



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



Laboratory Performance Assessment

2022/1

QS Fachgesellschaft Obst-Gemüse-Kartoffeln GmbH

Report

Test Material B

Pesticide Residues in Blueberry

June 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 "B". Each laboratory received a sample of blueberry with eight spiked pesticides. 31 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 "B" was distributed to thirty-one (31) 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 KLZH (Kantonales Labor Zürich), 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:

- 400 µg/kg 1-Naphthylacetamide,
- 40 µg/kg Azadirachtin,
- 300 µg/kg Clopyralid,
- 400 µg/kg Icaridin/Picaridin,
- 50 µg/kg Malathion,
- 310 µg/kg Phthalimide,
- 380 µg/kg THPI,
- 270 µg/kg Nicotine



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 "B" was calculated with the results from this proficiency testing round (Laboratory Performance Assessment 2022/1), because no previous proficiency testing data is available for the requested parameter matrix combination.

The homogeneity test was carried out at 10 representative random samples in double determination acc. to ISO 13528 (Intern. Harmonised Protocol).

The homogeneity tests are subcontracted by: Kantonales Labor Zürich (KLZH), Switzerland.

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

parameter	spiked level [$\mu\text{g}/\text{kg}$]	mean (homogeneity test) [$\mu\text{g}/\text{kg}$]	recovery (homogeneity test) [%]	standard deviation of the material homogeneity (s_{material}) [$\mu\text{g}/\text{kg}$]	test statistic [$\mu\text{g}/\text{kg}$]	evaluation of the homogeneity test $s_{\text{material}} < 30\%$ test statistic)
1-Naphthylacetamide	400	366	92	7	41	homogenous
Azadirachtin	40	37	92	0	9	homogenous
Clopyralid	300	288	96	0	77	homogenous
Icaridin/Picaridin	400	369	92	0	66	homogenous
Malathion	50	45	90	1	5	homogenous
Phthalimide	310	291	94	0	44	homogenous
THPI	380	348	92	0	78	homogenous
Nicotine	270	264	98	0	44	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-Naphthylacetamide,
- Azadirachtin,
- Clopyralid,
- Icaridin/Picaridin,
- Malathion,
- Phthalimide,
- THPI,
- Nicotine.

4. Criteria of assessment and test items

The test materials for the Laboratory Performance Assessment 2022/1 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.

In case of a positive result of nicotine with the multi-method, the laboratories are allowed to subcontract the analysis to another QS-approved laboratory as a confirmation analysis. The results were evaluated independently, whether the determination was performed by the participant themselves or subcontracted.

The analytes 1-Naphthylacetamide, Phthalimide, THPI and Malathion are components of sum-residue definitions. The sum-residues are shown informatively in tabular form.

All three test materials naturally contained a small amount of DEET (Diethyltoluamide) with < 3 µg/kg. Some participants reported traces of DEET.



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 "B" 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. Remarks and comments

- Lab 32 reported DEET < LoQ. The Lab also reported 1-Naphthylacetic acid: result: 289 µg/kg; recovery: 97.5%; LoQ: 10 µg/kg.

The test material contains 1-Naphthylacetamide but no 1- Naphthylacetic acid. Since 1- Naphthylacetamide cannot convert to 1-Naphthylacetic acid, the detection is considered a false positive.

- Lab 48, 50, 61 reported DEET < LoQ.
- Lab 57 reported DEET < LoQ (3µg/kg).
- Lab 36, 38, 47, 51 reported DEET < LoQ (5µg/kg).
- Lab 37 reported DEET < LoQ (8µg/kg).
- Lab 49 did not submit results within the reporting deadline. The test is thus considered failed.
- Lab 55 reported a detection of Matrine: result: 41 µg/kg; recovery: 88%; LoQ: 10µg/kg;

The analyte is not present in the test material and is evaluated as a false positive detection.



7. Results, tables and graphics

7.1 Summary

Table 1: Summarized laboratory rating in test material B

QS criteria	number of participants	percent of participants
passed	24	77
failed	7	23
total	31	100

Table 2: Number of satisfactory participants in test material B

QS criteria	number of satisfactory participants	number of participants	satisfactory %
all analyts identified	25	31	81
all analyts identified and reported in acceptable results	16	31	52
no false positive results	29	31	94



7.2 Rating of performance

Table 3: Rating

laboratory code	critterion 1 all analytes identified	critterion 2 number of acceptable results	critterion 3 number of false positive results	rating
31	yes	8	0	passed
32	yes	8	1	failed
33	yes	8	0	passed
34	yes	7	0	passed
35	yes	8	0	passed
36	yes	8	0	passed
37	yes	8	0	passed
38	yes	8	0	passed
39	no	4	0	failed
40	yes	8	0	passed
41	yes	7	0	passed
42	yes	6	0	passed
43	yes	6	0	passed
44	yes	7	0	passed
45	no	7	0	failed
46	yes	7	0	passed
47	yes	7	0	passed
48	yes	8	0	passed
49	no	0	0	failed
50	yes	8	0	passed
51	yes	8	0	passed
52	yes	8	0	passed
53	yes	8	0	passed
54	no	6	0	failed
55	no	2	1	failed
56	yes	8	0	passed
57	no	5	0	failed
58	yes	8	0	passed
59	yes	7	0	passed
60	yes	6	0	passed
61	yes	8	0	passed



Table 4: Number of satisfactory results in test material B

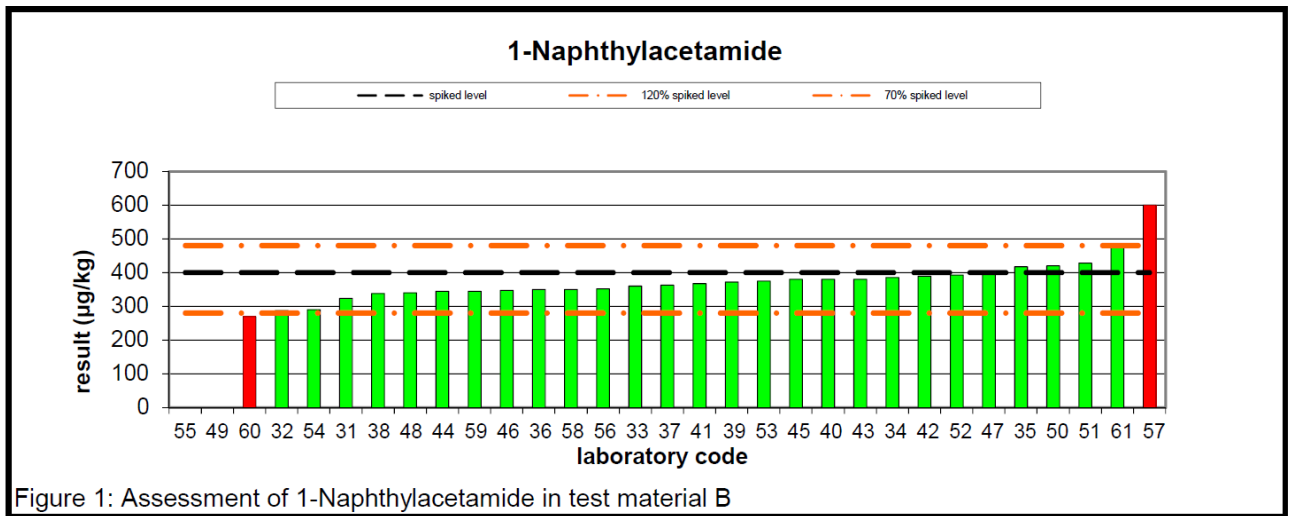
analyte	number of satisfactory results	total number of correct identification	satisfactory (%)
1-Naphthylacetamide	27	29	93
Azadirachtin	27	29	93
Clopyralid	25	28	89
Icaridin/Picaridin	26	27	96
Malathion	29	29	100
Phthalimide	26	30	87
THPI	26	29	90
Nicotine	26	27	96



7.3 Results of 1-Naphthylacetamide

Table 5: Results for 1-Naphthylacetamide in test material B

1-Naphthylacetamide - spiked level: 400 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 280-480
31	324	101	10	yes
32	287	94.2	10	yes
33	360	90	10	yes
34	386	90	10	yes
35	417	100.1	10	yes
36	350	95	10	yes
37	363	95	10	yes
38	338	100	10	yes
39	372	80	10	yes
40	380	98	5	yes
41	367	95	10	yes
42	389	108	10	yes
43	380	99	10	yes
44	345	82.5	3	yes
45	380	101	10	yes
46	347	90	5	yes
47	400	92	10	yes
48	340	97	10	yes
49				no
50	420	79	10	yes
51	428	103	10	yes
52	393	95.1	5	yes
53	375	106	10	yes
54	290	95	10	yes
55				no
56	352	95	10	yes
57	601	110	10	no
58	350	99	10	yes
59	345	88	10	yes
60	270	108	10	no
61	480	95	10	yes





7.4 Results of 1-Naphthylacetic acid sum

Table 6: Results for 1-Naphthylacetic acid sum* in test material B

1-Naphthylacetic acid sum*				
laboratory code	result (µg/kg) <i>only informative</i>	recovery (%)	LoQ (µg/kg)	evaluation
31	326			not part of the evaluation
32	580			
33				
34				
35				
36	353			
37	365			
38	339			
39	374			
40	382			
41	369			
42	391			
43				
44				
45	380			
46				
47	398			
48	342			
49				
50	422			
51	430			
52	395			
53	377			
54	292			
55				
56				
57				
58	352			
59	347			
60	271			
61	483			

* 1-Naphthylacetamide and 1-naphthylacetic acid (sum of 1-naphthylacetamide and 1-naphthylacetic acid and their salts, expressed as 1-naphthylacetic acid)



7.5 Results of Azadirachtin

Table 7: Results for Azadirachtin in test material B

Azadirachtin - spiked level: 40 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 28-48
31	35	91	10	yes
32	32	96.2	20	yes
33	36	95	10	yes
34	43	100	10	yes
35	42	99.9	10	yes
36	40	96	10	yes
37	35	98	10	yes
38	39	100	10	yes
39	49	92	5	no
40	42	95	5	yes
41	37	81	10	yes
42	40	94	10	yes
43	32	94	10	yes
44	38	87.9	3	yes
45	42	101	5	yes
46	40	95	5	yes
47	42	92	10	yes
48	48	95	10	yes
49				no
50	36	101	10	yes
51	36	98	10	yes
52	46	101.9	5	yes
53	41	100	10	yes
54				no
55	38	102	10	yes
56	35	100	10	yes
57	34.2	115	10	yes
58	40	88	10	yes
59	55	96	10	no
60	35	82	10	yes
61	42	95	10	yes

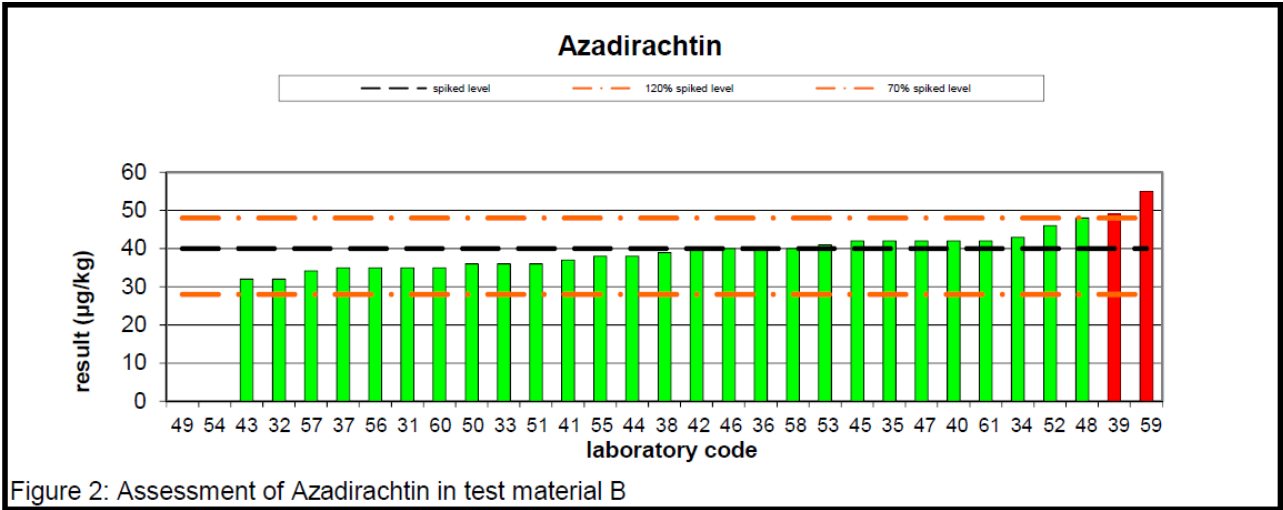


Figure 2: Assessment of Azadirachtin in test material B



7.6 Results of Clopyralid

Table 8: Results for Clopyralid in test material B

Clopyralid - spiked level: 300 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 210-360
31	228	82	10	yes
32	252	87.6	10	yes
33	240	83	10	yes
34	306	67	50	yes
35	275	89	10	yes
36	270	101	10	yes
37	329	97	10	yes
38	277	100	10	yes
39	280	107	5	yes
40	240	105	5	yes
41	185	76	50	no
42	398	91	10	no
43	230	95	10	yes
44	261	90.8	3	yes
45	230	80	10	yes
46	362	85	5	no
47	240	95	10	yes
48	270	83	10	yes
49				no
50	359	85	10	yes
51	245	78	50	yes
52	271	83.5	5	yes
53	254	101	10	yes
54				no
55				no
56	230	90	10	yes
57	288.3	108	10	yes
58	234	76	100	yes
59	279	89	10	yes
60	260	110	10	yes
61	240	95	10	yes

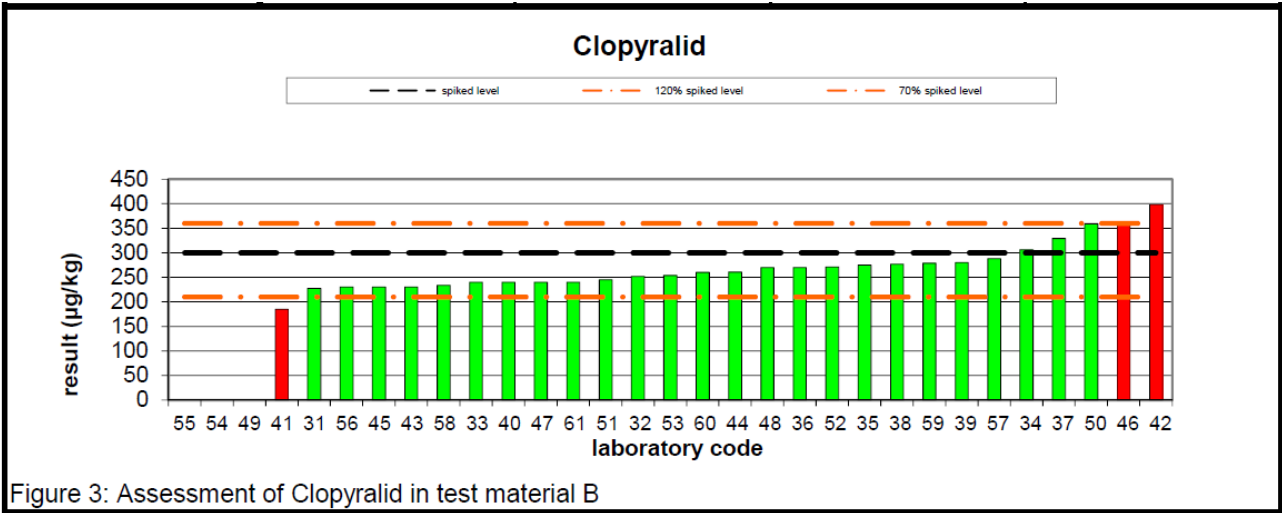


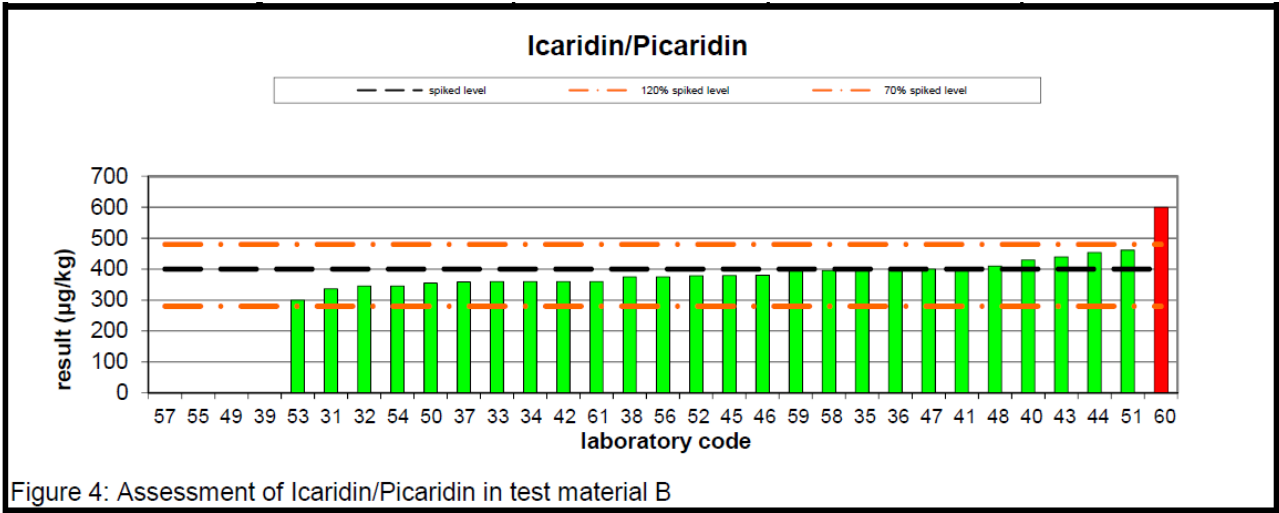
Figure 3: Assessment of Clopyralid in test material B



7.7 Results of Icaridin/Picaridin

Table 9: Results for Icaridin/Picaridin in test material B

Icaridin/Picaridin - spiked level: 400 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 280-480
31	336	107	10	yes
32	345	104.2	10	yes
33	360	80	10	yes
34	360	91	10	yes
35	400	83.6	10	yes
36	400	97	10	yes
37	359	104	10	yes
38	375	100	10	yes
39				no
40	430	--	5	yes
41	402	102	10	yes
42	360	102	10	yes
43	440	100	10	yes
44	454	89.6	3	yes
45	380	101	10	yes
46	381	100	5	yes
47	400	93	10	yes
48	410	96	10	yes
49				no
50	355	103	10	yes
51	461	82	10	yes
52	379	94.1	5	yes
53	300	90	10	yes
54	345	92	10	yes
55				no
56	375	105	10	yes
57				no
58	395	96	10	yes
59	394	96	5	yes
60	600	91	10	no
61	360	95	10	yes

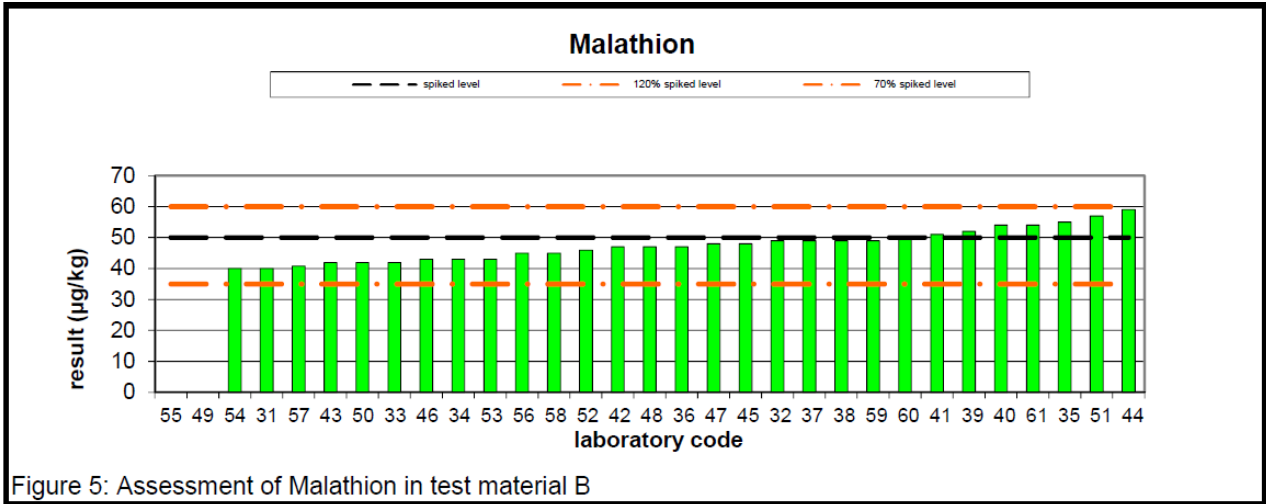




7.8 Results of Malathion

Table 10: Results for Malathion in test material B

Malathion - spiked level: 50 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 35-60
31	40	103	10	yes
32	49	100.8	10	yes
33	42	86	10	yes
34	43	95	10	yes
35	55	95.4	10	yes
36	47	99	10	yes
37	49	108	10	yes
38	49	100	10	yes
39	52	96	5	yes
40	54	106	5	yes
41	51	95	10	yes
42	47	119	10	yes
43	42	100	10	yes
44	59	91.3	3	yes
45	48	99	5	yes
46	43	107	5	yes
47	48	96	10	yes
48	47	93	10	yes
49				no
50	42	96	10	yes
51	57	85	10	yes
52	46	99.8	5	yes
53	43	88	10	yes
54	40	90	10	yes
55				no
56	45	95	10	yes
57	40.8	102	10	yes
58	45	104	10	yes
59	49	103	5	yes
60	50	104	5	yes
61	54	95	10	yes





7.9 Results of Malathion sum

Table 11: Results for Malathion sum*

Malathion sum*				
laboratory code	result (µg/kg) <i>only informative</i>	recovery (%)	LoQ (µg/kg)	evaluation
31				not part of the evaluation
32				
33				
34				
35				
36				
37	49			
38	49			
39	52			
40	54			
41	51			
42	47			
43	42			
44				
45	48			
46				
47	48			
48	47			
49				
50				
51				
52	46			
53	43			
54	40			
55				
56	45			
57				
58	45			
59	49			
60	50			
61	54			

* Malathion (sum of malathion and malaaxon, expressed as malathion)



7.10 Results of Phthalimide

Table 12: Results for Phthalimide in test material B

Phthalimide - spiked level: 310 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 217-372
31	252	87	10	yes
32	331	94	10	yes
33	300	95	10	yes
34	243	100	20	yes
35	355	102	10	yes
36	290	102	10	yes
37	236	80	10	yes
38	280	100	10	yes
39	148	87	5	no
40	240	95	10	yes
41	285	120	20	yes
42	290	100	10	yes
43	170	88	10	no
44	435	88.4	3	no
45	340	95	10	yes
46	294	95	5	yes
47	210	90	10	no
48	280	92	5	yes
49				no
50	288	73	10	yes
51	332	81	10	yes
52	307	101.3	5	yes
53	286	115	10	yes
54	290	97	10	yes
55	260	102	10	yes
56	285	90	10	yes
57	274.6	116	10	yes
58	289	105	10	yes
59	237	96	10	yes
60	300	99	5	yes
61	315	95	10	yes

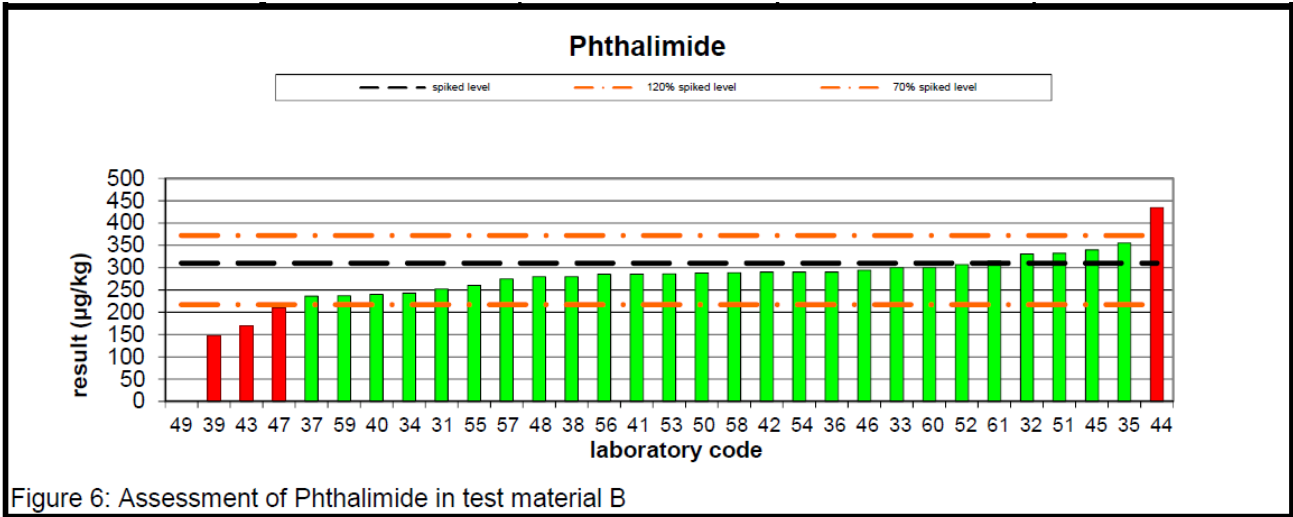


Figure 6: Assessment of Phthalimide in test material B



7.11 Results for Folpet (R) sum

Table 13: Results for Folpet (R) sum * in test material B

Folpet (R) sum *				
laboratory code	result (µg/kg) <i>only informative</i>	recovery (%)	LoQ (µg/kg)	evaluation
31	509			not part of the evaluation
32				
33				
34				
35				
36	586			
37	476			
38	564			
39	296			
40	485			
41	576			
42	583			
43	340			
44				
45	690			
46	588			
47	420			
48	565			
49				
50	581			
51	669			
52	620			
53	577			
54	586			
55	520			
56	574			
57	549.3			
58	582			
59	478			
60	606			
61	632			

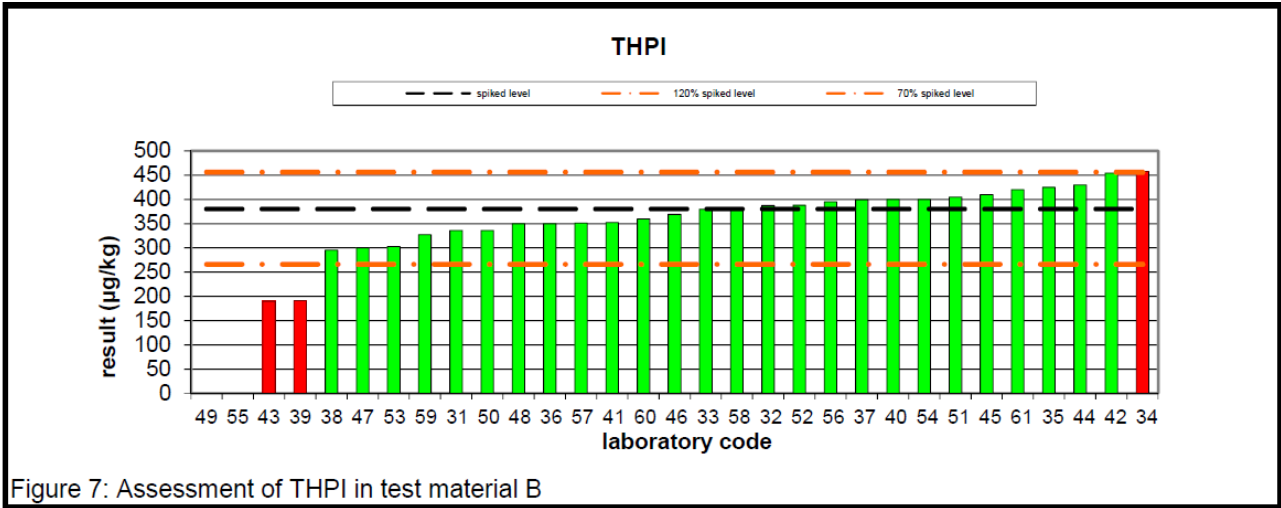
* Sum of folpet and phthalimide, expressed as folpet (R)



7.12 Results for THPI

Table 14: Results for THPI in test material B

THPI - spiked level: 380 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 266-456
31	336	84	10	yes
32	387	104.5	10	yes
33	380	95	10	yes
34	457	70	10	no
35	425	101.7	10	yes
36	350	96	10	yes
37	399	90	10	yes
38	295	100	10	yes
39	191	79	5	no
40	400	102	10	yes
41	352	98	20	yes
42	454.5	103	10	yes
43	190	96	10	no
44	430	91.2	3	yes
45	410	95	10	yes
46	369	92	5	yes
47	300	94	10	yes
48	350	92	5	yes
49				no
50	336	78	10	yes
51	405	77	10	yes
52	388	98.9	5	yes
53	303	120	10	yes
54	400	97	10	yes
55				no
56	395	100	10	yes
57	351	96	10	yes
58	382	94	10	yes
59	327	100	10	yes
60	360	130	5	yes
61	420	95	10	yes





7.13 Results for Captan (R) sum

Table 15: Results for Captan (R) sum * in test material B

Captan (R) sum *				
laboratory code	result (µg/kg) <i>only informative</i>	recovery (%)	LoQ (µg/kg)	evaluation
31	669			not part of the evaluation
32				
33				
34				
35				
36	693			
37	793			
38	587			
39	380			
40	795			
41	700			
42	900			
43	380			
44				
45	820			
46	738			
47	600			
48	696			
49				
50	668			
51	805			
52	771			
53	602			
54	795			
55				
56	785			
57	702			
58	760			
59	650			
60	716			
61	836			

* Sum of captan and THPI expressed as captan (R)

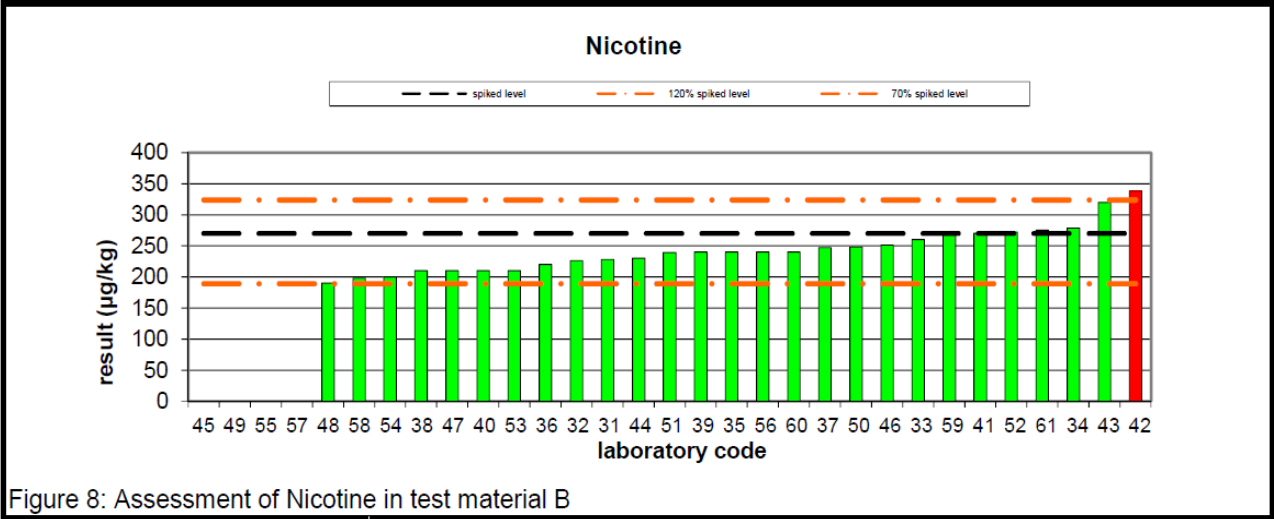


7.14 Results for Nicotine

Table 16: Results for Nicotine in test material B

Nicotine - spiked level: 270 µg/kg				
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	accepted range (µg/kg): 189-324
31	228	98	10	yes
32	226	92	10	yes
33	260	85	10	yes
34 *	279	88	10	yes
35	240	97.7	10	yes
36	220	95	10	yes
37	247	93	10	yes
38	210	100	10	yes
39	240	84	5	yes
40	210	97	5	yes
41	270	84	10	yes
42	338	61	100	no
43	320	109	10	yes
44	230	90.4	3	yes
45				no
46	251	107	5	yes
47	210	90	10	yes
48	190	92	10	yes
49				no
50	248	98	10	yes
51	239	70	10	yes
52 *	272	87.7	5	yes
53	210	103	10	yes
54	200	88	10	yes
55				no
56	240	95	10	yes
57				no
58	198	72	50	yes
59	267	91	10	yes
60 *	240	80	10	yes
61 *	275	95	10	yes

* quantification by single method





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



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