Bundesverband
Naturkost Naturwaren

Laboratory Performance Assessment

Analysis of several analytes in organic sunflower oil:

- ***Pesticides***
- ***Phthalates***
- ***PAH (polyaromatic hydrocarbons)***

Report

September 2019

Bundesverband
Naturkost Naturwaren

Summary

The laboratory performance assessment related to Pesticides, Phthalates and PAHs in sunflower oil was designed and organised by Lach & Bruns in September 2019 on behalf of BNN e.V. (Bundesverband Naturkost Naturwaren).

The test material was prepared of organic sunflower oil. In total, seventeen (17) analytes were present in the test material. Sixteen (16) analytes were spiked while PBO (Piperonylbutoxid) was already present as an incurred residue:

Pesticides:
Deltamethrin, Dieldrin, Dimoxystrobin, Imazamox, PBO.

Phthalates:
Benzylbutylphhtalat, Dibutylphthalate, Diethylhexylphthalate, Diiso-nonylphthalate, Dimethylphthalate, Di-n-octylphthalate.

PAHs:
Benzo[a]pyrene, Chrysene, Benzo[a]anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Dibenzo[a,h]anthracene.

The test material was distributed to twenty-two (22) participants across four (4) European countries (Germany, Italy, The Netherlands, Spain):

Pesticides: 20 participants
Phthalates: 6 participants
PAHs: 5 participants.

Some laboratories took part in more than one of the a.m. sub-groups. Two (2) laboratories took part on a voluntary basis in the pesticide testing, as they do not hold an approval for pesticides in edible oil at the moment.

Each laboratory received 40 ml of the prepared sunflower oil. The laboratories testing for phthalates and PAH received both a spiked sample and a blank sample to be able to adjust their findings if deemed necessary. No information with respect to the identity or the number of spiked analytes was provided to the laboratories in advance.

The performance assessment considers the following test criteria:

- No *false positive results*.
- Correct *identification* of the analytes, thus no false negatives. If an analyte is not within the current scope of a laboratory, it is considered as “out of scope” (oos).
- Correct quantification of the analytes in terms of 70 to 120 % recovery of the spiked value. At least 75% of the reported results must have been evaluated as passed according to the trueness criterion (recovery of spike).

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

Pesticides

Criterion	**Criterion passed**
Correct *identification* of all 5 analytes	15 out of 20 laboratories (75 %)
Correct *quantification* of minimum 4 out of 5 analytes (requirement of BNN to participate with success)	17 out of 20 laboratories (85 %)
Correct *quantification* of all 5 analytes	12 out of 20 laboratories (60 %)

The overall performance of the laboratories analysing pesticides in vegetable oils is quite good. Only 6 results out of 100 results in total (5 pesticides and 20 participants) are outside the target areas, while 5 labs have not included Imazamox so far into their analytical scope. In total, 89% of the reported results (89 out of 100) are correct, which is an extraordinary positive outcome of a ring test.

Phthalates

Criterion	**Criterion passed**
Correct *identification* of all 6 analytes	5 out of 6 laboratories (83 %)
Correct *quantification* of minimum 5 out of 6 analytes (requirement of BNN to participate with success)	5 out of 6 laboratories (83 %)
Correct *quantification* of all 6 analytes	3 out of 6 laboratories (50 %)

The overall performance of the laboratories approved by BNN e.V. for phthalates in vegetable oils is good. Only 8 results out of 36 results in total (6 phthalates and 6 participants) are outside the target areas. As a consequence, 78% of the results (28 out of 36) are within the target areas.

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PAHs

Criterion	**Criterion passed**
Correct *identification* of all 6 analytes	5 out of 5 laboratories (100 %)
Correct *quantification* of minimum 5 out of 6 analytes (requirement of BNN to participate with success)	4 out of 5 laboratories (80 %)
Correct *quantification* of all 6 analytes	1 out of 5 laboratories (20 %)

The overall performance of the laboratories approved by BNN e.V. for PAH in vegetable oils is good. Only 5 results out of 30 results in total (6 PAHs and 5 participants) are outside the target areas. As a consequence, 83 % of the results (25 out of 30) are within the target areas.

Assessment of the competence of the laboratories to evaluate the analytical results:

The correct application of the specific legal regulations and of the specific guidelines of BNN related to pesticides and phthalates is assessed, too.

The evaluation of the results related to the EU pesticide MRL regulation (EC) no.396/2005 is done in a correct way by almost all laboratories. Nevertheless, some shortcomings have been identified, which are summarised on pages 14 to 16 of this report. The application of the BNN orientation value of 0,01 mg/kg is well known and well done by the majority of the laboratories. The second specification of the BNN orientation value, which is the maximum number of pesticides, is not taken into consideration by several labs. This indicates an area of improvement.

All six participating laboratories correctly applied the BNN reference value for DEHP and DBP (1 mg/kg) resp. the reference value for all other Phthalates and Adipates (5 mg/kg) taking into consideration the expanded measurement uncertainty of 50%.

Also, all five participating laboratories applied and cited regulation (EC) no. 1881/2006 resp. the related MRLs of Benzo[a]pyrene and the sum of four listed PAHs is.

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1. Test material preparation and design

1.1 Test material preparation

The test material was prepared on August 22nd 2019 and consequently stored in a fridge (8°C, in darkness). Test samples were sent to the participating laboratories on September 9th 2019. Sending conditions were as follows: The samples were stored on Styrofoam boxes and cooled with cooling elements, although they didn't directly contact the cooling elements as they were packed in bubble wrap.

The test material, as well as the blank material, was stored in EPA-screw top vials G40 with metal lids and Teflon seals. The vials were heated before to 450°C to avoid active substance contamination. The Teflon seals, as well as all other glass ware, was rinsed extensively before use. Hexane and Dichloromethane were used for the rinsing process.

The test material and the blank material (for phthalates and PAH) were extracted from organic sunflower oil which was stirred in a beaker glass for 1 hour to ensure a homogeneous distribution of already present phthalates and PAHs in the raw material. Samples to a volume of 40 ml each were bottled as blank material to determine background concentration. The left-over homogenised sunflower oil was spiked with pesticides, phthalates and PAHs. This was done through a toluene solution, which was added to the sample material gradually under continuous stirring of the sample material. In order to ensure a homogeneous distribution the spiked test material was further stirred for 2 hours more. The spiked test material was then bottled in 40 ml quantities. The laboratories testing for phthalates and PAH received both a spiked sample and a blank sample to be able to adjust their findings if deemed necessary, in order to more accurately quantify the active substances.

The test material was spiked with 4 pesticides (Dimoxystrobin, Imazamox, Deltamethrin, Dieldrin), 6 Phthalates (Benzylbutylphthalate, Dibutylphthalate, Diethylhexylphthalate, Diiso-nonylphthalate, Dimethylphthalate, Di-n-octylphthalate) and 6 PAHs (Benzo[a]pyrene, Chrysene, Benzo[a]anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Dibenzo[a,h]anthracene). Laboratories were expected to find all substances in the respective tests and to quantify them according to the trueness criterion (ref.: part 2.1). Additionally, laboratories participating in the pesticide test were expected to identify PBO and to quantify it according to the comparability criterion (ref.: 2.2).

1.2 Homogeneity test

Independent testing of the blank material detected a concentration of PBO of 0,27mg/kg, concentrations 0,03 mg/kg for Diethylhexylphthalate and Diisononylphthalate respectively, as well as 0,5 µg/kg for Chrysene. While PBO was not spiked, it was identified by all laboratories that participated in the pesticide method ring test, confirming the background concentration found by the independent test. Recovery rate of all spiked substances was between 88% and 111% in the spiked samples when adjusting for background concentrations found in the blank samples. The independent testing used two samples each of both the spiked material and the blank material. Averages of the results were used to calculate recovery rates.

Chart 1: recovery rates pesticides

Parameter	spiked level	result A	result B	average AB	spike level recovery rate (in %)	blank result A	blank result B
Deltamethrin	0,035	0,031	0,034	0,033	93		
Dieldrin	0,028	0,025	0,024	0,025	88		
Dimoxystrobin	0,040	0,042	0,042	0,042	105		
Imazamox	0,045	0,045	0,049	0,047	104		
PBO	/	0,027	0,026	0,027	/	0,027	0,027

all values in mg/kg if not stated otherwise

Chart 2: recovery rates phthalates

Parameter	spiked level	result A*	result B*	average AB*	spike level recovery rate (in %)	blank result A	blank result B	average blank
Benzylbutyl-phthalate	1,25	1,09	1,12	1,11	89			
Diethylhexyl-phthalate	0,72	6,95	7,31	7,13	99	0,03	0,03	0,03
Di-n-octyl-phthalate	1,25	1,31	1,31	1,31	105			
Dibutyl-phthalate	0,57	0,54	0,53	0,54	94			
Diisononyl-phthalate	6,35	6,92	7,17	7,04	111	0,03	0,03	0,03
Dimethyl-phthalate	1,25	1,12	1,12	1,12	90			

all values in mg/kg if not stated otherwise

*adjusted for blank results if present

Chart 3: recovery rates PAHs

Parameter	spiked level	result A*	result B*	average AB*	spike level recovery rate (in %)	blank result A	blank result B	average blank
Benzo[a]anthracene	1,5	1,34	1,47	1,4	94	n.d.	n.d.	/
Benzo[a]pyrene	2,2	2,41	2,37	2,39	109	n.d.	n.d.	/
Benzo[b]fluoranthene	3,0	2,95	2,89	2,92	97	n.d.	n.d.	/
Benzo[k]fluoranthene	4,0	n.a.	n.a.	n.a.	/	n.a.	n.a.	/
Chrysene	4,5	4,74	4,92	4,83	107	0,50	0,47	0,49
Dibenzo[a,h]anthracene	6,0	n.a.	n.a.	n.a.	/	n.a.	n.a.	/

all values in µg/kg if not stated otherwise

*adjusted for blank results / n.a. = not analysed / n.d. = not detected, below reporting limit

2. Statistical evaluation of results

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 *analyte A* (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 *analyte B* (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).

[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.

Comparability criterion

The comparability of results is evaluated according to the z-score model based on an assigned value and the target standard deviation (acc. to Horwitz).

Assigned value

The assigned value x_{pt} is the robust mean, which is derived from the results of the participants according to ISO13528, Algorithm A[2]. The Winsorisation algorithm is applied to minimise the influence of outliers.

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

z-score

The z-score is derived of the result x_i of each participant, the assigned value x_{pt} and the target standard deviation according to Horwitz σ_H[2,3]:

$$z - score = \frac{x_i - x_{pt}}{\sigma_H}$$

3. Results

3.1 Pesticides

12 of the 20 laboratories that participated in the pesticide method ring test identified and correctly quantified all 5 active substances, these being Dimoxystrobin, Imazamox, Deltamethrin, Dieldrin and PBO (labs 1, 2, 4, 5, 6, 8, 9, 13, 15, 16, 17, 19).

15 laboratories identified all substances, while 5 did not identify Imazamox due to Imazamox not being within the scope of their multi-methods (labs 3, 10, 12, 14, 18). All of those 5 laboratories identified all other active substances. 3 of them correctly quantified all other active substances (labs 10, 12, 14). Particular notice should be given to lab 1, who despite not including Imazamox in their multi-method did identify and correctly quantify it regardless.

All laboratories correctly quantified Dimoxystrobin. All laboratories that identified Dimoxystrobin also quantified it correctly.

2 laboratories failed to correctly quantify Deltamethrin (labs 3, 11), 4 laboratories failed to quantify Dieldrin correctly (labs 7, 11, 18, 20).

All 20 laboratories passed the comparability criterion for the correct quantification of PBO.

[2] Statistical methods for use in proficiency testing by interlaboratory comparison. ISO 13528:2015. Corrected version 2016-10-15

[3] Horwitz W. Evaluation of Analytical Methods Used for Regulation of Foods and Drugs. Anal Chem. 1982;54(1):67A–76A.

Lab 1 also identified and quantified Hexachlorobenzene (HCB). As the reported level is at very low traces (0,002 mg/kg) this result is not considered as false positive.

The percentage of laboratories passing the respective trueness or comparability criterion for the active substances ranges from 80% for Dieldrin to 100% for Dimoxystrobin, Imazamox and PBO, with Deltamethrin at 90%.

There seems to be a trend towards under-quantification for Dieldrin, with 18 of the 20 reported results being lower than 90% of the spiked level.

To summarise:

- **Labs 2, 4, 5, 6, 8, 9, 13, 15, 16, 17 and 19** identified and **correctly quantified 5 out of 5 active substances.**
- **Lab 1** found and **correctly quantified all 4 active substances covered by their multi-method.** They also identified and **correctly quantified Imazamox**, which was not included in their multi-method.
- **Labs 10, 12 and 14** identified and **correctly quantified 4 out of 4 substances covered by their multi-method** (as Imazamox is currently out of their scope).
- **Labs 7 and 20** identified all 5 active substances and **correctly quantified 4 out of 5 active substances.**
- **Labs 3 and 18** identified all 4 active substances covered by their multi-method and **correctly quantified 3 out of 4 active substances covered by their multi-method** (as Imazamox is currently out of their scope).
- **Lab 11** identified all 5 active substances and **correctly quantified just 3 out of 5 active substances.**

3.2 Phthalates

Only 3 of the 6 participating laboratories for the phthalate method ring test identified and **correctly quantified all active substances** (**labs 23, 24, 26**).

5 Labs identified all substances, with lab 21 failed to identify Diethylhexylphthalate due to an inappropriate high limit of quantification at 1 mg/kg, which is above the spiked level and even above the 120% limit for the trueness criterion.

Lab 21 did however identify and correctly quantify all active substances present above their respective limit of quantification. **They correctly quantified 5 out of 5 active substances present above their limit of quantification.**

Lab 22, while identifying all substances, failed to correctly quantify Diisononylphthalate but correctly quantified all other substances. **They correctly quantified 5 out of 6 active substances**

Lab 25 failed to correctly quantify 4 of the 6 active substances. While they identified all active substances they only correctly quantified Diisononylphthalate and Di-n-octyl-phthalate. They failed to quantify Benzylbutylphthalate, Dibutylphthalate, Diethylhexyl-phthalate, and Dimethylphthalate. As a consequence, **they correctly quantified just 2 out of 6 active substances.**

Labs 23, 24, 25 and 26 also reported Diisodecylphthalate ranging from 0,206 mg/kg to 1,21 mg/kg. Lab 26 also reported 2-Ethylhexyldiphenylphosphat at a level of 0,108 mg/kg.

Success rates for correct quantification ranged from 66,67% for Diethylhexylphthalate to 100% for Di-n-octylphthalate with 83,33% for Benzylbutylphthalate, Dibutylphthalate, Diisononylphthalate, and Dimethylphthalate.

3.3 PAHs

All 5 participating laboratories identified all 6 active substances.

Only 1 of the 5 participating laboratories for the PAH method ring test **correctly quantified all 6 active substances** (**lab 32**).

Labs 31 and 33 managed to quantify Benzo[a]pyrene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, and Dibenzo[a,h]anthracene correctly. They both failed to quantify Benzo[a]anthracene however. **They correctly quantified 5 out of 6 active substances.**

Lab 34, in addition to, also failed to correctly quantify Benzo[b]fluoranthene but correctly quantified Benzo[a]pyrene, Chrysene, Benzo[a]anthracene, Benzo[k]fluoranthene, and Dibenzo[a,h]anthracene. **They correctly quantified 5 out of 6 active substances.**

Lab 35 only managed to correctly quantify Benzo[a]pyrene, Chrysene, Benzo[b]fluoranthene, and Dibenzo[a,h]anthracene. They failed to correctly quantify, Benzo[a]anthracene, and Benzo[b]fluoranthene. **They correctly quantified just 4 out of 6 active substances.**

Labs 32, 33 and 35 also found Benzo[g,h,i]perylen ranging from 0,3 mµ/kg to 0,4 mµ/kg. Labs 32 and 33 also found Indeno[1,2,3-cd]pyrene ranging from 0,3 mµ/kg to 1,4 mµ/kg. Labs 33 and 35 also found Benzo[j]fluoranthene ranging from 0,2 mµ/kg to 0,4 mµ/kg.

Success rates for correct quantification ranged from 40% for Benzo[a]anthracene to 100% for Benzo[a]pyrene, Chrysene, and Dibenzo[a]anthracene with 80% for Benzo[b]fluor-anthene and Benzo[k]fluoranthene.

4. Conclusions

Pesticides

- All laboratories managed to identify Dimoxystrobin, Deltamethrin, Dieldrin and PBO.
- All 14 laboratories who had Imazamox included in the scope of their multi-method managed to identify and correctly quantify Imazamox. Lab 1 also managed to identify and correctly quantify Imazamox although it was not in the scope of their multi-method.
- All laboratories correctly quantified Dimoxystrobin, while 90% correctly quantified Deltamethrin and 80% correctly quantified Dieldrin.
- All laboratories passed the comparability criterion for PBO with z-scores reaching from -1,2 to 1,7.
- Lab 3 didn't correctly quantify Deltamethrin, while labs 7, 18 and 20 didn't correctly quantify Dieldrin. Lab 11 didn't correctly quantify neither Deltamethrin nor Dieldrin. All others correctly quantified all substances within the scope of their respective multi-method.

The overall performance of the laboratories for pesticides in vegetable oils is quite good. Only 6 results out of 100 results in total (5 pesticides and 20 participants) are outside the target areas, while 5 labs have not included Imazamox so far into their analytical scope. In total, 89% of the reported results (89 out of 100) are correct, which is an extraordinary positive outcome of a ring test.

Interestingly, the few deviations are related to 2 pesticides (Deltamethrin, Dieldrin), which are covered by the gas chromatographic separation and subsequent detection (f.ex. GC/MSMS). As the instrumental approaches are more and more switched to liquid chromatographic separation (LC/MSMS) it seems, that the experience and competence related to GC-techniques is somewhat decreasing.

Phthalates

- All laboratories managed to identify Benzylbutylphthalate, Dibutylphthalate, Diisononylphthalate, Dimethylphthalate, and Di-n-octylphthalate.
- Lab 21 did not manage to identify Diethylhexylphthalate and lab 25 reported < LQ due to inappropriate reporting limits of 1,0 mg/kg in case of lab 21 and 0,5 mg/kg in case of lab 25. All other laboratories correctly quantified Diethylhexylphthalate.
- In addition to Diethylhexylphthalate lab 25 also failed to correctly quantify Benzylbutylphthalate, Dibutylphthalate, and Dimethylphthalate. All other laboratories correctly quantified these active substances.
- Lab 22 failed to correctly quantify Diisononylphthalate. All other laboratories correctly quantified this active substance.
- All laboratories correctly quantified Di-n-octylphthalate.

The overall performance of the laboratories approved by BNN e.V. for phthalates in vegetable oils is good. Only 8 results out of 36 results in total (6 phthalates and 6 participants) are outside the target areas. As a consequence, 78% of the results (28 out of 36) are within the target areas.

One (21) lab should take action to reduce its reporting limit for Diethylhexylphthalate, as this phthalate is of high importance.

Lab (25) failed in the correct quantification of 4 out of the 6 phthalates and should investigate their analytical approach.

The other 4 labs (22, 23, 24, and 26) performed very well with just one slight underestimation (lab 22, Diisononylphthalate).

PAHs

- All laboratories correctly identified all active substances. All laboratories further correctly quantified Benzo[a]pyrene, Chrysene, and Dibenzo[a,h]anthracene.
- Three labs (31, 33, 35) labs failed to correctly quantify Benzo[a]anthracene.
- Lab 35 also failed to correctly quantify Benzo[k]fluoranthene. All other laboratories correctly quantified these active substances.
- Lab 34 failed to correctly quantify Benzo[b]fluoranthene. All other laboratories correctly quantified this active substance.

The overall performance of the laboratories approved by BNN e.V. for PAH in vegetable oils is good. Only 5 results out of 30 results in total (6 PAHs and 5 participants) are outside the target areas. As a consequence, 83 % of the results (25 out of 30) are within the target areas.

The only conspicuous result is related to Benzo[a]anthracene, as the median of the participants (1,87 µg/kg) is outside the target area between 1,1 to 1,8 µg/kg. As the spikes of the other PAH are not in question and the homogeneity test confirmed the spiking level of Benzo[a]anthracene, these results of the participants are surprising. It might be possible, that the slight overestimation is based on the settings of the baseline of the peak of Benzo[a]anthracene. In sunflower oil samples the baseline is elevated at this retention time and forms a kind of a small hill. If this “hill” is included during integration of the peak area, the result is higher compared to an integration of the peak area without this elevation.

5. Assessment of evaluation competencies

Pesticides

1. Compliance check with Regulation (EU) No. 396/2005, taking into consideration processing factors and labelling of their source / explanation of assumptions on which the processing factor is based on.
2. Highlighting the specialty of PBO: No MRL published in Regulation (EU) No. 396/2005 thus references to other regulations if known (f. ex. such as the German "Rückstandshöchstmengenverordnung (RHmV)".
3. Application of the BNN guideline value for single substances (0,010 mg/kg) taking into consideration the expanded measurement uncertainty of 50% → possible exceeding of Dimoxystrobin and – if detected – Imazamox, depending on detected levels and applied processing factors.
4. Application of BNN guideline for multiple substances (not more than 2 ≧ 0,010 mg/kg): Not exceeded (referred to re-calculated levels for sunflower seeds).
5. Recommendation for analyses of the raw material (sunflower seeds).

Laboratory code	Evaluation of results
1	1. ⊗ 2. ⊗ 3. ⊗ 4. O 5. ⊗
2	1. ⊗ 2. ⊗ 3. ⊗ 4. ⊗ 5. O Refers to old Regulation (EU) 2092/91
3	1. ⊗ 2. O 3. ⊗ 4. ⊗ 5. O
4	1. ⊗ 2. O 3. ⊗ 4. O 5. O
5	1. ⊗ 2. O[1] 3. ⊗ 4. O 5. O
6	1. ⊗ 2. ⊗ 3. ⊗ 4. O 5. O
7	1. ⊗ 2. ⊗ 3. O 4. ⊗ 5. O
8	Only verification of analytical competence
9	1. ⊗ 2. O 3. ⊗ 4. ⊗ 5. ⊗
10	1. ⊗ 2. O 3. ⊗ 4. ⊗ 5. ⊗
11	1. ⊗[2] 2. ⊗[3] 3. O 4. O 5. O
12	1. ⊗ 2. ⊗ 3. ⊗ 4. O 5. ⊗
13	1. O[4] 2. O 3. ⊗ 4. ⊗ 5. O
14	1. ⊗ 2. ⊗ 3. ⊗ 4. ⊗ 5. ⊗
15	1. ⊗[5] 2. ⊗ 3. O[6] 4. O[7] 5. O
16	1. ⊗[8] 2. O 3. ⊗[9] 4. ⊗[10] 5. O
17	1. O[11] 2. O 3. O[12] 4. O[13] 5. O
18	1. ⊗ 2. ⊗ 3. ⊗ 4. ⊗ 5. ⊗
19	1. ⊗ 2. ⊗ 3. ⊗ 4. ⊗ 5. ⊗
20	1. ⊗ 2. ⊗[14] 3. ⊗[15] 4. ⊗ 5. O

⊗ = requirement met
O = requirement NOT met

Lab No. 5:
[1]Remark: The MRL of the German “RHmV” is listed in a table, but no source (“RHmV”) is allocated to the “national” MRL.

Lab No 11:
[2]MRLs according to Reg. (EC) No. 396/2005 are listed in a table, but no reference to this regulation is reported (just “MRL EU”). [3]MRL according to “MRL NL” is listed in a table, but no source (national regulation?) is reported.

Lab No. 13:
[4]Detected levels of Sunflower oil are allocated to MRL of sunflower seeds, which is misleading. No indication of application of any processing factor is provided. The “MRL” of PBO as listed in the table refers NOT to Regulation (EC) No. 396/2005 but to the national German Regulation “Rückstandshöchsmengenverordnung (RHmV)”.

Lab No. 15:
[5]No details published about applied processing factors, or any other explanation of how the laboratory concludes the compliance with EU-MRL.
[6]No information reported why the laboratory concludes, that the sample does not meet BNN requirements.
[7]An internet link was provided, while the application of the multiple residue policy – “not more than 2
≧ 0,010 mg/kg, NOT taking into consideration the expanded measurement uncertainty” - was not explained in detail.

Lab No. 16:
[8]Correct MRLs according to Regulation (EC) No. 396/2005 are listed in the table - however, the regulation itself (thus “(EC) No. 396/2005”) is not mentioned anywhere in the test report.
[9]An internet link was provided, while the application of the guideline value (0,010 mg/kg taking into consideration the expanded measurement uncertainty) was not explained in detail.
[10]An internet link was provided, while the application of the multiple residue policy – “not more than 2
≧ 0,010 mg/kg, NOT taking into consideration the expanded measurement uncertainty” - was not explained in detail.

Lab 17:
[11]No evaluation according to the requirements or Reg. (EC) No. 396/2005.
[12]The application of the guideline value (0,010 mg/kg taking into consideration the expanded measurement uncertainty) was not explained in detail.
[13]The application of the multiple residue policy – “not more than 2 ≧ 0,010 mg/kg NOT taking into consideration the expanded measurement uncertainty” - was not explained in detail. Deltamethrin, Dimoxystrobin and Imazamox are all reported > 0,010 mg/kg
→ 3 pesticides, which exceeds the multi-residue policy of BNN. BNN requirements ARE NOT MET!

Lab 20:
[14]No reference for PBO is provided like f. ex. national MRLs such as the German "Rückstandshöchstmengenverordnung" (RHmV), where an MRL of 3,0 mg/kg for PBO is listed.
[15]The BNN guideline value of 0,010 mg/kg DOES NOT apply for PBO (https://n-bnn.de/sites/default/dateien/BNN-Orientierungswert_EN_09042019.pdf)!

Phthalates

- Application of the BNN reference value for DEHP and DBP (1 mg/kg) resp. the reference value for all other Phthalates and Adipates (5 mg/kg) taking into consideration the expanded measurement uncertainty of 50% → exceeding of DiNP.

Laboratory code	Evaluation of results related to BNN reference values
21	Yes, done in a correct way (also DiNP).
22	Yes, done in a correct way. Analytical result of DiNP < 5 mg/kg, therefore no specific evaluation of DiNP.
23	Yes, done in a correct way (also DiNP).
24	Yes, done in a correct way (also DiNP).
25	Yes, done in a correct way (also DiNP).
26	Yes, done in a correct way. Analytical result of DiNP < 5 mg/kg, therefore no specific evaluation of DiNP.

PAHs (Polyaromatic Hydrocarbons)

- Application and citation of regulation (EC) no. 1881/2006 resp. the related MRLs of 2,0 µg/kg for Benzo[a]pyrene and 10,0 µg/kg for the sum of Benzo[a]pyrene, Benzo[a]anthracene, Benzo[b]fluoranthene, and Chrysene ("PAH-4").

Laboratory code	Evaluation of results related to the MRLs of reg. (EC) 1881/2006
31	Yes, done in a correct way.
32	Yes, done in a correct way.
33	Yes, done in a correct way.
34	Yes, done in a correct way.
35	Yes, done in a correct way. Analytical result of Benzo[a]pyrene < 2,0 µg/kg, therefore, no specific evaluation of Benzo[a]pyrene.

6. Tables and figures

Table 1. Summary of the overall performance - ***pesticides***

yes: correctly quantified; no: quantification not satisfying

Laboratory code	Dimoxystrobin	Imazamox	Deltamethrin	Dieldrin	PBO (z-score)
1	yes	yes	yes	yes	-0,1
2	yes	yes	yes	yes	0,1
3	yes	oos*	no	yes	0,7
4	yes	yes	yes	yes	0,3
5	yes	yes	yes	yes	-0,1
6	yes	yes	yes	yes	-0,1
7	yes	yes	yes	no	0,1
8	yes	yes	yes	yes	0,3
9	yes	yes	yes	yes	-0,1
10	yes	oos*	yes	yes	0,3
11	yes	yes	no	no	0,1
12	yes	oos*	yes	yes	-0,1
13	yes	yes	yes	yes	-0,4
14	yes	oos*	yes	yes	-1,2
15	yes	yes	yes	yes	-0,1
16	yes	yes	yes	yes	-0,1
17	yes	yes	yes	yes	1,7
18	yes	oos*	yes	no	-0,6
19	yes	yes	yes	yes	0,5
20	yes	yes	yes	no	-0,1
number trueness criterion passed	20	15	18	16	20** (comparability)
success rate	100%	100% resp. 75%*	90%	80%	100%

*oos: Imazamox was out of scope for lab codes 3, 10, 12, 14, 18.
**the comparability criterion was used instead of the trueness criterion for the evaluation of PBO.

*Table 2. Summary of the overall performance - **phthalates***

yes: correctly quantified; no: quantification not satisfying

Laboratory code	Benzyl-butyl-phthalate	Dibutyl-phthalate	Diethyl-hexyl-phthalate	Diisononyl-phthalate	Dimethyl-phthalate	Di-n-octyl-phthalate
21	yes	yes	no*	yes	yes	yes
22	yes	yes	yes	no	yes	yes
23	yes	yes	yes	yes	yes	yes
24	yes	yes	yes	yes	yes	yes
25	no	no	no	yes	no	yes
26	yes	yes	yes	yes	yes	yes
number trueness criterion passed	5	5	4	5	5	6
success rate	83,33%	83,33%	66,67%	83,33%	83,33%	100%

** Reporting limit not appropriate (too high)*

*Table 3. Summary of the overall performance - **PAH***

yes: correctly quantified; no: quantification not satisfying

Laboratory code	Benzo[a]-pyrene	Chrysene	Benzo[a]-anthracene	Benzo[b]-fluoranthene	Benzo[k]-fluoranthene	Dibenzo[a,h]-anthracene
31	yes	yes	no	yes	yes	yes
32	yes	yes	yes	yes	yes	yes
33	yes	yes	no	yes	yes	yes
34	yes	yes	yes	no	yes	yes
35	yes	yes	no	yes	no	yes
number trueness criterion passed	5	5	2	4	4	5
success rate	100%	100%	40%	80%	80%	100%

Table 4. Results of Dimoxystrobin

	Dimoxystrobin			
	Spiked level [mg/kg]			0,040
	Accepted range [mg/kg]	0,028	-	0,048

Laboratory code	Result [mg/kg]	RL [mg/kg]	Result in % of the spiked level	Trueness criterion passed
1	0,037	0,005	93	yes
2	0,035	0,01	88	yes
3	0,039	0,010	98	yes
4	0,044	0,01	110	yes
5	0,037	0,01	93	yes
6	0,030	0,010	75	yes
7	0,035	0,020	88	yes
8	0,047	0,01	118	yes
9	0,032	0,01	80	yes
10	0,037	0,010	93	yes
11	0,035	0,01	88	yes
12	0,033	0,01	83	yes
13	0,035	0,01	88	yes
14	0,035	0,01	88	yes
15	0,039	0,010	98	yes
16	0,043	0,01	108	yes
17	0,038	0,010	95	yes
18	0,037	0,010	93	yes
19	0,036	0,01	90	yes
20	0,040	0,005	100	yes

Table 5. Results of Imazamox

	Imazamox			
	Spiked level [mg/kg]			0,045
	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	0,041		91	yes
2	0,050	0,01	111	yes
3	o. o. s.		/	/
4	0,045	0,01	100	yes
5	0,042	0,01	93	yes
6	0,048	0,010	107	yes
7	0,038	0,010	84	yes
8	0,054	0,01	120	yes
9	0,047	0,01	104	yes
10	o. o. s.		/	/
11	0,054	0,01	120	yes
12	o. o. s.		/	/
13	0,043	0,01	96	yes
14	o. o. s.		/	/
15	0,050	0,010	111	yes
16	0,048	0,01	107	yes
17	0,038	0,010	84	yes
18	o. o. s.		/	/
19	0,047	0,01	104	yes
20	0,052	0,005	116	yes

Lab code 3, 10, 12, 14, 18 did not have Imazamox in their scope for the multi-method

Table 6. Results of Deltamethrin

	Deltamethrin			
	Spiked level [mg/kg]			0,035
	Accepted range [mg/kg]	0,024	-	0,042

Laboratory code	Result [mg/kg]	RL [mg/kg]	Result in % of the spiked level	Trueness criterion passed
1	0,041	0,005	117	yes
2	0,035	0,01	100	yes
3	0,047	0,010	134	no
4	0,042	0,01	120	yes
5	0,034	0,01	97	yes
6	0,036	0,010	103	yes
7	0,033	0,010	94	yes
8	0,041	0,01	117	yes
9	0,039	0,01	111	yes
10	0,035	0,010	100	yes
11	0,049	0,01	140	no
12	0,031	0,01	89	yes
13	0,034	0,01	97	yes
14	0,039	0,02	111	yes
15	0,039	0,010	111	yes
16	0,036	0,01	103	yes
17	0,038	0,010	109	yes
18	0,033	0,010	94	yes
19	0,039	0,01	111	yes
20	0,039	0,005	111	yes

Table 7. Results of Dieldrin

	Dieldrin			
	Spiked level [mg/kg]			0,028
	Accepted range [mg/kg]	0,019	-	0,034
Laboratory code	**Result [mg/kg]**	**RL [mg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
1	0,021	0,001	75	yes
2	0,029	0,01	104	yes
3	0,023	0,010	82	yes
4	0,021	0,01	75	yes
5	0,025	0,01	89	yes
6	0,024	0,010	86	yes
7	0,017	0,005	61	no
8	0,0228	0,01	81	yes
9	0,020	0,005	71	yes
10	0,024	0,010	86	yes
11	0,035	0,01	125	no
12	0,021	0,01	75	yes
13	0,025	0,01	89	yes
14	0,021	0,005	75	yes
15	0,024	0,005	86	yes
16	0,023	0,01	82	yes
17	0,020	0,010	71	yes
18	0,018	0,010	64	no
19	0,025	0,01	89	yes
20	0,018	0,005	64	no

Table 8. Results of PBO

	PBO	
	Assigned value [mg/kg]	0,0217
Laboratory Code	**Result [mg/kg]**	**z-score**
1	0,021	-0,1
2	0,022	0,1
3	0,025	0,7
4	0,023	0,3
5	0,021	-0,1
6	0,021	-0,1
7	0,022	0,1
8	0,0230	0,3
9	0,021	-0,1
10	0,023	0,3
11	0,022	0,1
12	0,021	-0,1
13	0,020	-0,4
14	0,016	-1,2
15	0,021	-0,1
16	0,021	-0,1
17	0,030	1,7
18	0,019	-0,6
19	0,024	0,5
20	0,021	-0,1

Table 9. Results of Benzylbutylphthalate

	Benzylbutylphthalate			
	Spiked level [mg/kg]			1,250
	Accepted range [mg/kg]	0,870	-	1,500
Laboratory code	**Result [mg/kg]**	**RL [mg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
21	1,2	0,3	96	yes
22	1,3	0,050	104	yes
23	1,3	0,1	104	yes
24	1,09	0,05	87	yes
25	1,597	0,01	128	no
26	1,11	0,010	89	yes

Table 10. Results of Dibutylphthalate

	Dibutylphthalate			
	Spiked level [mg/kg]			0,570
	Accepted range [mg/kg]	0,390	-	0,684
Laboratory code	**Result [mg/kg]**	**RL [mg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
21	0,56	0,3	98	yes
22	0,52	0,050	91	yes
23	0,48	0,1	84	yes
24	0,50	0,05	88	yes
25	0,739	0,01	130	no
26	0,492	0,025	86	yes

Table 11. Results of Diethylhexylphthalate

	Diethylhexylphthalate			
	Spiked level [mg/kg]			0,720
	Accepted range [mg/kg]	0,500	-	0,870
Laboratory code	**Result [mg/kg]**	**RL [mg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
21	n.r.	1,00	0	no
22	0,68	0,050	94	yes
23	0,73	0,1	101	yes
24	0,73	0,05	101	yes
25	< RL	0,5	0	no
26	0,713	0,050	99	yes

n.r. = not reported; < RL = below reporting limit

Table 12. Results of Diisononylphthalate

	Diisononylphthalate			
	Spiked level [mg/kg]			6,350
	Accepted range [mg/kg]	4,440	-	7,620
Laboratory code	**Result [mg/kg]**	**RL [mg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
21	6,3	5	99	yes
22	4,1	0,050	65	no
23	6,0	0,5	94	yes
24	5,84	0,25	92	yes
25	5,405	0,02	85	yes
26	4,59	0,050	72	yes

Table 13. Results of Dimethylphthalate

	Dimethylphthalate			
	Spiked level [mg/kg]			1,250
	Accepted range [mg/kg]	0,870	-	1,500
Laboratory code	**Result [mg/kg]**	**RL [mg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
21	1,3	0,5	104	yes
22	1,2	0,050	96	yes
23	1,2	0,1	96	yes
24	1,24	0,05	99	yes
25	1,854	0,01	148	no
26	1,13	0,025	90	yes

Table 14. Results of Di-n-octylphthalate

	Di-n-octylphthalate			
	Spiked level [mg/kg]			1,250
	Accepted range [mg/kg]	0,870	-	1,500
Laboratory code	**Result [mg/kg]**	**RL [mg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
21	1,2	0,5	96	yes
22	1,0	0,050	80	yes
23	0,95	0,1	76	yes
24	1,2	0,05	96	yes
25	0,956	0,05	76	yes
26	1,07	0,050	86	yes

Table 15. Results of Benzo[a]pyrene

	Benzo[a]pyrene			
	Spiked level [µg/kg]			2,2
	Accepted range [µg/kg]	1,5	-	2,6
Laboratory code	**Result [µg/kg]**	**RL [µg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
31	1,93	1	88	yes
32	2,2	0,10	100	yes
33	2,6	0,2	118	yes
34	2,43	0,9	110	yes
35	1,5	0,1	68	yes

Table 16. Results of Chrysene

	Chrysene			
	Spiked level [µg/kg]			4,5
	Accepted range [µg/kg]	3,2	-	5,4
Laboratory code	**Result [µg/kg]**	**RL [µg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
31	4,48	1	100	yes
32	5,0	0,10	111	yes
33	4,9	0,2	109	yes
34	4,53	0,9	101	yes
35	4,2	0,1	93	yes

Table 17. Results of Benzo[a]anthracene

	Benzo[a]anthracene			
	Spiked level [µg/kg]			1,5
	Accepted range [µg/kg]	1,1	-	1,8
Laboratory code	**Result [µg/kg]**	**RL [µg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
31	1,87	1	125	no
32	1,7	0,10	113	yes
33	2,0	0,2	133	no
34	1,82	0,9	121	yes
35	2,0	0,1	133	no

Table 18. Results of Benzo[b]fluoranthene

	Benzo[b]fluoranthene			
	Spiked level [µg/kg]			3,0
	Accepted range [µg/kg]	2,1	-	3,6
Laboratory code	**Result [µg/kg]**	**RL [µg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
31	3,24	1	108	yes
32	3,2	0,10	107	yes
33	3,4	0,2	113	yes
34	3,71	0,9	124	no
35	3,6	0,1	120	yes

Table 19. Results of Benzo[k]fluoranthene

	Benzo[k]fluoranthene			
	Spiked level [µg/kg]			4,0
	Accepted range [µg/kg]	2,8	-	4,8
Laboratory code	**Result [µg/kg]**	**RL [µg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
31	3,52	1	88	yes
32	3,6	0,10	90	yes
33	4,0	0,2	100	yes
34	3,23	1,0	81	yes
35	4,9	0,1	123	no

Table 20. Results of Dibenzo[a,h]anthracene

	Dibenzo[a,h]anthracene			
	Spiked level [µg/kg]			6,0
	Accepted range [µg/kg]	4,2	-	7,2
Laboratory code	**Result [µg/kg]**	**RL [µg/kg]**	**Result in % of the spiked level**	**Trueness criterion passed**
31	5,23	1	87	yes
32	5,6	0,10	93	yes
33	5,7	0,2	95	yes
34	6,20	1,0	103	yes
35	5,3	0,1	88	yes

Figures

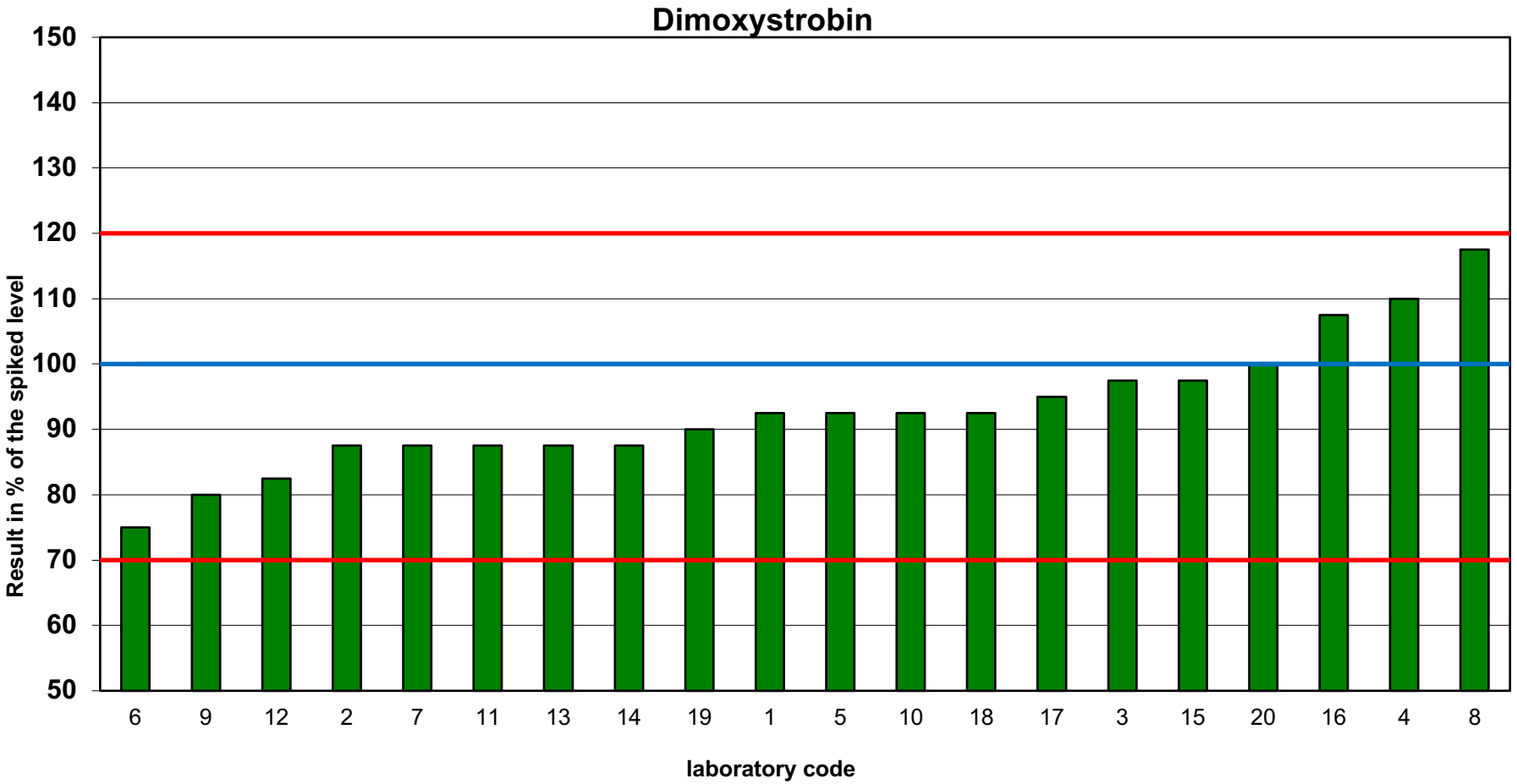

Figure 1 Assessment of Dimoxystrobin
Green: satisfactory results, red: dissatisfactory results

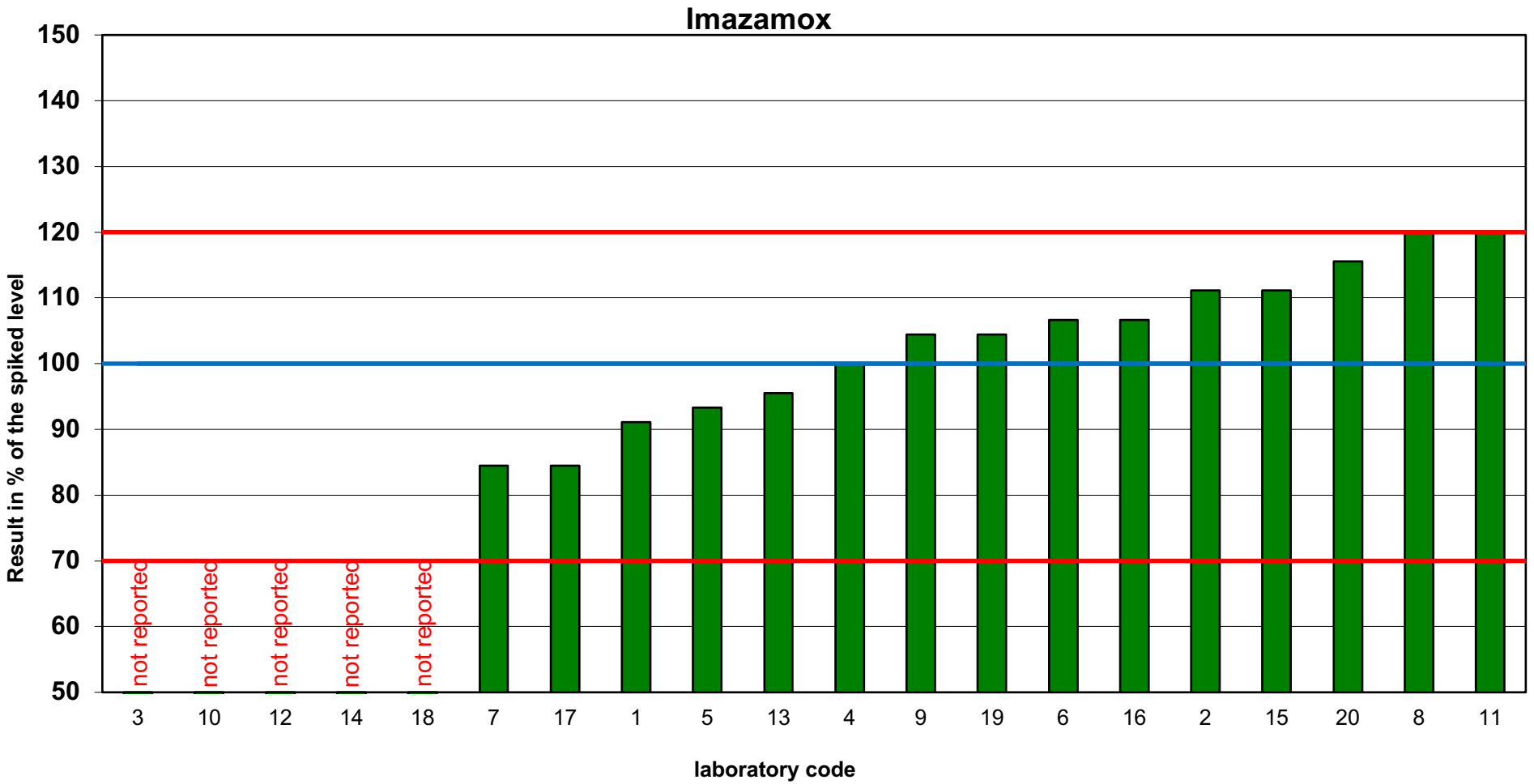

Figure 2 Assessment of Imazamox
Green: satisfactory results, red: dissatisfactory results

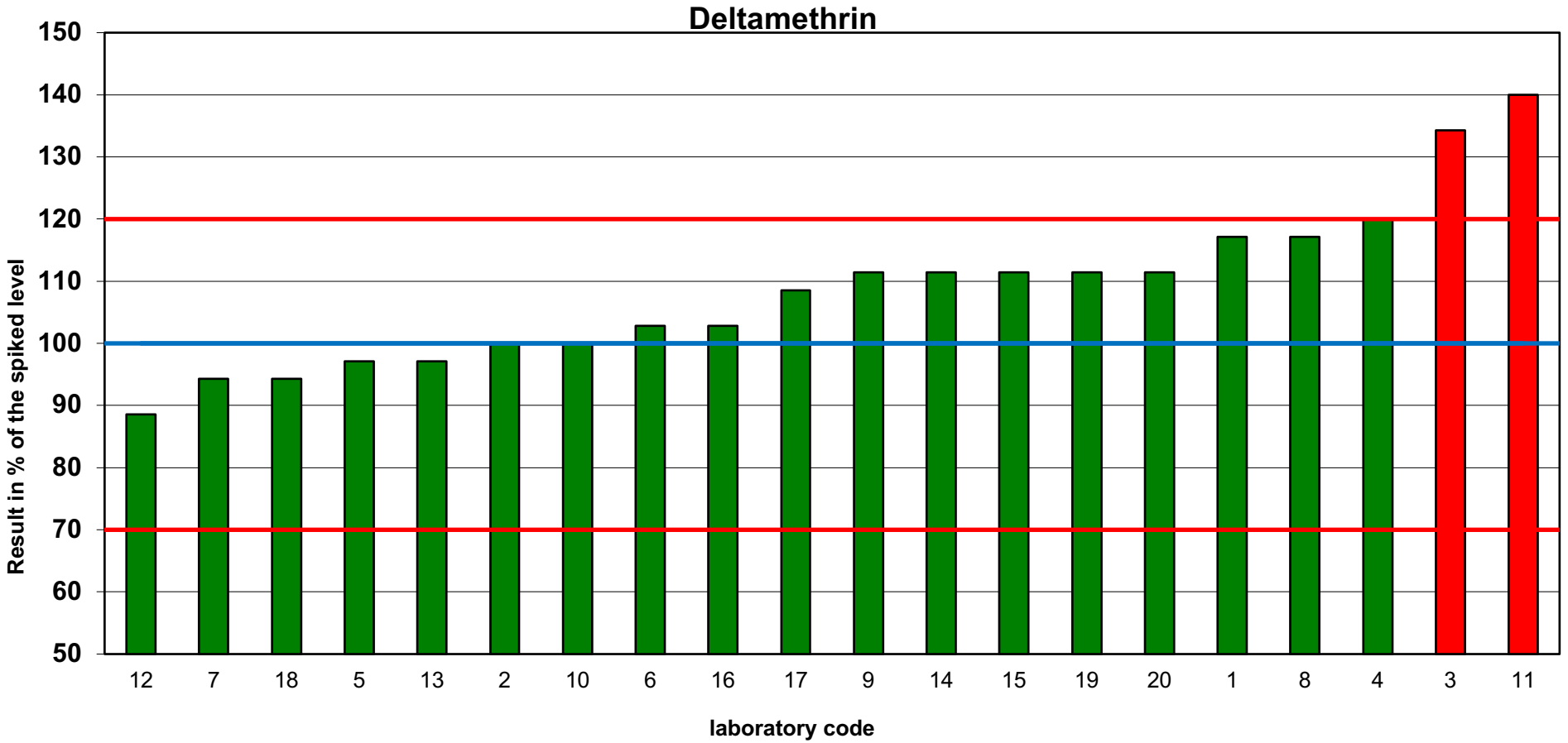

Figure 3 Assessment of Deltamethrin
Green: satisfactory results, red: dissatisfactory results

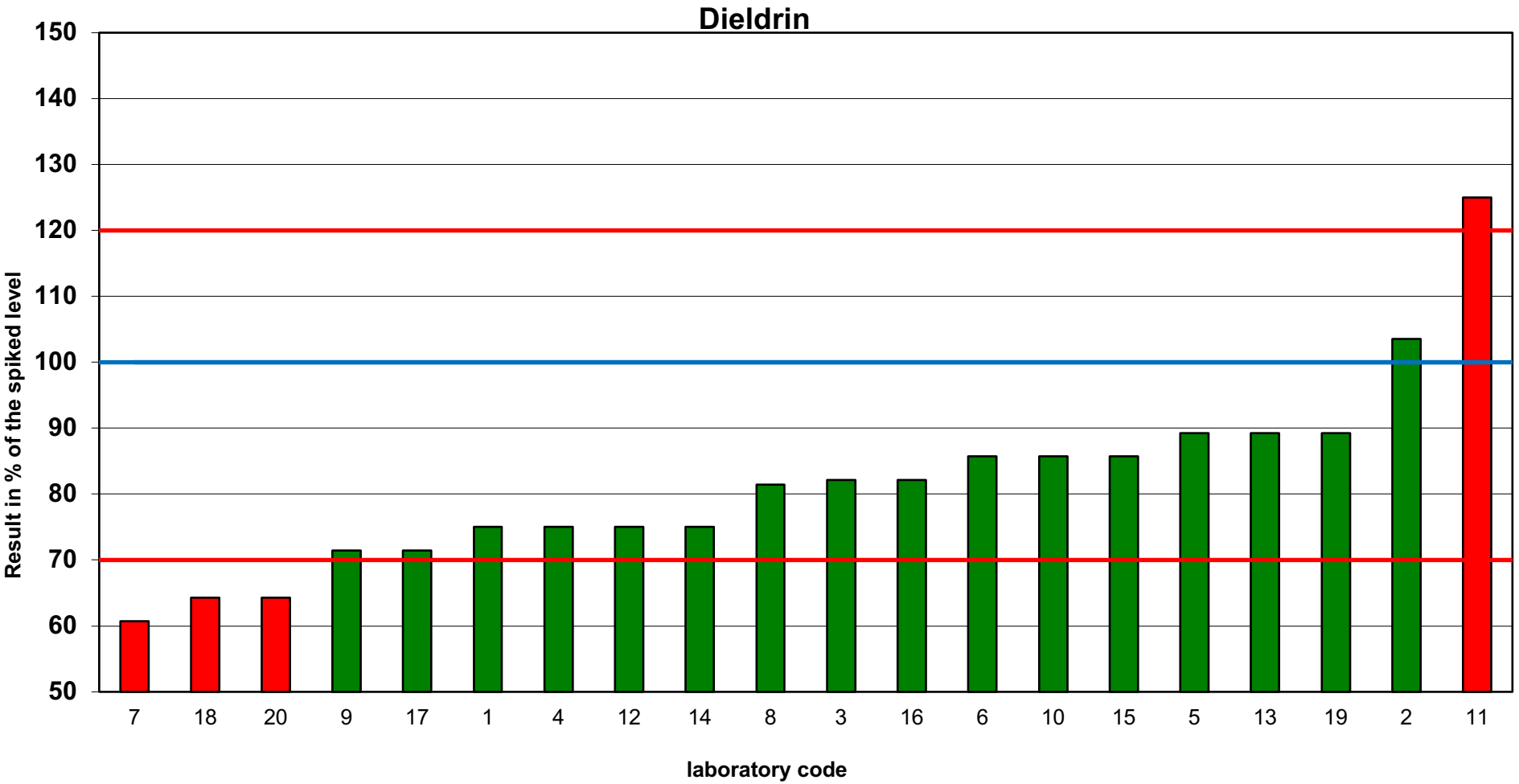

Figure 4 Assessment of Dieldrin
Green: satisfactory results, red: dissatisfactory results

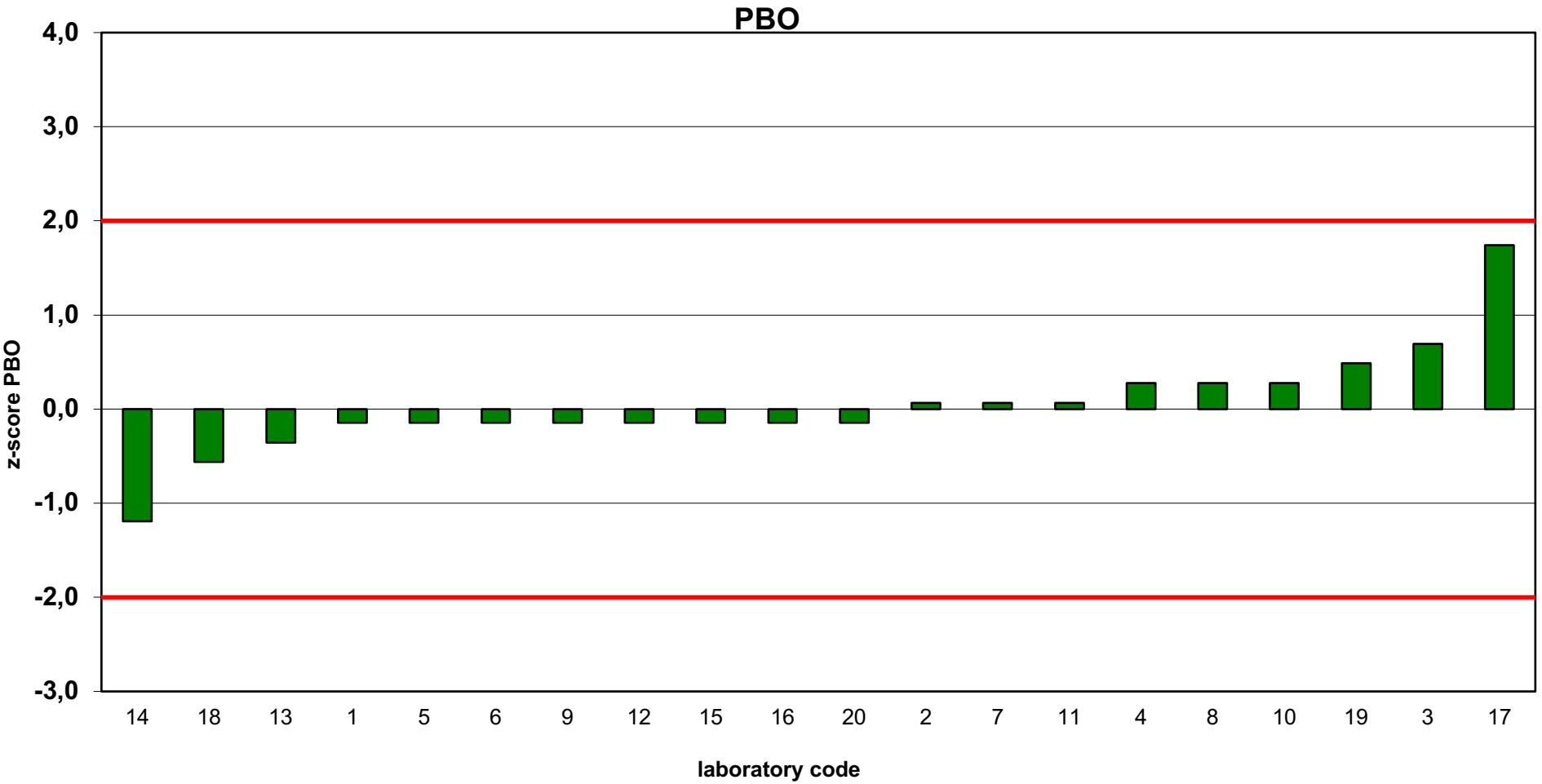

Figure 5 Assessment of PBO
Green: satisfactory results, red: dissatisfactory results

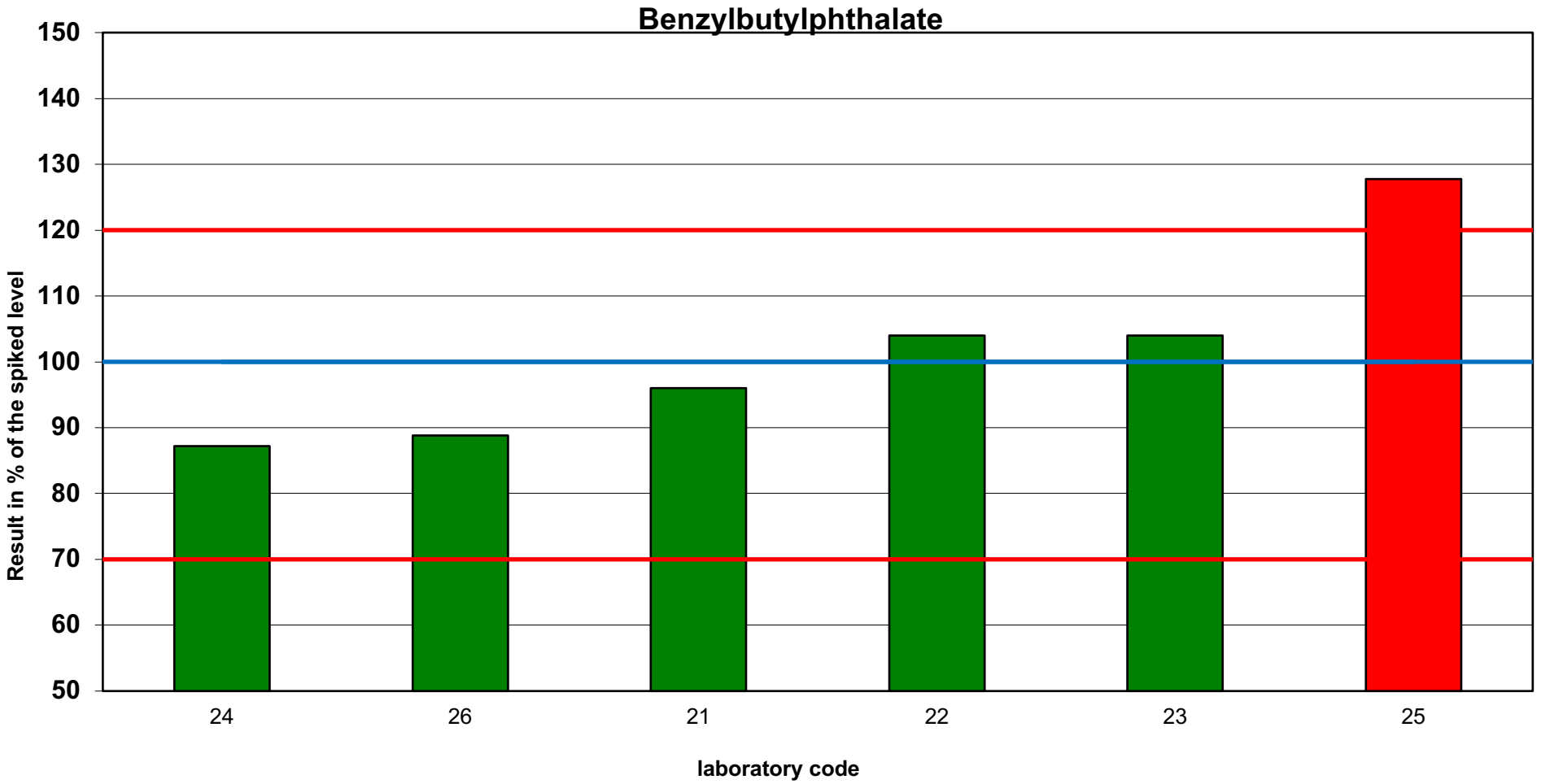

Figure 6 Assessment of Benzylbutylphthalate
Green: satisfactory results, red: dissatisfactory results

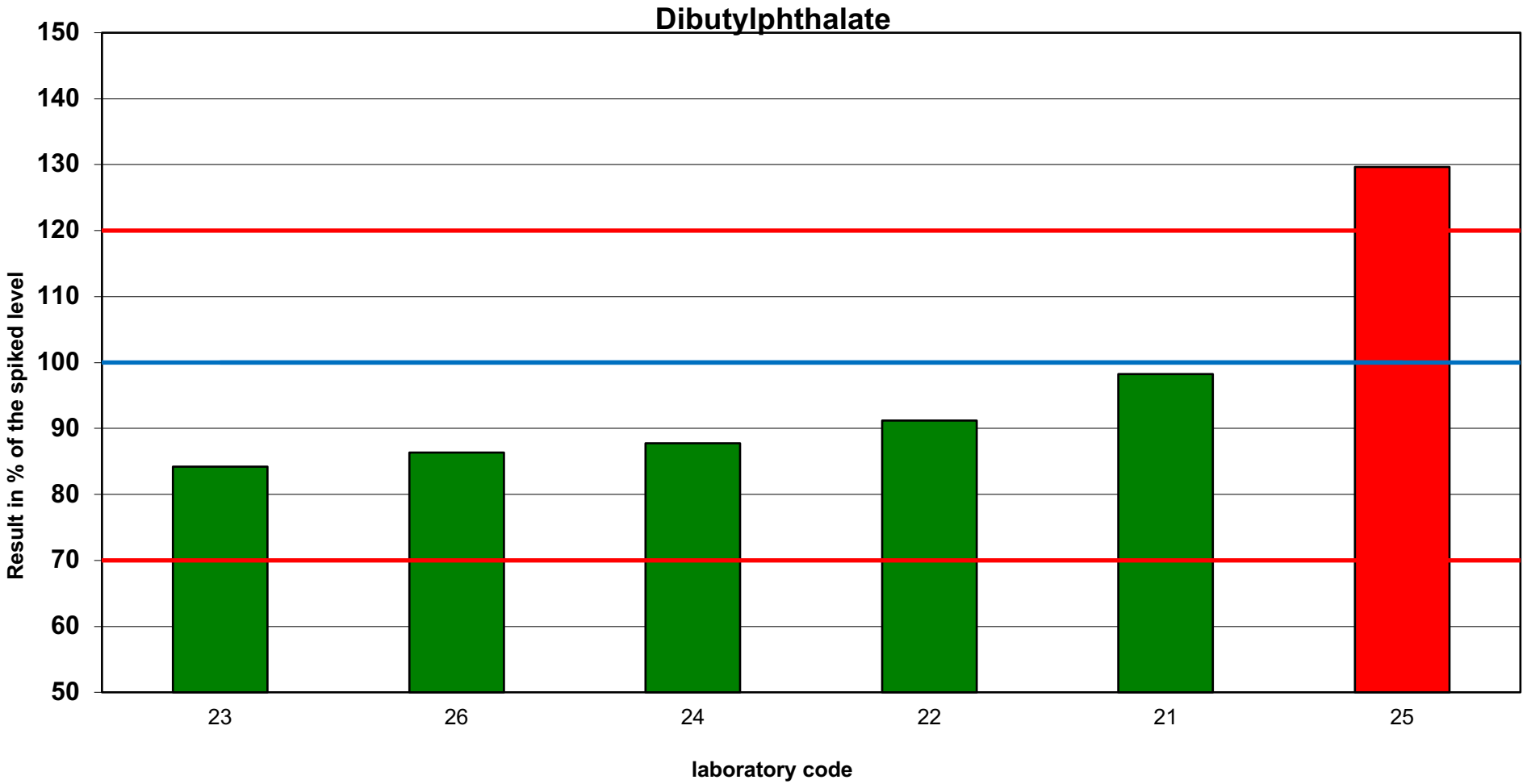

Figure 7 Assessment of Dibutylphthalate
Green: satisfactory results, red: dissatisfactory results

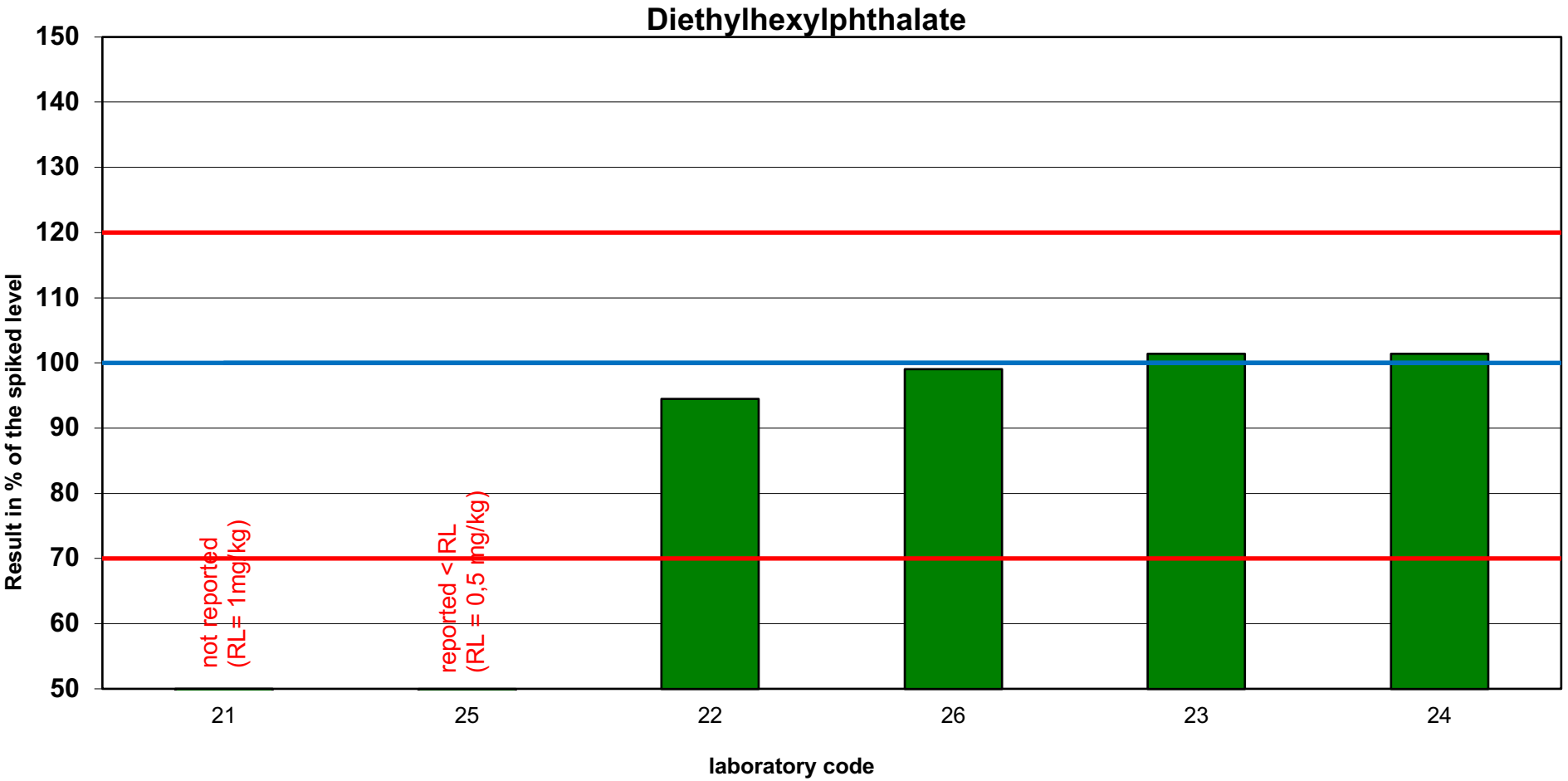

Figure 8 Assessment of Diethylhexylphthalate
Green: satisfactory results, red: dissatisfactory results

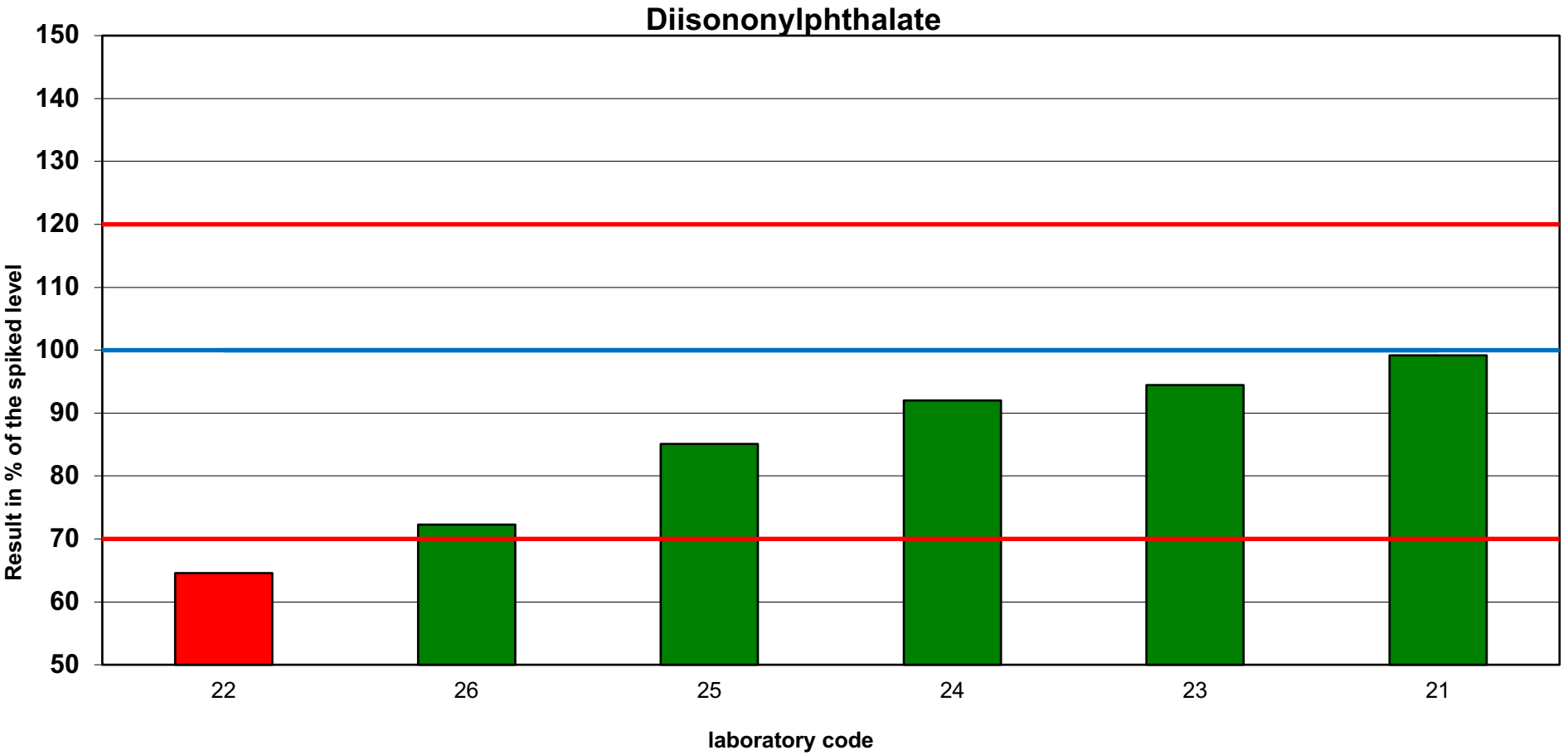

Figure 9 Assessment of Diisononylphthalate
Green: satisfactory results, red: dissatisfactory results

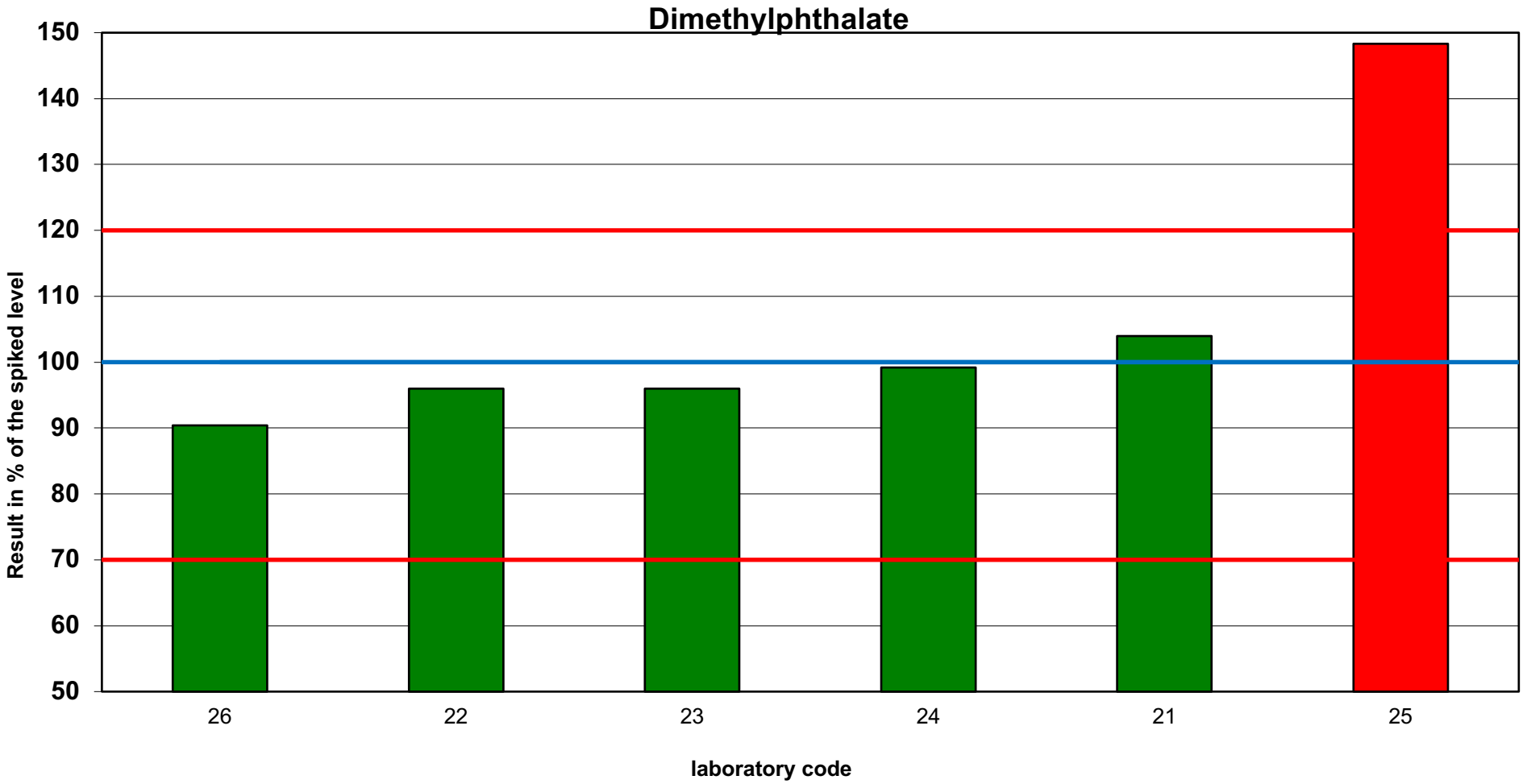

Figure 10 Assessment of Dimethylphthalate
Green: satisfactory results, red: dissatisfactory results

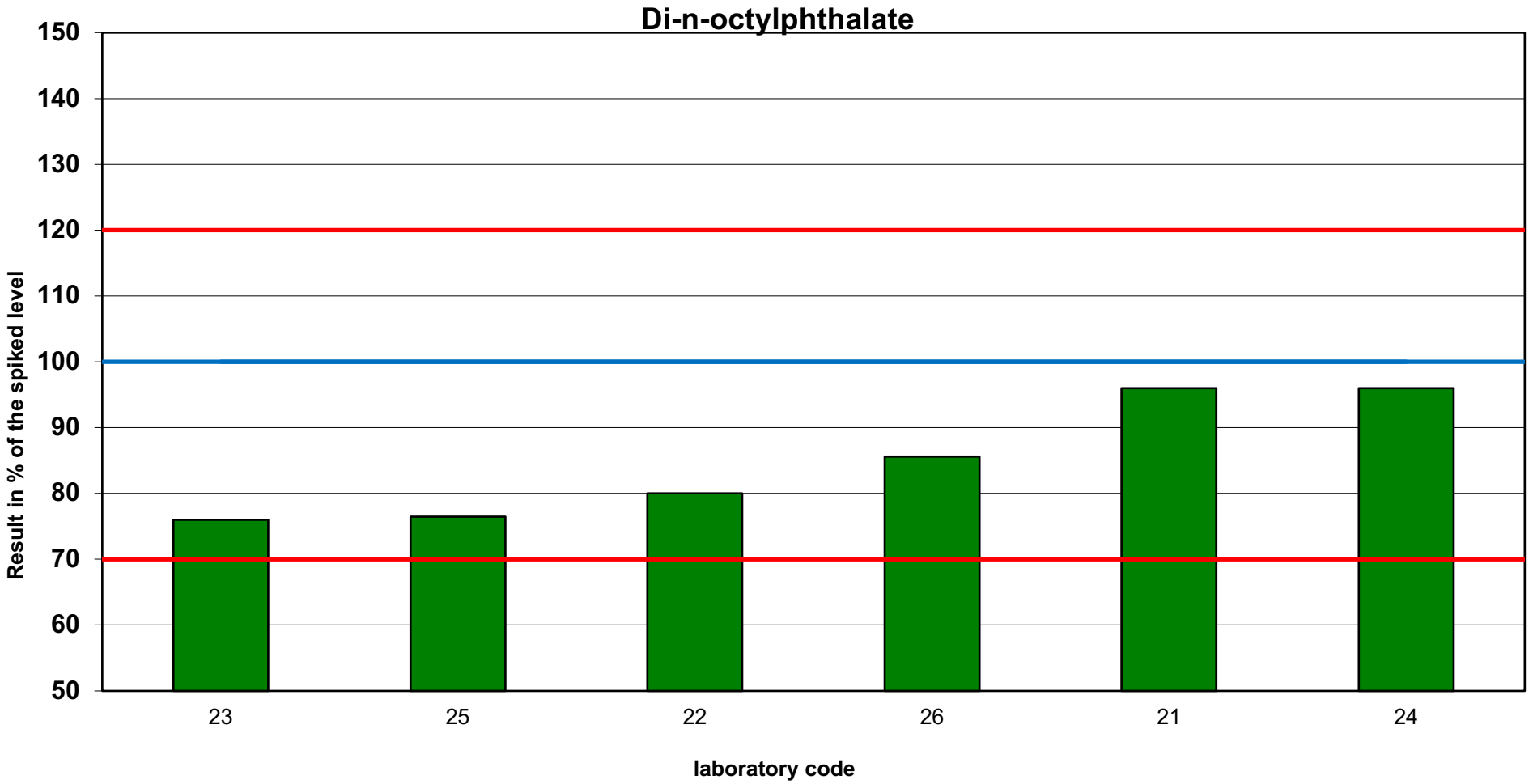

Figure 11 Assessment of Di-n-octylphthalate
Green: satisfactory results, red: dissatisfactory results

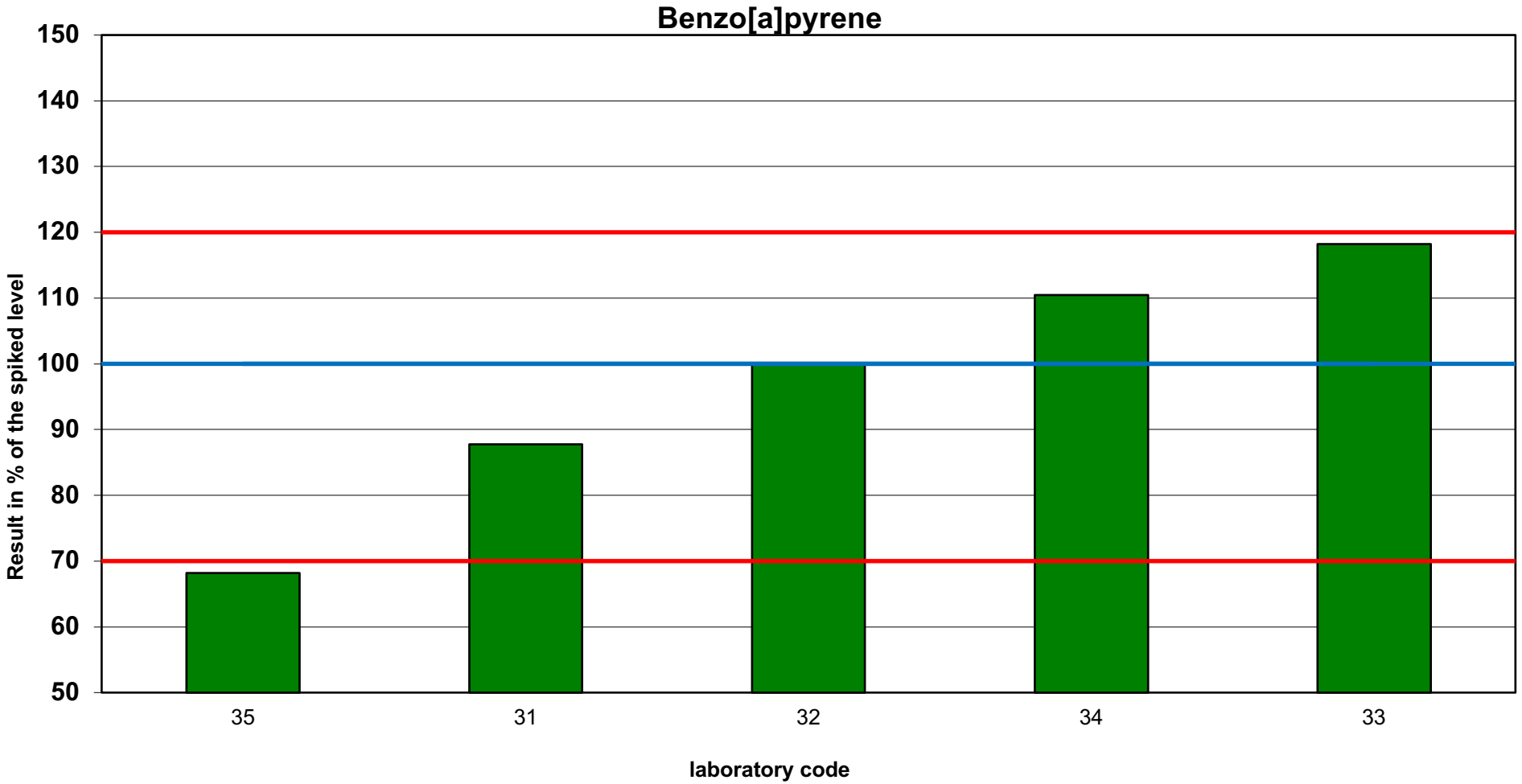

Figure 12 Assessment of Benzo[a]pyrene
Green: satisfactory results, red: dissatisfactory results

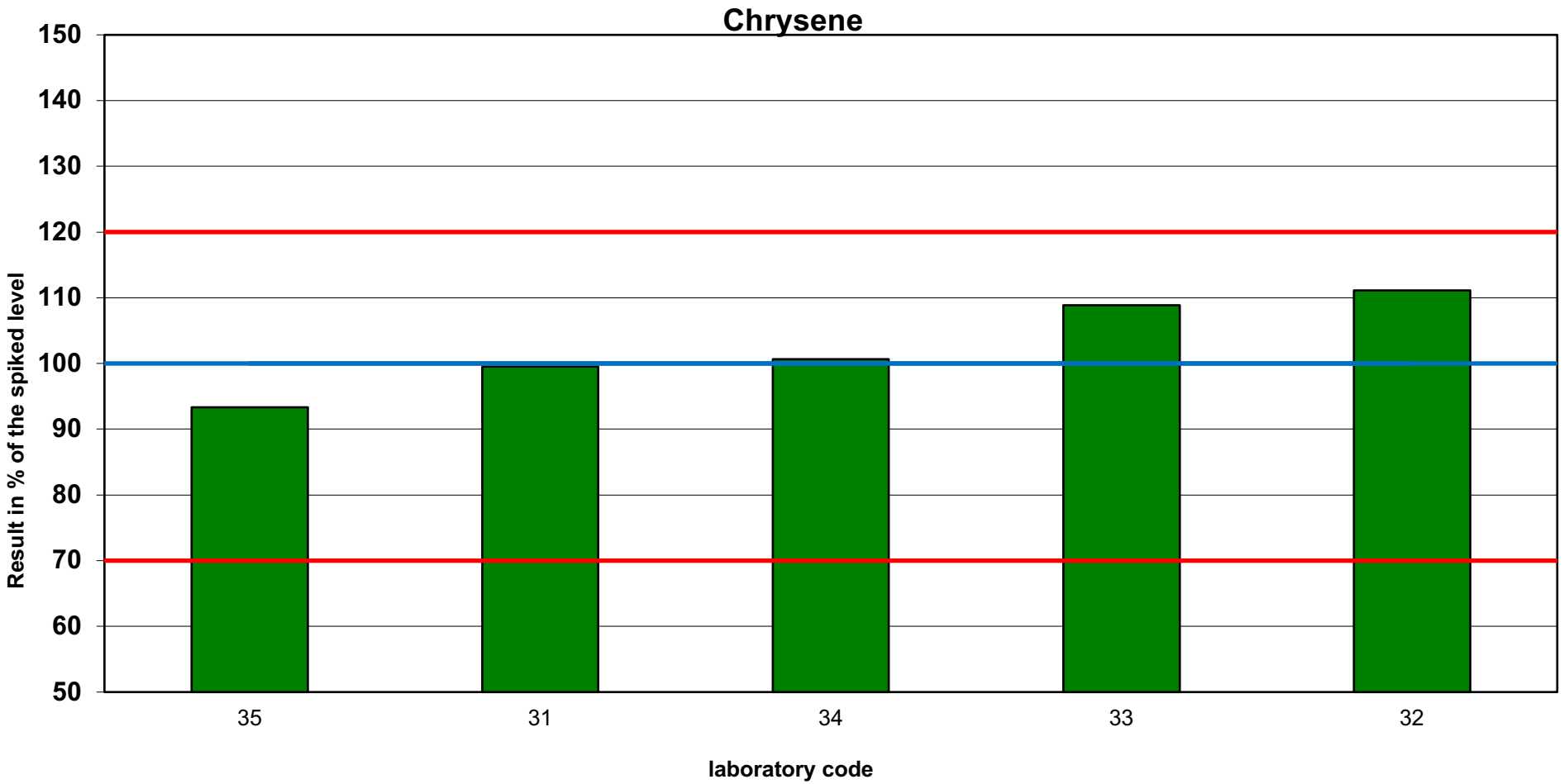

Figure 13 Assessment of Chrysene
Green: satisfactory results, red: dissatisfactory results

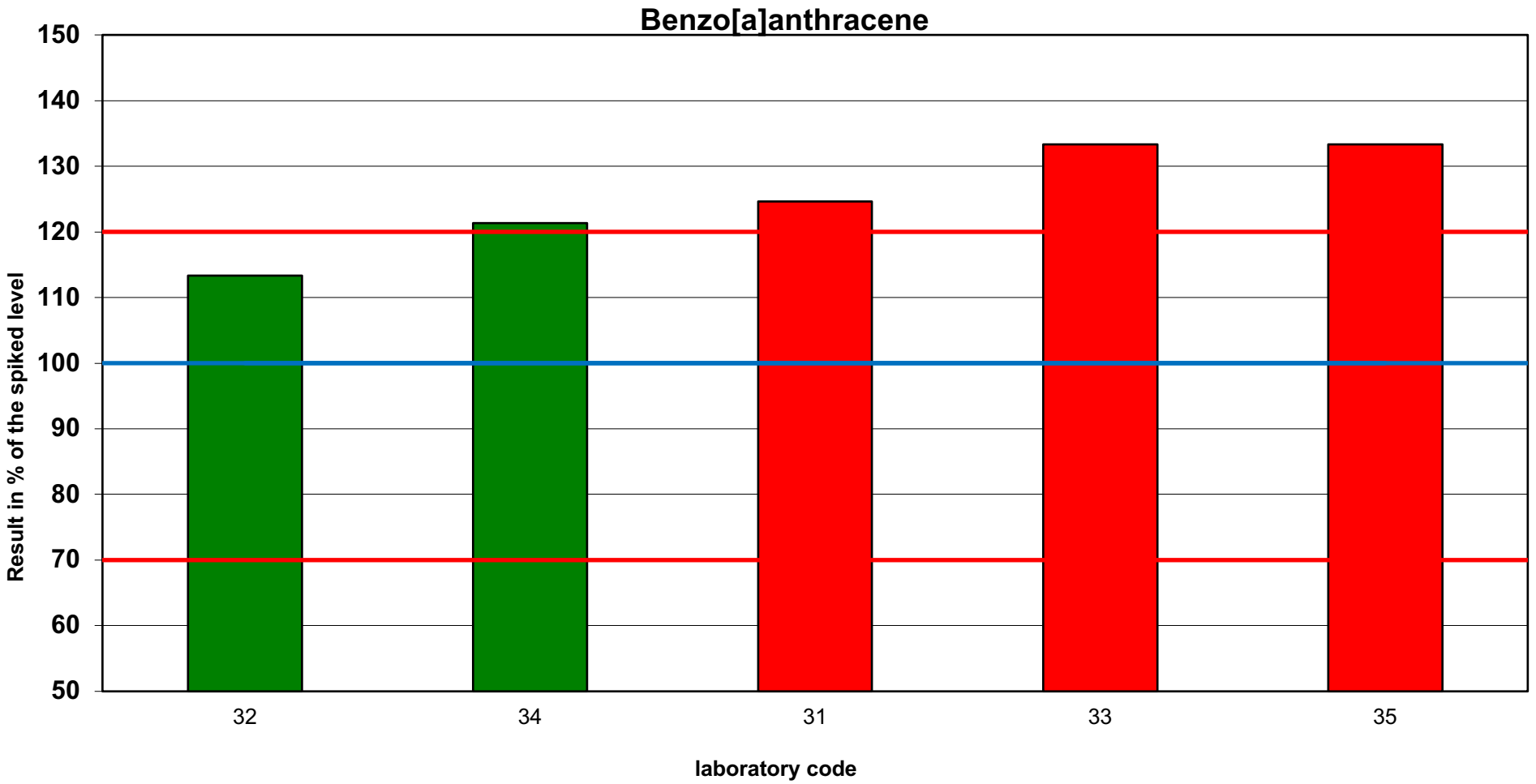

Figure 14 Assessment of Benzo[a]anthracene
Green: satisfactory results, red: dissatisfactory results

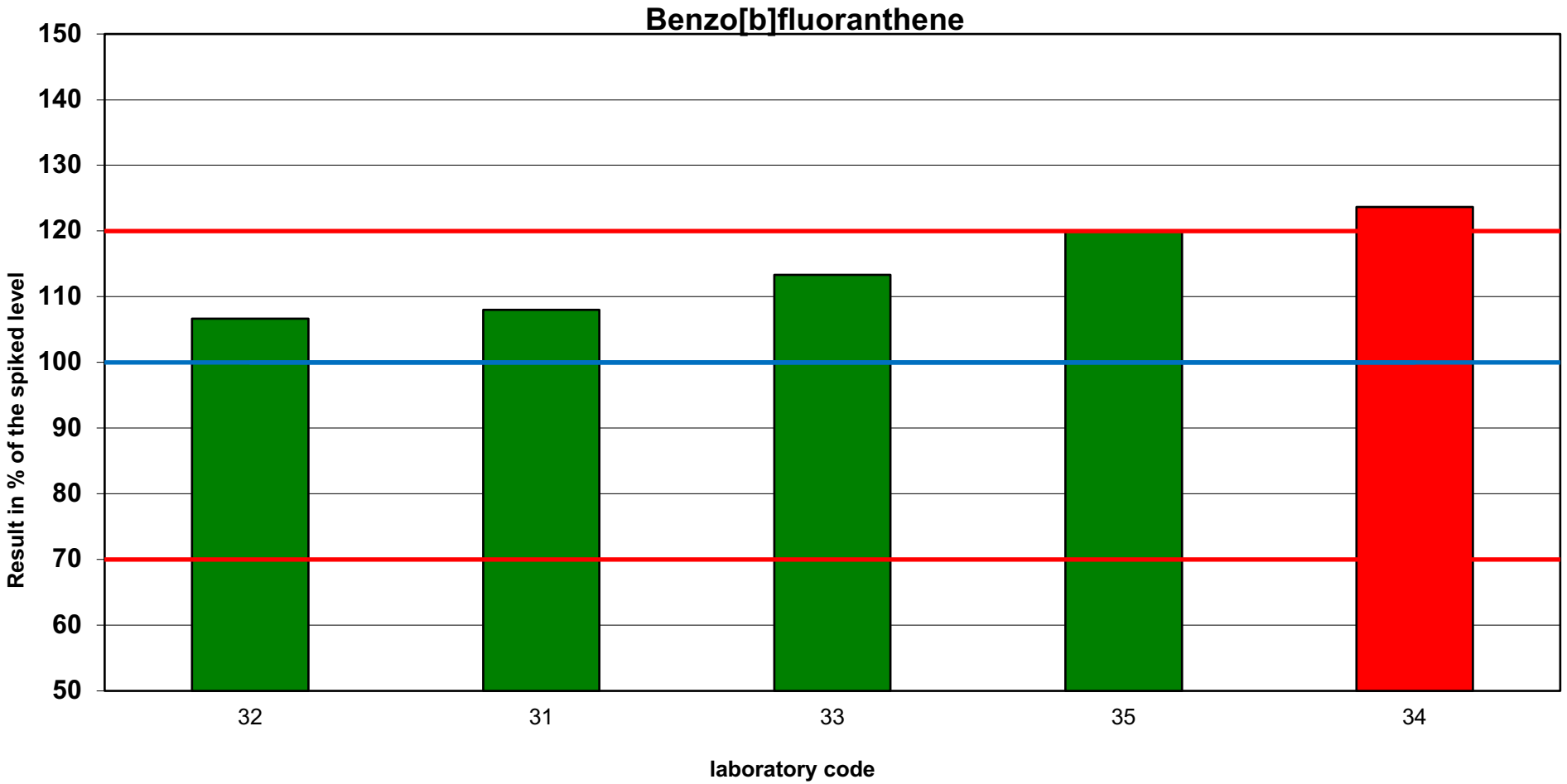

Figure 15 Assessment of Benzo[b]fluoranthene
Green: satisfactory results, red: dissatisfactory results

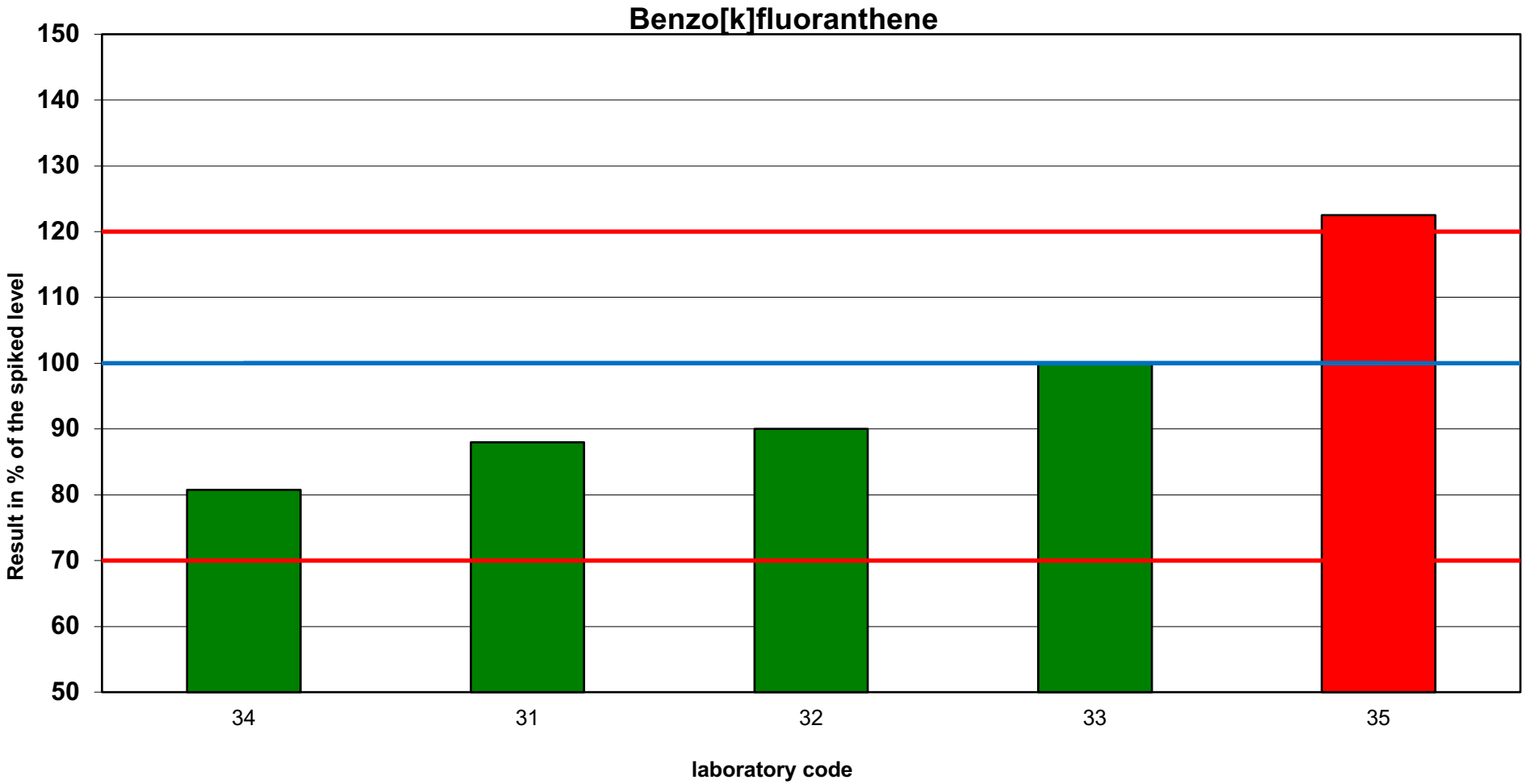

Figure 16 Assessment of Benzo[k]fluoranthene
Green: satisfactory results, red: dissatisfactory results

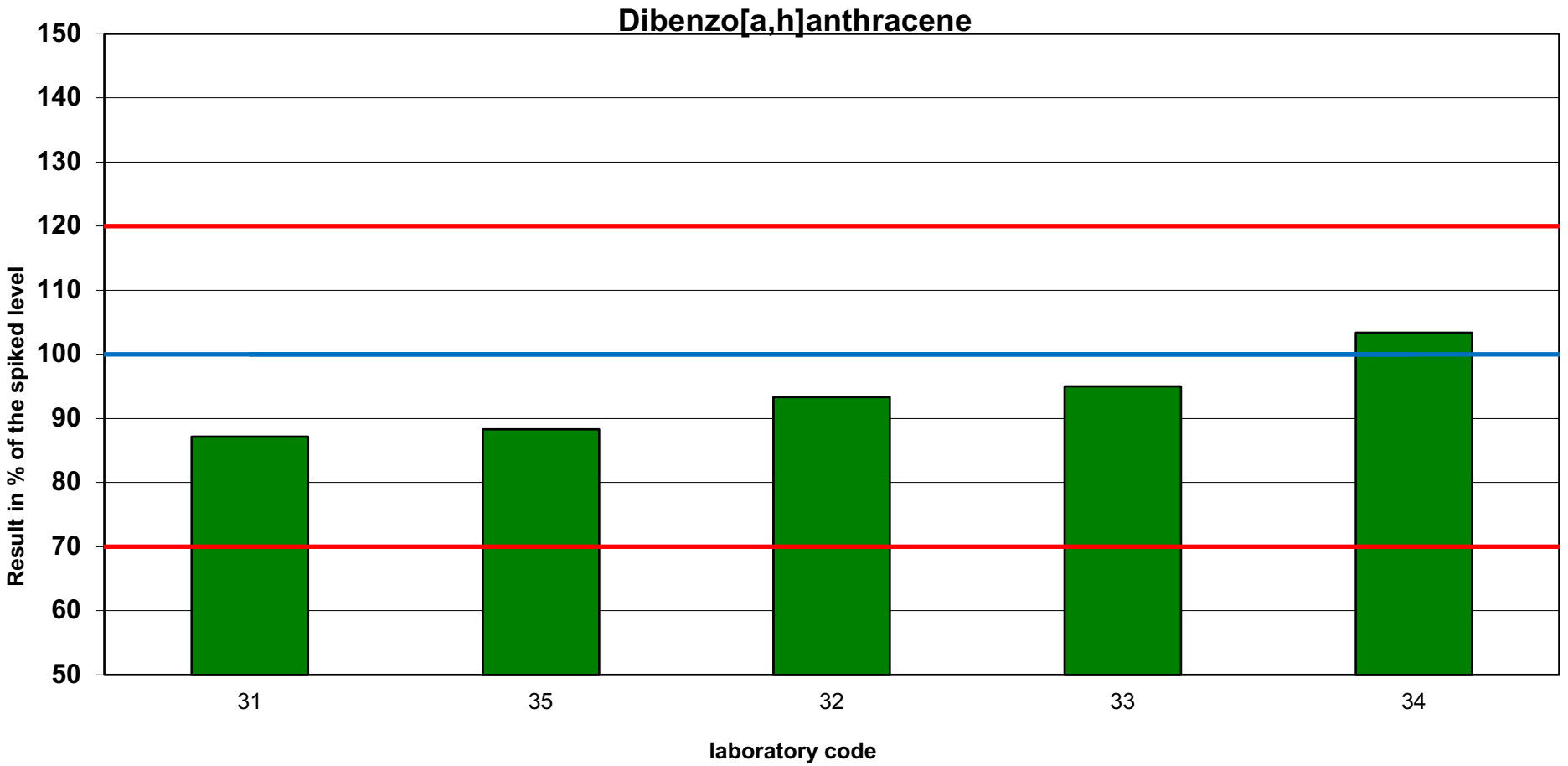

Figure 17 Assessment of Dibenzo[a,h]anthracene
Green: satisfactory results, red: dissatisfactory result