Australian Government
Department of Industry, Innovation and Science
National Measurement Institute

Proficiency Test Report AQA 18-07 Pesticides in Fruit & Vegetables

July 2017

ACKNOWLEDGMENTS

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I would like to thank the management and staff of the participating laboratories for supporting the study. It is only through widespread participation that we can provide an effective service to laboratories.

The assistance of the following NMI staff members in the planning, conduct and reporting of the study is acknowledged.

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I would like to thank Department of Economic Development, Jobs, Transport and Resources (DEDJTR), Victoria for supplying the incurred sample.

Paul Armishaw

Manager, Chemical Reference Values
105 Delhi Rd, Riverside Corporate Park, North Ryde NSW 2113
P O Box 138, North Ryde NSW 1670

Phone: 61-2-9449 0149

paul.armishaw@measurement.gov.au

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SUMMARY

Proficiency test AQA 18-07 Pesticides in Fruit and Vegetables was conducted in May 2018; twenty-two laboratories submitted results.

Three sets of test samples were prepared at the NMI laboratory in North Ryde, NSW. Samples S1 and S2 were purchased from a Sydney organic fruit and vegetable wholesaler. Sample S3 lemon was obtained from DEDJTR Victoria.

Sample **S1** was prepared from pureed tomato to which was added pesticide standard solutions.

Sample **S2** was prepared from pureed kale to which was added pesticide standard solutions.

Sample **S3** was prepared from pureed lemons that contained incurred pesticides and to which was added extra pesticide standard solution.

Spiked puree Samples S1, S2 and S3 were dispensed into 120 g portions. Participants were also provided with 120 g portions of unspiked Samples S1 and S2. No unspiked matrix was provided for Sample S3.

Of a possible 264 numeric results a total of 142 were submitted. One hundred and ten results (42%) were reported as Not Tested (NT).

The assigned values were the robust average of participants' results.

Traceability: The consensus of participants' results is not traceable to any external reference, so although expressed in SI units, metrological traceability has not been established.

The outcomes of the study was assessed against the aim as follows:

Assess the proficiency of laboratories measuring pesticides in fruits and vegetables;

Laboratory performance was assessed using both *z*-scores and E_n-scores.

Of the 139 results for which z-scores were calculated, 110 (79%) returned $|z| \leq 2$ indicating a satisfactory performance.

Of the 139 results for which E_n-scores were calculated, 102 (73%) returned $|E_n| \leq 1$ indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory **7, 15** had satisfactory z-scores and E_n-scores for all eleven analytes.

Laboratories **2**, **3**, **12** and **17** did not report results for analytes for which they tested and that were present in the test samples (a total of 6 false negatives).

Laboratories **3**, **11**, **15**, **19** and **21** reported results for analytes not added to the test samples (a total of 8 analytes).

Develop participants' practical application of traceability and measurement uncertainty and provide information that will assist their uncertainty estimates.

Of 142 numerical results, 122 (86%) were reported with an associated expanded measurement uncertainty. Laboratories **2**, **9**, **13** and **22** did not report an estimate of measurement uncertainty, while laboratory **19** reported an estimate of measurement uncertainty only for some analytes. Laboratories **9** and **22** were not accredited.

The magnitude of these uncertainties was within the range 0.24 – 90% relative.

Evaluate the laboratories' test methods.

Participants used a variety of methods and no significant trends with any particular sample preparation method or instrumental technique was evident.

1 INTRODUCTION

1.1 NMI Proficiency Testing Program

The National Measurement Institute (NMI) is responsible for Australia's national measurement infrastructure, providing a range of services including a chemical proficiency testing program.

Proficiency testing (PT) is: 'evaluation of participant performance against pre-established criteria by means of interlaboratory comparison'.[1] NMI PT studies target chemical testing in areas of high public significance such as trade, environment, law enforcement and food safety. NMI offers studies in:

- pesticide residues in fruit and vegetables, soil and water;
- petroleum hydrocarbons in soil and water;
- inorganic analytes in soil, water, food and pharmaceuticals;
- PFAS in soil, water and biota;
- controlled drug assay;
- allergens in food; and
- folic acid in flour.

1.2 Study Aims

The aims of the study were to:

- assess the proficiency of laboratories measuring pesticides in fruit and vegetable;
- develop participants' practical application of traceability and measurement uncertainty and provide information that will assist their uncertainty estimates; and
- evaluate the laboratories' test methods.

The choice of the test method was left to the participating laboratories.

1.3 Study Conduct

The conduct of NMI proficiency tests is described in the NMI Chemical Proficiency Testing Study Protocol.[2] The statistical methods used are described in the NMI Chemical Proficiency Testing Statistical Manual.[3] These documents have been prepared with reference to ISO 17043[1] and The International Harmonized Protocol for Proficiency Testing of (Chemical) Analytical Laboratories.[4] This study falls within the scope of NMI's accreditation as a proficiency testing provider.

2 STUDY INFORMATION

2.1 Selection of Pesticides and Matrices

When selecting matrices and pesticides for this study, consideration was given to:

- a variety of pesticides amenable to both gas chromatography and liquid chromatography;
- a variety of matrices;
- the availability of matrix material with incurred analytes,
- feedback from participants;
- current Australian agricultural practice; and
- Australian maximum residue limits (MRLs) promulgated in the Food Standards Code for Australia & New Zealand.[5]

The spiked pesticide concentrations and MRLs are presented in Table 1.

Table 1 Pesticides spiked into the test samples

Sample and matrix	Spiked concentration (mg/kg)	U[a] (mg/kg)	MRL (mg/kg)
S1 Tomato puree			
Deltamethrin	0.748	0.037	0.1
Endosulfan sulfate[b]	1.469	0.073	-
Imidacloprid[c]	0.352	0.018	0.5
Methamidophos	0.151	0.008	2
S2 Kale puree			
Azoxystrobin	0.850	0.043	2
Imidacloprid	0.250	0.013	0.5
Spinosad[d]	0.568	0.028	0.5
S3 Lemon puree			
Clothianidin	Incurred	-	T0.2
Imazalil	Incurred	-	10
Methidathion	Incurred	-	2
Omethoate	0.230	0.012	5
Thiabendazole[e]	Incurred	-	10

[a] Expanded uncertainty at 95% confidence interval using a coverage factor of 2
[b] Sum of A- and B- endosulfan and endosulfan sulfate
[c] Sum of imidacloprid and metabolites containing the 6-chloropyridinylmethylene moiety, expressed as imidacloprid.
[d] Sum of spinosyn A and spinosyn D
[e] Sum of thiabendazole and 5-hydroxylthiabendazole, expressed as thiabendazole
T denotes that the maximum residue limit is a temporary maximum residue limit

2.2 Study Timetable

The timetable of the study was:

Invitation issued: 06 April 2018
Samples dispatched: 07 May 2018
Results due: 04 June 2018
Interim report issued: 13 June 2018

2.3 Participation

A total of one hundred and sixteen international, national, state government and private laboratories were invited to participate.

Twenty-two laboratories agreed to participate and submitted results. Participant laboratories are listed in Appendix 1.

2.4 Test Material Specification

Three test samples were prepared.

Sample S1 was prepared by spiking pureed tomatoes which had been passed through a 850 µm sieve.

Sample S2 was prepared by spiking pureed kale which had been passed through a 850 µm sieve.

Sample S3 Lemons with incurred pesticides were pureed, spiked with an additional analyte and dispensed into glass jars.

2.5 Laboratory Code

To ensure confidentiality, all laboratories that agreed to participate were assigned a random code number.

2.6 Sample Preparation and Homogeneity

The preparation of the study samples is described in Appendix 2.

No homogeneity testing was conducted. These samples were prepared and packaged using a process that has been demonstrated to produce homogeneous samples for previous NMI PTs of pesticides in fruit and vegetables. The results of the study gave no reason to question the homogeneity of these samples.

2.7 Stability of Analytes

No stability studies were undertaken. Reports in the Joint FAO/WHO Meeting on Pesticide Residues (JMPR) database[6] together with previous use of these analytes in NMI PT studies, gave some assurance that the pesticides selected were stable in frozen fresh produce.

To assess possible instability, the results returned by participants for spiked analytes in Samples S1, S2 and S3 were compared to the spiked concentration. Robust averages of participant results were 58-102% of the spiked levels so gave no reason to question the stability of the pesticides. The stability of methamidophos in tomato sample, the analyte with 58% recovery, has been demonstrated in AQA 11-03.[7]

2.8 Samples Storage and Despatch

The test samples were stored in a freezer at approximately -20°C prior to dispatch. The samples were packaged into insulated polystyrene foam boxes and dispatched by courier.

The following items were also sent to participants:

- a covering letter which included a description of the test samples and instructions for participants;
- a faxback form for participants to confirm the receipt and condition of the test samples; and
- an electronic results sheet was e-mailed to participants.

2.9 Instructions to Participants

Participants were given a list of possible pesticides (Table 2), the incurred test samples and the ones that were spiked contained pesticides from this list.

They were asked to test for pesticides and report results as they would to a client, applying the limit of reporting of the method used. Specific instructions were:

- Quantitatively analyse the samples using your normal test method.
- The unspiked material need not be analysed, it is provided for participants to use if they wish.
- Participants need not test for all listed analytes.
- For each analyte in each sample report a single result expressed as if reporting to a client (i.e. corrected for recovery or not, according to your standard procedure). This figure will be used in all statistical analyses in the study report.

- For each analyte in each sample report the associated expanded measurement uncertainty (e.g. 0.50 ± 0.02 mg/kg).
- Report any listed pesticide not tested as NT.
- Do **not** correct results for any pesticide found in the unspiked sample.
- No limit of reporting has been set for this study. Report results as you would to a client, applying the limit of reporting of the method used for analysis.
- Report the basis of your uncertainty estimates (e.g. uncertainty budget, repeatability precision, long term result variability).
- If determined, report your percentage recovery. This will be presented in the report for information only.
- Return the completed results sheet by e-mail to proficiency@measurement.gov.au.
- Please return the completed result sheet by 04 June 2018. Late results cannot be included in the study report.

Table 2 List of possible analytes

2,4-D	Diazinon	Methidathion
Abamectin	Dicofol	Methomyl
alpha-Endosulfan	Dieldrin	Methomyl oxime
Azinphos-methyl	Dimethoate	Mevinphos
Azoxystrobin	Dithiocarbamates	Monocrotophos
beta-Endosulfan	Endosulfan Sulfate	Omethoate
Bifenazate	Fenamiphos	Parathion
Bifenthrin	Fenitrothion	Parathion Methyl
Buprofezin	Fenthion	Penconazole
Captan	Fenthion sulfone	Permethrin
Carbaryl	Fenthion sulfoxide	Pirimicarb
Carbendazim	Fenvalerate	pp-DDT
Chlorfenvinphos	Imazalil	Procymidone
Chlorothalonil	Imidacloprid	Profenofos
Chlorpyrifos	Indoxacarb	Propargite
Clothianidin	Iprodione	Pyraclostrobin
Cyfluthrin	Linuron	Spinosad
Cyhalothrin	Maldison	Thiabendazole
Cypermethrin	Metalaxyl	Triadimefon
Deltamethrin	Methamidophos	

2.10 Interim Report

An interim report was e-mailed to participants on 13 June 2018.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Test Method Summary

Participants were requested to provide information about their test methods. This is transcribed in Appendix 5.

3.2 Basis of Participants' Measurement Uncertainty Estimates

Table 3 Basis of expanded measurement uncertainty estimate

Lab Code	Approach to Estimating MU	Information Sources for MU Estimation		Guide Document
		Precision	Method Bias	
1	Top Down - precision and estimates of the method and laboratory bias	Control samples Duplicate analysis	Recoveries of sample spike Standard purity	Eurachem/CITAC Guide
2				
3	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control samples Duplicate analysis Instrument calibration	CRM Instrument calibration Recoveries of sample spike Standard purity	Eurachem/CITAC Guide
4	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control samples Duplicate analysis	Instrument calibration Recoveries of sample spike Standard purity	Eurachem/CITAC Guide
5	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control samples Duplicate analysis	Instrument calibration Recoveries of sample spike Standard purity	Eurachem/CITAC Guide
6	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration	Recoveries of sample spike	NMI Uncertainty Course
7	Top Down - precision and estimates of the method and laboratory bias	Control samples	Laboratory bias from PT studies Recoveries of sample spike	Eurachem/CITAC Guide
8	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis		
9				
10	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis		NATA Technical Note 33
11	Top Down - precision and estimates of the method and laboratory bias	Control samples	Instrument calibration Recoveries of sample spike	Eurachem/CITAC Guide
12	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Duplicate analysis	Recoveries of sample spike	Eurachem/CITAC Guide
13				
14	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration	Recoveries of sample spike	NATA Technical Note 33
15	Horwitz formula	Control samples Duplicate analysis Instrument calibration	Instrument calibration Recoveries of sample spike Standard purity	NMI Uncertainty Course
16	Top Down - precision and estimates of the method and laboratory bias	Control samples	CRM Recoveries of sample spike Standard purity	NATA Technical Note 33

Lab Code	Approach to Estimating MU	Information Sources for MU Estimation		Guide Document
		Precision	Method Bias	
17	Standard deviation of replicate analyses multiplied by 2 or 3			
18	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis Instrument calibration	Instrument calibration Recoveries of sample spike	Eurachem/CITAC Guide
19	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analysis	Instrument calibration Recoveries of sample spike Standard purity	Eurachem/CITAC Guide
20	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis	CRM Instrument calibration	NATA Technical Note 33
21	Top Down - precision and estimates of the method and laboratory bias		Recoveries of sample spike	NATA Technical Note 33
22				

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 4 to 15 with resultant summary statistics: robust average, median, mean, maximum, minimum, robust standard deviation (Robust SD) and robust coefficient of variation (Robust CV).

Bar charts of results and performance scores are presented in Figures 2 to 13.

An example chart with interpretation guide is shown in Figure 1.

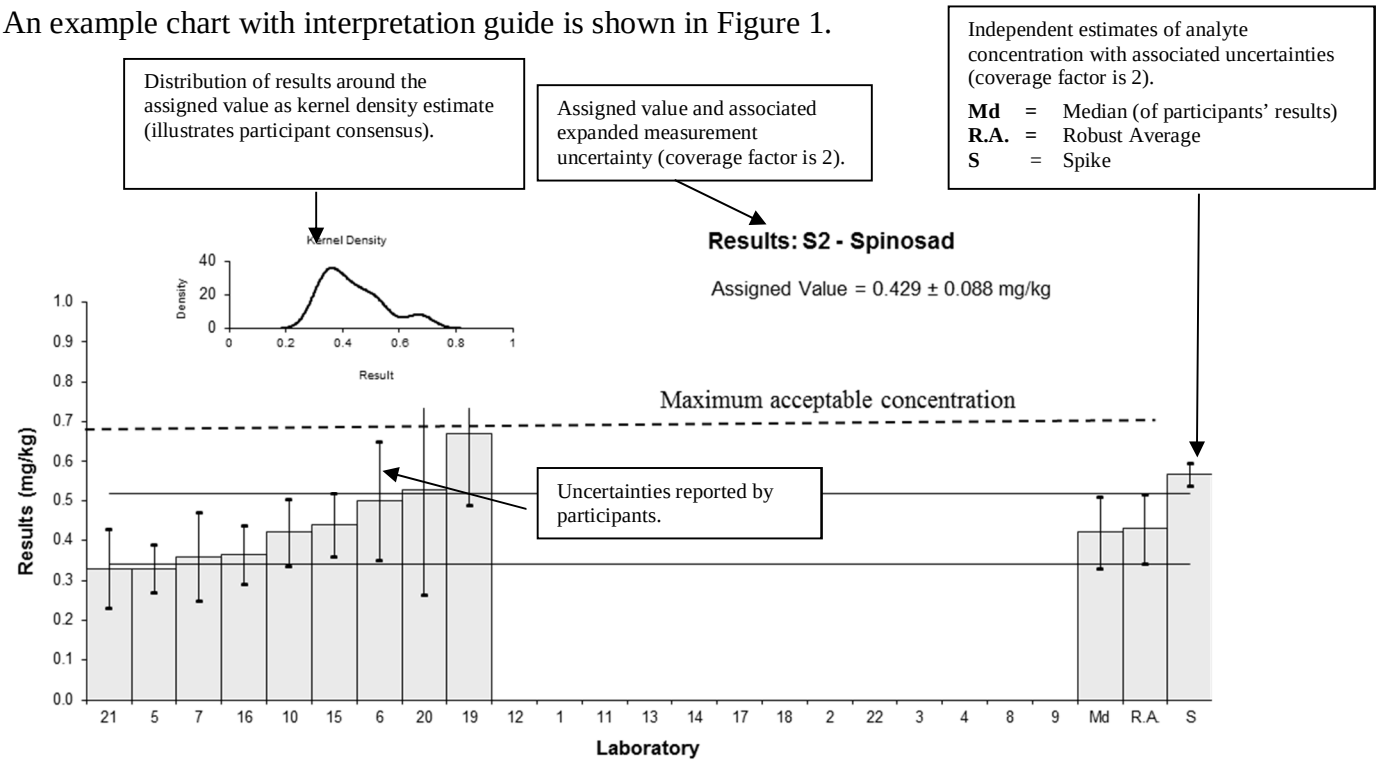


Figure 1 Guide to presentation of results

4.2 Assigned Value

The assigned value is defined as: 'value attributed to a particular property of a proficiency test item'.[1]

For a proficiency test, the assigned value is the best available measurement of the true concentration of an analyte in the test sample.

4.3 Between-Laboratory Coefficient of Variation

The between-laboratory coefficient of variation (CV) is a measure of the between laboratory variation that in the judgement of the study organiser would be expected from participants given the sample concentration.

4.4 Target Standard Deviation

The target standard deviation (σ) is the product of the assigned value (X) and the between-laboratory coefficient of variation (CV, Equation 1). This value is used in the calculation of z-scores. It is important to note that the target standard deviation is not the standard deviation of participant results.

$$\sigma = X * CV \qquad \text{Equation 1}$$

4.5 z-Score

For each participant result a z-score is calculated according to Equation 2 below:

$$z = \frac{(\chi - X)}{\sigma} \qquad \text{Equation 2}$$

where:

z is z-score
χ is the participant result
X is the study assigned value
σ is the target standard deviation from Equation 1

A z-score with absolute value (|z|):

- $|z| \leq 2$ is satisfactory;
- $2 < |z| < 3$ is questionable; and
- $|z| \geq 3$ is unsatisfactory.

4.6 E_n-Score

The E_n-score is complementary to the z-score in assessment of laboratory performance. E_n-score takes account of measurement uncertainty and is calculated according to Equation 3 below:

$$E_n = \frac{(\chi - X)}{\sqrt{U_\chi^2 + U_X^2}} \qquad \text{Equation 3}$$

where:

E_n is E_n-score
χ is a participant's result
X is the assigned value
U_χ is the expanded measurement uncertainty of the participant's result
U_X is the expanded measurement uncertainty of the assigned value

An E_n-score with absolute value ($|E_n|$):

- $|E_n| \leq 1$ is satisfactory; and
- $|E_n| > 1$ is unsatisfactory.

4.7 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025:2017[8] must establish and demonstrate the traceability and measurement uncertainty associated with their test results. Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem /CITAC Guide.[9]

4.8 Robust Average

The robust averages and associated expanded measurement uncertainties were calculated using the procedure described in 'ISO13528:2015, Statistical methods for use in proficiency testing by interlaboratory comparisons'.[10]

5 TABLES AND FIGURES

Table 4

Sample Details

Sample No.	S1
Matrix.	Tomato
Analyte.	Deltamethrin
Units	mg/kg

Participant Results

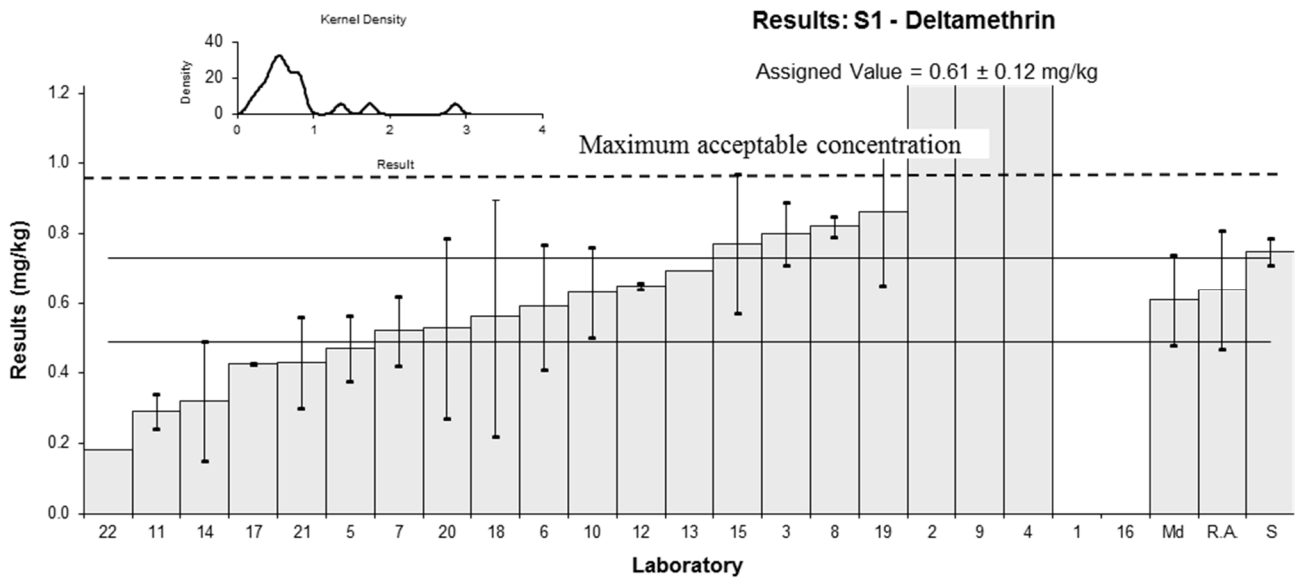
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	1.36	NR	NR	8.20	6.25
3*	0.80	0.09	100	2.00	1.00
4	2.86	0.44	100.33	24.59	4.93
5	0.47	0.094	70	-1.53	-0.92
6	0.59	0.18	70	-0.22	-0.09
7	0.52	0.10	80	-0.98	-0.58
8*	0.82	0.03	NR	2.00	1.00
9	1.74	NR	NR	12.35	9.42
10	0.63	0.13	97	0.22	0.11
11	0.29	0.05	89	-3.50	-2.46
12	0.65	0.008	90.2	0.44	0.33
13	0.695	NR	92	0.93	0.71
14	0.319	0.17	93	-3.18	-1.40
15	0.77	0.2	97	1.75	0.69
16	NT	NT	NT		
17	0.426	0.0016	97	-2.01	-1.53
18	0.56	0.34	82	-0.55	-0.14
19*	0.86	0.21	105	2.00	1.00
20	0.53	0.258	120	-0.87	-0.28
21	0.43	0.13	87	-1.97	-1.02
22	0.18	NR	NR	-4.70	-3.58

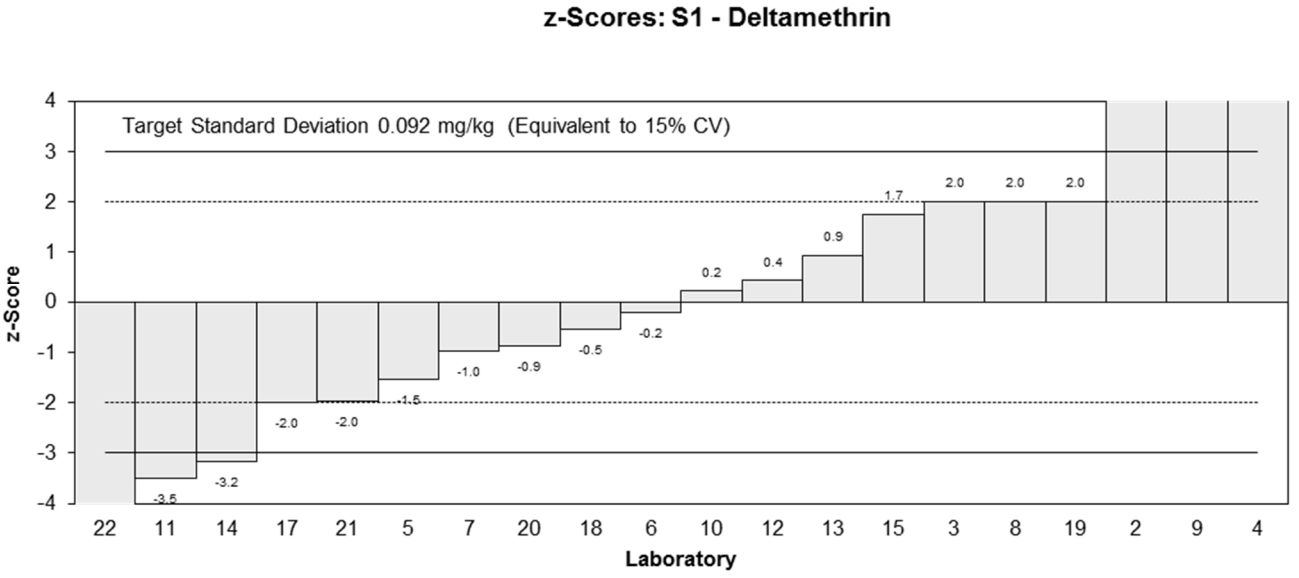
Statistics

Assigned Value**	0.61	0.12
Spike	0.75	0.04
Maximum acceptable conc.	0.93	
Robust Average	0.64	0.17
Median	0.61	0.13
Mean	0.78	
N	20	
Max.	2.86	
Min.	0.18	
Robust SD	0.30	
Robust CV	47%	

*z-score adjusted to 2 (see Section 6.3).

**Robust average excluding laboratories 2, 4, 9, 11 and 22.


Kernel Density
Density
Result
Results: S1 - Deltamethrin
Assigned Value = 0.61 ± 0.12 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
22 11 14 17 21 5 7 20 18 6 10 12 13 15 3 8 19 2 9 4 1 16 Md R.A. S


z-Scores: S1 - Deltamethrin
Target Standard Deviation 0.092 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
22 11 14 17 21 5 7 20 18 6 10 12 13 15 3 8 19 2 9 4

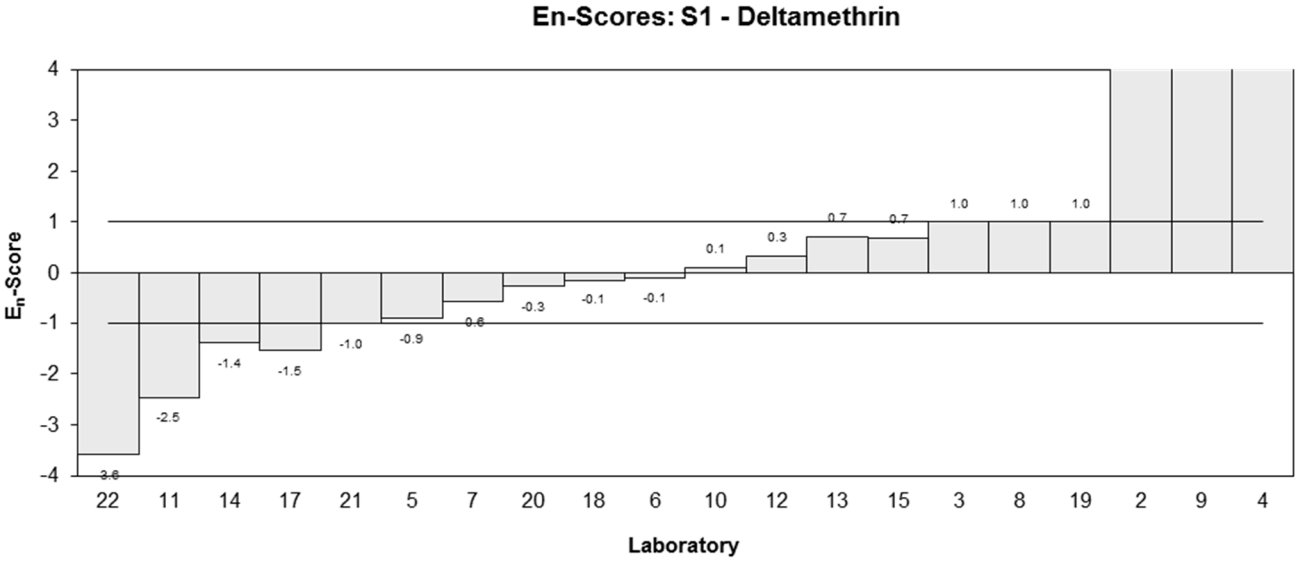

En-Scores: S1 - Deltamethrin
En-Score
Laboratory
22 11 14 17 21 5 7 20 18 6 10 12 13 15 3 8 19 2 9 4

Figure 2

Table 5

Sample Details

Sample No.	S1
Matrix.	Tomato
Analyte.	Endosulfan sulfate
Units	mg/kg

Participant Results

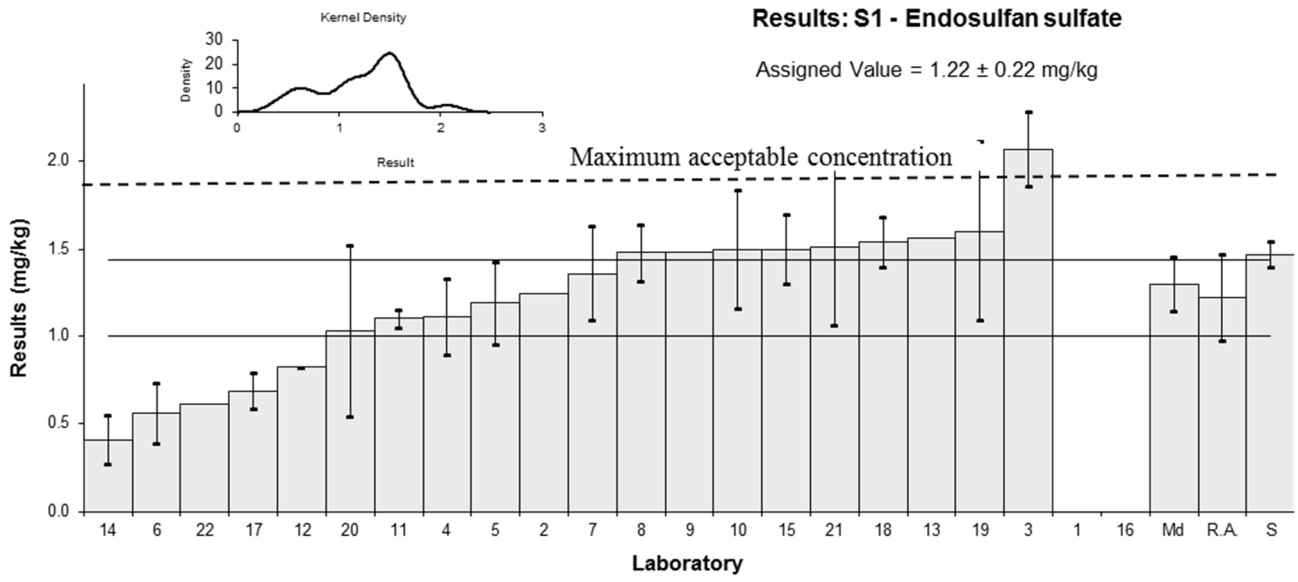
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	1.24	NR	NR	0.11	0.09
3	2.07	0.21	75	4.64	2.79
4	1.11	0.22	93.11	-0.60	-0.35
5	1.19	0.238	76	-0.16	-0.09
6	0.56	0.17	88	-3.61	-2.37
7	1.36	0.27	74	0.77	0.40
8	1.48	0.16	NR	1.42	0.96
9	1.48	NR	NR	1.42	1.18
10	1.5	0.34	110	1.53	0.69
11	1.10	0.05	103	-0.66	-0.53
12	0.82	0.002	83.9	-2.19	-1.82
13	1.56	NR	90	1.86	1.55
14	0.41	0.14	86	-4.43	-3.11
15	1.5	0.2	98	1.53	0.94
16	NT	NT	NT		
17	0.688	0.0998	78	-2.91	-2.20
18	1.54	0.14	135	1.75	1.23
19*	1.6	0.512	93	2.00	0.68
20	1.03	0.49	88	-1.04	-0.35
21	1.51	0.45	86	1.58	0.58
22	0.61	NR	NR	-3.33	-2.77

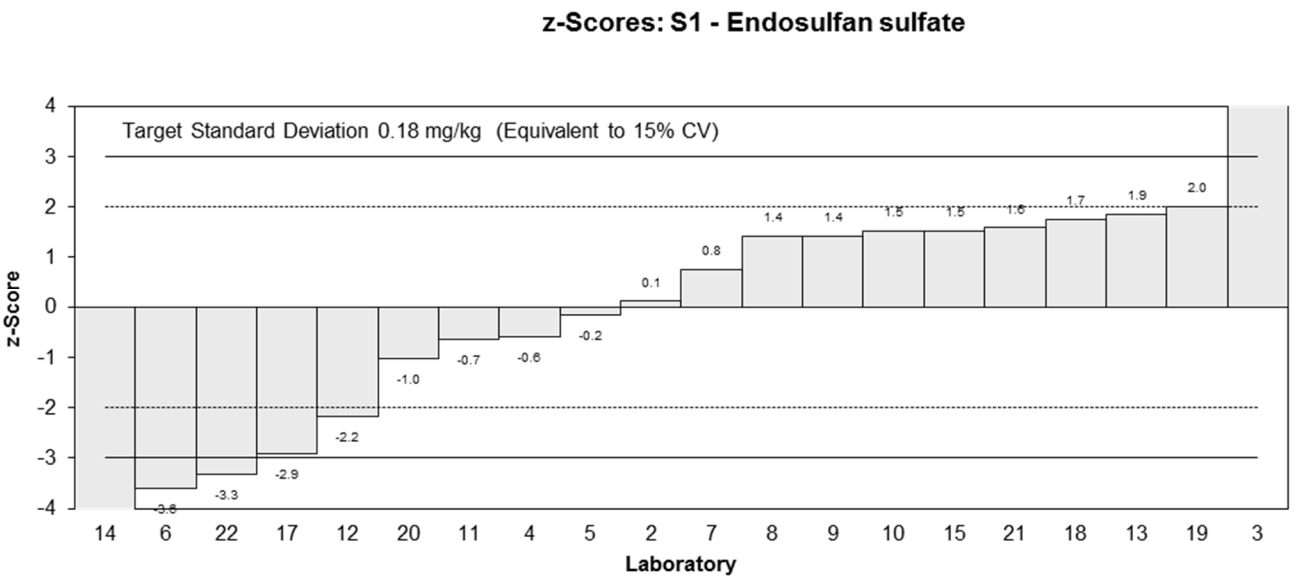
Statistics

Assigned Value*	1.22	0.22
Spike	1.47	0.07
Maximum acceptable conc.	1.83	
Robust Average	1.22	0.25
Median	1.30	0.16
Mean	1.22	
N	20	
Max.	2.07	
Min.	0.41	
Robust SD	0.45	
Robust CV	37%	

*z-score adjusted to 2 (see Section 6.3).

**Robust average excluding laboratories 3 and 14.


Kernel Density
Density
Result
Results: S1 - Endosulfan sulfate
Assigned Value = 1.22 ± 0.22 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
14 6 22 17 12 20 11 4 5 2 7 8 9 10 15 21 18 13 19 3 1 16 Md R.A. S


z-Scores: S1 - Endosulfan sulfate
Target Standard Deviation 0.18 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
14 6 22 17 12 20 11 4 5 2 7 8 9 10 15 21 18 13 19 3
-3.6 -3.3 -2.9 -2.2 -1.0 -0.7 -0.6 -0.2 0.1 0.8 1.4 1.4 1.5 1.5 1.6 1.7 1.9 2.0

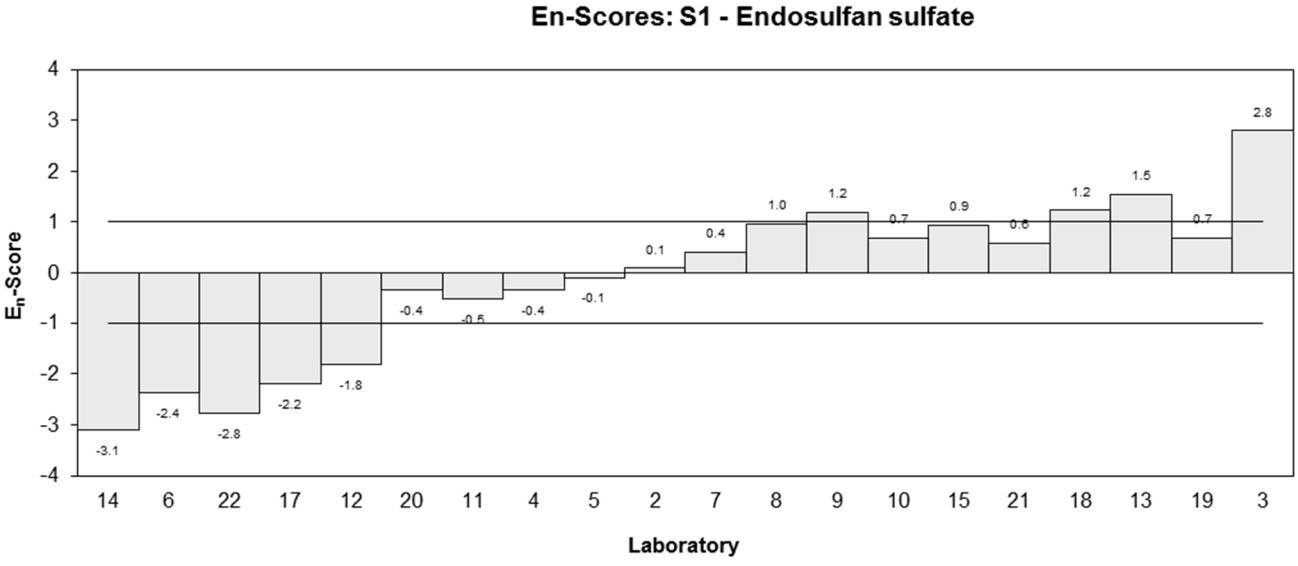

En-Scores: S1 - Endosulfan sulfate
En-Score
Laboratory
14 6 22 17 12 20 11 4 5 2 7 8 9 10 15 21 18 13 19 3
-3.1 -2.4 -2.8 -2.2 -1.8 -0.4 -0.5 -0.4 -0.1 0.1 0.4 1.0 1.2 0.7 0.9 0.6 1.2 1.5 0.7 2.8

Figure 3

Table 6

Sample Details

Sample No.	S1
Matrix.	Tomato
Analyte.	Imidacloprid
Units	mg/kg

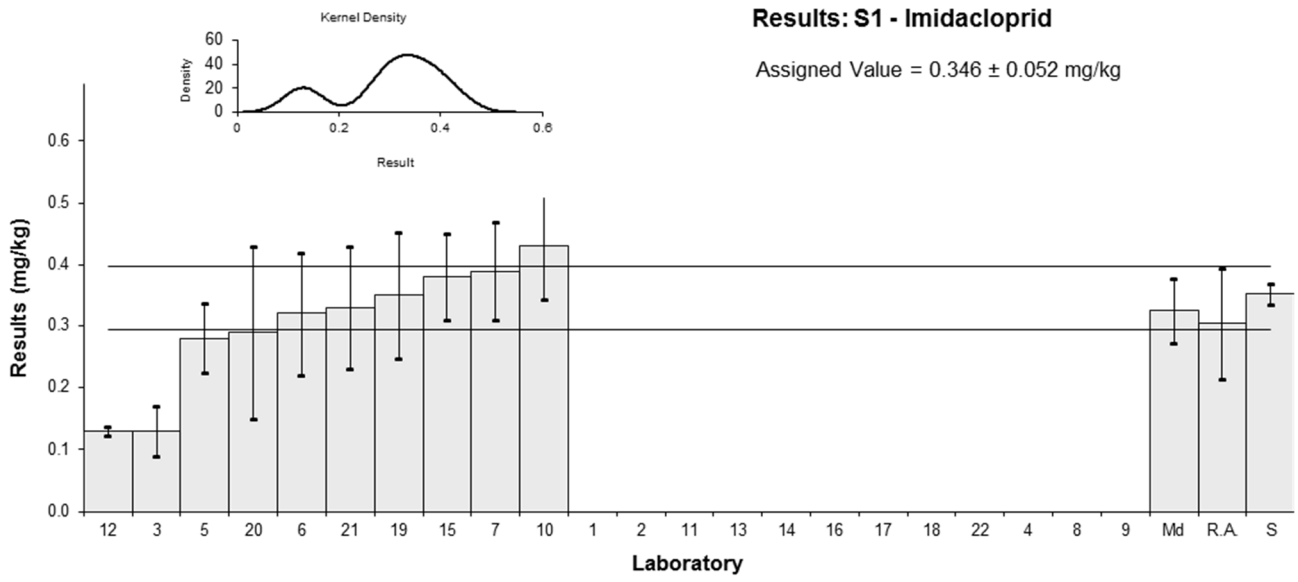
Participant Results

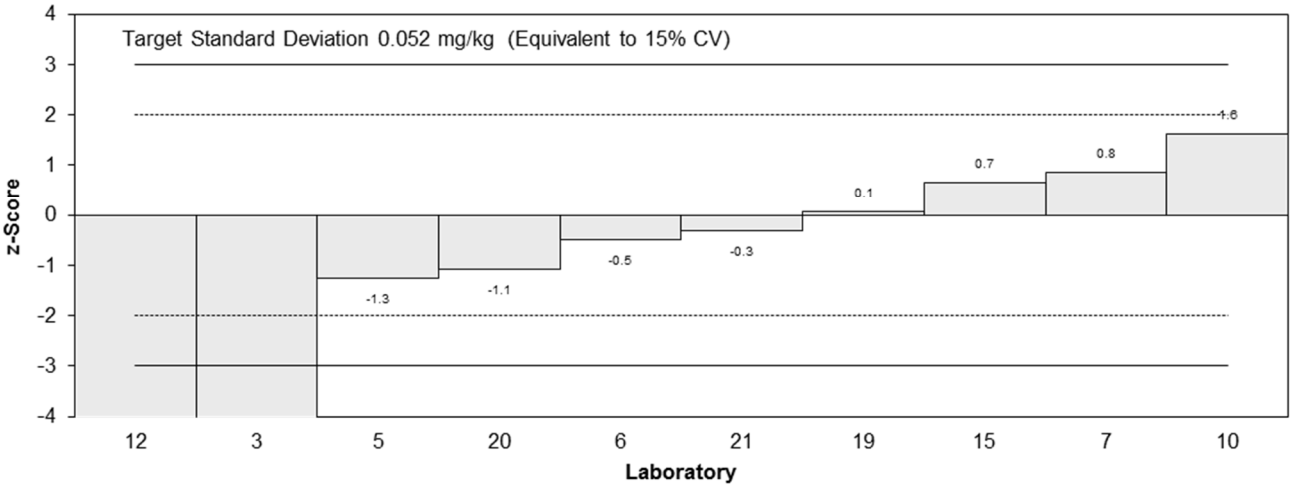
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NR	NR	NR		
3	0.13	0.04	85	-4.16	-3.29
4	NT	NT	NT		
5	0.28	0.056	83	-1.27	-0.86
6	0.32	0.10	105	-0.50	-0.23
7	0.39	0.06	107	0.85	0.55
8	NT	NT	NT		
9	NT	NT	NT		
10	0.43	0.087	105	1.62	0.83
11	NT	NT	NT		
12	0.13	0.008	79.2	-4.16	-4.11
13	NT	NT	NT		
14	NT	NT	NT		
15	0.38	0.07	97	0.66	0.39
16	NT	NT	NT		
17	NT	NT	NT		
18	NT	NT	NT		
19	0.35	0.102	74	0.08	0.03
20	0.29	0.14	75	-1.08	-0.37
21	0.33	0.10	95	-0.31	-0.14
22	NT	NT	NT		

Statistics

Assigned Value*	0.346	0.052
Spike	0.352	0.018
Robust Average	0.304	0.090
Median	0.325	0.053
Mean	0.303	
N	10	
Max.	0.43	
Min.	0.13	
Robust SD	0.114	
Robust CV	38%	

*Robust average excluding laboratories 3 and 12.


Kernel Density
Density
Result
Results: S1 - Imidacloprid
Assigned Value = 0.346 ± 0.052 mg/kg
Results (mg/kg)
Laboratory
12 3 5 20 6 21 19 15 7 10 1 2 11 13 14 16 17 18 22 4 8 9 Md R.A. S


z-Scores: S1 - Imidacloprid
Target Standard Deviation 0.052 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
12 3 5 20 6 21 19 15 7 10
-1.3
-1.1
-0.5
-0.3
0.1
0.7
0.8
1.6

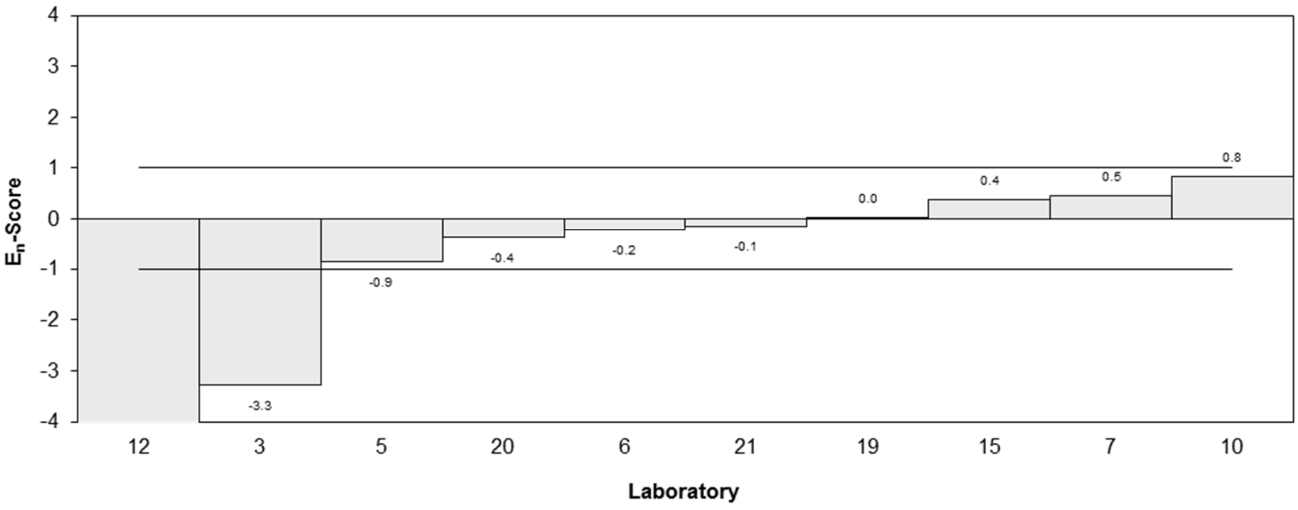

En-Scores: S1 - Imidacloprid
En-Score
Laboratory
12 3 5 20 6 21 19 15 7 10
-3.3
-0.9
-0.4
-0.2
-0.1
0.0
0.4
0.5
0.8

Figure 4

Table 7

Sample Details

Sample No.	S1
Matrix.	Tomato
Analyte.	Methamidophos
Units	mg/kg

Participant Results

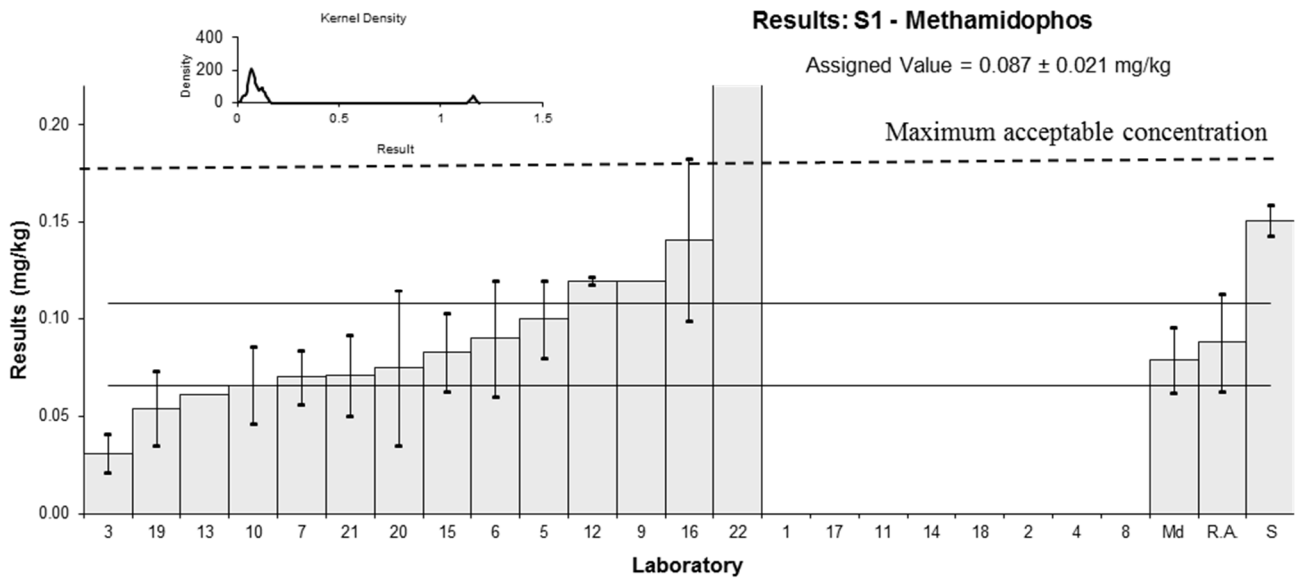
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	0.031	0.01	72	-4.29	-2.41
4	NT	NT	NT		
5	0.10	0.020	117	1.00	0.45
6	0.090	0.030	55	0.23	0.08
7	0.070	0.08	81	-1.30	-0.21
8	NT	NT	NT		
9*	0.12	NR	NR	2.00	1.00
10	0.066	0.02	93	-1.61	-0.72
11	NT	NT	NT		
12*	0.12	0.002	83.9	2.00	1.00
13	0.061	NR	79	-1.99	-1.24
14	NT	NT	NT		
15	0.083	0.02	76	-0.31	-0.14
16*	0.141	0.042	116	2.00	1.00
17	NR	NR	NR		
18	NT	NT	NT		
19	0.054	0.019	62	-2.53	-1.17
20	0.075	0.04	98	-0.92	-0.27
21	0.071	0.021	62	-1.23	-0.54
22	1.16	NR	NR	82.22	51.10

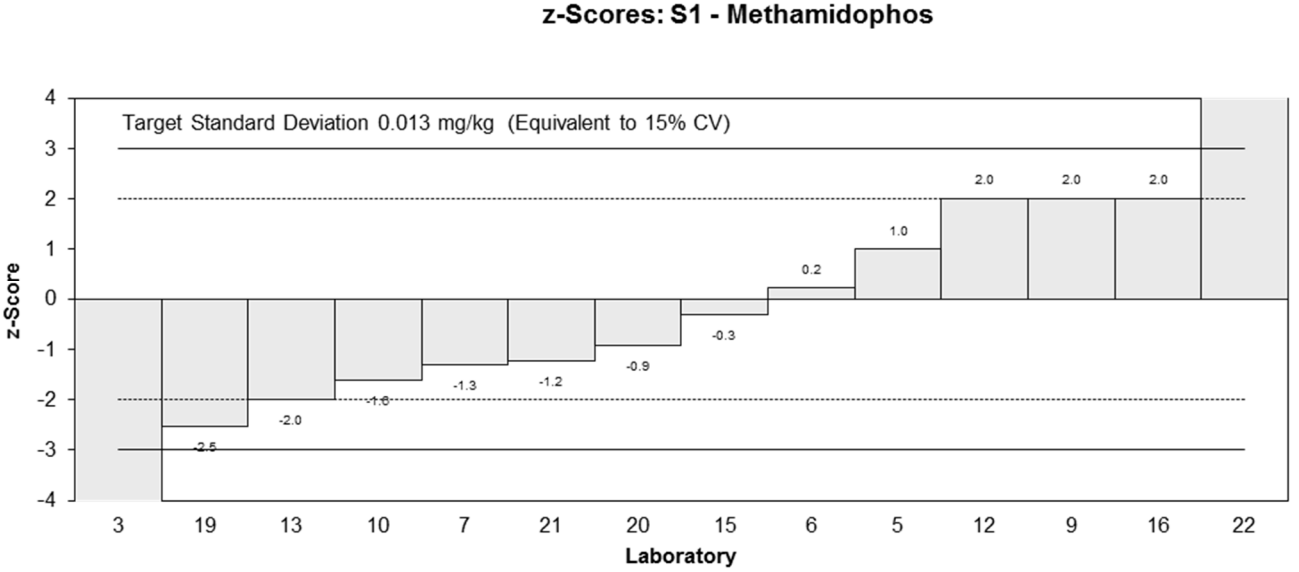
Statistics

Assigned Value**	0.087	0.021
Spike	0.151	0.008
Maximum acceptable conc.	0.177	
Robust Average	0.088	0.025
Median	0.079	0.017
Mean	0.160	
N	14	
Max.	1.16	
Min.	0.031	
Robust SD	0.038	
Robust CV	43%	

*z-score adjusted to 2 (see Section 6.3).

**Robust average excluding laboratories 3 and 22.


Kernel Density
Density
Result
Results: S1 - Methamidophos
Assigned Value = 0.087 ± 0.021 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
3 19 13 10 7 21 20 15 6 5 12 9 16 22 1 17 11 14 18 2 4 8 Md R.A. S


z-Scores: S1 - Methamidophos
Target Standard Deviation 0.013 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
3 19 13 10 7 21 20 15 6 5 12 9 16 22

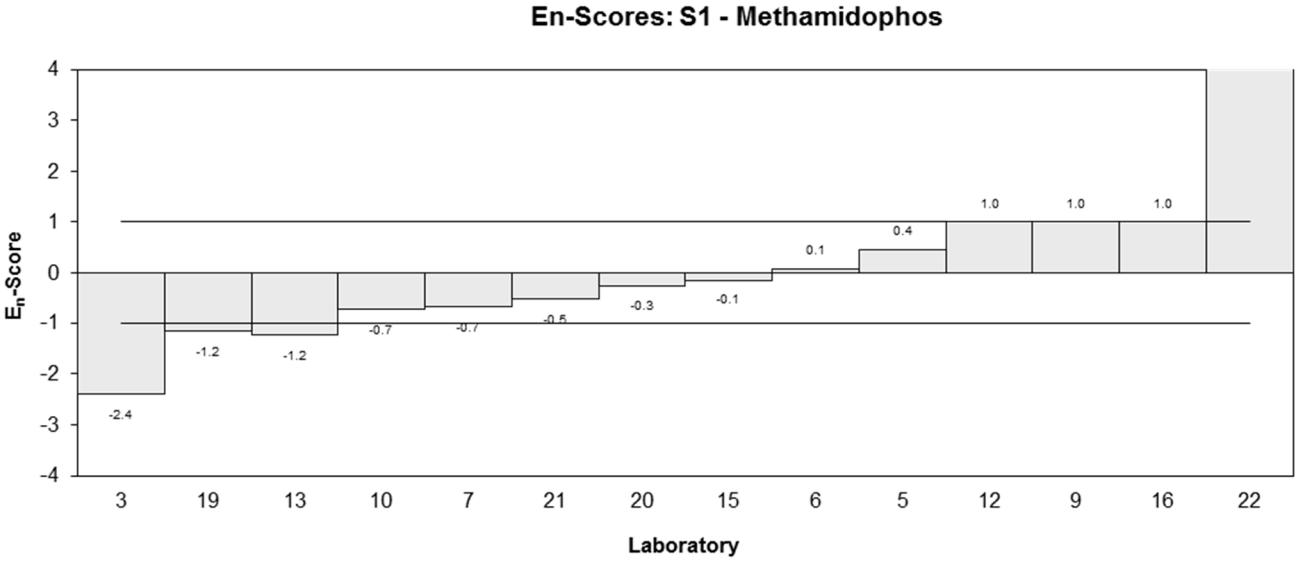

En-Scores: S1 - Methamidophos
En-Score
Laboratory
3 19 13 10 7 21 20 15 6 5 12 9 16 22

Figure 5

Table 8

Sample Details

Sample No.	S2
Matrix.	Kale
Analyte.	Azoxystrobin
Units	mg/kg

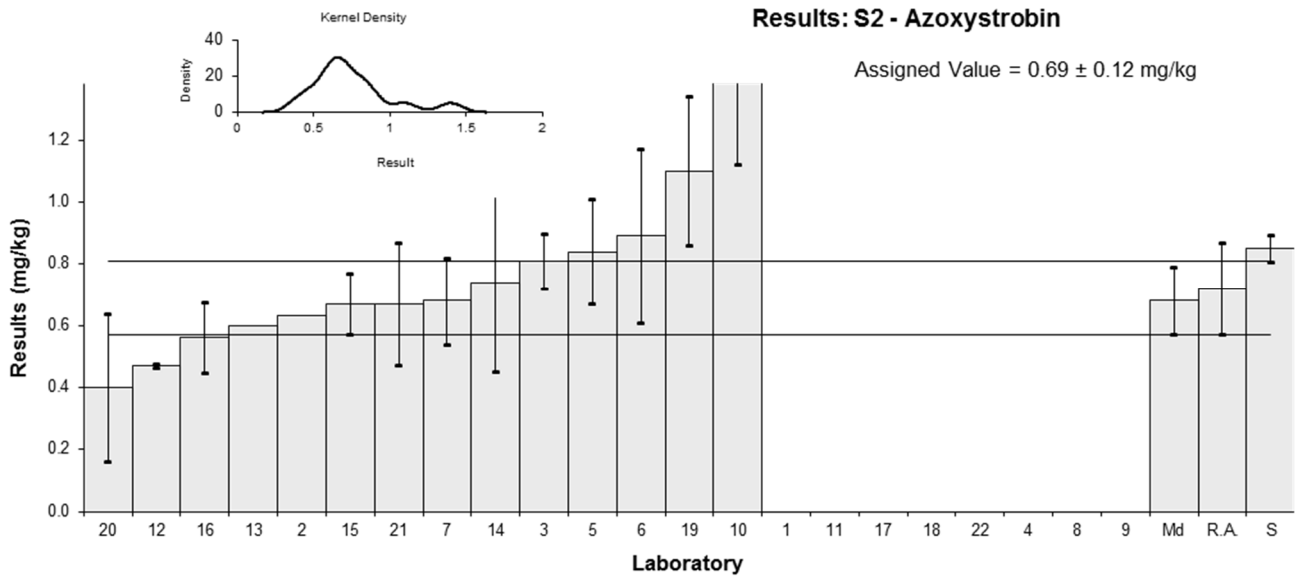
Participant Results

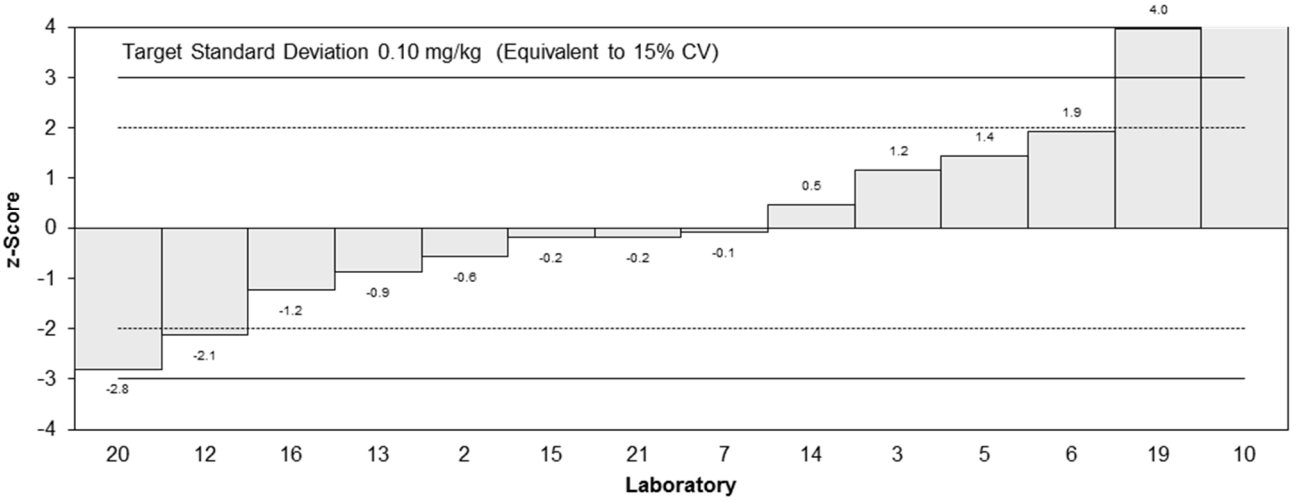
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	0.63	NR	NR	-0.58	-0.50
3	0.81	0.09	80	1.16	0.80
4	NT	NT	NT		
5	0.84	0.168	80	1.45	0.73
6	0.89	0.28	100	1.93	0.66
7	0.68	0.14	107	-0.10	-0.05
8	NT	NT	NT		
9	NT	NT	NT		
10	1.4	0.28	64	6.86	2.33
11	NT	NT	NT		
12	0.47	0.008	85.1	-2.13	-1.83
13	0.60	NR	109	-0.87	-0.75
14	0.74	0.29	95	0.48	0.16
15	0.67	0.1	89	-0.19	-0.13
16	0.561	0.112	88	-1.25	-0.79
17	NT	NT	NT		
18	NT	NT	NT		
19	1.1	0.24	47	3.96	1.53
20	0.40	0.238	70	-2.80	-1.09
21	0.67	0.20	102	-0.19	-0.09
22	NT	NT	NT		

Statistics

Assigned Value	0.69	0.12
Spike	0.850	0.043
Robust Average	0.72	0.15
Median	0.68	0.11
Mean	0.747	
N	14	
Max.	1.4	
Min.	0.4	
Robust SD	0.22	
Robust CV	31%	

*Robust average excluding laboratory 10.


Kernel Density
Density
Result
Results: S2 - Azoxystrobin
Assigned Value = 0.69 ± 0.12 mg/kg
Results (mg/kg)
Laboratory
20 12 16 13 2 15 21 7 14 3 5 6 19 10 1 11 17 18 22 4 8 9 Md R.A. S


z-Scores: S2 - Azoxystrobin
Target Standard Deviation 0.10 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
20 12 16 13 2 15 21 7 14 3 5 6 19 10
-2.8 -2.1 -1.2 -0.9 -0.6 -0.2 -0.2 -0.1 0.5 1.2 1.4 1.9 4.0

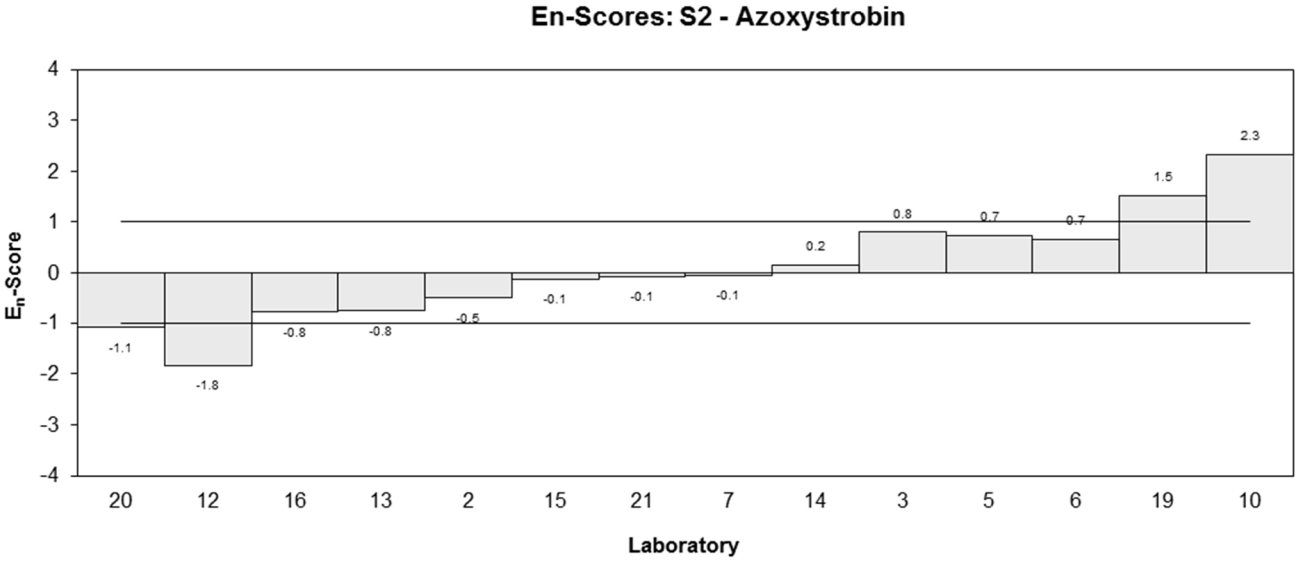

En-Scores: S2 - Azoxystrobin
En-Score
Laboratory
20 12 16 13 2 15 21 7 14 3 5 6 19 10
-1.1 -1.8 -0.8 -0.8 -0.5 -0.1 -0.1 -0.1 0.2 0.8 0.7 0.7 1.5 2.3

Figure 6

Table 9

Sample Details

Sample No.	S2
Matrix.	Kale
Analyte.	Imidacloprid
Units	mg/kg

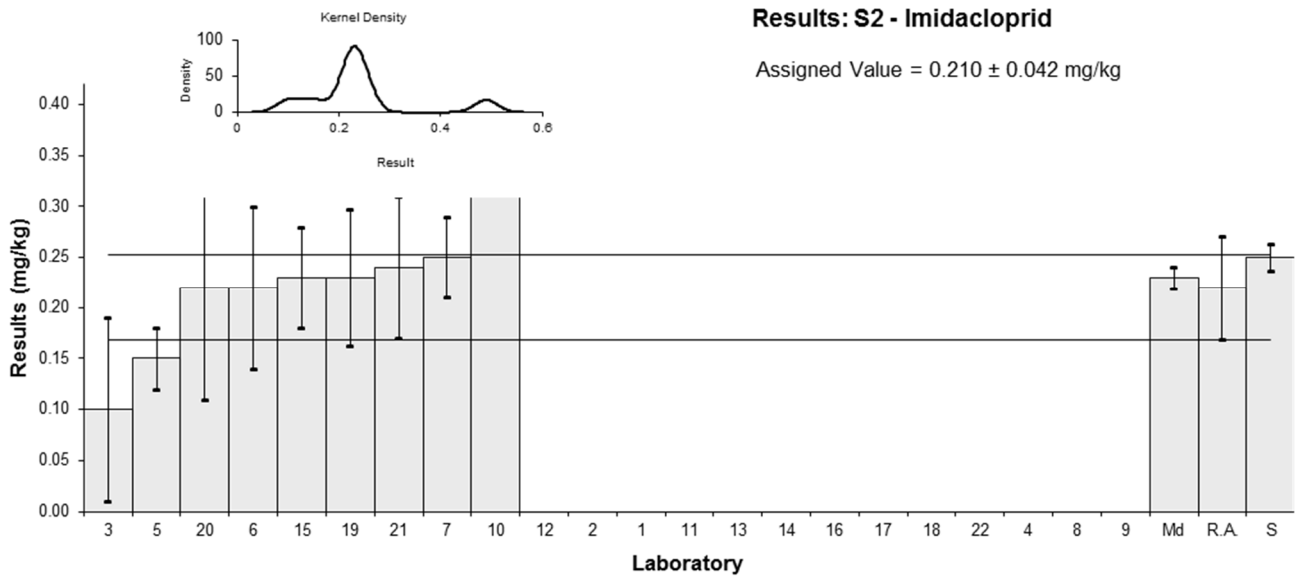
Participant Results

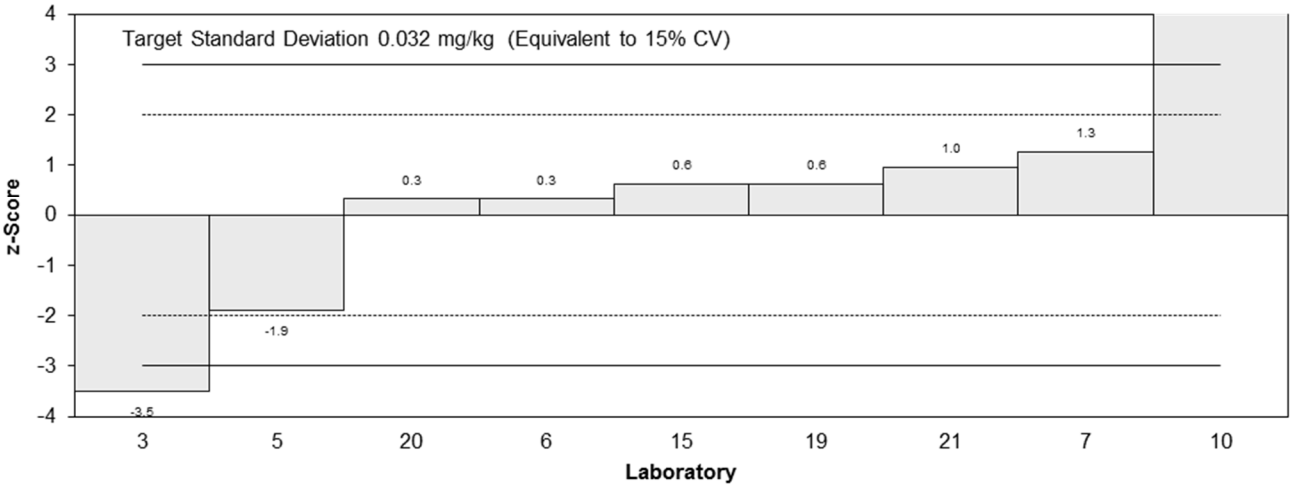
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NR	NR	NR		
3	0.10	0.09	80	-3.49	-1.11
4	NT	NT	NT		
5	0.15	0.030	65	-1.90	-1.16
6	0.22	0.08	105	0.32	0.11
7	0.25	0.04	115	1.27	0.69
8	NT	NT	NT		
9	NT	NT	NT		
10	0.49	0.098	78	8.89	2.63
11	NT	NT	NT		
12	NR	NR	NR		
13	NT	NT	NT		
14	NT	NT	NT		
15	0.23	0.05	88	0.63	0.31
16	NT	NT	NT		
17	NT	NT	NT		
18	NT	NT	NT		
19	0.23	0.067	52	0.63	0.25
20	0.22	0.11	75	0.32	0.08
21	0.24	0.07	110	0.95	0.37
22	NT	NT	NT		

Statistics

Assigned Value	0.210	0.042
Spike	0.250	0.013
Robust Average	0.220	0.051
Median	0.230	0.011
Mean	0.237	
N	9	
Max.	0.49	
Min.	0.1	
Robust SD	0.061	
Robust CV	28%	

*Robust average excluding laboratory 10.


Kernel Density
Density
Result
Results: S2 - Imidacloprid
Assigned Value = 0.210 ± 0.042 mg/kg
Results (mg/kg)
Laboratory
3 5 20 6 15 19 21 7 10 12 2 1 11 13 14 16 17 18 22 4 8 9 Md R.A. S


z-Scores: S2 - Imidacloprid
Target Standard Deviation 0.032 mg/kg (Equivalent to 15% CV)
z-Score
-3.5
-1.9
0.3
0.3
0.6
0.6
1.0
1.3
Laboratory
3 5 20 6 15 19 21 7 10

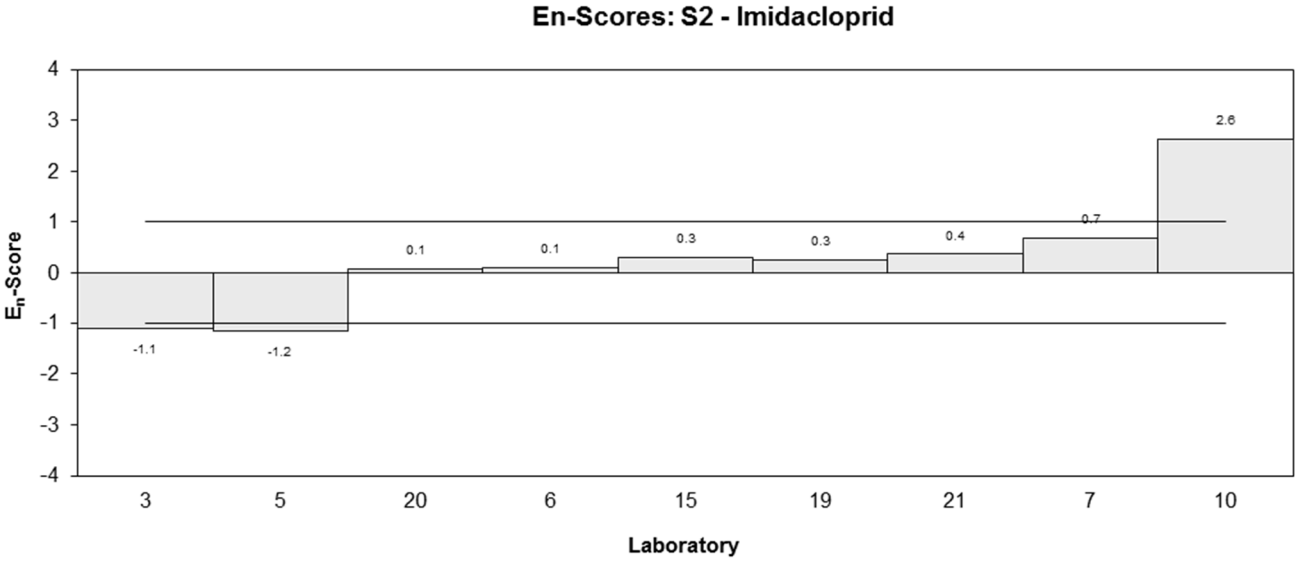

En-Scores: S2 - Imidacloprid
En-Score
-1.1
-1.2
0.1
0.1
0.3
0.3
0.4
0.7
2.6
Laboratory
3 5 20 6 15 19 21 7 10

Figure 7

Table 10

Sample Details

Sample No.	S2
Matrix.	Kale
Analyte.	Spinosad
Units	mg/kg

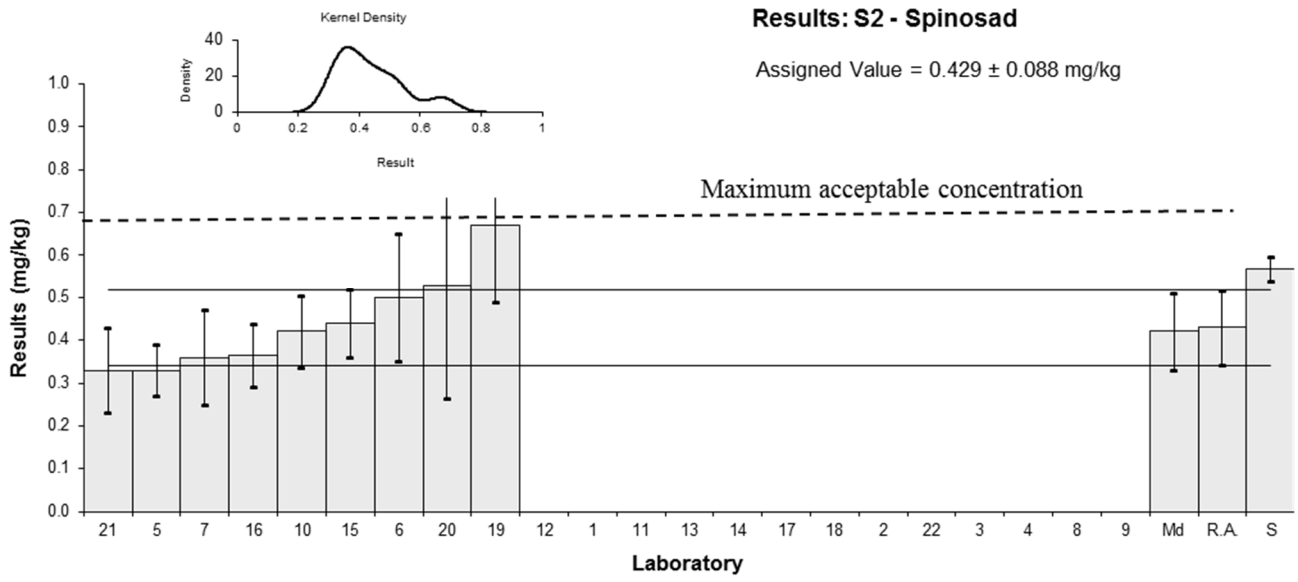
Participant Results

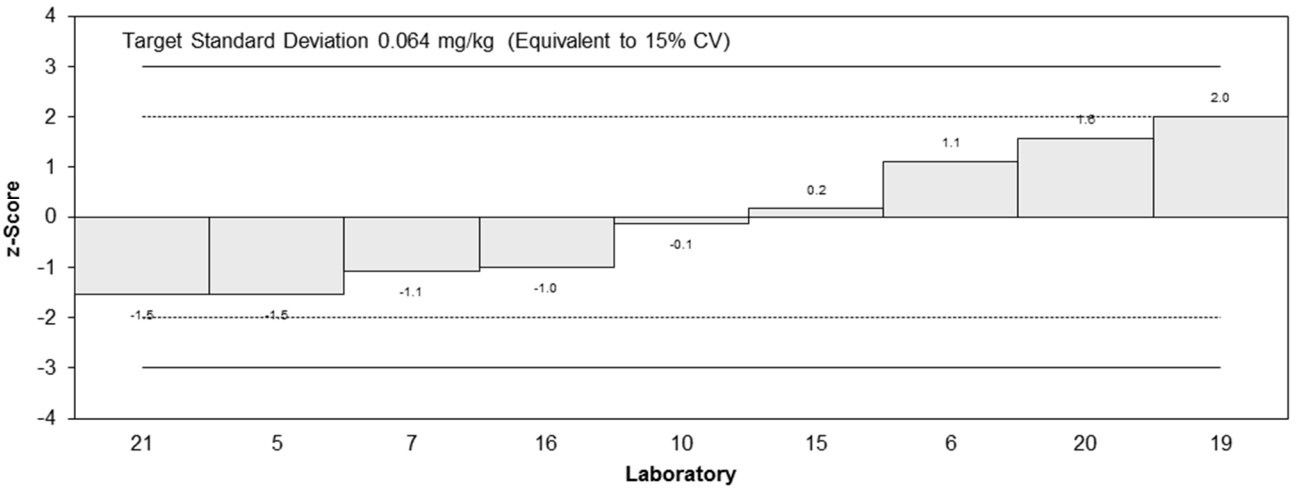
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	NT	NT	NT		
4	NT	NT	NT		
5	0.33	0.060	79	-1.54	-0.93
6	0.50	0.15	89	1.10	0.41
7	0.36	0.11	104	-1.07	-0.49
8	NT	NT	NT		
9	NT	NT	NT		
10	0.42	0.084	110	-0.14	-0.07
11	NT	NT	NT		
12	NR	NR	NR		
13	NT	NT	NT		
14	NT	NT	NT		
15	0.44	0.08	81	0.17	0.09
16	0.365	0.073	NR	-0.99	-0.56
17	NT	NT	NT		
18	NT	NT	NT		
19*	0.67	0.18	63	2.00	1.00
20	0.53	0.265	107	1.57	0.36
21	0.33	0.10	76	-1.54	-0.74
22	NT	NT	NT		

Statistics

Assigned Value	0.429	0.088
Spike	0.568	0.028
Maximum acceptable conc.	0.696	
Robust Average	0.429	0.088
Median	0.420	0.091
Mean	0.438	
N	9	
Max.	0.67	
Min.	0.33	
Robust SD	0.105	
Robust CV	25%	

*z-score adjusted to 2 (see Section 6.3).


Kernel Density
Density
Result
Results: S2 - Spinosad
Assigned Value = 0.429 ± 0.088 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
21 5 7 16 10 15 6 20 19 12 1 11 13 14 17 18 2 22 3 4 8 9 Md R.A. S


z-Scores: S2 - Spinosad
Target Standard Deviation 0.064 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
21 5 7 16 10 15 6 20 19
-1.5 -1.5 -1.1 -1.0 -0.1 0.2 1.1 1.6 2.0

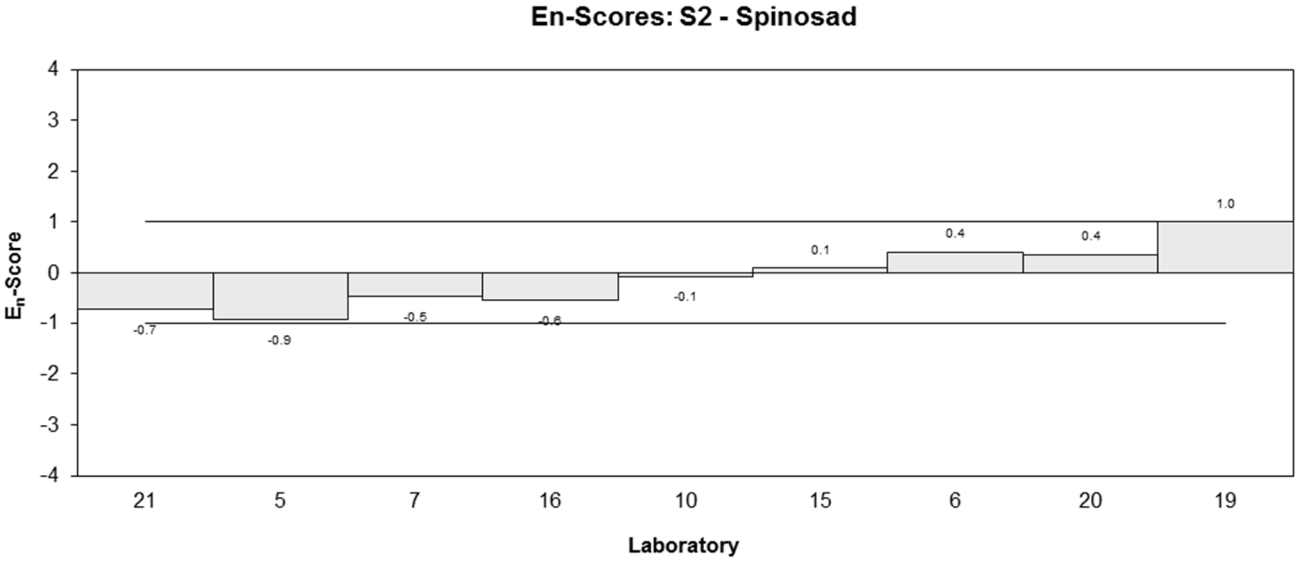

En-Scores: S2 - Spinosad
En-Score
Laboratory
21 5 7 16 10 15 6 20 19
-0.7 -0.9 -0.5 -0.6 -0.1 0.1 0.4 0.4 1.0

Figure 8

Table 11

Sample Details

Sample No.	S3
Matrix.	Lemon
Analyte.	Clothianidin
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	Recovery
1	NT	NT	NT
2	NT	NT	NT
3	NT	NT	NT
4	NT	NT	NT
5	NR	NR	NR
6	<0.01	NR	NR
7	0.017	0.003	106
8	NT	NT	NT
9	NT	NT	NT
10	NR	NR	NR
11	NT	NT	NT
12	NR	NR	NR
13	NT	NT	NT
14	NT	NT	NT
15	0.010	0.005	94
16*	< 0.011	0.01	96
17	NT	NT	NT
18	NT	NT	NT
19	0.010	NR	NR
20	NT	NT	NT
21	<0.01	NR	87
22	NT	NT	NT

*Laboratory 16 reported after the release of the interim report that their result is 0.011 and not <0.011.

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Median	0.010	
Mean	0.012	
N	3	
Max.	0.017	
Min.	0.01	

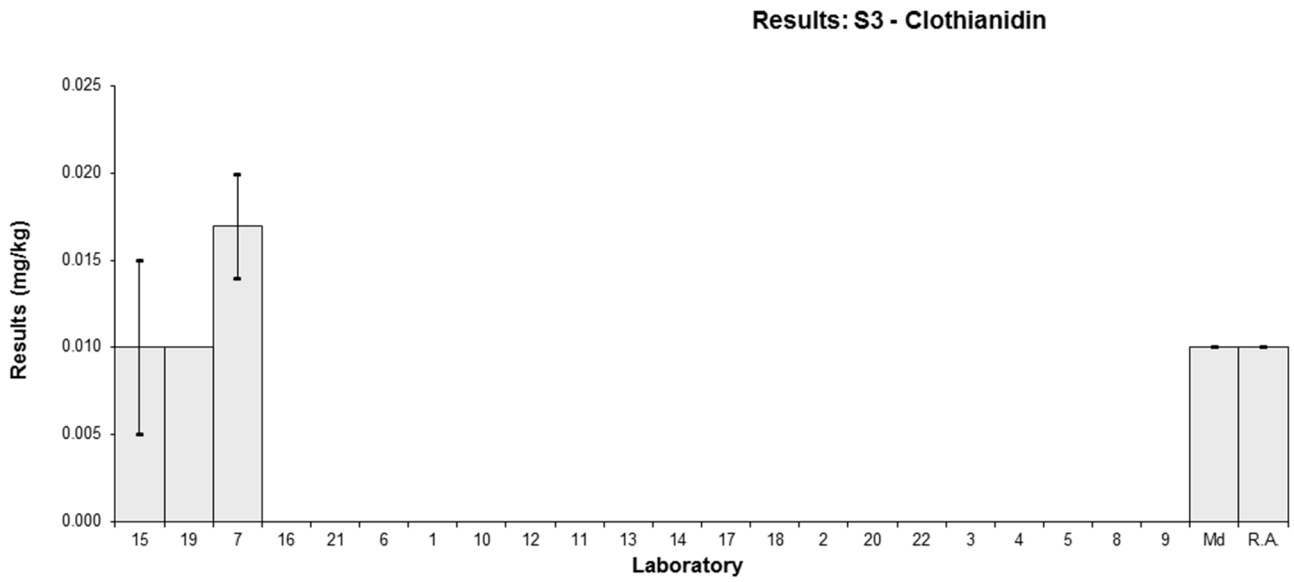

Results: S3 - Clothianidin
Results (mg/kg)
0.025
0.020
0.015
0.010
0.005
0.000
15 19 7 16 21 6 1 10 12 11 13 14 17 18 2 20 22 3 4 5 8 9 Md R.A.
Laboratory

Figure 9

Table 12

Sample Details

Sample No.	S3
Matrix.	Lemon
Analyte.	Imazalil
Units	mg/kg

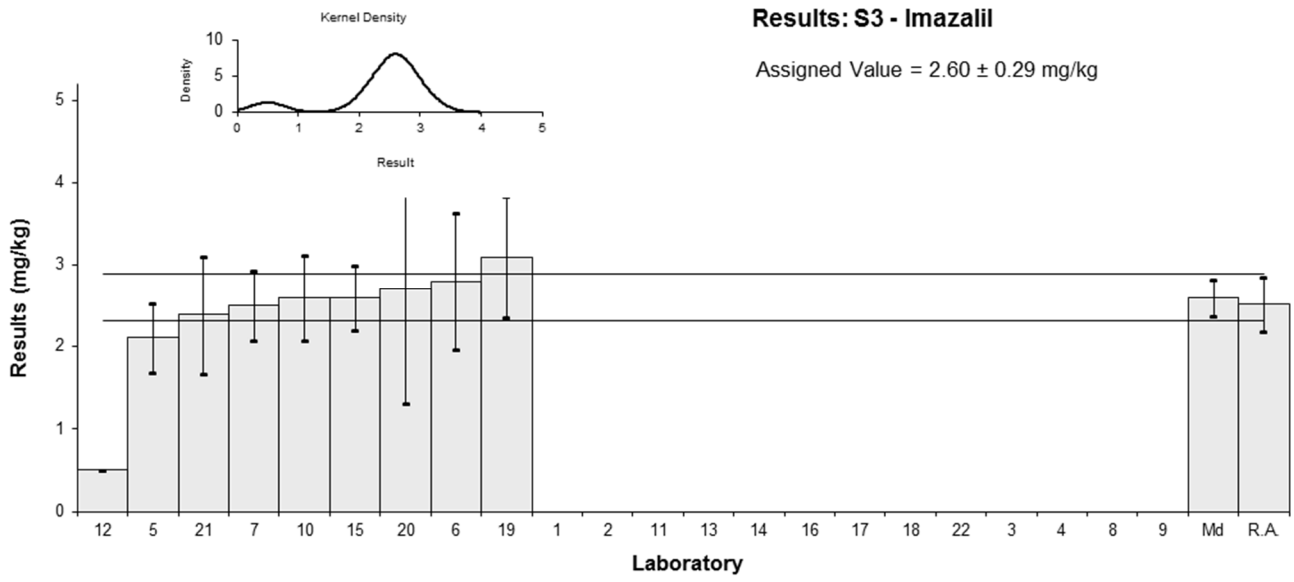
Participant Results

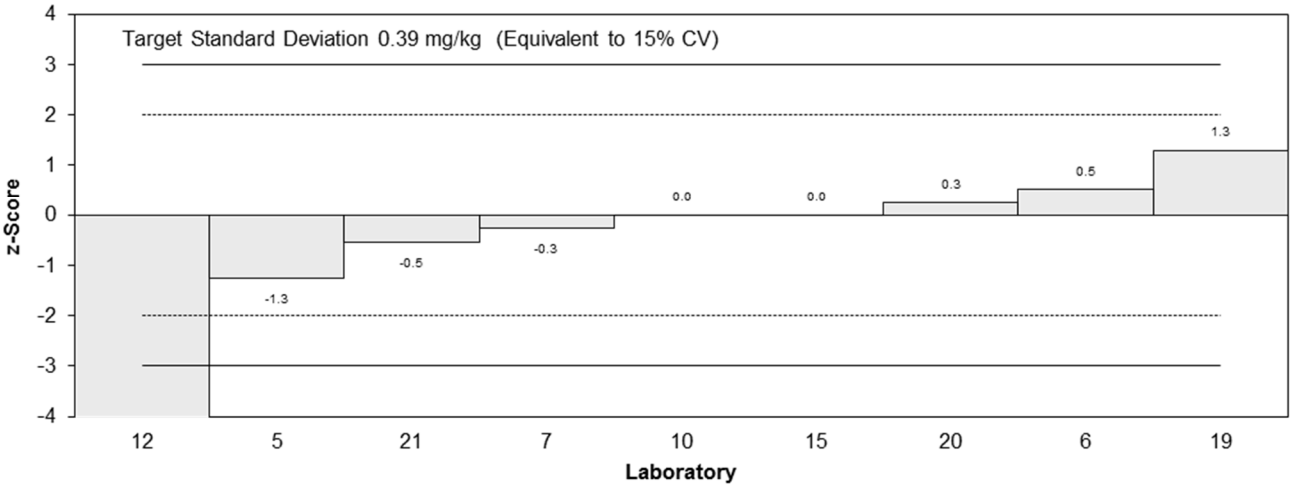
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NR	NR	NR		
3	NT	NT	NT		
4	NT	NT	NT		
5	2.11	0.422	75	-1.26	-0.96
6	2.8	0.84	100	0.51	0.23
7	2.50	0.43	106	-0.26	-0.19
8	NT	NT	NT		
9	NT	NT	NT		
10	2.6	0.52	NR	0.00	0.00
11	NT	NT	NT		
12	0.50	0.005	82.5	-5.38	-7.24
13	NT	NT	NT		
14	NT	NT	NT		
15	2.6	0.4	105	0.00	0.00
16	NT	NT	NT		
17	NT	NT	NT		
18	NT	NT	NT		
19	3.1	0.74	NT	1.28	0.63
20	2.7	1.39	75	0.26	0.07
21	2.39	0.72	87	-0.54	-0.27
22	NT	NT	NT		

Statistics

Assigned Value*	2.60	0.29
Spike	Not Spiked	
Robust Average	2.52	0.33
Median	2.60	0.23
Mean	2.37	
N	9	
Max.	3.1	
Min.	0.5	
Robust SD	0.40	
Robust CV	16%	

*Robust average excluding laboratory 12.


Kernel Density
Density
Result
Results: S3 - Imazalil
Assigned Value = 2.60 ± 0.29 mg/kg
Results (mg/kg)
Laboratory
12 5 21 7 10 15 20 6 19 1 2 11 13 14 16 17 18 22 3 4 8 9 Md R.A.


z-Scores: S3 - Imazalil
Target Standard Deviation 0.39 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
12 5 21 7 10 15 20 6 19
-1.3 -0.5 -0.3 0.0 0.0 0.3 0.5 1.3

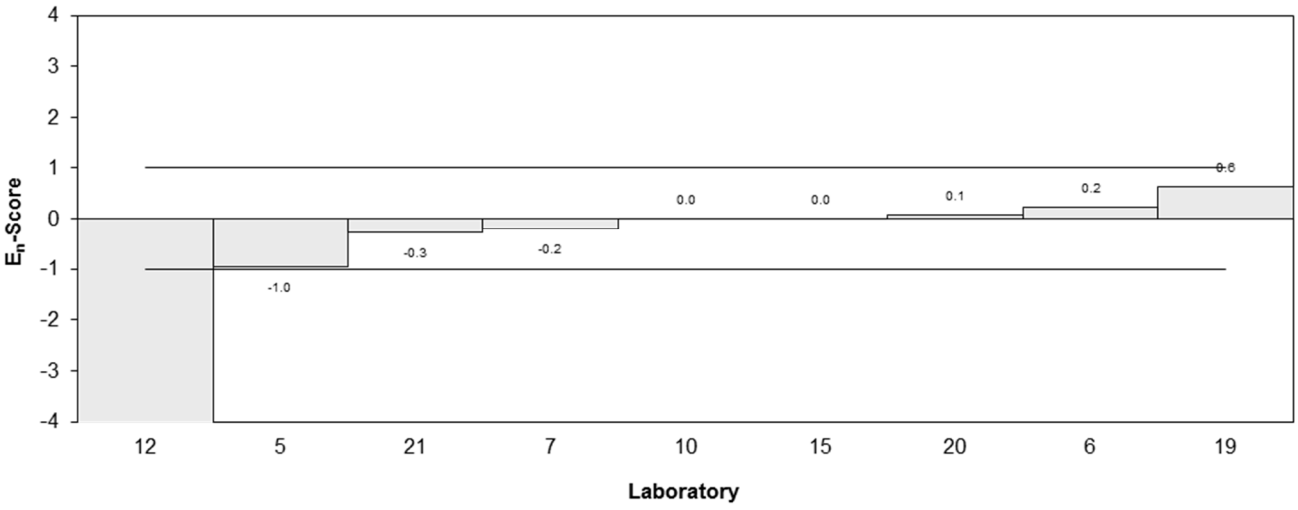

En-Scores: S3 - Imazalil
En-Score
Laboratory
12 5 21 7 10 15 20 6 19
-1.0 -0.3 -0.2 0.0 0.0 0.1 0.2 0.6

Figure 10

Table 13

Sample Details

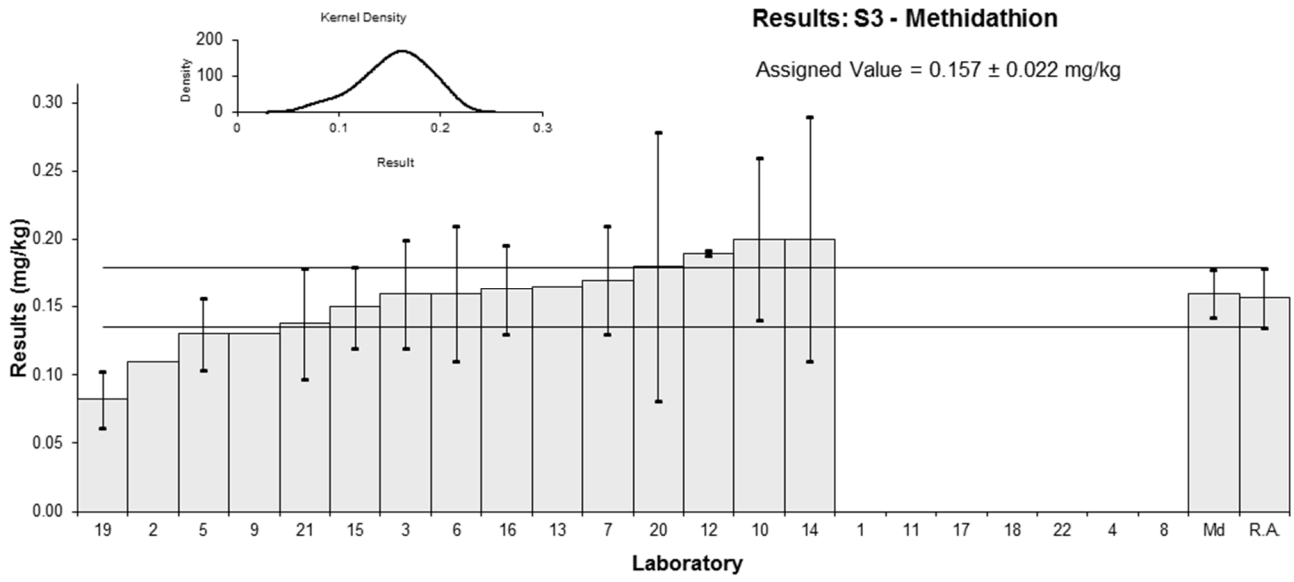
Sample No.	S3
Matrix.	Lemon
Analyte.	Methidathion
Units	mg/kg

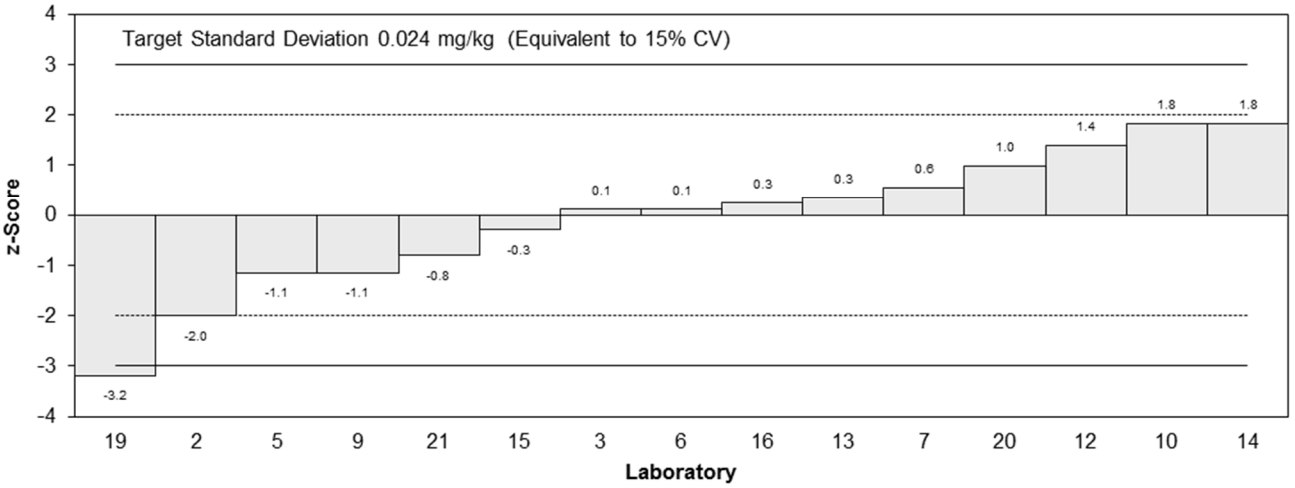
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	0.11	NR	NR	-2.00	-2.14
3	0.16	0.04	75	0.13	0.07
4	NT	NT	NT		
5	0.13	0.026	112	-1.15	-0.79
6	0.16	0.05	86	0.13	0.05
7	0.17	0.04	105	0.55	0.28
8	NT	NT	NT		
9	0.13	NR	NR	-1.15	-1.23
10	0.20	0.06	NR	1.83	0.67
11	NT	NT	NT		
12	0.19	0.002	71.2	1.40	1.49
13	0.165	NR	90	0.34	0.36
14	0.20	0.090	93	1.83	0.46
15	0.15	0.03	106	-0.30	-0.19
16	0.163	0.033	106	0.25	0.15
17	NT	NT	NT		
18	NT	NT	NT		
19	0.082	0.021	NT	-3.18	-2.47
20	0.18	0.099	100	0.98	0.23
21	0.138	0.041	70	-0.81	-0.41
22	NT	NT	NT		

Statistics

Assigned Value	0.157	0.022
Spike	Not Spiked	
Robust Average	0.157	0.022
Median	0.160	0.018
Mean	0.155	
N	15	
Max.	0.2	
Min.	0.082	
Robust SD	0.033	
Robust CV	21%	


Kernel Density
Density
Result
Results: S3 - Methidathion
Assigned Value = 0.157 ± 0.022 mg/kg
Results (mg/kg)
Laboratory
19 2 5 9 21 15 3 6 16 13 7 20 12 10 14 1 11 17 18 22 4 8 Md R.A.


z-Scores: S3 - Methidathion
Target Standard Deviation 0.024 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
19 2 5 9 21 15 3 6 16 13 7 20 12 10 14
-3.2 -2.0 -1.1 -1.1 -0.8 -0.3 0.1 0.1 0.3 0.3 0.6 1.0 1.4 1.8 1.8

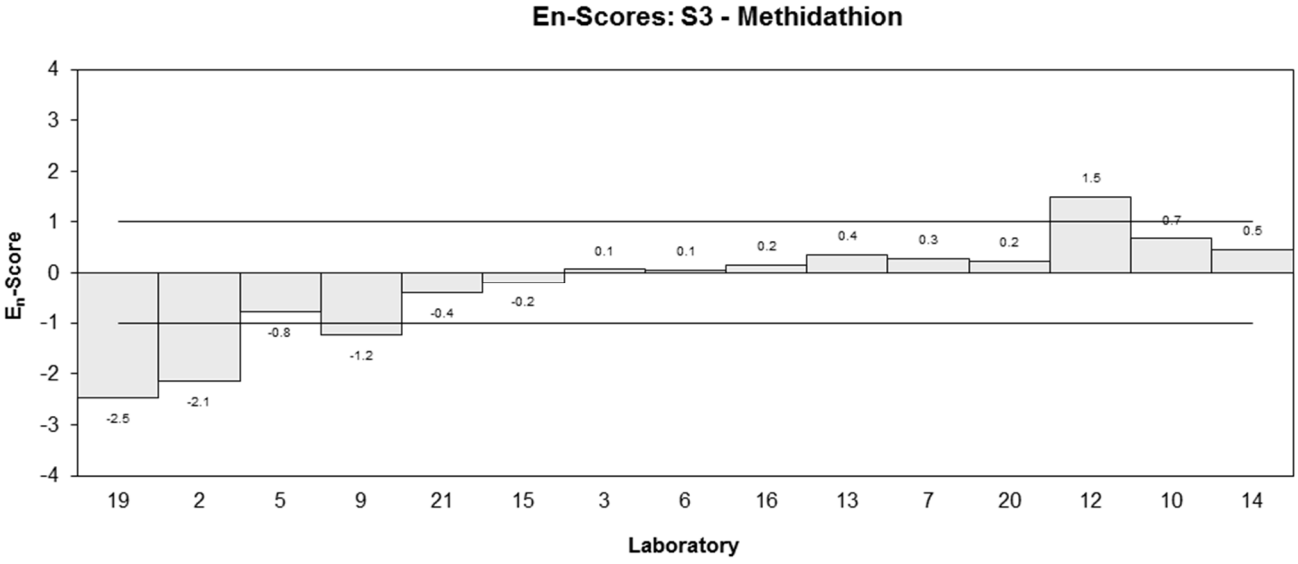

En-Scores: S3 - Methidathion
En-Score
Laboratory
19 2 5 9 21 15 3 6 16 13 7 20 12 10 14
-2.5 -2.1 -0.8 -1.2 -0.4 -0.2 0.1 0.1 0.2 0.4 0.3 0.2 1.5 0.7 0.5

Figure 11

Table 14

Sample Details

Sample No.	S3
Matrix.	Lemon
Analyte.	Omethoate
Units	mg/kg

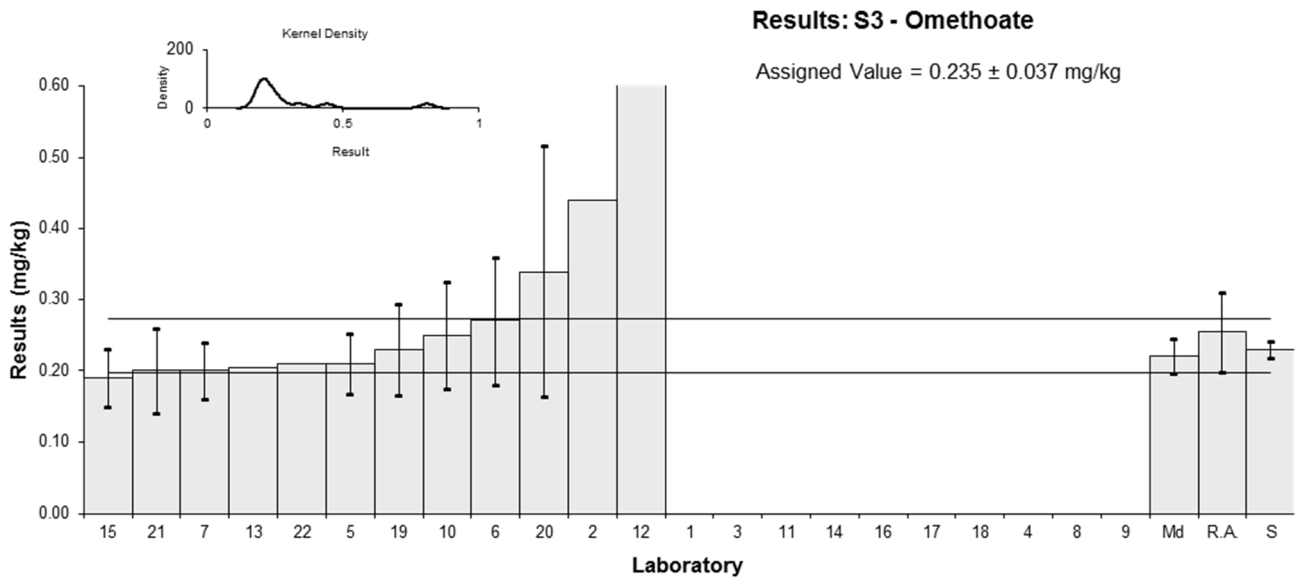
Participant Results

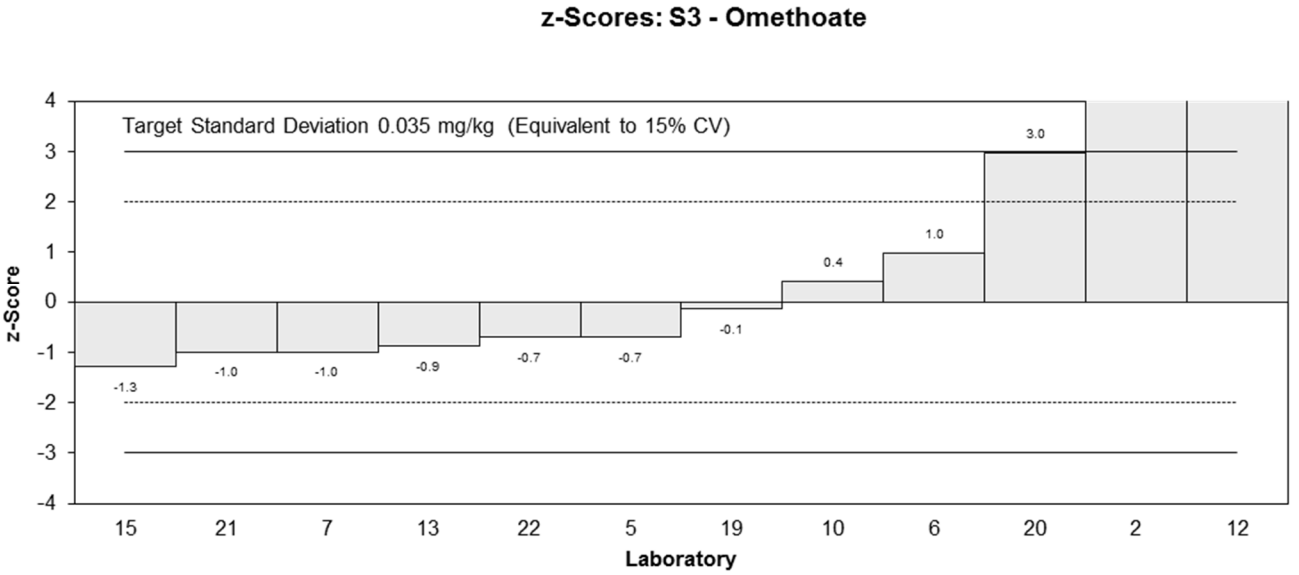
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	0.44	NR	NR	5.82	5.54
3	NR	NR	NR		
4	NT	NT	NT		
5	0.21	0.042	87	-0.71	-0.45
6	0.27	0.09	100	0.99	0.36
7	0.20	0.04	97	-0.99	-0.64
8	NT	NT	NT		
9	NT	NT	NT		
10	0.25	0.075	NR	0.43	0.18
11	NT	NT	NT		
12	0.81	0.002	98.6	16.31	15.52
13	0.204	NR	74	-0.88	-0.84
14	NT	NT	NT		
15	0.19	0.04	98	-1.28	-0.83
16	NT	NT	NT		
17	NT	NT	NT		
18	NT	NT	NT		
19	0.23	0.064	NR	-0.14	-0.07
20	0.34	0.176	89	2.98	0.58
21	0.20	0.06	79	-0.99	-0.50
22	0.21	NR	NR	-0.71	-0.68

Statistics

Assigned Value*	0.235	0.037
Spike	0.230	0.012
Robust Average	0.254	0.056
Median	0.220	0.024
Mean	0.296	
N	12	
Max.	0.81	
Min.	0.19	
Robust SD	0.077	
Robust CV	30%	

*Robust average excluding laboratory 12.


Results: S3 - Omethoate
Assigned Value = 0.235 ± 0.037 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
15 21 7 13 22 5 19 10 6 20 2 12 1 3 11 14 16 17 18 4 8 9 Md R.A. S


z-Scores: S3 - Omethoate
Target Standard Deviation 0.035 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
15 21 7 13 22 5 19 10 6 20 2 12
-1.3 -1.0 -1.0 -0.9 -0.7 -0.7 -0.1 0.4 1.0 3.0

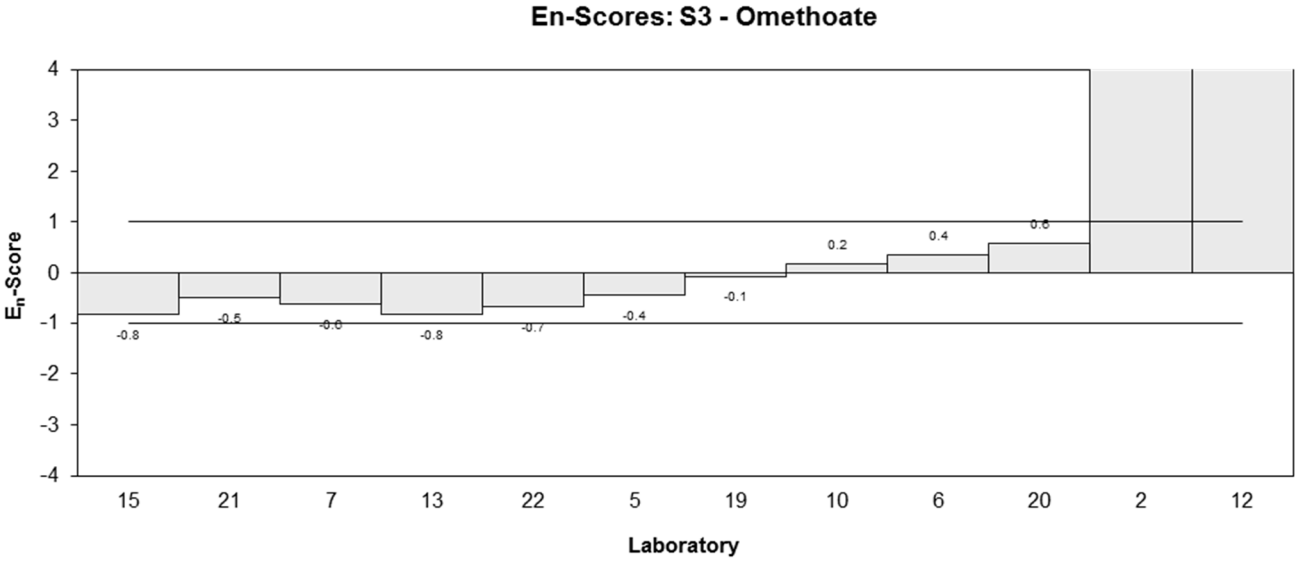

En-Scores: S3 - Omethoate
En-Score
Laboratory
15 21 7 13 22 5 19 10 6 20 2 12
-0.8 -0.5 -0.0 -0.8 -0.7 -0.4 -0.1 0.2 0.4 0.6

Figure 12

Table 15

Sample Details

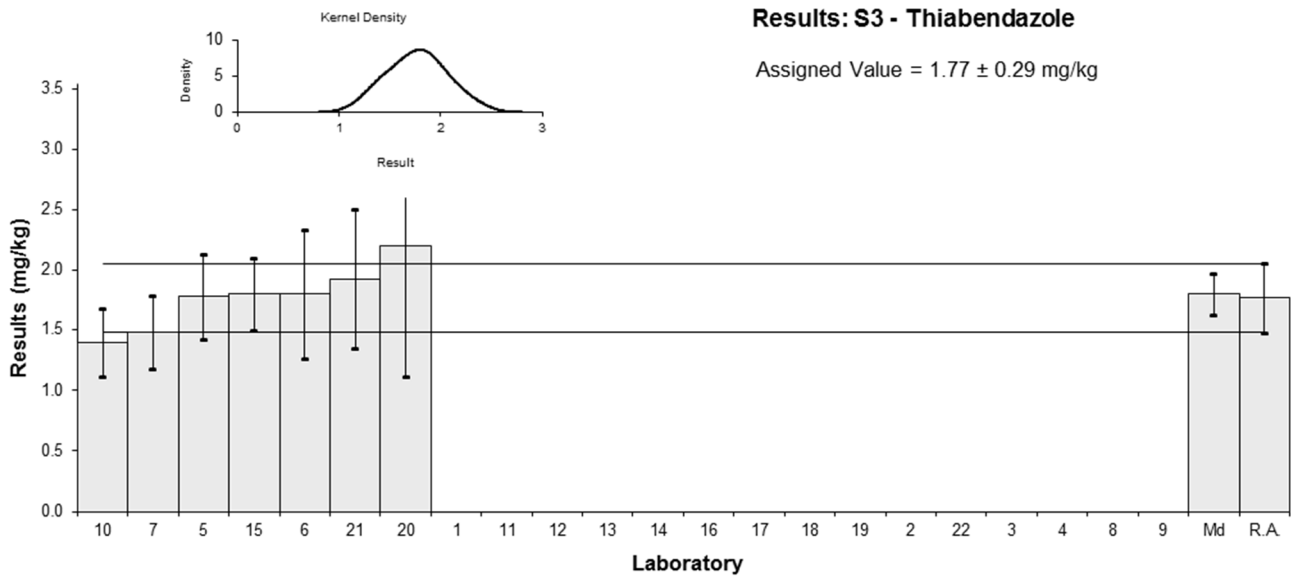
Sample No.	S3
Matrix.	Lemon
Analyte.	Thiabendazole
Units	mg/kg

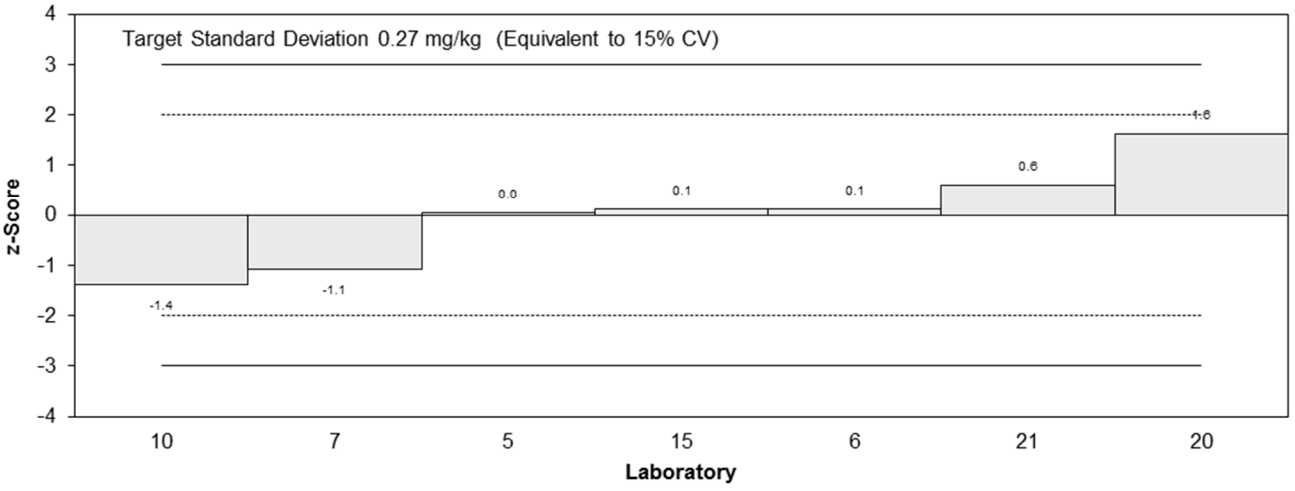
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
2	NT	NT	NT		
3	NT	NT	NT		
4	NT	NT	NT		
5	1.78	0.356	76	0.04	0.02
6	1.8	0.54	100	0.11	0.05
7	1.48	0.30	78	-1.09	-0.70
8	NT	NT	NT		
9	NT	NT	NT		
10	1.4	0.28	NR	-1.39	-0.92
11	NT	NT	NT		
12	NT	NT	NT		
13	NT	NT	NT		
14	NT	NT	NT		
15	1.8	0.3	100	0.11	0.07
16	NT	NT	NT		
17	NT	NT	NT		
18	NT	NT	NT		
19	NT	NT	NT		
20	2.2	1.082	79	1.62	0.38
21	1.93	0.58	92	0.60	0.25
22	NT	NT	NT		

Statistics

Assigned Value	1.77	0.29
Spike	Not Spiked	
Robust Average	1.77	0.29
Median	1.80	0.18
Mean	1.77	
N	7	
Max.	2.2	
Min.	1.4	
Robust SD	0.30	
Robust CV	17%	


Kernel Density
Density
Result
Results: S3 - Thiabendazole
Assigned Value = 1.77 ± 0.29 mg/kg
Results (mg/kg)
Laboratory
10 7 5 15 6 21 20 1 11 12 13 14 16 17 18 19 2 22 3 4 8 9 Md R.A.


z-Scores: S3 - Thiabendazole
Target Standard Deviation 0.27 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
10 7 5 15 6 21 20
-1.4
-1.1
0.0
0.1
0.1
0.6
1.6

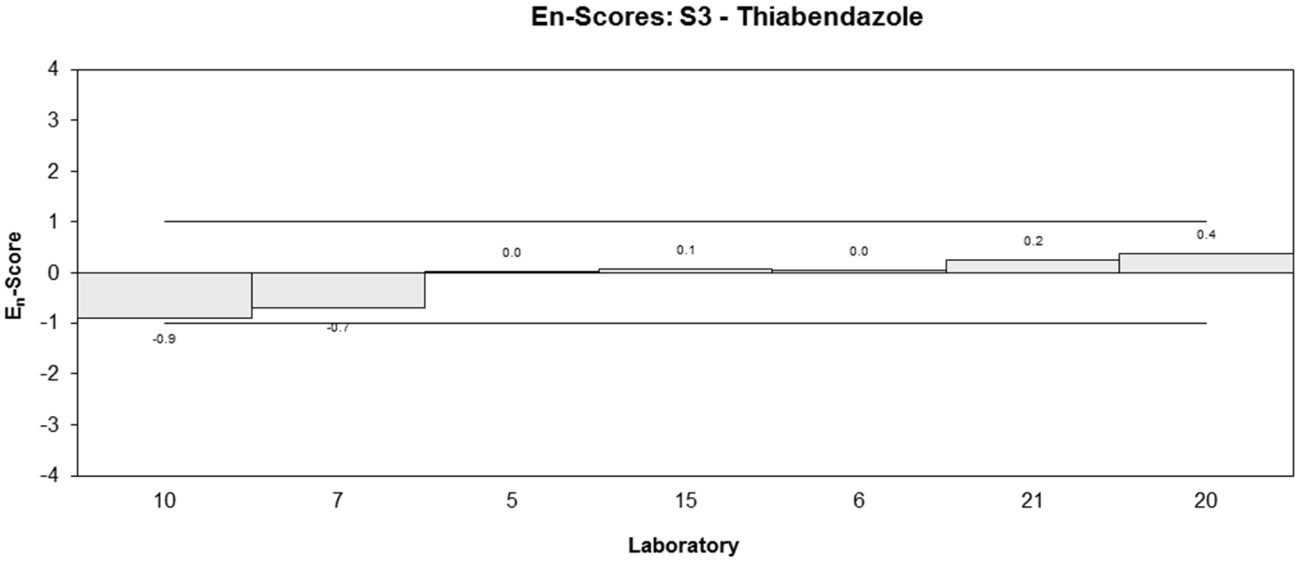

En-Scores: S3 - Thiabendazole
En-Score
Laboratory
10 7 5 15 6 21 20
-0.9
-0.7
0.0
0.1
0.0
0.2
0.4

Figure 13

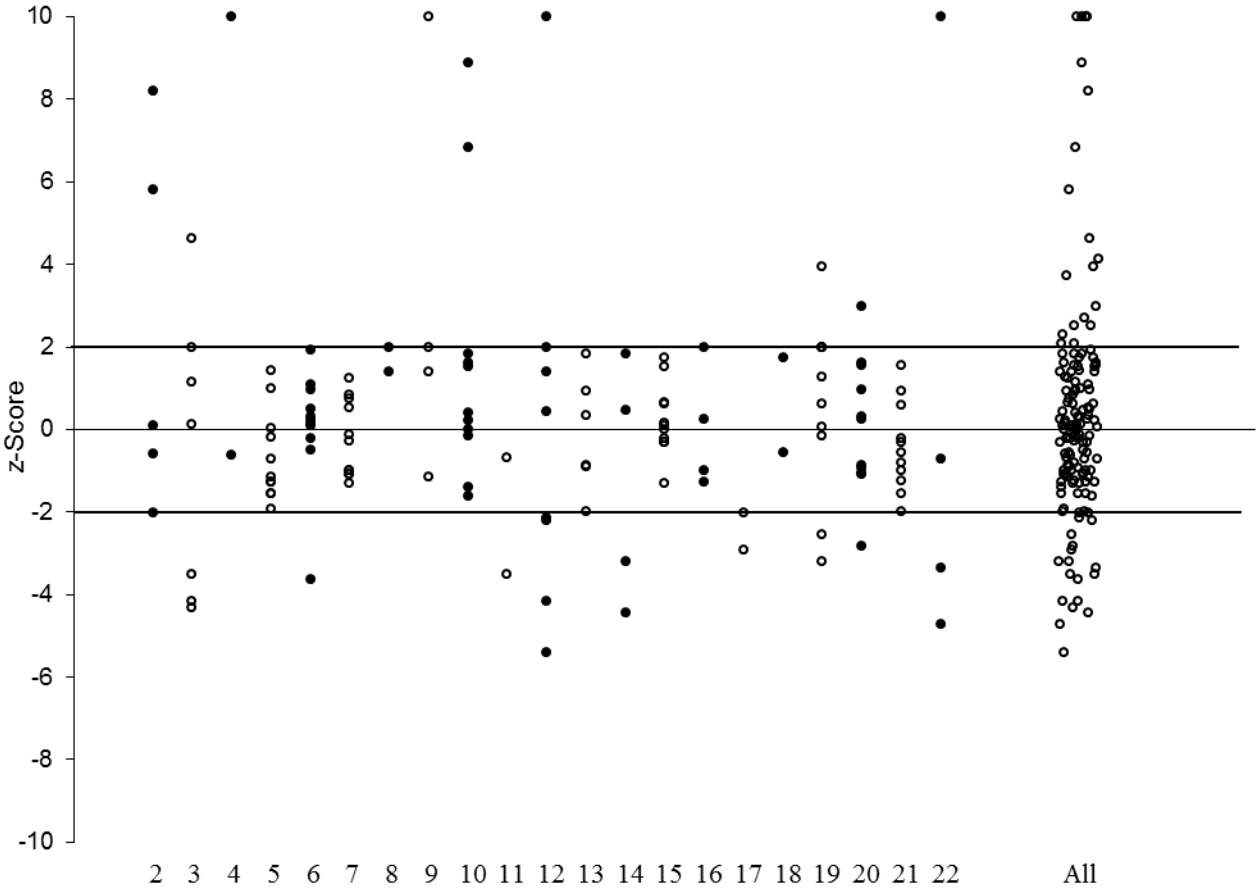


Figure 14 z-Score by laboratory

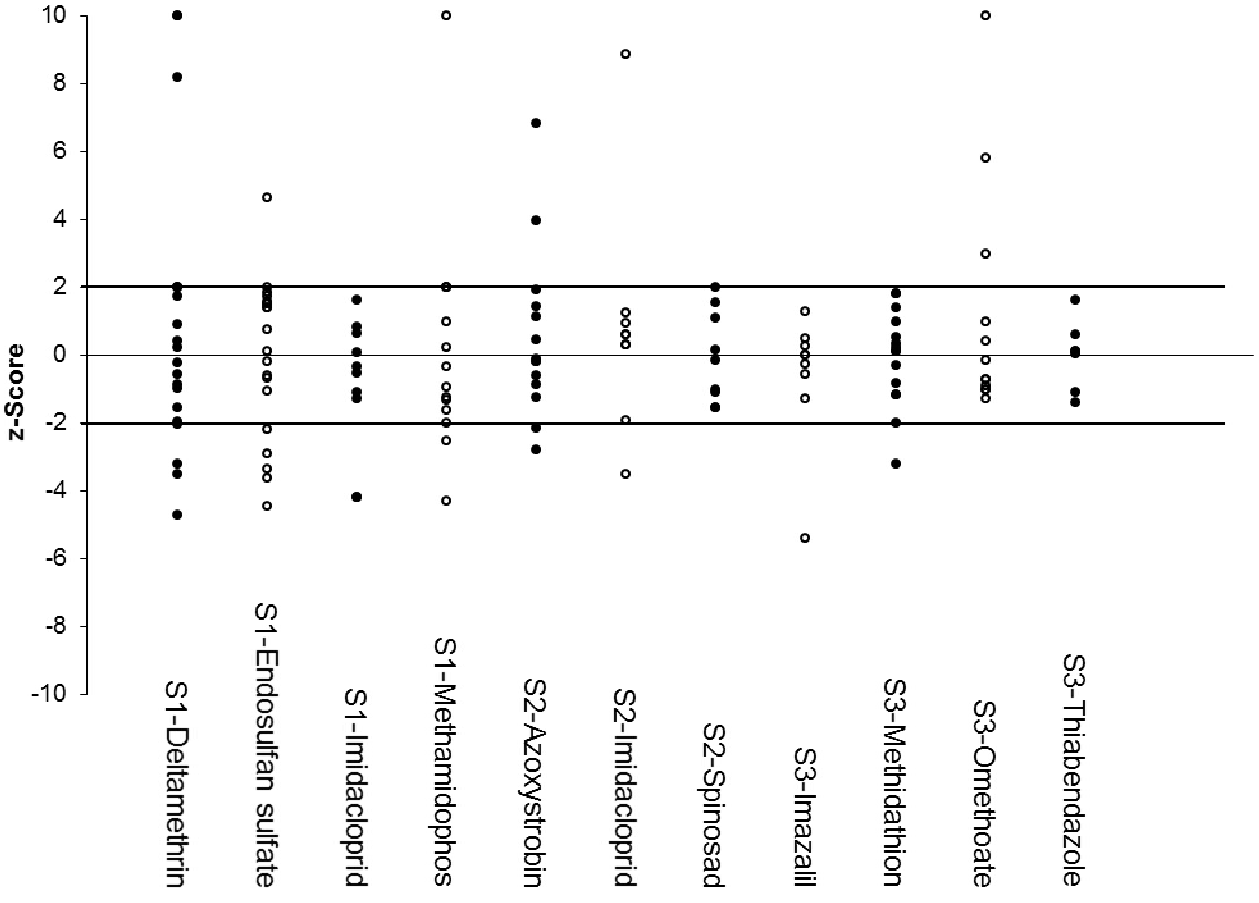


Figure 15 z-Score by analyte

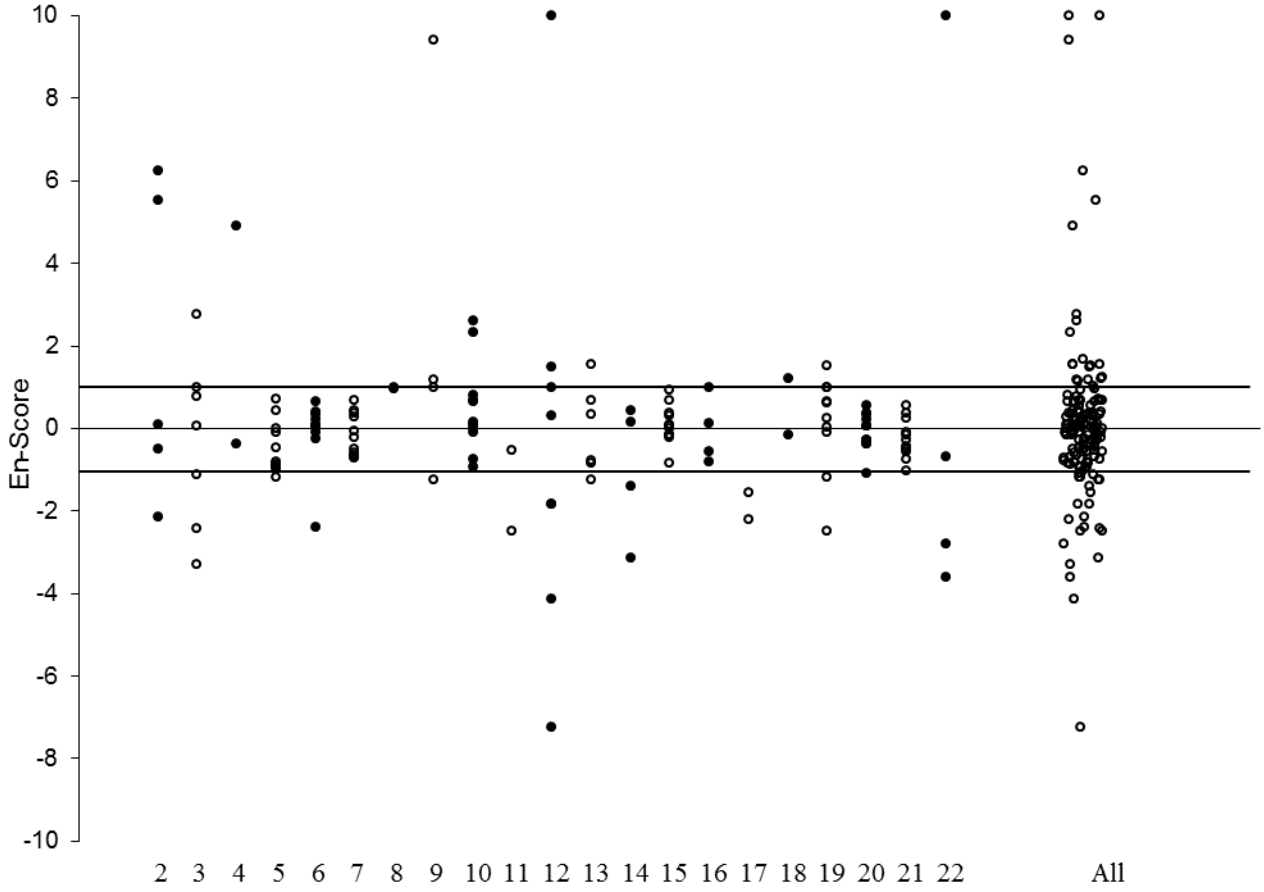


Figure 16 Summary of E_n-scores by laboratory

6 DISCUSSION OF RESULTS

6.1 Assigned Value

The robust averages of participants' results were used as the assigned values. The robust averages and associated expanded uncertainties were calculated using the procedure described in 'ISO13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparisons'.[10] Appendix 3 sets out the calculation for the expanded uncertainty of the robust average of methidathion in Sample S3.

No assigned value was set for clothianidin in Sample S3 because there were only a few results reported.

The assigned values for the spiked analytes were within the range 58% - 102% of the spiked level, providing additional support for the assigned values (Table 14).

Traceability: The consensus of participants' results is not traceable to any external reference, so although expressed in SI units, metrological traceability has not been established.

Table 16 Spiked and Assigned Values

Sample	Pesticide	Assigned Value (mg/kg)	Spiked concentration (mg/kg)	Assigned/spiked (%)
S1	Deltamethrin	0.61	0.75	82
S1	Endosulfan sulfate	1.22	1.47	83
S1	Imidacloprid	0.346	0.352	98
S1	Methamidophos	0.087	0.151	58
S2	Azoxystrobin	0.69	0.85	81
S2	Imidacloprid	0.21	0.25	84
S2	Spinosad	0.429	0.568	76
S3	Omethoate	0.235	0.230	102

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded uncertainty associated with their results and the basis of this uncertainty estimate (Table 3).

With the issue of ISO Standard 17025,[8] there is a requirement for the evaluation of the measurement uncertainty of chemical measurements.

Of 142 numerical results, 122 (86%) were reported with an associated expanded measurement uncertainty. Laboratories **2**, **9**, **13** and **22** did not report an estimate of measurement uncertainty, while laboratory **19** reported an estimate of measurement uncertainty only for some analytes. Laboratories **9** and **22** were not accredited.

The magnitude of these uncertainties was within the range 0.24 – 90% relative. Of the 122 expanded uncertainties reported, 19 were less than fifteen percent relative and 8 were over 50%. The study coordinator believes that a relative expanded measurement uncertainty of less than 15% and more than 50% may be unrealistic for routine measurement of a pesticide residue.

Laboratories having a satisfactory z-score and an unsatisfactory E_n-score are likely to have underestimated the expanded measurement uncertainty associated with their result.

In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write the uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example instead of 0.688 ± 0.0998 mg/kg the recommended format is 0.69 ± 0.10 mg/kg.[8]

6.3 z-Scores

Based on practical experience and published models the expected between-laboratory coefficient of variation (CV) should be approximately 15% for the concentrations of pesticides in the study samples. A target standard deviation equivalent to 15% CV was used to calculate z-scores for all analytes. The between laboratory coefficient of variation predicted by the modified Horwitz equation[11] is presented for comparison in Table 17.

Table 17 Target standard deviations and modified Horwitz values

Sample	Pesticide	Assigned value (mg/kg)	Modified Horwitz CV (%)	Target SD (as CV) (%)	Participants' SD (as CV) (%)
S1	Deltamethrin	0.61	17	15	47
S1	Endosulfan sulfate	1.22	16	15	37
S1	Imidacloprid	0.346	19	15	38
S1	Methamidophos	0.087	22	15	43
S2	Azoxystrobin	0.69	17	15	31
S2	Imidacloprid	0.21	20	15	28
S2	Spinosad	0.429	18	15	25
S3	Imazalil	2.60	14	15	16
S3	Methidathion	0.157	21	15	21
S3	Thiabendazole	1.77	15	15	17
S3	Omethoate	0.235	20	15	30

To account for possible bias in the consensus value due to laboratories using inefficient extraction techniques, z-scores were adjusted for deltamethrin, endosulfan sulfate and methamidophos in Sample S1 and spinosad in Sample S2 so that some z-scores greater than 2 were set at 2. This ensured that laboratories reporting results close to the spiked concentration were not penalised. A maximum acceptable concentration was set to two target standard deviations more than the spiked level. Scores of less than 2 were left unaltered.

Of the 139 results for which z-scores were calculated, 110 (79%) returned $|z| \leq 2$ indicating a satisfactory performance.

The dispersal of participants' z-scores is presented in Figure 14. The dispersal of z-scores for each analyte is presented in Figure 15.

Seven laboratories reported results for all analytes spiked into the samples.

Laboratories **5**, **7**, **15** and **21** returned satisfactory z-scores for all eleven analytes for which z-scores were calculated.

6.4 E_n-Score

Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score.

Of the 139 results for which E_n-scores were calculated, 102 (73%) returned $|E_n| \leq 1$ indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

The dispersal of participants' E_n-scores is graphically presented in Figure 16.

Laboratories **7** and **15** returned satisfactory E_n-scores for all eleven analytes.

6.5 False Negatives

Four laboratories reported a false negative – a pesticide present for which they tested but did not report a result. These are listed in Table 18.

Table 18 False negatives

Sample	Analyte	Lab Code
S1	Imidaclorpid	2
	Methamidophos	17
S2	Imidacloprid	2, 12
	Spinosad	12
S3	Imazalil	2
	Omethoate	3

6.6 Reporting of Pesticides not spiked in the PT samples

Five laboratories reported at least one pesticide which was not added by the study coordinator to the test material. These pesticides are listed by laboratory and sample in Table 19.

Table 19 Pesticides not added in the test materials

Lab. Code	Sample	Pesticide	Concentration (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
3	S2	Omethoate	1.02	0.09	85
11	S3	Cypermethrin	0.02	0.05	89
11	S3	Chlorpyrifos	0.01	0.05	70
11	S2	Deltamethrin	0.40	0.05	103
15	S3	2.4-D	0.012	0.004	92
19	S2	Spinetoram	0.014	NR	51
19	S1	pp-DDT	0.124	0.04	85
21	S2	Dithiocarbamates	0.02	0.01	108

Laboratories 7, 19 and 20 reported traces of beta-endosulfan and laboratory 11 traces of alpha and beta-endosulfan. These are likely a minor (<1%) impurity in the endosulfan sulfate standard used to spike the sample.

6.7 Participants' Analytical Methods

Participants were asked to provide descriptions of their measurement methods in a methods' questionnaire incorporated into the results sheet. This information is presented as Appendix 5. The study coordinator thanks those laboratories that completed the methods questionnaire.

Acetonitrile, ethyl acetate, dichloromethane (DCM), hexane, methanol, water and combination of these substances were used as extraction solvents. Laboratories performed a

variety of clean-up methods including dispersive SPE, florisil, silica gel and primary/secondary amines (PSA). Most methods used by participants were based around the QuEChERS[12] extraction and clean-up procedure (Figures 17-18).

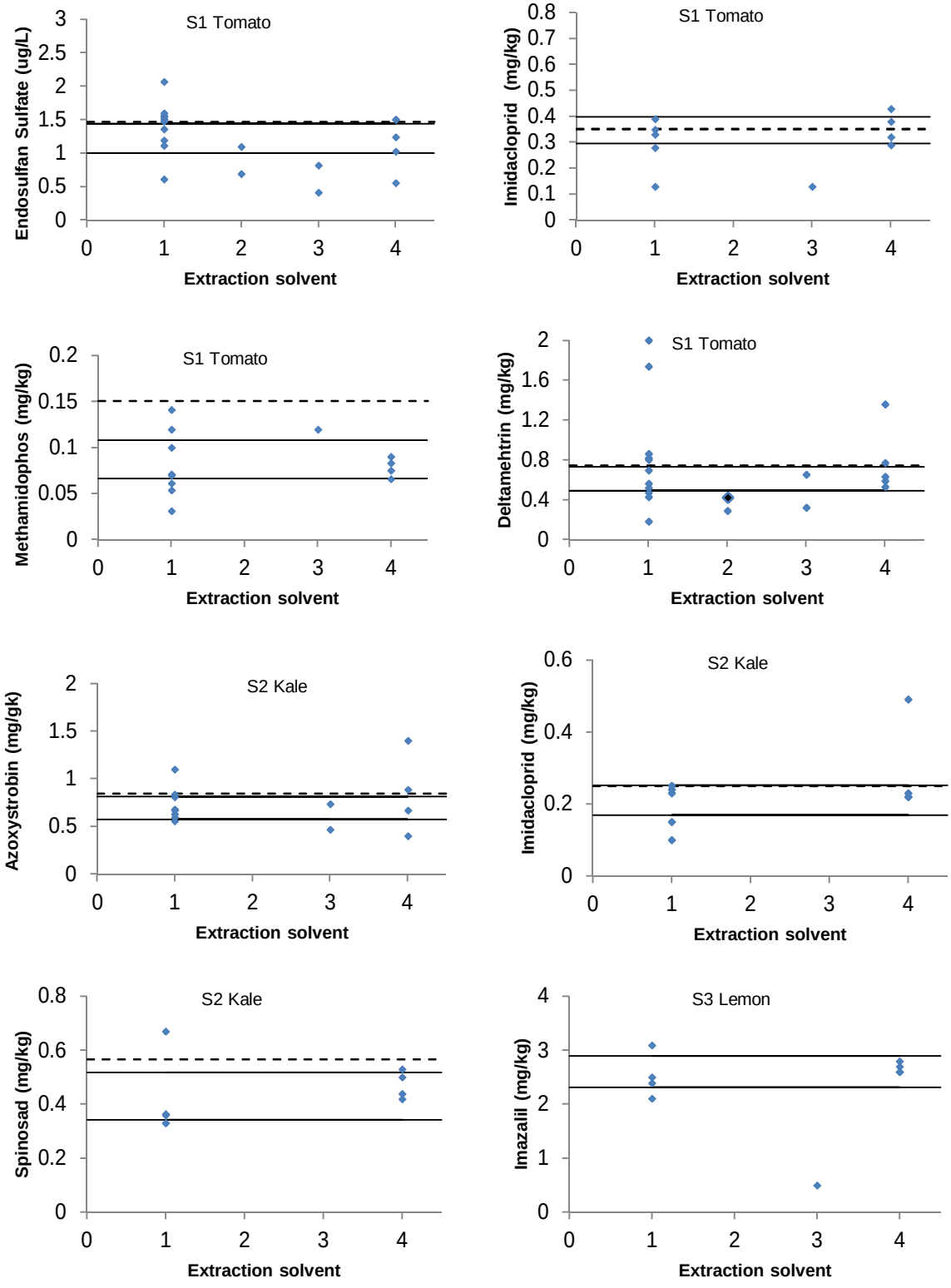


Figure 17 Results vs Extraction Solvent

1 = acetonitrile, 2 = Acetonitrile/other, 3 = Ethyl acetate, 4 = Other/Not specified

Horizontal lines are the upper and lower 95% confidence interval of the assigned value, the dotted line is the spiked value

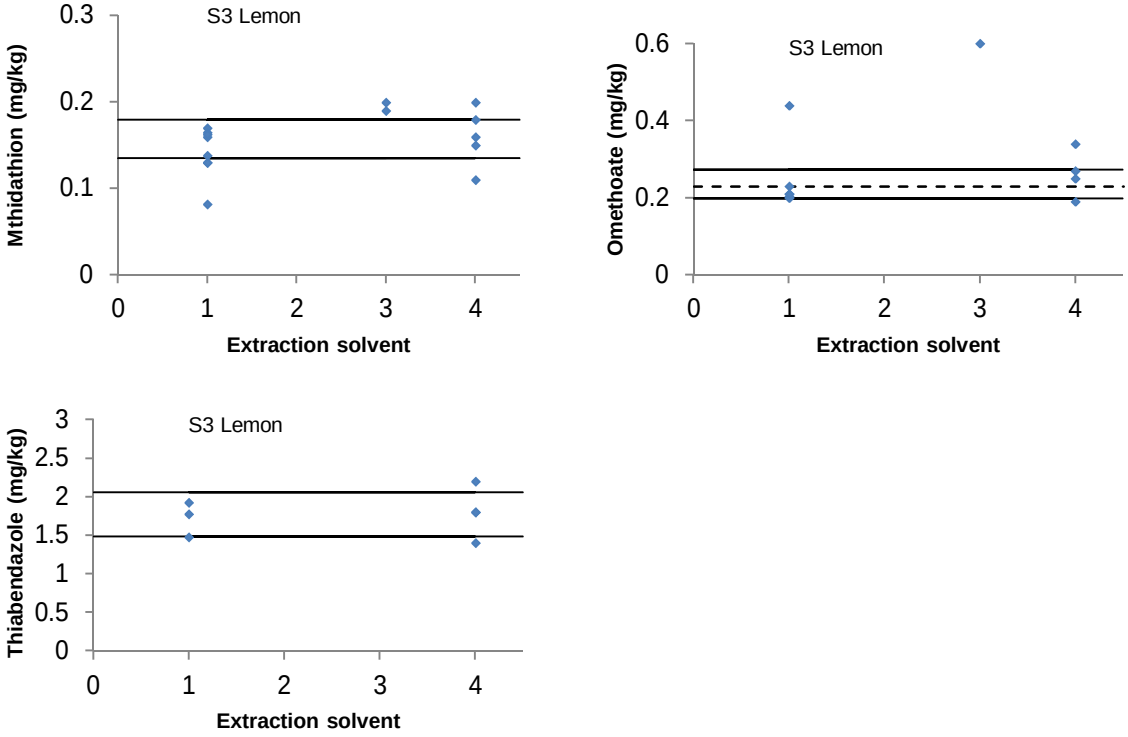


Figure 18 (cont'd) Results vs Extraction Solvent
1 = acetonitrile, 2 = Acetonitrile/other, 3 = Ethyl acetate, 4 = Other/Not specified
Horizontal lines are the upper and lower 95% confidence interval of the assigned value, the dotted line is the spiked value

Participants reported using GC-ECD/FPD, GC-MS(MS) and LC-MS(MS). A plot of result versus the instrument used is presented in Figures 19-21. No trends with the analytical instruments were observed.

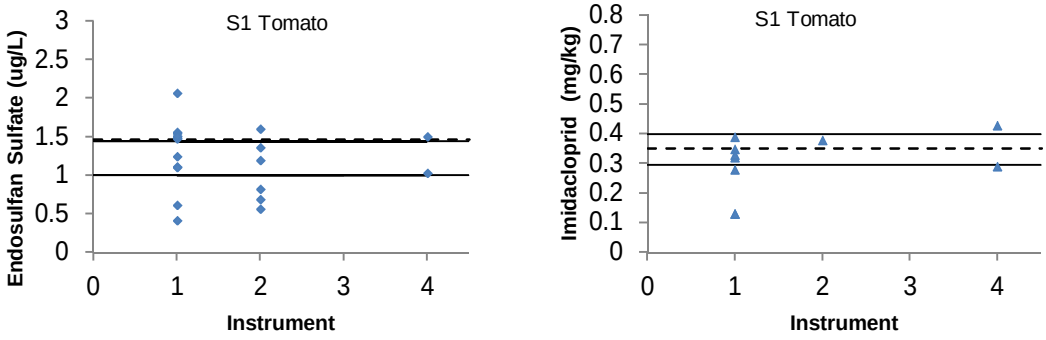


Figure 19 Results vs Instrument technique
1 = GC-ECD/FPD 2 = GC-MS(MS), 3 = LC-MS(MS), 4 = Combination/Not specified
Horizontal lines are the upper and lower 95% confidence interval of the assigned value; the dotted line is the spiked value

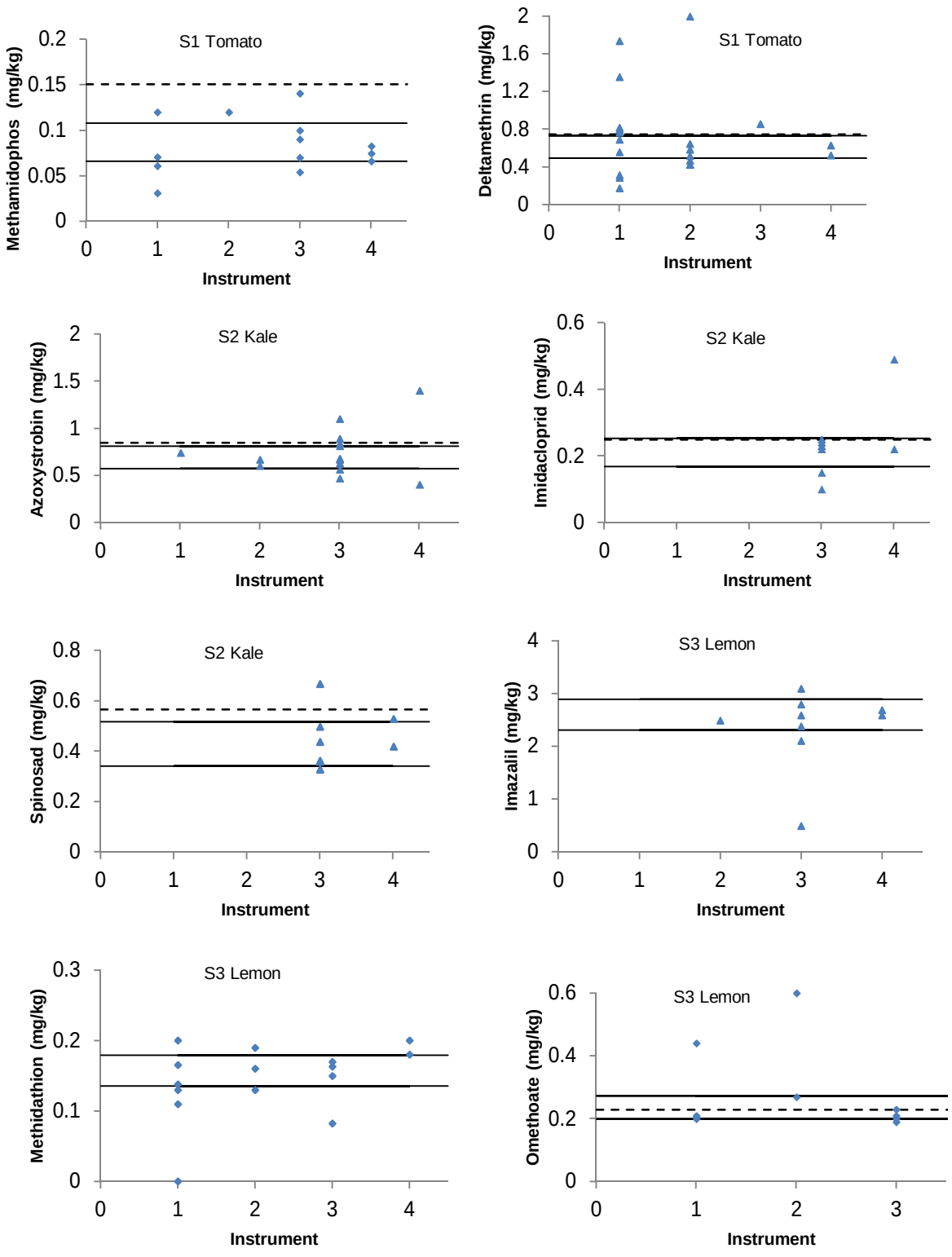


Figure 20 (cont'd) Results vs Instrument technique
1 = GC-ECD/FPD 2 = GC-MS(MS), 3 = LC-MS(MS), 4 = Combination/Not specified
Horizontal lines are the upper and lower 95% confidence interval of the assigned value; the dotted line is the spiked value

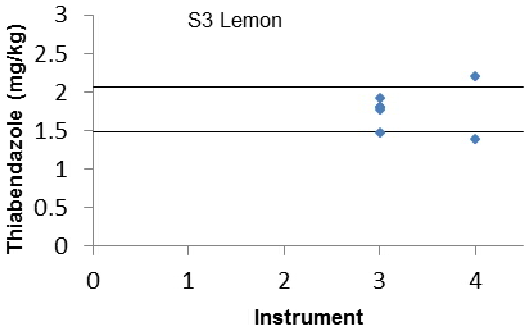


Figure 21 (cont'd) Results vs Instrument technique
1 = GC-ECD/FPD 2 = GC-MS(MS), 3 = LC-MS(MS), 4 = Combination/Not specified
Horizontal lines are the upper and lower 95% confidence interval of the assigned value; the dotted line is the spiked value

Recoveries were reported within the range 47% to 135%. Four laboratories reported that their results had been corrected for recovery.

6.8 Certified Reference Materials (CRM)

Participants were requested to indicate on the result sheet whether certified or matrix reference materials had been used as part of the quality assurance for the analysis. One laboratory reported using certified matrix reference materials. Fourteen laboratories reported using 'certified standards' from:

- Dr Ehrenstorfer
- Restek
- Sigma Aldrich
- AccuStandards

These materials may not meet the internationally-recognised definition of a Certified Reference Material:

> ***'reference material**, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures'* [13]

7 REFERENCES

[1] ISO/IEC 17043 2010, *Conformity assessment – General requirements for Proficiency Testing.*

[2] NMI 2016, *Chemical Proficiency Testing Study Protocol*, viewed 17 July 2018, < http://www.measurement.gov.au>.

[3] NMI 2016, *Chemical Proficiency Testing Statistical Manual*, viewed 17 July 2018, <http://www.measurement.gov.au >.

[4] Thompson, M. Ellison, SLR. & Wood, R 2005, 'The International Harmonized Protocol For Proficiency Testing Of (Chemical) Analytical Laboratories', *Pure Appl. Chem*, vol 78, pp 145-196.

[5] Federal Register of Legislation, *Australia New Zealand Food Standards Code – Schedule 20 – Maximum residue limits*, viewed 15 June 2018, <https://www.legislation.gov.au/Details/F2018C00379>.

[6] Food and Agriculture Organization of the United Nations, *AGP – JMPR reports and evaluations*, viewed 2 July 2018, <http://www.fao.org/agriculture/crops/thematic-sitemap/theme/pests/jmpr/jmpr-rep/en/>.

[7] NMI 2011, *AQA 11-03 Pesticides in Fruit and Vegetables*

[8] ISO/IEC 17025:2017, *General requirements for the competence of testing and calibration laboratories.*

[9] EURACHEM/CITAC Guide CG 4, QUAM:2012.P1, *Quantifying Uncertainty in Analytical Measurement*, 3rd edition, viewed 6 June 2018, <http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf>.

[10] ISO/IEC 13528:2015, *Statistical methods for use in proficiency testing by interlaboratory comparisons.*

[11] Thompson, M 2000, 'Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing', *Analyst*, vol 125, pp 385-386.

[12] Anastassiades, M, Lehotay, SJ, Štajnbaher, D & Schenck, FJ 2003, 'Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and Dispersive Solid-Phase Extraction for the Determination of Pesticide Residues in Produce', *JAOAC Int*., vol 86 (2), pp 412-431.

[13] BIPM, JCGM 200:2012, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM)*, 3rd edition, viewed 5 June 2018, <http://www.bipm.org/en/publications/guides/vim.html>.

APPENDIX 1 - PARTICIPANT LABORATORIES

Agriculture Research Centre Department of Agriculture Sabah, MALAYSIA	Agrifood Technology, VIC
ALS Scoresby, VIC	AMAL Analytical, VIC
Baguio Pesticide Analytical Laboratory, PHILIPPINES	Biosecurity Queensland Chemical Residues Laboratory, QLD
Cagayan de Oro Pesticide Analytical Laboratory, PHILIPPINES	Cebu Pesticides Analytical Laboratories, PHILIPPINES
Central Laboratory (Thailand) Co., Ltd, Bangkok Branch, THAILAND	Davao Pesticide Analytical Laboratory, PHILIPPINES
Eurofins Agroscience Testing NZ Ltd, NEW ZEALAND	National Measurement Institute VIC
Northern Plant Regulatory, THAILAND	Office of Agricultural Research & Development Region 1, THAILAND
Office of Agricultural Research and Development Region 6, THAILAND	Office of Environment and Heritage, Department of Premier and Cabinet Environmental Protection Science, NSW
OMIC Australia, VIC	Overseas Merchandise Inspection Co., Ltd, THAILAND
Pesticides Analytical Laboratory Section Bureau of Plant Industry - Quezon, PHILIPPINES	Royal Project Foundation (Thailand) Plant Protection Centre, THAILAND
Symbio Alliance QLD	The Australian Wine Research Institute SA

APPENDIX 2 - SAMPLE PREPARATION, HOMOGENEITY TESTING

Test Sample Preparation

Preparation of Samples S1 (Tomato) and S2 (Kale)

Tomatoes and kale were bought from a Sydney organic fruit and vegetable wholesaler. Samples were rinsed using tap water and allowed to air dry.

The whole tomato, including the peel, was chopped, pureed and passed through an 850 µm sieve. Kale was pureed and water added during the blending process. After blending the pureed was passed through an 850 µm sieve. Each sieved puree was continuously stirred while 120 g aliquots were dispensed into 200 mL amber bottles to provide unspiked samples. The remaining puree was spiked with aliquots of each pesticide standard solution, stirred for at least two hours and bottled. Each bottle was then labelled and shrink-wrapped in plastic film and placed in a freezer.

Preparation of Sample S3 (Lemon)

Lemons supplied by DEDJTR Victoria contained incurred pesticides and was used to prepare Sample S3.
5147.7 g of lemons, including rind, were placed in a stainless steel drum and blended using a stick mixer to form a puree. An amount of 1946.3 g of water was added to the puree to enable the sieving through an 850 µm sieve. The sieved puree was spiked with omethoate and stirred for at least two hours. The bottles were labelled, shrink-wrapped and placed in a freezer.

The formulated concentration and the relevant Australian maximum residue limits (MRL) are presented in Table 1.

Expanded uncertainties were estimated for the spiked concentration. Contributions to these uncertainties included the gravimetric and volumetric operation involved in spiking the samples and the purity of the pesticide reference standards. The expanded uncertainty of the spiked concentration at approximately 95% confidence was estimated to be 5% relative for all pesticides. Stability was not considered in the uncertainty budget and so the expanded uncertainty related to the concentration of pesticide at the time of spiking.

Homogeneity Testing

The process used to prepare the samples was the same as the one used in the previous NMI proficiency tests of pesticides in fruit and vegetables. This process has been demonstrated to produce homogeneous samples and no homogeneity testing was conducted.

APPENDIX 3 - ROBUST AVERAGE AND THE ASSOCIATED UNCERTAINTY

The robust average was calculated using the procedure described in 'ISO13258:2015, Statistical methods for use in proficiency testing by interlaboratory comparisons–Annex C.'[10] The uncertainty was estimated as:

$$u_{rob\ av} = 1.25 * S_{rob\ av} / \sqrt{p} \qquad \text{Equation 4}$$

where:

$u_{rob\ av}$	robust average standard uncertainty
$S_{rob\ av}$	robust average standard deviation
p	number of results

The expanded uncertainty ($U_{rob\ av}$) is the standard uncertainty multiplied by a coverage factor of 2 at approximately 95% confidence level.

A worked example is set out below in table 20.

Table 20 Uncertainty of robust average for Methidathion in Sample S3

No. results (p)	15
Robust Average	0.1568 mg/kg
$S_{rob\ av}$	0.0335 mg/kg
$u_{rob\ av}$	0.0108 mg/kg
k	2
$U_{rob\ av}$	0.0216 mg/kg

The robust average for Methidathion in Sample S3 is 0.157 ± 0.022 mg/kg.

APPENDIX 4 - ACRONYMS AND ABBREVIATIONS

CITAC	Co-operation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DCM	Dichloromethane
DEDJTR	Department of Economic Development, Jobs, Transport and Resources Victoria
$\lvert E_n \rvert$	Absolute value of an E_n-score
GC-MS	Gas Chromatography Mass Spectrometry
GC-ECD	Gas Chromatography Electron Capture Detector
GC-FPD	Gas Chromatography Flame Photometric Detector
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
LC-MS	Liquid Chromatography Mass Spectrometry
Max	Maximum value in a set of results
Md	Median value in a set of results
Min	Minimum value in a set of results
MRL	Maximum Residue Limits
NATA	National Association of Testing Authorities
NMI	National Measurement Institute (Australia)
NR	Not Reported
NT	Not Tested
PT	Proficiency Test
PSA	Primary/Secondary amines
QuEChERS	Quick Easy Cheap Effective Rapid Safe (an extraction technique)
R.A.	Robust average
Robust CV	Robust Coefficient of Variation
Robust SD	Robust Standard Deviation
S	Spiked or formulated concentration of a PT sample
SPE	Solid phase extraction
Target SD	Target standard deviation
σ	Target standard deviation
$\lvert z \rvert$	Absolute value of a z-score

APPENDIX 5 - PARTICIPANTS' TEST METHODS

Table 21 Test methods Sample S1 Tomato Endosulfan Sulfate

Lab. Code	Sample Weight (g)	Extraction	Clean-up	Extraction solvent	Measurement technique
1					
2	25	Liquid-Liquid	silica-gel	DCM	GCECD
3	10	solvent extraction	PSA+GCB	1%acetic in acetronitrile	GCECD
4	15	Modified QuEChERS	C18 SPE, CGB/PSA SPE	Acetonitrile	GCmECD
5	10	QuEChERS	d-SPE	Acetonitrile	GC-MS/MS
6	10	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ
7	10	QUECHERS	PSA	Acetonitrile	GCMSMS
8	15	Liquid-Liquid	PSA, C18	Acetonitrile	GC-ECD
9	10	QuEChERS	QuEChERS	1%acetic acid in acetonitrile	GCECD
10					
11	10	SPE	C18/envicarb/ Florisil	Acetonitrile/Acetone /Hexane	GC-ECD
12	10	Liquid-Liquid		ethyl acetate	GCMSMS
13	10	QuEChERS	PSA	0.1% Acetic acid in Acetonitrile	GCECD
14	24.2	Liquid-Liquid	Quechers	Ethyl Acetate	GCECD
15	20	Liquid-Liquid		Acetone,DCM,Hexane	GCMS,GC ECD
16	15	QuEChERS			
17	10	Liquid-Liquid	SPE-GCB / C-18/ florisil	Acetonitrile / Acetone / n-hexane	GCMSMS
18	10	SPE	C18, envicarb and florisil	Acetonitrile	GCECD
19	10	QuEChERS	PSA	Acetonitrile	GCMSMS
20					
21	10	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4	acetonitrile	GC-ECD
22	15	Liquid-liquid	Dispersive-SPE	Acetonitrile	GC-uECD

Table 22 Test methods Sample S1 Tomato Imidacloprid

Lab. Code	Extraction	Clean-up	Extraction solvent	Measurement technique
1				
2	QuEChERS		Acetronitrile	LC-MS/MS
3	QuEChERS	PSA+GCB	1%acetic in acetronitrile	LCMSMS
4				
5	QuEChERS	d-SPE	Acetonitrile	LC-MS/MS
6	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ
7	QUECHERS	PSA	Acetonitrile	LCMSMS
8				
9				
10				
11				
12	Liquid-Liquid		ethyl acetate	LCMSMS
13				
14				
15	Liquid-Liquid		Acetone,DCM,Hexane	LCMS
16				
17				
18				
19	QuEChERS		Acetonitrile	LCMSMS
20				
21	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	ACN	LC-MS/MS
22				

Table 23 Test methods Sample S1 Tomato Methamidophos

Lab. Code	Extraction	Clean-up	Extraction solvent	Measurement technique
1				
2	Liquid-Liquid		DCM	GCFPD
3	solvent extraction	PSA+GCB	1%acetic in acetronitrile	GCFPD
4				
5	QuEChERS	d-SPE	Acetonitrile	LC-MS/MS
6	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ
7	QUECHERS	PSA	Acetonitrile	LCMSMS
8				
9	QuEChERS	QuEChERS	1%acetic acid in acetonitrile	GCFPD
10				
11				
12	Liquid-Liquid		ethyl acetate	GCMSMS
13	QuEChERS	PSA	0.1% Acetic acid in Acetonitrile	GCFPD
14				
15	Liquid-Liquid	Acetone,DCM,Hexane	GCMS,LCMS	
16	QuEChERS	PSA	Acetonitrile	LC/MS/MS
17				
18				
19	QuEChERS		Acetonitrile	LCMSMS
20				
21	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	ACN	GC-FPD
22	Liquid-liquid	Dispersive-SPE	Acetonitrile	GC-FPD

Table 24 Test methods Sample S1 Tomato Deltamethrin

Lab. Code	Extraction	Clean-up	Extraction solvent	Measurement technique
1				
2	Liquid-Liquid		DCM	GCECD
3	QuEChERS	PSA+GCB	1%acetic in acetronitrile	GCECD
4	Modified QuEChERS	C18 SPE, CGB/PSA SPE	Acetonitrile	GCmECD
5	QuEChERS	d-SPE	Acetonitrile	GC-MS/MS
6	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ
7	QUECHERS	PSA	Acetonitrile	GCMSMS
8	Liquid-Liquid	PSA, C18	Acetonitrile	GC-ECD
9	QuEChERS	QuEChERS	1%acetic acid in acetonitrile	GCECD
10				
11	SPE	C18/envicarb/ Florisil	Acetonitrile/Acetone /Hexane	GC-ECD
12	Liquid-Liquid		ethyl acetate	GCMSMS
13	QuEChERS	PSA	0.1% Acetic acid in Acetonitrile	GCECD
14	Liquid-Liquid	Quechers	Ethyl Acetate	GCECD
15	Liquid-Liquid		Acetone,DCM,Hexane	GCMS,GC ECD
16				
17	Liquid-Liquid	SPE-GCB / C-18/ florisil	Acetonitrile / Acetone / n-hexane	GCMSMS
18	SPE	C18, envicarb and florisil	Acetonitrile	GCECD
19	QuEChERS		Acetonitrile	LCMSMS
20				
21	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	ACN	GC-MS
22	Liquid-liquid	Dispersive-SPE	Acetonitrile	GC-uECD

Table 25 Test methods Sample S2 Kale Azoxystrobin

Lab. Code	Sample Weight (g)	Extraction	Clean-up	Extraction solvent	Measurement technique
1					
2					
3	10	QuEChERS	PSA+GCB	1%acetic in acetronitrile	LCMSMS
4	15				
5	10	QuEChERS	d-SPE	Acetonitrile	LC-MS/MS
6	10	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ
7	10	QUECHERS	PSA	Acetonitrile	LCMSMS
8					
9	10				
10					
11	10				
12	10	Liquid-Liquid		ethyl acetate	LCMSMS
13	10	QuEChERS	PSA	0.1% Acetic acid in Acetonitrile	GCMSMS
14	24.8	Liquid-Liquid	Quechers	Ethyl Acetate	GCECD/NPD
15	20	Liquid-Liquid		Acetone,DCM,Hexane	GCMS, LCMS
16	15	QuEChERS	PSA	Acetonitrile	LC/MS/MS
17					
18	10				
19	10	QuEChERS		Acetonitrile	LCMSMS
20					
21	10	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	ACN	GC-MS
22	15				

Table 26 Test methods Sample S2 Kale Imidacloprid

Lab. Code	Extraction	Clean-up	Extraction solvent	Measurement technique
1				
2				
3	QuEChERS	PSA+GCB	1%acetic in acetronitrile	LCMSMS
4				
5	QuEChERS	d-SPE	Acetonitrile	LC-MS/MS
6	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ
7	QUECHERS	PSA	Acetonitrile	LCMSMS
8				
9				
10				
11				
12	Liquid-Liquid	ethyl acetate	LCMSMS	
13				
14				
15	Liquid-Liquid	Acetone,DCM,Hexane	LCMS	
16				
17				
18				
19	QuEChERS		Acetonitrile	LCMSMS
20				
21	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	ACN	LC-MS/MS
22				

Table 27 Test methods Sample S2 Kale Spinosad

Lab. Code	Extraction	Clean-up	Extraction solvent	Measurement technique
1				
2				
3				
4				
5	QuEChERS	d-SPE	Acetonitrile	LC-MS/MS
6	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ
7	QUECHERS	PSA	Acetonitrile	LCMSMS
8				
9				
10				
11				
12	Liquid-Liquid		ethyl acetate	LCMSMS
13				
14				
15	Liquid-Liquid		Acetone,DCM,Hexane	LCMS
16	QuEChERS	PSA	Acetonitrile	LC/MS/MS
17				
18				
19	QuEChERS		Acetonitrile	LCMSMS
20				
21	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	ACN	LC-MS/MS
22				

Table 28 Test methods Sample S3 Lemon Imazalil

Lab. Code	Sample Weight (g)	Extraction	Clean-up	Extraction solvent	Measurement technique
1					
2					
3	10				
4	15				
5	10	QuEChERS	d-SPE	Acetonitrile	LC-MS/MS
6	10	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ
7	10	QUECHERS	PSA	Acetonitrile	GCMSMS
8					
9	10				
10					
11	10				
12	10	Liquid-Liquid		ethyl acetate	LCMSMS
13	10				
14	24.7				
15	20	Liquid-Liquid		Acetone,DCM,Hexane	LCMS,GCMS
16	15				
17					
18	10				
19	10	QuEChERS		Acetonitrile	LCMSMS
20					
21	10	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	ACN	LC-MS/MS
22	15				

Table 29 Test methods Sample S3 Lemon Methidathion

Lab. Code	Clean-up	Extraction	Extraction solvent	Measurement technique
1				
2			DCM	GC FPD
3	QuEChERS	PSA+GCB	1%acetic in acetronitrile	GCFPD
4				
5	QuEChERS	d-SPE	Acetonitrile	GC-MS/MS
6	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ
7	QUECHERS	PSA	Acetonitrile	LCMSMS
8				
9	QuEChERS	QuEChERS	1%acetic acid in acetonitrile	GCFPD
10				
11				
12	Liquid-Liquid	ethyl acetate	GCMSMS	
13	QuEChERS	PSA	0.1% Acetic acid in Acetonitrile	GCFPD
14	Liquid Liquid	Quechers	Ethyl Acetate	GC ECD NPD
15	Liquid-Liquid	Acetone,DCM,Hexane	GCMS,LCMS	
16	QuEChERS	PSA	Acetonitrile	LC/MS/MS
17				
18				
19	QuEChERS		Acetonitrile	LCMSMS
20				
21	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	ACN	GC-FPD
22				

Table 30 Test methods Sample S3 Lemon Omethoate

Lab. Code	Clean-up	Extraction	Extraction solvent	Measurement technique
1				
2	Liquid-liquid		DCM	GCFPD
3	QuEChERS	PSA+GCB	1%acetic in acetronitrile	GCFPD
4				
5	QuEChERS	d-SPE	Acetonitrile	LC-MS/MS
6	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ
7	QUECHERS	PSA	Acetonitrile	LCMSMS
8				
9				
10				
11				
12	Liquid-Liquid	ethyl acetate	GCMSMS	
13	QuEChERS	PSA	0.1% Acetic acid in Acetonitrile	GCFPD
14				
15	Liquid-Liquid	Acetone,DCM,Hexane	GCMS,LCMS	
16				
17				
18				
19	QuEChERS		Acetonitrile	LCMSMS
20				
21	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	ACN	GC-FPD
22	Liquid-liquid	Dispersive-SPE	Acetonitrile	GC-FPD

Table 31 Test methods Sample S3 Lemon Thiabendazole

Lab. Code	Clean-up	Extraction	Extraction solvent	Measurement technique
1				
2				
3				
4				
5	QuEChERS	d-SPE	Acetonitrile	LC-MS/MS
6	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ
7	QUECHERS	PSA	Acetonitrile	LCMSMS
8				
9				
10				
11				
12				
13				
14				
15	Liquid-Liquid	Acetone,DCM,Hexane	LCMS	
16				
17				
18				
19	QuEChERS		Acetonitrile	
20				
21	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	ACN	LC-MS/MS
22				

Table 32 Test methods Sample S3 Lemon Clothianidin

Lab. Code	Clean-up	Extraction	Extraction solvent	Measurement technique
1				
2				
3				
4				
5				
6	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ
7	QUECHERS	PSA	Acetonitrile	LCMSMS
8				
9				
10				
11				
12	Liquid-Liquid	ethyl acetate	LCMSMS	
13				
14				
15	Liquid-Liquid	Acetone,DCM,Hexane	LCMS	
16	QuEChERS	PSA	Acetonitrile	LC/MS/MS
17				
18				
19	QuEChERS		Acetonitrile	LCMSMS
20				
21	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	ACN	LC-MS/MS
22				

END OF REPORT