

University of Stuttgart
Germany



Analytische Qualitätssicherung Baden-Württemberg

Proficiency Test 2/22
- TW S7 – Trifluoroacetic acid in drinking water -

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 July 2022

**AQS Baden-Württemberg at
Institute of Sanitary Engineering,
Water Quality and Solid Waste Management
at University of Stuttgart
Bandtäle 2
70569 Stuttgart-Büsnau
Germany
<http://www.aqsbw.de>
Tel.: +49 (0)711 / 685-65446
Fax: +49 (0)711 / 685-53769
E-Mail: info@aqsbw.de**

Responsibilities:

Scientific director:	Dr.-Ing. Michael Koch	
PT coordinator:	Dr.-Ing. Frank Baumeister	
Assistant PT coordinator	Dipl.-Biol. Biljana Marić	
Sample preparation	Dr. Vasil Valkov (IWW)	
Release of the report:	Dr.-Ing. Michael Koch	on 27.07.2022
Version of the report	1	

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Appendix B

Appendix C

TFA 1.....	C-1
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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:

- **Trifluoroacetic 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 22.02.2022 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 $\mu\text{g/l}$ with three significant digits.

6. Submission of the results

The deadline for the submission of results was on 14.03.2022.

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.

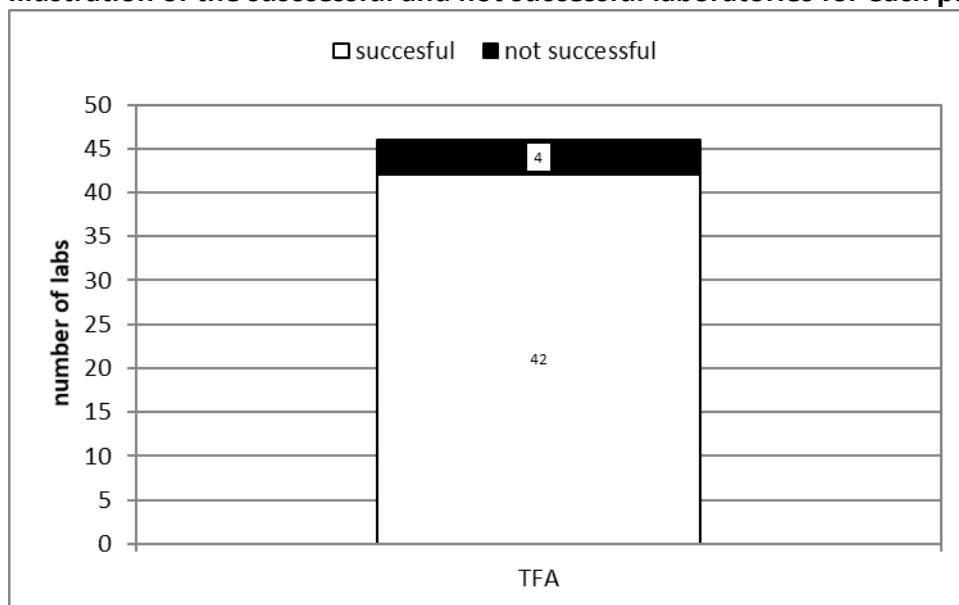
This PT was evaluated as follows:

Assigned value x_{pt}:	Reference value						
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:	<table style="border: none;"> <tr> <td style="padding-right: 20px;">$z_u \leq 2.0$</td> <td>successful</td> </tr> <tr> <td>$2.0 < z_u < 3.0$</td> <td>questionable</td> </tr> <tr> <td>$z_u \geq 3.0$</td> <td>unsatisfactory</td> </tr> </table>	$ z_u \leq 2.0$	successful	$2.0 < z_u < 3.0$	questionable	$ z_u \geq 3.0$	unsatisfactory
$ z_u \leq 2.0$	successful						
$2.0 < z_u < 3.0$	questionable						
$ z_u \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:	43 3 laboratories did not report any results
Number of reported values	137
Number of accepted values:	121 (88,3 %)

Illustration of the successful 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.agsbw.de/pdf/ausw_berichte_v1_en.pdf.

10. Measurement uncertainty

General:

Number of labs with valid values	46
Number of labs with valid values and reported measurement uncertainties	28 (60,9 %)
Number of valid values	137
Number of valid values with measurement uncertainties	83 (60,6 %)

Measurement uncertainties against the accreditation status

Accreditation status of the values	Number of values	Number of values with measurement uncertainty
accredited	77	56 (72,7 %)
not accredited	36	18 (50 %)
not specified	24	9 (37,5 %)

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 $z_U \leq 2,0$	72
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	12 (16,7 %)

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

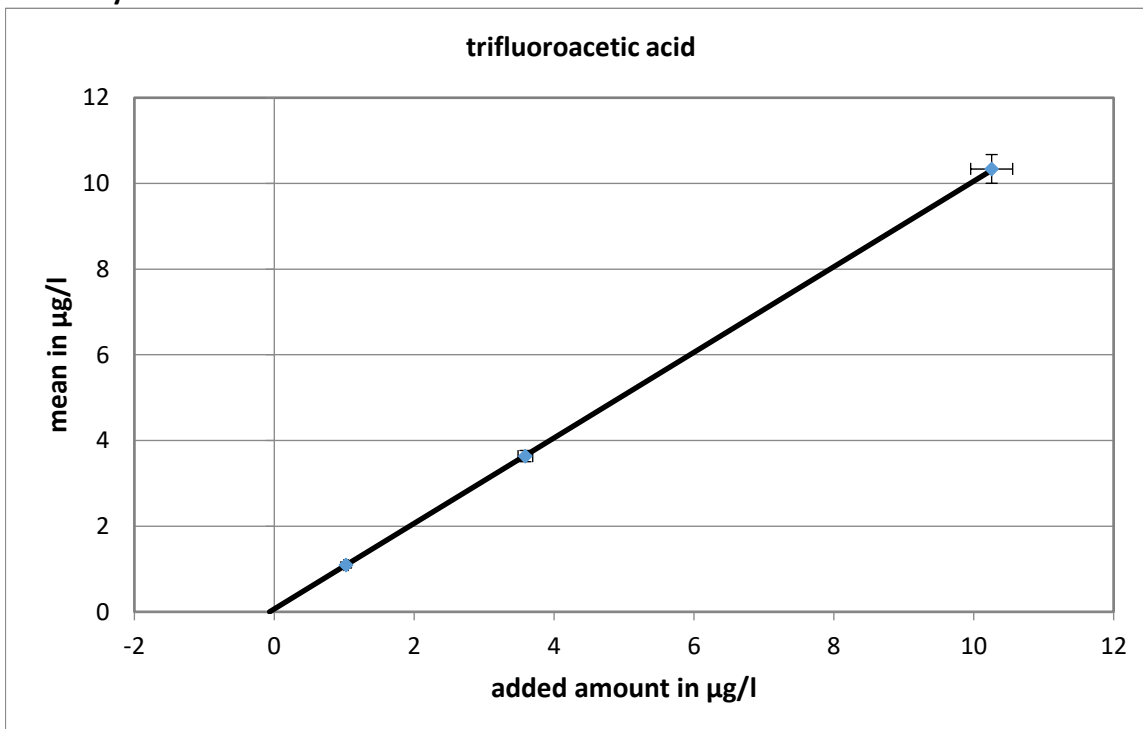
12. Internet

The report is available on the following webpage: http://www.aqsbw/pdf/report_267.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	1,093	6,72	0,1879	0,1879	17,20	1,507	0,7437	37,90	-31,93	46	0	3	6,5
2	3,657	3,41	0,3557	0,3557	9,73	4,406	2,977	20,50	-18,60	46	1	5	13,0
3	10,32	2,98	0,8900	0,8900	8,62	12,19	8,613	18,05	-16,56	44	4	4	17,8
sum										136	5	12	12,5

Recovery and matrix content

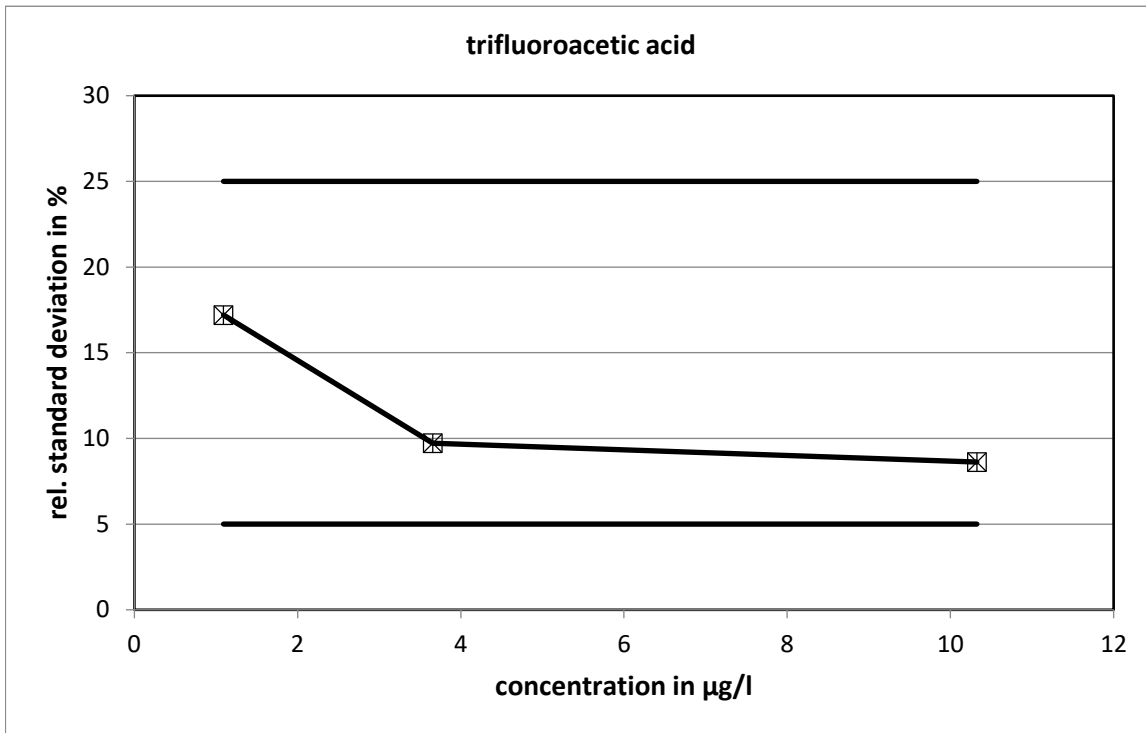


slope of the regression: 0,999; recovery rate: 99,9 %

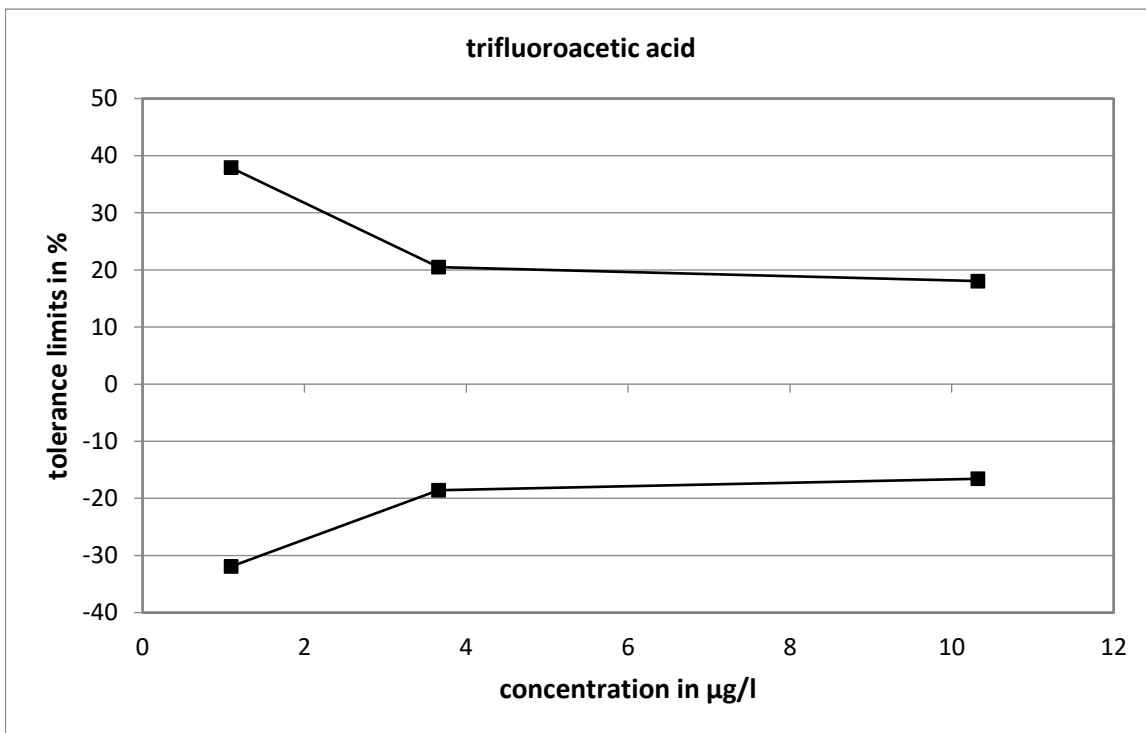
neg. x-axis intercept = matrix content: 0,067 µg/l

expanded uncertainty of the matrix content: 0,067 µg/l = 100 %

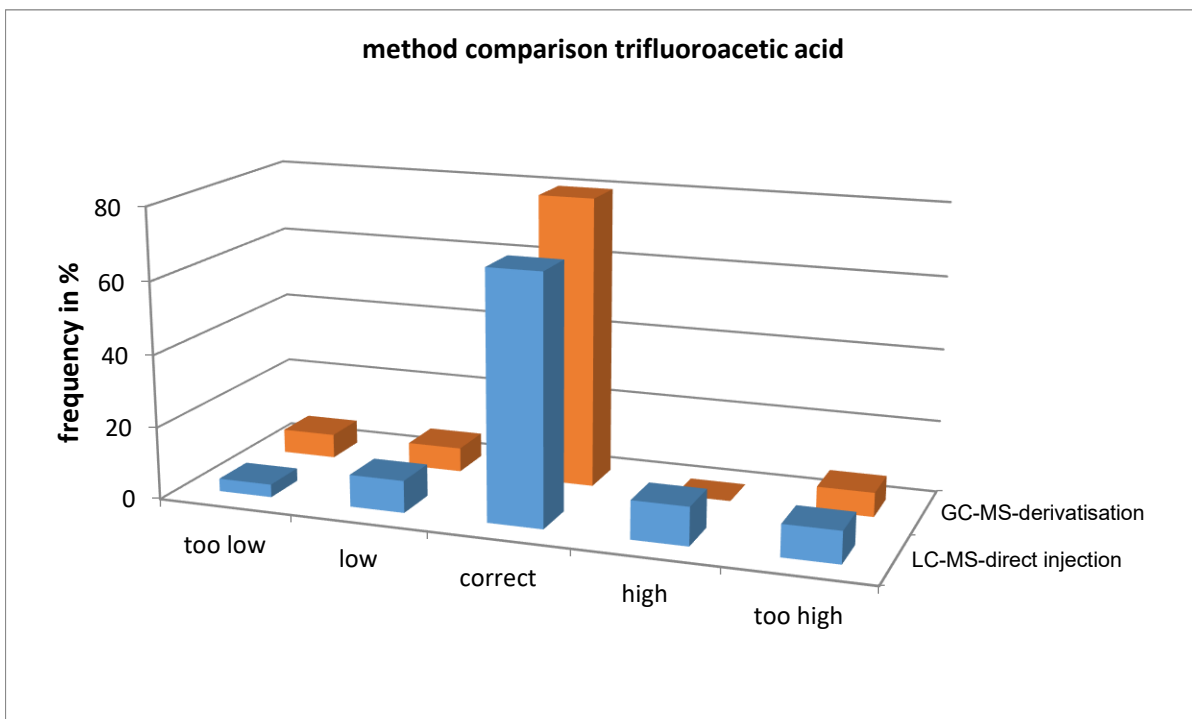
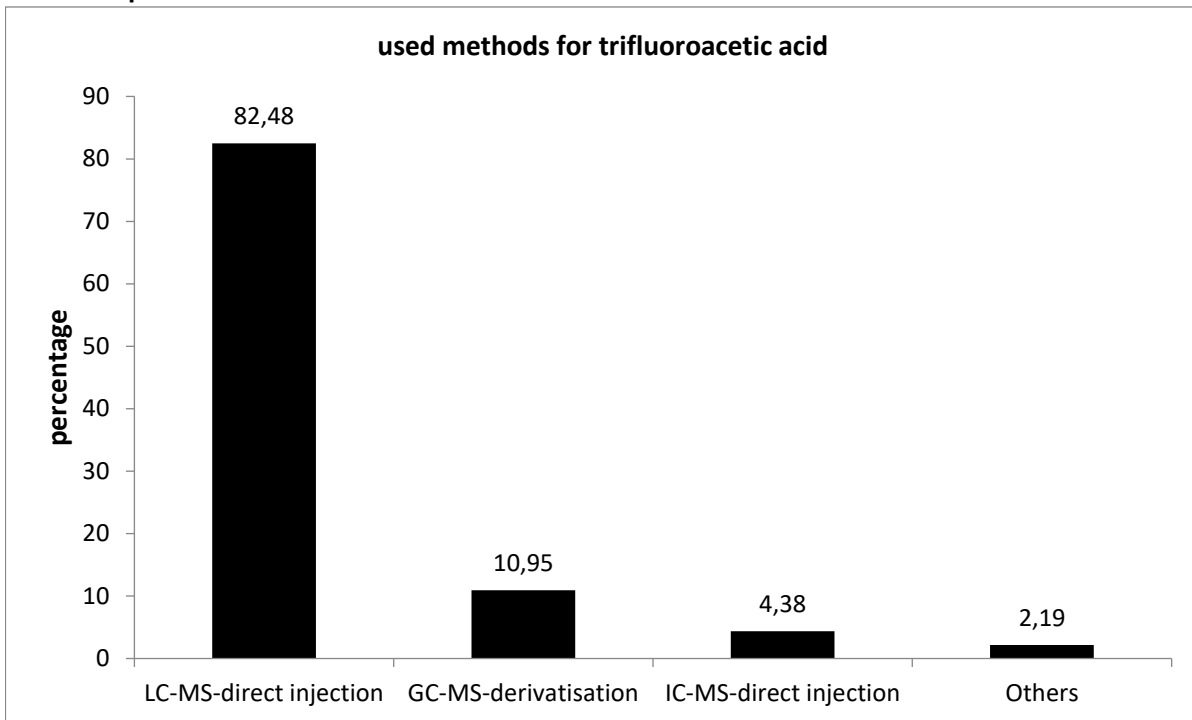
Relative standard deviation and tolerance limits



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



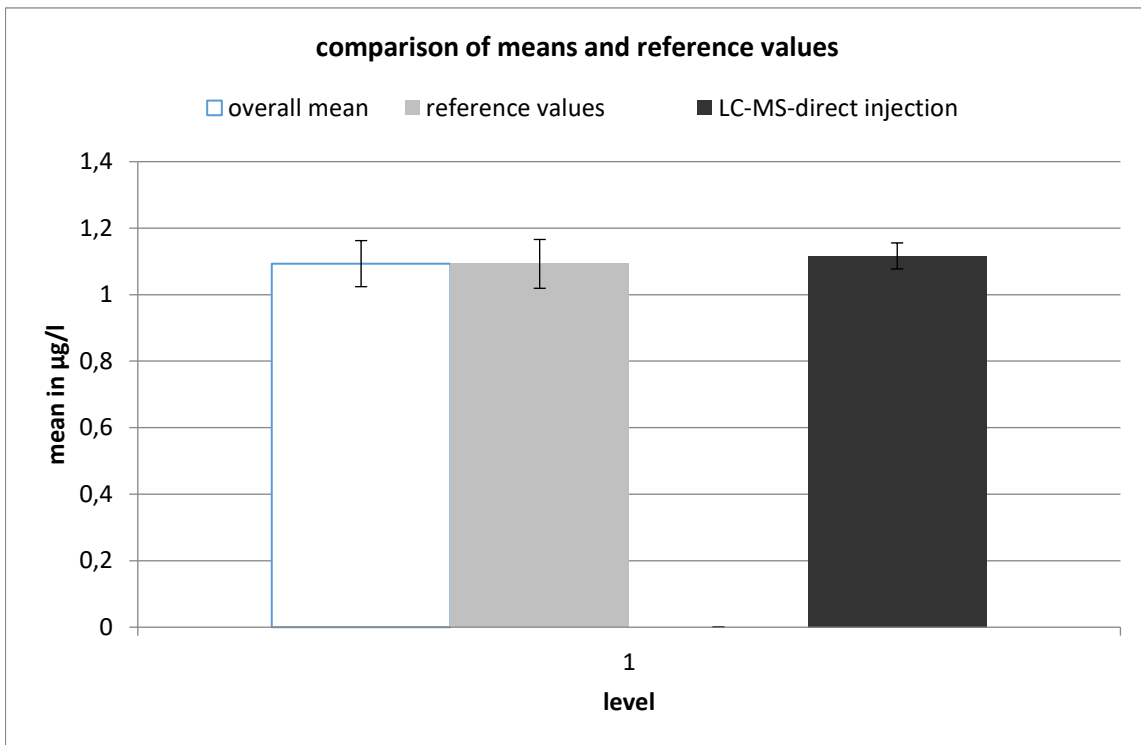
Method specific evaluation

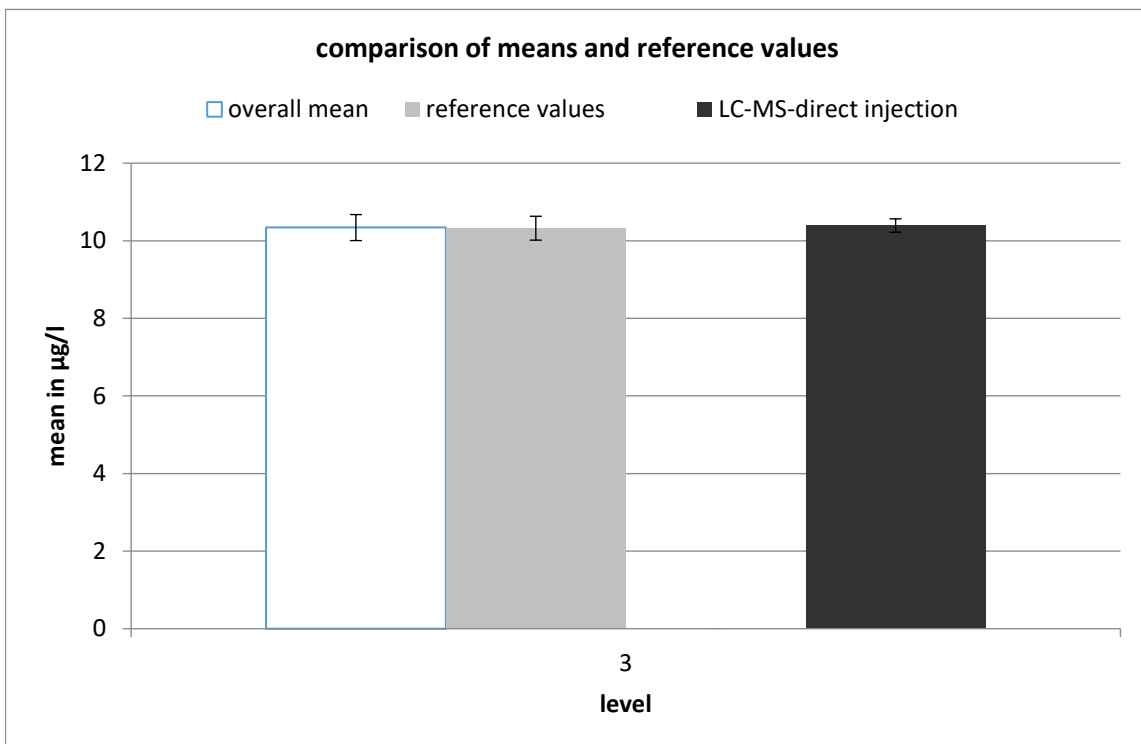
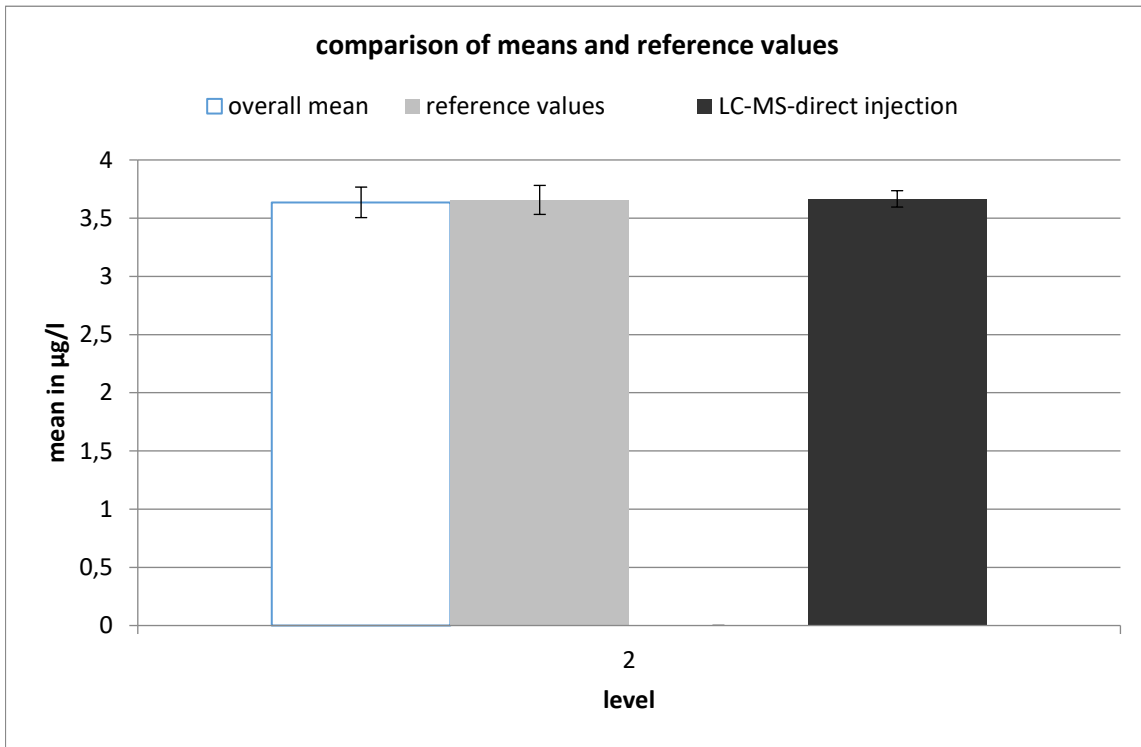


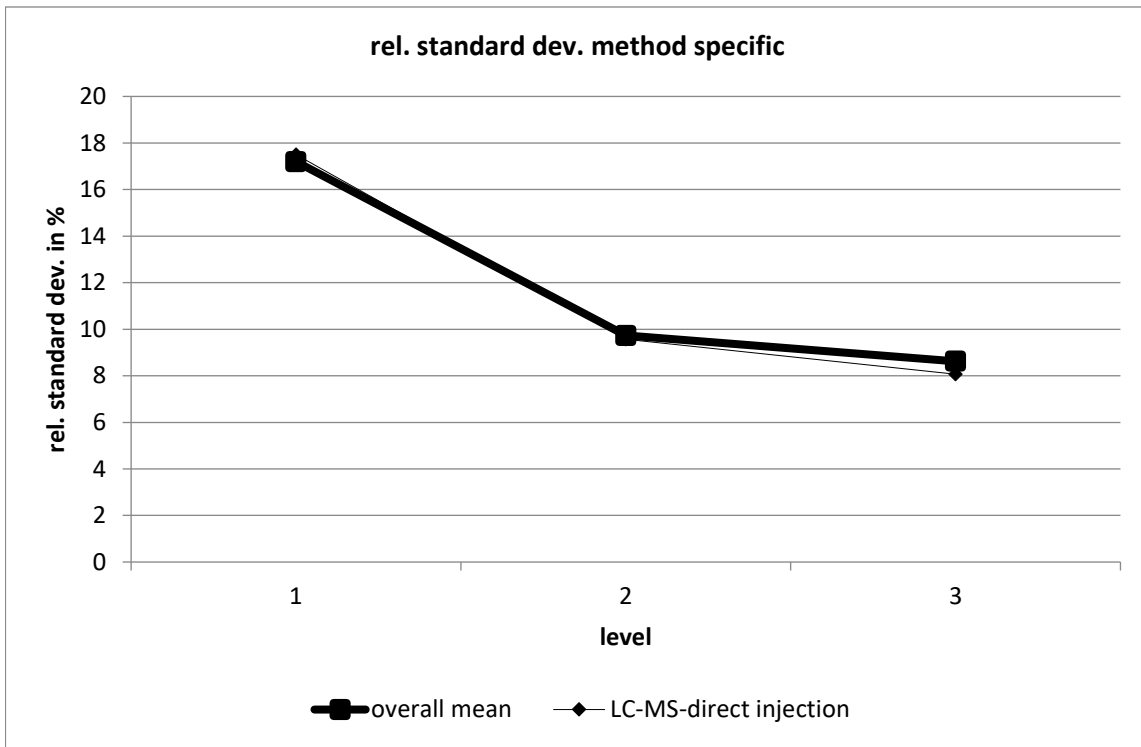
The differences between the methods were not significant.

Comparison of means and reference values

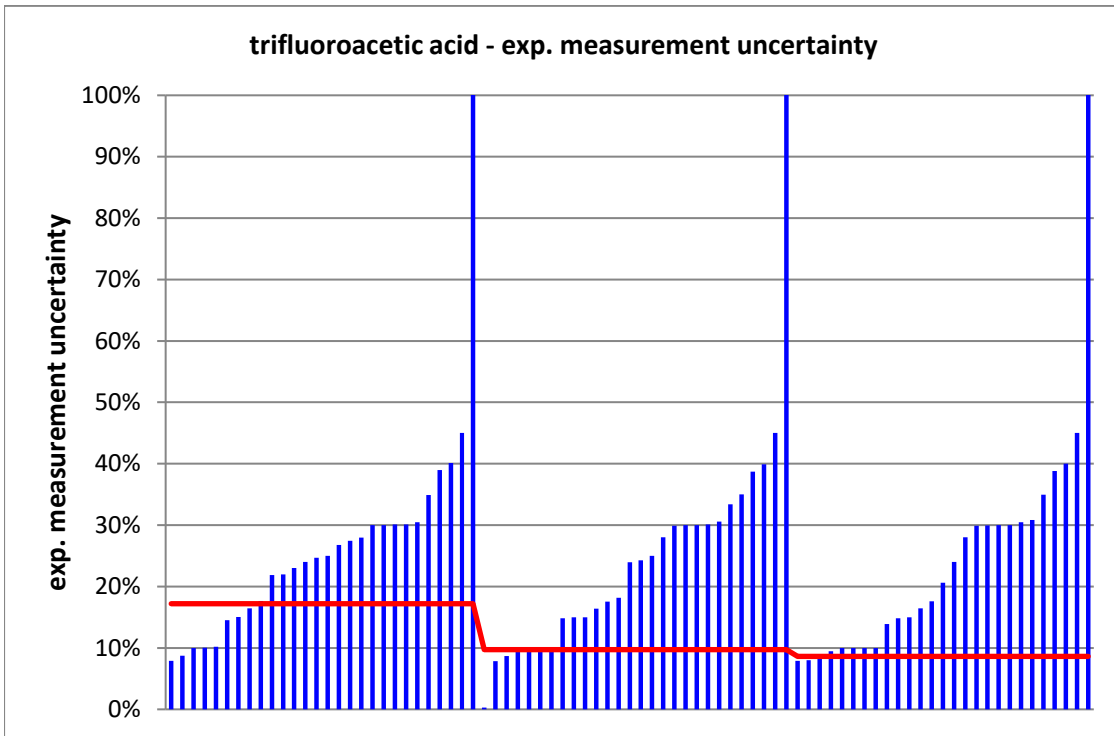
level	mean [µg/l]	exp. uncertainty [µg/l]	exp. uncertainty [%]	reference value [µg/l]	exp. uncertainty [µg/l]	exp. uncertainty [%]
1	1,093	0,069	6,3	1,093	0,073	6,7
2	3,636	0,131	3,6	3,657	0,125	3,4
3	10,34	0,34	3,2	10,32	0,31	3,0







LC-MS-direct injection									
level	robust mean [$\mu\text{g/l}$]	exp. unc. of the mean [$\mu\text{g/l}$]	exp. unc. of the mean [%]	robust standard deviation [$\mu\text{g/l}$]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	1,116	0,039	3,504	0,195	17,5	39	1	2	7,692
2	3,666	0,07	1,916	0,351	9,571	39	2	3	12,82
3	10,39	0,172	1,658	0,838	8,069	37	4	3	18,92

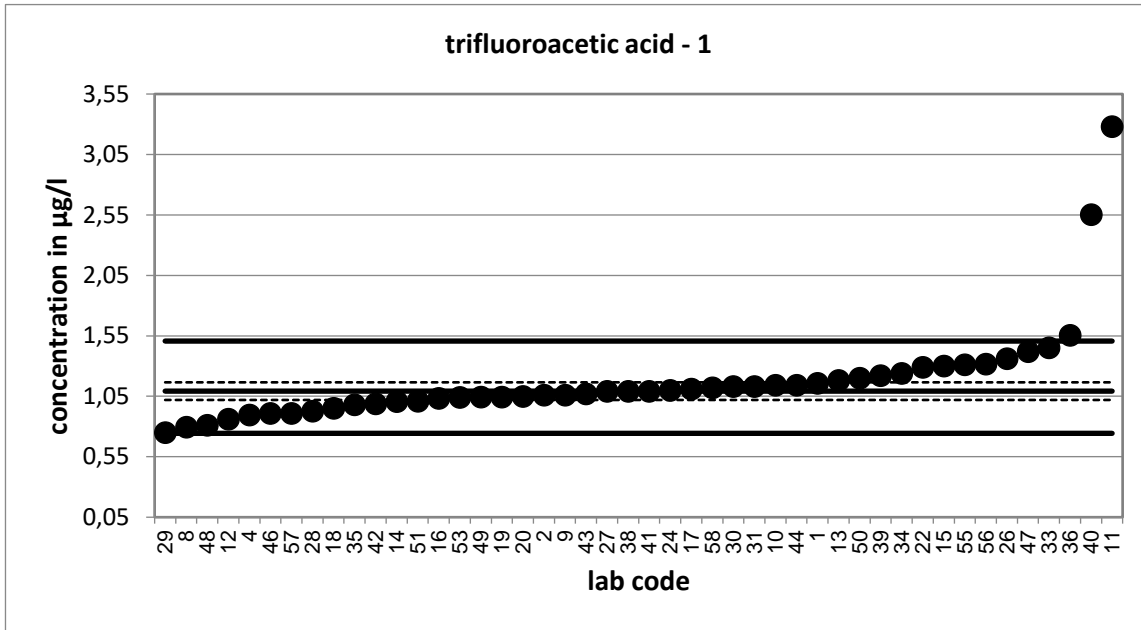


Strongly deviating values are not shown in the diagram.

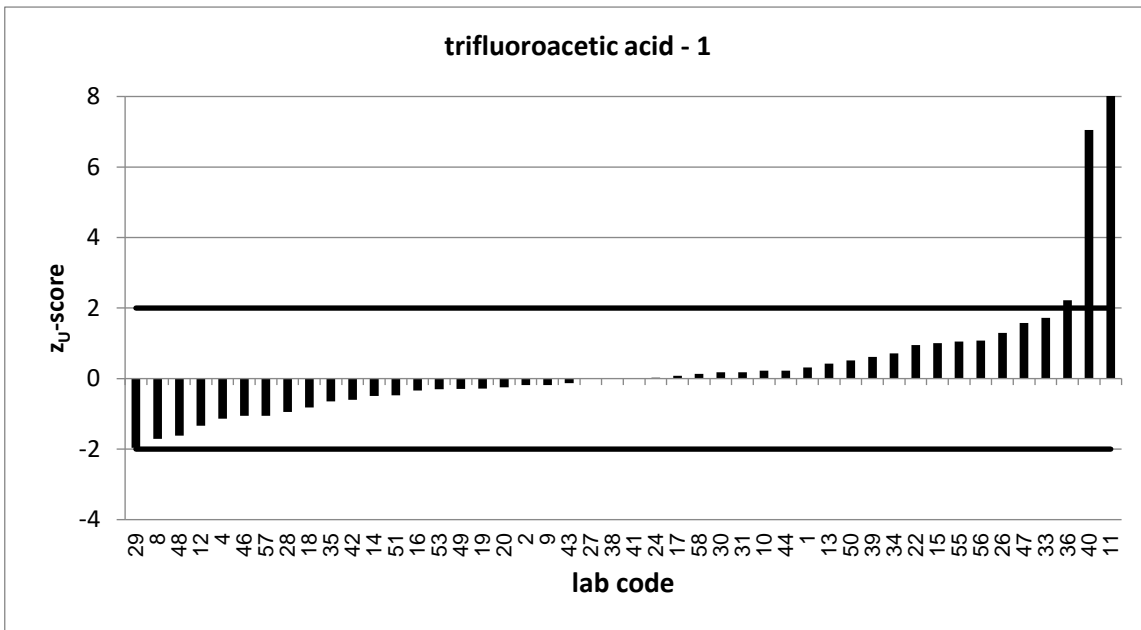
PT 2/22 - TW S7		trifluoroacetic acid - 1			
assigned value [$\mu\text{g/l}$]*		1,093 \pm 0,073			
upper tolerance limit [$\mu\text{g/l}$]		1,507			
lower tolerance limit [$\mu\text{g/l}$]		0,7437			
lab code	result [$\mu\text{g/l}$]	\pm	z-score	Z _U -score	assessm.**
1	1,158	25	0,0	0,3	s
2	1,06			-0,2	s
4	0,894			-1,1	s
8	0,7945			-1,7	s
9	1,06			-0,2	s
10	1,14	0,201	0,4	0,2	s
11	3,28	0,9	4,8	10,6	u
12	0,86	0,189	-2,3	-1,3	s
13	1,18			0,4	s
14	1,0062	0,101	-1,4	-0,5	s
15	1,301			1,0	s
16	1,0338			-0,3	s
17	1,11			0,1	s
18	0,95	0,285	-1,0	-0,8	s
19	1,043			-0,3	s
20	1,049	0,105	-0,7	-0,2	s
22	1,29	0,45	0,9	1,0	s
24	1,0984	0,096	0,1	0,0	s
26	1,36	0,53	1,0	1,3	s
27	1,09			0,0	s
28	0,928	0,232	-1,4	-0,9	s
29	0,75			-2,0	s
30	1,13			0,2	s
31	1,13	0,089	0,6	0,2	s
33	1,45	0,218	3,1	1,7	s
34	1,24	0,18	1,5	0,7	s
35	0,98	0,1	-1,8	-0,6	s
36	1,553	0,466	2,0	2,2	q
38	1,09	0,179	0,0	0,0	s
39	1,22	0,367	0,7	0,6	s
40	2,5515			7,0	u
41	1,09			0,0	s
42	0,988			-0,6	s
43	1,07			-0,1	s
44	1,14	0,343	0,3	0,2	s
46	0,908	0,218	-1,6	-1,1	s
47	1,42	0,57	1,1	1,6	s
48	0,81	0,2	-2,7	-1,6	s
49	1,042	0,24	-0,4	-0,3	s
50	1,2			0,5	s
51	1,01	0,221	-0,7	-0,5	s
53	1,04	0,317	-0,3	-0,3	s
55	1,31	0,59	0,7	1,1	s
56	1,316	0,368	1,2	1,1	s
57	0,908			-1,1	s
58	1,12	0,3	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%

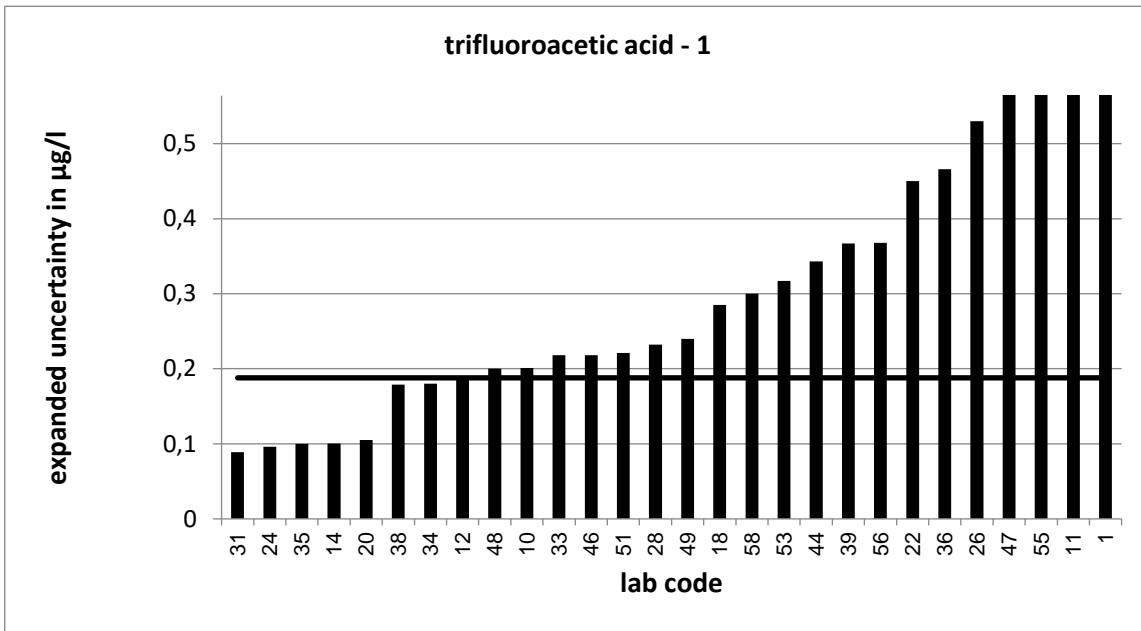
** s = satisfactory, q = questionable, u = unsatisfactory



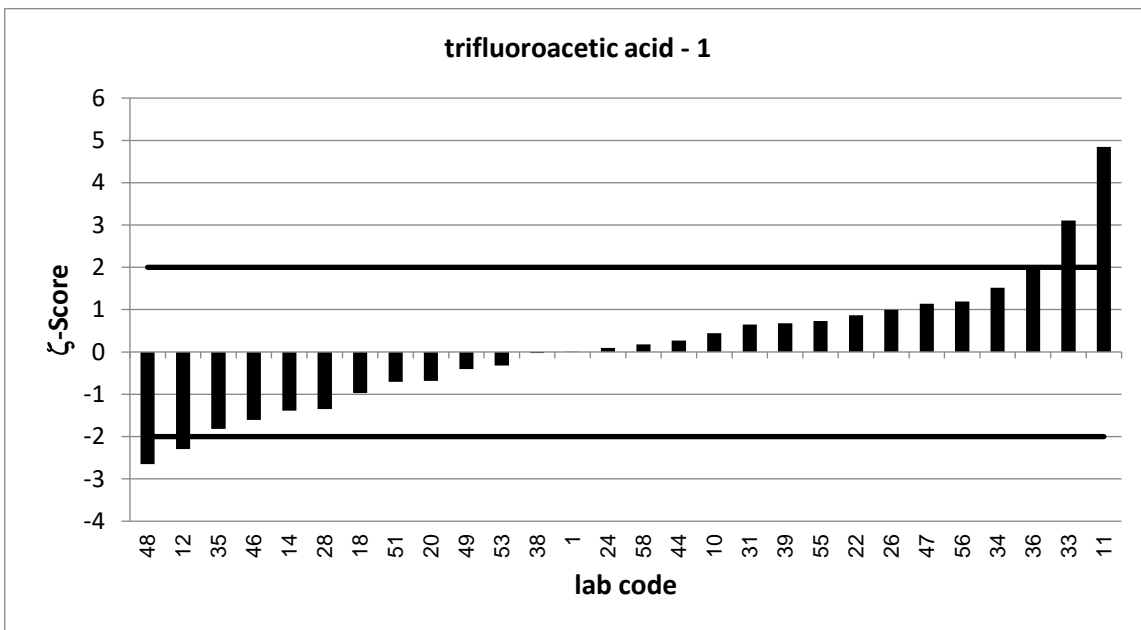
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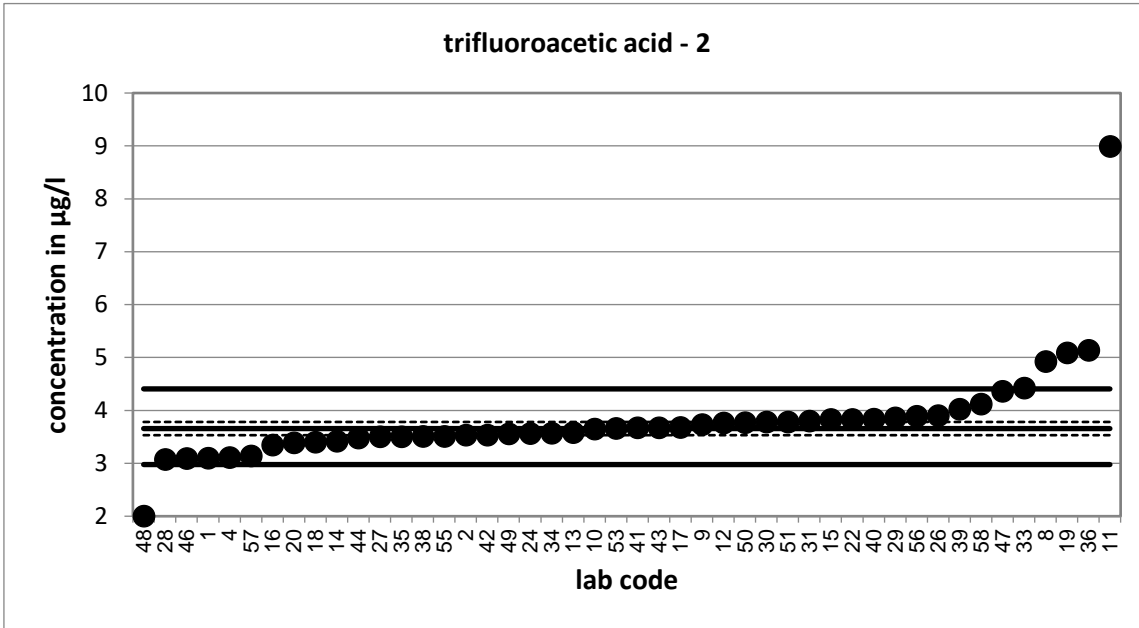
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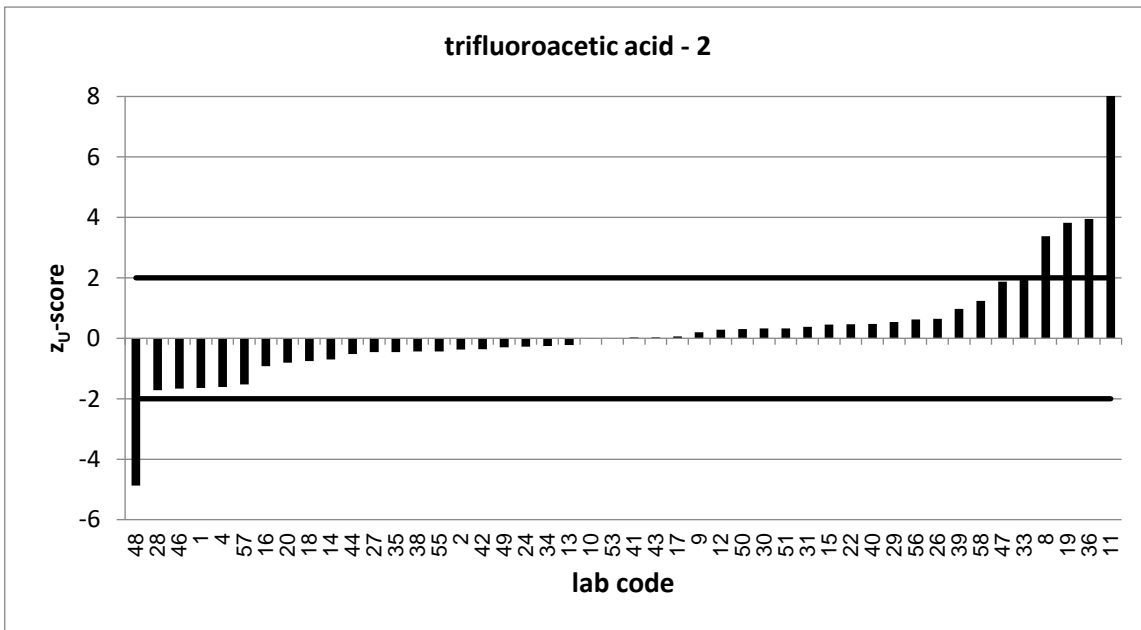
PT 2/22 - TW S7		trifluoroacetic acid - 2			
assigned value [$\mu\text{g/l}$]*		3,657 \pm 0,125			
upper tolerance limit [$\mu\text{g/l}$]		4,406			
lower tolerance limit [$\mu\text{g/l}$]		2,977			
lab code	result [$\mu\text{g/l}$]	\pm	z-score	Z _U -score	assessm.**
1	3,099	25	0,0	-1,6	s
2	3,53			-0,4	s
4	3,11			-1,6	s
8	4,922			3,4	u
9	3,73			0,2	s
10	3,65	0,641	0,0	0,0	s
11	8,99	3	3,6	14,2	u
12	3,764	0,685	0,3	0,3	s
13	3,58			-0,2	s
14	3,4182	0,342	-1,3	-0,7	s
15	3,827			0,5	s
16	3,343			-0,9	s
17	3,68			0,1	s
18	3,4	1,02	-0,5	-0,8	s
19	5,089			3,8	u
20	3,384	0,338	-1,5	-0,8	s
22	3,83	1,34	0,3	0,5	s
24	3,5635	0,31	-0,6	-0,3	s
26	3,9	1,51	0,3	0,6	s
27	3,5			-0,5	s
28	3,072	0,768	-1,5	-1,7	s
29	3,86			0,5	s
30	3,78			0,3	s
31	3,8	0,298	0,9	0,4	s
33	4,42	0,662	2,3	2,0	s
34	3,57	0,53	-0,3	-0,3	s
35	3,5	0,35	-0,8	-0,5	s
36	5,135	1,541	1,9	3,9	u
38	3,51	0,576	-0,5	-0,4	s
39	4,02	1,21	0,6	1,0	s
40	3,834			0,5	s
41	3,67			0,0	s
42	3,535			-0,4	s
43	3,67			0,0	s
44	3,48	1,04	-0,3	-0,5	s
46	3,09	0,74	-1,5	-1,7	s
47	4,36	1,74	0,8	1,9	s
48	2	0,3	-10,2	-4,9	u
49	3,555	0,01	-1,6	-0,3	s
50	3,77			0,3	s
51	3,78	0,384	0,6	0,3	s
53	3,66	1,12	0,0	0,0	s
55	3,51	1,58	-0,2	-0,4	s
56	3,889	1,089	0,4	0,6	s
57	3,136			-1,5	s
58	4,12	1	0,9	1,2	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%

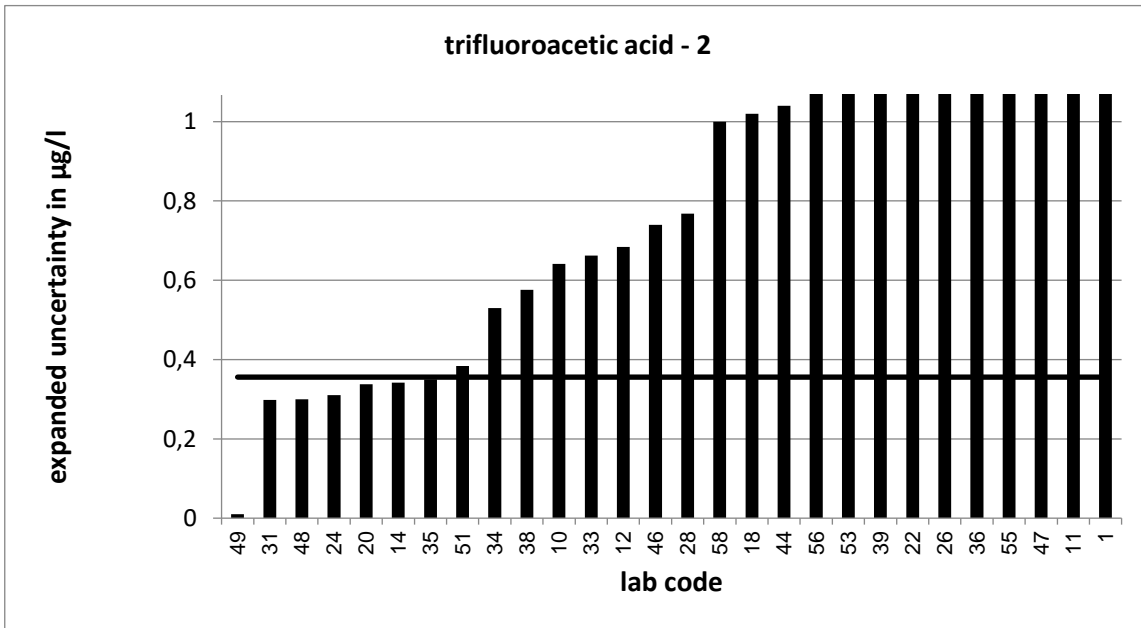
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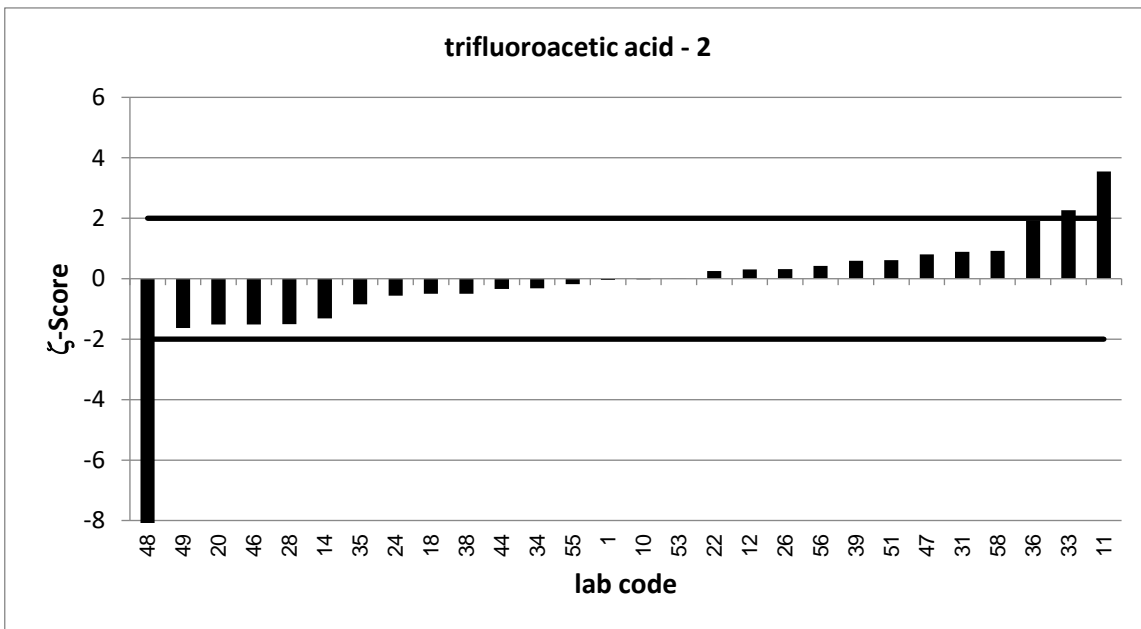
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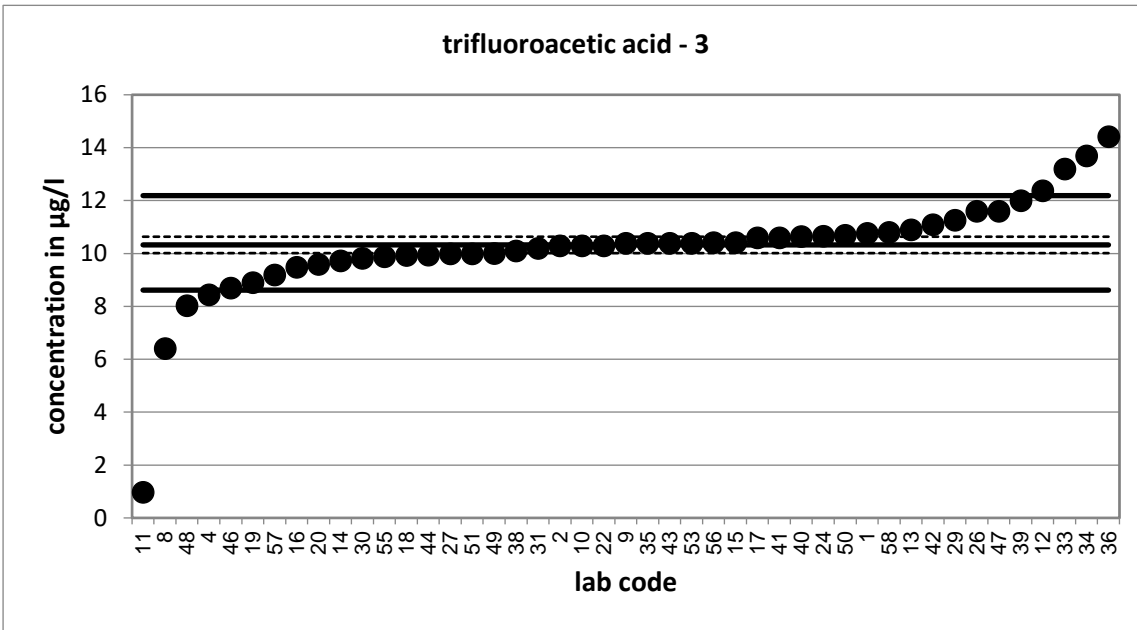


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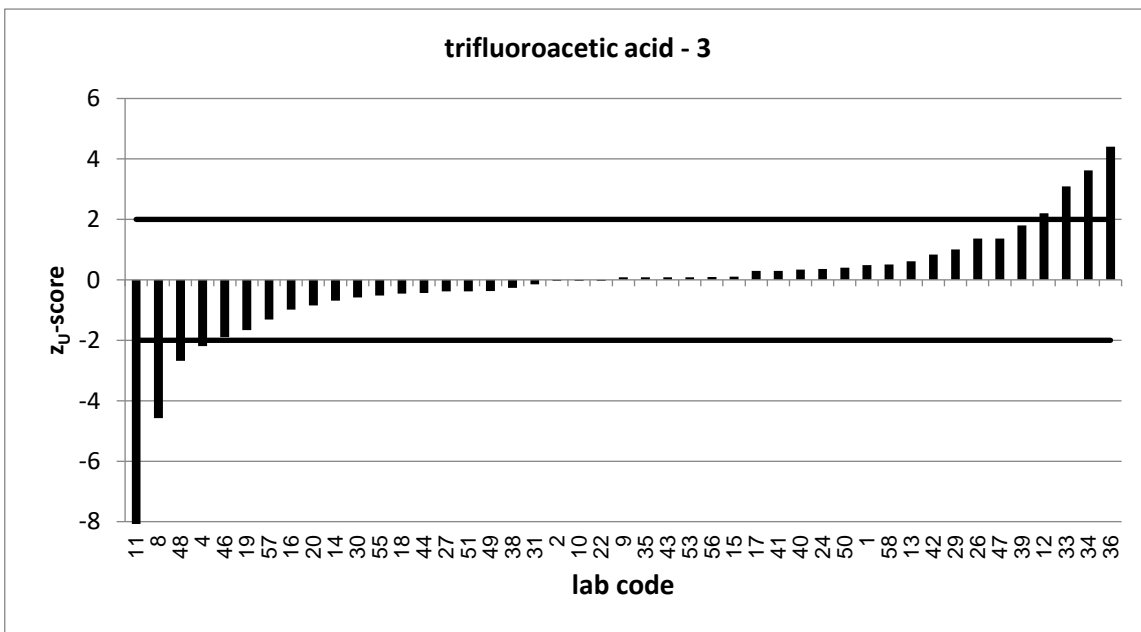
PT 2/22 - TW S7		trifluoroacetic acid - 3			
assigned value [$\mu\text{g/l}$]*		10,32 \pm 0,31			
upper tolerance limit [$\mu\text{g/l}$]		12,19			
lower tolerance limit [$\mu\text{g/l}$]		8,613			
lab code	result [$\mu\text{g/l}$]	\pm	z-score	Z _U -score	assessm.**
1	10,774	25	0,0	0,5	s
2	10,3			0,0	s
4	8,45			-2,2	q
8	6,413			-4,6	u
9	10,4			0,1	s
10	10,3	1,81	0,0	0,0	s
11	0,973	0,3	-43,5	-10,9	u
12	12,377	2,554	1,6	2,2	q
13	10,9			0,6	s
14	9,7338	0,973	-1,2	-0,7	s
15	10,42			0,1	s
16	9,481			-1,0	s
17	10,6			0,3	s
18	9,93	2,98	-0,3	-0,5	s
19	8,9			-1,7	s
20	9,599	0,96	-1,4	-0,8	s
22	10,3	3,6	0,0	0,0	s
24	10,6564	0,921	0,7	0,4	s
26	11,6	4,5	0,6	1,4	s
27	10			-0,4	s
29	11,26			1,0	s
30	9,83			-0,6	s
31	10,2	0,803	-0,3	-0,1	s
33	13,2	1,98	2,9	3,1	u
34	13,7	2,03	3,3	3,6	u
35	10,4	1,04	0,1	0,1	s
36	14,43	4,33	1,9	4,4	u
38	10,1	1,66	-0,3	-0,3	s
39	12	3,59	0,9	1,8	s
40	10,644			0,3	s
41	10,6			0,3	s
42	11,1			0,8	s
43	10,4			0,1	s
44	9,95	2,98	-0,2	-0,4	s
46	8,7	2,09	-1,5	-1,9	s
47	11,6	4,64	0,5	1,4	s
48	8,03	0,8	-5,4	-2,7	q
49	10,009	0,8	-0,7	-0,4	s
50	10,7			0,4	s
51	10	0,947	-0,6	-0,4	s
53	10,4	3,17	0,0	0,1	s
55	9,88	4,45	-0,2	-0,5	s
56	10,415	2,916	0,1	0,1	s
57	9,202			-1,3	s
58	10,8	1,5	0,6	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%

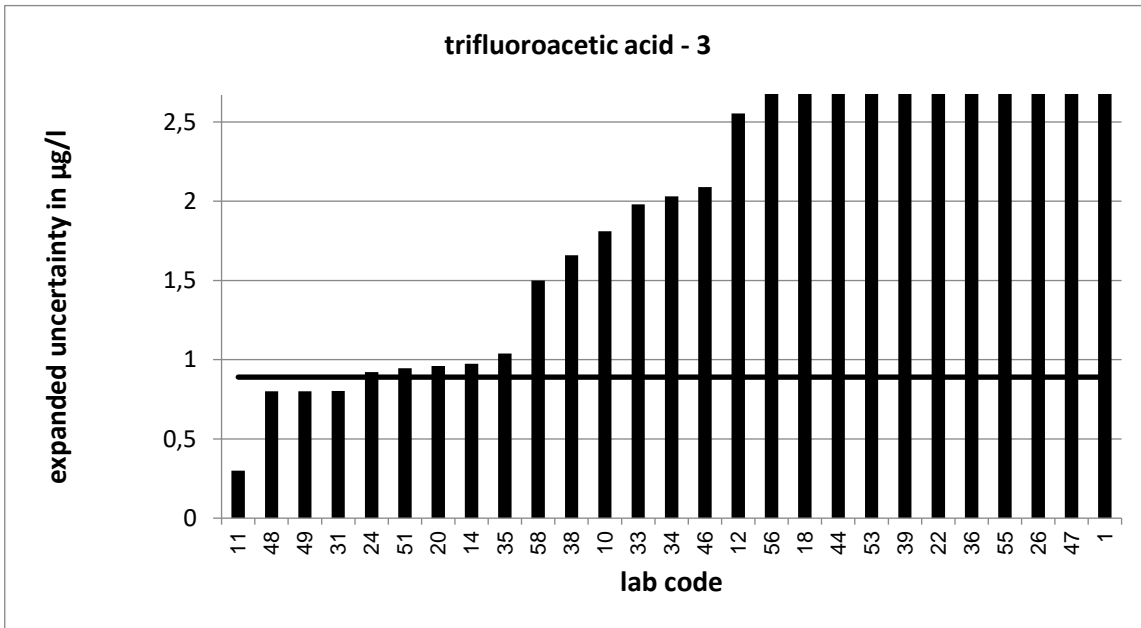
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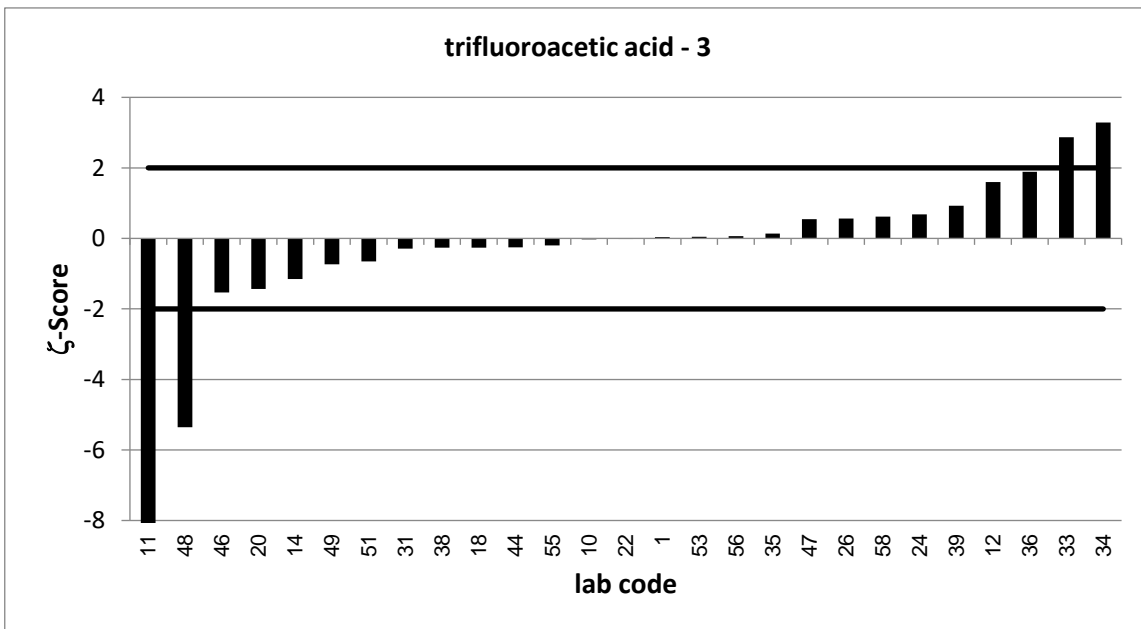
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