Qualitätssicherung. **Vom Landwirt bis zur Ladentheke.**

QS. Ihr Prüfsystem für Lebensmittel.

Laboratory Performance Assessment

Spring 2020

QS Fachgesellschaft Obst-Gemüse-Kartoffeln GmbH

Report

Test Material A

Pesticide Residues in red oak leaf lettuce

September 2020

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1. Scope of proficiency testing (PT)

This proficiency testing was run by QS Fachgesellschaft Obst-Gemüse-Kartoffeln GmbH. This proficiency testing represents an ability test. It is used to be an external quality assurance and shows on each testing field the performance/ability of the laboratory.

This report refers to the performance assessment of laboratories which analysed test material "A". Each laboratory received a sample of red oak leaf lettuce with eight spiked pesticides. 30 participants reported results and were evaluated.

The evaluation and reporting was subcontracted to DRRR GmbH.

2. Test items and homogeneity

QS required three different materials in terms of spiked pesticides. Thus, the three test materials partly differed in the type of spiked pesticides as well as in the levels of spiked pesticides. Test material "A" was distributed to thirty (30) participants. The test material for this Performance Assessment was prepared by the GLP department of LUFA Speyer, Germany. The homogeneity test was performed by the AGES (Östereichische Agentur für Gesundheit und Ernährungssicherheit), Austria and the Kantonales Labor Zürich (KLZH), Switzerland.

The material was distributed into labelled bottles with at least 200 g in each. The bottles were stored at -20 °C in the dark until distribution.

The following pesticides were spiked to give the approximate final concentrations:

- 250 µg/kg benalaxyl-M,
- 50 µg/kg buprofezin,
- 800 µg/kg fluopyram,
- 130 µg/kg iprovalicarb,
- 600 µg/kg metaflumizone,
- 200 µg/kg pencycuron,
- 40 µg/kg spirotetramat-enol,
- 45000 µg/kg bromide.

2.1 Summary of results of homogeneity testing

The homogeneity test was carried out at all requested parameters to get information about the principal suitability of the material for this proficiency testing. If the standard deviation ($s_{material}$) of the material homogeneity is smaller than 30 % of a test statistic the samples are classified as homogenous. The test statistic is usually calculated of all previous proficiency testings with this material type determining the relative mean standard deviation as well as extended uncertainty of the relative mean standard deviation of all previous proficiency testings with this material type. The relative values are referred to absolute values related to the actual value of the material and are added to obtain the test statistic. When this rule could not be followed it will be proved if the higher variance is usual for this material type. The test statistic for the evaluation of the homogeneity test of test material "A" was calculated with the results from this proficiency testing round (Laboratory Performance Assessment Spring 2020), because no previous proficiency testing data is available for the requested parameter matrix combination.

The homogeneity test was carried out at 5 representative random samples for bromide and 10 for the other parameters in double determination acc. to ISO 13528 (Intern. Harmonised Protocol).

The homogeneity test was subcontracted by:

AGES (Österreichische Agentur für Gesundheit und Ernährungssicherheit), Austria and Kantonales Labor Zürich (KLZH), Switzerland.

In the following table the evaluation of the homogeneity test is shown:

parameter	spiked level *[µg/kg]*	mean (homogeneity test) *[µg/kg]*	recovery (homogeneity test) *[%]*	standard deviation of the material homogeneity ($s_{material}$) *[µg/kg]*	test statistic *[µg/kg]*	evaluation of the homogeneity test ($s_{material}$ < 30 % test statistic)
benalaxyl-M	250	254	102	3	40	**homogenous**
buprofezin	50	52	104	2	9	**homogenous**
fluopyram	800	744	93	0	67	**homogenous**
iprovalicarb	130	126	97	4	17	**homogenous**
metaflumizone	600	552	92	0	175	**homogenous**
pencycuron	200	195	97	9	32	**homogenous**
spirotetramat-enol	40	41	102	1	8	**homogenous**
bromide	45000	44224	98	1077	6330	**homogenous**

3. Requested testing parameters

The participants were requested to report which pesticides the samples had been analysed for. The results had to be reported without consideration of the recovery. The participants were asked to report also recovery rates for the quantified pesticides. The limit of quantification (LoQ) had to be specified for all sought and found pesticides. The laboratories were requested to identify and quantify the following eight pesticides.

- benalaxyl-M,
- buprofezin,
- fluopyram,
- iprovalicarb,
- metaflumizone,
- pencycuron,
- spirotetramat-enol,
- bromide.

4. Criteria of assessment and test items

The test materials for the Laboratory Performance Assessment Spring 2020 of QS Fachgesellschaft Obst-Gemüse-Kartoffeln GmbH were prepared by the GLP department of LUFA Speyer to provide individual test material tailored to QS needs.

The sample should be analysed according to the QS control plan (without analysis of dithiocarbamates and nitrate). The sample was declared as a product of Italian origin. For this reason, the chloride/bromide ratio had to be determined and reported according to the QS control plan. The chloride contents and the chloride/bromide ratio determined by the laboratories are purely informative. This means, the determination of the chloride content and the chloride/bromide ratio is not included in the evaluation of the competence test. The results are shown on the last page of this report.

The analysis of the parameter total inorganic bromide could be subcontracted as a single method to a QS authorized laboratory. This result was evaluated independently whether the determination was performed by the participant themselves or subcontracted.

All three test materials naturally contained a small amount of perchlorate (< 20 µg/kg) as well as chlorate in the range of 700 µg/kg. Three laboratories have confirmed the chlorate content and also the low amount of perchlorate. However, these active substances were not the subject of the competence test and are therefore not relevant for the evaluation of the test.

All three test materials naturally contained a small amount of spirotetramate-BYI08330-ketohydroxy (< 10 µg/kg). Some participants reported traces of spirotetramate-BYI08330-ketohydroxy. A conversion from the spiked active substance spirotetramat-enol is unlikely. According to EFSA (2013 and 2019) spirotetramat-enol is stable, even under hydrolysis conditions.

The performance assessment considers the following test criteria:

- No false negative results are reported (thus identification of all eight pesticides)
- No false positive results are reported
- Correct quantification of at least six pesticides related to the recovery criteria. Analytical results between 70 % and 120% of the spiked levels have been considered satisfying.

5. Demonstration of the results

Each laboratory was given a number (laboratory code).

A summarized evaluation of the laboratory performance is shown in table 1 to 4 according to the test criteria.

The results of all participants analysing test material "A" are presented in tables 5 to 13. Each table follows a diagram with the individual results in ascending order. The diagrams include the spiked level and the accepted range of the respective pesticide.

6. Remarks and comments

- The labs 3, 10, 11, 12 and 15 reported spirotetramat-BYI08330-ketohydroxy in traces (< 10 µg/kg).
- The lab 13 reported oxydiazon: 43 µg/kg; recovery: 91%; LoQ: 10 µg/kg. This was evaluated false positive.
- The lab 23 reported chlorate: 690 µg/kg; recovery: 114%; LoQ: 10 µg/kg and perchlorate: 17 µg/kg; recovery: 94%; LoQ: 2 µg/kg.

7. Results, tables and graphics

7.1 Summary

Table 1: Summarized laboratory rating in test material A

QS criteria	number of participants	percent of participants
passed	28	93
failed	2	7
total	30	100

Table 2: Number of satisfactory participants in test material A

QS criteria	number of satisfactory participants	number of participants	satisfactory %
all analyts identified	29	30	97
all analyts identified and reported in acceptable results	24	30	80
no false positive results	29	30	97

7.2 Rating of performance

Table 3: Rating

Laboratory code	**criterion 1** all analytes identified	**criterion 2** number of acceptable results	**criterion 3** number of false positive results	rating
1	yes	8	0	**passed**
2	yes	7	0	**passed**
3	yes	8	0	**passed**
4	yes	8	0	**passed**
5	yes	8	0	**passed**
6	yes	7	0	**passed**
7	yes	8	0	**passed**
8	yes	8	0	**passed**
9	yes	8	0	**passed**
10	yes	8	0	**passed**
11	yes	8	0	**passed**
12	yes	8	0	**passed**
13	no	5	1	**failed**
14	yes	8	0	**passed**
15	yes	8	0	**passed**
16	yes	6	0	**passed**
17	yes	8	0	**passed**
18	yes	8	0	**passed**
19	yes	5	0	**failed**
20	yes	8	0	**passed**
21	yes	8	0	**passed**
22	yes	8	0	**passed**
23	yes	8	0	**passed**
24	yes	8	0	**passed**
25	yes	7	0	**passed**
26	yes	8	0	**passed**
27	yes	8	0	**passed**
28	yes	8	0	**passed**
29	yes	8	0	**passed**
30	yes	8	0	**passed**

Table 4: Number of satisfactory results in test material A

analyte	number of satisfactory results	total number of correct identification	satisfactory (%)
benalaxyl-M	30	30	100
buprofezin	30	30	100
fluopyram	28	30	93
iprovalicarb	29	30	97
metaflumizone	27	30	90
pencycuron	29	30	97
spirotetramat-enol	28	29	97
bromide	28	30	93

7.3 Results of Benalaxyl-M

Table 5: Results for benalaxyl-M in test material A

benalaxyl-M - spiked level: 250 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 175-300
1	250	117	10	**yes**
2	240	106	10	**yes**
3	239	88	10	**yes**
4	215	90	10	**yes**
5	278	96	10	**yes**
6	230	111	10	**yes**
7	250	88	10	**yes**
8	260	100	10	**yes**
9	288	85	10	**yes**
10	236	100	10	**yes**
11	255	119.3	10	**yes**
12	286	108	10	**yes**
13	289	89	10	**yes**
14	251	105	10	**yes**
15	251	98	10	**yes**
16	257	98	10	**yes**
17	256	82	10	**yes**
18	280	97	10	**yes**
19	285	95	10	**yes**
20	272	97.5	10	**yes**
21	217	100	10	**yes**
22	210	101	10	**yes**
23	210	96	10	**yes**
24	250	88.7	5	**yes**
25	225	103.7	5	**yes**
26	270	107	5	**yes**
27	260	106.9	10	**yes**
28	282	99	10	**yes**
29	233	89	10	**yes**
30	270	95	10	**yes**

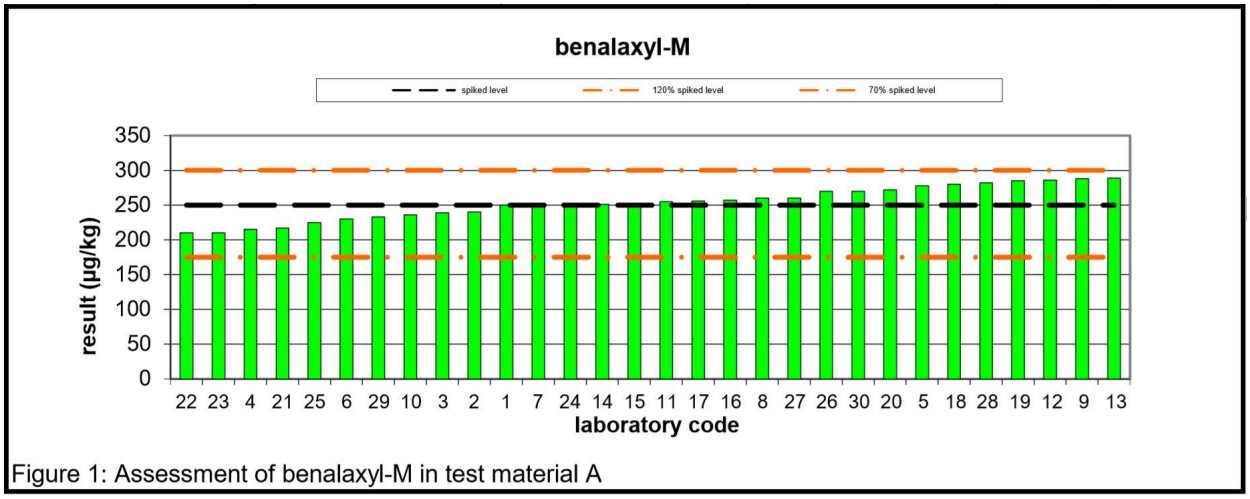

Figure 1: Assessment of benalaxyl-M in test material A

7.4 Results of Buprofezin

Table 6: Results for buprofezin in test material A

buprofezin – spiked level: 50 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 35-60
1	47	116	10	yes
2	53	104	10	yes
3	60	93	10	yes
4	45	90	10	yes
5	49.8	100	10	yes
6	47	93	10	yes
7	50	91	10	yes
8	47	115	10	yes
9	48	93	10	yes
10	42	90	10	yes
11	50	93.7	10	yes
12	54	100	10	yes
13	48	99	10	yes
14	48	98	10	yes
15	48	89	10	yes
16	47	98	10	yes
17	50	97	10	yes
18	48	99	10	yes
19	36	91	10	yes
20	54	92	10	yes
21	42	100	10	yes
22	42	101	10	yes
23	37	95	10	yes
24	50	90	5	yes
25	44	96.8	5	yes
26	50	110	5	yes
27	45	99	10	yes
28	53	99	10	yes
29	46	91	10	yes
30	48	105	10	yes

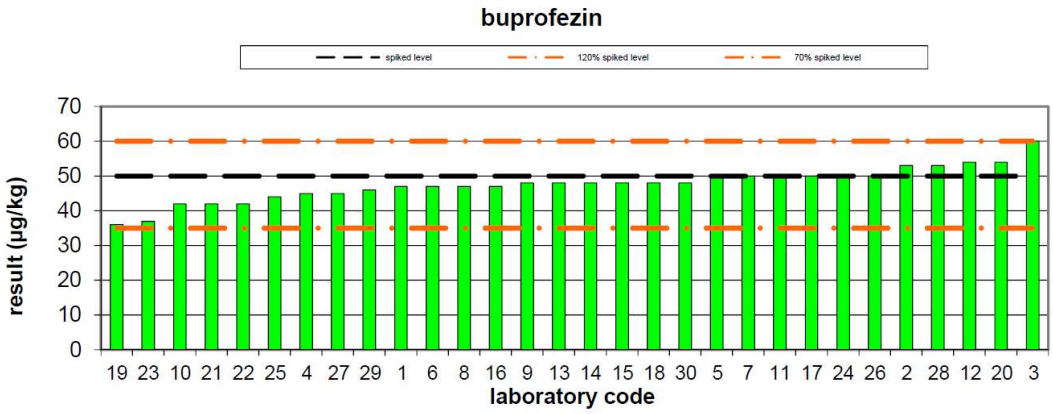

Figure 2: Assessment of buprofezin in test material A

7.5 Results of Fluopyram

Table 7: Results for fluopyram in test material A

fluopyram – spiked level: 800 µg/kg				
laboratory code	result (µg/kg)	Recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 560-960
1	740	112	10	yes
2	720	103	10	yes
3	749	86	10	yes
4	700	90	10	yes
5	628	99	10	yes
6	752	101	10	yes
7	650	87	10	yes
8	790	112	10	yes
9	780	99	10	yes
10	703	95	10	yes
11	842	98.3	10	yes
12	770	109	10	yes
13	843	99	10	yes
14	799	105	10	yes
15	767	96	10	yes
16	1032	104	10	no
17	710	80.6	10	yes
18	748	98	10	yes
19	1200	99	10	no
20	879	98.1	10	yes
21	700	98	10	yes
22	650	103	10	yes
23	740	85	10	yes
24	750	92	5	yes
25	795	103	5	yes
26	880	105	5	yes
27	800	102.1	10	yes
28	830	98	10	yes
29	654	87	10	yes
30	800	101	10	yes

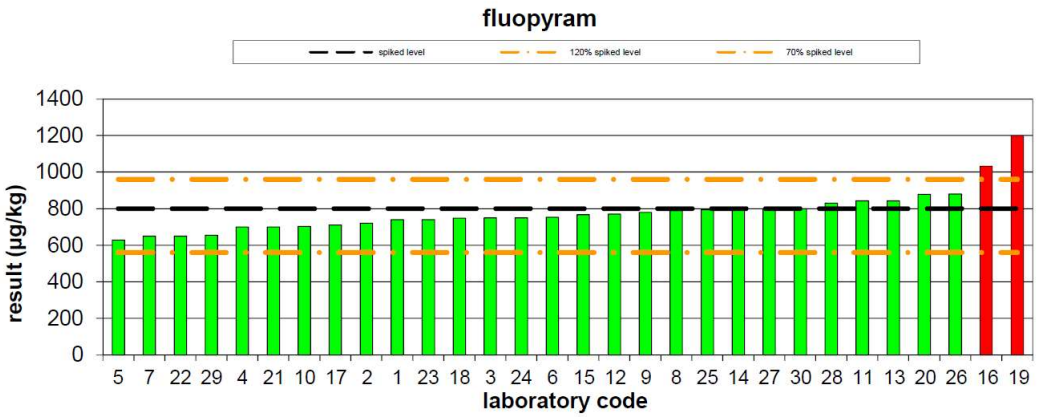

Figure 3: Assessment of fluopyram in test material A

7.6 Results of Iprovalicarb

Table 8: Results for iprovalicarb in test material A

iprovalicarb – spiked level: 130 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 91-156
1	126	112	10	**yes**
2	141	103	10	**yes**
3	120	91	10	**yes**
4	115	90	5	**yes**
5	118	100	10	**yes**
6	130	106	10	**yes**
7	143	100	5	**yes**
8	110	115	10	**yes**
9	132	96	10	**yes**
10	102	105	10	**yes**
11	140	97.4	10	**yes**
12	134	102	10	**yes**
13	132	96	10	**yes**
14	128	97	10	**yes**
15	111	101	10	**yes**
16	146	99	10	**yes**
17	128	80.2	10	**yes**
18	135	96	10	**yes**
19	204	103	10	**no**
20	146	105	5	**yes**
21	130	95	10	**yes**
22	105	107	10	**yes**
23	96	85	10	**yes**
24	130	110	5	**yes**
25	118	103	5	**yes**
26	138	06	5	**yes**
27	112	96.2	10	**yes**
28	139	103	10	**yes**
29	117	91	10	**yes**
30	115	90	10	**yes**

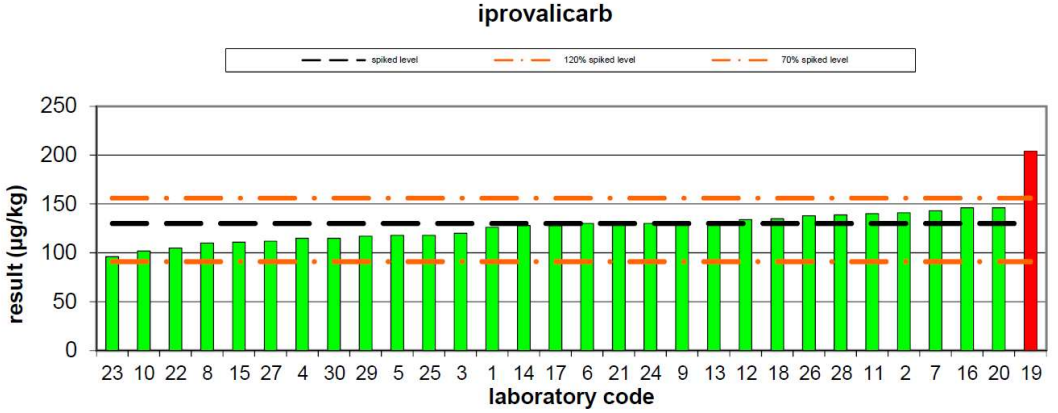

Figure 4: Assessment of iprovalicarb in test material A

7.7 Results of Metaflumizone

Table 9: Results for metaflumizone in test material A

metaflumizone – spiked level: 600 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 420-720
1	600	104	10	**yes**
2	547	98	10	**yes**
3	497	99	10	**yes**
4	450	90	5	**yes**
5	623	100	10	**yes**
6	516	94	10	**yes**
7	613	108	5	**yes**
8	583	115	10	**yes**
9	598	112	10	**yes**
10	520	85	10	**yes**
11	536	82.3	10	**yes**
12	587	92	10	**yes**
13	370	96	10	**no**
14	720	99	10	**yes**
15	527	91	10	**yes**
16	809	106	10	**no**
17	629	86.5	10	**yes**
18	640	105	10	**yes**
19	840	89	10	**no**
20	600	94.9	10	**yes**
21	600	85	10	**yes**
22	560	94	10	**yes**
23	540	89	10	**yes**
24	550	105	5	**yes**
25	603	96.5	5	**yes**
26	650	98	5	**yes**
27	570	92.2	10	**yes**
28	682	115	10	**yes**
29	493	86	10	**yes**
30	590	115	10	**Yes**

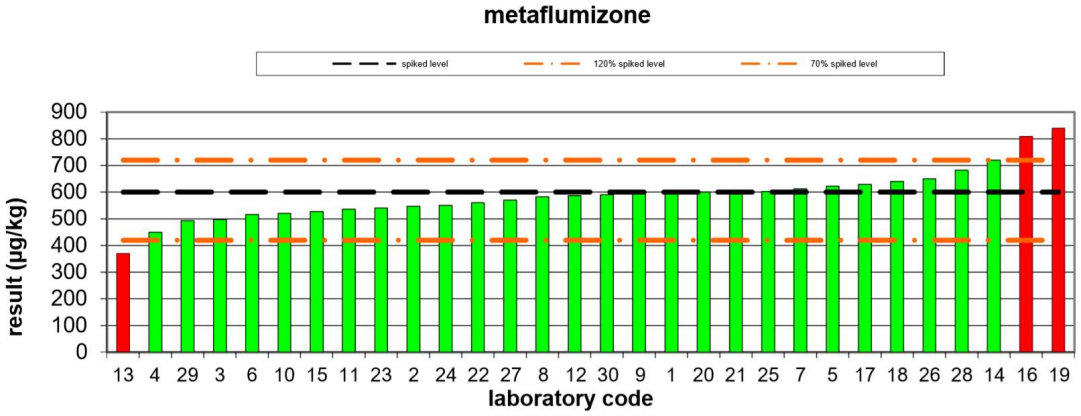

Figure 5: Assessment of metaflumizone in test material A

7.8 Results of Pencycuron

Table 10: Results for pencycuron in test material A

pencycuron – spiked level: 200 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	Accepted rance (µg/kg): 140-240
1	192	82	10	yes
2	186	103	10	yes
3	198	103	10	yes
4	190	90	10	yes
5	214	100	10	yes
6	191	96	10	yes
7	191	95	5	yes
8	210	112	10	yes
9	204	101	10	yes
10	200	90	10	yes
11	176	93.8	10	yes
12	195	98	10	yes
13	256	78	10	no
14	200	103	10	yes
15	201	95	10	yes
16	217	102	10	yes
17	185	81.2	10	yes
18	203	99	10	yes
19	240	105	20	yes
20	192	94.8	10	yes
21	170	100	10	yes
22	210	106	10	yes
23	140	87	10	yes
24	220	105.5	5	yes
25	186	96.5	5	yes
26	190	97	5	yes
27	200	106.6	10	yes
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29	184	90	10	yes
30	213	112	10	yes

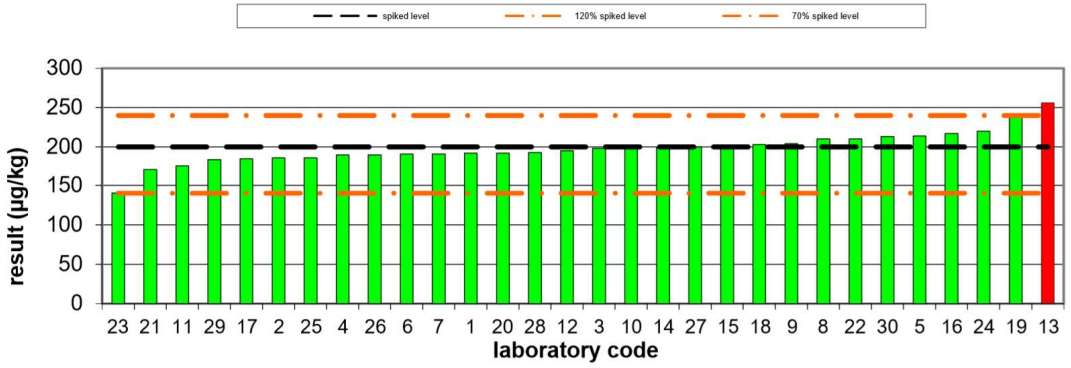

Figure 6: Assessment of pencycuron in test material A

7.9 Results of Spirotetramat-enol

Table 11: Results for spirotetramat-enol in test material A

spirotetramat-enol – spiked level: 40 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 28-48
1	42	83	10	yes
2	34	95	10	yes
3	40	95	10	yes
4	35	90	10	yes
5	32.7	100	10	yes
6	37	94	10	yes
7	47	88	5	yes
8	36	116	10	yes
9	42	79	10	yes
10	35	90	10	yes
11	33	106.1	10	yes
12	43	59	10	yes
13				no
14	40	86	10	yes
15	40	97	10	yes
16	36	103	10	yes
17	42	80.1	10	yes
18	37	90	10	yes
19	36	120	10	yes
20	35	86	10	yes
21	36	84	10	yes
22	35	94	10	yes
23	32	100	10	yes
24	36	95	5	yes
25	49	96.5	5	no
26	42	95	5	yes
27	36	98.9	10	yes
28	39	98	10	yes
29	32	91	10	yes
30	36	116	10	yes

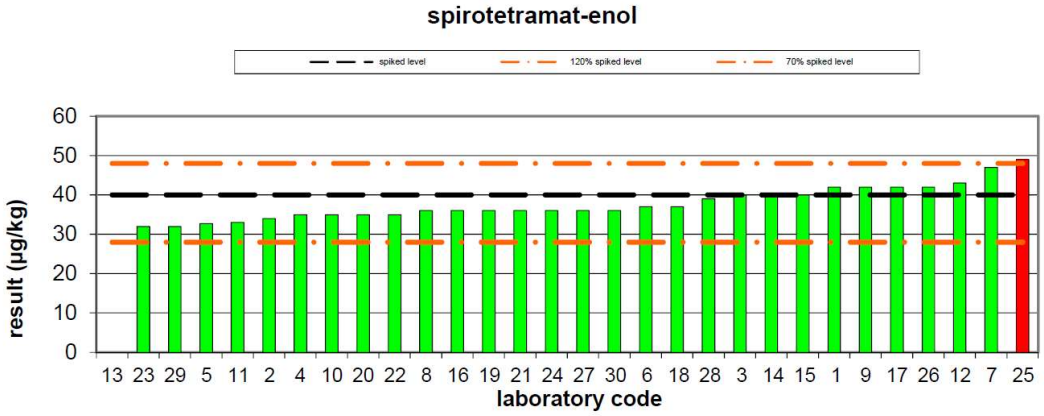

Figure 7: Assessment of spirotetramat-enol in test material A

7.10 Results of Bromide

Table 12: Results for bromide in test material A

bromide – spiked level: 45000 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 31500-54000
1	49300	102	500	**yes**
2	55600	103	1000	**no**
3	47000	96	3000	**yes**
4	42000	92	5000	**yes**
5 *	38600	75	1000	**yes**
6 *	60800	120	1000	**no**
7 *	42300	75	1000	**yes**
8	46000	95	1000	**yes**
9	48000	90	1000	**yes**
10	41000	108	100	**yes**
11 *	36000			**yes**
12	46000		100	**yes**
13	36000	75	5000	**yes**
14	49500	89	1000	**yes**
15	41300	92	500	**yes**
16	42740	97	500	**yes**
17	49345	99	10	**yes**
18 *	53980			**yes**
19 *	42060	95	1000	**yes**
20	46000	96	1000	**yes**
21	48000	90	50	**yes**
22 *	34000	104	5000	**yes**
23	45800	100	10000	**yes**
24 *	45000	120	50	**yes**
25	44461		130	**yes**
26	46000	95	200	**yes**
27	42000	101.7	3000	**yes**
28 *	47000	100	1000	**yes**
29	42300	83	3000	**yes**
30 *	41100	95	500	**yes**

* The analysis was subcontracted

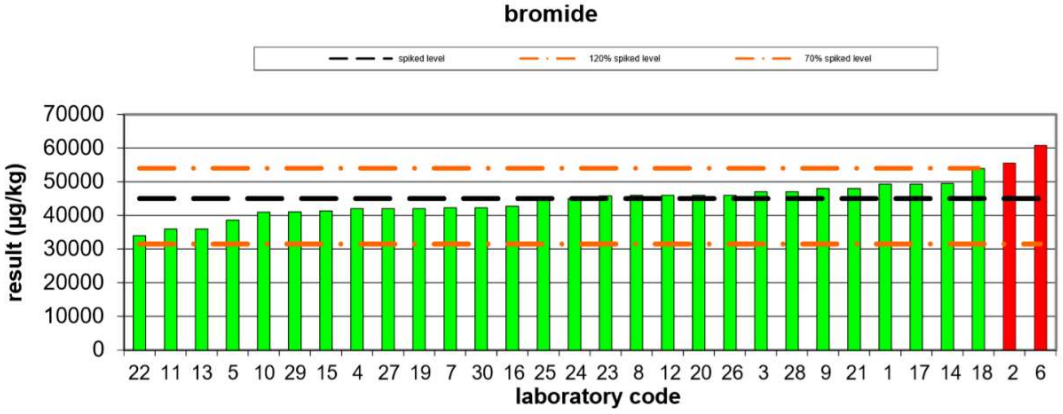

Figure 8: Assessment of bromide in test material A

7.11 Results of Chloride

Table 13: Results for chloride in test material A

chloride		
laboratory code	result (µg/kg)	chloride/bromide ratio
1 *	740000	15.01
2 *	608000	10.9
3	480000	10.2
4	700000	16.7
5 *	455000	11.8
6 *	522000	8:1
7 *	466000	
8	560000	12.2
9	630000	13:1
10	564000	14
11 *	423000	
12	599000	13.0
13 *	674000	
14 *	714000	14.45
15	591000	14:1
16	567160	13.27
17	629000	12.7
18	613000	11
19 *	558260	13.3
20	600000	13
21	638000	13
22 *	520000	15
23	540000	11.8
24		
25	120000	36.8
26	615000	
27	516000	12.28
28	715000	15.2
29	629000	14.9
30 *	603600	14.7

* The analysis was subcontracted

QS. Ihr Prüfsystem für Lebensmittel.

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