QS – Ihr Prüfsystem
für Lebensmittel

Confirmation of participation

The laboratory

Chemisches Labor Dr. Mang

Humperdinckstraße 28

60598 Frankfurt

has successfully participated in the 7th Laboratory Performance Assessment

„Pesticide Residues in Parsley Purée"

The laboratory's code in the report is:77.

The laboratory performance assessment was performed by

QS Fachgesellschaft Obst Gemüse Kartoffeln GmbH.

Bonn, November 20th 2009

Dr. Hermann-Josef Nienhoff
Managing Director

QS – Ihr Prüfsystem für Lebensmittel

7th Laboratory Performance Assessment

QS Fachgesellschaft – Obst-Gemüse-Kartoffeln GmbH

in co-operation with

Lach & Bruns, Consultant Chemists

Report

Test Material C

Pesticide Residues in Parsley Purée

September-November 2009

Summary

The Test Materials for the 7th Laboratory Performance Assessment of QS Fachgesellschaft Obst-Gemüse-Kartoffeln GmbH were prepared by the GLP department of LUFA Speyer in summer / autumn 2009 to provide individual Test Material tailored to QS needs. For the second time QS introduced Test Material with incurred pesticides thus the Parsley has been treated with three pesticides in total during the agricultural production.

QS also required four different materials in terms of spiked pesticides. Thus, the four Test Materials differed in the number of spiked pesticides as well as in the levels of spiked pesticides. Test Material "C" was distributed to twenty three (23) participants.

This report refers to the performance assessment of laboratories which analysed Test Material "C". Each laboratory received minimum 100 g Parsley purée with incurred and spiked pesticides. 23 participants (of test material "C") kept the term for the submission of results.

The laboratories were requested to identify and quantify 6 resp. 7 pesticides. These were Biphenyl (spiked), Cyromazine (spiked), Difenoconazole (incurred), Nitenpyram (spiked), Pirimicarb (incurred), and Quinoxyfen (spiked). The pesticide Metalaxyl (incurred) was present in the Test Material at low levels (≤10 µg/kg). The results of Metalaxyl are provided for information only in order to evaluate the laboratories' analytical performances at the low concentration levels and they are not considered for the assessment of the participants performances.

The performance assessment considers the following aspects:

- No *false negative* results are reported (thus identification of all six pesticides, see also table 5 to 7, p. 10-12)
- No *false positive* results are reported (see also table 2, p. 7)
- Correct quantification (either assessed by application of the z-score model or the 70 -120% recovery criteria – see also explanation next page)

The overall performance assessment results are summarised in the following table:

criteria	number of satisfactory participants	total number participants	**satisfactory %**
correctly identified all six pesticides > 20 µg/kg	17	23	**74**
correctly identified **AND** reported satisfactory results for all six pesticides	13	23	**57**

Assessment of quantification:

The z-scores were determined applying FAPAS® method [1, 2, 3]. The assigned values ($\hat{X}$) for the pesticide concentrations were calculated using Huber's algorithm. The target standard deviation (σ_p) was calculated using the appropriate form of Horwitz equation[4]. Results with z≤|2| are regarded as satisfactory. The applied robust statistics require a normal distribution of the analytical results. Outliers were identified according to the Grubbs test.

The performance assessment results are summarised in the following tables:

analyte	spiked value µg/kg	assigned value $\hat{X}$, µg/kg	number of satis-factory z-scores z≤|2|	total number of scores	satis-factory %
Difenoconazole	incurred residue	1627	18	22	**82**
Pirimicarb + P-desmethyl	incurred residue	705	23	23	**100**
Biphenyl	70	60	17	19	**89**
Nitenpyram	40	38	35	37	**95**
Quinoxyfen	80	67	20	22	**91**

The applied robust statistics assume that the distribution of the analytical results is roughly normal. However, the distribution of the *Cyromazine* and *Nitenpyram* results are atypical and the application of robust statistics gives misleading results. The standard deviations of the corresponding assigned values deviate considerably from the target standard deviations (see table 1, p. 7). Because of the target standard deviation of Nitenpyram (8 µg/kg) is at a very low level, these results have been evaluated using the z-score approach although the robust standard deviation was too high. Due to the inappropriate statistical evaluation of Cyromazine, another type of evaluation of the analytical results was applied. The obligatory method performance data of the *recovery* (70 – 120%)[6] was used to evaluate the laboratories' performances. Therefore, analytical results that lie between 70 and 120 per cent of the spiked levels are considered satisfactory (see also table 7: satisfactory results are marked with "*accept")*.

analyte	spiked level, µg/kg	number of satisfactory results (70-120% of the spiked level)	total number of scores	satisfactory %
Cyromazine	400	10	20	**50**

Contents

1. Test Material Preparation and Design

The material for this Performance Assessment was prepared by the GLP department of LUFA Speyer. The homogeneity tests were performed by the CVUA Stuttgart (European reference Laboratory for Residues of Pesticides). The results of homogeneity testing are presented in table 4, p. 8-9.

Difenoconazole, Metalaxyl and Pirimicarb were applied during the agricultural production of the Parsley and therefore are incurred pesticides. The following pesticides were spiked to give the approximate final concentrations: 70 µg/kg Biphenyl, 80 µg/kg Quinoxyfen, 40 µg/kg Nitenpyram and 400 µg/kg Cyromazine.

The Parsley purée was distributed into labelled bottles with at least 100 g in each. The bottles were stored at -20°C in the dark until distribution.

2. Results

The participants were requested to report which pesticides the parlsey purée had been analysed for. The results had to be reported without consideration of the recovery. The limit of quantification (LOQ) had to be specified for all pesticides.
Each laboratory was given a number (laboratory code). The results of all participants analysing Test Material C are presented in tables 5 to 8 (p. 10-12).

3. Statistical Evaluation of Results

The statistical procedure applied for this performance assessment is internationally accepted and used in inter-laboratory test series to achieve transparent and fair results. The method used follows recommendations given in the IUPAC/ISO/AOAC International Harmonised Protocol for the Proficiency Testing of Chemical Analytical Laboratories [5)].

3.1. Calculation of the Assigned Value, $\hat{X}$

The assigned value, $\hat{X}$, is derived as a robust mean from the results of all participants and presents the best estimate of the true concentration of the analyte.

The influence of outliers is minimised via Huber's method.

The uncertainty (*u)* of the robust mean is given by

$$u = \frac{\hat{\sigma}}{\sqrt{n}}$$

$\hat{\sigma}$ = the standard deviation of the robust mean (assigned value $\hat{X}$),
n = the number of data points used for calculation of $\hat{X}$

The values for $\hat{X}$, $\hat{\sigma}$, *u* and *n* are presented in table 1.

3.2. Target Standard Deviation for the Performance Assessment, σ_p

The target standard deviation for this laboratory test was derived from the appropriate form of the Horwitz equation. It predicts a standard deviation from a given concentration c, here is c the assigned value $\hat{X}$ **.**

There are three forms of the Horwitz equation for different analyte concentrations:

i) for analyte concentrations <120 ppb

$$\sigma_p = \frac{0.22c}{mr}$$

ii) for analyte concentrations ≥120 ppb and ≤13,8%

$$\sigma_p = \frac{0.02c^{0.8495}}{mr}$$

iii) for analyte concentrations >13,8%

$$\sigma_p = \frac{0.01c^{0.5}}{mr}$$

c = $\hat{X}$ **,** expressed as a dimensionless mass ratio, e. g. 1 ppm ≡ 10^{-6} or % ≡ 10^{-2}
mr = expressed as a dimensionless mass ratio, e. g. 1 ppm ≡ 10^{-6} or % ≡ 10^{-2}

3.3. Calculation of the Individual z-Scores

The z-scores for each participant and each analyte were calculated as:

$$z = \frac{x - \hat{X}}{\sigma_p}$$

where x = the reported result
$\hat{X}$ = the assigned value
σ_p = the target value of the standard deviation

If a participant did not identify one or more residues, these results were set equal to zero and the z-scores were calculated accordingly.

4. References

1) FAPAS®, 2002, *Protocol for the Food Analysis Performance Assessment Scheme Organisation and Analysis of Data*, 6th edition.
2) Lowthian, P.J. and Thompson, M., 2002, Bump-hunting for the proficiency tester-searching for multimodality, *Analyst*, **127**, 1359-1364.
3) Analytical Methods Committee, 1989, Robust statistics – How not to reject outliers Part 1. Basic concepts, *Analyst*, **114**, 1693-1697.
4) Thompson, M.., 2000, Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing, *Analyst*, **125**, 385-386.
5) 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*.*
6) *Method Validation and quality control procedures for pesticide residues analysis in food and feed*, Document No. SANCO/2007/3131, 31/October/2007 (Supersedes Document No. SANCO/10232/2006)

Assigned Values and Target Standard Deviations						
analyte	assigned value				target standard deviation	
	data points, *n*	robust mean, X, µg/kg	uncertainty, *u*	robust standard deviation, *σ*	derived from	σ_p, µg/kg
Biphenyl	19	70	2,98	13	Horwitz	13
Cyromazine	20	323	30,19	**135**	Horwitz	**61**
Difenoconazole	22	1627	80,59	**378**	Horwitz	**242**
*Metalaxyl**	*No statistics applied*					
Nitenpyram	21	38	2,40	**11**	Horwitz	**8**
Pirimicarb + P-desmethyl	23	705	19,39	93	Horwitz	119
Quinoxyfen	22	67	2,77	13	Horwitz	15

** italics indicate for information only*

Table 1: Assigned Values and Target Standard Deviations

laboratory code	pesticide residue	result (µg/kg)	recovery (%)	LoQ (µg/kg)
44	Diafenthiuron	82	-	5

Table 2: Additional Pesticide Residues Reported > 10 µg/kg

criteria	number of satisfactory participants	total number participants	**satisfactory %**
correctly identified all six pesticides	17	23	**74**
correctly identified **AND** reported satisfactory results for all six pesticides	13	23	**57**

Table 3: Number and Percentage of Participants Correctly Identifying and Reporting Satisfactory Results for all assessed Pesticides

test material	**Biphenyl**			
	1.Aufarbeitung	2. Aufarbeitung	**MW**	**Wiederfindung %**
PT C Nr.: 101	0,059	0,071	**0,065**	101
PT C Nr.: 106	0,062	0,063	**0,063**	
PT C Nr.: 111	0,067	0,060	**0,064**	**Standardabweichung**
PT C Nr.: 116	0,049	0,057	**0,053**	0,0064
PT C Nr.: 121	0,052	0,055	**0,054**	
PT C Nr.: 126	0,061	0,083	**0,072**	**Variation in %**
PT C Nr.: 131	0,058	0,052	**0,055**	10,8
PT C Nr.: 136	0,057	0,055	**0,056**	
PT C Nr.: 141	0,059	0,054	**0,057**	
PT C Nr.: 146	0,055	0,052	**0,054**	
mean	0,059		**0,059**	

Cyromazine (corrected by recovery)			
1.Aufarbeitung	2. Aufarbeitung	**MW**	**Wiederfindung %**
0,565	0,5580	**0,562**	28
0,558	0,5362	**0,547**	
0,540	0,5435	**0,542**	**Standardabweichung**
0,533	0,5072	**0,520**	0,0365
0,529	0,5399	**0,534**	
0,489	0,4964	**0,493**	**Variation in %**
0,514	0,5507	**0,533**	7,1
0,471	0,4891	**0,480**	
0,453	0,5036	**0,478**	
0,435	0,4638	**0,449**	
0,514		**0,514**	

test material	**Difenoconazole**			
	1.Aufarbeitung	2. Aufarbeitung	**MW**	**Wiederfindung(%)**
PT C Nr.: 101	1,48	1,46	**1,470**	
PT C Nr.: 106	1,5	1,45	**1,475**	
PT C Nr.: 111	1,49	1,46	**1,475**	**Standardabweichung**
PT C Nr.: 116	1,44	1,43	**1,435**	0,0455
PT C Nr.: 121	1,44	1,43	**1,435**	
PT C Nr.: 126	1,49	1,41	**1,450**	**Variation in %**
PT C Nr.: 131	1,44	1,4	**1,420**	3,2
PT C Nr.: 136	1,4	1,39	**1,395**	
PT C Nr.: 141	1,35	1,35	**1,350**	
PT C Nr.: 146	1,34	1,38	**1,360**	
mean	1,427		**1,427**	

Nitenpyram			
1.Aufarbeitung	2. Aufarbeitung	**MW**	**Wiederfindung %**
0,031	0,0302	**0,031**	74
0,03	0,0329	**0,031**	
0,032	0,032	**0,032**	**Standardabweichung**
0,031	0,0301	**0,031**	0,0016
0,029	0,0339	**0,031**	
0,0301	0,0281	**0,029**	**Variation in %**
0,0325	0,0301	**0,031**	5,4
0,0307	0,0293	**0,030**	
0,0282	0,0289	**0,029**	
0,0259	0,0276	**0,027**	
0,03		**0,03**	

Table 4(1): Homogeneity Data for Parsley Homogenate Sample (CVUA Stuttgart)

test material	Pirimicarb			
	1.Aufarbeitung	2. Aufarbeitung	MW	Wiederfindung %
PT C Nr.: 101	0,697	0,657	**0,677**	
PT C Nr.: 106	0,707	0,664	**0,686**	
PT C Nr.: 111	0,669	0,674	**0,672**	**Standardabweichung**
PT C Nr.: 116	0,655	0,641	**0,648**	0,0161
PT C Nr.: 121	0,664	0,655	**0,660**	
PT C Nr.: 126	0,699	0,644	**0,672**	**Variation in %**
PT C Nr.: 131	0,673	0,655	**0,664**	2,4
PT C Nr.: 136	0,638	0,643	**0,641**	
PT C Nr.: 141	0,634	0,651	**0,643**	
PT C Nr.: 146	0,645	0,642	**0,644**	
mean	0,66		**0,66**	

Pirimicarb-desmethyl			
1.Aufarbeitung	2. Aufarbeitung	MW	Wiederfindung %
0,046	0,051	**0,049**	
0,049	0,049	**0,049**	
0,053	0,053	**0,053**	**Standardabweichung**
0,045	0,050	**0,048**	0,02
0,045	0,051	**0,048**	
0,049	0,050	**0,050**	**Variation in %**
0,050	0,053	**0,052**	3,9
0,050	0,054	**0,052**	
0,046	0,055	**0,051**	
0,048	0,057	**0,053**	
0,050		**0,050**	

test material	Quinoxyfen			
	1.Aufarbeitung	2. Aufarbeitung	MW	Wiederfindung %
PT C Nr.: 101	0,0867	0,0844	**0,086**	110
PT C Nr.: 106	0,0785	0,0846	**0,082**	
PT C Nr.: 111	0,0785	0,0845	**0,082**	**Standardabweichung**
PT C Nr.: 116	0,0774	0,0786	**0,078**	0,0040
PT C Nr.: 121	0,0778	0,0812	**0,080**	
PT C Nr.: 126	0,0772	0,0775	**0,077**	**Variation in %**
PT C Nr.: 131	0,0775	0,0784	**0,078**	5
PT C Nr.: 136	0,0736	0,0772	**0,075**	
PT C Nr.: 141	0,0722	0,075	**0,074**	
PT C Nr.: 146	0,0694	0,0755	**0,072**	
mean	0,078		**0,078**	

Table 4(2): Homogeneity Data for Parsley Homogenate Sample (CVUA Stuttgart)

	Pirimicarb + P-desmethyl (assigned value 705 µg/kg)				**Difenoconazole** (assigned value 1627 µg/kg)			
laboratory code	result (µg/kg)	recovery (%) Pirimicarb/ P.desmethyl	LoQ (µg/kg)	z-score	result (µg/kg)	recovery (%)	LoQ (µg/kg)	z-score
3	669	98-100/89-103	5	-0,3	2254	84-96	10	**2,6**
4	795	90/95		0,8	2363	90		**3,0**
5	623	90		-0,7	**n.r.**			**-6,7**
10	752	90/78		0,4	2100	104		2,0
16	752	98/72		0,4	1535	103		-0,4
21	662	84		-0,4	1225	86		-1,7
23	740	93/83	10	0,3	1650	114	10	0,1
24	704	80/78		0,0	2031	76		1,7
25	795	88		0,8	1538	92		-0,4
30	593	90		-0,9	1340	85		-1,2
31	580	71	10	-1,0	1390	87	10	-1,0
35	815	86	10	0,9	1080	100	10	**-2,3**
41	814			0,9	1886			1,1
44	760	90	5	0,5	1649	90	5	0,1
47	614	96	10	-0,8	1890	95	10	1,1
50	631	104	10	-0,6	853	87	10	**-3,2**
51	755	100		0,4	1905	90		1,1
60	765	80	10	0,5	1550	85	10	-0,3
64	557	112	10	-1,2	1200	128	10	-1,8
66	810		10	0,9	1380		10	-1,0
73	699	94		0,0	1599	101		-0,1
77	576	96		-1,1	1436	96		-0,8
79	716	104	10	0,1	1986	90	10	1,5

* according to Grubbs

Table 5: Results and z-Scores for sum of Pirimicarb / Pirimicarb-desmethyl and Difenoconazole in Parsley Purée Test Material C

	Quinoxyfen assigned value 67 µg/kg / spiked level: 80 µg/kg				**Biphenyl** assigned value 60 µg/kg / spiked level: 70µg/kg			
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	z-score	result (µg/kg)	recovery (%)	LoQ (µg/kg)	z-score
3	50	97-104	10	-1,2	60	77-92	10	0,0
4	66,5	95		0,0	68,2	105		0,6
5	**n.r.**			**-4,5**	**n.r.**			**-4,5**
10	75,7	89		0,6	77	80		1,3
16	45	97		-1,5	73	98		1,0
21	66	92		-0,1	49	86		-0,9
23	72	100	10	0,3	59	95	10	-0,1
24	61	77		-0,4	61	90		0,0
25	71	87		0,3	66	102		0,4
30	83	87		1,1	50	92		-0,8
31	62	70	10	-0,3	82	70-120	10	1,6
35	60	95	10	-0,5	54	83	10	-0,5
41	88			1,4	68			0,6
44	68	90	5	0,1	55	70	5	-0,4
47	78	100	10	0,7	75	75	10	1,1
50	35	89	10	**-2,2**	32	96	10	**-2,1**
51	66	98		-0,1	50	100		-0,8
60	64	105	10	-0,2	67	105	10	0,5
64	55	126	10	-0,8	28	110	10	**-2,4**
66	44		10	-1,6	**n.r.**			**-4,5**
73	81	81		1,0	**n.r.**			**-4,5**
77	82	100		1,0	50	100		-0,8
79	79	100	10	0,8	**n.r.**			**-4,5**

Table 6: Results and z-Scores for Quinoxyfen and Biphenyl in Parsley Purée Test Material C

	Cyromazine assigned value 323 µg/kg / spiked level: 400 µg/kg				Nitenpyram assigned value 38 µg/kg / spiked level: 40 µg/kg			
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)	70-120%	result (µg/kg)	recovery (%)	LoQ (µg/kg)	z-score
3	318	89-98	10	accept	32	92-101	10	-0,7
4	102	70		-	22,4	80		-1,8
5	**n.r.**			-	**n.r.**			**-4,5**
10	417	72		accept	40,5	108		0,4
16	557	46		-	36	75		-0,2
21	31	70		-	41	122		0,4
23	315	36		accept	39	105		0,2
24	394	68		accept	39	72		0,2
25	764	92		-	52	85		1,7
30	235	85		-	35	89		-0,3
31	319	72	10	accept	50	116	10	1,5
35	378		10	accept	**n.r.**			**-4,5**
41	559			-	65			**3,3**
44	440	50	5	accept	26	80	5	-1,4
47	**n.r.**			-	49	71	10	1,4
50	251	75	5	-	24	95	5	-1,6
51	359	100		accept	33	79		-0,6
60	195	90	10	-	32	80	10	-0,7
64	387	79	10	accept	43	83	30	0,7
66	227		10	-	25		10	-1,5
73	131	77		-	52	60		1,7
77	293	76		accept	36	90		-0,2
79	**n.r.**			-	30	74	10	-0,9

Table 7: Results and Assessment/ z-Scores for Cyromazine and Nitenpyram in Parsley Purée Test Material C

	Metalaxyl		
laboratory code	result (µg/kg)	recovery (%)	LoQ (µg/kg)
3	8	93-107	5
4	5,7	95	
10	<10		
16	8	83	
21	7	76	
24	10	69	
25	7	112	
31	8	75	10
35	7		10
41	11		
44	10	100	5
47	7	100	5
50	8	91	5
60	10	80	10
64	<10	100	10

Table 8: Results for Metalaxyl in Parsley Purée Test Material C (for information only)

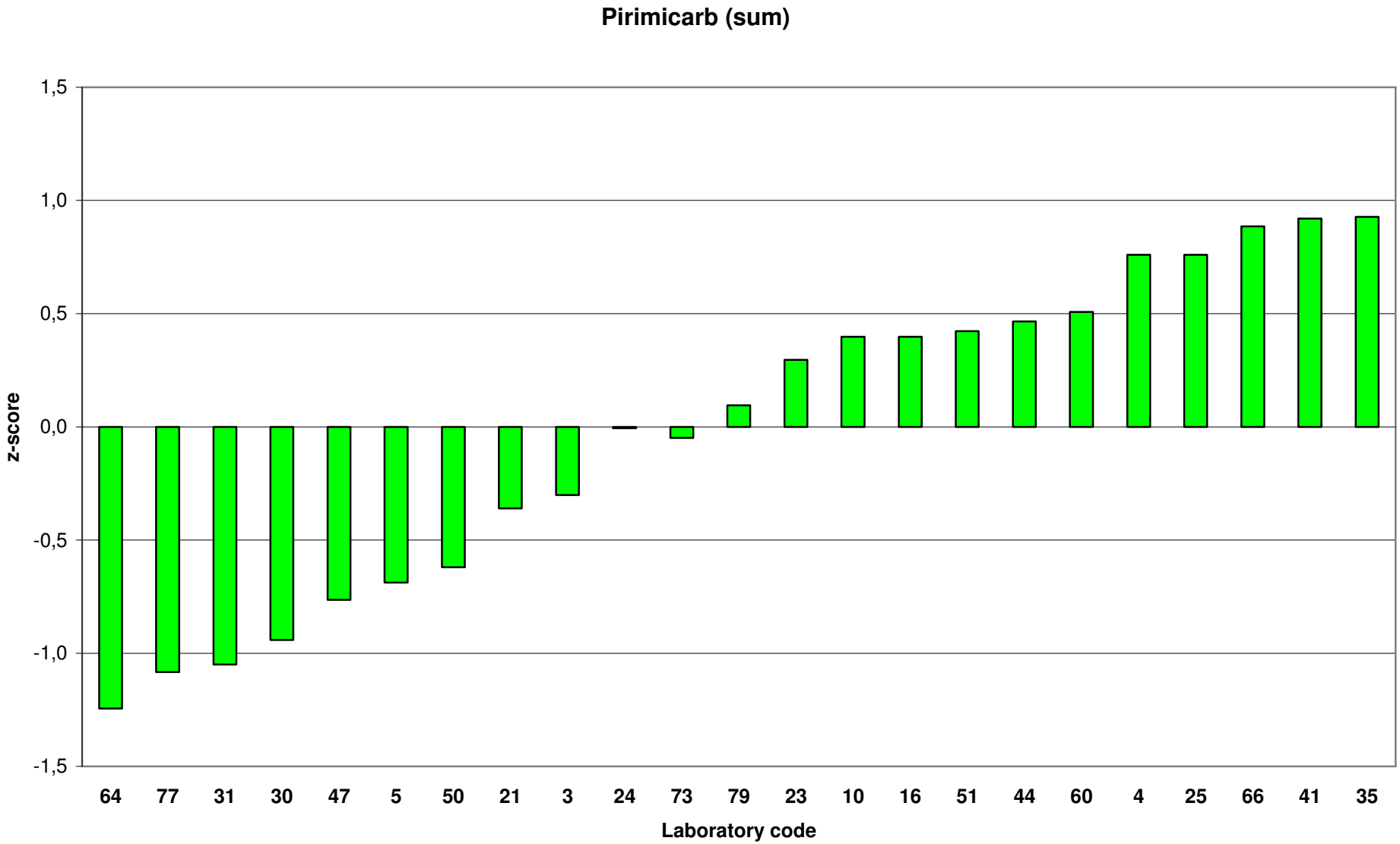

Figure 1: z-Scores for sum of Pirimicarb / Pirimicarb-desmethyl (705 µg/kg) in Parsley Purée Test Material C

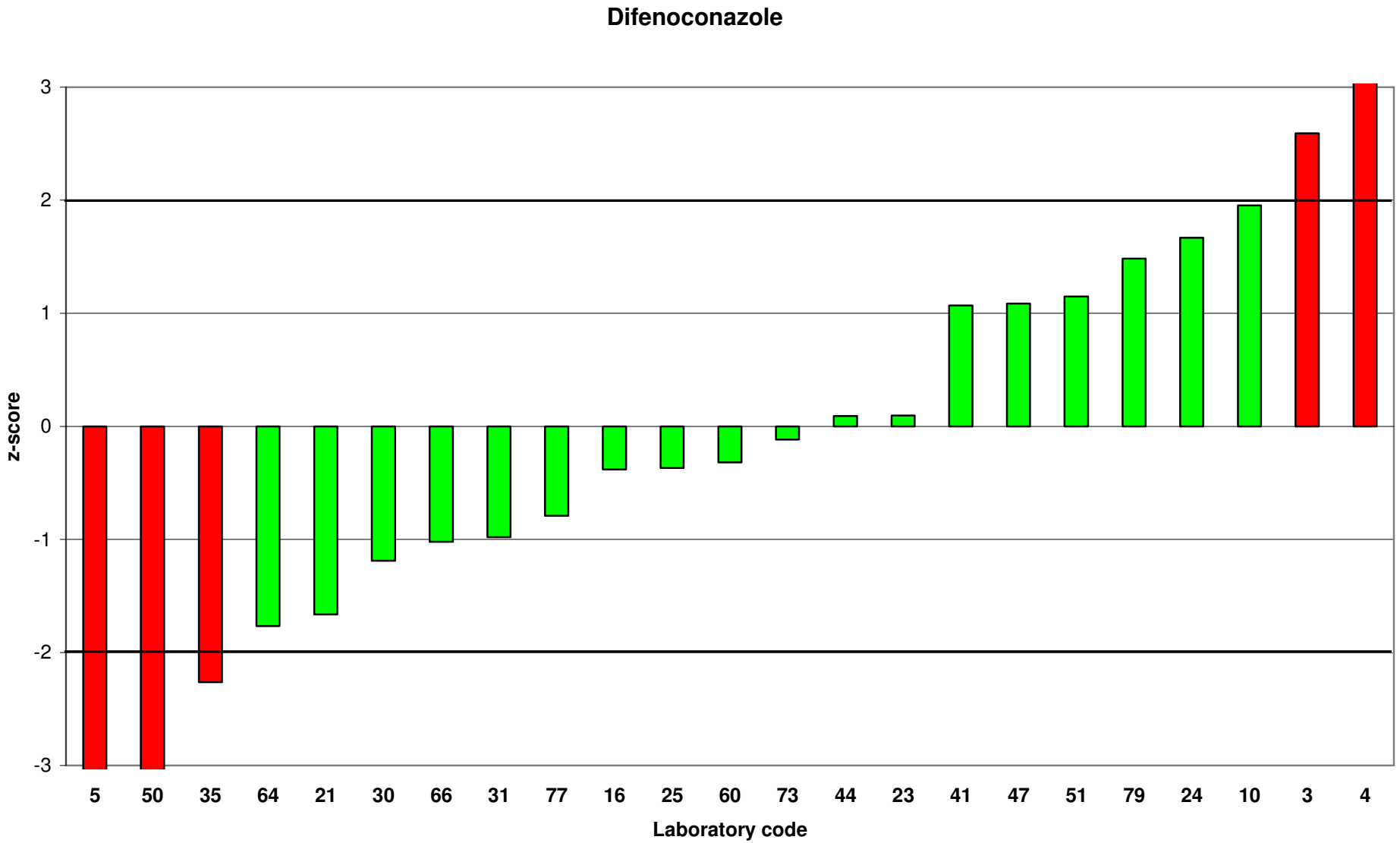

Figure 2: z-Scores for Difenoconazole (1627 µg/kg) in Parsley Purée Test Material C

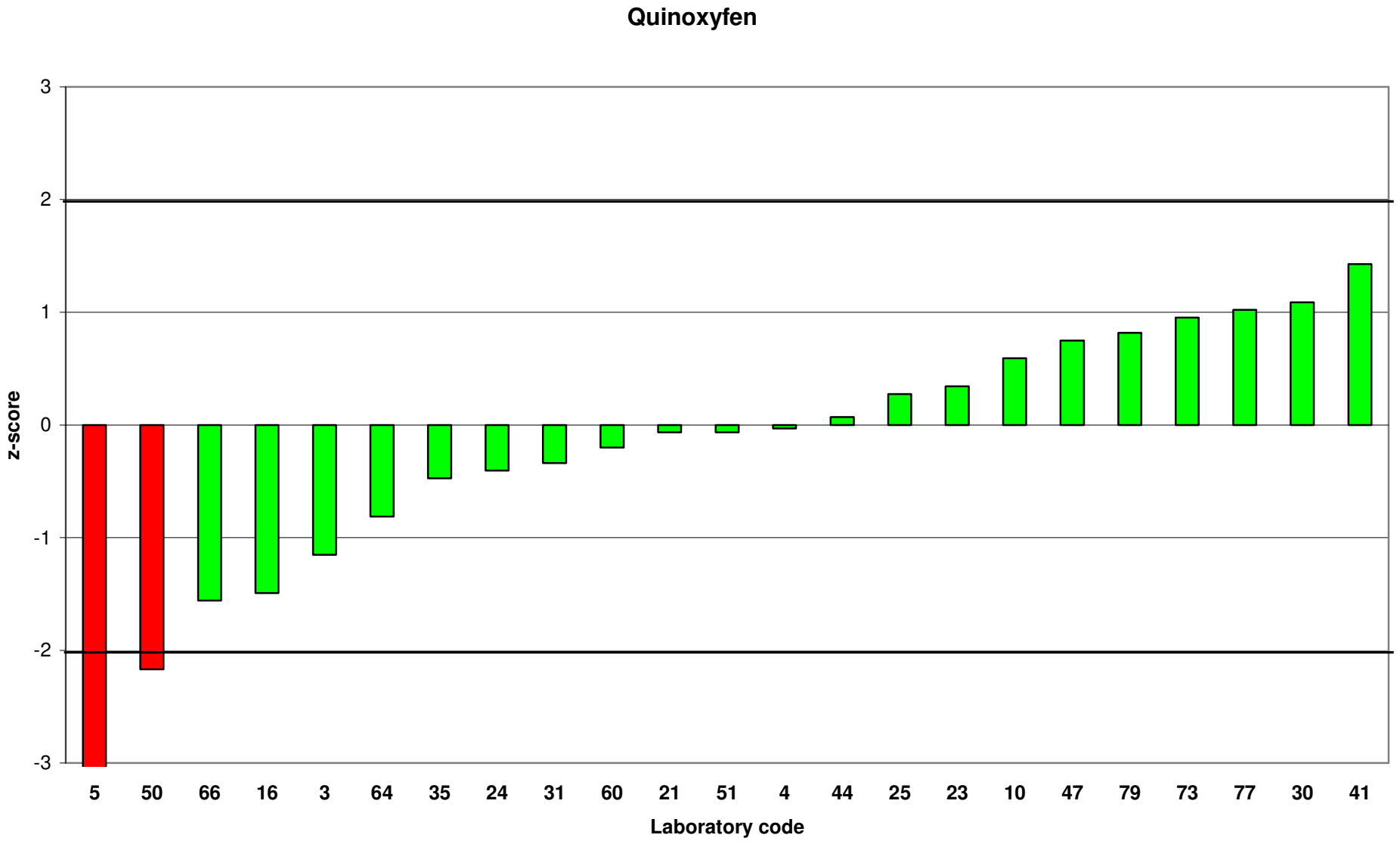

Figure 3: z-Scores for Quinoxyfen (67 µg/kg) in Parsley Purée Test Material C

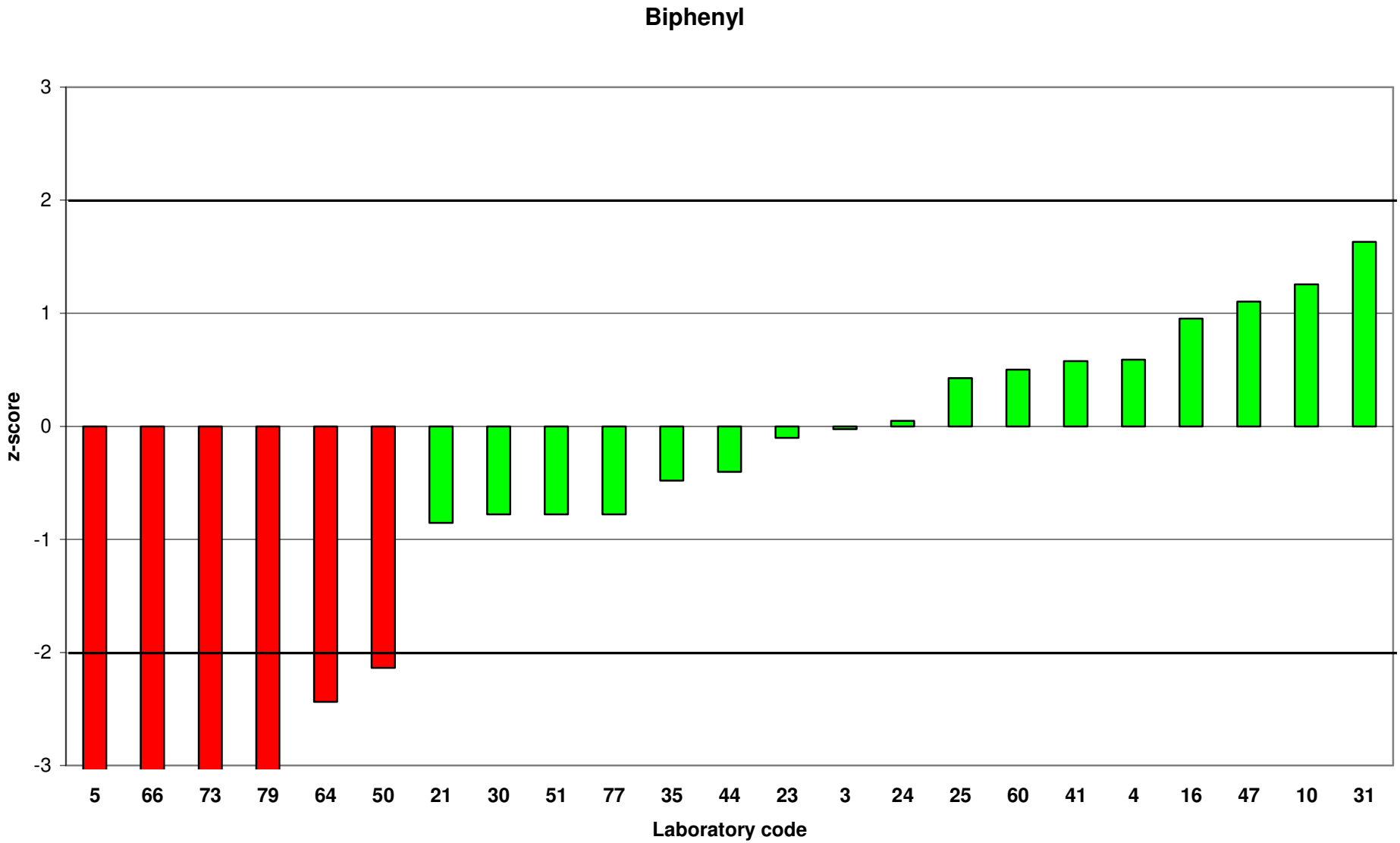

Figure 4: z-Scores for Biphenyl (60 µg/kg) in Parsley Purée Test Material C

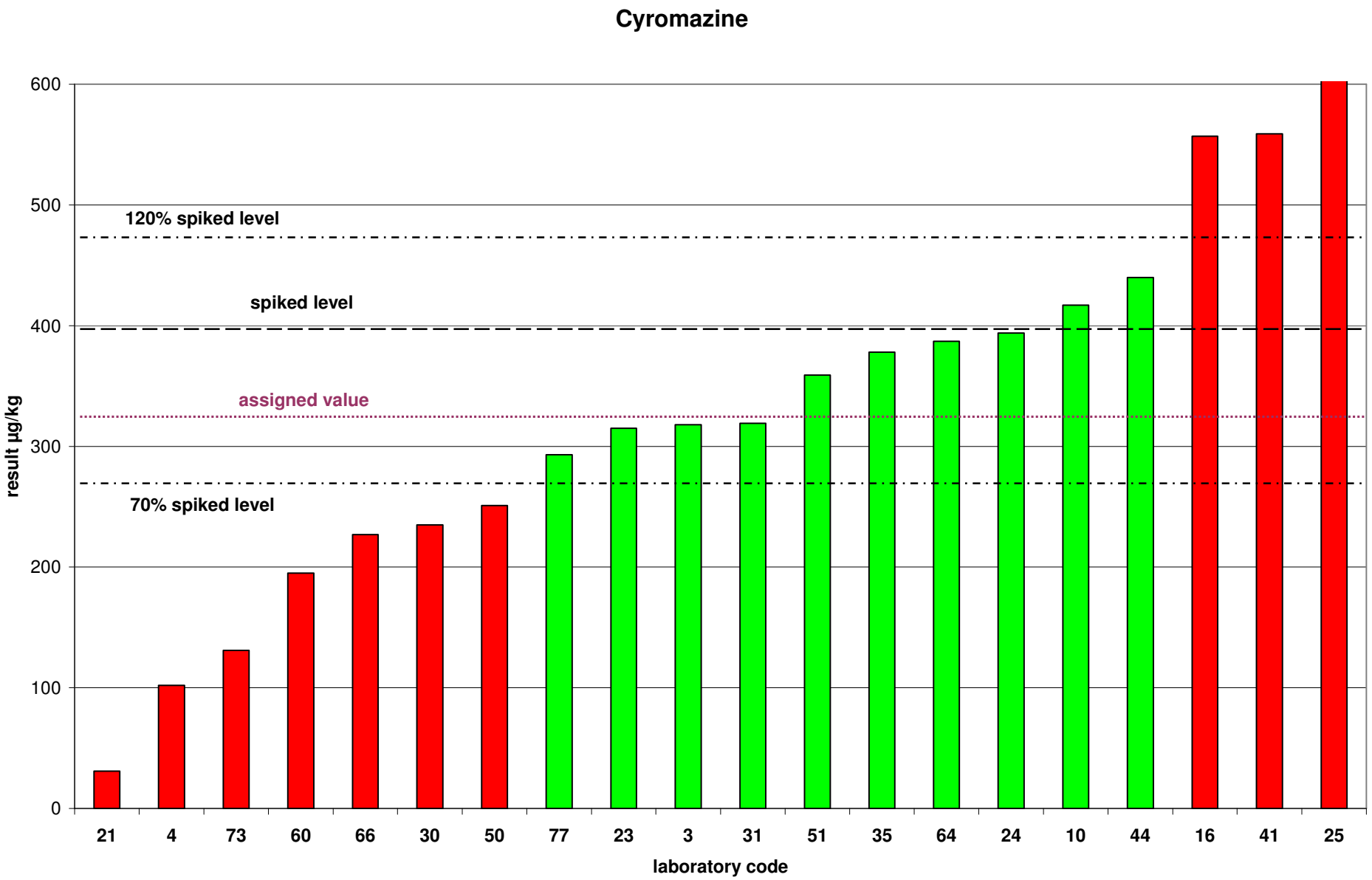

Figure 5: Assessment of Cyromazine (spiked level: 400 µg/kg) in Parsley Purée Test Material C

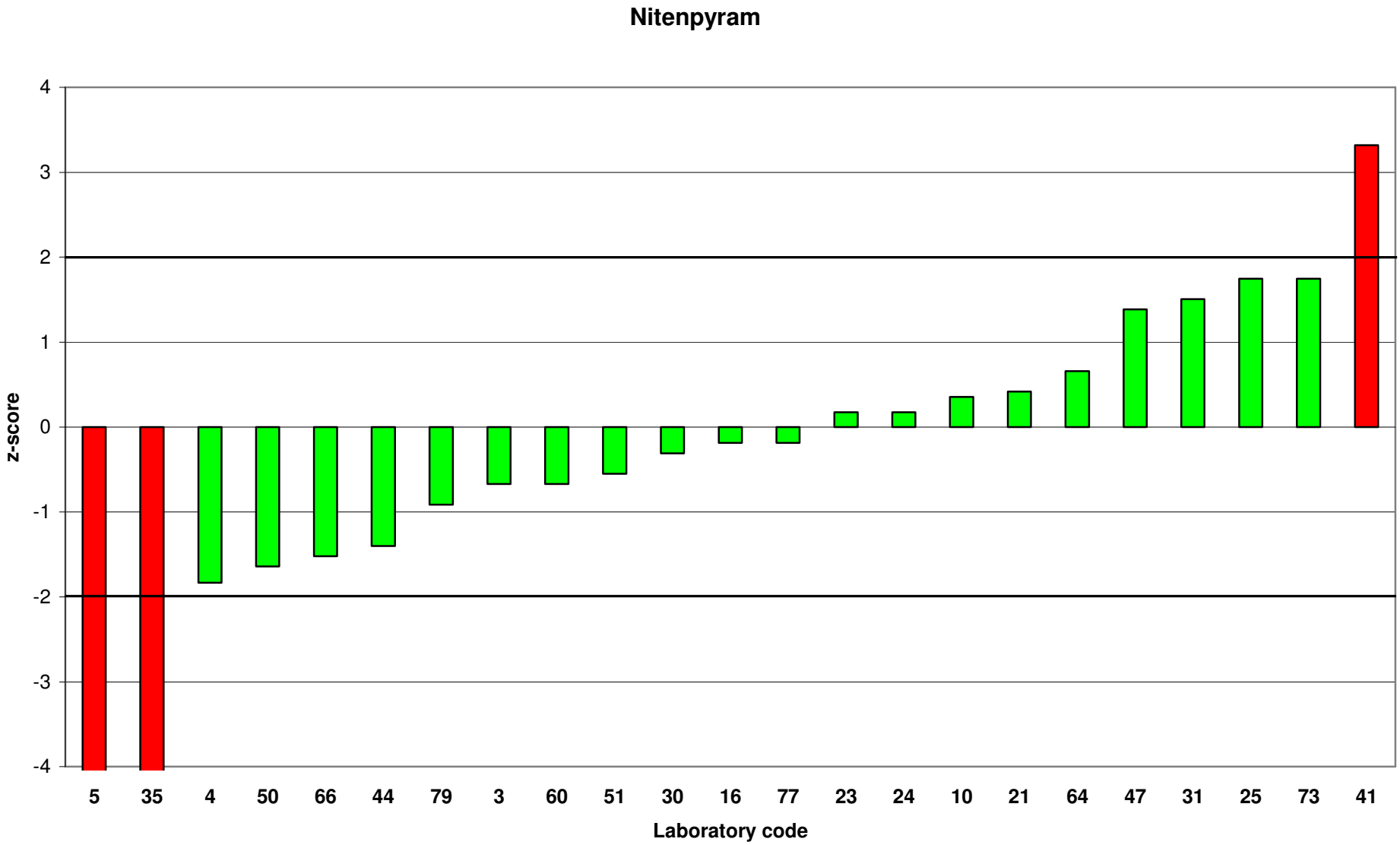

Figure 6: z-Scores for Nitenpyram (38 µg/kg) in Parsley Purée Test Material C