



Laboratory Performance Assessment

Winter 2012

Report

Pesticide residues in apple pulp purée

January 2013

Summary

The test material for the 2012 winter laboratory performance assessment of the Bundesverband Naturkost Naturwaren (BNN) e.V. was prepared by MPA Eberswalde GmbH in November 2012 to provide individual test material tailor-made for BNN needs.

The test material was prepared from organic apple pulp purée. The apple pulp purée was spiked with 13 pesticides at low levels (8-50 µg/kg) to represent typical levels of pesticide residues as expected in organic material.

The test material was distributed to nineteen participants from six European countries (Austria, Belgium, Germany, Italy, Spain, the Netherlands).

This report refers to the performance assessment of laboratories, which analysed the provided apple pulp purée test material. Each laboratory received minimum 250 g apple pulp purée spiked with an unknown number of pesticides. All 19 participants kept the term for the submission of results.

The laboratories were requested to identify and quantify 13 pesticides. These were Captan, Chlorpyrifos-methyl, Chlorpyrifos-ethyl, Diphenylamine, Dithianon, Fenhexamid, Iprodion, Myclobutanil, 2-Phenylphenol, Pirimicarb, Pyraclostrobin, Rotenone and Trifloxystrobin.

The performance assessment considers the following test criteria:

- No *false negative* results for all parameters have to be reported.
- *Correct* quantification related to the 70-120% recovery criteria (of the spiked value) for Captan, Chlorpyrifos-methyl, Diphenylamine, Fenhexamid, Myclobutanil, 2-Phenylphenol, Rotenone and Trifloxystrobin.
- Results not higher than 120% of the spiking level and not false negative were regarded as satisfactory for Chlorpyrifos-ethyl, Iprodion, Pirimicarb and Pyraclostrobin due to low spiking levels (<15 µg/kg).
- Dithianon is known to be instable under certain conditions. The prevention of losses during sample preparation is an analytical challenge for quantification of Dithianon. The assessment of the results revealed analytical difficulties for all participating laboratories and therefore no quantitative but a qualitative criterion was used for Dithianon in this report (detected or not detected).

The overall performance of the laboratory assessment (material apple pulp purée) is summarised in the table below:

Criteria	Number of satisfactory participants	Total number of participants	Satisfactory (%)
Correctly identified and / or quantified all thirteen pesticides	4	19	21

Assessment of quantification:

Analytical results between 70 and 120% of the spiked levels (criterion 70-120%) have been considered satisfying during the assessment of quantification for most of the parameters. Exceptions were Chlorpyriphos-ethyl and Pirimicarb, where due to low spiking levels (8 µg/kg) all results ≤10 µg/kg were considered satisfactory and Dithianon, where due to analytical difficulties in all laboratories the criterion detected or not detected was used.

Parameter	Spiked level (µg/kg)	Criterion	Number of satisfactory results	Total number of participants	Satisfactory (%)
Captan	25	70-120%	6	19	32
Chlorpyriphos-ethyl	8	≤10 µg/kg	19	19	100
Chlorpyriphos-methyl	15	70-120%	15	19	79
Diphenylamine	30	70-120%	11	19	58
Dithianon	50	detected yes/no	14	19	74
Fenhexamid	22	70-120%	17	19	89
Iprodion	12	70-120% or detected < 10 µg/kg	18	19	95
Myclobutanil	15	70-120%	19	19	100
2-Phenylphenol	35	70-120%	10	19	53
Pirimicarb	8	≤10 µg/kg	19	19	100
Pyraclostrobin	12	70-120% or detected < 10 µg/kg	18	19	95
Rotenone	24	70-120%	16	19	84
Trifloxystrobin	18	70-120%	18	19	95

Table of contents

	Page
Summary	2
1. Test material preparation and design	5
2. Results	5
Table 1. Results for Captan and Chlorpyrifos-methyl in apple pulp purée test material	7
Table 2. Results for Diphenylamine and Fenhexamid in apple pulp purée test material	8
Table 3. Results for Myclobutanil and 2-Phenylphenol in apple pulp purée test material	9
Table 4. Results for Rotenone and Trifloxystrobin in apple pulp purée test material	10
Table 5. Results for Chlorpyrifos-ethyl and Iprodion in apple pulp purée test material	11
Table 6. Results for Pirimicarb and Pyraclostrobin in apple pulp purée test material	12
Table 7. Results for Dithianon in apple pulp purée test material	13
Figure 1. Assessment of Captan (spiked level: 25 µg/kg) in apple pulp purée	14
Figure 2. Assessment of Chlorpyrifos-methyl (spiked level: 15 µg/kg) in apple pulp purée	15
Figure 3. Assessment of Diphenylamine (spiked level: 30 µg/kg) in apple pulp purée	16
Figure 4. Assessment of Fenhexamid (spiked level: 22 µg/kg) in apple pulp purée	17
Figure 5. Assessment of Myclobutanil (spiked level: 15 µg/kg) in apple pulp purée	18
Figure 6. Assessment of 2-Phenylphenol (spiked level: 35 µg/kg) in apple pulp purée	19
Figure 7. Assessment of Rotenone (spiked level: 24 µg/kg) in apple pulp purée	20
Figure 8. Assessment of Trifloxystrobin (spiked level: 18 µg/kg) in apple pulp purée	21
3. Homogeneity testing	22
Table 8. Results from homogeneity testing for Captan, Chlorpyrifos-ethyl and -methyl	22
Table 9. Results from homogeneity testing for Diphenylamine, Dithianon and Fenhexamid	23
Table 10. Results from homogeneity testing for Iprodion, Myclobutanil, 2-Phenylphenol	24
Table 11. Results from homogeneity testing for Pirimicarb, Pyraclostrobin and Rotenone	25
Table 12. Results from homogeneity testing for Trifloxystrobin	26
4. Stability testing	26
Table 13. Results from stability testing for all pesticides in apple pulp purée	26

1. Test material preparation and design

The test material was based on apple pulp purée labelled as organic, provided by the company Bauck GmbH&Co KG. The material was tested in advance to show absence of pesticides at a level of 5 µg/kg.

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

25 µg/kg Captan, 8 µg/kg Chlorpyriphos-ethyl, 15 µg/kg Chlorpyriphos-methyl, 30 µg/kg diphenylamine, 50 µg/kg Dithianon, 22 µg/kg Fenhexamid, 12 µg/kg Iprodion, 15 µg/kg Myclobutanil, 35 µg/kg 2-Phenylphenol, 8 µg/kg Pirimicarb, 12 µg/kg Pyraclostrobin, 24 µg/kg Rotenone, 18 µg/kg Trifloxystrobin.

The apple pulp purée was distributed into labelled PE-bottles with at least 250 g in each. The bottles were stored at -20°C in the dark until distribution.

The test material for this performance assessment was analysed in advance, prepared and tested for homogeneity and stability by MPA Eberswalde GmbH. The results of homogeneity testing are presented in table 8 to 12 (pp. 22-26), the results of stability testing in table 13 (p. 26).

2. Statistical Evaluation of Results

The statistical procedure applied for this performance assessment follows recommendations given in the International Harmonised Protocol for the Proficiency Testing of Chemical Analytical Laboratories¹ and take into account the statistical methods for use in proficiency testing by inter-laboratory comparisons (ISO 13528²).

Calculation of the assigned value, \hat{X} :

The assigned value \hat{X} is derived as a robust mean from the results of all participants, which have reported quantified concentration levels of the assessed analytes. The influence of outliers is minimised via Huber's method.

3. Results

The participants were requested to report the pesticides the apple purée had been analysed for. The results had to be reported without consideration of the recovery unless reported differently by the participants. The participants were asked to report also recovery rates for the quantified pesticides.

The reporting limit (RL) had to be specified for all sought and found pesticides.

Each laboratory was given a number (laboratory code). The results of all participants analysing test material apple pulp purée are presented in tables 1 to 7 (pp. 7-13).

The results for all parameters with spiked levels at or above 15 µg/kg (Captan, Chlorpyriphos-methyl, Diphenylamine, Fenhexamid, Myclobutanil, 2-Phenylphenol, Rotenone, Trifloxystrobin) are presented in table 1-4 and subsequently in relation to the accepted range of 70-120% of the spiked level in figures 1 to 8 (pp. 14-21).

¹ Thompson, M., Ellison, S.L.R. and Wood, R., 2006, The International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories, Pure Appl. Chem., 78, No. 1, 145-196.

² International Organization for Standardization. ISO 13528: Statistical methods for use in proficiency testing by inter-laboratory comparisons. English version ISO 13528:2005.

For parameters with spiked levels below 15 µg/kg (Chlorpyrifos-ethyl, Iprodion, Pirimicarb, Pyraclostrobin) the results are shown in tables 5 to 7 for information purpose only. This is because of common reporting levels of many participants at 10 µg/kg.

For Dithianon only a qualitative conclusion can be drawn from the assessment of the results. The results of all laboratories that reported Dithianon as detected were regarded as satisfactory.

The following colours were used in figures 1 to 8 to highlight the results with respect to their quality: Bars in green are satisfactory results, bars in red are non satisfactory results (not reported results are additionally marked as ./.). Yellow bars are used for results not appropriate to check the requested pesticide level.

The terms "S.A. = standard addition", "det. = detectable", "#1 = RL too high, not appropriate to check organic samples", "./. = not appropriate for the requested pesticide level" apply to tables 1 to 7 and figures 1 and 8.

laboratory code	Captan spiked level: 25 µg/kg assigned value: 21 µg/kg				Chlorpyriphos-methyl spiked level: 15 µg/kg assigned value: 11 µg/kg			
	result (µg/kg)	recovery (%)	RL (µg/kg)	accepted range: 17-30 µg/kg	result (µg/kg)	recovery (%)	RL (µg/kg)	accepted range: 10-18 µg/kg
1	26	92	10	yes	11	99	10	yes
2	26	97	10	yes	11	116	10	yes
3	./.		50	#1	10	91	10	yes
4	./.		50	#1	<10	119	10	no
5	<20	100	20	#1	11	100	10	yes
6	19	95	10	yes	12	95	10	yes
7	11	92	5	no	12	94	5	yes
8	31	117	10	no	11	111	5	yes
9	20	92	5	yes	12	99	5	yes
10	14	94	10	no	11	86	10	yes
11	19	90	10	yes	11	100	10	yes
12	<10	77	10	no	<10	80	10	no
13	12	S.A.	10	no	11	S.A.	10	yes
14	./.		20	no	11	101	10	yes
15	19	100	5	yes	13	104	2	yes
16	./.			no	9	110	3	no
17	31	111	10	no	16	91	10	yes
18	./.		10	no	11	87,2	10	yes
19	<20		20	#1	<10		10	no

Table 1. Results for Captan and Chlorpyriphos-methyl in apple pulp purée test material

laboratory code	Diphenylamine spiked level: 30 µg/kg assigned value: 22 µg/kg				Fenhexamid spiked level: 22 µg/kg assigned value: 19 µg/kg			
	result (µg/kg)	recovery (%)	RL (µg/kg)	accepted range: 21-36 µg/kg	result (µg/kg)	recovery (%)	RL (µg/kg)	accepted range: 15-27 µg/kg
1	26	92	10	yes	20	90	10	yes
2	21	43	10	yes	23	94	10	yes
3	27	97	10	yes	15	107	10	yes
4	20	109	10	no	20	83	10	yes
5	20	100	20	no	14	81	10	no
6	30	95	10	yes	18	95	10	yes
7	22	94	5	yes	19	107	5	yes
8	27	98	10	yes	21	76	5	yes
9	22	102	5	yes	18	101	5	yes
10	19	86	10	no	18	123	10	yes
11	21	99	10	yes	18	97	10	yes
12	20	80	10	no	18	92	20	yes
13	18	93	10	no	18	86	10	yes
14	16	100	10	no	17	98	10	yes
15	25	100	10	yes	18	95	5	yes
16	18	100	10	no	19	90	5	yes
17	25	95	10	yes	22	120	10	yes
18	18	87	10	no	22	85,4	10	yes
19	24	S.A.	10	yes	28	S.A.	10	no

Table 2. Results for Diphenylamine and Fenhexamid in apple pulp purée test material

laboratory code	Myclobutanil spiked level: 15 µg/kg assigned value: 11 µg/kg				2-Phenylphenol spiked level: 35 µg/kg assigned value: 25 µg/kg			
	result (µg/kg)	recovery (%)	RL (µg/kg)	accepted range: 10-18 µg/kg	result (µg/kg)	recovery (%)	RL (µg/kg)	accepted range: 24-42 µg/kg
1	12	101	10	yes	35	100	10	yes
2	11	103	10	yes	16	107	10	no
3	10	110	10	yes	27	92	10	yes
4	11	114	10	yes	21	118	10	no
5	11	92	10	yes	29	100	10	yes
6	12	95	10	yes	30	95	10	yes
7	13	105	5	yes	22	98	5	no
8	17	103	5	yes	28	104	10	yes
9	12	97	5	yes	20	115	5	no
10	10	102	10	yes	24	100	10	yes
11	10	100	10	yes	26	100	10	yes
12	11	87	10	yes	22	71	10	no
13	10	84	10	yes	18	101	10	no
14	10	98	10	yes	22	100	10	no
15	12	102	1	yes	29	100	10	yes
16	11	95	5	yes	./.			no
17	16	92	10	yes	30	101	10	yes
18	12	97/101	10	yes	./.		10	no
19	11	S.A.	10	yes	34	S.A.	10	yes

Table 3. Results for Myclobutanil and 2-Phenylphenol in apple pulp purée test material

laboratory code	Rotenone spiked level: 24 µg/kg assigned value: 18 µg/kg				Trifloxystrobin spiked level: 18 µg/kg assigned value: 14 µg/kg			
	result (µg/kg)	recovery (%)	RL (µg/kg)	accepted range: 16-29 µg/kg	result (µg/kg)	recovery (%)	RL (µg/kg)	accepted range: 12-22 µg/kg
1	17	97	10	yes	16	93	10	yes
2	15	101	10	no	13	108	10	yes
3	23	92	10	yes	12	110,0	10	yes
4	19	91	10	yes	16	119	10	yes
5	16	83	10	yes	12	86	10	yes
6	18	95	10	yes	14	95	10	yes
7	17	105	5	yes	16	84	5	yes
8	21	100	10	yes	17	97	5	yes
9	18	98	5	yes	13	98	5	yes
10	19	94	10	yes	13	94	10	yes
11	25	100	10	yes	14	102	10	yes
12	18	101	10	yes	11	95	10	no
13	15	82	10	no	12	88	10	yes
14	21	71	10	yes	12	99	10	yes
15	21	107	2	yes	16	105	5	yes
16	21	90	5	yes	14	80	3	yes
17	17	105	20	yes	18	109	10	yes
18	17	S.A.		yes	13	103/95	10	yes
19	15	S.A.	10	no	13	S.A.	10	yes

Table 4. Results for Rotenone and Trifloxystrobin in apple pulp purée test material

laboratory code	Chlorpyriphos-ethyl spiked level: 8 µg/kg				Iprodion spiked level: 12 µg/kg			
	result (µg/kg)	recovery (%)	RL (µg/kg)	accepted range: det. <10 µg/kg	result (µg/kg)	recovery (%)	RL (µg/kg)	accepted range: <10-15 µg/kg
1	<10	97	10	yes	10	98	10	yes
2	<10	88	10	yes	9	97	10	yes
3	<10	98	10	yes	10	107,0	10	yes
4	<10	118	10	yes	<10	122	10	yes
5	6	90	5	yes	<10	89	10	yes
6	<10	95	10	yes	10	95	10	yes
7	7	90	5	yes	10	101	5	yes
8	5,7	119	5	yes	<10	102	10	yes
9	6	99	5	yes	9	103	5	yes
10	<10		10	yes	10	108	10	yes
11	6	99	10	yes	10	100	10	yes
12	<10	90	10	yes	10	93	10	yes
13	5	S.A.	5	yes	<10		10	yes
14	<10	100	10	yes	10	100	10	yes
15	7	105	1	yes	10	106	5	yes
16	5	100	3	yes	9	85	5	yes
17	<10		10	yes	<10		10	yes
18	<10	100,2	10	yes	./.		10	no
19	<10	S.A.	10	yes	11	S.A.	10	yes

Table 5. Results for Chlorpyriphos-ethyl and Iprodion in apple pulp purée test material

laboratory code	Pirimicarb spiked level: 8 µg/kg				Pyraclostrobin spiked level: 12 µg/kg			
	result (µg/kg)	recovery (%)	RL (µg/kg)	accepted range: det. <10 µg/kg	result (µg/kg)	recovery (%)	RL (µg/kg)	accepted range: <10–15 µg/kg
1	<10	96	10	yes	<10	97	10	yes
2	7	100	10	yes	10	106	10	yes
3	<10	102	10	yes	10	108	10	yes
4	<10	86	10	yes	11	97	10	yes
5	<10	83	10	yes	<10	86	10	yes
6	<10	95	10	yes	10	95	10	yes
7	7	102	5	yes	9	83	5	yes
8	10	88	10	yes	10	108	5	yes
9	6	97	5	yes	9	112	5	yes
10	<10		10	yes	10	94	10	yes
11	6	100	10	yes	<10		10	yes
12	<10	91	10	yes	11	104	10	yes
13	<10		10	yes	<10		10	yes
14	<10	96	10	yes	10	98	10	yes
15	7	103	1	yes	11	110	2	yes
16	7	80	5	yes	10	85	3	yes
17	<10		10	yes	11	99	10	yes
18	<10	97/92	10	yes	<10	99	10	yes
19	<10	S.A.	10	yes	20	S.A.	10	no

Table 6. Results for Pirimicarb and Pyraclostrobin in apple pulp purée test material

	Dithianon spiked level: 50 µg/kg			
laboratory code	result (µg/kg)	recovery (%)	RL (µg/kg)	accepted range: detected yes/no
1	<10	73	10	yes
2	8	82	10	yes
3	./.		10	no
4	./.		10	no
5	<10		10	yes
6	15	95	10	yes
7	16	./.	5	yes
8	<20	85	20	yes
9	8	81	5	yes
10	11	108	10	yes
11	11	S.A.		yes
12	<10	89	10	yes
13	./.			no
14	21	101	10	yes
15	5	97	5	yes
16	8	95	5	yes
17	./.			no
18	./.			no
19	22	S.A.	10	yes

Table 7. Results for Dithianon in apple pulp purée test material

Figure 1. Assessment of Captan (spiked level: 25 µg/kg) in apple pulp purée

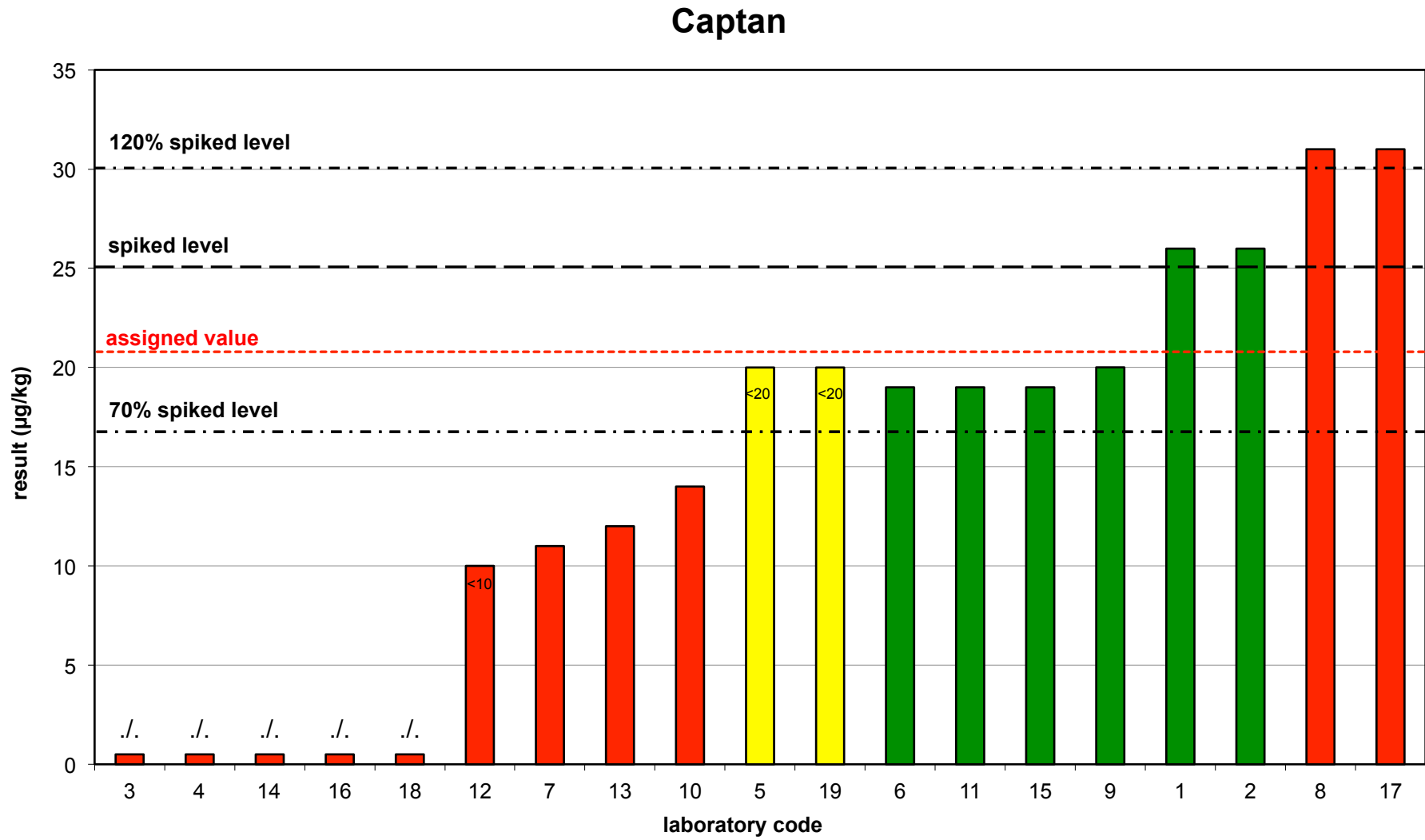


Figure 2. Assessment of Chlorpyrifos-methyl (spiked level: 15 µg/kg) in apple pulp purée

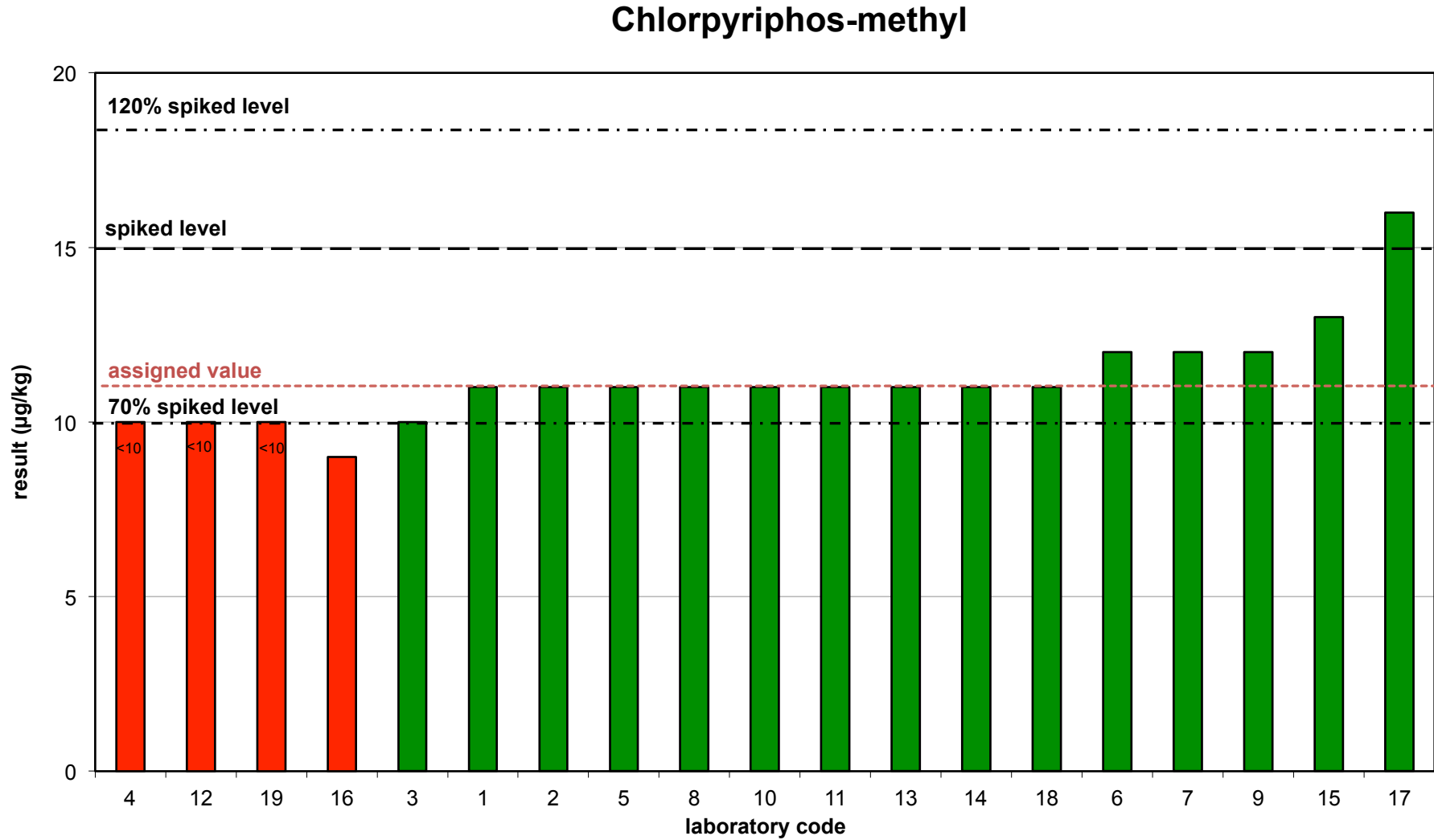


Figure 3. Assessment of Diphenylamine (spiked level: 30 µg/kg) in apple pulp purée

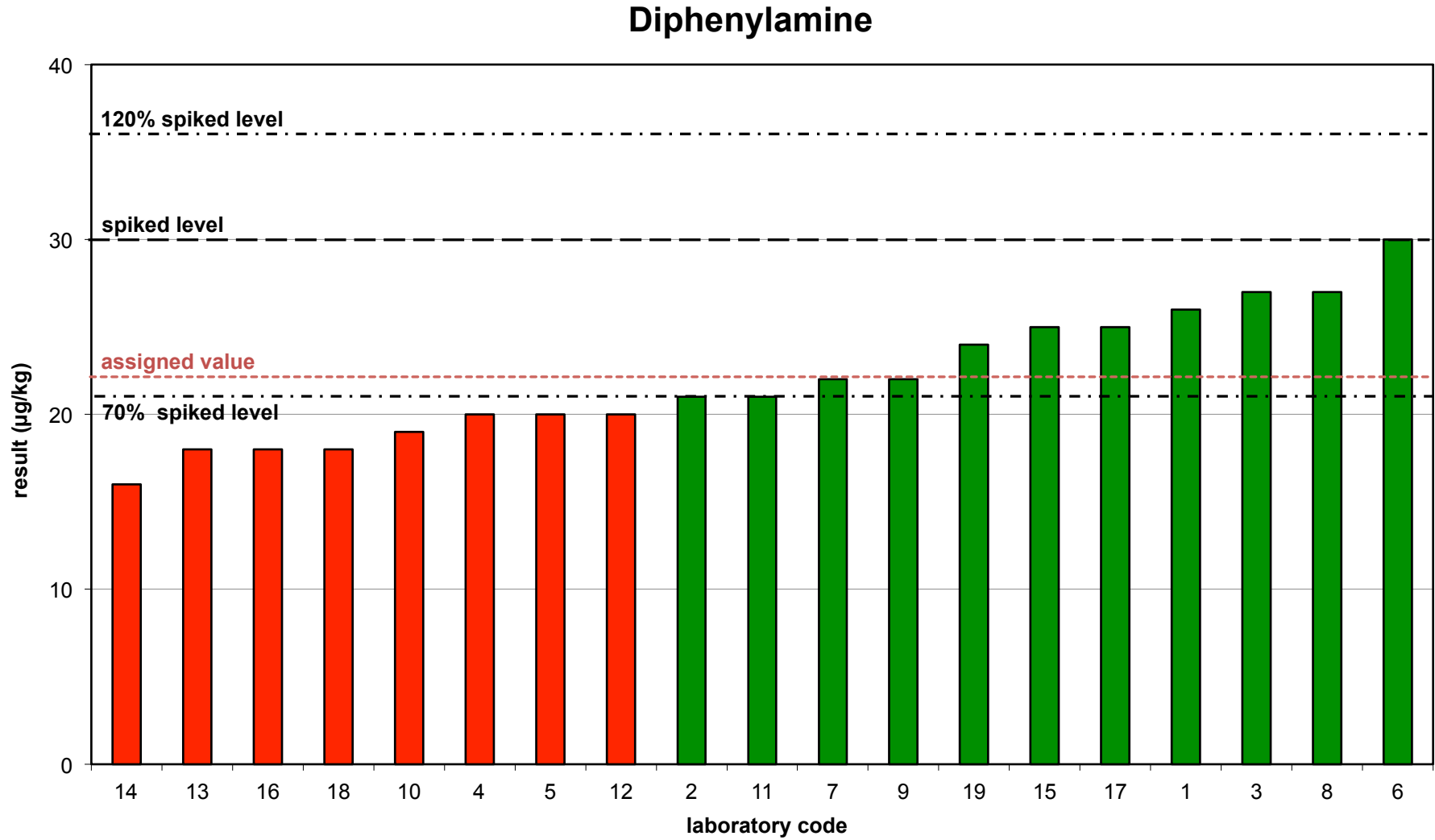


Figure 4. Assessment of Fenhexamid (spiked level: 22 µg/kg) in apple pulp purée

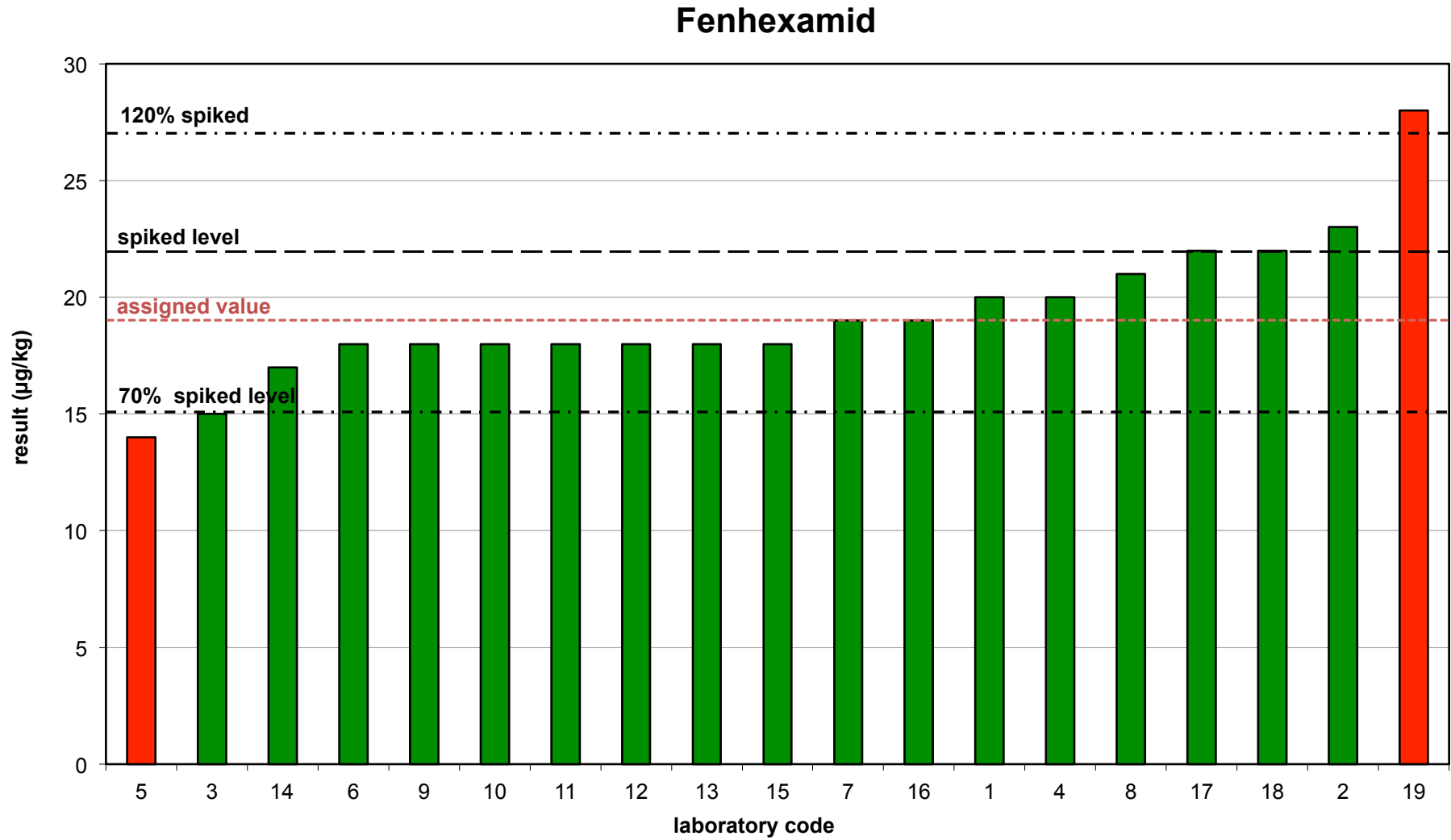


Figure 5. Assessment of Myclobutanil (spiked level: 15 µg/kg) in apple pulp purée

Myclobutanil

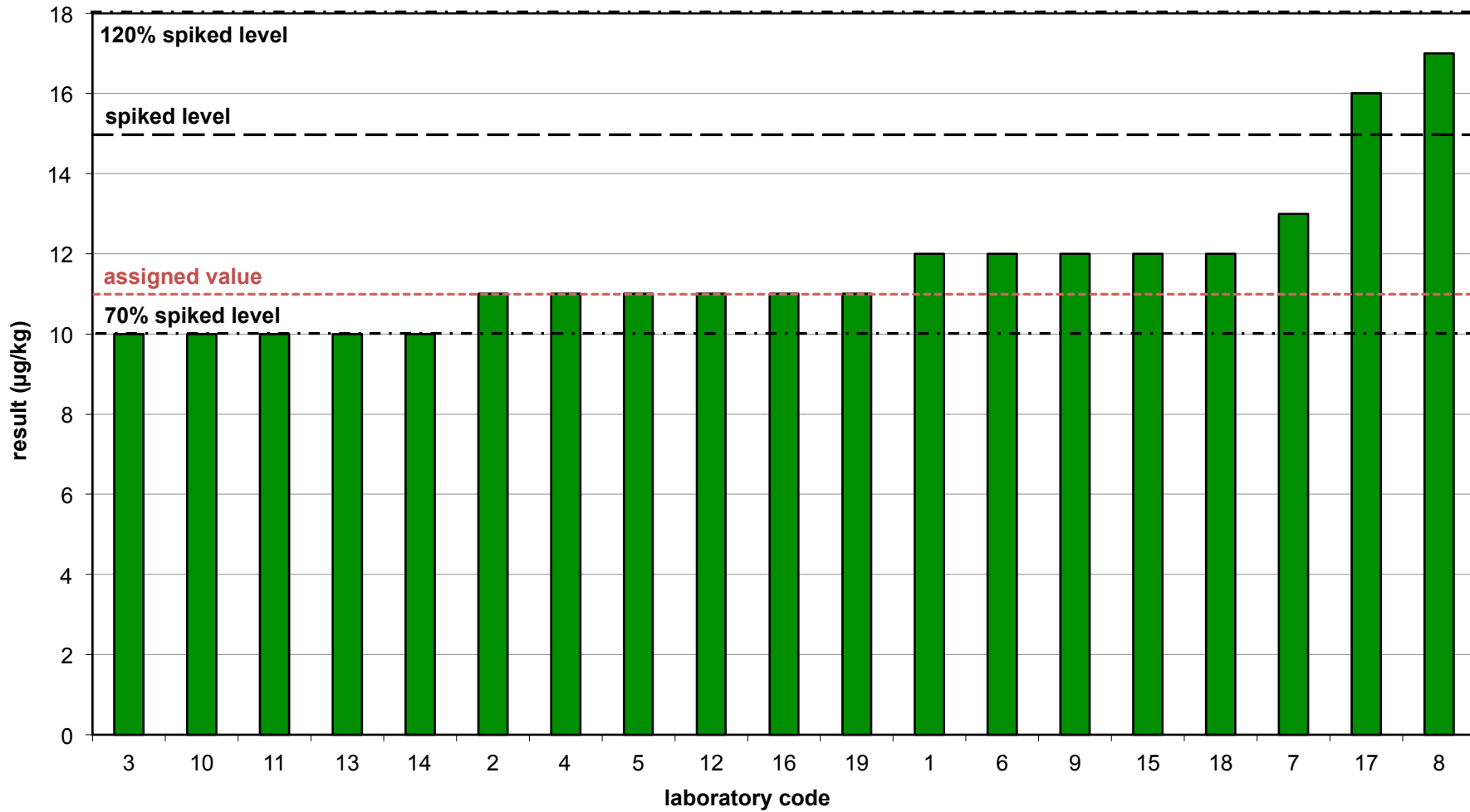


Figure 6. Assessment of 2-Phenylphenol (spiked level: 35 µg/kg) in apple pulp purée

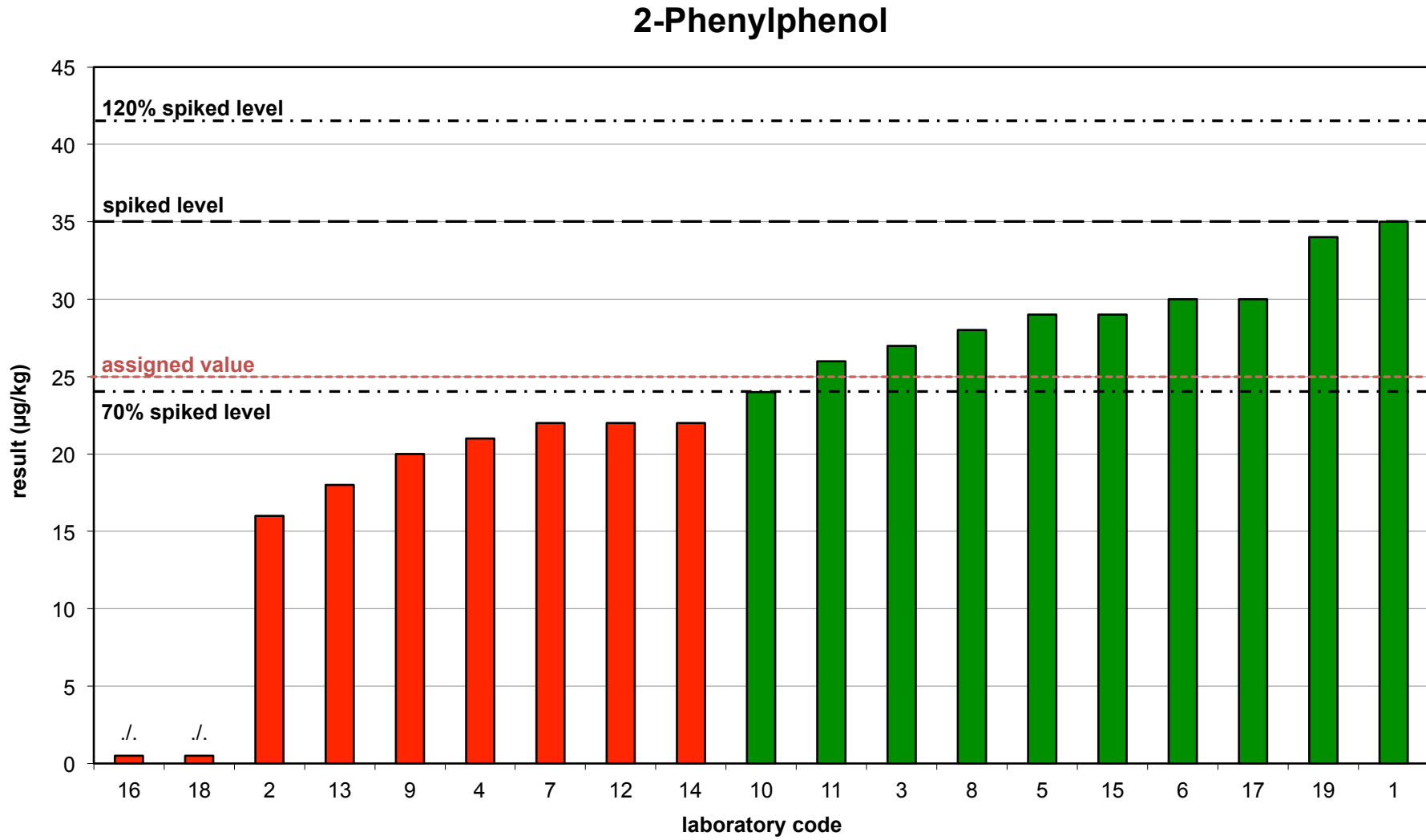


Figure 7. Assessment of Rotenone (spiked level: 24 µg/kg) in apple pulp purée

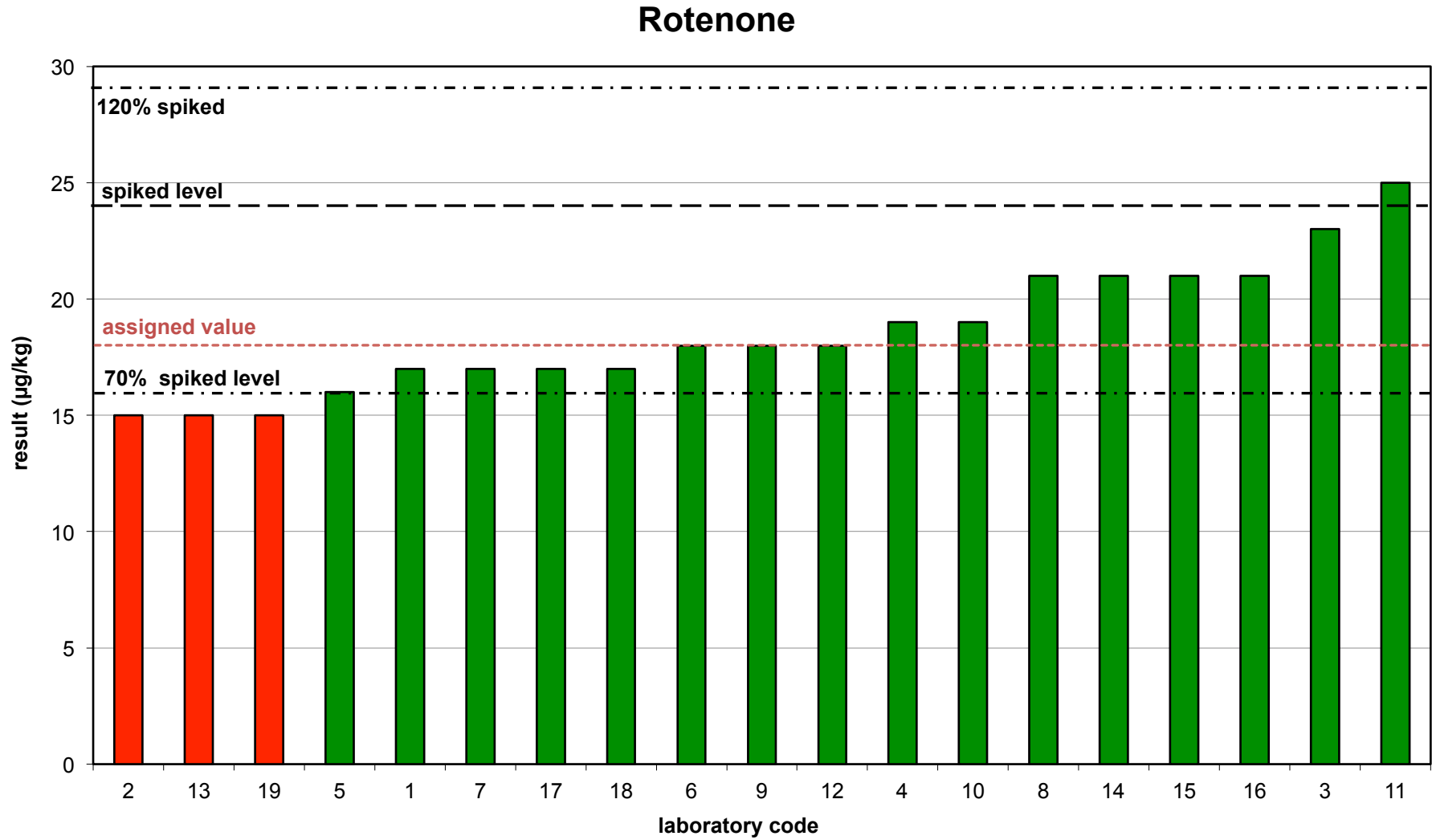
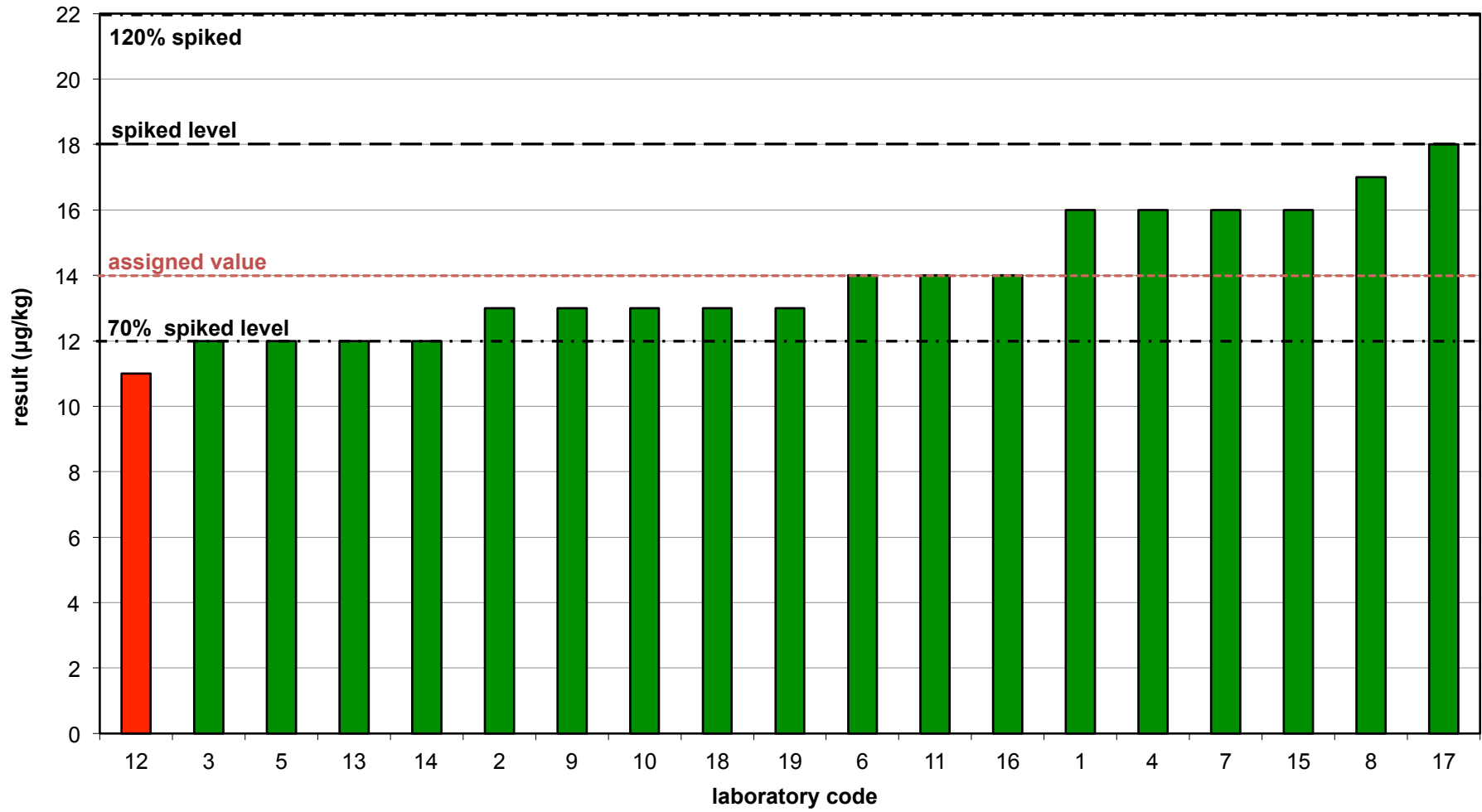


Figure 8. Assessment of Trifloxystrobin (spiked level: 18 µg/kg) in apple pulp purée

Trifloxystrobin



4. Homogeneity testing

The homogeneity testing were performed at MPA Eberswalde GmbH, Germany. Seven randomly chosen test material samples were analysed. The mean of the results of two injections for each sample was calculated and used for statistics to check the homogeneity of each of the 13 spiked pesticides in the test material.

Captan			
sample no.	injection 1	injection 2	mean (inj 1,2)
1	27.8	24.6	26.2
2	22.2	25.3	23.8
3	25.2	25.5	25.4
4	26.7	26.2	26.5
5	24.5	18.6	21.6
6	22.7	20.2	21.5
7	26.3	20.7	23.5
	mean [$\mu\text{g}/\text{kg}$]		24
	standard deviation [$\mu\text{g}/\text{kg}$]		2.1
	coefficient of variation [%]		8.6
	target value (spiked level) [$\mu\text{g}/\text{kg}$]		25
	recovery [%]		96

Chlorpyriphos-ethyl			
sample no.	injection 1	injection 2	mean (inj 1,2)
1	5.8	7.6	6.7
2	6.1	7.3	6.7
3	7.4	6.5	7
4	5.9	6.2	6.1
5	7.2	6.2	6.7
6	7.1	7.3	7.2
7	6	5.8	5.9
	mean [$\mu\text{g}/\text{kg}$]		6.6
	standard deviation [$\mu\text{g}/\text{kg}$]		0.5
	coefficient of variation [%]		7.1
	target value (spiked level) [$\mu\text{g}/\text{kg}$]		8
	recovery [%]		83

Chlorpyriphos-methyl			
sample no.	injection 1	injection 2	mean (inj 1,2)
1	14.3	14	14.2
2	13.4	13.3	13.4
3	13.1	13.5	13.3
4	14.1	14.4	14.3
5	12.8	13.6	13.2
6	12.7	13.8	13.3
7	14	13.6	13.8
	mean [$\mu\text{g}/\text{kg}$]		13.6
	standard deviation [$\mu\text{g}/\text{kg}$]		0.4
	coefficient of variation [%]		3.3
	target value (spiked level) [$\mu\text{g}/\text{kg}$]		15
	recovery [%]		91

Table 8. Results from homogeneity testing for Captan, Chlorpyriphos-ethyl and -methyl

Diphenylamine			
sample no.	injection 1	injection 2	mean (inj 1,2)
1	28.7	28.9	28.8
2	30.7	28.8	29.8
3	32.9	31.8	32.4
4	31.1	29.9	30.5
5	29.3	33	31.2
6	29.9	28.3	29.1
7	27.6	28.1	27.9
	mean [$\mu\text{g}/\text{kg}$]		29.9
	standard deviation [$\mu\text{g}/\text{kg}$]		1.5
	coefficient of variation [%]		5.1
	target value (spiked level [$\mu\text{g}/\text{kg}$])		30
	recovery [%]		100

Dithianon			
sample no.	injection 1	injection 2	mean (inj 1,2)
1	28.9	23.7	26.3
2	21	20.1	20.6
3	20	19	19.5
4	18.2	16.3	17.3
5	17.3	17.2	17.3
6	13.7	12.7	13.2
7	11.8	11.9	11.9
	mean [$\mu\text{g}/\text{kg}$]		18
	standard deviation [$\mu\text{g}/\text{kg}$]		4.8
	coefficient of variation [%]		26.8
	target value (spiked level [$\mu\text{g}/\text{kg}$])		50
	recovery [%]		36

Fenhexamid			
sample no.	injection 1	injection 2	mean (inj 1,2)
1	20.2	20.7	20.5
2	22.4	22.5	22.5
3	21.2	19.5	20.4
4	21.3	22.1	21.7
5	20	23.1	21.6
6	20.1	22.6	21.4
7	22.5	20.1	21.3
	mean [$\mu\text{g}/\text{kg}$]		21.3
	standard deviation [$\mu\text{g}/\text{kg}$]		0.7
	coefficient of variation [%]		3.4
	target value (spiked level) [$\mu\text{g}/\text{kg}$]		22
	recovery [%]		97

Table 9. Results from homogeneity testing for Diphenylamine, Dithianon and Fenhexamid

Iprodion			
sample no.	injection 1	injection 2	mean (inj 1,2)
1	11.2	11.2	11.2
2	11.4	11.6	11.5
3	11.3	10.3	10.8
4	10.1	10.9	10.5
5	9.8	11.4	10.6
6	10.1	10	10.1
7	10.2	9.7	10
	mean [$\mu\text{g}/\text{kg}$]		10.7
	standard deviation [$\mu\text{g}/\text{kg}$]		0.6
	coefficient of variation [%]		5.3
	target value (spiked level) [$\mu\text{g}/\text{kg}$]		12
	recovery [%]		89

Myclobutanil			
sample no.	injection 1	injection 2	mean (inj 1,2)
1	16.7	16.5	16.6
2	16	16.3	16.2
3	14.2	14.4	14.3
4	14.3	14.8	14.6
5	16.5	14.3	15.4
6	14	14.1	14.1
7	14	14.7	14.4
	mean [$\mu\text{g}/\text{kg}$]		15.1
	standard deviation [$\mu\text{g}/\text{kg}$]		1
	coefficient of variation [%]		6.7
	target value (spiked level) [$\mu\text{g}/\text{kg}$]		15
	recovery [%]		100

2-Phenylphenol			
sample no.	injection 1	injection 2	mean (inj 1,2)
1	33.2	32.4	32.8
2	32.4	33.1	32.8
3	32.7	32.5	32.6
4	30.1	32.5	31.3
5	31.4	30	30.7
6	29.9	30	30
7	29.8	28.3	29.1
	mean [$\mu\text{g}/\text{kg}$]		31.3
	standard deviation [$\mu\text{g}/\text{kg}$]		1.5
	coefficient of variation [%]		4.8
	target value (spiked level) [$\mu\text{g}/\text{kg}$]		35
	recovery [%]		89

Table 10. Results from homogeneity testing for Iprodion, Myclobutanil, 2-Phenylphenol

Pirimicarb			
sample no.	injection 1	injection 2	mean (inj 1,2)
1	7.6	8	7.8
2	8.1	8.2	8.2
3	7.8	8.3	8.1
4	7.5	8	7.8
5	8	7.8	7.9
6	8.1	7.6	7.9
7	7.8	7.3	7.6
mean [$\mu\text{g}/\text{kg}$]			7.9
standard deviation [$\mu\text{g}/\text{kg}$]			0.2
coefficient of variation [%]			2.5
target value (spiked level) [$\mu\text{g}/\text{kg}$]			8
recovery [%]			98

Pyraclostrobin			
sample no.	injection 1	injection 2	mean (inj 1,2)
1	12.6	12.1	12.4
2	12.8	12.1	12.5
3	11.3	10.9	11.1
4	11.2	11.3	11.3
5	11.1	10.5	10.8
6	10.3	10.7	10.5
7	10.4	10.5	10.5
mean [$\mu\text{g}/\text{kg}$]			11.3
standard deviation [$\mu\text{g}/\text{kg}$]			0.8
coefficient of variation [%]			7.3
target value (spiked level) [$\mu\text{g}/\text{kg}$]			12
recovery [%]			94

Rotenone			
sample no.	injection 1	injection 2	mean (inj 1,2)
1	24.8	22.4	23.6
2	22.8	21.1	22
3	24.1	24.1	24.1
4	22.8	22	22.4
5	22	23.8	22.9
6	23.4	23.1	23.3
7	21.8	24.4	23.1
mean [$\mu\text{g}/\text{kg}$]			23
standard deviation [$\mu\text{g}/\text{kg}$]			0.7
coefficient of variation [%]			3.1
target value (spiked level) [$\mu\text{g}/\text{kg}$]			24
recovery [%]			96

Table 11. Results from homogeneity testing for Pirimicarb, Pyraclostrobin and Rotenone

Trifloxystrobin			
sample no	injection 1	injection 2	mean (inj 1,2)
1	18.1	17.1	17.6
2	16.2	18.1	17.2
3	17	18.9	18
4	17.8	17.4	17.6
5	18.1	17.3	17.7
6	18	18.4	18.2
7	18.1	18.2	18.2
mean [$\mu\text{g}/\text{kg}$]			17.8
standard deviation [$\mu\text{g}/\text{kg}$]			0.4
coefficient of variation [%]			2.1
target value (spiked level) [$\mu\text{g}/\text{kg}$]			18
recovery [%]			99

Table 12. Results from homogeneity testing for Trifloxystrobin

5. Stability testing

MPA Eberswalde GmbH, Germany, performed the stability testing. Stability was tested for storage at -20°C from November 29th (preparation of test material) to December 17th, 2012.

The mean values from homogeneity testing (7 samples, 2 injections, November 29th, see paragraph 4) were used as reference.

For stability testing an extract was prepared from one randomly selected test material and analysed in a two-fold determination.

Mean values for stability testing for all pesticides in the apple pulp purée are shown in table 13.

Parameter	Mean value November 29 th	Mean value December 17 th
Captan	24.0	24.5
Chlorpyrifos-ethyl	6.6	7.5
Chlorpyrifos-methyl	13.6	13.9
Diphenylamine	29.9	31.6
<i>Dithianon</i>	28.8	23.9
Fenhexamid	21.3	21.7
Iprodion	10.7	11.5
Myclobutanil	15.1	13.9
2-Phenylphenol	31.3	31.2
Pirimicarb	7.9	7.6
Pyraclostrobin	11.3	11.2
Rotenone	23.0	23.5
Trifloxystrobin	17.8	16.1

Table 13. Results from stability testing for all pesticides in apple pulp purée