Bundesverband
Naturkost Naturwaren

Laboratory Performance Assessment

Analysis of Analytes in Dried Apple Chips

Report

September 2016

Bundesverband
Naturkost Naturwaren

Summary

The laboratory performance assessment related to analytes in dried apple chips was designed and organised by Lach & Bruns in cooperation with PROOF-ACS in September 2016 on behalf of BNN e.V. (Bundesverband Naturkost Naturwaren).

The test material was prepared of organic dried apple chips. Nine analytes were spiked to the apple chips:

> *Carbendazim, Carbofuran, Cyflufenamid, Folpet, Spirodiclofen, Tebuconazole, Tetrahydrophthalimide (THPI), Ethephon, and Phosphonic acid.*

The test material was distributed to twenty-six participants across five European countries (Belgium, Germany, Italy, Netherlands, Spain). Each laboratory received 200 g of the homogenised apple chips. No information with respect to the identity or the number of spiked multi-method analytes was provided to the laboratories in advance. In addition to analytes typically covered by the scope of multi-methods, the laboratories were instructed to analyse also for Ethephon and Phosphonic acid in the test sample. Thus, the laboratories were requested to identify the seven spiked multi-method analytes and to quantify nine analytes (multi-method analytes plus Ethephon and Phosphonic acid) in the test sample.

All participants kept the term of submission of results and were considered for evaluation.

The performance assessment considers the following test criteria:

- No *false positive results*.
- Correct *identification* of seven multi-method analytes. The presence of Ethephon and Phosphonic acid in the test sample was to be expected by the labs since they were instructed to analyse the test sample for both parameters.
- Correct *quantification* of nine analytes in terms of 70 to 120 % recovery of the spiked value.

Summary of the performance of the laboratories with respect to the identification and quantification of the analytes:

Criterion	**Criterion passed**
Correct *identification* of all seven multi-method analytes	23 out of 26 laboratories (88 %)
Correct *quantification* of all seven multi-method analytes	8 out of 26 laboratories (31 %)
Correct *quantification* of Ethephon	23 out of 26 laboratories (88 %)
Correct *quantification* of Phosphonic acid	19 out of 26 laboratories (73 %)
Correct *quantification* of all nine analytes	7 out of 26 laboratories (27 %)

Assessment of quantification

Analytical results between 70 and 120 % recovery of the spiked levels are considered satisfying for the assessment of the correct quantification of the pesticides.

Pesticide	Spiked level [mg/kg]	Assigned value [mg/kg]	Number of results	Correct quantification
Carbendazim	0.023	0.0221	26	24 out of 26 (92 %)
Carbofuran	0.015	0.0146	26	24 out of 26 (92 %)
Cyflufenamid	0.055	0.0505	26	26 out of 26 (100 %)
Folpet	0.045	0.0414	25	13 out of 26 (50 %)
Spirodiclofen	0.048	0.0479	26	24 out of 26 (92 %)
Tebuconazole	0.015	0.0146	26	24 out of 26 (92 %)
THPI	0.052	0.0464	24	24 out of 26 (92 %)
Ethephon	0.078	0.807	25	23 out of 26 (88 %)
Phosphonic acid	0.16	0.197	24	19 out of 26 (73 %)

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1. Test material preparation and design

The laboratory performance assessment was designed to verify the analytical competence related to BNN module-combination “A1 (pesticides) – B1/B2 (fresh and processed fruit and vegetable)”. As dried apples are a relevant product in the dried fruit market in the organic sector, apple chips were chosen as test material.

Seven analytes covered by multi-method analysis and two pesticides, which require single residue methods, were selected for the test:

> *Carbendazim, Carbofuran, Cyflufenamid, Folpet, Spirodiclofen, Tebuconazole, Tetrahydrophthalimide (THPI), Ethephon, and Phosphonic acid.*

An external laboratory prepared the test material under supervision of PROOF-ACS.

A subsample of the dried apple chips was analysed as blank material. Even though no incurred residues of the spiked pesticides were identified, incurred levels of about 0.015 mg/kg Phthalimide were identified in the blank sample (see section 3).

The dried apple chips were crumbled up by hand at room temperature. The spiking solution was added to the apple chips allowing to be soaked by the dried material. Thereafter, liquid nitrogen was added and the apple chips were milled and homogenised. Subsamples of 200 g were bottled and stored at -18 °C until shipment. Shipment was performed on dry ice in order to avoid any thawing of the test material, which might reduce the pourability of the material.

2. Statistical evaluation of results

2.1. Trueness criterion

The trueness criterion considers the correct quantification of the actual analyte concentration in the sample. The trueness of the results is assessed as the coverage of the spiked level in %. The coverage of the spiked level is calculated according to the equation below:

$$coverage\ of\ the\ spiked\ level = \frac{x}{sl} * 100$$

(x = reported result; sl = spiked level)

Accepted range:

Results, which correspond to a recovery of 70 to 120 % of the spiked level, are considered satisfying in this laboratory performance assessment in accordance with the guidelines of the BNN[1]. A non-commercial rounding is applied during the calculation of the accepted ranges (two significant figures).

Examples:

- A recovery of 70 % of the spiked level of Spirodiclofen (spiked level: 0.048 mg/kg) corresponds to an arithmetical value of 0.0336 mg/kg, which is rounded to the next lower figure: 0.033 mg/kg (slight increase of the accepted range).
- A recovery of 120 % of the spiked level of THPI (spiked level: 0.052 mg/kg) corresponds to an arithmetical value of 0.0624 mg/kg. 0.0624 mg/kg is rounded to the next higher figure: 0.063 mg/kg (also slight increase of the accepted range).

2.2. Assigned value

The assigned value $\hat{X}$ is the robust mean, which is derived from the results of the participants. It represents the statistical average (consensus) value of the results of the participants. The Winsorisation algorithm is applied to minimise the influence of outliers. As a first step the mean and the standard deviation of the results are calculated. After that, all results higher than the mean + 1.5-fold standard deviation are set to the mean + 1.5-fold standard deviation and results lower the mean - 1.5-fold standard deviation are set to the mean - 1.5-fold standard deviation. This procedure is repeated several times, until the robust mean remains the same[2].

The assigned values are subject to commercial rounding and are presented with an accuracy of three significant figures.

2.3. z-score

The z-score is derived from the result x of each participant according to the equation below. The z-score is applied to evaluate the comparability of the results. It is derived of the result x of each participant, the assigned value $\hat{X}$ and the target standard deviation $\hat{\sigma}_H$:

$$z - score = \frac{x - \hat{X}}{\hat{\sigma}_H}$$

The z-scores are provided for the assessment of the results of selected laboratories with respect to the quantification of Phosphonic acid (see section 3).

[1] BNN, Guidelines for laboratory approval by Bundesverband Naturkost Naturwaren (BNN) e. V. (Federal Association for Natural Foods and Natural Products inc. soc.), http://n-bnn.de/sites/default/dateien/GuidelinesBNNLabApprovalSeptember2015.pdf.

[2] Analytical Methods Committee, "Robust Statistics - How Not to Reject Outliers. Part 1. Basic Concepts," *The Analyst*, vol. 114, no. 12, p. 1693, 1989.

3. Results

The laboratories received the test samples without prior announcement. Upon receipt of the parcel, the laboratories were informed about the test, the type of test material and the scope of the test by an enclosed instruction letter. The laboratories were requested to apply the pesticide multi residue methods (with GC and LC modules) plus single residue methods for the quantification of Ethephon and Phosphonic acid.

Twenty-six laboratories across five European countries (Belgium, Germany, Italy, Netherlands, Spain) took part in the laboratory performance assessment. All participants kept the term of results submission and were considered for evaluation. Each laboratory was given a randomly selected identifier, hereinafter referred to as laboratory code.

The laboratories reported all sought and found pesticides, the corresponding recoveries, the reporting limits (RL) as well as the scope of the applied analytical methods.

A summary of the overall performance of the labs is provided in table 1. A more detailed evaluation of the results of the participants is presented in tables 2 to 11 (pp. 12-21) and in figures 1 to 10 (pp. 22-31).

All laboratories identified Carbendazim, Carbofuran, Cyflufenamid, Spirodiclofen, and Tebuconazole correctly. None of the labs reported false positive results. False negative results were reported for Folpet (lab 14), THPI (lab 10) and Phosphonic acid (lab 8).

More than 90 % of the laboratories (at least 24 out of 26 labs) quantified Carbendazim, Carbofuran, Cyflufenamid, Spirodiclofen, Tebuconazole and THPI correctly and passed the trueness criterion.

Folpet / Phthalimide

According to regulation (EU) No 2016/156 the new residue definition of Folpet applies from August 26, 2016. Phthalimide, the metabolite of Folpet, is now part of the residue definition ("*Folpet: Sum of folpet and phtalimide, expressed as folpet*"). However, in addition to being a metabolite of Folpet, Phthalimide might also be linked to other sources than the application of Folpet according to recent publications [3].

As a consequence, it is essential that the laboratories are able to distinguish between Folpet and Phthalimide, especially in cases of positive findings of Phthalimide in organic samples - without any Folpet detections. Only reporting the sum of Folpet and Phthalimide bears the risk of indicating false positive results for the pesticide Folpet in organic food samples [4].

[3] *relana® Position Paper No. 16-03 "Folpet/Phthalimid" version 2016/07/22* (www.relana-online.de)
[4] GDCh, Arbeitsgruppe Pestizide, Positionspapier „Keine zweifelsfreie Überwachung des Rückstandshöchstgehaltes von Folpet möglich. (https://www.gdch.de/fileadmin/downloads/Netzwerk_und_Strukturen/Fachgruppen/Lebensmittelchemiker/Arbeitsgruppen/pestizide/2016_positionspapier_phthalimid.pdf.

In this laboratory performance assessment, Folpet was spiked to the test material at a level of 0.045 mg/kg. In addition, the testing of the blank material revealed incurred residues of Phthalimide of about 0.015 mg/kg. This is in line with the levels that were generally reported as background levels in dried apples [3].

The correct quantification of Folpet was assessed in this laboratory performance assessment, while the reported levels of Phthalimide are presented for information purpose only (table 6 and figure 5).

Most of the laboratories reported results of both, Folpet and Phthalimide. 50 % of the laboratories (13 out of 26 labs) reported correct results of Folpet and passed the trueness criterion.

The laboratories, that did not report results of Phthalimide were contacted after having reported results, and they were asked if they quantified Phthalimide in the test sample as well - and if so, at which levels.

Lab 7 replied that it applies an analytical method based on the quantification of Phthalimide ("For folpet we have analysed fthalimide and expressed as folpet"). That kind of "indirect" quantification is applicable only if Folpet is completely converted to Phthalimide during the analytical process and if the instrumental system is free of phthalimide residues (resulting f. ex. from former analyses or other contamination sources). These perquisites have to be provided in any case. The result then represents the sum of Folpet and Phthalimide. However, this procedure bears the risk of overestimation if the necessary prerequisites are not provided. Furthermore, the results must be reported as "sum of Folpet and Phtalimide, expressed as Folpet" instead of "Folpet".

In this test, lab 7 overestimates the level of Folpet in the test material (recovery of 144 % of the spiked level). Lab 7 is not fit for reporting reliable results of Folpet and Phthalimide separately as required in general and in particular for organic samples.

Lab 3 replied "We didn't analyze Phthalimide, but only Folpet so we can't give you separately the Phthalimide result." Phthalimide is not part of the analytical scope according to the provided documents. The lab is thus not fit for verification of the levels of Folpet in food according to regulation (EU) No 2016/156.

Lab 14 only reported Phthalimide at a concentration level of 0.039 mg/kg. Having asked about the analytical details after lab 14 had reported the results, PROOF received the comment: "On a routine report Fthalimide is reported as Folpet (sum): 0.080 mg/kg. Traces of folpet (editor's note: *in the BNN test sample*) are detected below the LOQ 0.01 mg/kg." Taking into consideration the routines of Lab 14, the result of Folpet is considered "false negative". Lab 14 is not fit to report reliable results of Folpet and Phthalimide as required in general and in particular for organic samples.

Tetrahydrophthalimide (THPI)

The laboratory performance assessment took place one month before regulation (EU) No 2016/452 applied. The new residue definition of Captan includes Tetrahydrophthalimide (THPI), the main metabolite of Captan ("Sum of captan and THPI, expressed as captan").

The aim of including THPI into the test was to verify if the laboratories are prepared for the new residue definition and if the laboratories are able to provide reliable results of THPI.

All but three laboratories (Labs 7, 10, 15) reported results of THPI. Labs 7 and 15 were contacted after closing of the BNN test and they were asked if they analysed the test samples for THPI, and if they are able to provide results. Lab 10 did not report results of THPI, although it is covered by its analytical scope. THPI was thus considered “false negative” for lab 10.

Lab 7 reported a result of Captan. Upon request, the lab explained that it analysed for THPI and expressed the result as Captan. For the evaluation, the THPI result was calculated back to the Captan result by PROOF.

Lab 15 explained that at the time of the test, it was on the way to set up the analytical method of THPI but had not finished yet. Due to the fact that the new residue definition has not yet applied at the time of the BNN test, THPI was considered as “not in scope” (n.a.) for lab 15.

Ethephon

All but one laboratory (lab 5) reported results of Ethephon. Lab 5 explained that at the time of the test it had problems with the analytical system and was not able to quantify Ethephon.

23 out of 26 laboratories pass the trueness criterion.

Phosphonic acid

24 out of 26 laboratories reported results of Phosphonic acid.

Lab 8 explained on request that it quantified a level of Phosphonic acid below its reporting limit of 0.1 mg/kg and thus did not report Phosphonic acid. The result was considered false negative.

The reporting limits of two labs are not appropriate for the quantification of Phosphonic acid in organic products (lab 9: RL 0.5 mg/kg; lab 21: RL 0.3 mg/kg).

Lab 9 provided a comment explaining that in routine analyses, the lab subcontracts the analysis of Phosphonic acid in dried organic fruits to another lab.

Although the reporting limit of lab 21 is at 0.3 mg/kg, the lab reported a result of Phosphonic acid of 0.11 mg/kg. The result was considered for evaluation and is still within the accepted range.

The assigned value of Phosphonic acid of 0.197 mg/kg corresponds to a recovery of 123 % of the spiked level. The reported results of the laboratories thus indicate a general trend to overestimate the spiked level. The reason of the overestimation is not clear. The results of the homogeneity as well as the stability testing are close to the spiked level (homogeneity: 89 % / stability: 105 % recovery of the spiked level).

However, due to the observed trend the results of labs 6 (z-score: 0,8), 12 (z-score: 1,3), 17 (z-score: 0,6), 18 (z-score: 0,4), 19 (z-score: 0,3), and 25 (z-score: 0,3) are considered satisfying as they correspond to z-scores < 2.

The results of 19 out of 26 labs (73 %) are thus considered satisfying.

4. Conclusion

- All laboratories identified Carbendazim, Carbofuran, Cyflufenamid, Spirodiclofen, and Tebuconazole correctly.
- None of the laboratories reported false positive results.
- False negative results were reported for Folpet (lab 14), THPI (lab 10) and Phosphonic acid (lab 8).
- Each of the pesticides Carbendazim, Carbofuran, Cyflufenamid, Spirodiclofen, Tebuconazole, and THPI was quantified correctly by more than 90 % of the laboratories (at least 24 out of 26 labs).
- The most challenging parameter in the test is Folpet. Only 50 % of the laboratories were able to report correct results of this parameter.
- 88 % of the labs (23 out of 26) quantified Ethephon correctly.
- A tendency towards and overestimation is observed for Phosphonic acid. The results of 19 out of 26 labs (73 %) are considered satisfying.
- Seven laboratories quantified all nine parameters correctly (labs 2, 11, 18, 19, 22, and 25). Also lab 3 quantified all nine parameters correctly, however Phthalimide is not part of the analytical scope according to the provided documents. The lab is thus not fit for verification of the levels of Folpet in food according to regulation (EU) No 2016/156. The Phthalimid level was only repirted on request of PROOF after closind of the BNN test.

5. Tables and figures

Table 1. Summary of the overall performance

Lab code	Carben-dazim	Carbo-furan	Cyflu-fenamid	Folpet	Spiro-diclofen	Tebu-conazole	THPI	Ethephon	Phospho-nic acid	All parameters correct
1	no	yes	yes	yes	yes	yes	yes	yes	yes	no
2	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
3	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
4	yes	yes	yes	yes	no	yes	yes	yes	no	no
5	yes	yes	yes	yes	yes	yes	yes	**n.a.**	no	no
6	yes	yes	yes	no	yes	yes	yes	yes	yes*	no
7	yes	yes	yes	no	yes	yes	yes	yes	yes	no
8	yes	yes	yes	no	yes	yes	yes	no	**f. neg.**	no
9	yes	yes	yes	no	yes	yes	yes	yes	no	no
10	yes	no	yes	yes	yes	no	**f. neg.**	yes	yes	no
11	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
12	yes	yes	yes	no	yes	yes	yes	yes	yes*	no
13	no	yes	yes	no	yes	yes	yes	yes	yes	no
14	yes	yes	yes	**f. neg.**	yes	yes	yes	yes	no	no
15	yes	yes	yes	yes	yes	yes	**n.a.**	yes	yes	no
16	yes	yes	yes	no	yes	yes	yes	yes	no	no
17	yes	yes	yes	no	yes	yes	yes	yes	yes*	no
18	yes	yes	yes	yes	yes	yes	yes	yes	yes*	yes
19	yes	yes	yes	yes	yes	yes	yes	yes	yes*	yes
20	yes	yes	yes	no	yes	yes	yes	yes	yes	no
21	yes	no	yes	no	yes	no	yes	yes	yes	no
22	yes	yes	yes	yes	yes	yes	yes	yes	yes	yes
23	yes	yes	yes	no	yes	yes	yes	no	yes	no
24	yes	yes	yes	no	yes	yes	yes	yes	no	no
25	yes	yes	yes	yes	yes	yes	yes	yes	yes*	yes
26	yes	yes	yes	yes	no	yes	yes	yes	yes	no
Success rate	**92 %**	**92 %**	**100 %**	**50 %**	**92 %**	**92 %**	**92 %**	**88 %**	**73 %**	**27 %**

yes: correctly quantified; no: quantification not satisfying; f.neg.: false negative; n.a.: not analysed

Table 2. Results of Carbendazim

	Carbendazim					
	Spiked level [mg/kg]					0.023
	Assigned value [mg/kg]					0.0221
	Assigned value in % of spiked level					96
	Accepted range [mg/kg]			0.016	-	0.028
Laboratory code	**Result [mg/kg]**	**Recovery [%]**	**RL [mg/kg]**	**z-score**	**Result in % of the spiked level**	**Trueness criterion passed**
1	0.031	-	0.01	1.8	135	no
2	0.020	95	0.01	-0.4	87	yes
3	0.024	88	0.01	0.4	104	yes
4	0.022	101	0.01	0.0	96	yes
5	0.025	117	0.01	0.6	109	yes
6	0.020	88	0.01	-0.4	87	yes
7	0.025	100	0.01	0.6	109	yes
8	0.018	95	0.01	-0.8	78	yes
9	0.023	89	0.01	0.2	100	yes
10	0.019	99	0.01	-0.6	83	yes
11	0.023	84	0.01	0.2	100	yes
12	0.023	85.8	0.01	0.2	100	yes
13	0.013	78	0.005	-1.9	57	no
14	0.024	112	0.01	0.4	104	yes
15	0.021	93	0.01	-0.2	91	yes
16	0.027	70	0.01	1.0	117	yes
17	0.020	100	0.005	-0.4	87	yes
18	0.018	85	0.005	-0.8	78	yes
19	0.021	-	0.01	-0.2	91	yes
20	0.022	-	0.005	0.0	96	yes
21	0.023	101	0.005	0.2	100	yes
22	0.026	-	0.01	0.8	113	yes
23	0.02	66	0.01	-0.4	87	yes
24	0.022	96	0.01	0.0	96	yes
25	0.02	84	0.005	-0.4	87	yes
26	0.025	72	0.005	0.6	109	yes

Table 3. Results of Carbofuran

	Carbofuran			
	Spiked level [mg/kg]			0.015
	Assigned value [mg/kg]			0.0146
	Assigned value in % of spiked level			97
	Accepted range [mg/kg]	0.010	-	0.018

Laboratory code	Result [mg/kg]	RL [mg/kg]	Result in % of the spiked level	Trueness criterion passed
1	0.017	0.001	113	yes
2	0.013	0.01	87	yes
3	0.016	0.001	107	yes
4	0.012	0.01	80	yes
5	0.017	0.001	113	yes
6	0.015	0.001	100	yes
7	0.014	0.01	93	yes
8	0.017	0.001	113	yes
9	0.016	0.001	107	yes
10	0.019	0.01	127	no
11	0.014	0.01	93	yes
12	0.014	0.01	93	yes
13	0.013	0.003	87	yes
14	0.013	0.01	87	yes
15	0.016	0.01	107	yes
16	0.016	0.01	107	yes
17	0.016	0.001	107	yes
18	0.013	0.005	87	yes
19	0.012	0.01	80	yes
20	0.010	0.001	67	yes
21	0.019	0.001	127	no
22	0.015	0.001	100	yes
23	0.013	0.001	87	yes
24	0.013	0.01	87	yes
25	0.015	0.005	100	yes
26	0.013	0.01	87	yes

Table 4. Results of Cyflufenamid

	Cyflufenamid			
	Spiked level [mg/kg]			0.055
	Assigned value [mg/kg]			0.0505
	Assigned value in % of spiked level			92
	Accepted range [mg/kg]	0.038	-	0.066
Laboratory code	**Result [mg/kg]**	**RL [mg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
1	0.052	0.01	95	yes
2	0.046	0.01	84	yes
3	0.048	0.01	87	yes
4	0.045	0.01	82	yes
5	0.047	0.01	85	yes
6	0.056	0.01	102	yes
7	0.050	0.01	91	yes
8	0.045	0.01	82	yes
9	0.049	0.01	89	yes
10	0.065	0.01	118	yes
11	0.050	0.01	91	yes
12	0.052	0.01	95	yes
13	0.045	0.01	82	yes
14	0.043	0.01	78	yes
15	0.053	0.01	96	yes
16	0.054	0.01	98	yes
17	0.052	0.005	95	yes
18	0.058	0.01	105	yes
19	0.040	0.01	73	yes
20	0.050	0.005	91	yes
21	0.066	0.01	120	yes
22	0.051	0.01	93	yes
23	0.054	0.01	98	yes
24	0.054	0.01	98	yes
25	0.054	0.005	98	yes
26	0.047	0.01	85	yes

Table 5. Results of Folpet

	Folpet			
	Spiked level [mg/kg]			0.045
	Assigned value [mg/kg]			0.0414
	Assigned value in % of spiked level			92
	Accepted range [mg/kg]	0.031	-	0.054
Laboratory code	**Result [mg/kg]**	**RL [mg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
1	0.045	0.02	100	yes
2	0.039	0.01	87	yes
3	0.053	0.01	118	yes
4	0.050	0.01	111	yes
5	0.044	0.01	98	yes
6	0.055	0.01	122	no
7	0.065*	0.01	144	no
8	0.028	0.01	62	no
9	0.027	0.02	60	no
10	0.054	0.03	120	yes
11	0.041	0.01	91	yes
12	0.027	0.01	60	no
13	0.055	0.01	122	no
14	<0.01		-	**f. neg.****
15	0.045	0.01	100	yes
16	0.029	0.02	64	no
17	0.055	0.005	122	no
18	0.050	0.01	111	yes
19	0.040	0.02	89	yes
20	0.024	0.005	53	no
21	0.023	0.02	51	no
22	0.042	0.01	93	yes
23	0.028	0.01	62	no
24	0.016	0.01	36	no
25	0.054	0.005	120	yes
26	0.043	0.02	96	yes

* Lab 7 analysed Phthalimide and expressed the result as Folpet.
**f. neg.: false negative. Traces of Folpet were only reported on request after closing of BNN test.

Table 6. Results of Phthalimide

	Phthalimide	
Laboratory code	**Result [mg/kg]**	**RL [mg/kg]**
1	0.016	0.01
2	0.036	0.01
3	n.a.	
4	n.r.	
5	0.029	0.02
6	0.036	0.01
7	n.r.	
8	0.01	
9	0.031	0.01
10	n.r.	
11	0.039	0.01
12	0.034	0.01
13	0.03	0.005
14	0.039	0.01
15	0.050	0.01
16	0.037	0.02
17	0.044	0.005
18	0.029	0.01
19	0.018	0.02
20	0.016	0.005
21	0.027	0.05
22	0.040	0.01
23	0.032	0.01
24	0.042	0.01
25	0.037	0.005
26	0.019	0.01

n.a.: not analysed
n.r.: not reported

Table 7. Results of Spirodiclofen

	Spirodiclofen			
	Spiked level [mg/kg]			0.048
	Assigned value [mg/kg]			0.0479
	Assigned value in % of spiked level			100
	Accepted range [mg/kg]	0.033	-	0.058
Laboratory code	**Result [mg/kg]**	**RL [mg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
1	0.055	0.01	115	yes
2	0.042	0.01	88	yes
3	0.052	0.01	108	yes
4	0.028	0.01	58	no
5	0.051	0.01	106	yes
6	0.048	0.01	100	yes
7	0.046	0.01	96	yes
8	0.048	0.01	100	yes
9	0.048	0.01	100	yes
10	0.057	0.01	119	yes
11	0.045	0.01	94	yes
12	0.049	0.01	102	yes
13	0.050	0.003	104	yes
14	0.046	0.01	96	yes
15	0.051	0.01	106	yes
16	0.048	0.01	100	yes
17	0.043	0.005	90	yes
18	0.046	0.01	96	yes
19	0.044	0.01	92	yes
20	0.048	0.005	100	yes
21	0.043	0.01	90	yes
22	0.045	0.01	94	yes
23	0.053	0.01	110	yes
24	0.048	0.01	100	yes
25	0.048	0.005	100	yes
26	0.064	0.01	133	no

Table 8. Results of Tebuconazole

	Tebuconazole			
	Spiked level [mg/kg]			0.015
	Assigned value [mg/kg]			0.0146
	Assigned value in % of spiked level			97
	Accepted range [mg/kg]	0.010	-	0.018

Laboratory code	Result [mg/kg]	RL [mg/kg]	Result in % of the spiked level	Trueness criterion passed
1	0.014	0.01	93	yes
2	0.014	0.01	93	yes
3	0.013	0.01	87	yes
4	0.015	0.01	100	yes
5	0.015	0.01	100	yes
6	0.013	0.01	87	yes
7	0.013	0.01	87	yes
8	0.018	0.01	120	yes
9	0.014	0.01	93	yes
10	0.019	0.01	127	no
11	0.014	0.01	93	yes
12	0.014	0.01	93	yes
13	0.016	0.003	107	yes
14	0.014	0.01	93	yes
15	0.015	0.01	100	yes
16	0.016	0.01	107	yes
17	0.014	0.005	93	yes
18	0.017	0.01	113	yes
19	0.012	0.01	80	yes
20	0.015	0.005	100	yes
21	0.019	0.01	127	no
22	0.015	0.01	100	yes
23	0.012	0.01	80	yes
24	0.015	0.01	100	yes
25	0.015	0.005	100	yes
26	0.014	0.01	93	yes

Table 9. Results of THPI

	THPI			
	Spiked level [mg/kg]			0.052
	Assigned value [mg/kg]			0.0463
	Assigned value in % of spiked level			89
	Accepted range [mg/kg]	0.036	-	0.063
Laboratory code	**Result [mg/kg]**	**RL [mg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
1	0.055	0.01	106	yes
2	0.045	0.01	87	yes
3	0.054	0.01	104	yes
4	0.050	0.01	96	yes
5	0.041	0.01	79	yes
6	0.045	0.01	87	yes
7	0.046*	0.01	88	yes
8	0.052	0.01	100	yes
9	0.036	0.01	69	yes
10	n.r.		-	**f. neg.**
11	0.053	0.01	102	yes
12	0.044	0.01	85	yes
13	0.052	0.003	100	yes
14	0.043	0.01	83	yes
15	n.i.s		-	-
16	0.059	0.01	113	yes
17	0.042	0.005	81	yes
18	0.046	0.01	88	yes
19	0.040	0.01	77	yes
20	0.045	0.005	87	yes
21	0.041	-	79	yes
22	0.055	0.01	106	yes
23	0.041	0.01	79	yes
24	0.040	0.01	77	yes
25	0.042	0.005	81	yes
26	0.048	0.01	92	yes

f. neg.: false negative
n.i.s.: not in scope (method development has started already)
* Lab 7 reported THPI as Captan, thus the result of THPI was calculated back by PROOF.

Table 10. Results of Ethephon

	Ethephon			
	Spiked level [mg/kg]			0.078
	Assigned value [mg/kg]			0.0807
	Assigned value in % of spiked level			103
	Accepted range [mg/kg]	0.054	-	0.094

Laboratory code	Result [mg/kg]	RL [mg/kg]	Result in % of the spiked level	Trueness criterion passed
1	0.077	0.01	99	yes
2	0.080	0.01	103	yes
3	0.077	0.05	99	yes
4	0.074	0.01	95	yes
5	n.a.		-	no
6	0.062	0.01	79	yes
7	0.089	0.05	114	yes
8	0.10	0.01	128	no
9	0.088	0.01	113	yes
10	0.086	0.01	110	yes
11	0.082	0.01	105	yes
12	0.079	0.01	101	yes
13	0.070	0.01	90	yes
14	0.081	0.01	104	yes
15	0.089	0.01	114	yes
16	0.090	0.01	115	yes
17	0.074	0.01	95	yes
18	0.074	0.01	95	yes
19	0.086	0.01	110	yes
20	0.065	0.01	83	yes
21	0.074	0.02	95	yes
22	0.085	0.01	109	yes
23	0.11	0.05	141	no
24	0.079	0.01	101	yes
25	0.07	0.005	90	yes
26	0.090	0.02	115	yes

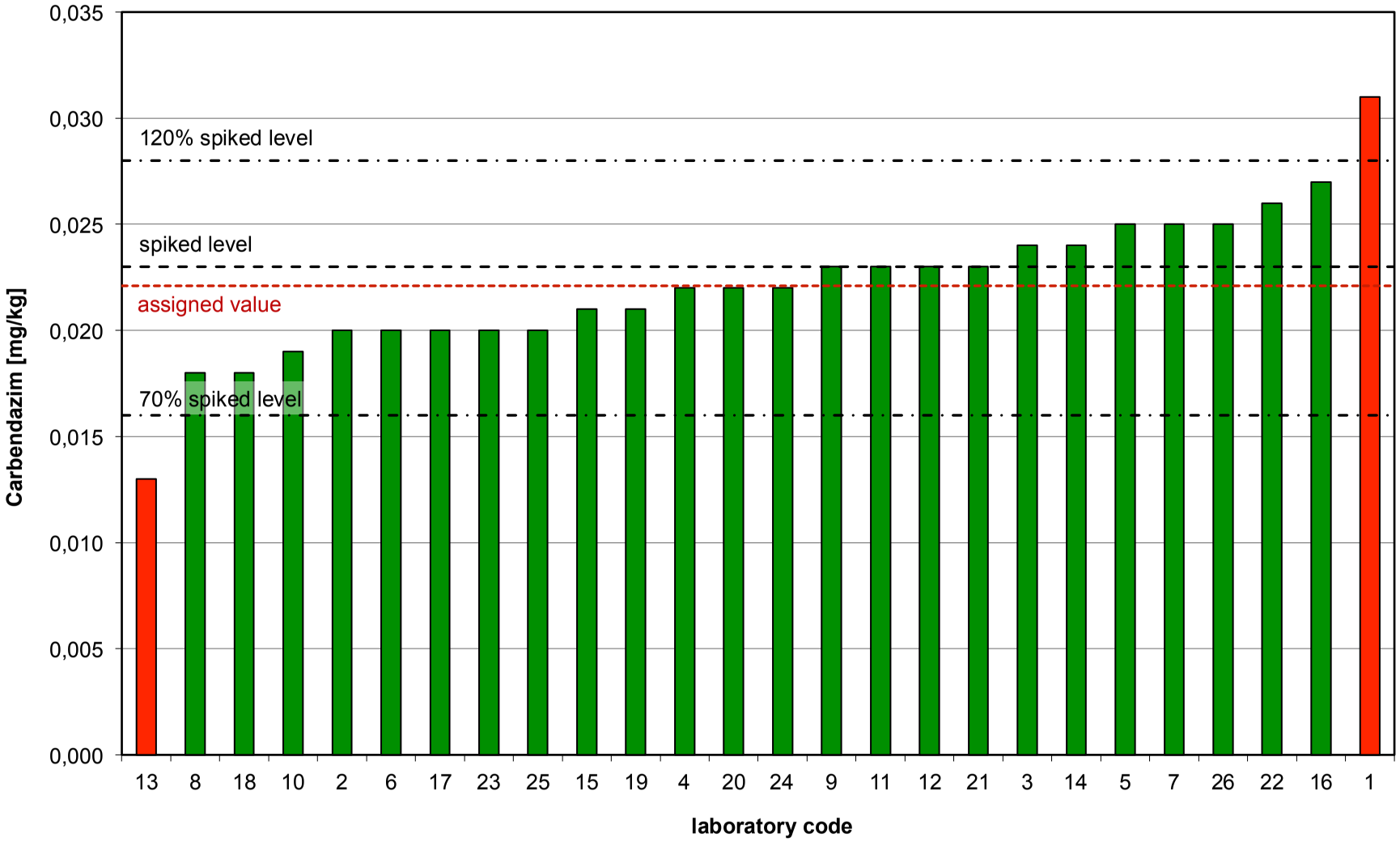
n.a.: not analysed

Table 11. Results of Phosphonic acid

	Phosphonic acid			
	Spiked level [mg/kg]			0,16
	Assigned value [mg/kg]			0,197
	Assigned value in % of spiked level			123
	Accepted range [mg/kg]	0,11	-	0.20
Laboratory code	**Result [mg/kg]**	**RL [mg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
1	0.19	0.1	119	yes
2	0.180	0.01	113	yes
3	0.14	0.075	88	yes
4	0.050	0.2	31	no
5	0.50	0.1	313	no
6	0.23	0.1	144	yes*
7	0.15	0.1	94	yes
8	<0.1	-	-	**f. neg.**
9	<0.50[#]	0.5	-	no
10	0.19	0.1	119	yes
11	0.18	0.01	113	yes
12	0.25	0.01	156	yes*
13	0.2	0.1	125	yes
14	0.33	0.1	206	no
15	0.123	0.05	77	yes
16	0.31	0.1	194	no
17	0.22	0.1	138	yes*
18	0.214	0.01	134	yes*
19	0.21	0.1	131	yes*
20	0.2	0.1	125	yes
21	<0.3 (0.11)	0.3	69	yes
22	0.17	0.1	106	yes
23	0.16	0.1	100	yes
24	0.31	0.01	194	no
25	0.207	0.01	129	yes*
26	0.185	0.05	116	yes

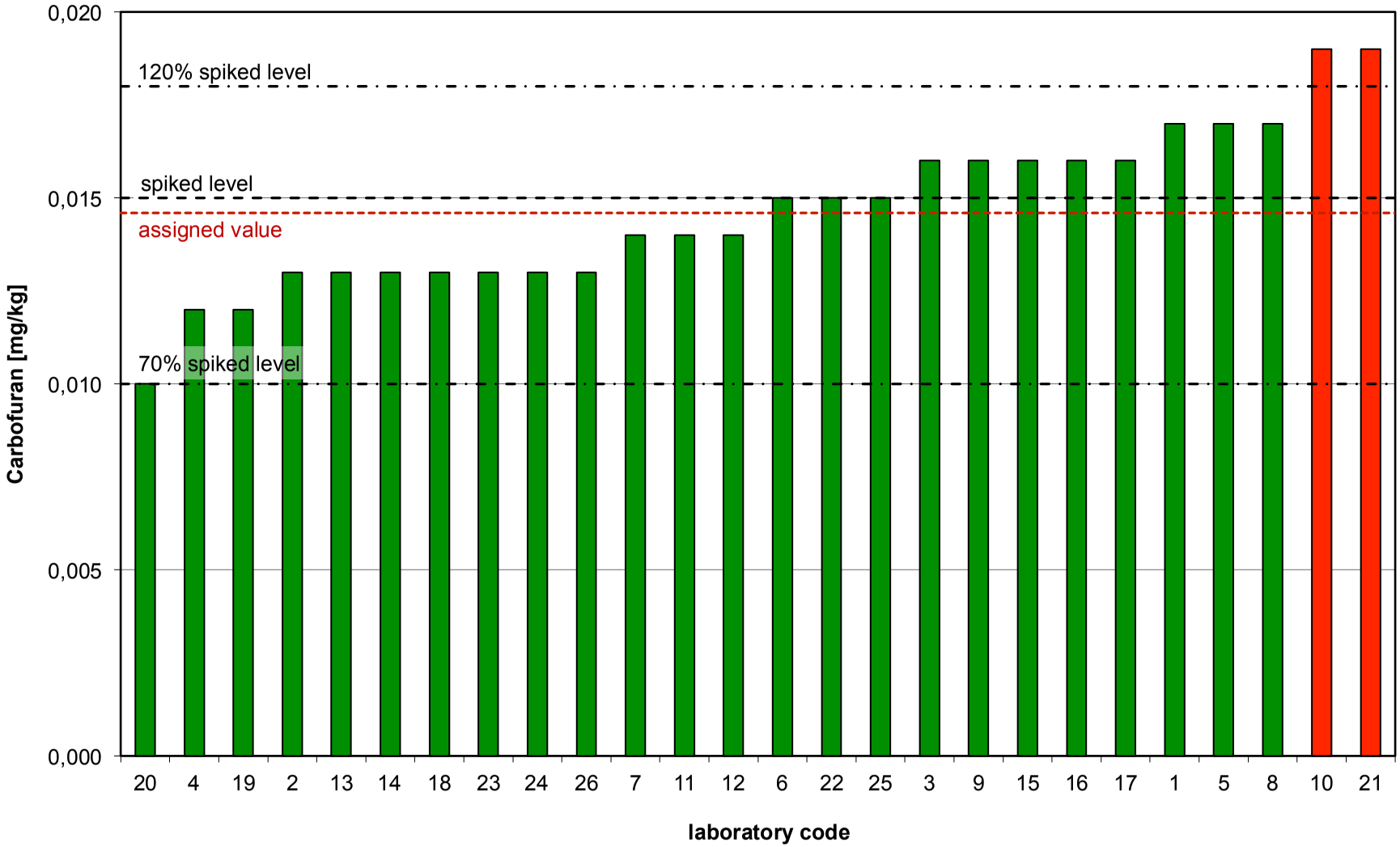
* The results of labs 6, 12, 17, 18, 19, and 25 are considered satisfying. See section 3 for details
[#] In routine, the analysis of dried organic samples is subcontracted
f. neg.: false negative

Figure 1. Assessment of Carbendazim



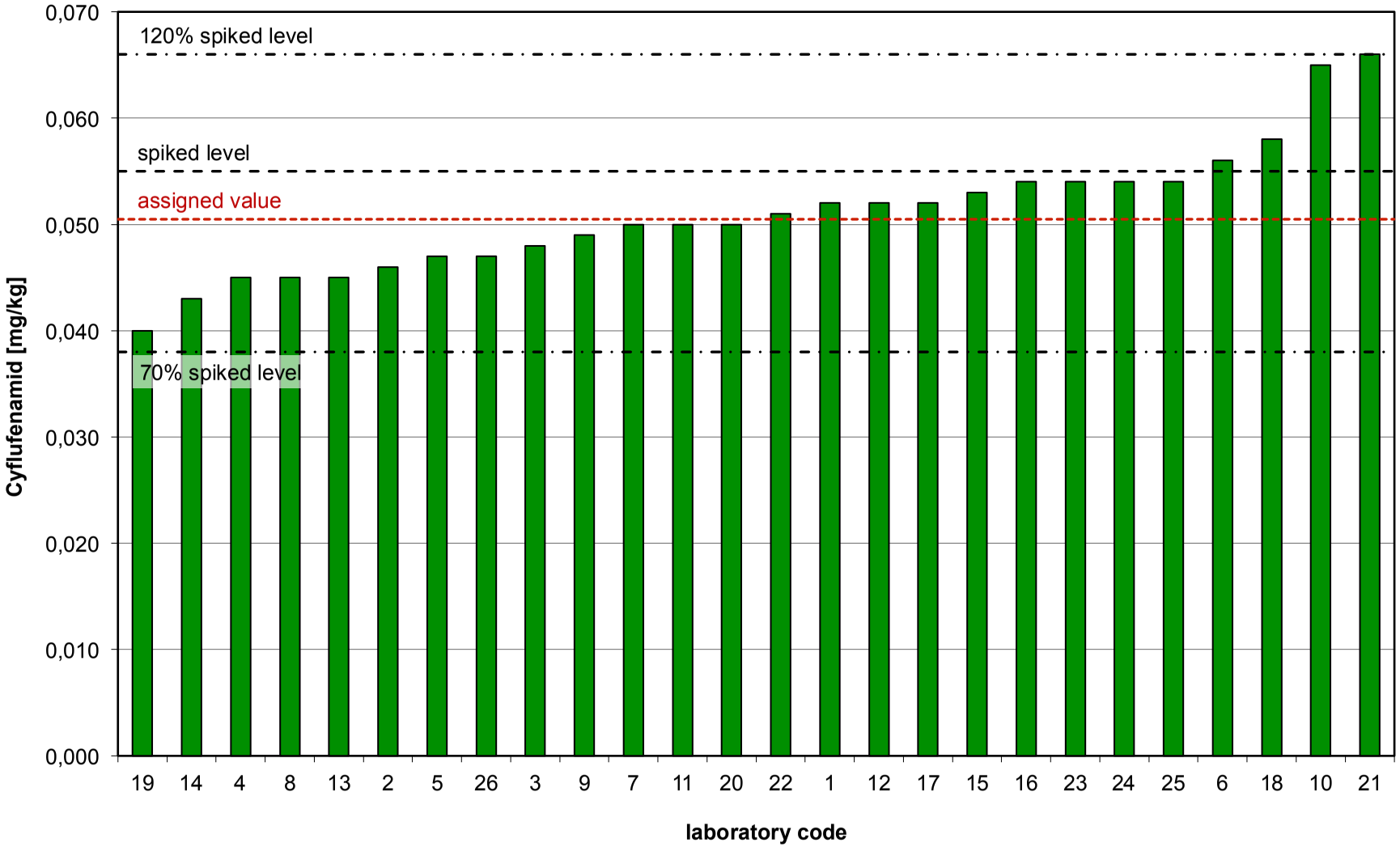
Green: satisfactory results, red: dissatisfactory results

Figure 2. Assessment of Carbofuran



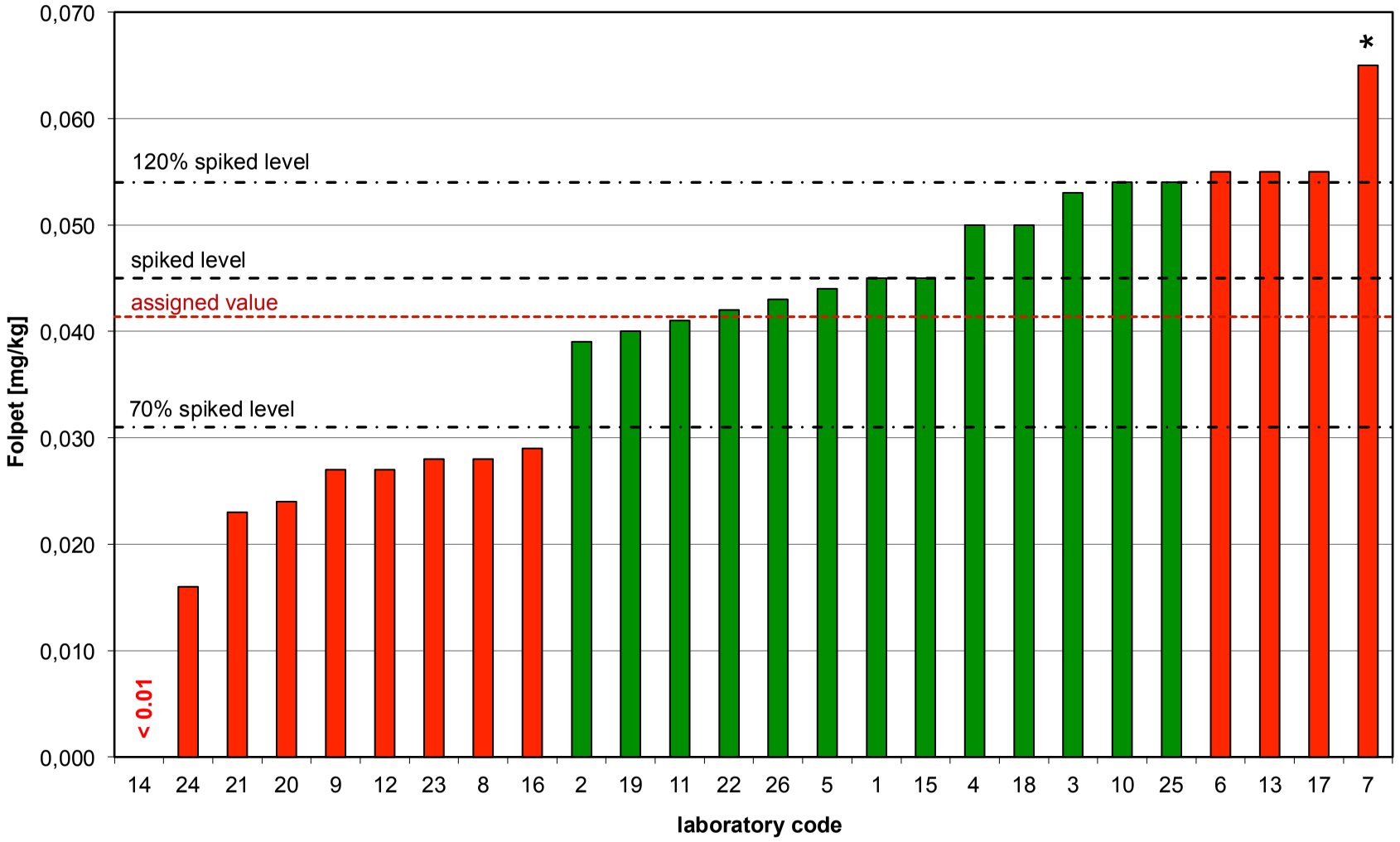
Green: satisfactory results, red: dissatisfactory results

Figure 3. Assessment of Cyflufenamid



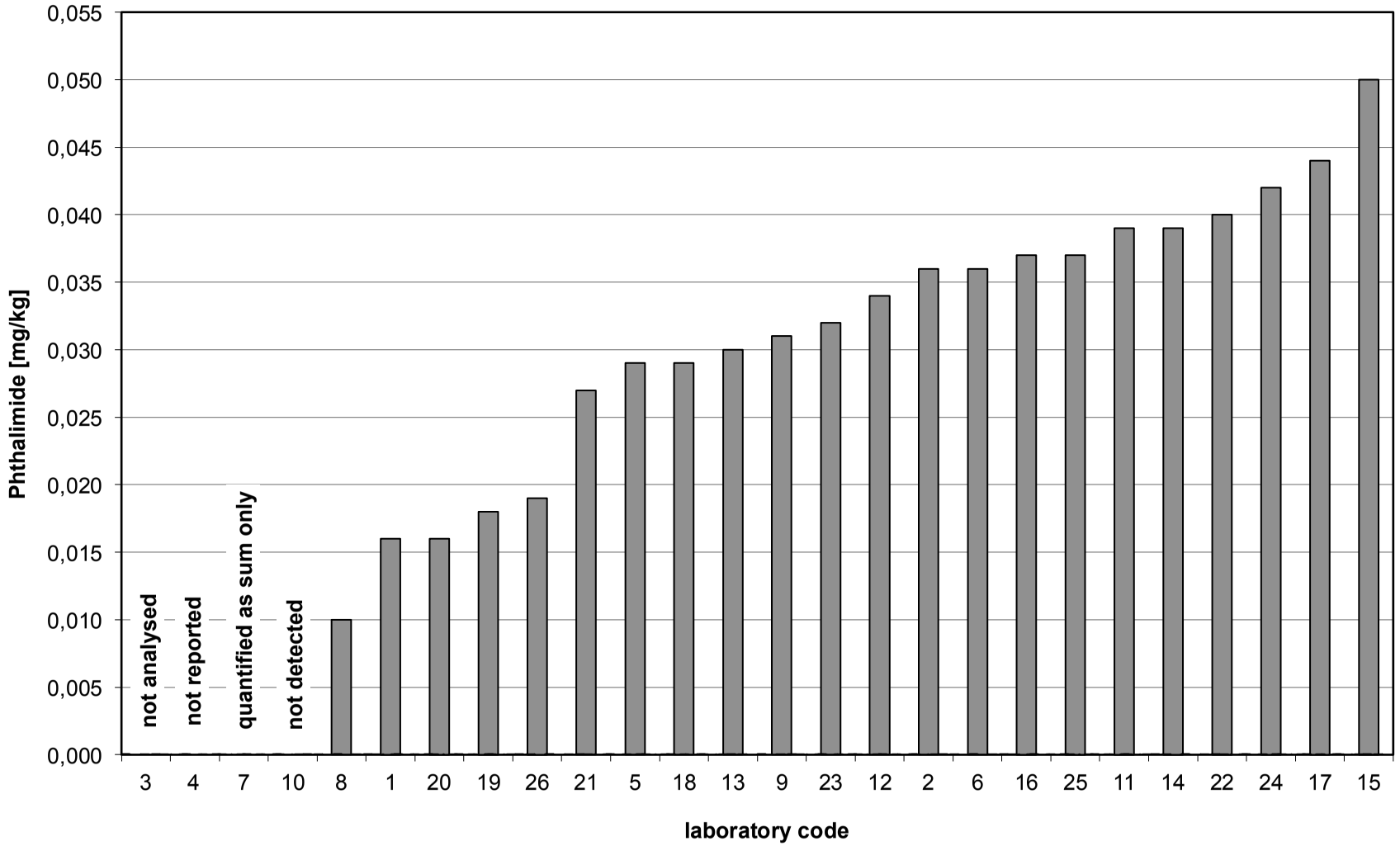
Green: satisfactory results, red: dissatisfactory results

Figure 4. Assessment of Folpet



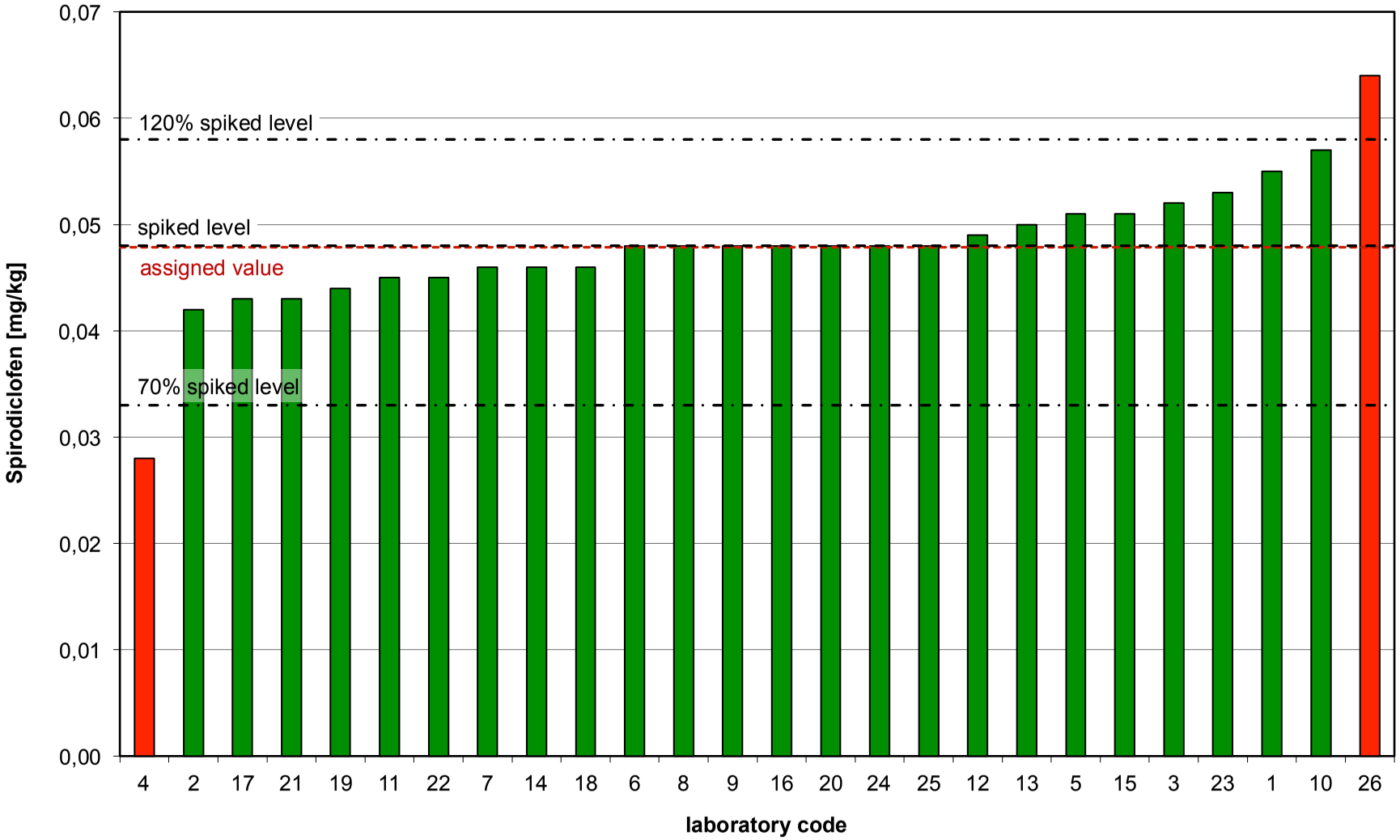
* Lab 7 analysed Phthalimide and expressed the result as Folpet. The result thus corresponds to the sum of Folpet and Phthalimide.
Green: satisfactory results, red: dissatisfactory results

Figure 5. Assessment of Phthalimide (unspiked, for information purpose only)



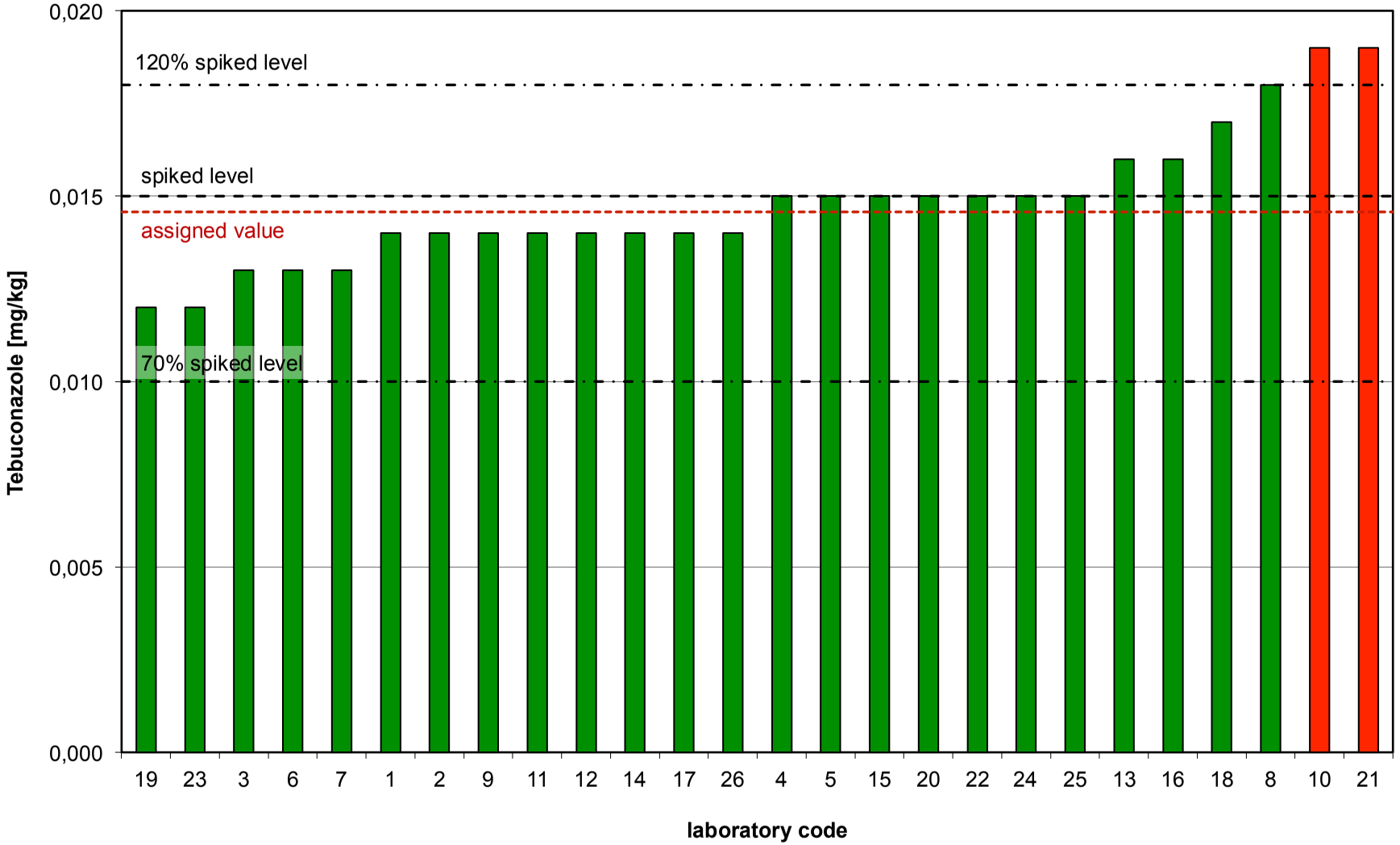
Green: satisfactory results, red: dissatisfactory results

Figure 6. Assessment of Spirodiclofen



Green: satisfactory results, red: dissatisfactory results

Figure 7. Assessment of Tebuconazole



Green: satisfactory results, red: dissatisfactory results

Figure 8. Assessment of THPI

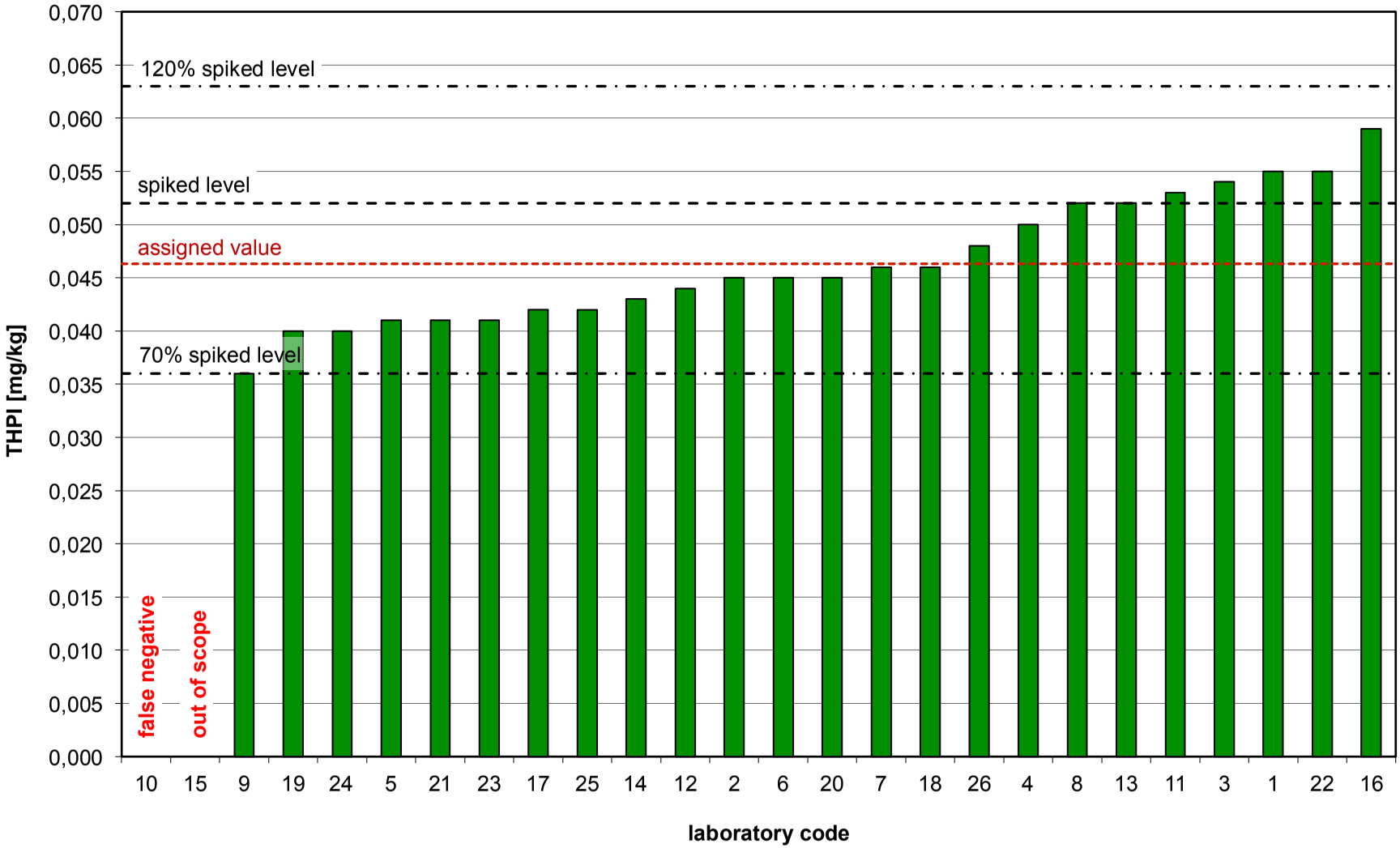


Figure 9. Assessment of Ethephon

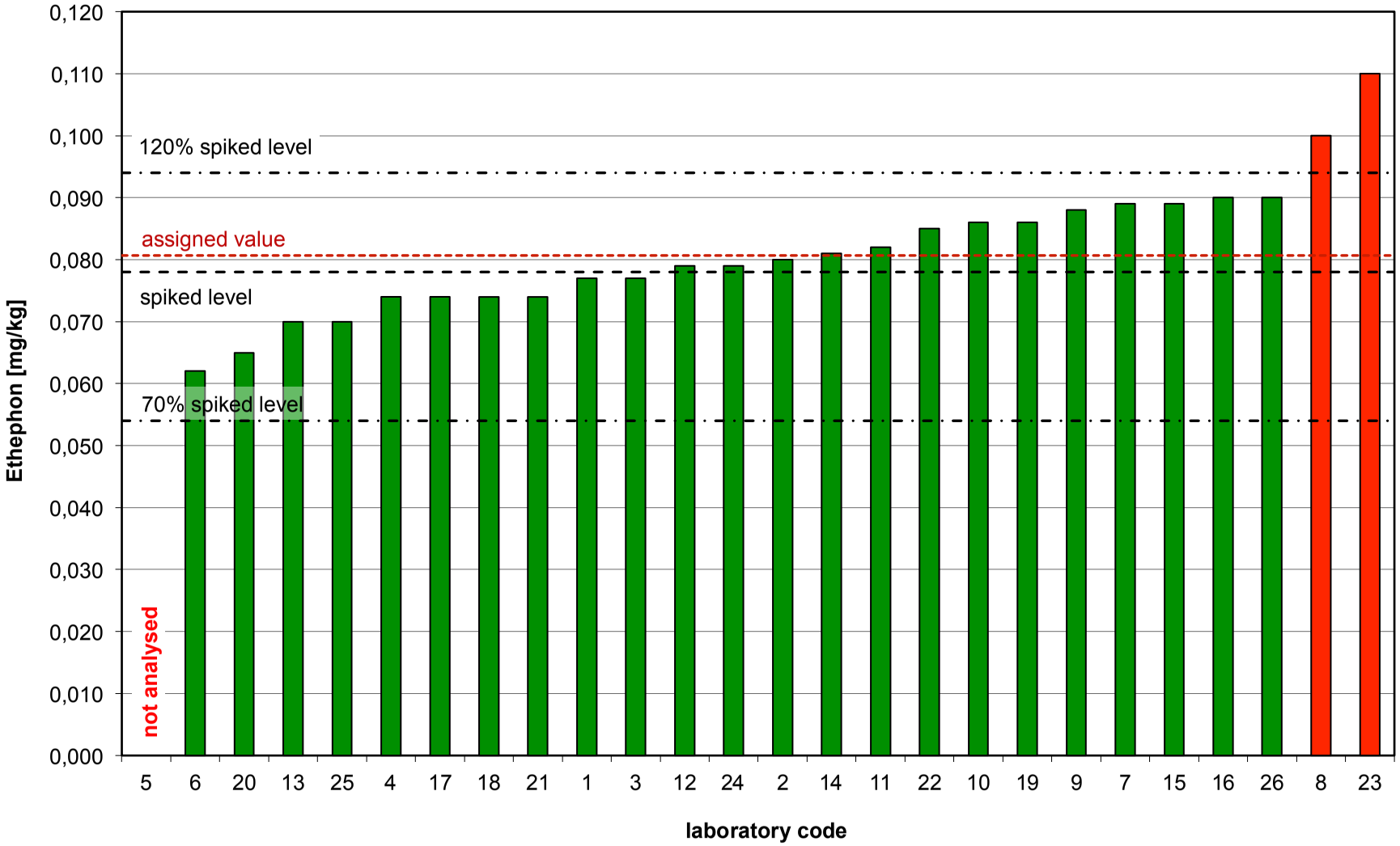
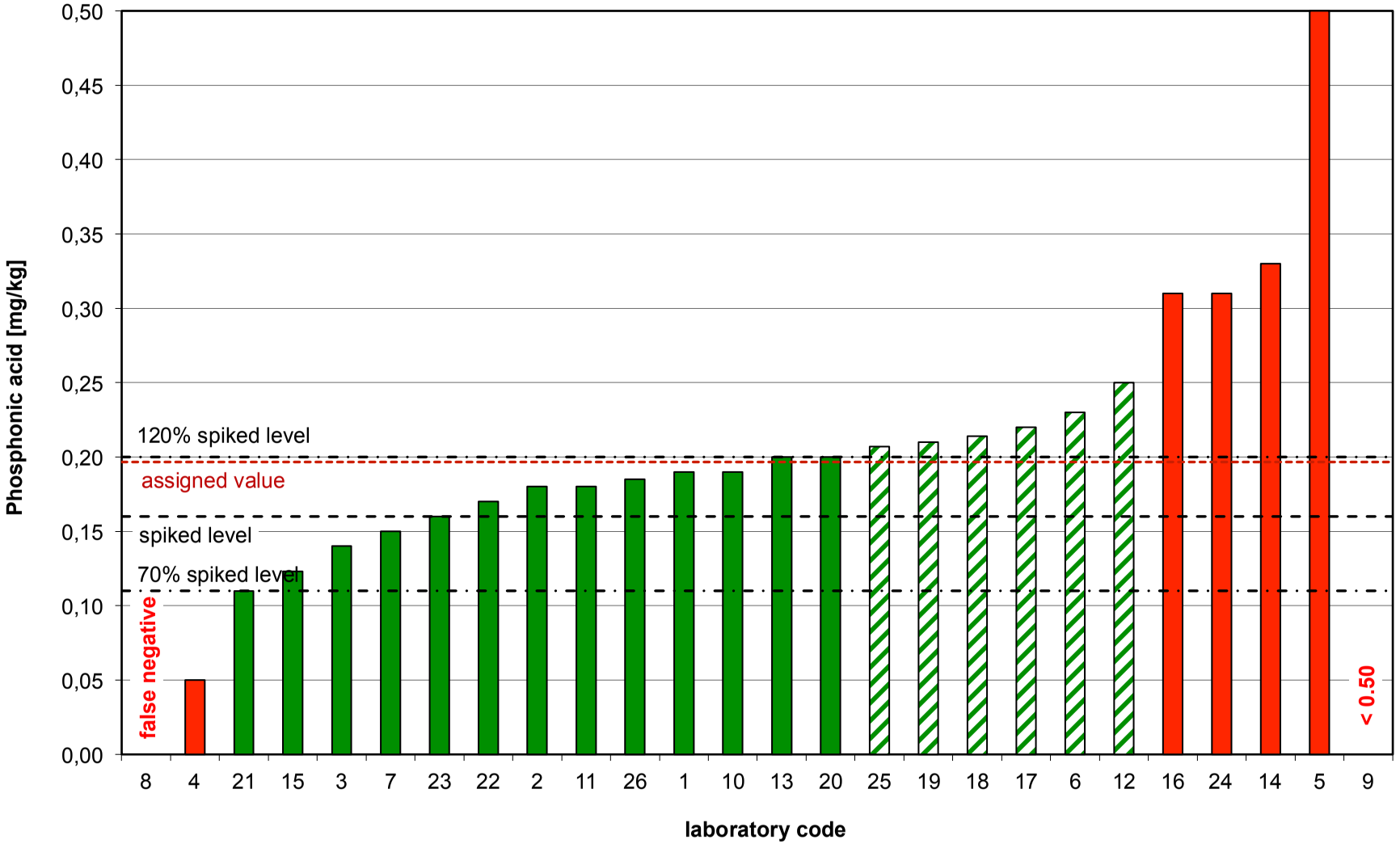


Figure 10. Assessment of Phosphonic acid



6. Homogeneity testing

Ten randomly chosen test samples were used for homogeneity testing. Each subsample was analysed for all spiked pesticides in duplicate. The results confirm the homogeneous distribution of the pesticides in the test material and the spiked levels (tables 12 and 13).

Table 12. Results of the homogeneity testing (part 1)

Subsample No.	Extraction No.	Carbendazim [mg/kg]	Carbofuran [mg/kg]	Cyflufenamid [mg/kg]	Folpet [mg/kg]
1	1	0.025	0.012	0.059	0.042
	2	0.024	0.013	0.058	0.043
2	1	0.024	0.012	0.058	0.047
	2	0.024	0.013	0.058	0.051
3	1	0.023	0.012	0.055	0.041
	2	0.024	0.013	0.059	0.048
4	1	0.023	0.013	0.058	0.044
	2	0.024	0.013	0.057	0.044
5	1	0.024	0.013	0.057	0.042
	2	0.022	0.013	0.058	0.043
6	1	0.023	0.013	0.059	0.044
	2	0.023	0.013	0.057	0.041
7	1	0.025	0.013	0.055	0.041
	2	0.023	0.012	0.055	0.041
8	1	0.024	0.013	0.059	0.043
	2	0.022	0.013	0.058	0.042
9	1	0.024	0.012	0.057	0.043
	2	0.022	0.012	0.056	0.043
10	1	0.023	0.012	0.055	0.048
	2	0.023	0.012	0.055	0.043
Mean [mg/kg]		0.0235	0.0126	0.0572	0.0437
Standard deviation [mg/kg]		0.00089	0.00050	0.0015	0.0027
Coefficient of variation [%]		3.8	4.0	2.6	6.3
Spiked level [mg/kg]		0.023	0.015	0.055	0.045
Recovery of the spiked level [%]		102	84	104	97

Table 13. Results of the homogeneity testing (part 2)

Subsample No.	Extraction No.	Spiro-diclofen [mg/kg]	Tebu-conazole [mg/kg]	THPI [mg/kg]	Ethephon [mg/kg]	Phosphonic acid [mg/kg]
1	1	0.050	0.014	0.049	0.084	0.15
	2	0.053	0.014	0.049	0.084	0.15
2	1	0.050	0.014	0.044	0.085	0.16
	2	0.050	0.015	0.046	0.084	0.16
3	1	0.048	0.013	0.046	0.082	0.16
	2	0.046	0.013	0.047	0.082	0.18
4	1	0.050	0.013	0.044	0.082	0.17
	2	0.053	0.013	0.045	0.085	0.18
5	1	0.049	0.013	0.045	0.087	0.15
	2	0.050	0.013	0.049	0.085	0.15
6	1	0.048	0.012	0.047	0.084	0.15
	2	0.046	0.012	0.042	0.084	0.17
7	1	0.056	0.015	0.049	0.090	0.15
	2	0.048	0.012	0.047	0.078	0.16
8	1	0.048	0.013	0.047	0.082	0.15
	2	0.046	0.012	0.046	0.086	0.14
9	1	0.047	0.013	0.047	0.087	0.15
	2	0.046	0.012	0.042	0.083	0.15
10	1	0.045	0.013	0.048	0.080	0.16
	2	0.047	0.013	0.045	0.084	0.15
Mean [mg/kg]		0.0488	0.0131	0.0462	0.0839	0.156
Standard deviation [mg/kg]		0.0028	0.00091	0.0021	0.0026	0.0089
Coefficient of variation [%]		5.7	7.0	4.6	3.1	5.7
Spiked level [mg/kg]		0.048	0.015	0.052	0.078	0.16
Recovery of the spiked level [%]		102	87	89	108	98

7. Stability testing

After the closure of transmission of results the test material was re-analysed to confirm the stability of the pesticides over the period of the test. The mean of the re-analysis was compared to the mean result of the homogeneity testing (table 14). The results confirm the stability of all analytes throughout the test (recoveries of 86 to 108 % of the homogeneity testing).

Table 14. Results of the stability testing

Pesticide	Mean result from homogeneity testing [mg/kg]	Mean level at closure of transmission of results [mg/kg]	Recovery compared to the mean of the homogeneity testing [%]
Carbendazim	0.0235	0.0232	99
Carbofuran	0.0126	0.0108	86
Cyflufenamid	0.0572	0.0519	91
Folpet	0.0437	0.0393	90
Spirodiclofen	0.0488	0.0479	98
Tebuconazole	0.0131	0.0135	103
THPI	0.0462	0.0472	102
Ethephon	0.0839	0.0817	97
Phosphonic acid	0.156	0.168	108