EURL-PROFICIENCY TEST-T02, 2014

Pesticide Residues in Tea Homogenate

Final Report

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CONTENTS

1. INTRODUCTION. 1
2. TEST ITEMS. 3
    2.1 Analytical method. 3
    2.2 Preparation of test items. 3
    2.3 Homogeneity test. 4
    2.4 Stability test. 5
    2.5 Distribution of test item and protocol to participants. 6
3. STATISTICAL METHODS. 7
    3.1 False positives and negatives. 7
    3.2 Estimation of the assigned values. 7
    3.3 Fixed target standard deviations. 8
    3.4 z-Scores. 8
    3.5 Combined z-scores. 9
4. RESULTS. 10
    4.1 Summary of reported results. 10
    4.2 Assigned values and target standard deviations. 13
    4.3 Assessment of laboratory performance. 14
5. CONCLUSIONS. 17
6. ACKNOWLEDGEMENTS. 20

APPENDIX 1. Homogeneity data. 21
APPENDIX 2. Histograms of residue data for each pesticide from all the laboratories. 23
APPENDIX 3. Results (mg/Kg) and z-scores for FFP RSD (25 %). 27
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %). 33
APPENDIX 5. 'Average of the Squared z-Score' (AZ^2) for laboratories in Category A. 61
APPENDIX 6. EUPT T02 – AZ^2 - Graphical representation for laboratories in Category A. 62
APPENDIX 7. Methods used by participants for determining pesticides.
(available in the EURL-FV web page in electronic format)

ANNEX 1. Protocols and instructions. Target list of pesticides to be sought. 63
ANNEX 2. List of laboratories that agreed to participate in EUPT-T02. 85

EURL-EUROPEAN UNION PROFICIENCY TEST 02
FOR THE DETERMINATION OF PESTICIDES IN TEA USING MULTIRESIDUE METHODS
2014

According to Article 28 of Regulation 396/2005/EC (23rd February, 2005) of the European Parliament and of the Council, concerning maximum residue levels for pesticides in or on food and feed of plant and animal origin[1], all laboratories analysing samples for the official control of pesticide residues shall participate in the European Union Proficiency Tests (EUPTs) for pesticide residues organised by the European Union. These proficiency tests are carried out on an annual basis in order to continuously improve the quality, accuracy and comparability of the residue data reported by EU Member States to the European Union, as well as other Member States, within the framework of the EU Multi-annual co-ordinated control programme and national monitoring programmes.

Regulation (EC) No 882/2004[2] lays down the general tasks, duties and requirements for European Union Reference Laboratories (EURLs)[3] for Food, Feed and Animal Health. Among these tasks is the provision for independently-organised comparative tests. The European Union Proficiency Test of pesticides in Tea 01 has been organised by the EURL in Fruit and Vegetables at the University of Almería, Spain[4].

Participation in this European Union Proficiency Test in Tea 02 was on a purely voluntary basis for EU laboratories. Nevertheless, all FV-NRLs and FV-Official laboratories involved in the determination of pesticide residues in fruit and vegetables were invited to take part. Additionally, laboratories from China, Saudi Arabia and Uruguay participated.

This report will be presented to the European Union Standing Committee for Animal Health and the Food Chain. In addition, DG-SANCO will have full access to all data from the EUPTs including the lab-code/lab-name key.

[1] Regulation (EC) No 396/2005, published in the OJ of the EU L70 on 16.03.2005, last amended by Regulation 839/2008 published in the OJ of the EU L234 on 30.08.2008.

[2] Regulation (EC) No 882/2004 of the European Parliament and of the Council on official controls performed to ensure compliance verification with feed and food law, animal health and animal welfare rules. Published in the OJ of the EU L191 on 28.05.2004.

[3] The Community Reference Laboratory (CRL) changed its name to the European Union Reference Laboratory (EURL) on 1st December 2009 as a result of the Treaty of Lisbon. OJ of the EU C306 on 17.12.2007.

[4] Commission Regulation (EC) No 776/2006 of 23rd May 2006 - amending Annex VII to Regulation (EC) No 882/2004 of the European Parliament and of the Council as regards European Union Reference Laboratories.

1. INTRODUCTION

Since 2012, there have been 120 rapid alerts through the Rapid Alert System for Food and Feed (RASFF)[5] concerning tea and herbal tea matrices. From them, 105 were border rejection, finding up to fourteen pesticides in one single sample with concentration range within 0.045-1.625 mg/kg. Taking into account that tea and other herbal teas have become more and more popular due to the health benefits associated with their consumption, and the contamination levels in these kinds of matrices, it is very important to know how efficient the analytical methods used by the laboratories are for reporting official results.

In view of the difficulties of this matrix type the EURL-FV considered to continue one year more with this voluntary basis proficiency test.

Fifty-one laboratories agreed to participate in European Union Proficiency Test in Tea 02.

The proficiency test was performed in 2014 using a tea homogenate. This proficiency test was based on the analysis of tea samples from China containing incurred pesticide residues. The tea was bought from a specialised shop for Chinese products, in Almería, Spain, containing incurred pesticides. Participating laboratories were not provided with a 'blank' tea homogenate.

The test item, over 15 g of tea homogenate containing pesticide residues, was shipped to participants on 8th September 2014. The deadline for results submission to the Organiser was 27th September 2014. The participants were provided with a list of one hundred and seventy-five target pesticide residues (Annex I) and were informed that any of these pesticides might be present in the test item. They were asked to determine the residue levels of all the pesticides that they detected and report the concentrations. This list of target pesticides also contained the Minimum Required Reporting Level (MRRL) for each pesticide fixed between 0.005 and 0.01 mg/Kg.

Pesticides considered as positives were those which were reported by the organiser and the majority of the participants. The median values of the results submitted by participants were used to obtain the assigned (true) values for each of the pesticide residues present. A fit-for-purpose relative target standard deviation (FFP RSD) of 25 % was chosen to calculate the target standard deviations (σ) as well as the z-scores for each pesticide.

For the assessment of overall laboratory performance, only the Average of the squared z-scores (AZ^2) has been used. Laboratories that have 'sufficient scope' and are able to detect at least 90 % of the pesticides present in the test item and report no false positives will be classified into Category A. Within this category, the laboratories have also been subclassified as 'good',

[5] http://ec.europa.eu/food/food/rapidalert/rasff_portal_database_en.htm

'satisfactory' or 'unsatisfactory', in relation to the overall accuracy of the results that they reported.

All the other laboratories have been classified into Category B because they have demonstrated 'insufficient scope'. For laboratories in Category B, individual z-scores have been calculated but their overall accuracy of their results has not been assessed. They have been listed in order of the number of pesticides sought and the number of acceptable z-scores achieved. In addition, the laboratories in the Category B table have been ranked according to the number of pesticides detected from the total number of pesticides taken into account for the statistical evaluation.

Laboratories that did not report results have not been classified into any category and are subsequently indicated in Annex 2 with the rest of laboratories that agreed to participate in EUPT-T02.

2. TEST ITEMS

2.1 Analytical method

The analytical method described briefly below was performed by the EURL-FV in order to conduct the homogeneity and stability tests. This was:

- Modified QuEChERS method[6]: The sample is extracted with acetonitrile using the same salts as for citrate QuEChERS, but firstly the tea was hydrated. In the clean-up step, calcium chloride was added instead of magnesium sulphate. The extract obtained was injected into both GC-MS and LC-MS based instruments.

Anthraquinone, bifenthrin, chlorfenapyr, chlorpyrifos, cyfluthrin, cypermethrin, dicofol, endosulfan alpha, endosulfan beta, endosulfan sulphate, fenpropathrin, lambda cyhalothrin and pyridaben were determined using GC-MS/MS. All other pesticides (Acetamiprid, buprofezin, carbendazim, fipronil, imidacloprid, methomyl and triazophos) were analysed using LC-MS/MS. For confirmation purposes, MS/MS spectra were used.

2.2 Preparation of the test item

One kilogram three hundred grams of dried green tea containing incurred pesticide residues was bought in a local shop in Almería (Spain). A subsample was taken and analysed to ascertain the pesticides present and to determine their concentrations. Following this, the entire sample was processed using a mill and then sieved through a mesh size of 0.5 mm. The milled tea was mixed in a constantly-spinning container for 20 hours to attain a homogeneous material. Approximately 15 g portions of the well-mixed homogenate were weighed into previously-labelled sealed plastic bags and stored in a fridge at 4 °C prior to distribution to participants.

[6] A. Lozano, Ł. Rajski, N .Belmonte-Valles, A. Uclés, S. Uclés, M. Mezcua, A. R. Fernández-Alba. Pesticide analysis in teas and chamomile by liquid chromatography and gas chromatography tandem mass spectrometry using a modified QuEChERS method: Validation and pilot survey in real samples. J. Chromatogr. A, 1268 (2012), 109-122.

2.3 Homogeneity test

Ten bags of the test item were randomly chosen from those stored in the fridge and analyses were performed on duplicate portions taken from each bag. The sequence of analyses was determined using a table of randomly-generated numbers. The injection sequence of the twenty extracts that were analysed by GC and LC was also randomly chosen. The quantification by GC and LC was performed using three points for standard addition in triplicate constructed from the test item.

The statistical evaluation was performed according to the International Harmonized Protocol published by IUPAC, ISO and AOAC[7]. The individual residue data from the homogeneity tests are given in Appendix 1. The results of the statistical analyses are given in Table 2.1. The acceptance criteria for the test item to be sufficiently homogenous for the proficiency test were that: $Ss^2 < c$, where Ss is the between-bottle sampling standard deviation and $c = F_1\sigma^2_{all} + F_2S^2_{an}$; F_1 and F_2 being constant values of 1.88 and 1.01, respectively, from the ten samples taken, and σ^2_{all} = 0.3 x FFP RSD(25 %) x the analytical sampling mean for all the pesticides.

Table 2.1. Statistical evaluation of the homogeneity test data (n = 20 analyses)

Pesticide	Mean Conc. (mg/Kg)	Ss^2	c	$Ss^2 < c$ Pass/Fail
Acetamiprid	0.223	0	9.16×10^{-4}	Pass
Anthraquinone	0.054	0	3.17×10^{-5}	Pass
Bifenthrin	0.777	2.51×10^{-5}	6.41×10^{-3}	Pass
Buprofezin	0.187	2.33×10^{-6}	6.47×10^{-4}	Pass
Carbendazim	0.022	8.46×10^{-6}	1.29×10^{-5}	Pass
Chlorfenapyr	1.195	1.88×10^{-3}	1.64×10^{-2}	Pass
Chlorpyrifos	0.043	2.12×10^{-5}	4.48×10^{-5}	Pass
Cyfluthrin	0.013	4.22×10^{-7}	1.89×10^{-6}	Pass
Cypermethrin	0.163	2.69×10^{-5}	3.39×10^{-4}	Pass
Dicofol*	0.069	1.52×10^{-6}	5.68×10^{-5}	Pass
Endosulfan alpha	0.035	1.46×10^{-6}	1.69×10^{-5}	Pass
Endosulfan beta	0.074	0	8.96×10^{-5}	Pass
Endosulfan sulfate	0.095	0	1.18×10^{-4}	Pass
Fenpropathrin	0.145	7.88×10^{-7}	2.41×10^{-4}	Pass
Fipronil	0.024	1.65×10^{-6}	7.99×10^{-6}	Pass
Imidacloprid	0.159	1.65×10^{-6}	2.85×10^{-4}	Pass
Lambda-Cyhalothrin	0.169	8.70×10^{-6}	3.23×10^{-4}	Pass
Methomyl	0.072	0	1.02×10^{-4}	Pass

[7] M. Thompson, S. L. R. Ellison, and R.Wood. The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories. Pure Appl. Chem., 2006, 78 (1), 145–196.

Pesticide	Mean Conc. (mg/Kg)	Ss^2	c	$Ss^2 < c$ Pass/Fail
Pyridaben	0.018	5.85×10^{-7}	3.74×10^{-6}	Pass
Triazophos	0.040	5.85×10^{-7}	2.36×10^{-5}	Pass

S_s: Between-Sampling Standard Deviation
*Dicofol degrades more than 50% at the used analytical method conditions.

As can be seen from Table 2.1., all the incurred pesticides in tea matrix passed the homogeneity test.

2.4 Stability tests

The analytical method described briefly in section 2.1 was also used for the stability tests.

The tests were performed on two occasions. On each occasion, a single bag stored in the fridge at 4°C was chosen randomly and duplicate analyses were performed.

The two occasions were:
- Day 1: coinciding with the first test item shipments, which took place on 8th September 2014.
- Day 2: shortly after the deadline for reporting results, on 27th September 2014.

The individual results are given in Table 2.2. In general, these tests did not show any significant decrease in the pesticide concentrations. This demonstrates that, for the duration of the proficiency test, and provided that the storage conditions prescribed were followed, the time elapsed until the participants performed the analysis would not have influenced their results.

Table 2.2. Statistical test for analytical precision and to demonstrate pesticides stability after a time-elapse interval.

Pesticide	Concentration (mg/kg)							
	Day 1 (1st analysis)	Day 1 (2nd analysis)	Mean 1	Day 2 (1st analysis)	Day 2 (2nd analysis)	Mean 2	(M2-M1) / M1	%
Acetamiprid	0.274	0.250	0.262	0.227	0.298	0.263	0.0019	0
Anthraquinone	0.058	0.055	0.057	0.051	0.052	0.052	-0.088	-9
Bifenthrin	0.779	0.778	0.778	0.802	0.799	0.801	0.029	3
Buprofezin	0.203	0.195	0.199	0.179	0.162	0.171	-0.143	-14
Carbendazim	0.020	0.022	0.021	0.021	0.018	0.020	-0.071	-7
Chlorfenapyr	1.045	1.062	1.054	1.036	1.003	1.020	-0.032	-3
Chlorpyrifos	0.044	0.046	0.045	0.041	0.043	0.042	-0.067	-7
Cyfluthrin	0.012	0.014	0.013	0.013	0.015	0.014	0.077	8
Cypermethrin	0.161	0.166	0.164	0.175	0.173	0.174	0.064	6
Dicofol*	0.047	0.044	0.046	0.058	0.052	0.055	0.209	21
Endosulfan alpha	0.042	0.037	0.040	0.032	0.036	0.034	-0.139	14

Pesticide	Concentration (mg/kg)							
	Day 1 (1st analysis)	Day 1 (2nd analysis)	Mean 1	Day 2 (1st analysis)	Day 2 (2nd analysis)	Mean 2	(M2-M1) / M1	%
Endosulfan beta	0.090	0.094	0.092	0.078	0.085	0.082	-0.114	-11
Endosulfan sulfate	0.083	0.085	0.084	0.096	0.097	0.097	0.149	15
Fenpropathrin	0.151	0.157	0.154	0.152	0.164	0.158	0.026	3
Fipronil	0.028	0.029	0.029	0.032	0.027	0.030	0.035	4
Imidacloprid	0.172	0.171	0.172	0.160	0.172	0.166	-0.032	-3
λ-Cyhalothrin	0.179	0.172	0.176	0.170	0.169	0.170	-0.034	-3
Methomyl	0.087	0.080	0.084	0.084	0.106	0.095	0.138	14
Pyridaben	0.015	0.016	0.016	0.016	0.018	0.017	0.097	10
Triazophos	0.046	0.047	0.047	0.045	0.051	0.048	0.032	3

*Dicofol degrades more than 50% at the used analytical method conditions.

2.5 Distribution of test item and protocol to participants

One bag of of the test item was shipped to each participant in boxes at ambient temperature. The samples were sent on 27th September 2014.

Before test item shipment, the laboratories received full instructions (The Specific Protocol) for the receipt, storage and analysis of the test items although they were encouraged to use their normal sample receipt procedure and method(s) of analysis. These instructions were uploaded onto the open site of the EURL-FV webpage as part of the Specific Protocol. The Application Form was sent to the participants by e-mail as an excel spreadsheet. The Target Pesticide List and the Minimum Required Reporting Levels (MRRLs), as established by the Organiser, were uploaded onto the EURL-FV open website.

3. STATISTICAL METHODS

3.1 False positives and negatives

3.1.1 False positives

These are results above the MRRLs that show the apparent presence of any pesticide that was listed in the Target Pesticide List, but which was: (i) not detected by the Organiser, even after repeated analyses, and (ii) not detected by most of the participating laboratories that had targeted that specific pesticide.

Results reported which were lower than the MRRL, have been disregarded and have not therefore been considered to be false positives.

No z-score values have been calculated for false positive results. Any laboratory reporting a false positive, even when reporting the necessary number of pesticides to obtain sufficient scope, has been classified into Category B.

3.1.2 False negatives

These are results for any pesticide reported by the laboratories as "analysed" but reported without numerical values, although they were detected by the Organiser and the majority of the participants that had targeted this specific pesticide, at, or above, the MRRL.

z-Scores have been calculated for all pesticides detected and reported at levels at, or above, the MRRL, including false negatives. However, these z-scores were not taken into account in assessing the 90 %, or more, of pesticides present in the sample needed to be classified into Category A.

3.2 Estimation of the assigned values

The assigned values for each pesticide were based on the median level of all the reported results, excluding outliers. Individual results without any numerical values reported, such as detected (D), were not considered. The spread of results for each pesticide was tested for multimodality.

Taking into account the regulation for robust analysis in ISO 13528[8], an uncertainty accompanied the assigned value for each pesticide, which was calculated according to the following equation:

$$u = \frac{1.25 \cdot \frac{CV(\%)}{100} \cdot \mu}{\sqrt{n}}$$

[8] ISO 13528:2005 "Statistical methods for use in proficiency testing by interlaboratory comparisons"

Where:

- u is the uncertainty in mg/Kg.
- CV (%) is the robust relative standard deviation.
- μ is the assigned value.
- n is the total number of laboratories reporting a result for each pesticide, excluding outliers.

3.3 Fixed target standard deviations

Based on the experience gained from previous EU proficiency tests and recommendations from the Advisory Group, a fixed relative standard deviation (FFP RSD) of 25 % was chosen[9]. This is in line with the internationally-accepted Target Measurement Uncertainty of 50 % for multiresidue analysis of pesticides[10], which is derived from, and linked to, the EUPTs.
The same target RSD has been applied to all the pesticides, independent of concentration. The target standard deviation (σ) for each individual pesticide was calculated by multiplying this FFP RSD by the assigned value. The FFP-RSD for each pesticide was compared to CV (%).

3.4 z-Scores

A z-score for each laboratory/pesticide combination was calculated according to the following equation:

$$z = (x-X) / \sigma$$

Where:

- x is the result reported by the participant, the MRRL or the RL (whichever one is lower) for those labs not having detected the presence of the pesticide in the sample.
- X is the assigned value.
- σ is the target standard deviation (the FFP-RSD of 25 % multiplied by the assigned value).

z-Score classification is as follows:

$|z| \leq 2$ Acceptable

$2 < |z| \leq 3$ Questionable

$|z| > 3$ Unacceptable

- Any z-score values of $|z| > 5$ have been reported as '5'.
- No z-score calculations have been performed for false positive results.

[9] P. Medina-Pastor, C. Rodriguez-Torreblanca, A. Andersson, A. R. Fernandez-Alba, European Commission proficiency tests for pesticide residues in fruits and vegetables, Trends in Analytical Chemistry, 2010, 29 (1), 70-83.

[10] P.Medina Pastor, A. Valverde, T. Pihlström, S. Masselter, M. Gamón, M. Mezcua, C. Rodríguez Torreblanca, A. R. Fernández-Alba, Comparative Study of the Main Top-down Approaches for the Estimation of Measurement Uncertainty in Multiresidue Analysis of Pesticides in Fruits and Vegetables, J. Agric. Food Chem., 2011, 59 (14), 7609-7619.

- For false negative results, the MRRL (or RL) has been used to calculate the z-score. These z-scores have also been included in the graphical representation, and are marked with an asterisk.

3.5 Combined z-scores

In order to evaluate each laboratory's overall performance according to the quality of its results and its scope, two classifications - Category A and B - were used. To be classified into Category A, laboratories had to detect (that is *sought and detected*) 90 % or more of the total number of pesticides present in the test item and report no false positives. If these two requirements were met, then the combined z-scores were calculated as the 'Average of the Squared z-scores' (AZ^2)[11].

3.5.1 The Average of the Squared z-Scores (AZ^2)

The 'Average of the Squared z-scores' was introduced for the first time in EUPT-12. The AZ^2 is calculated as follows:

$$AZ^2 = \frac{\sum_{i=1}^{n} Z_i^2}{n}$$

The formula is the sum of the z-scores value, multiplied by itself and divided by the number of z-scores (n) detected by each laboratory, including those from false negatives.

This formula is subsequently used to produce an overall classification of laboratories with three sub-classifications: 'good', 'satisfactory' and 'unsatisfactory'.

$|AZ^2| \leq 2$ Good

$2 < |AZ^2| \leq 3$ Satisfactory

$|AZ^2| > 3$ Unsatisfactory

In this way, a simple, single, combined value is also achieved, as with the previous formula. However, this time, it is more mathematically justifiable as it uses the actual z-score value rather than the factors 1, 3 and 5. Again, the aim is to encourage laboratories to not only improve the accuracy of their results but also to analyse a greater number of pesticides.

Laboratories that did not detect sufficient pesticides, or reported a false positive, have been placed in Category B and no combined z-score has been calculated.

In Appendices 5 and 6, only results of laboratories in Category A have been presented, along with their graphical representations.

[11] P . Medina-Pastor, M. Mezcua, C. Rodríguez-Torreblanca, A. R. Fernández-Alba, Laboratory assessment by combined z-score values in proficiency tests: experience gained through the European Union proficiency tests for pesticide residues in fruits and vegetables, Anal. Bioanal. Chem., 2010, 397, 3061–3070.

4. RESULTS

4.1 Summary of reported results

Fifty-one laboratories agreed to participate in this proficiency test and all but two submitted results. The results reported by all the laboratories are presented in this report. However, only results reported by laboratories from EU-countries and EFTA-countries (Norway) have been included in the statistical treatment. The results submitted by laboratories in China, Saudi Arabia and Uruguay have not been included. This last group totals four laboratories, two from China, one from Saudi Arabia and Uruguay. Twenty pesticides were present in the test sample. For all of them, except for carbendazim, chlorpyrifos, cyfluthrin, endosulfan alpha, pyridaben and triazophos, statistical results have been calculated and presented in this report because the pesticide MRRL was 0.010 mg/klg and the achieved concentration medians were 0.021, 0.031, 0.013, 0.028, 0.019 and 0.039 mg/kg, repectively. As stated in the general protocol, "In cases of the assigned value being less than a factor of 4 times the MRRL, false negatives will not be assigned as this is not statistically justifiable". For this reason, those pesticides will not be used for the laboratory evaluation. However, for informative purposes only, their histogram will be included in the Final Report. A summary of the reported results can be seen below in Table 4.1.

Table 4.1. Summary of Reported Results

Pesticides	No. of Reported Results	No. of False Negative Results	No. of Not Analysed Results	Percentage of Reported Results (out of 45)*
Acetamiprid	42	1	2	93
Anthraquinone	14	9	23	31
Bifenthrin	41	0	4	91
Buprofezin	42	1	2	93
Carbendazim**	33	8	4	73
Chlorfenapyr	38	0	7	84
Chlorpyrifos**	41	3	1	91
Cyfluthrin**	9	31	5	20
Cypermethrin	40	0	5	89
Dicofol	31	6	8	69
Endosulfan alpha**	37	4	4	82
Endosulfan beta	37	4	4	82
Endosulfan sulfate	42	0	3	93
Fenpropathrin	42	0	3	93
Fipronil	29	9	6	64
Imidacloprid	41	2	2	91
λ-Cyhalothrin	40	1	4	89
Methomyl	35	6	5	78
Pyridaben**	33	10	2	73
Triazophos**	39	3	3	87

* The % of Reported Results comes from 45 laboratories.
**Only for informative purpose (median < 4MRRL).

The laboratories that agreed to participate are listed in Annex 2. All analytical results reported by the participants are given in Appendix 3, whilst the analytical methods used are given in Appendix 7 (available in the EURL-FV web page in electronic format).

4.1.1 False positives

Six laboratories reported results for additional pesticides that were not present in the test item. These pesticides, and the residue levels reported, are presented in Table 4.2. together with the MRRL. Where the reported concentration of the erroneously-detected pesticide was higher than, or equal to, the assigned MRRL value in the Target Pesticide List (Annex 1), the result has been considered as a false positive.

One out of these six laboratories reporting a false positive result has not been classified into Category A despite achieving sufficient scope.

Table 4.2. Laboratories that reported as 'official concentration' results for pesticides which were not present in the test item

Lab. Code	Pesticide	Concentration (mg/kg)	Determination Technique	RL (mg/Kg)	MRRL (mg/Kg)
lab62	Chlorobenzilate	0.011	GC-MS (tQ)	0.01	0.02
lab103	Chlorothalonil	0.011	GC-MS (tQ)	0.01	0.02
lab103	Cyprodynil	0.013	GC-MS (tQ)	0.01	0.02
Lab138	Dichlorvos	0.010	GC-MS (tQ) and LC- MS (tQ)	0.01	0.02
Lab138	Diflubenzuron	0.030	GC-MS (tQ) and LC- MS (tQ)	0.01	0.02
Lab 139	Mepanipyrim	0.052	LC-MS (IT)	0.01	0.02
lab103	Mepanipyrim	0.012	LC- MS (tQ)	0.01	0.02
Lab121	Thiamethoxam	0.011	LC- MS (tQ)	0.01	0.02
lab91	Thiophanate methyl	0.020	LC- MS (tQ)	0.01	0.02

False positives from China, Arabia Saudi and Uruguay have not been included in this table.

If the residue levels reported were below the MRRLs, or if the pesticides did not appear in the pesticide target list included in Annex I, then they were not considered to be false positives.

4.1.2 False negatives

Table 4.3. summarises the results from laboratories that reported false negatives.

Table 4.3. Laboratories that failed to report pesticides which were present in the test item.

Laboratory Code	Acetamiprid	Anthraquinone	Bifenthrin	Buprofezin	Chlorfenapyr	Cypermethrin	Dicofol	Endosulfan beta	Endosulfan sulfate	Fenpropathrin	Fipronil	Imidacloprid	λ-Cyhalothrin	Methomyl	False negatives in total by laboratory
Lab003							ND				ND		ND	ND	4
Lab011							ND								1
Lab015							ND								1
Lab030											ND				1
Lab058											ND				1
Lab090							ND				ND				2
Lab091											ND				1
Lab096		ND						ND							2
Lab099											ND				1
Lab103		ND									ND				2
Lab105				ND											1
Lab110								ND							1
Lab112		ND													1
Lab115		ND						ND						ND	3
Lab119														ND	1
Lab121		ND													1
Lab133		ND						ND							2
Lab134												ND		ND	2
Lab138		ND									ND				2
Lab139		ND					ND							ND	3
Lab173	ND						ND					ND		ND	4
Lab185		ND									ND				2
False negatives in total by pesticide	1	9	0	1	0	0	6	4	0	0	9	2	1	6	

False negatives from China, Araba Saudi and Uruguay have not been included in this table.

4.1.3 Distribution of data

The distributions of the concentrations of the pesticides reported by the laboratories have been plotted as histograms after removing results that were distant from the main population in Appendix 2.

4.2 Assigned values and target standard deviations

The assigned values were based on the robust mean values calculated using all the reported results, but excluding those values that were far from the assigned value, i.e. outliers. The assigned values and the uncertainty for the fourteen pesticides are presented in Table 4.4.

The target standard deviation was calculated using a fixed FFP RSD value of 25 %. For comparison, a robust relative standard deviation (CV(%)) was also calculated for informative purposes. These RSDs can be seen in Table 4.4.

Table 4.4. Robust mean values, uncertainty and %RSDs for all pesticides present in the test item.

Pesticides	MRRL (mg/Kg)	Robust Mean (mg/Kg)	U (mg/kg)	FFP RSD (%)	CV (%)
Acetamiprid	0.01	0.307	0.013	25	22
Anthraquinone	0.01	0.048	0.006	25	39
Bifenthrin	0.01	0.643	0.031	25	25
Buprofezin	0.01	0.157	0.008	25	27
Chlorfenapyr	0.01	0.704	0.029	25	20
Cypermethrin	0.01	0.174	0.011	25	32
Dicofol	0.01	0.265	0.023	25	39
Endosulfan beta	0.01	0.065	0.006	25	42
Endosulfan sulfate	0.01	0.072	0.006	25	43
Fenpropathrin	0.01	0.115	0.005	25	22
Fipronil	0.005	0.022	0.001	25	19
Imidacloprid	0.01	0.121	0.007	25	29
λ-Cyhalothrin	0.01	0.160	0.009	25	27
Methomyl	0.01	0.072	0.003	25	21

4.3 Assessment of laboratory performance

4.3.1 z-Scores

z-Scores were calculated using the FFP RSD of 25 % for all the pesticides present. In Appendix 3, the individual z-scores are presented for each laboratory, together with the median values for each pesticide. The z-scores for China, Saudi Arabia and Uruguay have been included in Appendix 3 but have not been considered in the following table.

Table 4.5. Classification of z-scores for the pesticides reported

Pesticides	Acceptable (%)	Questionable (%)	Unacceptable (%)
Acetamiprid	85.7	4.8	9.5
Anthraquinone	56.5	4.3	39.1
Bifenthrin	85.4	9.8	4.9
Buprofezin	93.0	2.3	4.7
Chlorfenapyr	94.7	5.3	0.0
Cypermethrin	87.5	10.0	2.5
Dicofol	70.3	10.8	18.9
Endosulfan beta	75.6	7.3	17.1
Endosulfan sulfate	81.0	11.9	7.1
Fenpropathrin	95.2	0.0	4.8
Fipronil	73.7	2.6	23.7
Imidacloprid	81.4	9.3	9.3
λ-Cyhalothrin	92.7	4.9	2.4
Methomyl	82.9	2.4	14.6

z-Scores for false negative results have been calculated using the MRRL value given in the Target Pesticide List (Annex 1) or the RL value from the laboratory (whichever was lower).

In Appendix 4, graphical representations of the z-scores are presented. No z-scores have been calculated for false positive results. z-Scores for false negative results have been included on the chart and are indicated by an asterisk. The charts have been constructed using different colour bars according to the determination technique and the extraction method used for each particular pesticide.

4.3.2 Combined z-scores

As previously mentioned in Section 3.5, the AZ^2 formula alone has been applied to categorise laboratories into Category A and B.

The table in Appendix 5 shows the values of individual z-scores for each pesticide and the combined 'Average of the Squared z-scores' (AZ^2) for those laboratories in Category A. In this category are the laboratories that sought and detected thirteen or more compounds and did not report any false positive results. A graphical representation of the results for these laboratories can also be found in Appendix 6.

Twenty of the forty-five EU and EFTA laboratories that submitted results have been classified into Category A (44 %).
From the AZ^2, 85 percent were classed as 'good', 15 percent as 'satisfactory' and none of them were classed as 'unsatisfactory'.
Of the twenty-five laboratories in Category B, one would have been in Category A had they not reported a false positive result.

Table 4.6.1. shows the laboratories in Category A, the number of pesticides reported, the AZ^2 values and their subclassifications. Laboratories that reported false negative results in Category A are marked with an asterisk and laboratories with AZ^2 values greater than 3.0 have been marked with an '↑'.

Table 4.6.2. shows the laboratories in Category B, the number of results reported, and the number of acceptable z-scores. Laboratories reporting a false negative are marked with an asterisk and laboratories reporting a false positive are marked with a '+'.

The AZ^2 graphical representations for laboratories classified into Category A can be seen in Appendix 6. The National Reference Laboratories (NRLs) for Fruit and Vegetables have been plotted using a different colour.

Table 4.6.1. Performance and Classification of laboratories in Category A using the AZ^2 formula

Lab Code	No. of z-scores achieved in total (n)	AZ^2	Classification
Lab060	14	0.3	Good
Lab017	13	0.3	Good
Lab033	13	0.4	Good
Lab107	14	0.5	Good
Lab001	14	0.5	Good
Lab076	14	0.5	Good
Lab021	13	0.7	Good
Lab061	13	0.7	Good
Lab075	14	0.7	Good
Lab040	13	1.1	Good
Lab079	14	1.1	Good

Lab Code	No. of z-scores achieved in total (n)	AZ^2	Classification
Lab068	14	1.3	Good
Lab049	14	1.4	Good
Lab015*	13	1.5	Good
Lab151	13	1.6	Good
Lab031	13	1.6	Good
Lab053	14	1.9	Good
Lab112*	13	2.1	Satisfactory
Lab008	13	2.4	Satisfactory
Lab119*	13	2.5	Satisfactory

* Laboratories reporting a false negative result.
↑ Laboratories with AZ^2 values > 3

Table 4.6.2. Performance of laboratories in Category B.

Lab Code	No. of acceptable z-scores	No. of pesticides detected	No. of total z-scores	% No. of detected z-scores / No. of pesticides present
Lab062+	13	14	14	100
Lab105*	11	12	12	86
Lab011*	11	12	13	86
Lab030*	10	12	13	86
Lab091*	12	12	13	86
Lab096*	12	12	14	86
Lab099*	4	11	12	79
Lab103*	10	12	14	86
Lab110*	12	12	13	86
Lab133*	10	12	14	86
Lab138*	12	12	14	86
Lab185*	12	12	14	86
Lab139*	10	11	14	79
Lab090*	10	11	13	79
Lab121*	8	11	12	79
Lab140	8	11	11	79
Lab115*	10	10	13	71
Lab173*	6	9	12	64
Lab058*	5	8	9	57
Lab003*	4	7	11	50
Lab134*	5	7	9	50
Lab047	5	6	6	43
Lab130*	4	4	4	29
Lab029	3	3	3	21
Lab156	2	2	2	14

* Laboratories reporting a false negative result.
+ Laboratories reporting a false positive result.

5. CONCLUSIONS

Fifty-one laboratories agreed to participate in EUPT-T02. Out of these, two did not submit results. Four of those submitting results were not from EU or EFTA countries; therefore no statistical analysis was performed on their results.

The pesticides present in the tea test item were all incurred in the bought tea sample. Pesticides considered as positives were those which were reported by both the Organiser and the majority of participants.

For each laboratory/pesticide combination, z-scores based on the FFP RSD of 25 % have been calculated. The different chromatographic techniques used by the participant laboratories, whether gas or liquid, as well as the extraction method used, are shown in the z-score graphs. Asterisks have been used to mark each bar of the chart to represent a false negative result reported as 'ND' by a laboratory. Classification of z-score values into 'acceptable', 'questionable' or 'unacceptable' has also been undertaken.

The criterion of using the Average of Squared z-Scores formula has been used for the evaluation of the participant laboratories. Laboratories reporting thirteen or more quantitative results, and no false positive results, were considered to have sufficient scope and were therefore classified into Category A. Laboratories in Category A were also classed as 'good', 'satisfactory' or 'unsatisfactory'. Laboratories reporting false negatives were marked with an asterisk and those obtaining an AZ^2 value greater than 3 were marked with a '↑'.

Those laboratories that reported less than thirteen results were considered as having insufficient scope and were automatically classified into Category B, together with those reporting one, or more, false positive results. These laboratories have been categorised depending on the number of pesticides detected and quantified out of the total (fourteen). Laboratories reporting false negatives were marked with an asterisk. Laboratories having reported a false positive have been marked with a '+'.

The median value for each pesticide was used as the assigned value or "true" concentration, which was also used to calculate the z-scores. Results were required from the laboratories not only for the pesticides, as defined by the MRL definition, but also for all the individual components that are included in the MRL definition.

In this PT, all the participant laboratories have added water to hydrate the sample prior to the extraction process.

The difficulties of this matrix type have been evaluated as a consequence of the large amount of coextractive natural components provoking higher dispersion (CV) than in most fruits and vegetables. For antraquinone, dicofol, endosulfan beta and endosulfan sulfate (the CVs of 39,

39, 42 and 43%, respectively) are notable. It is worth to note that the population of the results for anthraquinone is only 14, so higher dispersion can be expected.

Overall, the results can be considered to be good with regard to the z-scores for each pesticide present in the test item. For the majority of the pesticides, a low number of unacceptable results were obtained in terms of z-scores, except for antraquinone, dicofol, endosulfan beta and fipronil (36.4, 18.9, 17.1 and 25.6 %, respectively).

As happened in the previous PT-T01, the small population of the results obtained from modified QuEChERS with calcium chloride and the large population of laboratories employing QuECHERS methodologies does not allow us to draw definitive conclusions about the improvemet due to the modification.

6. ACKNOWLEDGEMENTS

The Organiser is most grateful to the European Commission for funding this European Proficiency Test in Tea 02.

The Organiser wishes to thank the members of the Quality Control Group and the Scientific Committee for their invaluable expert advice. Many thanks also to the Statistical Group for their cooperation.

The Organiser wishes to give a special thank-you to the University of Almeria for the use of their facilities.

APPENDIX 1. Homogeneity data.

Acetamiprid (mg/Kg)		Anthraquinone (mg/Kg)		Bifenthrin (mg/Kg)		Buprofezin (mg/Kg)	
Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2
0.248	0.231	0.055	0.053	0.775	0.779	0.160	0.182
0.250	0.226	0.054	0.053	0.776	0.763	0.187	0.196
0.232	0.210	0.053	0.052	0.772	0.778	0.201	0.213
0.212	0.228	0.052	0.055	0.789	0.780	0.207	0.186
0.211	0.240	0.054	0.053	0.774	0.783	0.211	0.195
0.233	0.237	0.053	0.056	0.782	0.789	0.169	0.200
0.215	0.210	0.053	0.053	0.770	0.767	0.157	0.197
0.265	0.194	0.054	0.053	0.777	0.789	0.162	0.200
0.196	0.208	0.053	0.054	0.780	0.775	0.182	0.187
0.200	0.206	0.053	0.054	0.763	0.773	0.180	0.177

Carbendazim (mg/Kg)		Chlorfenapyr (mg/Kg)		Chlorpyrifos (mg/Kg)		Cyfluthrin (mg/Kg)	
Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2
0.019	0.022	1.196	1.150	0.044	0.053	0.013	0.013
0.025	0.024	1.195	1.125	0.056	0.044	0.014	0.013
0.020	0.025	1.212	1.151	0.033	0.031	0.013	0.014
0.017	0.015	1.151	1.203	0.033	0.042	0.012	0.012
0.028	0.026	1.189	1.210	0.049	0.044	0.013	0.013
0.025	0.030	1.295	1.304	0.037	0.047	0.014	0.014
0.021	0.017	1.195	1.119	0.047	0.040	0.012	0.013
0.019	0.024	1.258	1.244	0.040	0.040	0.013	0.013
0.026	0.021	1.154	1.102	0.047	0.045	0.014	0.014
0.024	0.020	1.254	1.188	0.048	0.050	0.014	0.014

Cypermethrin (mg/Kg)		Dicofol (mg/Kg)		Endosulfan alpha (mg/Kg)		Endosulfan beta (mg/Kg)	
Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2
0.154	0.139	0.068	0.066	0.034	0.035	0.071	0.078
0.157	0.169	0.067	0.068	0.035	0.030	0.072	0.066
0.169	0.178	0.069	0.068	0.036	0.037	0.083	0.069
0.176	0.169	0.065	0.067	0.033	0.035	0.069	0.071
0.171	0.157	0.073	0.066	0.038	0.039	0.077	0.081
0.167	0.163	0.070	0.065	0.033	0.032	0.075	0.078
0.163	0.160	0.069	0.064	0.035	0.032	0.086	0.069
0.162	0.164	0.071	0.074	0.032	0.036	0.077	0.071
0.159	0.173	0.069	0.074	0.036	0.032	0.071	0.071
0.151	0.165	0.071	0.069	0.037	0.034	0.074	0.072

APPENDIX 1. Homogeneity data.

Endosulfan sulfate (mg/Kg)		Fenpropathrin (mg/Kg)		Fipronil (mg/Kg)		Imidacloprid (mg/Kg)	
Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2
0.092	0.095	0.149	0.139	0.022	0.024	0.163	0.159
0.100	0.096	0.148	0.141	0.025	0.025	0.162	0.163
0.094	0.100	0.149	0.156	0.026	0.027	0.159	0.161
0.086	0.098	0.140	0.148	0.025	0.026	0.161	0.162
0.096	0.095	0.147	0.144	0.027	0.025	0.160	0.168
0.097	0.094	0.141	0.141	0.023	0.024	0.159	0.161
0.093	0.099	0.147	0.147	0.019	0.024	0.145	0.158
0.096	0.092	0.145	0.148	0.023	0.022	0.161	0.152
0.087	0.100	0.147	0.143	0.023	0.024	0.157	0.158
0.094	0.092	0.141	0.146	0.024	0.022	0.156	0.152

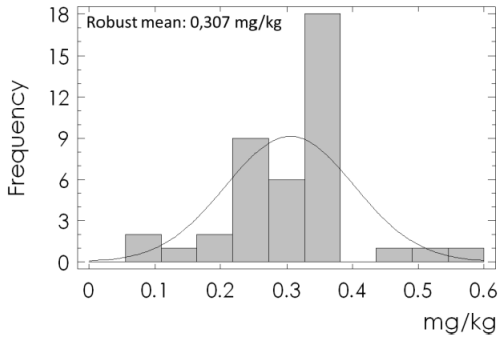
Lambda-Cyhalothrin (mg/Kg)		Methomyl (mg/Kg)		Pyridaben (mg/Kg)		Triazophos (mg/Kg)	
Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2	Replicate 1	Replicate 2
0.165	0.161	0.075	0.076	0.018	0.016	0.041	0.042
0.178	0.165	0.077	0.072	0.018	0.018	0.048	0.042
0.178	0.170	0.074	0.070	0.018	0.017	0.040	0.041
0.165	0.166	0.070	0.073	0.016	0.017	0.040	0.041
0.168	0.171	0.068	0.073	0.019	0.018	0.036	0.042
0.173	0.166	0.069	0.080	0.018	0.019	0.039	0.041
0.179	0.174	0.066	0.070	0.018	0.017	0.040	0.041
0.167	0.171	0.088	0.061	0.020	0.019	0.040	0.038
0.163	0.166	0.063	0.064	0.018	0.019	0.039	0.035
0.161	0.169	0.071	0.072	0.018	0.018	0.036	0.042

The sample numbers used for this test were: 36, 60, 27, 34, 15, 58, 04, 41, 25 and 01.

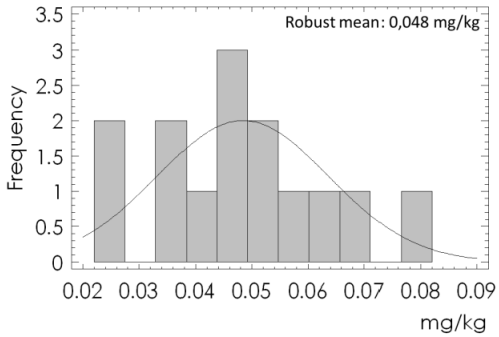
APPENDIX 2. Histograms of residue data for each pesticide from all the laboratories.

Results presented as histograms.

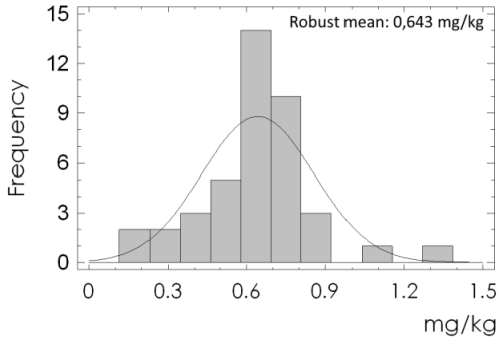
Acetamiprid



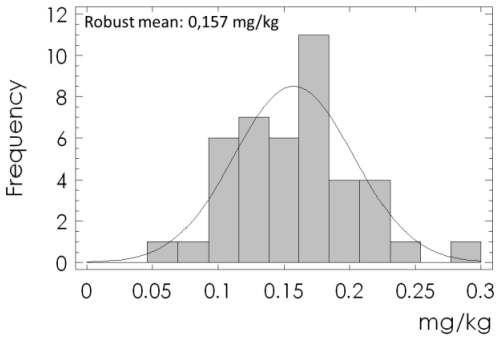
Anthraquinone



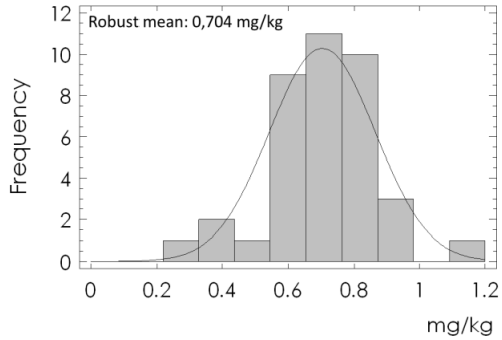
Bifenthrin



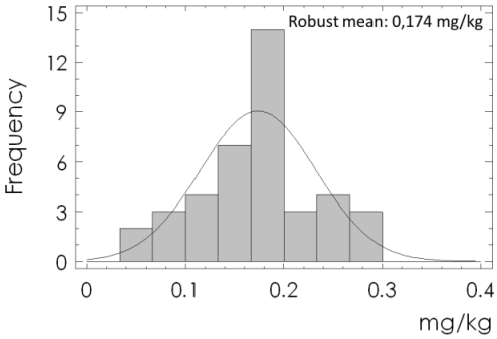
Buprofezin



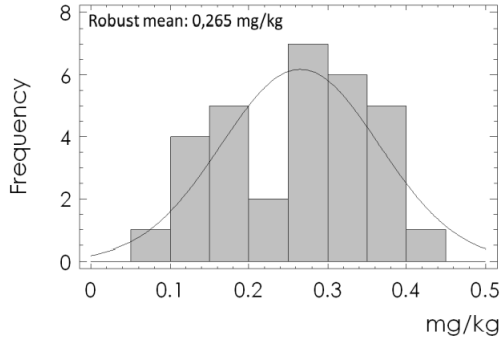
Chlorfenapyr



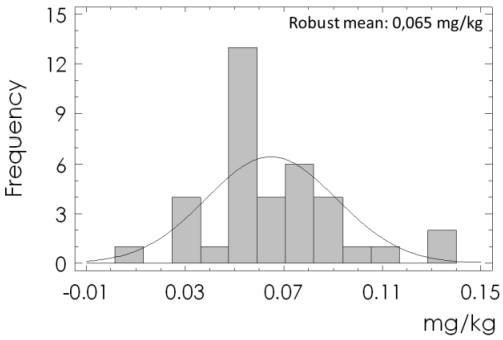
Cypermethrin



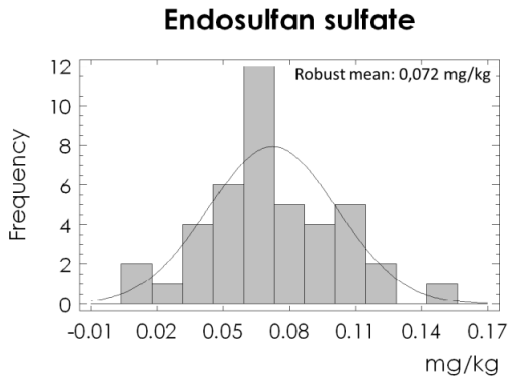
Dicofol

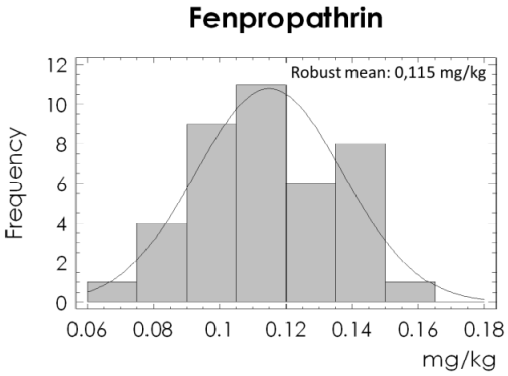


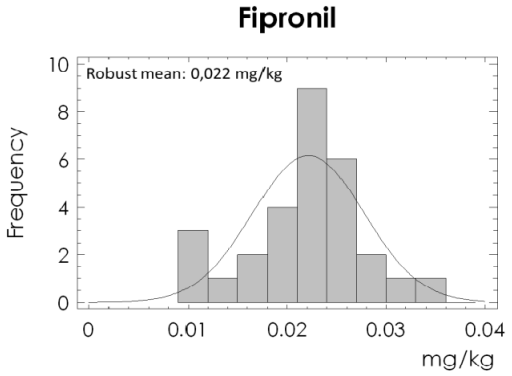
Endosulfan beta

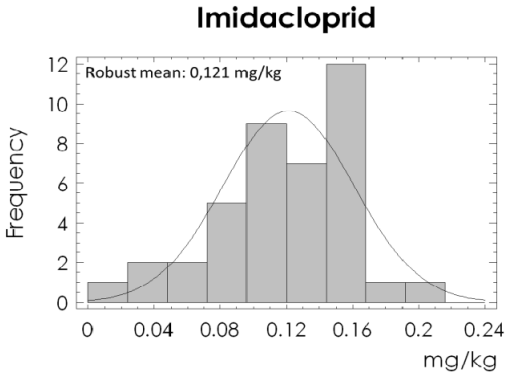


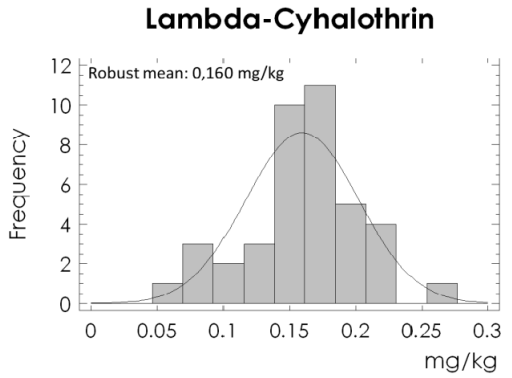
APPENDIX 2. Histograms of residue data for each pesticide from all the laboratories.

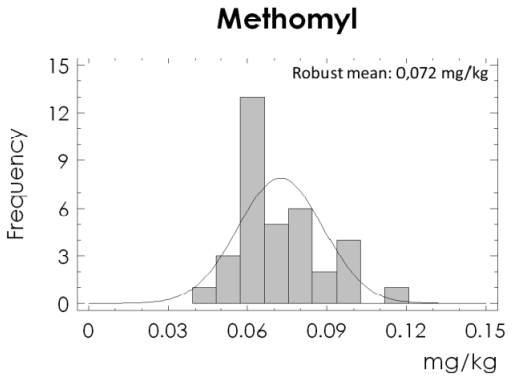








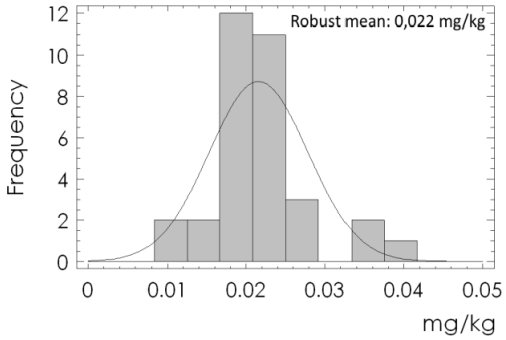




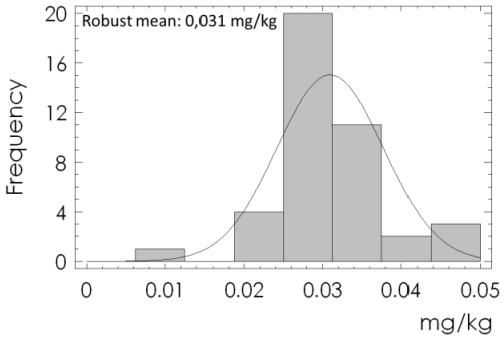
APPENDIX 2. Histograms of residue data for each pesticide from all the laboratories.

For informative purposes only (median < 4MRRL).

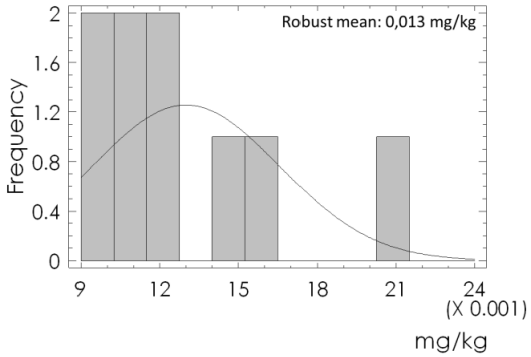
Carbendazim



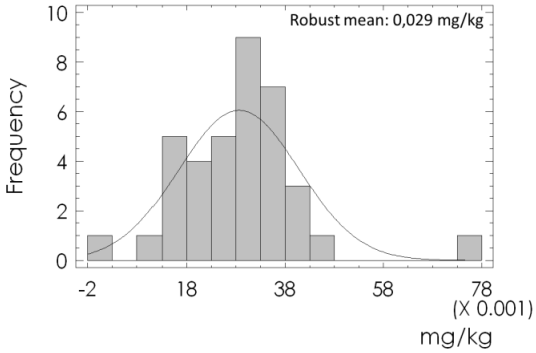
Chlorpyrifos



Cyfluthrin



Endosulfan alpha



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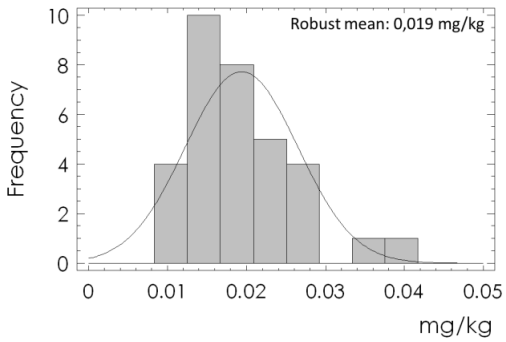
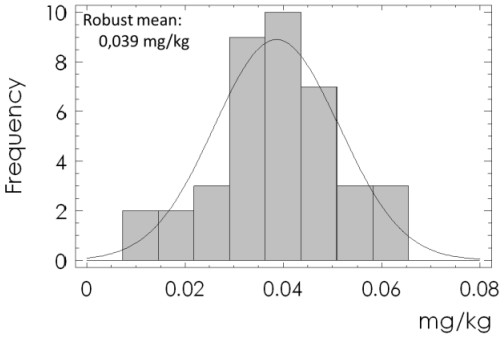


Triazophos



APPENDIX 3. Results (mg/kg) and z-scores for FFP RSD (25 %).

Results given by the laboratories (mg/kg) and their calculated z-score value using FFP RSD 25 %

Lab Code	Acetamiprid	z-Score (FFP RSD 25%)	Anthraquinone	z-Score (FFP RSD 25%)	Bifenthrin	z-Score (FFP RSD 25%)	Buprofezin	z-Score (FFP RSD 25%)	Carbendazim	z-Score (FFP RSD 25%)	Chlorfenapyr	z-Score (FFP RSD 25%)	Chlorpyrifos	z-Score (FFP RSD 25%)	Cyfluthrin	z-Score (FFP RSD 25%)
MRRL (mg/kg)	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Robust mean (mg/kg)	**0.307**		**0.048**		**0.643**		**0.157**		**0.022**		**0.704**		**0.031**		**0.013**	
Lab001	0.310	0.0	0.041	-0.6	0.720	0.5	0.150	-0.2	0.020	-0.4	0.620	-0.5	0.031	0.0	0.011	-0.6
Lab003	0.143	-2.1	NA		0.310	-2.1	0.101	-1.4	ND	-2.2	NA		0.026	-0.6	ND	-0.9
Lab008	0.329	0.3	0.059	0.9	1.094	2.8	0.233	1.9	0.026	0.7	0.799	0.5	0.031	-0.1	ND	-0.9
Lab011	0.290	-0.2	NA		0.830	1.2	0.180	0.6	0.021	-0.2	0.850	0.8	ND	-2.7	ND	-0.9
Lab015	0.369	0.8	0.027	-1.8	0.669	0.2	0.160	0.1	0.022	0.0	0.660	-0.3	0.029	-0.3	ND	-0.9
Lab017	0.336	0.4	NA		0.620	-0.1	0.165	0.2	0.020	-0.3	0.790	0.5	0.032	0.2	ND	-0.9
Lab019	0.356	0.6	0.056	0.7	0.888	1.5	0.145	-0.3	0.026	0.7	0.702	0.0	0.130	5.0	ND	-0.9
Lab021	0.340	0.4	0.064	1.3	0.694	0.3	0.172	0.4	0.022	0.0	0.850	0.8	0.035	0.5	ND	-0.9
Lab024	0.270	-0.5	NA		0.250	-2.4	NA		ND	-2.2	NA		ND	-2.7	ND	-0.9
Lab029	0.757	5.0	NA		NA		0.209	1.3	0.013	-1.6	NA		0.031	0.0	NA	
Lab030	0.231	-1.0	NA		0.298	-2.1	0.117	-1.0	ND	-2.2	0.743	0.2	0.031	0.0	ND	-0.9
Lab031	0.356	0.6	NA		0.564	-0.5	0.150	-0.2	0.035	2.4	0.774	0.4	0.034	0.4	0.012	-0.3
Lab033	0.262	-0.6	NA		0.723	0.5	0.128	-0.7	0.017	-0.9	0.715	0.1	0.033	0.3	0.011	-0.6
Lab040	0.376	0.9	NA		0.657	0.1	0.170	0.3	0.019	-0.5	0.906	1.1	0.031	0.0	ND	-0.9
Lab047	0.250	-0.7	NA		0.120	-3.3	0.110	-1.2	0.011	-2.0	NA		0.032	0.1	NA	
Lab049	0.334	0.4	0.045	-0.3	0.602	-0.3	0.166	0.2	0.022	0.0	0.771	0.4	0.032	0.1	0.012	-0.3
Lab052	0.371	0.8	0.043	-0.4	0.600	-0.3	0.171	0.4	0.026	0.7	0.654	-0.3	0.029	-0.3	ND	-3.4
Lab053	0.310	0.0	0.050	0.2	0.700	0.4	0.160	0.1	0.017	-0.9	1.110	2.3	0.026	-0.6	0.014	0.3
Lab058	NA		NA		0.885	1.5	0.279	3.1	NA		0.822	0.7	ND	-2.7	NA	
Lab060	0.296	-0.1	0.044	-0.3	0.657	0.1	0.168	0.3	0.020	-0.3	0.557	-0.8	0.027	-0.5	ND	-0.9
Lab061	0.367	0.8	NA		0.731	0.5	0.166	0.2	0.035	2.4	0.687	-0.1	0.031	0.0	ND	-0.9
Lab062	0.179	-1.7	0.038	-0.8	0.451	-1.2	0.129	-0.7	0.011	-2.1	0.593	-0.6	0.025	-0.8	ND	-0.9
Lab068	0.370	0.8	0.069	1.8	0.670	0.2	0.210	1.4	0.017	-0.9	0.730	0.1	0.034	0.4	0.021	2.5
Lab075	0.351	0.6	0.025	-1.9	0.803	1.0	0.203	1.2	0.026	0.7	0.722	0.1	0.028	-0.4	ND	-0.9
Lab076	0.208	-1.3	0.037	-0.9	0.647	0.0	0.129	-0.7	0.020	-0.4	0.687	-0.1	0.030	-0.1	ND	-0.9
Lab079	0.360	0.7	0.048	0.0	0.642	0.0	0.182	0.6	0.024	0.4	0.905	1.1	0.036	0.6	0.016	0.9
Lab089	No results reported															
Lab090	0.332	0.3	NA		0.647	0.0	0.166	0.2	ND	-2.2	0.708	0.0	0.047	2.1	ND	-0.9
Lab091	0.457	2.0	NA		0.550	-0.6	0.195	1.0	0.020	-0.4	0.585	-0.7	0.028	-0.4	ND	-0.9
Lab096	0.258	-0.6	ND	-3.2	0.511	-0.8	0.117	-1.0	0.025	0.5	0.652	-0.3	0.026	-0.6	ND	-0.9
Lab099	0.520	2.8	NA		0.210	-2.7	0.097	-1.5	ND	-2.2	0.250	-2.6	0.048	2.2	ND	-0.9
Lab103	0.227	-1.0	ND	-3.2	0.487	-1.0	0.104	-1.4	0.017	-0.9	0.473	-1.3	0.023	-1.0	ND	-0.9
Lab105	0.297	-0.1	NA		0.667	0.1	ND	-3.9	0.016	-1.1	0.697	0.0	0.029	-0.3	ND	-2.5
Lab107	0.351	0.6	0.053	0.4	0.662	0.1	0.183	0.7	0.023	0.1	0.635	-0.4	0.034	0.4	ND	-0.9
Lab110	0.334	0.4	NA		0.789	0.9	0.166	0.2	0.018	-0.7	0.903	1.1	0.023	-1.0	ND	-0.9
Lab112	0.360	0.7	ND	-3.2	0.680	0.2	0.220	1.6	0.017	-0.9	0.625	-0.4	0.038	0.9	ND	-0.9
Lab115	0.240	-0.9	ND	-3.2	0.720	0.5	0.150	-0.2	0.040	3.3	0.800	0.5	0.031	0.0	ND	-0.9
Lab116	0.255	-0.7	NA		0.255	-2.4	0.227	1.8	NA		0.730	0.1	ND	-2.7	ND	-0.9
Lab119	0.326	0.2	0.078	2.5	0.891	1.5	0.227	1.8	0.022	0.0	0.851	0.8	0.036	0.7	ND	-0.9
Lab121	0.551	3.2	ND	-3.2	NA		0.153	-0.1	0.024	0.4	NA		0.036	0.6	ND	-0.9

APPENDIX 3. Results (mg/Kg) and z-scores for FFP RSD (25%).

Lab Code	Acetamiprid	z-Score (FFP RSD 25%)	Anthraquinone	z-Score (FFP RSD 25%)	Bifenthrin	z-Score (FFP RSD 25%)	Buprofezin	z-Score (FFP RSD 25%)	Carbendazim	z-Score (FFP RSD 25%)	Chlorfenapyr	z-Score (FFP RSD 25%)	Chlorpyrifos	z-Score (FFP RSD 25%)	Cyfluthrin	z-Score (FFP RSD 25%)
MRRL (mg/kg)	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**	
Robust mean (mg/kg)	**0.307**		**0.048**		**0.643**		**0.157**		**0.022**		**0.704**		**0.031**		**0.013**	
Lab130	0.330	0.3	NA		NA		NA		ND	-2.2	NA		0.026	-0.6	NA	
Lab133	0.230	-1.0	ND	-3.2	0.670	0.2	0.130	-0.7	ND	-2.2	0.680	-0.1	ND	-2.7	ND	-0.9
Lab134	0.071	-3.1	NA		1.300	4.1	0.091	-1.7	NA		NA		0.028	-0.4	0.010	-0.9
Lab138	0.364	0.7	ND	-3.2	0.796	1.0	0.194	0.9	0.021	-0.2	0.841	0.8	0.027	-0.5	0.010	-0.9
Lab139	0.240	-0.9	ND	-3.2	0.585	-0.4	0.104	-1.4	ND	-2.2	0.393	-1.8	0.023	-1.0	ND	-0.9
Lab140	0.059	-3.2	NA		0.520	-0.8	0.120	-0.9	NA		0.630	-0.4	0.026	-0.6	ND	-0.9
Lab151	0.229	-1.0	NA		0.420	-1.4	0.111	-1.2	0.024	0.4	0.631	-0.4	0.041	1.3	ND	-0.9
Lab156	NA		NA		NA		NA		NA		NA		NA		NA	
Lab173	ND	-3.9	NA		0.380	-1.6	0.050	-2.7	ND	-2.2	0.390	-1.8	0.010	-2.7	ND	-0.9
Lab174	No results reported															
Lab185	0.379	0.9	ND	-3.2	0.773	0.8	0.198	1.0	0.027	0.9	0.709	0.0	0.044	1.7	ND	-0.9

APPENDIX 3. Results (mg/kg) and z-scores for FFP RSD (25 %).

Lab Code	Cypermethrin	z-Score (FFP RSD 25%)	Dicofol	z-Score (FFP RSD 25%)	Endosulfan alpha	z-Score (FFP RSD 25%)	Endosulfan beta	z-Score (FFP RSD 25%)	Endosulfan sulfate	z-Score (FFP RSD 25%)	Fenpropathrin	z-Score (FFP RSD 25%)	Fipronil	z-Score (FFP RSD 25%)	Imidacloprid	z-Score (FFP RSD 25%)
MRRL (mg/kg)	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.005**		**0.01**	
Robust mean (mg/kg)	**0.174**		**0.265**		**0.029**		**0.065**		**0.072**		**0.115**		**0.022**		**0.121**	
Lab001	0.160	-0.3	0.400	2.0	0.034	0.7	0.058	-0.4	0.088	0.9	0.120	0.2	0.025	0.5	0.130	0.3
Lab003	0.093	-1.9	ND	-3.8	NA		NA		0.125	2.9	0.099	-0.6	ND	-3.1	0.063	-1.9
Lab008	0.285	2.6	0.346	1.2	0.040	1.5	0.074	0.5	0.101	1.6	0.140	0.9	NA		0.130	0.3
Lab011	0.210	0.8	ND	-3.8	0.035	0.8	0.085	1.2	0.150	4.3	0.120	0.2	0.022	0.0	0.180	2.0
Lab015	0.154	-0.5	ND	-3.8	0.028	-0.1	0.056	-0.6	0.068	-0.2	0.098	-0.6	0.026	0.7	0.118	-0.1
Lab017	0.173	0.0	0.298	0.5	0.037	1.0	0.085	1.2	0.086	0.8	0.114	0.0	0.023	0.1	0.153	1.1
Lab019	0.130	-1.0	0.305	0.6	0.041	1.7	0.068	0.2	0.090	1.0	0.117	0.1	0.023	0.2	0.132	0.4
Lab021	0.175	0.0	NA		0.035	0.8	0.079	0.9	0.095	1.3	0.137	0.8	0.024	0.4	0.154	1.1
Lab024	NA		NA		NA		NA		NA		NA		0.070	5.0	0.120	0.0
Lab029	NA		NA		NA		NA		NA		NA		NA		0.336	5.0
Lab030	0.160	-0.3	0.117	-2.2	0.014	-2.1	0.052	-0.8	0.049	-1.3	0.098	-0.6	ND	-3.1	0.140	0.6
Lab031	0.185	0.3	0.260	-0.1	0.021	-1.1	0.132	4.1	0.057	-0.8	0.125	0.3	0.025	0.5	0.133	0.4
Lab033	0.181	0.2	0.228	-0.6	0.032	0.4	0.055	-0.6	0.063	-0.5	0.097	-0.6	0.021	-0.2	0.145	0.8
Lab040	0.177	0.1	0.281	0.2	0.036	1.0	0.090	1.5	0.088	0.9	0.114	0.0	0.034	2.2	0.156	1.2
Lab047	NA		NA		NA		NA		NA		0.110	-0.2	NA		0.110	-0.4
Lab049	0.239	1.5	0.380	1.7	0.074	5.0	0.075	0.6	0.119	2.6	0.164	1.7	0.027	0.9	0.162	1.4
Lab052	0.137	-0.9	0.606	5.0	0.025	-0.6	0.059	-0.4	0.076	0.2	0.128	0.5	0.023	0.2	0.147	0.9
Lab053	0.210	0.8	0.320	0.8	0.042	1.8	0.130	4.0	0.071	-0.1	0.150	1.2	0.030	1.5	0.130	0.3
Lab058	NA		0.299	0.5	ND	-2.6	0.110	2.8	0.104	1.8	0.260	5.0	ND	-3.1	NA	
Lab060	0.151	-0.5	0.345	1.2	0.029	0.0	0.066	0.1	0.071	-0.1	0.111	-0.1	0.020	-0.4	0.114	-0.2
Lab061	0.261	2.0	0.359	1.4	0.026	-0.4	0.056	-0.6	0.057	-0.8	0.118	0.1	0.023	0.2	0.145	0.8
Lab062	0.117	-1.3	0.443	2.7	0.014	-2.1	0.033	-2.0	0.041	-1.7	0.087	-1.0	0.016	-1.1	0.087	-1.1
Lab068	0.190	0.4	0.150	-1.7	0.034	0.7	0.049	-1.0	0.085	0.7	0.130	0.5	0.011	-2.0	0.093	-0.9
Lab075	0.168	-0.1	0.388	1.9	0.033	0.5	0.065	0.0	0.078	0.3	0.123	0.3	0.024	0.3	0.130	0.3
Lab076	0.126	-1.1	0.270	0.1	0.032	0.4	0.064	-0.1	0.082	0.6	0.093	-0.8	0.017	-0.9	0.092	-1.0
Lab079	0.192	0.4	0.348	1.3	0.032	0.4	0.086	1.3	0.105	1.8	0.111	-0.1	0.032	1.8	0.154	1.1
Lab089	No results reported															
Lab090	0.153	-0.5	ND	-3.8	0.028	-0.1	0.053	-0.8	0.111	2.2	0.078	-1.3	ND	-3.1	0.107	-0.5
Lab091	0.135	-0.9	0.184	-1.2	0.040	1.5	0.055	-0.6	0.065	-0.4	0.140	0.9	ND	-3.1	0.153	1.1
Lab096	0.126	-1.1	0.151	-1.7	0.019	-1.4	ND	-3.4	0.062	-0.6	0.095	-0.7	0.019	-0.5	0.141	0.7
Lab099	0.050	-2.9	NA		0.017	-1.7	0.030	-2.2	0.040	-1.8	0.085	-1.0	ND	-3.1	0.038	-2.7
Lab103	0.040	-3.1	0.305	0.6	0.015	-1.9	0.065	0.0	0.043	-1.6	0.315	5.0	ND	-3.1	0.095	-0.9
Lab105	0.195	0.5	0.109	-2.4	0.021	-1.1	0.051	-0.9	0.071	-0.1	0.143	1.0	0.020	-0.3	0.120	0.0
Lab107	0.206	0.7	0.169	-1.4	0.023	-0.8	0.051	-0.9	0.067	-0.3	0.098	-0.6	0.025	0.6	0.156	1.2
Lab110	0.174	0.0	0.179	-1.3	ND	-2.6	ND	-3.4	0.058	-0.8	0.123	0.3	0.023	0.2	0.120	0.0
Lab112	0.170	-0.1	0.280	0.2	0.034	0.7	0.073	0.5	0.082	0.6	0.150	1.2	0.025	0.5	0.200	2.6
Lab115	0.240	1.5	NA		ND	-2.6	ND	-3.4	0.066	-0.3	0.130	0.5	0.020	-0.4	0.089	-1.1
Lab116	0.730	5.0	NA		ND	-2.6	ND	-3.4	0.730	5.0	0.730	5.0	NA		NA	
Lab119	0.199	0.6	0.215	-0.8	0.024	-0.6	0.078	0.8	0.088	0.9	0.101	-0.5	0.026	0.7	0.035	-2.8
Lab121	0.274	2.3	0.349	1.3	0.046	2.3	0.048	-1.0	0.014	-3.2	0.094	-0.7	0.012	-1.8	0.156	1.2
Lab130	NA		NA		NA		NA		NA		0.150	1.2	NA		0.110	-0.4
Lab133	0.300	2.9	0.200	-1.0	ND	-2.6	ND	-3.4	0.110	2.1	0.110	-0.2	0.022	0.0	0.120	0.0

APPENDIX 3. Results (mg/Kg) and z-scores for FFP RSD (25%).

Lab Code	Cypermethrin	z-Score (FFP RSD 25%)	Dicofol	z-Score (FFP RSD 25%)	Endosulfan alpha	z-Score (FFP RSD 25%)	Endosulfan beta	z-Score (FFP RSD 25%)	Endosulfan sulfate	z-Score (FFP RSD 25%)	Fenpropathrin	z-Score (FFP RSD 25%)	Fipronil	z-Score (FFP RSD 25%)	Imidacloprid	z-Score (FFP RSD 25%)
MRRL (mg/kg)	**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.01**		**0.005**		**0.01**	
Robust mean (mg/kg)	**0.174**		**0.265**		**0.029**		**0.065**		**0.072**		**0.115**		**0.022**		**0.121**	
Lab134	0.190	0.4	NA		0.028	-0.1	0.034	-1.9	0.050	-1.2	NA		NA		ND	-3.7
Lab138	0.164	-0.2	0.371	1.6	0.026	-0.4	0.082	1.0	0.065	-0.4	0.131	0.6	ND	-3.1	0.160	1.3
Lab139	0.119	-1.3	ND	-3.8	0.018	-1.5	0.037	-1.7	0.036	-2.0	0.108	-0.2	0.011	-2.0	0.056	-2.1
Lab140	0.086	-2.0	0.120	-2.2	0.027	-0.3	0.056	-0.6	0.073	0.1	0.087	-1.0	NA		0.018	-3.4
Lab151	0.170	-0.1	0.060	-3.1	0.026	-0.4	0.097	2.0	0.058	-0.8	0.106	-0.3	0.024	0.4	0.110	-0.4
Lab156	NA		NA		0.002	-3.7	0.005	-3.7	0.004	-3.8	NA		NA		NA	
Lab173	0.100	-1.7	ND	-3.8	0.010	-2.6	0.030	-2.2	0.030	-2.3	0.070	-1.6	0.015	-1.3	ND	-3.7
Lab174	No results reported															
Lab185	0.255	1.9	0.291	0.4	0.029	0.0	0.056	-0.6	0.065	-0.4	0.140	0.9	ND	-3.1	0.147	0.9

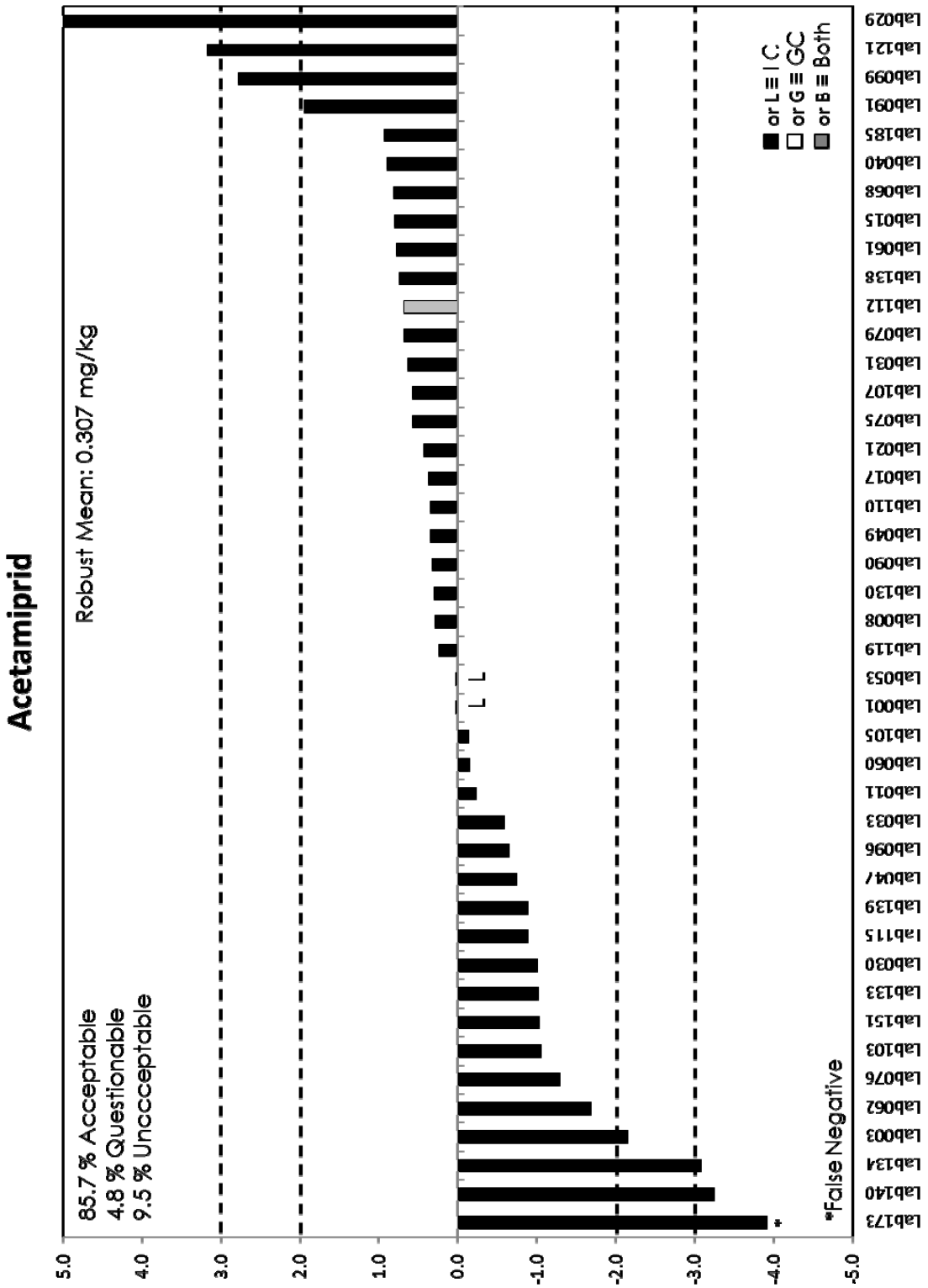
APPENDIX 3. Results (mg/kg) and z-scores for FFP RSD (25 %).

Lab Code	Lambda-Cyhalothrin	z-Score (FFP RSD 25%)	Methomyl	z-Score (FFP RSD 25%)	Pyridaben	z-Score (FFP RSD 25%)	Triazophos	z-Score (FFP RSD 25%)
MRRL (mg/kg)	**0.01**		**0.01**		**0.01**		**0.01**	
Robust mean (mg/kg)	**0.160**		**0.072**		**0.019**		**0.039**	
Lab001	0.143	-0.4	0.065	-0.4	0.015	-0.8	0.038	-0.1
Lab003	ND	-3.8	ND	-3.4	0.016	-0.6	0.033	-0.6
Lab008	0.263	2.6	0.078	0.3	0.027	1.8	0.036	-0.3
Lab011	0.120	-1.0	0.078	0.3	ND	-1.9	0.053	1.4
Lab015	0.176	0.4	0.061	-0.6	0.019	0.0	0.044	0.5
Lab017	0.166	0.2	0.080	0.5	0.020	0.2	0.047	0.8
Lab019	0.145	-0.4	ND	-3.4	0.029	2.1	0.053	1.4
Lab021	0.180	0.5	0.091	1.1	ND	-1.9	0.050	1.1
Lab024	0.140	-0.5	0.050	-1.2	NA		NA	
Lab029	NA		NA		0.029	2.1	NA	
Lab030	0.201	1.0	0.066	-0.3	0.011	-1.7	ND	-3.0
Lab031	0.138	-0.6	0.094	1.2	0.025	1.3	0.036	-0.3
Lab033	0.143	-0.4	0.049	-1.3	0.017	-0.4	0.036	-0.3
Lab040	0.172	0.3	0.098	1.4	0.028	1.9	0.052	1.3
Lab047	NA		0.062	-0.6	0.015	-0.8	0.034	-0.5
Lab049	0.199	1.0	0.075	0.2	0.035	3.4	0.062	2.4
Lab052	0.156	-0.1	ND	-3.7	0.021	0.4	0.051	1.2
Lab053	0.150	-0.3	0.067	-0.3	0.023	0.8	0.048	0.9
Lab058	0.168	0.2	NA		NA		0.060	2.2
Lab060	0.122	-1.0	0.060	-0.6	0.014	-1.1	0.044	0.5
Lab061	0.188	0.7	0.079	0.4	0.041	4.6	0.032	-0.7
Lab062	0.144	-0.4	0.043	-1.6	0.013	-1.3	0.039	0.0
Lab068	0.220	1.5	0.086	0.8	0.013	-1.3	0.043	0.4
Lab075	0.162	0.1	0.065	-0.4	0.026	1.5	0.041	0.2
Lab076	0.150	-0.3	0.076	0.2	ND	-1.9	0.037	-0.2
Lab079	0.215	1.4	0.065	-0.4	ND	-1.9	0.046	0.7
Lab089	No results reported							
Lab090	0.226	1.7	0.058	-0.8	ND	-1.9	0.027	-1.2
Lab091	0.195	0.9	0.095	1.3	0.010	-1.9	0.025	-1.4
Lab096	0.150	-0.3	0.064	-0.4	0.014	-1.1	0.027	-1.2
Lab099	0.055	-2.6	0.054	-1.0	ND	-1.9	ND	-3.0
Lab103	0.080	-2.0	0.055	-0.9	0.015	-0.8	ND	-3.0
Lab105	0.172	0.3	0.065	-0.4	0.016	-0.6	0.037	-0.2
Lab107	0.177	0.4	0.071	0.0	0.019	0.1	0.043	0.4
Lab110	0.180	0.5	0.065	-0.4	0.020	0.2	0.047	0.8
Lab112	0.175	0.4	0.120	2.7	0.018	-0.2	0.065	2.7
Lab115	0.190	0.8	ND	-3.4	ND	-1.9	0.039	0.0
Lab116	NA		NA		0.022	0.6	NA	
Lab119	0.170	0.3	ND	-3.4	0.022	0.6	0.057	1.8
Lab121	0.210	1.3	0.072	0.0	0.019	0.0	0.015	-2.5
Lab130	NA		0.060	-0.7	0.022	0.6	NA	
Lab133	0.150	-0.3	0.066	-0.3	ND	-1.9	0.031	-0.8

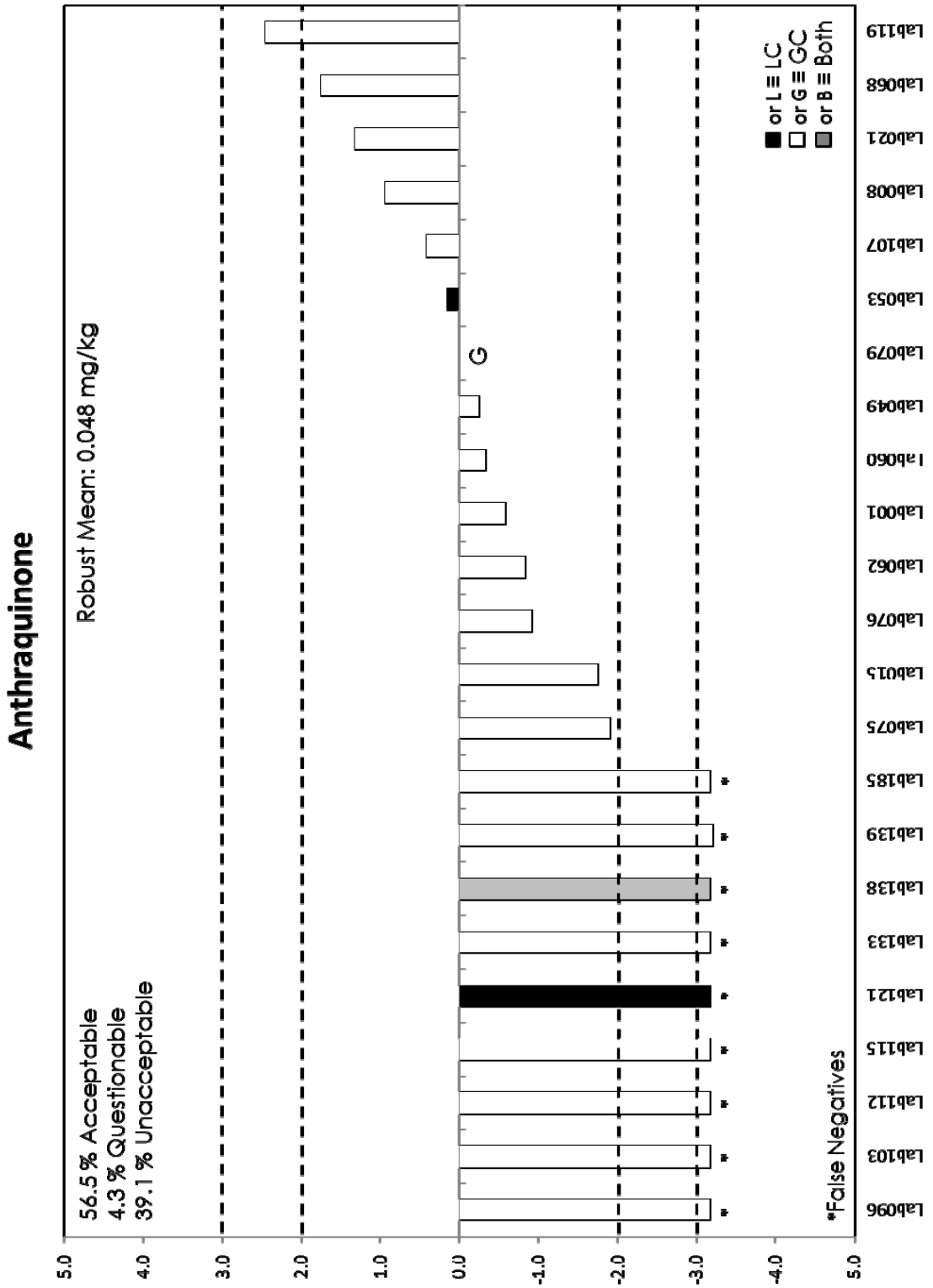
APPENDIX 3. Results (mg/Kg) and z-scores for FFP RSD (25%).

Lab Code	Lambda-Cyhalothrin	z-Score (FFP RSD 25%)	Methomyl	z-Score (FFP RSD 25%)	Pyridaben	z-Score (FFP RSD 25%)	Triazophos	z-Score (FFP RSD 25%)
MRRL (mg/kg)	**0.01**		**0.01**		**0.01**		**0.01**	
Robust mean (mg/kg)	**0.160**		**0.072**		**0.019**		**0.039**	
Lab134	0.150	-0.3	ND	-3.4	ND	-1.9	0.013	-2.7
Lab138	0.147	-0.3	0.080	0.4	0.020	0.2	0.039	0.0
Lab139	0.088	-1.8	ND	-3.4	0.012	-1.5	0.018	-2.2
Lab140	0.086	-1.9	NA		0.013	-1.3	0.032	-0.7
Lab151	0.113	-1.2	0.070	-0.1	0.022	0.6	0.031	-0.8
Lab156	NA		NA		NA		NA	
Lab173	0.100	-1.5	ND	-3.4	0.010	-1.9	0.010	-3.0
Lab174	No results reported							
Lab185	0.147	-0.3	0.102	1.7	ND	-1.9	0.041	0.2

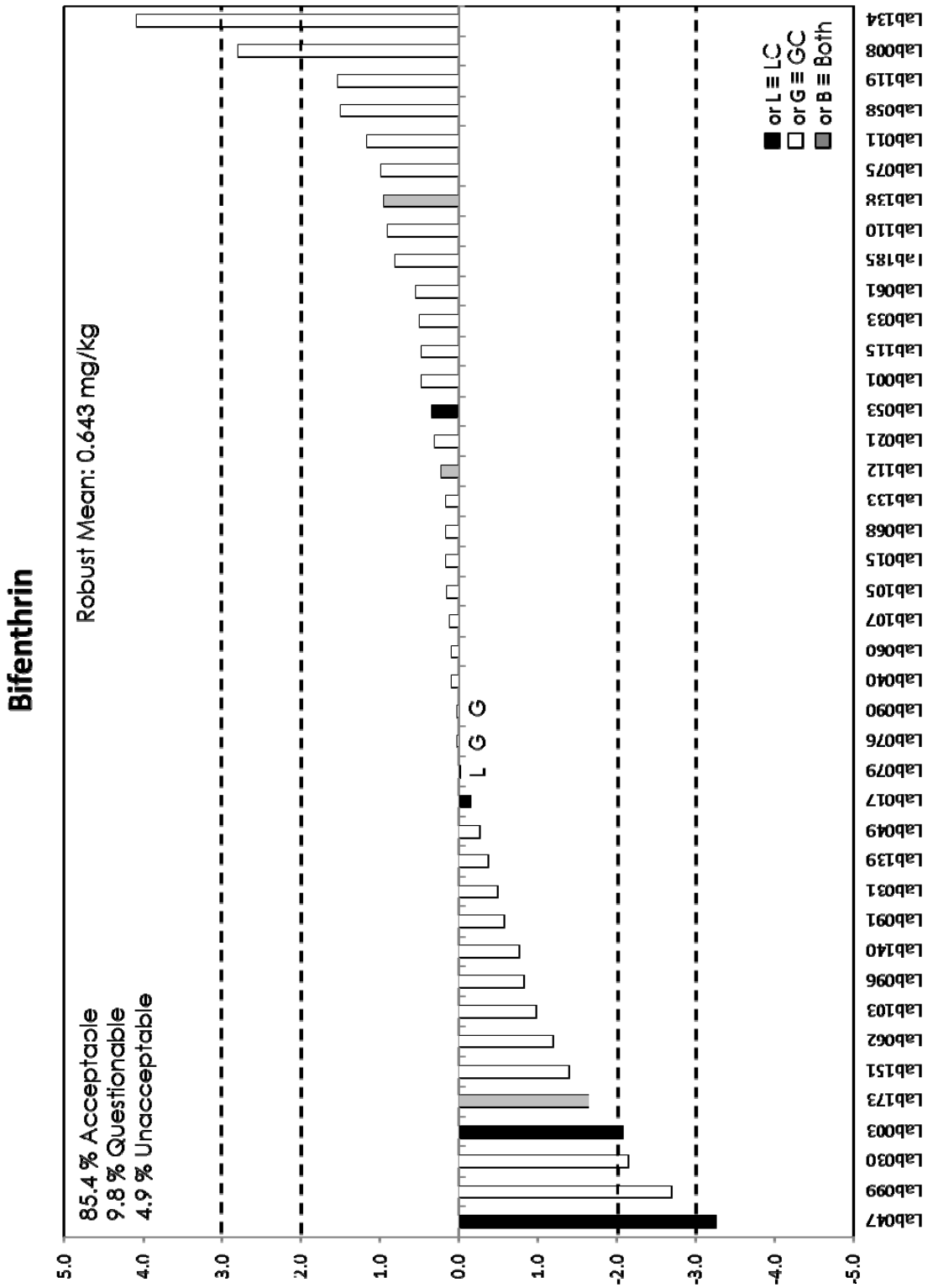
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



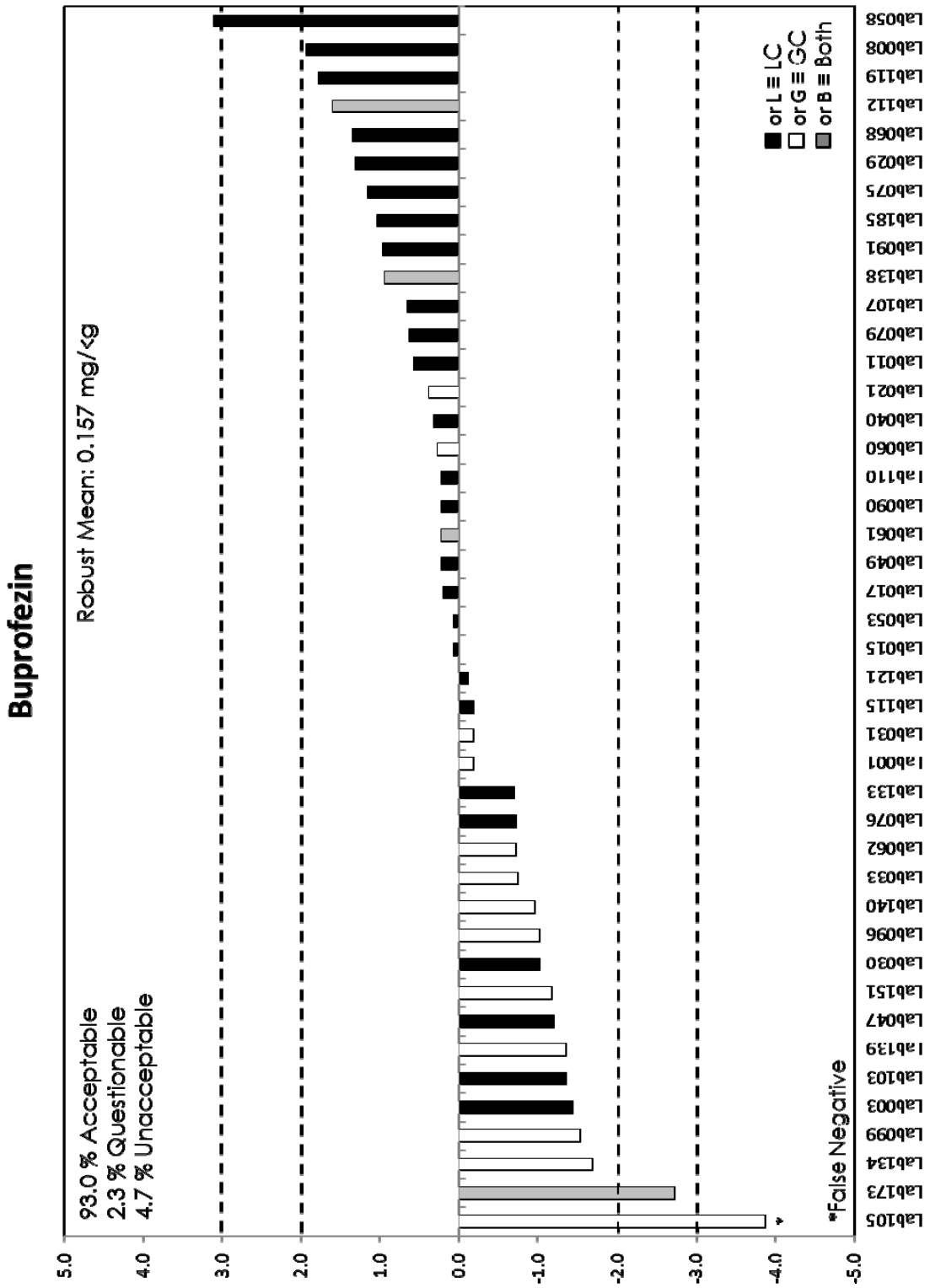
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



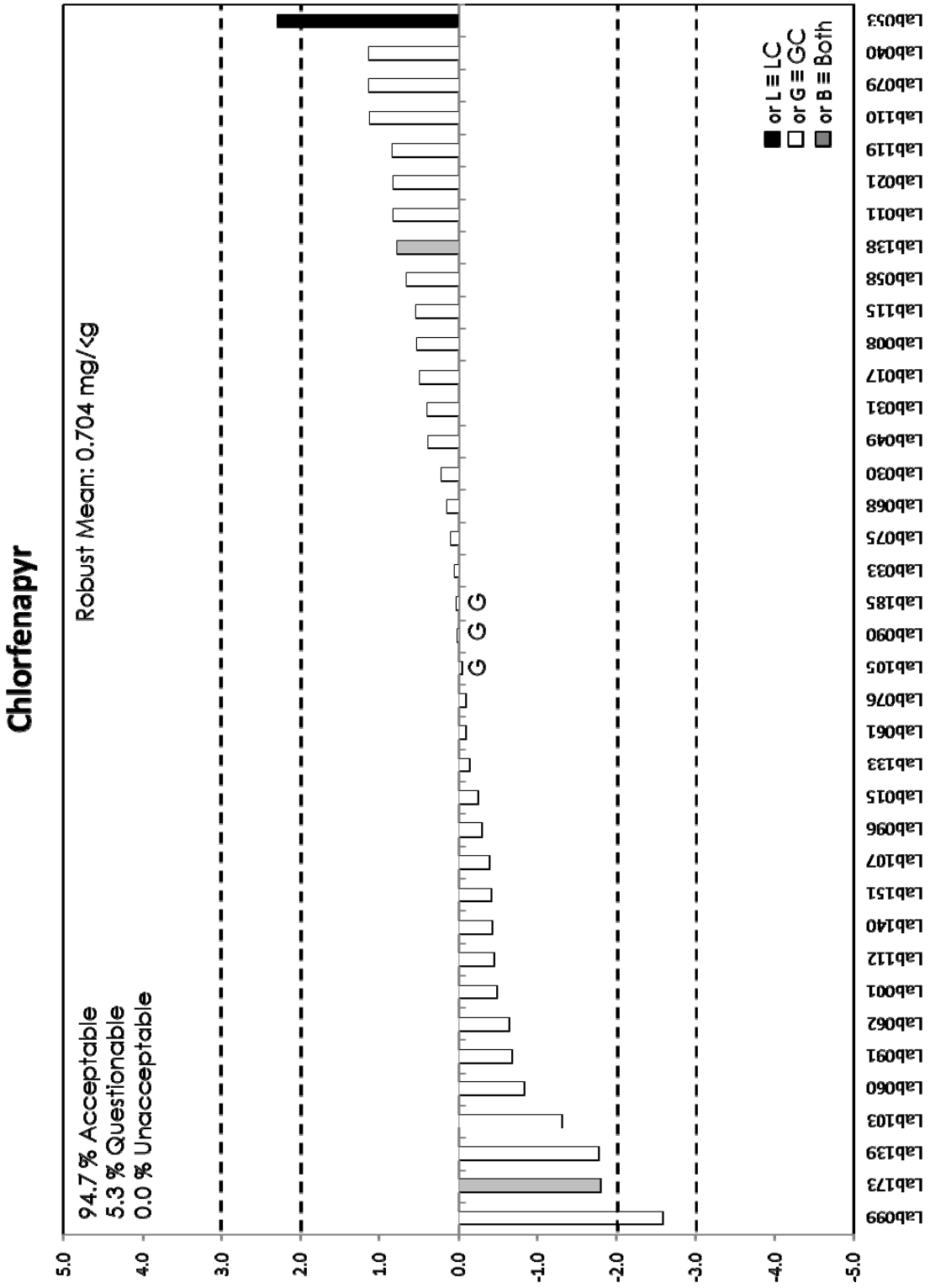
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



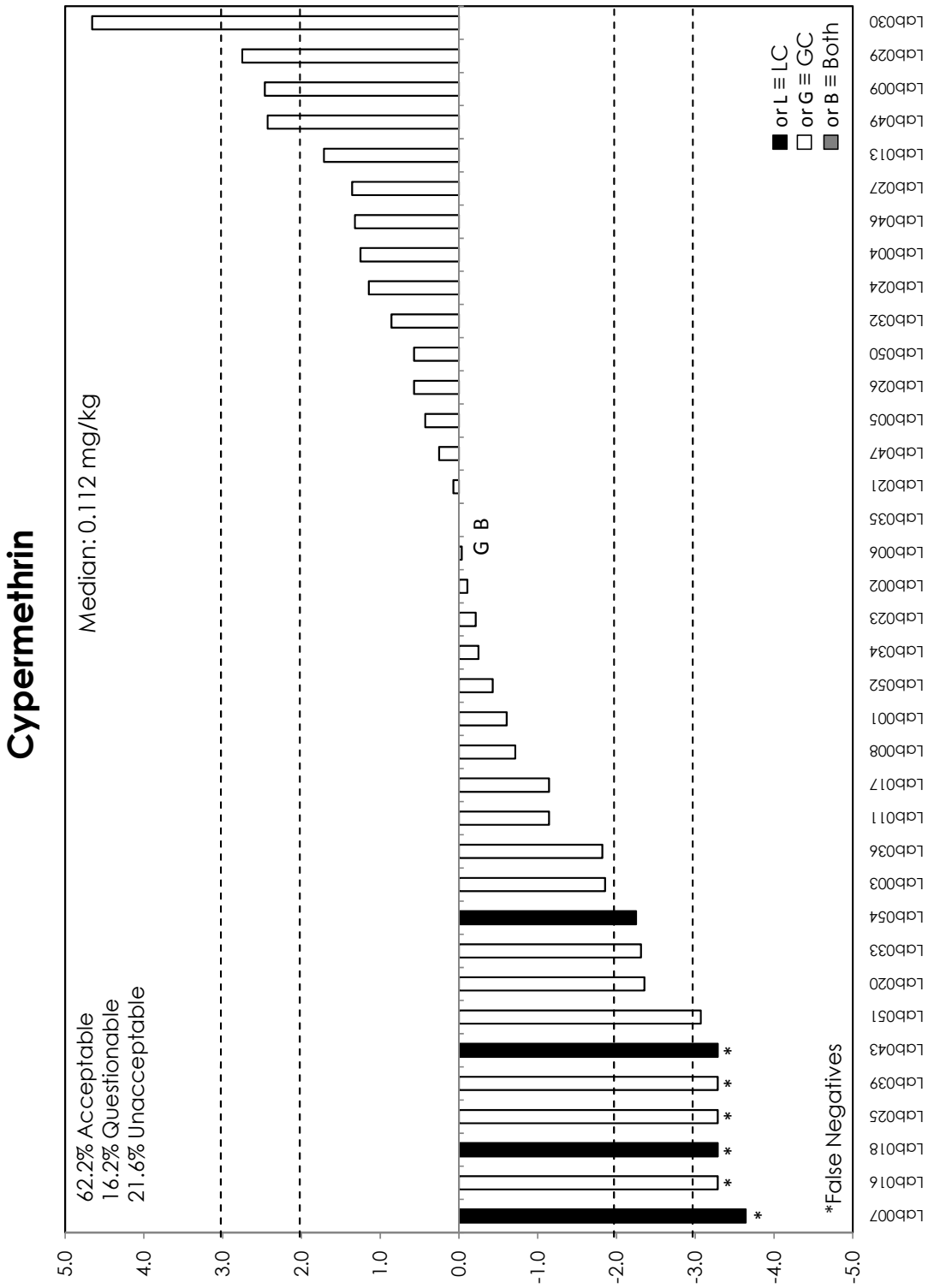
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



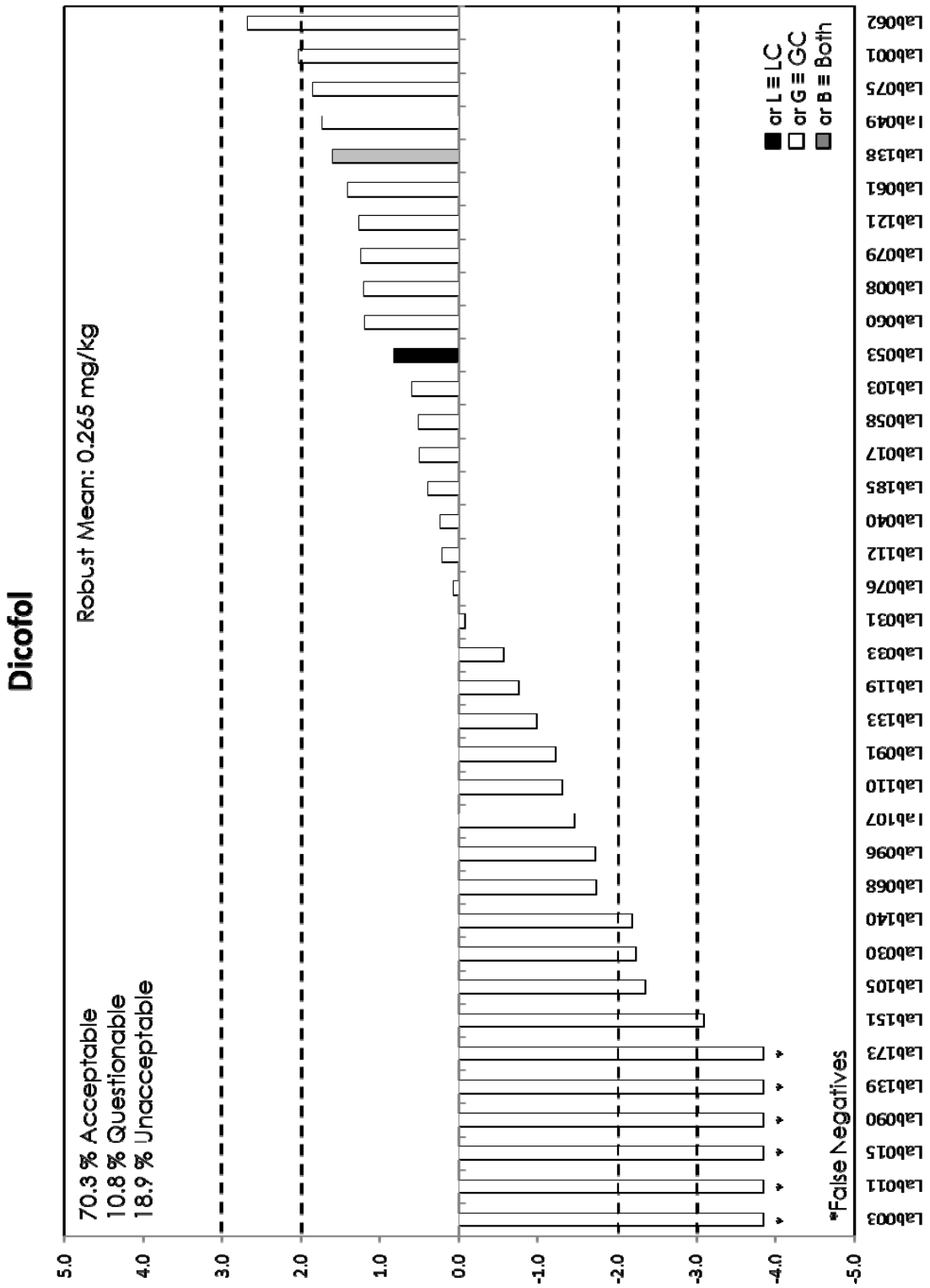
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



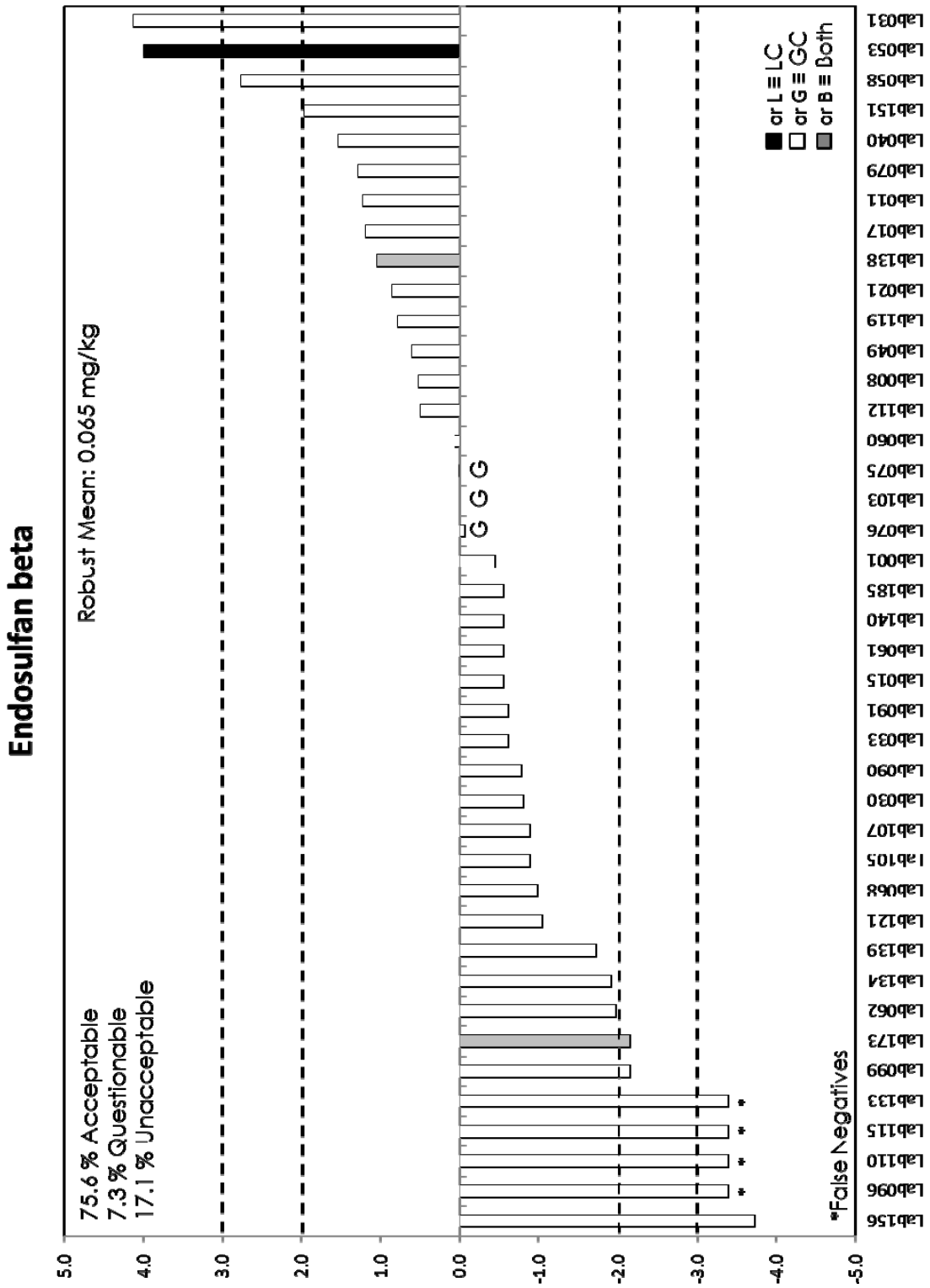
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



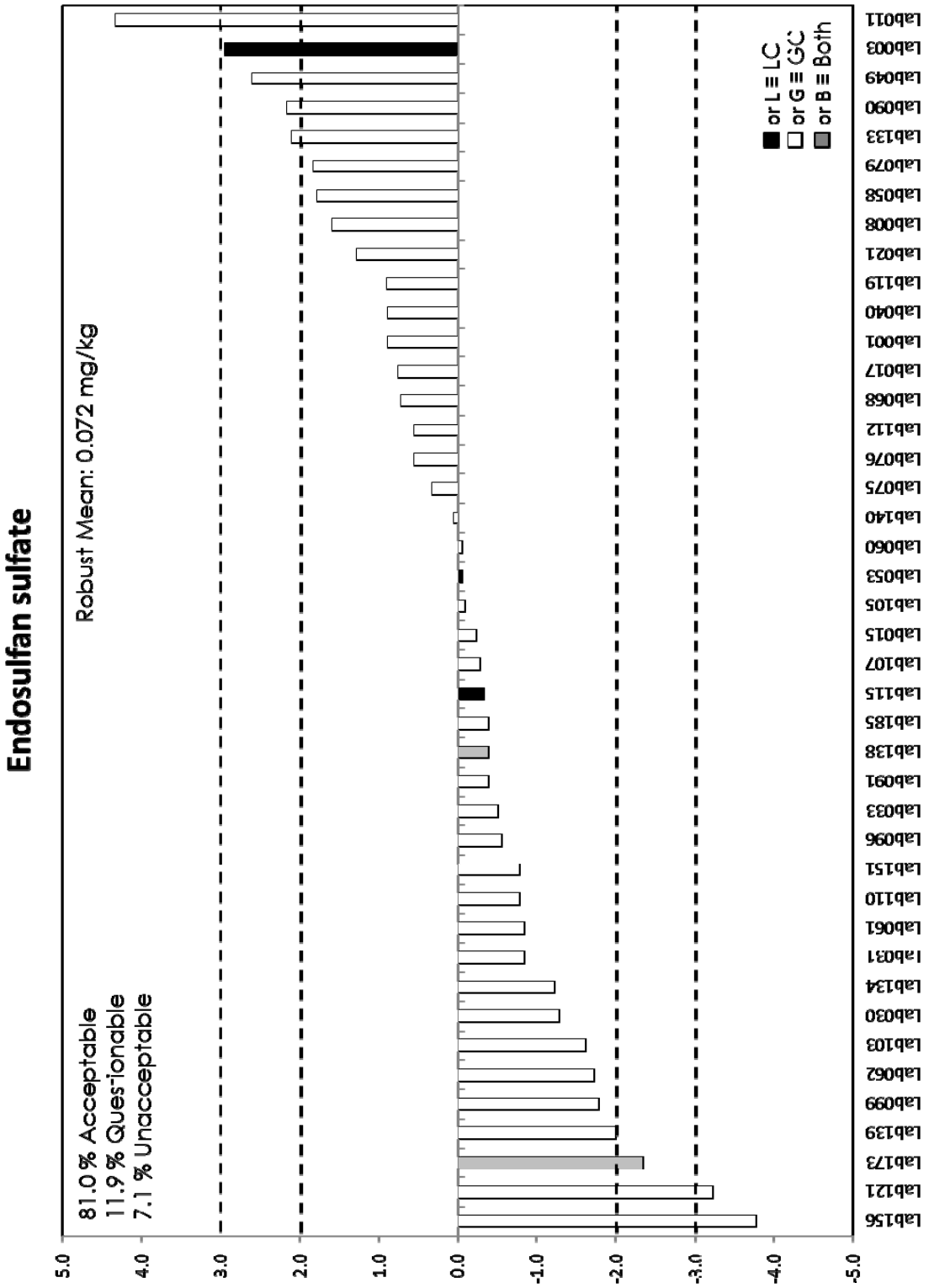
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



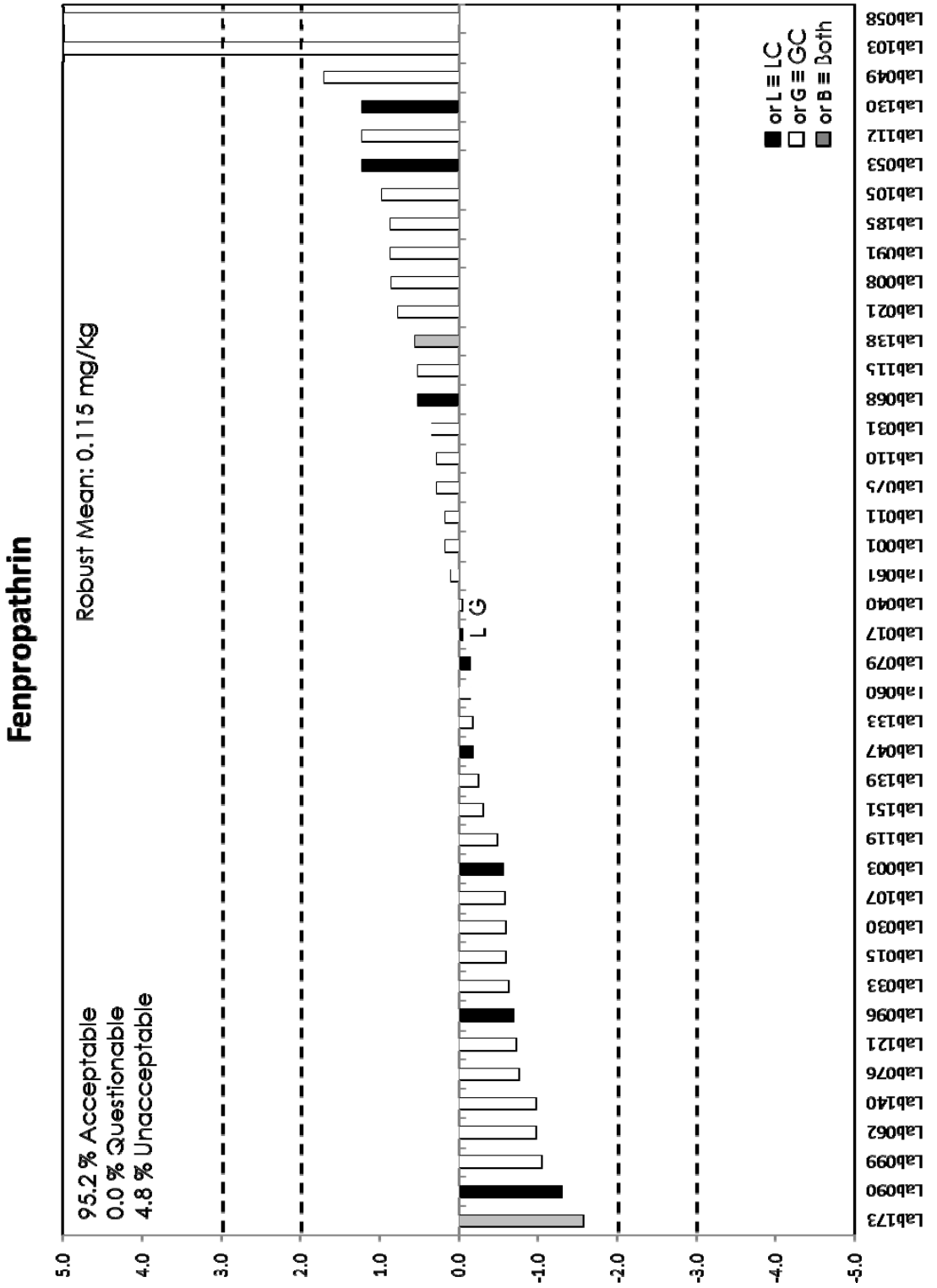
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



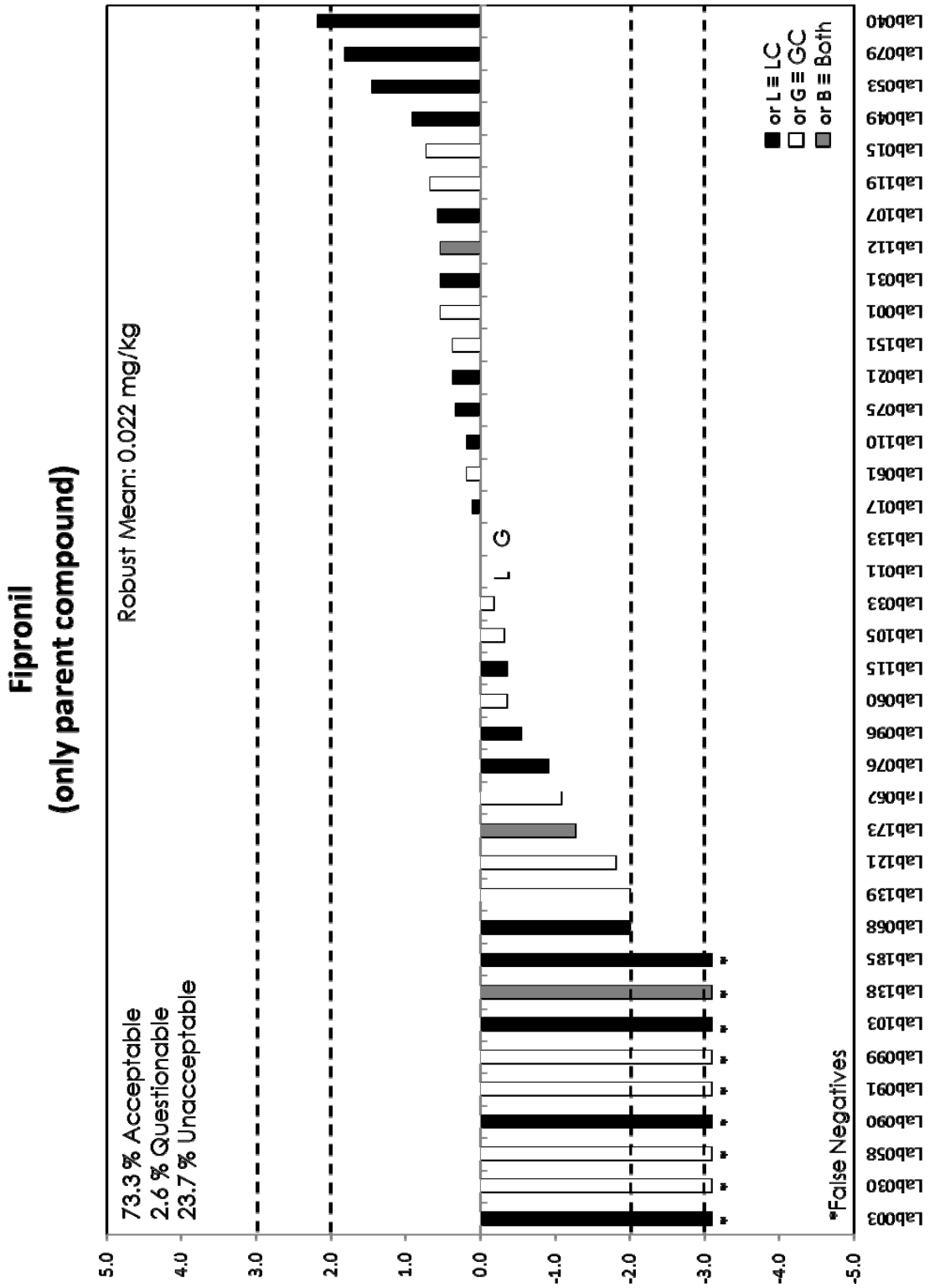
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



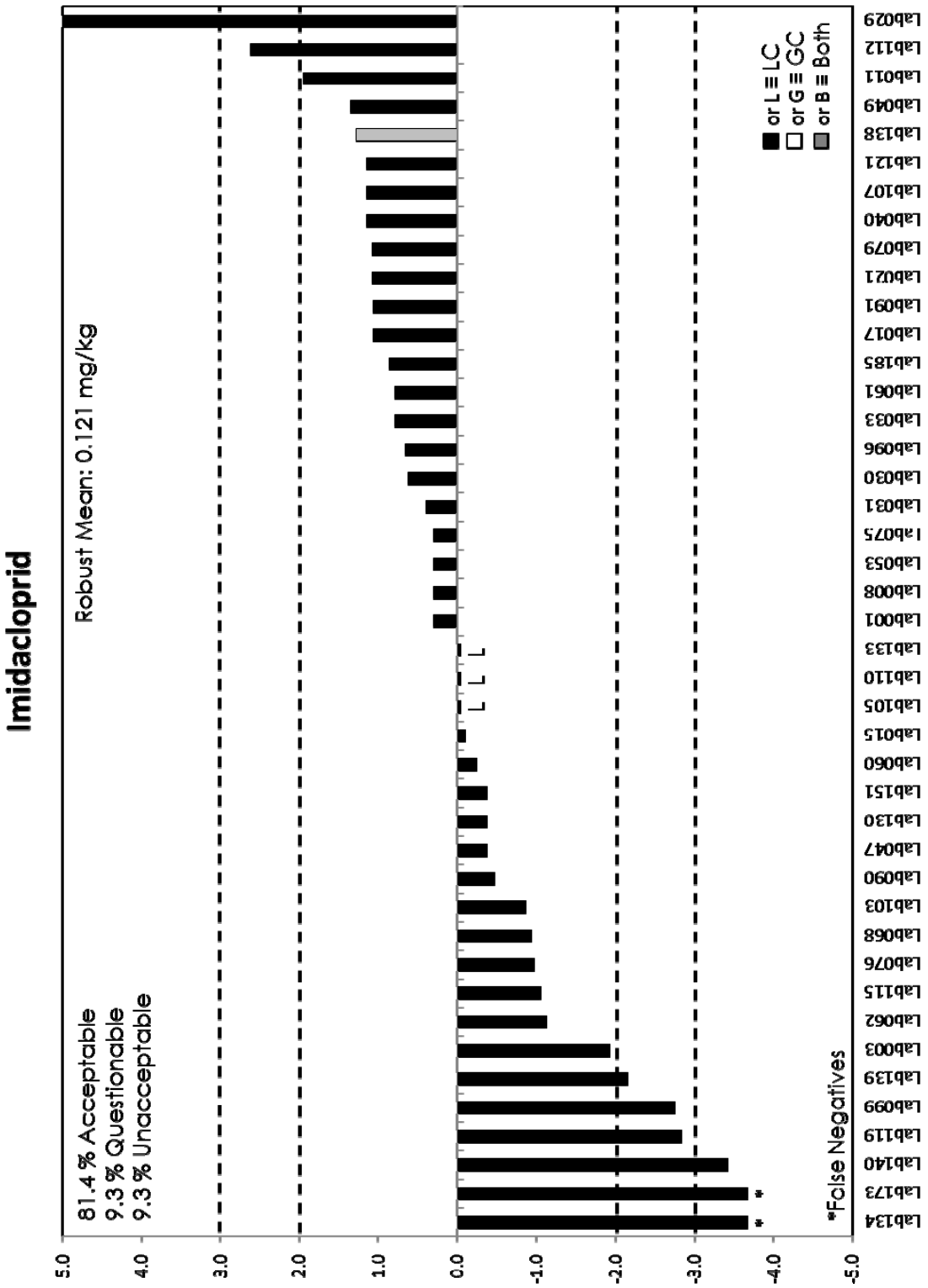
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



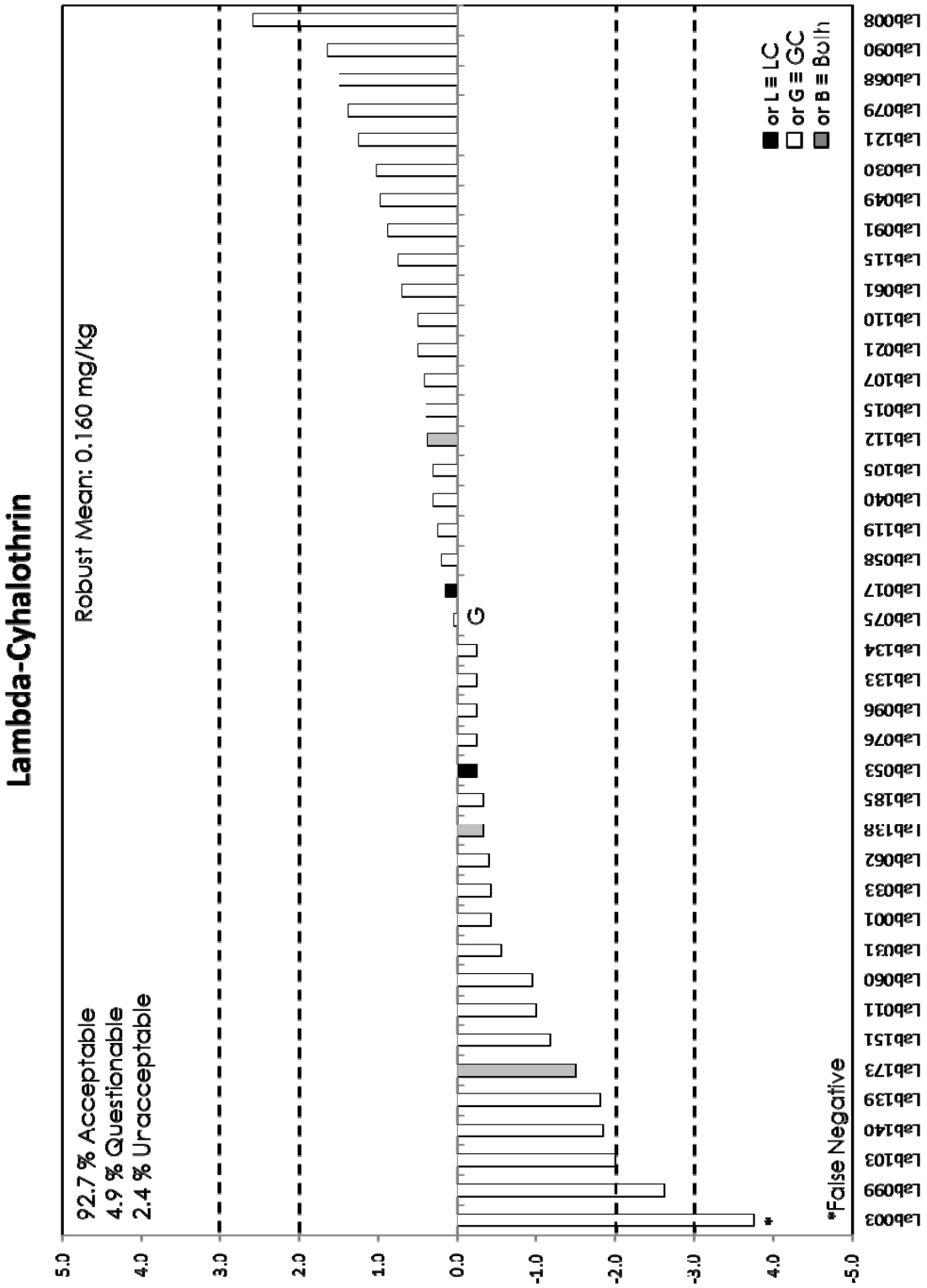
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



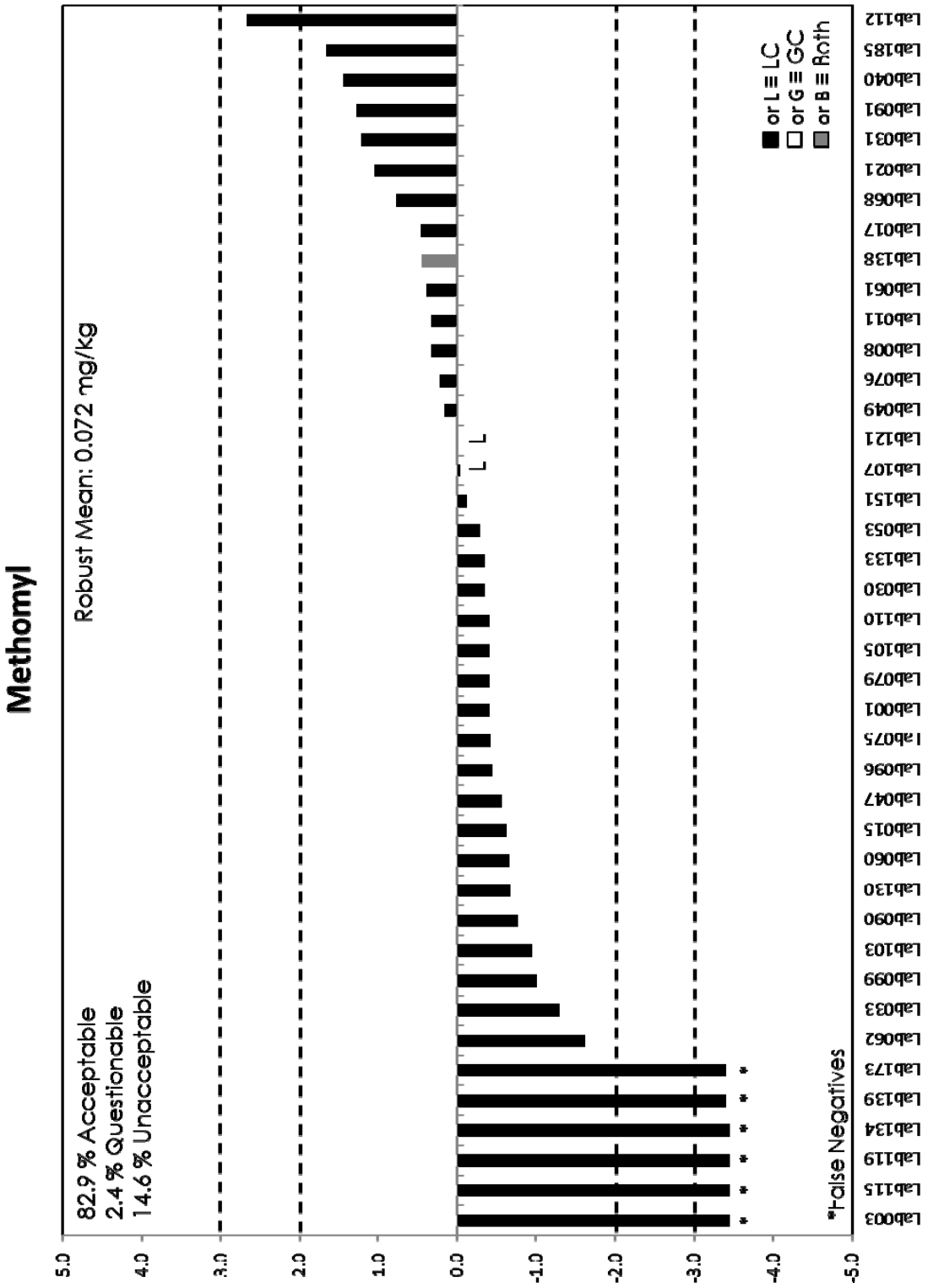
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



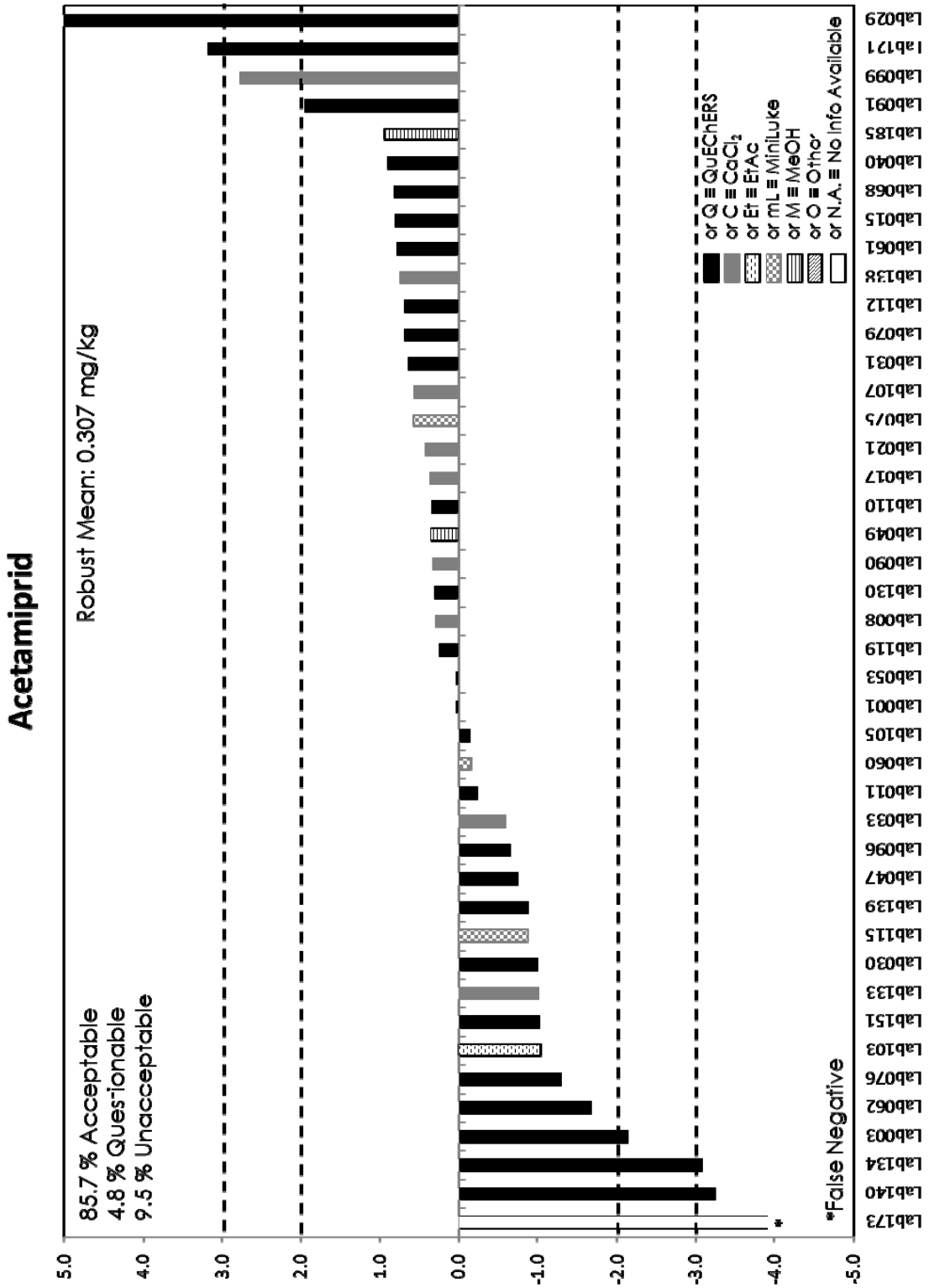
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



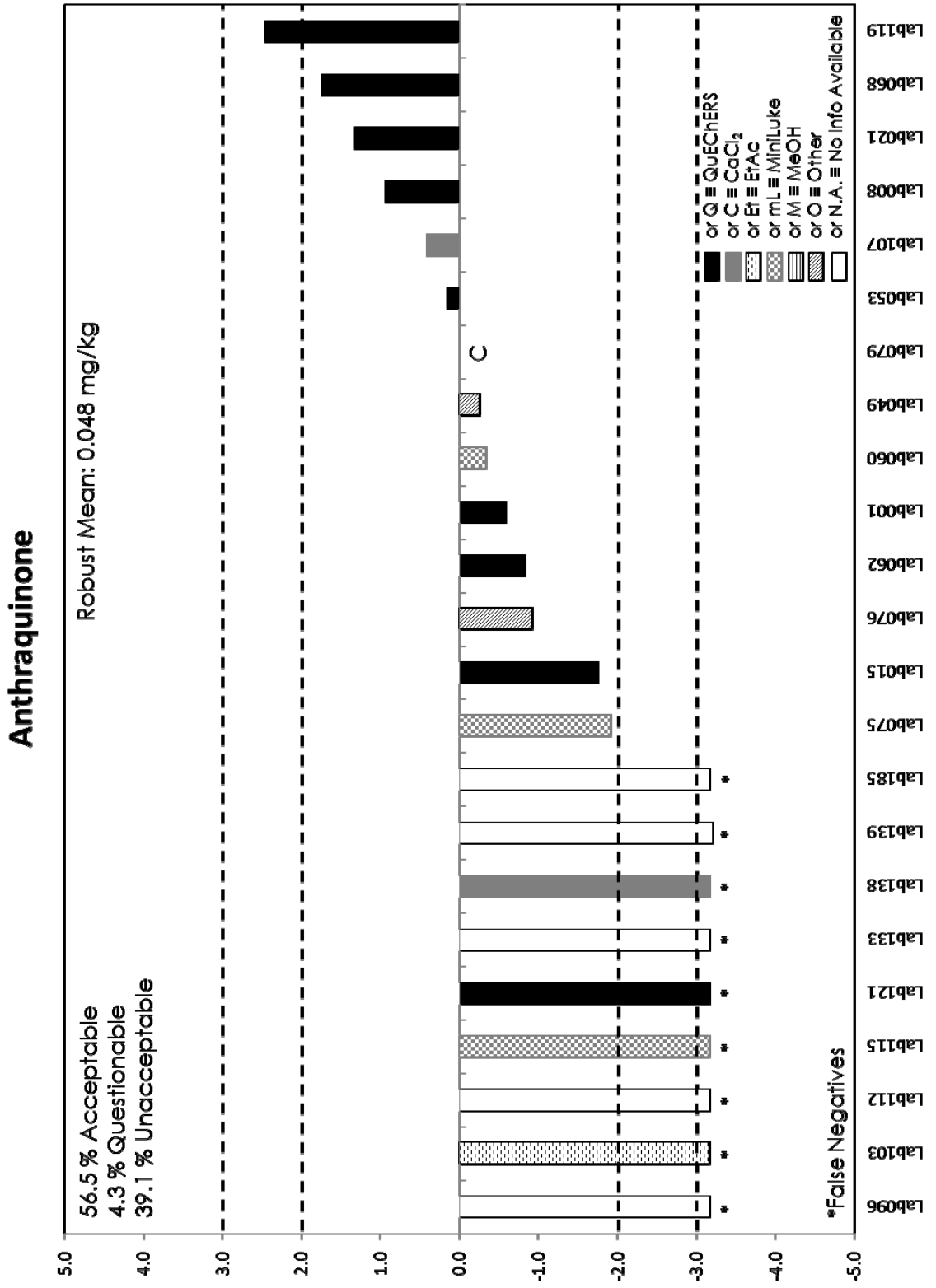
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



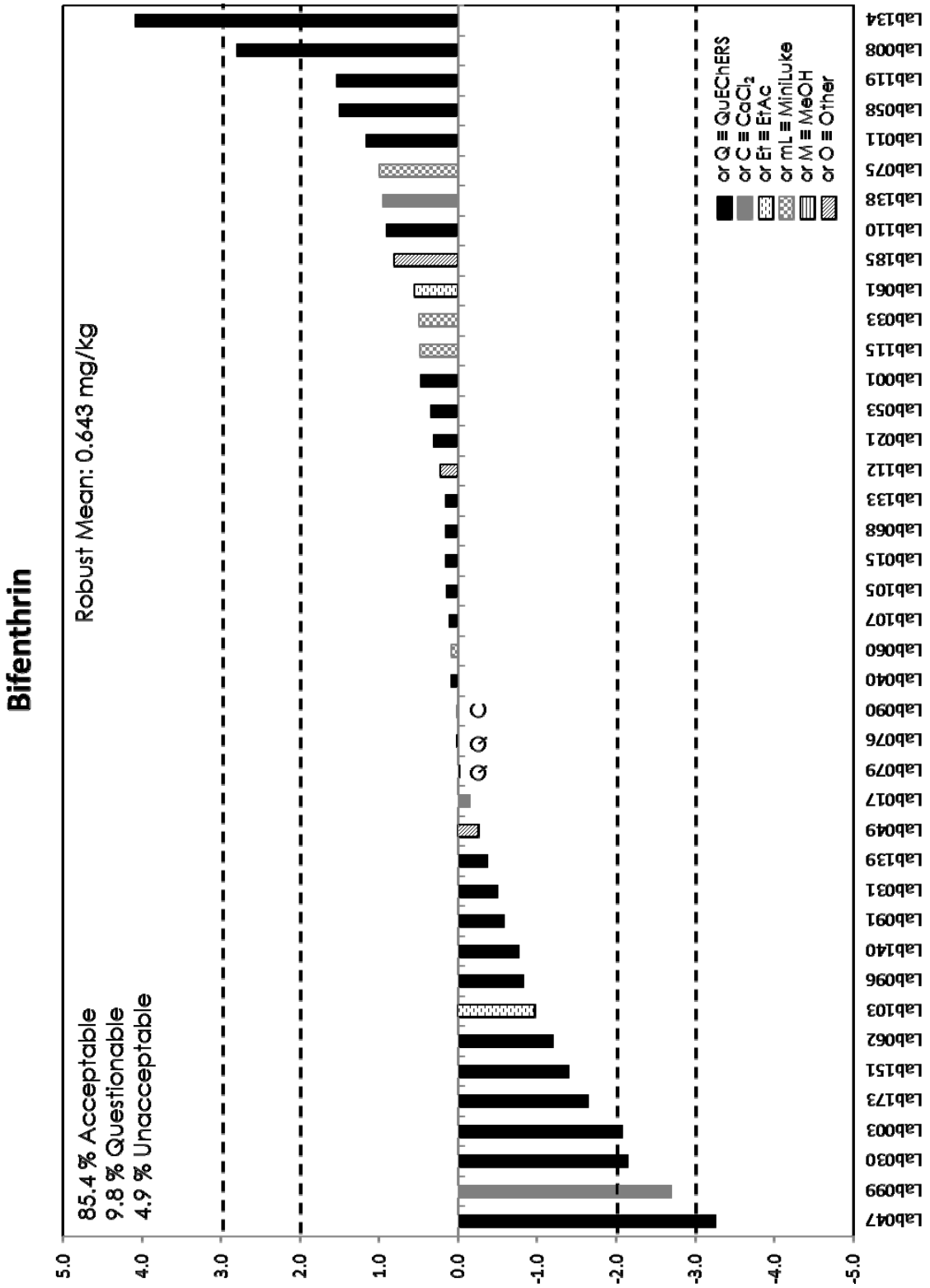
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



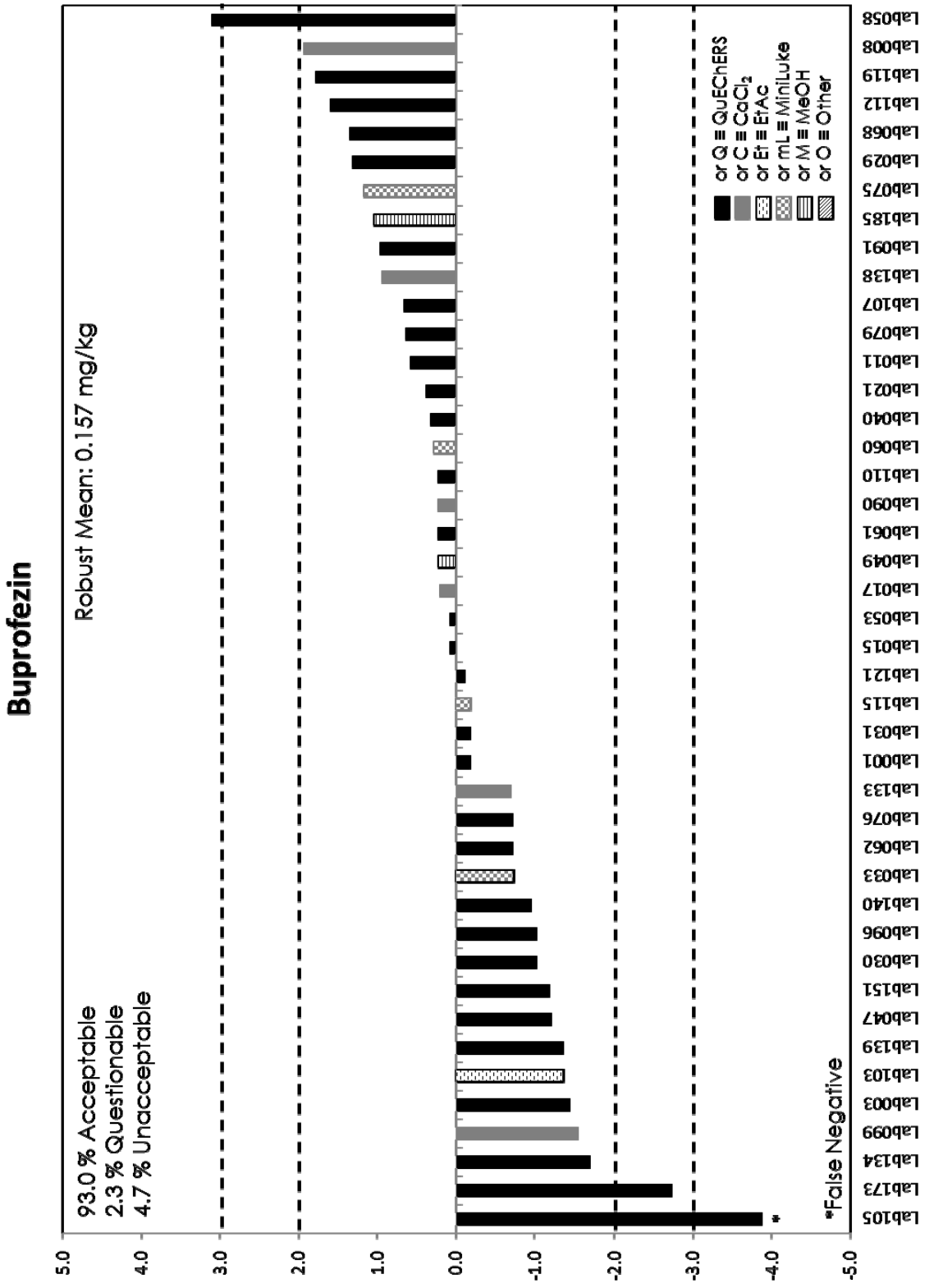
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



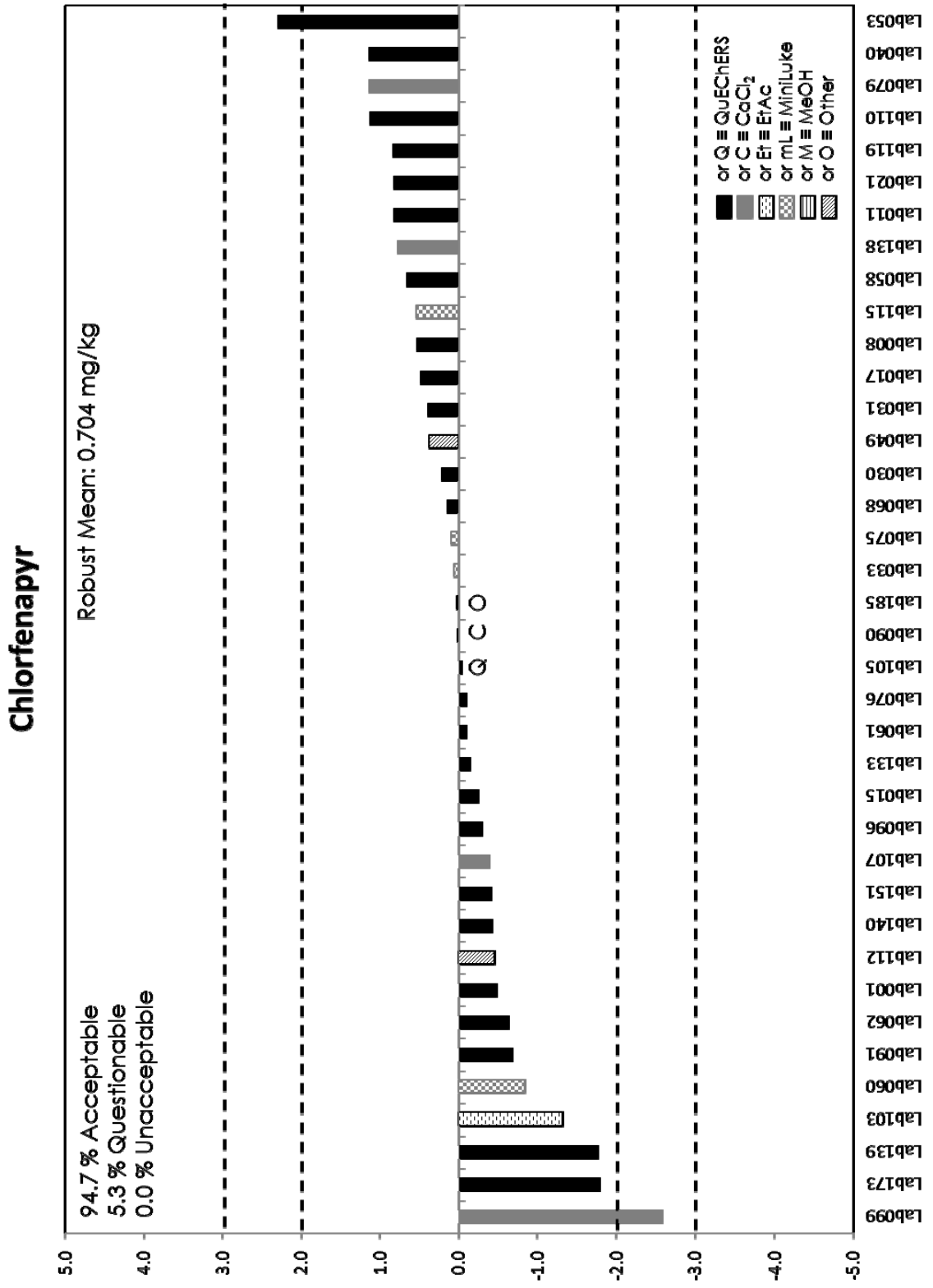
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



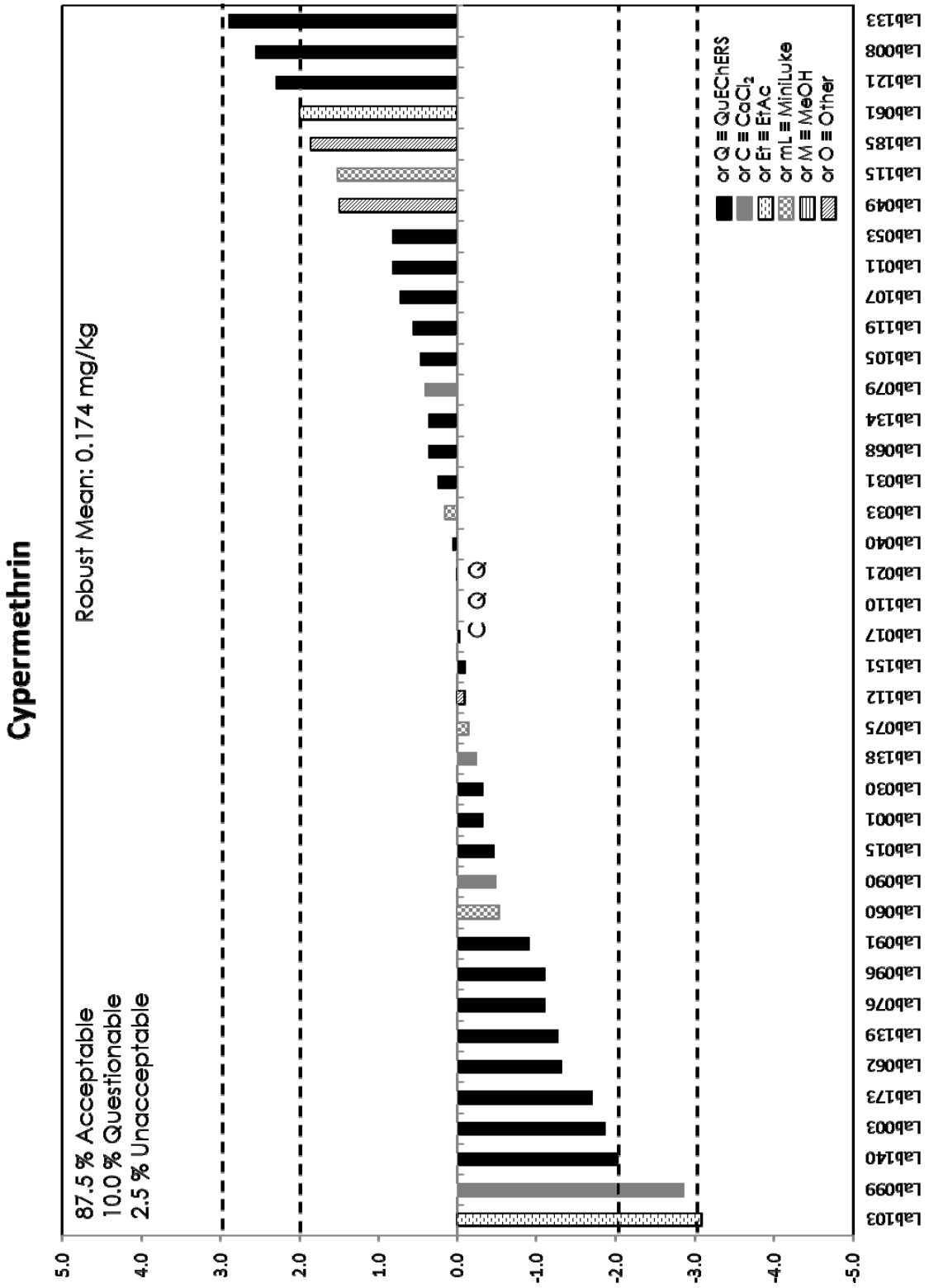
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



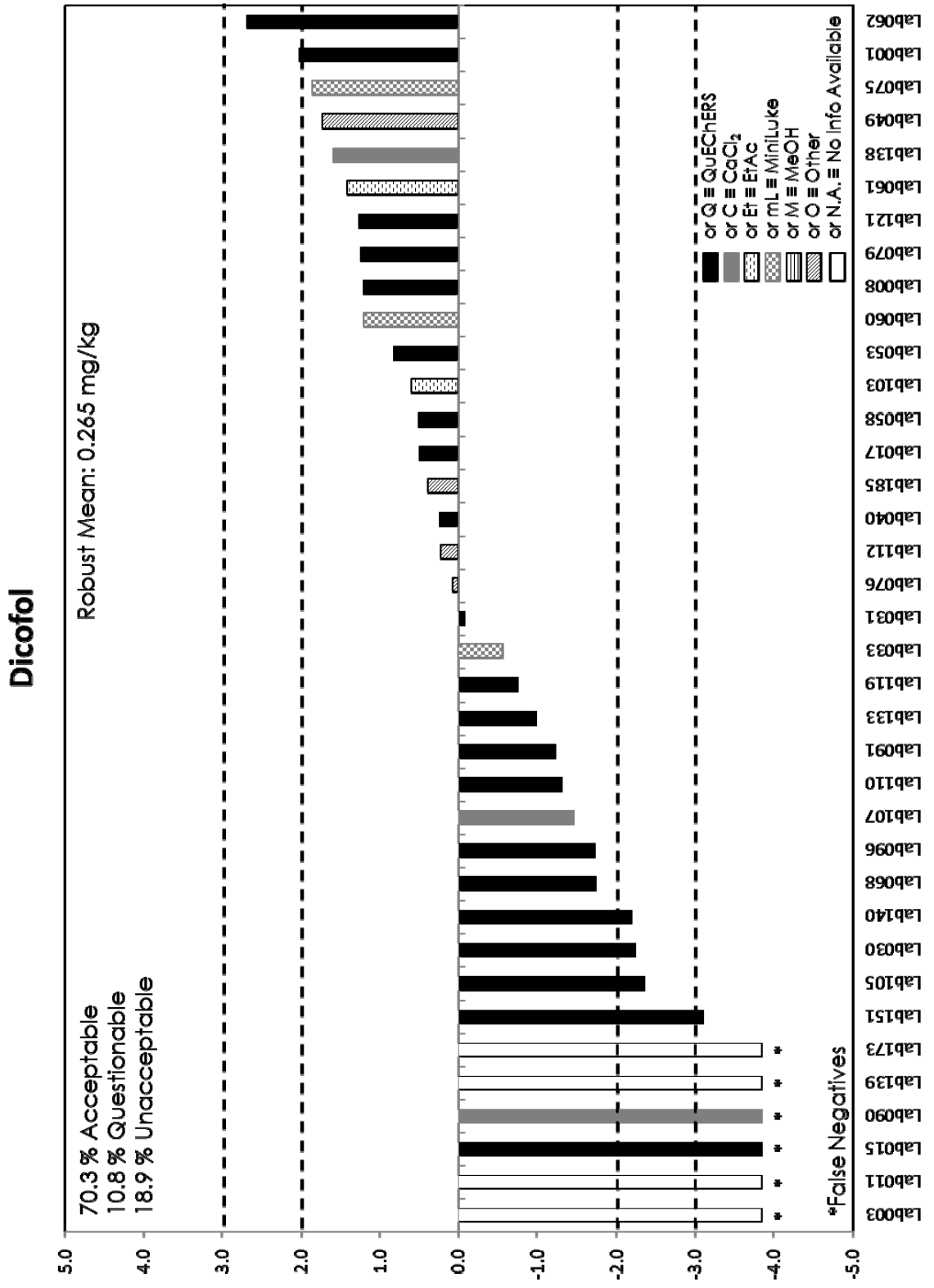
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



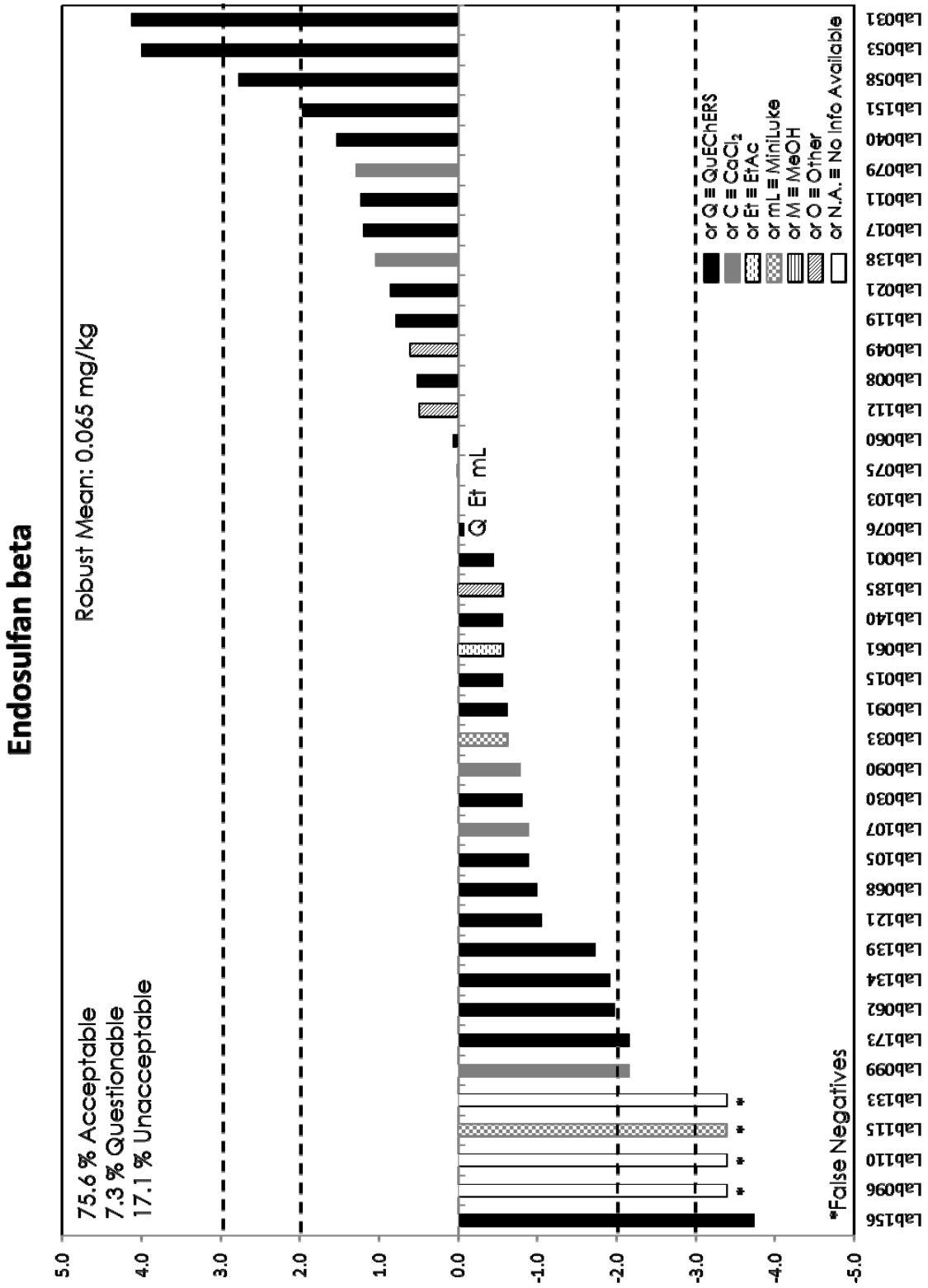
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



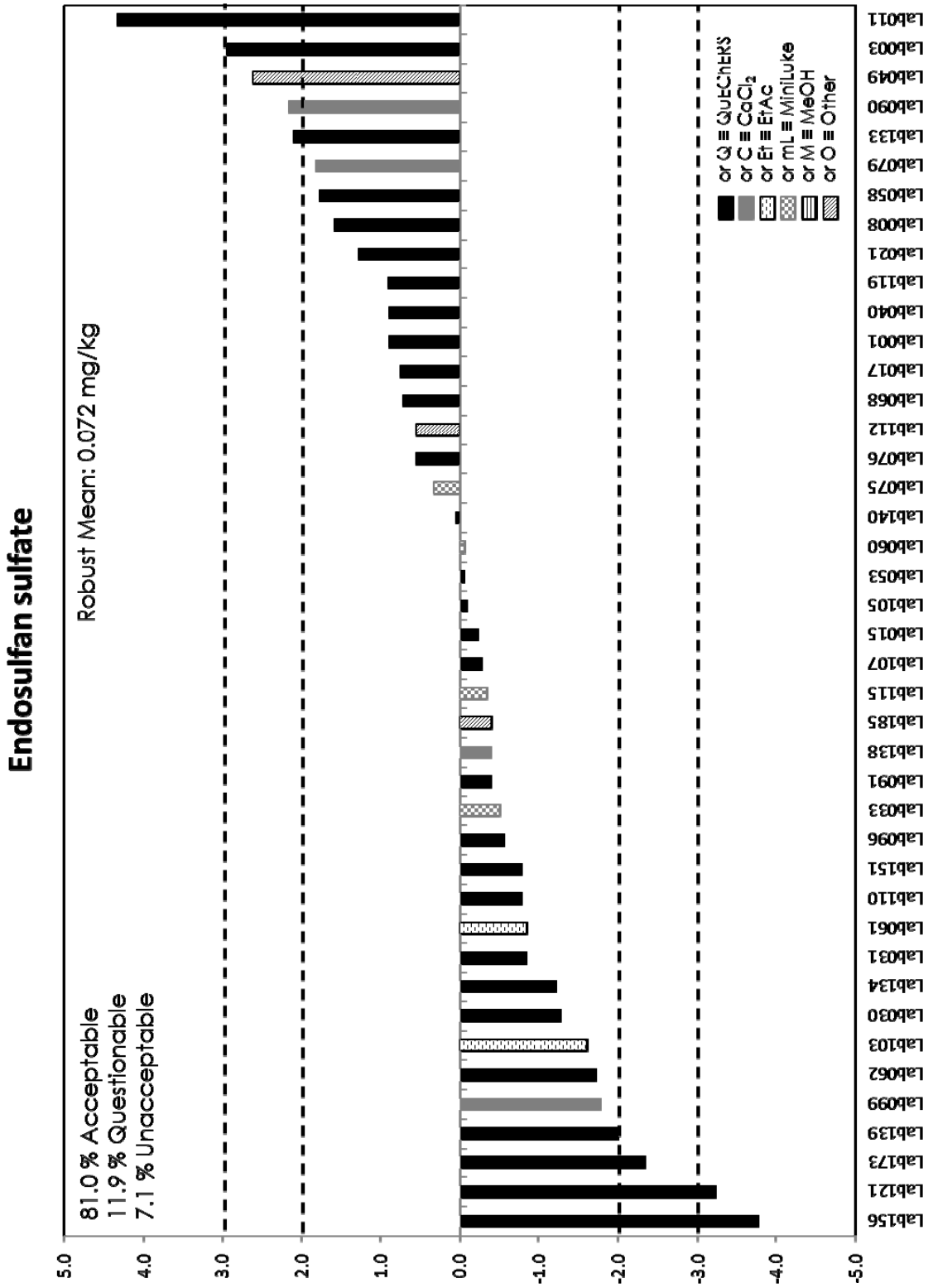
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



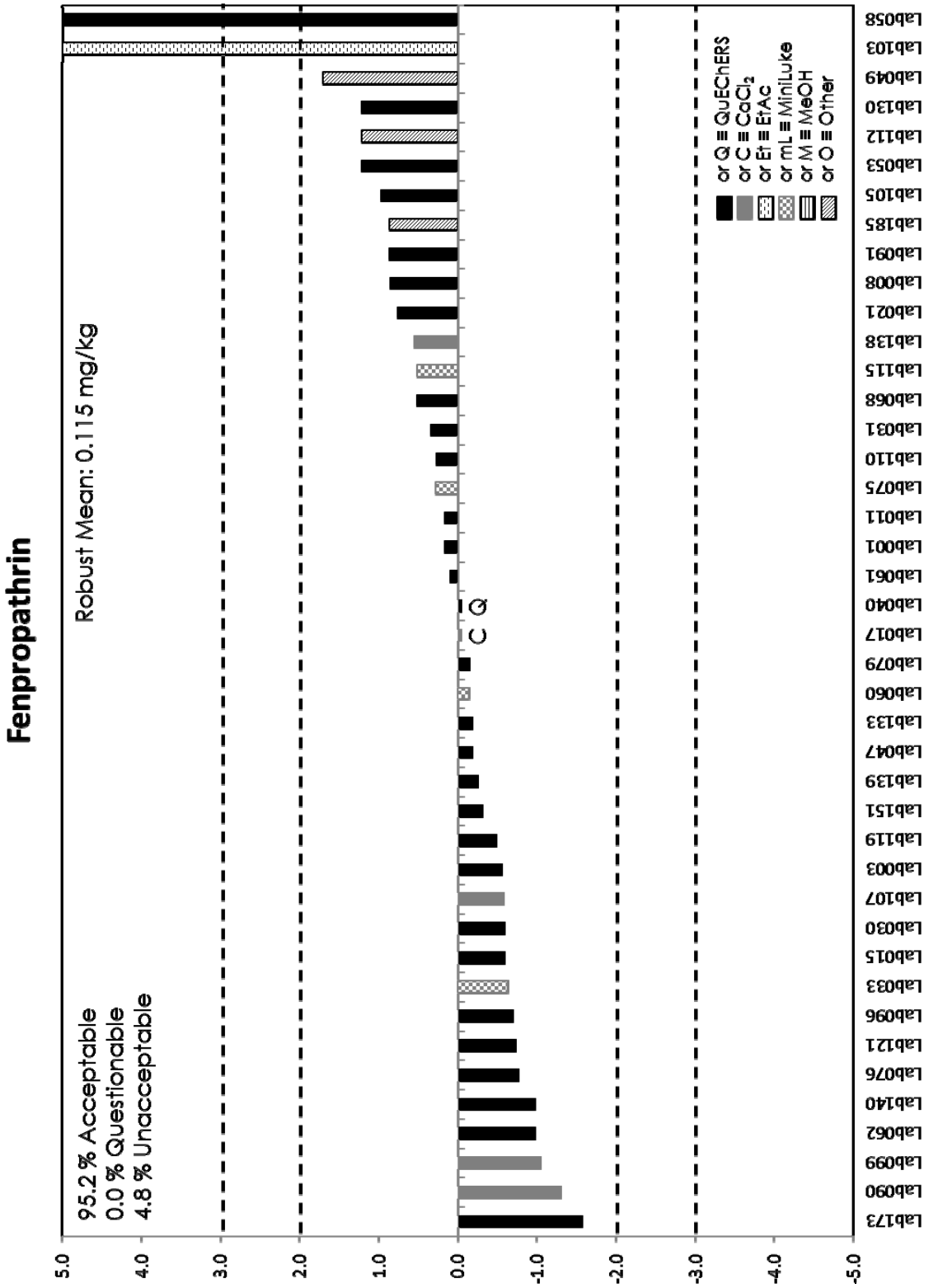
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



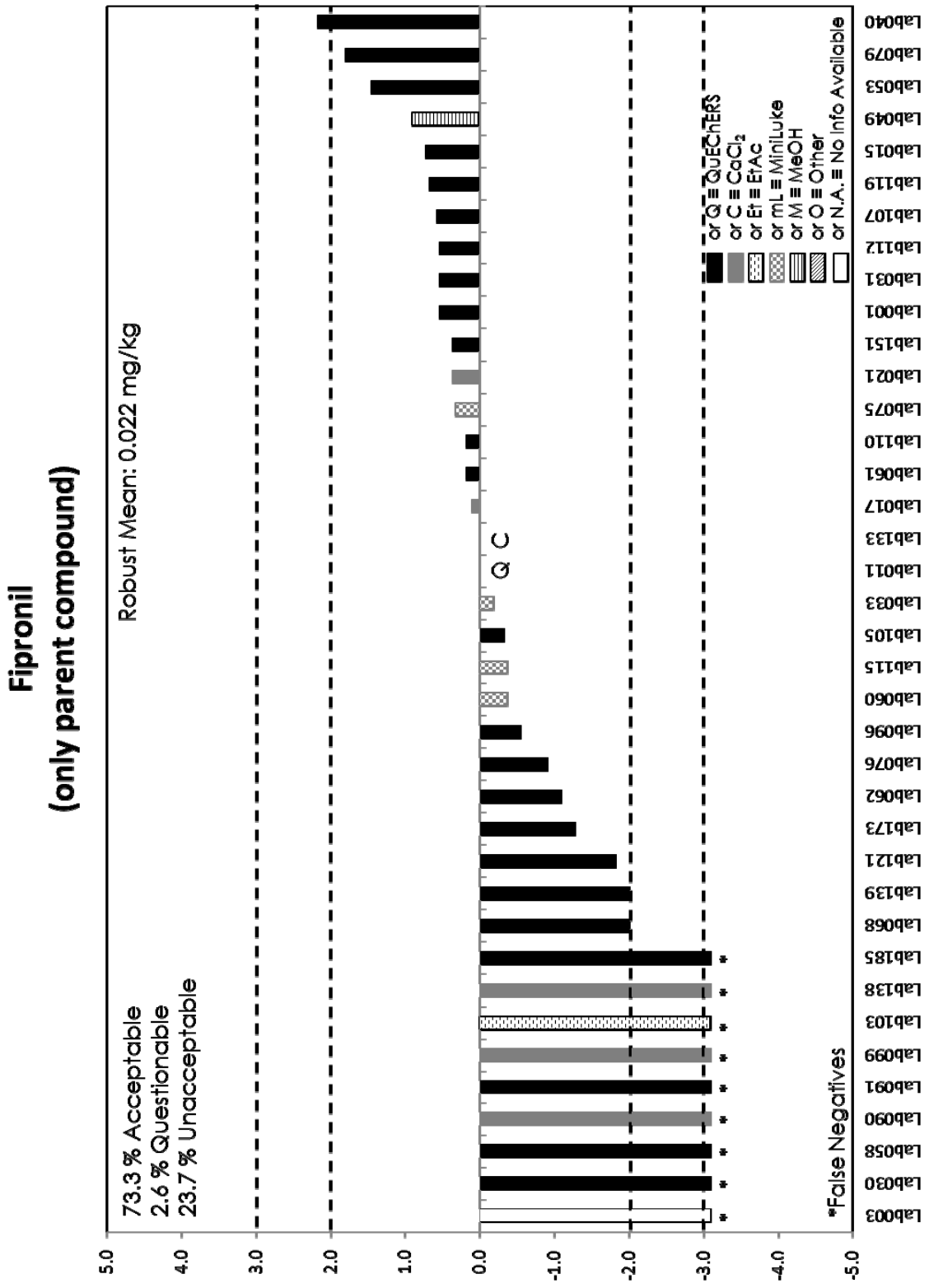
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



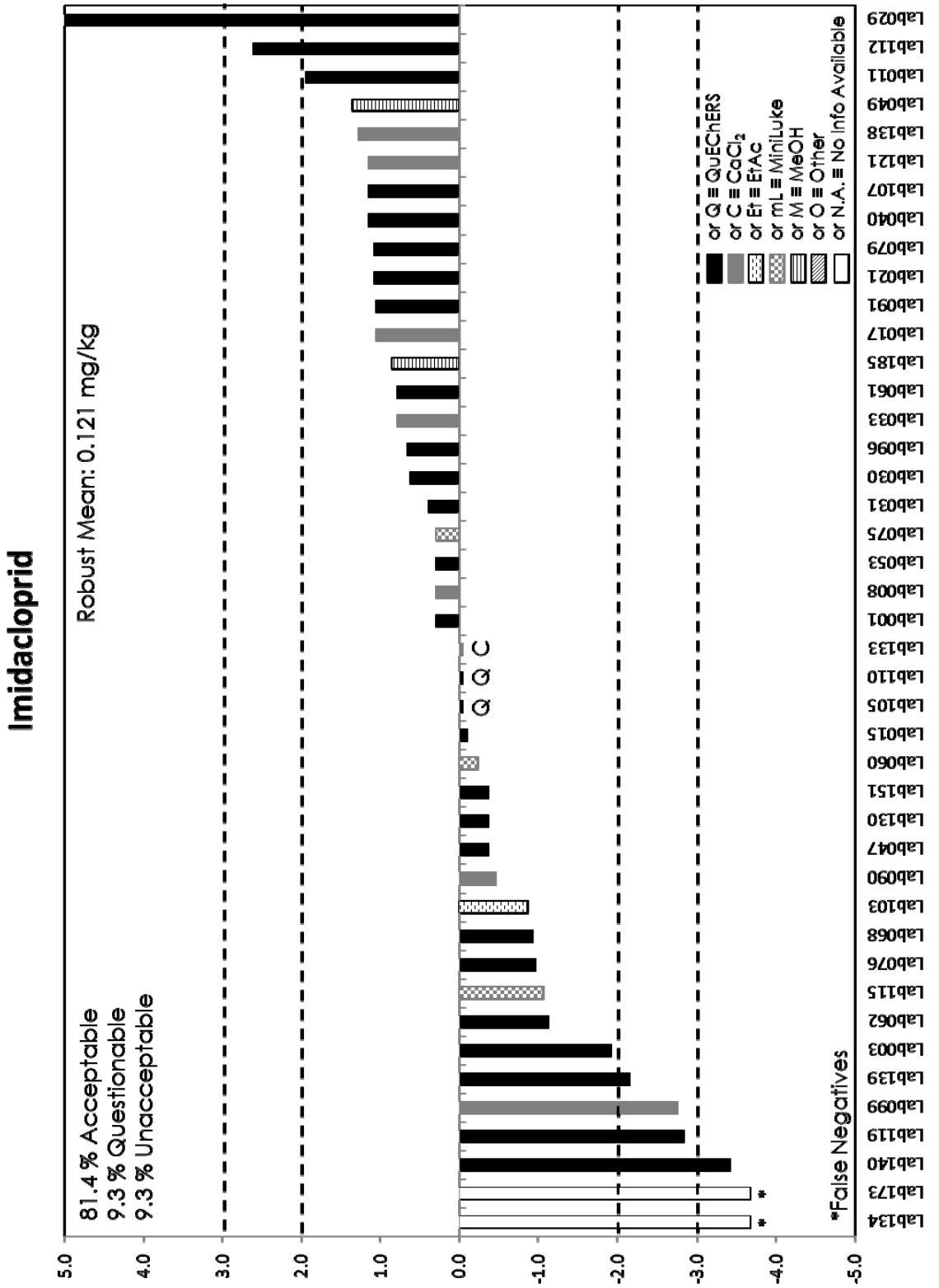
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



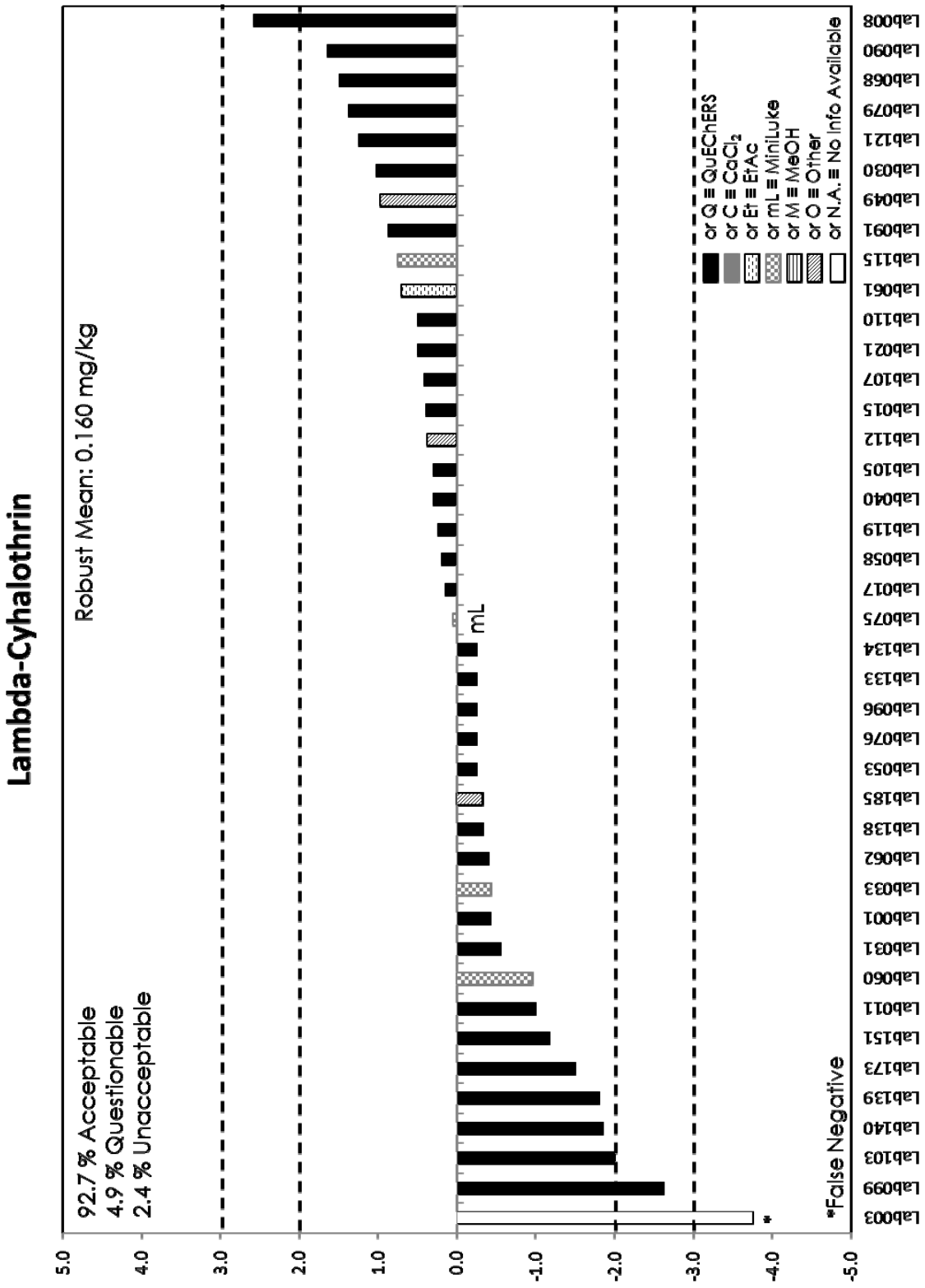
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



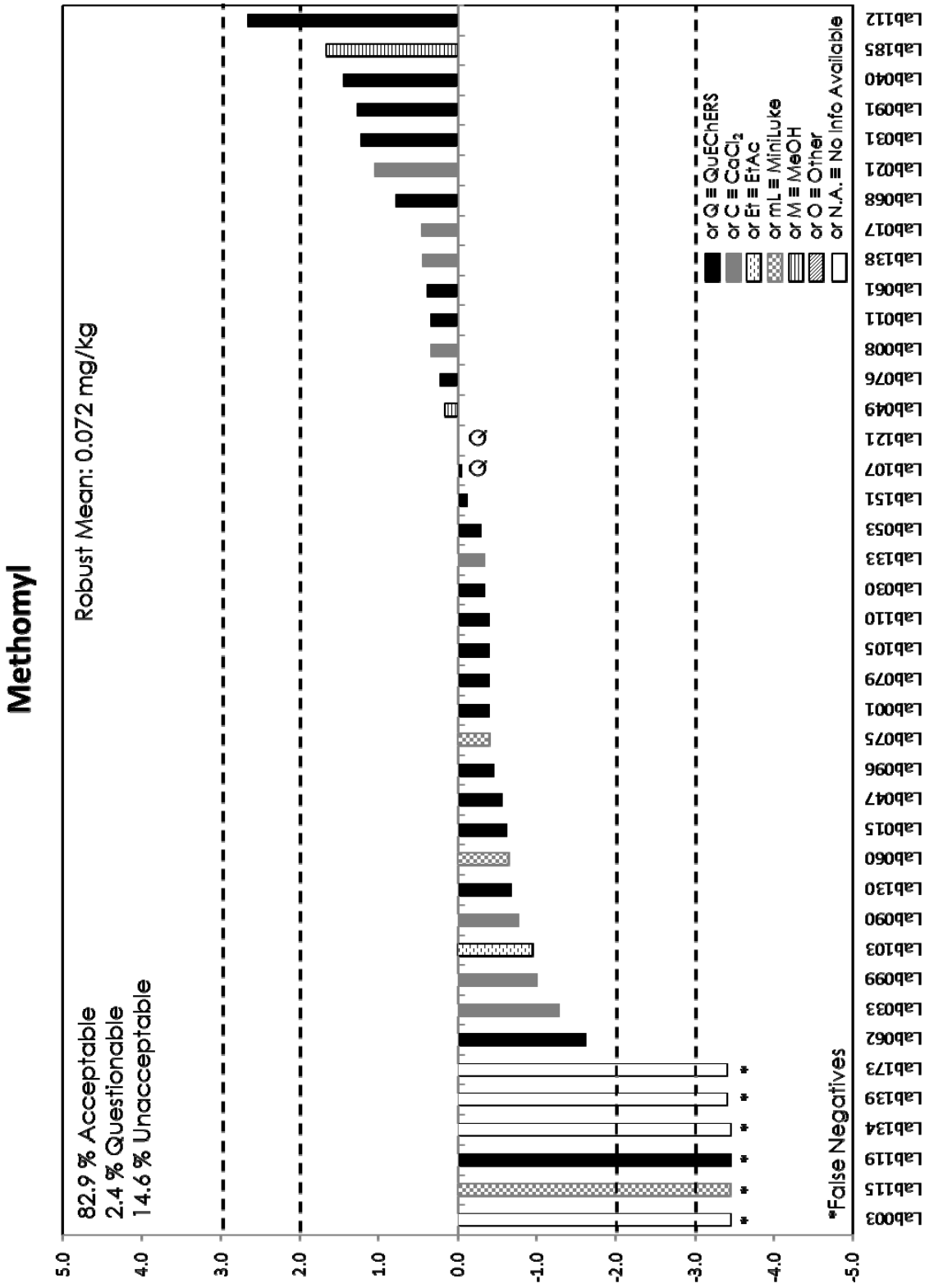
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



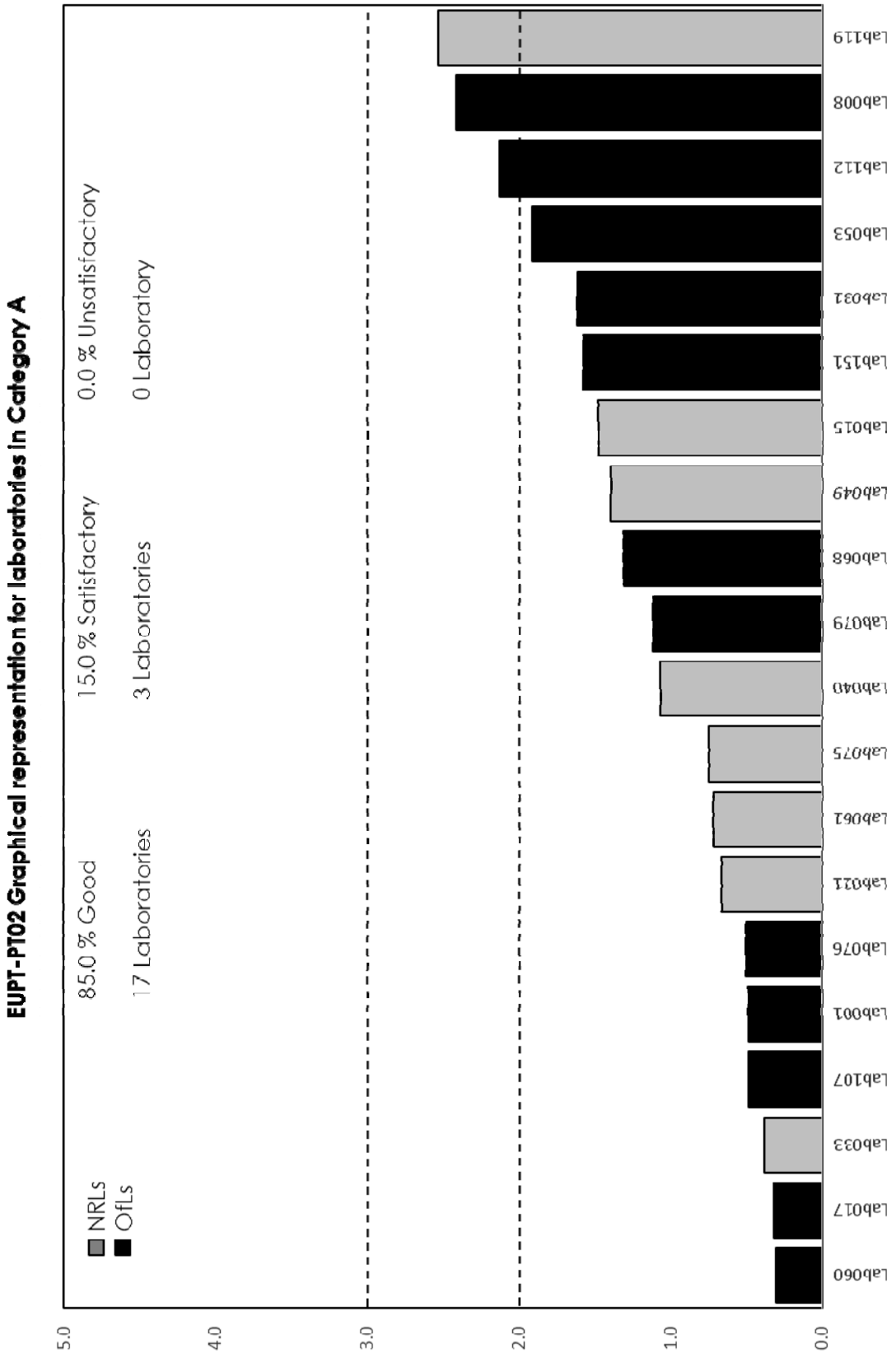
APPENDIX 4. Graphical representation of z-scores for FFP RSD (25 %).



APPENDIX 5. 'Average Sum of z-Scores' (AZ^2) for laboratories in Category A.

Lab Code	Acetamiprid	Anthraquinone	Bifenthrin	Buprofezin	Chlorfenapyr	Cypermethrin	Dicofol	Endosulfan beta	Endosulfan sulfate	Fenpropathrin	Fipronil	Imidacloprid	Lambda-Cyhalothrin	Methomyl	No. of Pesticides	AZ^2
	z-score															
1	0.0	13	0.5	-0.2	-0.5	-0.3	2.0	-0.4	0.9	0.2	0.5	0.3	-0.4	-0.4	14	0.5
8	0.3	13	2.8	1.9	0.5	2.6	1.2	0.5	1.6	0.9		0.3	2.6	0.3	13	2.4
15	0.8	13	0.2	0.1	-0.3	-0.5	-3.8	-0.6	-0.2	-0.6	0.7	-0.1	0.4	-0.6	13	1.5
17	0.4	13	-0.1	0.2	0.5	0.0	0.5	1.2	0.8	0.0	0.1	1.1	0.2	0.5	13	0.3
21	0.4	13	0.3	0.4	0.8	0.0		0.9	1.3	0.8	0.4	1.1	0.5	1.1	13	0.7
31	0.6	13	-0.5	-0.2	0.4	0.3	-0.1	4.1	-0.8	0.3	0.5	0.4	-0.6	1.2	13	1.6
33	-0.6	13	0.5	-0.7	0.1	0.2	-0.6	-0.6	-0.5	-0.6	-0.2	0.8	-0.4	-1.3	13	0.4
40	0.9	14	0.1	0.3	1.1	0.1	0.2	1.5	0.9	0.0	2.2	1.2	0.3	1.4	13	1.1
49	0.4	14	-0.3	0.2	0.4	1.5	1.7	0.6	2.6	1.7	0.9	1.4	1.0	0.2	14	1.4
53	0.0	14	0.4	0.1	2.3	0.8	0.8	4.0	-0.1	1.2	1.5	0.3	-0.3	-0.3	14	1.9
60	-0.1	13	0.1	0.3	-0.8	-0.5	1.2	0.1	-0.1	-0.1	-0.4	-0.2	-1.0	-0.6	14	0.3
61	0.8	14	0.5	0.2	-0.1	2.0	1.4	-0.6	-0.8	0.1	0.2	0.8	0.7	0.4	13	0.7
68	0.8	14	0.2	1.4	0.1	0.4	-1.7	-1.0	0.7	0.5	-2.0	-0.9	1.5	0.8	14	1.3
75	0.6	14	1.0	1.2	0.1	-0.1	1.9	0.0	0.3	0.3	0.3	0.3	0.1	-0.4	14	0.7
76	-1.3	14	0.0	-0.7	-0.1	-1.1	0.1	-0.1	0.6	-0.8	-0.9	-1.0	-0.3	0.2	14	0.5
79	0.7	14	0.0	0.6	1.1	0.4	1.3	1.3	1.8	-0.1	1.8	1.1	1.4	-0.4	14	1.1
107	0.6	13	0.1	0.7	-0.4	0.7	-1.4	-0.9	-0.3	-0.6	0.6	1.2	0.4	0.0	14	0.5
112	0.7	13	0.2	1.6	-0.4	-0.1	0.2	0.5	0.6	1.2	0.5	2.6	0.4	2.7	13	2.1
119	0.2	13	1.5	1.8	0.8	0.6	-0.8	0.8	0.9	-0.5	0.7	-2.8	0.3	-3.4	13	2.5
151	-1.0	14	-1.4	-1.2	-0.4	-0.1	-3.1	2.0	-0.8	-0.3	0.4	-0.4	-1.2	-0.1	13	1.6

APPENDIX 6. EUPT T02 – AZ2 - Graphical representation for laboratories in Category A



4th Edition
Revised 09 Jan., 2014

GENERAL PROTOCOL

for EU Proficiency Tests on Pesticide Residues in Food and Feed

Introduction

This protocol contains general procedures valid for all European Union Proficiency Tests (EUPTs) organised on behalf of the European Commission, DG-SANCO[1] by the four European Union Reference Laboratories (EURLs) for pesticide residues in food and feed. These EUPTs are directed at laboratories belonging to the Network[2] of National Reference Laboratories (NRLs) and Official Laboratories (OfLs) of the EU Member States. OfLs from EFTA countries and EU-Candidate countries are also welcome to participate in the EUPTs. OfLs from Third countries may be permitted to participate on a case-by-case basis.

The following four EURLs for pesticide residues were appointed by DG-SANCO based on regulation 882/2004/EC[3]:

- EURL for Fruits and Vegetables (EURL-FV)
- EURL for Cereals and Feedingstuff (EURL-CF)
- EURL for Food of Animal Origin and Commodities with High Fat Content (EURL-AO) and
- EURL for Single Residue Methods (EURL-SRM)

The aim of these EUPTs is to obtain information regarding the quality, accuracy and comparability of pesticide residue data in food and feed reported to the European Union within the framework of the national control programmes and the EU multiannual co-ordinated control programme[4]. Participating laboratories will be provided with an assessment of their analytical performance that they can use to demonstrate their analytical performance and compare themselves with other participating laboratories.

[1] DG-SANCO = European Commission, Health and Consumer Protection Directorate-General
[2] For more information about the EURL/NRL/OfL-Network please refer to the EURL-Web-portal under: http://www.eurl-pesticides.eu
[3] Regulation (EC) No 882/2004 of the European Parliament and of the Council on official controls performed to ensure the verification of compliance with feed and food law, animal health and animal welfare rules. Published at OJ of the EU L191 of 28.05.2004
[4] European Commission Proficiency Tests for Pesticide Residues in Fruits and Vegetables, Trends in Analytical Chemistry, 2010, 29 (1), 70 – 83.

EUPT-Organisers and Scientific Committee

EUPTs are organised by individual EURLs or by more than one EURL in joint cooperation.

An **Organising Team** is appointed from the EURL(s) in charge. This team is responsible for all administrative and technical matters concerning the organisation of the PT, e.g. PT-announcement, production of Test Item and Blank Material, the undertaking of homogeneity and stability tests, packing and shipment of the Test Item and Blank Material, handling and evaluation of the results and method information submitted by the participants and the drafting of the preliminary and final reports.

To complement the internal expertise of the EURLs, a group of external consultants that form the **EUPT-Scientific Committee** (EUPT-SC)[5] has been established and approved by DG SANCO. The EUPT-SC consists of expert scientists with many years of experience in PTs and/or pesticide residue analysis. The actual composition of the EUPT-SC, the affiliation of each member is shown on the EURL-Website. The members of the EUPT-SC will also be listed in the Specific Protocol and the Final Report of each EUPT.

The EUPT-SC is made up of the following two subgroups:

a) An independent **Quality Control Group** (EUPT-QCG) and

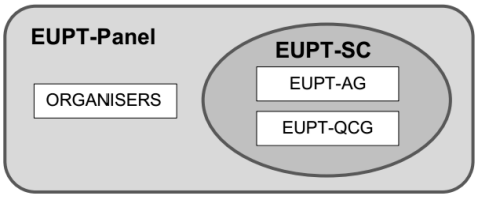
b) An **Advisory Group** (EUPT-AG)

The EUPT-SC's role is to help the organisers make decisions regarding the EUPT design: the selection of the commodity, the selection of pesticides to be included in the Target Pesticide List (see below), the establishment of the Minimum Required Reporting Levels (MRRLs), the statistical treatment and evaluation of participants results (in anonymous form), and the drafting and updating of documents such as the General and Specific PT Protocols and the Final EUPT-Reports.

The EUPT-QCG has the additional function of supervising the quality of EUPTs and of assisting the EURLs in confidential aspects such as the choice of the pesticides to be present in the Test Item and the concentrations at which they should be present.

The EUPT-SC typically meets once a year, after the EUPTs of all four pesticide EURLs have been conducted, to discuss the evaluation of the EUPT-results and to consult with the EURLs in their decision making. Upcoming EUPTs are also planned during these meetings.

The EUPT-Organising Team and the EUPT-SC together form the **EUPT-Panel**.



[5] Link to the List of current members of the EUPT Scientific Committee: http://www.eurl-pesticides.eu/library/docs/allcrl/EUPT-SC.pdf

The decisions of the EUPT-Panel will be documented.

This present EUPT General Protocol was jointly drafted by the EUPT-SC and the EURLs and was approved by DG-SANCO.

EUPT Participants

Within the European Union all NRLs operating in the same area as the organising EURL, as well as all OfLs whose scope overlaps with that of the EUPT, are legally obliged to participate in EUPTs. The legal obligation of NRLs and OfLs to participate in EUPTs arises from:

- Art. 28 of Reg. 396/2005/EC[6] (for all OfLs analyzing for pesticide residues within the framework of official controls[7] in food or feed)
- Art. 33 of Reg. 882/2004/EC (for all NRLs)

The four EURLs will annually issue and distribute, via the EURL-website, a joint list of all OfLs that must participate in each of the EUPTs to be conducted within a given year. The list of obliged labs will be updated every year to take account of any changes in the lab profiles. Interim updates will be issued to eliminate any possible errors.

NRLs are responsible for checking whether all relevant OfLs within their network are included in the list of obligated laboratories and whether the contact information and commodity-scopes are correct.

OfLs are furthermore urged to keep their own profiles within the EURL-DataPool up-to-date, especially their commodity and pesticide scopes and their contact information.

Labs that are obliged to participate in a given EUPT, and that are not able to participate, must provide the reasons for their non-participation without prejudice of any legal action taken against them for not participating. This also applies to any participating laboratories that then fail to report results.

Confidentiality and Communication

The proprietor of all EUPT data is DG-SANCO and thus has access to all information.

For each EUPT, the laboratories are given a unique code (lab code), initially only known to themselves and the Organisers. In the final EUPT-Report, the names of participating laboratories will not be linked to their laboratory codes. It should be noted, however, that the Organisers, at the request by DG-SANCO, may present the EUPT-results on a country-by-country basis. It may therefore be possible that a link between codes and laboratories could be made, especially for those countries where only one laboratory has participated. Furthermore, the EURLs reserve the

[6] Regulation (EC) No 396/2005, published at OJ of the EU L70 of 16.03.2005, as last amended by Regulation 839/2008 published at OJ of the EU L234 of 30.08.2008.

[7] Official controls in the sense of Reg. 882/2004/EC This includes labs involved in controls within the framework of national and/or EU-controlled programmes as well as labs involved in import controls according to regulation 669/2009/EC.

right to share EUPT results and codes amongst themselves: for example, for the purpose of evaluating overall lab or country performance as requested by DG-SANCO.

As laid down in Regulation 882/2004, NRLs are responsible for evaluating and improving their own OfL-Network. On request from the NRLs, the EURLs will provide them with the PT-codes of the participating OfLs belonging to their OfL-Network. This will allow NRLs to follow the participation and performance of the laboratories within their network.

Communication between participating laboratories during the test on matters concerning a PT exercise is not permitted from the start of the PT exercise until the distribution of the preliminary report.

For each EUPT the organising EURL prepares a specific EUPT-Website where all relevant documents in their latest version are linked.

The official language used in all EUPTs is English.

Announcement / Invitation Letter

At least 3 months before the Test Item of a given EUPT is distributed to the laboratories the EURLs will publish an Announcement/Invitation letter on the EURL-web-portal and distribute it via e-mail to the NRL/OfL mailing list available to the EURLs. This letter will inform about the commodity to be used as Test Item, as well as links to the tentative EUPT-Target Pesticide List and the tentative EUPT-Calendar.

Target Pesticide List

This list contains all analytes (pesticides and metabolites) to be sought, along with the Minimum Required Reporting Levels (MRRLs) valid for the specific EUPT. The MRRLs are typically based upon the lowest MRLs found either in Regulation 396/2005/EC or Commission Directive 2006/125/EC (Baby Food Directive).
Labs must express their results as stated in the Target Pesticides List.

Specific Protocol

For each EUPT the organizing EURL will publish a Specific Protocol at least 2 weeks before the Test Item is distributed to the participating laboratories. The Specific Protocol will contain all the information previously included in the Invitation Letter but in its final version, information on payment and delivery, instructions on how to handle the Test Item upon receipt and on how to submit results, as well as any other relevant information.

Homogeneity of the Test Item

The Test Item will be tested for homogeneity typically before distribution to participants. The homogeneity tests involve the analysis of two replicate analytical portions, taken from at least ten randomly chosen units of treated Test Item. Both, sample preparation and measurements should be conducted in random order.

The homogeneity test data are statistically evaluated according to the International Harmonized Protocols published by ISO and IUPAC. The acceptance criterion for the Test Items to be sufficiently homogeneous for the Proficiency Test is that s_{sam}^2 is less than c with s_{sam} being the between-bottle sampling standard deviation and $c = F_1 \times \sigma_{all}^2 + F_2 \times s_{an}^2$. F_1 and F_2 are constants, with values of 1.88 and 1.01, respectively, if 10 samples are used. $\sigma_{all}{}^2$= 0.3 × FFP-RSD[8] (25 %) × the analytical sampling mean for all pesticides, and san is the estimate of the analytical standard deviation.

The results of all homogeneity tests are presented to the EUPT-SC. In special cases where the above homogeneity test criteria are not met, the EUPT-SC considering all relevant aspects (e.g. the homogeneity results of other pesticides spiked at the same time, the overall distribution the participants' results, the analytical difficulties faced during the test, knowledge of the analytical behaviour of the pesticide question) may decide to overrule the test. The reasons of this overruling have to be transparently explained in the Final EUPT-Report.

Stability of the analytes contained in the Test Item

The Test Items will also be tested for stability - according to ISO 13528, Annex B. The time delay between the first and the last stability test must exceed the period of the EUPT-exercise. Typically the first analysis is carried out shortly before the shipment of the Test Items and the last one shortly after the deadline for submission of results. To better recognise trends and gain additional certainty one or more additional tests may be conducted by the Organisers. At least 6 sub-samples (analytical portions) should be analysed on each test day (e.g. 2 analytical portions withdrawn from three randomly chosen containers OR 6 portions withdrawn from a single container). In principle all pesticides contained in the Test Item should be checked for stability. However, in individual cases, where sufficient knowledge exists that the stability of a certain analyte is very unlikely to be significantly affected during storage (e.g. based on experience from past stability tests or knowledge of its physicochemical properties), the Organisers, after consultation with the EUPT-QCG, may decide to omit a specific stability test. The EUPT-SC will finally decide whether analytes for which the stability test was not undertaken will be included in the final report, considering all relevant aspects such as the distribution of the participant's results (CV (%)).

A pesticide is considered to be adequately stable if $|x_1 - y_i| \leq 0.3 \times \sigma$, where x_1 is the mean value of the first stability test, y_i the mean value of the last stability test and σ the standard deviation used for proficiency assessment (typically 25% of the assigned value).

The results of all stability tests are presented to the EUPT-SC. In special cases where the above stability test criteria are not met, the EUPT-SC considering all relevant aspects (e.g. the past experience with the stability of the compound, the overall distribution the participants' results, the analytical difficulties faced during the test, knowledge about the analytical behaviour of the pesticide question) may decide to overrule the test. The reasons of this overruling will be transparently explained in the Final EUPT-Report.

[8] FFP-RSD = fit for purpose relative standard deviation, see also p. 11.

The Organisers may also decide to conduct additional stability tests at different storage conditions than those recommended to the participants e.g. at ambient temperature.
Considering knowledge about the expected susceptibility of pesticides in the Test Item to possible losses, the Organisers will chose the shipment conditions to be such that pesticide losses are minimised (e.g. shipment of frozen samples, addition of dry ice). As shipment time can differ between labs/countries it is recommended that the Organisers conduct additional stability tests at conditions simulating shipment. Should critical losses be detected for certain pesticides the EUPT-SC will be informed (or the EUPT-QCG before or during the test). Case-by-case decisions may be taken considering all relevant aspects including the shipment time of the samples to each laboratory.

Methodologies to be used by the participants

Participating laboratories are instructed to use the analytical procedure(s) that they would routinely employ in official control activities (monitoring etc.). Where an analytical method has not yet been established routinely this should be stated.

General procedures for reporting results

Participating laboratories are responsible for reporting their own quantitative results to the Organiser within the stipulated deadline. Any pesticide that was targeted by a participating laboratory should be reported as "analysed". Each laboratory will be able to report only one result for each analyte detected in the Test Item. The concentrations of the pesticides detected should be expressed in 'mg/ kg' unless indicated otherwise in the specific protocol.
The Test Item is intentionally treated with pesticides whereas the Blank Material is analysed to ensure that it does not contain any of the pesticides in the Target Pesticides List, at or above, the specified MRRLs. Both the Test Item and Blank Material have to be analysed by the participating laboratories and any pesticide detected in them must be reported.

Correction of results for recovery

According to the Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed[9] , it is common practice that pesticide analysis results are not corrected for recovery, but may be corrected if the average recovery is significantly different from 100 % (typically if outside the 70 – 120 % range, but also exhibiting good precision). Other approaches for recovery correction explicitly allowed in the SANCO document are the use of stable isotope labelled analogues of the target analytes used as Internal Standards (ISTDs), the 'procedural calibration' approach as well as the approach of 'standard addition' with additions of analyte(s) being made to analytical portions. Where reported residue data have been automatically adjusted for recovery by the method, or have subsequently been adjusted using a recovery factor, this must be indicated on the specific field of the 'Result Submission Form'. Results may be corrected for recovery only in cases where this correction is applied in routine practice (including cases of MRLviolations). Laboratories are required to report whether their results were

[9] Document N° SANCO/12571/2013; Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Food and Feed

adjusted for recovery and, if a recovery factor was used, the recovery (in percentage) must also be reported. No recovery data are required where correction for recovery is automatic by using the 'standard addition approach, or isotopically-labelled internal standards (in both cases with spiking of the Test Item at the beginning of the extraction procedures). In these cases, the laboratories should report the actual approach that was followed.

Methodology information

All laboratories are requested to provide information on the analytical method(s) they have used. A compilation of the methodology information submitted by all participants is presented in an Annex of the final report or in a separate report. Where necessary the methods are evaluated and discussed, especially in those cases where the result distribution is not unimodal or very broad (e.g. CV > 35 %). If no sufficient information on the methodology used is provided, the Organiser reserves the right not to accept the analytical results reported by the participants concerned.

Results evaluation

The procedures used for the treatment and assessment of results are described below.

- ***False Positives***

These are results of pesticides from the Target Pesticides List, that are reported, at or above, their respective MRRL although they were: (i) not detected by the Organiser, even after repeated analyses, and/or (ii) not detected by the overwhelming majority (e.g. > 95 %) of the participating laboratories that had targeted the specific pesticides. In certain instances, case-by-case decisions by the EUPT-Panel may be necessary.
Any results reported lower than the MRRL will not be considered as false positives, even though these results should not have been reported.

- ***False Negatives***

These are results for pesticides reported by the laboratories as 'analysed' but without reporting numerical values although they were: a) used by the Organiser to treat the Test Item and b) detected by the Organiser as well as the majority of the participants that had targeted these specific pesticides at or above the respective MRRLs. Results reported as '< RL' (RL= Reporting Limit of the laboratory) will be considered as not detected and will be judged as false negatives. In certain instances, case-by-case decisions by the EUPT-Panel may be necessary.

In cases of the assigned value being less than a factor of 4 times the MRRL, false negatives will typically not be assigned. The EUPT-Panel may decide to take case-by-case decisions in this respect after considering all relevant factors such as the result distribution and the reporting limits of the affected labs.

- ***Estimation of the true concentration (μ)***

In order to minimise the influence of out-lying results on the statistical evaluation, the assigned value (= consensus concentration) will typically be estimated using robust statistics as described in ISO 13528:2009-01[10]. In special justifiable cases, the EUPT-Panel may decide to eliminate certain results traceably associated with gross errors (see "Omission or Exclusion of results" below) or to use only the results of a subgroup consisting of laboratories that have repeatedly demonstrated good performance for the specific compound in the past.

- ***Omission or Exclusion of results***

Before estimating the assigned value results associated with obvious mistakes have to be examined to decide whether they should be removed from the population. Such gross errors may include incorrect recording (e.g. due to transcription errors by the participant, decimal point faults or transposed digits, incorrect unit), calculation errors (e.g. missing factors), analysis of a wrong sample/extract (e.g. a spiked blank), use of wrong concentrations of standard solutions, incorrect data processing (e.g. integration of wrong peak), major deviations from the analytical procedure, inappropriate storage or transport conditions (in case of susceptible compounds), and the use of inappropriate procedures that demonstrably lead to significantly biased results (e.g. due to degradation or incomplete extraction). Where the Organisers (e.g. after the publication of the preliminary report) receive information of such gross errors, having a significant impact on a generated result, the affected results will be examined on a case-by-case basis to decide whether, or not, they should be excluded from the population used for robust statistics. Even results that cannot be specifically identified as outliers might be excluded. All decisions to omit/exclude results will be discussed with the EUPT-SC and the reasoning for the omission of each result clearly stated in the final EUPT-Report. However, z-scores will be calculated for all results irrespective of the fact that they were omitted from the calculation of the assigned value.

Omitted results might be interesting as they might give indications about possible source(s) of errors. The Organisers will thus ask the relevant lab(s) to provide feedback on possible sources of errors (see also "follow-up activities").

Any exclusion of results from the population is to be discussed within the EUPT-SC and the reasoning behind is to be revealed in the EUPT-final report.

Uncertainty of the assigned value

The uncertainty of the assigned values μi is calculated according to ISO 13528:2009-01 as:

$$\mu_i = 1.25 * \frac{S}{\sqrt{n}}$$

Where S is the robust standard deviation and *n* is the number of results.

[10] DIN ISO 13528:2009-01, Statistical methods for use in proficiency testing by interlaboratory comparisons, International Organization for Standardization. Therein a specific robust method for determination of the consensus mean and standard deviation without the need for removal of deviating results is described (Algorithm A in Annex C).

In certain cases and considering all relevant factors (e.g. the result distribution, multimodality), the number of submitted results, information regarding analyte homogeneity/stability, information regarding the use of methodologies that might produce a bias that were used by the participants), the EUPT-Panel may consider the assigned value of a specific analyte to be too uncertain and decide that the results should not be evaluated, or only evaluated for informative purposes. The provisions of ISO 13528:2009-01 concerning the uncertainty of the assigned value will be taken into account.

- ***Standard deviation of the assigned value (target standard deviation)***

The target standard deviation (δ) of the assigned value will be calculated using a Fit-For-Purpose Relative Standard Deviation (FFP-RSD) approach, as follows:

$$\delta = b_i * \mu_i \quad \text{with } b_i = 0.25 \text{ (25\% FFP-RSD)}$$

The percentage FFP-RSD is set at 25% based on experience from previous EUPTs[11]. The EUPT-Panel reserves the right to also employ other approaches on a case-by-case basis considering analytical difficulties and experience gained from previous proficiency tests.

For informative purposes the robust relative standard deviation (CV (%)) is calculated according to ISO 13528:2009-01; Chapter 5.6 (Consensus value from participants) following Algorithm A in Annex C.

- ***z-scores***

This parameter is calculated using the following formula:

$$z_i = (x_i - \mu_i) / \delta_i$$

Where: x_i is the value reported by the laboratory, μ_i the assigned value, and δ_i the standard deviation at that level for each pesticide (i). Z-scores will be rounded to one decimal place. For the calculation of combined z-scores (see below) the original z-scores will be used and rounded to one decimal place after calculation.

Any z-scores of > 5 will be reported as '>5' and a value of '5' will be used to calculate combined z-scores (see below).

z-Scores will be interpreted in the following way:

$\|z\| \leq 2.0$	Acceptable
$2.0 < \|z\| \leq 3.0$	Questionable
$\|z\| > 3.0$	Unacceptable

For results that are considered to be false negatives, z-scores will be calculated using the MRRL or RL (the laboratory's Reporting Limit) if the RL < MRRL. The EUPT-Panel will consider whether, or not, these values should appear in the z-score histograms.

[11] Comparative Study of the Main Top-down Approaches for the Estimation of Measurement Uncertainty in Multiresidue Analysis of Pesticides in Fruits and Vegetables. J. Agric. Food Chem., 2011, 59(14), 7609-7619.

ANNEX 1. Protocols and instructions. Target List of pesticides to be sought.

- ***Category A and B classification***

The EUPT-Panel will decide if and how to classify the laboratories into two categories - A or B. Currently, laboratories that have detected and quantified a sufficiently high percentage of the pesticides present in the Test Item (e.g. at least 90 %) and reported no false positives will have demonstrated 'sufficient scope' and can therefore be classified into Category A. The 90 % criterion will be applied following Table 1.

Table 1. No. of pesticides needed to be detected to have sufficient scope.

No. of Pesticides Present in the Sample (N)	90%	No. of Pesticides needed to be detected to have sufficient scope (n)	n
3	2.7	3	N
4	3.6	4	
5	4.5	4	N - 1
6	5.4	5	
7	6.3	6	
8	7.2	7	
9	8.1	8	
10	9.0	9	
11	9.9	10	
12	10.8	11	
13	11.7	12	
14	12.6	13	
15	13.5	13	N - 2
16	14.4	14	
17	15.3	15	
18	16.2	16	
19	17.1	17	
20	18.0	18	
21	18.9	19	
22	19.8	20	
23	20.7	21	
24	21.6	22	
25	22.5	22	N - 3
26	23.4	23	

- ***Overall performance of laboratories - combined z-scores***

For evaluation of the overall performance of laboratories within Category A, the Average of the Squared z-Score (AZ^2)[12,13] (see below) will be used. The AZ^2 is calculated as follows:

$$AZ^2 = \frac{\sum_{i=1}^{n} Z_i^2}{n}$$

Where n is the number of z-scores to be considered in the calculation. In the calculation of the AZ^2, z-scores higher than 5 will be classified as 5. Based on the AZ^2 achieved, the laboratories are classified as follows:

$AZ^2 \leq 2.0$	Good
$2.0 < AZ^2 \leq 3.0$	Satisfactory
$AZ^2 > 3.0$	Unsatisfactory

Combined z-scores are considered to be of lesser importance than the individual z-scores. The EUPT-Panel retains the right not to calculate AZ^2 if it is considered as not being useful or if the number of results reported by any participant is considered to be too low.

In the case of EUPT-SRMs, where only a few results per lab may be available, the Average of the Absolute z-scores (AAZ) may be calculated for informative purposes, but only for labs that have reported enough results to obtain 5 or more z-scores. For the calculation of the AAZ, z-scores higher than 5 will also be classified as 5.

Laboratories within Category B will be ranked according to the total number of pesticides that they correctly reported to be present in the Test Item. The number of acceptable z-scores achieved will be presented, too. The EURL-Panel retains the right to calculate combined z-scores (see above) also for labs within Category B, e.g. for informative purposes, provided that a minimum number of results (z-scores) are have been reported.

Publication of results

The EURLs will publish a preliminary report, containing tentative medians and z-score values for all pesticides present in the Test Item, within 2 months of the deadline for result submission.

The Final EUPT Report will be published after the EUPT-Panel has discussed the results. Taking into account that the EUPT-Panel meets normally only once a year (typically in late summer or autumn) to discuss the results of all EUPTs organised annually by the EURLs in the following year, the final report may be published up to 10 months after the deadline for results submission.

[12] Formerly named "Sum of squared z-scores (SZ^2)"

[13] Laboratory assessment by combined z-score values in proficiency tests: experience gained through the EUPT for pesticide residues in fruits and vegetables. Anal. Bioanal. Chem., 2010, 397, 3061–3070.

ANNEX 1. Protocols and instructions. Target List of pesticides to be sought.

Certificates of participation

Together with the Final EUPT-Report, the EURL Organiser will deliver a Certificate of Participation to each participating laboratory showing the z-scores achieved for each individual pesticide, the combined z-scores calculated (if any), and the classification into Category A or B.

Feedback

At any time before, during or after the PT participants have the possibility to contact the Organisers and make suggestions or indicate errors. After the distribution of the Final EUPT-Report, participating laboratories will be given the opportunity to give their feedback to the Organisers and make suggestions for future improvements.

Correction of errors

Should errors be discovered in any of the documents issued prior to the EUPT (Calendar, Target Pesticides List, Specific Protocol, General Protocol) the corrected documents will be uploaded onto the website and in the case of substantial errors the participants will be informed. **Before starting the exercise participants should make sure to download the latest version of these documents.**

If substantial errors are discovered in the Preliminary EUPT-Report the Organisers will distribute a new corrected version, where it will be stated that the previous version is no longer valid.

Where substantial errors are discovered in the Final EUPT-Report the EUPT-Panel will decide whether a corrigendum will be issued and how this should look. The online version of the final report will be replaced by the new one and all affected labs will be contacted.

Where errors are discovered in EUPT-Certificates the relevant laboratories will be sent new corrected ones. Where necessary the laboratories will be asked to return the old ones.

Follow-up activities

Laboratories are expected to undertake follow-up activities to trace back the sources of erroneous or strongly deviating results (typically those with with $|z| > 2.0$) - including all false positives and false negatives. Even results within $|z| < 2.0$ may have to be checked if there is indications of a significant positive or negative bias.
Upon request, the laboratory's corresponding NRL and EURL are to be informed of the outcome of any investigative activities for false positives, false negatives and for results with $|z| > 3.0$.
Concerning z-scores between 2.0 and 3.0 the communication of the outcome of traceability activities is optional but highly encouraged where the source of deviation could be identified and could be of interest to other labs.
According to instructions from DG-SANCO, the "Protocol for management of underperformance in comparative testing and/or lack of collaboration of National Reference Laboratories (NRLs) with EU Reference Laboratories (EURLs) activities" is to be followed.

ANNEX 1. Protocols and instructions. Target List of pesticides to be sought.

Disclaimer

The EUPT-Panel retains the right to change any parts of this EUPT – General Protocol based on new scientific or technical information. Any changes will be communicated in due course.

EUPT-T02 SPECIFIC PROTOCOL

European Union Proficiency Test for

Pesticide Residues in tea

(2014)

Introduction

This protocol is complementary to the General Protocol of EU Proficiency Tests (EUPTs) for Pesticide Residues in Food and Feed. This Proficiency Test is organised by the EURL for Pesticide Residues in Fruit and Vegetables covering Multiresidue Methods (MRM) of analysis.

Test item

This proficiency test is based on the analysis of tea samples from China containing incurred residues of pesticides. The samples were purchased in a specialised shop for tea in Almería, Spain.

The test item (dried green tea containing incurred pesticide residues) was ground, homogenised and sub-sampled into self-seal bags that had previously been coded.

Ten of those bags containing the test item have been chosen randomly, and analysed to check for homogeneity.

The test item is stored at 4ºC prior to shipment to participants.

Two bags, again chosen randomly, will be analysed by the Organiser over a period of time to confirm the stability of the pesticides in the test item (firstly, when the test items are shipped, then a few days after the receipt deadline for participants´ results).

Steps to follow

This Proficiency Test will be made up of the following steps:

1. To participate, each laboratory must complete and return the Application Form, sent to the participants by e-mail, before the deadline stipulated on the Calendar. The participants will also receive the Target Pesticide List, containing the Minimum Required Reporting Limits (MRRLs). Those MRRLs do not always correspond with the EU MRLs set for tea. Participation in this proficiency test remains on a voluntary basis.

2. Laboratories will then receive an e-mail confirming their participation in this exercise, and assigning them each a Laboratory Code.

3. The sample delivery will be provided free of charge for NRLs, and it will be 150 euros for the rest of the laboratories.

4. The sample will be delivered to the participant laboratories on September 8th 2014. At the same time they will receive by e-mail an Excel file where they will be able to report the results.

5. The deadline for submitting the results of this proficiency test is 27th September 2014.

6. The Organiser will evaluate the results at the end of the proficiency test, once the deadline for the receipt of results has passed. The Organiser will upload an electronic version onto the EURL-FV website and will send the electronic copy of the Final Report to each participant laboratory. This report will include information regarding the design of the test, the homogeneity and stability results, a statistical evaluation of the participant's results as well as graphical displays of the results and any conclusions. Further relevant information considered to be of value may also be included.

Amount of Test Item

Participants will receive:

- Approximately 15 g of incurred commercial tea.

Shipment of Test item

The test item will be packed in self-seal bags and into cardboard boxes protected with foam in the interior.

The shipment of the test item will be carried out over a one-week period from the 8th September 2014. The Organiser will try to ensure that all the packages arrive on the same day at each laboratory. An information message will be sent out by e-mail before shipment. Laboratories must make their own arrangements for the receipt of the package. They must inform the Organiser of any public holidays in their country/city during the delivery period given in the calendar, as well as making the necessary arrangements for receiving the shipment, even if the laboratory is closed.

Advice on Test item Handling

Once received, the test item should be stored at 4°C prior to analysis thus avoiding any possible deterioration/spoilage. The test item should be mixed thoroughly before taking the analytical portion(s).

All participants should use their own routine standard operating procedures for extraction, clean-up and analytical measurement and their own reference standards for identification and quantification.

ANNEX 1. Protocols and instructions. Target List of pesticides to be sought.

Test item Receipt

Once the laboratory has received the test item, its arrival must be reported to the Organiser by e-mail. The deadline for acceptance (or non-acceptance) is 12th September 2014. If the laboratory does not respond by this date, the Organiser will assume that the test item has been received and accepted.

If any laboratory has not received the test item by 12th September, they must inform the Organiser **immediately** by e-mail (cferrer@ual.es or analozano@ual.es)

Submission of results:

Once the laboratory has analysed the test item and is ready to submit their data, they must enter their results in the Excel file provided by the Organisers and send it to the following e-mail address: cferrer@ual.es.

All analyte concentrations must be expressed in mg/kg together with the associated recovery expressed as a percentage.

The number of significant figures should be based on the guidelines provided in SANCO/12571/2013. Additional significant figures may be recorded for the purpose of statistical analysis. Please bear this in mind when reporting data:

- Residue levels above the reporting level and < 10 mg/kg should be rounded to two significant figures.
- Residue levels ≥ 10 mg/kg may be rounded to three significant figures or to a whole number.

Results should not be reported where a pesticide was not detected or was detected below the laboratory's LOQ. In both cases, this should be recorded as 'ND' (Not Detected) or <LOQ. If a pesticide was not sought, it should be recorded as 'NA' (Not Analysed). The actual results/residue levels measured must be reported as numbers.

Further instructions on how to fill in the Excel file will be provided in the same file.

False Negatives

After the receipt of results, participant laboratories that have reported that they sought a pesticide present in the test item but did not find it (false negative) will be asked via e-mail about the analytical method used to determine that specific pesticide.

ANNEX 1. Protocols and instructions. Target List of pesticides to be sought.

Calendar

ACTIVITY	DATE
Sending Application Form to laboratories	2nd June 2014
Sending calendar and pesticides target list to participant laboratories.	2nd June 2014
Deadline for receiving Application Form from laboratories.	23rd June 2014
Sample distribution.	8th September 2014
Deadline for receiving results	27th September 2014
Preliminary Report: only results, no statistical treatment.	October 2014
Final Report	December 2014

Cost of test item shipment.

The sample delivery will be **150 €**. For NRLs it will be free of charge. Regarding payment procedures, each laboratory can specify their details and invoice requests when applying for the test. Payment details are as follows:

BANK NAME: CAJAMAR - Caja Rural Sociedad Corporativa de Crédito

BANK ACCOUNT HOLDER: Universidad de Almeria

BANK ADDRESS: Office Number 990. Universidad de Almeria. Spain

IBAN: ES0730580130172731005000

SWIFT: CCRIES2A

REFERENCE GIVEN: Invoice No. or Lab Code

Contact information

The official organising group details are as follows:

Universidad de Almería. Edificio Químicas CITE I

Ctra. Sacramento s/n

04120 La Cañada de San Urbano Almería - Spain

Fax No.: +34 950015008

ANNEX 1. Protocols and instructions. Target List of pesticides to be sought.

Organising team (e-mails and phone no.s):

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Ms. Ana Lozano EURL-FV analozano@ual.es +34 950015645
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Quality Control Group

Dr. Antonio Valverde, University of Almería, Spain
Mr. Stewart Reynolds, Senior Chemist, FERA, York, United Kingdom

Statistical Group

Dr. Carmelo Rodriguez, Senior Mathematician, University of Almeria, Spain

Advisory Group

Dr. Michelangelo Anastassiades, Senior Chemist, CVUA, Stuttgart, Germany.
Mr. Richard Fussell, Senior Chemist, FERA, York, United Kingdom.
Dr. Miguel Gamón, Senior Chemist, Laboratorio Agroalimentario, Valencia, Spain.
Dr. Magnus Jezussek, Senior Chemist, Erlangen, Germany.
Dr. André de Kok, Senior Chemist, NVWA, Wageningen, The Netherlands.
Mr. Ralf Lippold, Senior Chemist, CVUA, Freiburg, Germany.
Dr. Sonja Masselter, Senior Chemist, AGES, Innsbruck, Austria.
Dr. Tuija Pihlström, Senior Chemist NFA, Uppsala, Sweden.
Dr. Mette Erecius Poulsen, Senior Chemist, NFI, Copenhagen, Denmark.
Dr. Darinka Stajnbaher, Senior Chemist, Maribor, Slovenia.

TARGET PESTICIDE LIST FOR THE EUPT-T02

Pesticide	MRRL (mg/Kg)
3-hydroxy-carbofuran	0.01
Acephate	0.01
Acetamiprid	0.01
Acrinathrin	0.01
Aldicarb	0.01
Aldicarb Sulfone	0.01
Aldicarb Sulfoxide	0.01
Amitraz	0.01
Anthraquinone	0.01
Azinphos-methyl	0.01
Azoxystrobin	0.01
Benfuracarb	0.01
Bifenthrin	0.01
Bitertanol	0.01
Boscalid	0.01
Bromopropylate	0.01
Bromuconazole	0.01
Bupirimate	0.01
Buprofezin	0.01
Cadusafos	0.01
Captan	0.01
Carbaryl	0.01
Carbendazim (sum of benomyl and carbendazim expressed as carbendazim)	0.01
Carbofuran	0.01
Carbosulfan	0.01
Chlorfenapyr	0.01
Chlorfenvinphos	0.01
Chlorobenzilate	0.01
Chlorothalonil	0.01
Chlorpropham (only parent compound)	0.01
Chlorpyrifos	0.01
Chlorpyrifos-methyl	0.01
Clofentezine (only parent compound)	0.01
Clothianidin	0.01
Cyfluthrin (cyfluthrin incl. other mixtures of constituent isomers (sum of isomers))	0.01
Cypermethrin (cypermethrin incl. other mixtures of constituent isomers (sum of isomers))	0.01
Cyproconazole	0.01
Cyprodinil	0.01
Deltamethrin	0.01
Demeton-S-methylsulfone	0.01
Desmethyl-pirimicarb	0.01
Diazinon	0.01
Dichlofluanid (only parent compound)	0.01
Dichlorvos	0.01
Dicloran	0.01
Dicofol	0.01
Difenoconazole	0.01
Diflubenzuron	0.01
Dimethoate	0.01
Dimethomorph	0.01
Dimethylaminosulfotoluidide (DMST)	0.01
Diphenylamine	0.01
DMF (2,4-Dimethylformanilide)	0.01
DMPF (N-2,4-Dimethylphenyl-N-Methyl-formamidine)	0.01
Endosulfan alpha	0.01

ANNEX 1. Protocols and instructions. Target List of pesticides to be sought.

Pesticide	**MRRL** (mg/Kg)
Endosulfan beta	0.01
Endosulfan sulfate	0.01
EPN	0.01
Epoxiconazole	0.01
Ethion	0.01
Ethoprophos	0.01
Etofenprox	0.01
Fenamiphos	0.01
Fenamiphos sulfone	0.01
Fenamiphos sulfoxide	0.01
Fenarimol	0.01
Fenazaquin	0.01
Fenbuconazole	0.01
Fenhexamid	0.01
Fenitrothion	0.01
Fenoxycarb	0.01
Fenpropathrin	0.01
Fenpropimorph	0.01
Fenthion	0.01
Fenthion oxon	0.01
Fenthion oxon sulfone	0.01
Fenthion oxon sulfoxide	0.01
Fenthion sulfone	0.01
Fenthion sulfoxide	0.01
Fipronil (only parent compound)	**0.005**
Fludioxonil	0.01
Flufenoxuron	0.01
Fluopicolide	0.01
Fluquinconazole	0.01
Flusilazole	0.01
Flutolanil	0.01
Flutriafol	0.01
Folpet	0.01
Fosthiazate	0.01
Hexaconazole	0.01
Hexythiazox	0.01
Imazalil	0.01
Imidacloprid	0.01
Indoxacarb (Indoxacarb as sum of the isomers S and R)	0.01
Iprodione	0.01
Iprovalicarb	0.01
Isofenphos-methyl	0.01
Kresoxim-methyl	0.01
Lambda-Cyhalothrin	0.01
Linuron	0.01
Lufenuron	0.01
Malaoxon	0.01
Malathion	0.01
Mepanipyrim (only parent compound)	0.01
Metaflumizone	0.01
Metalaxyl and metalaxyl-M	0.01
Metconazole	0.01
Methamidophos	0.01
Methidathion	0.01
Methiocarb	0.01
Methiocarb sulfone	0.01
Methiocarb sulfoxide	0.01
Methomyl	0.01

ANNEX 1. Protocols and instructions. Target List of pesticides to be sought.

Pesticide	MRRL (mg/Kg)
Methoxyfenozide	0.01
Monocrotophos	0.01
Myclobutanil	0.01
Omethoate	0.01
Orthophenylphenol	0.01
Oxadixyl	0.01
Oxamyl	0.01
Oxydemeton-methyl	0.01
Paclobutrazole	0.01
Paraoxon-methyl	0.01
Parathion-ethyl	0.01
Parathion-methyl	0.01
Penconazole	0.01
Pencycuron	0.01
Pendimethalin	0.01
Phenthoate	0.01
Phosalone	0.01
Phosmet	0.01
Phosmet oxon	0.01
Phoxim	0.01
Pirimicarb	0.01
Pirimiphos-methyl	0.01
Prochloraz (only parent compound)	0.01
Procymidone	0.01
Profenofos	0.01
Propargite	0.01
Propiconazole	0.01
Propyzamide	0.01
Prothioconazole (Prothioconazole-desthio)	0.01
Prothiofos	0.01
Pyraclostrobin	0.01
Pyridaben	0.01
Pyrimethanil	0.01
Pyriproxyfen	0.01
Quinoxyfen	0.01
Spinosad (sum of spinosyn A and spinosyn D, expr. as spinosad)	0.01
Spirodiclofen	0.01
Spiroxamine	0.01
Tau-Fluvalinate	0.01
Tebuconazole	0.01
Tebufenozide	0.01
Tebufenpyrad	0.01
Teflubenzuron	0.01
Tefluthrin	0.01
Tetraconazole	0.01
Tetradifon	0.01
Thiabendazole	0.01
Thiacloprid	0.01
Thiamethoxam	0.01
Thiodicarb	0.01
Thiophanate-methyl	0.01
Tolclofos-methyl	0.01
Tolylfluanid	0.01
Triadimefon	0.01
Triadimenol	0.01
Triazophos	0.01
Trichlorfon (only parent compound)	0.01
Trifloxystrobin	0.01

ANNEX 1. Protocols and instructions. Target List of pesticides to be sought.

Pesticide	**MRRL** (mg/Kg)
Triflumuron	0.01
Trifluralin	0.01
Triticonazole	0.01
Vinclozolin (only parent compound)	0.01
Zoxamide	0.01

This list is based on Commission Regulation (EU) No 788/2012.

ANNEX 2. List of laboratories that agreed to participate in EUPT-T02.

COUNTRY	LABORATORY NAME	CITY	REPORTED RESULTS
Austria	Austrian Agency for Health and Food Safety, Institute for Food Safety, Department for Pesticide and Food Analytics (PLMA)	Innsbruck	YES
Belgium	Scientific Institute of Public Health	Brussels	YES
Belgium	Fytolab cvba	Zwijnaarde	YES
Belgium	LOVAP	Geel	YES
China	Key Laboratory of Food Safety Risk Assessment of Minstry of Health, China National Center for Food Safety Risk Assessment	Beijing	YES
China	Shanghai Municipal Center for Disease Control and Prevention	Shanghai	YES
Croatia	E.C. INSPEKT d.o.o.	Zagreb	YES
Croatia	EUROINSPEKT CROATIAKONTROLA d.o.o.	Zagreb	YES
Czech Republic	Czech Agriculture and Food Inspection Authority	Prague	YES
Czech Republic	Department of Food Analysis and Nutrition, Institute of Chemical Technology Prague (ICT Prague)	Prague	YES
Finland	Finnish Customs Laboratory	Espoo	YES
France	SCL-IDF-Massy	Massy Cedex	YES
France	GIRPA/FREDON PAYS DE LA LOIRE	Beaucouze	YES
France	CERECO SUD	Garons	YES
France	Laboratoire du SCL de Montpellier	Montpellier	YES
Germany	Federal Insitute of Food safety and Consumer Protection (BVL)	Berlin	YES
Germany	Landesamt für Verbraucherschutz	Saarbrücken	YES
Germany	Landesuntersuchungsanstalt für das Gesundheits- und Veterinärwesen Sachsen	Dresden	YES
Germany	Institut für Hygiene und Umwelt	Hamburg	YES
Germany	Chemical and Veterinary Analytical Institute Rhine-Ruhr-Wupper	Krefeld	YES
Germany	Chemisches und Veterinäruntersuchungsamt Stuttgart (CVUA Stuttgart)	Fellbach	YES
Germany	Landesuntersuchungsamt für Chemie, Hygiene und Veterinärmedizin	Bremen	YES
Germany	Berlin-Brandenburg State Laboratory	Berlin	YES
Germany	Eurofins Dr. Specht Laboratorien GmbH	Hamburg	YES
Germany	The Bavarian Health and Food Safety Authority	Erlangen	YES
Greece	PESTICIDE RESIDUES LABORATORY, BENAKI PHYTOPATHOLOGICAL INSTITUTE	Kiphissia (Athens)	YES

ANNEX 2. List of laboratories that agreed to participate in EUPT-T02.

COUNTRY	LABORATORY NAME	CITY	REPORTED RESULTS
Hungary	National Food Chain Safety Office, DPPSCA Pesticide Residue Analytical Laboratory, Miskolc	Miskolc	YES
Hungary	National Food Chain Safety Office, DPPSCA Pesticide Analytical Laboratory, Velence	Velence	YES
Ireland	The Pesticide Control Laboratory	Celbridge	YES
Italia	Laboratorio di Prevenzione - ASL Milano	Milano	YES
Italy	ARPAL - Dipartimento La Spezia - U.O. Laboratorio	La Spezia	YES
Italy	Arpa Emilia Romagma, Area Fitofarmaci	Ferrara	YES
Norway	Bioforsk, Plant Health and Plant Protection, Pesticide Chemistry	Aas	YES
Poland	Institute of Horticulture, Food Safety Laboratory	Skierniewice	YES
Poland	Voivodship Sanitary-Epidemiological Station in Warsaw - Pesticide Residue Laboratory, National Reference Laboratory for fruits, vegetables and cereals.	Warsaw	YES
Saudi Arabia	National Center for Monitoring Food Contaminants	Riyadh	YES
Slovakia	Veterinary and Food Institute in Bratislava	Bratislava	YES
Slovenia	National Laboratory of Health, Environment and Food (Department for Chemical Analysis Maribor)	Maribor	NO
Spain	LABORATORIO AGROALIMENTARIO DE EXTREMADURA	Cáceres	YES
Spain	Analytica Alimentaria GmbH, sucursal en España	Almeria	YES
Spain	CNTA	San Adrian (Navarra)	YES
Spain	LABORATORIOS ECOSUR, S.A.	Lorqui - Murcia	NO
Spain	LABORATORIO DE PRODUCCUÓN Y SANIDAD VEGETAL DE ALMERIA	Almería	YES
Spain	Laboratori Agroalimentari - DAAM (Generalitat de Catalunya)	Cabrils	YES
Spain	Laboratorio Arbitral Agroalimentario	Madrid	YES
Spain	LABORATORIO DE PRODUCCION Y SANIDAD VEGETAL. AGAPA. JUNTA DE ANDALUCIA	Mengibar (Jaén)	YES
Sweden	National Food Agency, Science Department	Uppsala	YES
The Netherlands	Groen Agro Control	Delfgauw	YES
The Netherlands	Laboratorium Zeeuws-Vlaanderen BV	Graauw	YES
The Netherlands	NVWA - Netherlands Food and Consumer Product Safety Authority	Wageningen	YES
Uruguay	Pharmacognosy & Natural Products G.A.C.T.	Montevideo	YES