Qualitätssicherung. **Vom Erzeuger bis zur Ladentheke.**

QS. Ihr Prüfsystem für Lebensmittel.

Laboratory Performance Assessment

Autumn 2019

QS Fachgesellschaft Obst-Gemüse-Kartoffeln GmbH

Report

Test Material A

Pesticide Residues in Raspberry

January 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 raspberry with eight spiked pesticides. 25 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 twenty-five (25) 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 (Österreichische Agentur für Gesundheit und Ernährungssicherheit), Austria.

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:

- 80 µg/kg Abamectin,
- 5000 µg/kg Bifenazate,
- 200 µg/kg Captan,
- 200 µg/kg Fludioxonil,
- 550 µg/kg Indoxacarb,
- 20 µg/kg Pyriproxyfen,
- 50 µg/kg Zoxamide,
- 1400 µg/kg Phosphonic acid.

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. For this laboratory performance assessment the double variation coefficient [%] according to Horwitz (HORWITZ, W. (1982): Evaluation of analytical methods used for regulation of foods and drugs. Anal Chem 54 (1): 67A-76A) converted to absolute values was used as the test statistic.

The homogeneity test was carried out at 10 representative random samples for all 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

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)
Abamectin	80	78	97	2	37	**homogenous**
Bifenazate	5000	4896	98	276	1239	**homogenous**
Captan	200	172	86	6	70	**homogenous**
Fludioxonil	200	198	99	2	82	**homogenous**
Indoxacarb	550	531	96	20	187	**homogenous**
Pyriproxyfen	20	20	98	1	11	**homogenous**
Zoxamide	50	49	98	1	25	**homogenous**
Phosphonic acid	1400	1357	97	22	413	**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.

- Abamectin,
- Bifenazate,
- Captan,
- Fludioxonil,
- Indoxacarb,
- Pyriproxyfen,
- Zoxamide,
- Phosphonic acid.

4. Criteria of assessment and test items

The test materials for the 2019 Autumn Laboratory Performance Assessment 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 test material was spiked only with abamectin, according to the certificate consisting of 96 % avermectin B1a and 2,4 % avermectin B1b. Since avermectin B1a was not converted into avermectin B1b during the analysis, only the avermectin B1a content was used for evaluation.

The test material was spiked only with bifenazate 5000 µg/kg. Since bifenazate diazine could be formed during sample preparation and measurement, the sum of bifenazate and bifenazate diazine was evaluated. The reported values for bifenazate and bifenazate diazine are shown in the tabular evaluation.

The test material was spiked with captan 200 µg/kg and not with tetrahydrophtalimide (THPI). Since THPI could be formed from captan during sample preparation and measurement in the GC system, the sum of captan and THPI was evaluated. The reported values for captan and THPI are shown in the tabular evaluation.

The test material was spiked only with phosphonic acid 1400 µg/kg and not with fosetyl. Since no conversion takes place during the analysis, only the value for the phosphonic acid was used for evaluation.

The analysis of the parameter phosphonic acid could be subcontracted as a single method to a QS authorized laboratory. These results were evaluated independently, whether the determination was performed by the participant themselves or subcontracted.

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 16. 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. Results, tables and graphics

6.1 Summary

Table 1: Summarized laboratory rating in test material A

QS criteria	number of participants	percent of participants
passed	20	80
failed	5	20
total	25	100

Table 2: Number of satisfactory participants in test material A

QS criteria	number of satisfactory participants	number of participants	satisfactory %
all analyts identified	25	25	100
all analyts identified and reported in acceptable results	9	25	36
no false positive results	25	25	100

6.2 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	7	0	**passed**
4	yes	8	0	**passed**
5	yes	5	0	**failed**
6	yes	8	0	**passed**
7	yes	3	0	**failed**
8	yes	7	0	**passed**
9	yes	7	0	**passed**
10	yes	8	0	**passed**
11	yes	8	0	**passed**
12	yes	7	0	**passed**
13	yes	5	0	**failed**
14	yes	6	0	**passed**
15	yes	8	0	**passed**
16	yes	7	0	**passed**
17	yes	8	0	**passed**
18	yes	7	0	**passed**
19	yes	5	0	**failed**
20	yes	8	0	**passed**
21	yes	8	0	**passed**
22	yes	6	0	**passed**
23	yes	7	0	**passed**
24	yes	5	0	**failed**
25	yes	7	0	**passed**

Table 4: Number of satisfactory results in test material A

analyte	number of satisfactory results	total number of correct identification	satisfactory (%)
abamectin	19	25	76
sum of bifenazate and bifenazate diazine, expressed as bifenazate	19	25	76
sum of captan and THPI, expressed as captan	17	25	68
fludioxonil	24	25	96
indoxacarb	25	25	100
pyriproxyfen	23	25	92
zoxamide	24	25	96
phosphonic acid	19	25	76

6.3 Results of Abamectin

Table 5: Results for Abamectin in test material A

abamectin - spiked level: 80 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 56-96
1	74	92	10	**yes**
2	93	84	10	**yes**
3	55	94	10	**no**
4	76	118	10	**yes**
5	53	143	10	**no**
6	70	96	10	**yes**
7	55	100	10	**no**
8	84	97	10	**yes**
9	80	99,6	10	**yes**
10	82	89	50	**yes**
11	71	100	10	**yes**
12	76	94	10	**yes**
13	47	98	10	**no**
14	91	110	10	**yes**
15	72	118	10	**yes**
16	60	109	10	**yes**
17	72	94	10	**yes**
18	64	109	10	**yes**
19	97	96	10	**no**
20	70	109	10	**yes**
21	84	91	10	**yes**
22	71	86	10	**yes**
23	81	84	10	**yes**
24	54,6	123	10	**no**
25	61	97	5	**yes**

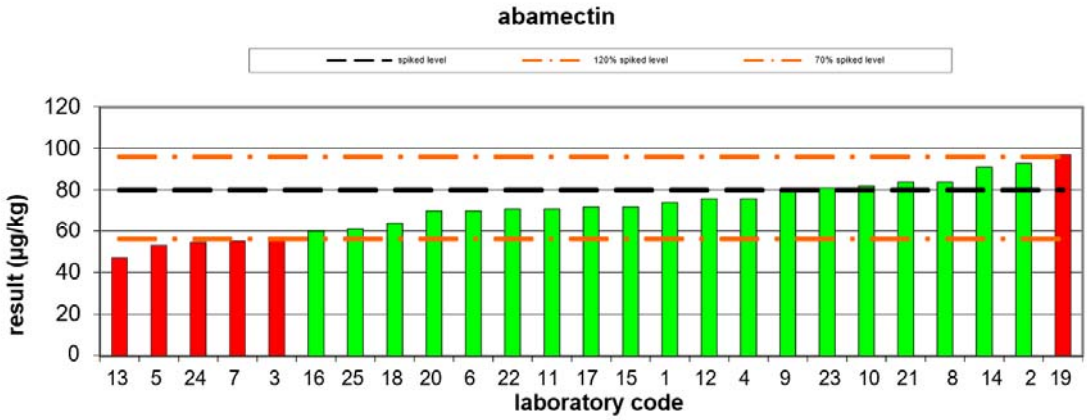

Figure 1: Assessment of abamectin in test material A

6.4 Results of Bifenazate

Table 6: Results for bifenazate in test material A

bifenazate				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	evaluation
1	5229	89	10	see table 8: Results for sum of bifenazate and bifenazate diazine, expressed as bifenazate in test material A
2	4500	89	10	
3	4900	92	10	
4	4615	107	10	
5	4423	100	1	
6	4200	82	10	
7	7000	83	5	
8	4622	95	10	
9	3410	124,8	10	
10	3504	100	10	
11	5580	100	10	
12	4500	88	10	
13	3595	103	10	
14	5200	72,3	10	
15	3300	84	10	
16	4604	91	10	
17	4400	100	10	
18	4700	95	10	
19	3372	90	10	
20	5750	105	10	
21	4700	91	10	
22	6448	99	10	
23	5523	94	10	
24	9806,3	105	10	
25	3500	90	5	

Table 7: Results for bifenazate diazine in test material A

bifenazate diazine				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	evaluation
1	<LoQ	93	10	see table 8: Results for sum of bifenazate and bifenazate diazine, expressed as bifenazate in test material A
2				
3				
4	48	95	10	
5	2098	94	10	
6				
7	100	88	5	
8	293	108	10	
9	82	93,6	10	
10				
11	10	100	10	
12	21	89	10	
13	<LoQ			
14				
15	300	96	10	
16	157		10	
17	63	101	10	
18	15	95	10	
19	53	93	10	
20				
21				
22				
23	68	92	10	
24				
25				

Table 8: Results for sum of bifenazate and bifenazate diazine, expressed as bifenazate in test material A

sum of bifenazate and bifenazate diazine, expressed as bifenazate - spiked level: 5000 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 3500-6000
1	5229			**yes**
2	4500			**yes**
3	4900			**yes**
4	4663			**yes**
5	6533			**no**
6	4200			**yes**
7	7100			**no**
8	4917			**yes**
9	3493			**no**
10	3504			**yes**
11	5590			**yes**
12	4521			**yes**
13	3595			**yes**
14	5200			**yes**
15	3558			**yes**
16	4762			**yes**
17	4500			**yes**
18	4715			**yes**
19	3425			**no**
20	5750			**yes**
21	4700			**yes**
22	6450			**no**
23	5591			**yes**
24	9806,3			**no**
25	3500			**yes**

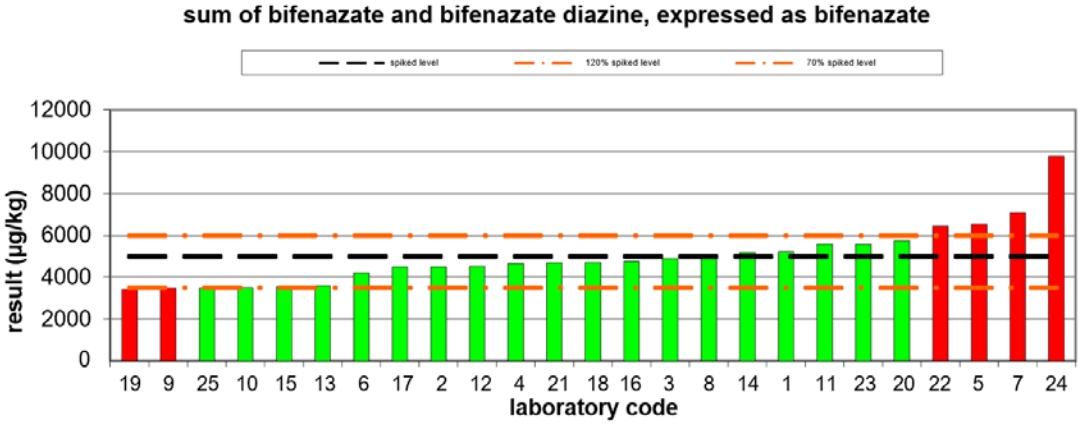

Figure 2: Assessment of sum of bifenazate and bifenazate diazine, expressed as bifenazate in test material A

6.5 Results of Captan

Table 9: Results for captan in test material A

captan				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	evaluation
1	240	94	10	see table 11: Results for sum of captan and THPI, expressed as captan in test material A
2				
3	210	80	10	
4	177	101	10	
5	165	118	5	
6	<LoQ			
7	<LoQ		5	
8	198	108	20	
9	110	108,3	10	
10	88	95	10	
11	88	100	10	
12	170	90	10	
13	126	85	10	
14	266	103	10	
15	50	83	10	
16	181	104	10	
17	110	76	10	
18	123	91	10	
19	105	90	10	
20	135	77	10	
21	156	97	10	
22	169	100	10	
23	67	90	10	
24	<LoQ			
25	50	70	10	

Table 10: Results for tetrahydrophthalimide (THPI) in test material A

tetrahydrophthalimide (THPI)				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	evaluation
1	<LoQ	95	10	see table 11: Results for sum of captan and THPI, expressed as captan in test material A
2	68	115	10	
3				
4	18	88	10	
5	57	86	5	
6	106	90	10	
7	118	98,6	5	
8				
9	56	119,5	10	
10	50	90	10	
11	51	100	10	
12	43	96	10	
13	<LoQ			
14	154	106	10	
15	54	89	10	
16				
17	40	86	10	
18	78	91	10	
19	45	89	10	
20	35	82	10	
21				
22	20	100	10	
23	61	90	10	
24	161,2	67	10	
25	100	80	10	

Table 11: Results for sum of captan and THPI, expressed as captan in test material A

sum of captan and THPI, expressed as captan - spiked level: 200 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 140-240
1	240			**yes**
2	135			**no**
3	210			**yes**
4	213			**yes**
5	278			**no**
6	210			**yes**
7	235			**yes**
8	198			**yes**
9	221			**yes**
10	187			**yes**
11	190			**yes**
12	255			**no**
13	126			**no**
14	420			**no**
15	158			**yes**
16	181			**yes**
17	190			**yes**
18	278			**no**
19	194			**yes**
20	205			**yes**
21	156			**yes**
22	189			**yes**
23	188			**yes**
24	320,5			**no**
25	249			**no**

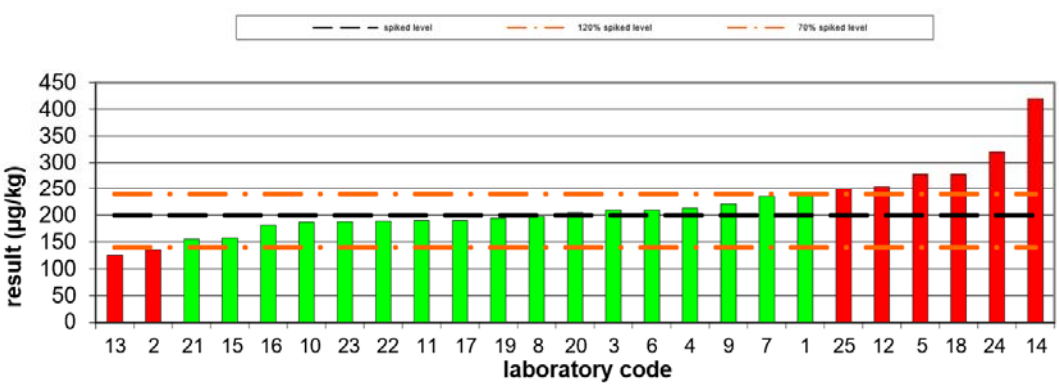

Figure 3: Assessment of sum of captan and THPI, expressed as captan in test material A

6.6 Results of Fludioxonil

Table 12: Results for fludioxonil in test material A

fludioxonil - spiked level: 200 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 140-240
1	186	101	10	yes
2	185	88	10	yes
3	180	80	10	yes
4	180	118	10	yes
5	233	73	1	yes
6	175	96	10	yes
7	185	98,6	5	yes
8	179	104	10	yes
9	194	97,8	10	yes
10	198	86	10	yes
11	215	100	10	yes
12	185	89	10	yes
13	185	96	10	yes
14	176	118	10	yes
15	200	92	10	yes
16	130	92	10	no
17	170	99,8	10	yes
18	158	99	10	yes
19	190	85	10	yes
20	188	82	10	yes
21	180	87	10	yes
22	196	96	10	yes
23	183	81	10	yes
24	183,1	97	10	yes
25	176	101	5	yes

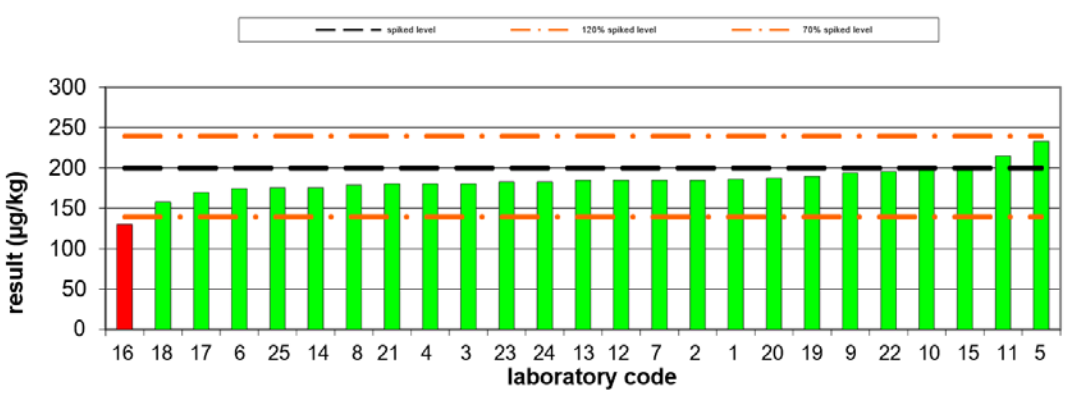

Figure 4: Assessment of fludioxonil in test material A

6.7 Results of Indoxacarb

Table 13: Results for indoxacarb in test material A

indoxacarb - spiked level: 550 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 385-660
1	515	96	10	yes
2	470	96	10	yes
3	510	87	10	yes
4	504	114	10	yes
5	481	107	5	yes
6	600	87	10	yes
7	440	99	5	yes
8	531	77	10	yes
9	513	105,7	10	yes
10	504	101	10	yes
11	587	100	10	yes
12	565	93	10	yes
13	620	110	10	yes
14	480	80,6	10	yes
15	560	89	10	yes
16	506	78	10	yes
17	600	95,5	10	yes
18	486	104	10	yes
19	550	110	10	yes
20	475	100	10	yes
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22	572	85	10	yes
23	474	89	10	yes
24	535	114	10	yes
25	520	97	5	yes

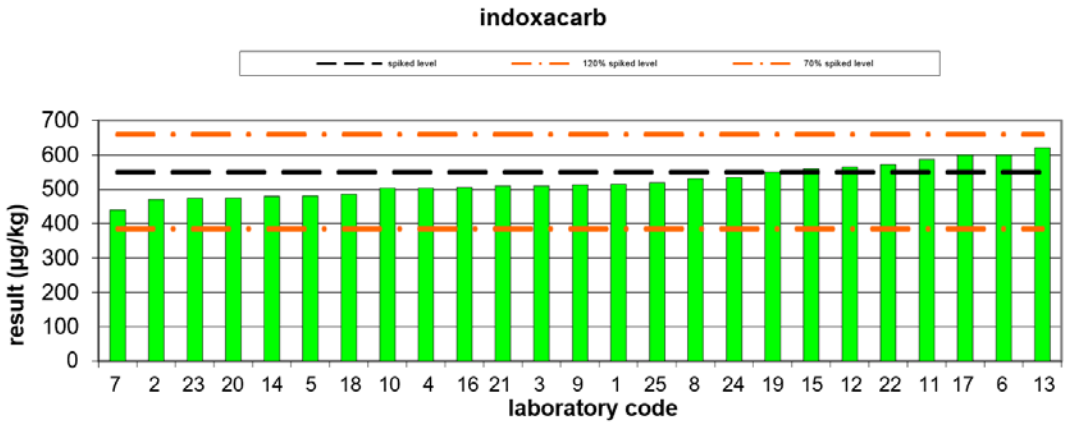

Figure 5: Assessment of indoxacarb in test material A

6.8 Results of Pyriproxyfen

Table 14: Results for pyriproxyfen in test material A

pyriproxyfen - spiked level: 20 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 14-24
1	20	96	10	yes
2	15	87	10	yes
3	18	85	10	yes
4	20	115	10	yes
5	17	97	1	yes
6	18	77	10	yes
7	27	99	5	no
8	21	99	10	yes
9	20	94,4	10	yes
10	20	96	10	yes
11	23	100	10	yes
12	20	92	10	yes
13	22	90	10	yes
14	21	102	10	yes
15	20	118	10	yes
16	19	97	10	yes
17	20	99	10	yes
18	19	108	10	yes
19	20	90	10	yes
20	20	114	10	yes
21	22	87	10	yes
22	26	93	10	no
23	19	95	10	yes
24	15,7	107	10	yes
25	18	98	5	yes

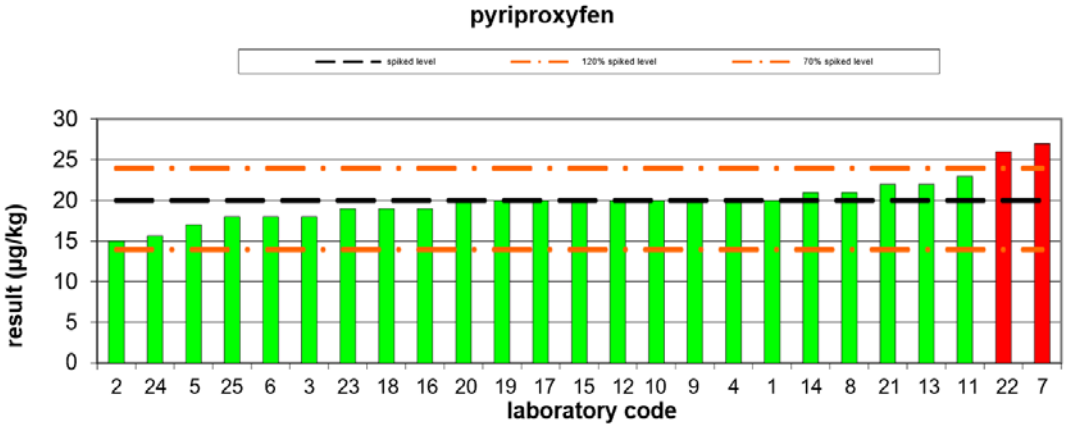

Figure 6: Assessment of pyriproxyfen in test material A

6.9 Results of Zoxamide

Table 15: Results for zoxamide in test material A

zoxamide - spiked level: 50 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 35-60
1	59	89	10	yes
2	54	90	10	yes
3	48	86	10	yes
4	51	105	10	yes
5	47	100	1	yes
6	48	100	10	yes
7	92	99	5	no
8	52	92	10	yes
9	48	98	10	yes
10	48	103	10	yes
11	54	100	10	yes
12	52	103	10	yes
13	56	100	10	yes
14	53	110	10	yes
15	46	114	50	yes
16	51	103	10	yes
17	57	96,6	10	yes
18	49	114	10	yes
19	57	100	10	yes
20	45	104	10	yes
21	56	98	10	yes
22	52	89	10	yes
23	55	99	10	yes
24	42,2	82	10	yes
25	48	104	5	yes

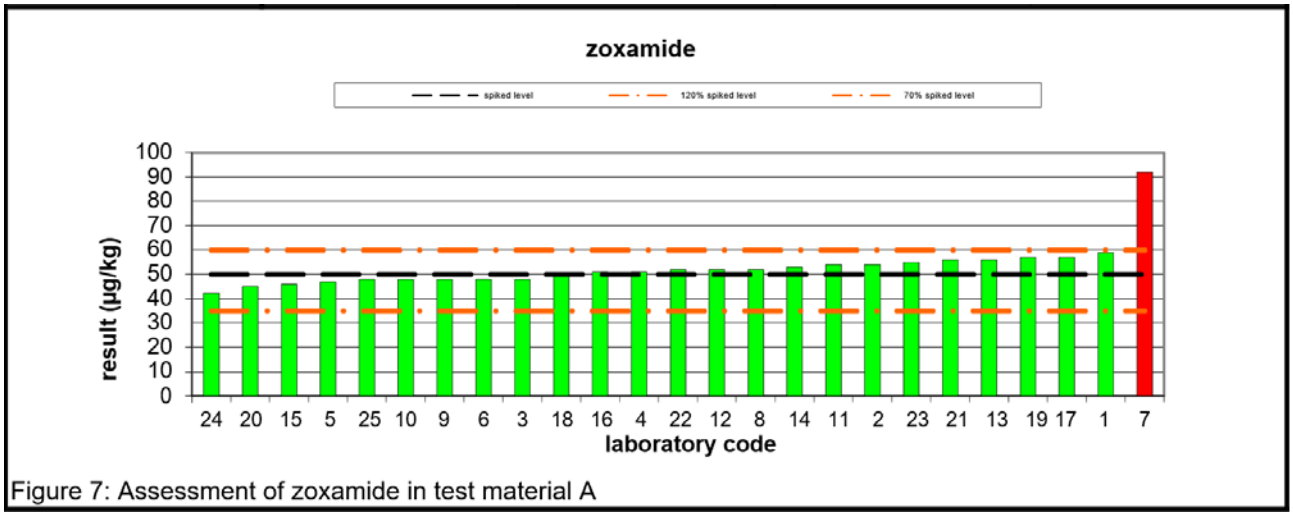

Figure 7: Assessment of zoxamide in test material A

6.10 Results of Phosphonic acid

Table 16: Results for phosphonic acid in test material A

phosphonic acid - spiked level: 1400 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 980-1680
1	1308	99	50	yes
2	1125	111	10	yes
3	1100	81	100	yes
4	1162	92	10	yes
5	1251	97	100	yes
6 *	1250	105	50	yes
7	1720			no
8 *	1887	99	50	no
9	1420	99,6	10	yes
10	1599	87	10	yes
11	1342	100	100	yes
12	1180	86	10	yes
13	1700	92	10	no
14	2200	81,8	10	no
15	1200	98	10	yes
16	1537	109	100	yes
17	1400	105	10	yes
18	1306	93	10	yes
19	2650	108	100	no
20	1670	97	10	yes
21 *	1400	77	50	yes
22	1156	95	10	yes
23	1805	79,3	10	no
24 *	1400	105	10	yes
25	1250	91	10	yes

* The analysis was subcontracted

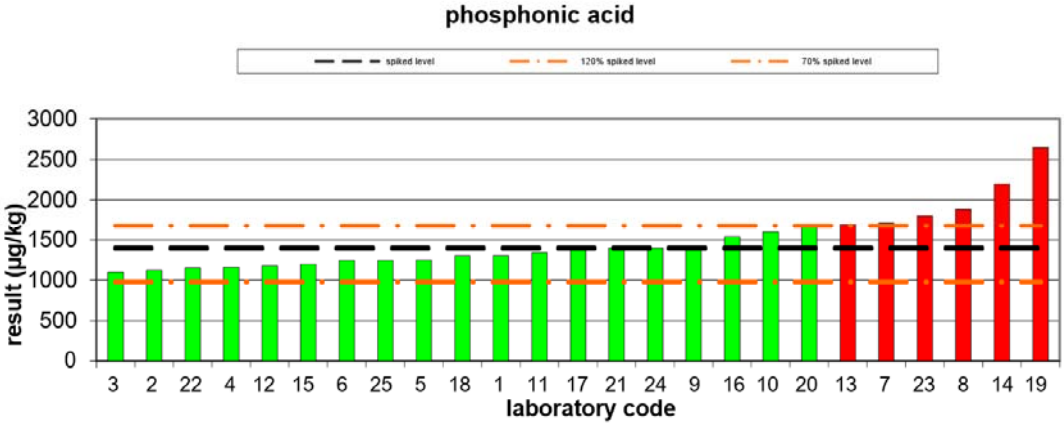

Figure 8: Assessment of phosphonic acid in test material A

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