University of Stuttgart
Germany

iswa

Analytische Qualitätssicherung Baden-Württemberg

Proficiency Test 11/23
- TW S10 – epichlorohydrin, acrylamide in drinking water -

Final report

provided by
AQS Baden-Württemberg at
Institute for Sanitary Engineering, Water Quality and Solid Waste Management,
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AQS Baden-Württemberg

Stuttgart, in April 2024

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Release of the report:	Dr.-Ing. Michael Koch 4.4.2024
Version of the report	1

List of contents

1. General

This PT was provided in the context of the AQS Baden-Württemberg drinking water PT scheme. In this round following parameter were to be determined.

- epichlorohydrin
- acrylamide

The PT was executed according to the recommendations of the German Federal Environment Agency from December 2003. These recommendations "for the execution of PTs for the measurement of chemical parameter and indicator parameter for the external quality control of drinking water laboratories" (Bundesgesundheitsblatt 46 12, 1094-1095) require, that drinking water laboratories must demonstrate their competence for all parameters they are accredited for or they want to be accredited for by a successful participation in a PT round within a cycle of 2-3 years.

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 epichlorohydrin in 1000-ml-glass bottles with screw cap. Preservation by cooling.

- 3 samples for the determination of acrylamide in 500-ml-glas bottles with screw cap. Preservation by cooling.

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

3. Sample preparation

The samples for the determination of the above mentioned parameters were based on a real drinking water matrix.

The drinking water was filtered by using 5 µm and 1 µm filter cartridges to eliminate particles. To reduce germs, the drinking water was irradiated with ultraviolet light and pasteurised at 80°C in a stainless steel vessel overnight. During pasteurisation, the drinking water was aerated with a mixture composed of carbon dioxide and nitrogen to prevent calcium carbonate precipitation.

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

4. Sample distribution

The samples were dispatched on 04 December 2023 by express service (GoExpress).

5. Analytical methods

The participants were free to choose a suitable method, but a limit of quantification of 0,04 µg/l for epichlorohydrin and 0,05 µg/l for acrylamide 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 samples had to be analysed in duplicate over the complete method (sample preparation and measurement). The participants were asked to report the results in µg/l with three significant digits.

6. Submission of the results

The deadline for the submission of results was on 22 December 2023.

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}:	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:	35
Number of reported values	168
Number of accepted values:	146 (86,9 %)

Illustration of the susscessful and not successful laboratories for each parameter
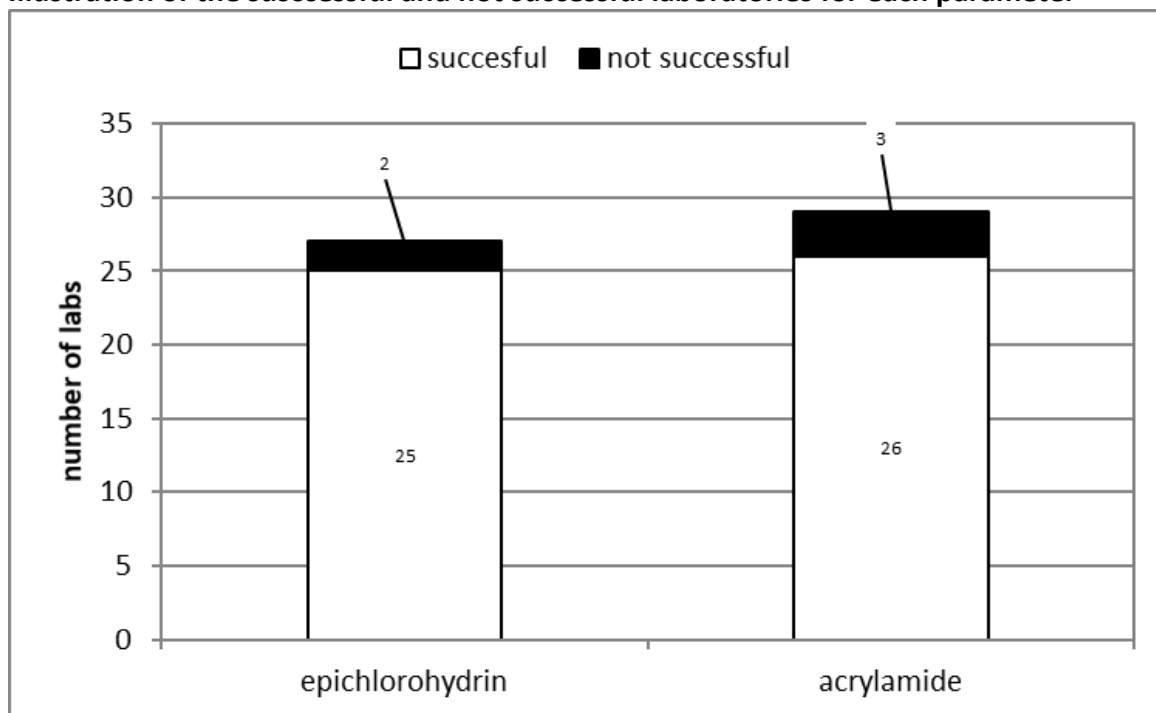
9. Explanation for the appendices

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	25 (71,4 %)
Number of valid values	168
Number of valid values with measurement uncertainties	117 (69,6 %)

Measurement uncertainties against the accreditation status

Accreditation status of the values	Number of values	Number of values with measurement uncertainty
accredited	153	102 (66,6 %)
not accredited	15	15 (100 %)
not specified	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 $|z_U| \leq 2{,}0$	105
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	16 (15,2 %)

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
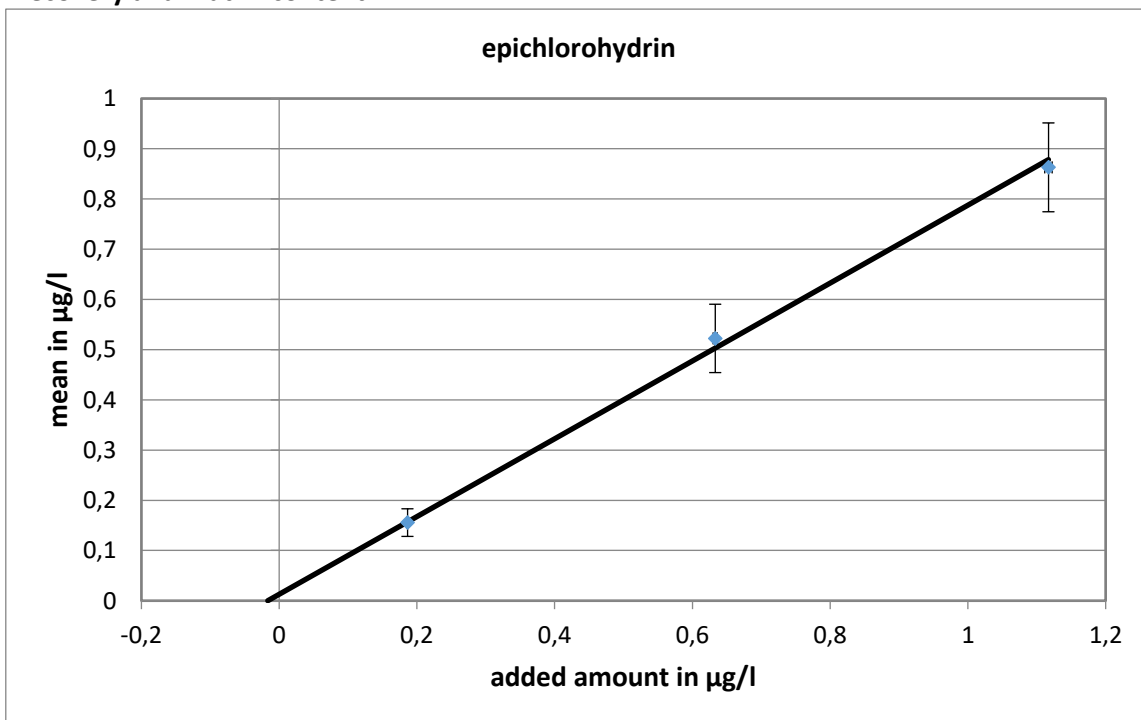
12.   Internet

The report is available on the following webpage:
http://www.aqsbw/pdf/287/report_287.pdf

epichlorohydrin

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	0,1555	17,68	0,0572	0,0389	25,00	0,2457	0,0853	57,99	-45,19	27	3	1	14,8
2	0,5224	13,03	0,1415	0,1306	25,00	0,8253	0,2863	57,99	-45,19	27	1	2	11,1
3	0,8630	10,25	0,1838	0,1838	21,30	1,279	0,5267	48,19	-38,97	27	1	1	7,4
									sum	81	5	4	11,1

Recovery and matrix content

slope of the regression: 0,775; recovery rate: 77,5 %

neg. x-axis intercept = matrix content: 0,0165 µg/l

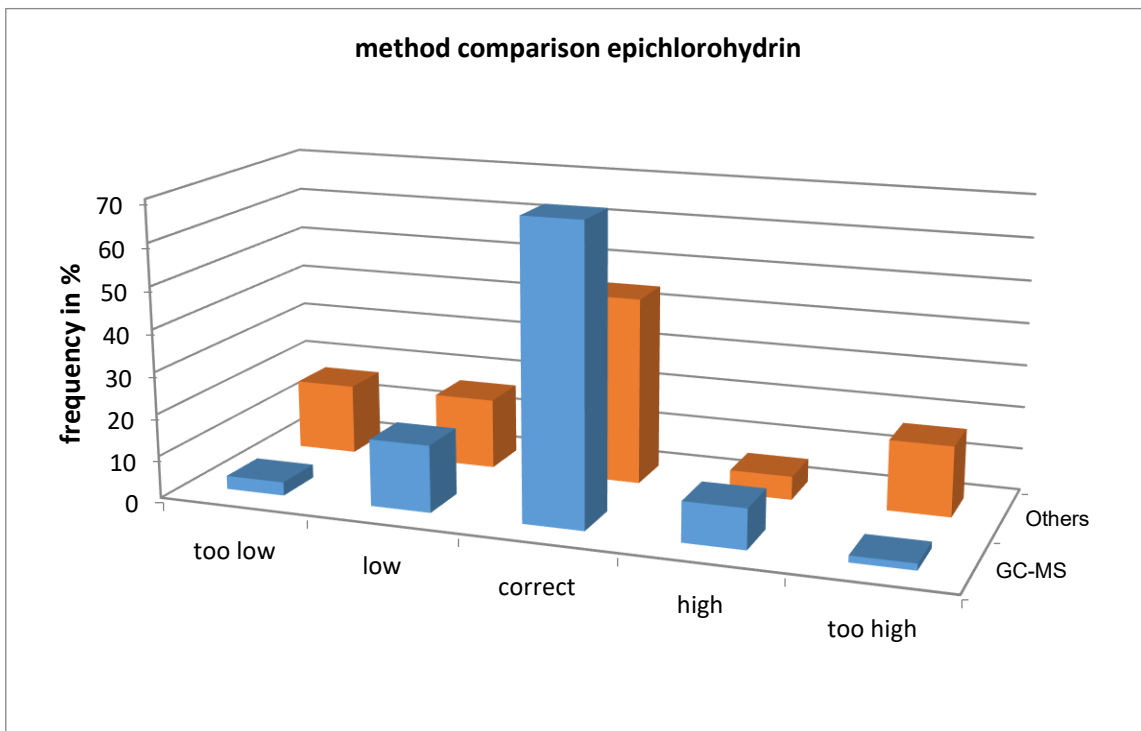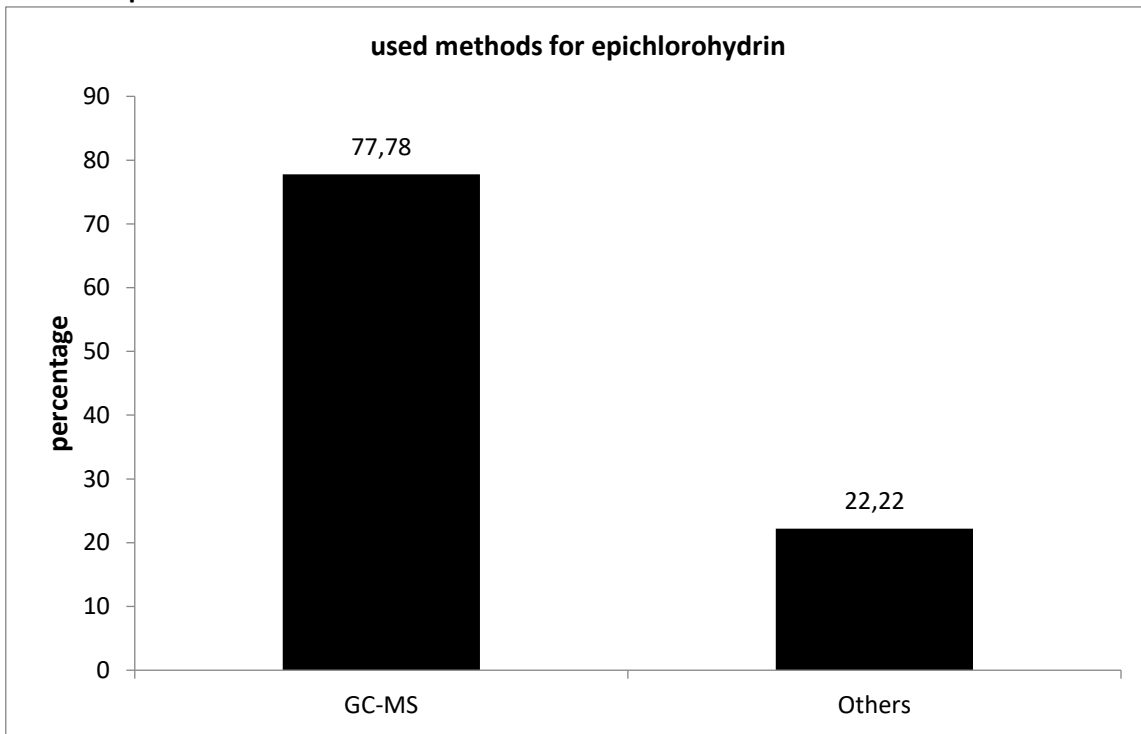expanded uncertainty of the matrix content: 0,0165 µg/l = 100 %

Relative standard deviation and tolerance limits

epichlorohydrin
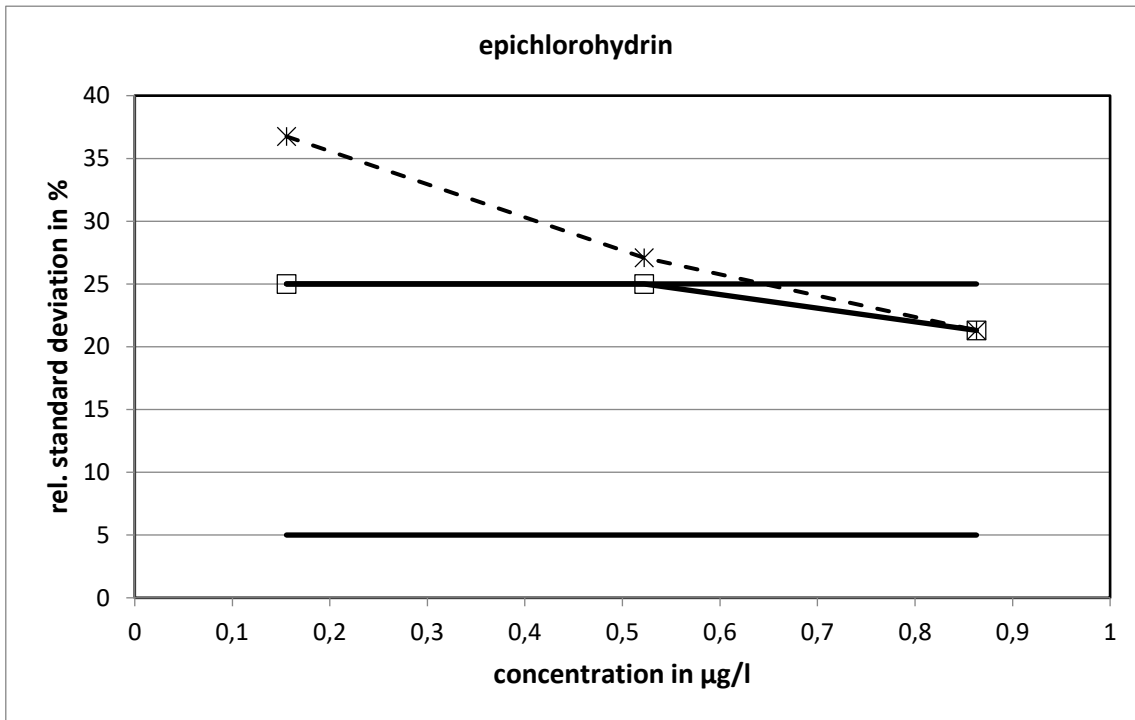
The relative standard deviations calculated with the Q-method reached the upper limit with two concentration levels.

epichlorohydrin

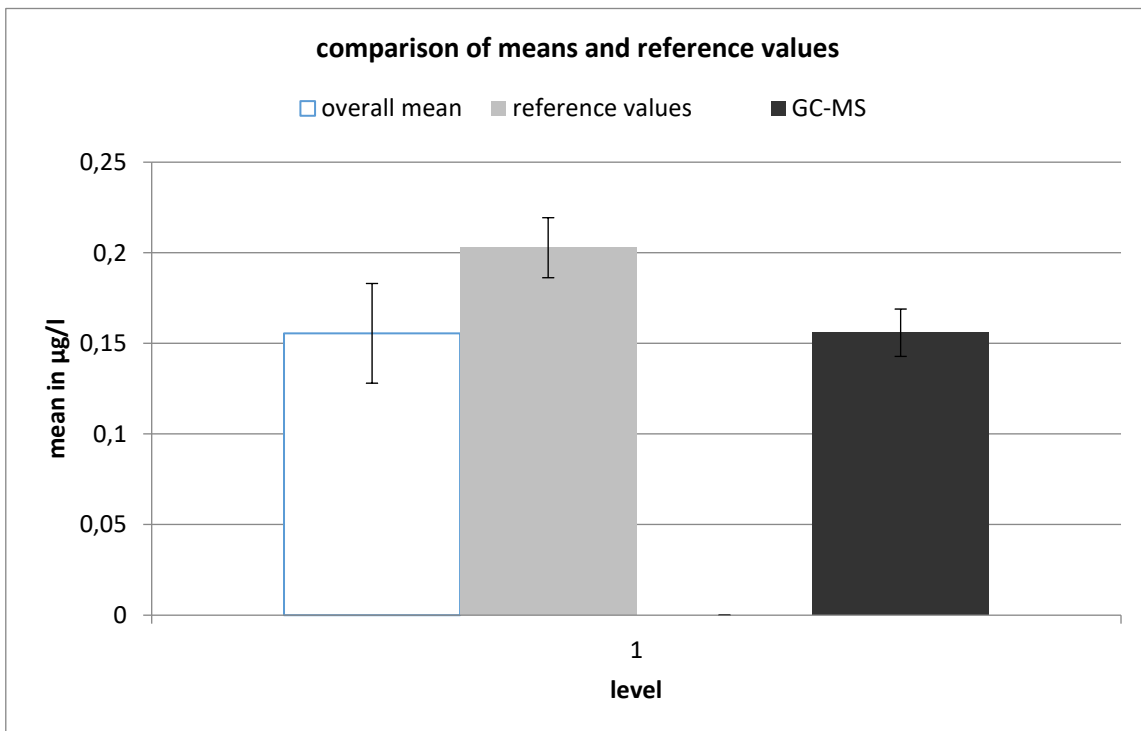**Method specific evaluation**

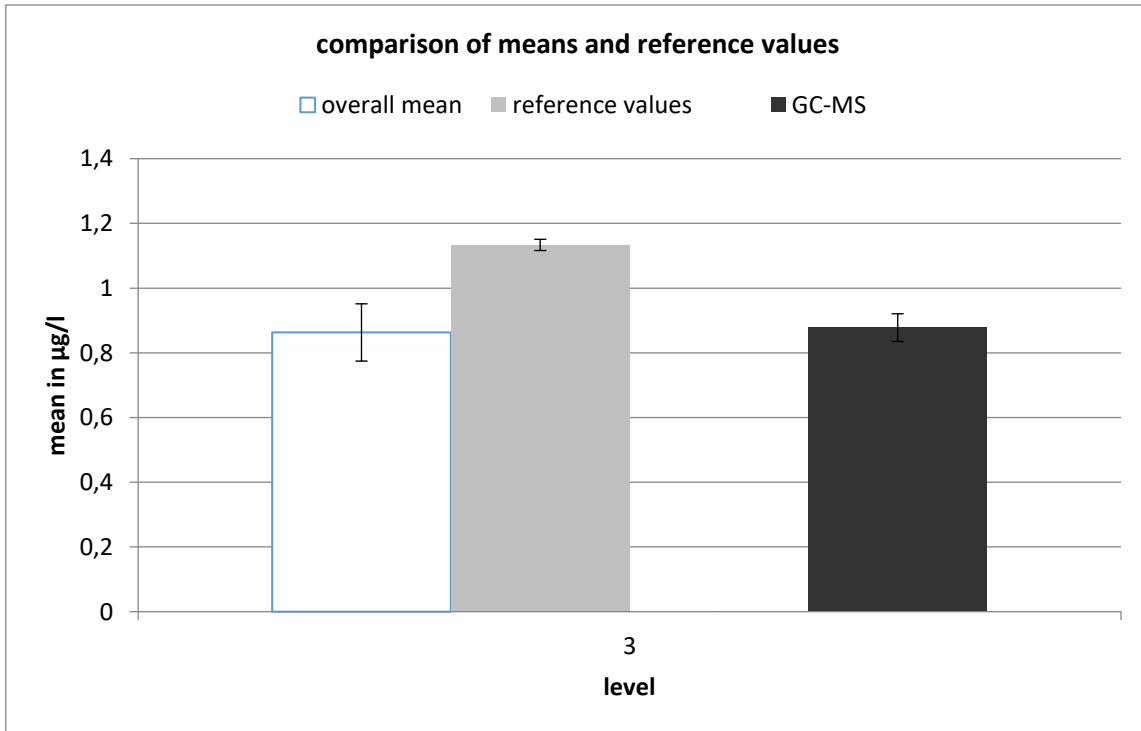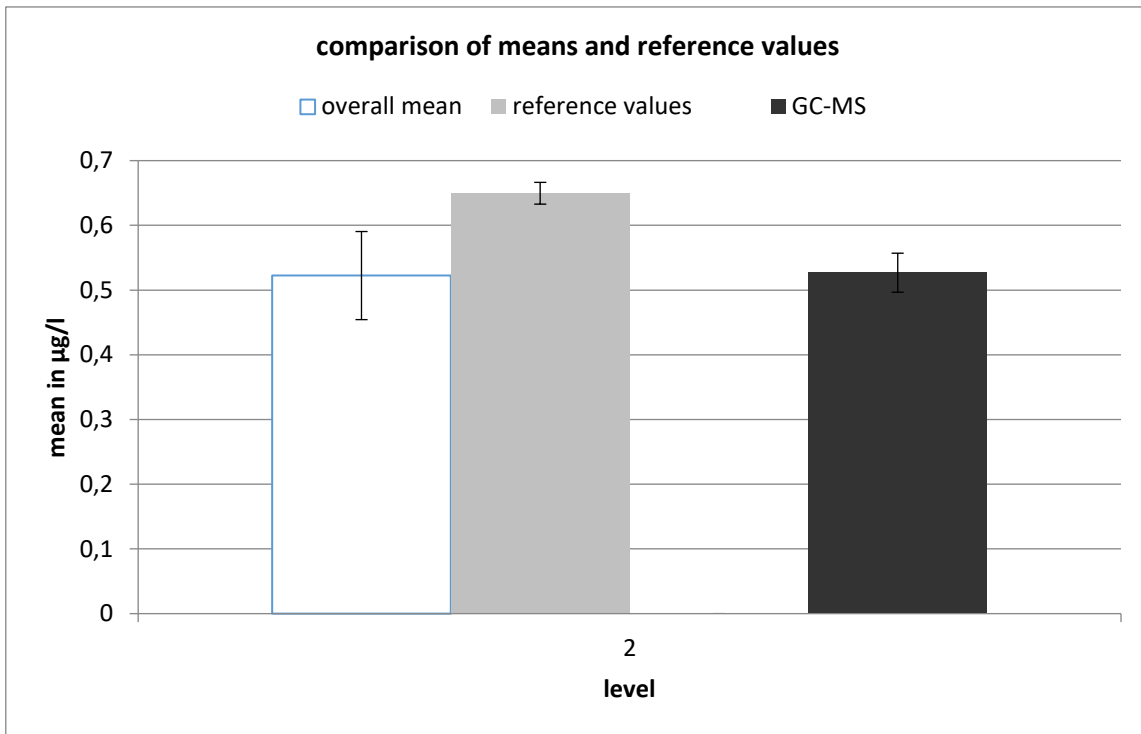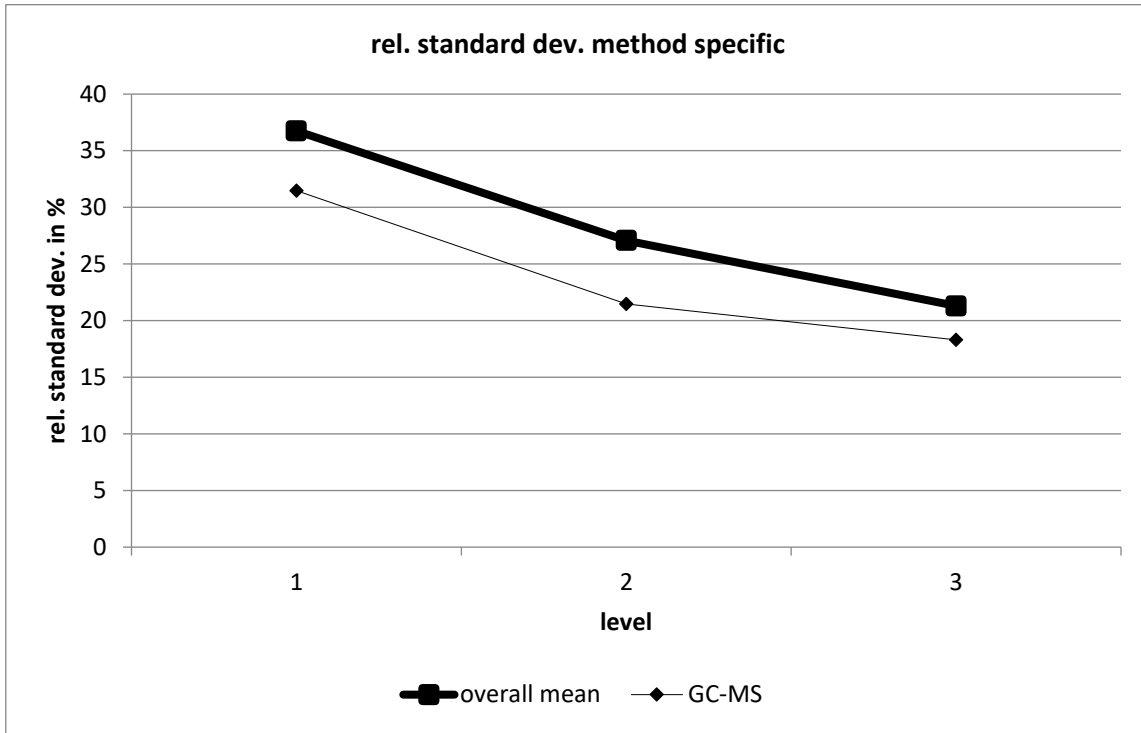### used methods for epichlorohydrin
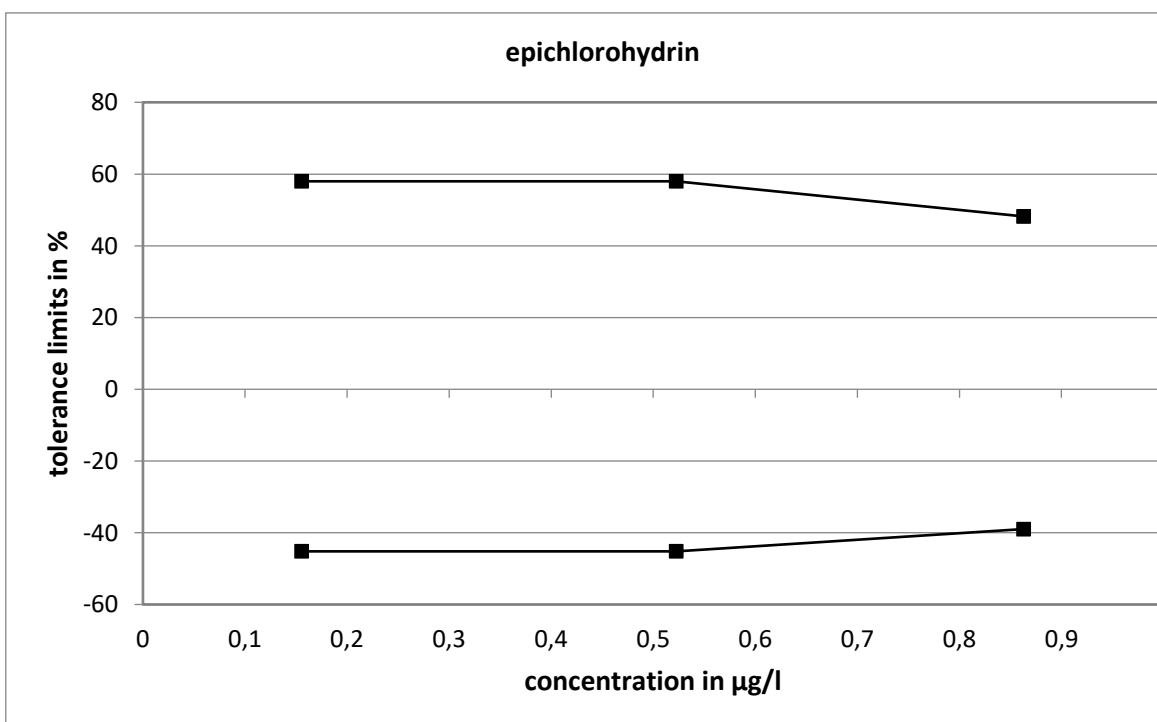
method comparison epichlorohydrin

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

Comparison of means and reference values

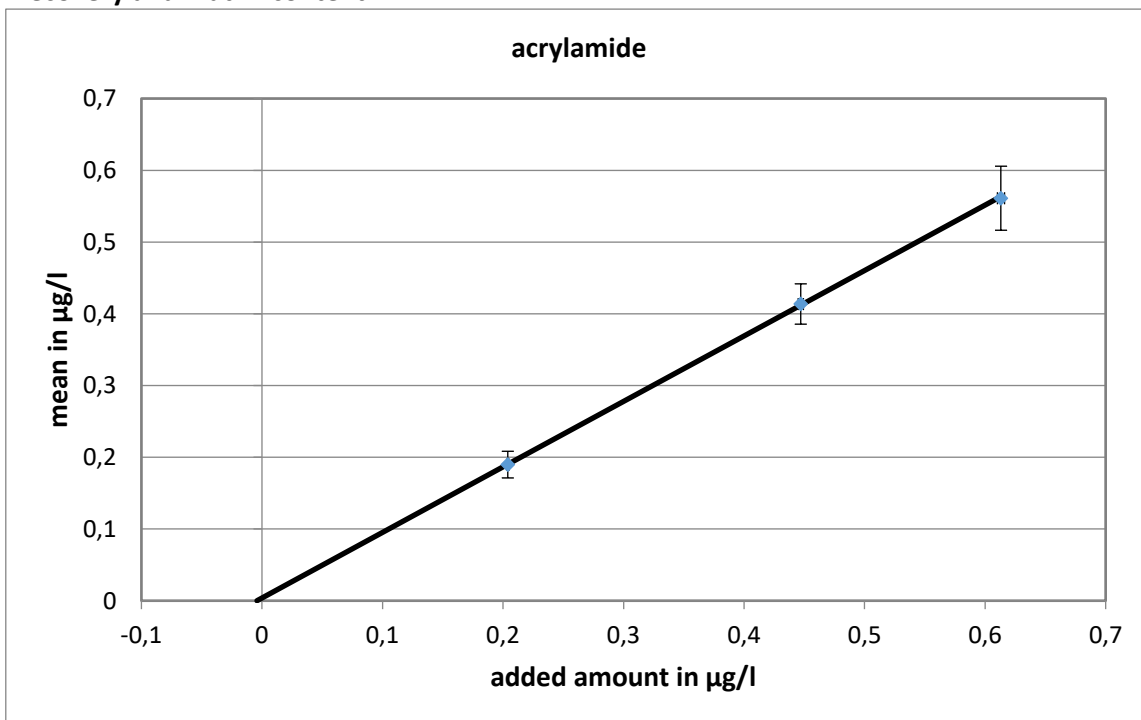| level	mean [µg/l]	exp. uncertainty [µg/l]	exp. uncertainty [%]	reference value [µg/l]	exp. uncertainty [µg/l]	exp. uncertainty [%]
1	0,1555	0,0275	17,7	0,2028	0,0166	8,2
2	0,5224	0,0681	13,0	0,6496	0,0168	2,6
3	0,8630	0,0884	10,2	1,1334	0,0174	1,5

comparison of means and reference values

comparison of means and reference values

comparison of means and reference values

rel. standard dev. method specific

| GC-MS									
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	0,1559	0,0131	8,3882	0,0491	31,475	22	3	0	13,64
2	0,5268	0,0302	5,7251	0,1132	21,483	22	1	1	9,091
3	0,8778	0,0428	4,8776	0,1607	18,302	22	1	0	4,545

acrylamide

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	0,1897	9,81	0,0401	0,0401	21,13	0,2803	0,1163	47,74	-38,67	29	3	1	13,8
2	0,4136	6,79	0,0605	0,0605	14,62	0,5447	0,3003	31,70	-27,40	29	4	0	13,8
3	0,5611	7,96	0,0962	0,0962	17,14	0,7729	0,3825	37,75	-31,82	29	3	0	10,3
									sum	87	10	1	12,6

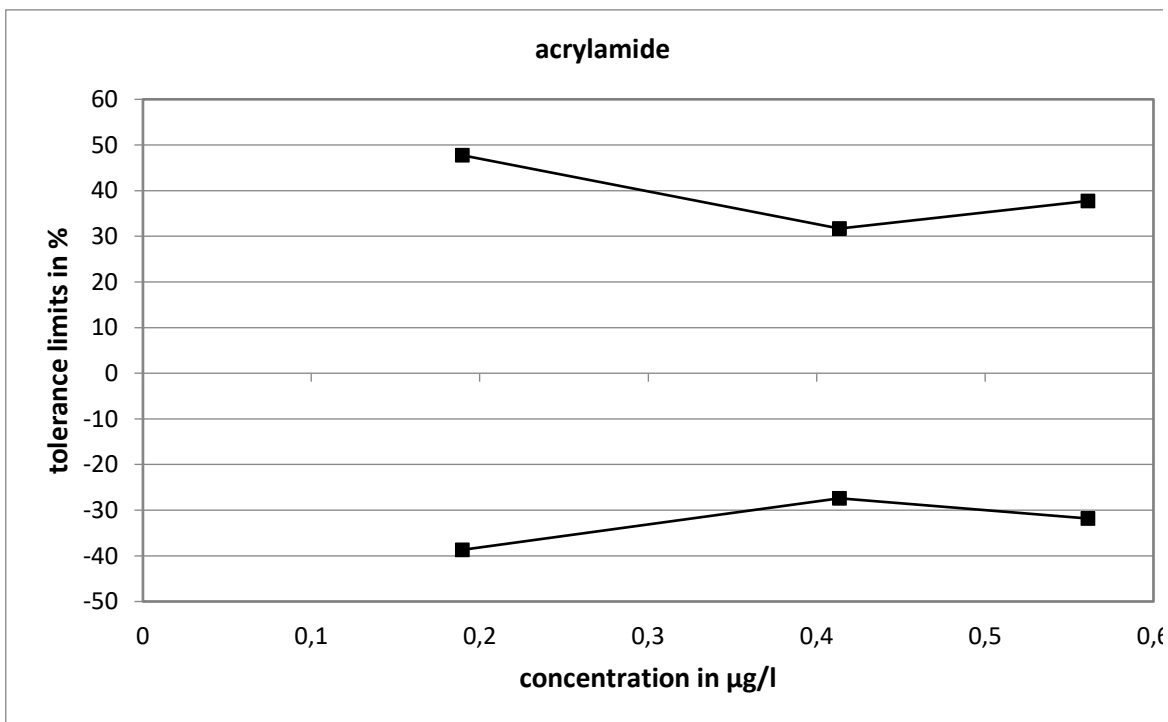**Recovery and matrix content**

slope of the regression: 0,913; recovery rate: 91,3 %

neg. x-axis intercept = matrix content: 0,0041 µg/l

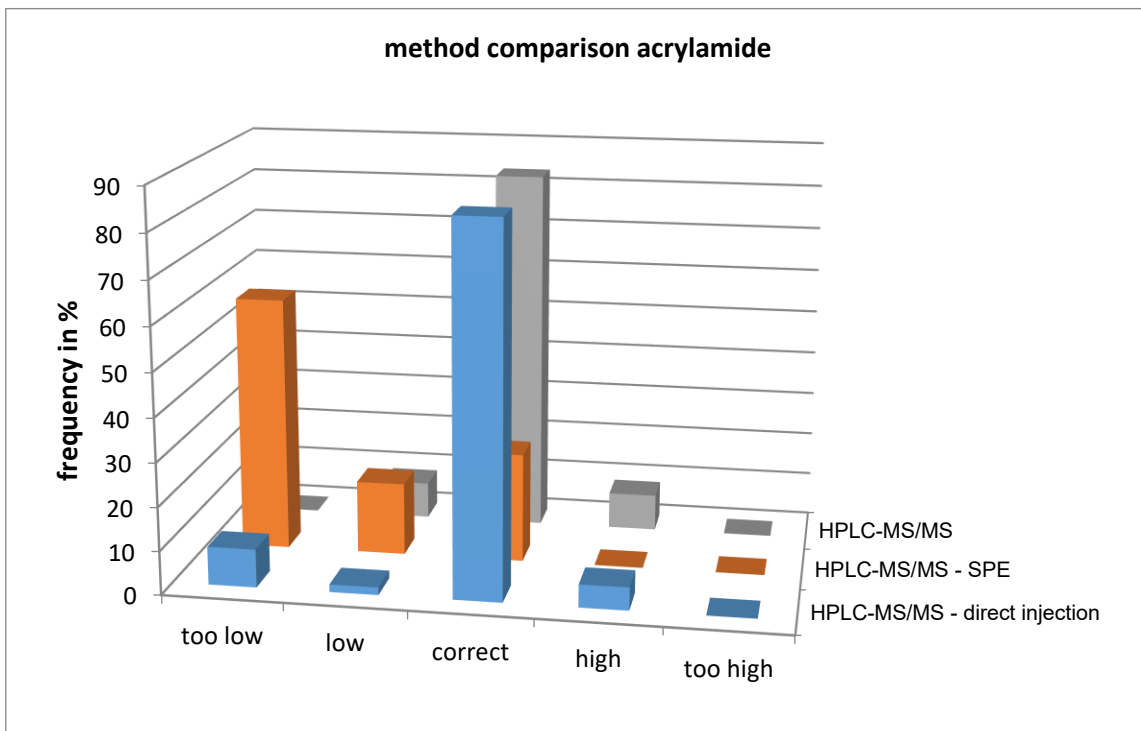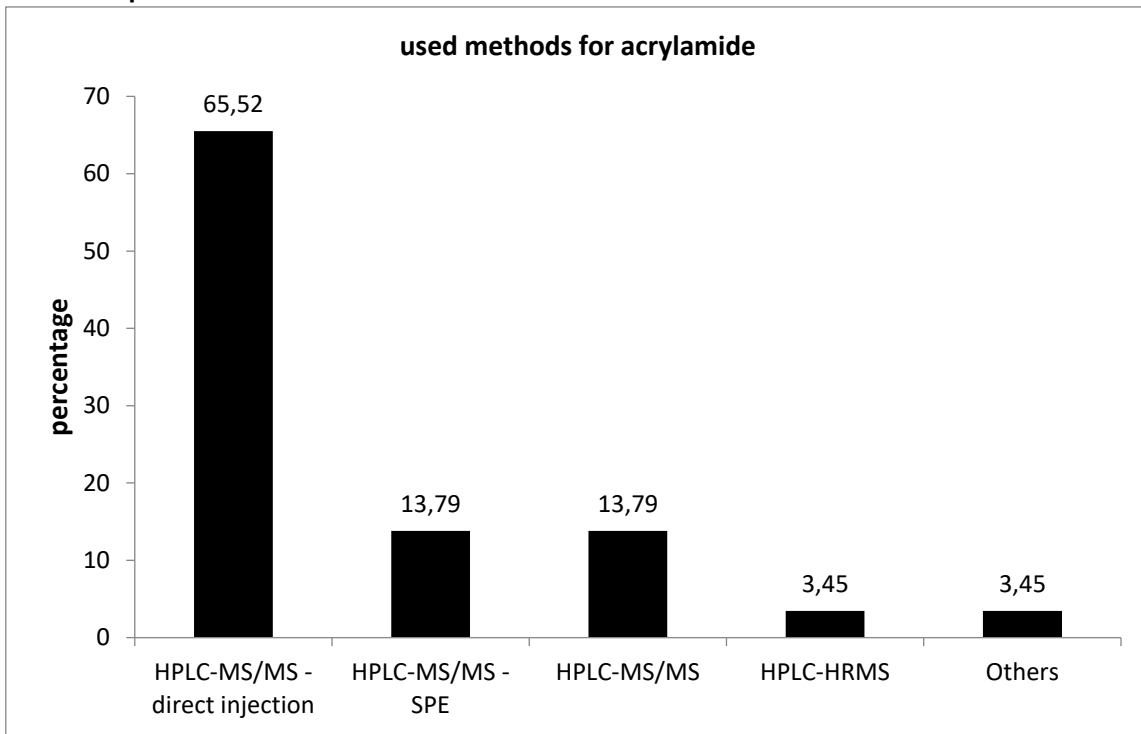expanded uncertainty of the matrix content: 0,0041 µg/l = 100 %

Relative standard deviation and tolerance limits

acrylamide
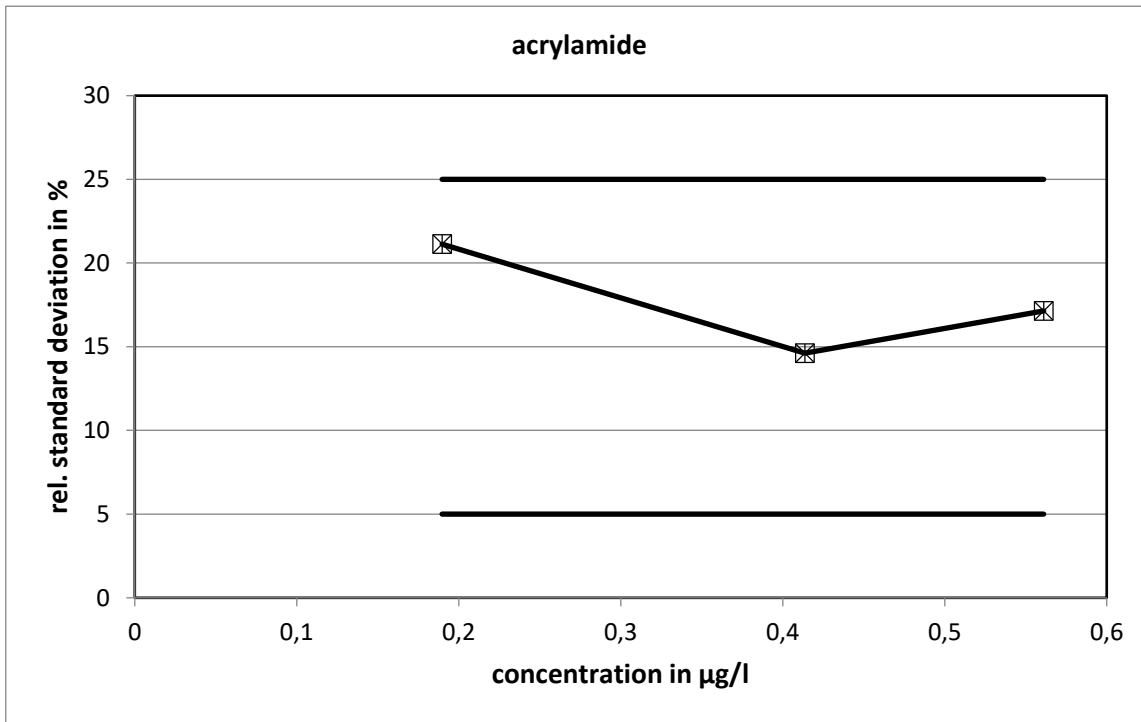
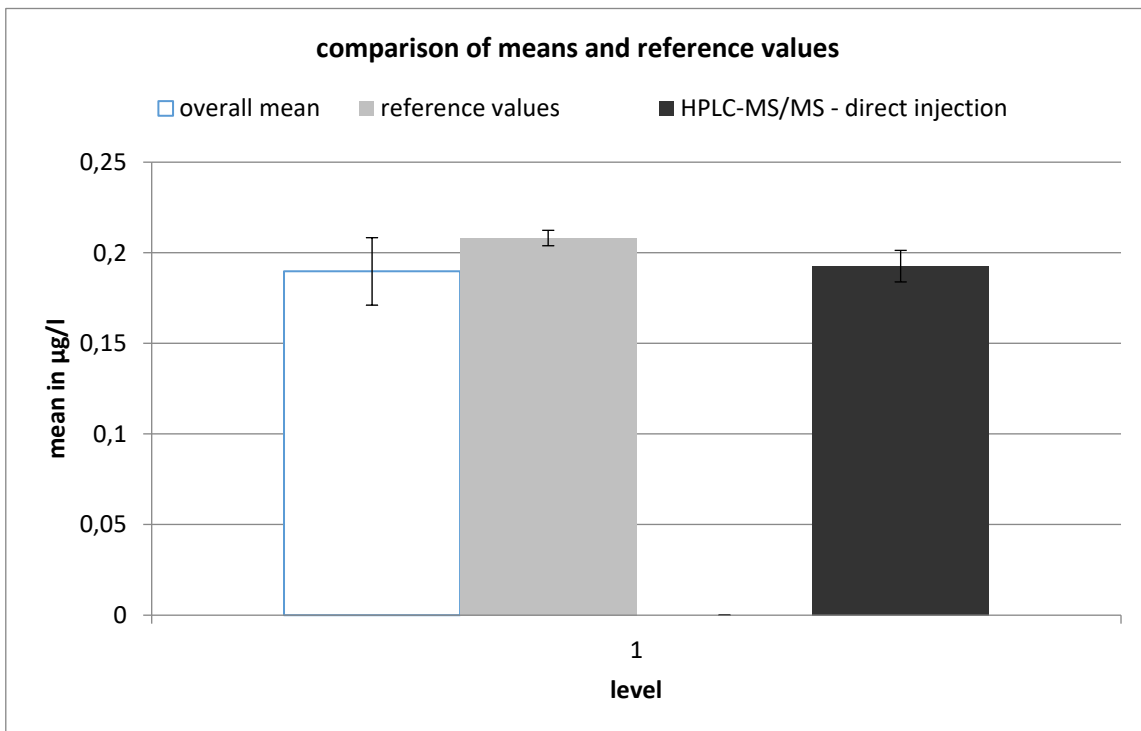The relative standard deviations calculated with the Q-method reached not the limits.

acrylamide

Method specific evaluation

used methods for acrylamide
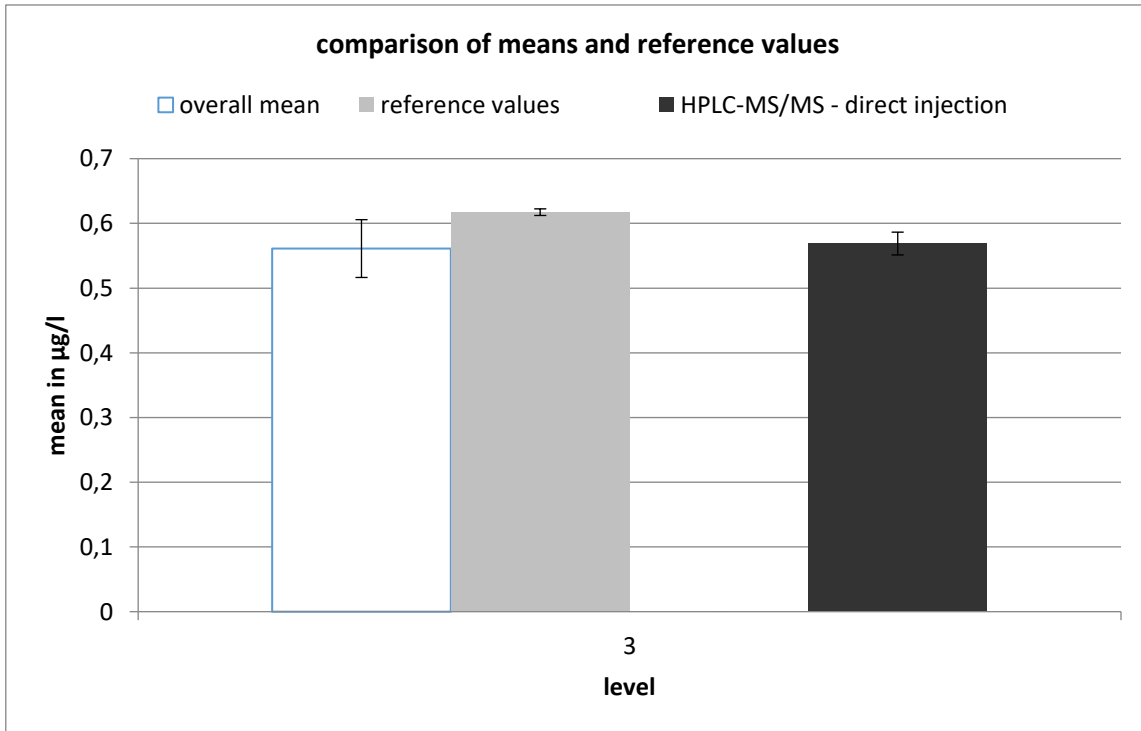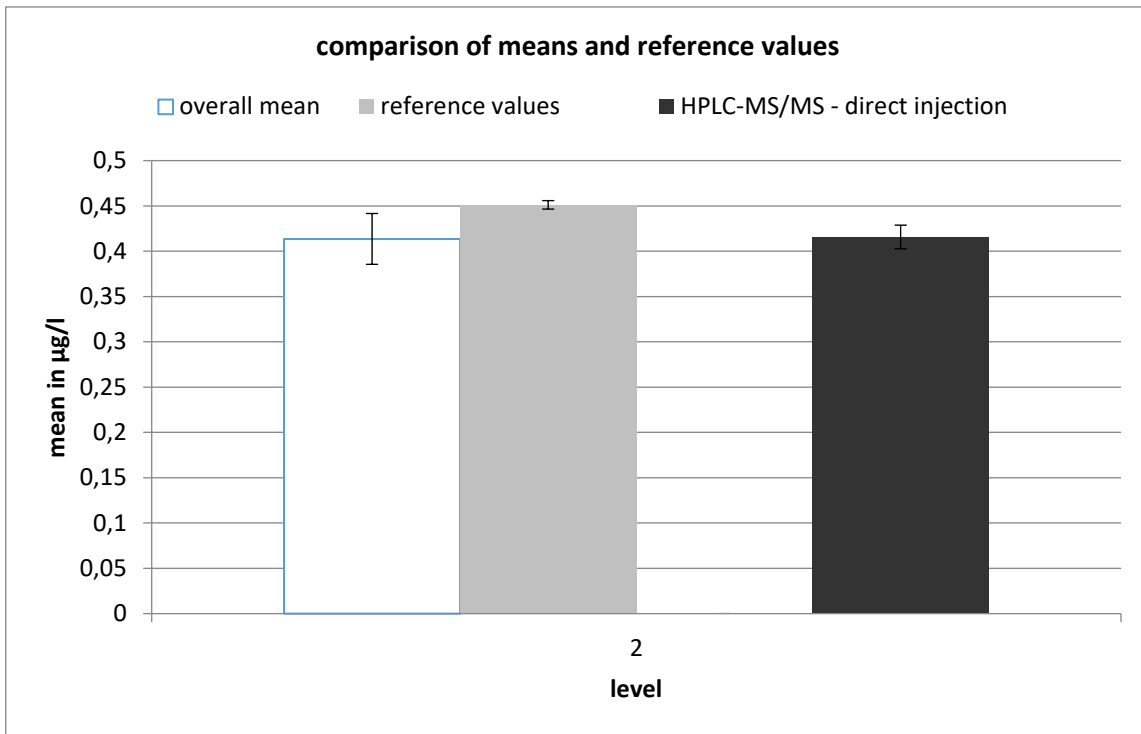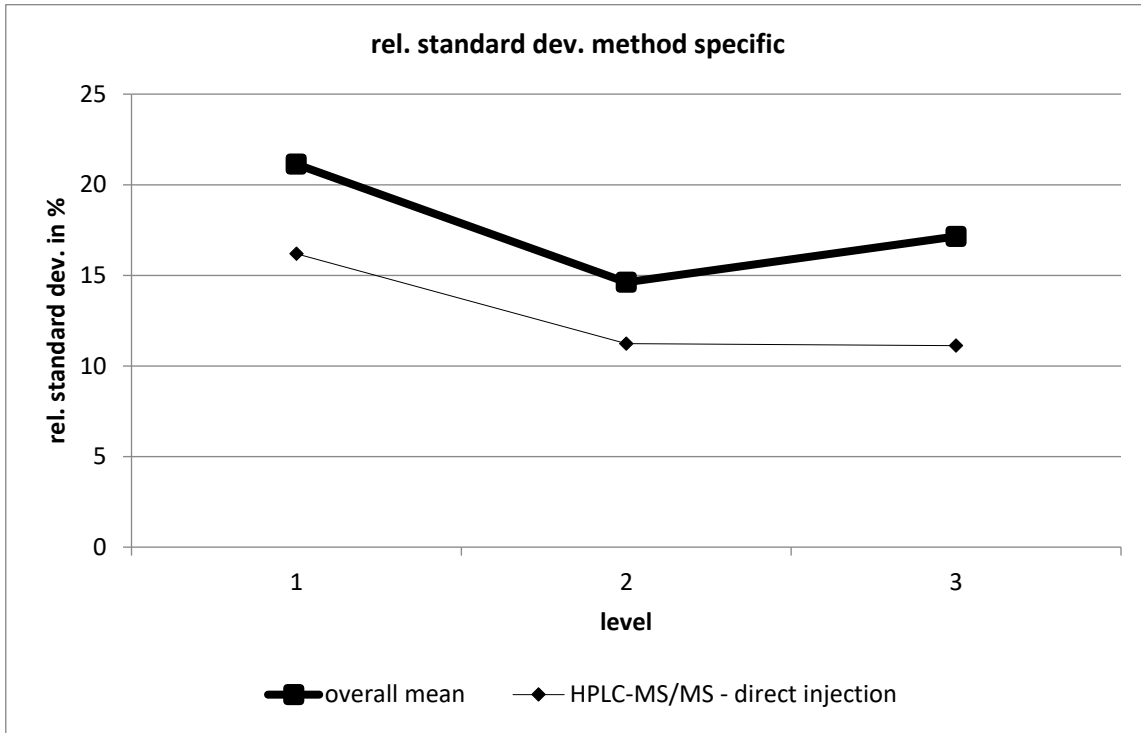

method comparison acrylamide

The values determined with HPLC-MS/MS - direct injection showed the closest statistical distribution.

Comparison of means and reference values

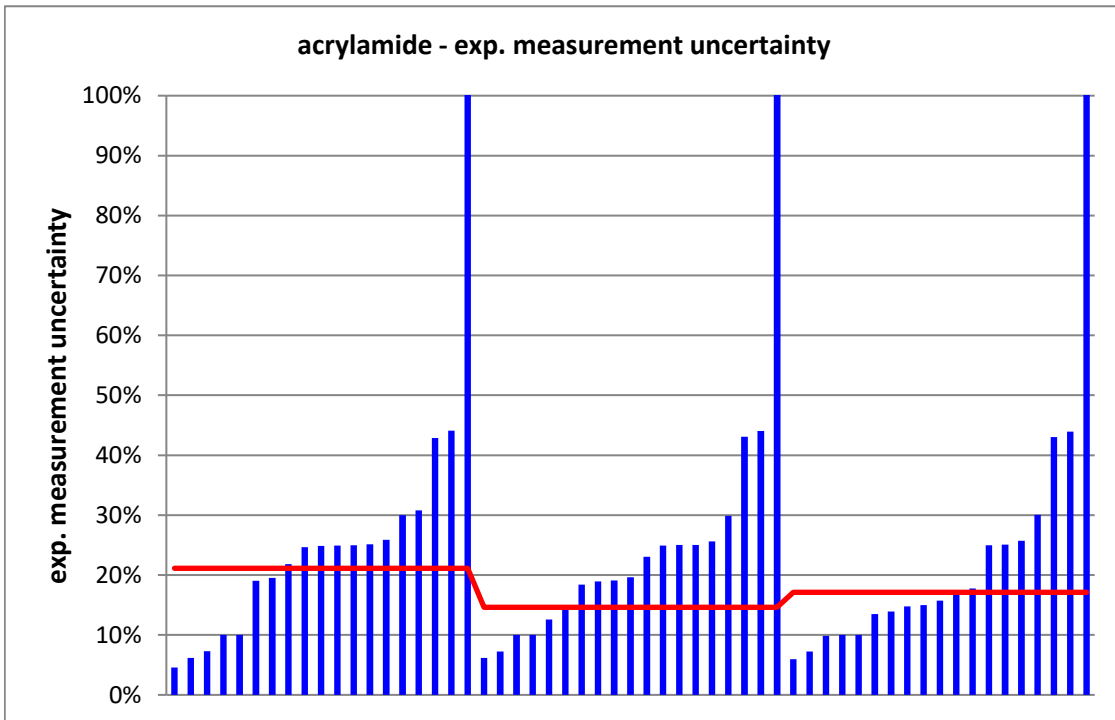| level	mean [µg/l]	exp. uncertainty [µg/l]	exp. uncertainty [%]	reference value [µg/l]	exp. uncertainty [µg/l]	exp. uncertainty [%]
1	0,1897	0,0186	9,8	0,2081	0,0043	2,0
2	0,4136	0,0281	6,8	0,4512	0,0047	1,0
3	0,5611	0,0446	8,0	0,6173	0,0051	0,8

comparison of means and reference values

□ overall mean   ■ reference values   ■ HPLC-MS/MS - direct injection

comparison of means and reference values

comparison of means and reference values

rel. standard dev. method specific

HPLC-MS/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	0,1926	0,0087	4,5247	0,0312	16,188	20	2	1	15
2	0,4158	0,0131	3,1399	0,0467	11,234	20	1	1	10
3	0,5688	0,0177	3,1078	0,0632	11,119	20	2	1	15
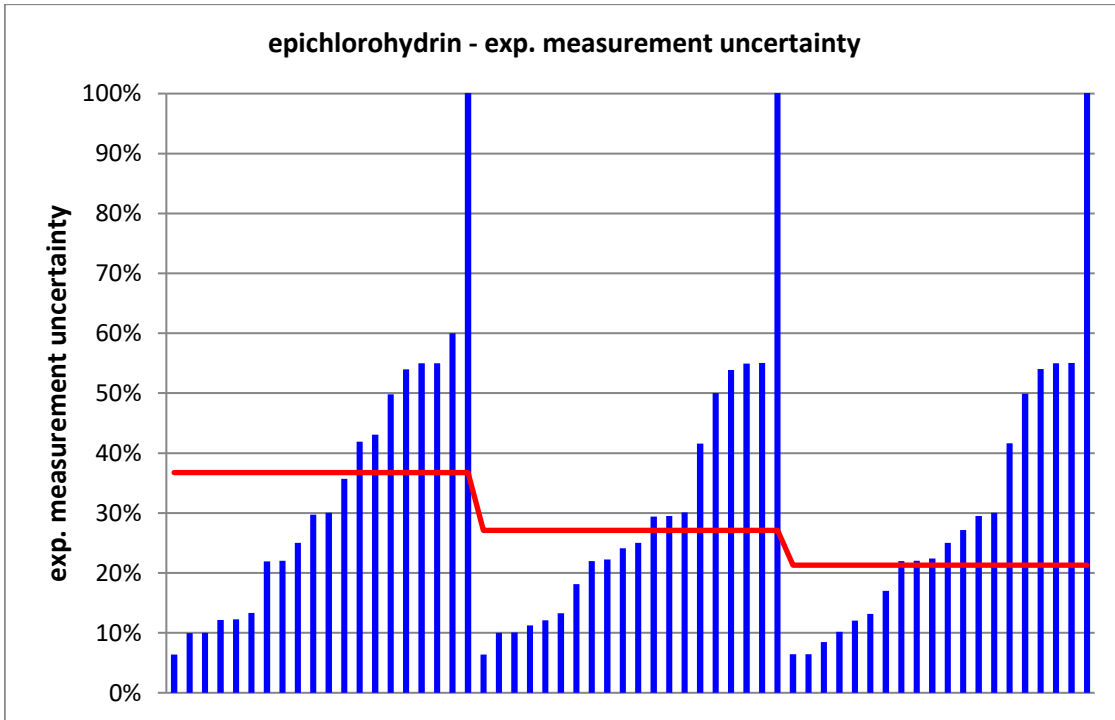
epichlorohydrin - exp. measurement uncertainty

Strongly deviating values are not illustrated.

acrylamide - exp. measurement uncertainty
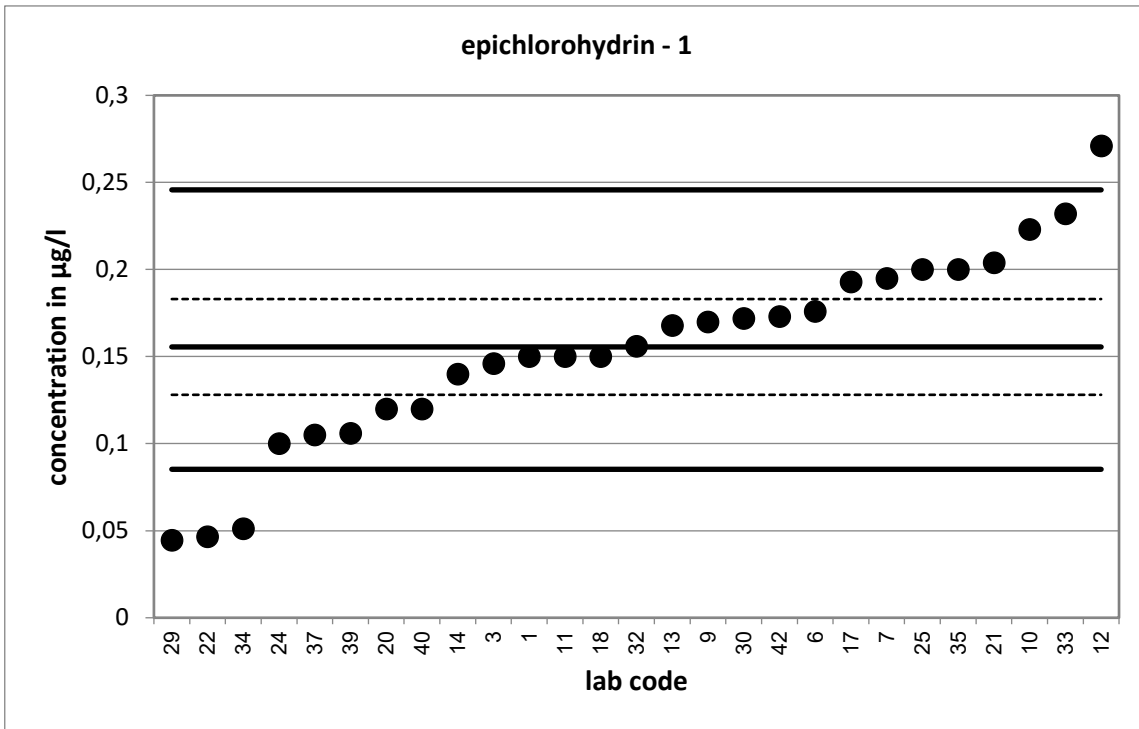
Strongly deviating values are not illustrated.

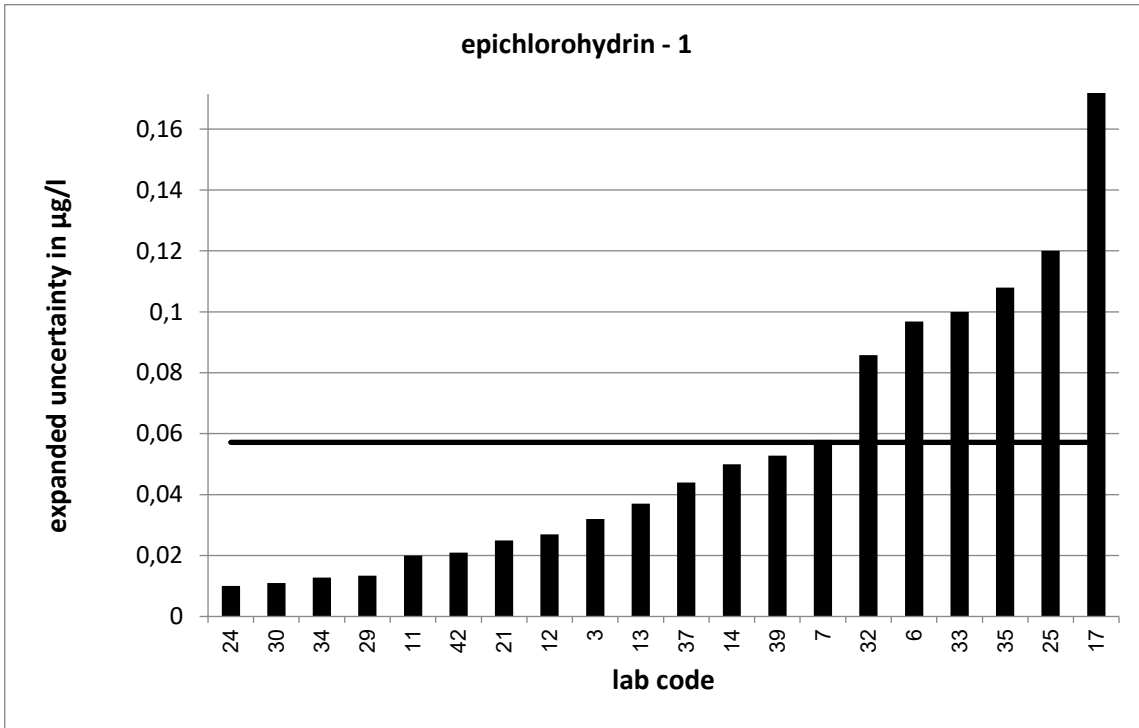| PT 11/23 - TW S10	epichlorohydrin - 1				
assigned value [µg/l]*		0,1555	± 0,0275		
upper tolerance limit [µg/l]		0,2457			
lower tolerance limit [µg/l]		0,08526			
lab code	result [µg/l]	±	z-score	z_U-score	assessm.**
1	0,15			-0,2	s
3	0,146	0,032	-0,5	-0,3	s
6	0,176	0,097	0,4	0,5	s
7	0,195	0,058	1,2	0,9	s
9	0,17			0,3	s
10	0,223			1,5	s
11	0,15	0,02	-0,3	-0,2	s
12	0,271	0,027	6,0	2,6	q
13	0,168	0,037	0,5	0,3	s
14	0,14	0,05	-0,5	-0,4	s
17	0,193	7	0,0	0,8	s
18	0,15			-0,2	s
20	0,12			-1,0	s
21	0,204	0,025	2,6	1,1	s
22	0,0466			-3,1	u
24	0,1	0,01	-3,8	-1,6	s
25	0,2	0,12	0,7	1,0	s
29	0,0446	0,013	-7,3	-3,2	u
30	0,172	0,011	1,1	0,4	s
32	0,156	0,086	0,0	0,0	s
33	0,232	0,1	1,5	1,7	s
34	0,0512	0,013	-6,9	-3,0	u
35	0,2	0,108	0,8	1,0	s
37	0,105	0,044	-1,9	-1,4	s
39	0,106	0,053	-1,7	-1,4	s
40	0,12			-1,0	s
42	0,173	0,021	1,0	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%
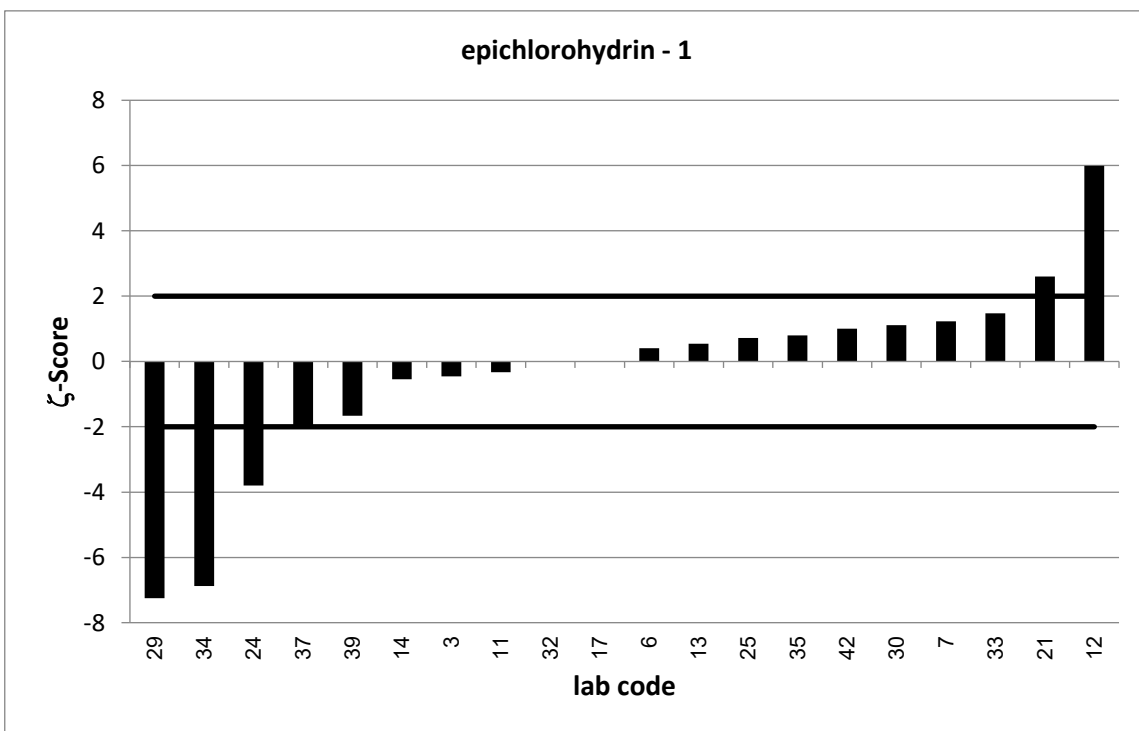** s = satisfactory, q = questionable, u = unsatisfactory

epichlorohydrin - 1

Strongly deviating values are not shown in the diagram.

epichlorohydrin - 1

epichlorohydrin - 1
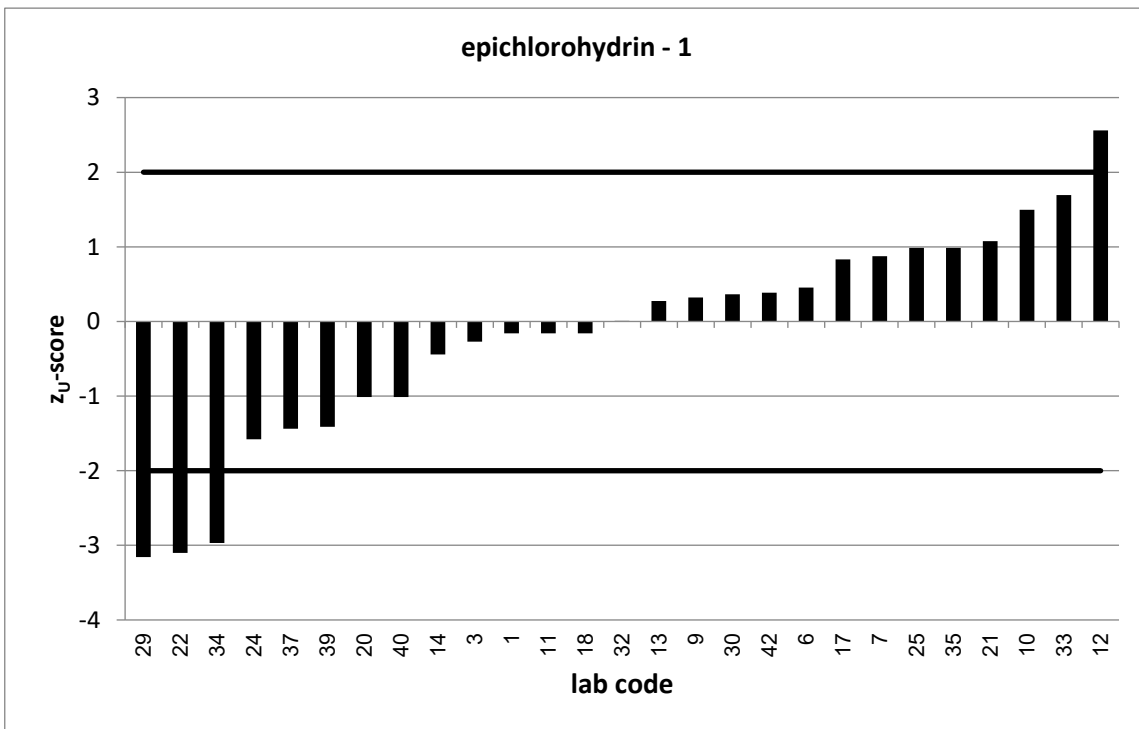
Strongly deviating values are not correctly shown in the diagram.

epichlorohydrin - 1

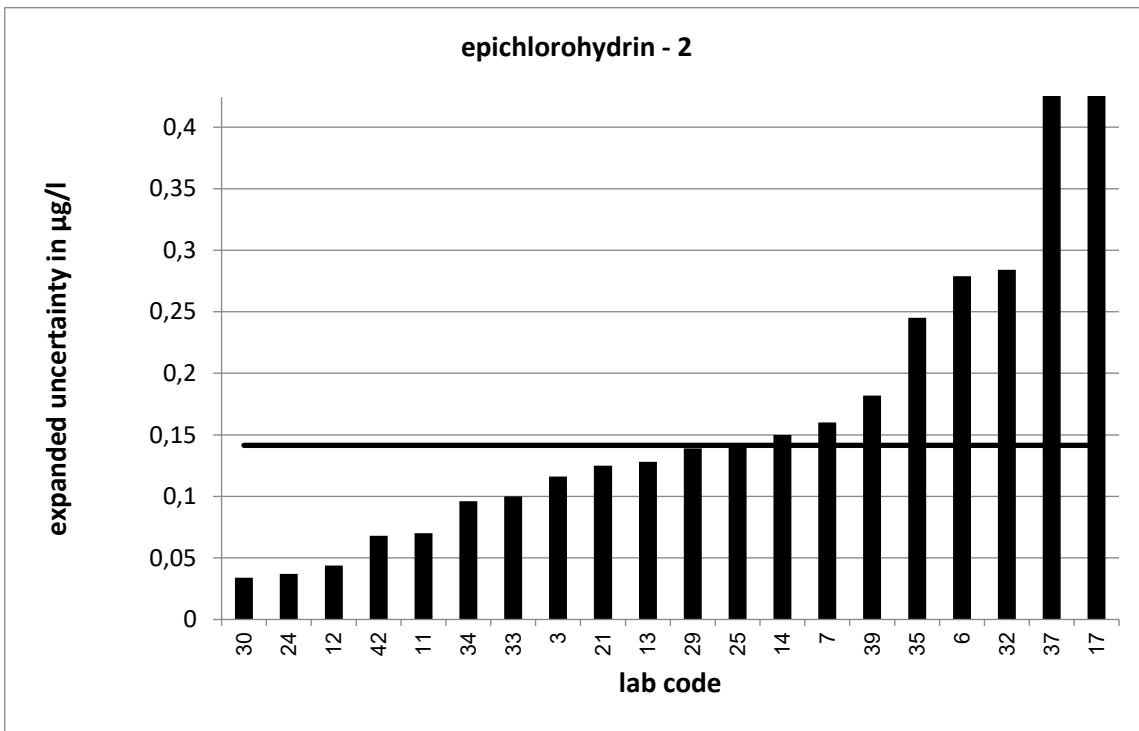| PT 11/23 - TW S10	epichlorohydrin - 2				
assigned value [µg/l]*		0,5224	± 0,0681		
upper tolerance limit [µg/l]		0,8253			
lower tolerance limit [µg/l]		0,2863			
lab code	result [µg/l]	±	z-score	z_U-score	assessm.**
1	0,532			0,1	s
3	0,521	0,116	0,0	0,0	s
6	0,507	0,279	-0,1	-0,1	s
7	0,542	0,16	0,2	0,1	s
9	0,67			1,0	s
10	0,701			1,2	s
11	0,527	0,07	0,1	0,0	s
12	0,437	0,044	-2,1	-0,7	s
13	0,583	0,128	0,8	0,4	s
14	0,51	0,15	-0,2	-0,1	s
17	0,667	7	0,0	1,0	s
18	0,513			-0,1	s
20	0,439			-0,7	s
21	0,69	0,125	2,4	1,1	s
22	0,197			-2,8	q
24	0,367	0,037	-4,0	-1,3	s
25	0,581	0,14	0,8	0,4	s
29	0,462	0,139	-0,8	-0,5	s
30	0,533	0,034	0,3	0,1	s
32	0,517	0,284	0,0	0,0	s
33	0,891	0,1	6,1	2,4	q
34	0,384	0,096	-2,4	-1,2	s
35	0,455	0,245	-0,5	-0,6	s
37	1,06	0,441	2,4	3,5	u
39	0,364	0,182	-1,6	-1,3	s
40	0,373			-1,3	s
42	0,563	0,068	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%
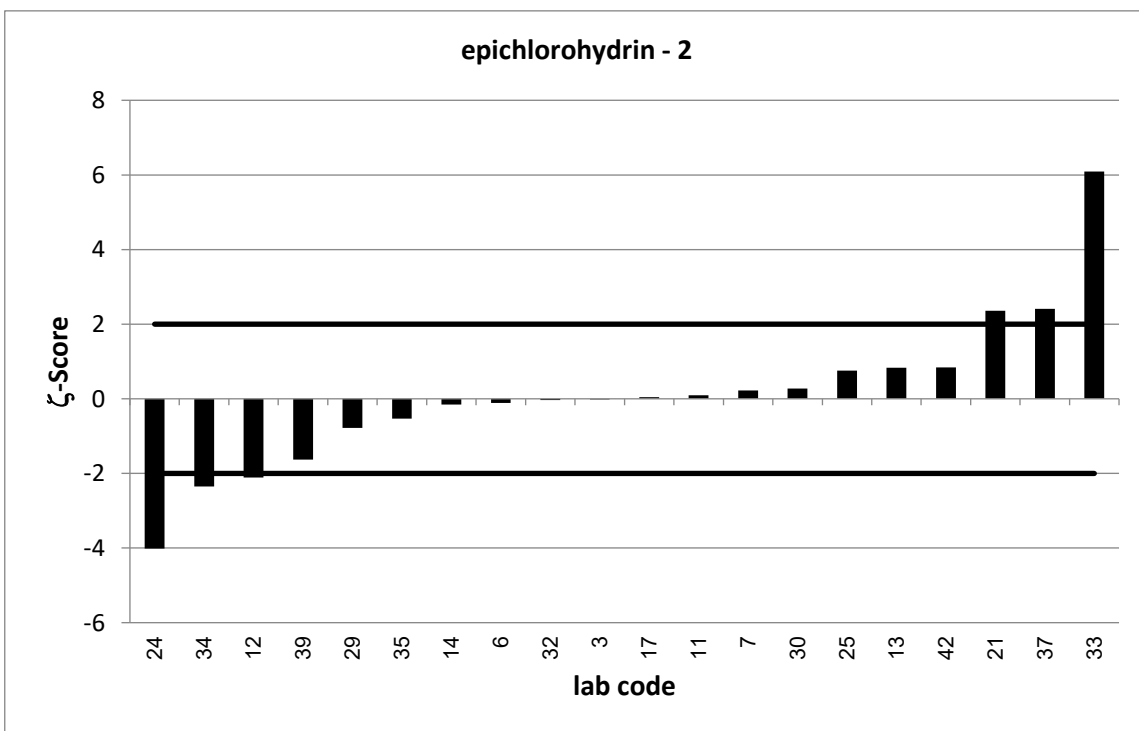** s = satisfactory, q = questionable, u = unsatisfactory

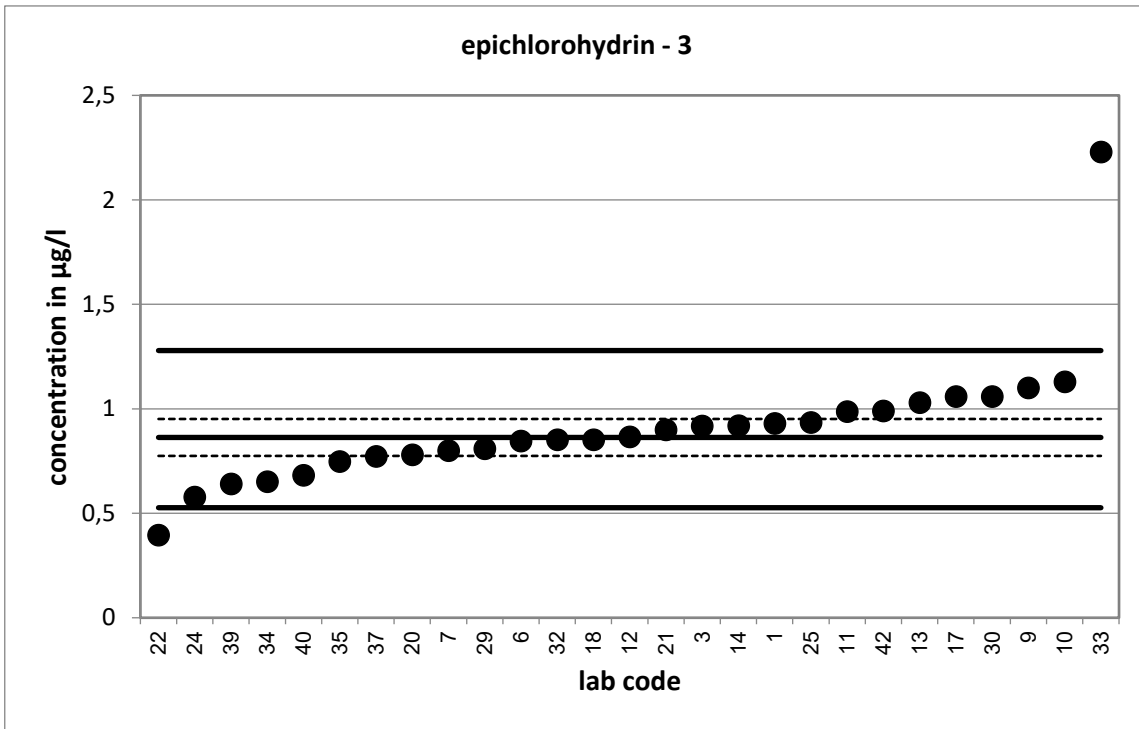epichlorohydrin - 2

Strongly deviating values are not shown in the diagram.
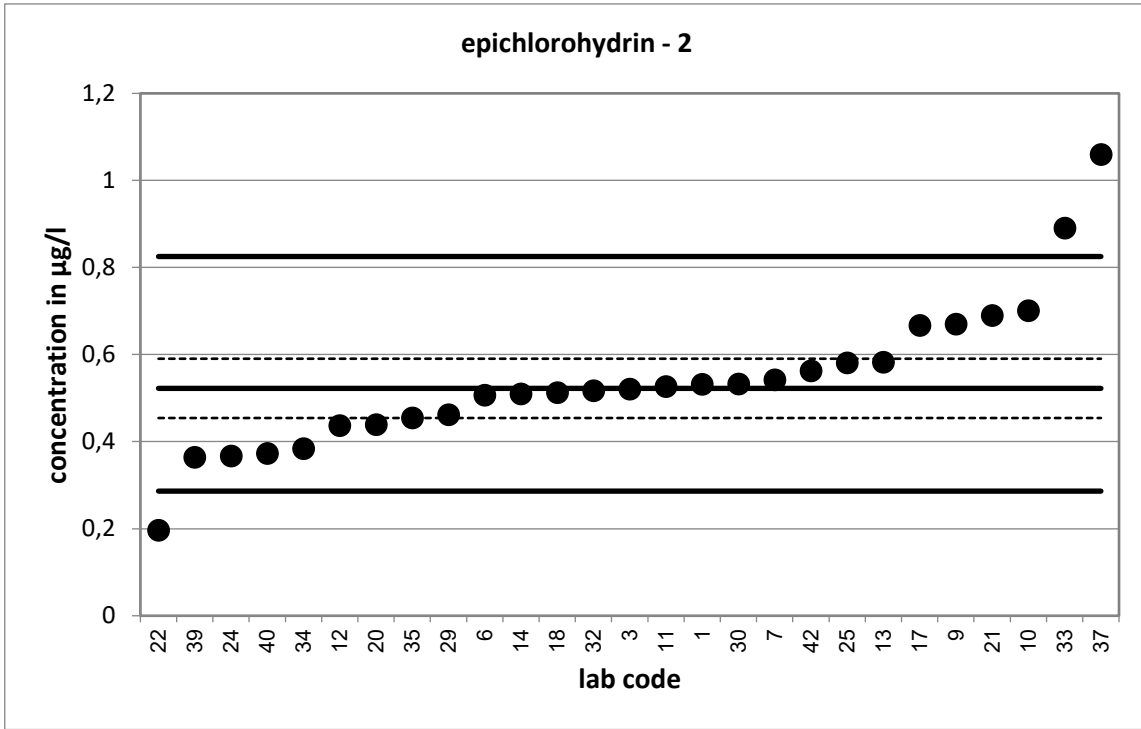
epichlorohydrin - 2

epichlorohydrin - 2
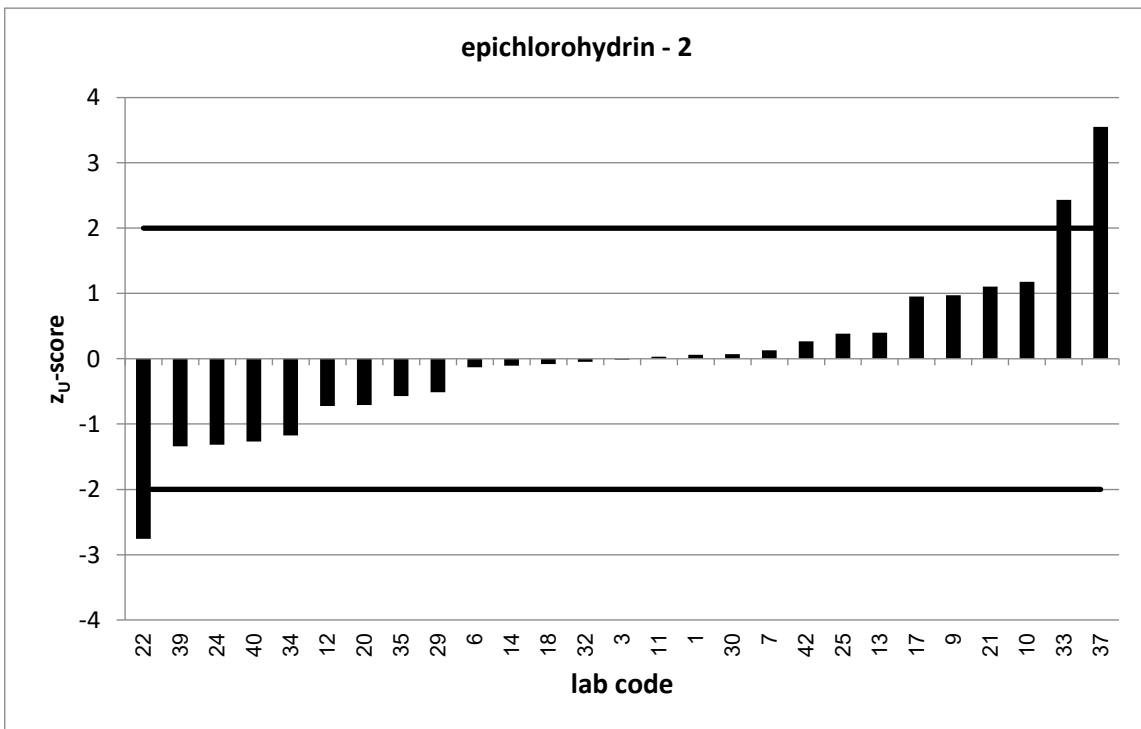
Strongly deviating values are not correctly shown in the diagram.

epichlorohydrin - 2

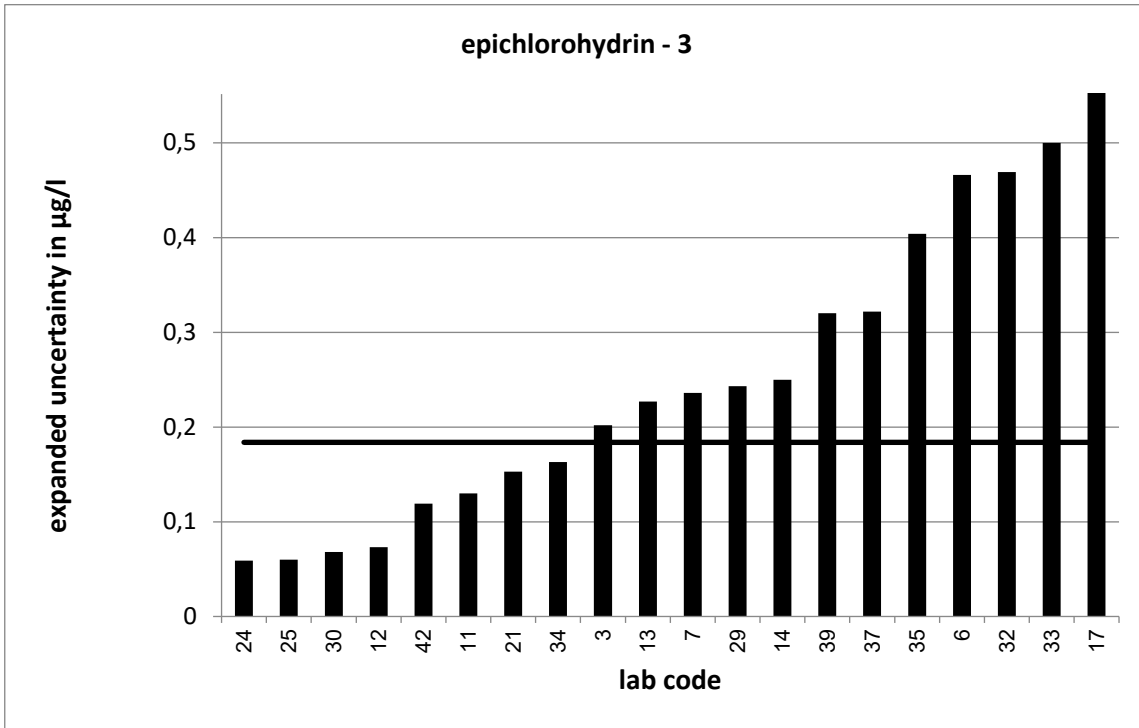| PT 11/23 - TW S10	epichlorohydrin - 3				
assigned value [µg/l]*		0,863	± 0,0884		
upper tolerance limit [µg/l]		1,279			
lower tolerance limit [µg/l]		0,5267			
lab code	result [µg/l]	±	z-score	z_U-score	assessm.**
1	0,93			0,3	s
3	0,918	0,202	0,5	0,3	s
6	0,847	0,466	-0,1	-0,1	s
7	0,8	0,236	-0,5	-0,4	s
9	1,1			1,1	s
10	1,13			1,3	s
11	0,987	0,13	1,6	0,6	s
12	0,867	0,073	0,1	0,0	s
13	1,03	0,227	1,4	0,8	s
14	0,92	0,25	0,4	0,3	s
17	1,059	7	0,1	0,9	s
18	0,853			-0,1	s
20	0,78			-0,5	s
21	0,9	0,153	0,4	0,2	s
22	0,396			-2,8	q
24	0,579	0,059	-5,3	-1,7	s
25	0,935	0,06	1,3	0,3	s
29	0,809	0,243	-0,4	-0,3	s
30	1,06	0,068	3,5	0,9	s
32	0,852	0,469	0,0	-0,1	s
33	2,23	0,5	5,4	6,6	u
34	0,652	0,163	-2,3	-1,3	s
35	0,748	0,404	-0,6	-0,7	s
37	0,773	0,322	-0,5	-0,5	s
39	0,641	0,32	-1,3	-1,3	s
40	0,682			-1,1	s
42	0,99	0,119	1,7	0,6	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%
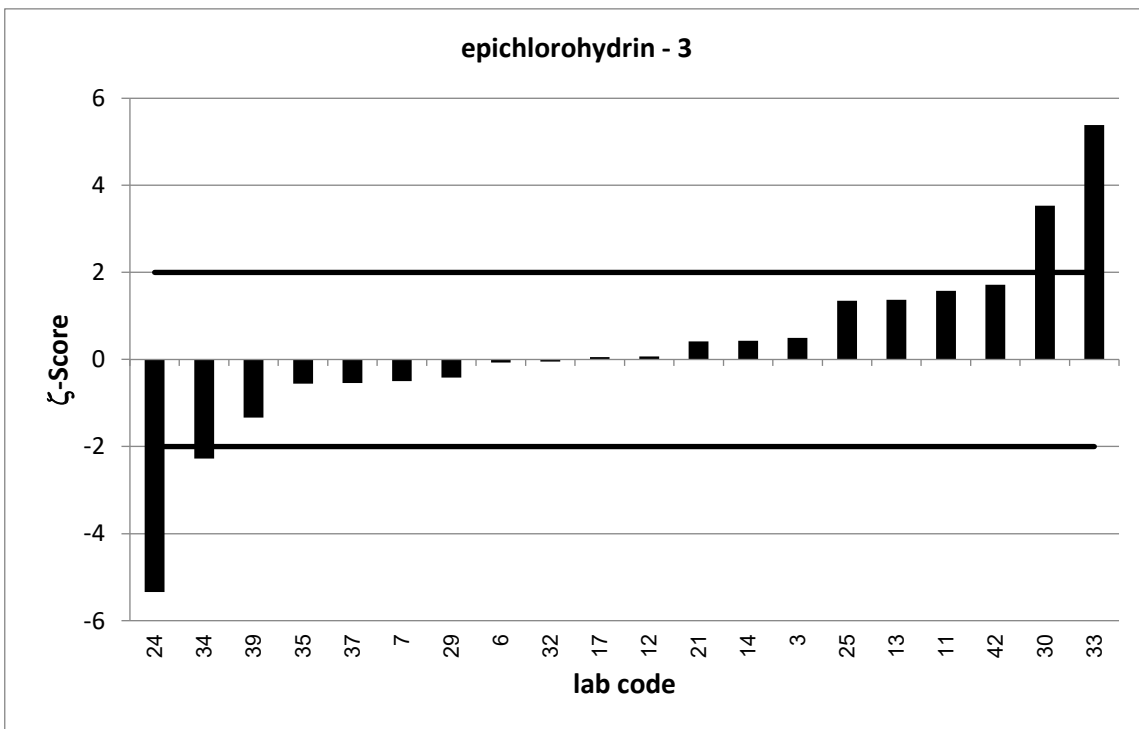
** s = satisfactory, q = questionable, u = unsatisfactory

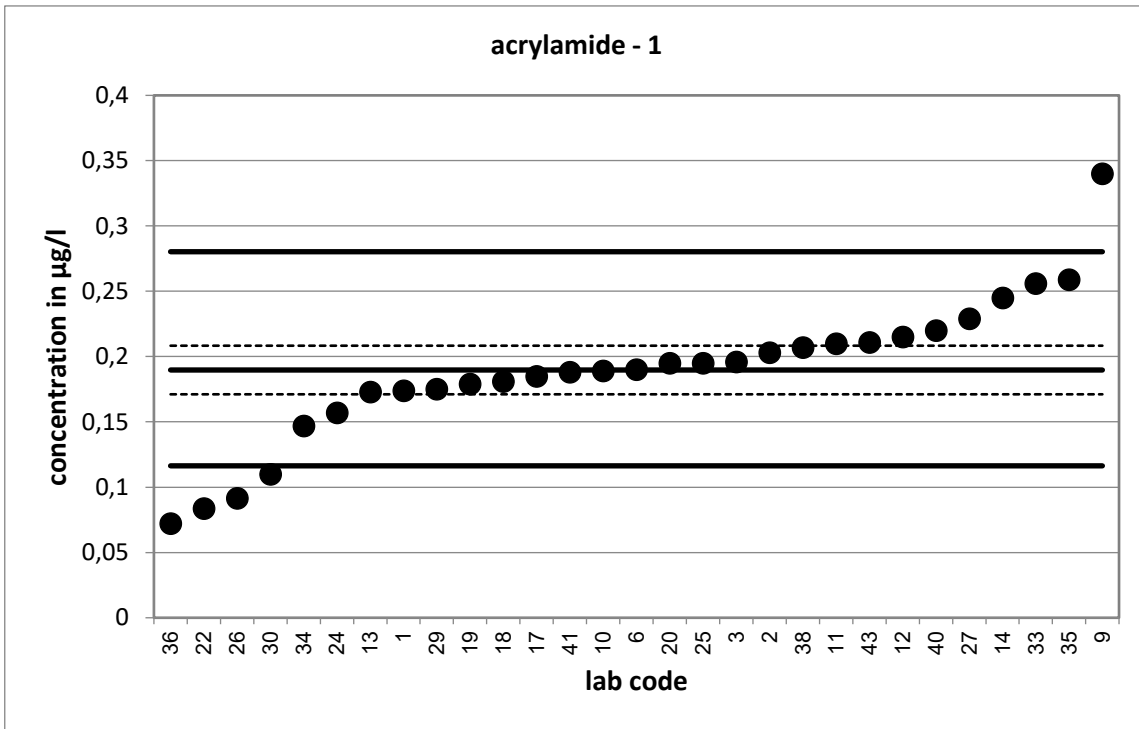epichlorohydrin - 3

Strongly deviating values are not shown in the diagram.

epichlorohydrin - 3

epichlorohydrin - 3

Strongly deviating values are not correctly shown in the diagram.

epichlorohydrin - 3
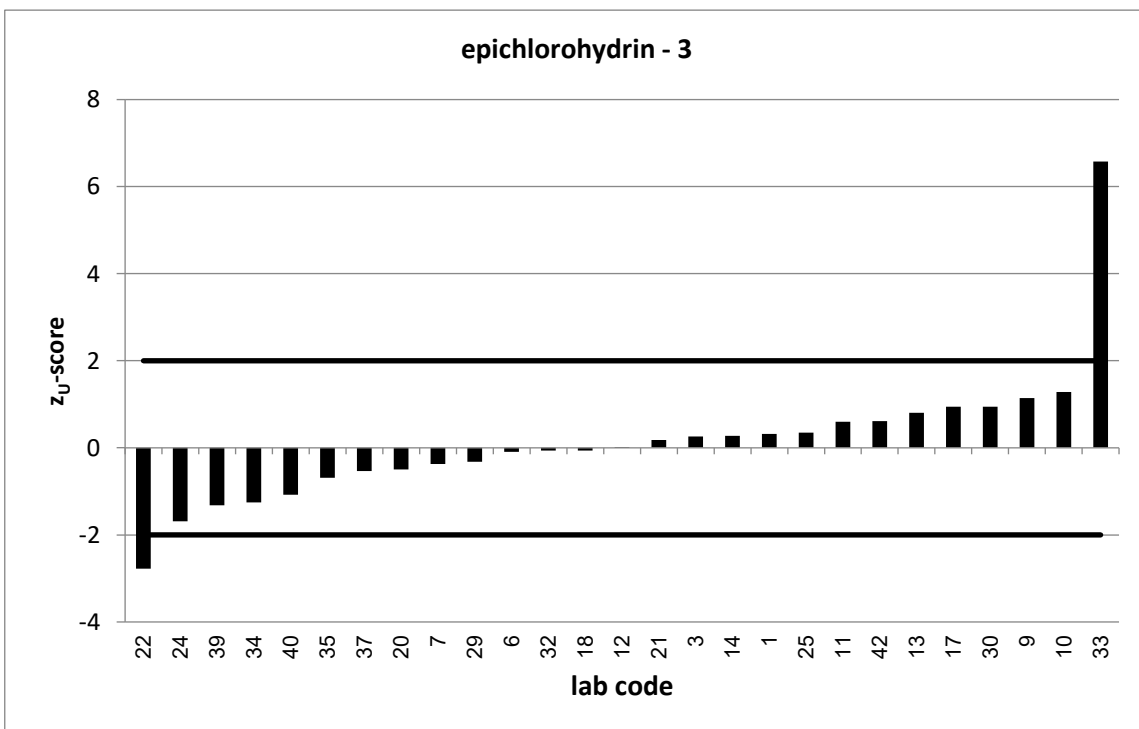
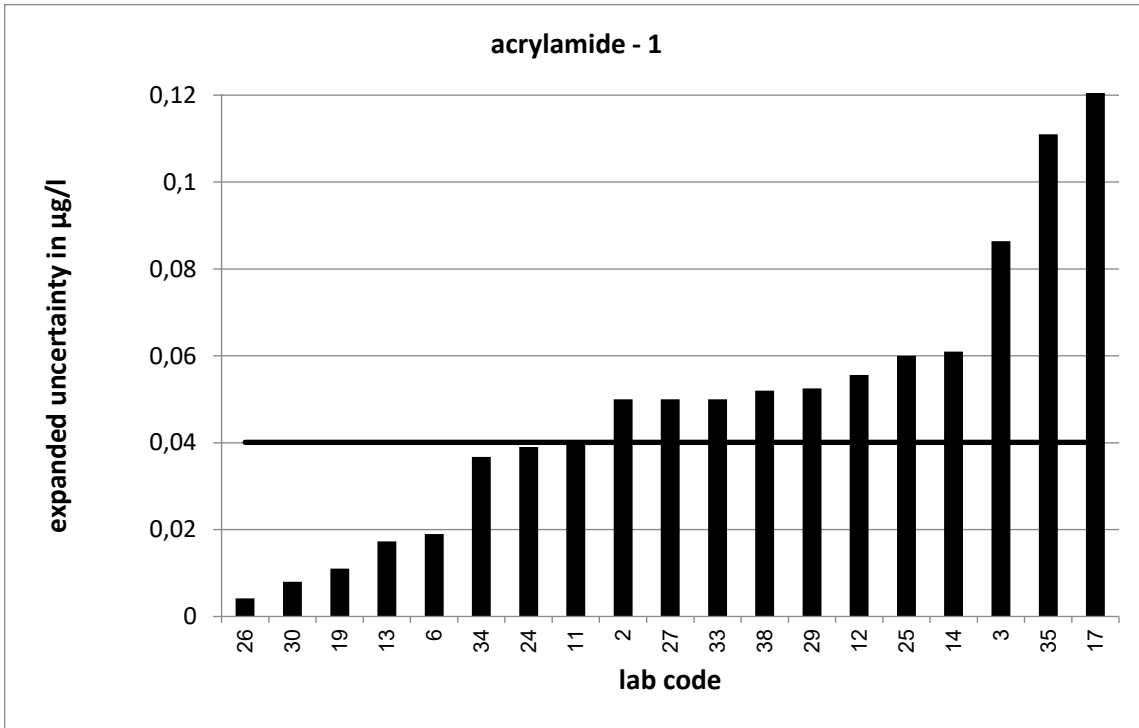| PT 11/23 - TW S10	acrylamide - 1				
assigned value [µg/l]*		0,1897	± 0,0186		
upper tolerance limit [µg/l]		0,2803			
lower tolerance limit [µg/l]		0,1163			
lab code	result [µg/l]	±	z-score	z_U-score	assessm.**
1	0,174			-0,4	s
2	0,203	0,05	0,5	0,3	s
3	0,196	0,086	0,1	0,1	s
6	0,19	0,019	0,0	0,0	s
9	0,34			3,3	u
10	0,189			0,0	s
11	0,21	0,04	0,9	0,4	s
12	0,215	0,056	0,9	0,6	s
13	0,173	0,017	-1,3	-0,5	s
14	0,245	0,061	1,7	1,2	s
17	0,185	5	0,0	-0,1	s
18	0,181			-0,2	s
19	0,179	0,011	-1,0	-0,3	s
20	0,195			0,1	s
22	0,0836			-2,9	q
24	0,157	0,039	-1,5	-0,9	s
25	0,195	0,06	0,2	0,1	s
26	0,0916	0,004	-10,3	-2,7	q
27	0,229	0,05	1,5	0,9	s
29	0,175	0,053	-0,5	-0,4	s
30	0,11	0,008	-7,9	-2,2	q
33	0,256	0,05	2,5	1,5	s
34	0,147	0,037	-2,1	-1,2	s
35	0,259	0,111	1,2	1,5	s
36	0,0722			-3,2	u
38	0,207	0,052	0,6	0,4	s
40	0,22			0,7	s
41	0,188			0,0	s
43	0,211			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%
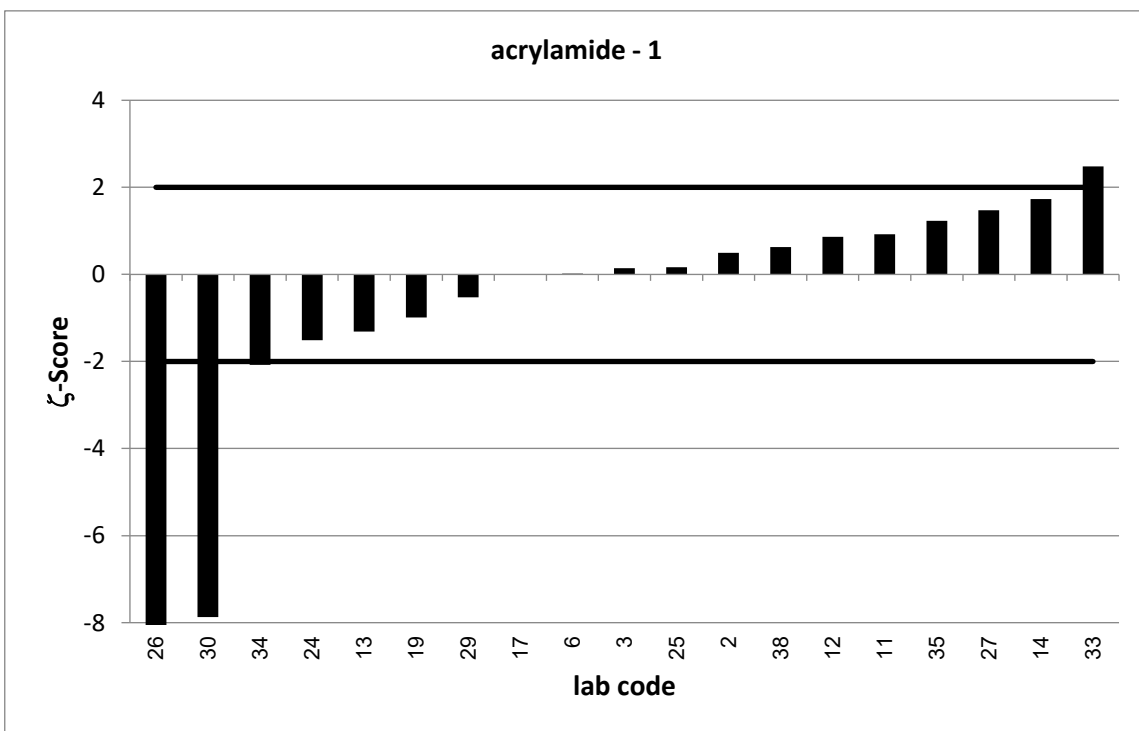** s = satisfactory, q = questionable, u = unsatisfactory

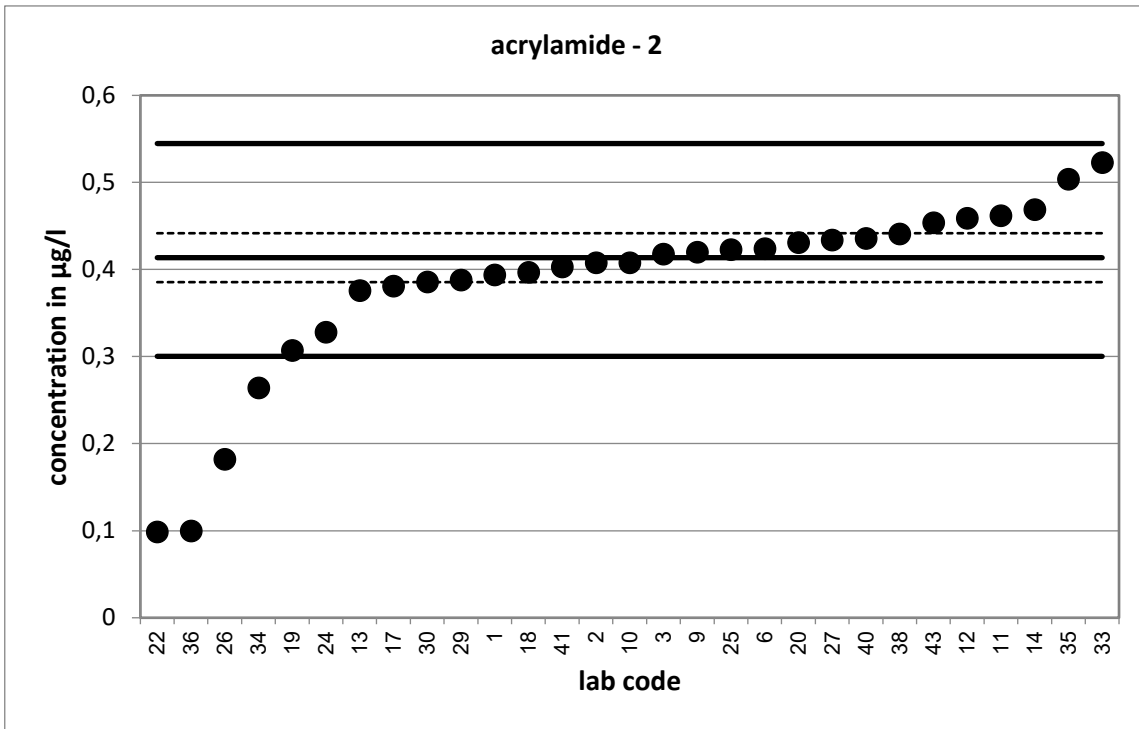**acrylamide - 1**

Strongly deviating values are not shown in the diagram.

acrylamide - 1

acrylamide - 1

Strongly deviating values are not correctly shown in the diagram.

acrylamide - 1

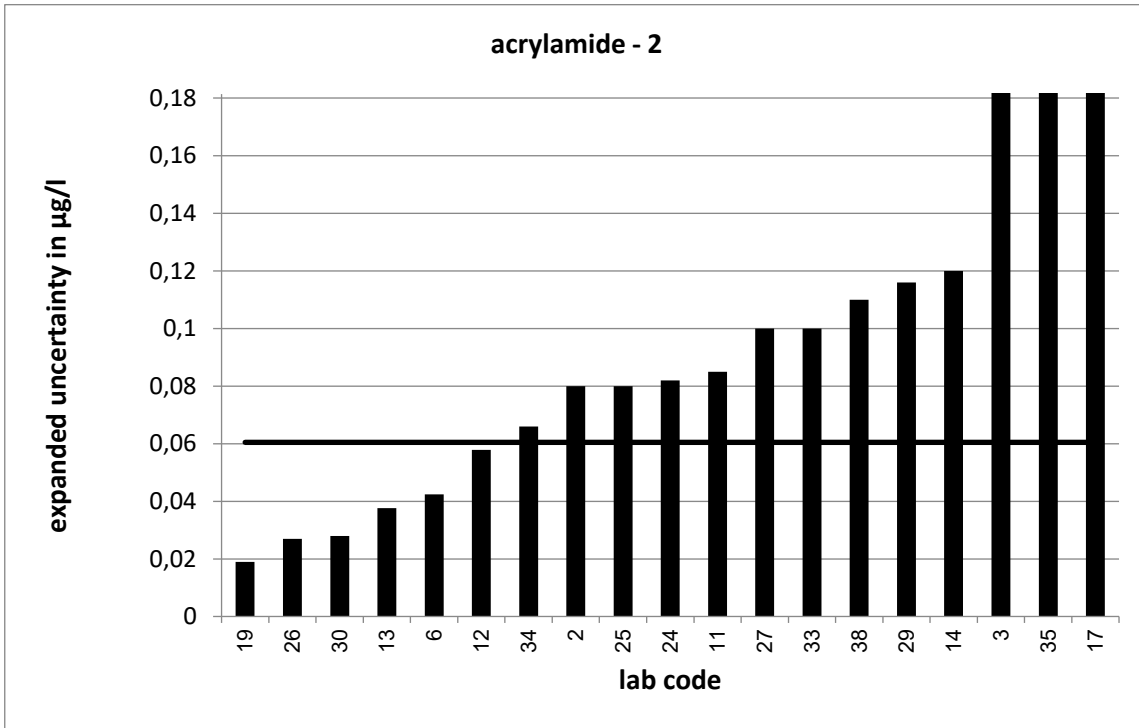| PT 11/23 - TW S10	acrylamide - 2				
assigned value [µg/l]*		0,4136	± 0,0281		
upper tolerance limit [µg/l]		0,5447			
lower tolerance limit [µg/l]		0,3003			
lab code	result [µg/l]	±	z-score	z_U-score	assessm.**
1	0,394			-0,3	s
2	0,408	0,08	-0,1	-0,1	s
3	0,418	0,184	0,0	0,1	s
6	0,424	0,042	0,4	0,2	s
9	0,42			0,1	s
10	0,408			-0,1	s
11	0,462	0,085	1,1	0,7	s
12	0,459	0,058	1,4	0,7	s
13	0,376	0,038	-1,6	-0,7	s
14	0,469	0,12	0,9	0,8	s
17	0,381	5	0,0	-0,6	s
18	0,397			-0,3	s
19	0,307	0,019	-6,3	-1,9	s
20	0,431			0,3	s
22	0,0988			-5,6	u
24	0,328	0,082	-2,0	-1,5	s
25	0,423	0,08	0,2	0,1	s
26	0,1823	0,027	-11,9	-4,1	u
27	0,434	0,1	0,4	0,3	s
29	0,388	0,116	-0,4	-0,5	s
30	0,386	0,028	-1,4	-0,5	s
33	0,523	0,1	2,1	1,7	s
34	0,264	0,066	-4,2	-2,6	q
35	0,504	0,217	0,8	1,4	s
36	0,0998			-5,5	u
38	0,441	0,11	0,5	0,4	s
40	0,436			0,3	s
41	0,403			-0,2	s
43	0,454			0,6	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%
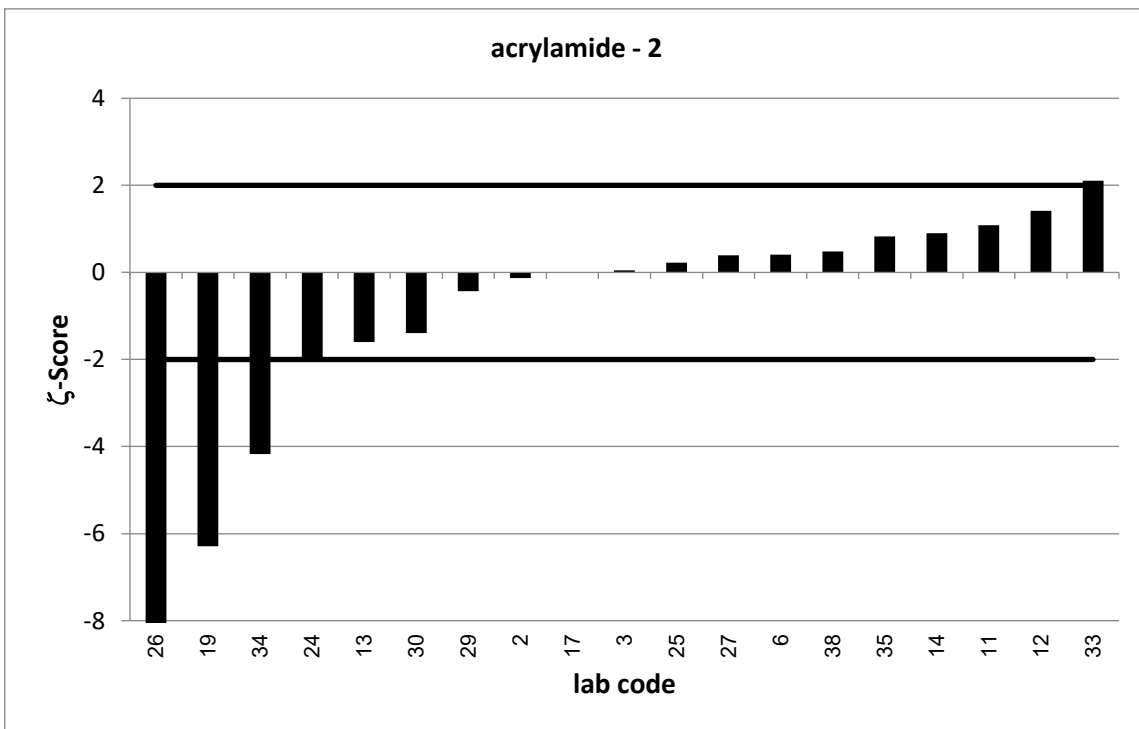** s = satisfactory, q = questionable, u = unsatisfactory

acrylamide - 2

Strongly deviating values are not shown in the diagram.

acrylamide - 2

acrylamide - 2
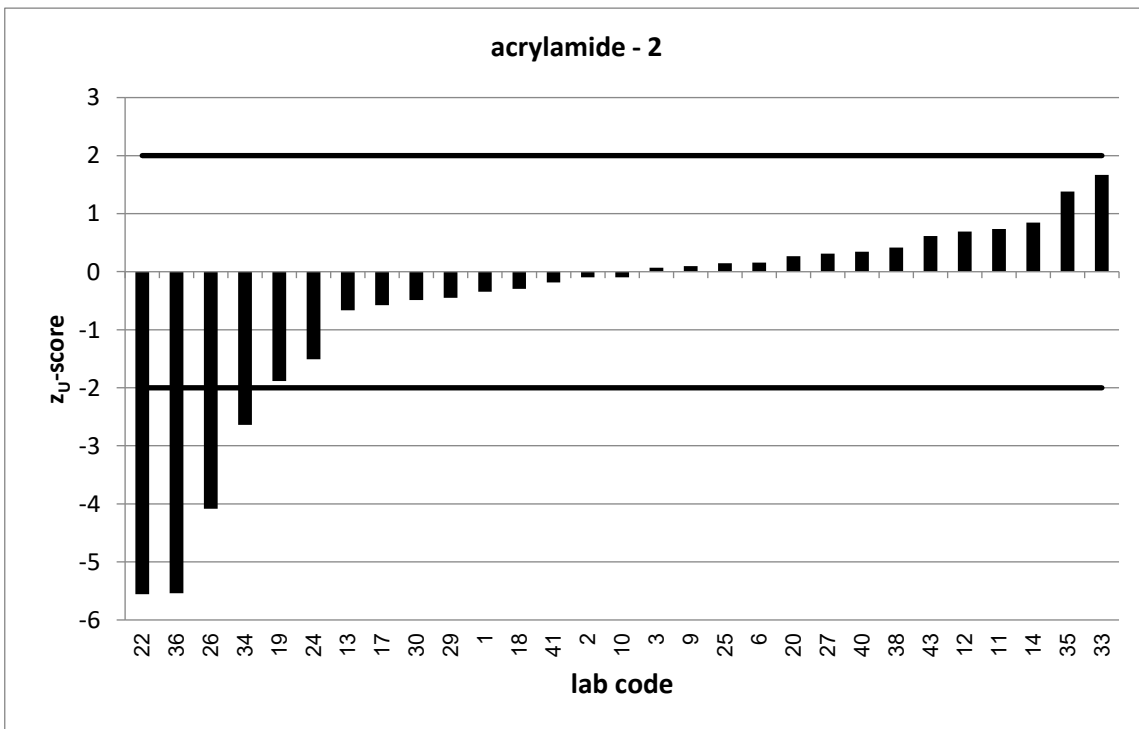
Strongly deviating values are not correctly shown in the diagram.

acrylamide - 2
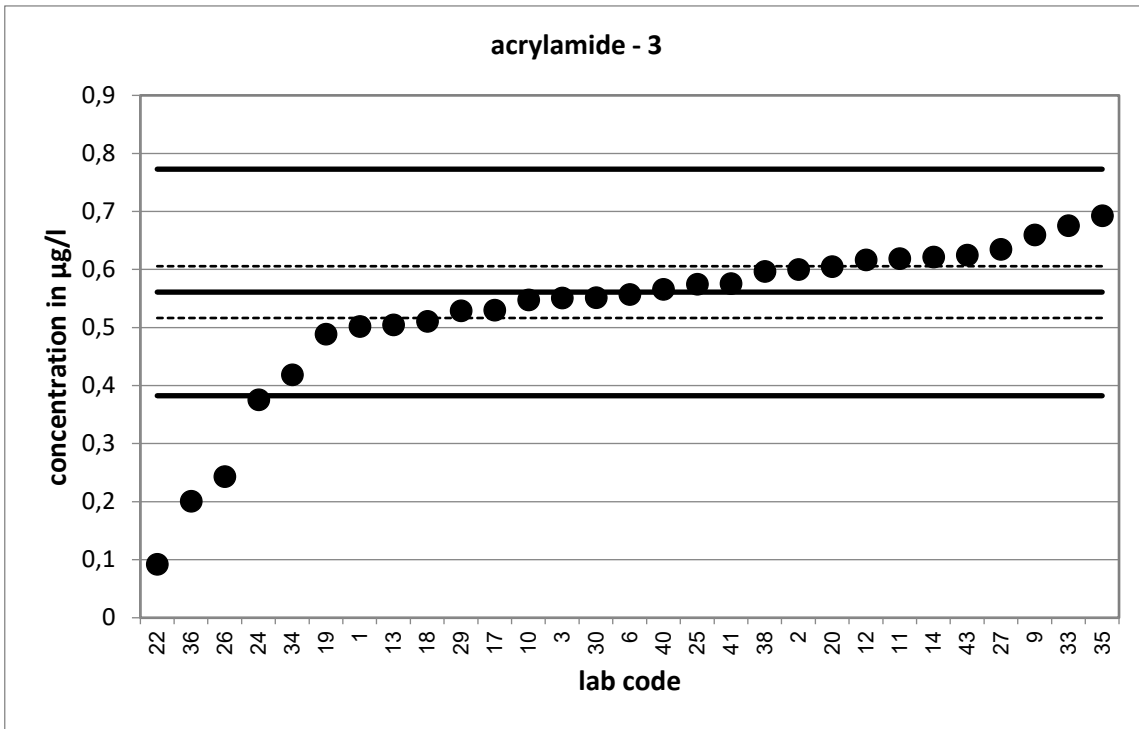
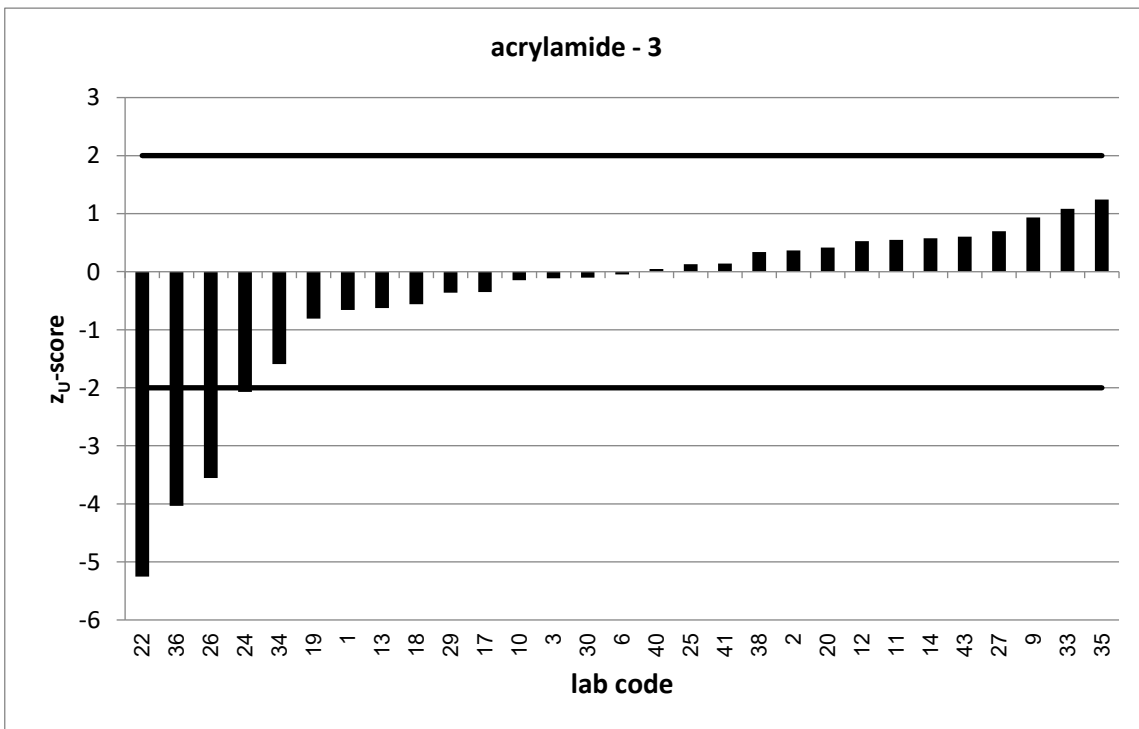Strongly deviating values are not correctly shown in the diagram.

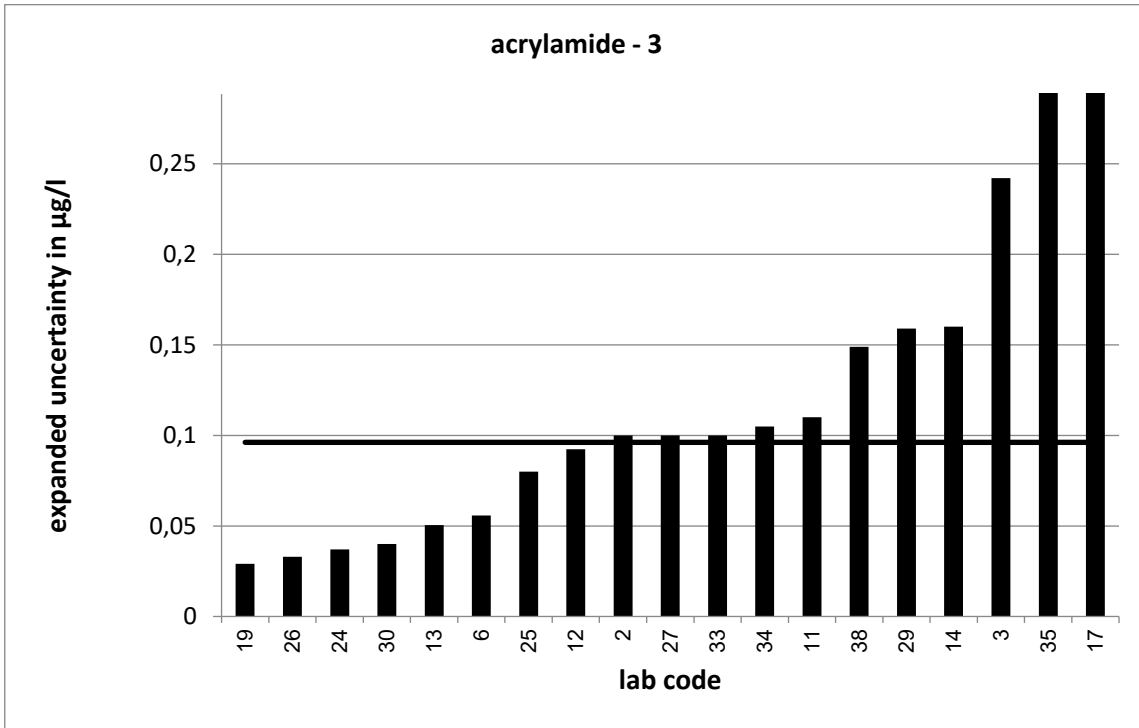| PT 11/23 - TW S10	acrylamide - 3				
assigned value [µg/l]*		0,5611	± 0,0446		
upper tolerance limit [µg/l]		0,7729			
lower tolerance limit [µg/l]		0,3825			
lab code	result [µg/l]	±	z-score	z_U-score	assessm.**
1	0,502			-0,7	s
2	0,6	0,1	0,7	0,4	s
3	0,551	0,242	-0,1	-0,1	s
6	0,557	0,056	-0,1	0,0	s
9	0,66			0,9	s
10	0,548			-0,1	s
11	0,619	0,11	1,0	0,5	s
12	0,617	0,092	1,1	0,5	s
13	0,505	0,051	-1,7	-0,6	s
14	0,622	0,16	0,7	0,6	s
17	0,53	5	0,0	-0,3	s
18	0,511			-0,6	s
19	0,489	0,029	-2,7	-0,8	s
20	0,605			0,4	s
22	0,0922			-5,3	u
24	0,376	0,037	-6,4	-2,1	q
25	0,575	0,08	0,3	0,1	s
26	0,2436	0,033	-11,4	-3,6	u
27	0,635	0,1	1,4	0,7	s
29	0,529	0,159	-0,4	-0,4	s
30	0,552	0,04	-0,3	-0,1	s
33	0,676	0,1	2,1	1,1	s
34	0,419	0,105	-2,5	-1,6	s
35	0,693	0,298	0,9	1,2	s
36	0,201			-4,0	u
38	0,597	0,149	0,5	0,3	s
40	0,566			0,0	s
41	0,576			0,1	s
43	0,625			0,6	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%
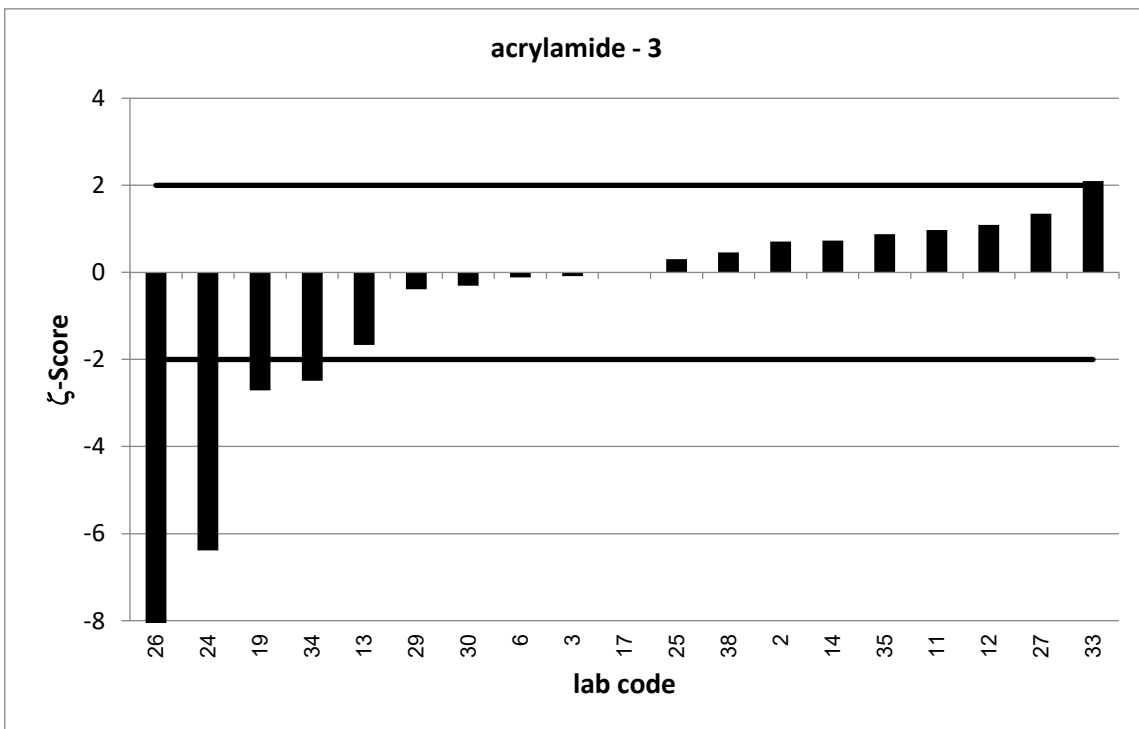** s = satisfactory, q = questionable, u = unsatisfactory

acrylamide - 3

Strongly deviating values are not shown in the diagram.

acrylamide - 3

acrylamide - 3

Strongly deviating values are not correctly shown in the diagram.

acrylamide - 3

Strongly deviating values are not correctly shown in the diagram.