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

QS. Ihr Prüfsystem für Lebensmittel.

Laboratory Performance Assessment

2021/2

QS Fachgesellschaft Obst-Gemüse-Kartoffeln GmbH

Report

Test Material A

Pesticide Residues in Potato

January 2022

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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 potato with nine spiked pesticides. 26 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-six (26) 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).

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:

- 600 µg/kg 1,4-Dimethylnaphthaline,
- 80 µg/kg Cyantraniliprole,
- 200 µg/kg Flufenacet-sulfonic acid (ESA),
- 100 µg/kg Flutolanil,
- 60 µg/kg Quizalofop-P free acid
- 200 µg/kg Quizalofop-P-ethyl
- *245 µg/kg Quizalofop-P sum (calculated; sum of quizalofop, its salts, its esters (including propaquizafop) and its conjugates, expressed as quizalofop (any ratio of constituent isomers)),*
- 50 µg/kg Oxathiapiprolin,
- 50 µg/kg Tolclophos-methyl,
- 120.2 µg/kg Lead (spiked with lead acetate trihydrate; conversion factor 1.830)

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 samples 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)
1,4-Dimethylnaphthaline	600	579	97	13	201	**homogenous**
Cyantraniliprole	80	79	99	0	37	**homogenous**
Flufenacet-sulfonic acid (ESA)	200	199	100	0	81	**homogenous**
Flutolanil	100	101	101	2	46	**homogenous**
Quizalofop-P sum	245	226	92	10	90	**homogenous**
Oxathiapiprolin	50	45	90	0	21	**homogenous**
Tolclophos-methyl	50	51	102	0	24	**homogenous**
Lead	120.2	122	101	8	53	**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.

- 1,4-Dimethylnaphthaline,
- Cyantraniliprole,
- Flufenacet-sulfonic acid (ESA),
- Flutolanil,
- Quizalofop-P sum,
- Oxathiapiprolin,
- Tolclophos-methyl,
- Lead

4. Criteria of assessment and test items

The test materials for the Laboratory Performance Assessment 2021/2 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 total bromide and maleic hydrazite, but an additional test for the heavy metals lead and cadmium.

The analysis of the parameter lead and cadmium could be subcontracted to a QS authorized laboratory. Also, the confirmatory analysis of positive results for the phenoxyalkanecarboxylic acids quizalofop free acid/quizalofop P-ethyl in the multi-method by means of the single method of the hydrolysis could be subcontracted to a QS authorized laboratory. The results were evaluated independently, whether the determination was performed by the participant themselves or subcontracted.

All three test materials naturally contained a small amount of cadmium (14 µg/kg, mean value from 3 measurements by AGES). The participants also reported cadmium residues. The results are presented informatively. Cadmium was not the subject of the competence test and is therefore not relevant for the evaluation of the test.

The substance 1,4-Dimethylnaphthaline could only be evaluated qualitatively. The stability tests showed a loss of 17 % - 24 % of the spiked amount after 8 weeks. Since the defined residue

level of 600 µg/kg could not be guaranteed, no quantitative evaluation was performed. However, a significant residue level above the limit of quantification was present during the period of the laboratory performance assessment.

The test material was spiked with Flufenacet-sulfonic acid (ESA) 200 µg/kg only and not with the parent substance Flufenacet. Since no conversion takes place during the analysis, only the value for Flufenacet-sulfonic acid (ESA) was used for evaluation.

The test material was spiked with Quizalofop-P free acid 60 µg/kg and 200 µg/kg of the ester Quizalofop- P-ethyl. Since conversion occurs during analysis/hydrolysis, the reported sum value was used for evaluation here. The reported values for Quizalofop-P free acid and Quizalofop-P-ethyl are shown in the tabular evaluation.

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 five pesticides related to the recovery criteria of the quantitative evaluations. 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 with evaluated results 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

- Lab 8: reports a detection of Indolylacetic acid: result: 205.94 µg/kg; recovery: 94.77 %; LoQ: 10 µg/kg;

  The substance is a phytohormone that was not subject of the competence test, therefore the detection is not relevant for the evaluation of the test.

- Lab 10: reports a detection of bromide: 2929 µg/kg; recovery: 82 %; LoQ: 1000 µg/kg;

  The substance is determined by a single method. However, the substance was not subject of the competence test, therefore the detection is not relevant for the evaluation of the test.

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	17	65
failed	9	35
total	26	100

Table 2: Number of satisfactory participants in test material A

QS criteria	number of satisfactory participants	number of participants	satisfactory %
all analyts identified	19	26	73
all analyts identified and reported in acceptable results	8	26	31
no false positive results	26	26	100

7.2 Rating of performance

Table 3: Rating

laboratory code	**criterion 1** all analytes identified	**criterion 2** number of acceptable results of the quanti-tative evaluations	**criterion 3** number of false positive results	**rating**
1	yes	5	0	**passed**
2	yes	7	0	**passed**
3	no	6	0	**failed**
4	no	4	0	**failed**
5	no	4	0	**failed**
6	yes	7	0	**passed**
7	yes	6	0	**passed**
8	no	6	0	**failed**
9	yes	7	0	**passed**
10	no	4	0	**failed**
11	yes	7	0	**passed**
12	yes	7	0	**passed**
13	yes	6	0	**passed**
14	yes	6	0	**passed**
15	yes	6	0	**passed**
16	yes	4	0	**failed**
17	yes	4	0	**failed**
18	yes	6	0	**passed**
19	yes	5	0	**passed**
20	yes	7	0	**passed**
21	no	3	0	**failed**
22	no	5	0	**failed**
23	yes	6	0	**passed**
24	yes	6	0	**passed**
25	yes	7	0	**passed**
26	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 (%)
1,4-Dimethylnaphthaline	23	23	100
Cyantraniliprole	23	26	88
Flufenacet-sulfonic acid (ESA)	12	20	60
Flutolanil	24	26	92
Quizalofop-P sum	18	25	72
Oxathiapiprolin	24	26	92
Tolclophos-methyl	25	25	100
Lead	22	25	88

7.3 Results of 1,4-Dimethylnaphthaline

Table 5: Results for 1,4-Dimethylnaphthaline in test material A

1,4-Dimethylnaphthaline - spiked level: 600 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): > 0
1	450	100	10	**yes**
2	533	82	10	**yes**
3	367	107	10	**yes**
4				**no**
5	536	116	10	**yes**
6	420	92	10	**yes**
7	350	96	10	**yes**
8				**no**
9	390	80	20	**yes**
10	378	91	10	**yes**
11	430	94.2	5	**yes**
12	467	91	10	**yes**
13	373	115	10	**yes**
14	440.5	89	10	**yes**
15	350	95	10	**yes**
16	265	81	10	**yes**
17	460	120	10	**yes**
18	410	106	10	**yes**
19	380	110	10	**yes**
20	408	98	10	**yes**
21				**no**
22	360	95	10	**yes**
23	439	95	10	**yes**
24	539	105	10	**yes**
25	300	111	10	**yes**
26	440	85	10	**yes**

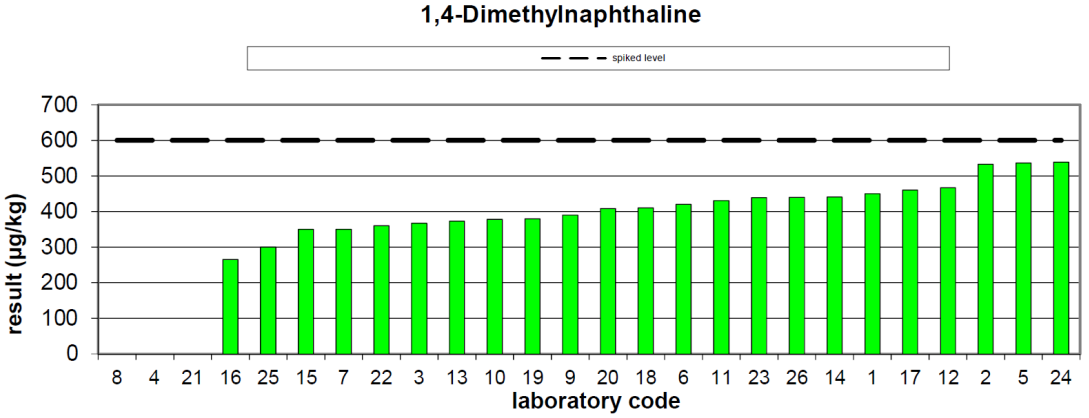

Figure 1: Assessment of 1,4-Dimethylnaphthaline in test material A

7.4 Results of Cyantraniliprole

Table 6: Results for Cyantraniliprole in test material A

Cyantraniliprole - spiked level: 80 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 56-96
1	98	110	10	**no**
2	92	90	10	**yes**
3	74	101	10	**yes**
4	83	103	10	**yes**
5	95	104	10	**yes**
6	78	95	10	**yes**
7	72	103	10	**yes**
8	94.04	88.15	10	**yes**
9	70	120	10	**yes**
10	87	92	10	**yes**
11	74	86,9	5	**yes**
12	84	89	10	**yes**
13	80	96.2	10	**yes**
14	70.8	102	10	**yes**
15	78	90	10	**yes**
16	165	108	10	**no**
17	36	101	10	**no**
18	92	105	10	**yes**
19	76	97	10	**yes**
20	72	100	10	**yes**
21	85	93.1	3	**yes**
22	69	96	10	**yes**
23	96	95	10	**yes**
24	93	86	10	**yes**
25	84	102	10	**yes**
26	77	110	10	**yes**

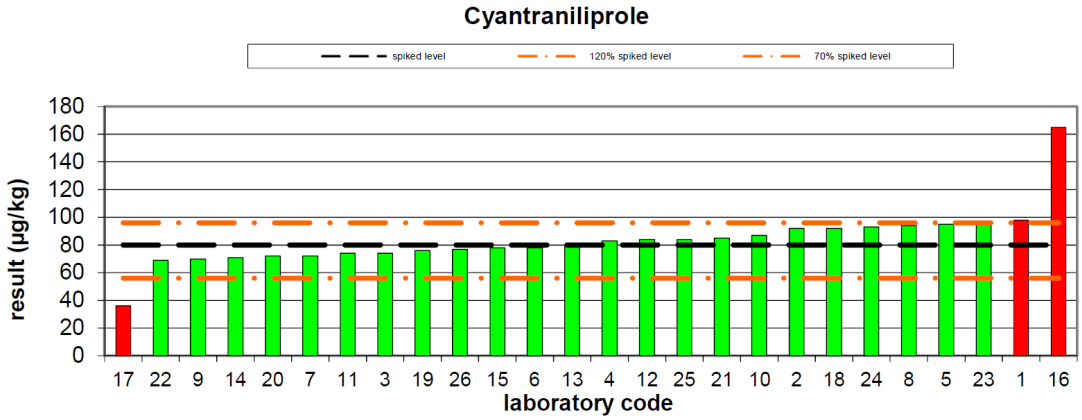

Figure 2: Assessment of Cyantraniliprole in test material A

7.5 Results of Flufenacet-sulfonic acid (ESA)

Table 7: Results for Flufenacet-sulfonic acid (ESA) in test material A

Flufenacet-sulfonic acid (ESA) - spiked level: 200 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 140-240
1	94	71	10	**no**
2	147	80	10	**yes**
3				**no**
4				**no**
5	80	95	10	**no**
6	140	75	10	**yes**
7	175	90	10	**yes**
8				**no**
9	187	100	10	**yes**
10				**no**
11	192	93.1	5	**yes**
12	140	97	10	**yes**
13	96	96.4	10	**no**
14	213.5	86	10	**yes**
15	193	90	10	**yes**
16	27	72	10	**no**
17	110	101	10	**no**
18	117	93	10	**no**
19	85	99	10	**no**
20	168	83	10	**yes**
21				**no**
22				**no**
23	225	90	10	**yes**
24	130	76	10	**no**
25	216	93	10	**yes**
26	180	75	10	**yes**

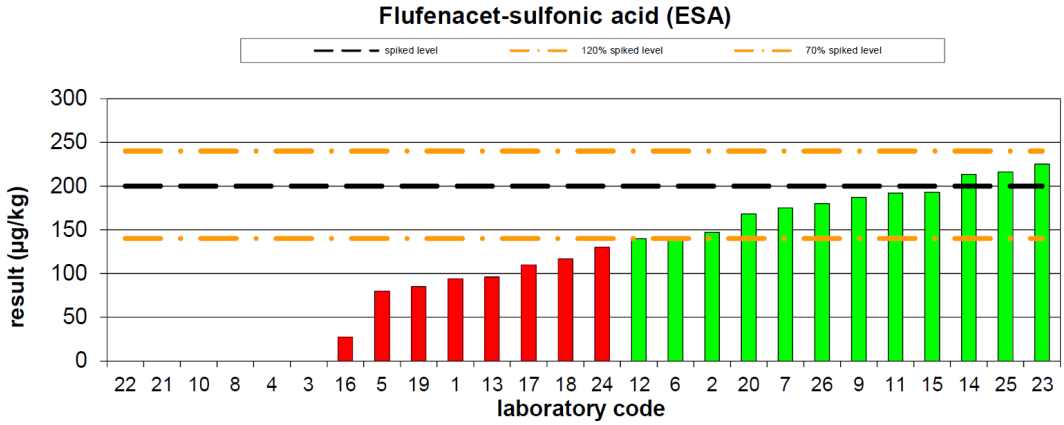

Figure 3: Assessment of Flufenacet-sulfonic acid (ESA) in test material A

7.6 Results of Flufenacet sum

Table 8: Results for Flufenacet sum* in test material A

Flufenacet sum*				
laboratory code	result (µg/kg) *only informative*	recovery (%)	LoQ (µg/kg)	evaluation
1				not part of the evaluation
2	147			
3				
4				
5	98			
6	172			
7				
8				
9	229			
10				
11				
12	185			
13	127			
14	256			
15	255			
16	33			
17	130			
18	142			
19	110			
20	222			
21				
22				
23	298			
24	172			
25	285			
26	239			

* Flufenacet (sum of all compounds containing the N fluorophenyl-N-isopropyl moiety expressed as flufenacet)

7.7 Results of Flutolanil

Table 9: Results for Flutolanil in test material A

Flutolanil - spiked level: 100 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 70-120
1	78	100	10	**yes**
2	85	82	10	**yes**
3	80	104	10	**yes**
4	88	97	10	**yes**
5	82	94	10	**yes**
6	102	93	10	**yes**
7	70	97	10	**yes**
8	104.15	91.33	10	**yes**
9	91	80	10	**yes**
10	121	117	10	**no**
11	86	92.1	5	**yes**
12	108	96	10	**yes**
13	92	103.5	10	**yes**
14	79.8	80	10	**yes**
15	90	85	10	**yes**
16	113	116	10	**yes**
17	100	92	10	**yes**
18	94	108	10	**yes**
19	93	80	10	**yes**
20	90	90	10	**yes**
21	87	91.1	3	**yes**
22	95	101	10	**yes**
23	59	90	10	**no**
24	103	86	10	**yes**
25	90	104	10	**yes**
26	107	105	10	**yes**

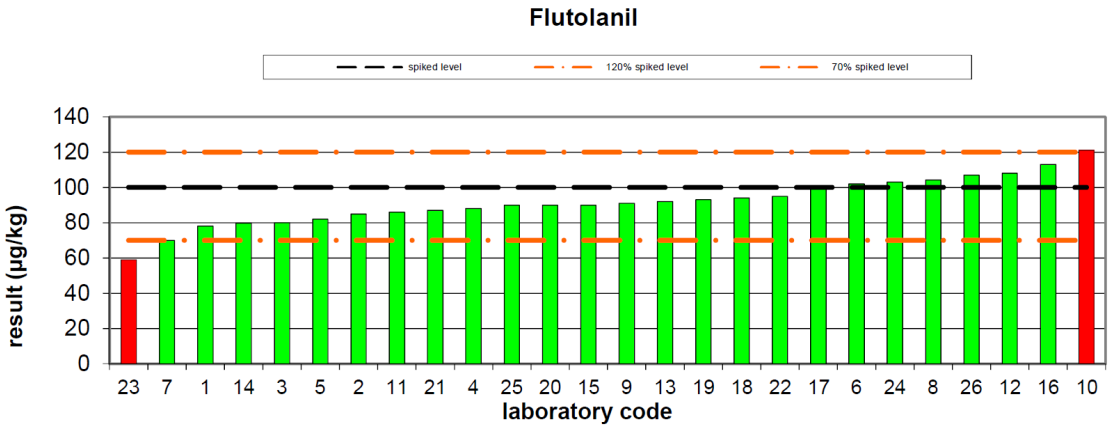

Figure 4: Assessment of Flutolanil in test material A

7.8 Results of Quizalofop-P free acid

Table 10: Results for Quizalofop-P free acid in test material A

Quizalofop-P free acid - spiked level: 60 µg/kg				
laboratory code	result (µg/kg) *only informative*	recovery (%)	LoQ (µg/kg)	evaluation
1	230	110	10	not part of the evaluation
2				
3	180			
4	114	74	10	
5	321	100	1	
6	204	90	10	
7	120	100	10	
8	222.65	85.66	10	
9	248	81	10	
10	231	90	10	
11	231	88.8	5	
12	151	93	10	
13	106	85,4	10	
14	191	90	10	
15				
16	57	89	10	
17	170	104	10	
18	110	93	10	
19	130	73	10	
20	216			
21	86	93.9	3	
22				
23	220	86	10	
24	161	84	10	
25	240	91	10	
26	180	110	10	

7.9 Results of Quizalofop-P-ethyl

Table 11: Results for Quizalofop-P-ethyl in test material A

Quizalofop-P-ethyl - spiked level: 200 µg/kg				
laboratory code	result (µg/kg) *only informative*	recovery (%)	LoQ (µg/kg)	evaluation
1	19	84	10	not part of the evaluation
2				
3	<BG			
4	46	94	10	
5	3	117	1	
6	30	90	10	
7	49	98	10	
8				
9				
10	24	81	10	
11				
12	33	94	10	
13	69	86.8	10	
14				
15				
16				
17	53	106	10	
18	24	97	10	
19				
20	28			
21	14	89,3	3	
22				
23	21	110	10	
24	87	86	10	
25	<BG			
26				

7.10 Results of Quizalofop-P sum

Table 12: Results for Quizalofop-P sum** in test material A

Quizalofop-P sum** - spiked level calculated: 245 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 172-294
1	290		10	**yes**
2	212	80	10	**yes**
3	197	101	10	**yes**
4	154			**no**
5	324			**no**
6	232		10	**yes**
7*	120	90	10	**no**
8	222.65		10	**yes**
9	248			**yes**
10	453	95	10	**no**
11	231			**yes**
12	182	94	10	**yes**
13	174	85.4	10	**yes**
14	191	90	10	**yes**
15	200		10	**yes**
16	57			**no**
17	260	102	10	**yes**
18	268	94	10	**yes**
19	130	73	10	**no**
20	240	116	10	**yes**
21	99		3	**no**
22				**no**
23	239		10	**yes**
24	241		10	**yes**
25	264	85	10	**yes**
26	230	115	10	**yes**

* subcontracted: hydrolysis Quizalofop
** Quizalofop (sum of quizalofop, its salts, its esters (including propaquizafop) and its conjugates, expressed as quizalofop (any ratio of constituent isomers))

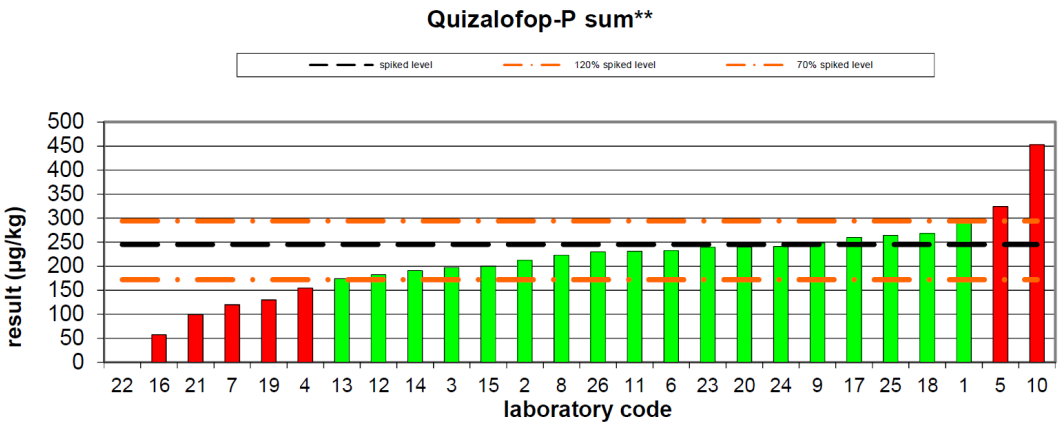

Figure 5: Assessment of Quizalofop-P sum** in test material A

7.11 Results for Oxathiapiprolin

Table 13: Results for Oxathiapiprolin in test material A

Oxathiapiprolin - spiked level: 50 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 35-60
1	52	110	10	yes
2	40	95	10	yes
3	43	103	10	yes
4	48	102	10	yes
5	41	93	10	yes
6	46	96	10	yes
7	42	102	10	yes
8	43.55	95.44	10	yes
9	39	120	10	yes
10	55	96	10	yes
11	43	101	5	yes
12	46	92	10	yes
13	44	90.5	10	yes
14	39.6	132	10	yes
15	32	100	10	no
16	60	113	10	yes
17	50	95	10	yes
18	38	97	10	yes
19	41	86	10	yes
20	36	90	10	yes
21	71	91.3	3	no
22	41	94	10	yes
23	43	95	10	yes
24	55	96	10	yes
25	36	97	10	yes
26	59	125	10	yes

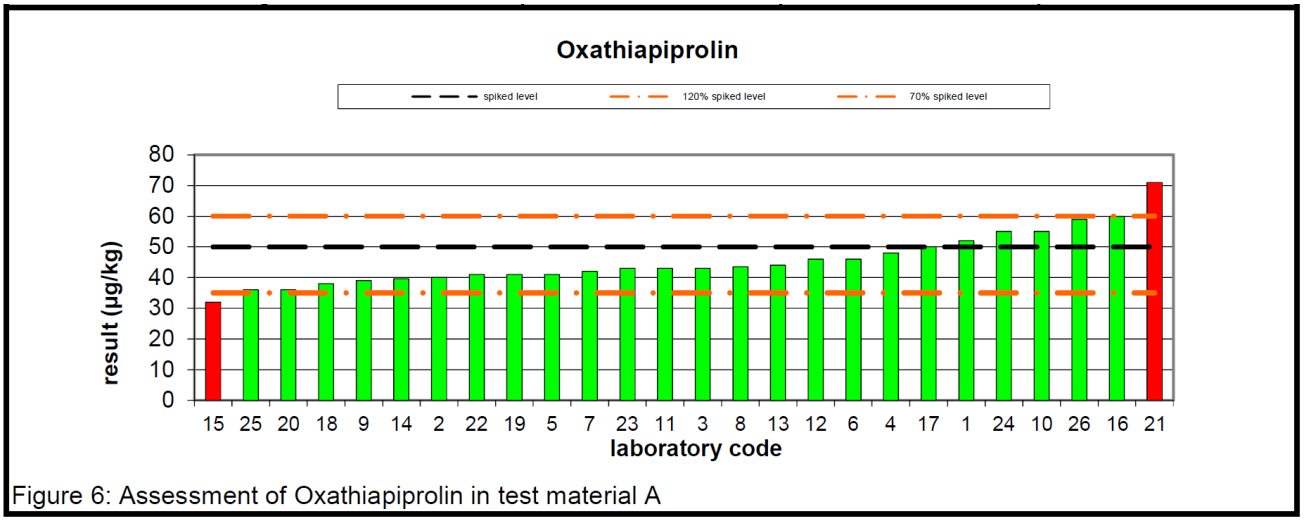

Figure 6: Assessment of Oxathiapiprolin in test material A

7.12 Results for Tolclophos-methyl

Table 14: Results for Tolclophos-methyl in test material A

Tolclophos-methyl - spiked level: 50 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 35-60
1	56	110	10	yes
2	48	91	10	yes
3	42	103	10	yes
4	39	94	10	yes
5				no
6	42	88	10	yes
7	36	106	10	yes
8	44.27	92.79	10	yes
9	42	90	10	yes
10	43	101	10	yes
11	50	93.2	5	yes
12	47	99	10	yes
13	46	100	10	yes
14	46.5	97	10	yes
15	35	105	10	yes
16	57	112	10	yes
17	56	98	10	yes
18	39	94	10	yes
19	43	87	10	yes
20	42	97	10	yes
21	39	92.4	3	yes
22	45	96	10	yes
23	44	110	10	yes
24	50	95	10	yes
25	42	102	10	yes
26	46	85	10	yes

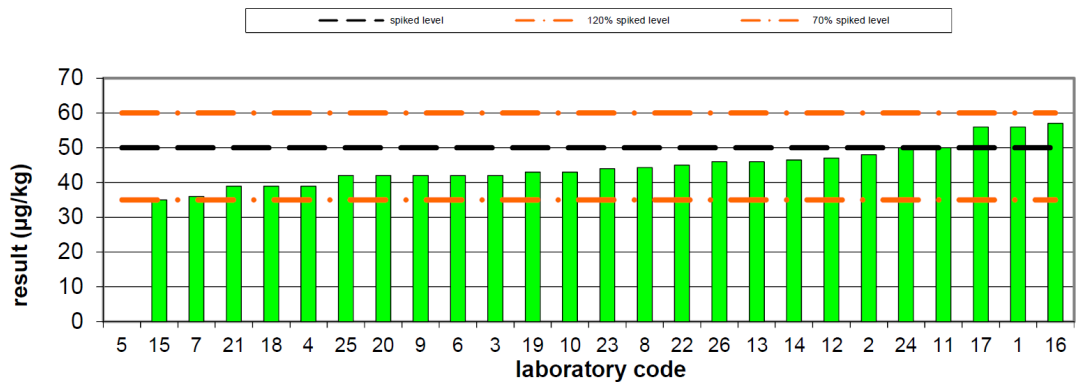

Figure 7: Assessment of Tolclophos-methyl in test material A

7.13 Results for Lead

Table 15: Results for Lead in test material A

Lead - spiked level calculated**: 120,2 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 84-144
1	114	105	10	yes
2	144	96	10	yes
3	126	90	10	yes
4	2170	100	30	no
5	117	103.6	5	yes
6*	140	94	20	yes
7*	100	99	20	yes
8	122.01	99.23	30	yes
9	101	98	10	yes
10	137	96	5	yes
11	95	90.2	0.2	yes
12	130	101	1	yes
13*	120		6.25	yes
14	57.2	92	10	no
15*	120		10	yes
16	118	115	50	yes
17	1066	108	10	no
18*	110	112	100	yes
19*	130	96	10	yes
20	100	87	10	yes
21				no
22	128	109	5	yes
23	115	90	20	yes
24	100	95	10	yes
25	108		10	yes
26	135	100	10	yes

* The analysis was subcontracted

** spiked with lead acetate trihydrate; conversion factor 1.830

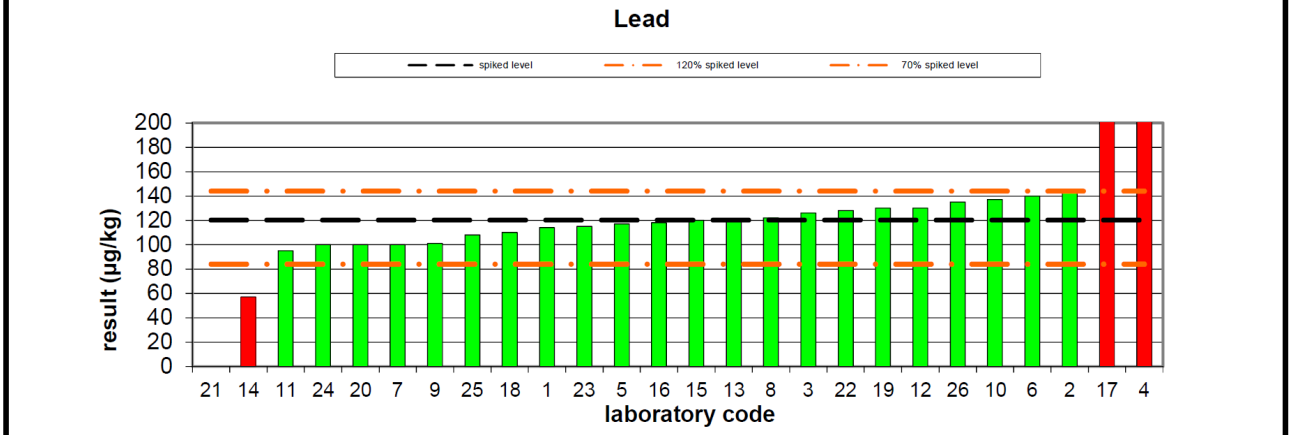

Figure 8: Assessment of Lead in test material A

7.14 Results for Cadmium

Table 16: Results for Cadmium in test material A

Cadmium				
laboratory code	result (µg/kg) *only informative*	recovery (%)	LoQ (µg/kg)	evaluation
1	13			not part of the evaluation
2	14			
3	14			
4	3040			
5	13.1			
6*	14			
7*	12			
8	583.74			
9	12			
10	15			
11	10			
12	14			
13*	13.6			
14	13.5			
15*	11			
16	11			
17	124			
18*	12			
19*	14			
20	11			
21				
22	14			
23	15			
24	12			
25	12			
26	15			

* The analysis was subcontracted

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