University of Stuttgart
Germany

Analytische Qualitätssicherung Baden-Württemberg

Proficiency Test 5/18
- TW S7 – Trifluoroacetic acid in drinking water -
Trifluoroacetic acid (TFA)

Final report

provided by
AQS Baden-Württemberg at
Institute for Sanitary Engineering, Water Quality and Solid Waste Management,
University of Stuttgart
Bandtäle 2, 70569 Stuttgart-Büsnau, Germany

And
IWW Water Center
Moritzstr. 26, 45476 Mülheim an der Ruhr, Germany

Stuttgart, in September 2018

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Responsibilities:

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Release of the report:	Dr.-Ing. Michael Koch	on 05.09.18
Version of the report	1	

List of contents

1. 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).

The following parameter was offered:

- **Trifluoracetic acid (TFA); CAS-No.: 76-05-1**

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

2. PT design

Each participant received the following samples:

- 3 samples for the determination of TFA in 50-ml-plastic tubes.

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

3. Sample preparation

The samples for the determination of TFA 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.

4. Sample distribution

The samples were dispatched on 05 June 2018 by express service

5. Analytical methods

The participants were free to choose a suitable method, but a limit of quantification of 0.03 µg/l was required.

The participants were informed that the samples had to be analysed in the own laboratory, with own personal and own equipment. Subcontracting of the analysis was not allowed.

The participants were informed to cool the samples after receipt and to start with the analysis one day after receipt at the latest.

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

6. Submission of the results

The deadline for the submission of results was on 25 June 2018.

7. Basic principle of evaluation and assessment

The basic principle of the evaluation and assessment of the PTs from AQS Baden-Württemberg are described in the document „Evaluation of the PTs and information for the report“, which can be downloaded from www.aqsbw.de/pdf/ausw_berichte_v1_en.pdf.

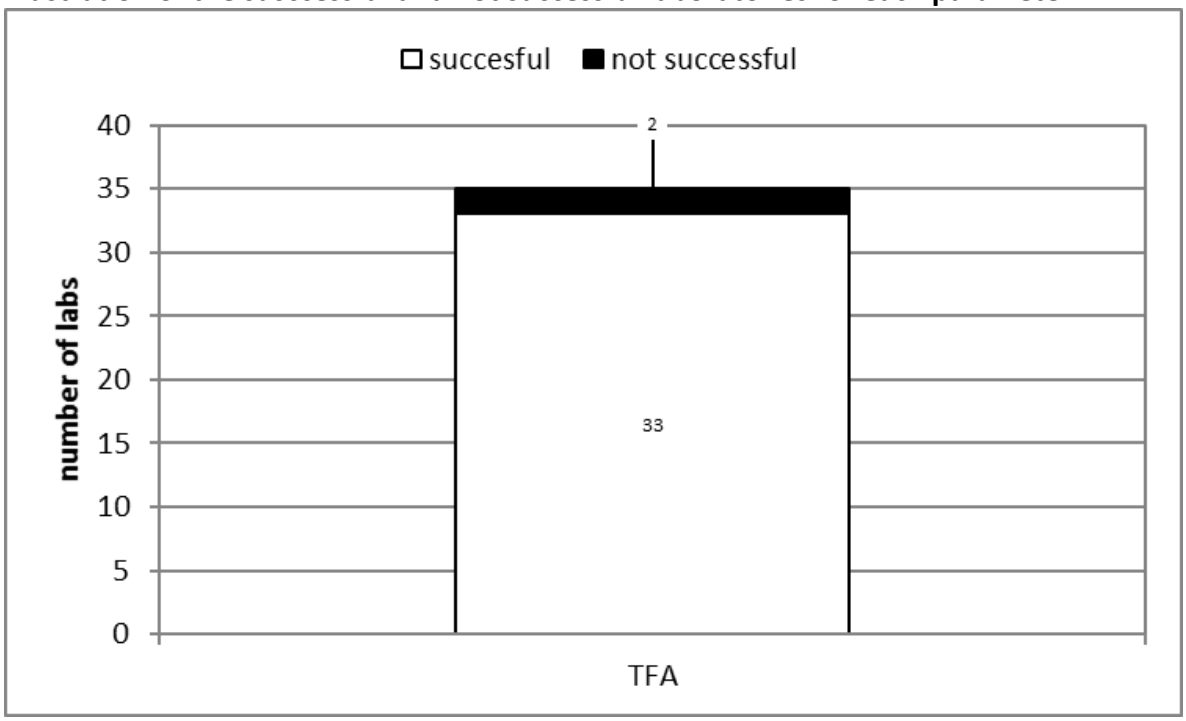
This PT was evaluated as follows:

Assigned value x_{pt}:	Reference value Consensus value (Hampel estimator)
Standard deviation for proficiency assessment σ_{pt}:	Q method
Upper limit of σ_{pt}:	25 %
Lower limit of σ_{pt}:	5 %
Assessment:	z_U-Score
Classification of the single results:	$\lvert z_u \rvert \leq 2.0$ successful $2.0 < \lvert z_u \rvert < 3.0$ questionable $\lvert z_u \rvert \geq 3.0$ unsatisfactory
Parameter assessment:	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).

8. Evaluation

Number of participants:	39 4 laboratories did not report any results
Number of reported values	105
Number of accepted values:	95 (90,5 %)

Illustration of the susccessful and not successful laboratories for each parameter



9. Explanation for the appendices

The explanations for the appendices can be found in the document „Evaluation of the PTs and information for the report“, which can be downloaded from www.aqsbw.de/pdf/ausw_berichte_v1_en.pdf.

10. Measurement uncertainty

General:

Number of labs with valid values	35
Number of labs with valid values and reported measurement uncertainties	16 (45,7 %)
Number of valid values	105
Number of valid values with measurement uncertainties	48 (45,7 %)

Measurement uncertainties against the accreditation status

Accreditation status of the values	Number of values	Number of values with measurement uncertainty
accredited	45	27 (60 %)
not accredited	45	21 (46,7 %)
not specified	15	0 (0 %)

Interpretation of the reported measurement uncertainties:
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.

Number of values with reported measurement uncertainty having a $|z_U| \leq 2,0$	43
Number of values with a magnitude of ζ-scores > 2 The own requirements of the laboratory are not fulfilled and the estimation of the measurement uncertainty is too low	6 (14 %)

11. Traceable reference values

The explanations about traceable reference values can be found in the document „Evaluation of the PTs and information for the report", which can be downloaded from www.aqsbw.de/pdf/ausw_berichte_v1_en.pdf

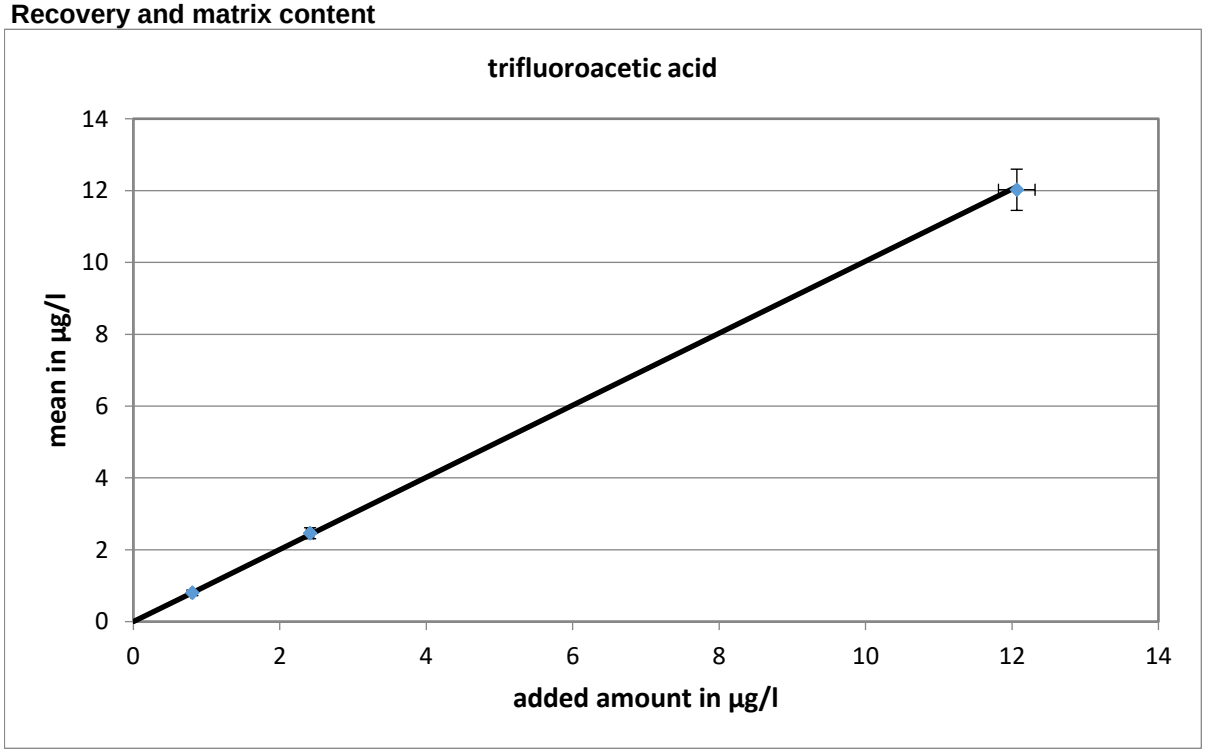
12. Internet

The report is available on the following webpage: http://www.aqsbw/pdf/report518.pdf

trifluoroacetic acid

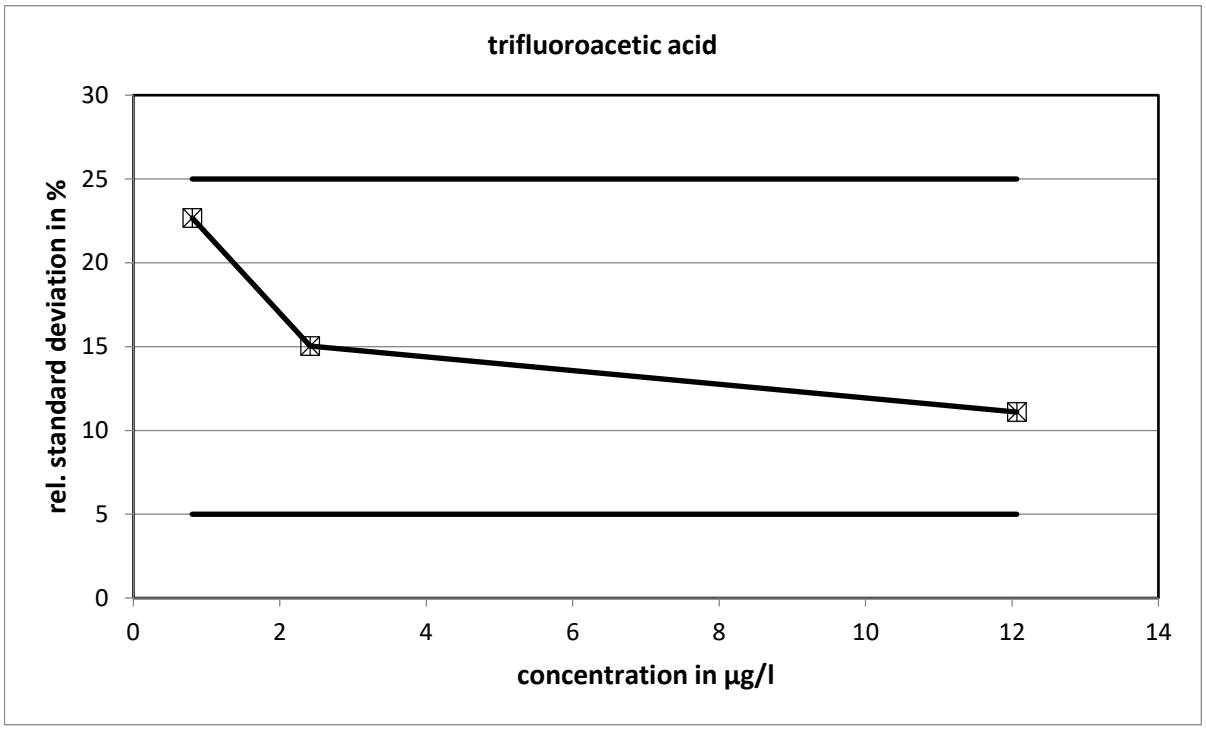
level	assigned value [µg/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [µg/l]	standard deviation for proficiency assessment [µg/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [µg/l]	lower tolerance limit [µg/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,8043	2,09	0,1824	0,1824	22,68	1,221	0,4723	51,81	-41,28	34	2	3	14,3
2	2,413	2,07	0,3626	0,3626	15,03	3,200	1,734	32,61	-28,15	35	1	2	8,6
3	12,06	2,07	1,339	1,339	11,10	14,91	9,520	23,57	-21,09	34	1	1	5,7
									sum	103	4	6	9,7

Recovery and matrix content

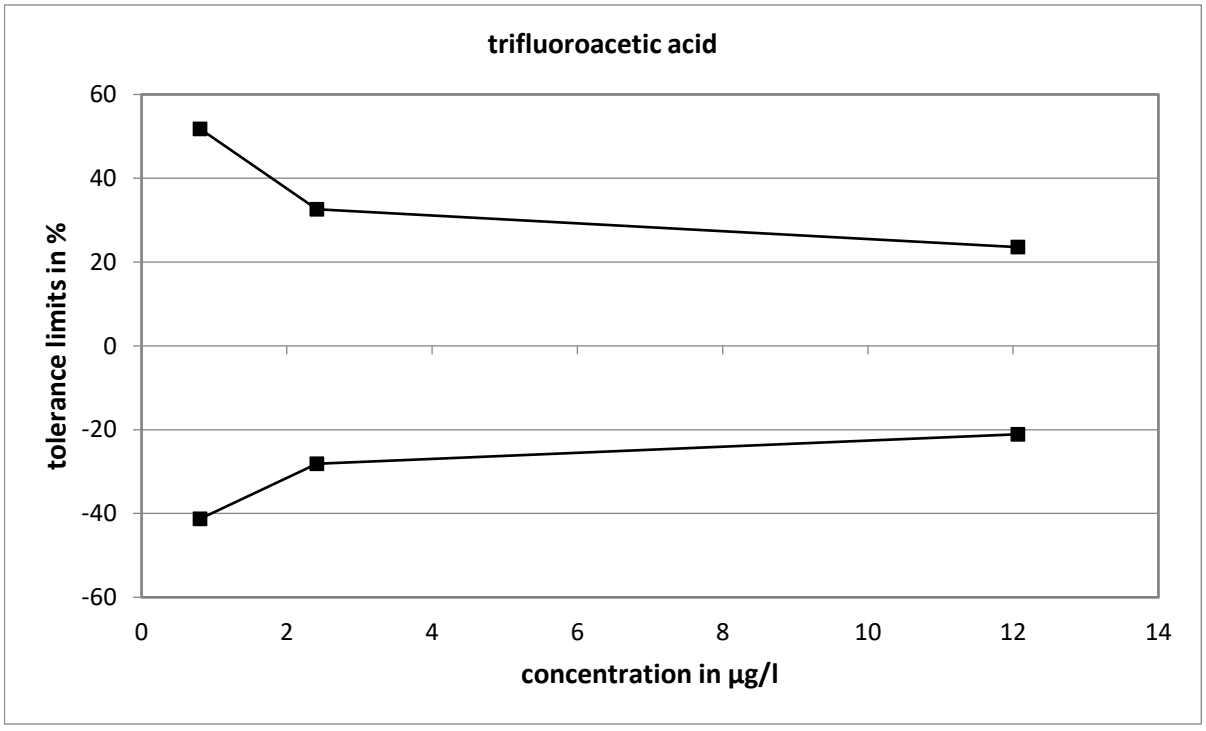


slope of the regression: 1,003; average recovery: 100,3 %

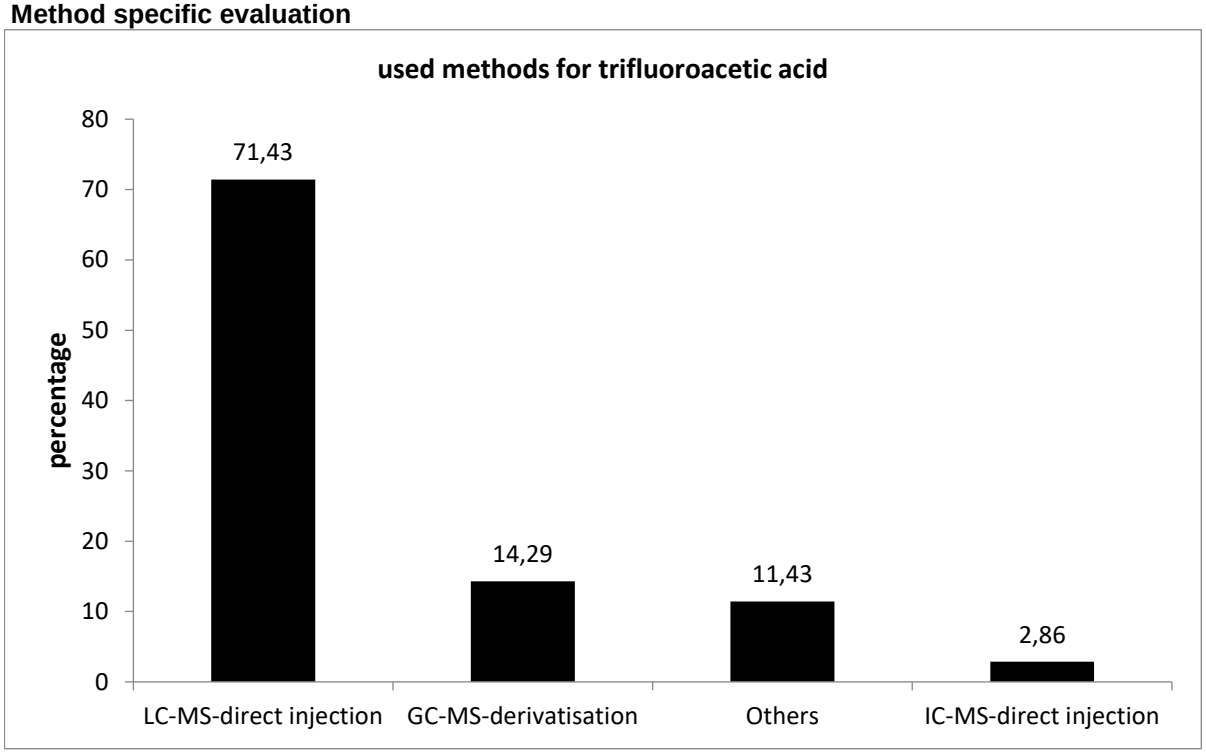
Relative standard deviation and tolerance limits

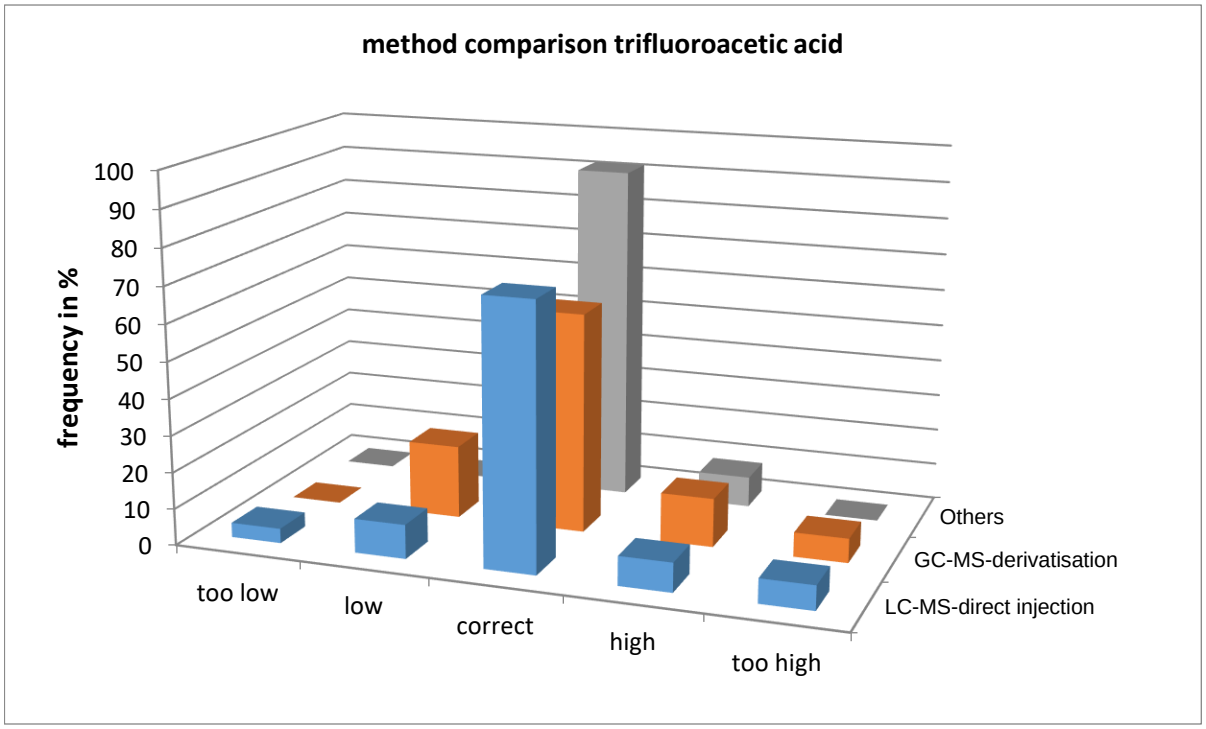


The relative standard deviations calculated with the Q-method did not reach the limits.



Method specific evaluation

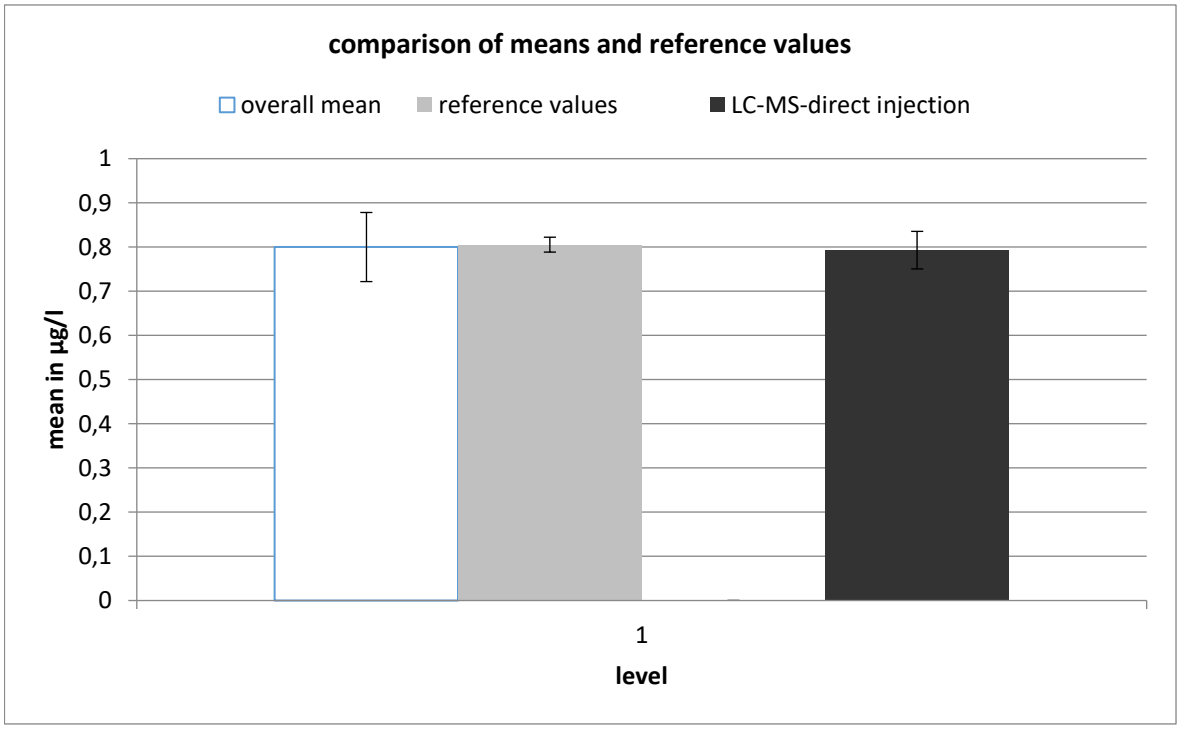


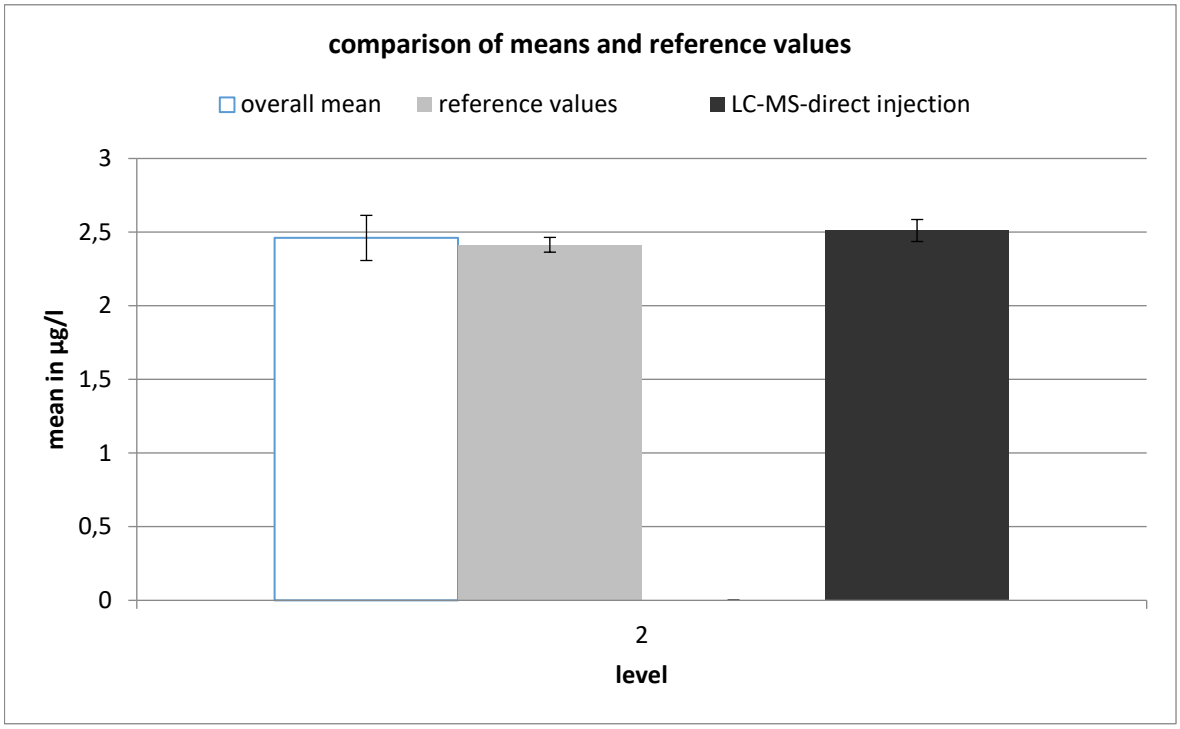


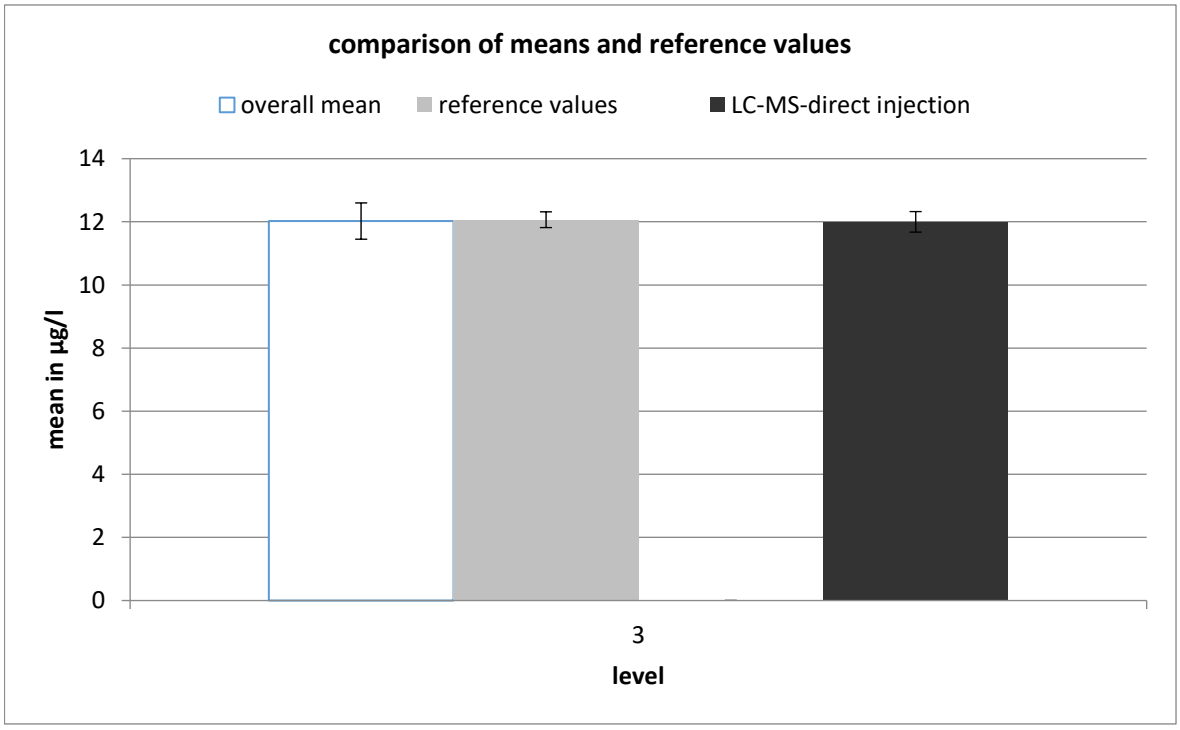
The values determined with GC-MS-derivatisation showed a slightly broader distribution.

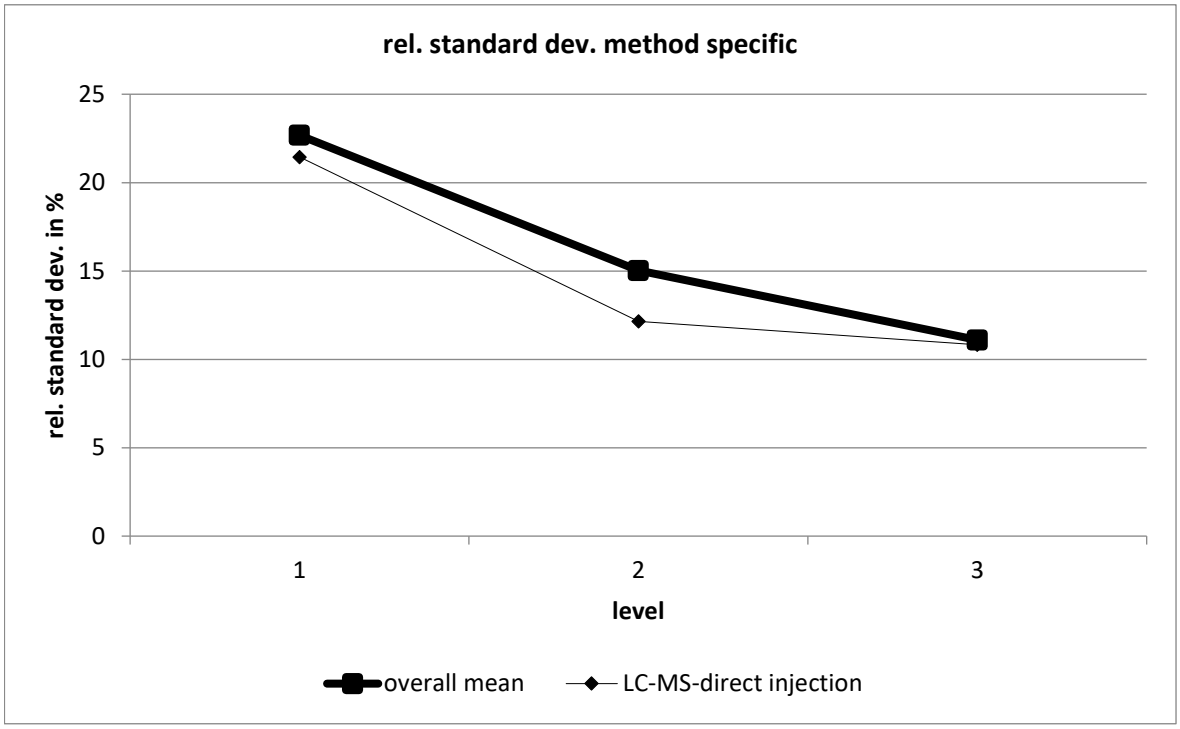
Comparison of means and reference values

level	mean [µg/l]	exp. uncertainty [µg/l]	exp. uncertainty [%]	reference value [µg/l]	exp. uncertainty [µg/l]	exp. uncertainty [%]
1	0,8000	0,0782	9,8	0,8054	0,0168	2,1
2	2,460	0,153	6,2	2,414	0,050	2,1
3	12,02	0,57	4,8	12,07	0,25	2,1

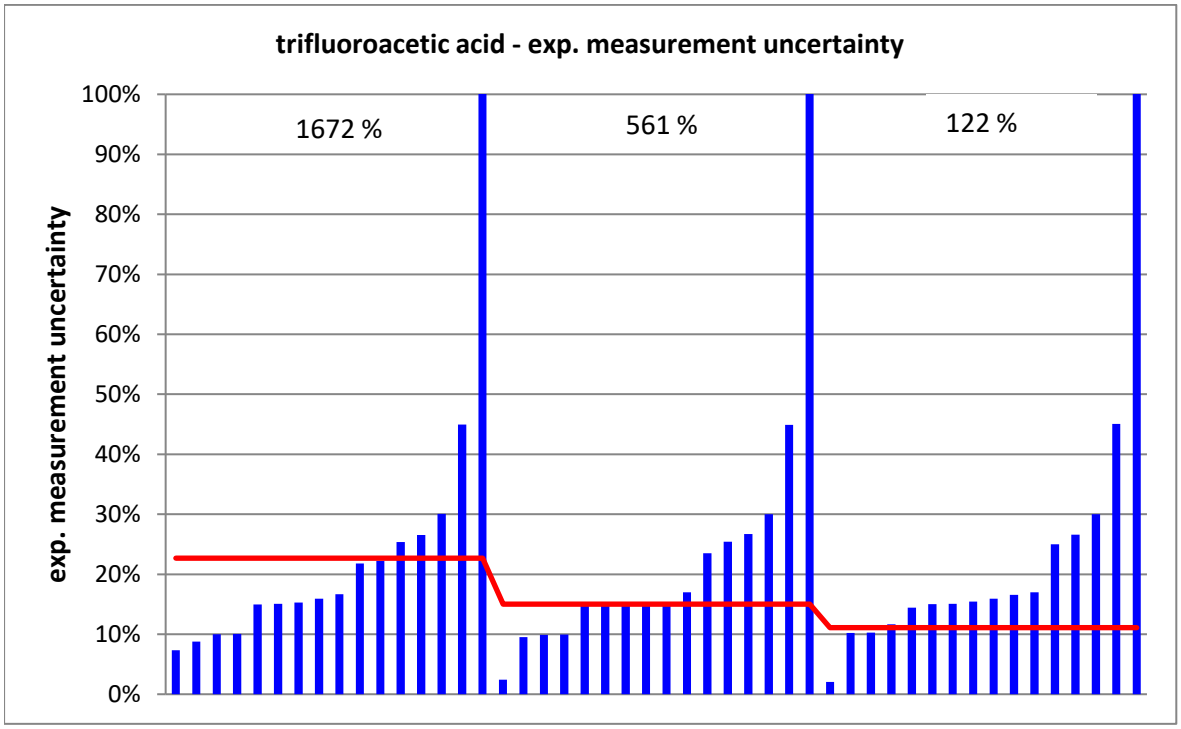



comparison of means and reference values
overall mean
reference values
LC-MS-direct injection
mean in µg/l
3
2,5
2
1,5
1
0,5
0
2
level


comparison of means and reference values
overall mean
reference values
LC-MS-direct injection
mean in µg/l
14
12
10
8
6
4
2
0
3
level



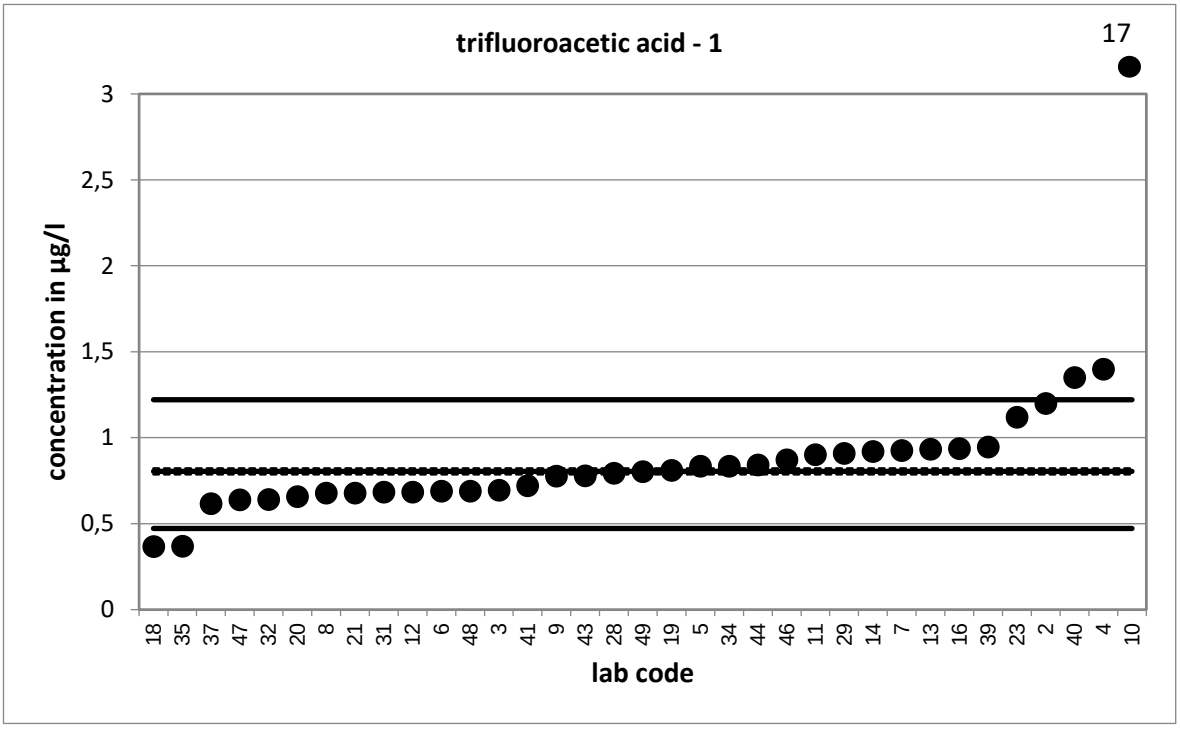
LC-MS-direct injection									
level	robust mean [µg/l]	exp. unc. of the mean [µg/l]	exp. unc. of the mean [%]	robust standard deviation [µg/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	0,793	0,043	5,362	0,17	21,45	25	2	3	20
2	2,511	0,075	2,977	0,305	12,14	26	3	2	19,23
3	12	0,325	2,707	1,299	10,83	25	1	0	4

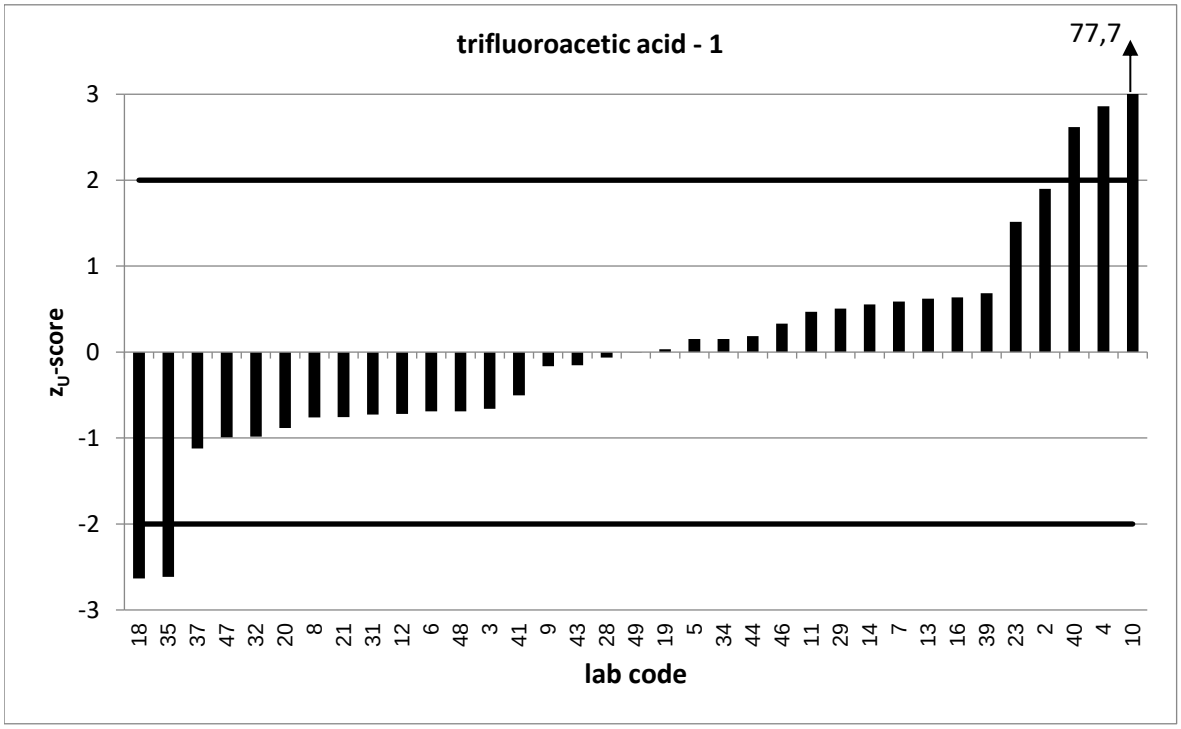

trifluoroacetic acid - exp. measurement uncertainty
exp. measurement uncertainty
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
1672 %
561 %
122 %

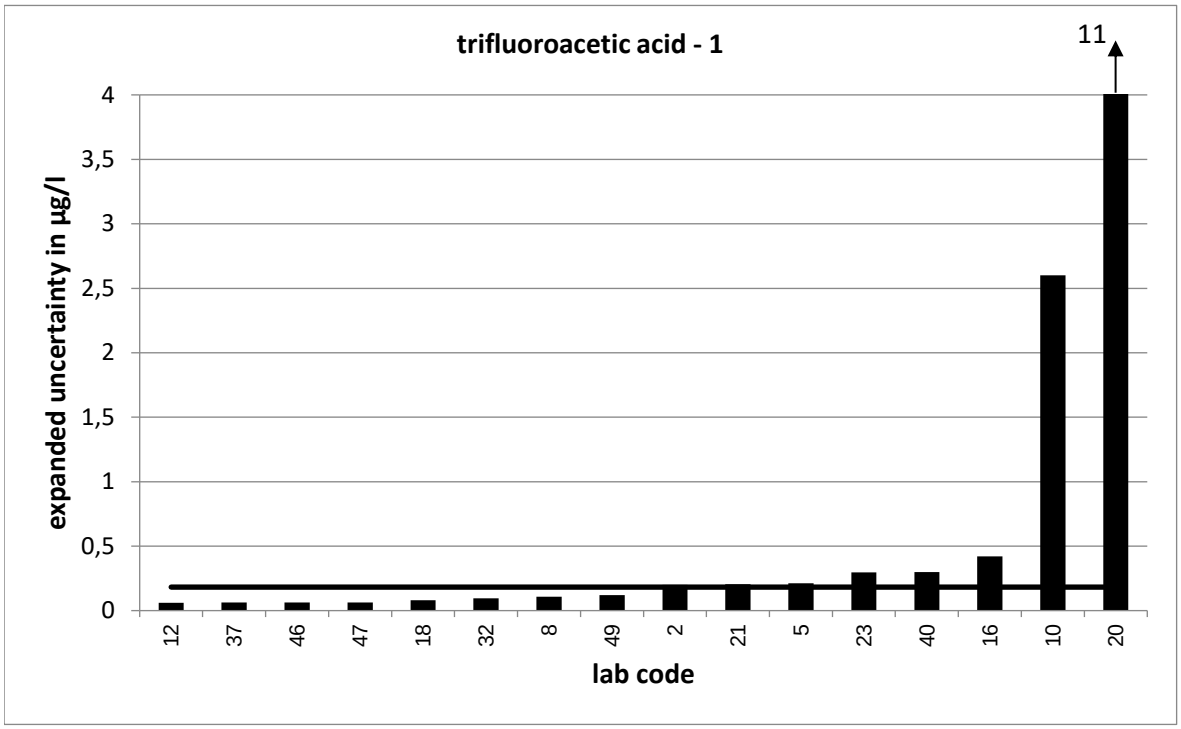
PT 5/18 - TW S7		trifluoroacetic acid - 1			
assigned value [µg/l]*		0,8043	± 0,0168		
upper tolerance limit [µg/l]		1,221			
lower tolerance limit [µg/l]		0,4723			
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
2	1,2	0,2	3,9	1,9	s
3	0,695			-0,7	s
4	1,4			2,9	q
5	0,836	0,212	0,3	0,2	s
6	0,69			-0,7	s
7	0,927			0,6	s
8	0,678	0,108	-2,3	-0,8	s
9	0,777			-0,2	s
10	17	2,6	12,5	77,7	u
11	0,902			0,5	s
12	0,685	0,06	-3,8	-0,7	s
13	0,934			0,6	s
14	0,92			0,6	s
16	0,937	0,421	0,6	0,6	s
18	0,367	0,08	-10,7	-2,6	q
19	0,811			0,0	s
20	0,658	11	0,0	-0,9	s
21	0,679	0,204	-1,2	-0,8	s
23	1,12	0,297	2,1	1,5	s
28	0,794			-0,1	s
29	0,91			0,5	s
31	0,684			-0,7	s
32	0,641	0,096	-3,4	-1,0	s
34	0,836			0,2	s
35	0,37			-2,6	q
37	0,618	0,062	-5,8	-1,1	s
39	0,947			0,7	s
40	1,35	0,3	3,6	2,6	q
41	0,721			-0,5	s
43	0,779			-0,2	s
44	0,843			0,2	s
46	0,873	0,064	2,1	0,3	s
47	0,64	0,064	-5,0	-1,0	s
48	0,69			-0,7	s
49	0,804	0,121	0,0	0,0	s

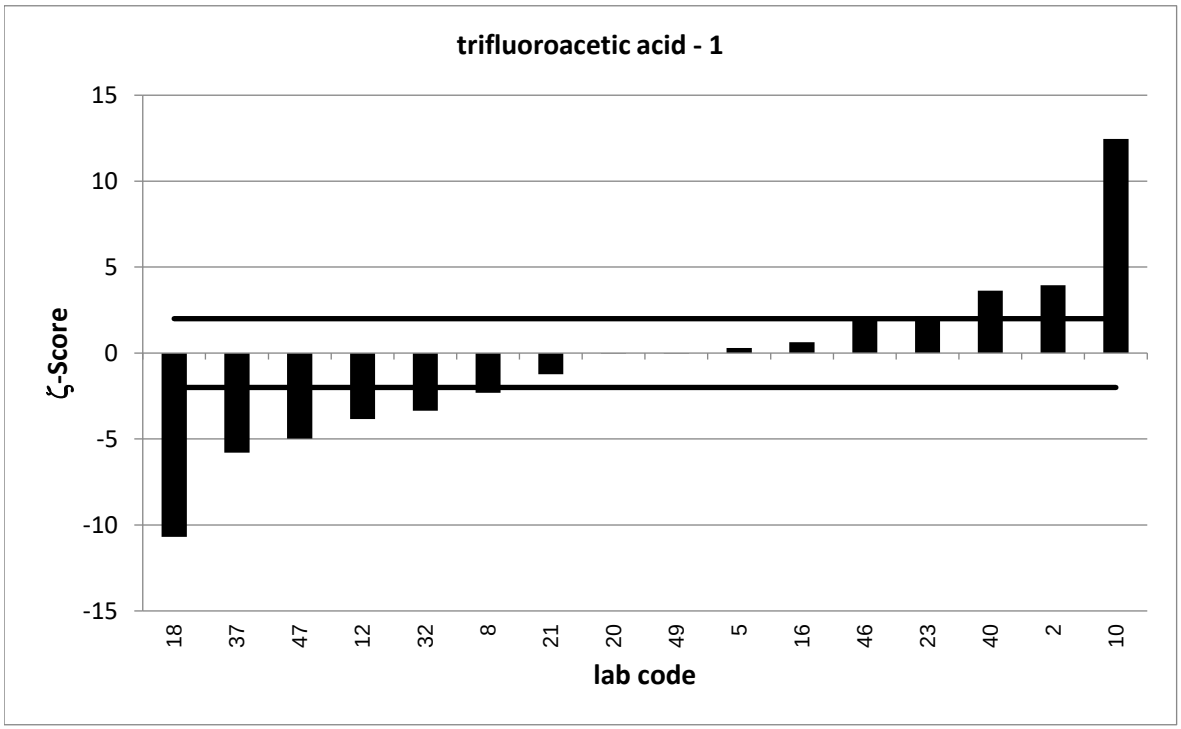
* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

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


trifluoroacetic acid - 1
17
concentration in µg/l
3
2,5
2
1,5
1
0,5
0
18 35 37 47 32 20 8 21 31 12 6 48 3 41 9 43 28 49 19 5 34 44 46 11 29 14 7 13 16 39 23 2 40 4 10
lab code


trifluoroacetic acid - 1
77,7
z_U-score
3
2
1
0
-1
-2
-3
18 35 37 47 32 20 8 21 31 12 6 48 3 41 9 43 28 49 19 5 34 44 46 11 29 14 7 13 16 39 23 2 40 4 10
lab code

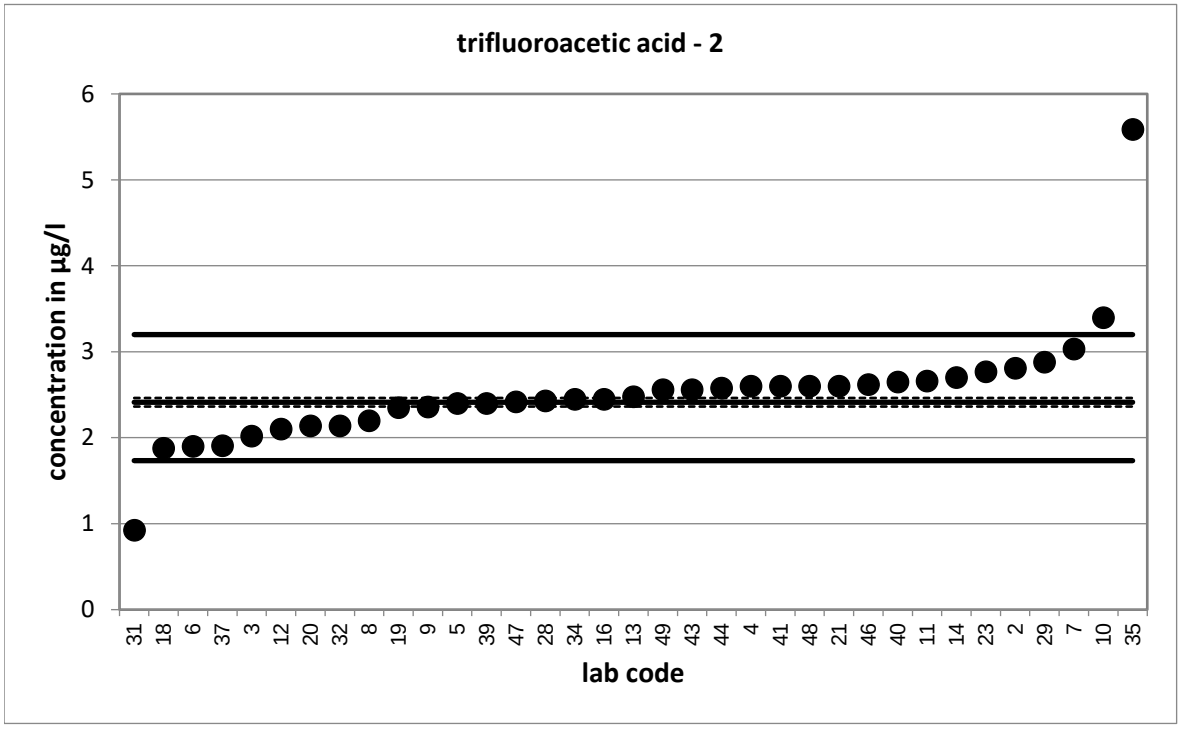

trifluoroacetic acid - 1
11
expanded uncertainty in µg/l
4
3,5
3
2,5
2
1,5
1
0,5
0
12
37
46
47
18
32
8
49
2
21
5
23
40
16
10
20
lab code

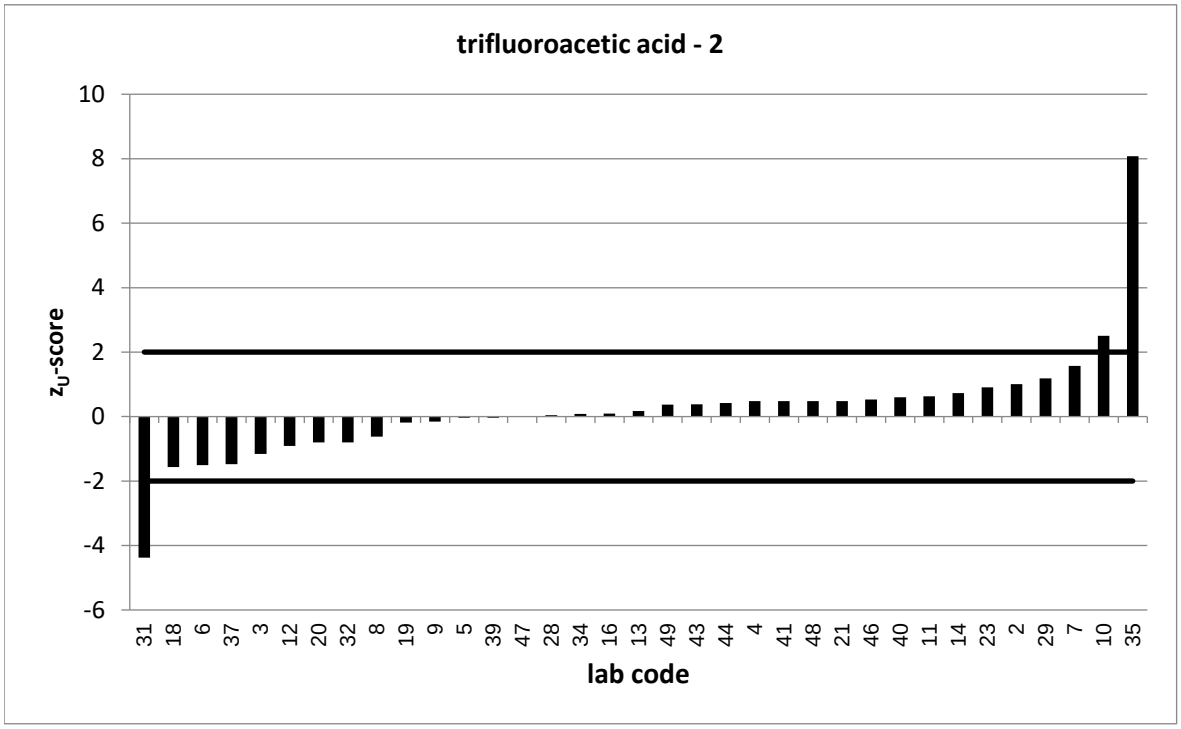

trifluoroacetic acid - 1
ζ-Score
15
10
5
0
-5
-10
-15
18
37
47
12
32
8
21
20
49
5
16
46
23
40
2
10
lab code

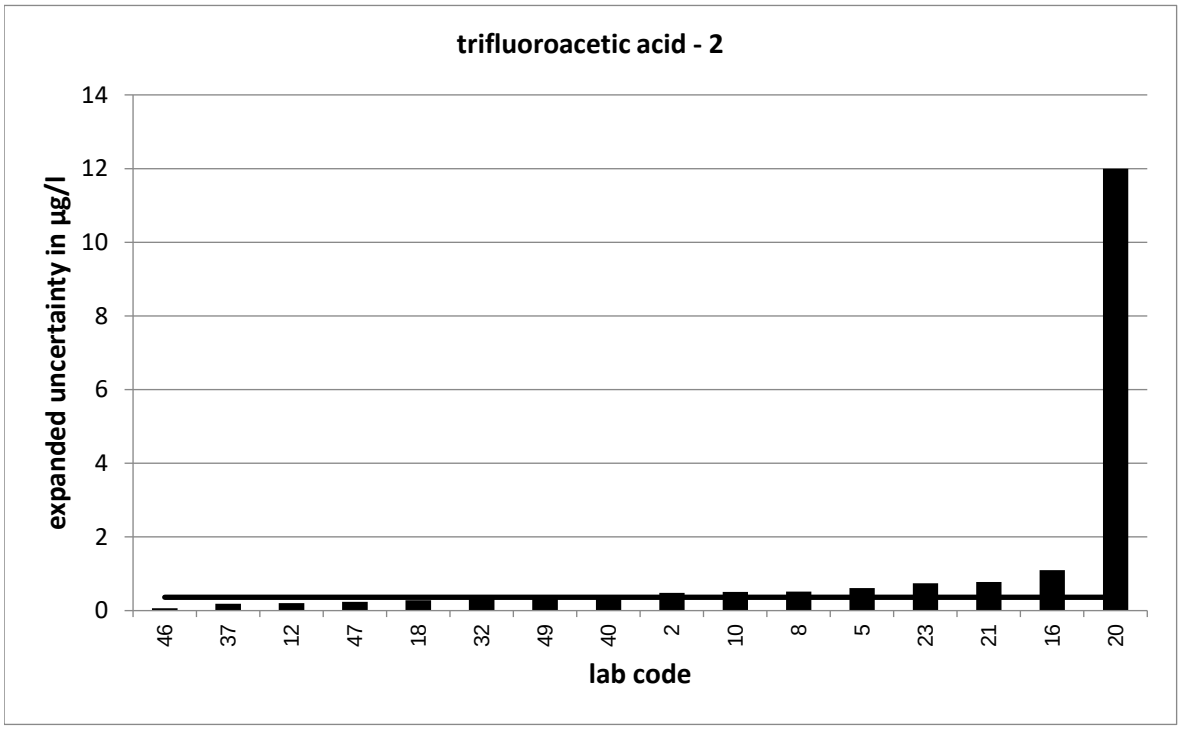
PT 5/18 - TW S7		trifluoroacetic acid - 2			
assigned value [µg/l]*		2,413	± 0,05		
upper tolerance limit [µg/l]		3,2			
lower tolerance limit [µg/l]		1,734			
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
2	2,81	0,478	1,7	1,0	s
3	2,02			-1,2	s
4	2,6			0,5	s
5	2,4	0,61	0,0	0,0	s
6	1,9			-1,5	s
7	3,033			1,6	s
8	2,2	0,517	-0,8	-0,6	s
9	2,36			-0,2	s
10	3,4	0,51	3,9	2,5	q
11	2,66			0,6	s
12	2,102	0,2	-3,0	-0,9	s
13	2,48			0,2	s
14	2,7			0,7	s
16	2,45	1,1	0,1	0,1	s
18	1,88	0,28	-3,7	-1,6	s
19	2,35			-0,2	s
20	2,14	12	0,0	-0,8	s
21	2,603	0,781	0,5	0,5	s
23	2,77	0,739	1,0	0,9	s
28	2,43			0,0	s
29	2,88			1,2	s
31	0,9259			-4,4	u
32	2,14	0,32	-1,7	-0,8	s
34	2,447			0,1	s
35	5,59			8,1	u
37	1,91	0,19	-5,1	-1,5	s
39	2,4			0,0	s
40	2,65	0,4	1,2	0,6	s
41	2,6			0,5	s
43	2,562			0,4	s
44	2,58			0,4	s
46	2,62	0,064	5,1	0,5	s
47	2,42	0,24	0,1	0,0	s
48	2,6			0,5	s
49	2,56	0,39	0,7	0,4	s

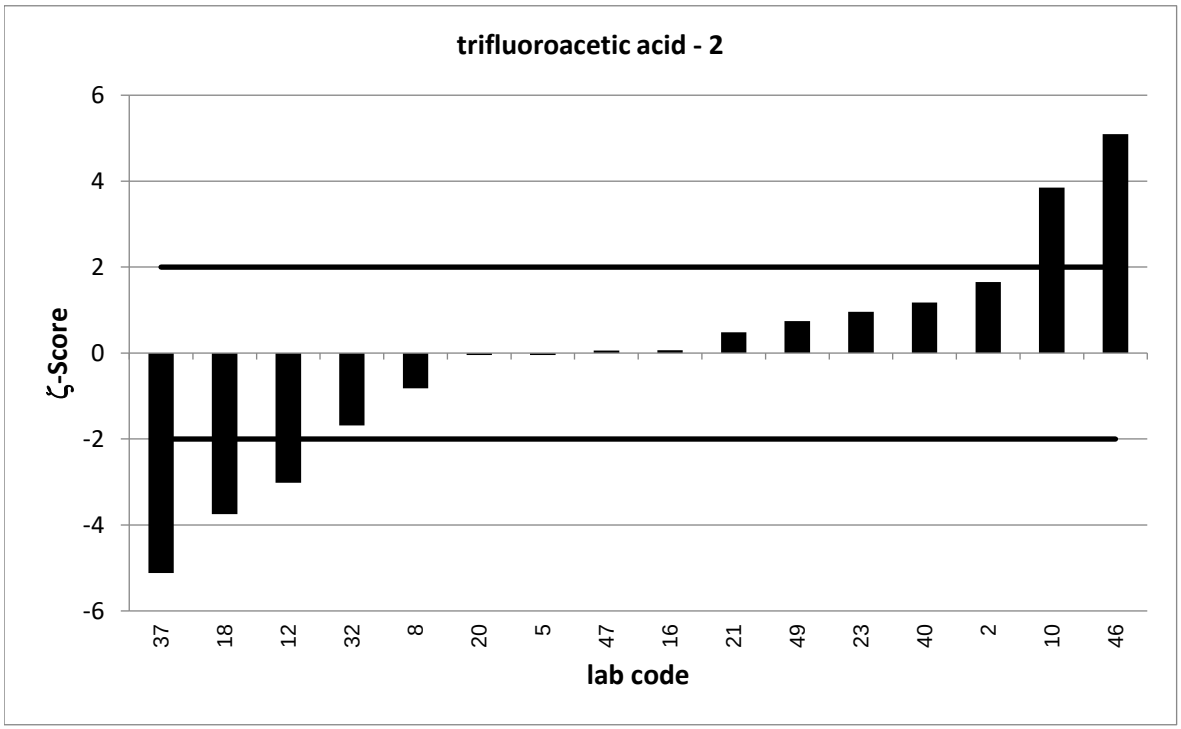
* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

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


trifluoroacetic acid - 2
concentration in µg/l
0
1
2
3
4
5
6
31 18 6 37 3 12 20 32 8 19 9 5 39 47 28 34 16 13 49 43 44 4 41 48 21 46 40 11 14 23 2 29 7 10 35
lab code


trifluoroacetic acid - 2
z_U-score
10
8
6
4
2
0
-2
-4
-6
31 18 6 37 3 12 20 32 8 19 9 5 39 47 28 34 16 13 49 43 44 4 41 48 21 46 40 11 14 23 2 29 7 10 35
lab code

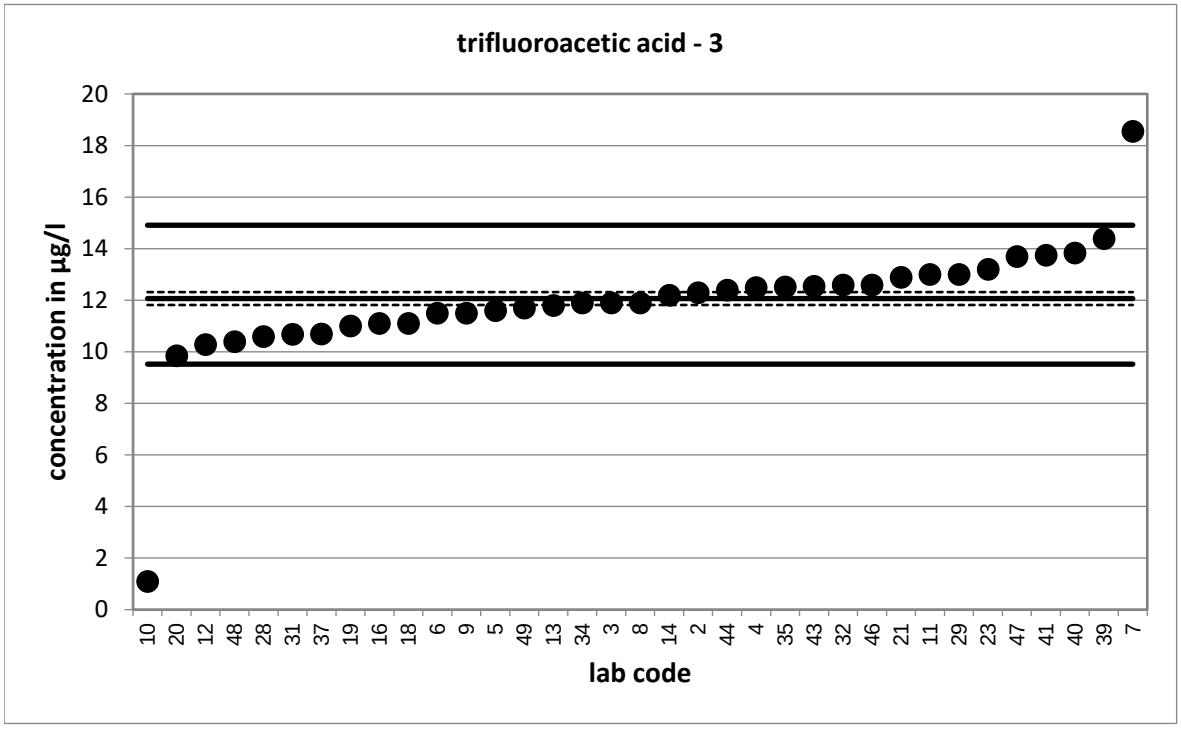

trifluoroacetic acid - 2
expanded uncertainty in µg/l
14
12
10
8
6
4
2
0
46
37
12
47
18
32
49
40
2
10
8
5
23
21
16
20
lab code

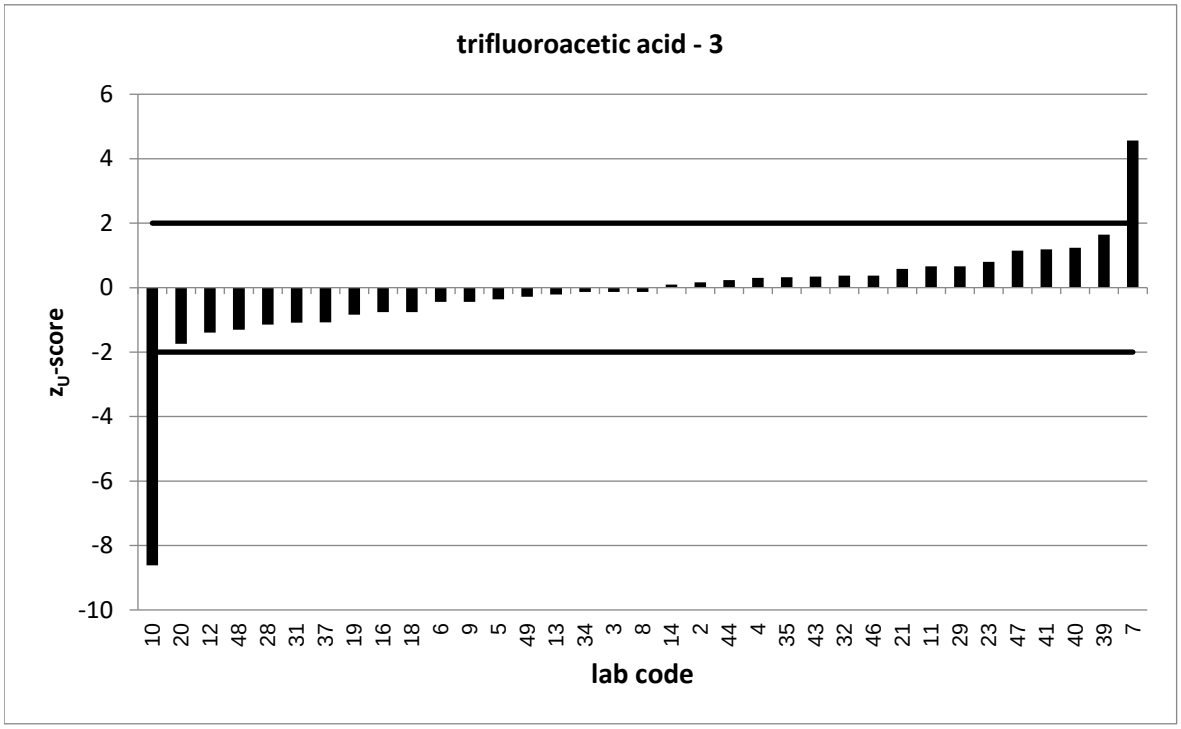

trifluoroacetic acid - 2
ζ-Score
6
4
2
0
-2
-4
-6
37
18
12
32
8
20
5
47
16
21
49
23
40
2
10
46
lab code

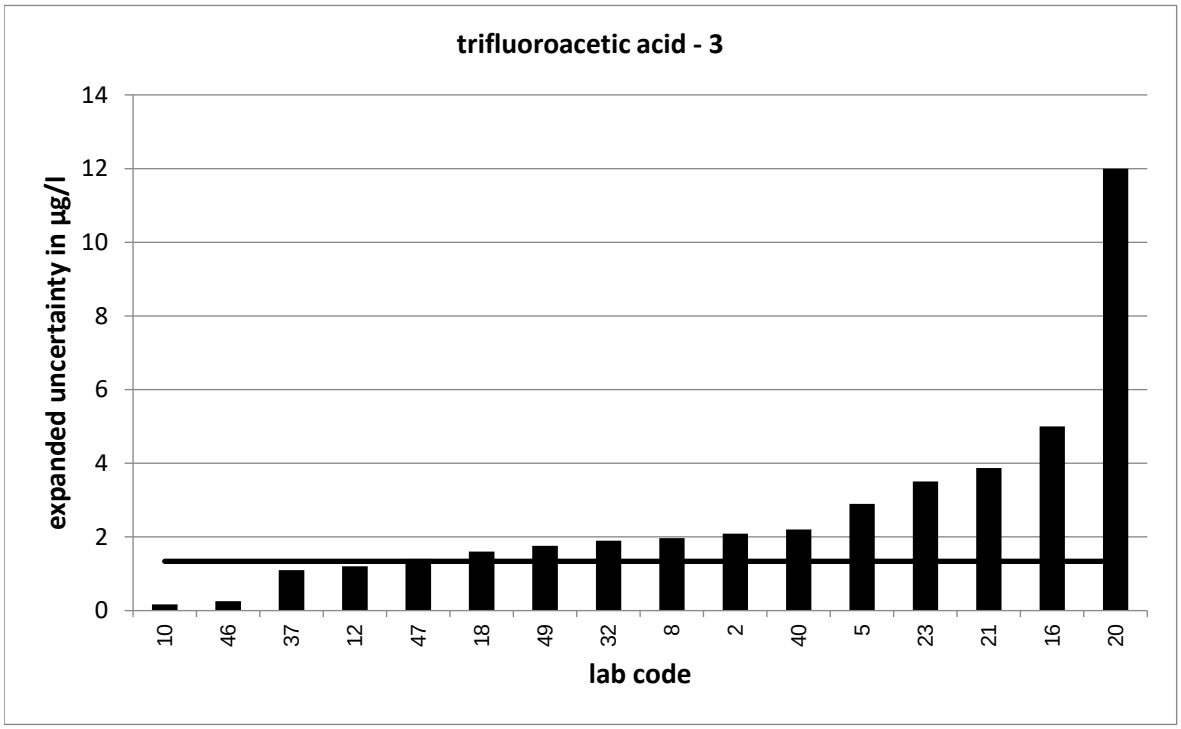
PT 5/18 - TW S7		trifluoroacetic acid - 3			
assigned value [µg/l]*		12,06	± 0,25		
upper tolerance limit [µg/l]		14,91			
lower tolerance limit [µg/l]		9,52			
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
2	12,3	2,09	0,2	0,2	s
3	11,9			-0,1	s
4	12,5			0,3	s
5	11,6	2,9	-0,3	-0,4	s
6	11,5			-0,4	s
7	18,555			4,6	u
8	11,9	1,97	-0,2	-0,1	s
9	11,5			-0,4	s
10	1,1	0,17	-72,6	-8,6	u
11	13			0,7	s
12	10,29	1,2	-2,9	-1,4	s
13	11,8			-0,2	s
14	12,2			0,1	s
16	11,1	5	-0,4	-0,8	s
18	11,1	1,6	-1,2	-0,8	s
19	11			-0,8	s
20	9,85	12	-0,4	-1,7	s
21	12,89	3,867	0,4	0,6	s
23	13,2	3,51	0,6	0,8	s
28	10,6			-1,2	s
29	13			0,7	s
31	10,688			-1,1	s
32	12,6	1,9	0,6	0,4	s
34	11,894			-0,1	s
35	12,52			0,3	s
37	10,7	1,1	-2,4	-1,1	s
39	14,4			1,6	s
40	13,83	2,2	1,6	1,2	s
41	13,75			1,2	s
43	12,55			0,3	s
44	12,4			0,2	s
46	12,6	0,256	3,0	0,4	s
47	13,7	1,4	2,3	1,2	s
48	10,4			-1,3	s
49	11,7	1,76	-0,4	-0,3	s

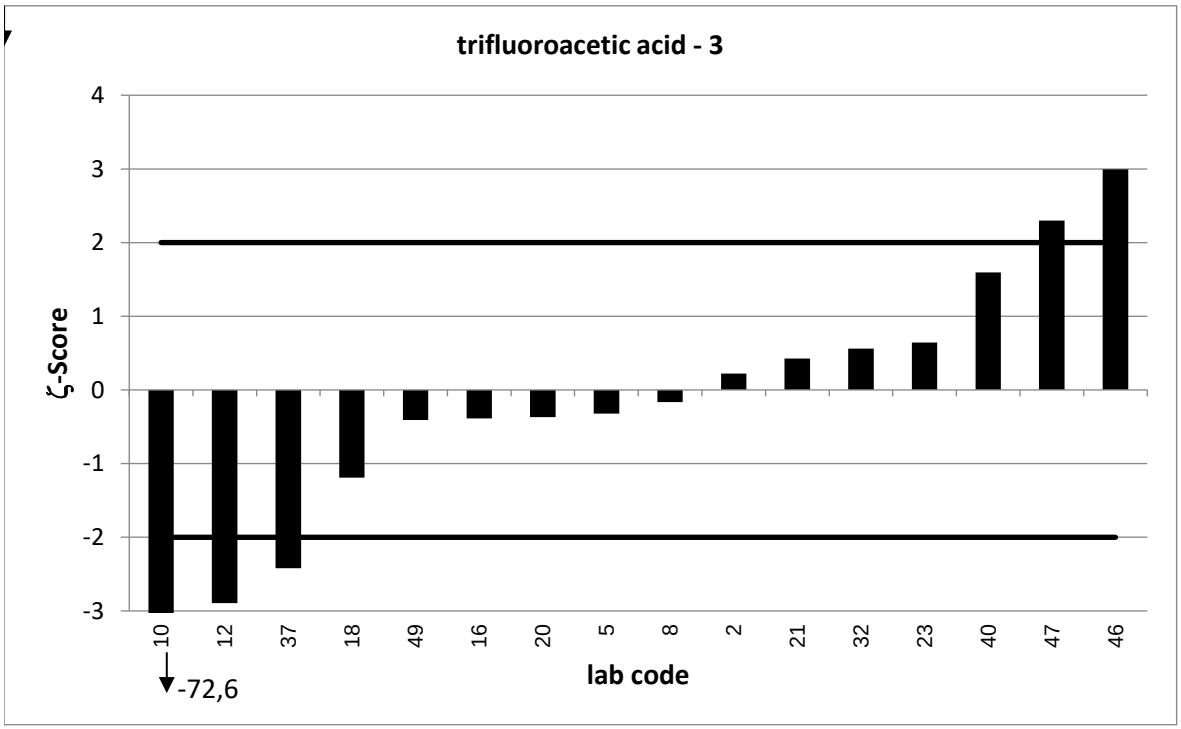
* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%

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


trifluoroacetic acid - 3
concentration in µg/l
0
2
4
6
8
10
12
14
16
18
20
10 20 12 48 28 31 37 19 16 18 6 9 5 49 13 34 3 8 14 2 44 4 35 43 32 46 21 11 29 23 47 41 40 39 7
lab code


trifluoroacetic acid - 3
z_U-score
6
4
2
0
-2
-4
-6
-8
-10
10 20 12 48 28 31 37 19 16 18 6 9 5 49 13 34 3 8 14 2 44 4 35 43 32 46 21 11 29 23 47 41 40 39 7
lab code


trifluoroacetic acid - 3
expanded uncertainty in µg/l
14
12
10
8
6
4
2
0
10
46
37
12
47
18
49
32
8
2
40
5
23
21
16
20
lab code


trifluoroacetic acid - 3
ζ-Score
4
3
2
1
0
-1
-2
-3
10
12
37
18
49
16
20
5
8
2
21
32
23
40
47
46
-72,6
lab code