Analytische Qualitätssicherung Baden-Württemberg

Proficiency Test 3/18
- TW S5 – Sulfonylurea herbicides -
amidosulfuron, metsulfuron-methyl, rimsulfuron, thifensulfuron-methyl, triasulfuron

Final report

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Release of the report:	Dr.-Ing. Michael Koch on 06.06.2018
Version of the report	1

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<u>Appendix A</u>

<u>Appendix B</u>

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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). In this round following parameters were to be determined:

- **amidosulfuron**, CAS No. 120923-37-7
- **metsulfuron-methyl**, CAS No. 74223-64-6
- **rimsulfuron**, CAS No. 122931-48-0
- **thifensulfuron-methyl**, CAS No. 79277-27-3
- **triasulfuron**, CAS No. 82097-50-5

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 x 1 sample for the determination of amidosulfuron, metsulfuron-methyl, rimsulfuron, thifensulfuron-methyl, triasulfuron in 1000-ml-glass bottles with ground glass plug. Preservation with sodium azide.

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

3. Sample preparation

The samples for the determination of the sulfonyurea herbicides 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 27 March 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 for all parameters 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 16 April 2018. Results submitted after the deadline were not accepted.

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:	$\left\| z_u \right\| \leq 2,0$ successful $2,0 < \left\| z_u \right\| < 3,0$ questionable $\left\| z_u \right\| \geq 3,0$ 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:	25
Number of reported values	351
Number of accepted values:	305 (86,89 %)

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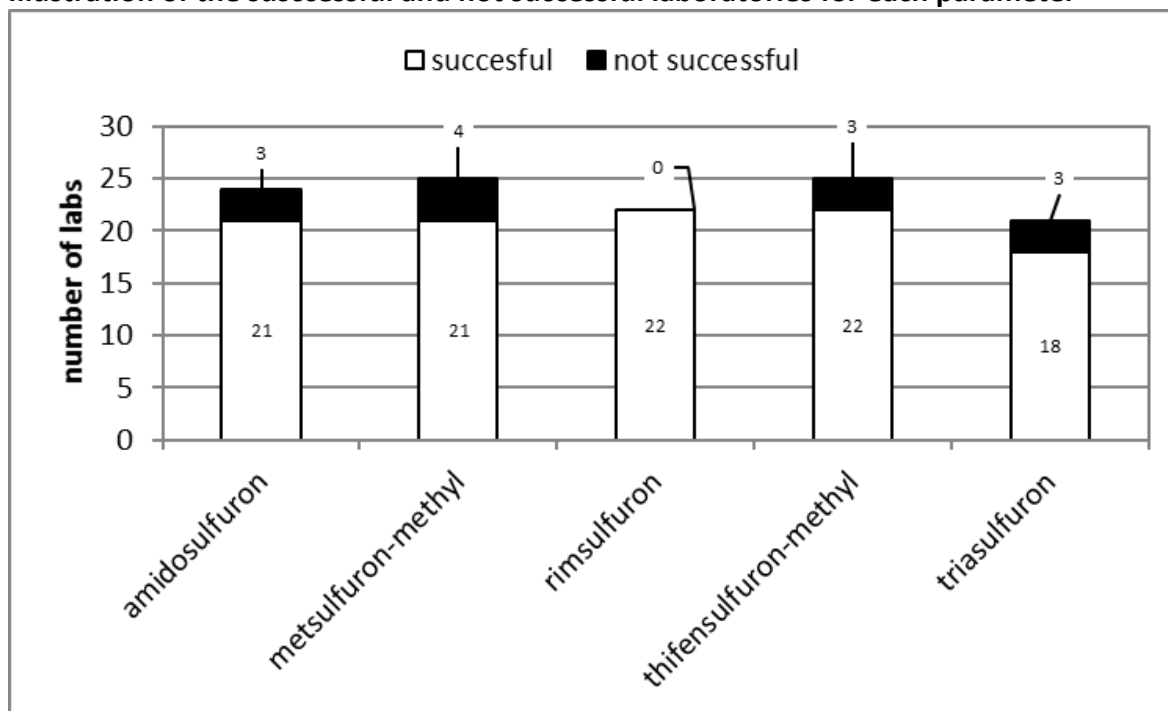
9. Explanation for the appendices

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	25
Number of labs with valid values and reported measurement uncertainties	13 (52 %)
Number of valid values	351
Number of valid values with measurement uncertainties	180 (51,3 %)

Measurement uncertainties against the accreditation status

Accreditation status of the values	Number of values	Number of values with measurement uncertainty
accredited	300	180 (60 %)
not accredited	15	0 (0 %)
not specified	36	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 $|z_U| \leq 2,0$	161
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	36 (22,4 %)

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
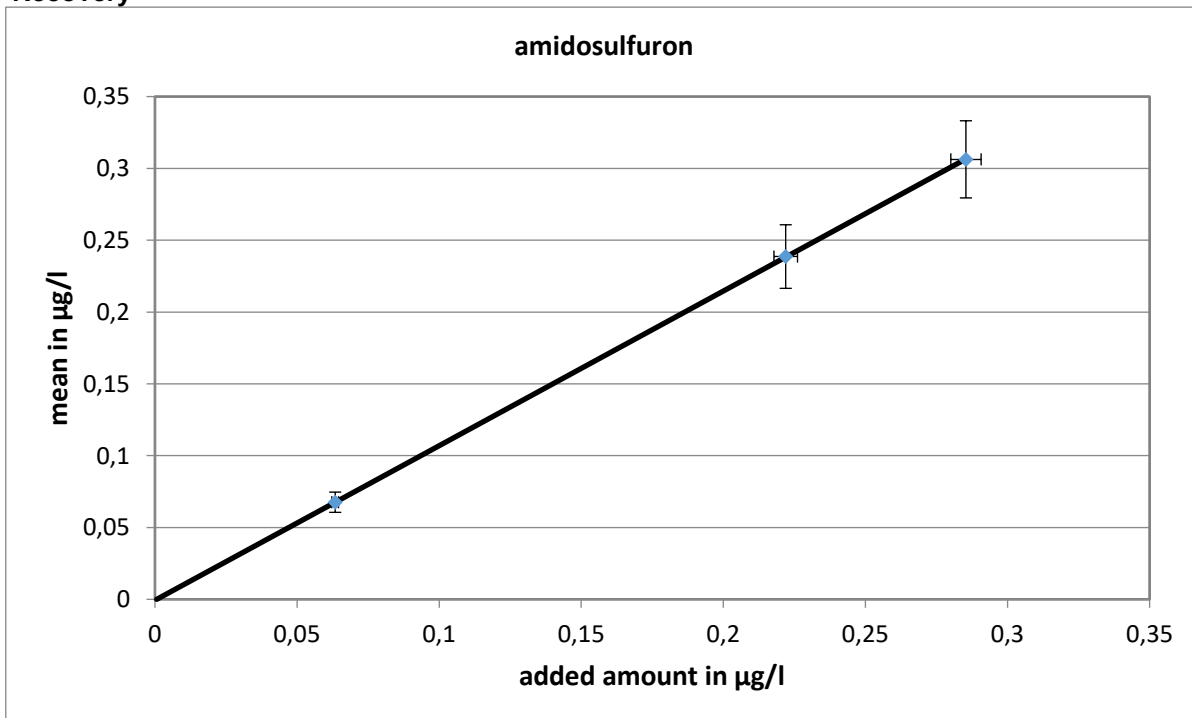
12.   Internet

The report is available on the following webpage: http://www.aqsbw/pdf/report318.pdf
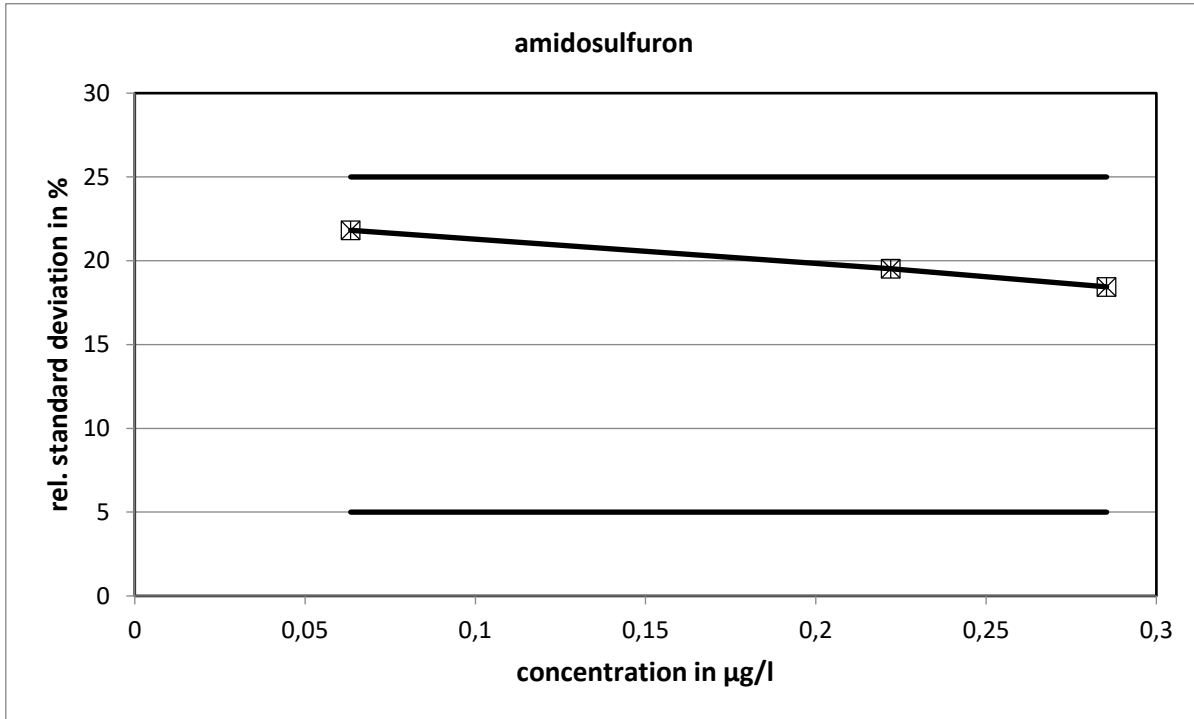
amidosulfuron

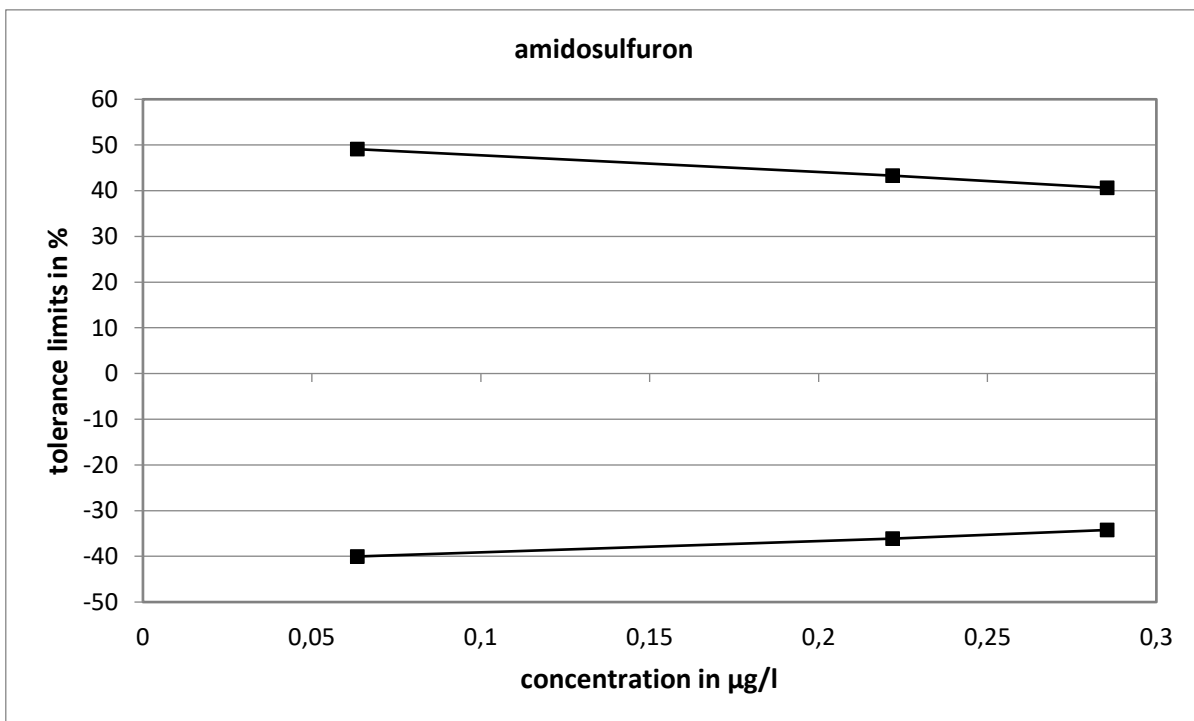| level	assigned value [µg/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [µg/l]	standard deviation for proficiency assessment [µg/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [µg/l]	lower tolerance limit [µg/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,0634	2,10	0,0138	0,0138	21,82	0,0945	0,0380	49,08	-40,03	24	1	2	12,5
2	0,2220	1,89	0,0433	0,0433	19,53	0,3180	0,1418	43,28	-36,12	24	1	2	12,5
3	0,2854	1,88	0,0526	0,0526	18,44	0,4013	0,1877	40,63	-34,23	24	1	2	12,5
									sum	72	3	6	12,5

Recovery

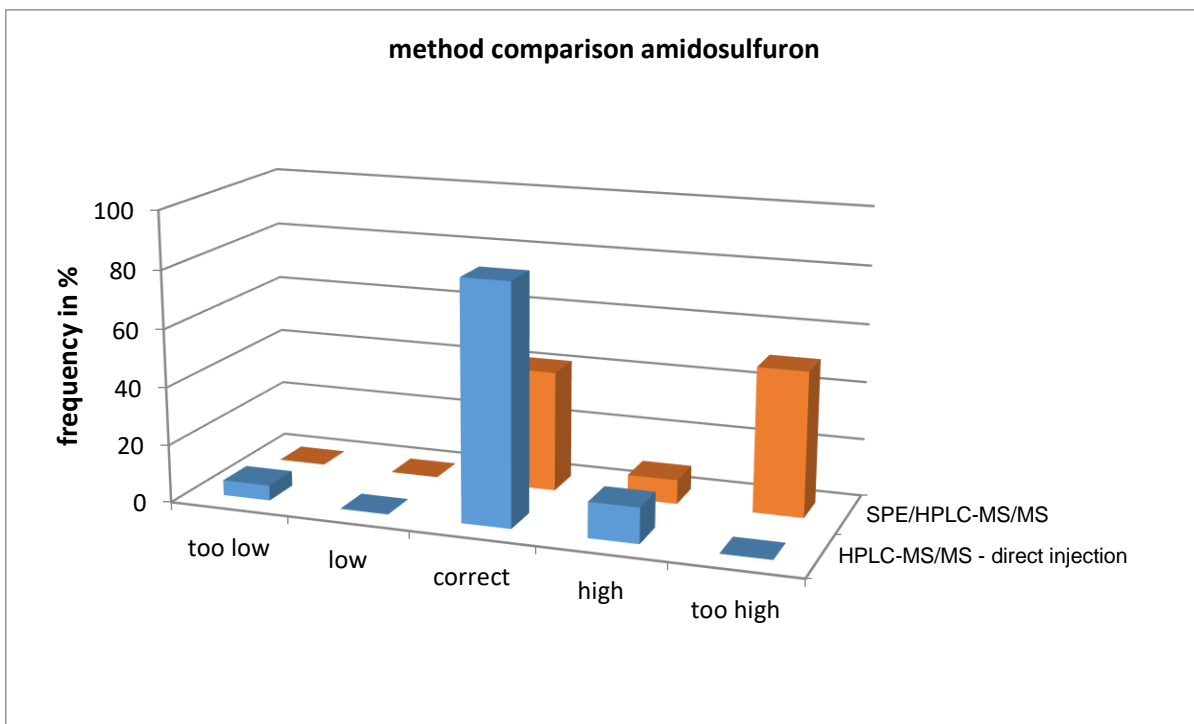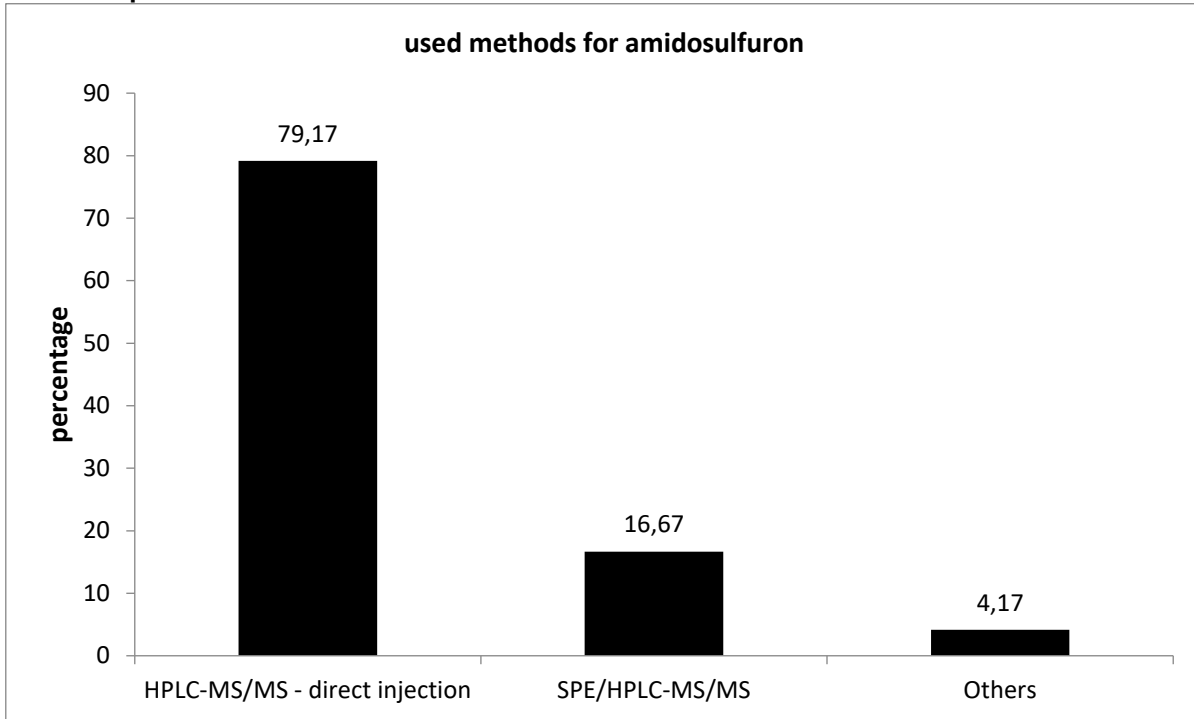slope of the regression: 1,077; recovery rate: 107,7 %

Relative standard deviation and tolerance limits

amidosulfuron

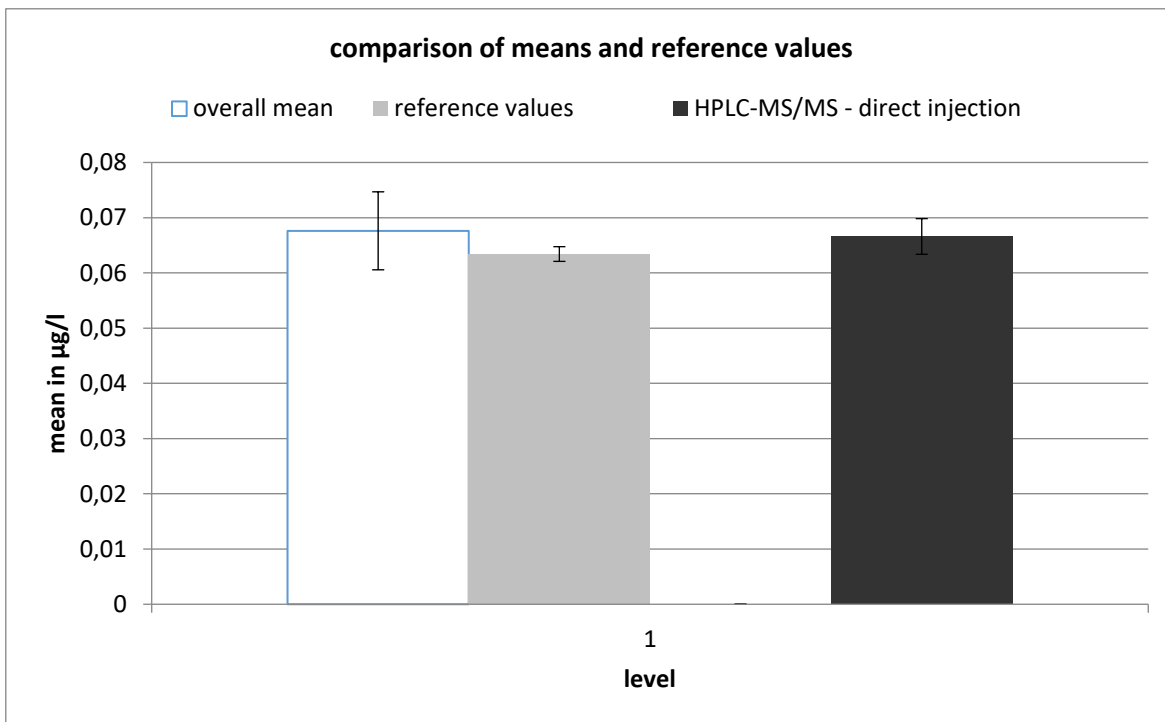The relative standard deviations calculated with the Q method did not reach the limits.

amidosulfuron

Method specific evaluation

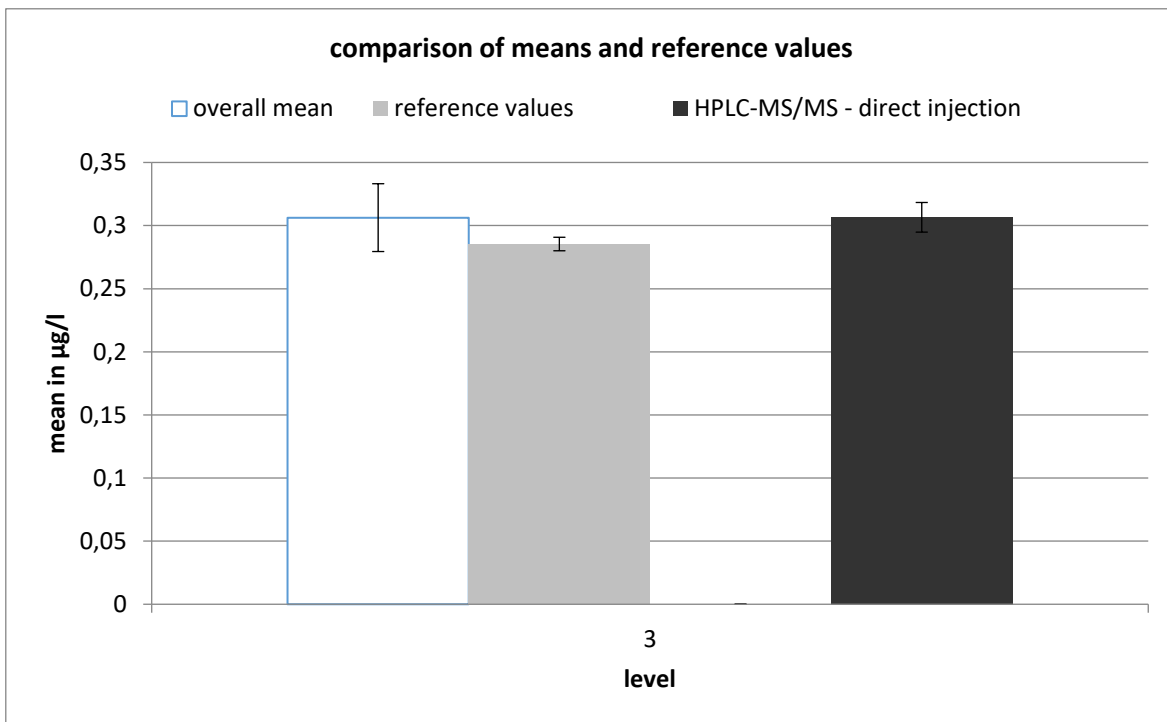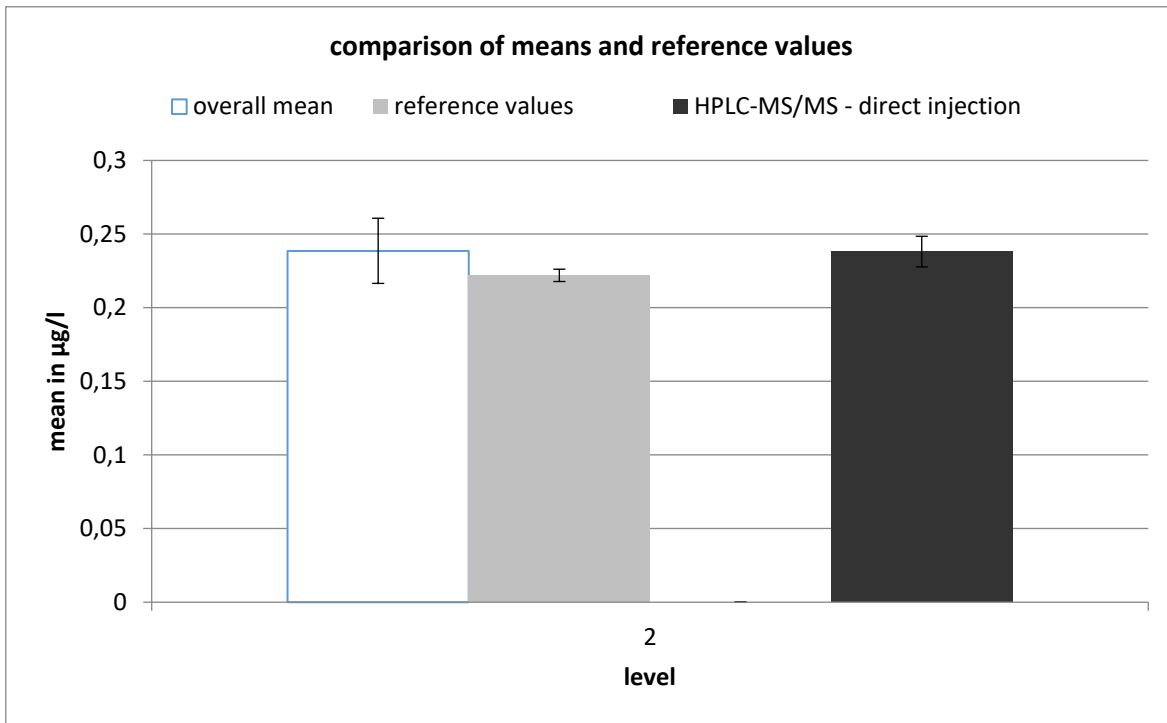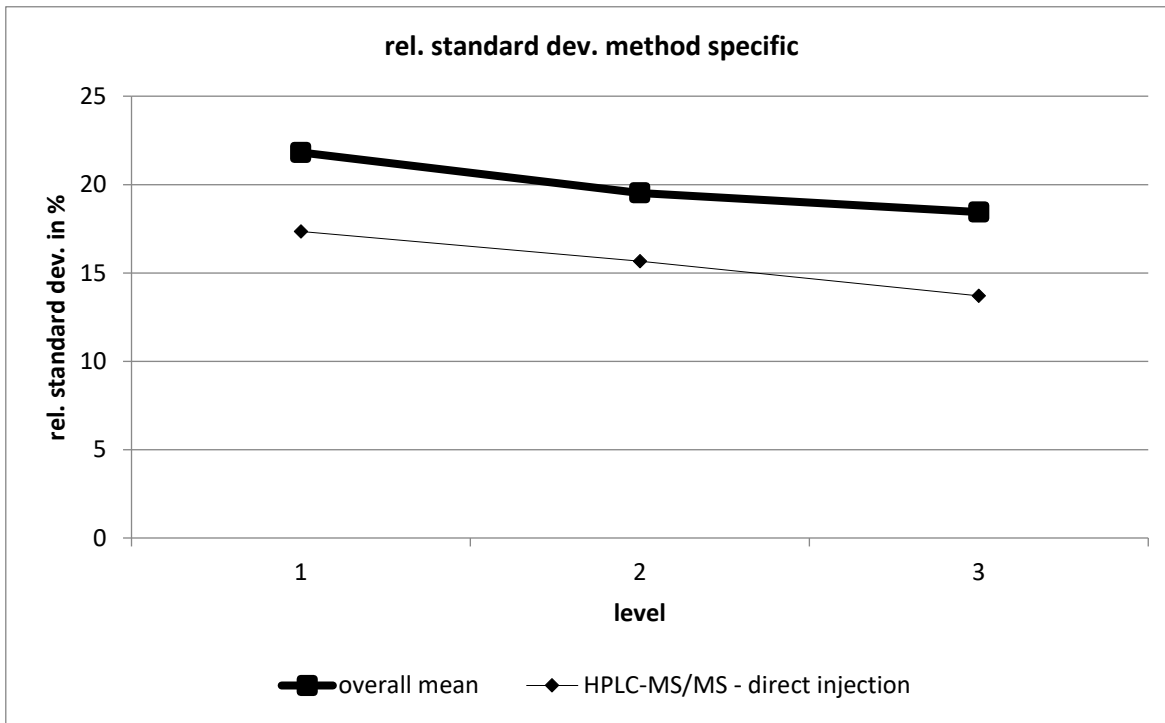## used methods for amidosulfuron

method comparison amidosulfuron

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	0,0676	0,0071	10,4	0,0634	0,0013	2,1
2	0,2386	0,0221	9,3	0,2220	0,0042	1,9
3	0,3063	0,0269	8,8	0,2854	0,0054	1,9

comparison of means and reference values

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

comparison of means and reference values

☐ overall mean ▨ reference values ▪ HPLC-MS/MS - direct injection

comparison of means and reference values

☐ overall mean ▨ reference values ▪ HPLC-MS/MS - direct injection

rel. standard dev. method specific

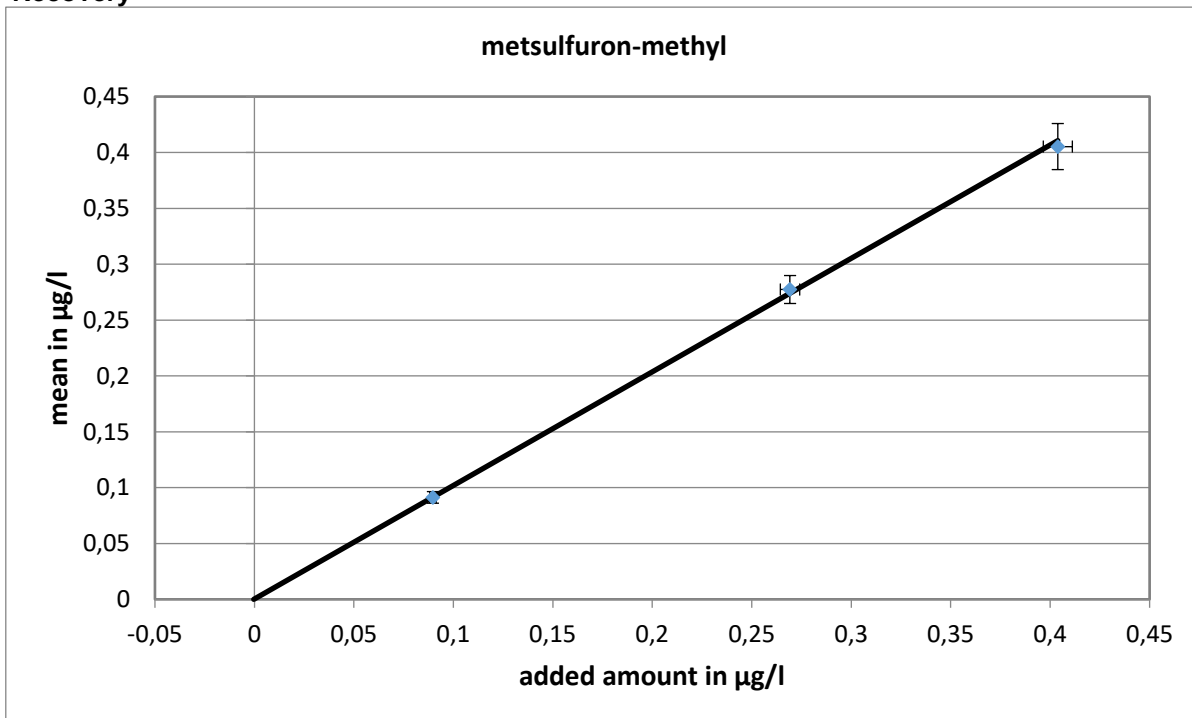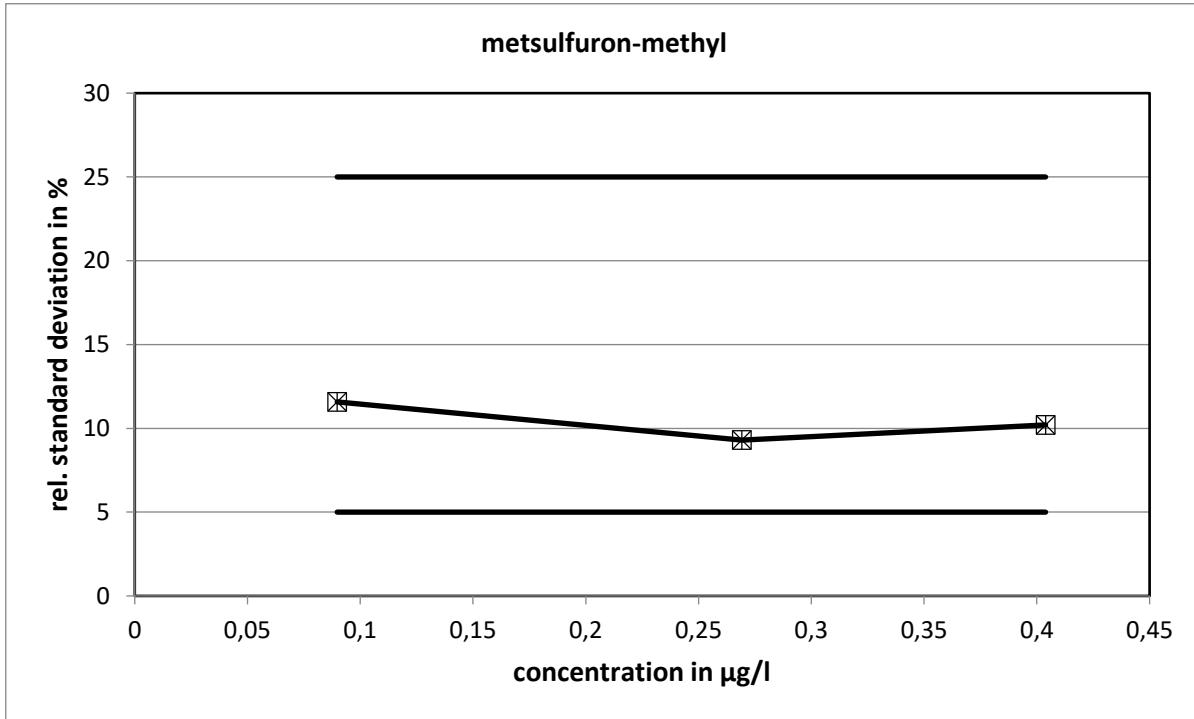| HPLC-MS/MS - direct injection									
level	robust mean [µg/l]	exp. unc. of the mean [µg/l]	exp. unc. of the mean [%]	robust standard deviation [µg/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	0,067	0,003	4,848	0,012	17,35	20	2	0	10
2	0,238	0,01	4,379	0,037	15,67	20	2	0	10
3	0,307	0,012	3,83	0,042	13,7	20	2	0	10

metsulfuron-methyl

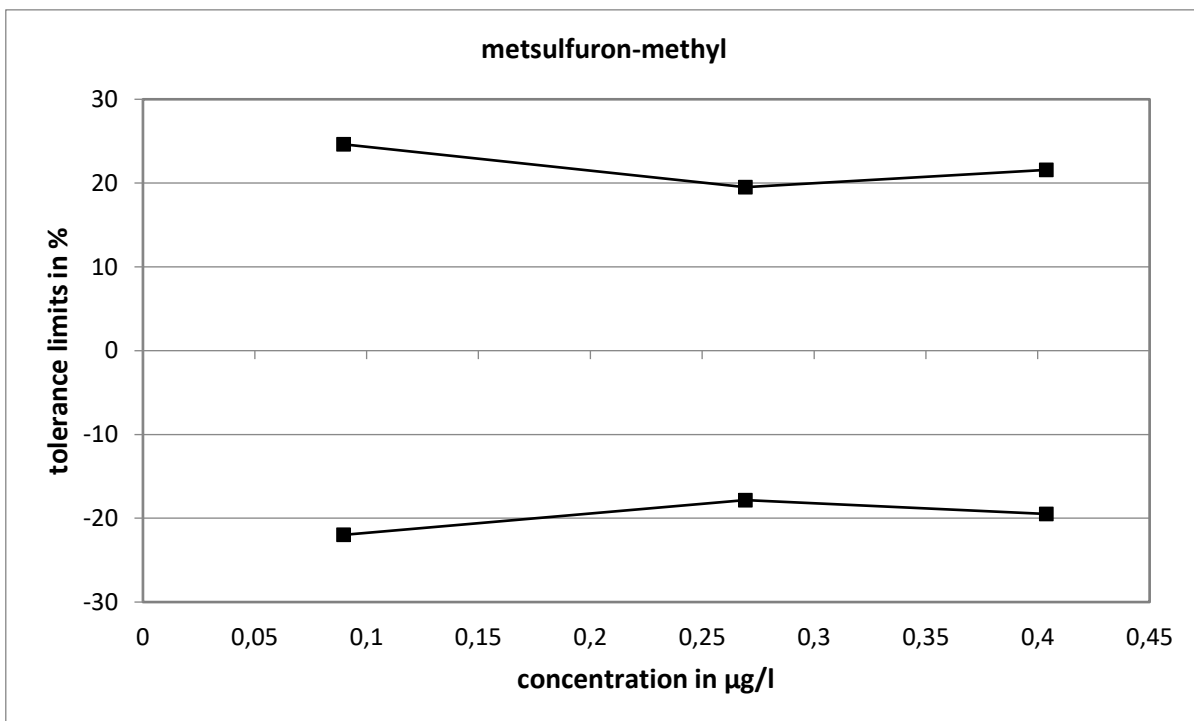| level	assigned value [µg/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [µg/l]	standard deviation for proficiency assessment [µg/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [µg/l]	lower tolerance limit [µg/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,0897	1,84	0,0104	0,0104	11,58	0,1118	0,0700	24,62	-21,98	25	1	2	12,0
2	0,2692	1,81	0,0250	0,0250	9,30	0,3218	0,2212	19,51	-17,83	25	2	3	20,0
3	0,4039	1,81	0,0412	0,0412	10,21	0,4910	0,3252	21,57	-19,48	25	2	2	16,0
									sum	75	5	7	16,0

Recovery

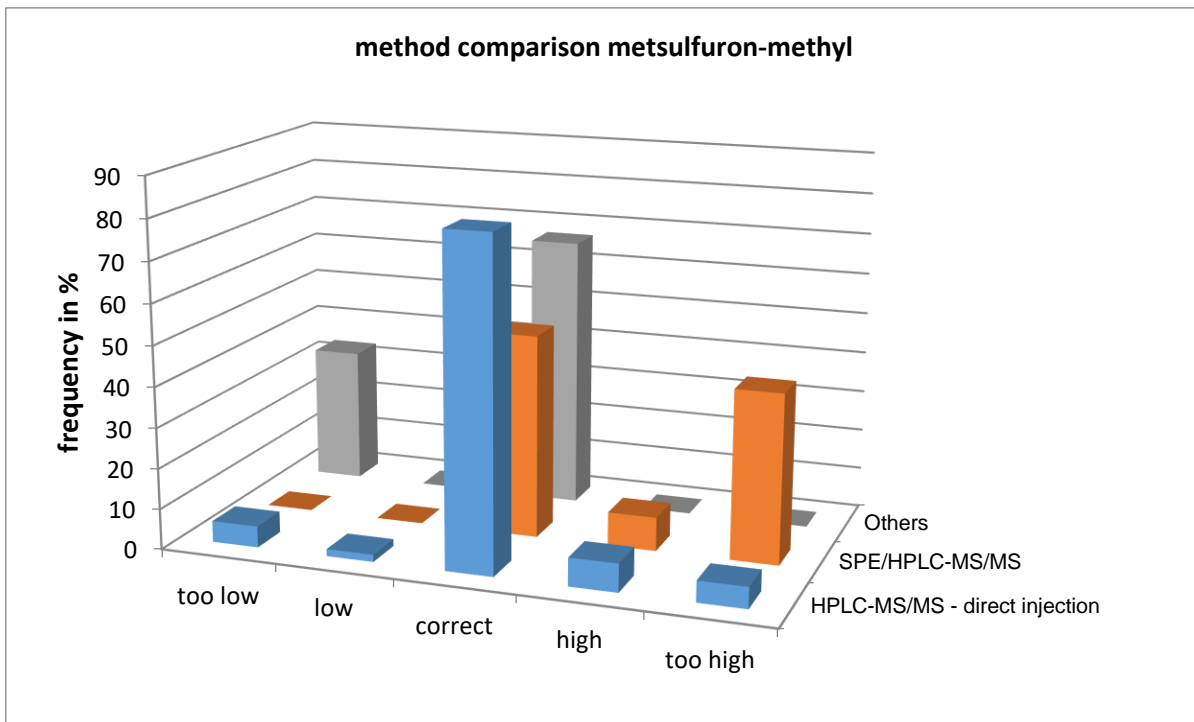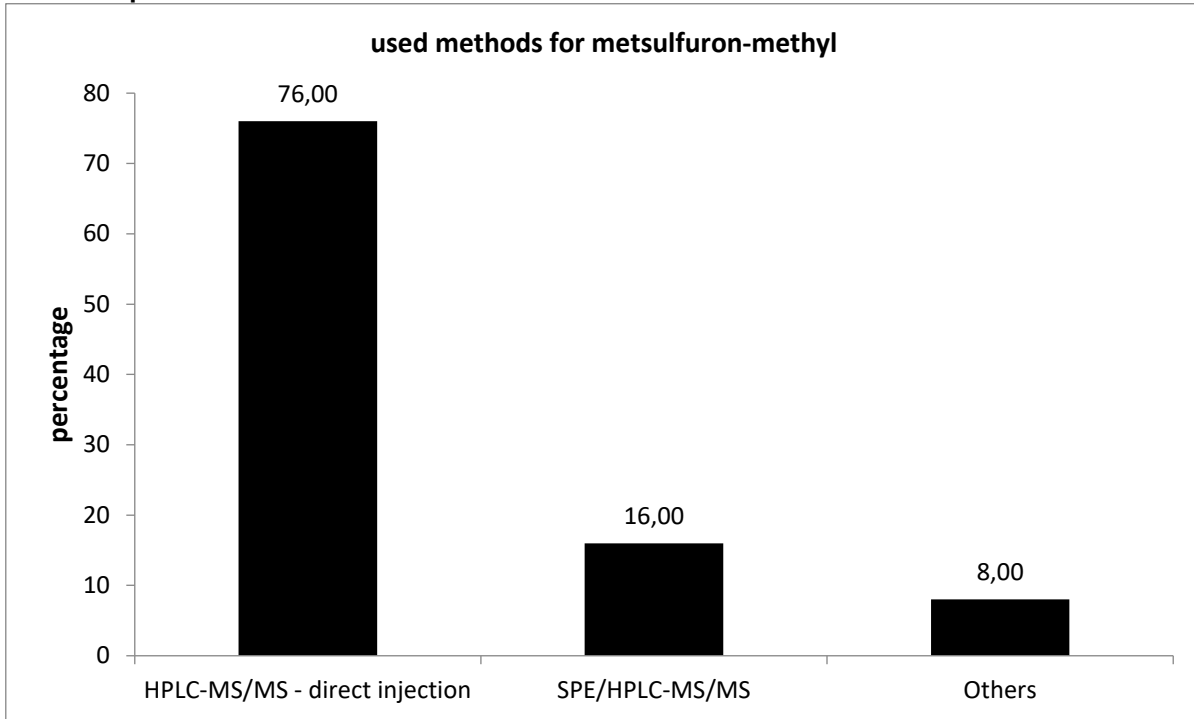slope of the regression: 1,016; recovery rate: 101,6 %

Relative standard deviation and tolerance limits

The relative standard deviations calculated with the Q method did not reach the limits.
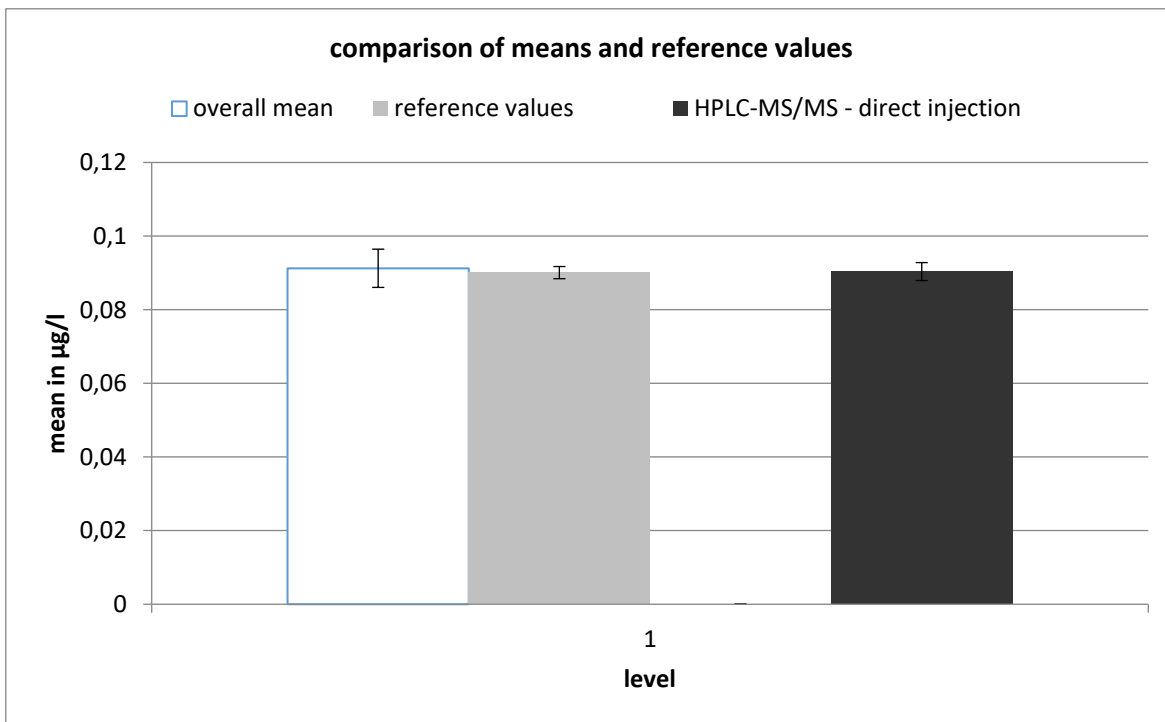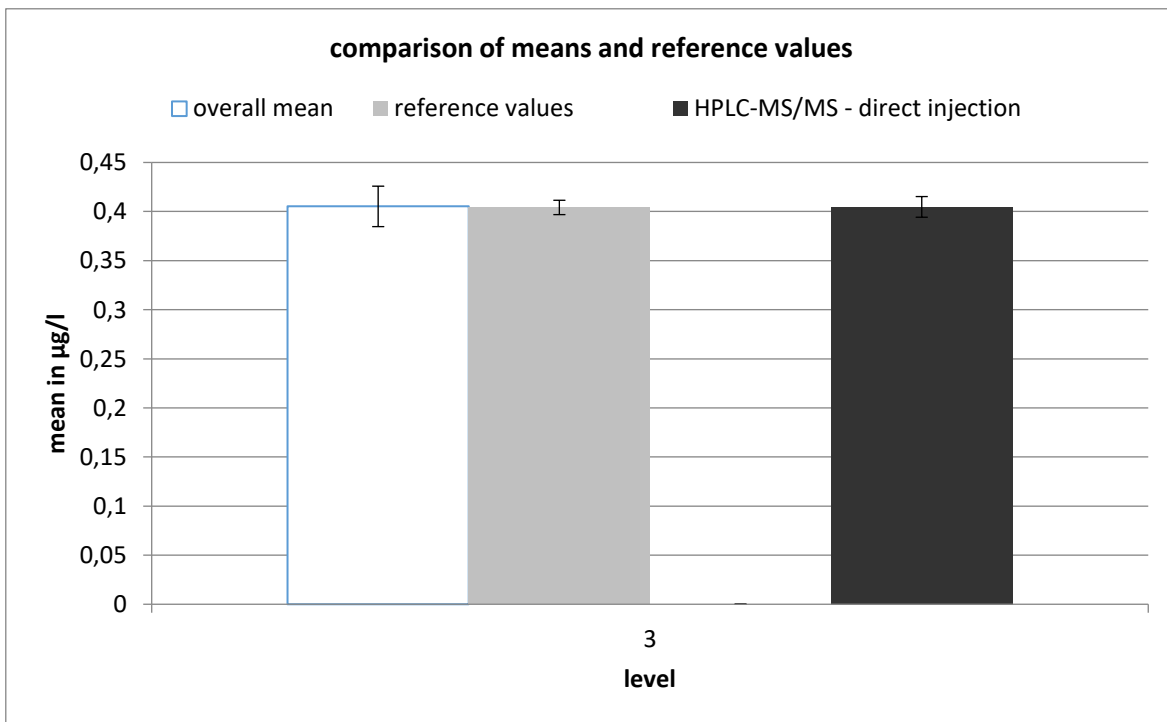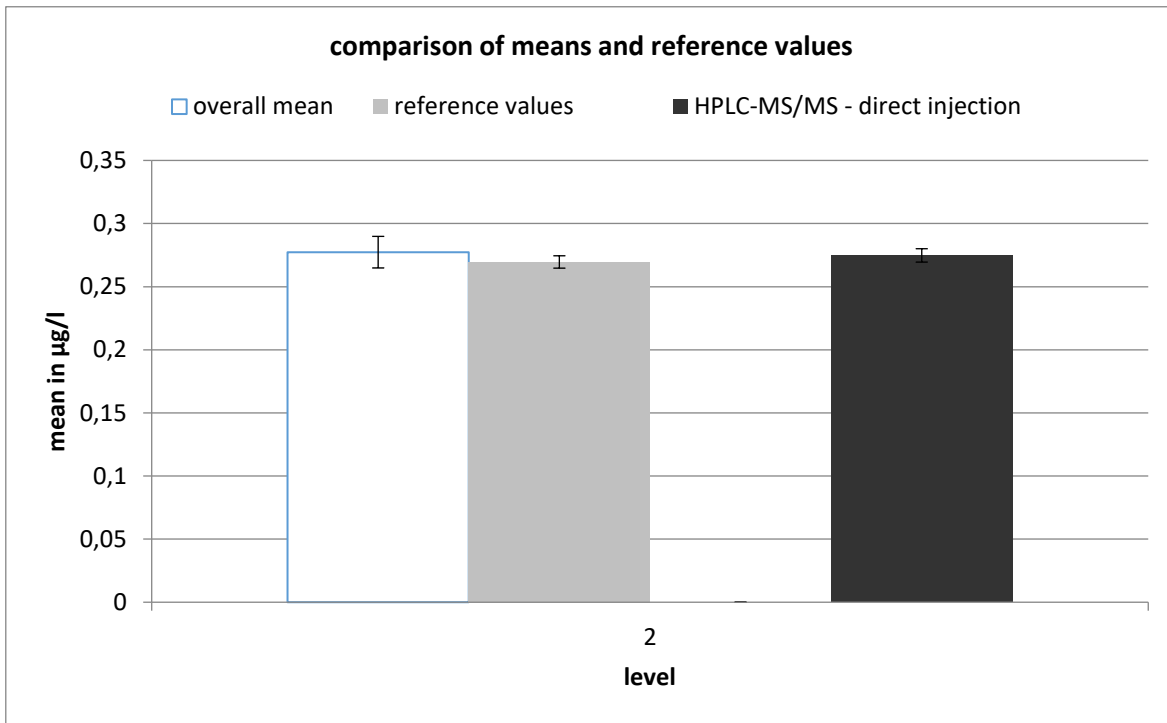
Method specific evaluation

used methods for metsulfuron-methyl

method comparison metsulfuron-methyl

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	0,0913	0,0052	5,7	0,0901	0,0017	1,8
2	0,2773	0,0125	4,5	0,2696	0,0049	1,8
3	0,4053	0,0206	5,1	0,4042	0,0073	1,8

comparison of means and reference values

comparison of means and reference values

rel. standard dev. method specific

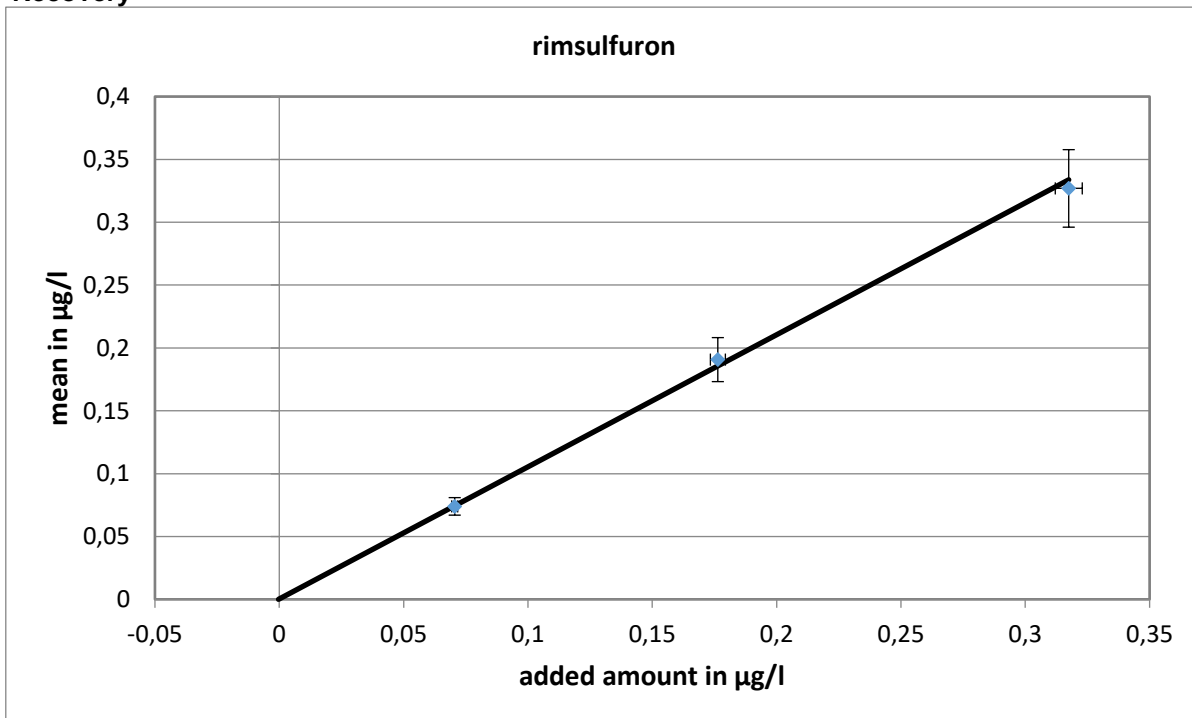Legend: overall mean — HPLC-MS/MS - direct injection

HPLC-MS/MS - direct injection

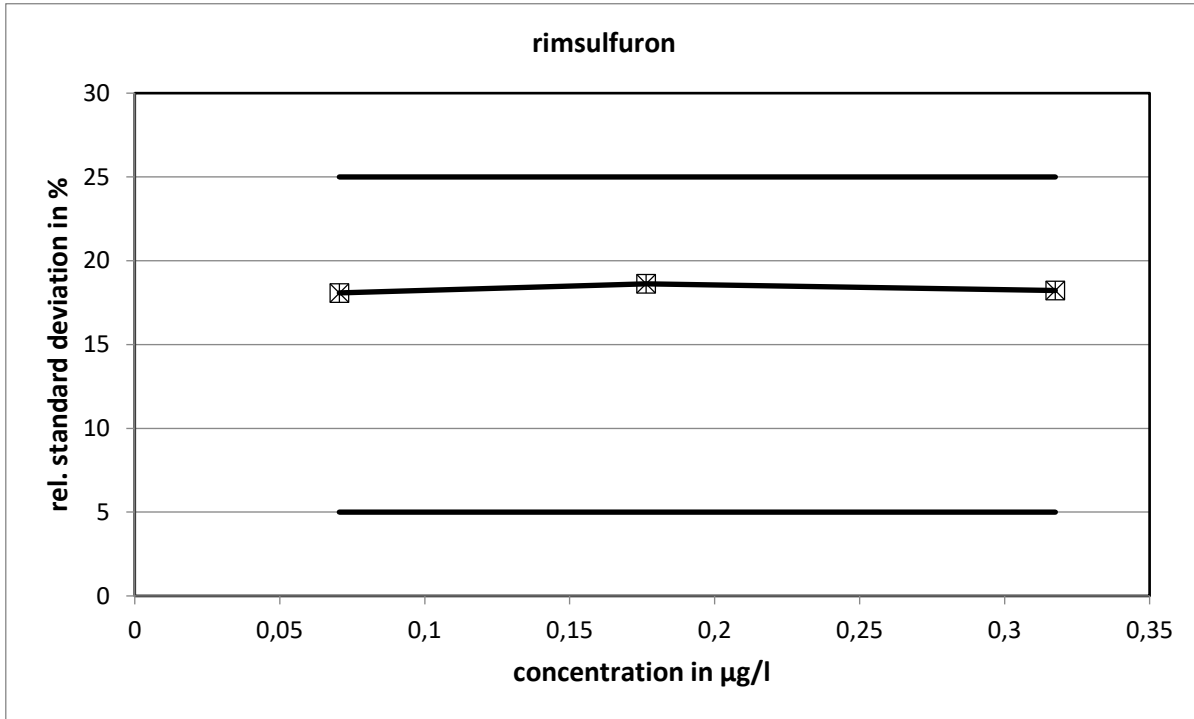| level	robust mean [µg/l]	exp. unc. of the mean [µg/l]	exp. unc. of the mean [%]	robust standard deviation [µg/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	0,09	0,002	2,697	0,009	9,648	20	2	1	15
2	0,275	0,005	1,922	0,019	6,875	20	2	1	15
3	0,405	0,011	2,602	0,038	9,308	20	2	1	15

rimsulfuron

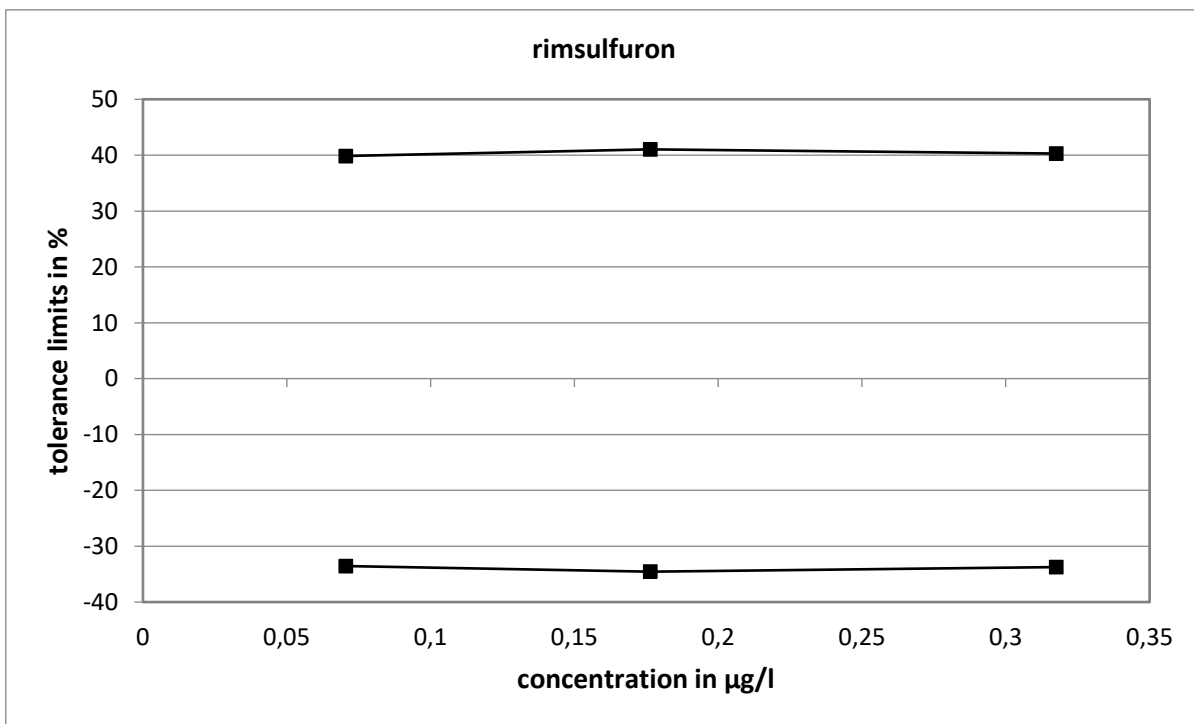| level	assigned value [µg/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [µg/l]	standard deviation for proficiency assessment [µg/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [µg/l]	lower tolerance limit [µg/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,0706	1,76	0,0128	0,0128	18,08	0,0987	0,0469	39,85	-33,56	21	1	0	4,5
2	0,1764	1,71	0,0328	0,0328	18,62	0,2488	0,1154	41,03	-34,56	22	0	0	0,0
3	0,3175	1,71	0,0579	0,0579	18,23	0,4454	0,2103	40,28	-33,77	22	1	0	4,5
									sum	65	2	0	3,1

Recovery

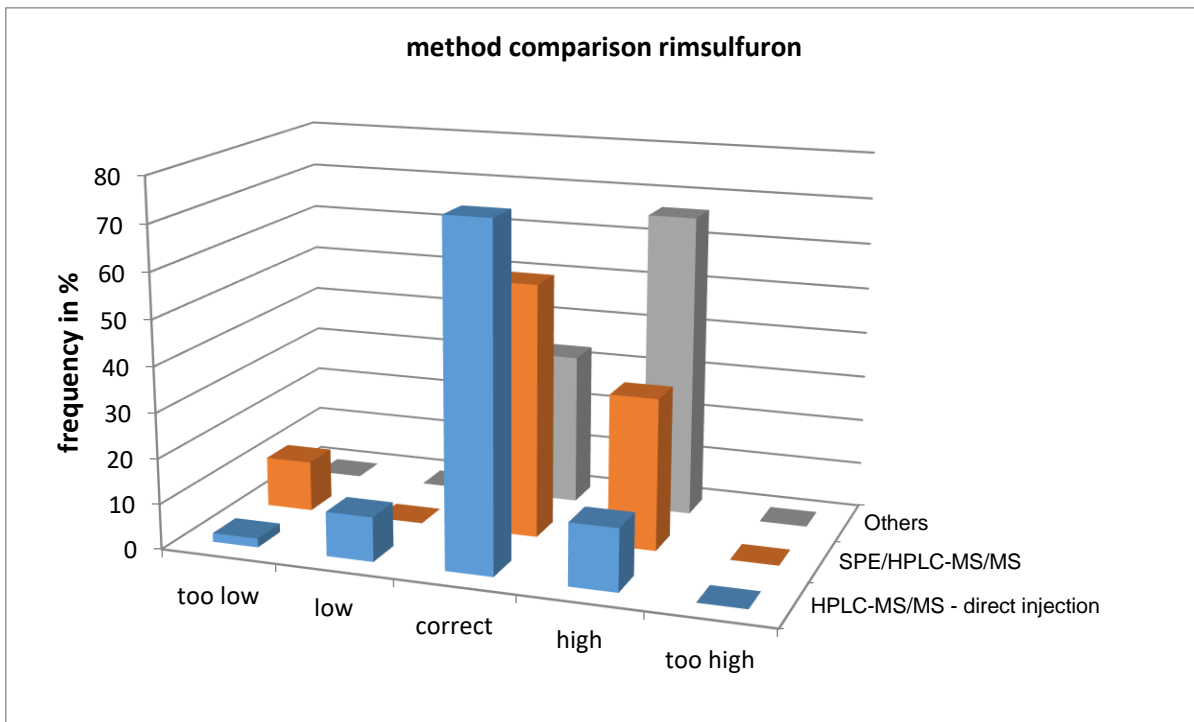slope of the regression: 1,05; recovery rate: 105 %
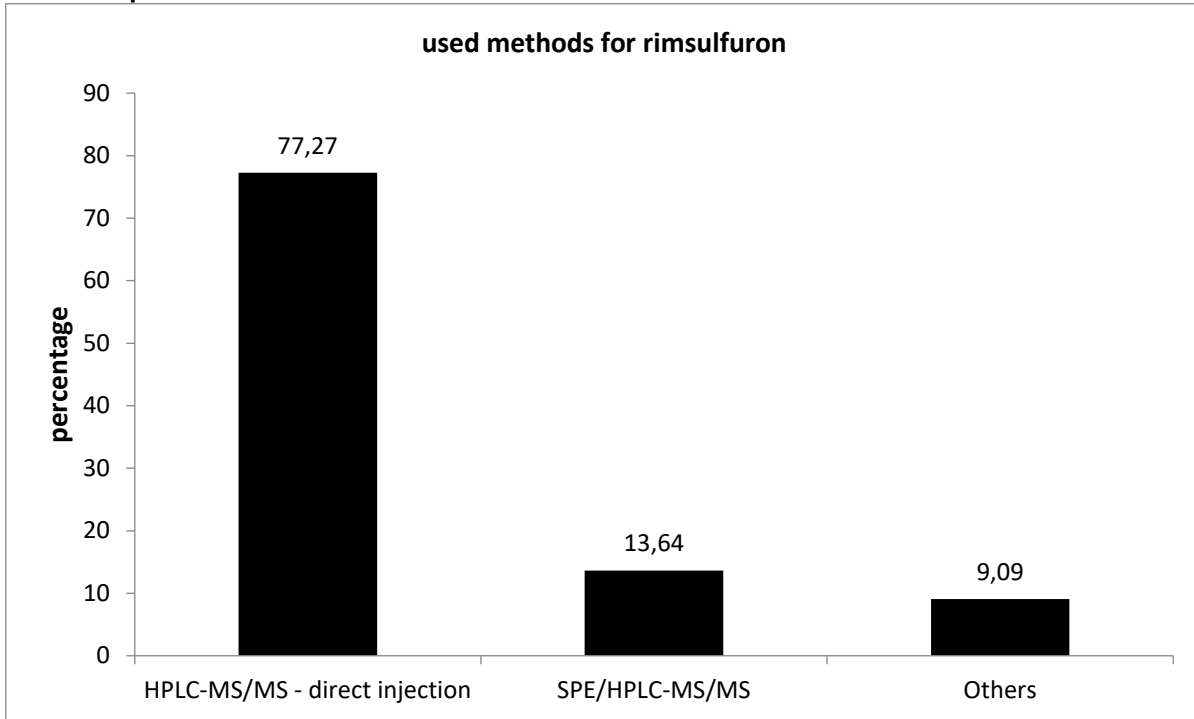
Relative standard deviation and tolerance limits

rimsulfuron

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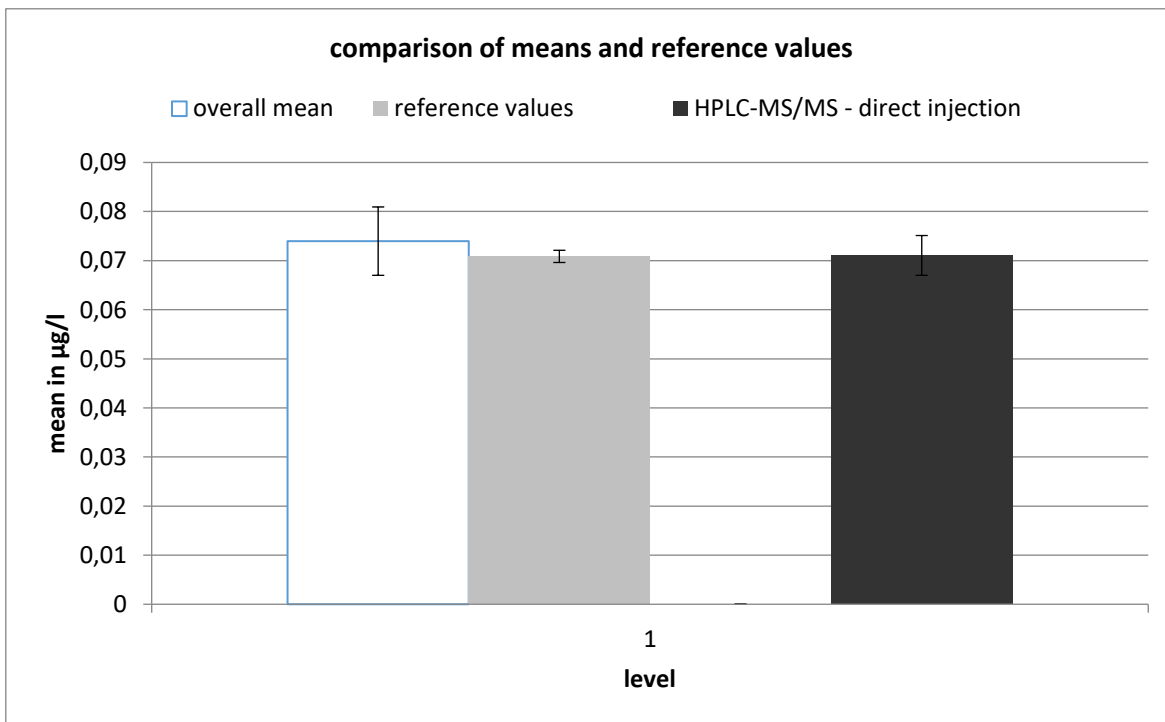

rimsulfuron

Method specific evaluation

used methods for rimsulfuron

method comparison rimsulfuron

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	0,0740	0,0070	9,4	0,0709	0,0012	1,8
2	0,1907	0,0175	9,2	0,1767	0,0030	1,7
3	0,3269	0,0308	9,4	0,3178	0,0054	1,7

comparison of means and reference values

comparison of means and reference values

rel. standard dev. method specific

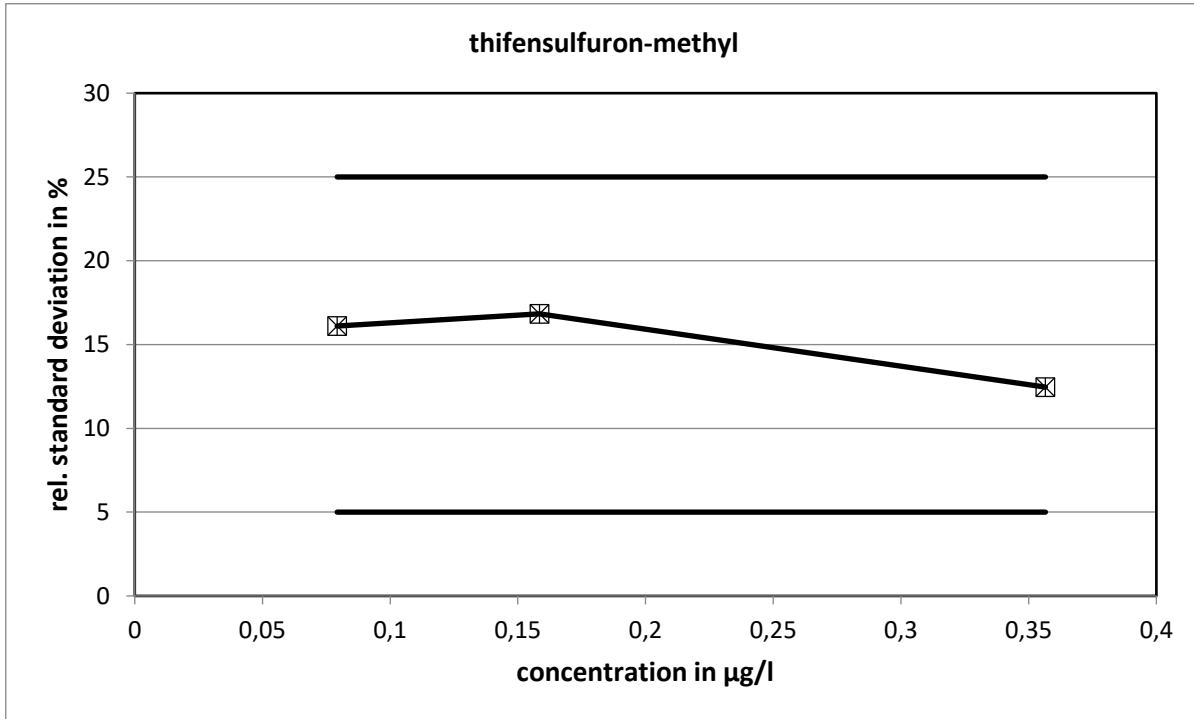| HPLC-MS/MS - direct injection									
level	robust mean [µg/l]	exp. unc. of the mean [µg/l]	exp. unc. of the mean [%]	robust standard deviation [µg/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	0,071	0,004	5,705	0,014	19,36	18	0	1	5,556
2	0,183	0,009	4,755	0,03	16,14	18	0	1	5,556
3	0,324	0,017	5,371	0,059	18,23	18	1	0	5,556

thifensulfuron-methyl

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	0,0792	8,08	0,0128	0,0128	16,10	0,1071	0,0554	35,18	-30,05	24	1	2	12,5
2	0,1585	8,20	0,0267	0,0267	16,83	0,2171	0,1089	36,97	-31,30	26	2	3	19,2
3	0,3566	6,22	0,0444	0,0444	12,46	0,4517	0,2726	26,67	-23,56	25	2	3	20,0
									sum	75	5	8	17,3

Recovery
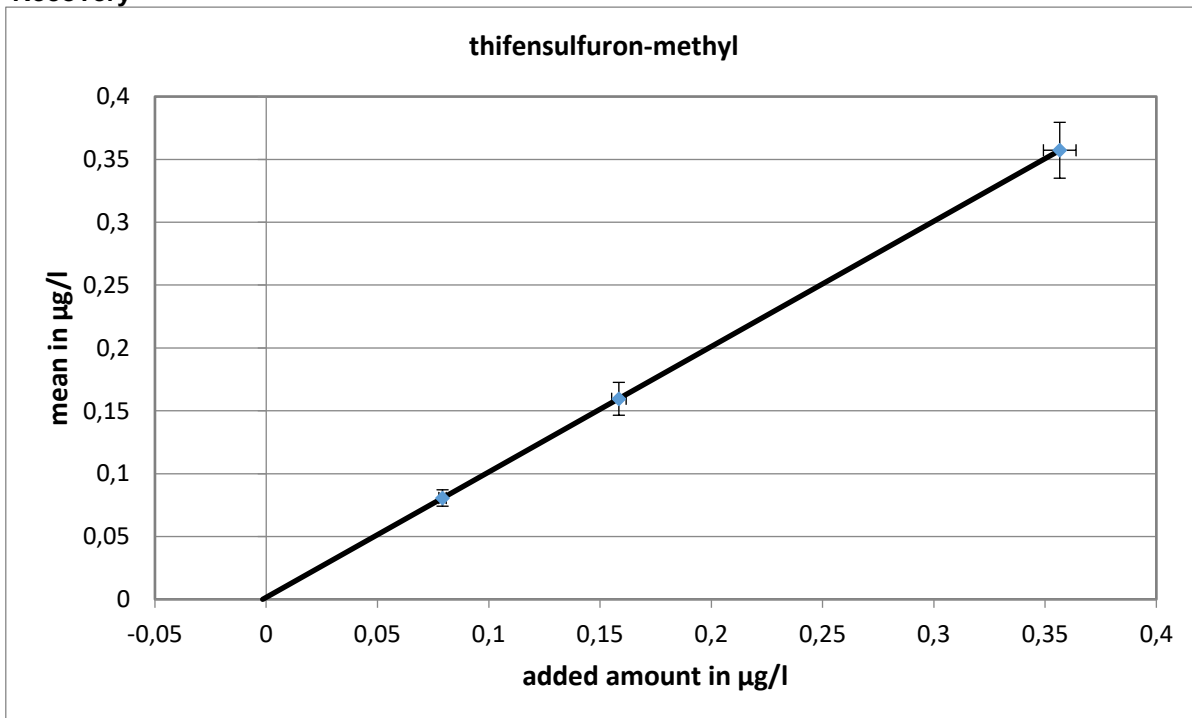
slope of the regression: 0,997; recovery rate: 99,7 %
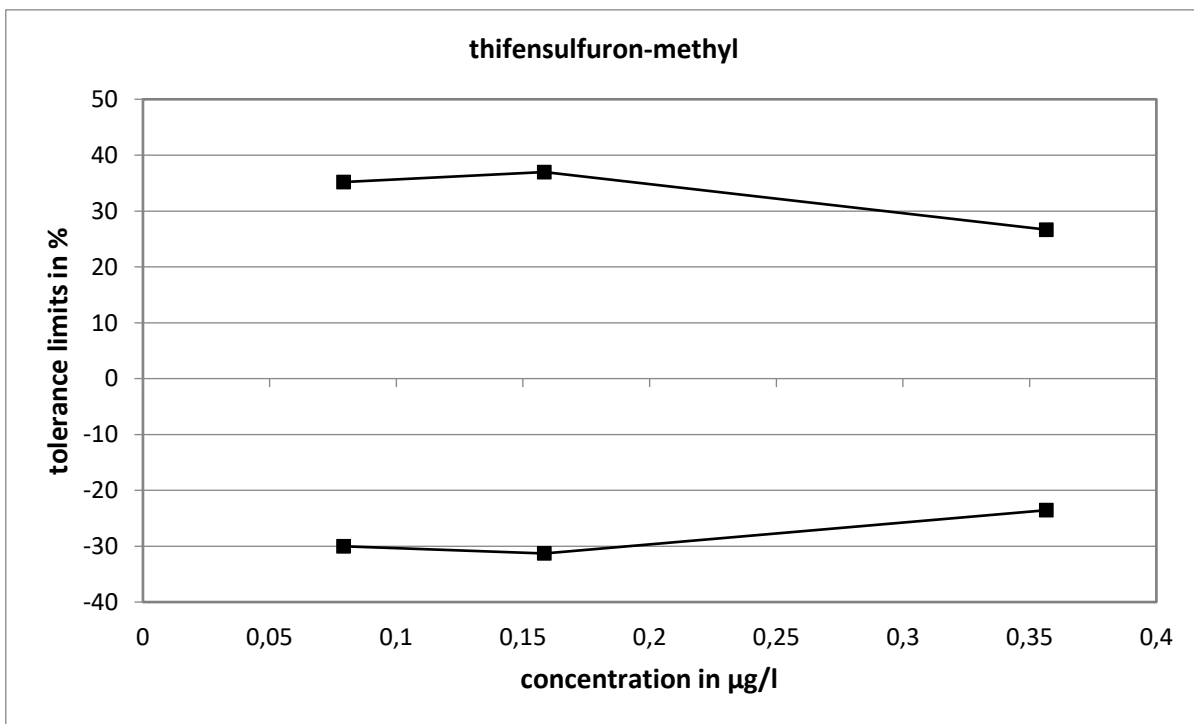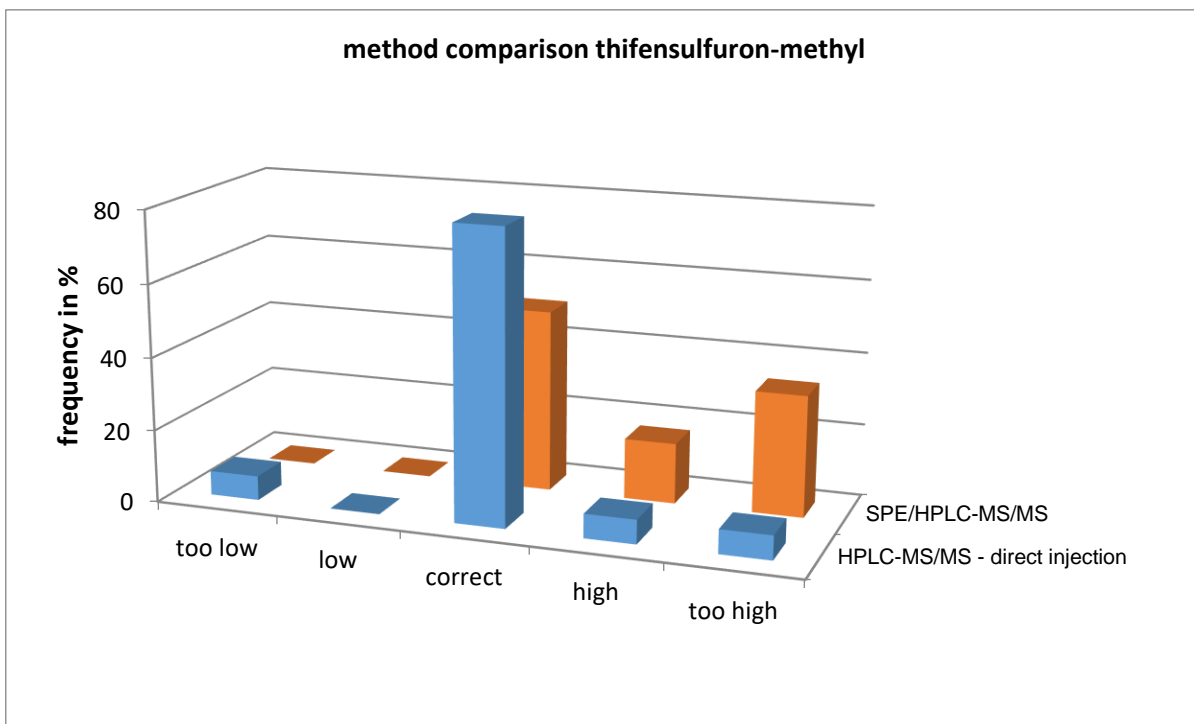
Relative standard deviation and tolerance limits

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

Method specific evaluation

used methods for thifensulfuron-methyl

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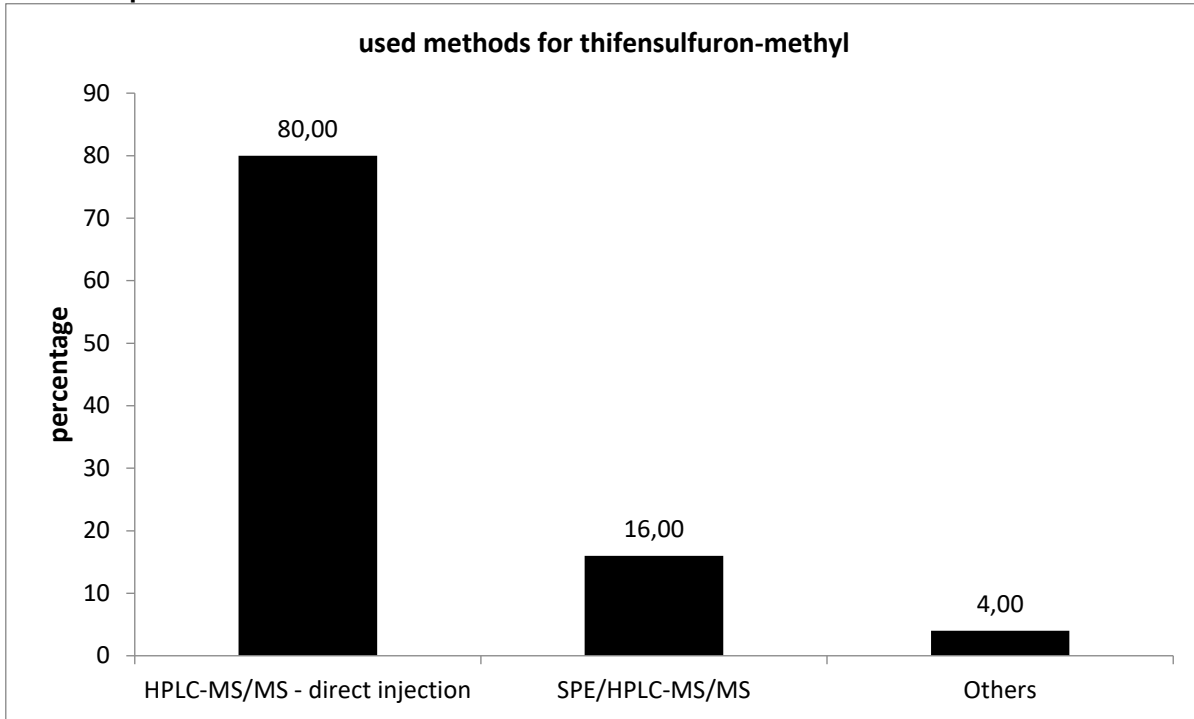
The values determined with HPLC-MS/MS - direct injection showed the closest statistical distribution.

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	0,0806	0,0065	8,1	0,0808	0,0023	2,8
2	0,1596	0,0131	8,2	0,1601	0,0036	2,3
3	0,3573	0,0222	6,2	0,3582	0,0075	2,1

comparison of means and reference values

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

mean in µg/l

level
2

comparison of means and reference values

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

mean in µg/l

level
3

rel. standard dev. method specific

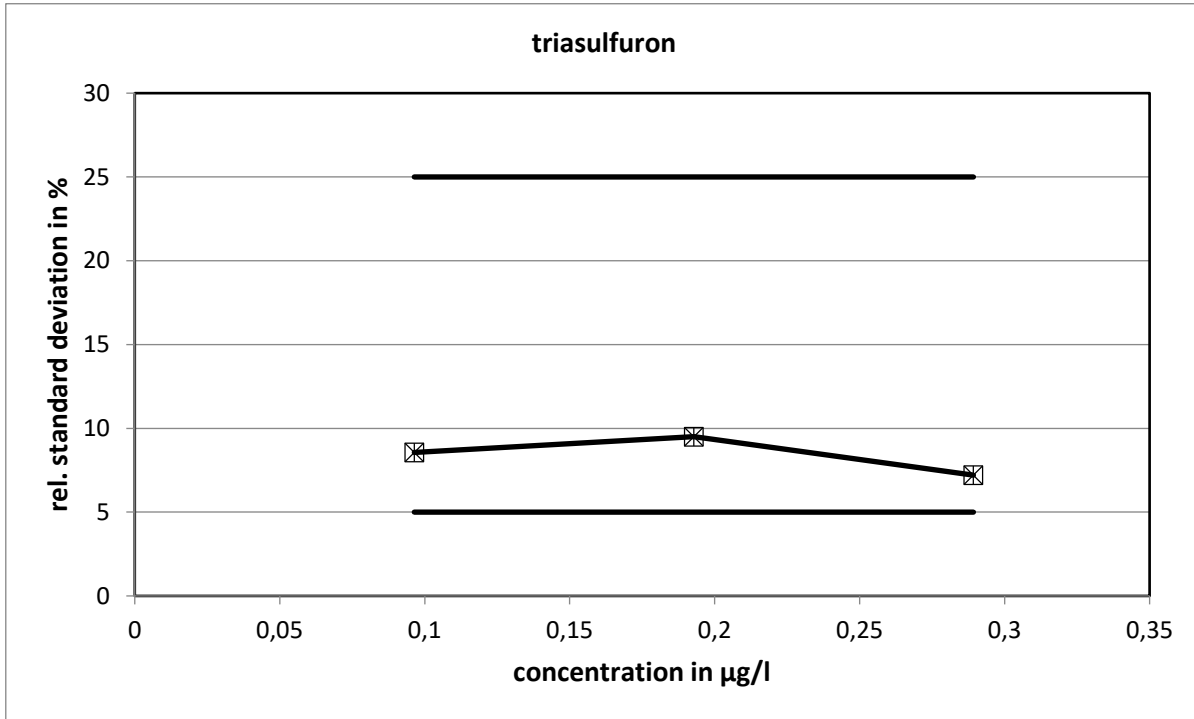| HPLC-MS/MS - direct injection									
level	robust mean [µg/l]	exp. unc. of the mean [µg/l]	exp. unc. of the mean [%]	robust standard deviation [µg/l]	robust standard deviation [%]	number of results	out below	out above	out [%]
1	0,079	0,002	3,106	0,009	11,11	20	2	2	20
2	0,158	0,006	3,593	0,021	13,48	22	3	1	18,18
3	0,357	0,011	2,957	0,039	10,84	21	2	3	23,81

triasulfuron

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	0,0964	2,92	0,0083	0,0083	8,57	0,1137	0,0805	17,93	-16,47	21	0	3	14,3
2	0,1928	2,12	0,0183	0,0183	9,50	0,2313	0,1577	19,97	-18,21	21	0	3	14,3
3	0,2892	1,94	0,0208	0,0208	7,21	0,3325	0,2489	14,96	-13,94	21	1	3	19,0
									sum	63	1	9	15,9

Recovery and matrix content
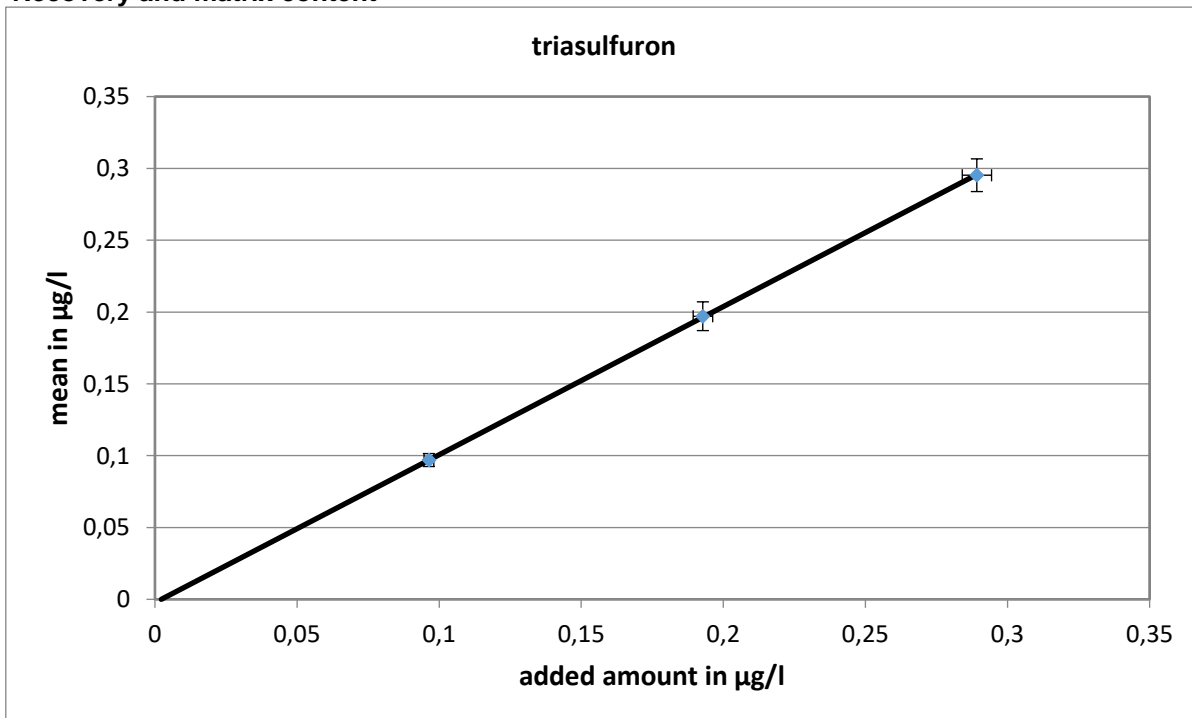
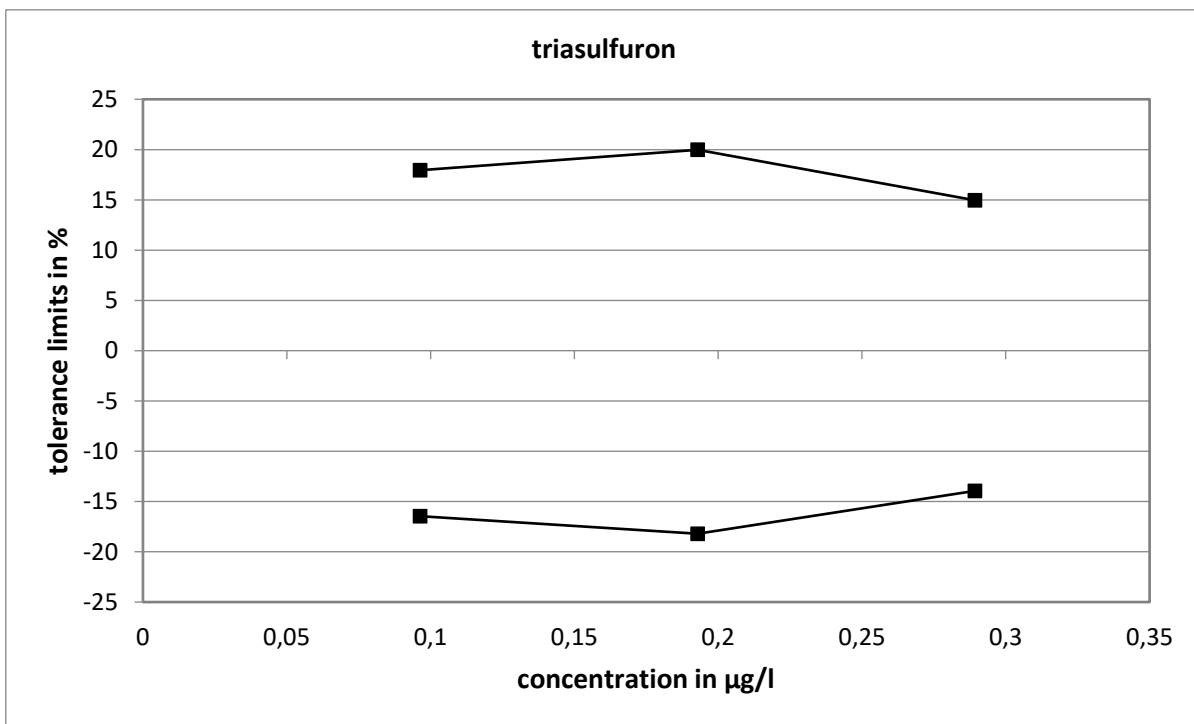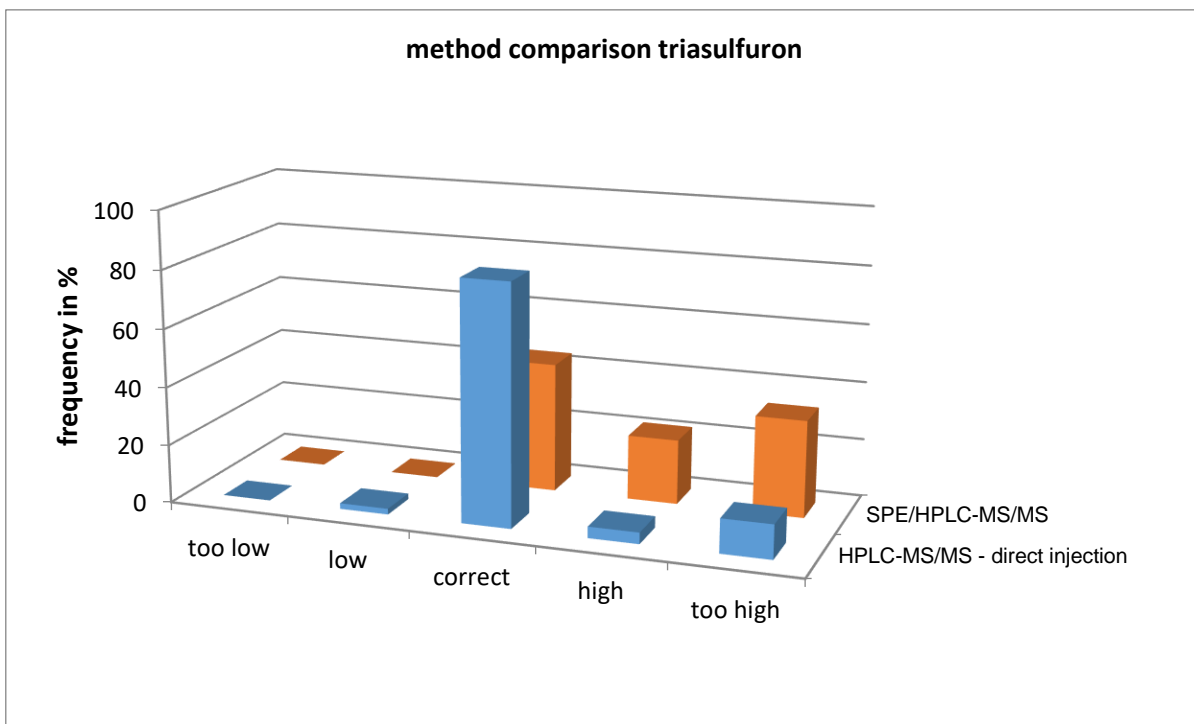slope of the regression: 1,03; recovery rate: 103 %

Relative standard deviation and tolerance limits

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

Method specific evaluation

used methods for triasulfuron

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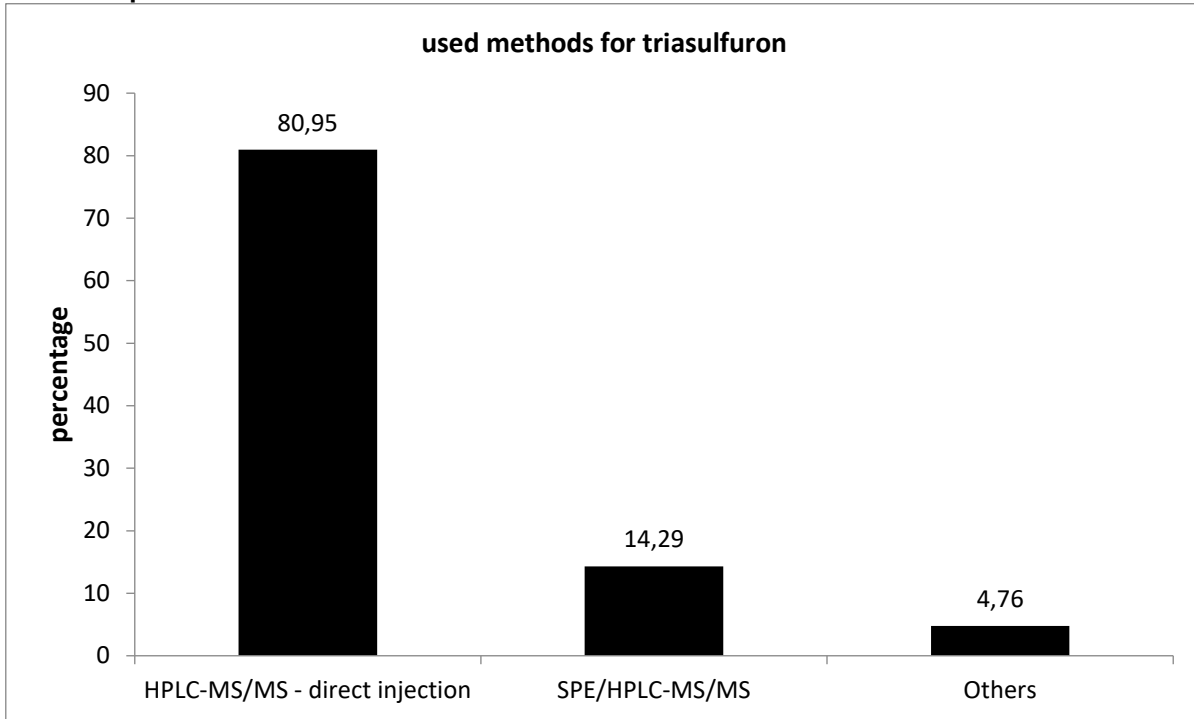
The values determined with HPLC-MS/MS - direct injection showed the closest statistical distribution.

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	0,0970	0,0045	4,6	0,0964	0,0028	2,9
2	0,1971	0,0100	5,1	0,1928	0,0041	2,1
3	0,2952	0,0114	3,9	0,2892	0,0056	1,9

comparison of means and reference values

☐ overall mean   ▤ reference values   ■ HPLC-MS/MS - direct injection

comparison of means and reference values

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

comparison of means and reference values

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

rel. standard dev. method specific

Legend: overall mean ▪▪▪ HPLC-MS/MS - direct injection ◆

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	0,097	0,002	1,863	0,006	6,323	18	0	3	16,67
2	0,196	0,004	2,166	0,014	7,35	18	0	3	16,67
3	0,294	0,005	1,63	0,016	5,533	18	0	3	16,67

amidosulfuron - exp. measurement uncertainty

16610 %   4615 %   5560 %

metsulfuron-methyl - exp. measurement uncertainty

24667 %   8290 %   3603 %

rimsulfuron - exp. measurement uncertainty

53770 %   7925 %   4982 %

thifensulfuron-methyl - exp. measurement uncertainty

38611 %   18503 %   5962 %

triasulfuron - exp. measurement uncertainty
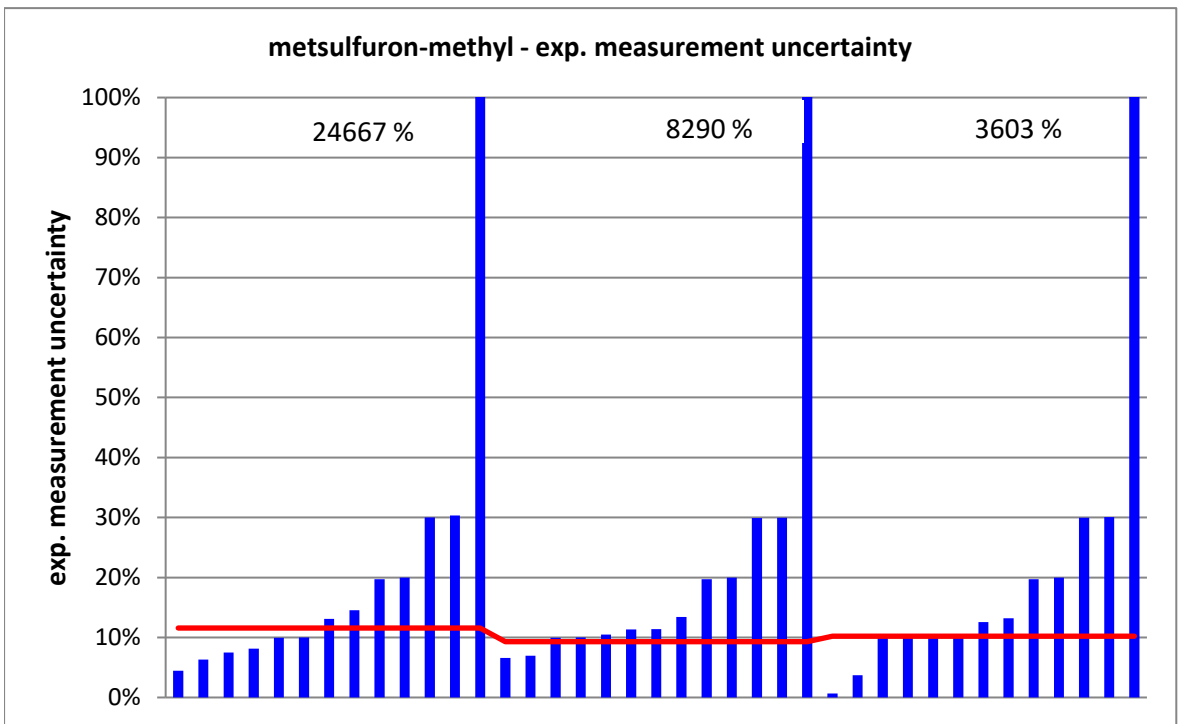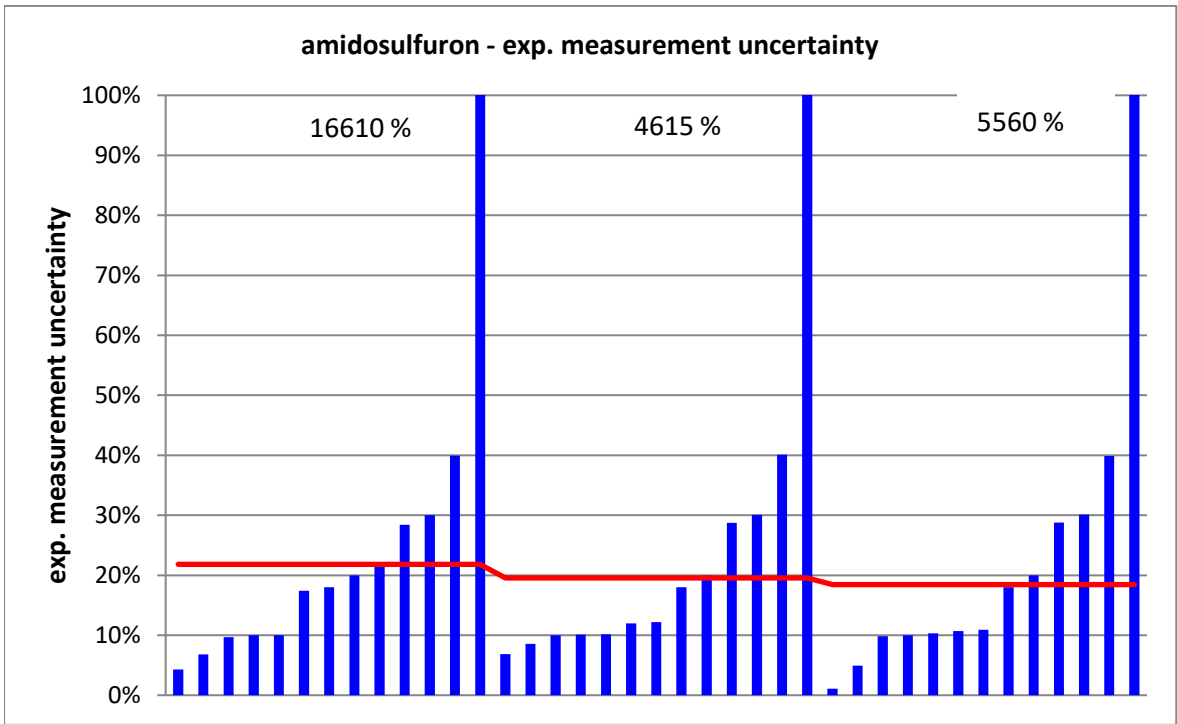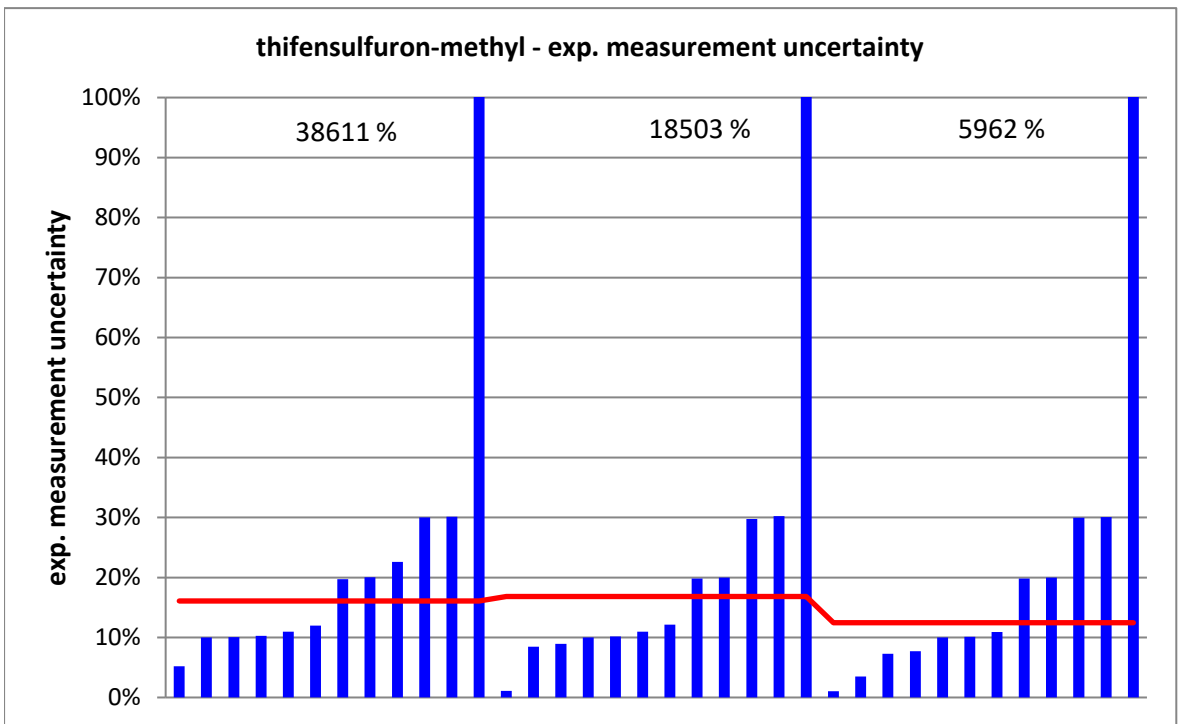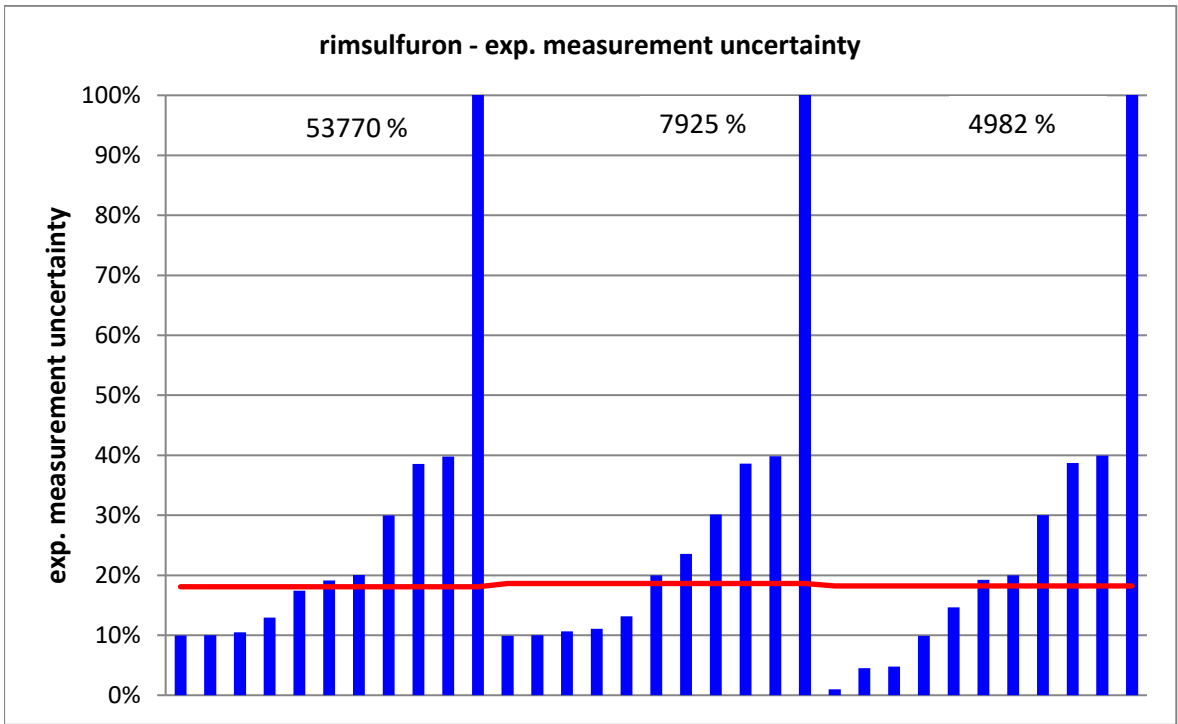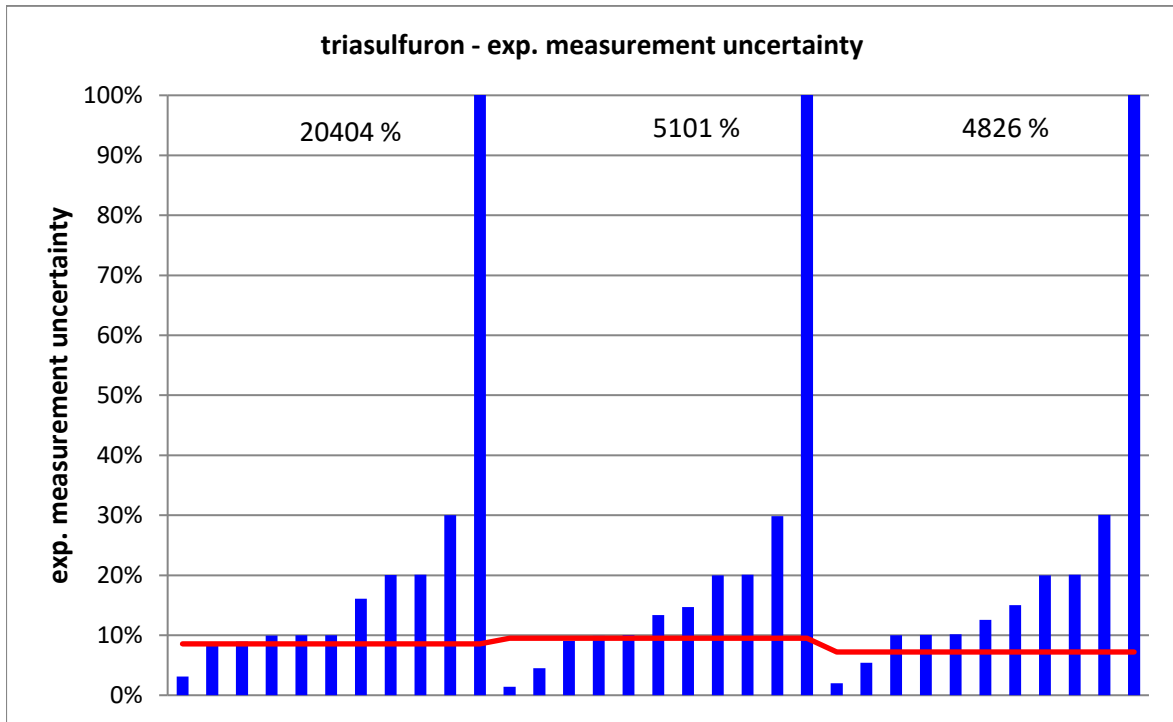
PT 3/18 - TW S5	amidosulfuron - 1				
assigned value [µg/l]*		0,06342	± 0,00133		
upper tolerance limit [µg/l]		0,09455			
lower tolerance limit [µg/l]		0,03803			
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
1	0,079	0,003	8,5	1,0	s
2	0,059	0,004	-2,1	-0,3	s
4	0,0691	0,014	0,8	0,4	s
5	0,069	0,012	0,9	0,4	s
7	0,075			0,7	s
8	0,058			-0,4	s
9	0,0696	0,015	0,8	0,4	s
10	0,081	0,023	1,5	1,1	s
11	0,076			0,8	s
12	0,059	9,8	0,0	-0,3	s
13	0,0723	0,022	0,8	0,6	s
14	0,069			0,4	s
15	0,0603			-0,2	s
16	0,031	0,003	-19,8	-2,6	q
17	0,0616			-0,1	s
18	0,0681	0,007	1,3	0,3	s
23	0,166			6,6	u
25	0,0591	0,006	-1,4	-0,3	s
26	0,0977	0,039	1,8	2,2	q
27	0,0527	0,009	-2,2	-0,8	s
29	0,085			1,4	s
31	0,0604			-0,2	s
33	0,071			0,5	s
35	0,0658			0,2	s

* The stated uncertainty of the assigned value is the expanded uncertainty with a coverage factor k=2 corresponding to a confidence level of about 95%
** s = satisfactory, q = questionable, u = unsatisfactory

amidosulfuron - 1

amidosulfuron - 1

amidosulfuron - 1
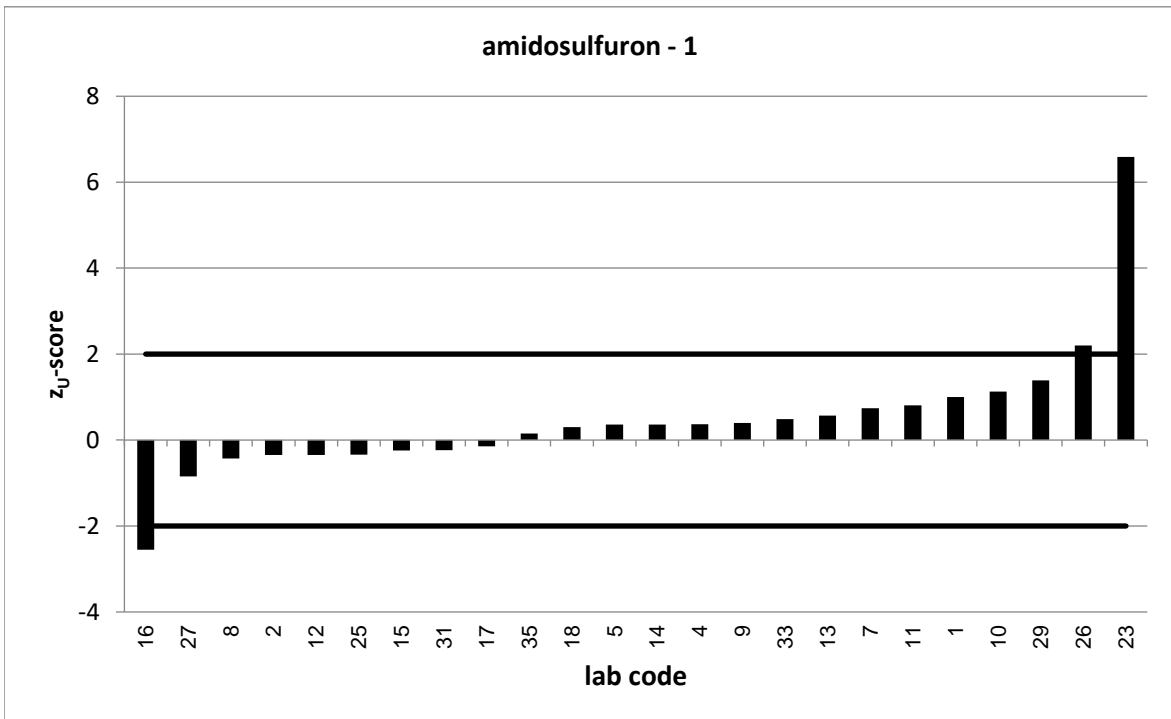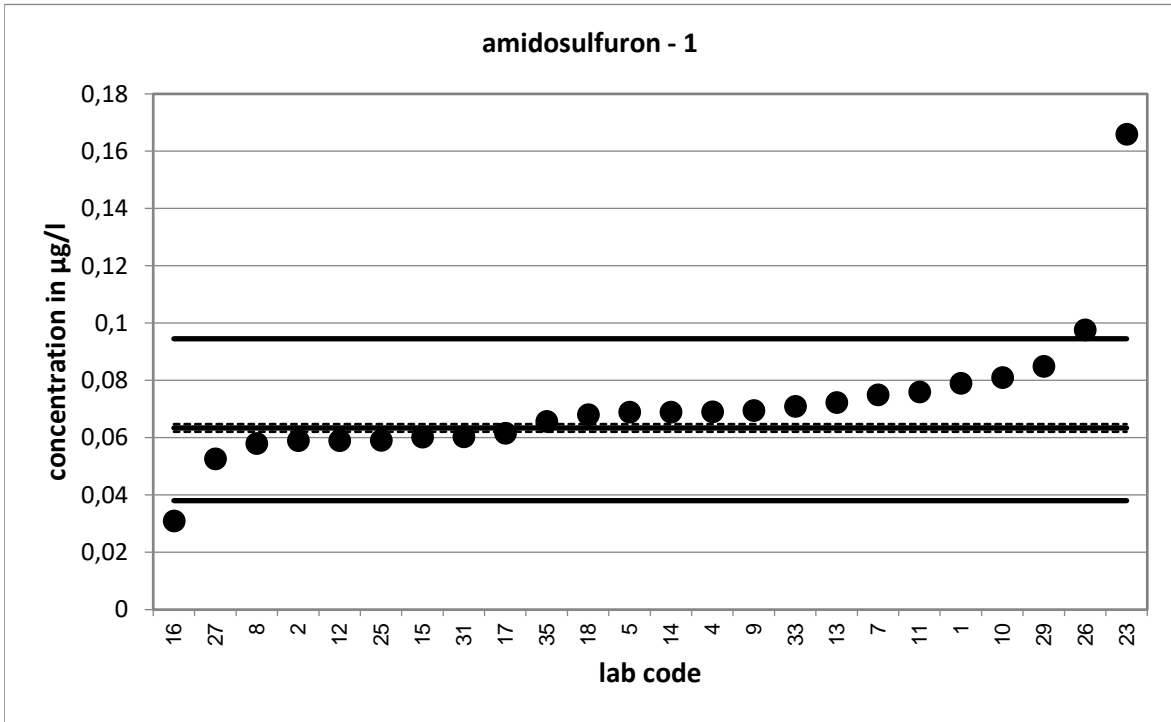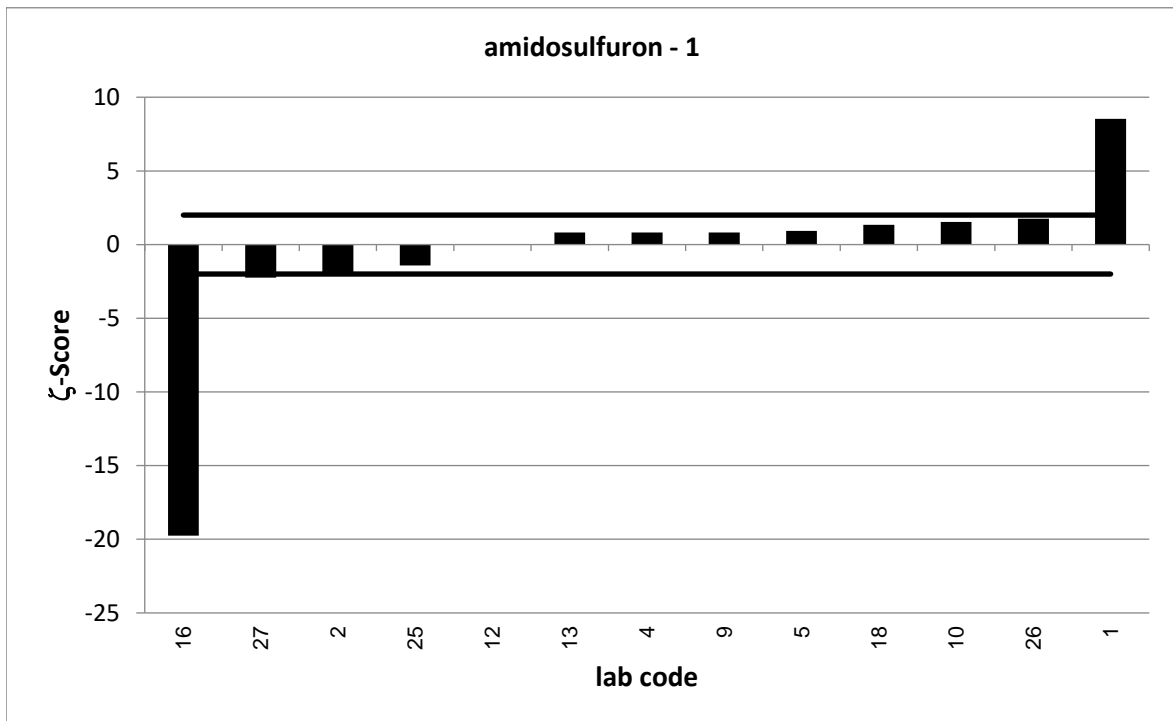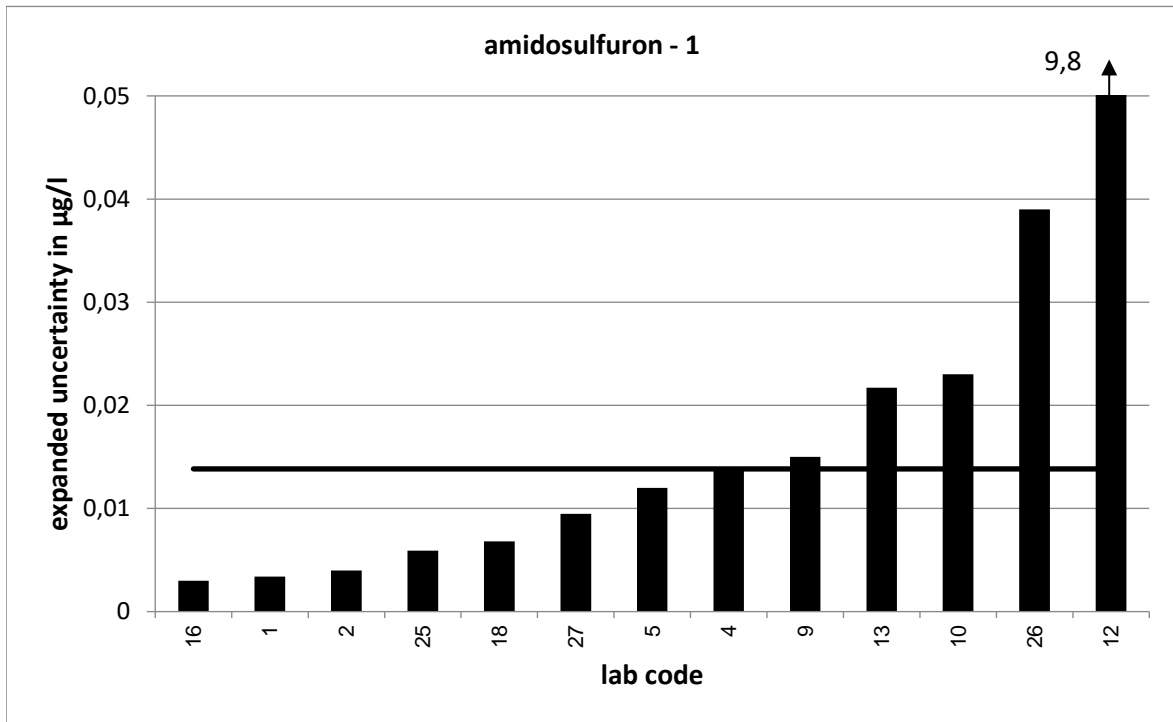
amidosulfuron - 1

PT 3/18 - TW S5	amidosulfuron - 2				
assigned value [µg/l]*		0,222	± 0,0042		
upper tolerance limit [µg/l]		0,318			
lower tolerance limit [µg/l]		0,1418			
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
1	0,264	0,018	4,5	0,9	s
2	0,189	0,023	-2,8	-0,8	s
4	0,25	0,05	1,1	0,6	s
5	0,233	0,02	1,1	0,2	s
7	0,265			0,9	s
8	0,204			-0,4	s
9	0,275	0,033	3,2	1,1	s
10	0,289	0,083	1,6	1,4	s
11	0,233			0,2	s
12	0,208	9,6	0,0	-0,3	s
13	0,256	0,077	0,9	0,7	s
14	0,257			0,7	s
15	0,226			0,1	s
16	0,109	0,011	-19,2	-2,8	q
17	0,223			0,0	s
18	0,244	0,024	1,8	0,5	s
23	0,438			4,5	u
25	0,216	0,022	-0,5	-0,1	s
26	0,374	0,15	2,0	3,2	u
27	0,2	0,036	-1,2	-0,5	s
29	0,3			1,6	s
31	0,215			-0,2	s
33	0,236			0,3	s
35	0,233411			0,2	s

* The stated uncertainty of the assigned value is the expanded
uncertainty with a coverage factor k=2 corresponding to a
confidence level of about 95%
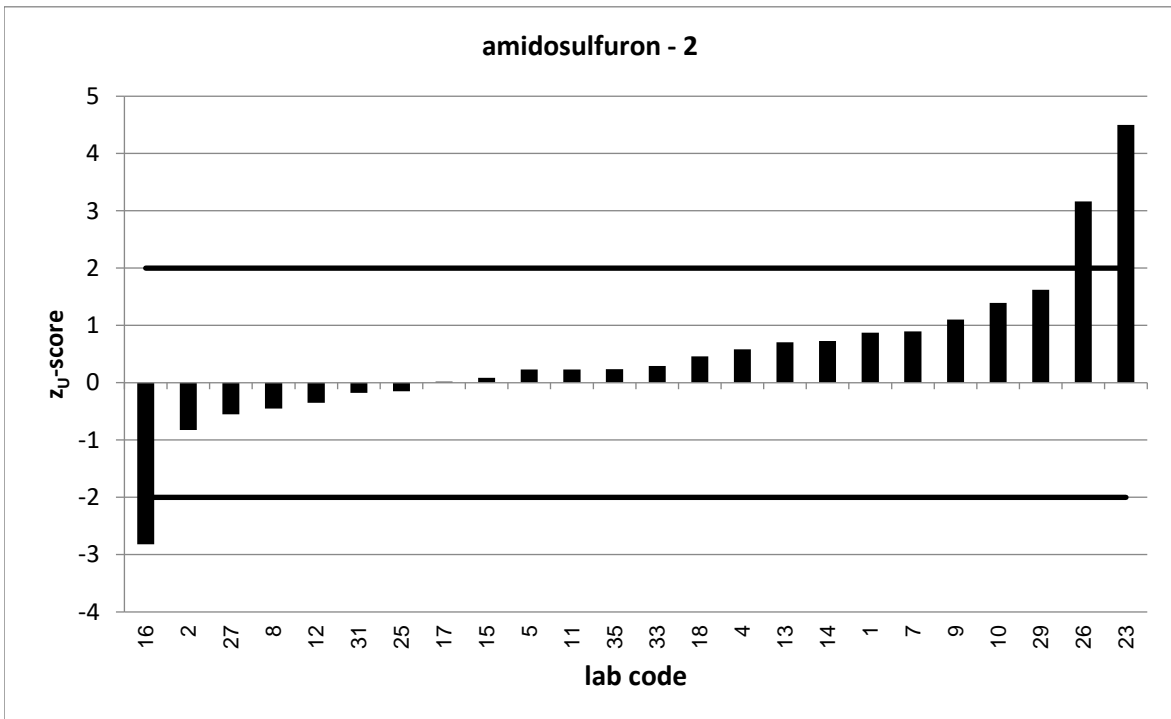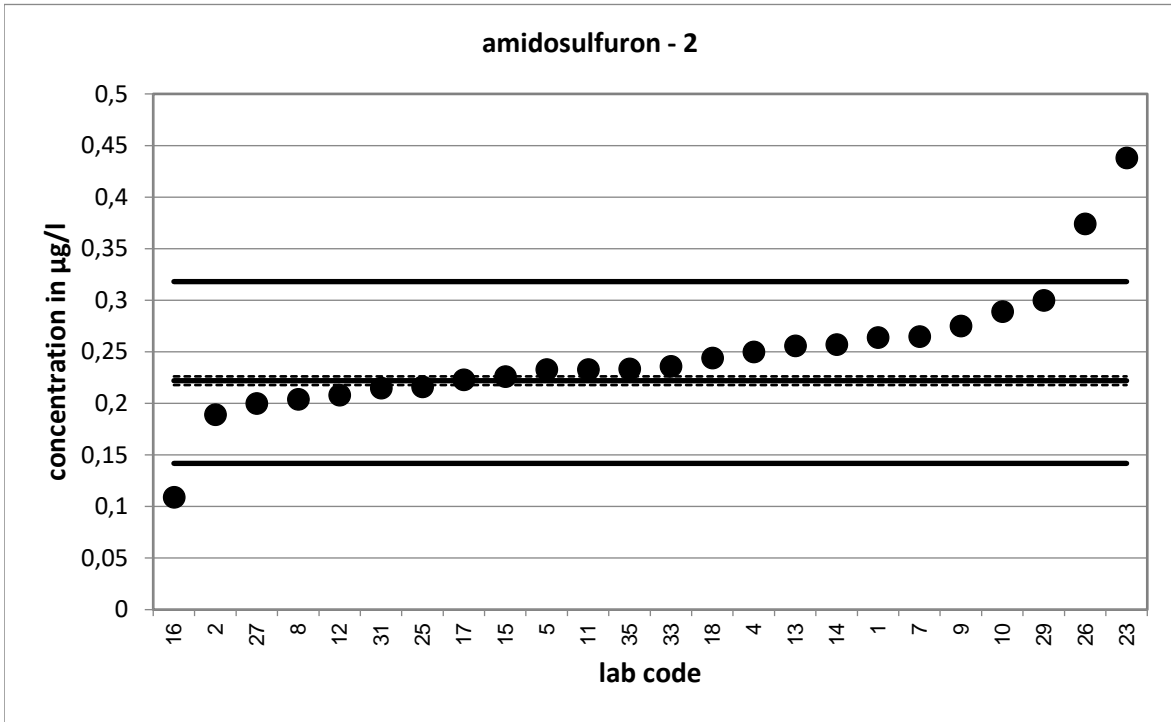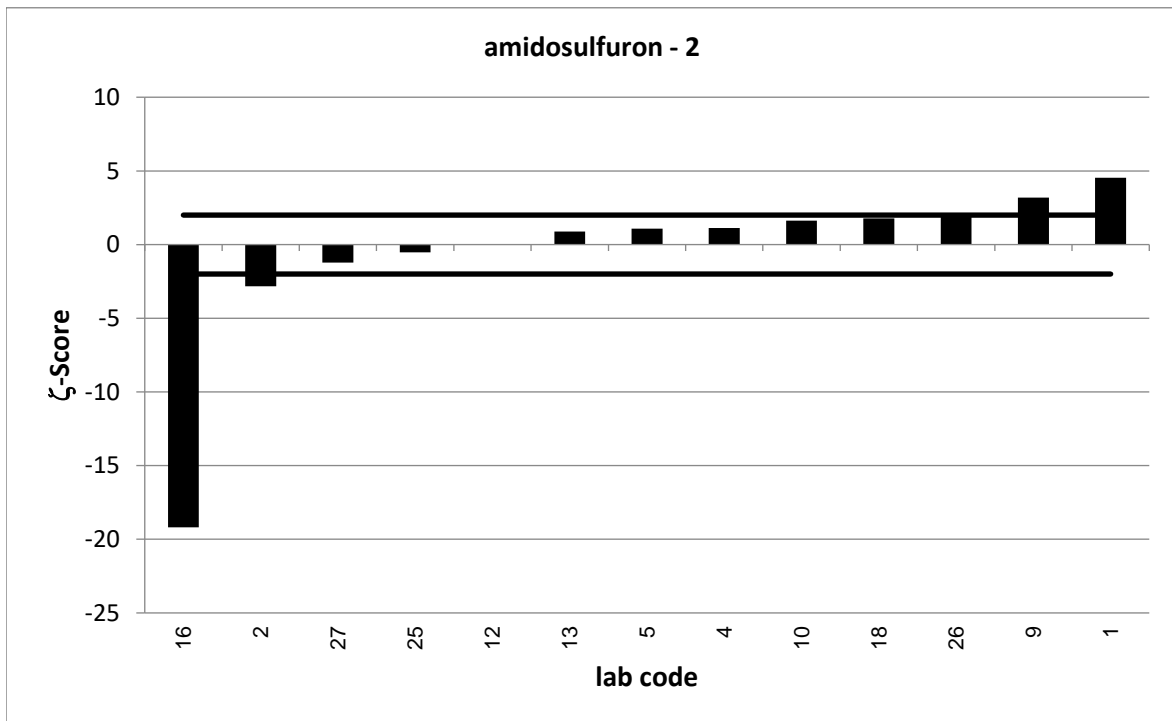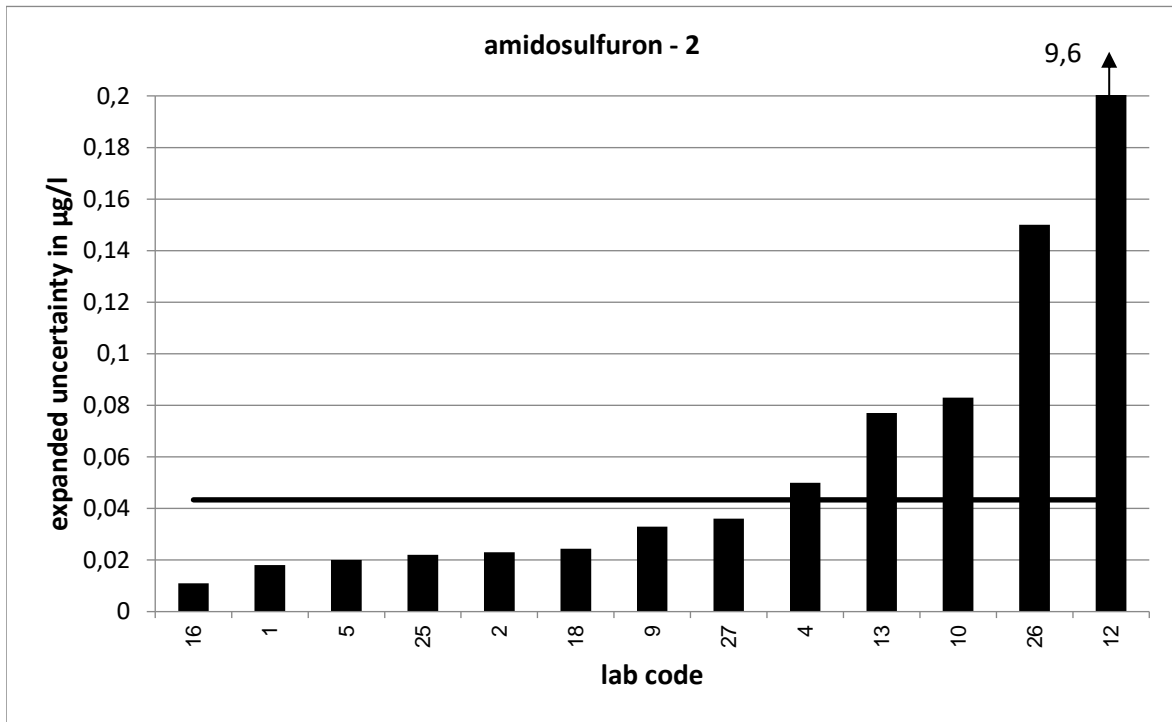** s = satisfactory, q = questionable, u = unsatisfactory

amidosulfuron - 2

amidosulfuron - 2

amidosulfuron - 2

amidosulfuron - 2

PT 3/18 - TW S5	amidosulfuron - 3				
assigned value [µg/l]*	0,2854	± 0,0054			
upper tolerance limit [µg/l]	0,4013				
lower tolerance limit [µg/l]	0,1877				
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
1	0,341	0,004	17,1	1,0	s
2	0,247	0,027	-2,8	-0,8	s
4	0,317	0,063	1,0	0,5	s
5	0,303	0,015	2,2	0,3	s
7	0,312			0,5	s
8	0,264			-0,4	s
9	0,32	0,033	2,1	0,6	s
10	0,365	0,105	1,5	1,4	s
11	0,29			0,1	s
12	0,268	14,9	0,0	-0,4	s
13	0,322	0,097	0,8	0,6	s
14	0,336			0,9	s
15	0,308			0,4	s
16	0,14	0,015	-18,3	-3,0	u
17	0,288			0,0	s
18	0,337	0,034	3,0	0,9	s
23	0,963			11,7	u
25	0,274	0,027	-0,8	-0,2	s
26	0,441	0,176	1,8	2,7	q
27	0,255	0,046	-1,3	-0,6	s
29	0,384			1,7	s
31	0,282			-0,1	s
33	0,33			0,8	s
35	0,2807			-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%
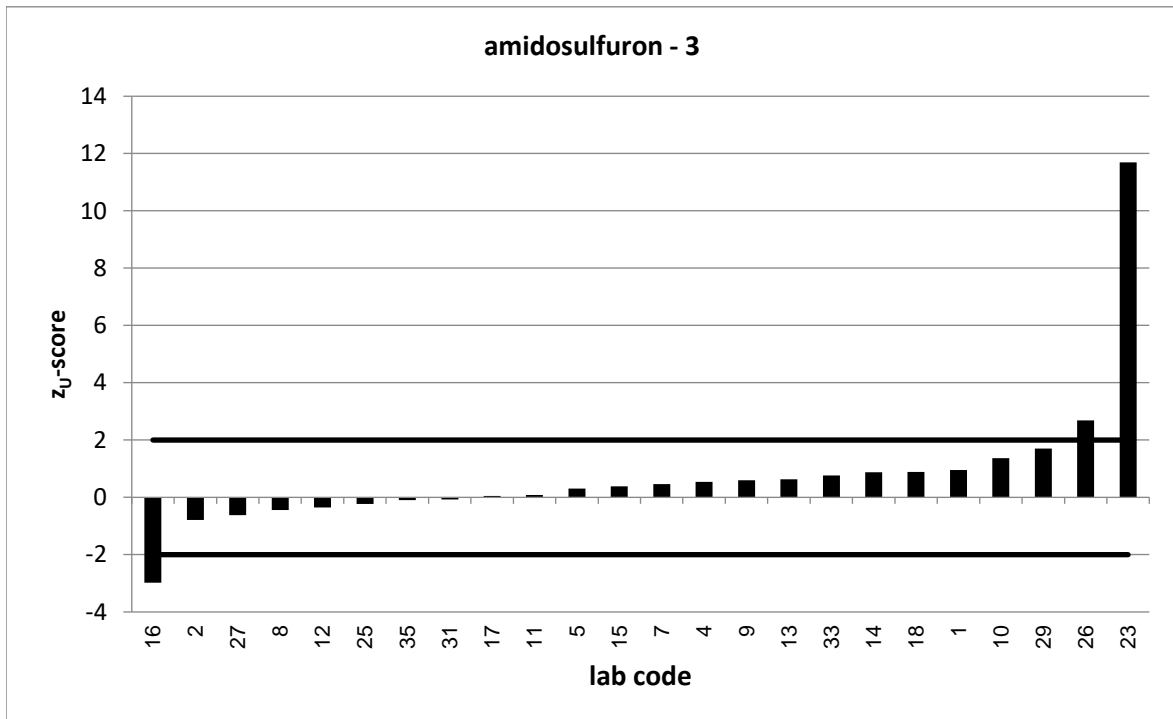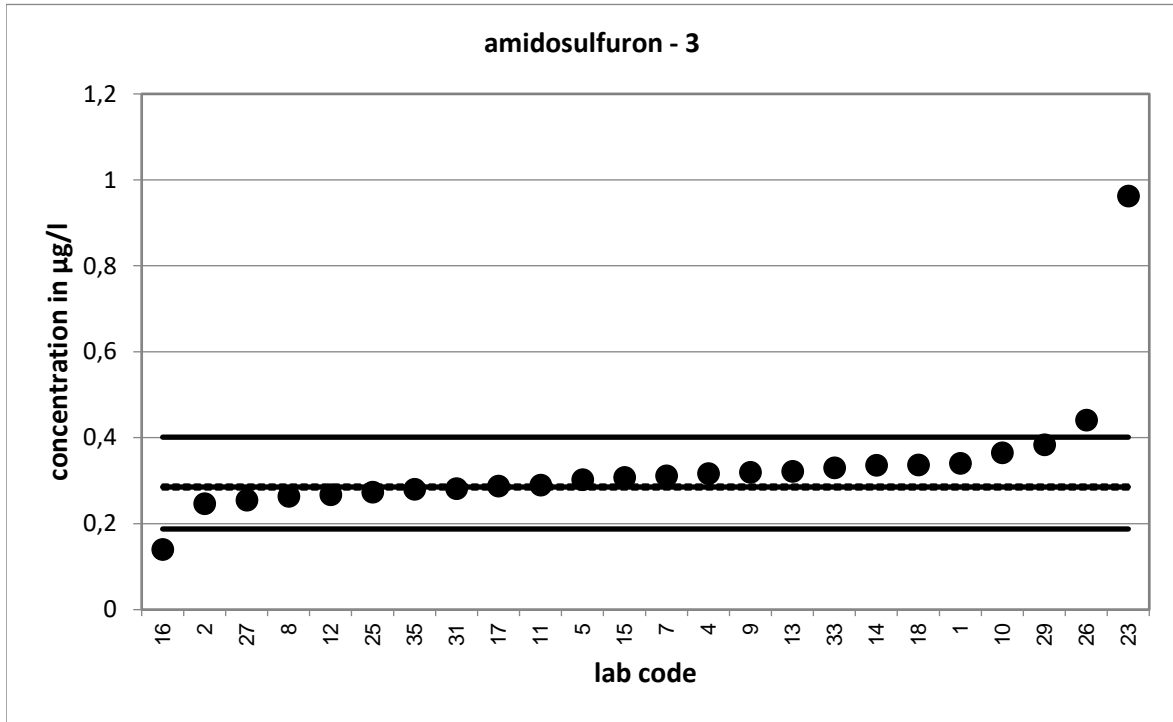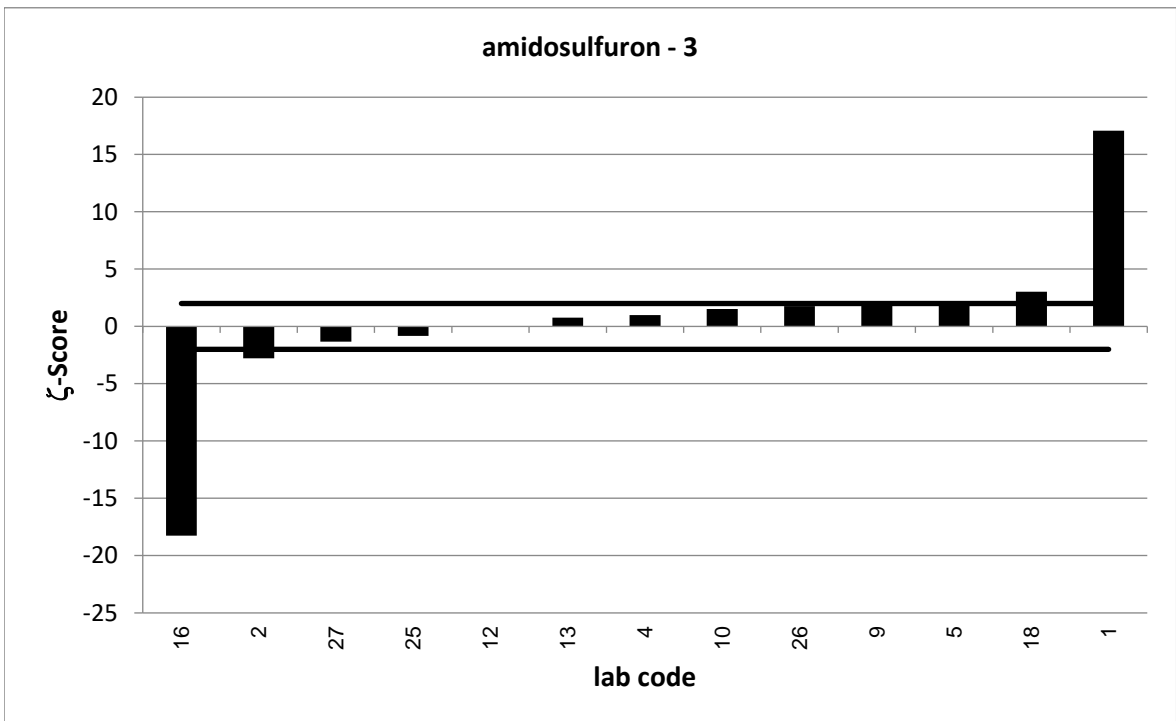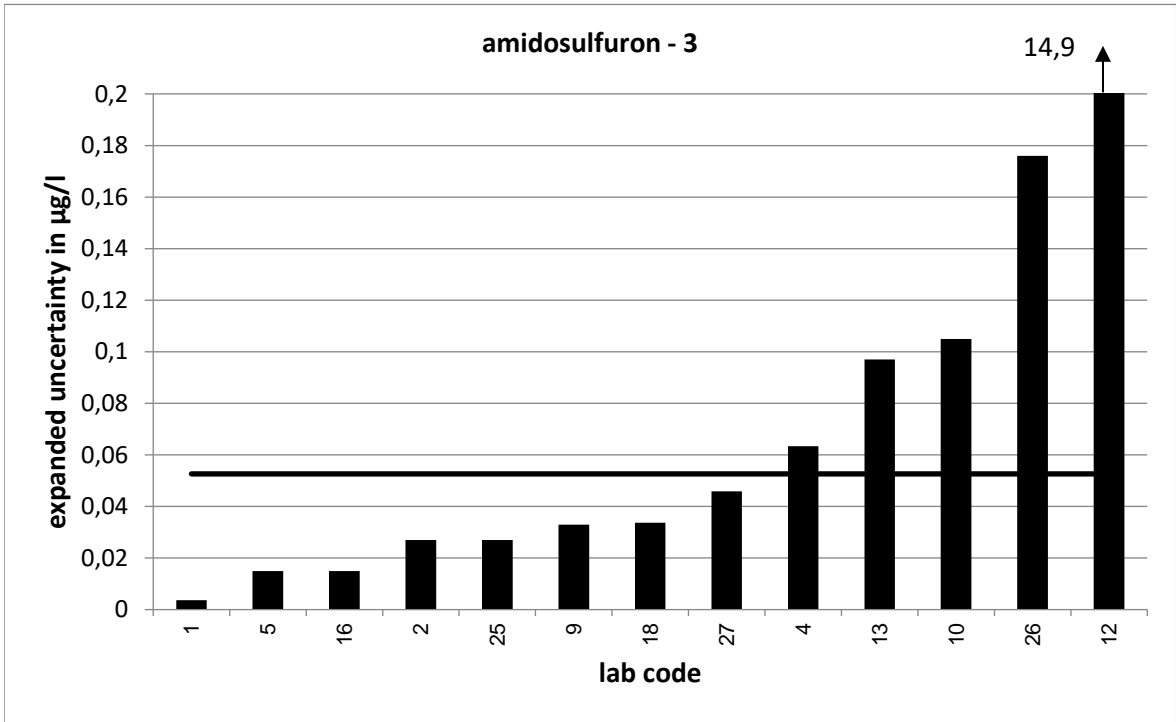** s = satisfactory, q = questionable, u = unsatisfactory

amidosulfuron - 3

amidosulfuron - 3

amidosulfuron - 3

amidosulfuron - 3

PT 3/18 - TW S5	metsulfuron-methyl - 1				
assigned value [µg/l]*	0,08975	± 0,00166			
upper tolerance limit [µg/l]	0,1118				
lower tolerance limit [µg/l]	0,07002				
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
1	0,094	0,004	1,9	0,4	s
2	0,08	0,006	-3,1	-1,0	s
4	0,0836	0,017	-0,7	-0,6	s
5	0,086	0,007	-1,0	-0,4	s
7	0,087			-0,3	s
8	0,085			-0,5	s
9	0,0953	0,006	1,8	0,5	s
10	0,0918	0,012	0,3	0,2	s
11	0,097			0,7	s
12	0,09	22,2	0,0	0,0	s
13	0,0809	0,024	-0,7	-0,9	s
14	0,095			0,5	s
15	0,0823			-0,8	s
16	0,055	0,008	-8,5	-3,5	u
17	0,0918			0,2	s
18	0,102	0,01	2,4	1,1	s
23	0,246			14,1	u
25	0,0915	0,009	0,4	0,2	s
26	0,112	0,034	1,3	2,0	s
27	0,0847	0,017	-0,6	-0,5	s
29	0,098			0,7	s
30	0,089			-0,1	s
31	0,122			2,9	q
33	0,093			0,3	s
35	0,0978			0,7	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%
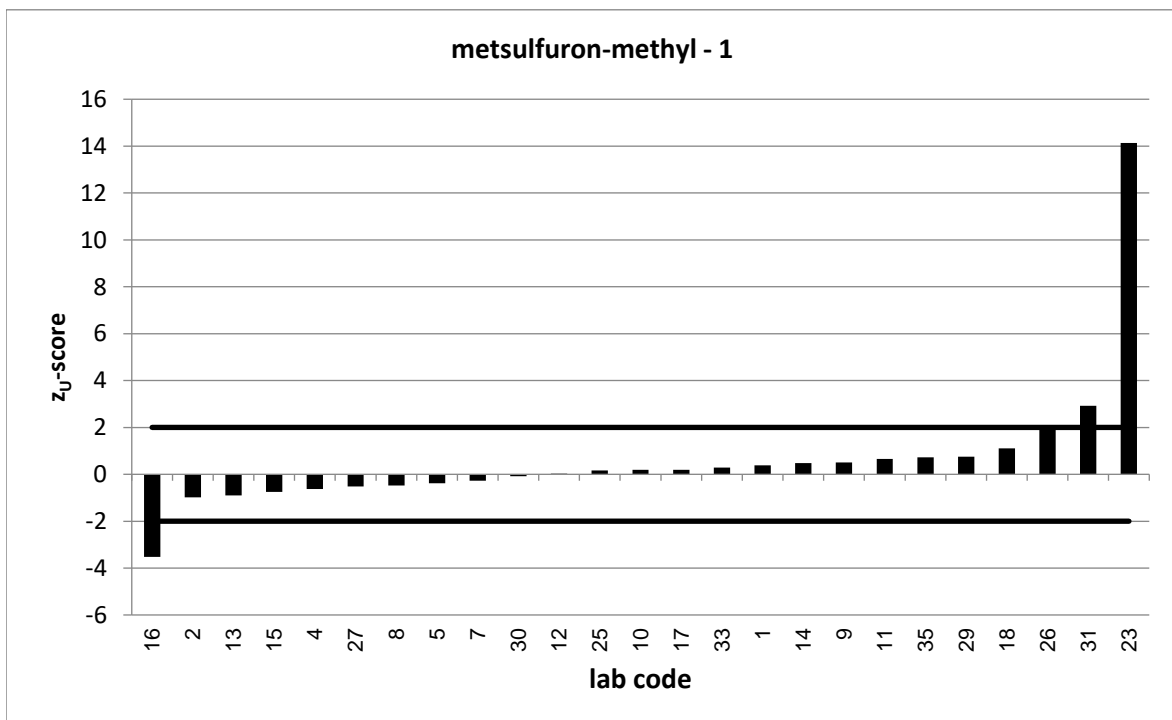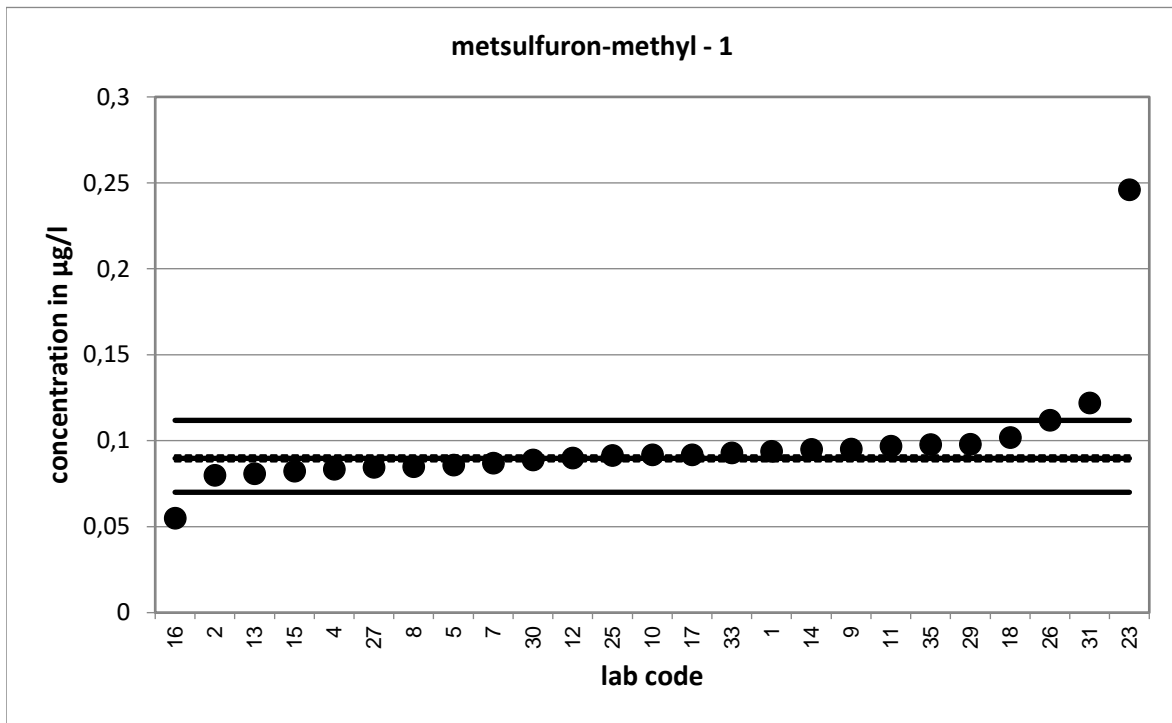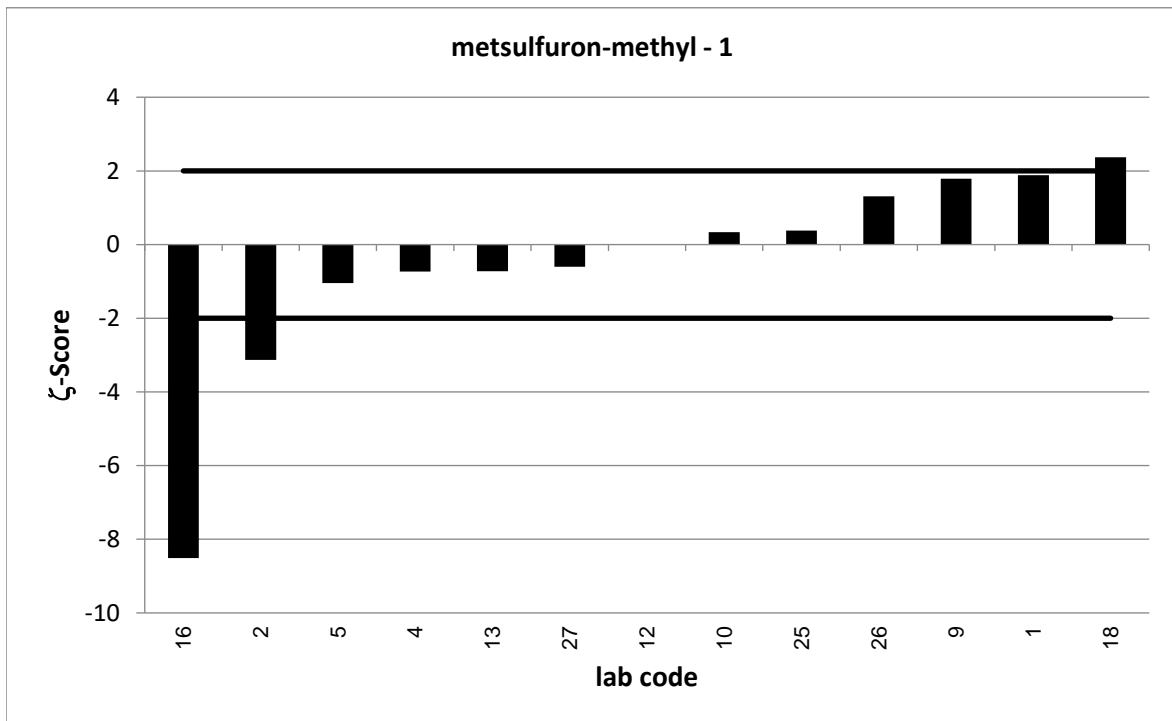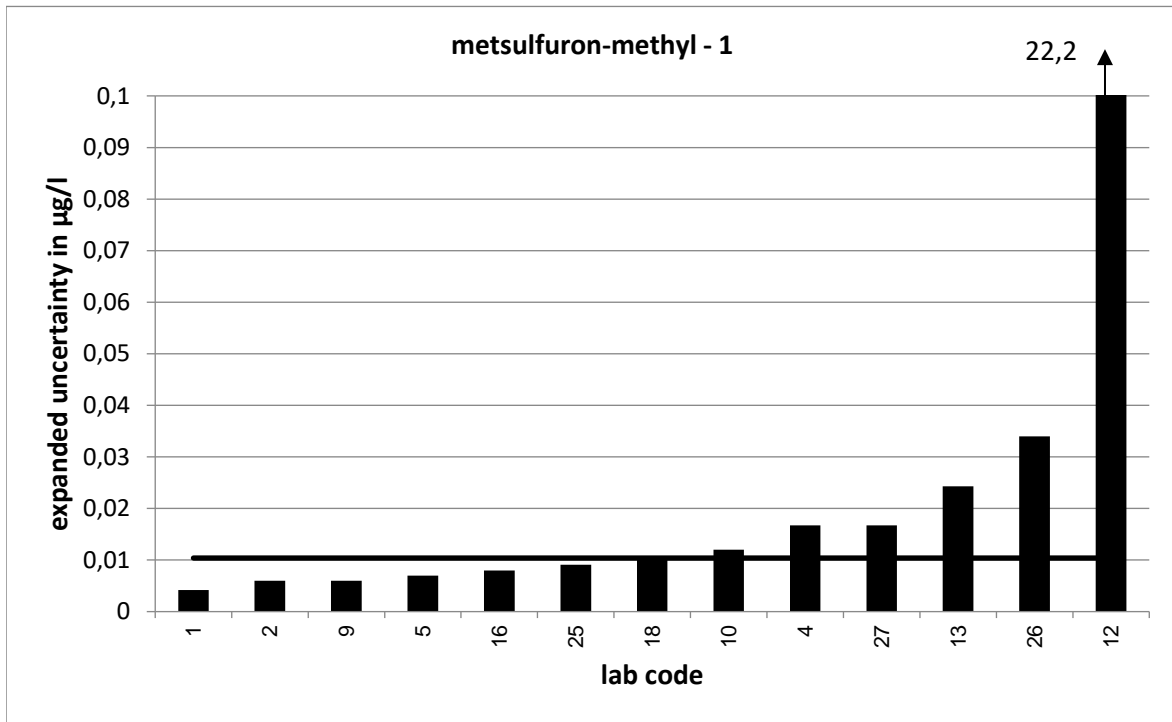** s = satisfactory, q = questionable, u = unsatisfactory

metsulfuron-methyl - 1

metsulfuron-methyl - 1

metsulfuron-methyl - 1

metsulfuron-methyl - 1

PT 3/18 - TW S5	metsulfuron-methyl - 2				
assigned value [µg/l]*		0,2692	± 0,0049		
upper tolerance limit [µg/l]		0,3218			
lower tolerance limit [µg/l]		0,2212			
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
1	0,294	0,019	2,5	0,9	s
2	0,215	0,015	-6,9	-2,3	q
4	0,256	0,051	-0,5	-0,6	s
5	0,264	0,03	-0,3	-0,2	s
7	0,284			0,6	s
8	0,268			-0,1	s
9	0,286	0,03	1,1	0,6	s
10	0,276	0,037	0,4	0,3	s
11	0,272			0,1	s
12	0,269	22,3	0,0	0,0	s
13	0,251	0,075	-0,5	-0,8	s
14	0,282			0,5	s
15	0,274			0,2	s
16	0,168	0,019	-10,3	-4,2	u
17	0,276			0,3	s
18	0,304	0,03	2,3	1,3	s
23	0,475			7,8	u
25	0,272	0,027	0,2	0,1	s
26	0,324	0,097	1,1	2,1	q
27	0,263	0,052	-0,2	-0,3	s
29	0,305			1,4	s
30	0,275			0,2	s
31	0,348			3,0	u
33	0,257			-0,5	s
35	0,2839			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%
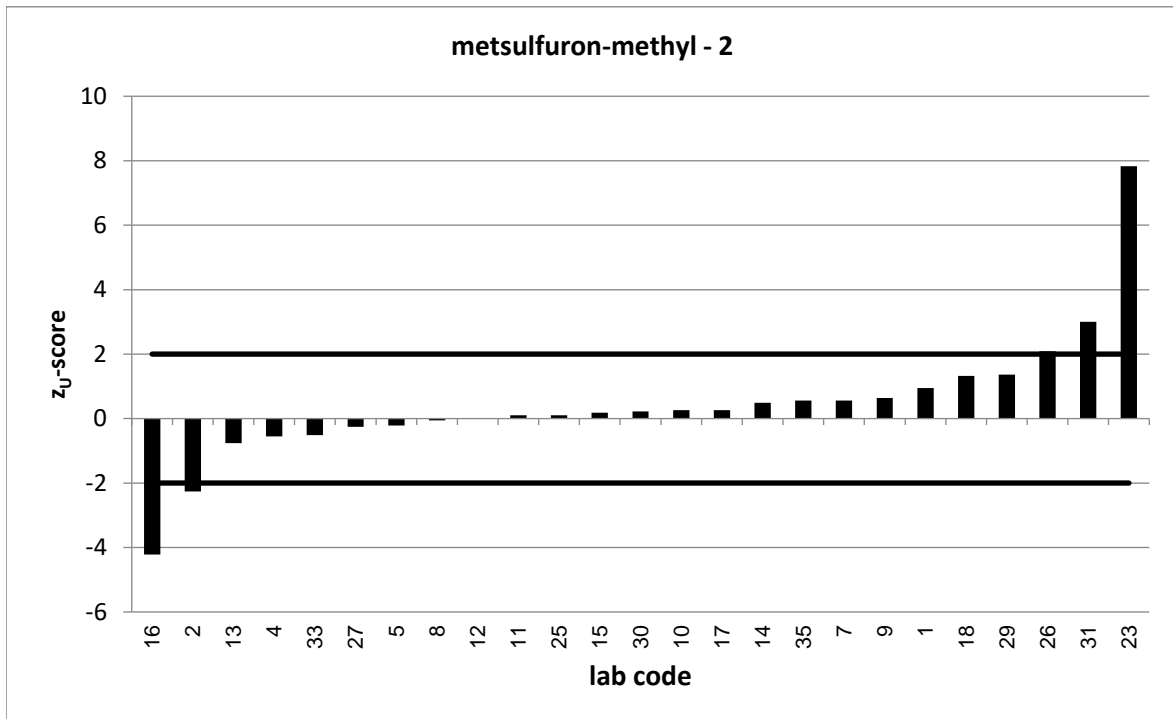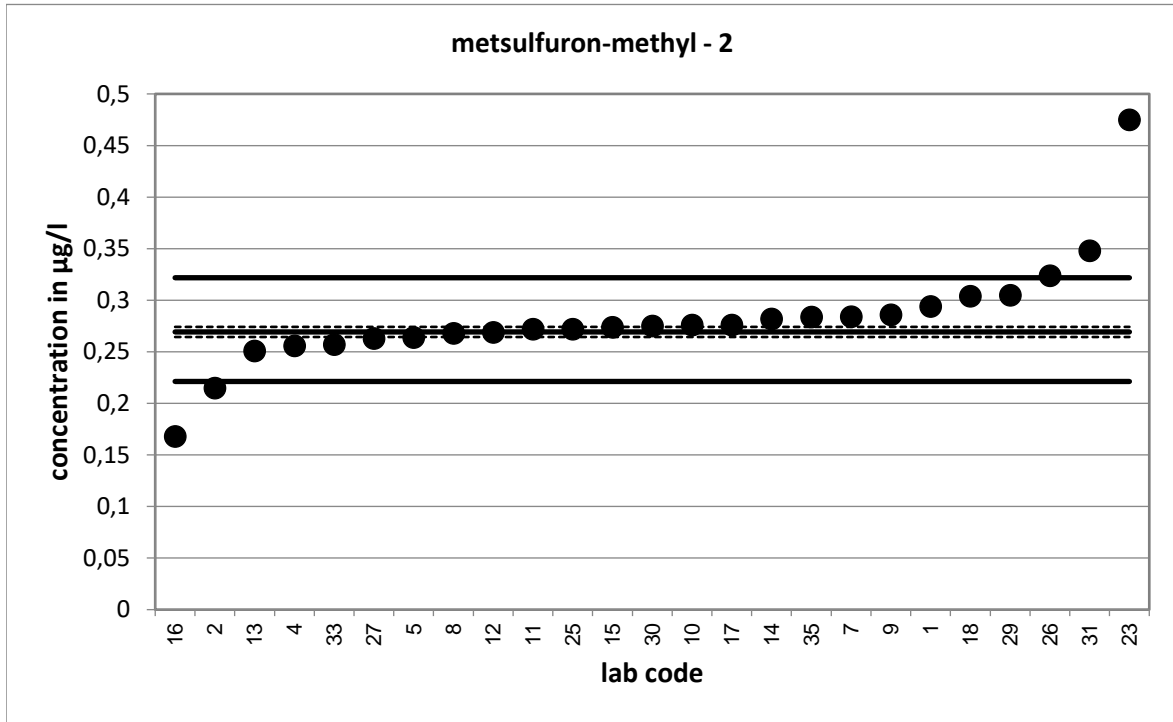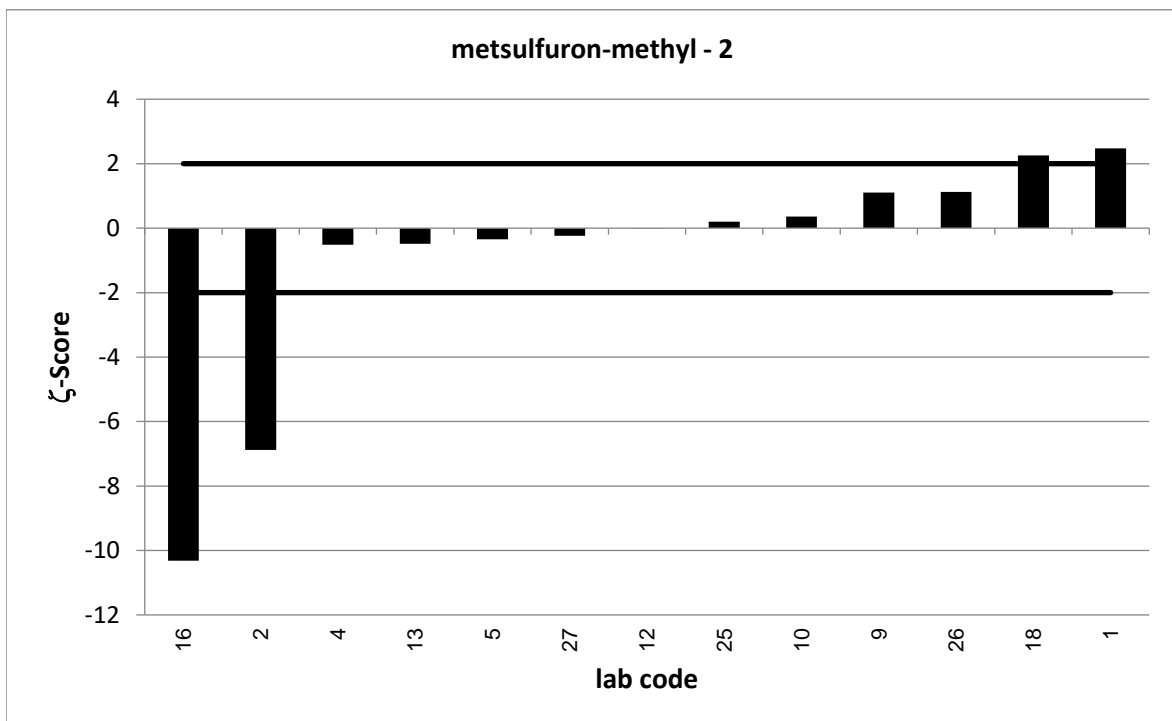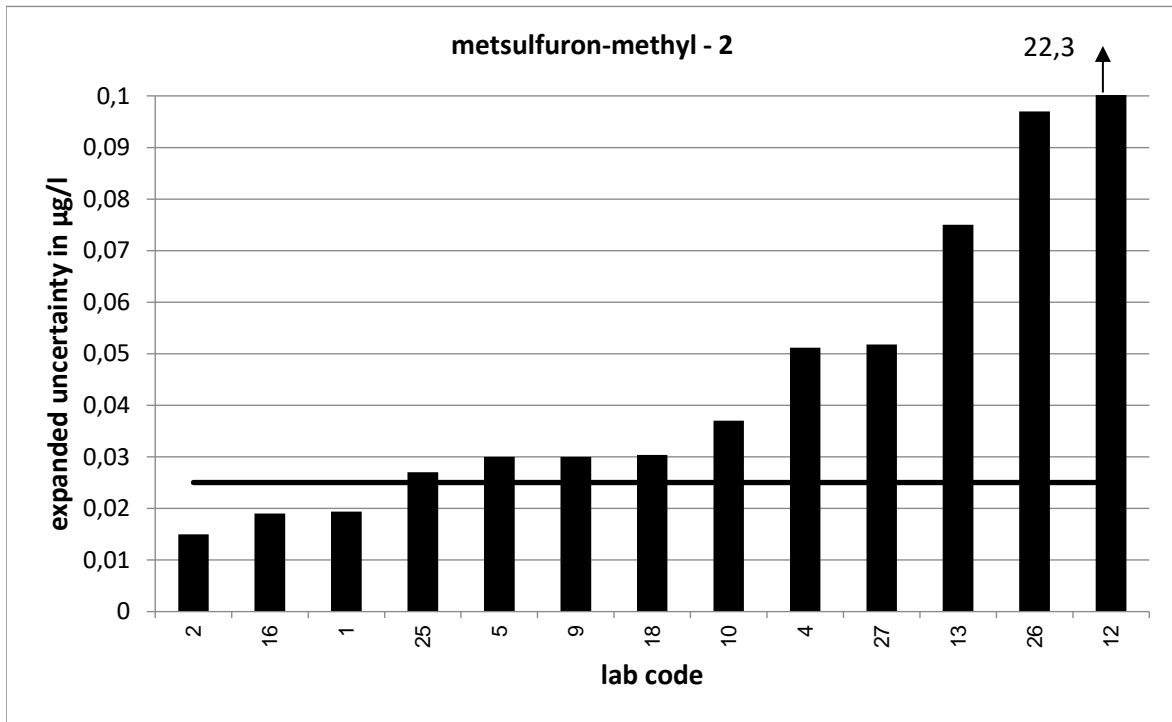** s = satisfactory, q = questionable, u = unsatisfactory

metsulfuron-methyl - 2

metsulfuron-methyl - 2

metsulfuron-methyl - 2

metsulfuron-methyl - 2

PT 3/18 - TW S5	metsulfuron-methyl - 3				
assigned value [µg/l]*		0,4039	± 0,0073		
upper tolerance limit [µg/l]		0,491			
lower tolerance limit [µg/l]		0,3252			
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
1	0,433	0,003	7,4	0,7	s
2	0,322	0,012	-11,7	-2,1	q
4	0,381	0,076	-0,6	-0,6	s
5	0,398	0,042	-0,3	-0,1	s
7	0,437			0,8	s
8	0,395			-0,2	s
9	0,398	0,05	-0,2	-0,1	s
10	0,416	0,055	0,4	0,3	s
11	0,384			-0,5	s
12	0,408	14,7	0,0	0,1	s
13	0,374	0,112	-0,5	-0,8	s
14	0,417			0,3	s
15	0,424			0,5	s
16	0,254	0,026	-11,1	-3,8	u
17	0,418			0,3	s
18	0,361	0,036	-2,3	-1,1	s
23	0,796			9,0	u
25	0,4	0,04	-0,2	-0,1	s
26	0,486	0,146	1,1	1,9	s
27	0,397	0,078	-0,2	-0,2	s
29	0,461			1,3	s
30	0,399			-0,1	s
31	0,512			2,5	q
33	0,375			-0,7	s
35	0,4015			-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%
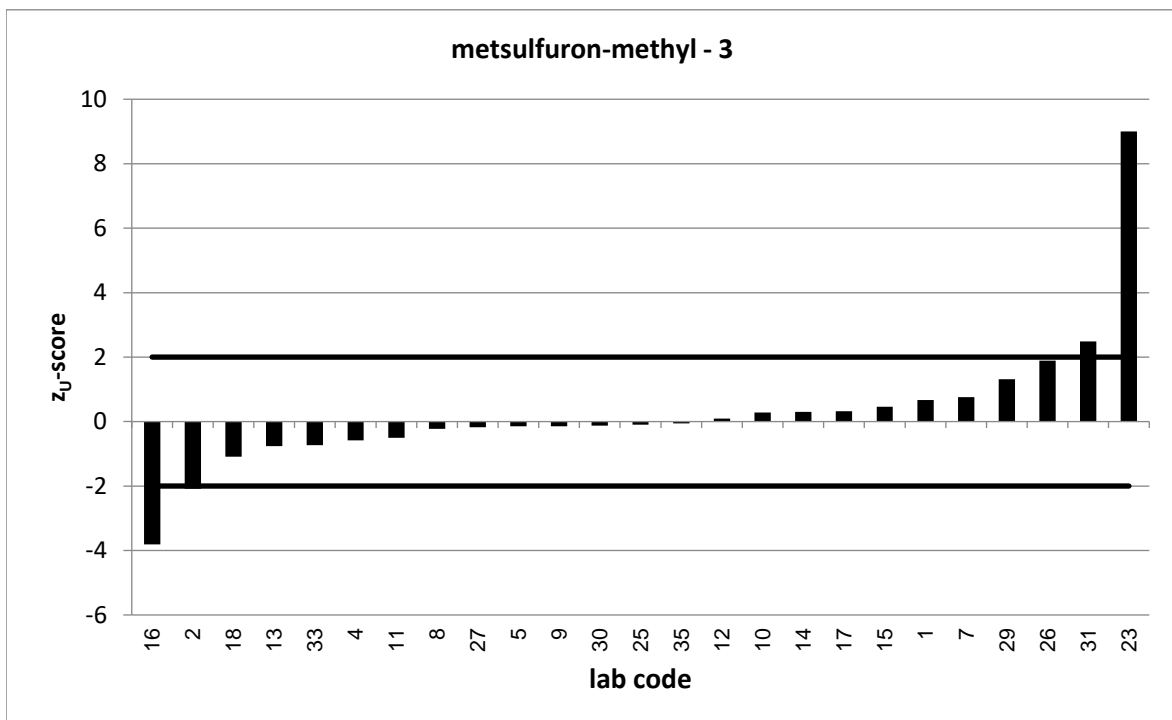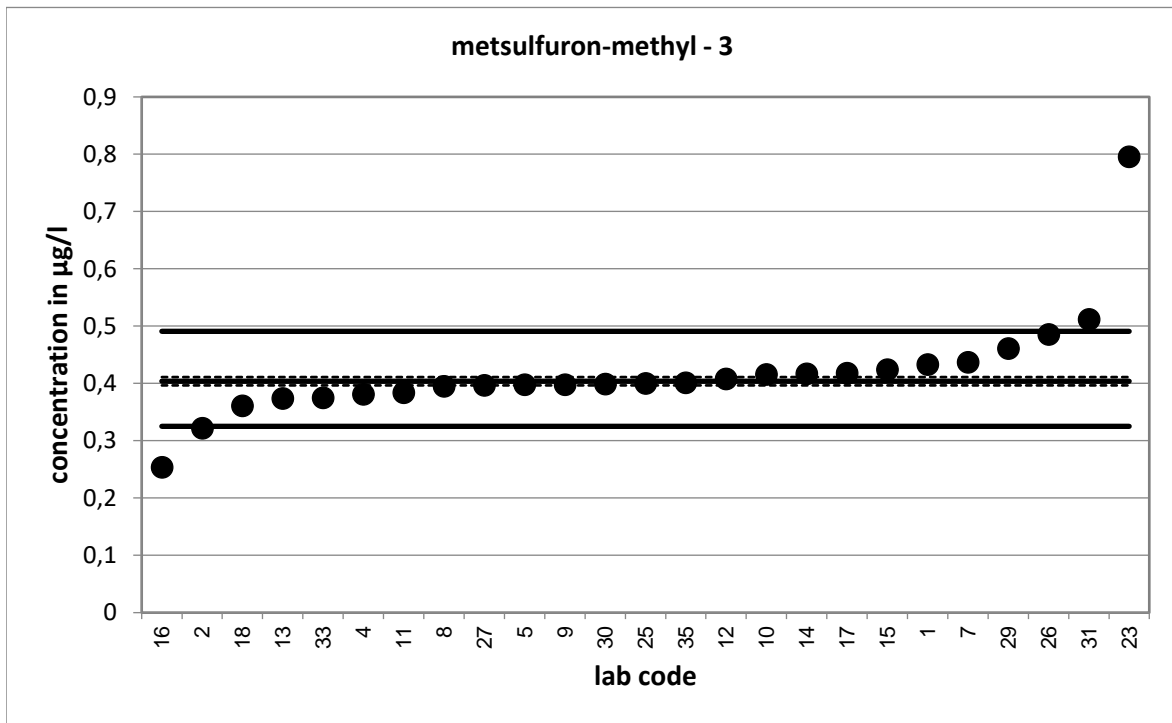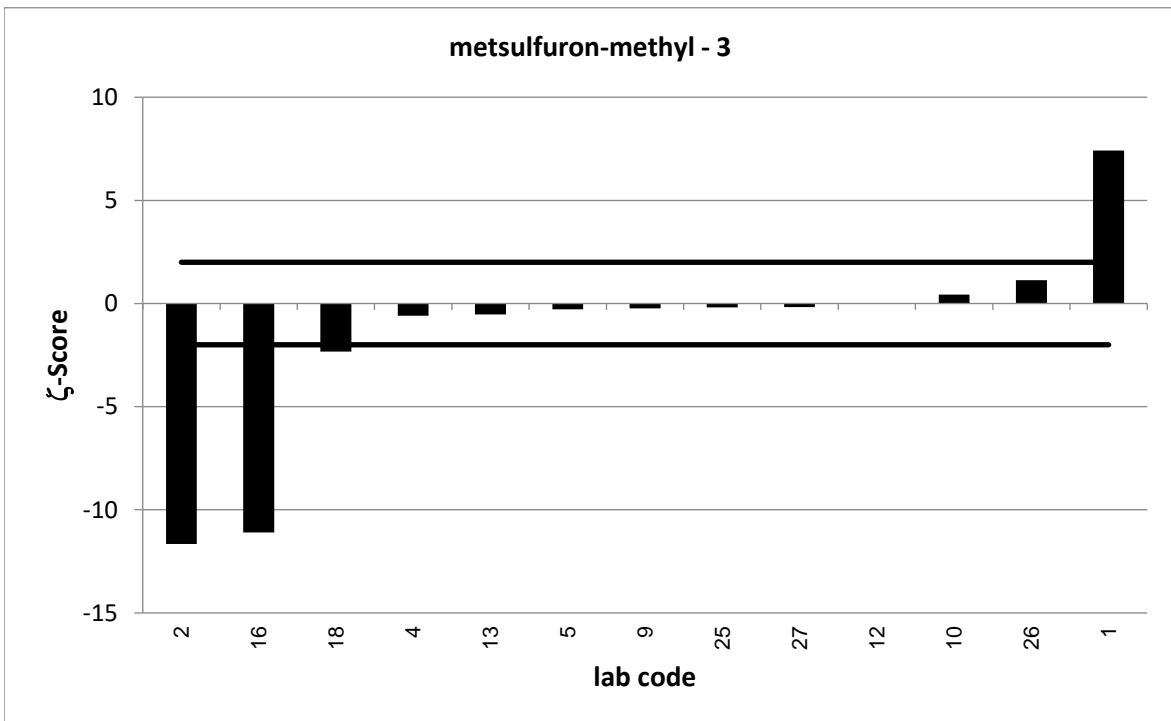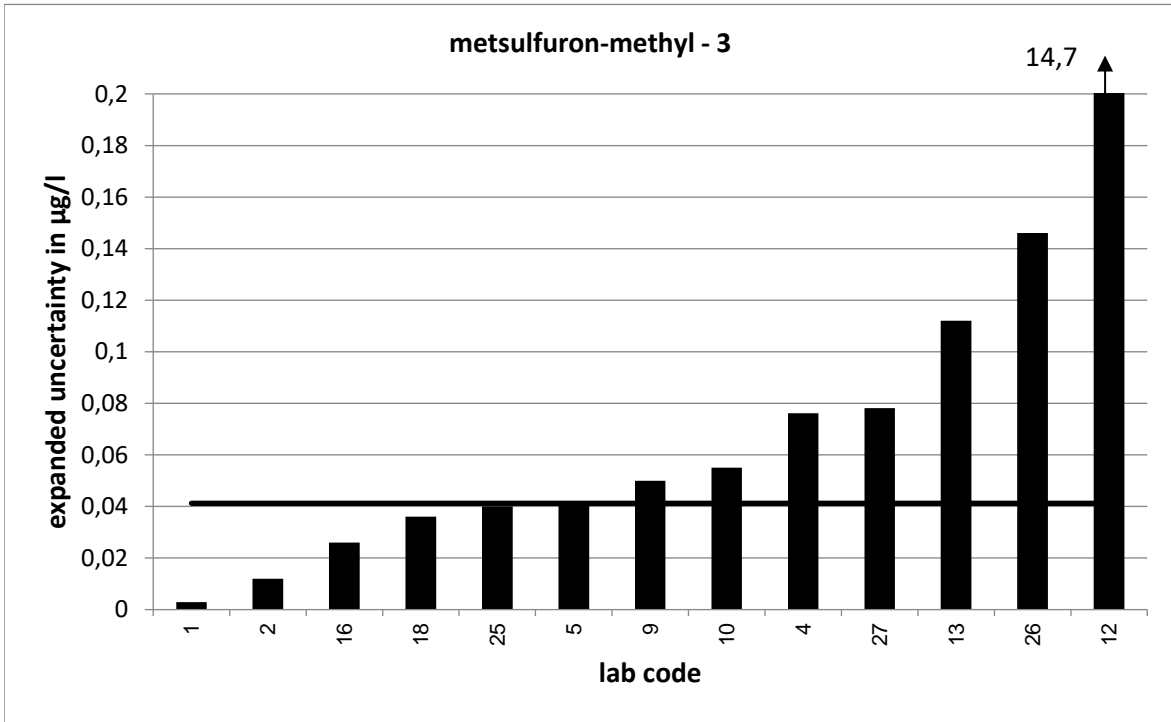** s = satisfactory, q = questionable, u = unsatisfactory

metsulfuron-methyl - 3

metsulfuron-methyl - 3

metsulfuron-methyl - 3

metsulfuron-methyl - 3

PT 3/18 - TW S5	rimsulfuron - 1				
assigned value [µg/l]*		0,07055	± 0,00124		
upper tolerance limit [µg/l]		0,09867			
lower tolerance limit [µg/l]		0,04688			
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
2	0,085	0,011	2,6	1,0	s
4	0,0754	0,015	0,6	0,3	s
5	0,086	0,009	3,4	1,1	s
7	0,075			0,3	s
8	0,063			-0,6	s
9	0,0516	0,009	-4,2	-1,6	s
10	0,0855			1,1	s
11	0,064			-0,6	s
12	0,061	32,8	0,0	-0,8	s
13	0,0808	0,024	0,8	0,7	s
14	0,081			0,7	s
15	0,0601			-0,9	s
16	0,047	0,009	-5,2	-2,0	s
17	0,0676			-0,2	s
18	0,0692	0,007	-0,4	-0,1	s
23	0,0064			-5,4	u
25	0,0713	0,007	0,2	0,1	s
26	0,0905	0,036	1,1	1,4	s
27	0,0781	0,03	0,5	0,5	s
29	0,088			1,2	s
33	0,086			1,1	s
35	0,0762			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%
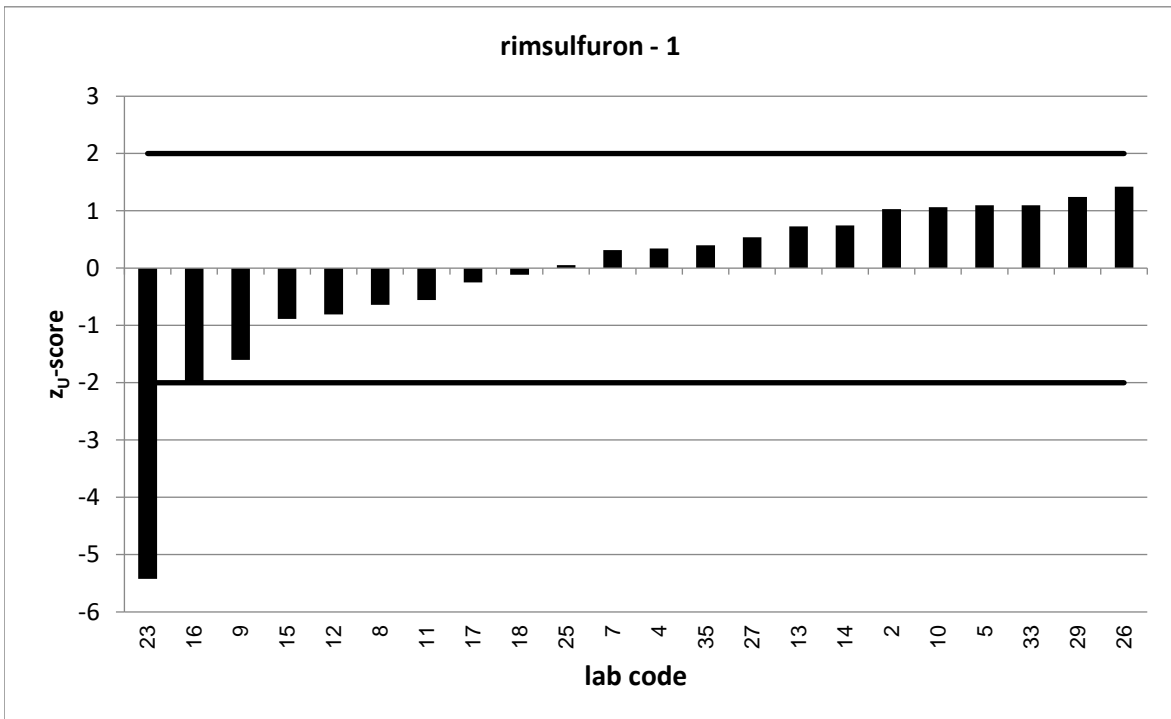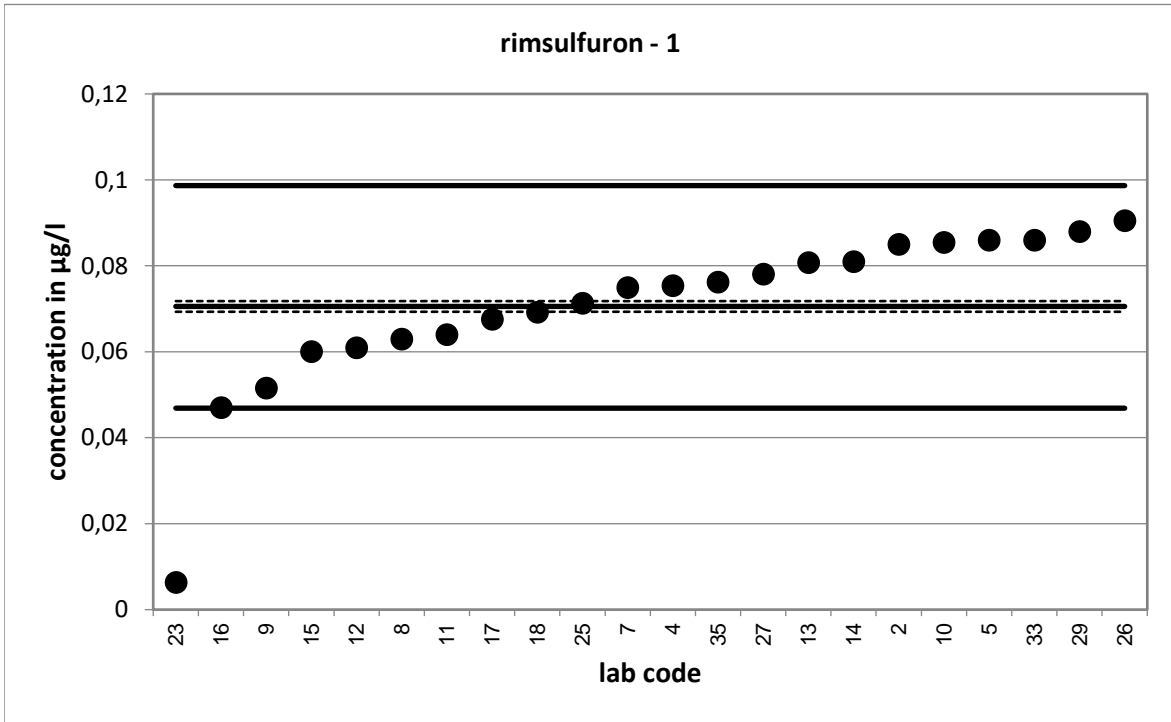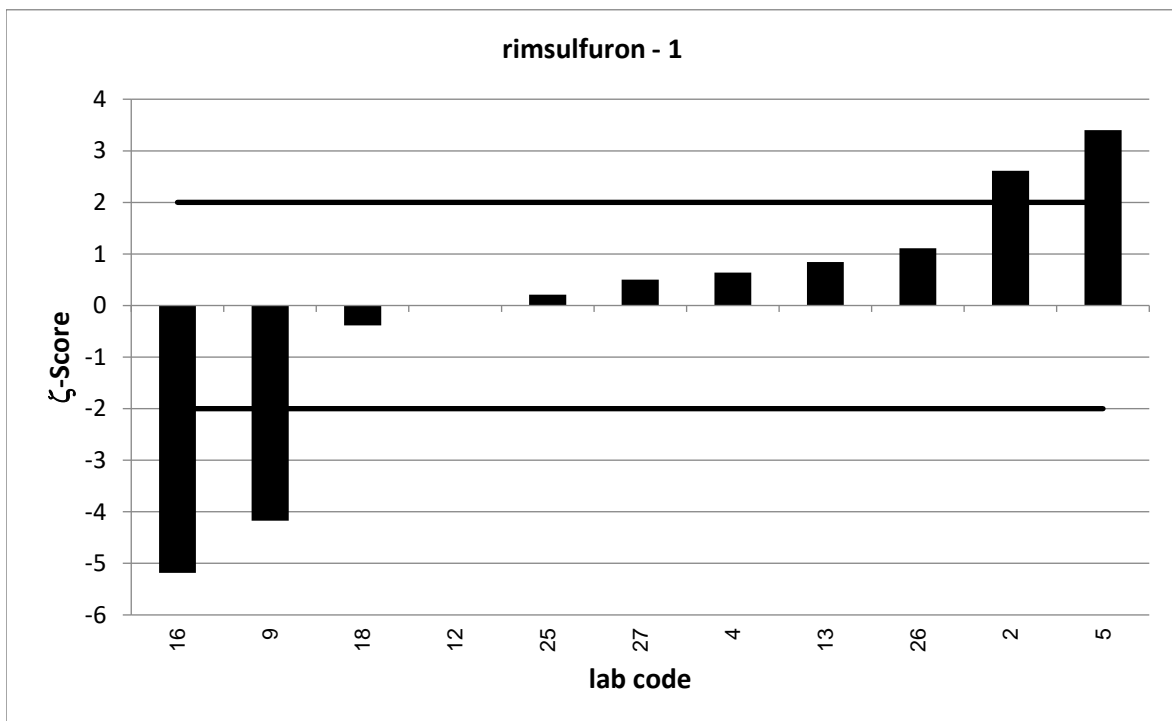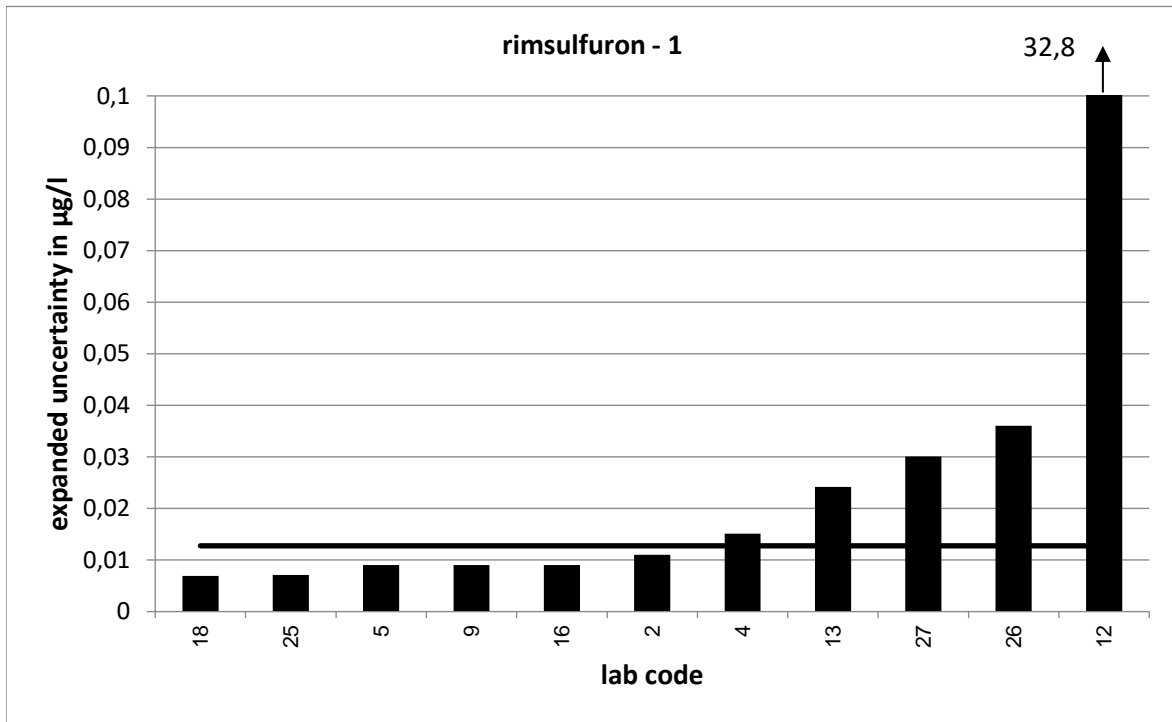** s = satisfactory, q = questionable, u = unsatisfactory

rimsulfuron - 1

rimsulfuron - 1

rimsulfuron - 1

32,8

rimsulfuron - 1

PT 3/18 - TW S5	rimsulfuron - 2				
assigned value [µg/l]*		0,1764	± 0,003		
upper tolerance limit [µg/l]		0,2488			
lower tolerance limit [µg/l]		0,1154			
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
2	0,199	0,022	2,0	0,6	s
4	0,197	0,039	1,0	0,6	s
5	0,216	0,023	3,4	1,1	s
7	0,18			0,1	s
8	0,166			-0,3	s
9	0,137	0,018	-4,3	-1,3	s
10	0,22			1,2	s
11	0,171			-0,2	s
12	0,159	12,6	0,0	-0,6	s
13	0,219	0,066	1,3	1,2	s
14	0,212			1,0	s
15	0,161			-0,5	s
16	0,136	0,032	-2,5	-1,3	s
17	0,173			-0,1	s
18	0,176	0,018	0,0	0,0	s
23	0,231			1,5	s
25	0,182	0,018	0,6	0,2	s
26	0,236	0,094	1,3	1,6	s
27	0,202	0,078	0,7	0,7	s
29	0,206			0,8	s
33	0,212			1,0	s
35	0,1952			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%
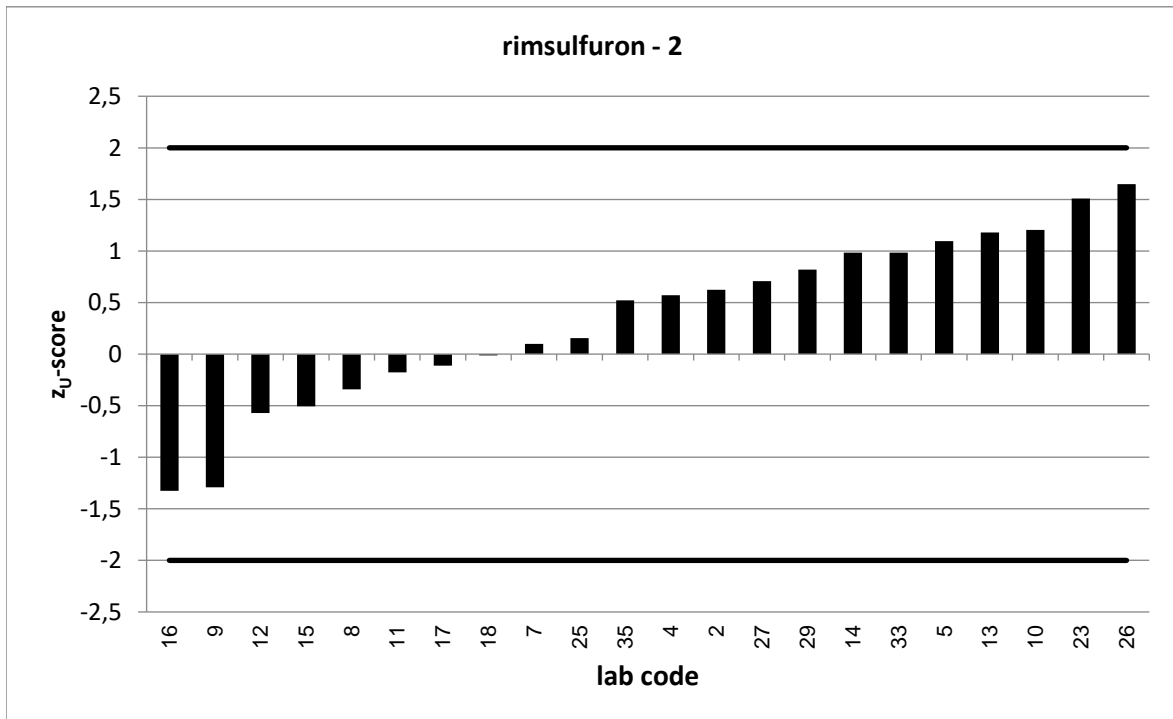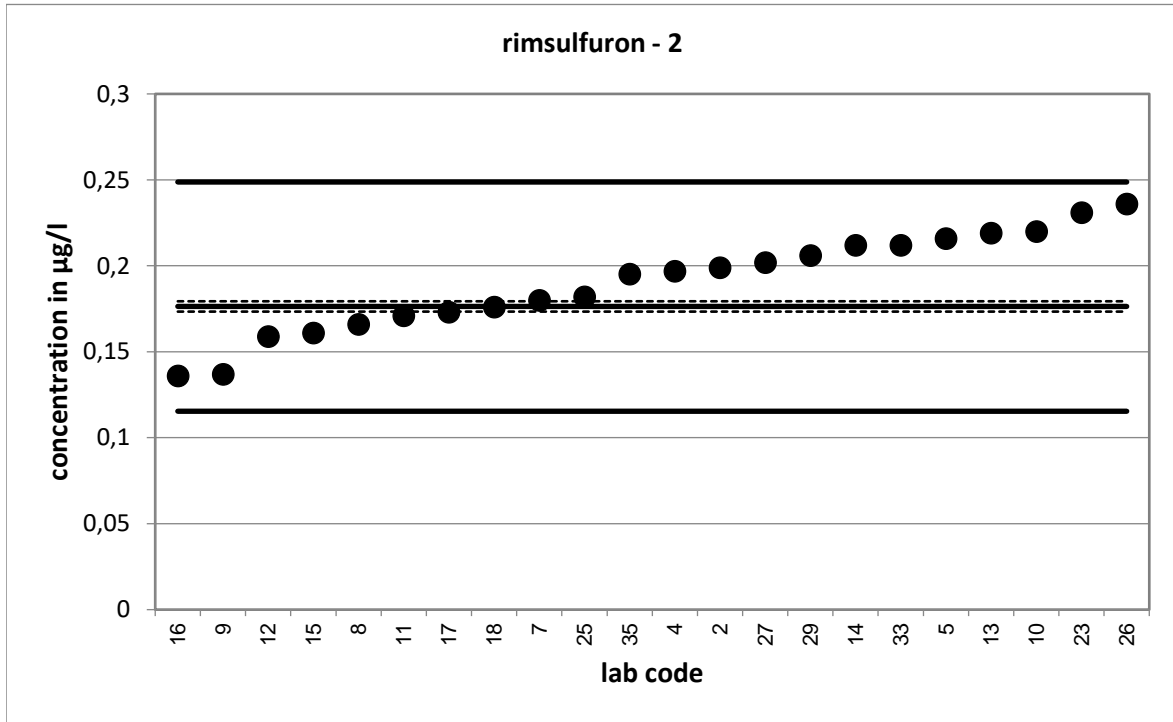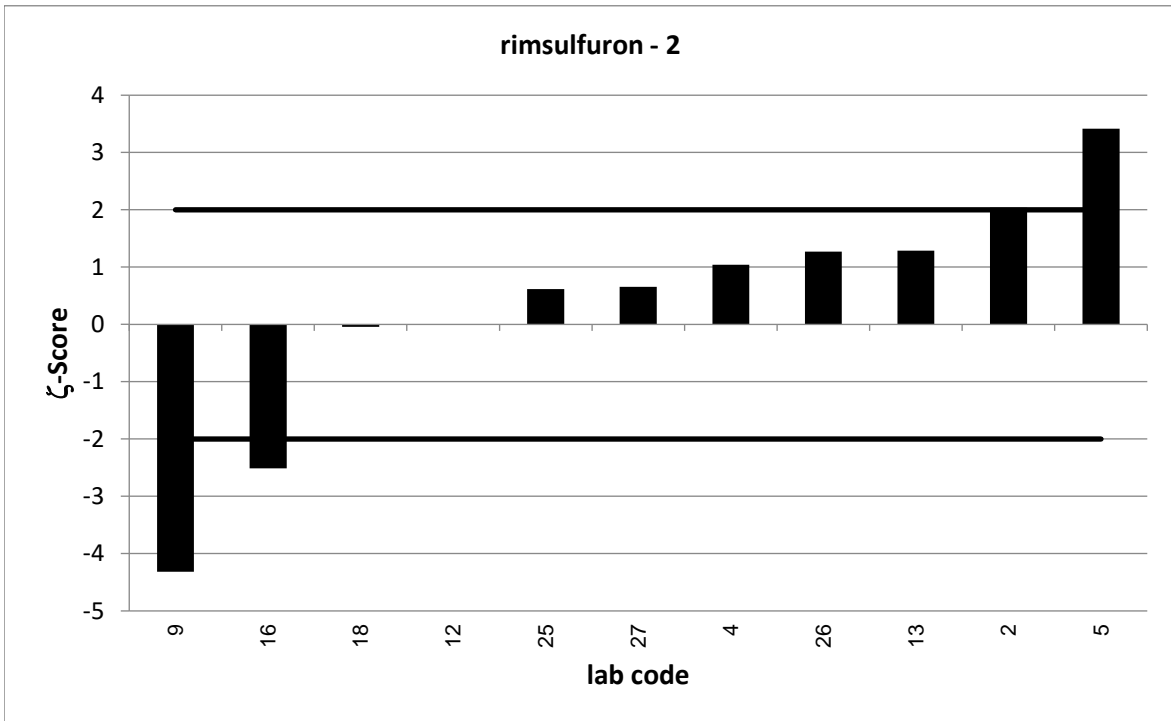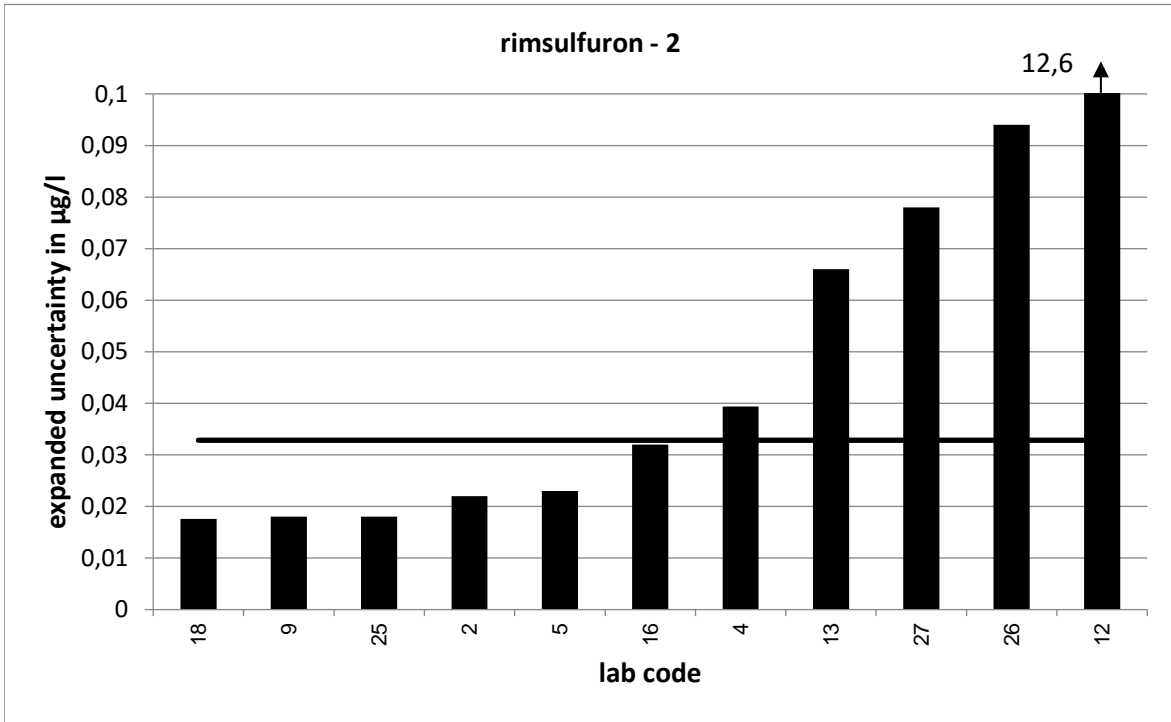** s = satisfactory, q = questionable, u = unsatisfactory

rimsulfuron - 2

rimsulfuron - 2

rimsulfuron - 2

rimsulfuron - 2

PT 3/18 - TW S5	rimsulfuron - 3				
assigned value [µg/l]*		0,3175	± 0,0054		
upper tolerance limit [µg/l]		0,4454			
lower tolerance limit [µg/l]		0,2103			
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
2	0,314	0,046	-0,2	-0,1	s
4	0,352	0,07	1,0	0,5	s
5	0,399	0,018	8,7	1,3	s
7	0,328			0,2	s
8	0,295			-0,4	s
9	0,251	0,012	-10,1	-1,2	s
10	0,397			1,2	s
11	0,3			-0,3	s
12	0,283	14,1	0,0	-0,6	s
13	0,39	0,117	1,2	1,1	s
14	0,37			0,8	s
15	0,289			-0,5	s
16	0,203	0,039	-5,8	-2,1	q
17	0,302			-0,3	s
18	0,315	0,003	-0,8	0,0	s
23	0,271			-0,9	s
25	0,323	0,032	0,3	0,1	s
26	0,358	0,143	0,6	0,6	s
27	0,354	0,137	0,5	0,6	s
29	0,363			0,7	s
33	0,357			0,6	s
35	0,3416			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%
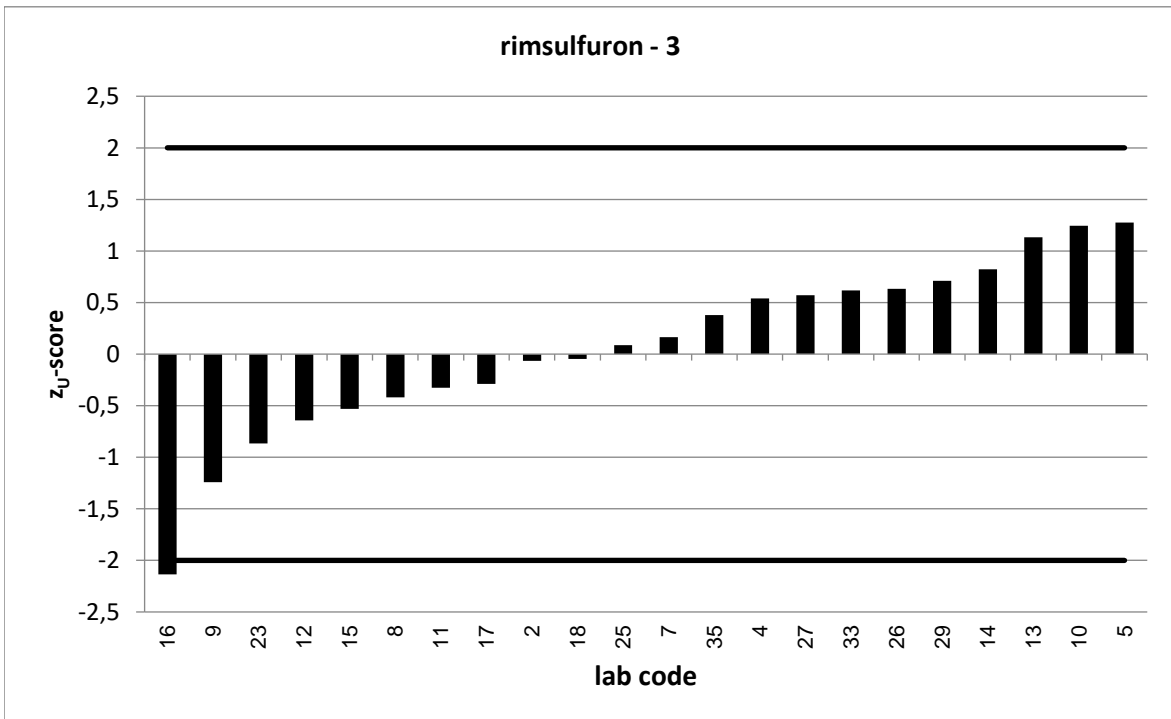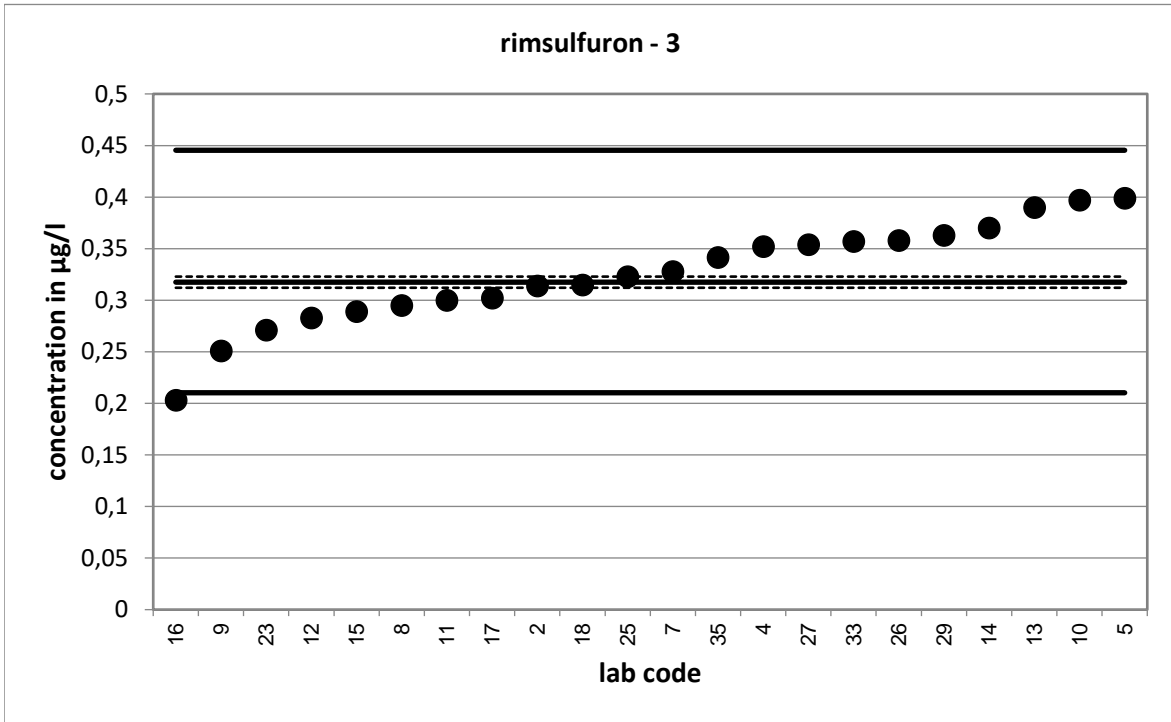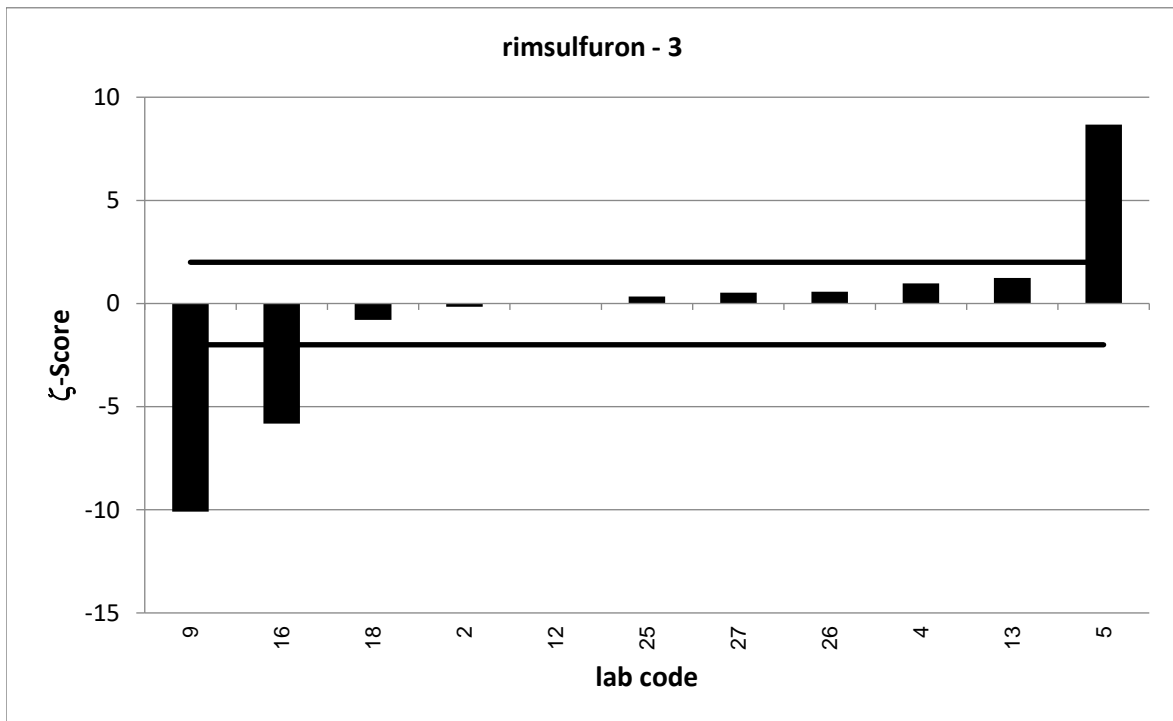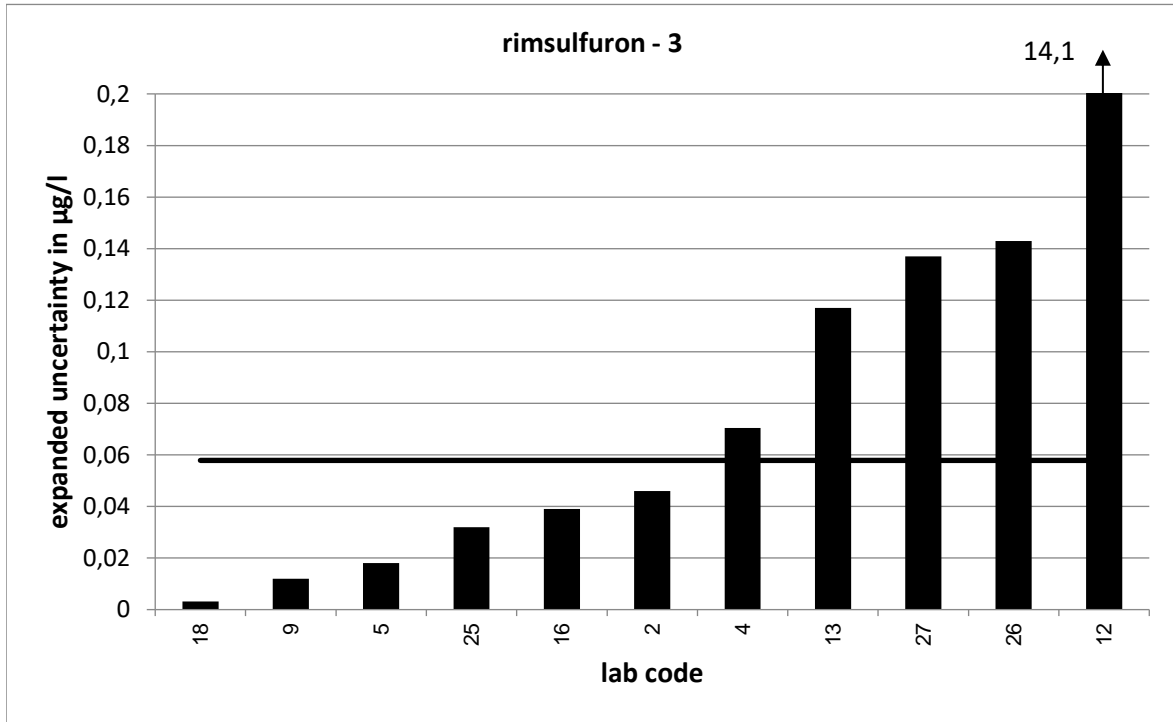** s = satisfactory, q = questionable, u = unsatisfactory

rimsulfuron - 3

rimsulfuron - 3

rimsulfuron - 3

rimsulfuron - 3

PT 3/18 - TW S5	thifensulfuron-methyl - 1				
assigned value [µg/l]*		0,07924	± 0,00227		
upper tolerance limit [µg/l]		0,1071			
lower tolerance limit [µg/l]		0,05543			
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
1	0,087	0,005	3,1	0,6	s
2	0,064	0,007	-4,1	-1,3	s
4	0,0728	0,015	-0,9	-0,5	s
5	0,078	0,008	-0,3	-0,1	s
7	0,084			0,3	s
8	0,081			0,1	s
9	0,0797	0,018	0,1	0,0	s
10	0,0984			1,4	s
11	0,077			-0,2	s
12	0,072	27,8	0,0	-0,6	s
13	0,0756	0,023	-0,3	-0,3	s
14	0,083			0,3	s
15	0,0697			-0,8	s
16	0,05	0,006	-9,1	-2,5	q
17	0,0842			0,4	s
18	0,0845	0,008	1,2	0,4	s
23	0,127			3,4	u
25	0,0745	0,008	-1,2	-0,4	s
26	0,103	0,031	1,5	1,7	s
27	0,0755	0,015	-0,5	-0,3	s
29	0,095			1,1	s
31	0,176			6,9	u
33	0,076			-0,3	s
35	0,0896			0,7	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%
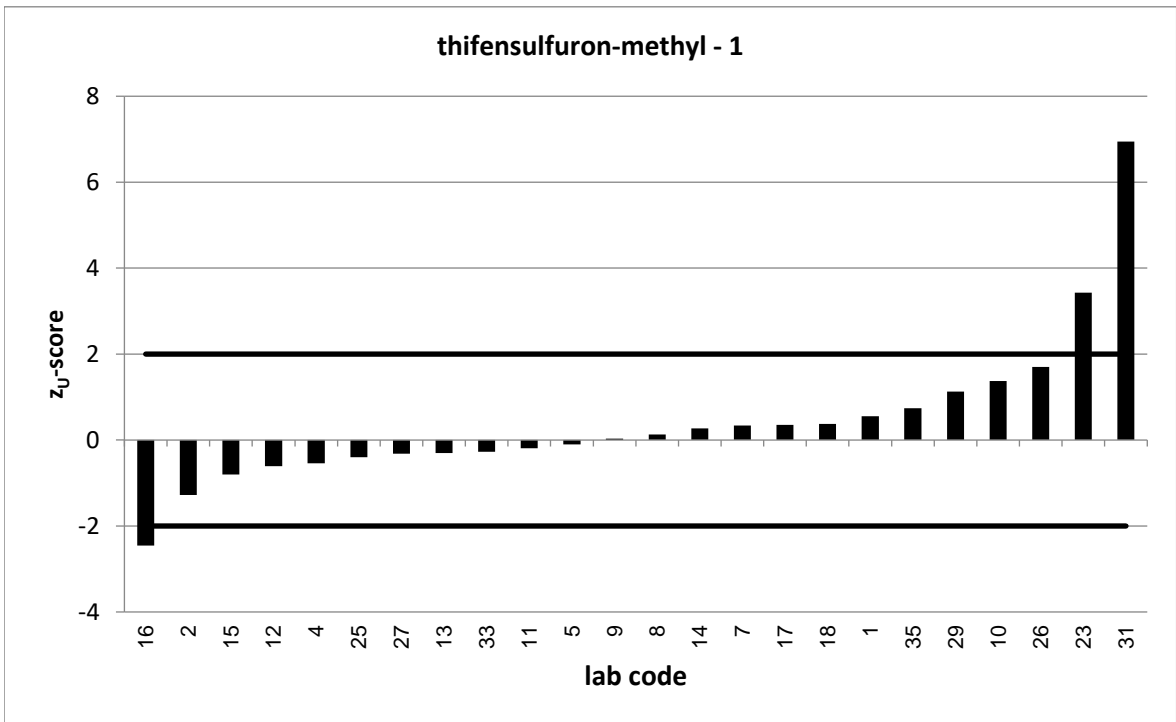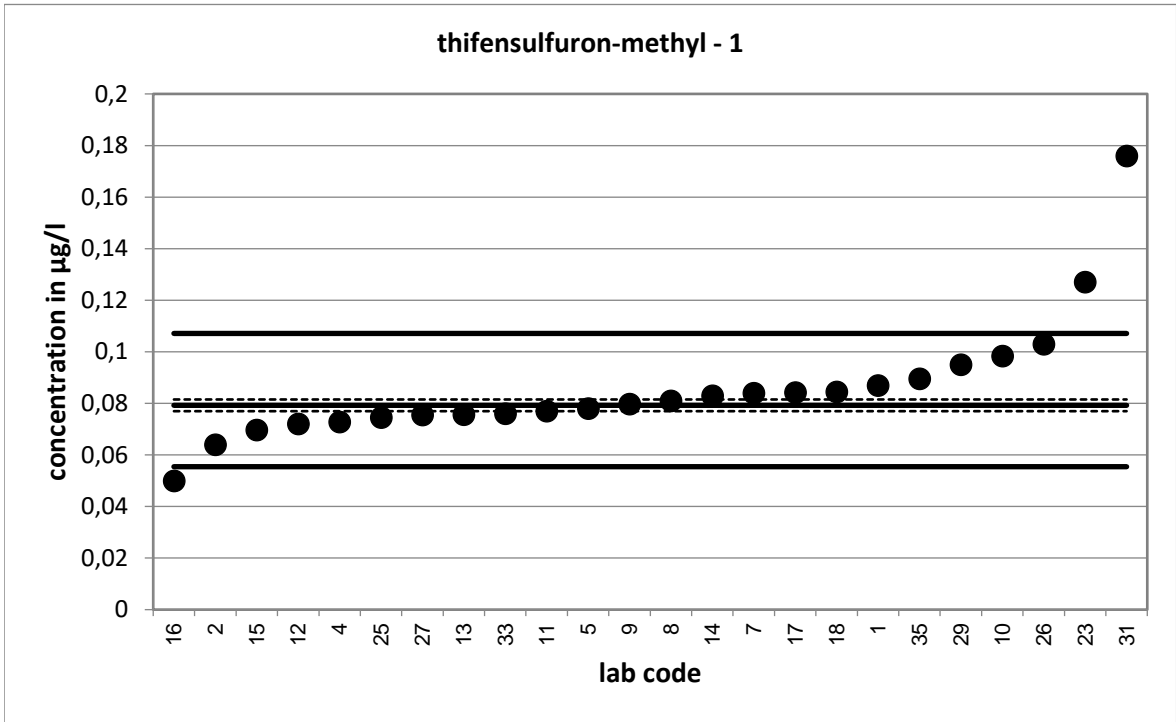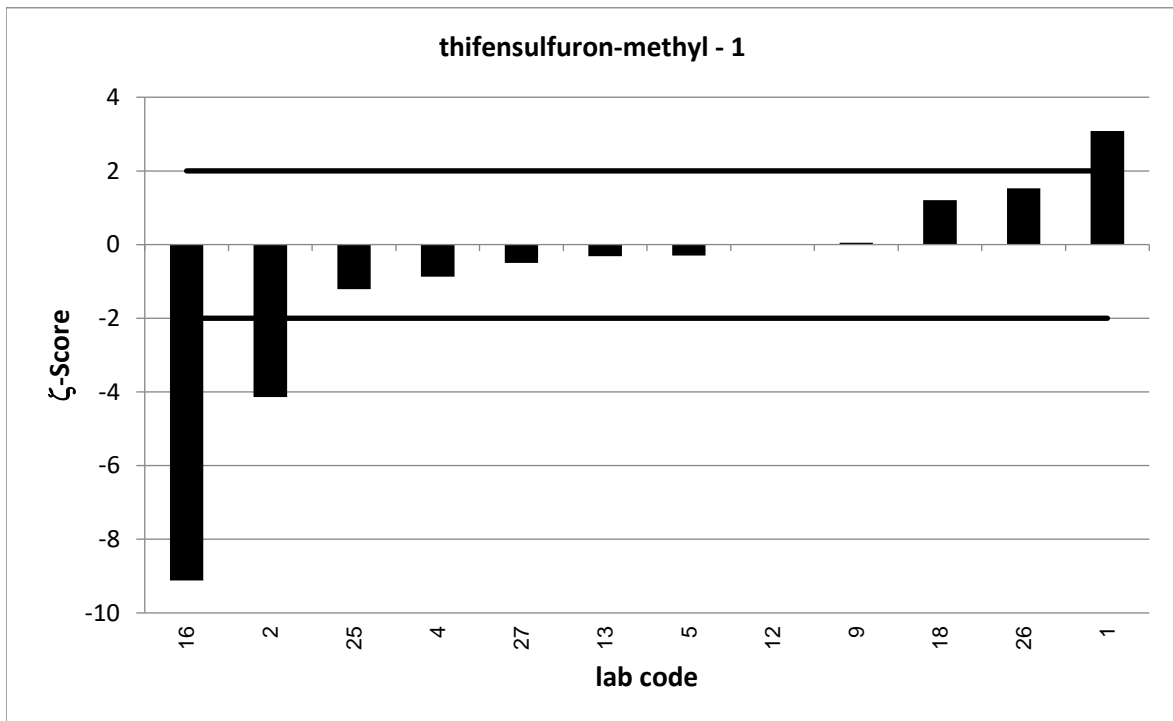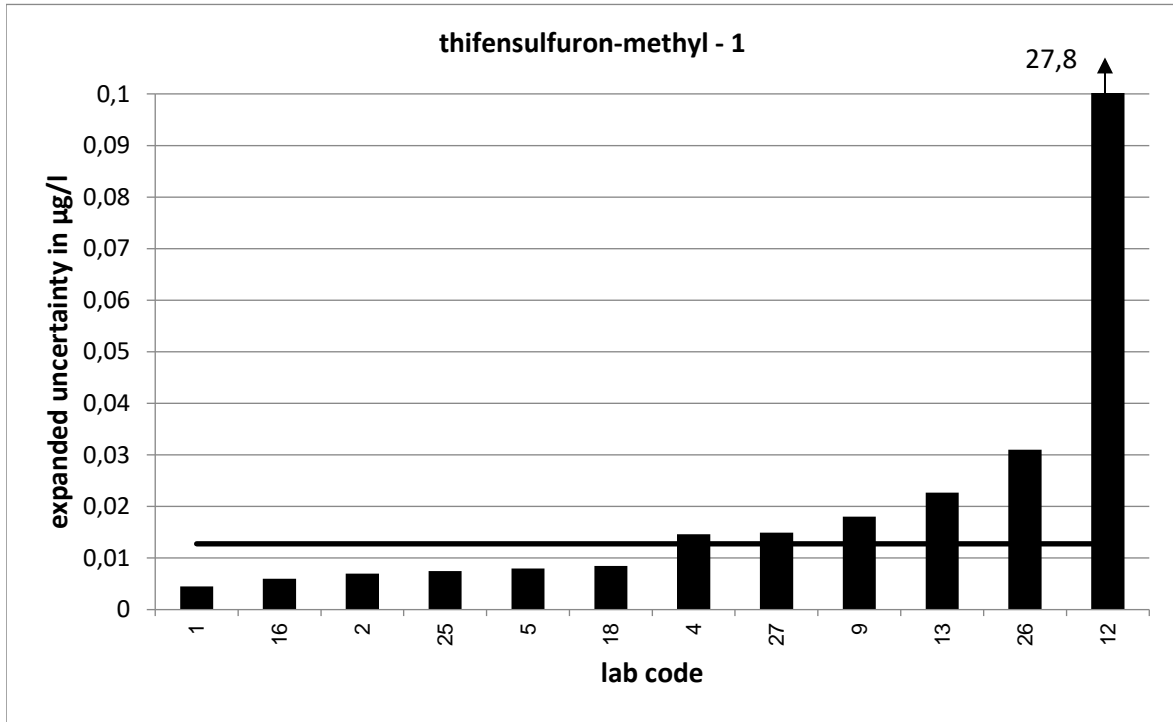** s = satisfactory, q = questionable, u = unsatisfactory

thifensulfuron-methyl - 1

thifensulfuron-methyl - 1

thifensulfuron-methyl - 1

expanded uncertainty in µg/l vs lab code: 1, 16, 2, 25, 5, 18, 4, 27, 9, 13, 26, 12 (27,8)

thifensulfuron-methyl - 1

ζ-Score vs lab code: 16, 2, 25, 4, 27, 13, 5, 12, 9, 18, 26, 1

PT 3/18 - TW S5	thifensulfuron-methyl - 2				
assigned value [µg/l]*		0,1585	± 0,0036		
upper tolerance limit [µg/l]		0,2171			
lower tolerance limit [µg/l]		0,1089			
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
1	0,174	0,002	7,6	0,5	s
2	0,123	0,011	-6,1	-1,4	s
4	0,146	0,029	-0,8	-0,5	s
5	0,154	0,013	-0,7	-0,2	s
7	0,172			0,5	s
8	0,159			0,0	s
9	0,164	0,018	0,6	0,2	s
10	0,202			1,5	s
11	0,158			0,0	s
12	0,147	27,2	0,0	-0,5	s
13	0,148	0,044	-0,5	-0,4	s
14	0,169			0,4	s
15	0,143			-0,6	s
16	0,099	0,012	-9,5	-2,4	q
17	0,168			0,3	s
18	0,182	0,018	2,5	0,8	s
23	0,259			3,4	u
25	0,148	0,015	-1,4	-0,4	s
26	0,225	0,068	2,0	2,3	q
27	0,153	0,03	-0,4	-0,2	s
29	0,183			0,8	s
30	0,079			-3,2	u
30	0,16			0,1	s
31	0,368			7,2	u
33	0,151			-0,3	s
35	0,168			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%
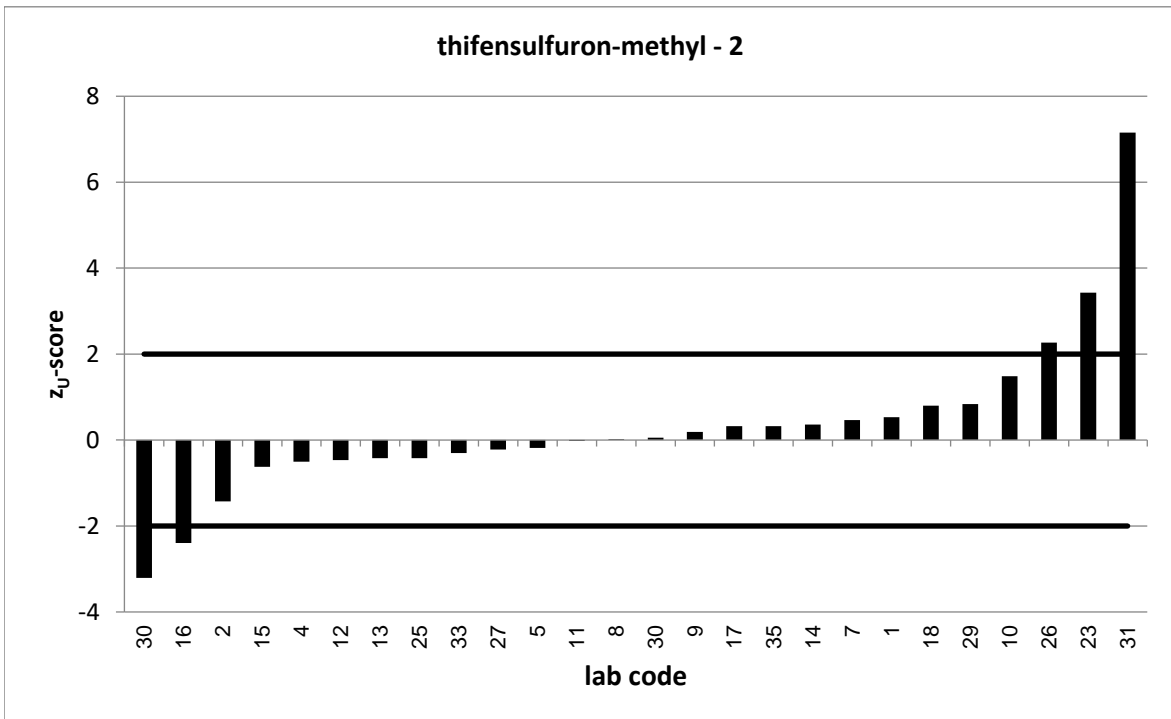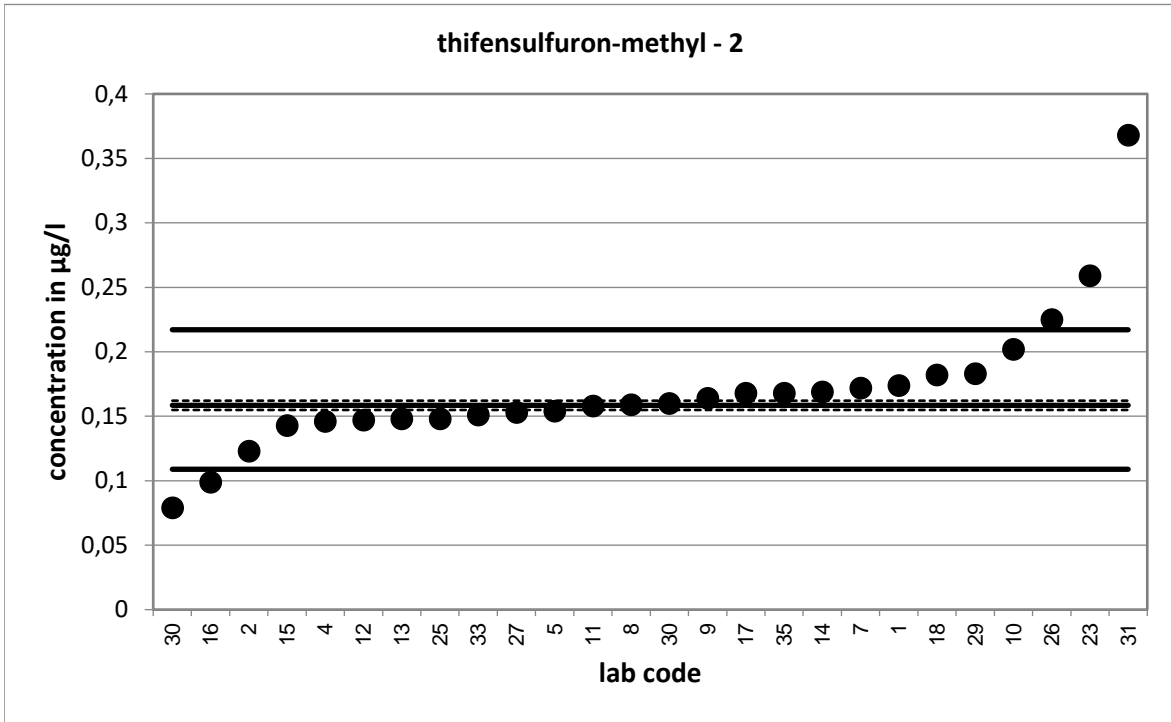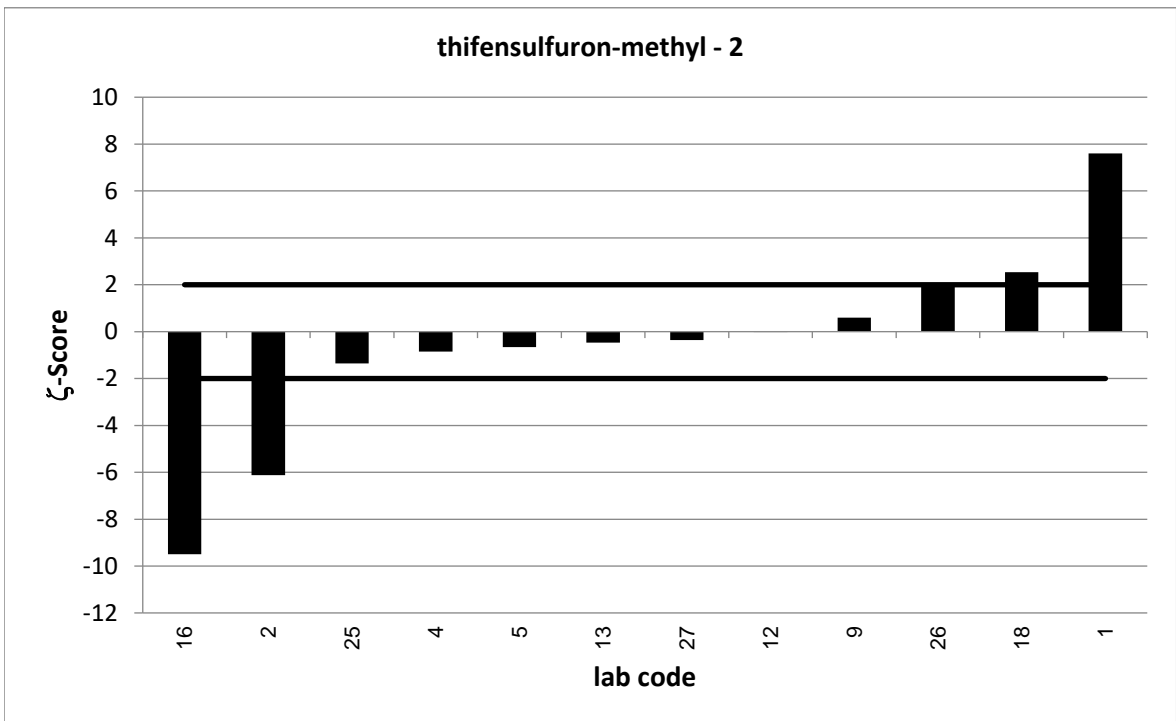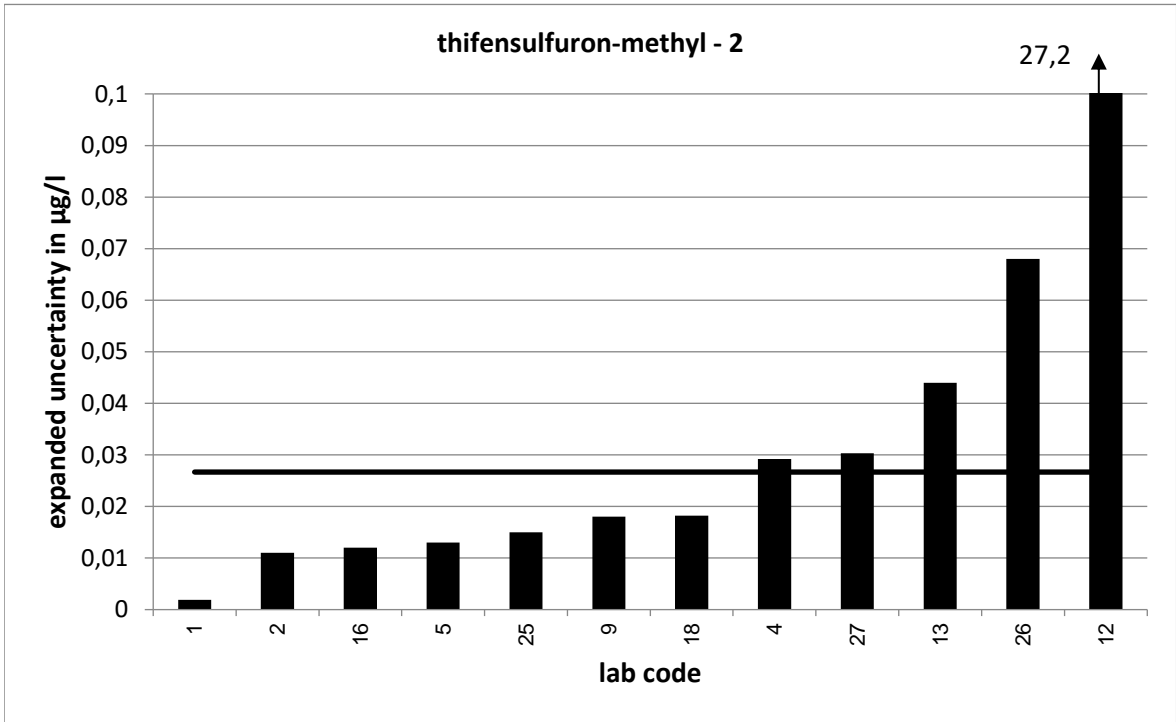** s = satisfactory, q = questionable, u = unsatisfactory

thifensulfuron-methyl - 2

thifensulfuron-methyl - 2

thifensulfuron-methyl - 2

thifensulfuron-methyl - 2

PT 3/18 - TW S5	thifensulfuron-methyl - 3				
assigned value [µg/l]*		0,3566	± 0,0075		
upper tolerance limit [µg/l]		0,4517			
lower tolerance limit [µg/l]		0,2726			
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
1	0,375	0,004	4,4	0,4	s
2	0,26	0,02	-9,0	-2,3	q
4	0,339	0,068	-0,5	-0,4	s
5	0,345	0,012	-1,6	-0,3	s
7	0,373			0,3	s
8	0,364			0,2	s
9	0,366	0,04	0,5	0,2	s
10	0,448			1,9	s
11	0,338			-0,4	s
12	0,317	18,9	0,0	-0,9	s
13	0,326	0,098	-0,6	-0,7	s
14	0,381			0,5	s
15	0,343			-0,3	s
16	0,206	0,015	-18,0	-3,6	u
17	0,364			0,2	s
18	0,368	0,037	0,6	0,2	s
23	0,699			7,2	u
25	0,337	0,034	-1,1	-0,5	s
26	0,434	0,13	1,2	1,6	s
27	0,346	0,069	-0,3	-0,3	s
29	0,5			3,0	u
30	0,384			0,6	s
31	0,835			10,1	u
33	0,355			0,0	s
35	0,335			-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%
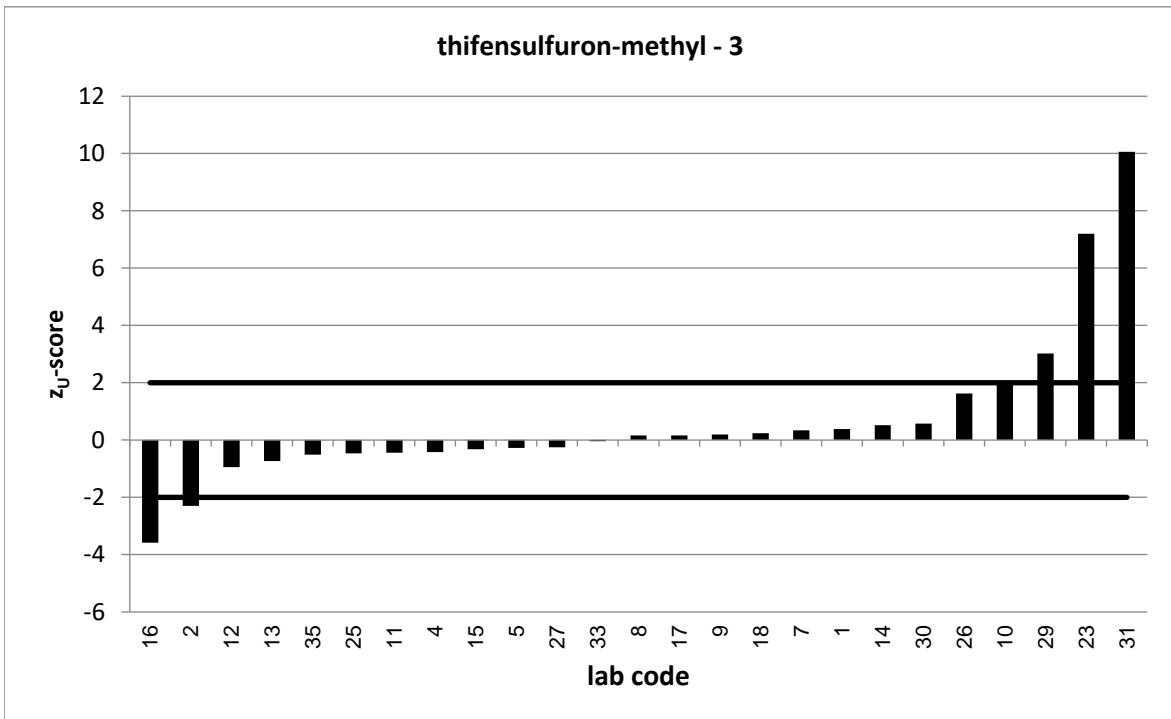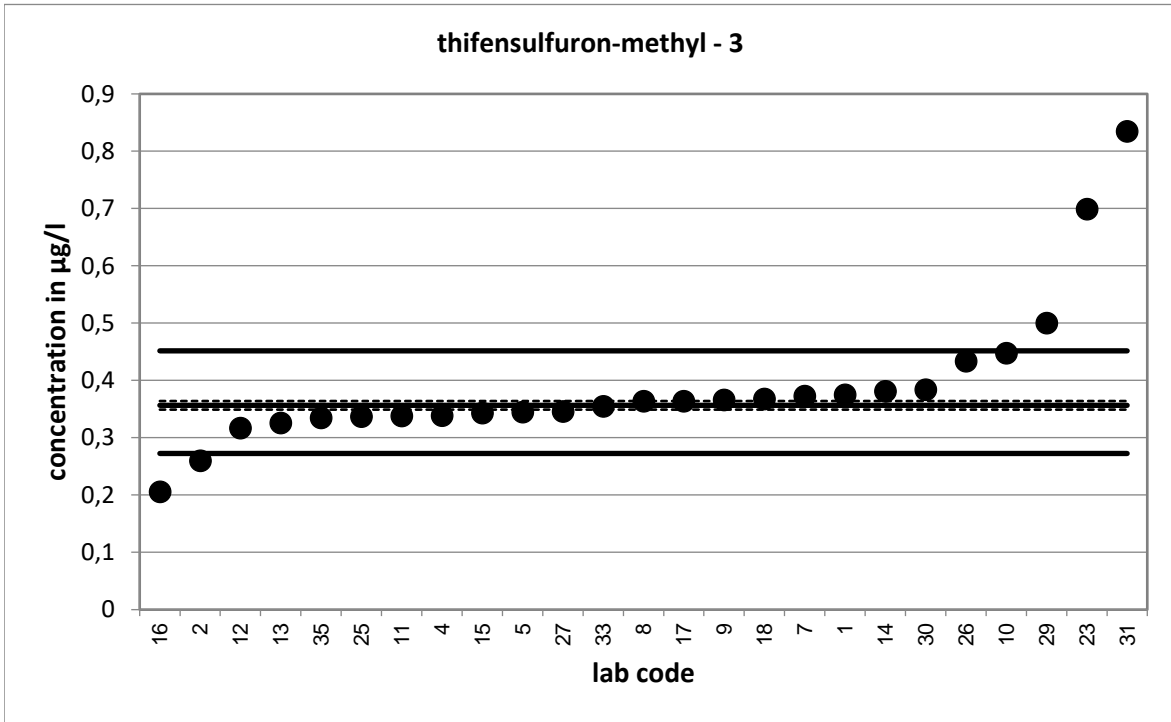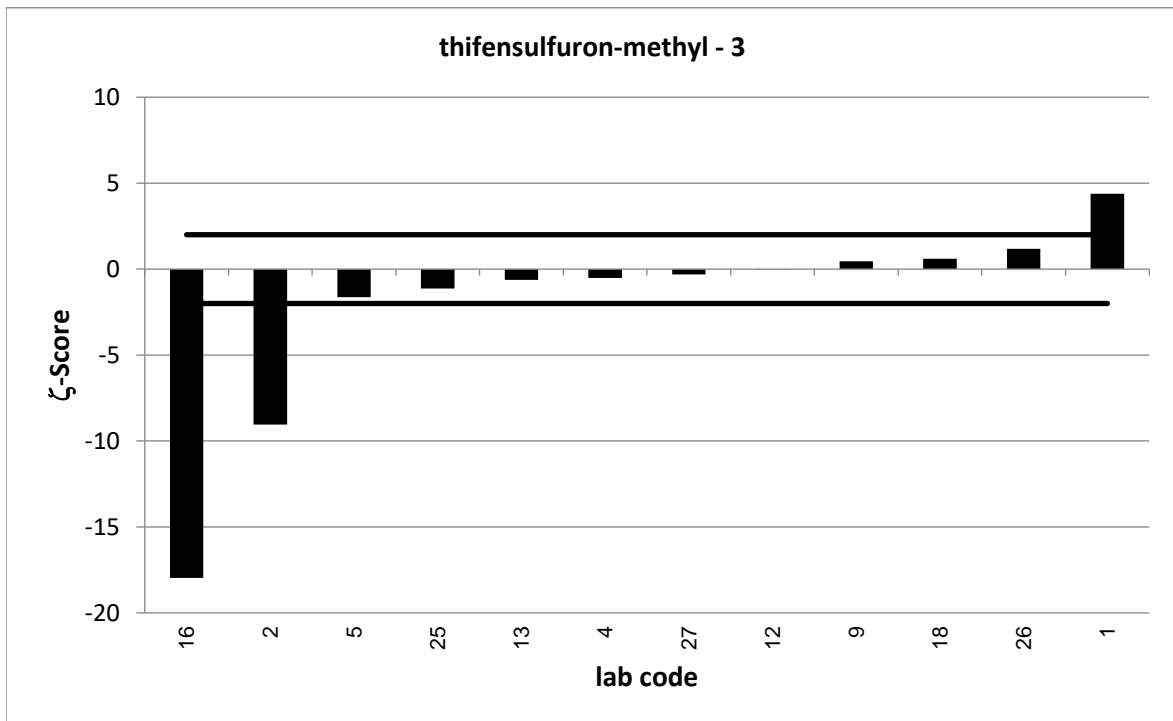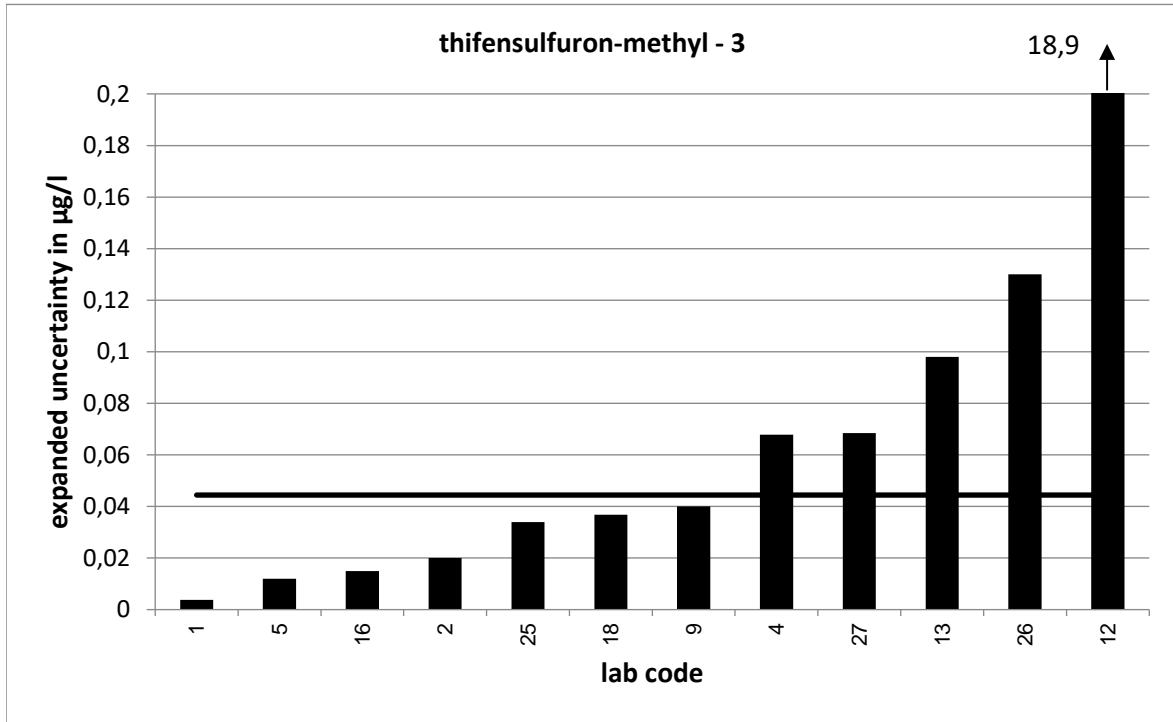** s = satisfactory, q = questionable, u = unsatisfactory

thifensulfuron-methyl - 3

thifensulfuron-methyl - 3

thifensulfuron-methyl - 3

thifensulfuron-methyl - 3

PT 3/18 - TW S5	triasulfuron - 1				
assigned value [µg/l]*		0,09641	± 0,00281		
upper tolerance limit [µg/l]		0,1137			
lower tolerance limit [µg/l]		0,08053			
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
1	0,105	0,009	1,8	1,0	s
2	0,087	0,014	-1,3	-1,2	s
4	0,0993	0,02	0,3	0,3	s
5	0,097	0,008	0,1	0,1	s
8	0,097			0,1	s
9	0,0968	0,003	0,2	0,0	s
10	0,118			2,5	q
11	0,096			-0,1	s
12	0,099	20,2	0,0	0,3	s
13	0,0919	0,028	-0,3	-0,6	s
14	0,101			0,5	s
15	0,0859			-1,3	s
16	0,09	0,009	-1,4	-0,8	s
17	0,0959			-0,1	s
18	0,109	0,011	2,2	1,5	s
23	0,176			9,2	u
25	0,0963	0,01	0,0	0,0	s
27	0,0912	0,018	-0,6	-0,7	s
29	0,134			4,3	u
33	0,099			0,3	s
35	0,0957			-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%
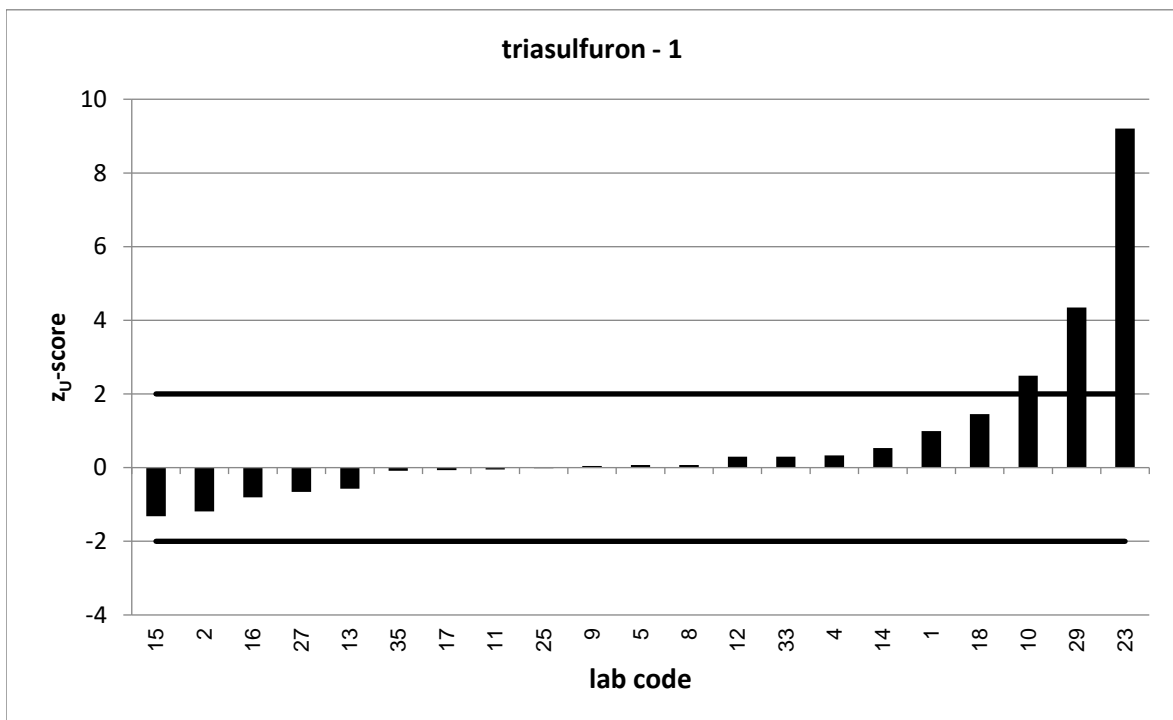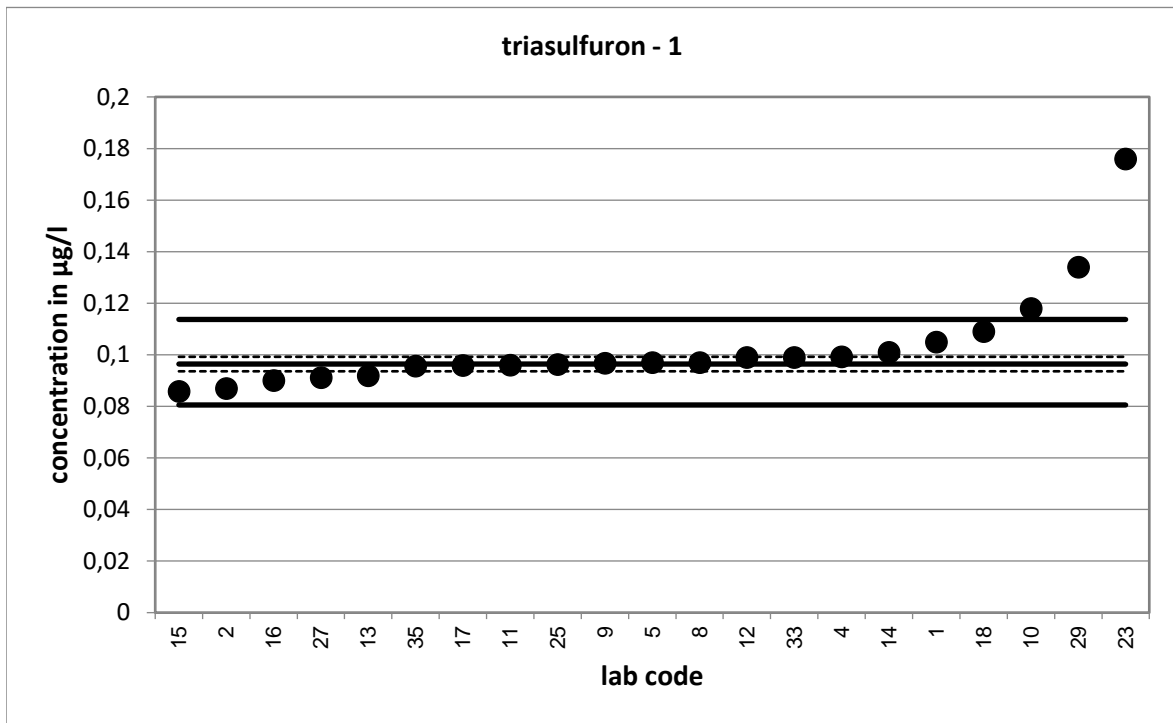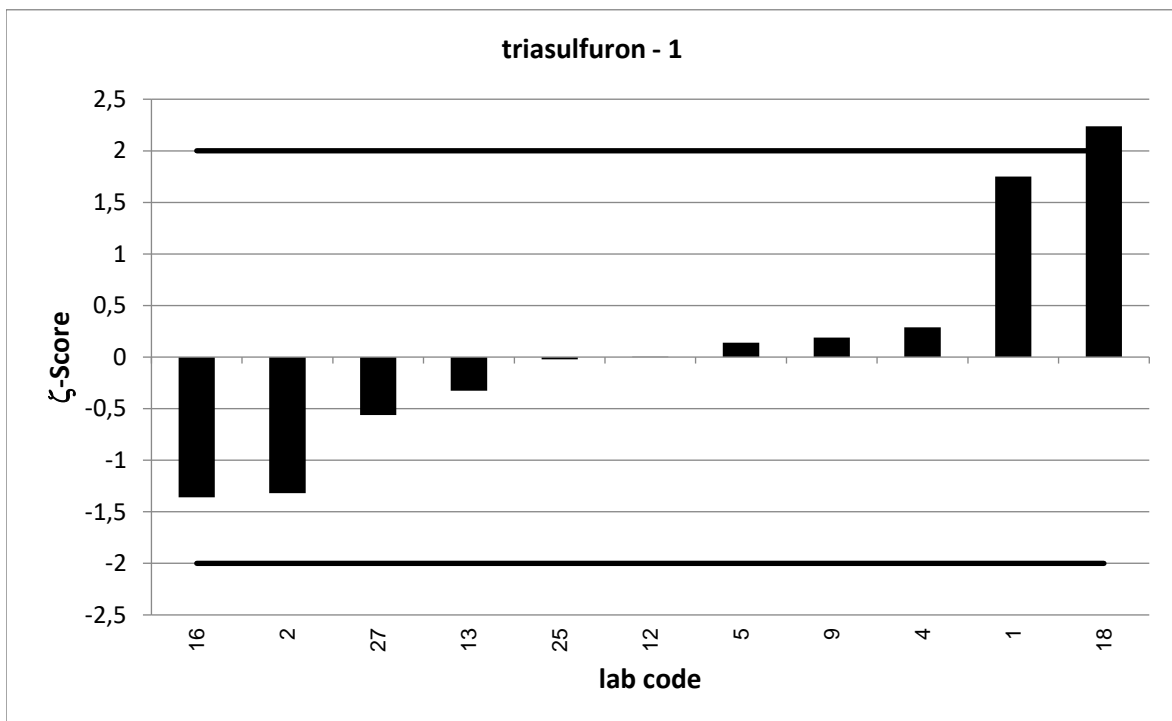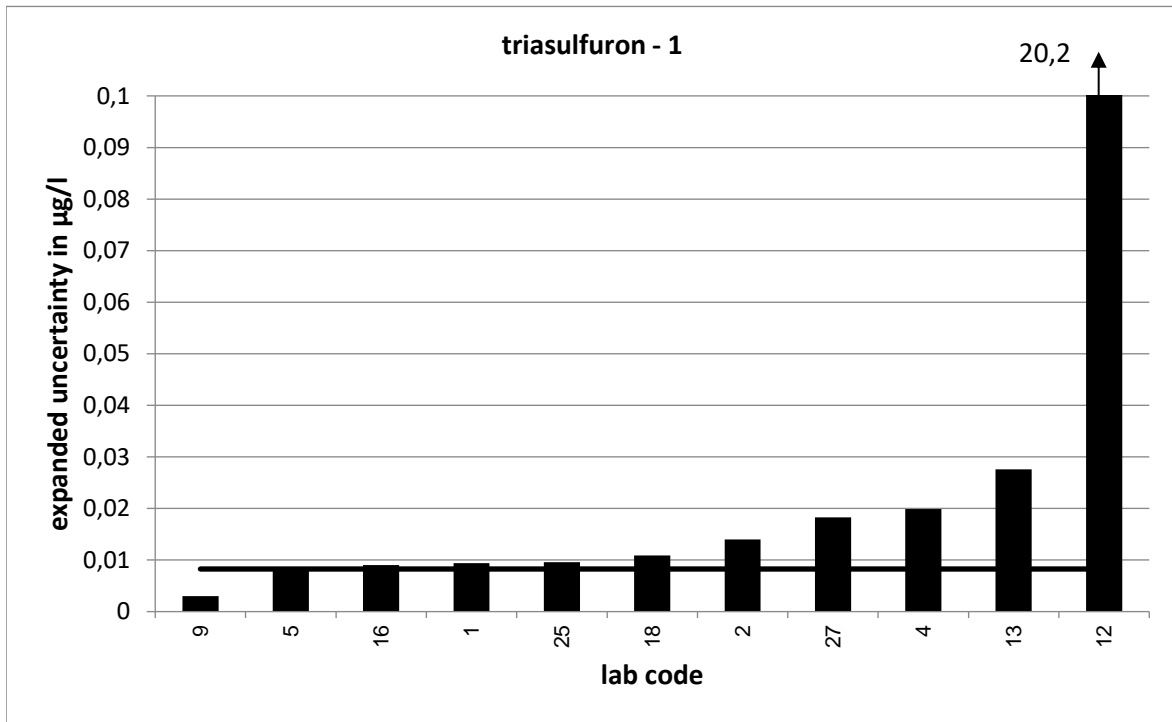** s = satisfactory, q = questionable, u = unsatisfactory

triasulfuron - 1

triasulfuron - 1

PT 3/18 - TW S5	triasulfuron - 2				
assigned value [µg/l]*		0,1928	± 0,0041		
upper tolerance limit [µg/l]		0,2313			
lower tolerance limit [µg/l]		0,1577			
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
1	0,195	0,003	0,9	0,1	s
2	0,17	0,025	-1,8	-1,3	s
4	0,197	0,039	0,2	0,2	s
5	0,199	0,009	1,2	0,3	s
8	0,198			0,3	s
9	0,199	0,018	0,7	0,3	s
10	0,237			2,3	q
11	0,201			0,4	s
12	0,198	10,1	0,0	0,3	s
13	0,181	0,054	-0,4	-0,7	s
14	0,206			0,7	s
15	0,183			-0,6	s
16	0,187	0,025	-0,5	-0,3	s
17	0,19			-0,2	s
18	0,216	0,022	2,1	1,2	s
23	0,301			5,6	u
25	0,192	0,019	-0,1	0,0	s
27	0,181	0,036	-0,6	-0,7	s
29	0,249			2,9	q
33	0,185			-0,4	s
35	0,2146			1,1	s

* The stated uncertainty of the assigned value is the expanded
uncertainty with a coverage factor k=2 corresponding to a
confidence level of about 95%
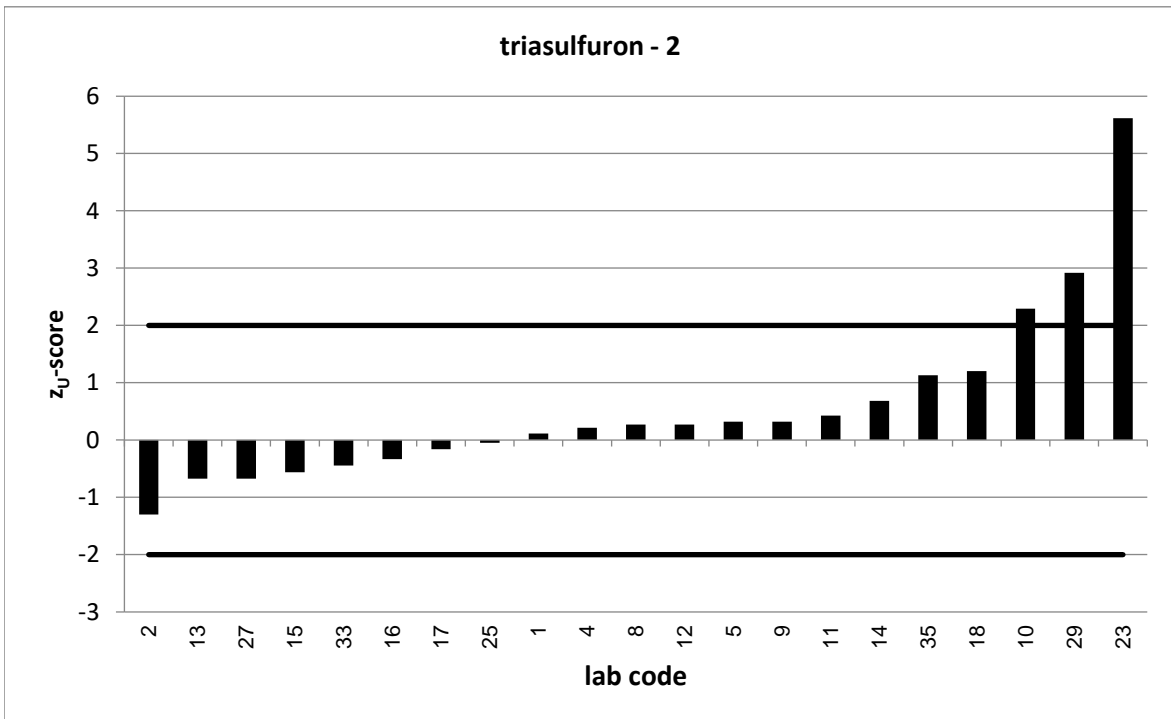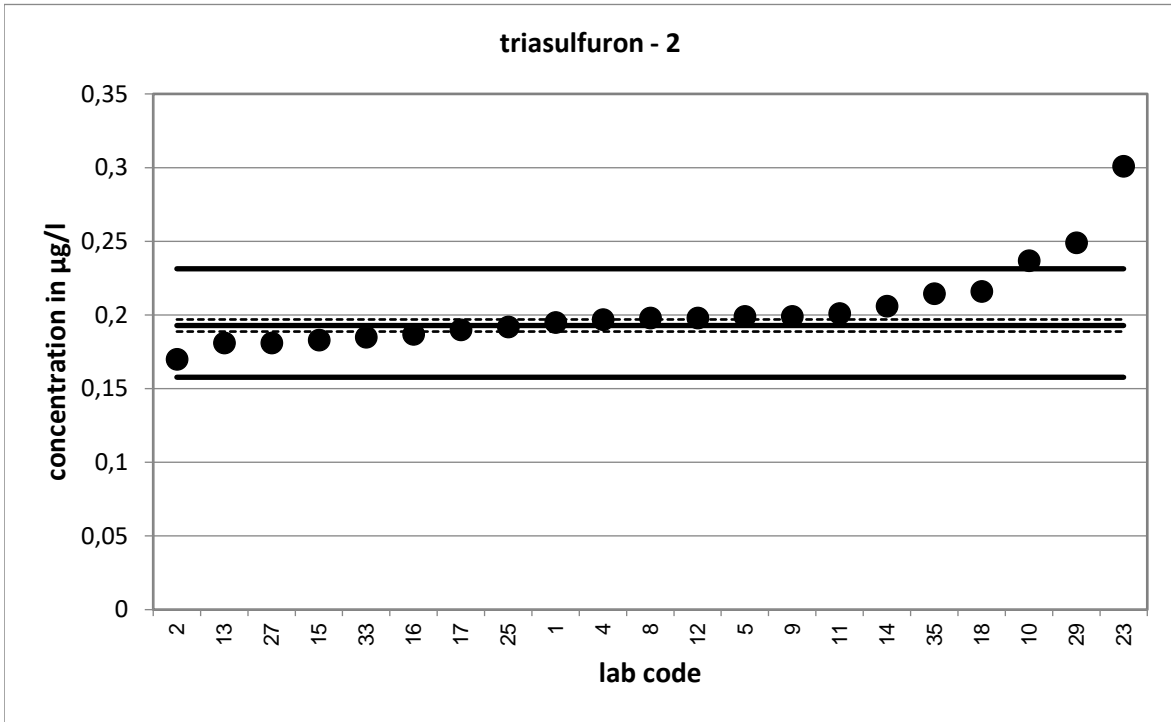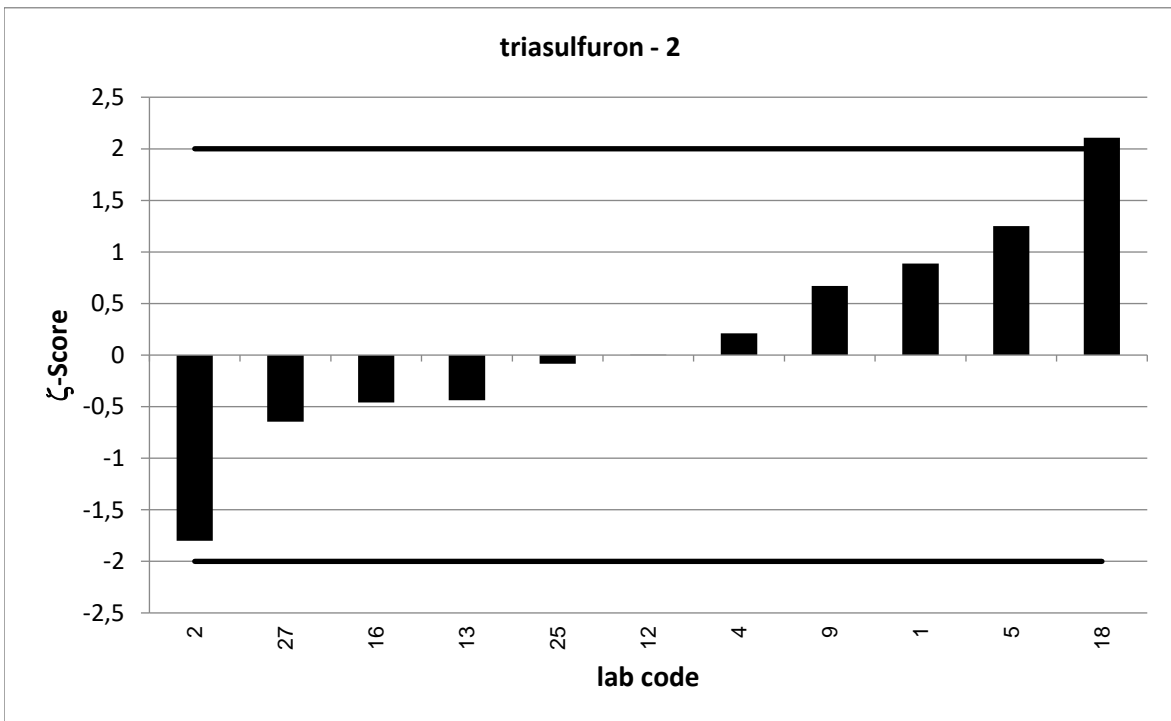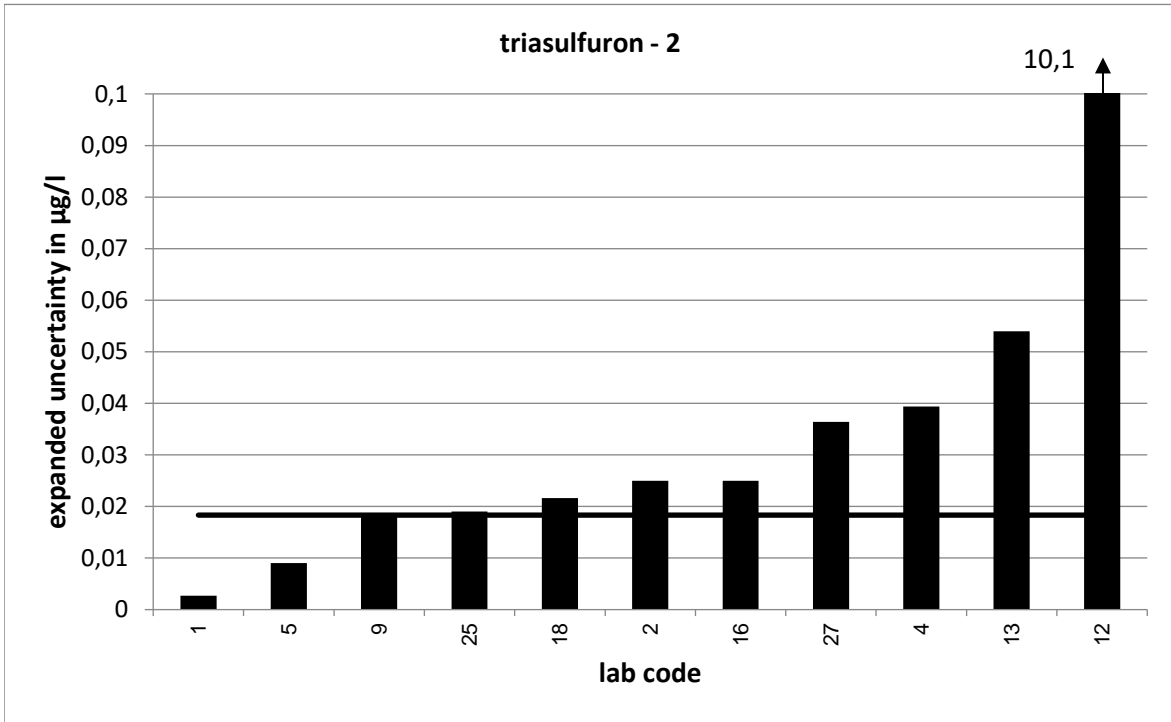** s = satisfactory, q = questionable, u = unsatisfactory

triasulfuron - 2

triasulfuron - 2

triasulfuron - 2

triasulfuron - 2

PT 3/18 - TW S5	triasulfuron - 3				
assigned value [µg/l]*		0,2892	± 0,0056		
upper tolerance limit [µg/l]		0,3325			
lower tolerance limit [µg/l]		0,2489			
lab code	result [µg/l]	±	ζ-score	z_U-score	assessm.**
1	0,313	0,006	5,7	1,1	s
2	0,246	0,037	-2,3	-2,1	q
4	0,293	0,059	0,1	0,2	s
5	0,296	0,016	0,8	0,3	s
8	0,304			0,7	s
9	0,296	0,03	0,4	0,3	s
10	0,342			2,4	q
11	0,283			-0,3	s
12	0,288	13,9	0,0	-0,1	s
13	0,276	0,083	-0,3	-0,7	s
14	0,309			0,9	s
15	0,281			-0,4	s
16	0,279	0,035	-0,6	-0,5	s
17	0,294			0,2	s
18	0,302	0,03	0,8	0,6	s
23	0,399			5,1	u
25	0,288	0,029	-0,1	-0,1	s
27	0,275	0,055	-0,5	-0,7	s
29	0,35			2,8	q
33	0,304			0,7	s
35	0,3069			0,8	s

* The stated uncertainty of the assigned value is the expanded
uncertainty with a coverage factor k=2 corresponding to a
confidence level of about 95%
** s = satisfactory, q = questionable, u = unsatisfactory

triasulfuron - 3

triasulfuron - 3

triasulfuron - 3

triasulfuron - 3