

**University of Stuttgart**  
Germany



# Analytische Qualitätssicherung Baden-Württemberg

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Proficiency Test 7/21  
- TW S5 – Sulfonylurea herbicides -  
amidosulfuron, metsulfuron-methyl, rimsulfuron,  
thifensulfuron-methyl, triasulfuron

## 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 February 2022

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<b>Version of the report</b>	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). 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 sulfonyleurea herbicides were based on a real ground water matrix. 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 26 October 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  $\mu\text{g/l}$  with three significant digits.

## 6. Submission of the results

The deadline for the submission of results was on 22 November 2021. 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](http://www.aqsbw.de/pdf/ausw_berichte_v1_en.pdf).

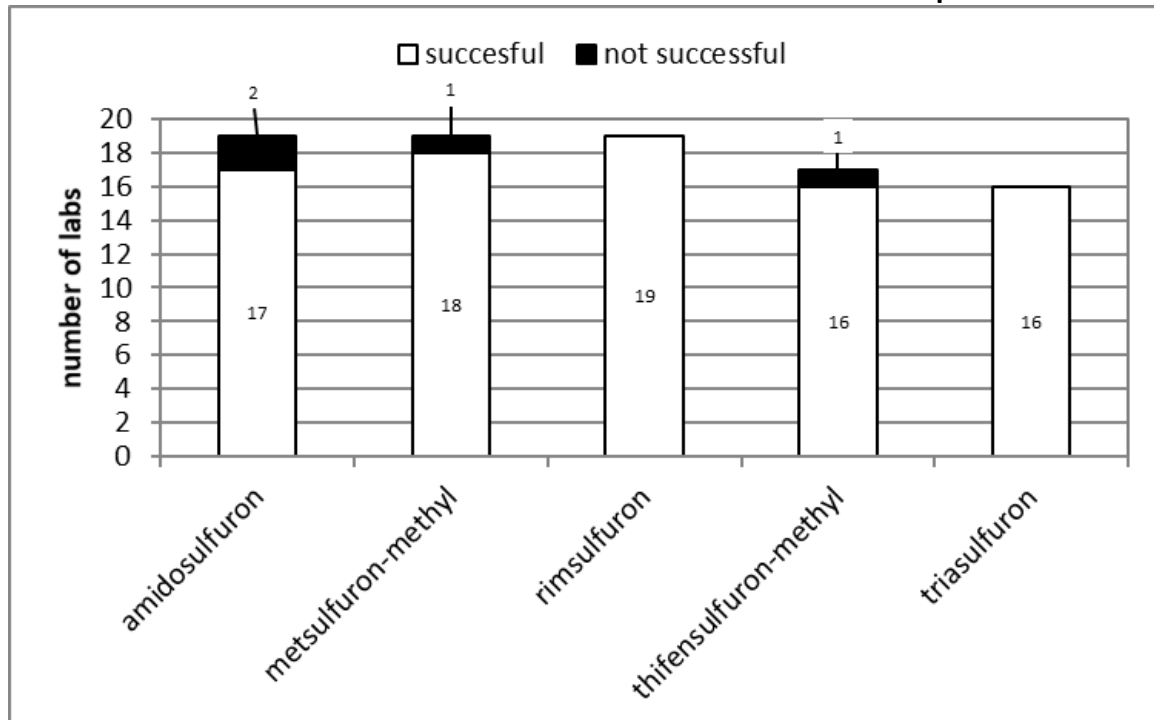
This PT was evaluated as follows:

<b>Assigned value <math>x_{pt}</math>:</b>	Robust mean value from participants' results (Hampel-estimator)						
<b>Standard deviation for proficiency assessment <math>\sigma_{pt}</math>:</b>	Q method						
<b>Upper limit of <math>\sigma_{pt}</math>:</b>	25 %						
<b>Lower limit of <math>\sigma_{pt}</math>:</b>	5 %						
<b>Assessment:</b>	$z_U$ -Score						
<b>Classification of the single results:</b>	<table style="border: none;"> <tr> <td style="padding-right: 20px;"><math> z_u  \leq 2,0</math></td> <td>successful</td> </tr> <tr> <td><math>2,0 &lt;  z_u  &lt; 3,0</math></td> <td>questionable</td> </tr> <tr> <td><math> z_u  \geq 3,0</math></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						
<b>Parameter assessment:</b>	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

<b>Number of participants:</b>	21
<b>Number of reported values</b>	270
<b>Number of accepted values:</b>	249 (92,2 %)

### 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.aqsbw.de/pdf/ausw\\_berichte\\_v1\\_en.pdf](http://www.aqsbw.de/pdf/ausw_berichte_v1_en.pdf).

## 10. Measurement uncertainty

### General:

Number of labs with valid values	19
Number of labs with valid values and reported measurement uncertainties	12 (63,1 %)
Number of valid values	270
Number of valid values with measurement uncertainties	168 (62,2 %)

**Measurement uncertainties against the accreditation status**

Accreditation status of the values	Number of values	Number of values with measurement uncertainty
accredited	237	168 (70,9 %)
not accredited	3	0
not specified	30	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  $\zeta$ -score.  $|\zeta| > 2$  means that the “own” requirements (defined in terms of estimated uncertainty) are not fulfilled.

<b>Number of values with reported measurement uncertainty having a <math> z_U  \leq 2,0</math></b>	153
<b>Number of values with a magnitude of <math>\zeta</math>-scores <math>&gt; 2</math></b> The own requirements of the laboratory are not fulfilled and the estimation of the measurement uncertainty is too low	10 (6,5 %)

**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](http://www.aqsbw.de/pdf/ausw_berichte_v1_en.pdf)

**12. Internet**

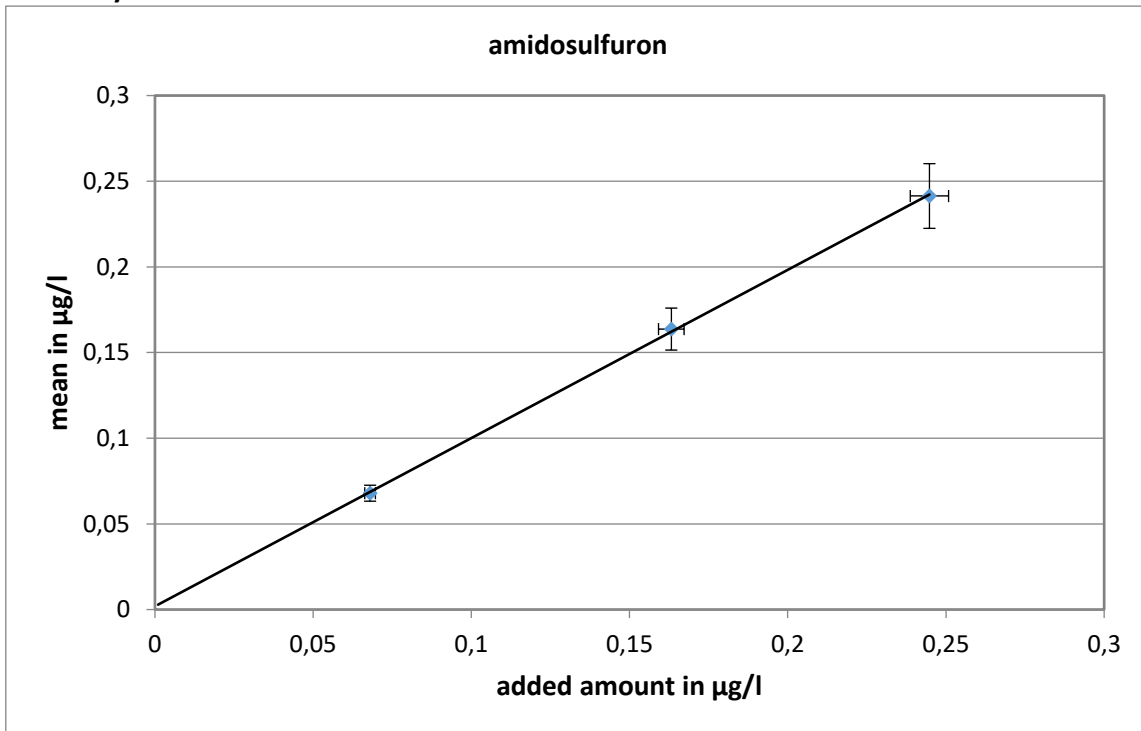
The report is available on the following webpage:  
[http://www.aqsbw/pdf/261/report\\_261.pdf](http://www.aqsbw/pdf/261/report_261.pdf)



# amidosulfuron

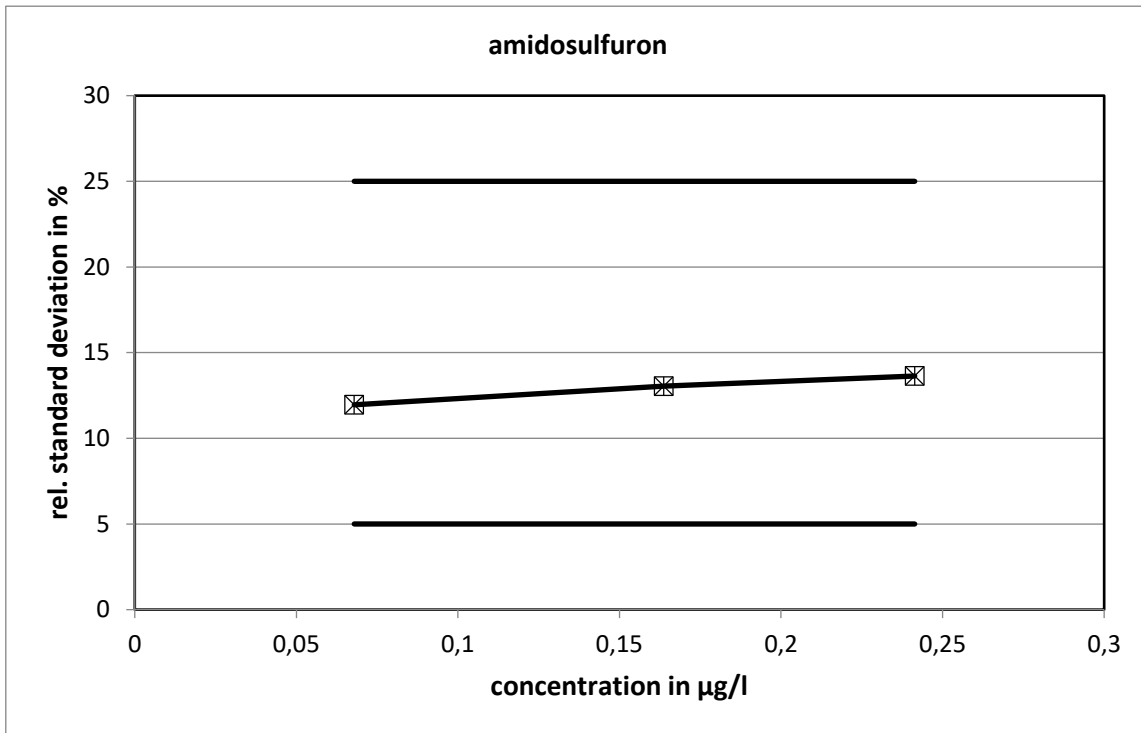
level	assigned value [µg/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [µg/l]	standard deviation for proficiency assessment [µg/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [µg/l]	lower tolerance limit [µg/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,0679	6,86	0,0081	0,0081	11,96	0,0853	0,0525	25,51	-22,65	19	0	2	10,5
2	0,1637	7,48	0,0214	0,0214	13,05	0,2096	0,1234	28,02	-24,61	19	0	1	5,3
3	0,2414	7,82	0,0329	0,0329	13,64	0,3123	0,1794	29,39	-25,66	19	0	2	10,5
sum										57	0	5	8,8

## Recovery and matrix content

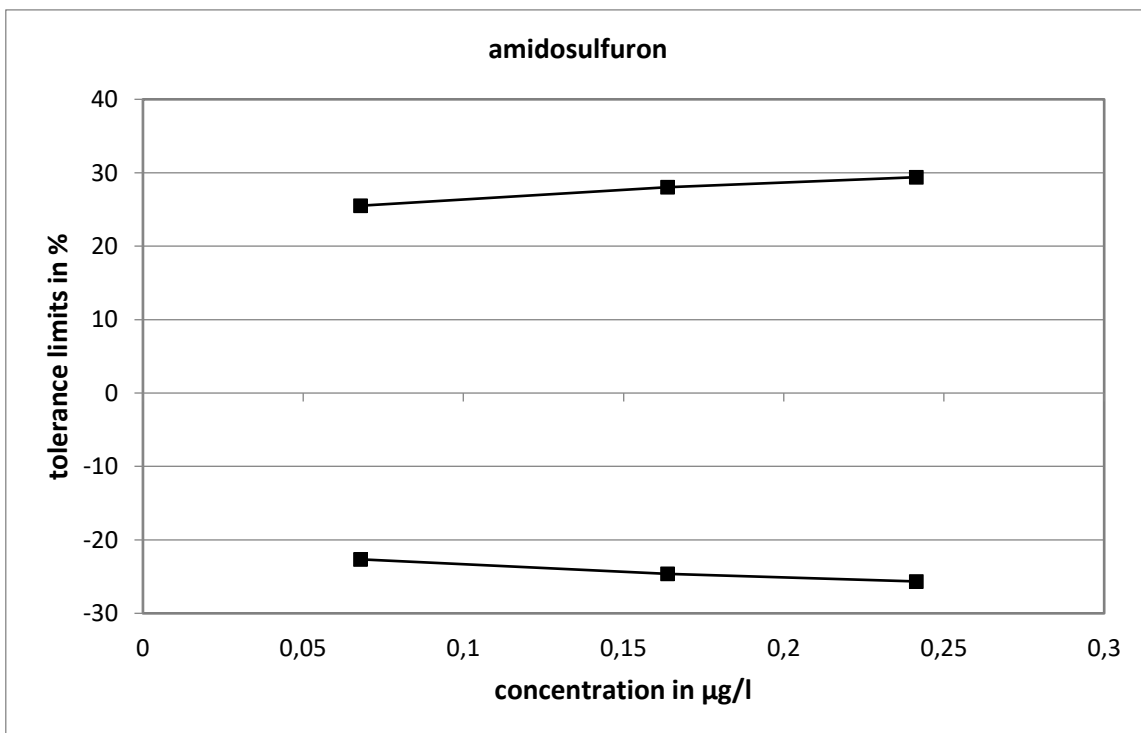


average recovery rate: 98,2 %

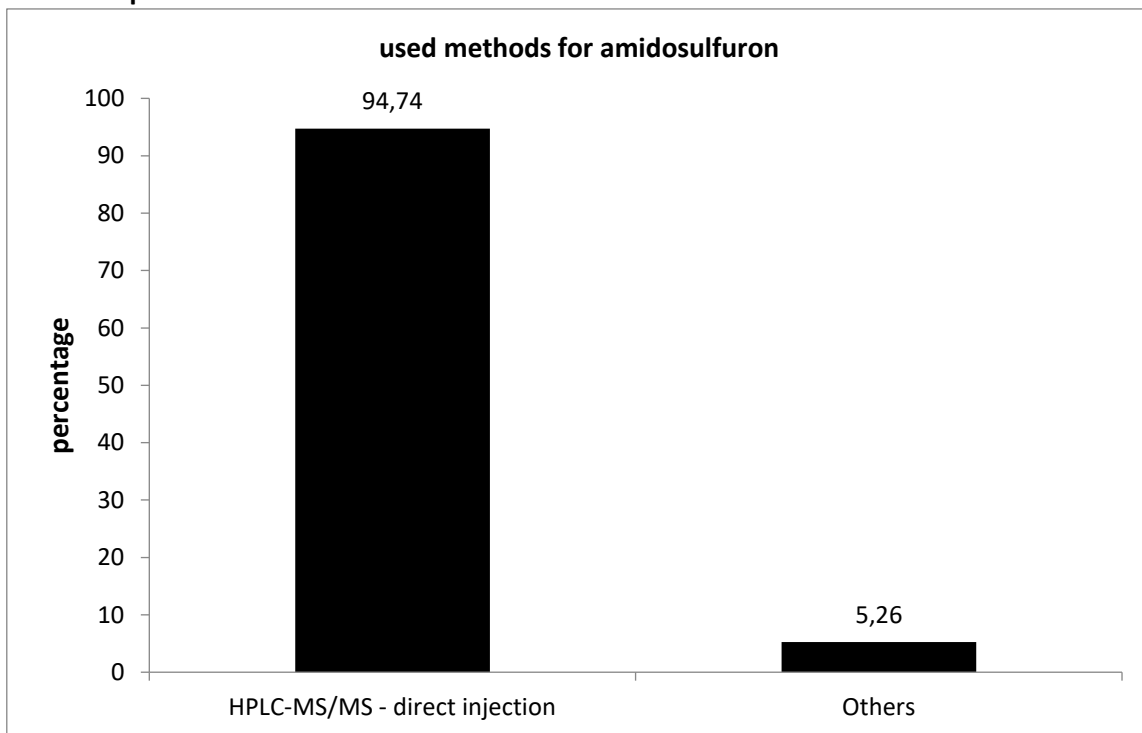
Relative standard deviation and tolerance limits



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



**Method specific evaluation**

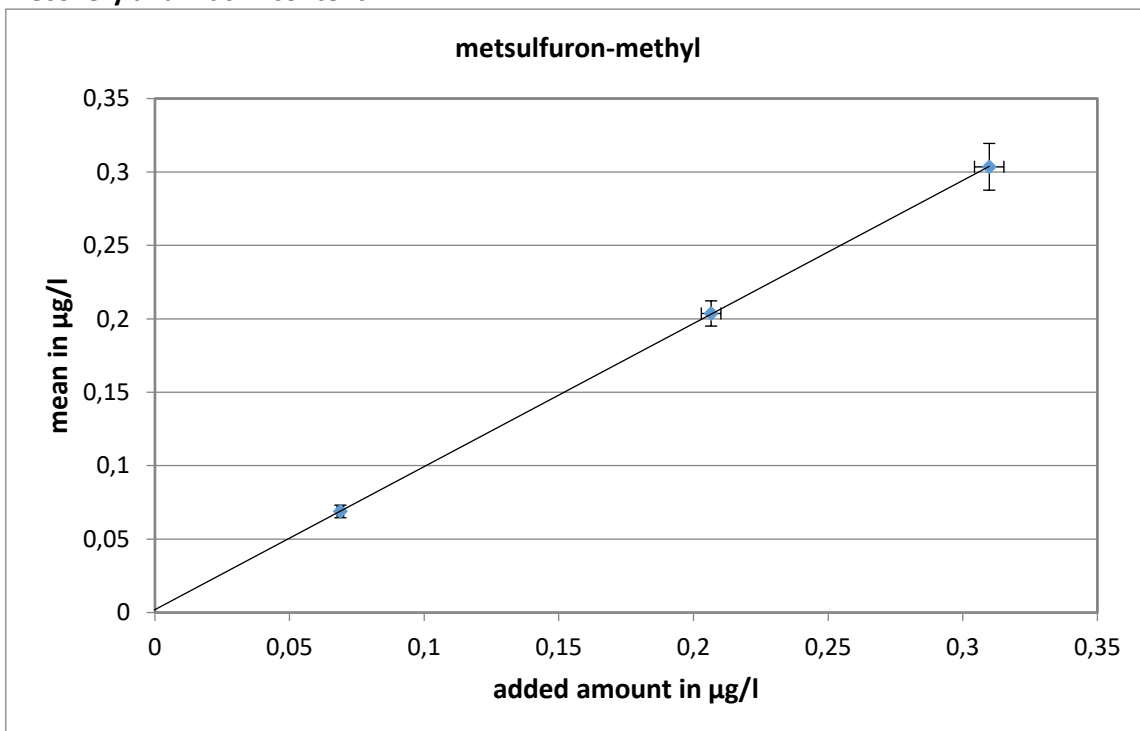


There is no method comparison, because almost all used HPLC-MS/MS - direct injection.

# metsulfuron-methyl

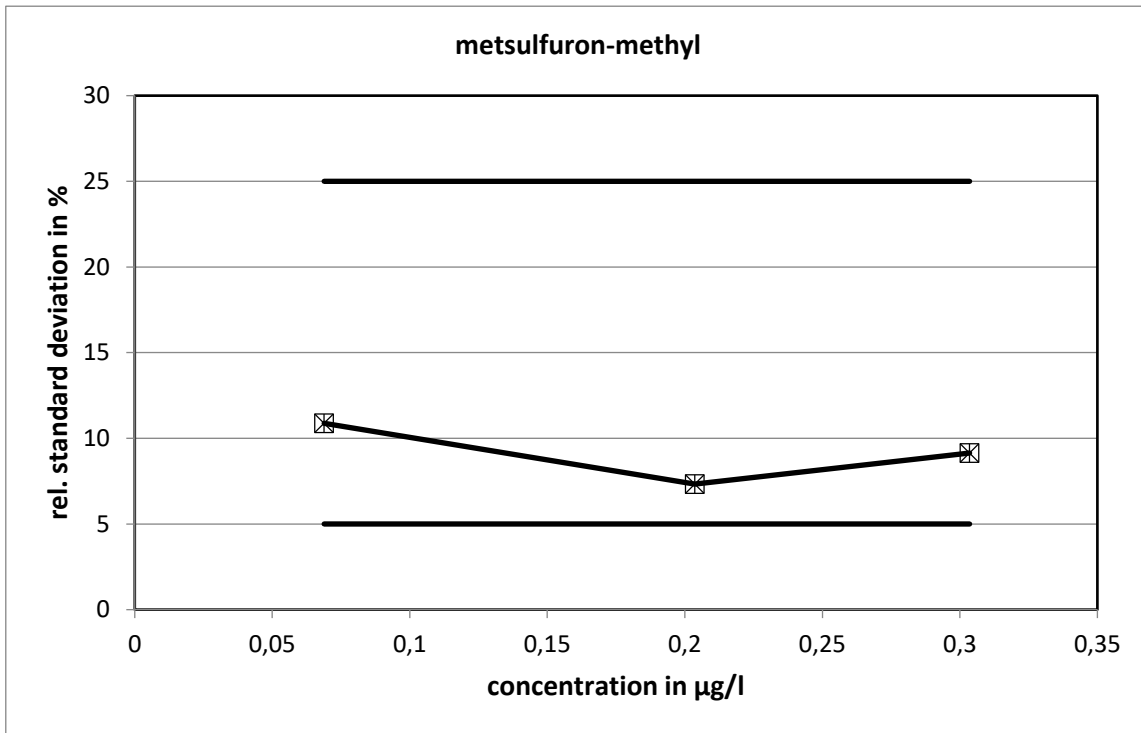
level	assigned value [µg/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [µg/l]	standard deviation for proficiency assessment [µg/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [µg/l]	lower tolerance limit [µg/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,0689	6,24	0,0075	0,0075	10,88	0,0847	0,0546	23,07	-20,69	19	1	0	5,3
2	0,2037	4,20	0,0149	0,0149	7,33	0,2347	0,1748	15,24	-14,16	19	1	0	5,3
3	0,3035	5,24	0,0277	0,0277	9,14	0,3618	0,2504	19,19	-17,52	19	1	0	5,3
sum										57	3	0	5,3

## Recovery and matrix content

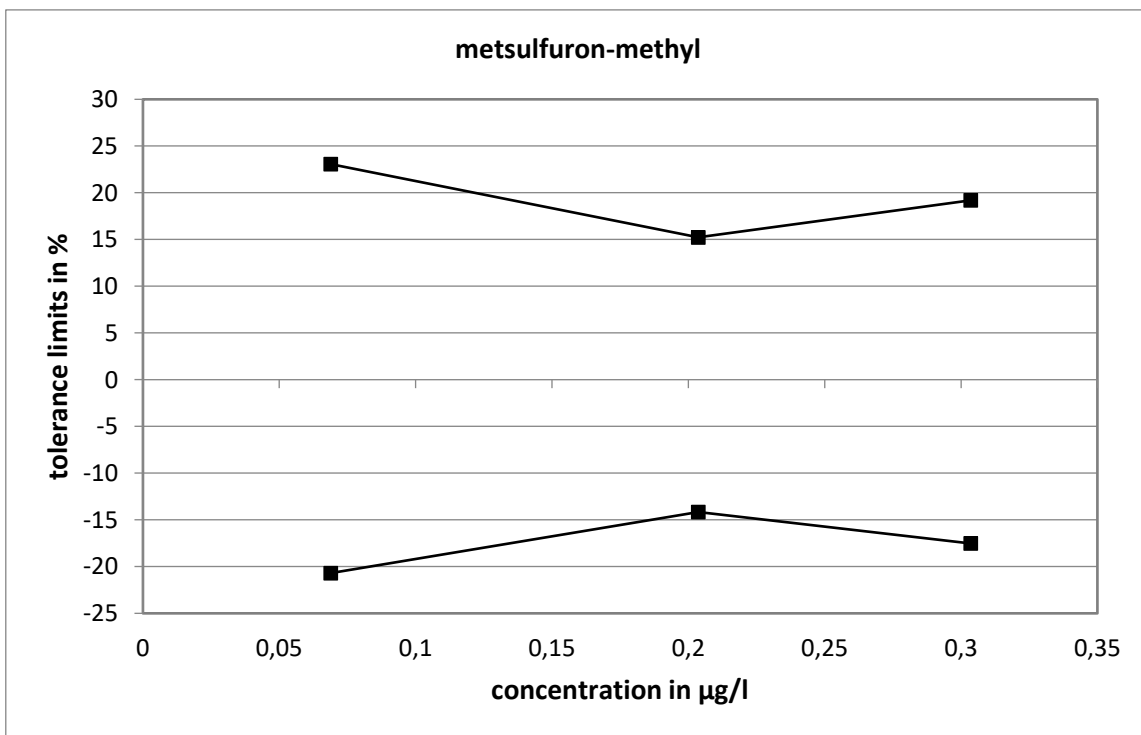


average recovery rate: 97,4 %

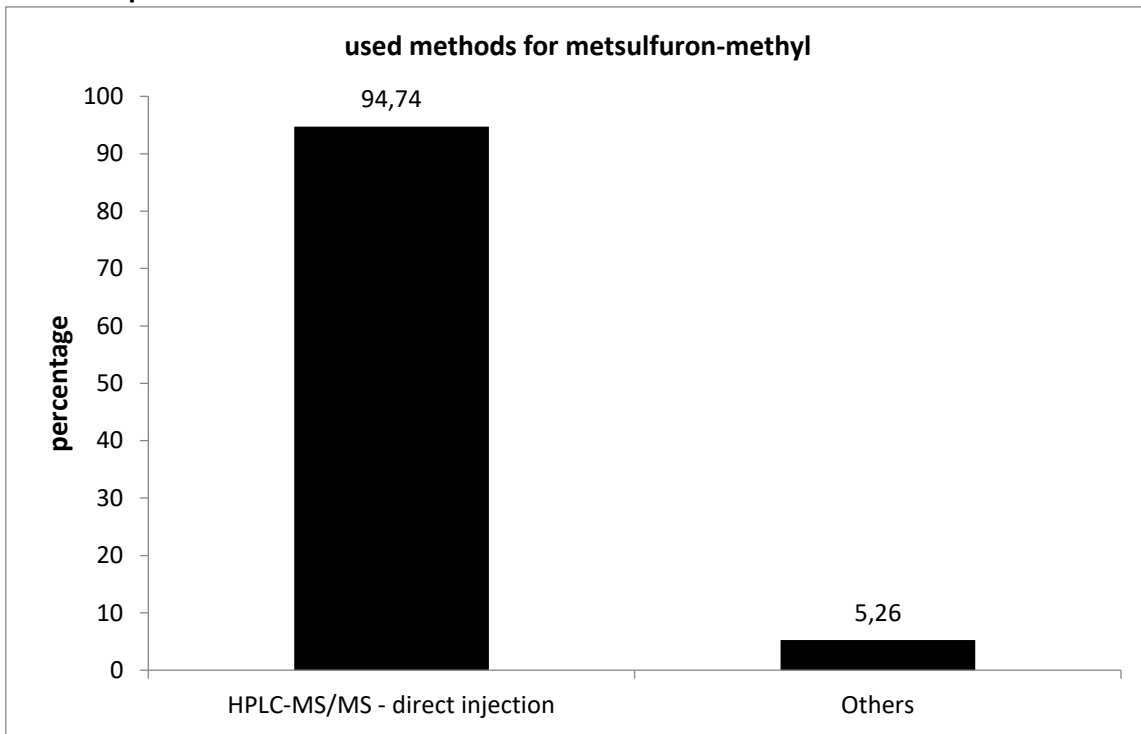
Relative standard deviation and tolerance limits



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



**Method specific evaluation**

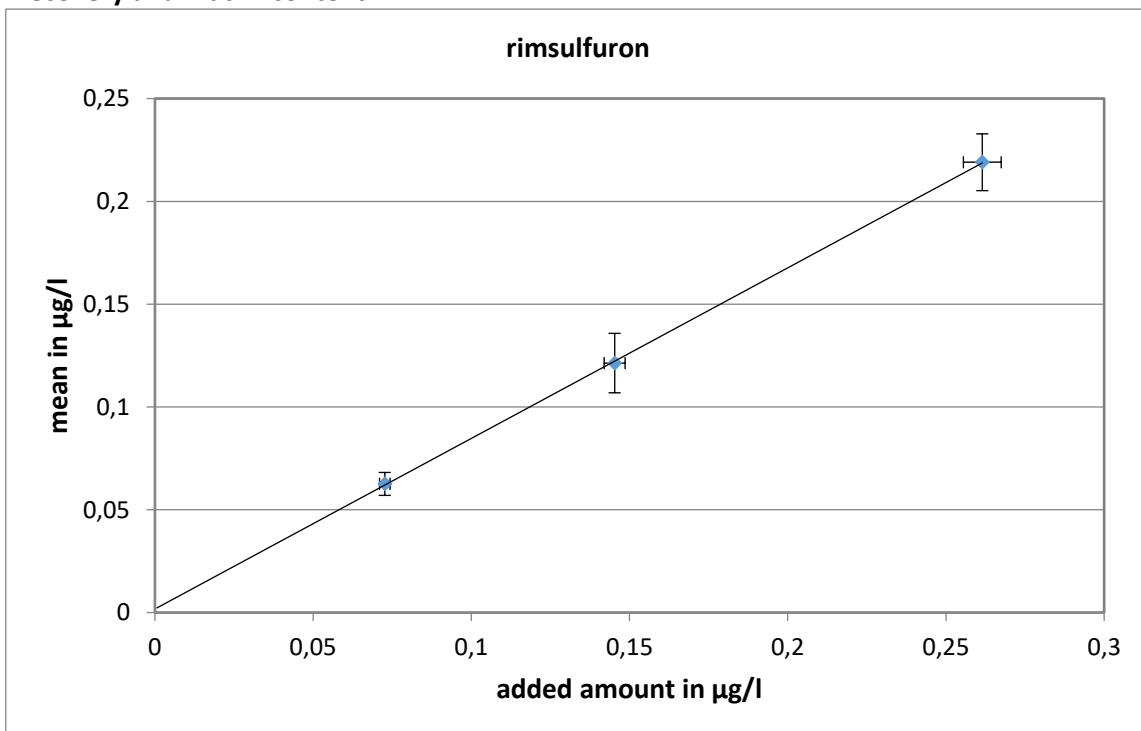


There is no method comparison, because almost all used HPLC-MS/MS - direct injection.

# 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	0,0626	8,92	0,0097	0,0097	15,56	0,0838	0,0444	33,93	-29,06	19	0	0	0,0
2	0,1213	11,92	0,0252	0,0252	20,79	0,1782	0,0751	46,86	-38,09	19	1	0	5,3
3	0,2190	6,31	0,0241	0,0241	11,00	0,2701	0,1732	23,34	-20,91	19	1	3	21,1
sum										57	2	3	8,8

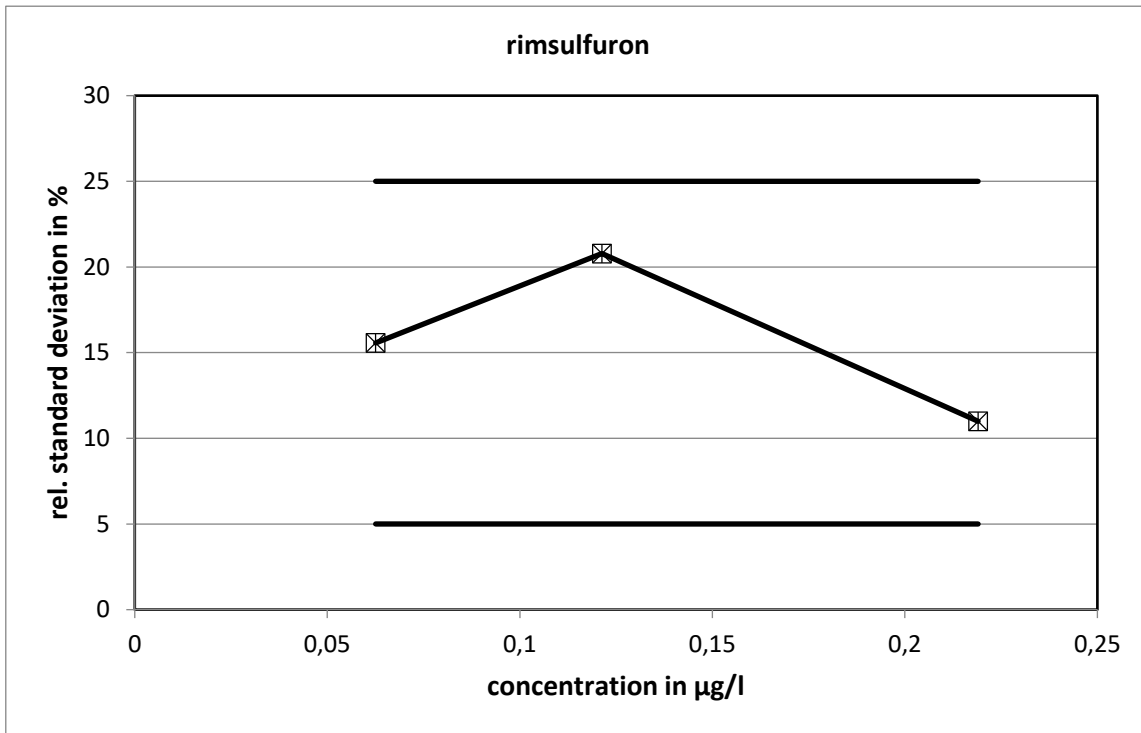
## Recovery and matrix content



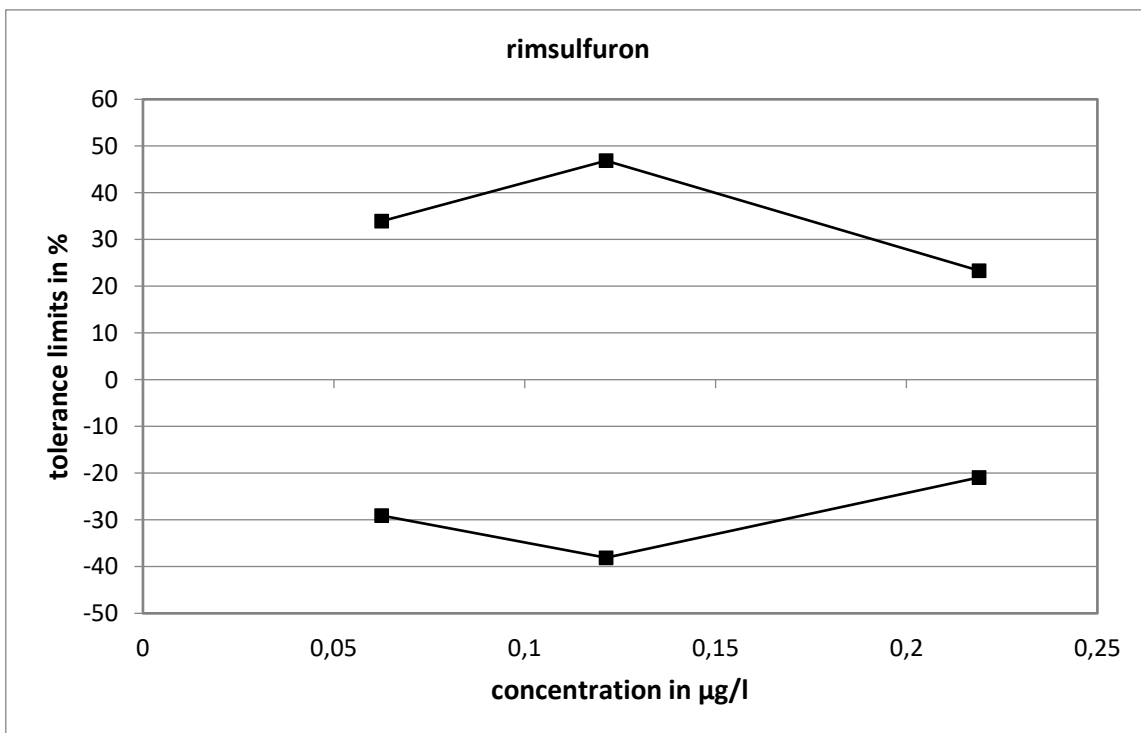
average recovery rate: 83 %

There are doubts about the trueness of the spiking, but the reasons were not found.

Relative standard deviation and tolerance limits

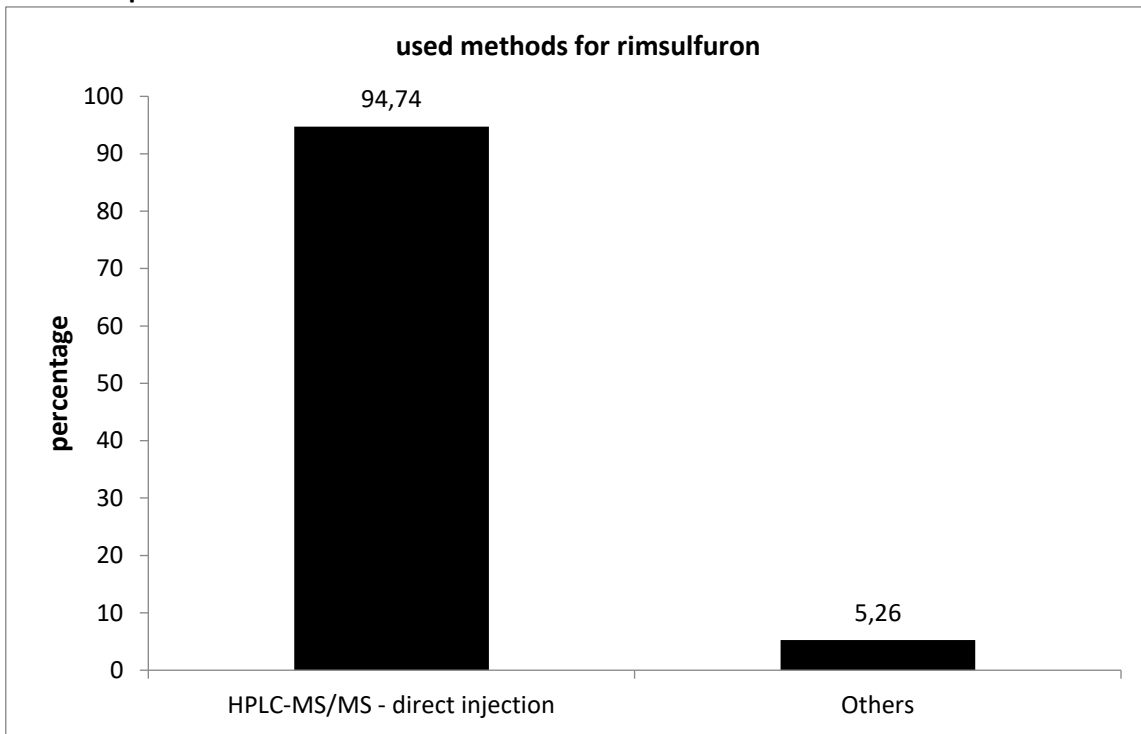


The relative standard deviation calculated with the Q-method did not reach the limits.





**Method specific evaluation**

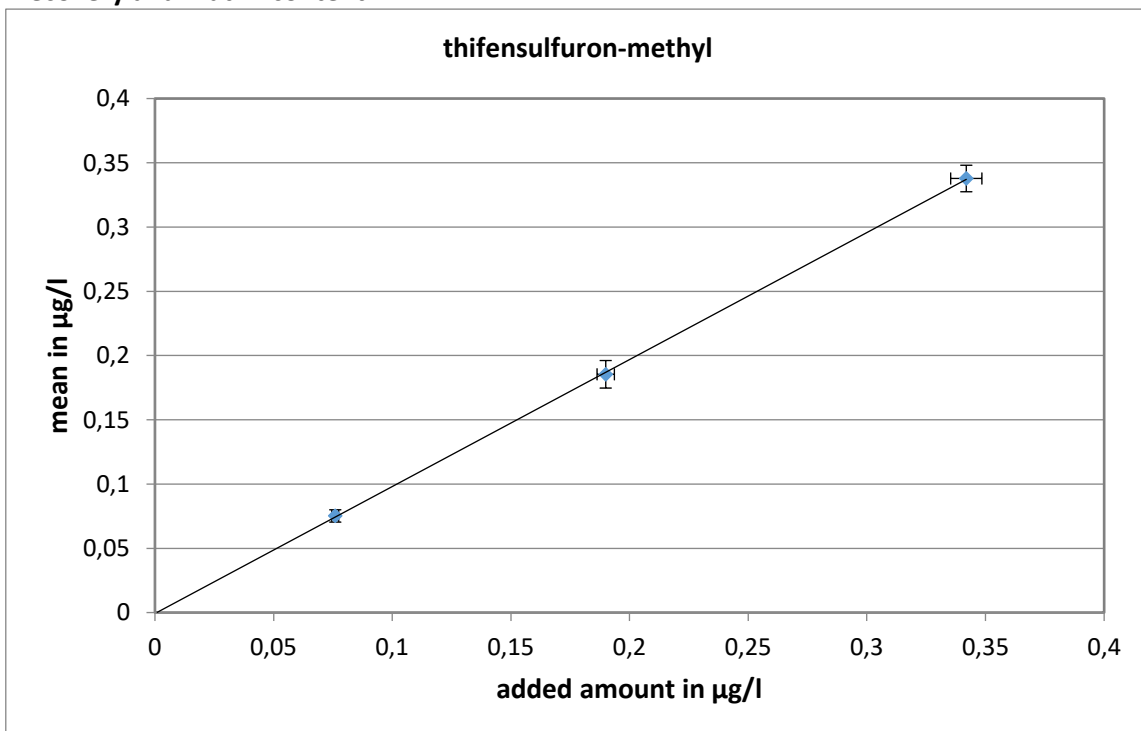


There is no method comparison, because almost all used HPLC-MS/MS - direct injection.

# thifensulfuron-methyl

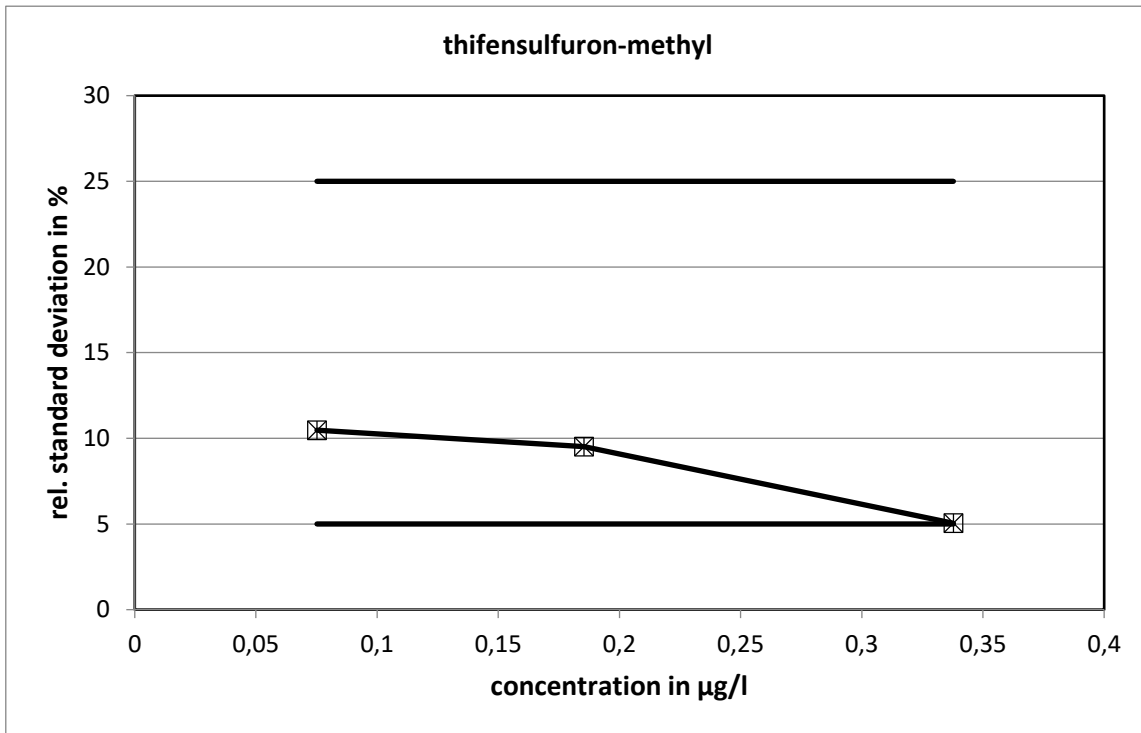
level	assigned value [µg/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [µg/l]	standard deviation for proficiency assessment [µg/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [µg/l]	lower tolerance limit [µg/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,0752	6,35	0,0079	0,0079	10,48	0,0919	0,0602	22,17	-19,97	17	0	1	5,9
2	0,1854	5,77	0,0177	0,0177	9,52	0,2226	0,1516	20,03	-18,22	17	0	1	5,9
3	0,3378	3,06	0,0170	0,0170	5,04	0,3727	0,3045	10,35	-9,84	17	2	2	23,5
sum										51	2	4	11,8

## Recovery and matrix content

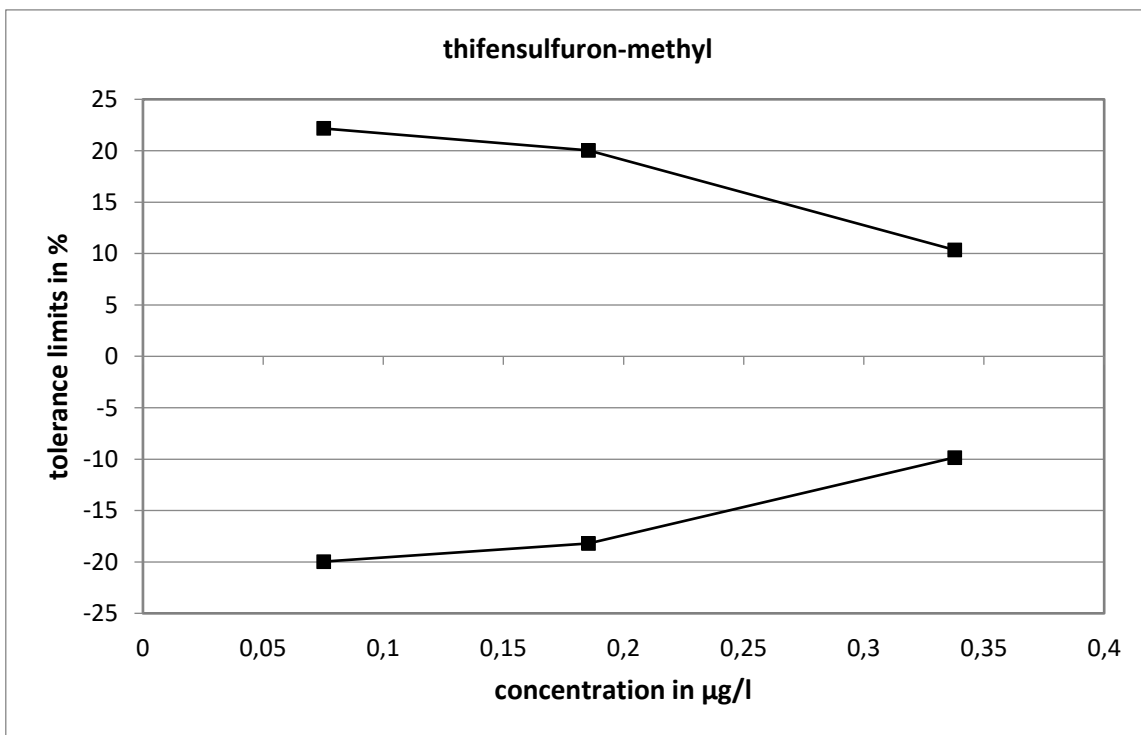


average recovery rate: 98,8 %

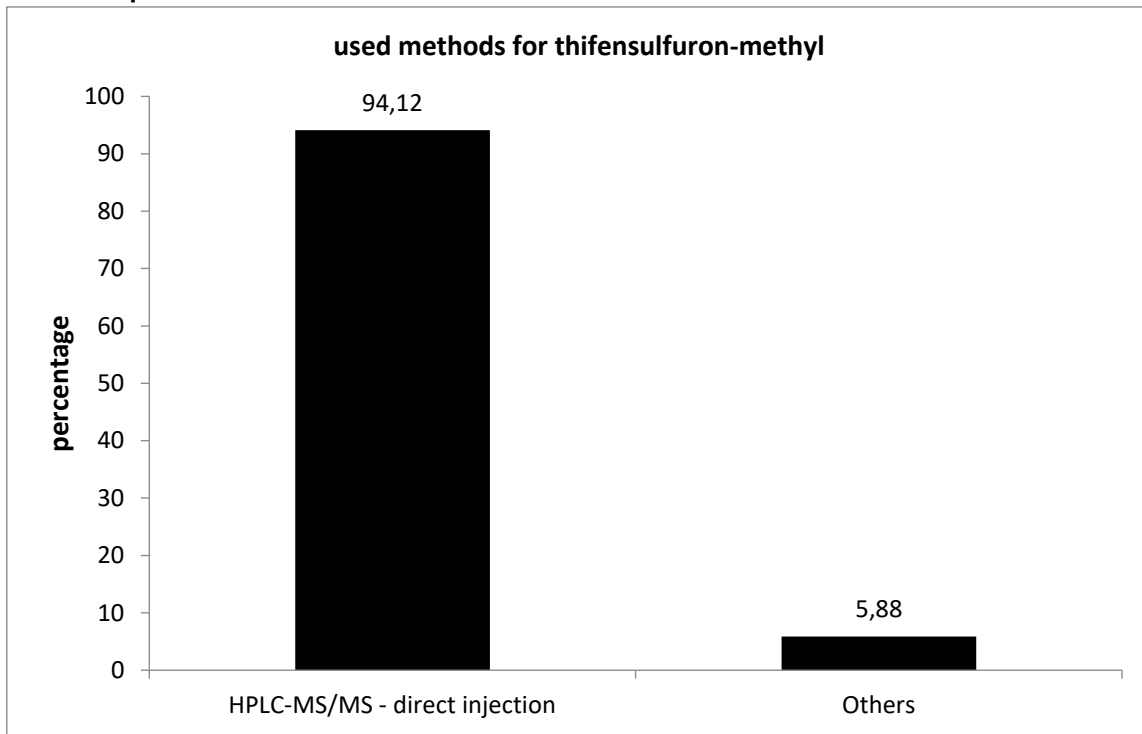
Relative standard deviation and tolerance limits



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



**Method specific evaluation**

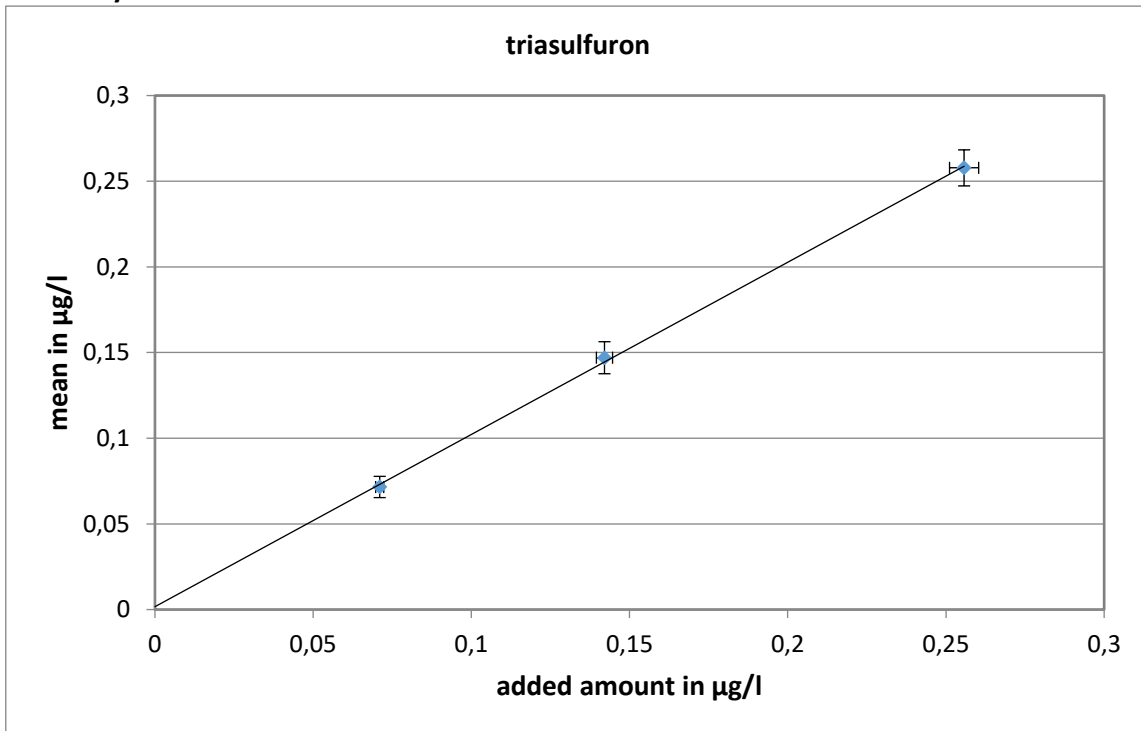


There is no method comparison, because almost all used HPLC-MS/MS - direct injection.

# triasulfuron

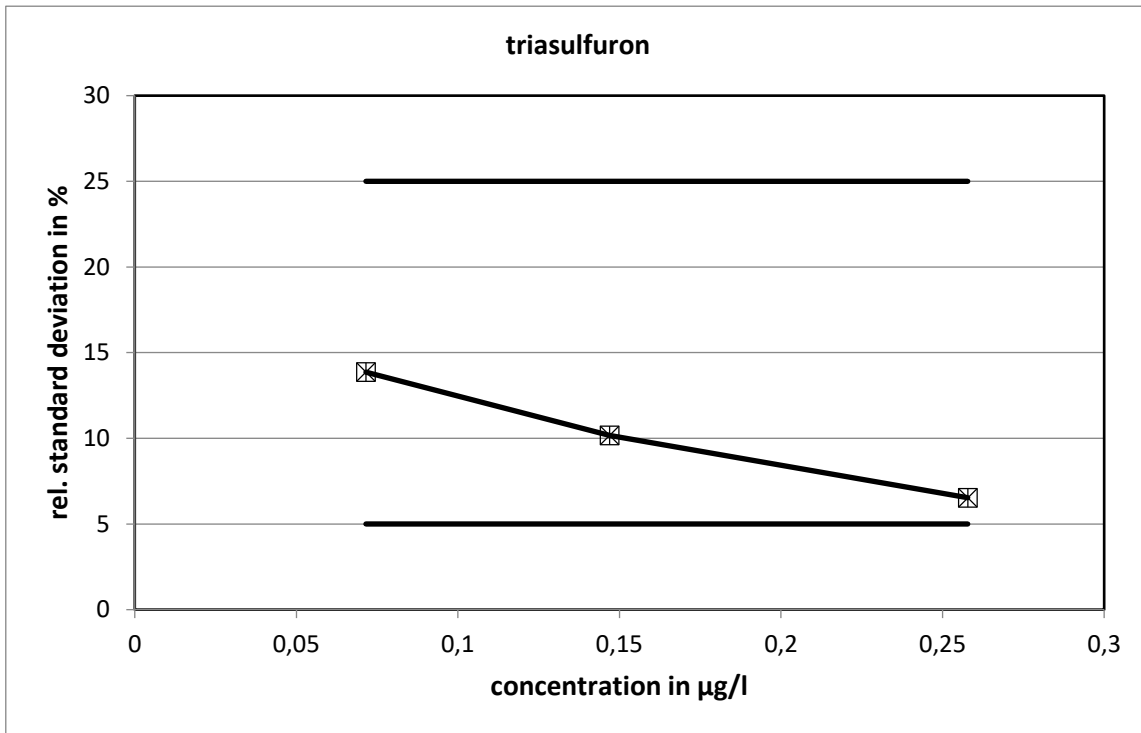
level	assigned value [µg/l]	expanded uncertainty of the assigned value [%]	standard deviation, calculated using robust statistics [µg/l]	standard deviation for proficiency assessment [µg/l]	standard deviation for proficiency assessment [%]	upper tolerance limit [µg/l]	lower tolerance limit [µg/l]	upper tolerance limit [%]	lower tolerance limit [%]	number of results	out below	out above	out [%]
1	0,0715	8,66	0,0099	0,0099	13,86	0,0929	0,0529	29,92	-26,06	16	0	0	0,0
2	0,1470	6,36	0,0150	0,0150	10,17	0,1786	0,1184	21,49	-19,41	16	0	0	0,0
3	0,2578	4,08	0,0168	0,0168	6,53	0,2926	0,2251	13,52	-12,67	16	0	2	12,5
sum										48	0	2	4,2

## Recovery and matrix content

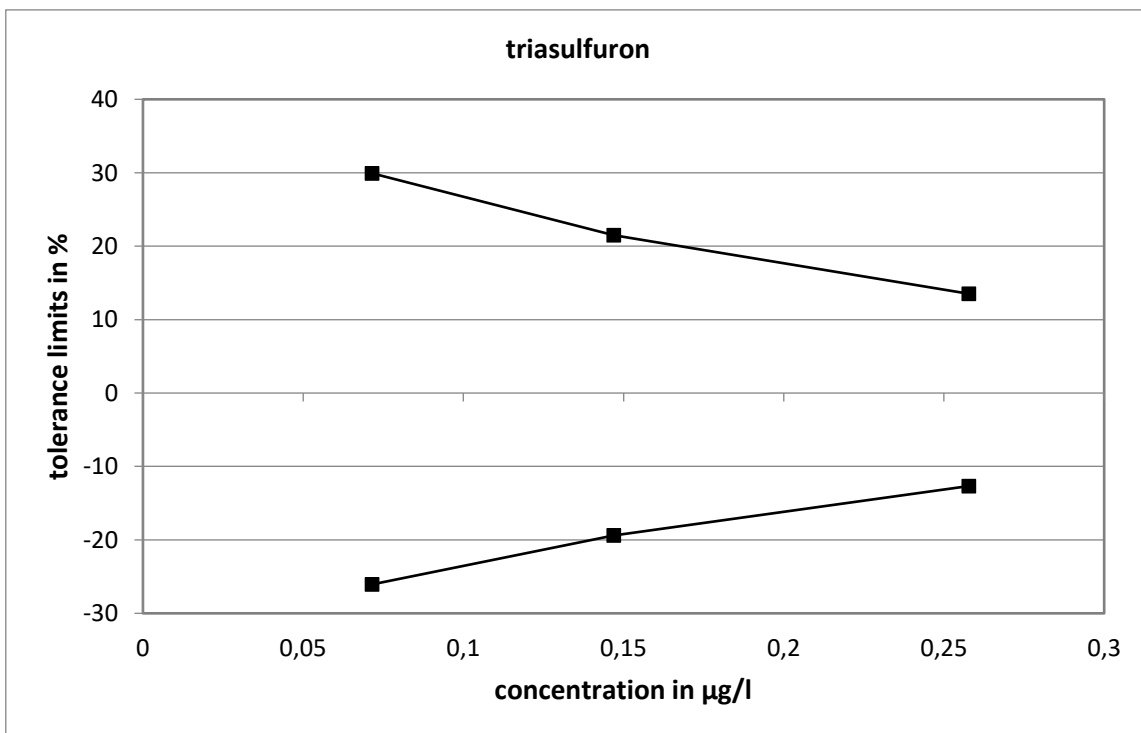


average recovery rate: 100,5 %

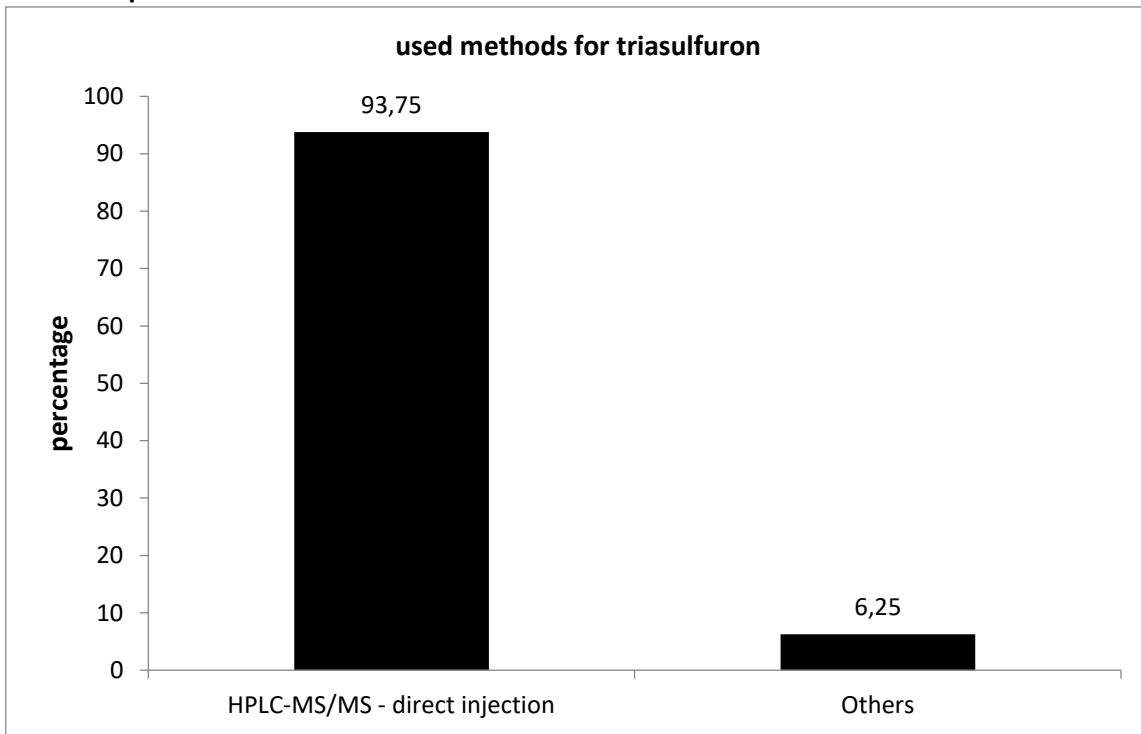
Relative standard deviation and tolerance limits



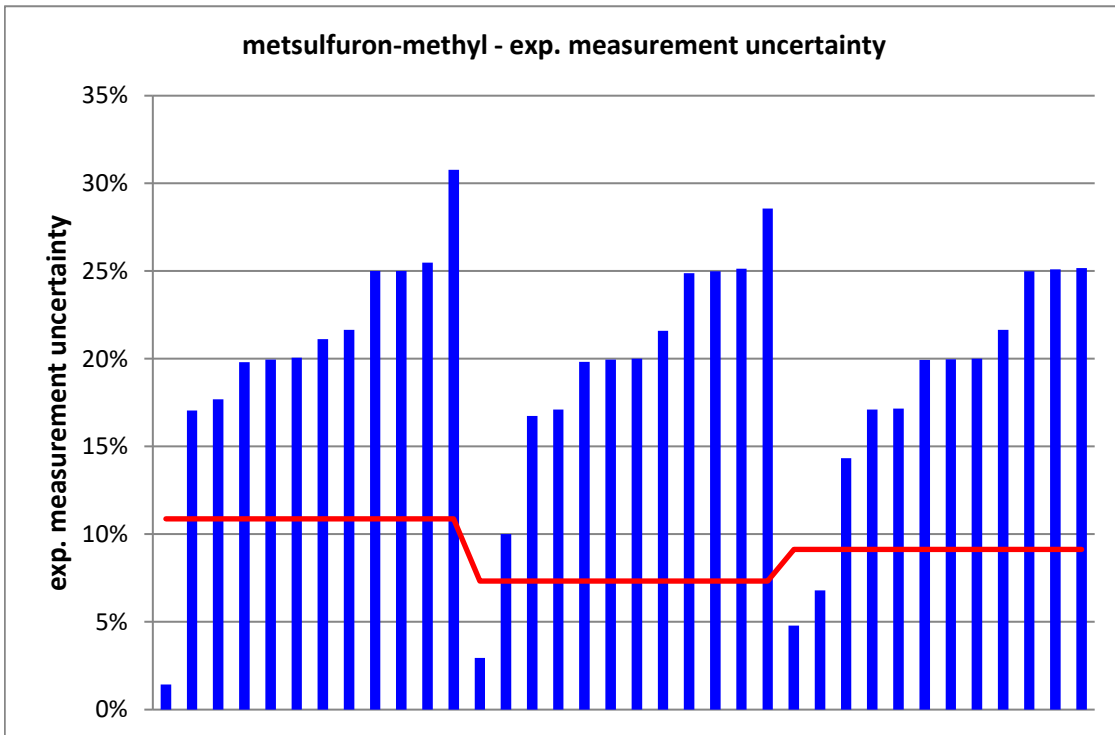
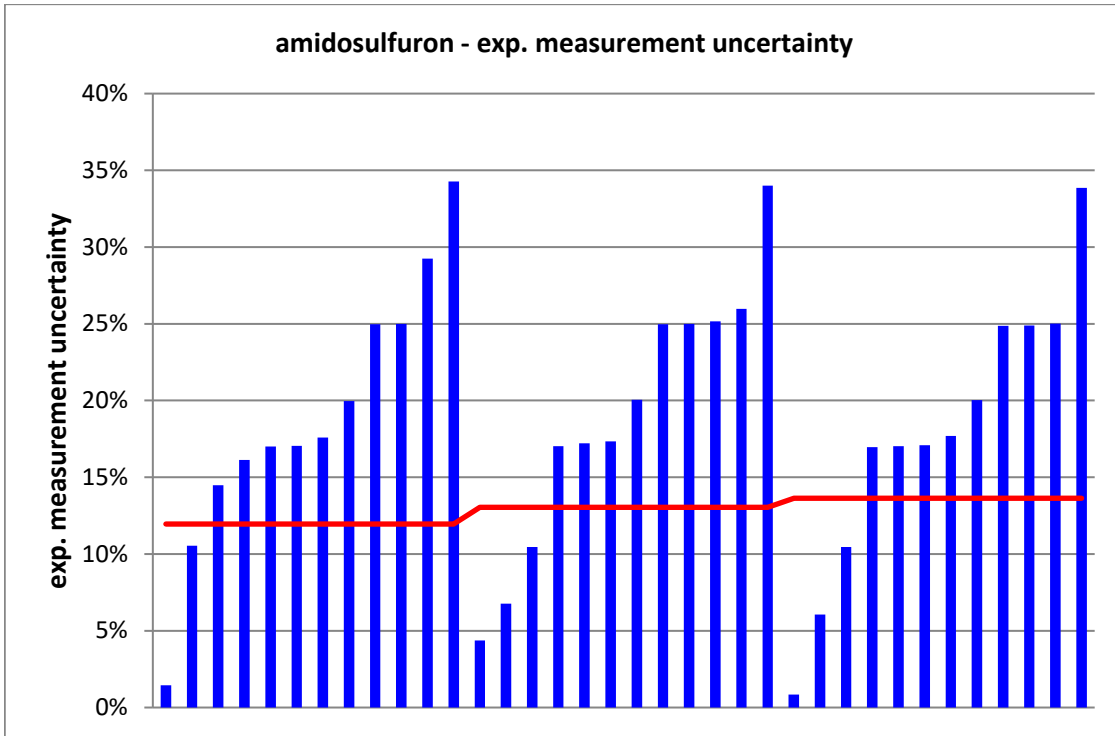
The relative standard deviation calculated with the Q-method did not reach the limits.



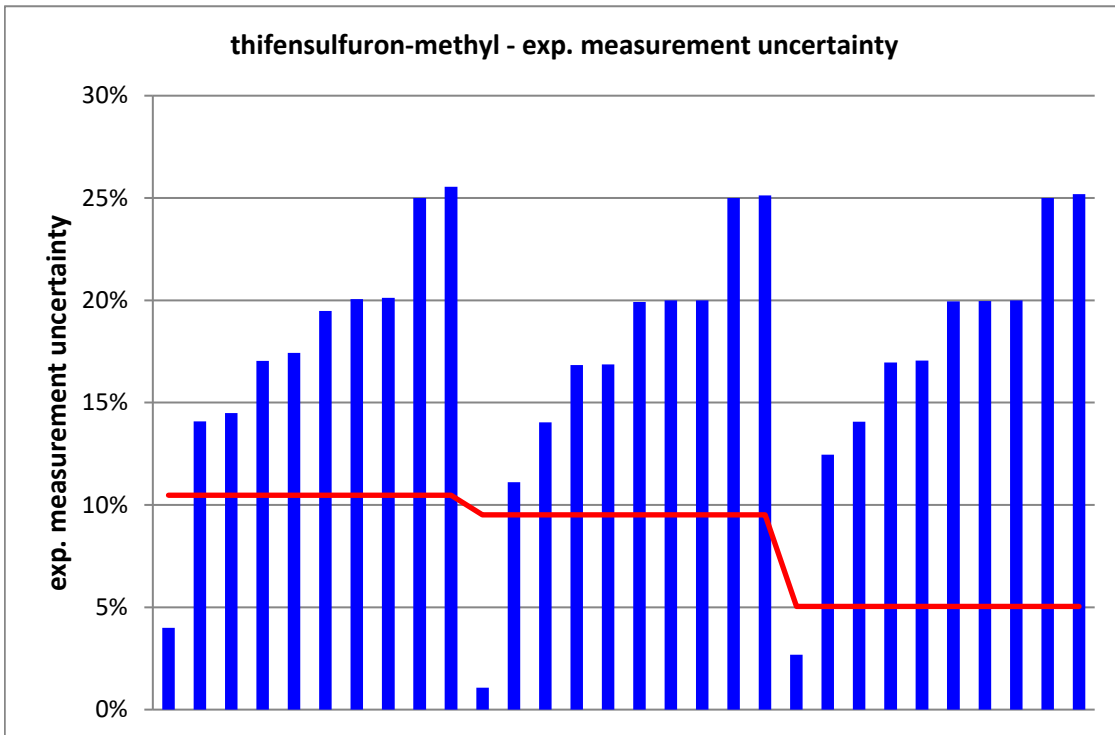
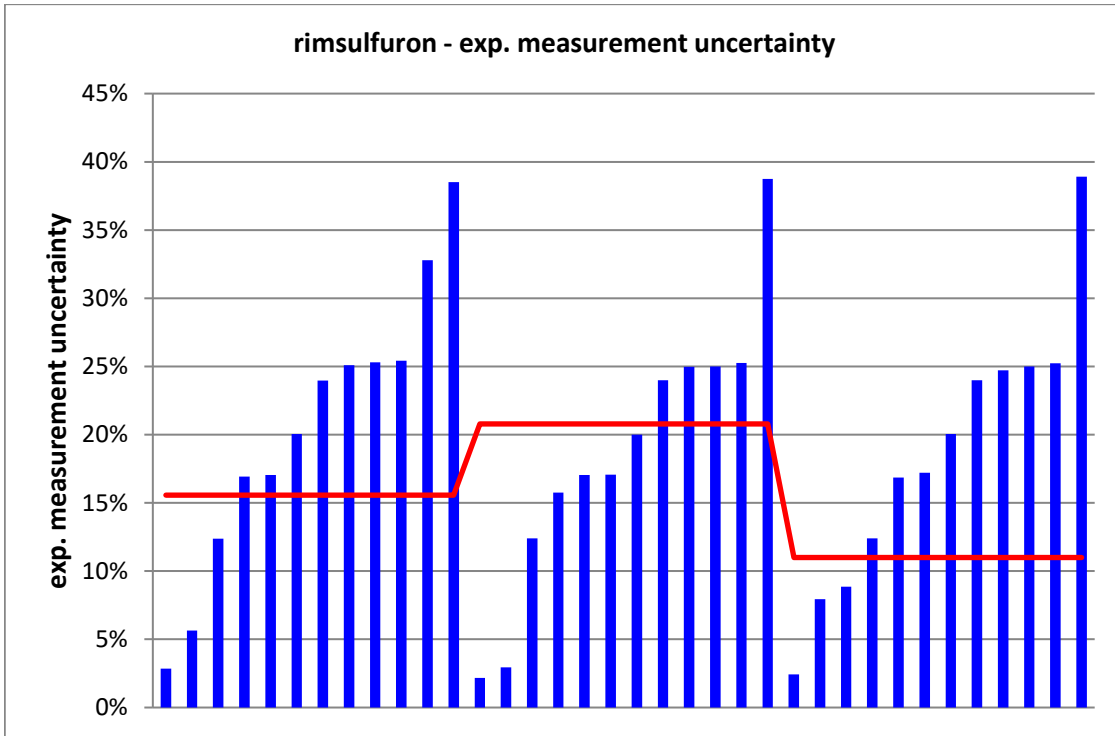
**Method specific evaluation**

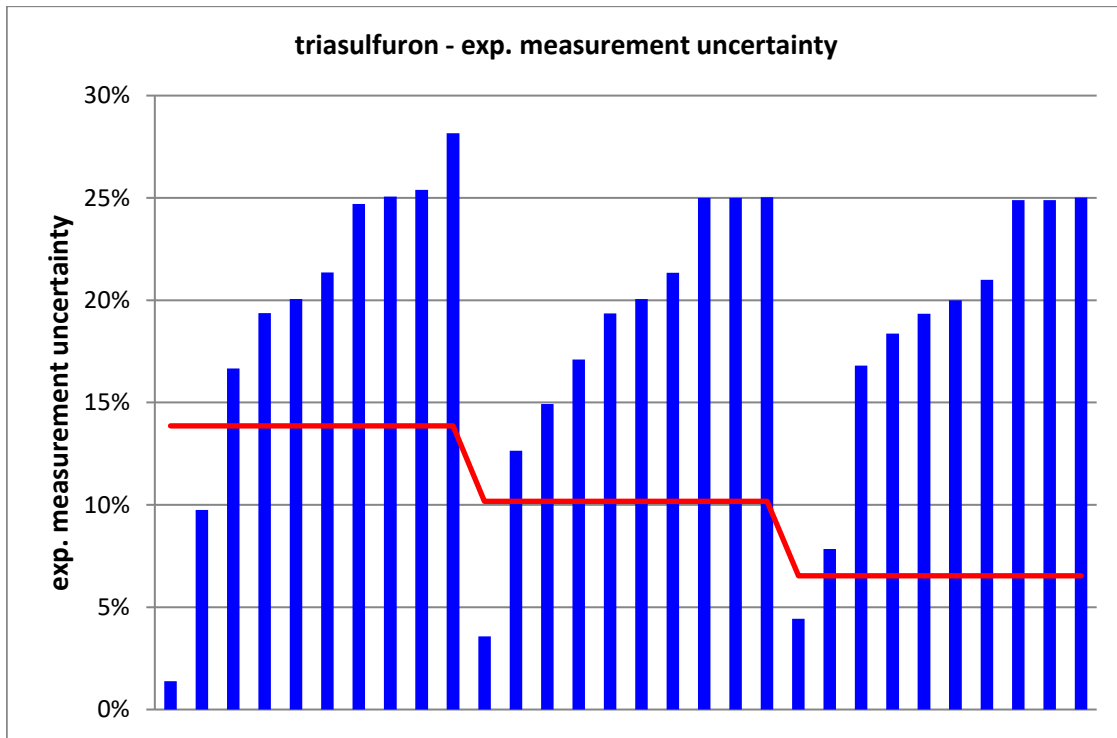


There is no method comparison, because almost all used HPLC-MS/MS - direct injection.





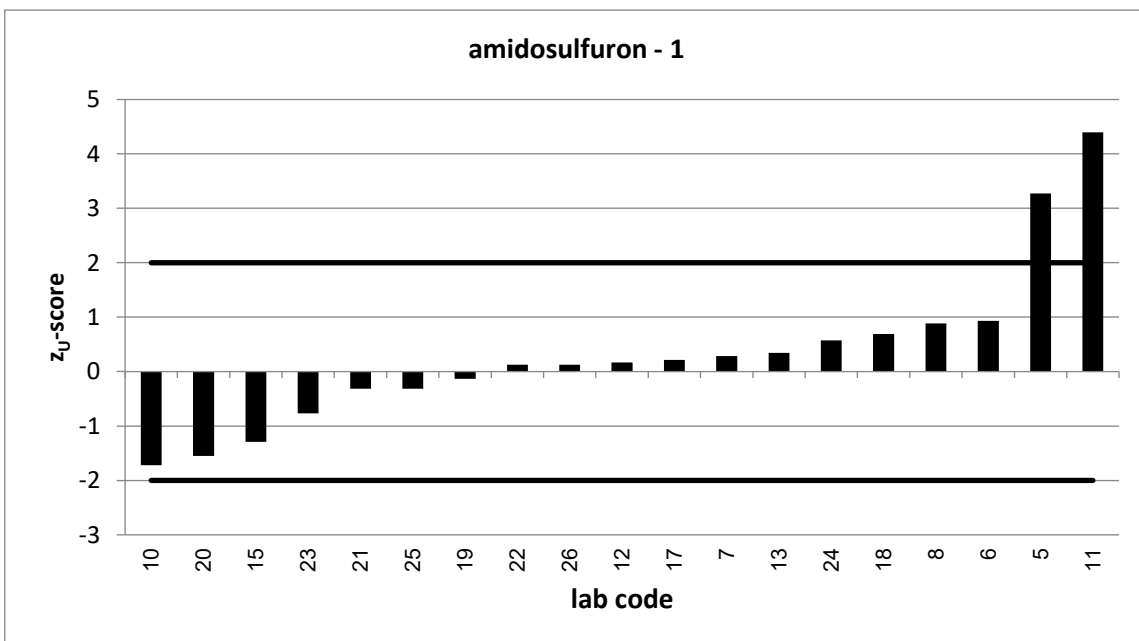
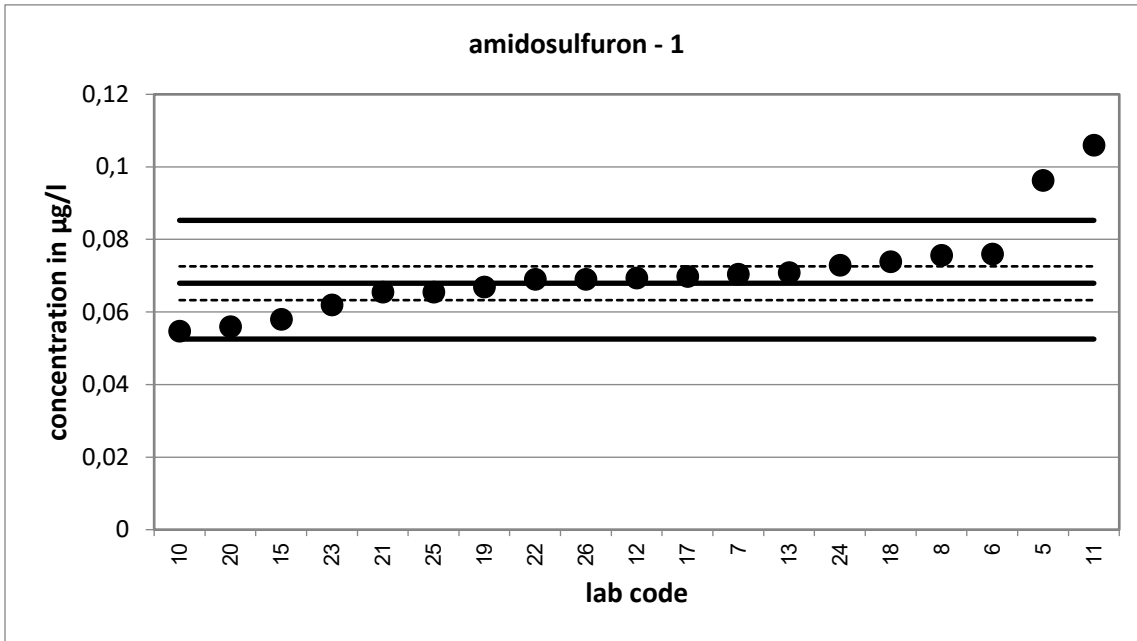


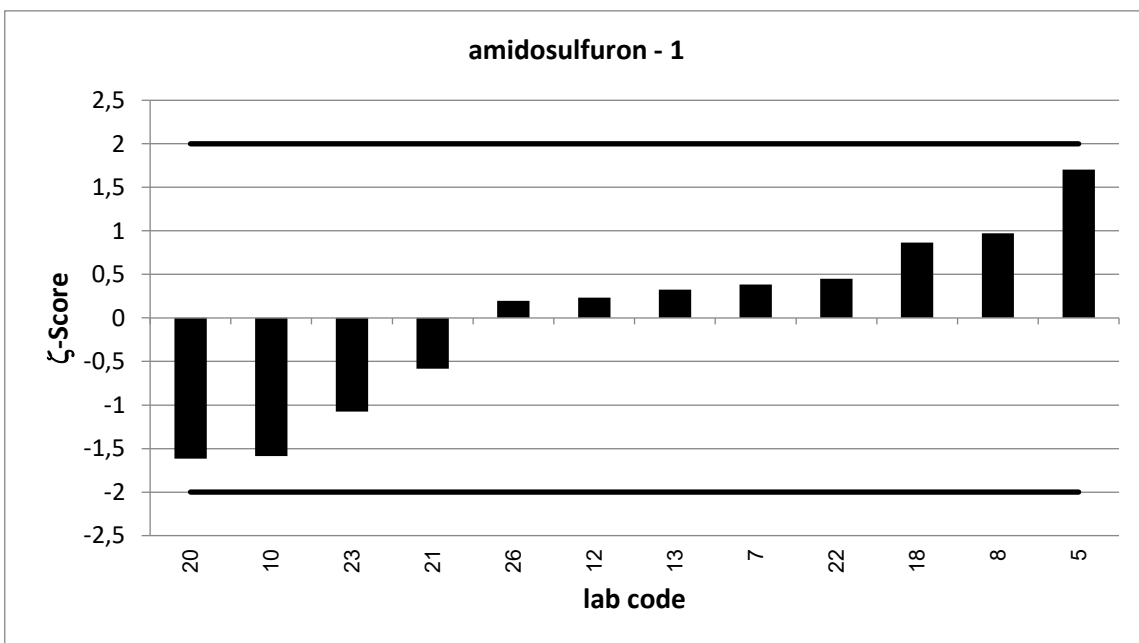
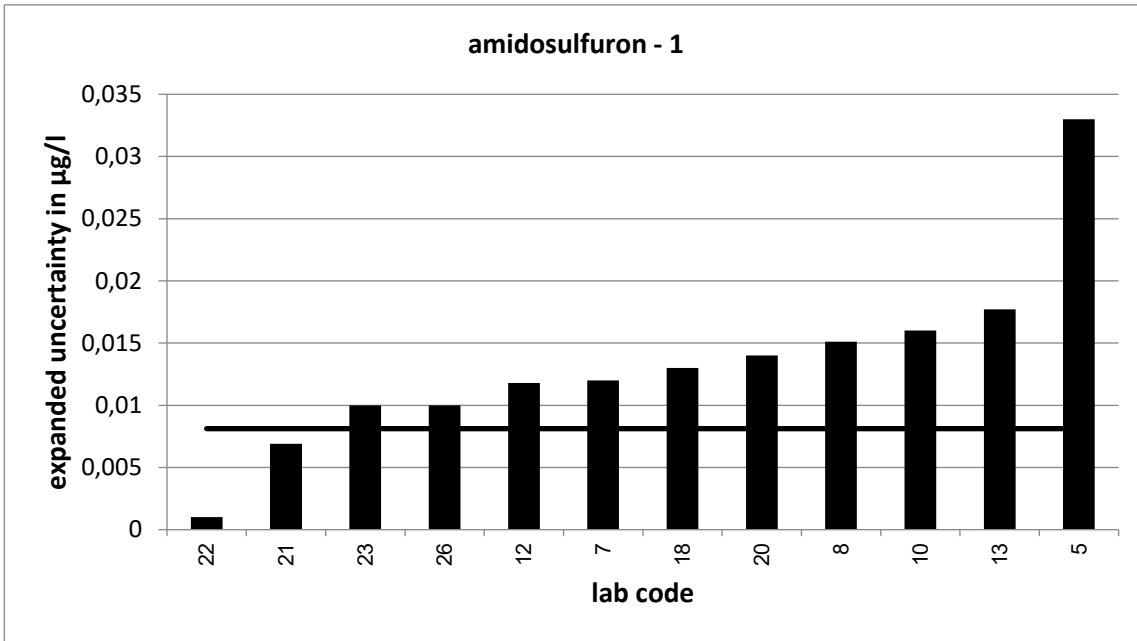


PT 7/21 - TW S5		amidosulfuron - 1			
assigned value [ $\mu\text{g/l}$ ]*		0,06792 $\pm$ 0,00466			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,08525			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,05254			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	z-score	Z <sub>U</sub> -score	assessm.**
5	0,0963	0,033	1,7	3,3	u
6	0,076			0,9	s
7	0,0704	0,012	0,4	0,3	s
8	0,0756	0,015	1,0	0,9	s
10	0,0547	0,016	-1,6	-1,7	s
11	0,106			4,4	u
12	0,0694	0,012	0,2	0,2	s
13	0,0709	0,018	0,3	0,3	s
15	0,058			-1,3	s
17	0,0698			0,2	s
18	0,0739	0,013	0,9	0,7	s
19	0,0669			-0,1	s
20	0,056	0,014	-1,6	-1,6	s
21	0,0655	0,007	-0,6	-0,3	s
22	0,069	0,001	0,5	0,1	s
23	0,062	0,01	-1,1	-0,8	s
24	0,0729			0,6	s
25	0,0655			-0,3	s
26	0,069	0,01	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

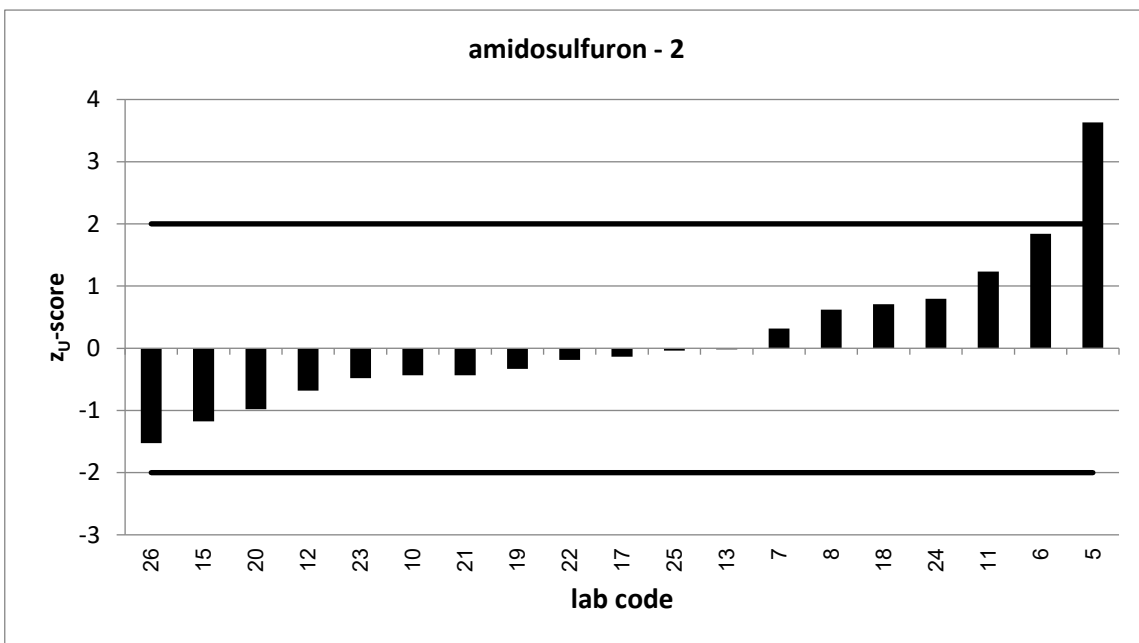
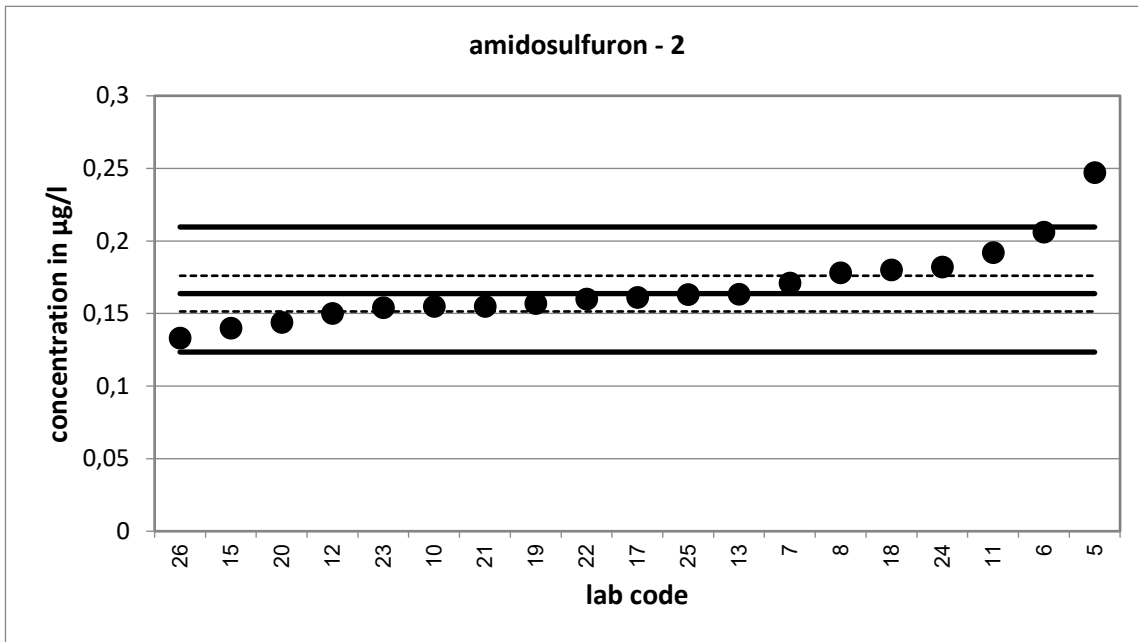


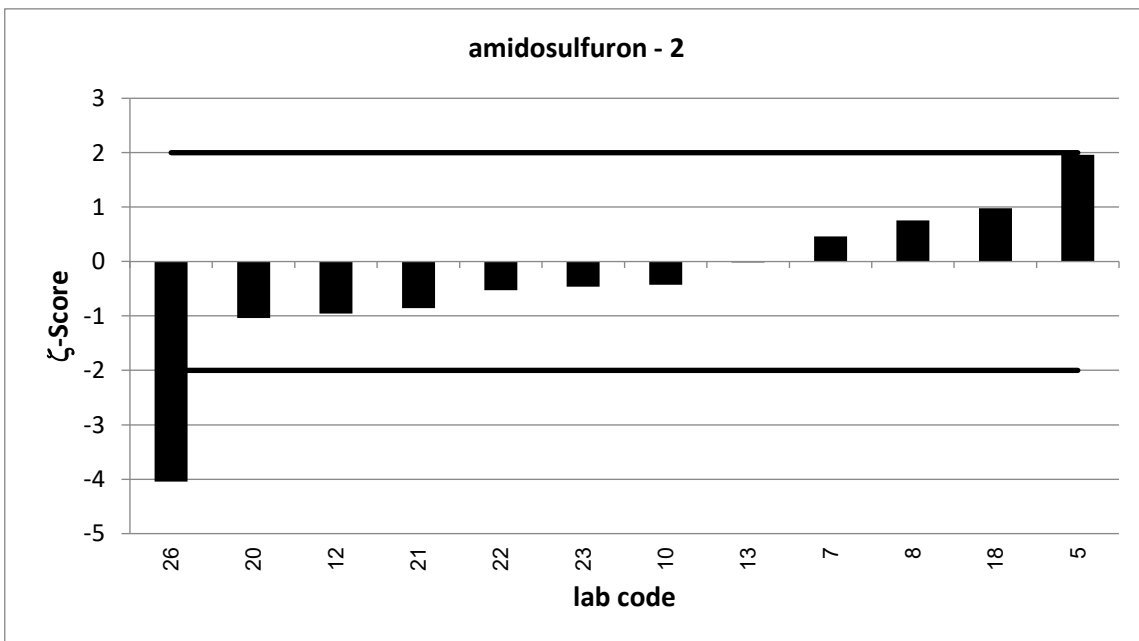
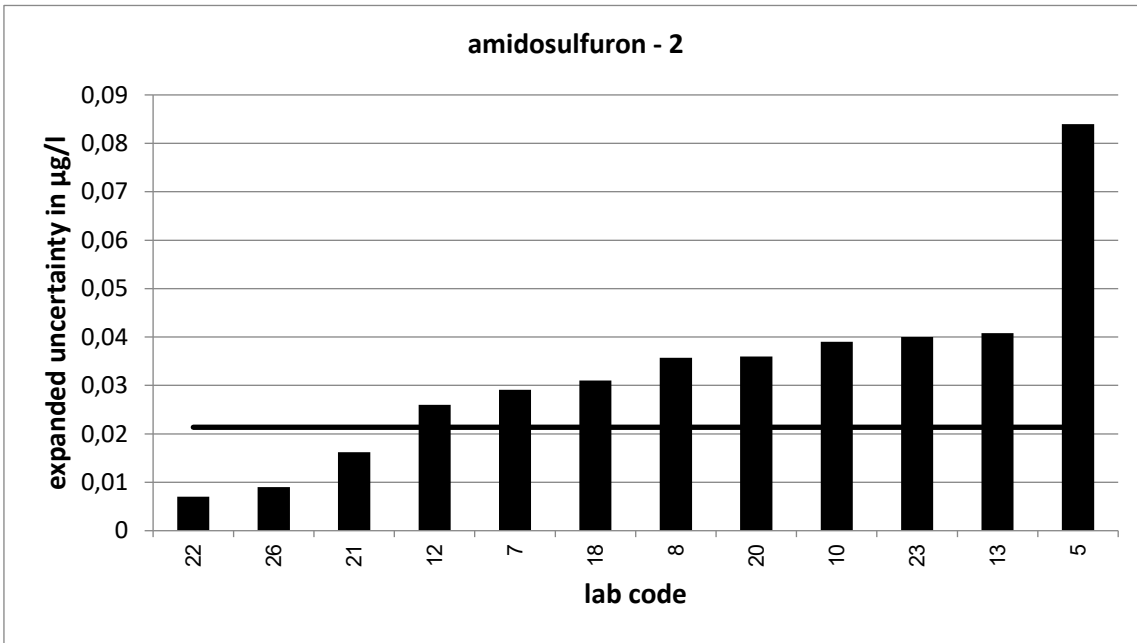


PT 7/21 - TW S5		amidosulfuron - 2			
assigned value [ $\mu\text{g/l}$ ]*		0,1637 $\pm$ 0,0123			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,2096			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,1234			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	z-score	Z <sub>U</sub> -score	assessm.**
5	0,247	0,084	2,0	3,6	u
6	0,206			1,8	s
7	0,171	0,029	0,5	0,3	s
8	0,178	0,036	0,8	0,6	s
10	0,155	0,039	-0,4	-0,4	s
11	0,192			1,2	s
12	0,15	0,026	-1,0	-0,7	s
13	0,1634	0,041	0,0	0,0	s
15	0,14			-1,2	s
17	0,161			-0,1	s
18	0,18	0,031	1,0	0,7	s
19	0,157			-0,3	s
20	0,144	0,036	-1,0	-1,0	s
21	0,155	0,016	-0,9	-0,4	s
22	0,16	0,007	-0,5	-0,2	s
23	0,154	0,04	-0,5	-0,5	s
24	0,182			0,8	s
25	0,163			0,0	s
26	0,133	0,009	-4,0	-1,5	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



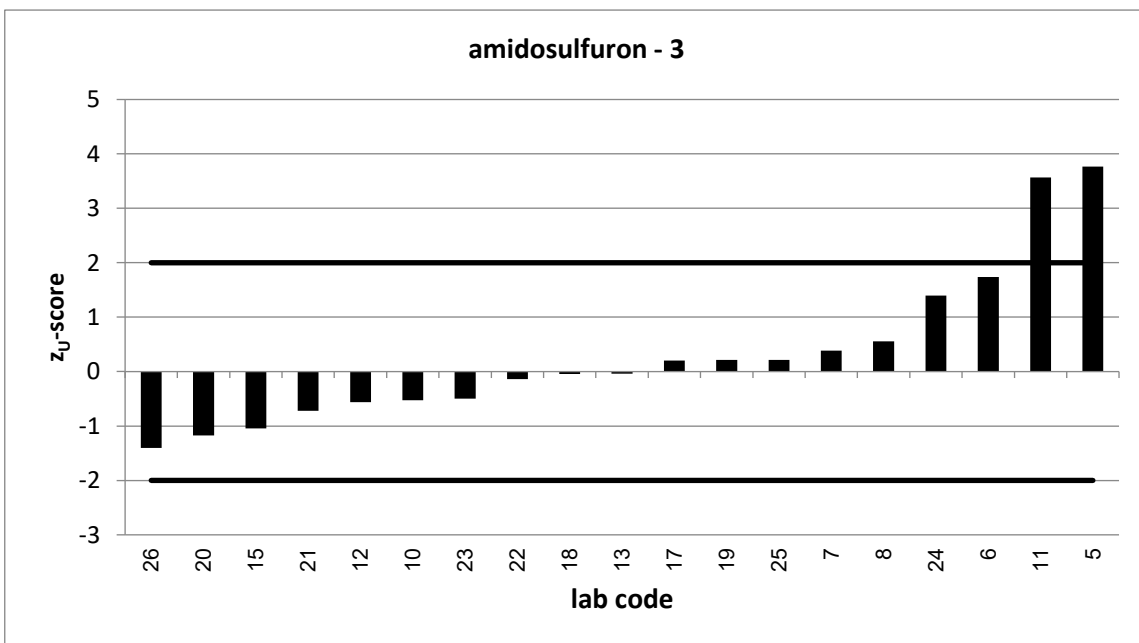
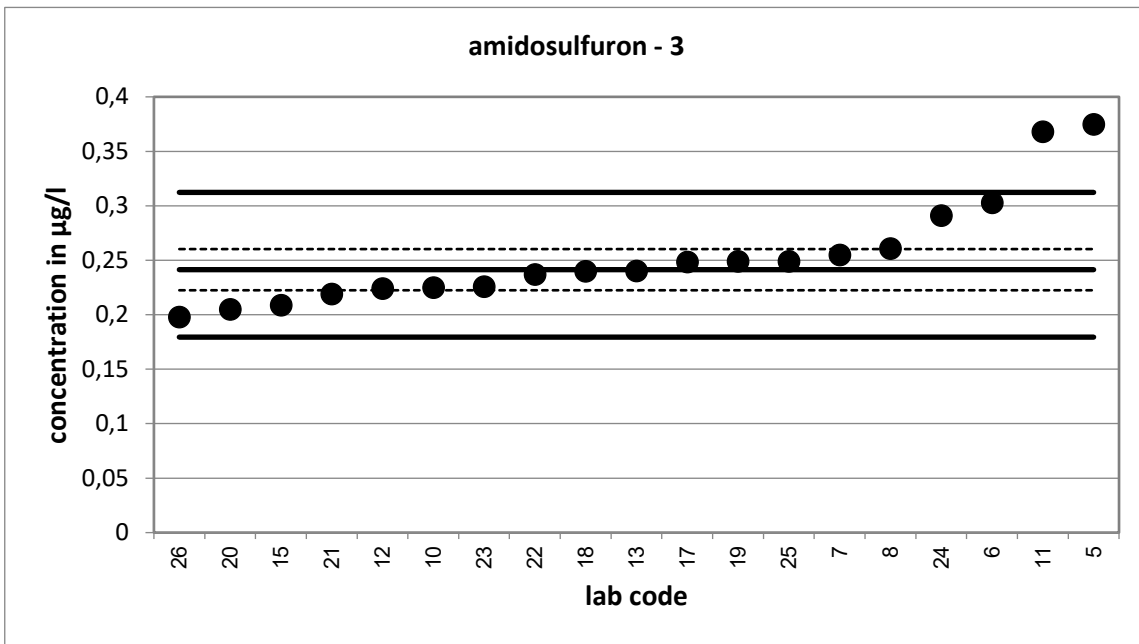


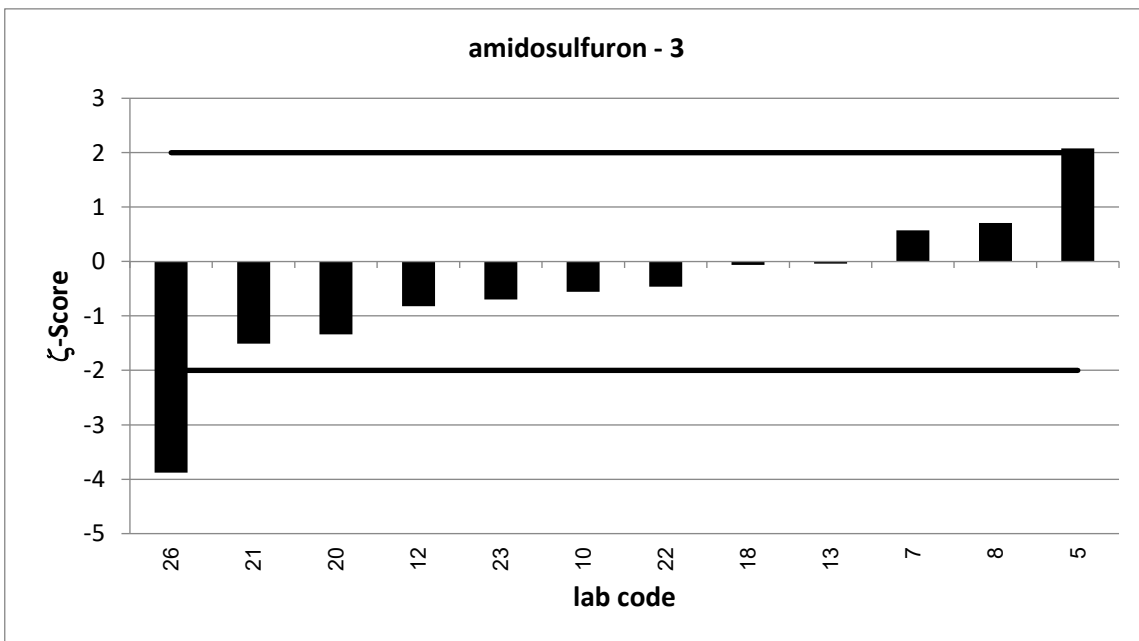
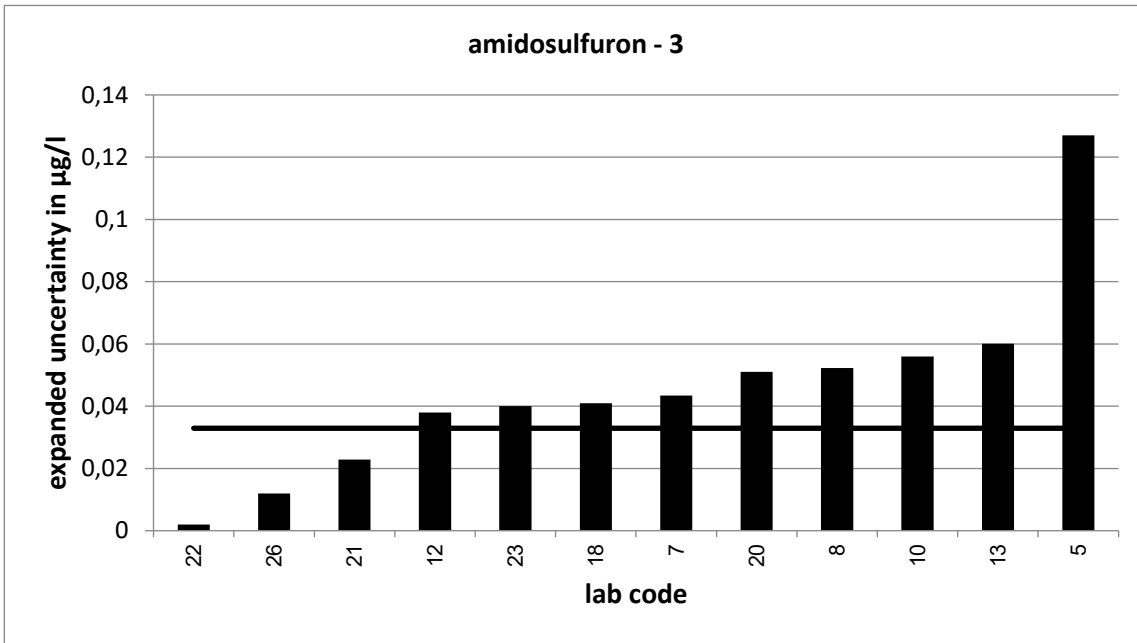


PT 7/21 - TW S5		amidosulfuron - 3			
assigned value [ $\mu\text{g/l}$ ]*		0,2414 $\pm$ 0,0189			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,3123			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,1794			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	z-score	Z <sub>U</sub> -score	assessm.**
5	0,375	0,127	2,1	3,8	u
6	0,303			1,7	s
7	0,255	0,043	0,6	0,4	s
8	0,261	0,052	0,7	0,6	s
10	0,225	0,056	-0,6	-0,5	s
11	0,368			3,6	u
12	0,224	0,038	-0,8	-0,6	s
13	0,2402	0,06	0,0	0,0	s
15	0,209			-1,0	s
17	0,2486			0,2	s
18	0,24	0,041	-0,1	0,0	s
19	0,249			0,2	s
20	0,205	0,051	-1,3	-1,2	s
21	0,219	0,023	-1,5	-0,7	s
22	0,237	0,002	-0,5	-0,1	s
23	0,226	0,04	-0,7	-0,5	s
24	0,291			1,4	s
25	0,249			0,2	s
26	0,198	0,012	-3,9	-1,4	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

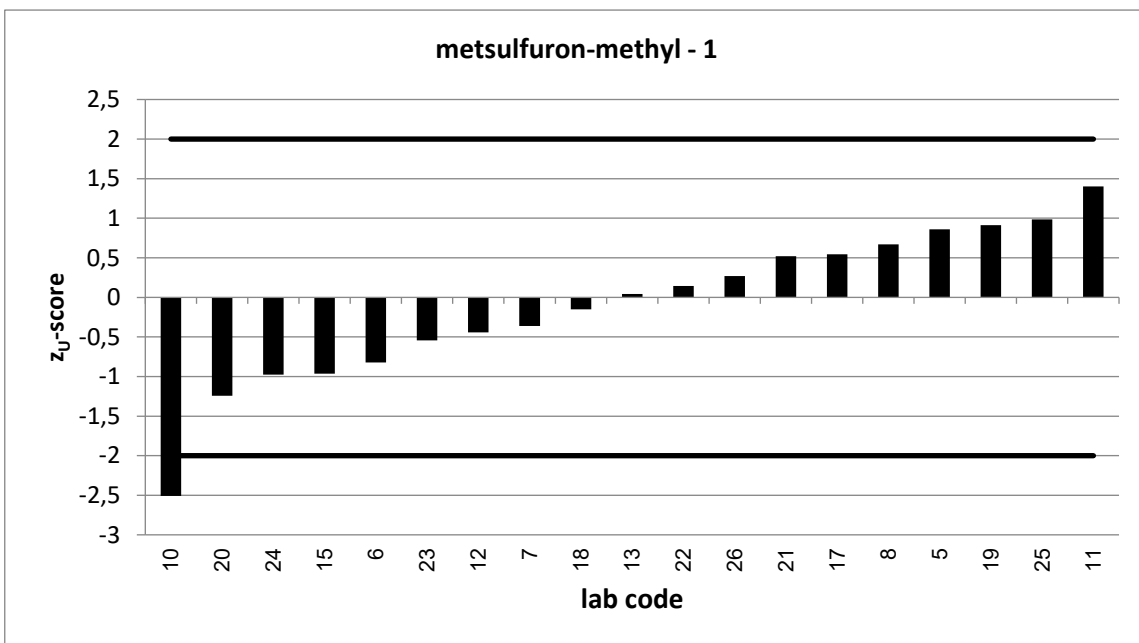
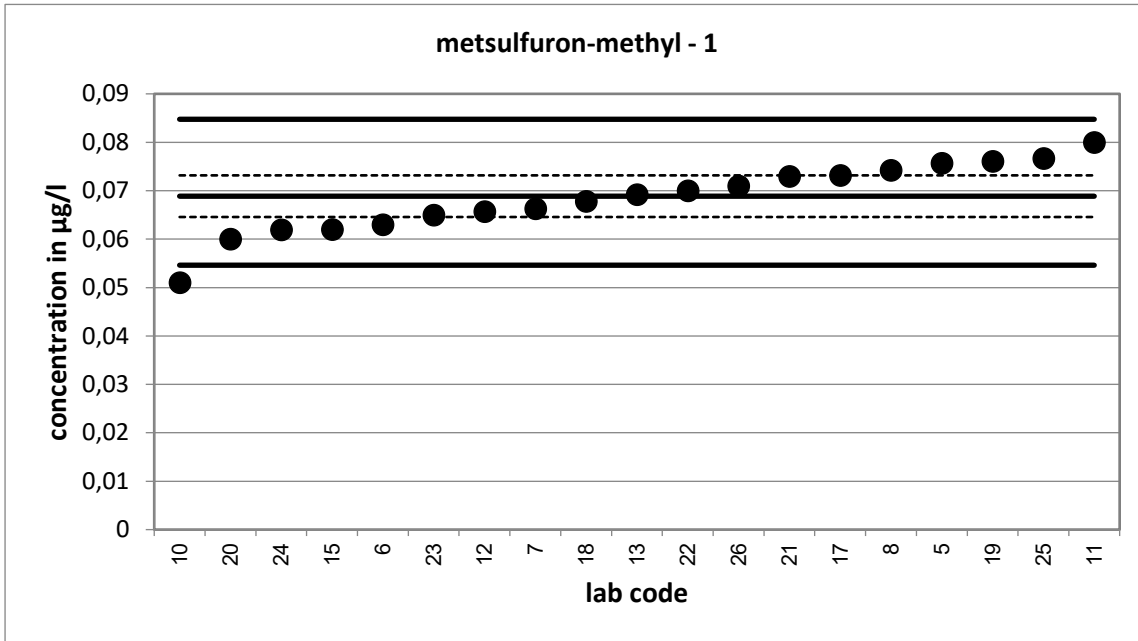


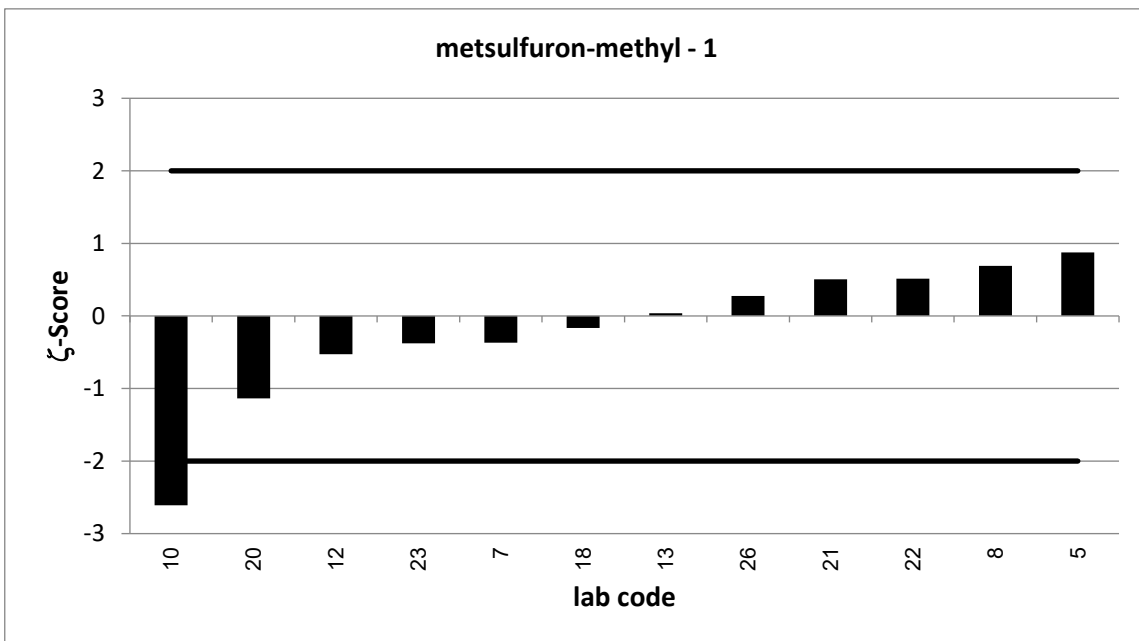
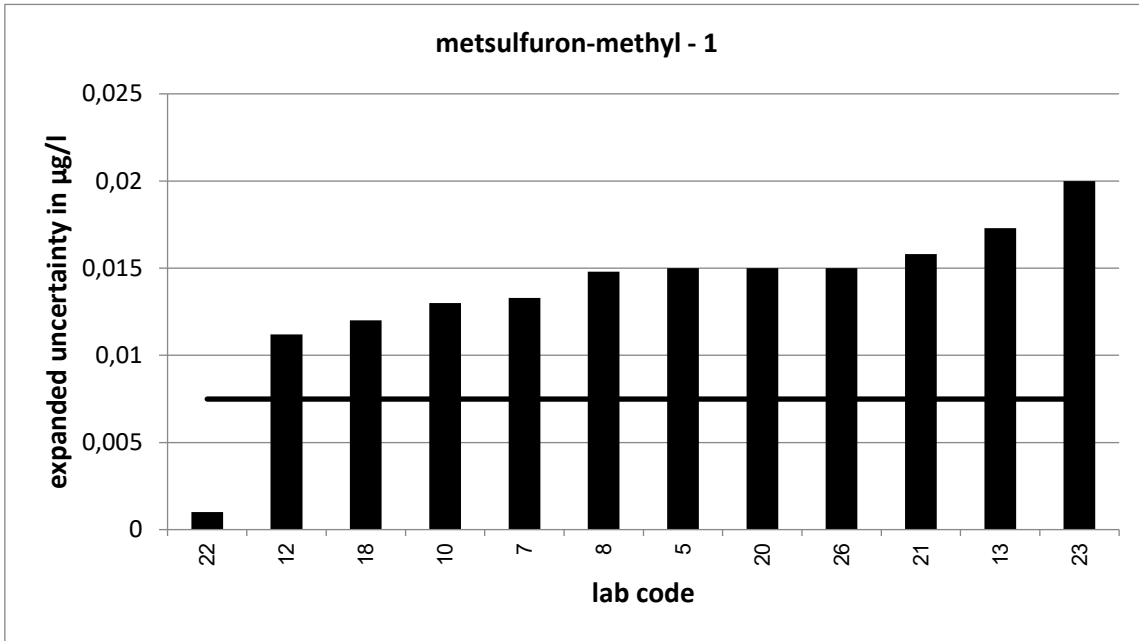


PT 7/21 - TW S5		metsulfuron-methyl - 1			
assigned value [ $\mu\text{g/l}$ ]*		0,06887 $\pm$ 0,0043			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,08475			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,05461			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	z-score	Z <sub>U</sub> -score	assessm.**
5	0,0757	0,015	0,9	0,9	s
6	0,063			-0,8	s
7	0,0663	0,013	-0,4	-0,4	s
8	0,0742	0,015	0,7	0,7	s
10	0,051	0,013	-2,6	-2,5	q
11	0,08			1,4	s
12	0,0657	0,011	-0,5	-0,4	s
13	0,0692	0,017	0,0	0,0	s
15	0,062			-1,0	s
17	0,0732			0,5	s
18	0,0678	0,012	-0,2	-0,1	s
19	0,0761			0,9	s
20	0,06	0,015	-1,1	-1,2	s
21	0,073	0,016	0,5	0,5	s
22	0,07	0,001	0,5	0,1	s
23	0,065	0,02	-0,4	-0,5	s
24	0,0619			-1,0	s
25	0,0767			1,0	s
26	0,071	0,015	0,3	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

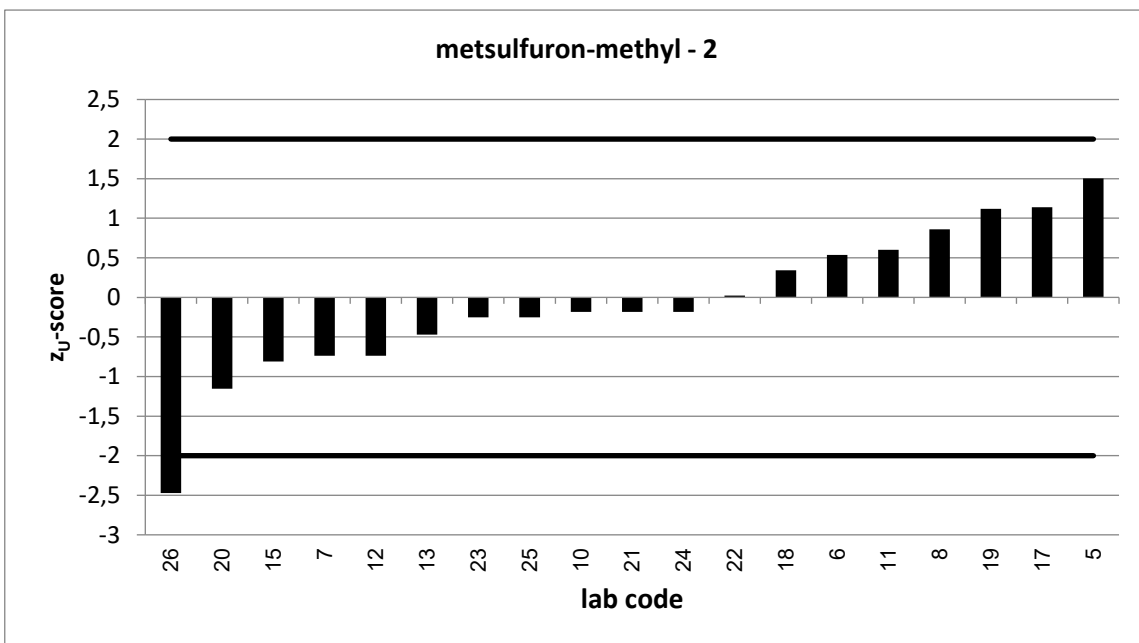
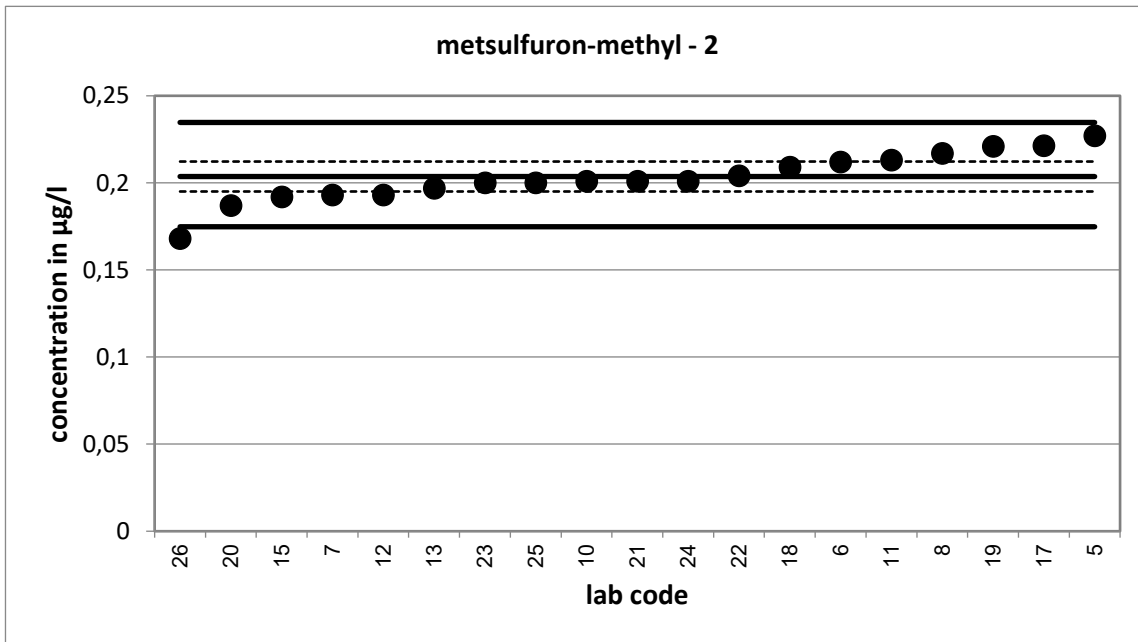




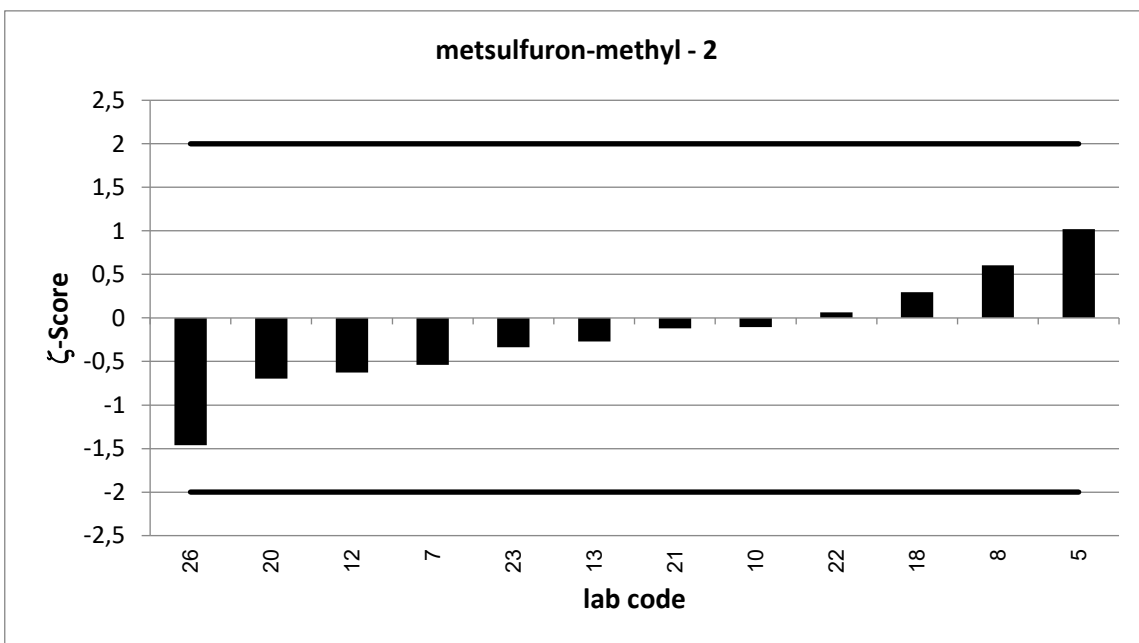
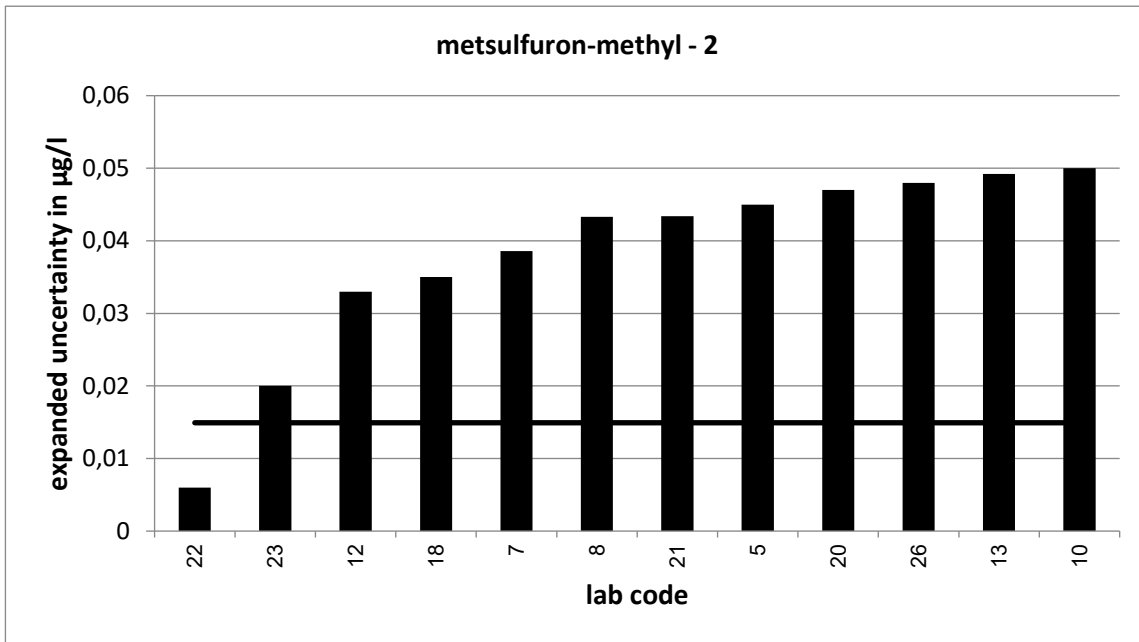
PT 7/21 - TW S5		metsulfuron-methyl - 2			
assigned value [ $\mu\text{g/l}$ ]*		0,2037 $\pm$ 0,0086			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,2347			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,1748			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	z-score	Z <sub>U</sub> -score	assessm.**
5	0,227	0,045	1,0	1,5	s
6	0,212			0,5	s
7	0,193	0,039	-0,5	-0,7	s
8	0,217	0,043	0,6	0,9	s
10	0,201	0,05	-0,1	-0,2	s
11	0,213			0,6	s
12	0,193	0,033	-0,6	-0,7	s
13	0,1969	0,049	-0,3	-0,5	s
15	0,192			-0,8	s
17	0,2213			1,1	s
18	0,209	0,035	0,3	0,3	s
19	0,221			1,1	s
20	0,187	0,047	-0,7	-1,2	s
21	0,201	0,043	-0,1	-0,2	s
22	0,204	0,006	0,1	0,0	s
23	0,2	0,02	-0,3	-0,3	s
24	0,201			-0,2	s
25	0,2			-0,3	s
26	0,168	0,048	-1,5	-2,5	q

\* 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



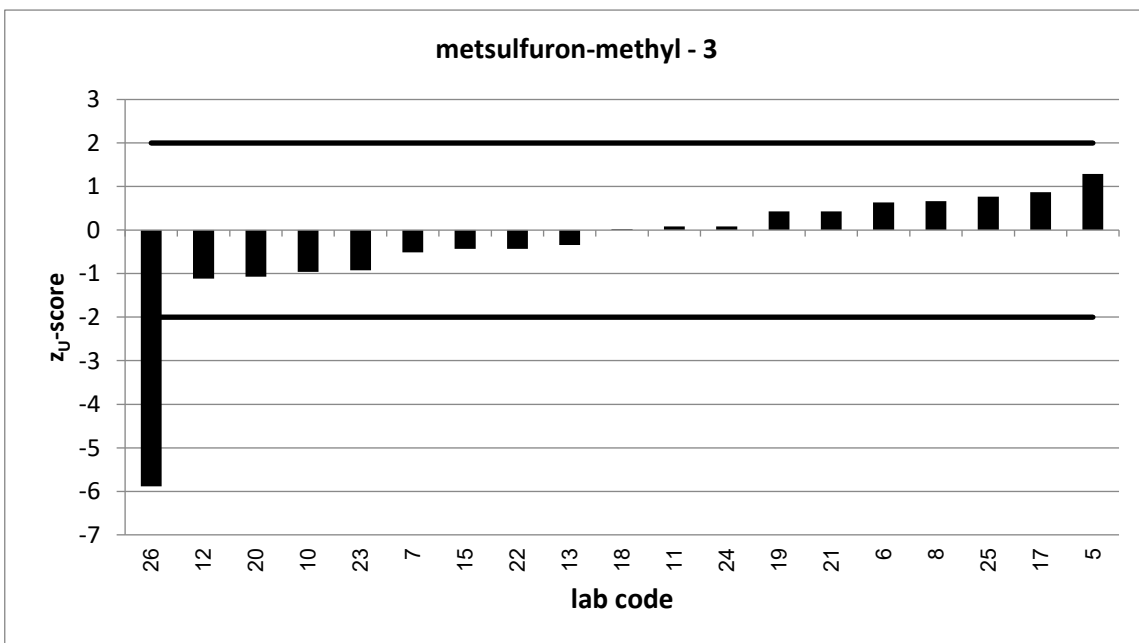
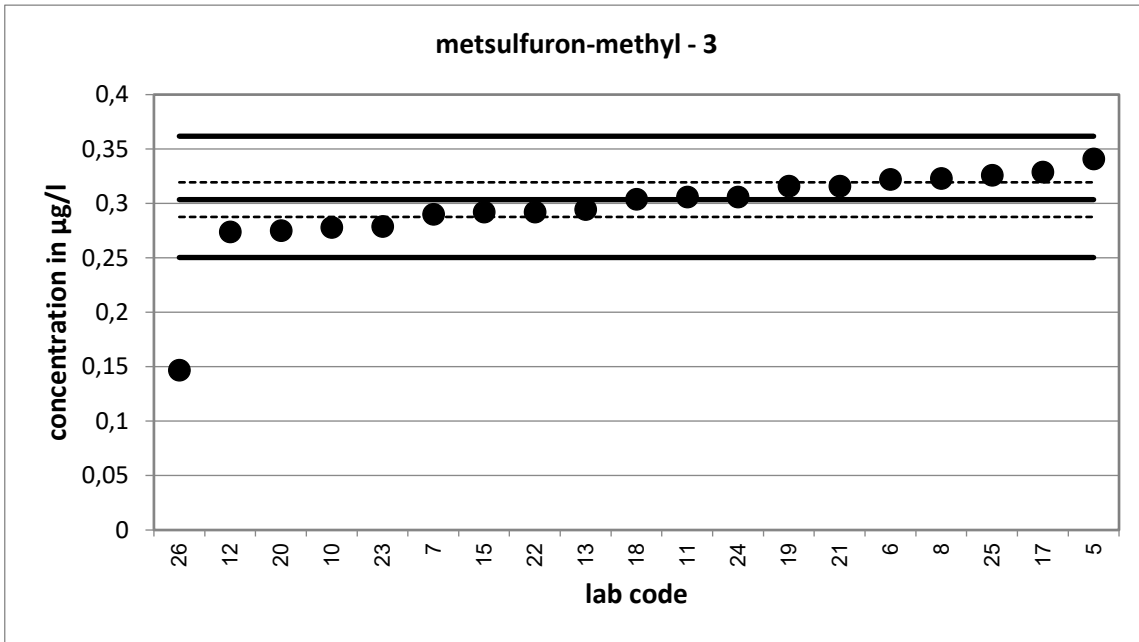


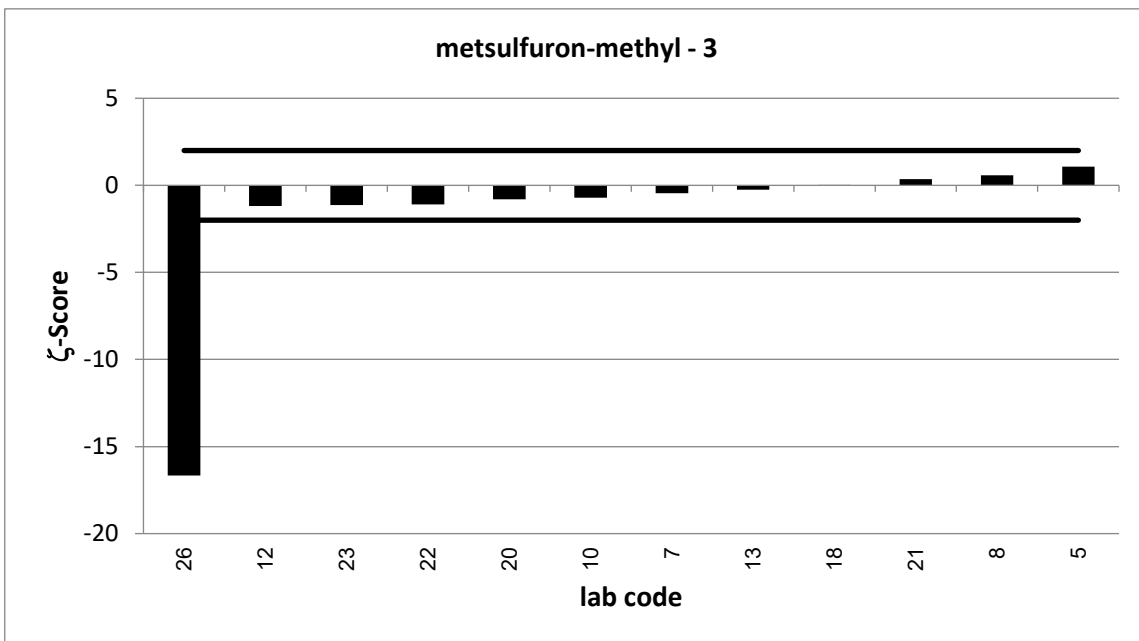
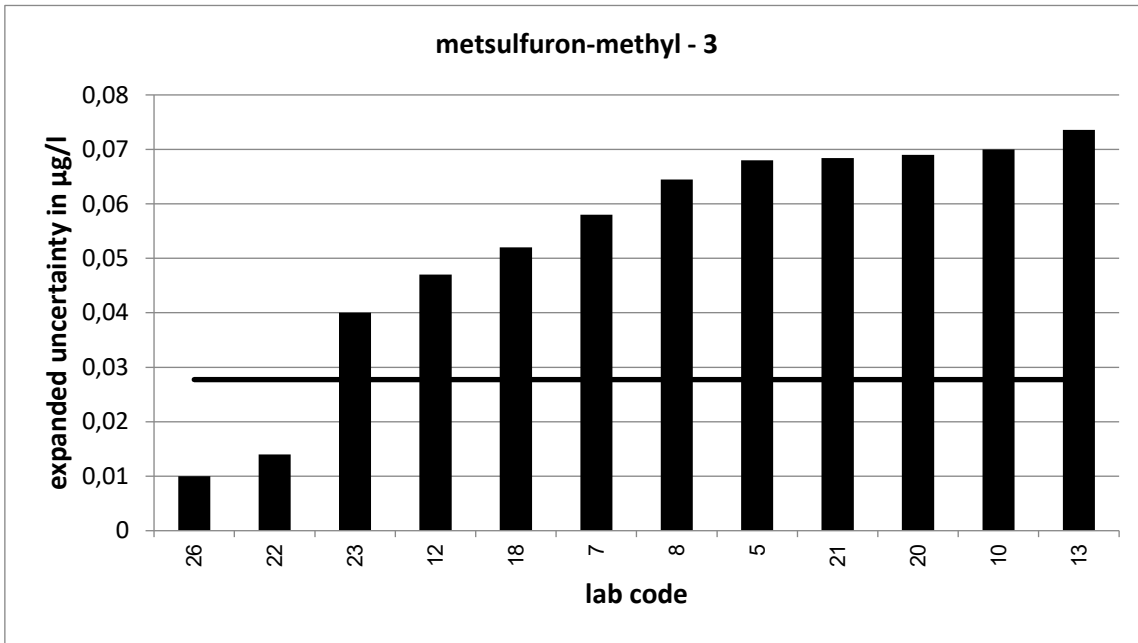


PT 7/21 - TW S5		metsulfuron-methyl - 3			
assigned value [ $\mu\text{g/l}$ ]*		0,3035 $\pm$ 0,0159			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,3618			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,2504			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	z-score	Z <sub>U</sub> -score	assessm.**
5	0,341	0,068	1,1	1,3	s
6	0,322			0,6	s
7	0,29	0,058	-0,4	-0,5	s
8	0,323	0,065	0,6	0,7	s
10	0,278	0,07	-0,7	-1,0	s
11	0,306			0,1	s
12	0,274	0,047	-1,2	-1,1	s
13	0,2945	0,074	-0,2	-0,3	s
15	0,292			-0,4	s
17	0,329			0,9	s
18	0,304	0,052	0,0	0,0	s
19	0,316			0,4	s
20	0,275	0,069	-0,8	-1,1	s
21	0,316	0,068	0,4	0,4	s
22	0,292	0,014	-1,1	-0,4	s
23	0,279	0,04	-1,1	-0,9	s
24	0,306			0,1	s
25	0,326			0,8	s
26	0,147	0,01	-16,7	-5,9	u

\* 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

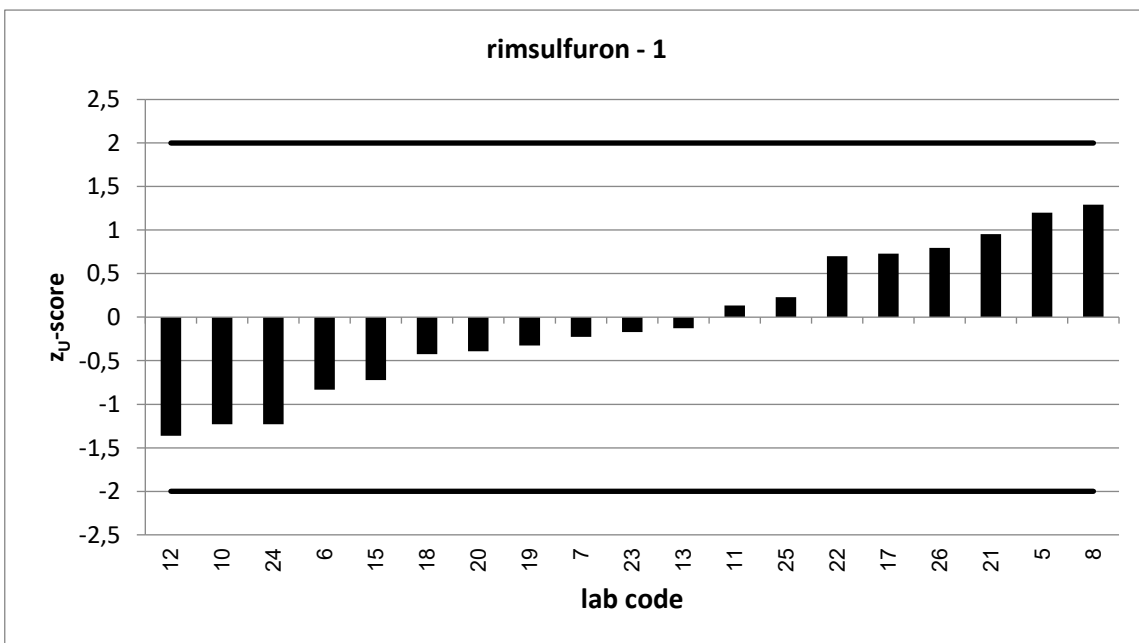
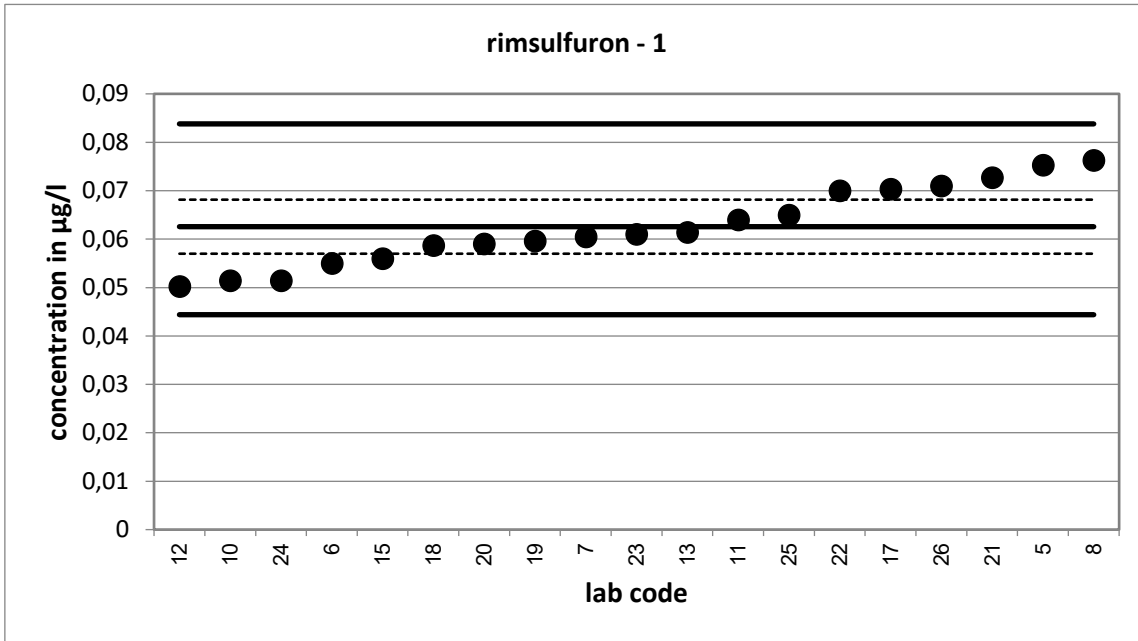


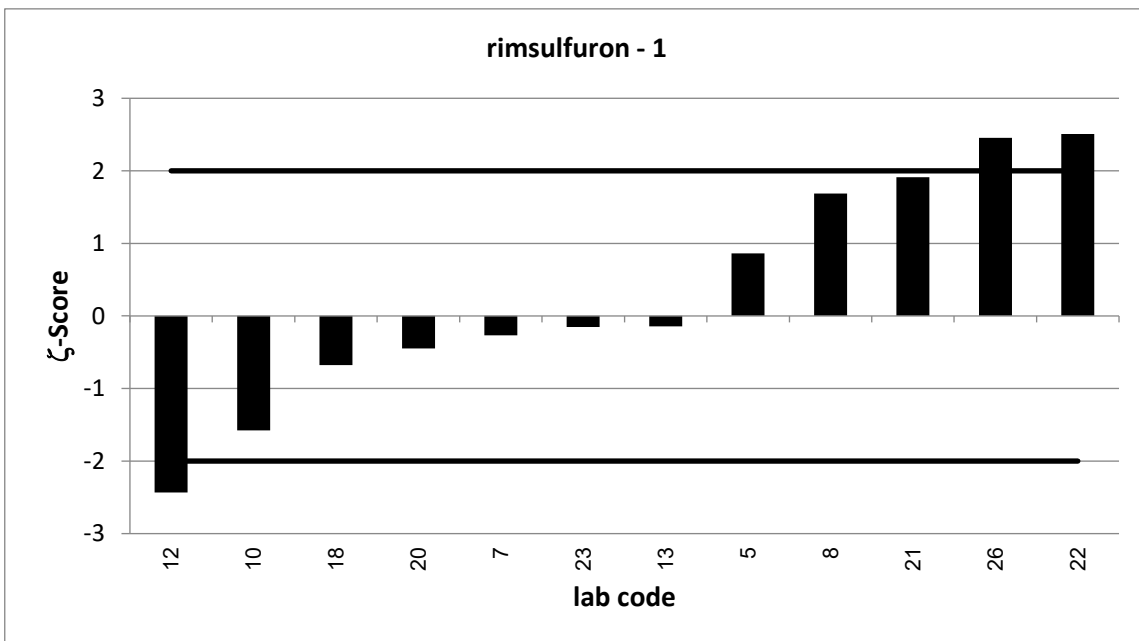
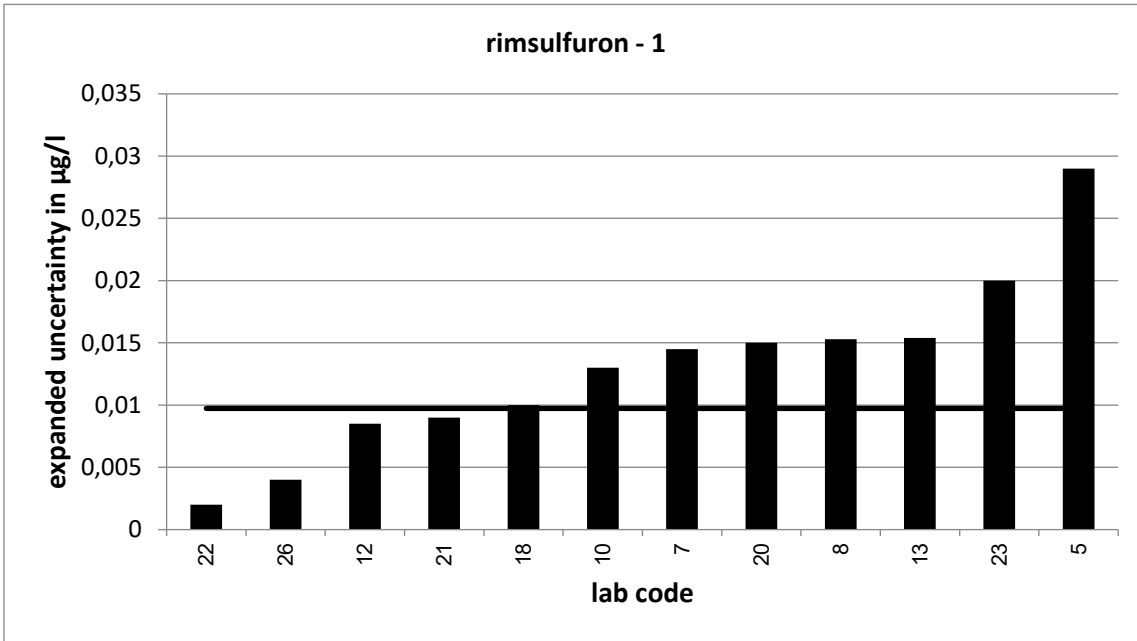


PT 7/21 - TW S5		rimsulfuron - 1			
assigned value [ $\mu\text{g/l}$ ]*		0,06257 $\pm$ 0,00558			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,0838			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,04439			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	z-score	Z <sub>U</sub> -score	assessm.**
5	0,0753	0,029	0,9	1,2	s
6	0,055			-0,8	s
7	0,0605	0,015	-0,3	-0,2	s
8	0,0763	0,015	1,7	1,3	s
10	0,0514	0,013	-1,6	-1,2	s
11	0,064			0,1	s
12	0,0502	0,009	-2,4	-1,4	s
13	0,0614	0,015	-0,1	-0,1	s
15	0,056			-0,7	s
17	0,0703			0,7	s
18	0,0587	0,01	-0,7	-0,4	s
19	0,0596			-0,3	s
20	0,059	0,015	-0,4	-0,4	s
21	0,0727	0,009	1,9	1,0	s
22	0,07	0,002	2,5	0,7	s
23	0,061	0,02	-0,2	-0,2	s
24	0,0514			-1,2	s
25	0,065			0,2	s
26	0,071	0,004	2,5	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



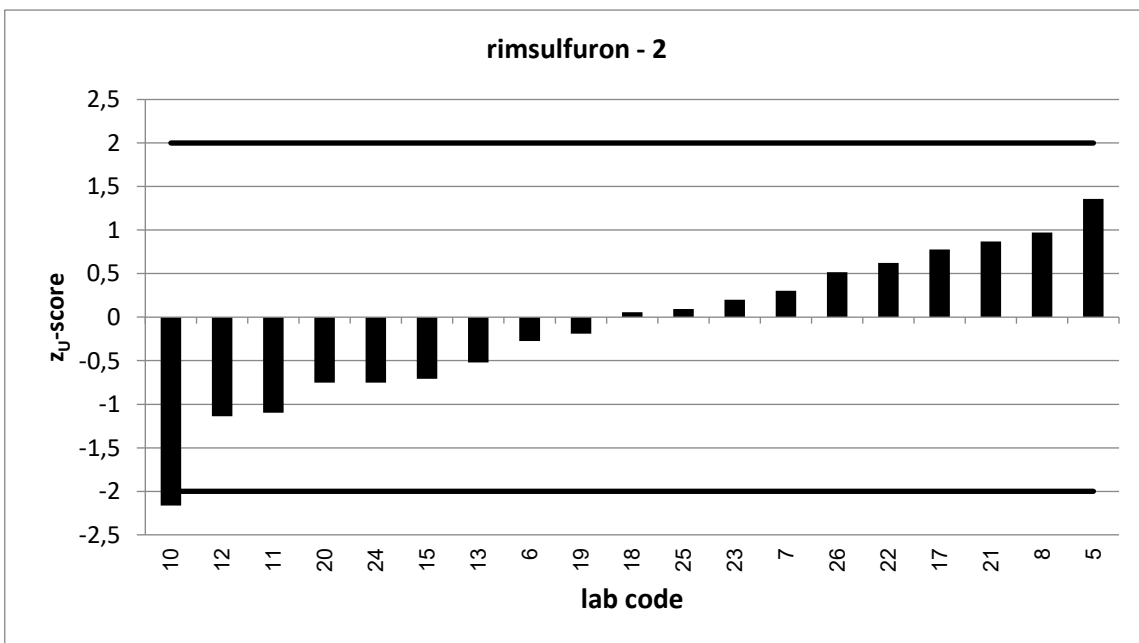
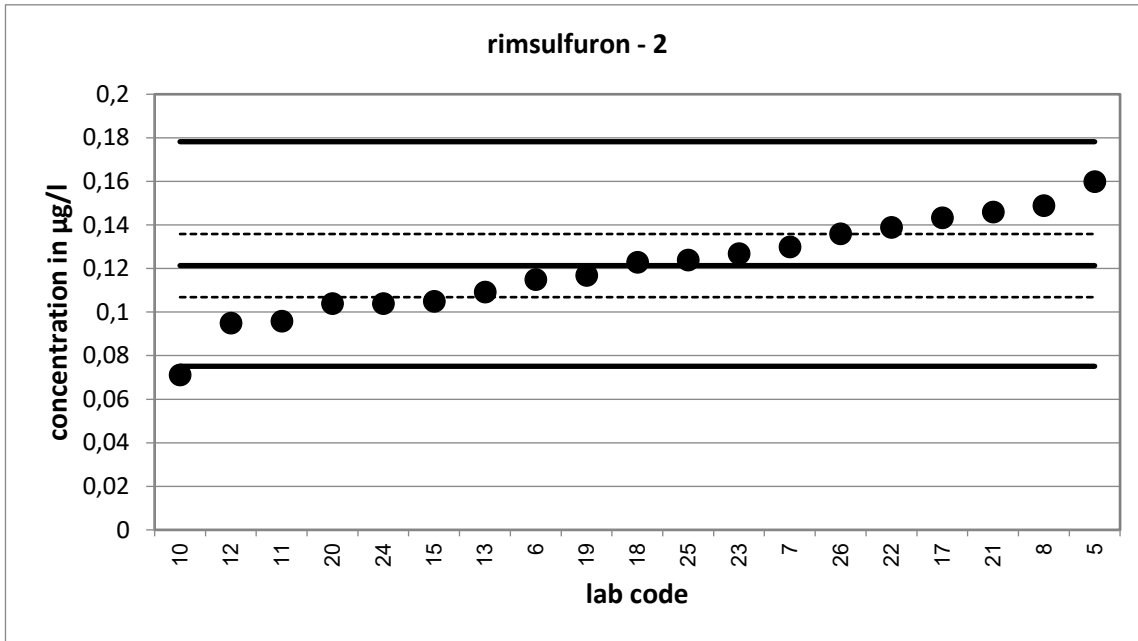


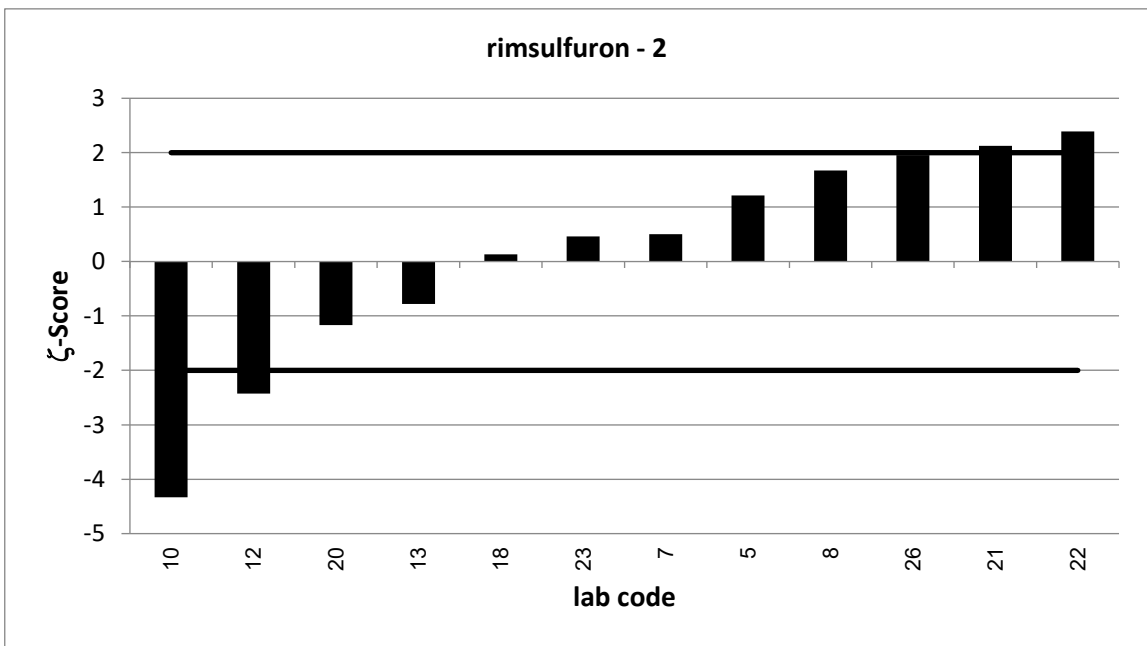
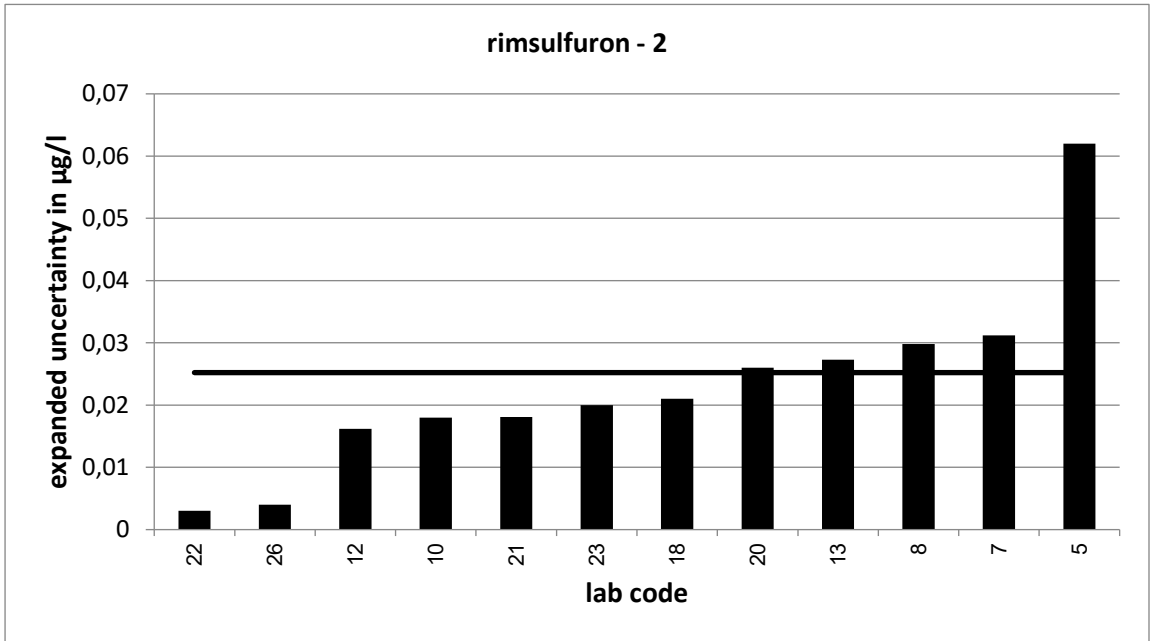
PT 7/21 - TW S5		rimsulfuron - 2			
assigned value [ $\mu\text{g/l}$ ]*		0,1213 $\pm$ 0,0145			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,1782			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,07511			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	z-score	Z <sub>U</sub> -score	assessm.**
5	0,16	0,062	1,2	1,4	s
6	0,115			-0,3	s
7	0,13	0,031	0,5	0,3	s
8	0,149	0,03	1,7	1,0	s
10	0,0713	0,018	-4,3	-2,2	q
11	0,096			-1,1	s
12	0,095	0,016	-2,4	-1,1	s
13	0,1093	0,027	-0,8	-0,5	s
15	0,105			-0,7	s
17	0,1434			0,8	s
18	0,123	0,021	0,1	0,1	s
19	0,117			-0,2	s
20	0,104	0,026	-1,2	-0,8	s
21	0,146	0,018	2,1	0,9	s
22	0,139	0,003	2,4	0,6	s
23	0,127	0,02	0,5	0,2	s
24	0,104			-0,8	s
25	0,124			0,1	s
26	0,136	0,004	2,0	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



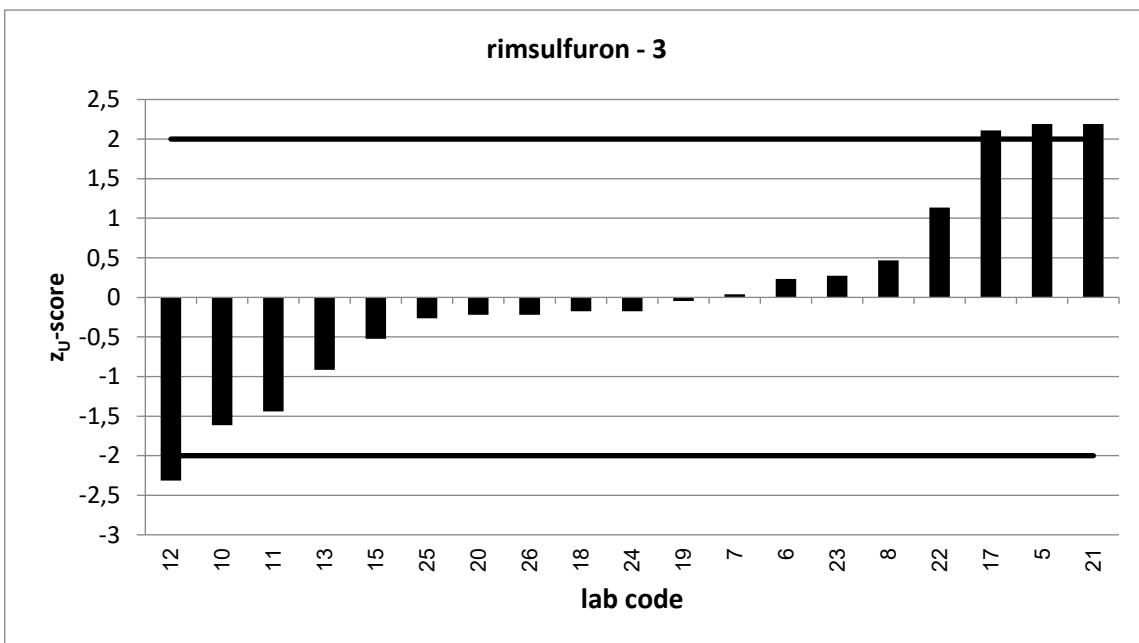
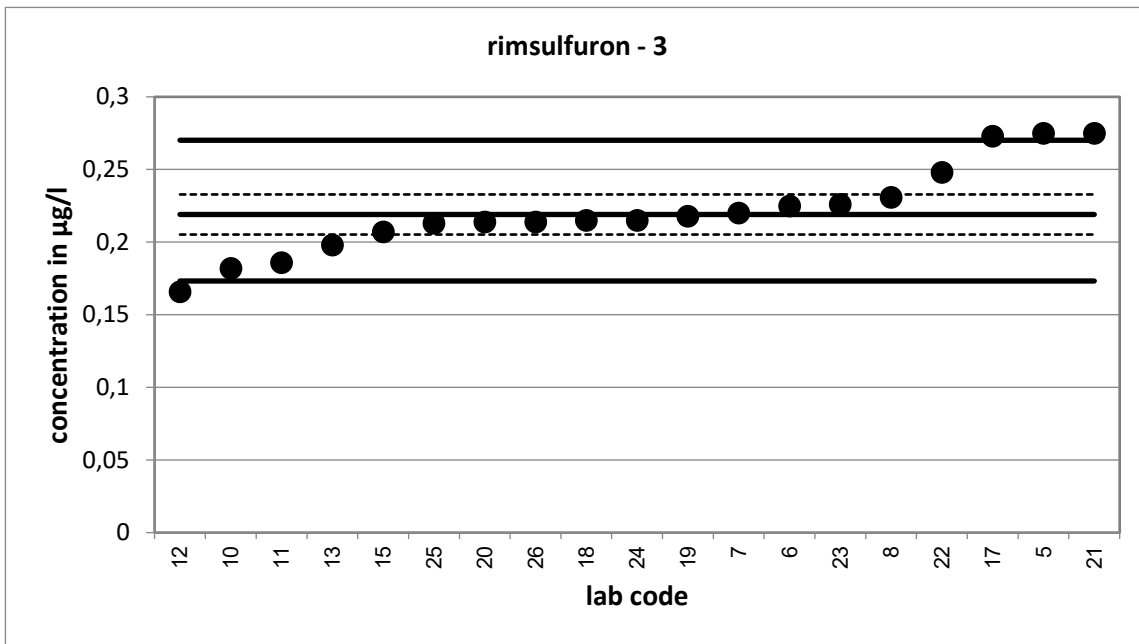


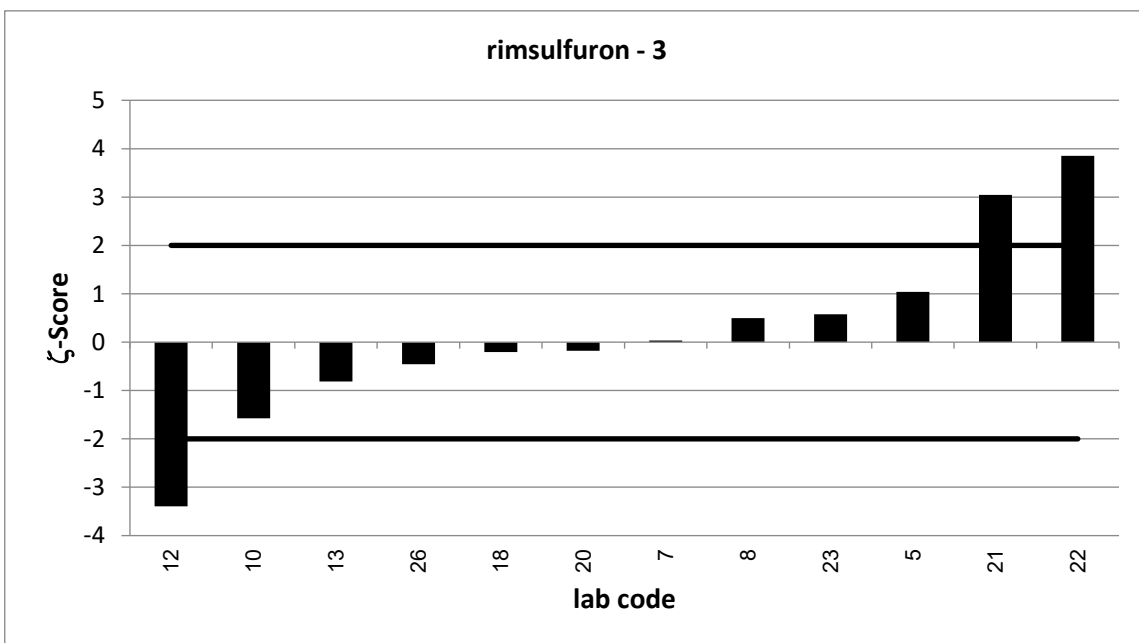
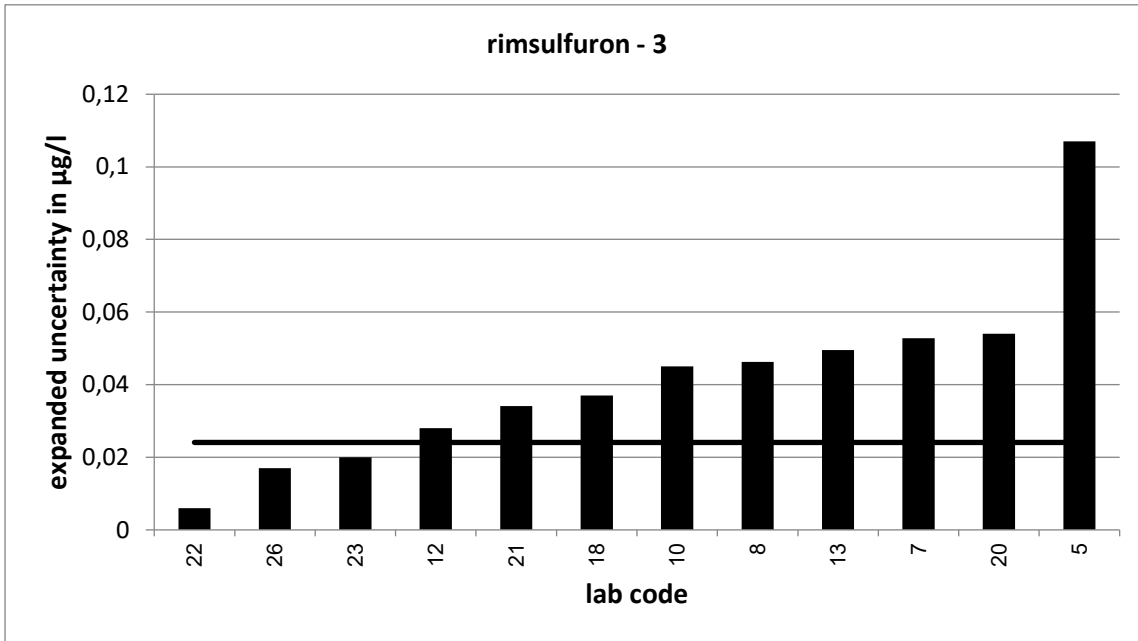


PT 7/21 - TW S5		rimsulfuron - 3			
assigned value [ $\mu\text{g/l}$ ]*		0,219 $\pm$ 0,0138			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,2701			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,1732			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	z-score	Z <sub>U</sub> -score	assessm.**
5	0,275	0,107	1,0	2,2	q
6	0,225			0,2	s
7	0,22	0,053	0,0	0,0	s
8	0,231	0,046	0,5	0,5	s
10	0,182	0,045	-1,6	-1,6	s
11	0,186			-1,4	s
12	0,166	0,028	-3,4	-2,3	q
13	0,1981	0,05	-0,8	-0,9	s
15	0,207			-0,5	s
17	0,2729			2,1	q
18	0,215	0,037	-0,2	-0,2	s
19	0,218			0,0	s
20	0,214	0,054	-0,2	-0,2	s
21	0,275	0,034	3,0	2,2	q
22	0,248	0,006	3,8	1,1	s
23	0,226	0,02	0,6	0,3	s
24	0,215			-0,2	s
25	0,213			-0,3	s
26	0,214	0,017	-0,5	-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

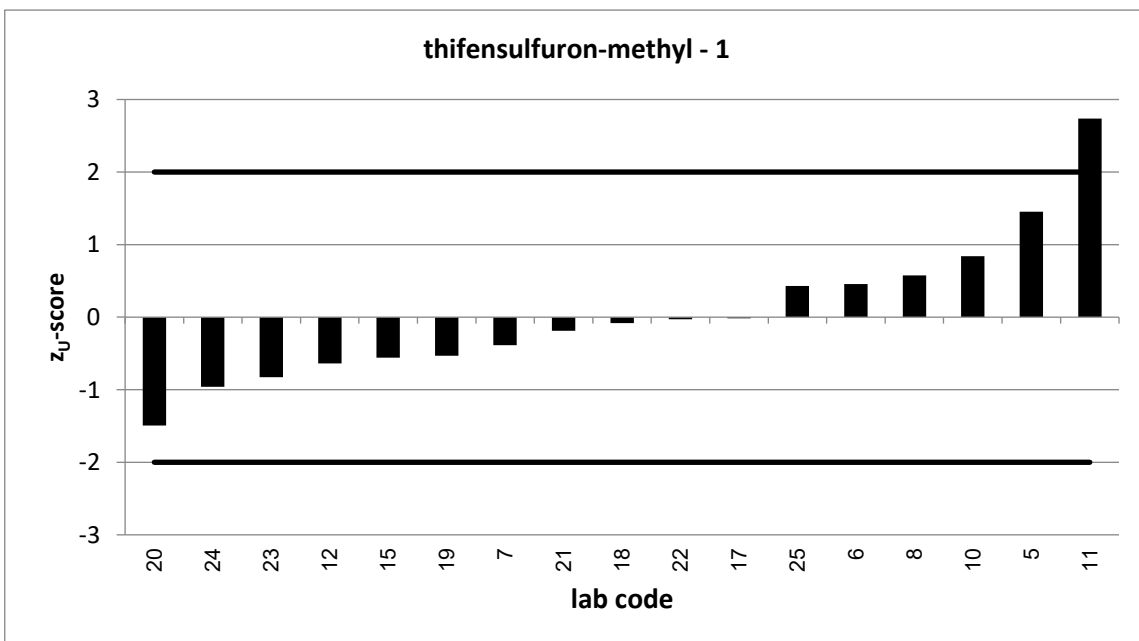
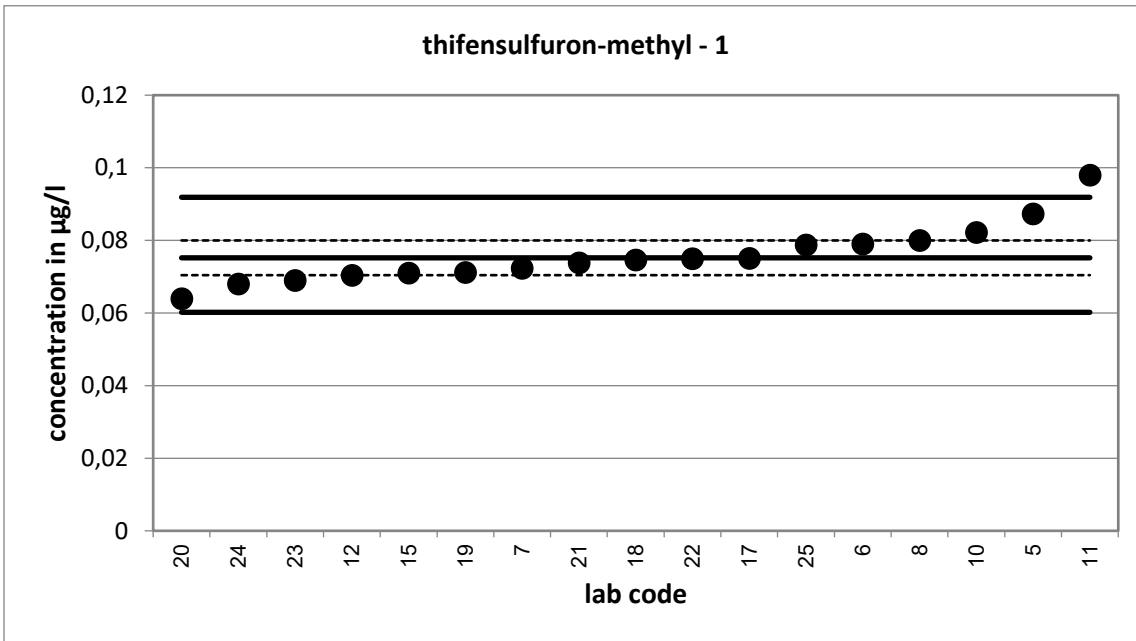


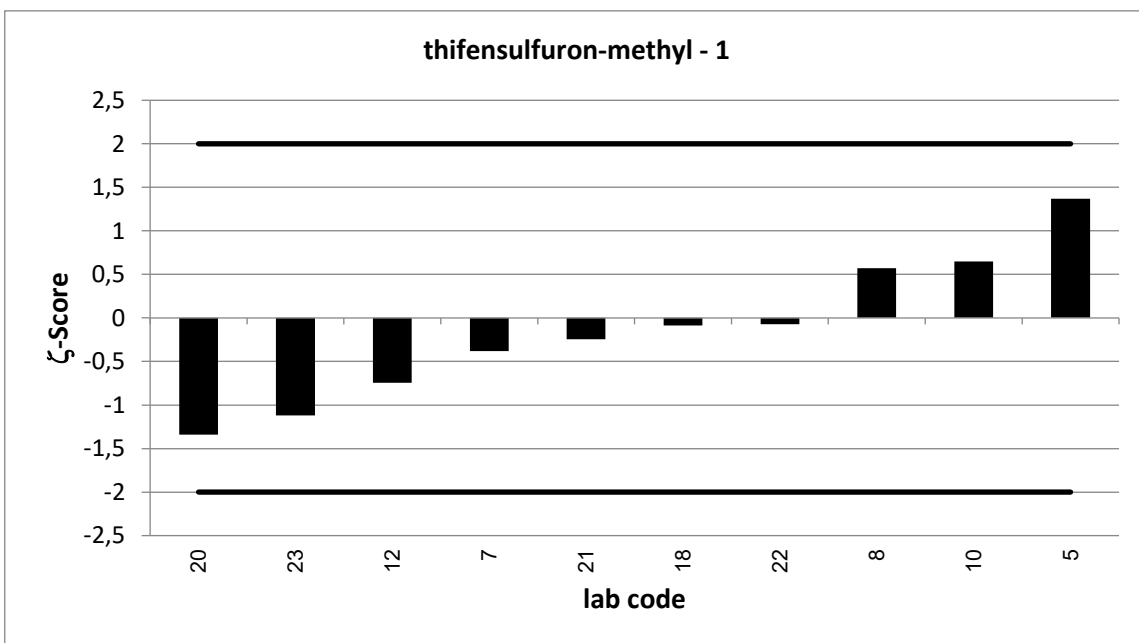
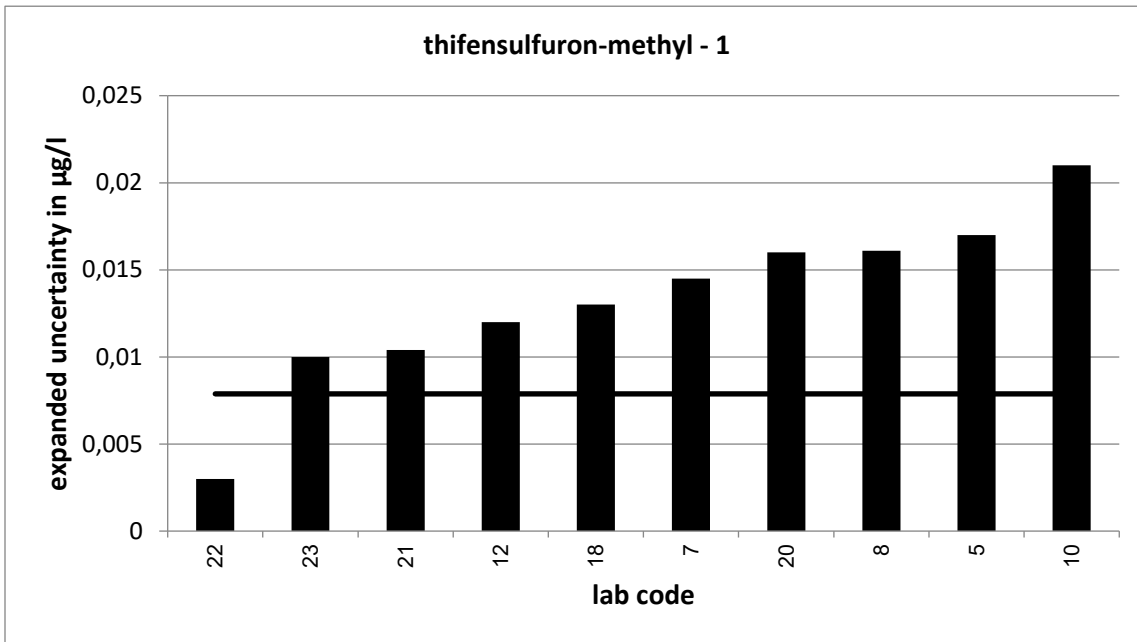


PT 7/21 - TW S5		thifensulfuron-methyl - 1			
assigned value [ $\mu\text{g/l}$ ]*		0,0752 $\pm$ 0,00478			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,09187			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,06019			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	z-score	Z <sub>U</sub> -score	assessm.**
5	0,0873	0,017	1,4	1,5	s
6	0,079			0,5	s
7	0,0723	0,015	-0,4	-0,4	s
8	0,08	0,016	0,6	0,6	s
10	0,0822	0,021	0,6	0,8	s
11	0,098			2,7	q
12	0,0704	0,012	-0,7	-0,6	s
15	0,071			-0,6	s
17	0,0751			0,0	s
18	0,0746	0,013	-0,1	-0,1	s
19	0,0712			-0,5	s
20	0,064	0,016	-1,3	-1,5	s
21	0,0738	0,01	-0,2	-0,2	s
22	0,075	0,003	-0,1	0,0	s
23	0,069	0,01	-1,1	-0,8	s
24	0,068			-1,0	s
25	0,0788			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



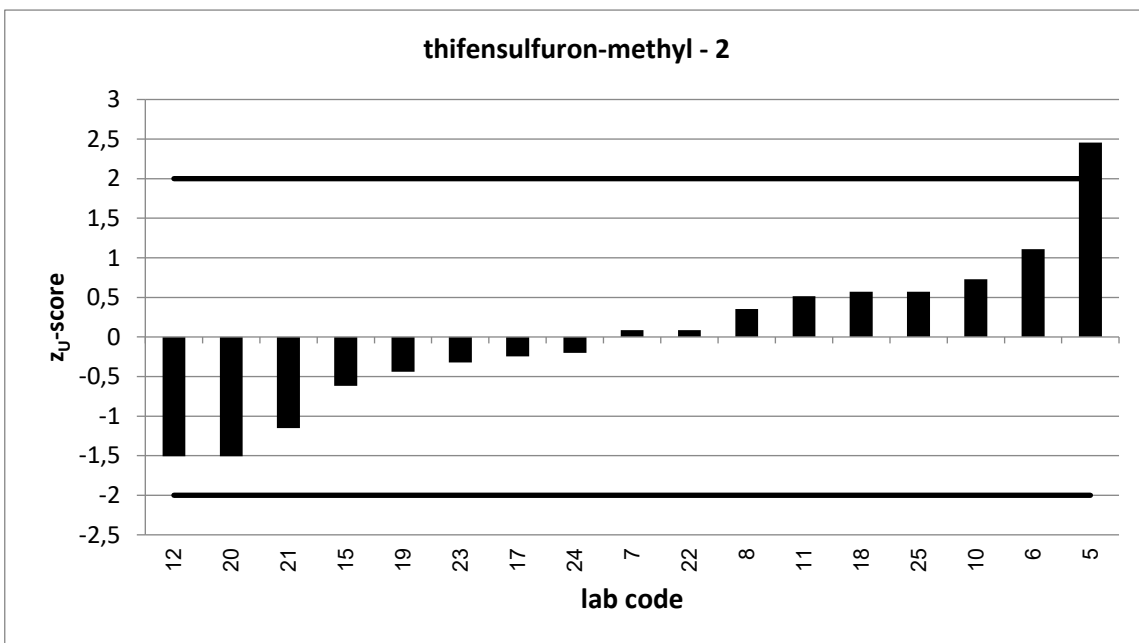
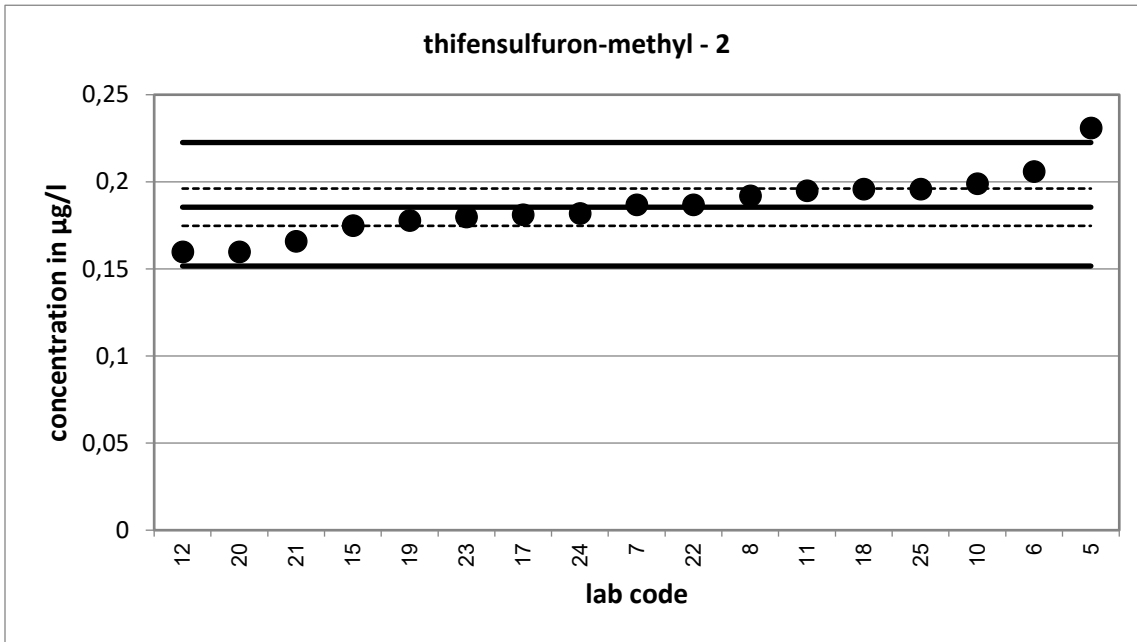


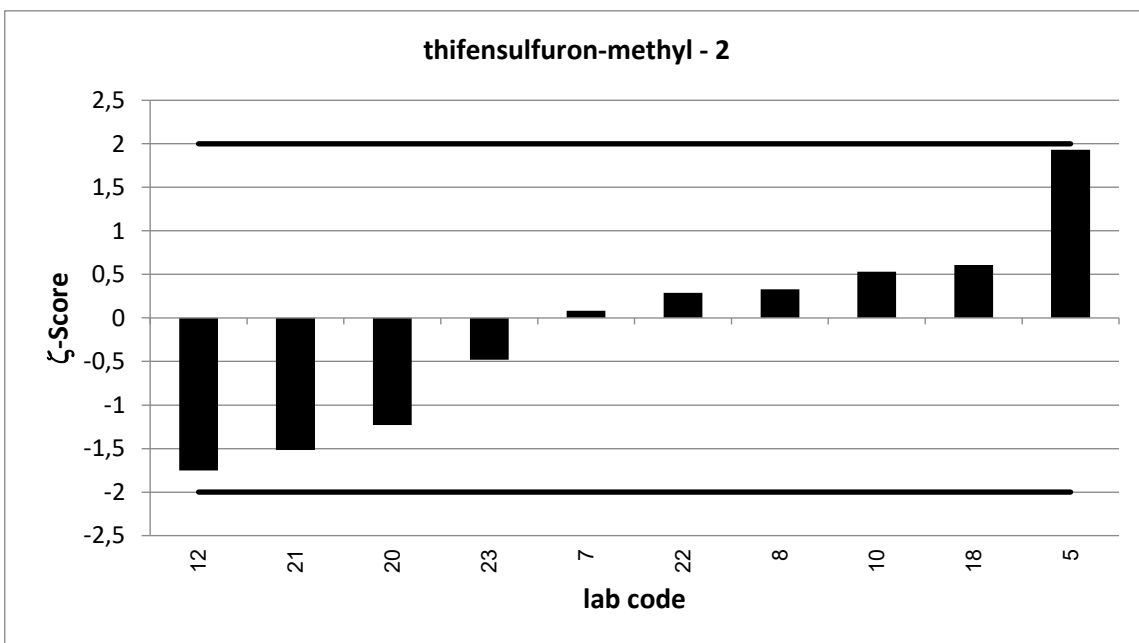
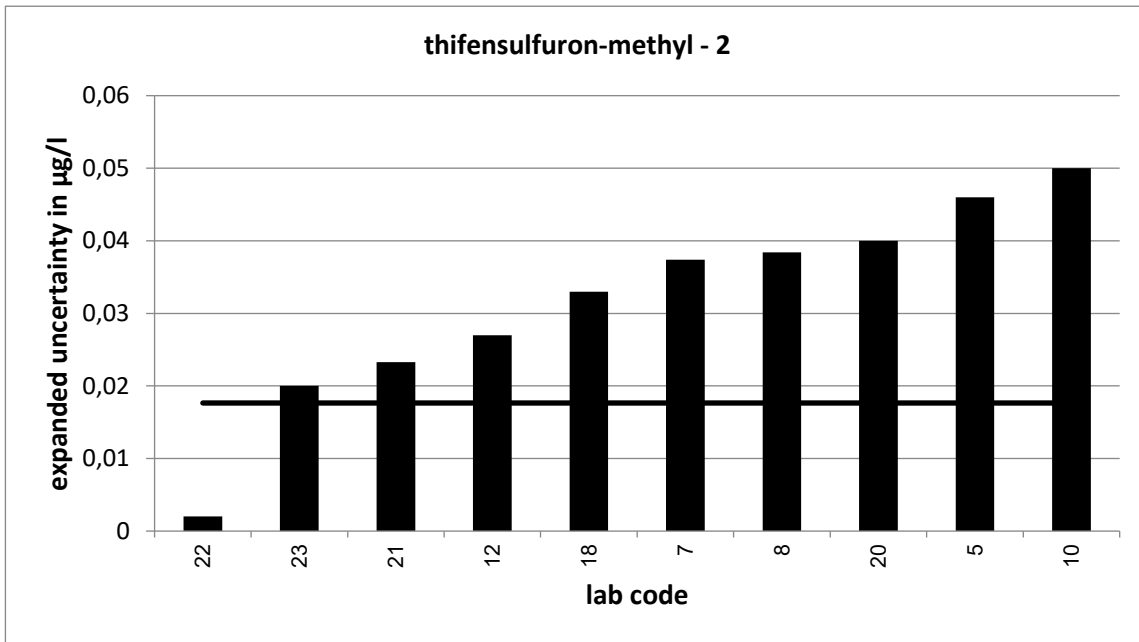


PT 7/21 - TW S5		thifensulfuron-methyl - 2			
assigned value [ $\mu\text{g/l}$ ]*		0,1854 $\pm$ 0,0107			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,2226			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,1516			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	z-score	Z <sub>U</sub> -score	assessm.**
5	0,231	0,046	1,9	2,5	q
6	0,206			1,1	s
7	0,187	0,037	0,1	0,1	s
8	0,192	0,038	0,3	0,4	s
10	0,199	0,05	0,5	0,7	s
11	0,195			0,5	s
12	0,16	0,027	-1,8	-1,5	s
15	0,175			-0,6	s
17	0,1813			-0,2	s
18	0,196	0,033	0,6	0,6	s
19	0,178			-0,4	s
20	0,16	0,04	-1,2	-1,5	s
21	0,166	0,023	-1,5	-1,2	s
22	0,187	0,002	0,3	0,1	s
23	0,18	0,02	-0,5	-0,3	s
24	0,182			-0,2	s
25	0,196			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

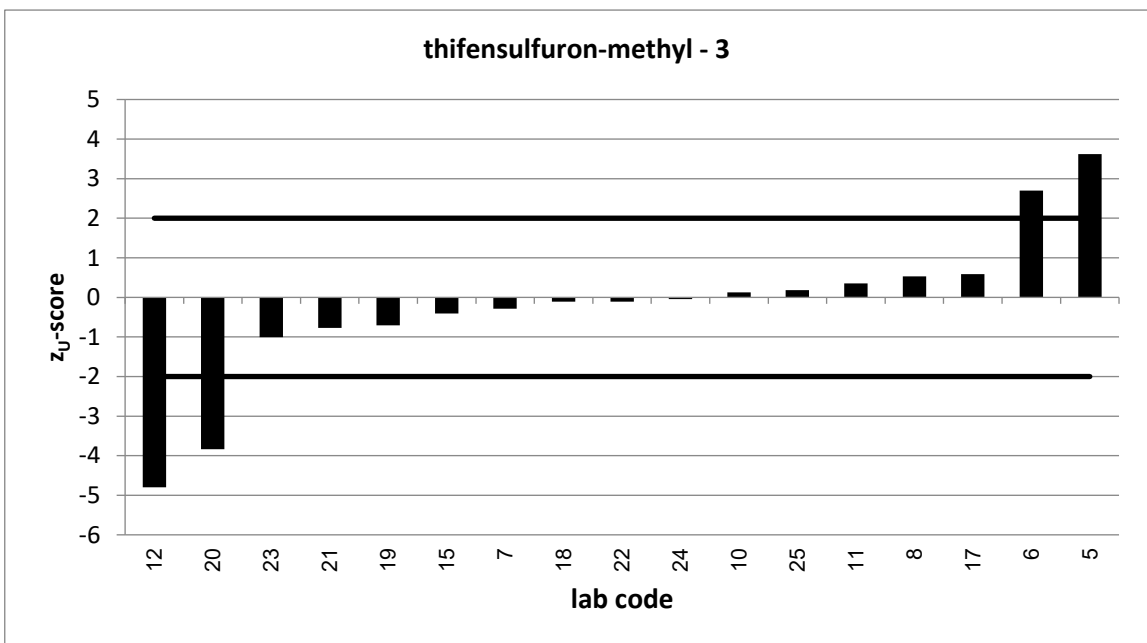
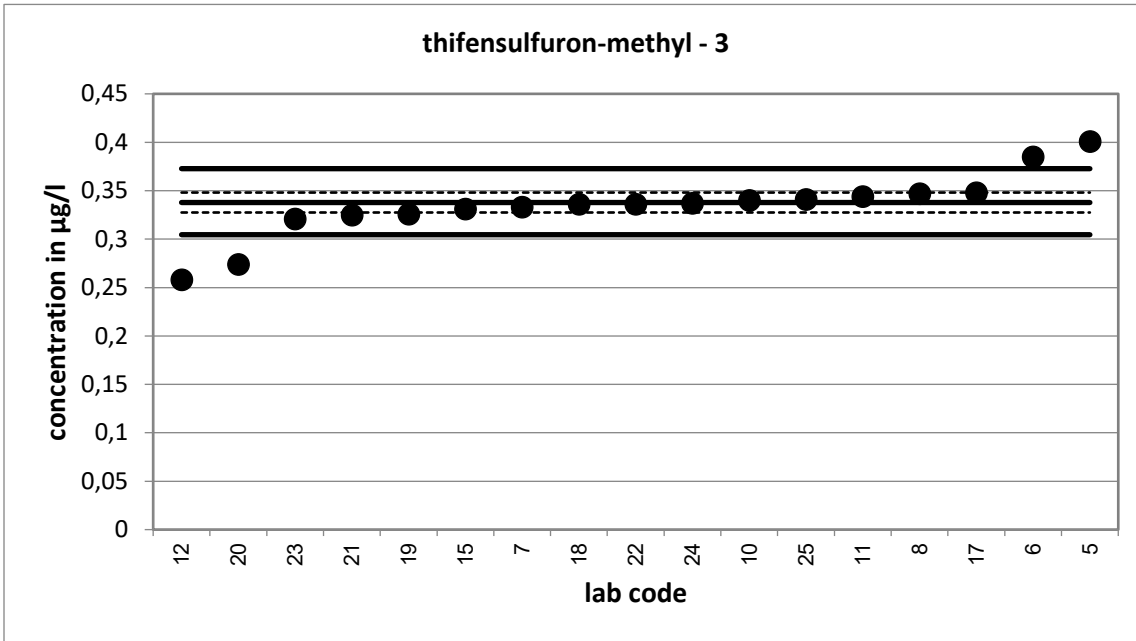


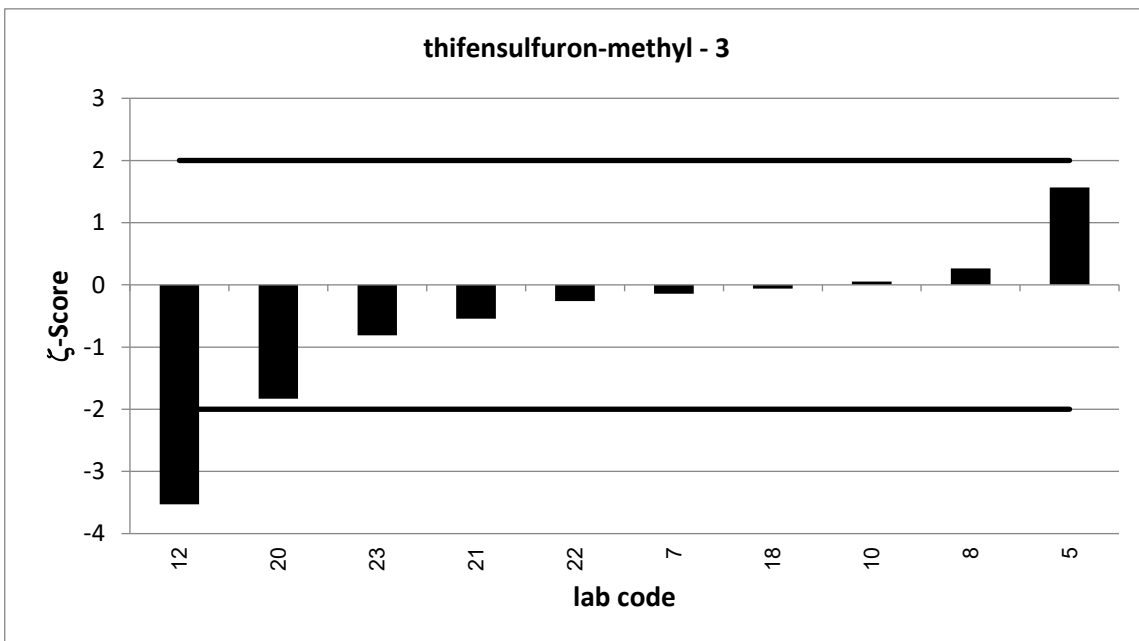
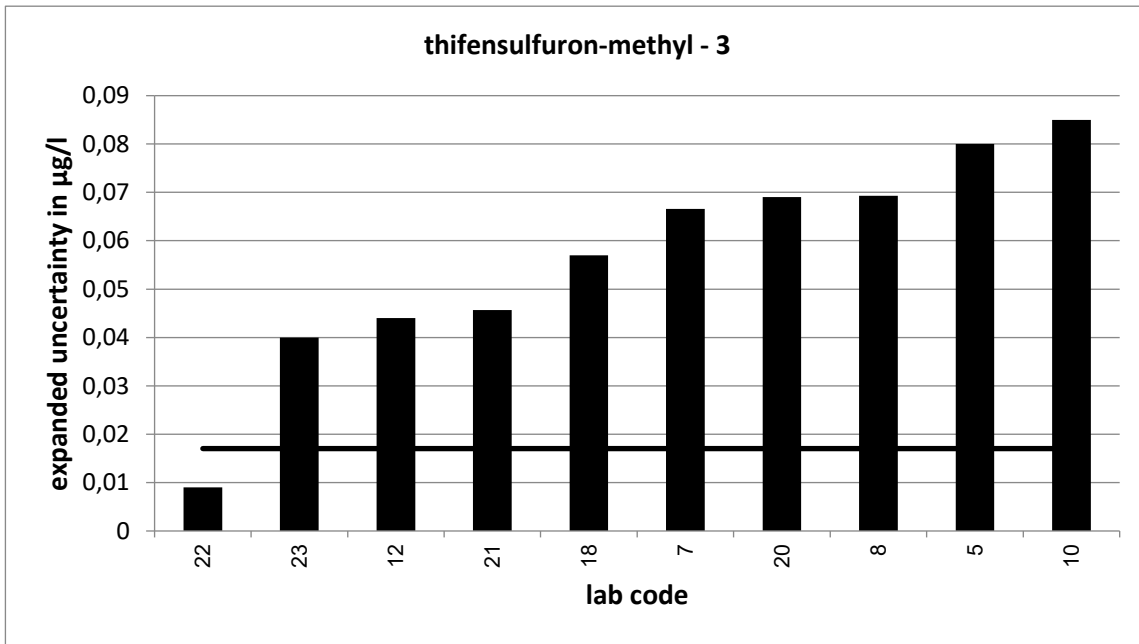


PT 7/21 - TW S5		thifensulfuron-methyl - 3			
assigned value [ $\mu\text{g/l}$ ]*		0,3378 $\pm$ 0,0103			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,3727			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,3045			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	z-score	Z <sub>U</sub> -score	assessm.**
5	0,401	0,08	1,6	3,6	u
6	0,385			2,7	q
7	0,333	0,067	-0,1	-0,3	s
8	0,347	0,069	0,3	0,5	s
10	0,34	0,085	0,1	0,1	s
11	0,344			0,4	s
12	0,258	0,044	-3,5	-4,8	u
15	0,331			-0,4	s
17	0,348			0,6	s
18	0,336	0,057	-0,1	-0,1	s
19	0,326			-0,7	s
20	0,274	0,069	-1,8	-3,8	u
21	0,325	0,046	-0,5	-0,8	s
22	0,336	0,009	-0,3	-0,1	s
23	0,321	0,04	-0,8	-1,0	s
24	0,337			0,0	s
25	0,341			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

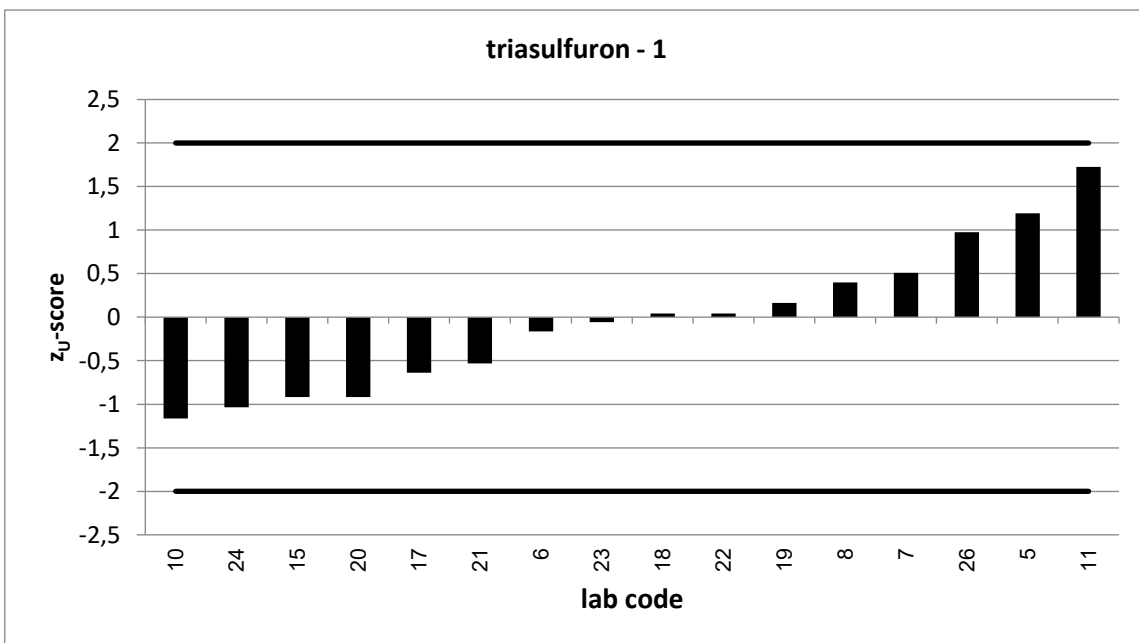
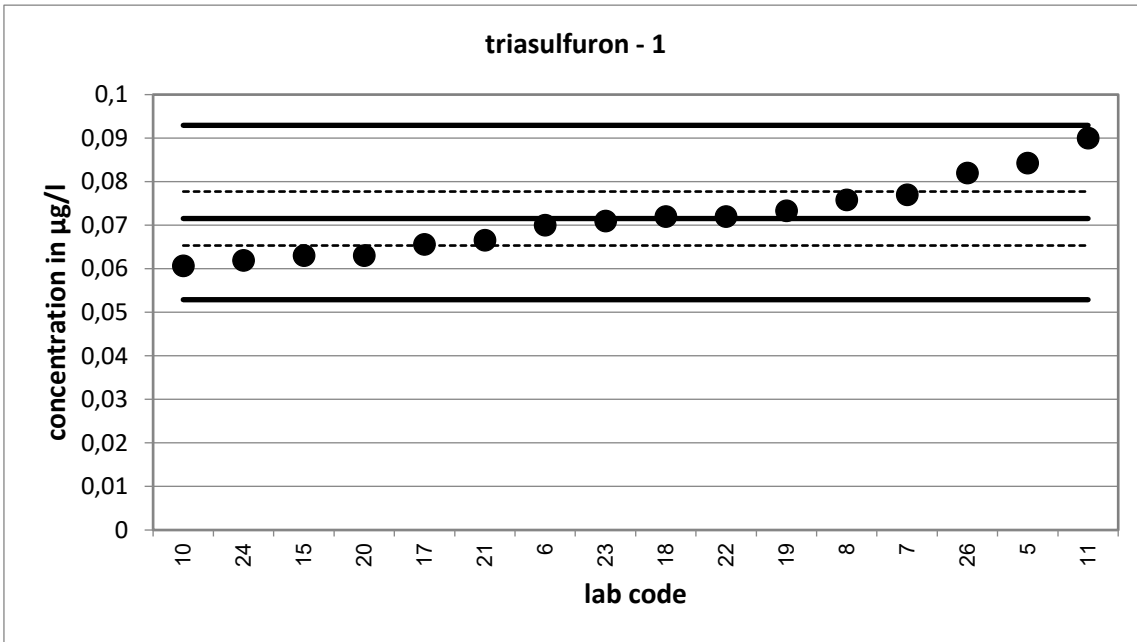




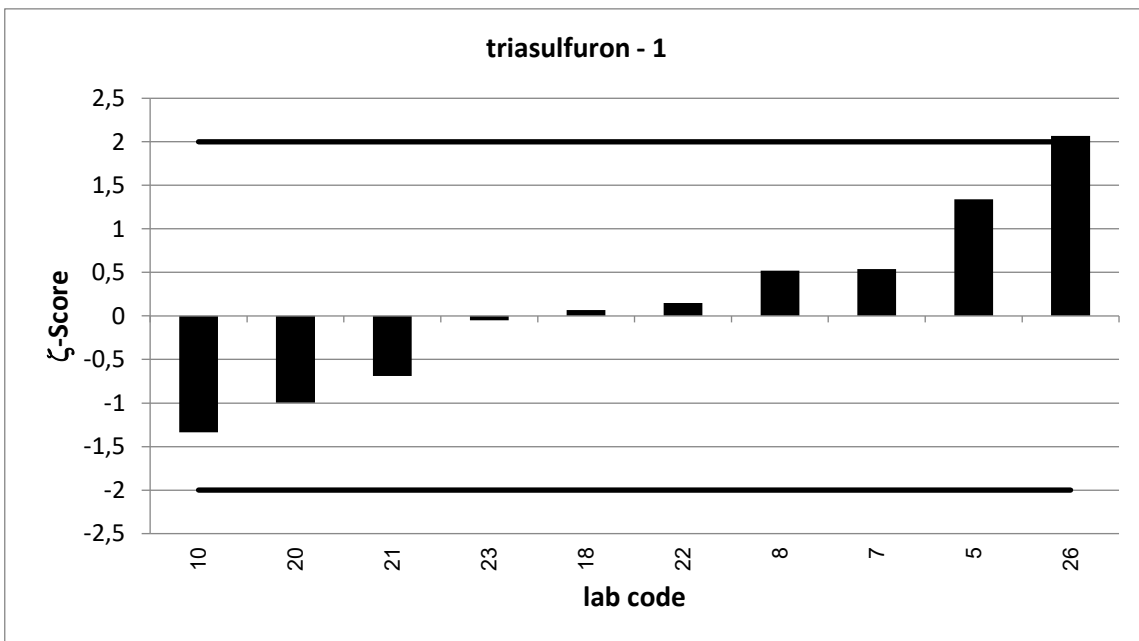
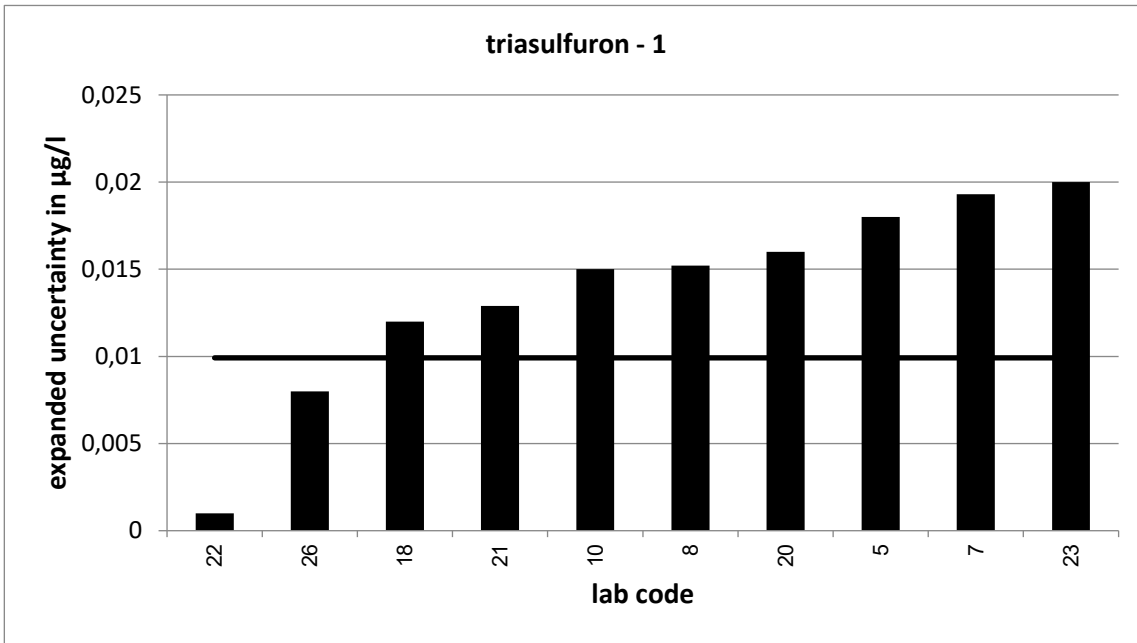
PT 7/21 - TW S5		triasulfuron - 1			
assigned value [ $\mu\text{g/l}$ ]*		0,07154 $\pm$ 0,0062			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,09294			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,0529			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	z-score	Z <sub>U</sub> -score	assessm.**
5	0,0843	0,018	1,3	1,2	s
6	0,07			-0,2	s
7	0,077	0,019	0,5	0,5	s
8	0,0758	0,015	0,5	0,4	s
10	0,0607	0,015	-1,3	-1,2	s
11	0,09			1,7	s
15	0,063			-0,9	s
17	0,0656			-0,6	s
18	0,072	0,012	0,1	0,0	s
19	0,0733			0,2	s
20	0,063	0,016	-1,0	-0,9	s
21	0,0666	0,013	-0,7	-0,5	s
22	0,072	0,001	0,1	0,0	s
23	0,071	0,02	-0,1	-0,1	s
24	0,0619			-1,0	s
26	0,082	0,008	2,1	1,0	s

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

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



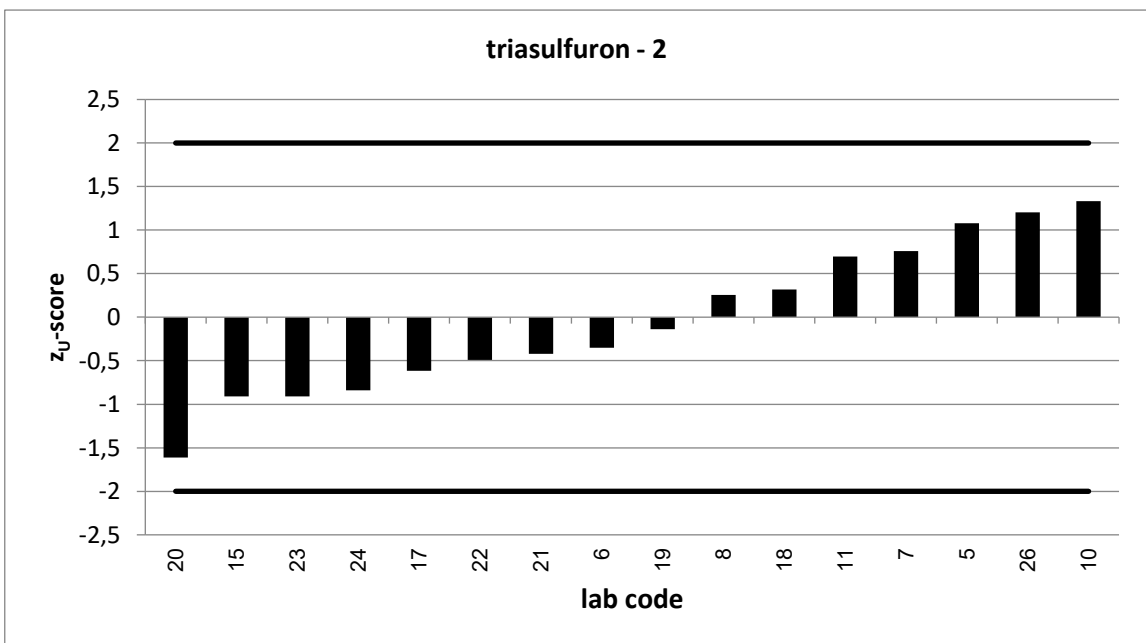
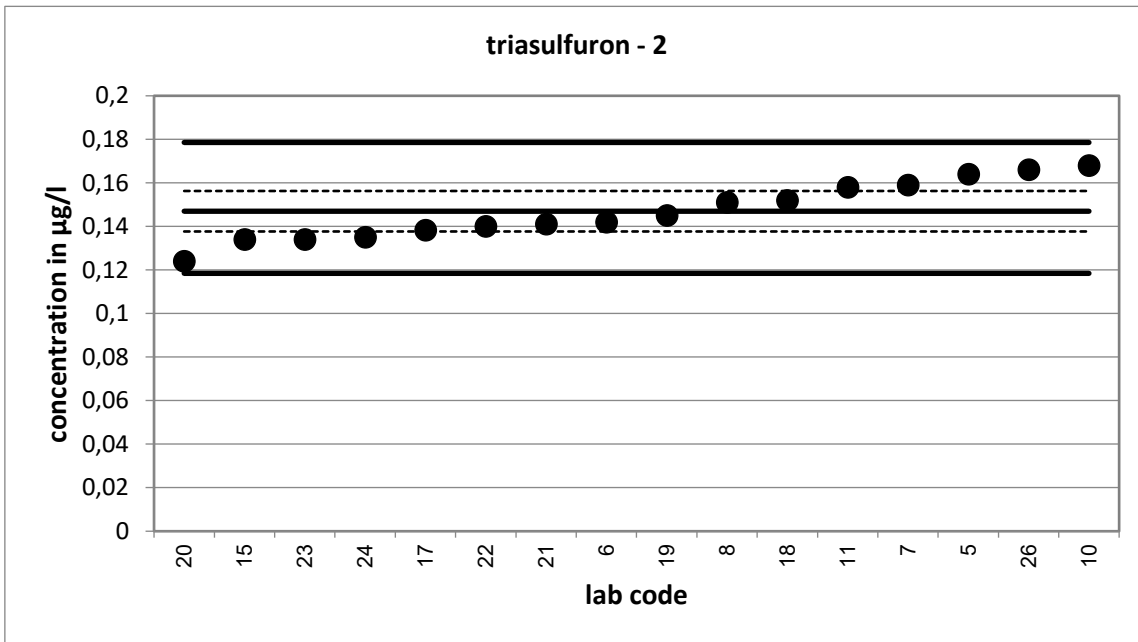


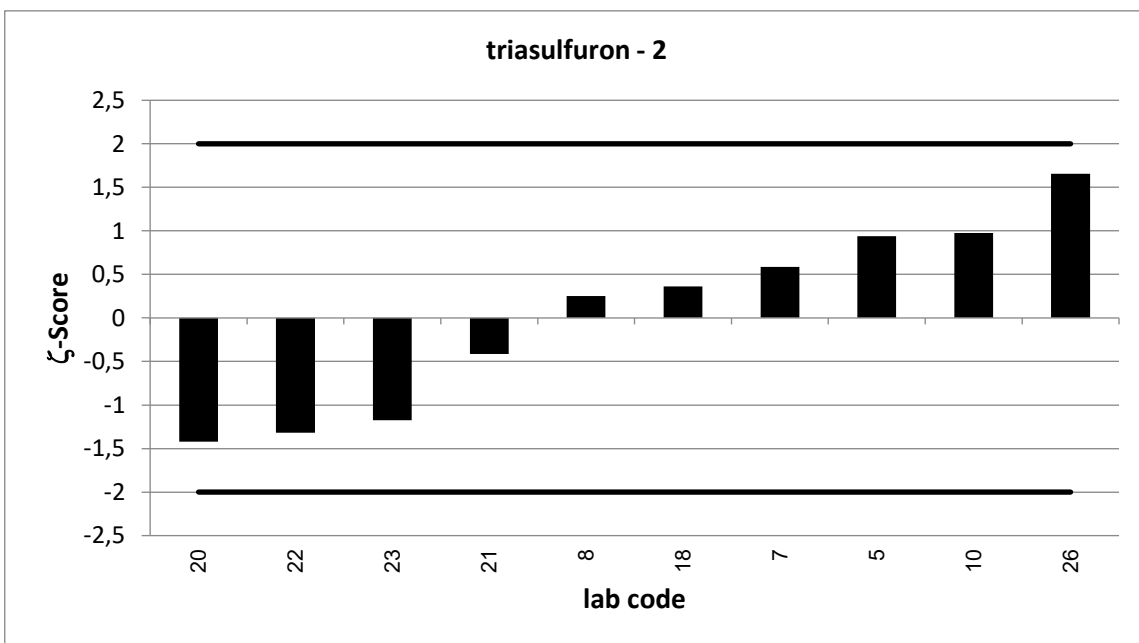
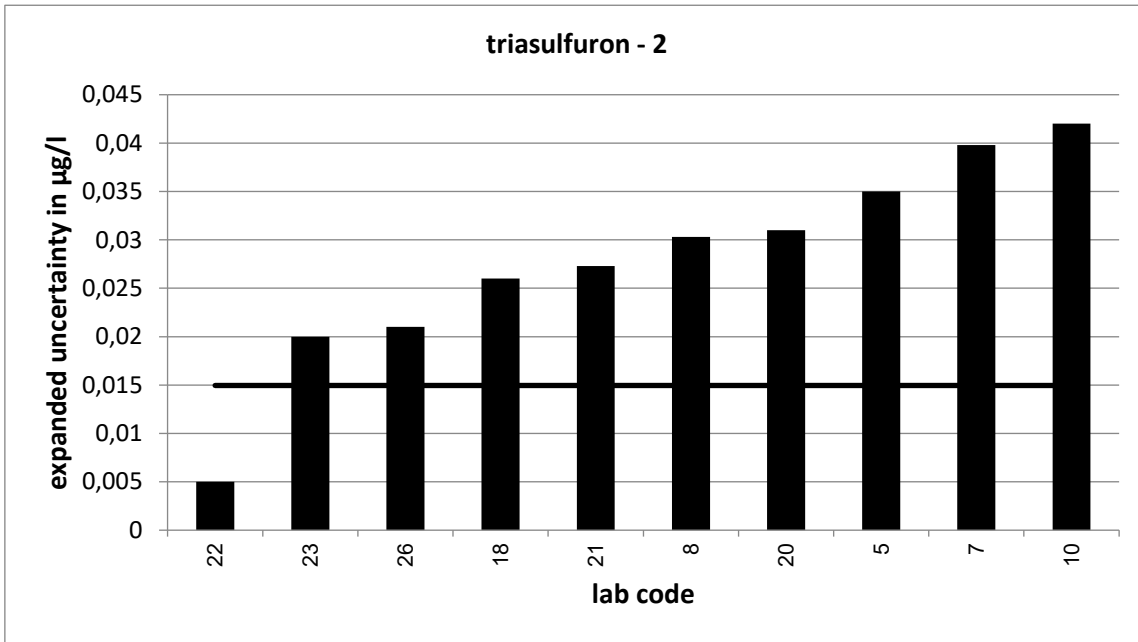


PT 7/21 - TW S5		triasulfuron - 2			
assigned value [ $\mu\text{g/l}$ ]*		0,147 $\pm$ 0,0093			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,1786			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,1184			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	z-score	Z <sub>U</sub> -score	assessm.**
5	0,164	0,035	0,9	1,1	s
6	0,142			-0,3	s
7	0,159	0,04	0,6	0,8	s
8	0,151	0,03	0,3	0,3	s
10	0,168	0,042	1,0	1,3	s
11	0,158			0,7	s
15	0,134			-0,9	s
17	0,1382			-0,6	s
18	0,152	0,026	0,4	0,3	s
19	0,145			-0,1	s
20	0,124	0,031	-1,4	-1,6	s
21	0,141	0,027	-0,4	-0,4	s
22	0,14	0,005	-1,3	-0,5	s
23	0,134	0,02	-1,2	-0,9	s
24	0,135			-0,8	s
26	0,166	0,021	1,7	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%

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





PT 7/21 - TW S5		triasulfuron - 3			
assigned value [ $\mu\text{g/l}$ ]*		0,2578 $\pm$ 0,0105			
upper tolerance limit [ $\mu\text{g/l}$ ]		0,2926			
lower tolerance limit [ $\mu\text{g/l}$ ]		0,2251			
lab code	result [ $\mu\text{g/l}$ ]	$\pm$	z-score	Z <sub>U</sub> -score	assessm.**
5	0,3	0,063	1,3	2,4	q
6	0,254			-0,2	s
7	0,275	0,069	0,5	1,0	s
8	0,268	0,054	0,4	0,6	s
10	0,241	0,06	-0,6	-1,0	s
11	0,313			3,2	u
15	0,246			-0,7	s
17	0,2715			0,8	s
18	0,25	0,042	-0,4	-0,5	s
19	0,253			-0,3	s
20	0,225	0,056	-1,2	-2,0	s
21	0,27	0,052	0,5	0,7	s
22	0,248	0,011	-1,3	-0,6	s
23	0,255	0,02	-0,2	-0,2	s
24	0,254			-0,2	s
26	0,245	0,045	-0,6	-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

