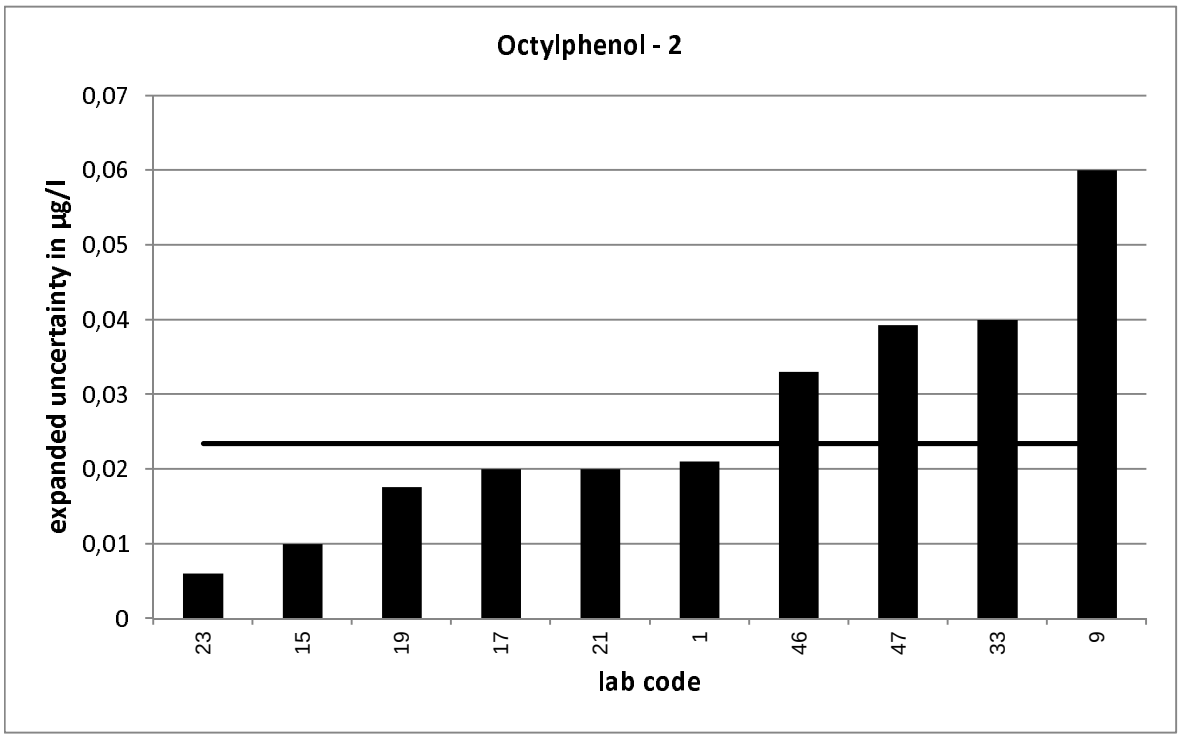

Octylphenol - 1
ζ-Score
6
5
4
3
2
1
0
-1
-2
-3
23
21
19
47
33
46
17
1
15
9
lab code

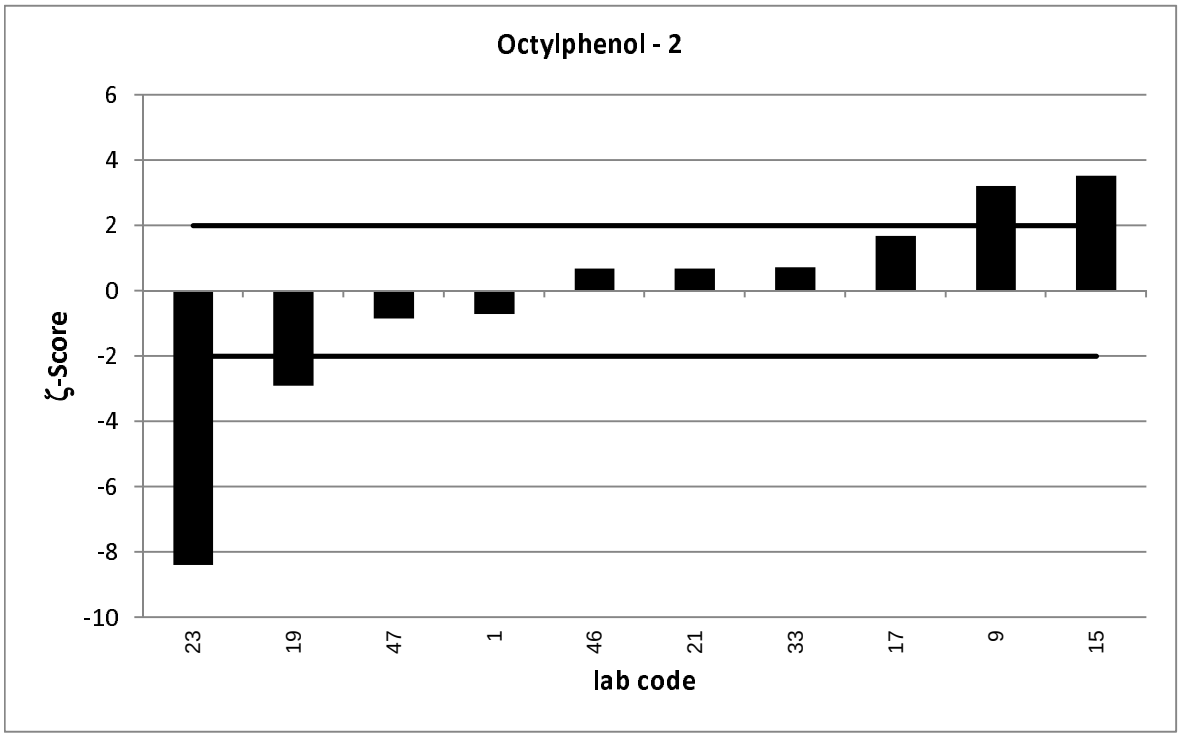
PT 2/14 - TW S3		Octylphenol - 2			
assigned value [µg/l]*			0,1153	± 0,0098	
upper tolerance limit [µg/l]			0,1703		
lower tolerance limit [µg/l]			0,07068		
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.
1	0,107	0,021	-0,7	-0,4	+
4	0,11			-0,2	+
6	0,107			-0,4	+
9	0,213	0,06	3,2	3,5	-
10	0,051			-2,9	-
12	0,1			-0,7	+
14	0,111			-0,2	+
15	0,14	0,01	3,5	0,9	+
16	0,099			-0,7	+
17	0,134	0,02	1,7	0,7	+
18	0,129			0,5	+
19	0,086	0,018	-2,9	-1,3	+
21	0,123	0,02	0,7	0,3	+
23	0,0671	0,006	-8,4	-2,2	-
24	0,102			-0,6	+
26	0,115			0,0	+
28	0,111			-0,2	+
29	0,13			0,5	+
31	0,12			0,2	+
33	0,13	0,04	0,7	0,5	+
34	0,123			0,3	+
35	0,081			-1,5	+
37	0,108			-0,3	+
38	0,0487			-3,0	-
40	0,24			4,5	-
41	0,11			-0,2	+
42	0,113			-0,1	+
43	0,12			0,2	+
44	0,176			2,2	-
45	0,1181			0,1	+
46	0,127	0,033	0,7	0,4	+
47	0,0981	0,039	-0,8	-0,8	+

* 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%


Octylphenol - 2
concentration in µg/l
0,3
0,25
0,2
0,15
0,1
0,05
0
38 10 23 35 19 47 16 12 24 1 6 37 4 41 14 28 42 26 45 31 43 21 34 46 18 29 33 17 15 44 9 40
lab code

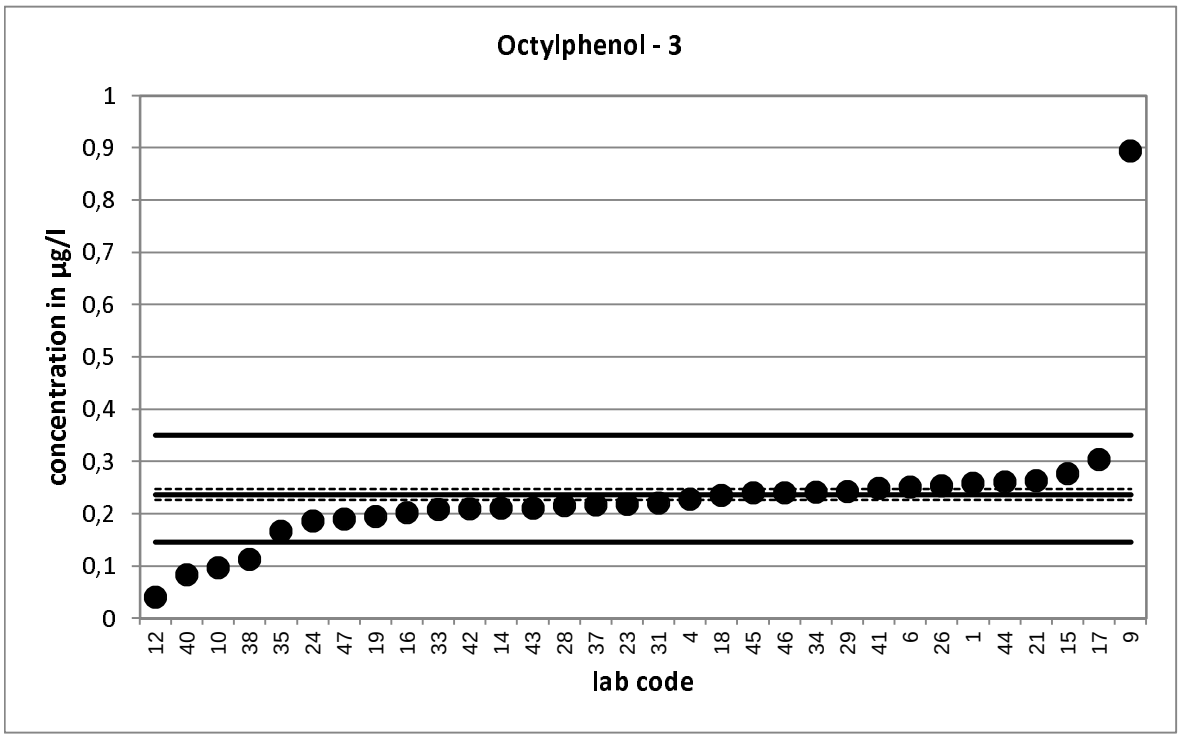

Octylphenol - 2
z_U-score
5
4
3
2
1
0
-1
-2
-3
-4
38 10 23 35 19 47 16 12 24 1 6 37 4 41 14 28 42 26 45 31 43 21 34 46 18 29 33 17 15 44 9 40
lab code

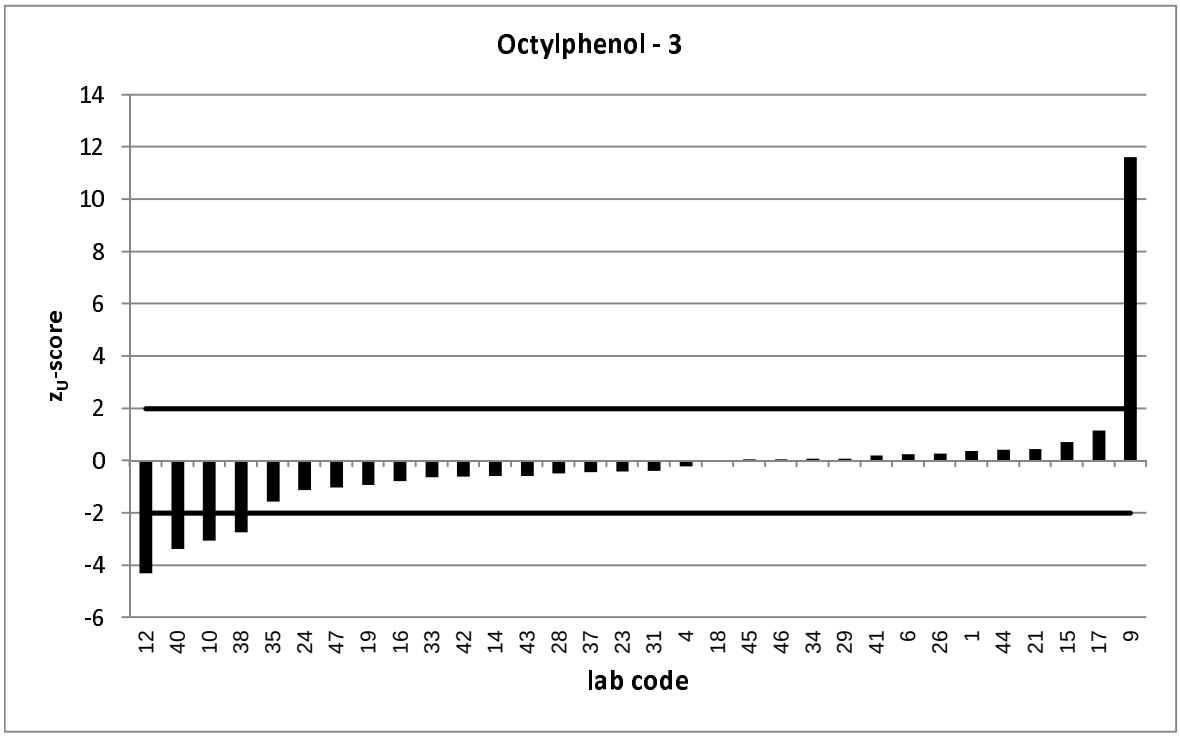

Octylphenol - 2
expanded uncertainty in µg/l
0,07
0,06
0,05
0,04
0,03
0,02
0,01
0
23
15
19
17
21
1
46
47
33
9
lab code

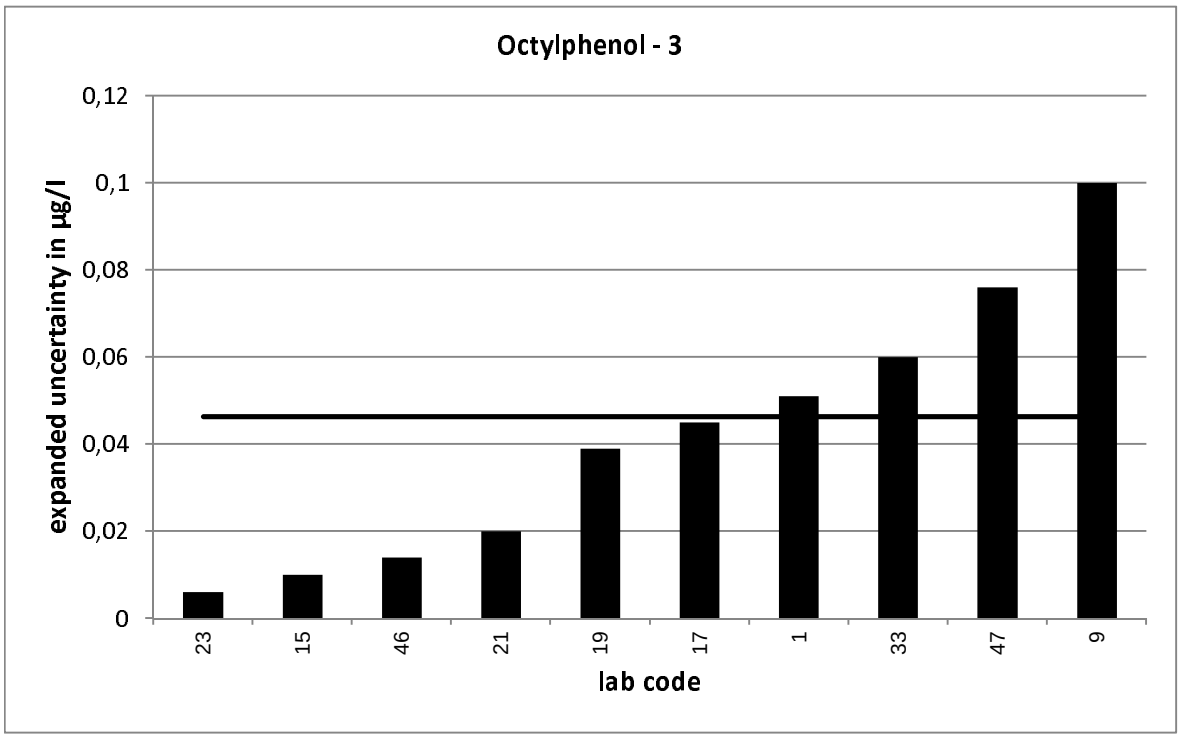

Octylphenol - 2
ζ-Score
6
4
2
0
-2
-4
-6
-8
-10
23
19
47
1
46
21
33
17
9
15
lab code

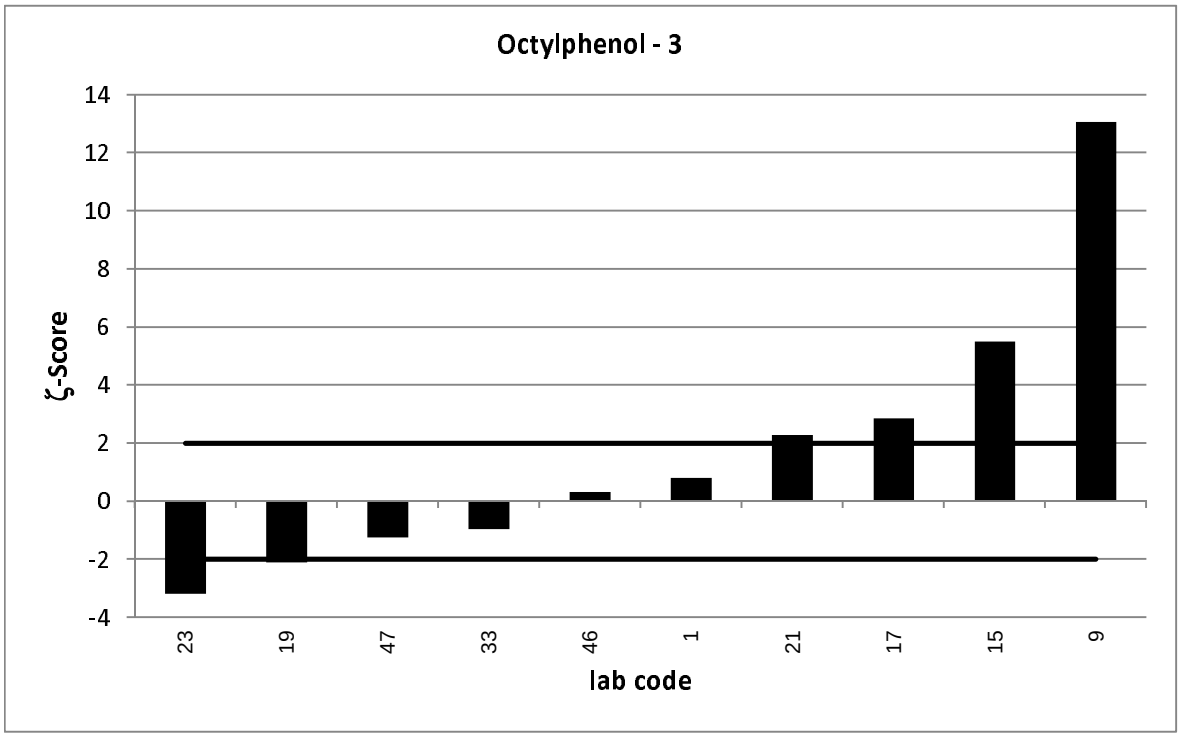
PT 2/14 - TW S3		Octylphenol - 3			
assigned value [µg/l]*			0,2372	± 0,0104	
upper tolerance limit [µg/l]			0,3502		
lower tolerance limit [µg/l]			0,1455		
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.
1	0,258	0,051	0,8	0,4	+
4	0,227			-0,2	+
6	0,251			0,2	+
9	0,894	0,1	13,1	11,6	-
10	0,097			-3,1	-
12	0,04			-4,3	-
14	0,21			-0,6	+
15	0,277	0,01	5,5	0,7	+
16	0,202			-0,8	+
17	0,303	0,045	2,9	1,2	+
18	0,235			0,0	+
19	0,195	0,039	-2,1	-0,9	+
21	0,263	0,02	2,3	0,5	+
23	0,218	0,006	-3,2	-0,4	+
24	0,186			-1,1	+
26	0,253			0,3	+
28	0,215			-0,5	+
29	0,242			0,1	+
31	0,22			-0,4	+
33	0,208	0,06	-1,0	-0,6	+
34	0,241			0,1	+
35	0,166			-1,6	+
37	0,217			-0,4	+
38	0,112			-2,7	-
40	0,083			-3,4	-
41	0,248			0,2	+
42	0,209			-0,6	+
43	0,21			-0,6	+
44	0,261			0,4	+
45	0,2399			0,0	+
46	0,24	0,014	0,3	0,1	+
47	0,19	0,076	-1,2	-1,0	+

* 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%


Octylphenol - 3
concentration in µg/l
1
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
12 40 10 38 35 24 47 19 16 33 42 14 43 28 37 23 31 4 18 45 46 34 29 41 6 26 1 44 21 15 17 9
lab code

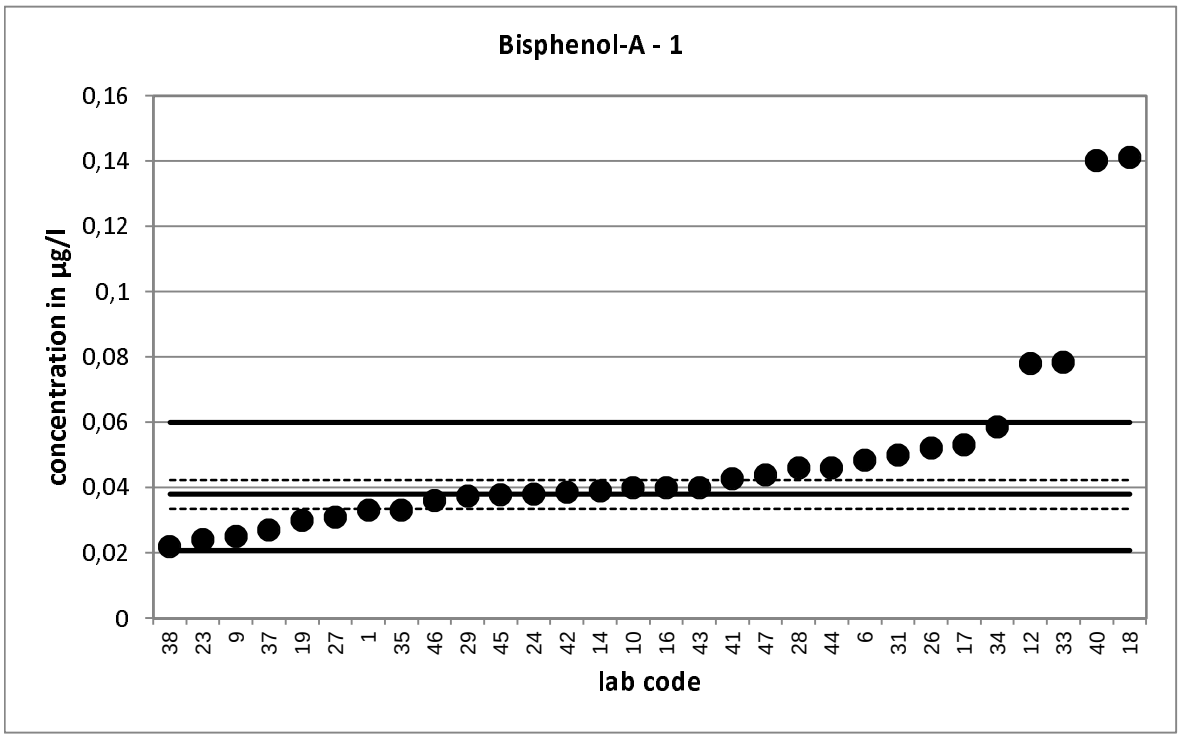

Octylphenol - 3
z_U-score
14
12
10
8
6
4
2
0
-2
-4
-6
12 40 10 38 35 24 47 19 16 33 42 14 43 28 37 23 31 4 18 45 46 34 29 41 6 26 1 44 21 15 17 9
lab code

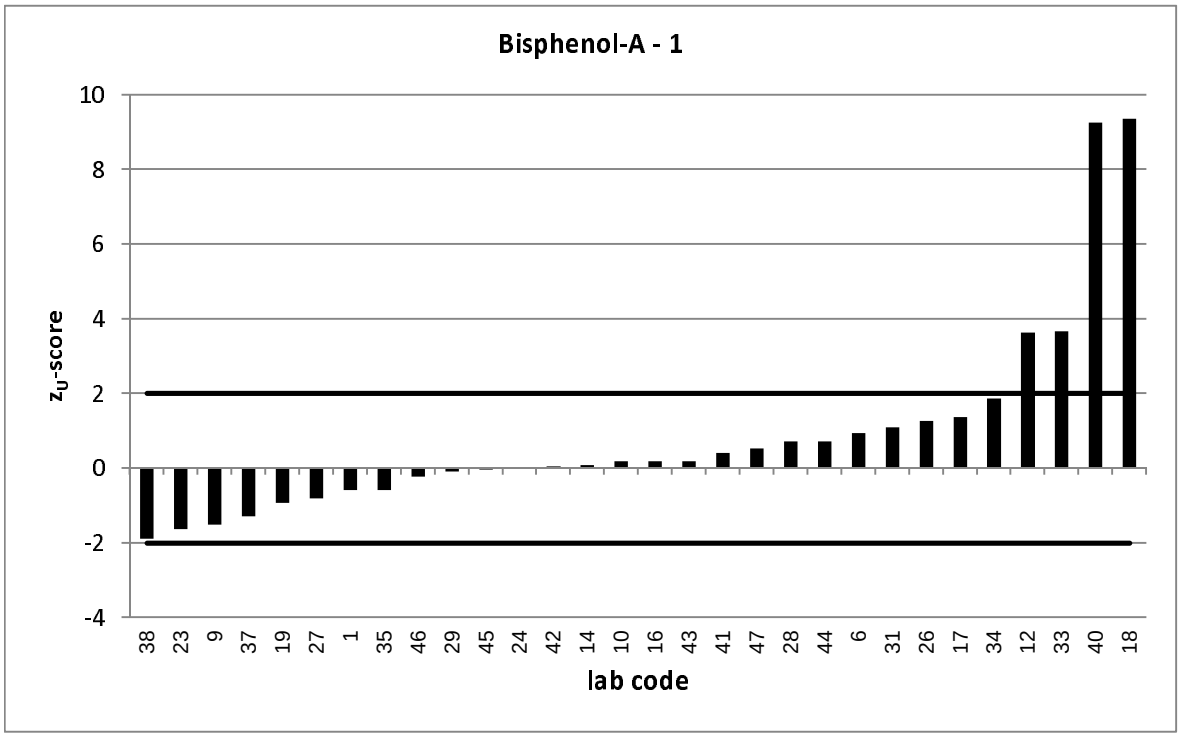

Octylphenol - 3
expanded uncertainty in µg/l
0,12
0,1
0,08
0,06
0,04
0,02
0
23
15
46
21
19
17
1
33
47
9
lab code

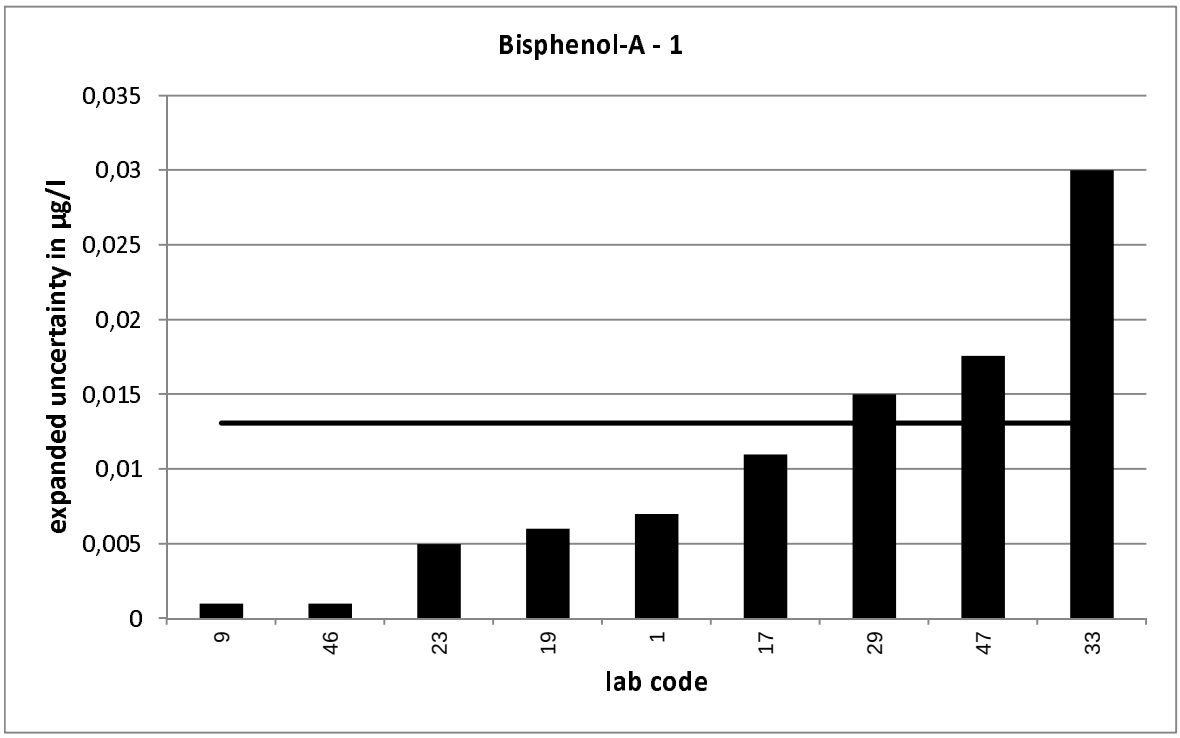

Octylphenol - 3
ζ-Score
14
12
10
8
6
4
2
0
-2
-4
23
19
47
33
46
1
21
17
15
9
lab code

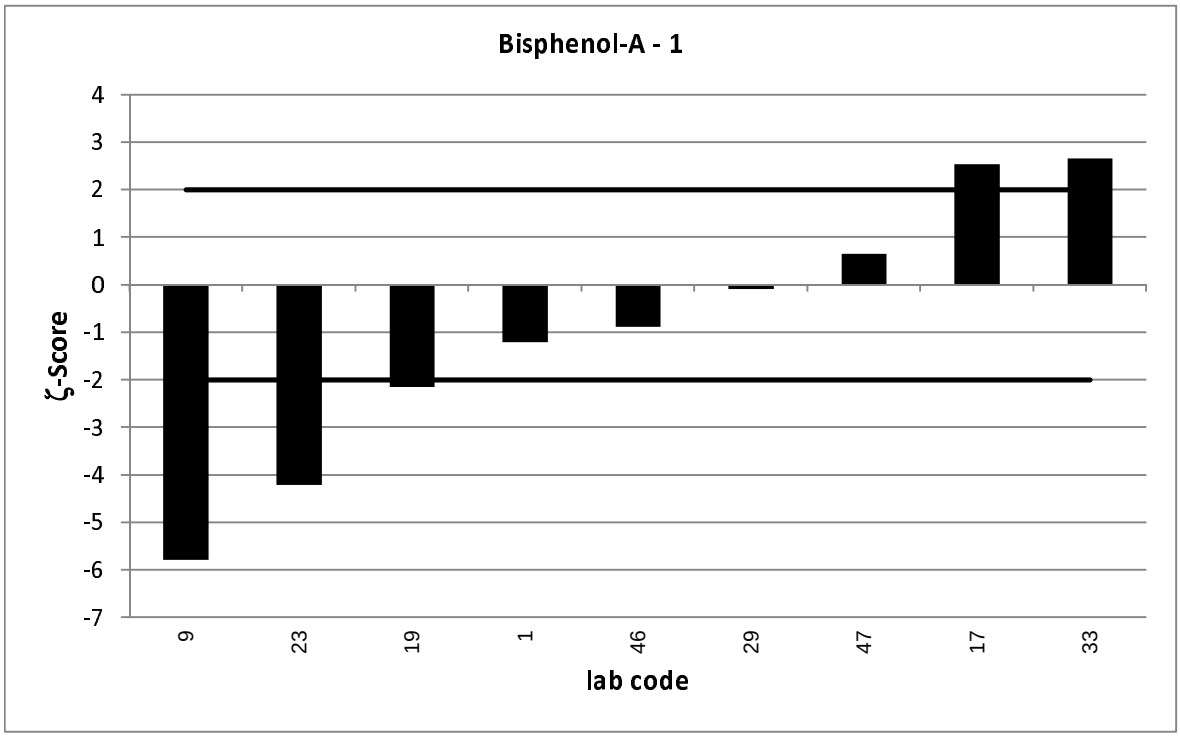
PT 2/14 - TW S3		Bisphenol-A - 1			
assigned value [µg/l]*			0,03799	± 0,00438	
upper tolerance limit [µg/l]			0,06002		
lower tolerance limit [µg/l]			0,02082		
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.
1	0,033	0,007	-1,2	-0,6	+
6	0,0484			0,9	+
9	0,025	0,001	-5,8	-1,5	+
10	0,04			0,2	+
12	0,078			3,6	-
14	0,039			0,1	+
16	0,04			0,2	+
17	0,053	0,011	2,5	1,4	+
18	0,141			9,4	-
19	0,03	0,006	-2,2	-0,9	+
23	0,024	0,005	-4,2	-1,6	+
24	0,038			0,0	+
26	0,052			1,3	+
27	0,031			-0,8	+
28	0,046			0,7	+
29	0,0373	0,015	-0,1	-0,1	+
31	0,05			1,1	+
33	0,0783	0,03	2,7	3,7	-
34	0,0585			1,9	+
35	0,033			-0,6	+
37	0,027			-1,3	+
38	0,0218			-1,9	+
40	0,14			9,3	-
41	0,0426			0,4	+
42	0,0385			0,0	+
43	0,04			0,2	+
44	0,046			0,7	+
45	0,0377			0,0	+
46	0,036	0,001	-0,9	-0,2	+
47	0,0439	0,018	0,7	0,5	+

* 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%


Bisphenol-A - 1
concentration in µg/l
0,16
0,14
0,12
0,1
0,08
0,06
0,04
0,02
0
38 23 9 37 19 27 1 35 46 29 45 24 42 14 10 16 43 41 47 28 44 6 31 26 17 34 12 33 40 18
lab code

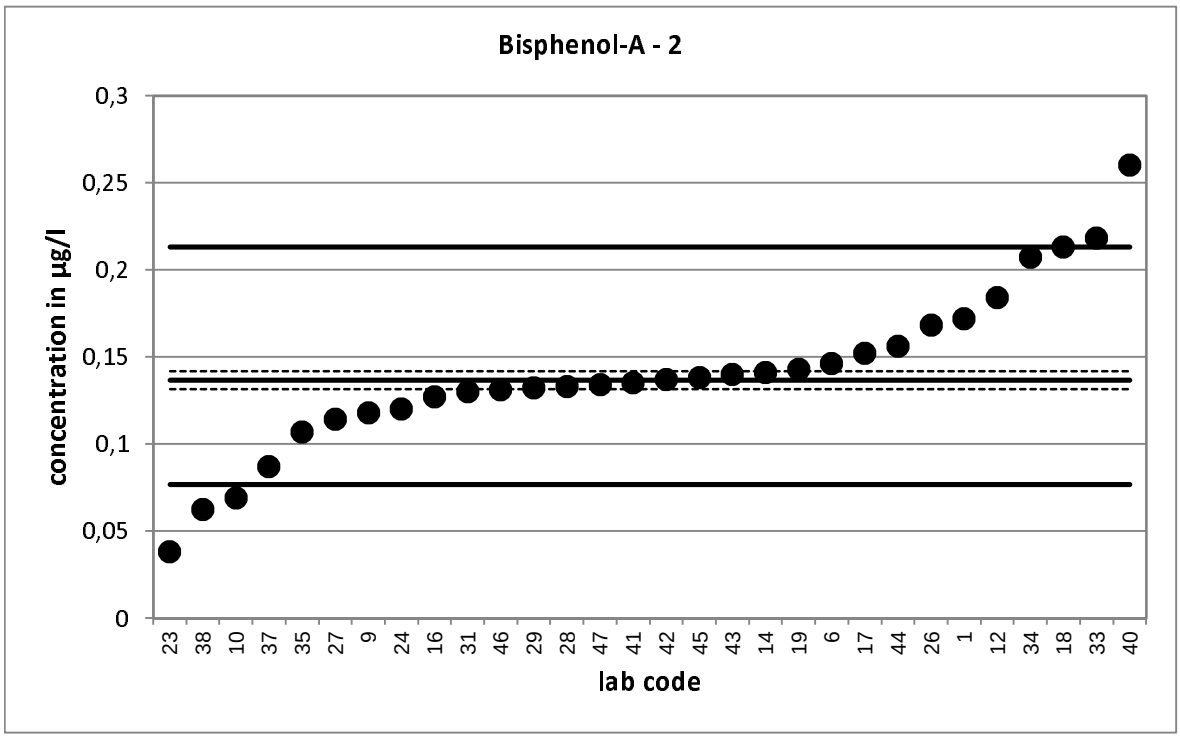

Bisphenol-A - 1
z_U-score
10
8
6
4
2
0
-2
-4
38 23 9 37 19 27 1 35 46 29 45 24 42 14 10 16 43 41 47 28 44 6 31 26 17 34 12 33 40 18
lab code

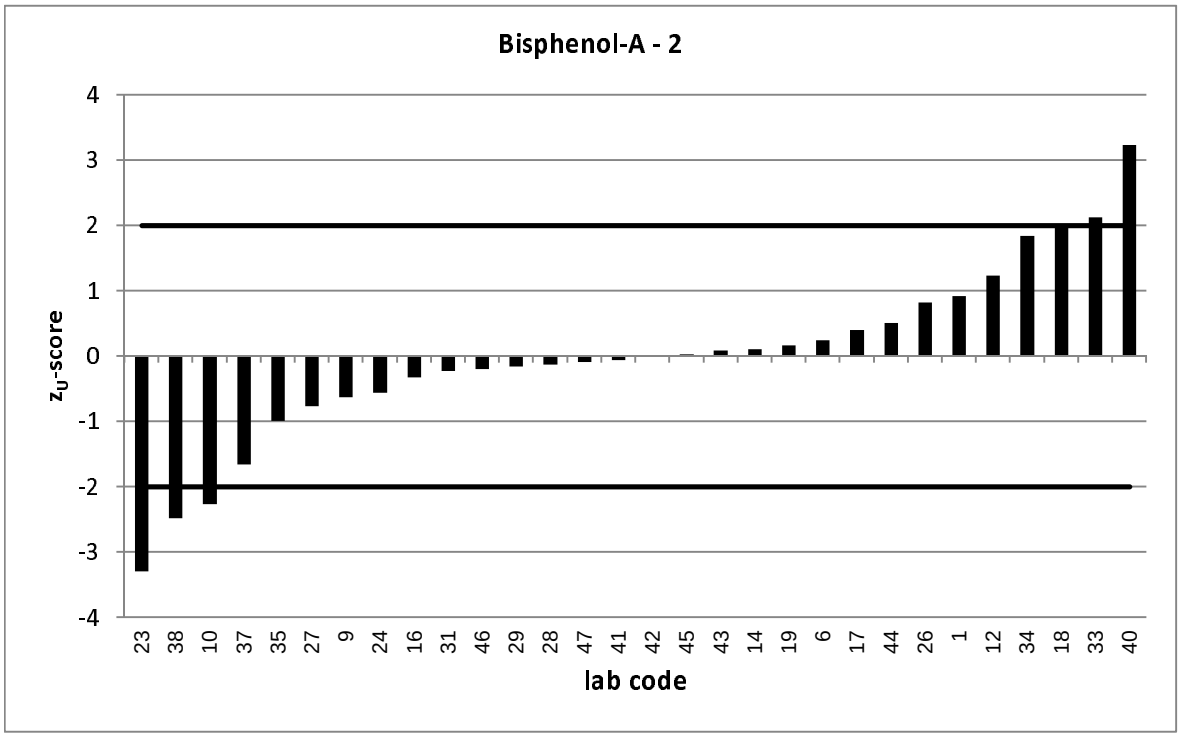

Bisphenol-A - 1
expanded uncertainty in µg/l
0,035
0,03
0,025
0,02
0,015
0,01
0,005
0
9
46
23
19
1
17
29
47
33
lab code

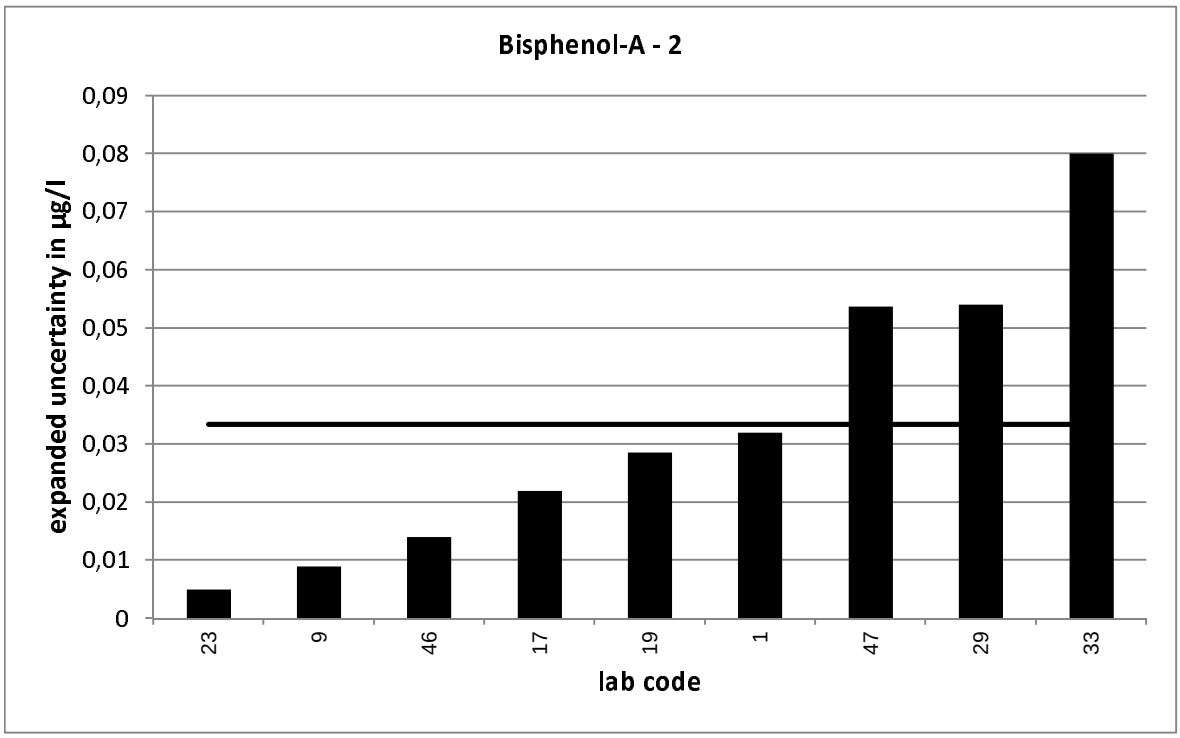

Bisphenol-A - 1
ζ-Score
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
9
23
19
1
46
29
47
17
33
lab code

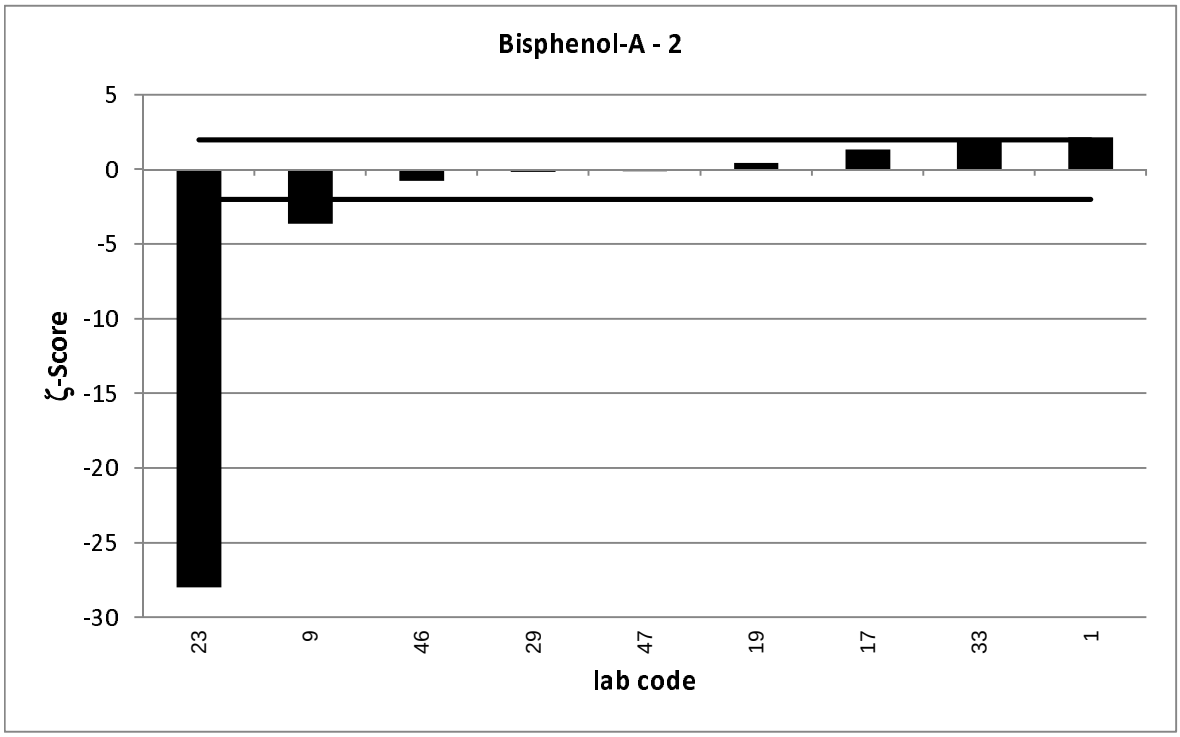
PT 2/14 - TW S3		Bisphenol-A - 2			
assigned value [µg/l]*			0,1368	± 0,005	
upper tolerance limit [µg/l]			0,213		
lower tolerance limit [µg/l]			0,07683		
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.
1	0,172	0,032	2,2	0,9	+
6	0,146			0,2	+
9	0,118	0,009	-3,6	-0,6	+
10	0,069			-2,3	-
12	0,184			1,2	+
14	0,141			0,1	+
16	0,127			-0,3	+
17	0,152	0,022	1,4	0,4	+
18	0,213			2,0	+
19	0,143	0,029	0,4	0,2	+
23	0,038	0,005	-28,0	-3,3	-
24	0,12			-0,6	+
26	0,168			0,8	+
27	0,114			-0,8	+
28	0,133			-0,1	+
29	0,132	0,054	-0,2	-0,2	+
31	0,13			-0,2	+
33	0,218	0,08	2,0	2,1	-
34	0,207			1,8	+
35	0,107			-1,0	+
37	0,087			-1,7	+
38	0,0625			-2,5	-
40	0,26			3,2	-
41	0,135			-0,1	+
42	0,137			0,0	+
43	0,14			0,1	+
44	0,156			0,5	+
45	0,1379			0,0	+
46	0,131	0,014	-0,8	-0,2	+
47	0,134	0,054	-0,1	-0,1	+

* 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%


Bisphenol-A - 2
concentration in µg/l
0,3
0,25
0,2
0,15
0,1
0,05
0
23 38 10 37 35 27 9 24 16 31 46 29 28 47 41 42 45 43 14 19 6 17 44 26 1 12 34 18 33 40
lab code

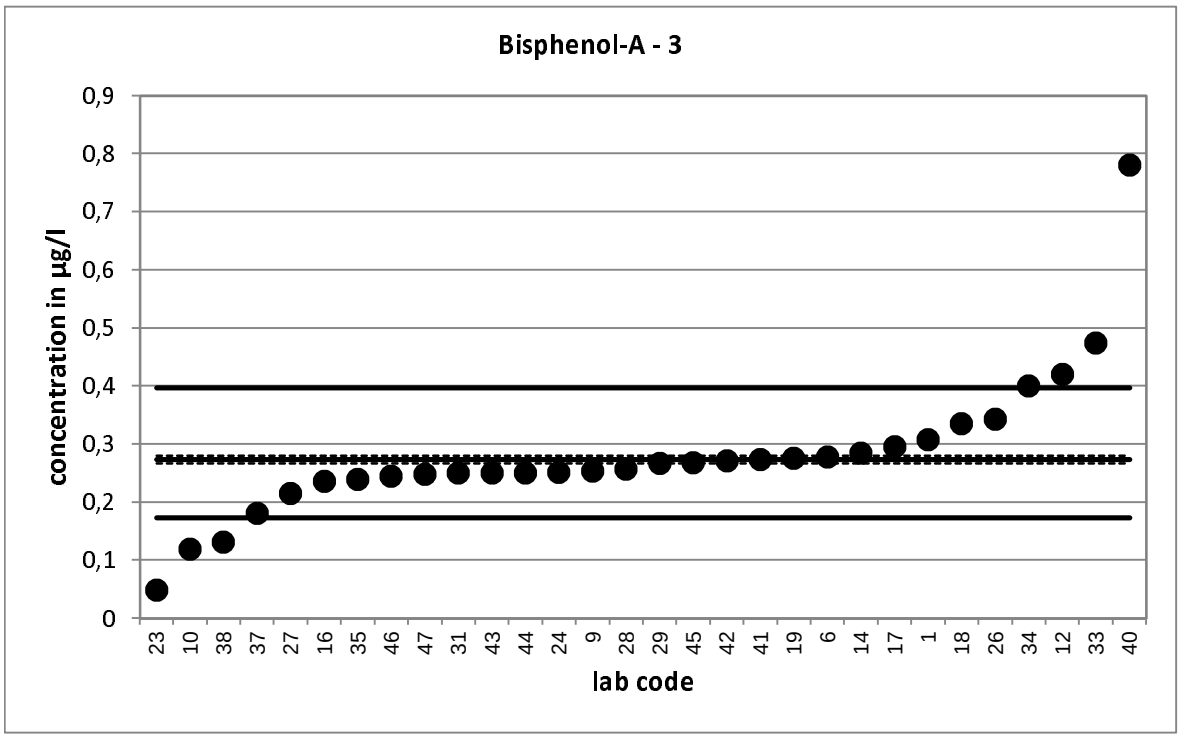

Bisphenol-A - 2
z_U-score
4
3
2
1
0
-1
-2
-3
-4
23 38 10 37 35 27 9 24 16 31 46 29 28 47 41 42 45 43 14 19 6 17 44 26 1 12 34 18 33 40
lab code

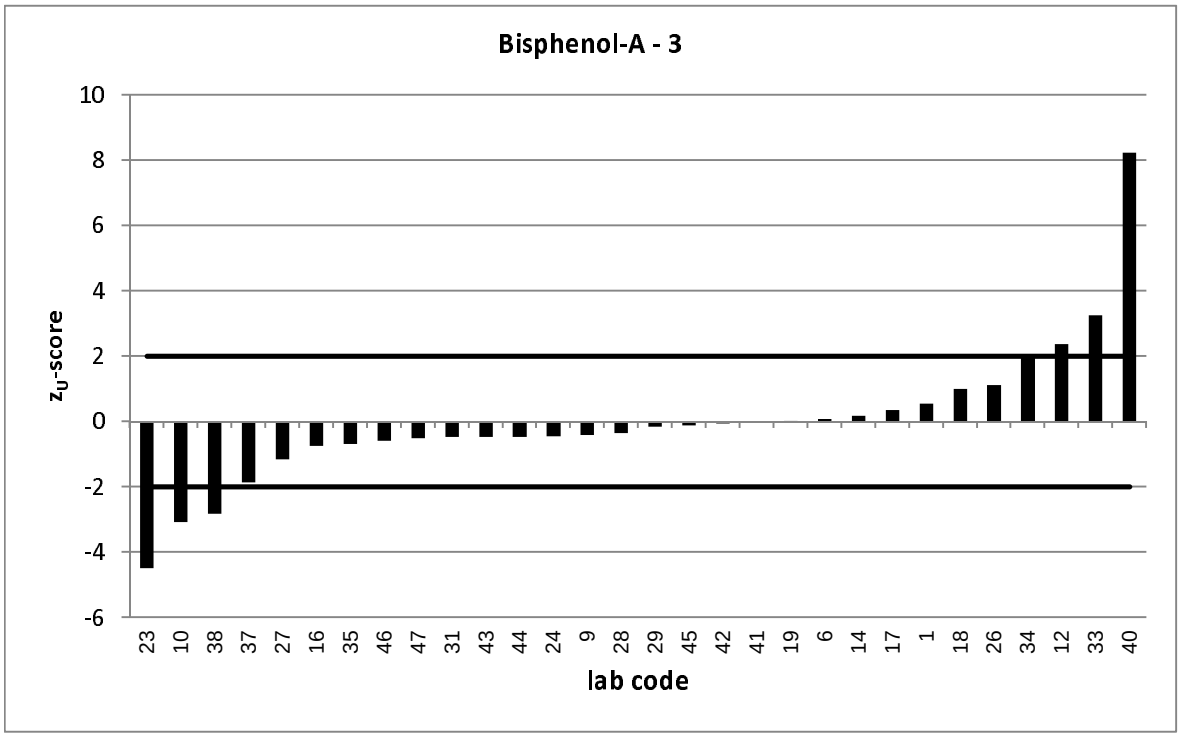

Bisphenol-A - 2
expanded uncertainty in µg/l
0,09
0,08
0,07
0,06
0,05
0,04
0,03
0,02
0,01
0
23
9
46
17
19
1
47
29
33
lab code

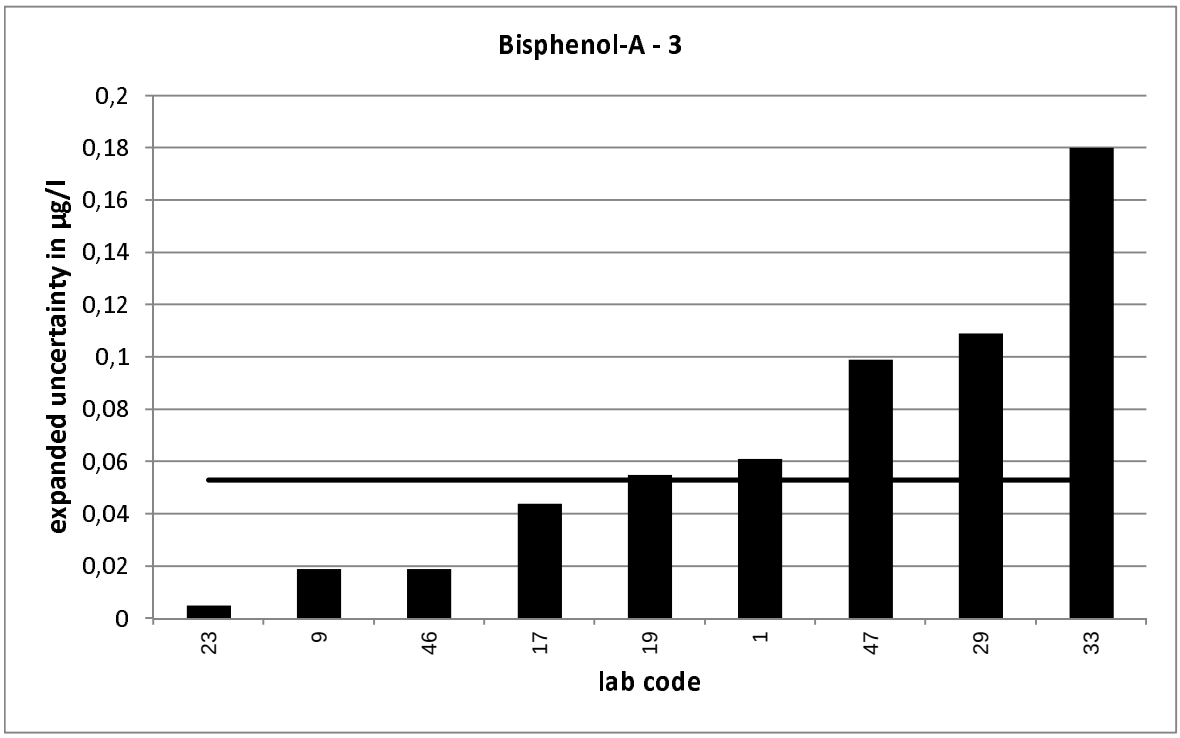

Bisphenol-A - 2
ζ-Score
5
0
-5
-10
-15
-20
-25
-30
23
9
46
29
47
19
17
33
1
lab code

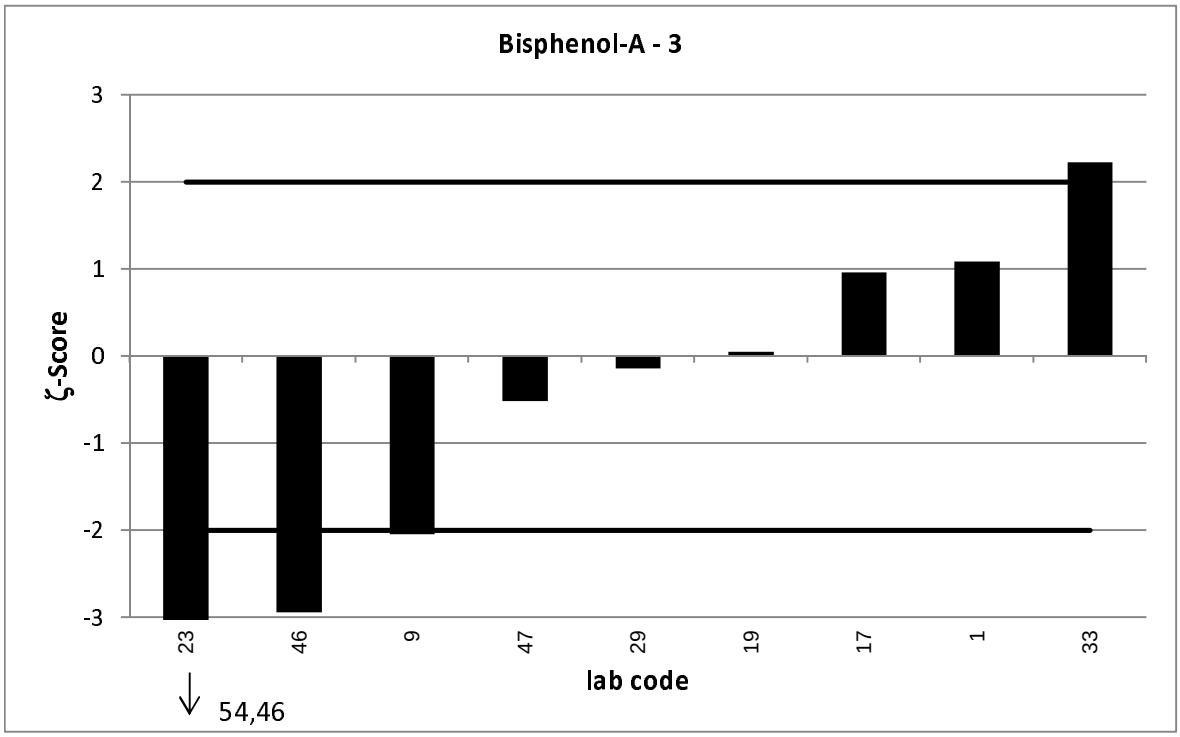
PT 2/14 - TW S3		Bisphenol-A - 3			
assigned value [µg/l]*			0,2735	± 0,0066	
upper tolerance limit [µg/l]			0,3965		
lower tolerance limit [µg/l]			0,1728		
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.
1	0,307	0,061	1,1	0,5	+
6	0,278			0,1	+
9	0,253	0,019	-2,0	-0,4	+
10	0,119			-3,1	-
12	0,42			2,4	-
14	0,284			0,2	+
16	0,236			-0,7	+
17	0,295	0,044	1,0	0,3	+
18	0,335			1,0	+
19	0,275	0,055	0,1	0,0	+
23	0,048	0,005	-54,5	-4,5	-
24	0,251			-0,4	+
26	0,342			1,1	+
27	0,215			-1,2	+
28	0,256			-0,3	+
29	0,266	0,109	-0,1	-0,1	+
31	0,25			-0,5	+
33	0,474	0,18	2,2	3,3	-
34	0,4			2,1	-
35	0,239			-0,7	+
37	0,18			-1,9	+
38	0,131			-2,8	-
40	0,78			8,2	-
41	0,273			0,0	+
42	0,271			-0,1	+
43	0,25			-0,5	+
44	0,25			-0,5	+
45	0,2673			-0,1	+
46	0,244	0,019	-2,9	-0,6	+
47	0,248	0,099	-0,5	-0,5	+

* 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%


Bisphenol-A - 3
concentration in µg/l
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
23 10 38 37 27 16 35 46 47 31 43 44 24 9 28 29 45 42 41 19 6 14 17 1 18 26 34 12 33 40
lab code


Bisphenol-A - 3
z_U-score
10
8
6
4
2
0
-2
-4
-6
23 10 38 37 27 16 35 46 47 31 43 44 24 9 28 29 45 42 41 19 6 14 17 1 18 26 34 12 33 40
lab code


Bisphenol-A - 3
expanded uncertainty in µg/l
0,2
0,18
0,16
0,14
0,12
0,1
0,08
0,06
0,04
0,02
0
23
9
46
17
19
1
47
29
33
lab code


Bisphenol-A - 3
ζ-Score
3
2
1
0
-1
-2
-3
23
46
9
47
29
19
17
1
33
lab code
54,46