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

Proficiency Test Report AQA 19-08 Pesticides in Fruit & Vegetables

August 2019

ACKNOWLEDGMENTS

This study was conducted by the National Measurement Institute (NMI). Support funding was provided by the Australian Government Department of Industry, Innovation and Science.

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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SUMMARY

Proficiency test AQA 19-08 Pesticides in Fruit and Vegetables was conducted in May 2019; seventeen laboratories submitted results.

Four sets of test samples were prepared at the NMI laboratory in North Ryde, NSW.

Sample **S1** was prepared from pureed tomato to which was added pesticide standard solutions. This sample is the same as the one distributed in AQA 18-07 as Sample S1.

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

Sample **S3** was prepared from pureed apples to which was added pesticide standard solution.

Sample **S4** was prepared from pureed potatoes to which was added pesticide standard solution.

Each spiked puree was dispensed into 120 g portions. Participants were also provided with 120 g portions of unspiked Samples S1, S2, S3 and S4.

Of a possible 238 numeric results a total of 147 were submitted. Seventy results (29%) 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 137 results for which z-scores were calculated, 115 (84%) returned $|z| \leq 2$ indicating a satisfactory performance.

Of the 137 results for which E_n-scores were calculated, 111 (81%) returned $|E_n| \leq 1$ indicating agreement of the participant's result with the assigned value within their respective expanded uncertainties.

Laboratory **20** had satisfactory z-scores and E_n-scores for all twelve analytes for which scores were calculated.

Laboratories **1**, **4**, **12**, **17** and **18** 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 **6** and **7** reported results for analytes not added to the test samples (a total of 10 analytes).

A high number of Not Tested analytes (~40%) were recorded against Sample S2 Cauliflower and Sample S4 Potato.

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

Of 162 numerical results, 142 (88%) were reported with an associated expanded measurement uncertainty. Laboratories **10**, **12** and **15** did not report an estimate of measurement uncertainty for all or some analytes. Laboratories **9** and **20** reported very large measurement uncertainties estimates, likely relative measurement uncertainties instead of absolute.

The magnitude of these uncertainties was within the range 0.05 – 86% relative, excluding laboratories 9 and 20.

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 Cauliflower puree			
Iprodione	0.802	0.040	T0.1
Methomyl	2.59	0.13	2
Omethoate	3.10	0.16	2
S3 Apple puree			
Azinpos-methyl	1.400	0.070	1
Chlorpyrifos	0.701	0.035	T0.5
Diazinon	0.799	0.040	0.5
S4 Potato puree			
Azoxystrobin	2.79	0.14	7
Endosulfan sulfate[b]	1.208	0.060	-
Imidacloprid[c]	0.551	0.028	0.3
Thiabendazole[d]	3.47	0.17	5

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

2.2 Study Timetable

The timetable of the study was:

Invitation issued:	10 April 2019
Samples dispatched:	07 May 2019
Results due:	03 June 2019
Interim report issued:	19 June 2019

2.3 Participation

A total of seventy-eight international, national, state government and private laboratories were invited to participate.

Seventeen laboratories agreed to participate and submitted results.

2.4 Test Material Specification

Four test samples were prepared.

Sample S1 was prepared in March 2018 by spiking pureed tomatoes which had been passed through a 850 µm sieve. This sample is the same as Sample S1 in AQA 18-07[6] .
Sample S2 was prepared by spiking pureed cauliflower which had been passed through a 850 µm sieve.
Sample S3 was prepared by spiking pureed apple which had been passed through a 850 µm sieve.
Sample S4 was prepared by spiking pureed potato which had been passed through a 850 µm sieve.

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 1.

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[7] 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 were compared to the spiked concentration. Robust averages were 54-96% of the spiked levels which gave no reason to question the stability of the pesticides. Methamidophos low recovery in tomato Sample S1 (54%) was similar to the one obtained in AQA 18-07 (58%) which may indicate participants' having difficulties with the extraction of this analyte rather than stability issues.[6,8] A stability check for Sample S1 is detailed in Appendix 1.

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 03 June 2019. 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 19 June 2019.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Test Method Summary

Participants were requested to provide information about their test methods. This is transcribed in Appendix 4.

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	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples Spiked Samples	Recoveries of Spiked Samples	Eurachem/CITAC Guide
4	Top Down - precision and estimates of the method and laboratory bias	Control Samples Spiked Samples	Recoveries of Spiked Samples Standard Purity	CAC/GL 59-2006 Guidelines on Estimation of Uncertainty of Results
6	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis Instrument Calibration	Recoveries of Spiked Samples	NMI Uncertainty Course
7	Top Down - precision and estimates of the method and laboratory bias	Control Samples Spiked Samples Duplicate Analysis Instrument Calibration	Laboratory Bias from PT Studies Recoveries of Spiked Samples	Eurachem/CITAC Guide
8	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate Analysis		
9	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Duplicate Analysis	Recoveries of Spiked Samples	NATA Technical Note 33
10				
11	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate Analysis	Recoveries of Spiked Samples Instrument Calibration Standard Purity	Eurachem/CITAC Guide
12	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples Spiked Samples Duplicate Analysis Instrument Calibration	Recoveries of Spiked Samples	Eurachem/CITAC Guide
13	Top Down - precision and estimates of the method and laboratory bias	Control Samples Spiked Samples	Recoveries of Spiked Samples Standard Purity	NATA Technical Note 33
14	Top Down - precision and estimates of the method and laboratory bias	Spiked Samples	Recoveries of Spiked Samples	NATA Technical Note 33
15	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Duplicate Analysis	Recoveries of Spiked Samples Instrument Calibration Standard Purity	Eurachem/CITAC Guide
16	Horwitz formula	Control Samples Duplicate Analysis Instrument Calibration	Certified Reference Materials Recoveries of Spiked Samples Standard Purity	NMI Uncertainty Course
17	Top Down - precision and estimates of the method and laboratory bias	Control Samples	Recoveries of Spiked Samples Standard Purity	Codex CAC/GL 59-2006 Guidelines on Estimation of Uncertainty of Results
18	Standard deviation of replicate analyses multiplied by 2 or 3	Spiked Samples		
19	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis Instrument Calibration	Recoveries of Spiked Samples Instrument Calibration Standard Purity	Eurachem/CITAC Guide
20			Recoveries of Spiked Samples	

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 4 to 17 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 15.

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

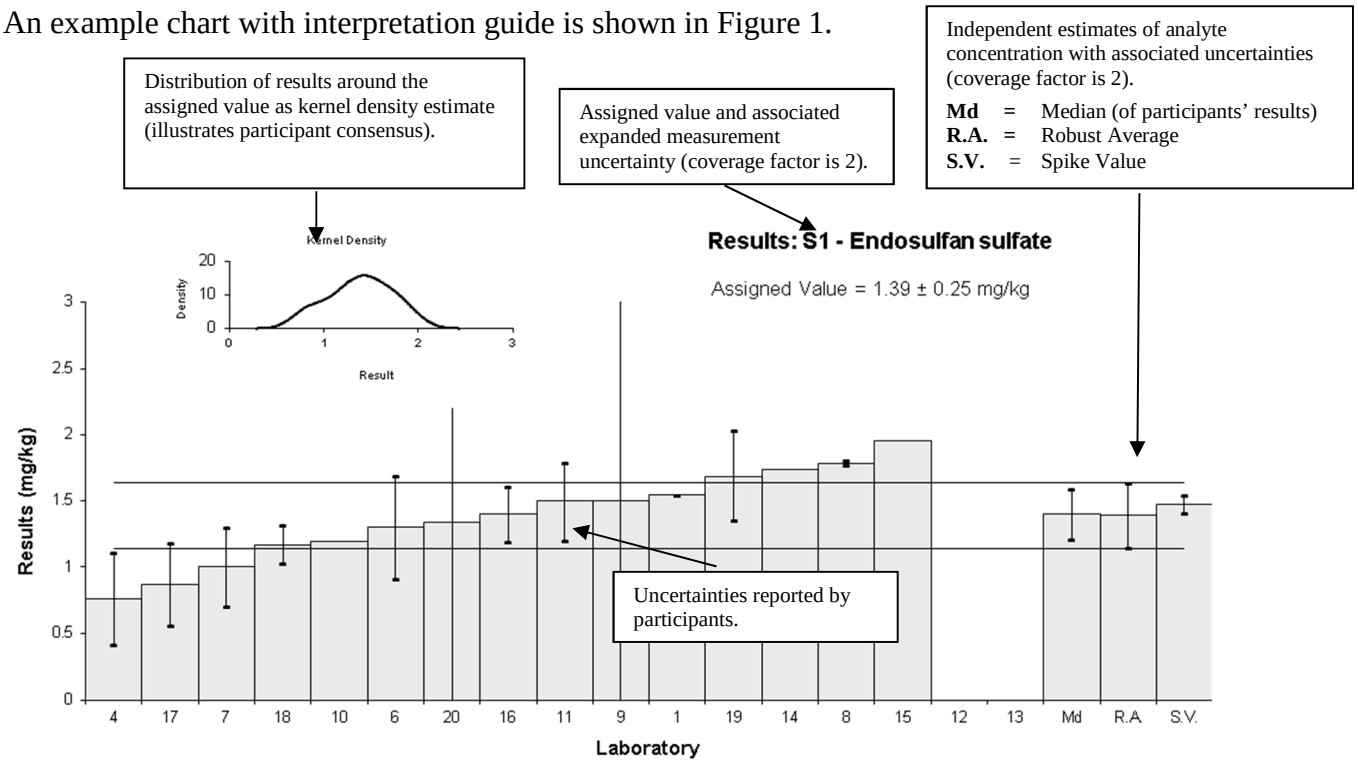


Figure 1 Guide to presentation of results

4.2 Assigned Value

The assigned value is defined as: 'value attributed to a particular quantity and accepted, sometimes by convention, as having an uncertainty appropriate for a given purpose.'[3]

For a proficiency test, the assigned value is the best available measurement of the true concentration of an analyte in the test sample. For this PT study the assigned values were the robust average of the participants' results.

4.3 Robust Average

The robust averages and associated expanded measurement uncertainties were calculated using the procedure described in 'Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO13528:2015'.[9]

4.4 Performance Coefficient of Variation (PCV)

The performance coefficient of variation (PCV) is a measure of the between laboratories variation that in the judgement of the study organiser would be expected from participants given the sample concentration. It is important to note that this is a performance measure set by the study coordinator; it is not the robust coefficient of variation (robust CV) of participants' results.

4.5 Target Standard Deviation

The target standard deviation (σ) is the product of the assigned value (*X)* and the performance coefficient of variation (PCV) as presented in Equation 1.

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

This value is used for calculation of participant z-score.

4.6 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.

4.7 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.

4.8 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025:2017[10] 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.[11]

5 TABLES AND FIGURES

Table 4

Sample Details

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

Participant Results

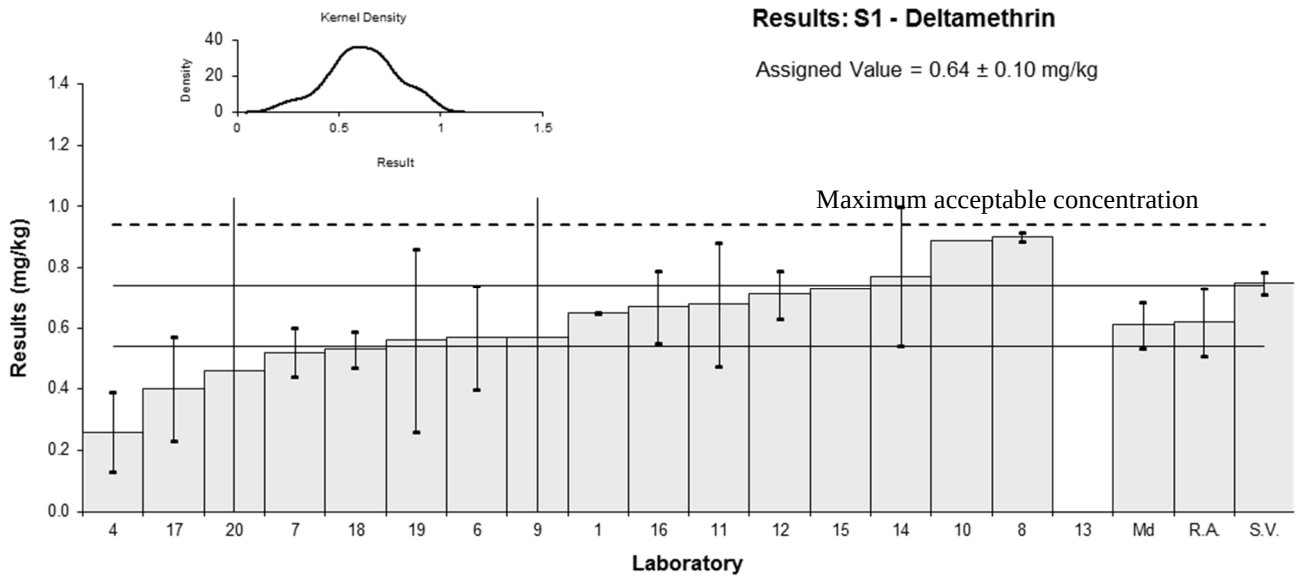
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.65	0.002	89	0.10	0.10
4	0.26	0.13	85	-3.96	-2.32
6	0.57	0.17	88	-0.73	-0.35
7	0.52	0.08	65	-1.25	-0.94
8*	0.90	0.015	NR	2.00	1.00
9	0.57	15.79	102.4	-0.73	0.00
10*	0.89	NR	NR	2.00	1.00
11	0.679	0.203	85	0.41	0.17
12	0.71	0.08	102.5	0.73	0.55
13	NT	NT	NT		
14	0.77	0.23	105	1.35	0.52
15	0.73	NR	113	0.94	0.90
16	0.67	0.12	98	0.31	0.19
17	0.40	0.17	96	-2.50	-1.22
18	0.53	0.06	100	-1.15	-0.94
19	0.56	0.30	122	-0.83	-0.25
20	0.46	30	NR	-1.88	-0.01

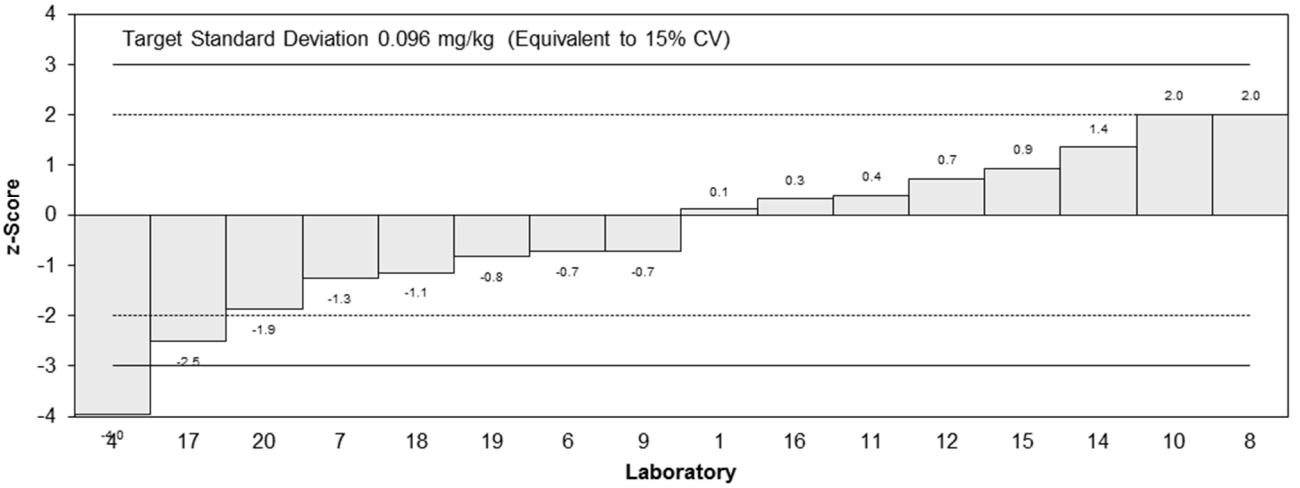
Statistics

Assigned Value**	0.64	0.10
Spike	0.748	0.037
Robust Average	0.62	0.11
Maximum acceptable conc.	0.94	
Median	0.610	0.075
Mean	0.617	
N	16	
Max.	0.9	
Min.	0.26	
Robust SD	0.16	
Robust CV	26%	

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

**Robust average excluding laboratory 4.


Kernel Density
Density
Result
Results: S1 - Deltamethrin
Assigned Value = 0.64 ± 0.10 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
4 17 20 7 18 19 6 9 1 16 11 12 15 14 10 8 13 Md R.A. S.V.


z-Scores: S1 - Deltamethrin
Target Standard Deviation 0.096 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
4 17 20 7 18 19 6 9 1 16 11 12 15 14 10 8

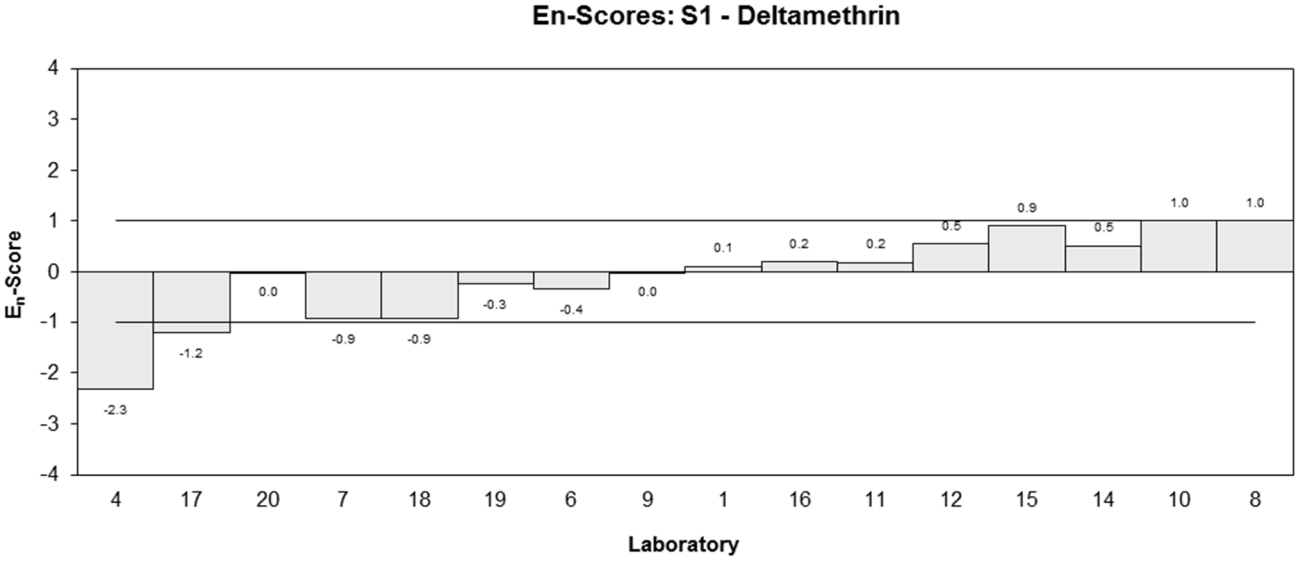

En-Scores: S1 - Deltamethrin
En-Score
Laboratory
4 17 20 7 18 19 6 9 1 16 11 12 15 14 10 8

Figure 2

Table 5

Sample Details

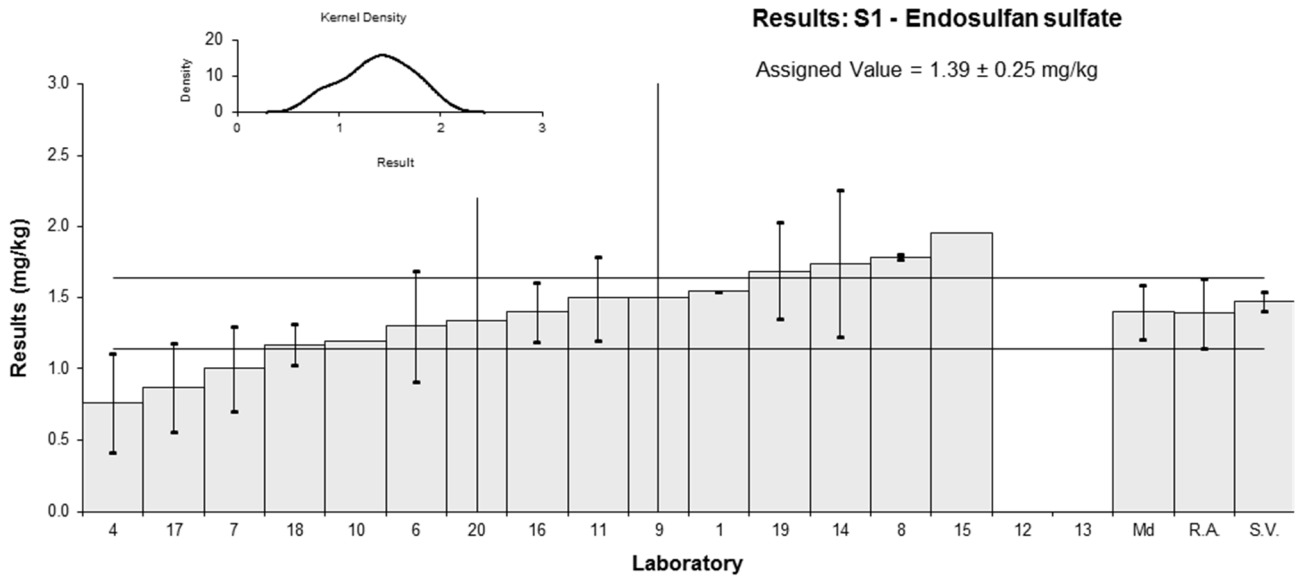
Sample No.	S1
Matrix.	Tomato
Analyte.	Endosulfan sulfate
Units	mg/kg

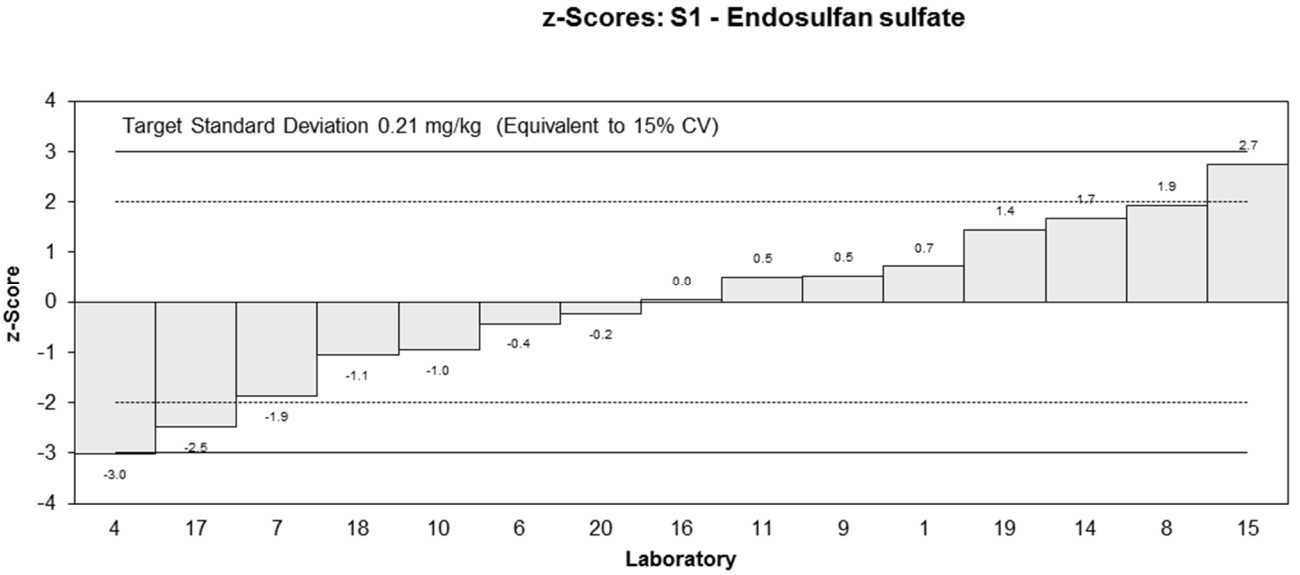
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	1.54	0.002	92	0.72	0.60
4	0.76	0.35	95	-3.02	-1.46
6	1.3	0.39	87	-0.43	-0.19
7	1.0	0.3	62	-1.87	-1.00
8	1.79	0.015	NR	1.92	1.60
9	1.5	33.11	95.6	0.53	0.00
10	1.19	NR	NR	-0.96	-0.80
11	1.494	0.299	92	0.50	0.27
12	NT	NT	NT		
13	NT	NT	NT		
14	1.74	0.52	96	1.68	0.61
15	1.96	NR	117	2.73	2.28
16	1.4	0.21	98	0.05	0.03
17	0.87	0.31	106	-2.49	-1.31
18	1.17	0.14	128	-1.06	-0.77
19	1.69	0.34	120	1.44	0.71
20	1.34	30	NR	-0.24	0.00

Statistics

Assigned Value	1.39	0.25
Spike	1.47	0.07
Robust Average	1.39	0.25
Median	1.40	0.19
Mean	1.38	
N	15	
Max.	1.96	
Min.	0.76	
Robust SD	0.38	
Robust CV	27%	


Kernel Density
Density
Result
Results: S1 - Endosulfan sulfate
Assigned Value = 1.39 ± 0.25 mg/kg
Results (mg/kg)
Laboratory
4 17 7 18 10 6 20 16 11 9 1 19 14 8 15 12 13 Md R.A. S.V.


z-Scores: S1 - Endosulfan sulfate
Target Standard Deviation 0.21 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
4 17 7 18 10 6 20 16 11 9 1 19 14 8 15
-3.0 -2.5 -1.9 -1.1 -1.0 -0.4 -0.2 0.0 0.5 0.5 0.7 1.4 1.7 1.9 2.7

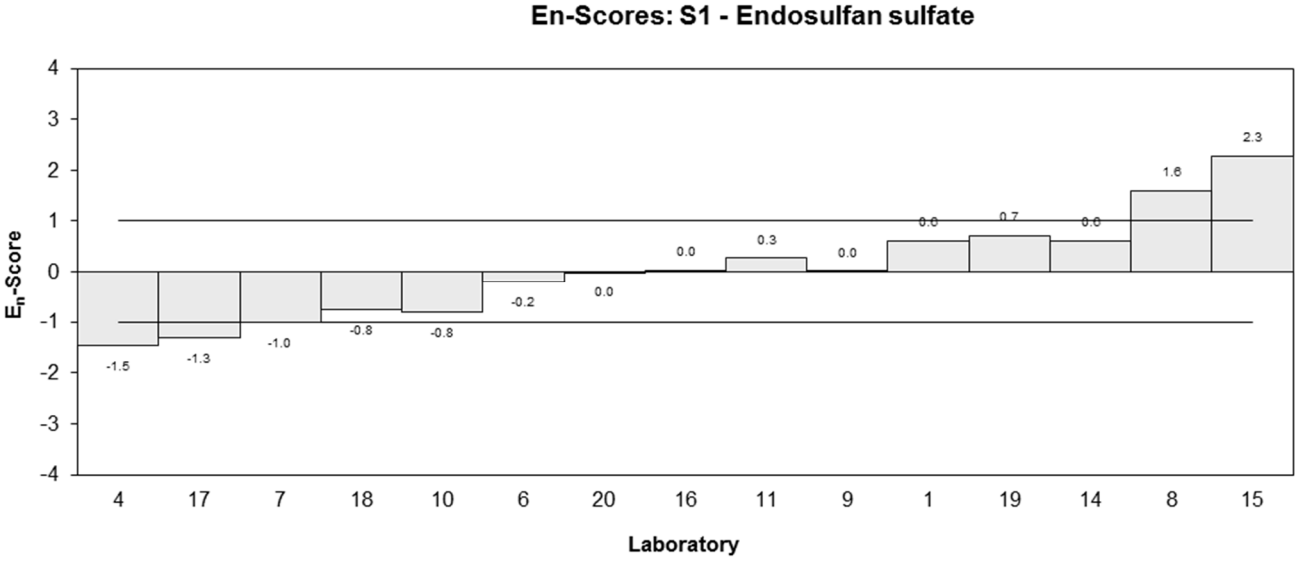

En-Scores: S1 - Endosulfan sulfate
En-Score
Laboratory
4 17 7 18 10 6 20 16 11 9 1 19 14 8 15
-1.5 -1.3 -1.0 -0.8 -0.8 -0.2 0.0 0.0 0.3 0.0 0.6 0.7 0.6 1.6 2.3

Figure 3

Table 6

Sample Details

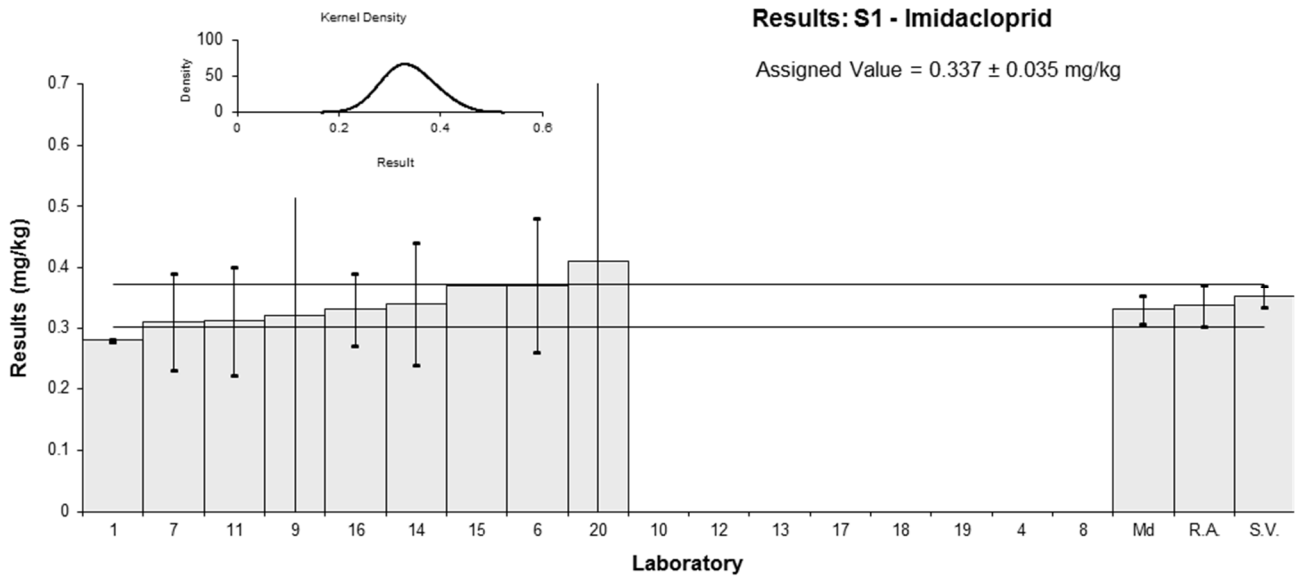
Sample No.	S1
Matrix.	Tomato
Analyte.	Imidacloprid
Units	mg/kg

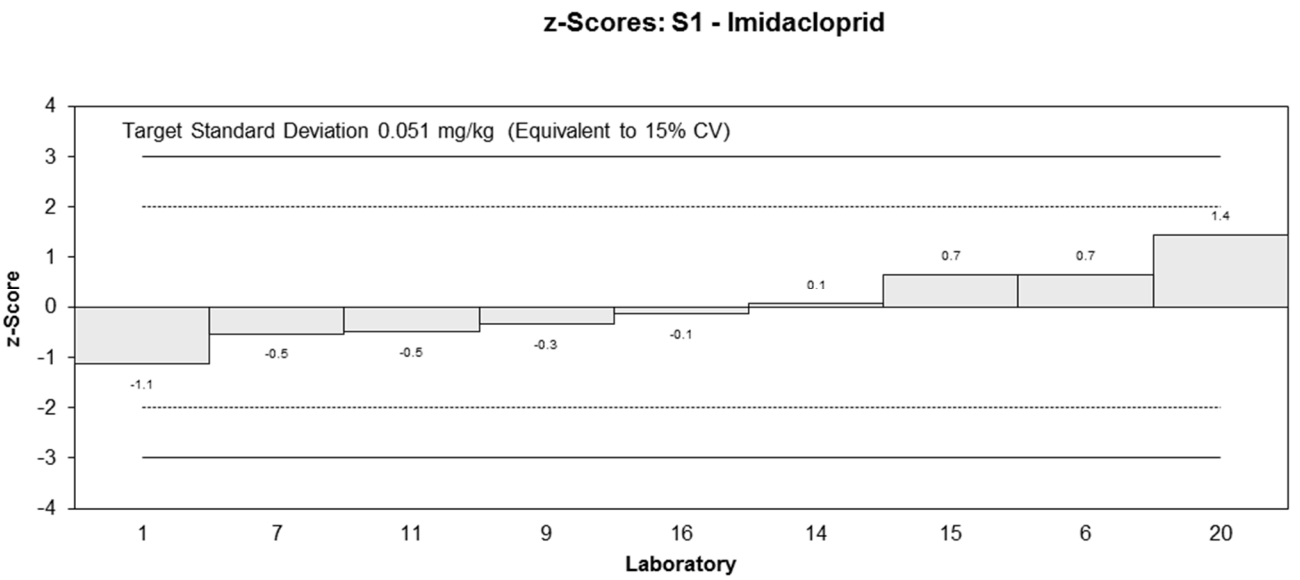
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.28	0.002	89	-1.13	-1.63
4	NT	NT	NT		
6	0.37	0.11	104	0.65	0.29
7	0.31	0.08	116	-0.53	-0.31
8	NT	NT	NT		
9	0.32	21.54	105.5	-0.34	0.00
10	NT	NT	NT		
11	0.312	0.09	98	-0.49	-0.26
12	NT	NT	NT		
13	NT	NT	NT		
14	0.34	0.1	98	0.06	0.03
15	0.37	NR	101	0.65	0.94
16	0.33	0.06	96	-0.14	-0.10
17	NT	NT	NT		
18	NT	NT	NT		
19	NT	NT	NT		
20	0.41	30	NR	1.44	0.00

Statistics

Assigned Value	0.337	0.035
Spike	0.352	0.018
Robust Average	0.337	0.035
Median	0.330	0.023
Mean	0.338	
N	9	
Max.	0.41	
Min.	0.28	
Robust SD	0.042	
Robust CV	12%	


Kernel Density
Density
Result
Results: S1 - Imidacloprid
Assigned Value = 0.337 ± 0.035 mg/kg
Results (mg/kg)
Laboratory
1 7 11 9 16 14 15 6 20 10 12 13 17 18 19 4 8 Md R.A. S.V.


z-Scores: S1 - Imidacloprid
Target Standard Deviation 0.051 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
1 7 11 9 16 14 15 6 20
-1.1 -0.5 -0.5 -0.3 -0.1 0.1 0.7 0.7 1.4

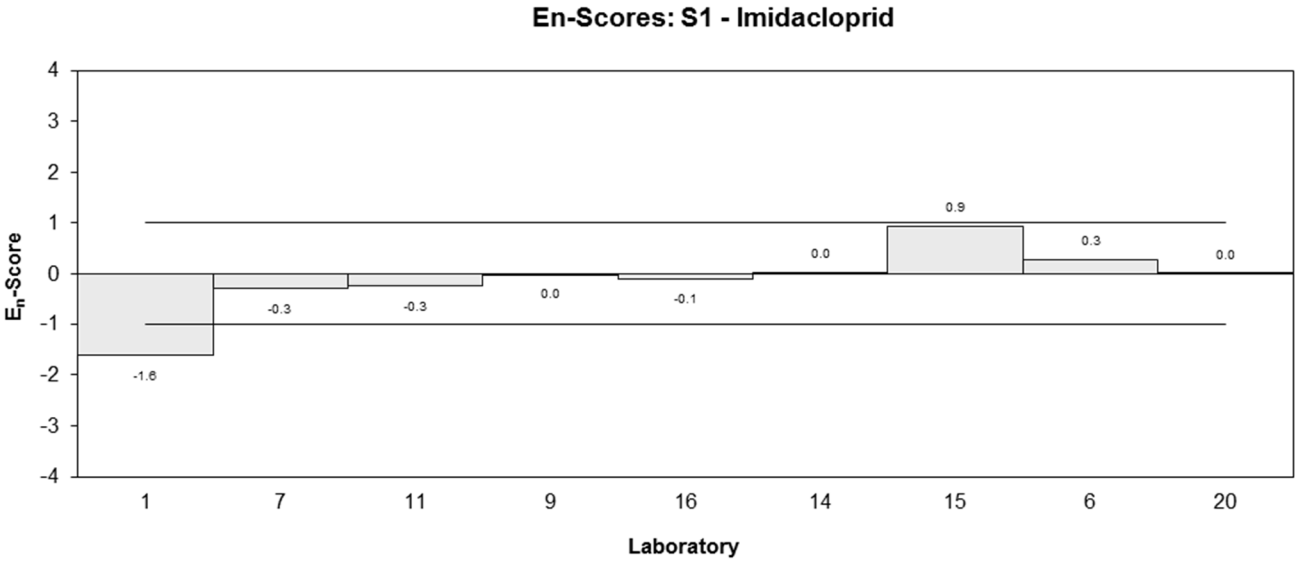

En-Scores: S1 - Imidacloprid
En-Score
Laboratory
1 7 11 9 16 14 15 6 20
-1.6 -0.3 -0.3 0.0 -0.1 0.0 0.9 0.3 0.0

Figure 4

Table 7

Sample Details

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

Participant Results

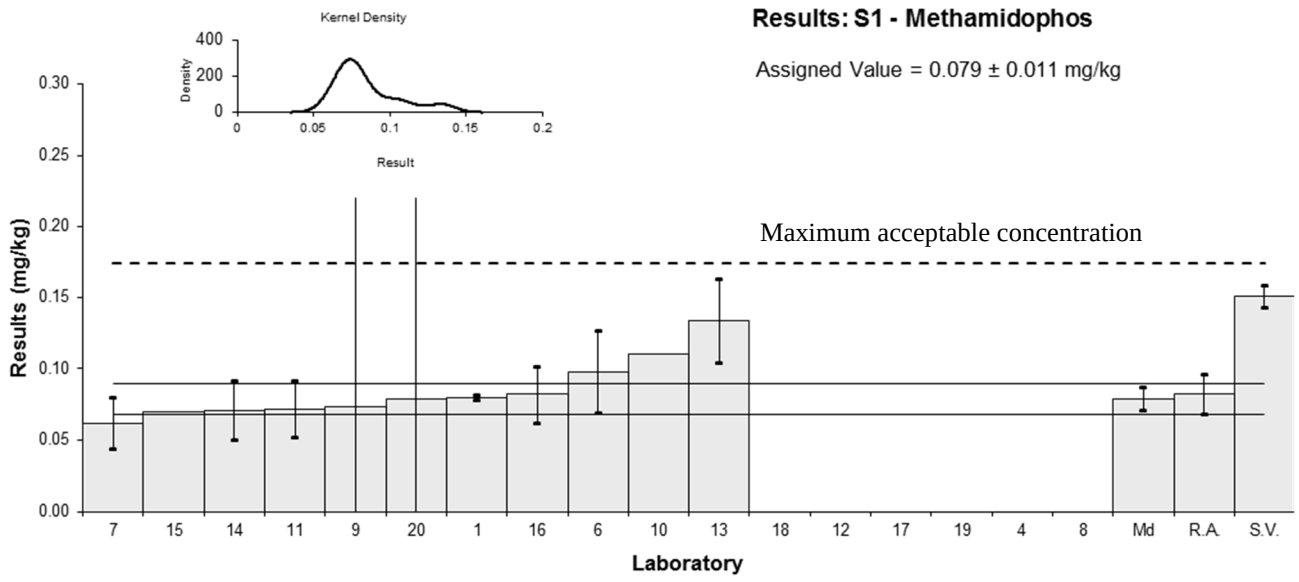
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.08	0.002	85	0.08	0.09
4	NT	NT	NT		
6	0.098	0.029	87	1.60	0.61
7	0.062	0.018	82	-1.43	-0.81
8	NT	NT	NT		
9	0.073	29.6	101.9	-0.51	0.00
10*	0.11	NR	NR	2.00	1.00
11	0.072	0.02	96	-0.59	-0.31
12	NR	NR	NR		
13*	0.134	0.03	111	2.00	1.00
14	0.071	0.021	85	-0.68	-0.34
15	0.07	NR	77	-0.76	-0.82
16	0.082	0.020	56	0.25	0.13
17	NT	NT	NT		
18	NR	NR	NR		
19	NT	NT	NT		
20	0.079	30	NR	0.00	0.00

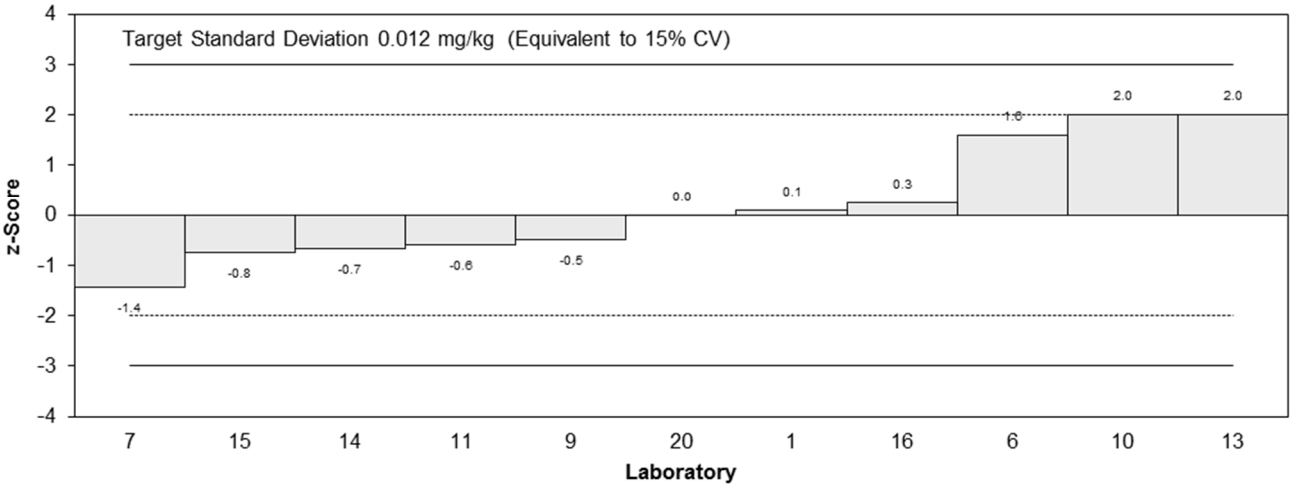
Statistics

Assigned Value**	0.079	0.011
Spike	0.151	0.008
Maximum acceptable conc.	0.175	
Robust Average	0.082	0.014
Median	0.0790	0.0080
Mean	0.0846	
N	11	
Max.	0.134	
Min.	0.062	
Robust SD	0.014	
Robust CV	17%	

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

**Robust average excluding laboratory 13.


Kernel Density
Density
Result
Results: S1 - Methamidophos
Assigned Value = 0.079 ± 0.011 mg/kg
Maximum acceptable concentration
Results (mg/kg)
Laboratory
7 15 14 11 9 20 1 16 6 10 13 18 12 17 19 4 8 Md R.A. S.V.


z-Scores: S1 - Methamidophos
Target Standard Deviation 0.012 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
7 15 14 11 9 20 1 16 6 10 13
-1.4 -0.8 -0.7 -0.6 -0.5 0.0 0.1 0.3 1.6 2.0 2.0

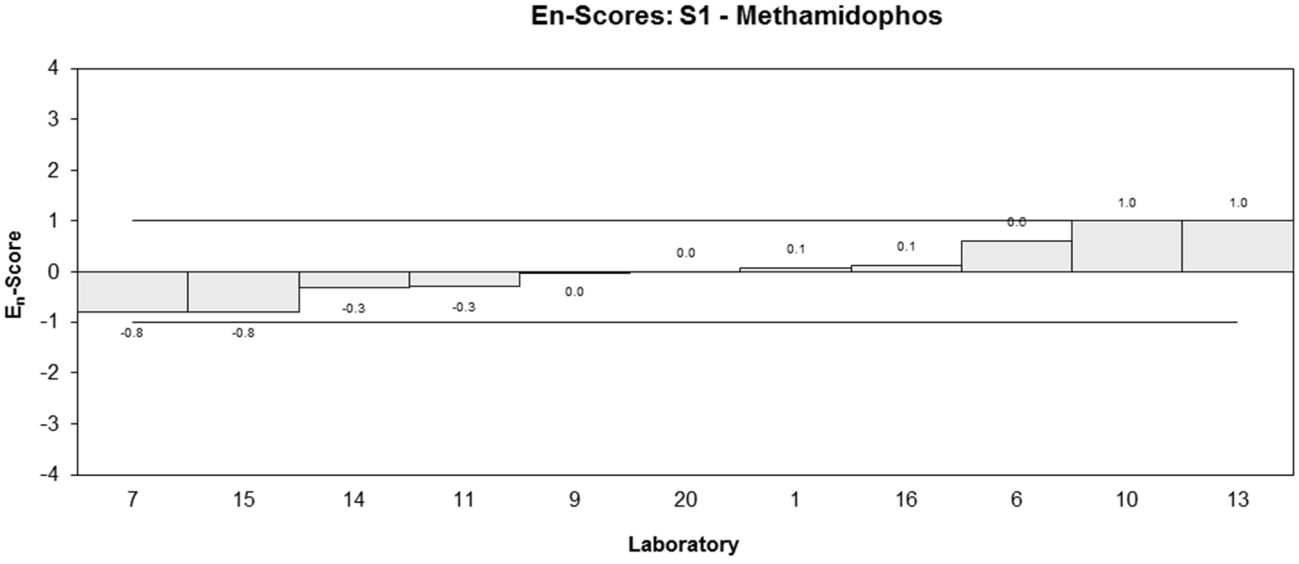

En-Scores: S1 - Methamidophos
En-Score
Laboratory
7 15 14 11 9 20 1 16 6 10 13
-0.8 -0.8 -0.3 -0.3 0.0 0.0 0.1 0.1 0.6 1.0 1.0

Figure 5

Table 8

Sample Details

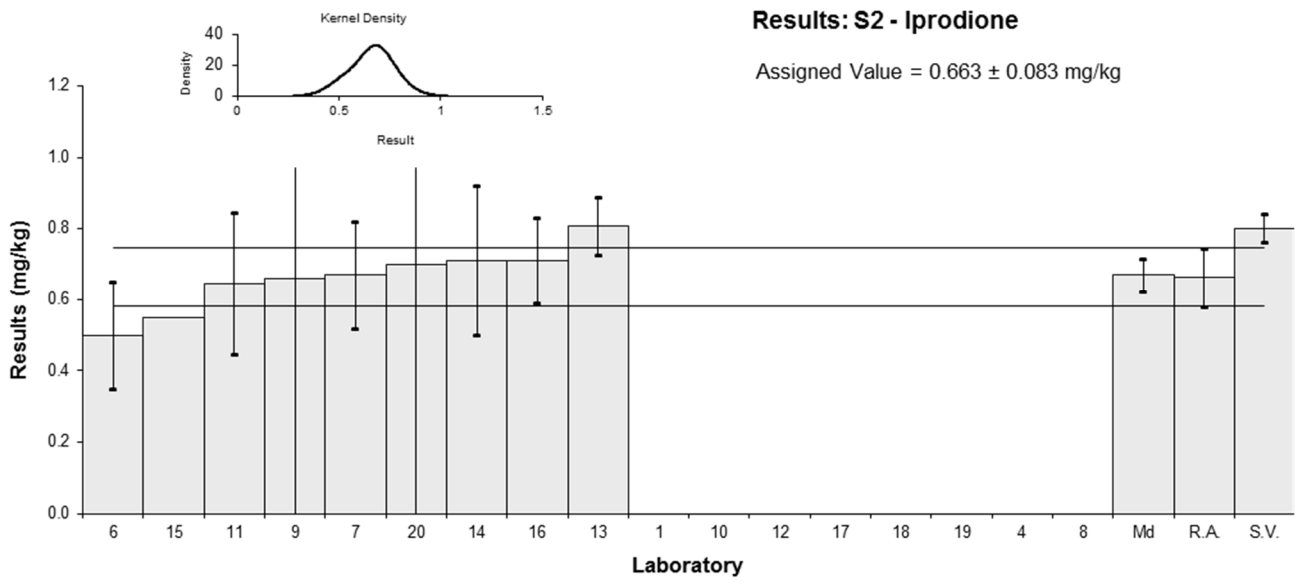
Sample No.	S2
Matrix.	Cauliflower
Analyte.	Iprodione
Units	mg/kg

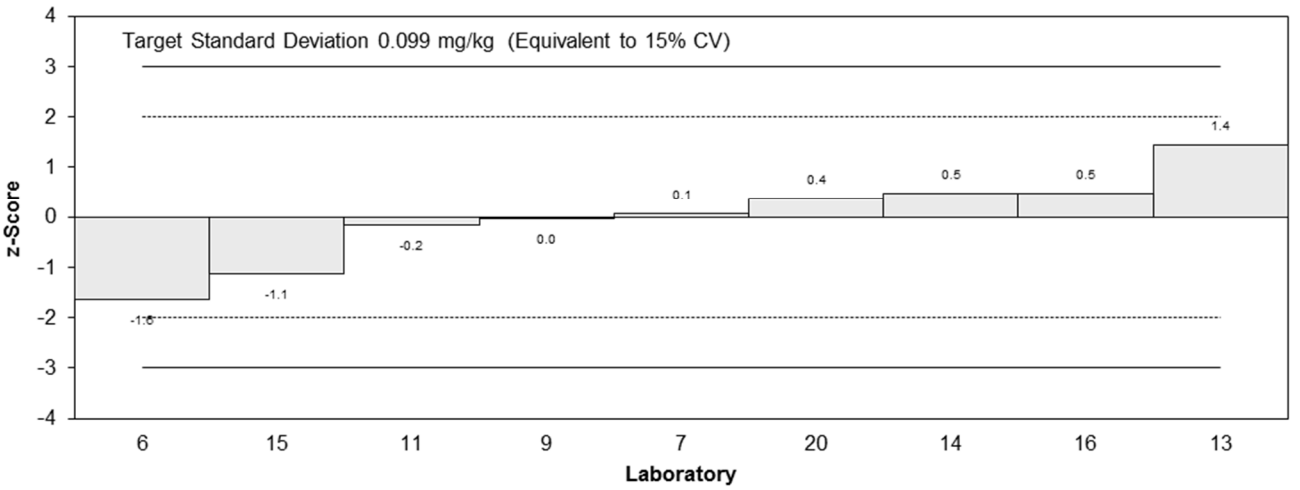
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NT	NT	NT		
4	NT	NT	NT		
6	0.50	0.15	82	-1.64	-0.95
7	0.67	0.15	98	0.07	0.04
8	NT	NT	NT		
9	0.66	33.24	91.1	-0.03	0.00
10	NT	NT	NT		
11	0.647	0.2	88	-0.16	-0.07
12	NT	NT	NT		
13	0.807	0.081	93	1.45	1.24
14	0.71	0.21	115	0.47	0.21
15	0.55	NR	81	-1.14	-1.36
16	0.71	0.12	97	0.47	0.32
17	NT	NT	NT		
18	NT	NT	NT		
19	NT	NT	NT		
20	0.70	30	NR	0.37	0.00

Statistics

Assigned Value	0.663	0.083
Spike	0.802	0.040
Robust Average	0.663	0.083
Median	0.670	0.046
Mean	0.662	
N	9	
Max.	0.807	
Min.	0.5	
Robust SD	0.10	
Robust CV	15%	


Kernel Density
Density
Result
Results: S2 - Iprodione
Assigned Value = 0.663 ± 0.083 mg/kg
Results (mg/kg)
Laboratory
6 15 11 9 7 20 14 16 13 1 10 12 17 18 19 4 8 Md R.A. S.V.


z-Scores: S2 - Iprodione
Target Standard Deviation 0.099 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
6 15 11 9 7 20 14 16 13
-1.6 -1.1 -0.2 0.0 0.1 0.4 0.5 0.5 1.4

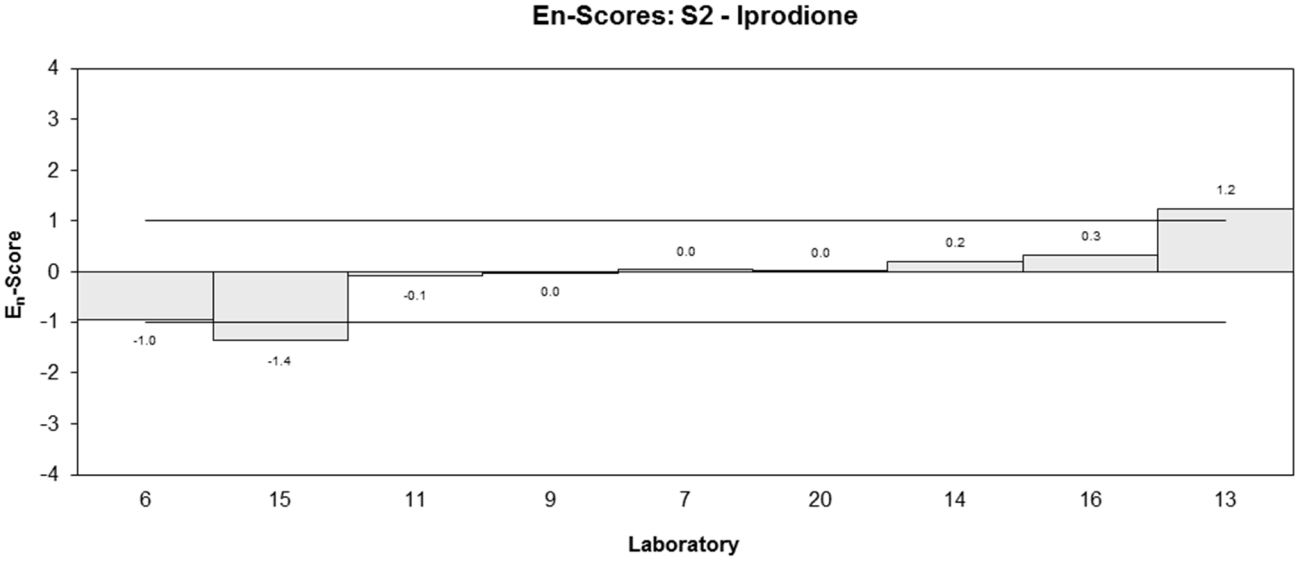

En-Scores: S2 - Iprodione
En-Score
Laboratory
6 15 11 9 7 20 14 16 13
-1.0 -1.4 -0.1 0.0 0.0 0.0 0.2 0.3 1.2

Figure 6

Table 9

Sample Details

Sample No.	S2
Matrix.	Cauliflower
Analyte.	Methomyl
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	Recovery
1	0.56	0.002	89
4	NT	NT	NT
6	0.21	0.063	86
7	0.43	0.09	95
8	NT	NT	NT
9	0.18	30.47	106.6
10	NT	NT	NT
11	0.250	0.05	98
12	NT	NT	NT
13	0.315	0.032	94
14	0.20	0.06	113
15	0.51	NR	81
16	0.43	0.08	98
17	NT	NT	NT
18	NT	NT	NT
19	NT	NT	NT
20	0.29	30	NR

Statistics

Assigned Value	Not Set	
Spike	2.59	0.13
Robust Average	0.34	0.12
Median	0.30	0.12
Mean	0.34	
N	10	
Max.	0.56	
Min.	0.18	
Robust SD	0.11	
Robust CV	32%	

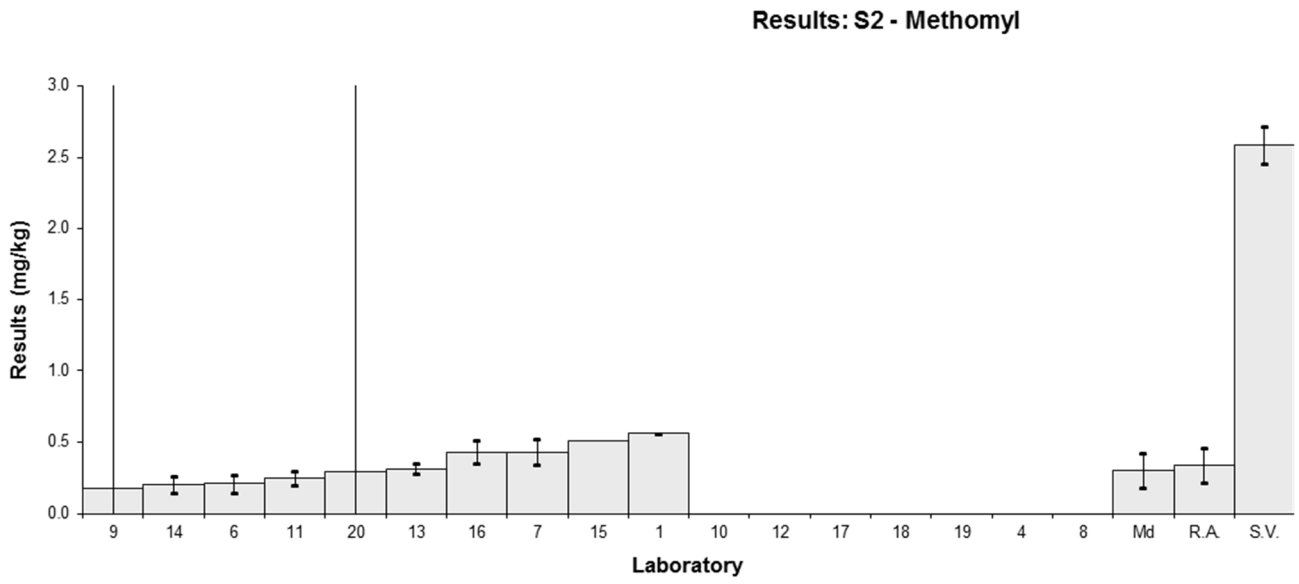

Results: S2 - Methomyl
Results (mg/kg)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
9
14
6
11
20
13
16
7
15
1
10
12
17
18
19
4
8
Md
R.A.
S.V.
Laboratory

Figure 7

Table 10

Sample Details

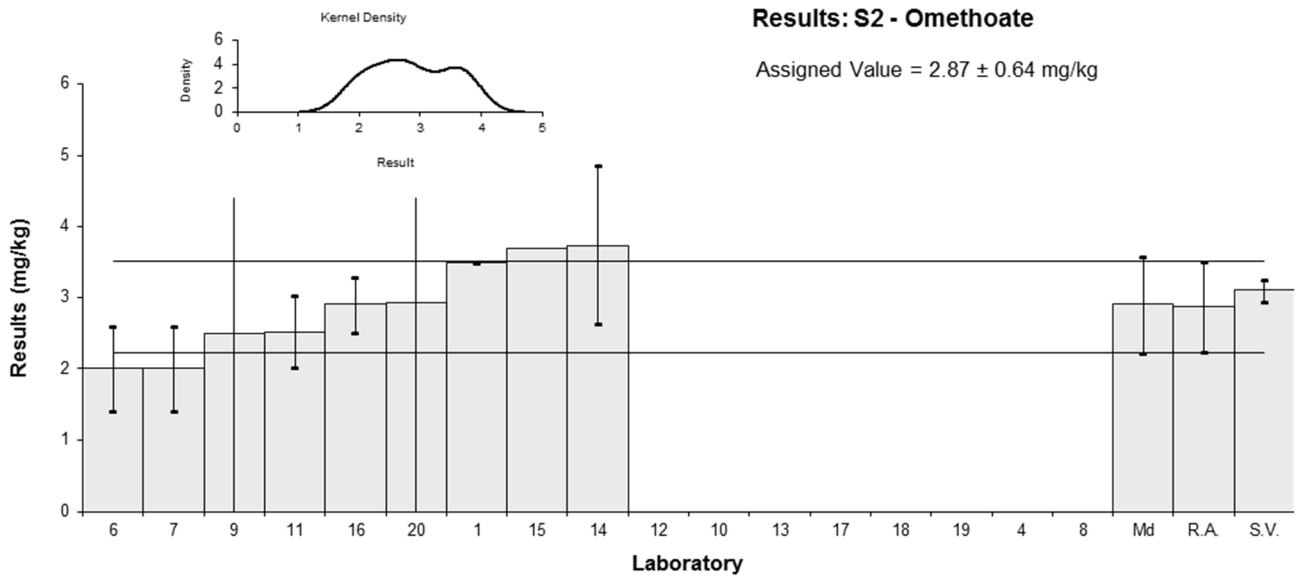
Sample No.	S2
Matrix.	Cauliflower
Analyte.	Omethoate
Units	mg/kg

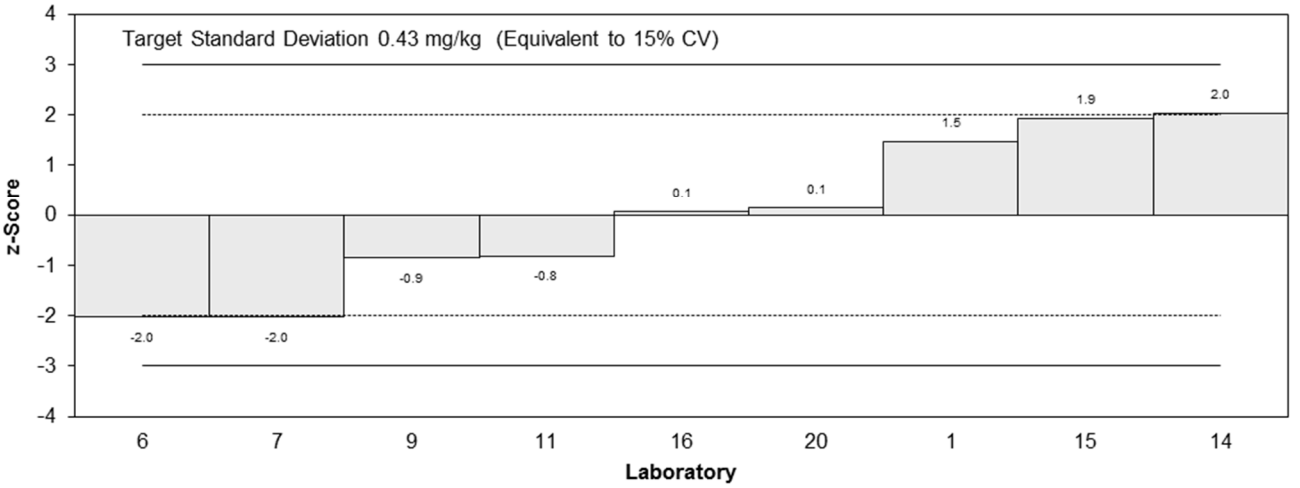
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	3.5	0.002	88	1.46	0.98
4	NT	NT	NT		
6	2.0	0.60	96	-2.02	-0.99
7	2.0	0.6	91	-2.02	-0.99
8	NT	NT	NT		
9	2.5	23.79	104.0	-0.86	-0.02
10	NT	NT	NT		
11	2.519	0.5	96	-0.82	-0.43
12	NR	NR	NR		
13	NT	NT	NT		
14	3.74	1.12	100	2.02	0.67
15	3.70	NR	112	1.93	1.30
16	2.9	0.4	85	0.07	0.04
17	NT	NT	NT		
18	NT	NT	NT		
19	NT	NT	NT		
20	2.93	30	NR	0.14	0.00

Statistics

Assigned Value	2.87	0.64
Spike	3.10	0.16
Robust Average	2.87	0.64
Median	2.90	0.68
Mean	2.87	
N	9	
Max.	3.74	
Min.	2	
Robust SD	0.76	
Robust CV	26%	


Kernel Density
Density
Result
Results: S2 - Omethoate
Assigned Value = 2.87 ± 0.64 mg/kg
Results (mg/kg)
Laboratory
6 7 9 11 16 20 1 15 14 12 10 13 17 18 19 4 8 Md R.A. S.V.


z-Scores: S2 - Omethoate
Target Standard Deviation 0.43 mg/kg (Equivalent to 15% CV)
z-Score
-2.0 -2.0 -0.9 -0.8 0.1 0.1 1.5 1.9 2.0
Laboratory
6 7 9 11 16 20 1 15 14

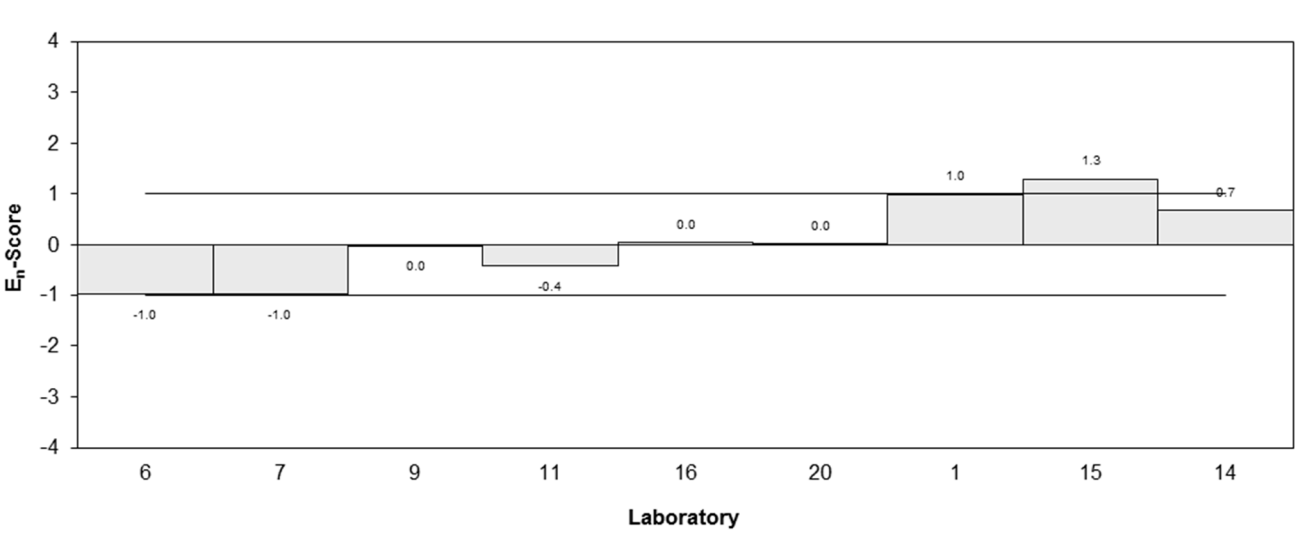

En-Scores: S2 - Omethoate
En-Score
-1.0 -1.0 0.0 -0.4 0.0 0.0 1.0 1.3 0.7
Laboratory
6 7 9 11 16 20 1 15 14

Figure 8

Table 11

Sample Details

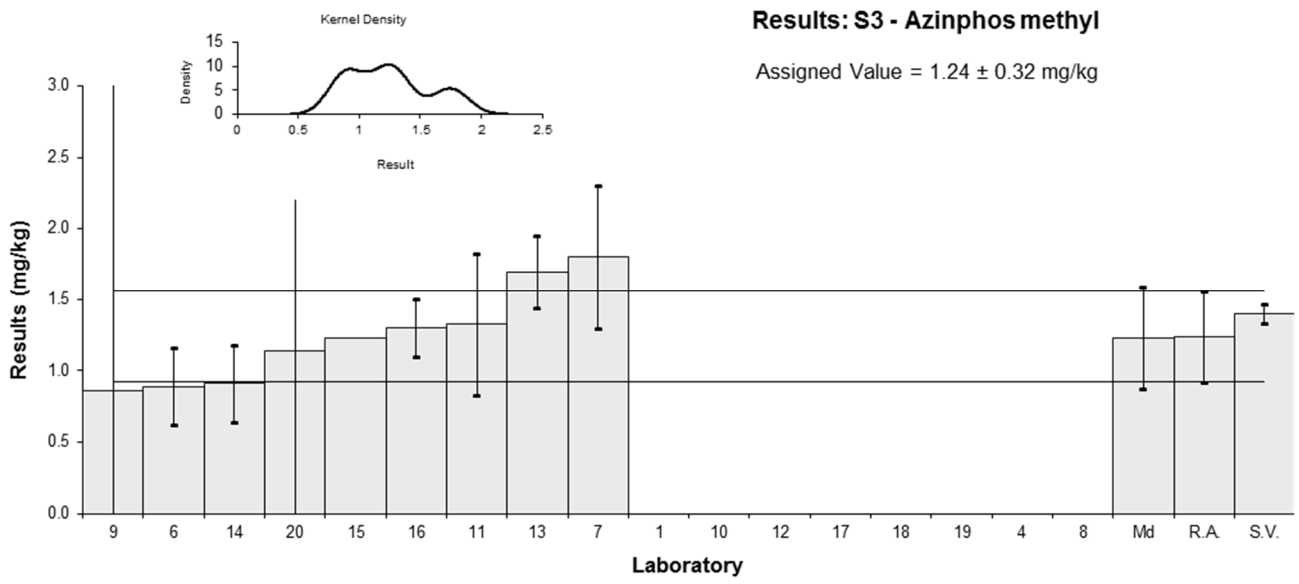
Sample No.	S3
Matrix.	Apple
Analyte.	Azinphos methyl
Units	mg/kg

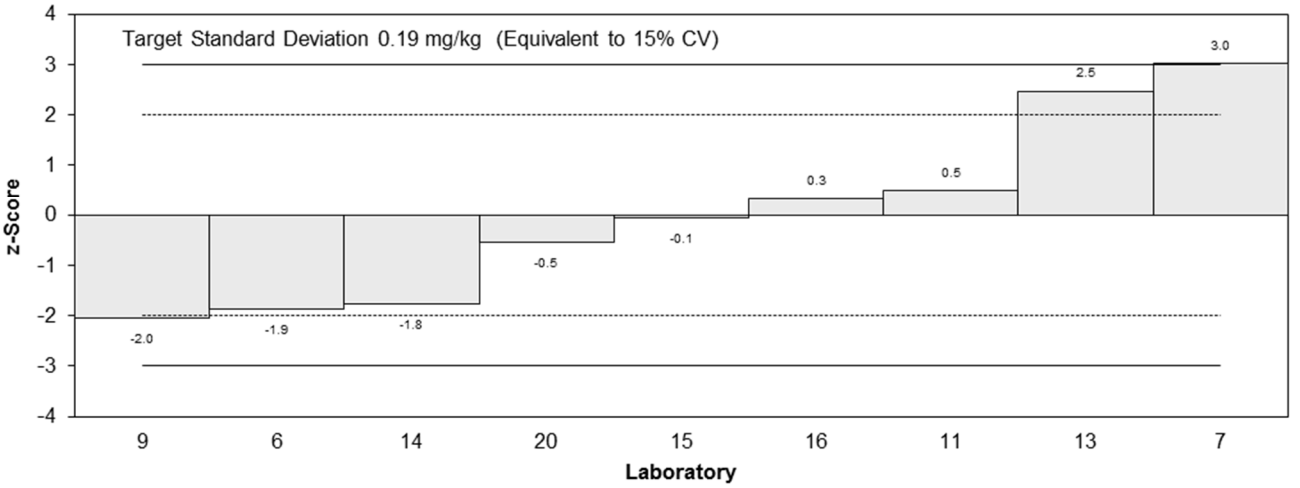
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	NR	NR	NR		
4	NT	NT	NT		
6	0.89	0.27	85	-1.88	-0.84
7	1.8	0.5	103.5	3.01	0.94
8	NT	NT	NT		
9	0.86	26.59	85.9	-2.04	-0.01
10	NT	NT	NT		
11	1.331	0.5	103	0.49	0.15
12	NT	NT	NT		
13	1.697	0.255	86	2.46	1.12
14	0.91	0.27	103	-1.77	-0.79
15	1.23	NR	77	-0.05	-0.03
16	1.3	0.2	95	0.32	0.16
17	NT	NT	NT		
18	NT	NT	NT		
19	NT	NT	NT		
20	1.14	30	NR	-0.54	0.00

Statistics

Assigned Value	1.24	0.32
Spike	1.40	0.07
Robust Average	1.24	0.32
Median	1.23	0.36
Mean	1.24	
N	9	
Max.	1.8	
Min.	0.86	
Robust SD	0.38	
Robust CV	31%	


Kernel Density
Density
Result
Results: S3 - Azinphos methyl
Assigned Value = 1.24 ± 0.32 mg/kg
Results (mg/kg)
Laboratory
9 6 14 20 15 16 11 13 7 1 10 12 17 18 19 4 8 Md R.A. S.V.


z-Scores: S3 - Azinphos methyl
Target Standard Deviation 0.19 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
9 6 14 20 15 16 11 13 7
-2.0 -1.9 -1.8 -0.5 -0.1 0.3 0.5 2.5 3.0

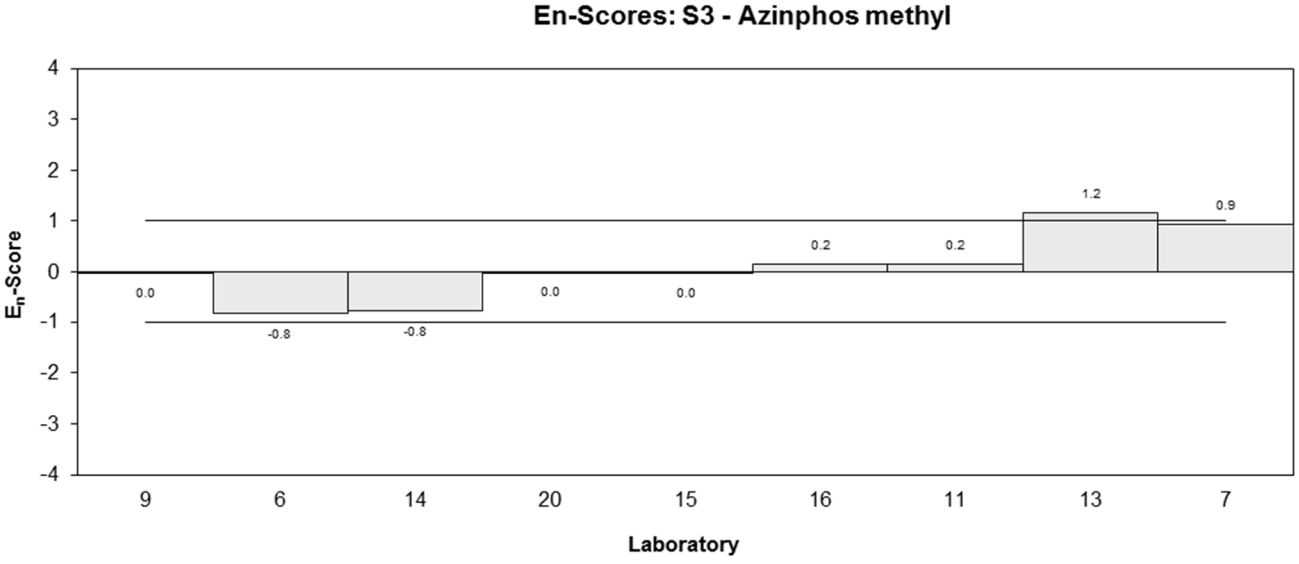

En-Scores: S3 - Azinphos methyl
En-Score
Laboratory
9 6 14 20 15 16 11 13 7
0.0 -0.8 -0.8 0.0 0.0 0.2 0.2 1.2 0.9

Figure 9

Table 12

Sample Details

Sample No.	S3
Matrix.	Apple
Analyte.	Chlorpyrifos
Units	mg/kg

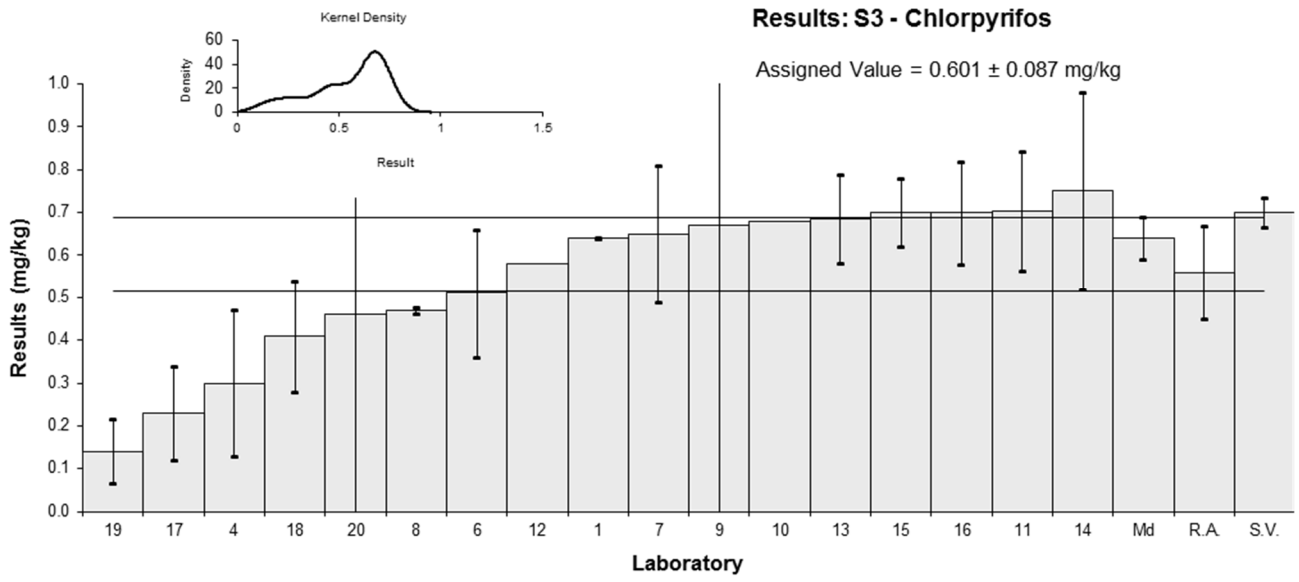
Participant Results

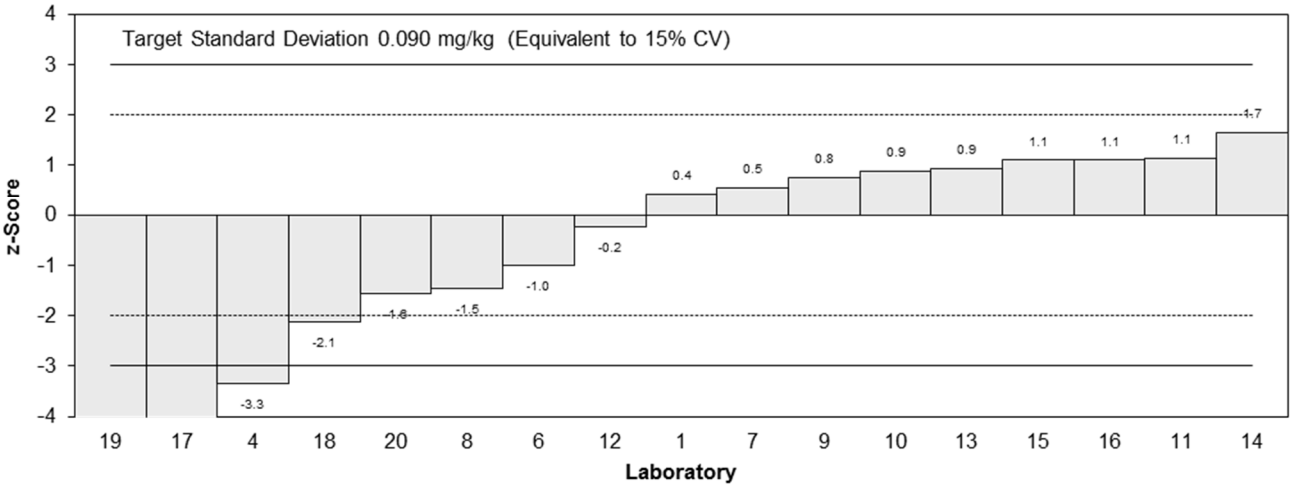
Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.64	0.002	92	0.43	0.45
4	0.30	0.17	82	-3.34	-1.58
6	0.51	0.15	77	-1.01	-0.52
7	0.65	0.16	119	0.54	0.27
8	0.47	0.0070	NR	-1.45	-1.50
9	0.67	27.55	99.9	0.77	0.00
10	0.68	NR	NR	0.88	0.91
11	0.704	0.14	76	1.14	0.62
12	0.58	NR	NR	-0.23	-0.24
13	0.685	0.103	91	0.93	0.62
14	0.75	0.23	86	1.65	0.61
15	0.70	0.08	94	1.10	0.84
16	0.70	0.12	95	1.10	0.67
17	0.23	0.11	116	-4.12	-2.65
18	0.41	0.13	64	-2.12	-1.22
19	0.14	0.075	53	-5.11	-4.01
20	0.46	30	NR	-1.56	0.00

Statistics

Assigned Value*	0.601	0.087
Spike	0.701	0.035
Robust Average	0.56	0.11
Median	0.640	0.049
Mean	0.546	
N	17	
Max.	0.75	
Min.	0.14	
Robust SD	0.13	
Robust CV	23%	

*Robust average excluding laboratories 17 and 19.


Kernel Density
Density
Result
Results: S3 - Chlorpyrifos
Assigned Value = 0.601 ± 0.087 mg/kg
Results (mg/kg)
Laboratory
19 17 4 18 20 8 6 12 1 7 9 10 13 15 16 11 14 Md R.A. S.V.


z-Scores: S3 - Chlorpyrifos
Target Standard Deviation 0.090 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
19 17 4 18 20 8 6 12 1 7 9 10 13 15 16 11 14
-3.3 -2.1 -1.6 -1.5 -1.0 -0.2 0.4 0.5 0.8 0.9 0.9 1.1 1.1 1.1 1.7

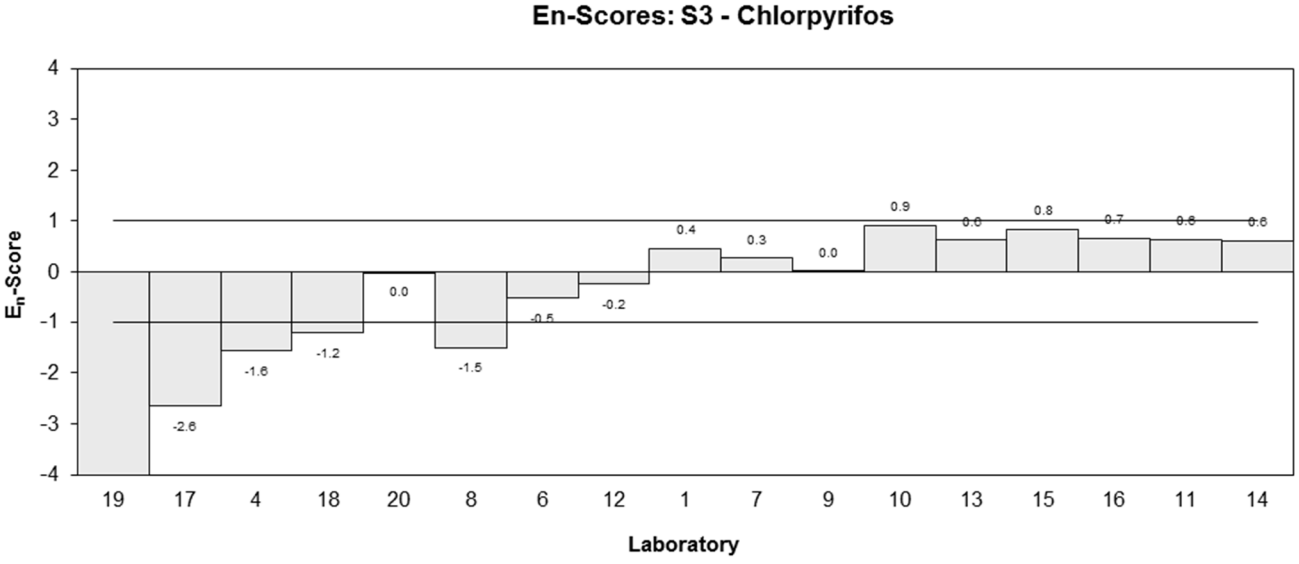

En-Scores: S3 - Chlorpyrifos
En-Score
Laboratory
19 17 4 18 20 8 6 12 1 7 9 10 13 15 16 11 14
-2.6 -1.6 -1.2 0.0 -1.5 -0.5 -0.2 0.4 0.3 0.0 0.9 0.6 0.8 0.7 0.6 0.6

Figure 10

Table 13

Sample Details

Sample No.	S3
Matrix.	Apple
Analyte.	Diazinon
Units	mg/kg

Participant Results

Lab Code	Result	Uncertainty	Recovery
1	0.28	0.002	92
4	NR	NR	NR
6	0.23	0.069	62
7	0.37	0.07	106
8	0.46	0.00091	NR
9	0.37	34.84	99.0
10	0.35	NR	NR
11	0.321	0.1	84
12	0.51	0.05	97.5
13	0.188	0.02	88
14	0.63	0.19	82
15	0.47	NR	99
16	0.58	0.10	94
17	NR	NR	NR
18	0.30	0.05	62
19	0.11	0.095	92
20	0.22	30	NR

Statistics

Assigned Value	Not Set	
Spike	0.799	0.040
Robust Average	0.36	0.11
Median	0.350	0.099
Mean	0.359	
N	15	
Max.	0.63	
Min.	0.11	
Robust SD	0.12	
Robust CV	33%	

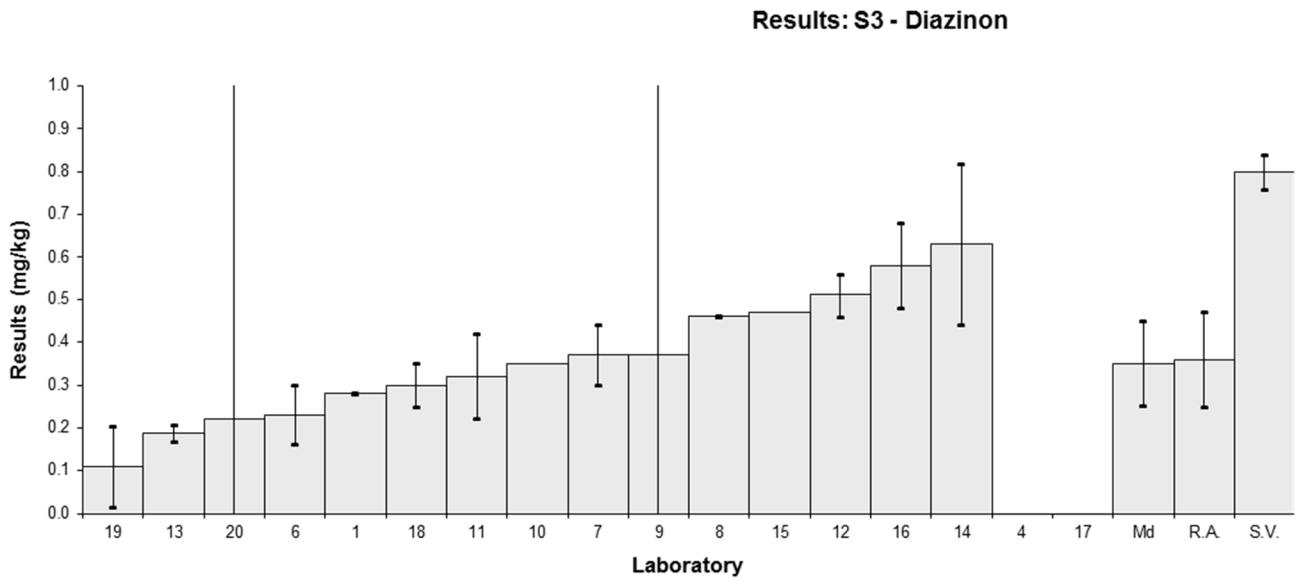

Results: S3 - Diazinon
Results (mg/kg)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
19
13
20
6
1
18
11
10
7
9
8
15
12
16
14
4
17
Md
R.A.
S.V.
Laboratory

Figure 11

Table 14

Sample Details

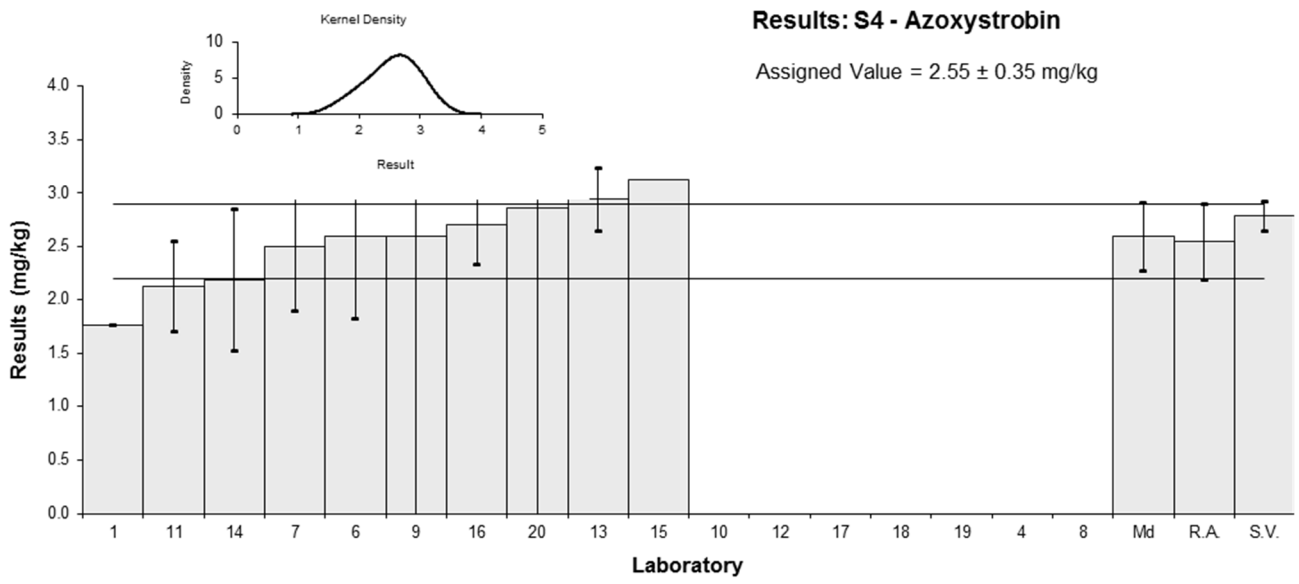
Sample No.	S4
Matrix.	Potato
Analyte.	Azoxystrobin
Units	mg/kg

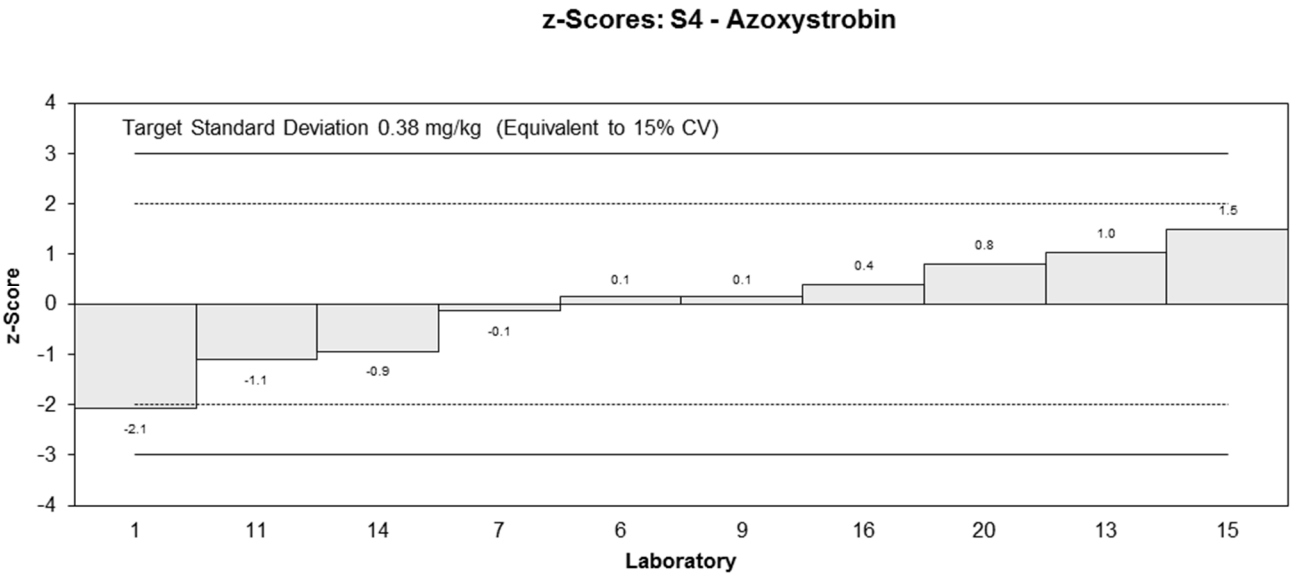
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	1.76	0.002	86	-2.07	-2.26
4	NT	NT	NT		
6	2.6	0.78	97	0.13	0.06
7	2.5	0.6	82	-0.13	-0.07
8	NT	NT	NT		
9	2.6	30.3	98.0	0.13	0.00
10	NT	NT	NT		
11	2.13	0.43	94	-1.10	-0.76
12	NT	NT	NT		
13	2.947	0.295	96	1.04	0.87
14	2.19	0.66	80	-0.94	-0.48
15	3.12	NR	110	1.49	1.63
16	2.7	0.36	96	0.39	0.30
17	NT	NT	NT		
18	NT	NT	NT		
19	NT	NT	NT		
20	2.86	30	NR	0.81	0.01

Statistics

Assigned Value	2.55	0.35
Spike	2.79	0.14
Robust Average	2.55	0.35
Median	2.60	0.32
Mean	2.54	
N	10	
Max.	3.12	
Min.	1.76	
Robust SD	0.44	
Robust CV	17%	


Kernel Density
Density
Result
Results: S4 - Azoxystrobin
Assigned Value = 2.55 ± 0.35 mg/kg
Results (mg/kg)
Laboratory
1 11 14 7 6 9 16 20 13 15 10 12 17 18 19 4 8 Md R.A. S.V.


z-Scores: S4 - Azoxystrobin
Target Standard Deviation 0.38 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
1 11 14 7 6 9 16 20 13 15
-2.1 -1.1 -0.9 -0.1 0.1 0.1 0.4 0.8 1.0 1.5

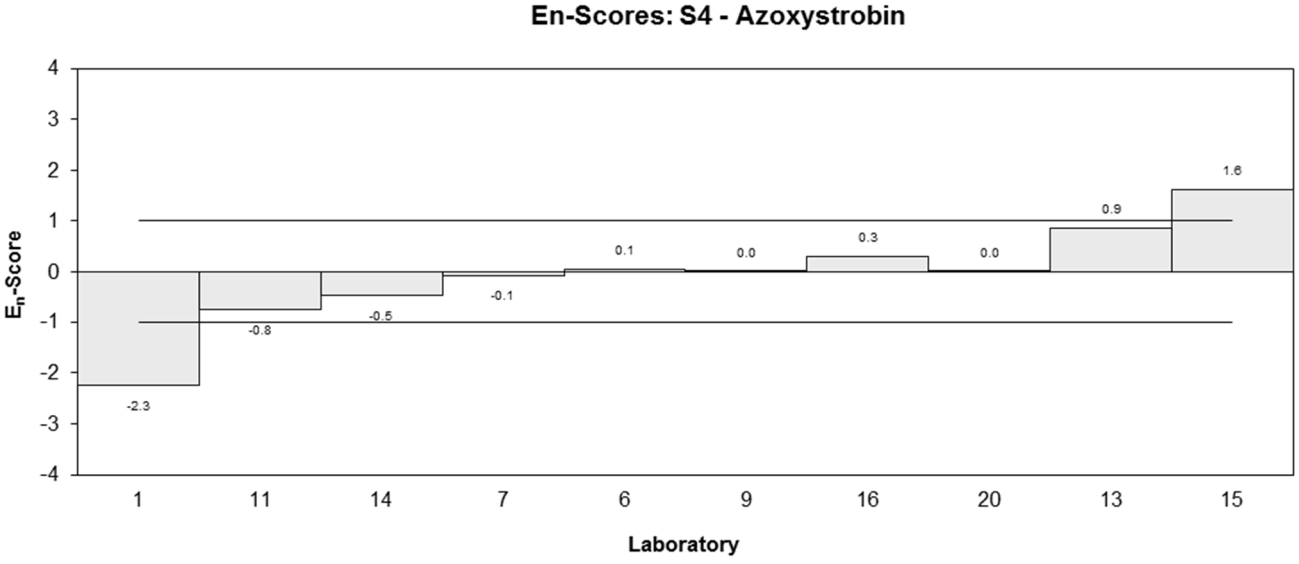

En-Scores: S4 - Azoxystrobin
En-Score
Laboratory
1 11 14 7 6 9 16 20 13 15
-2.3 -0.8 -0.5 -0.1 0.1 0.0 0.3 0.0 0.9 1.6

Figure 12

Table 15

Sample Details

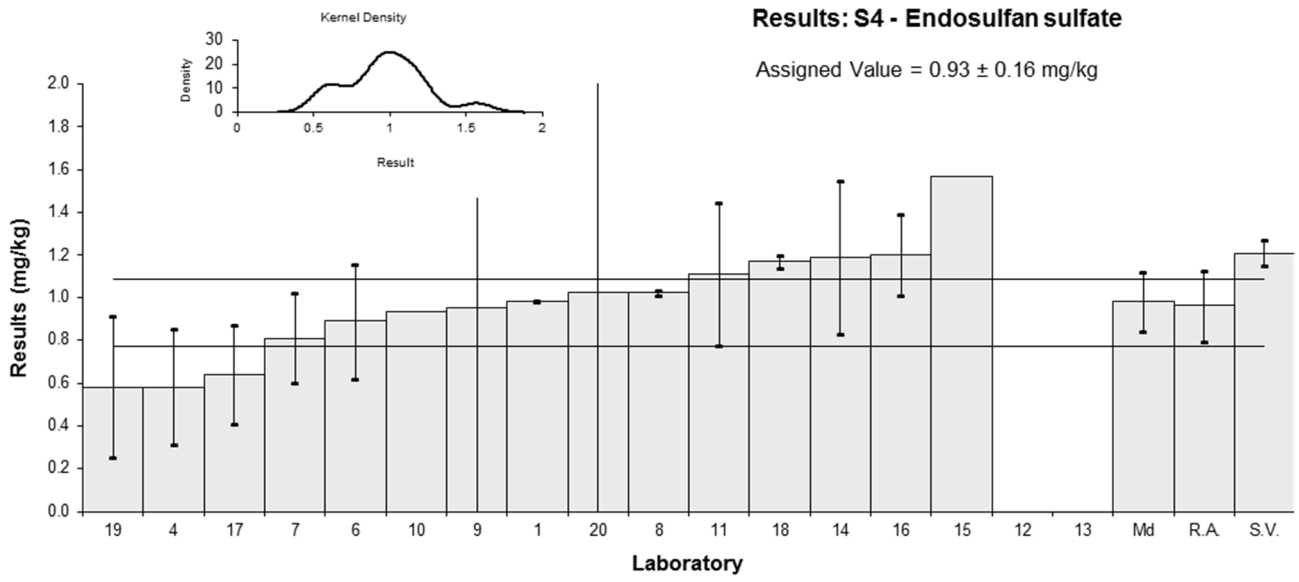
Sample No.	S4
Matrix.	Potato
Analyte.	Endosulfan sulfate
Units	mg/kg

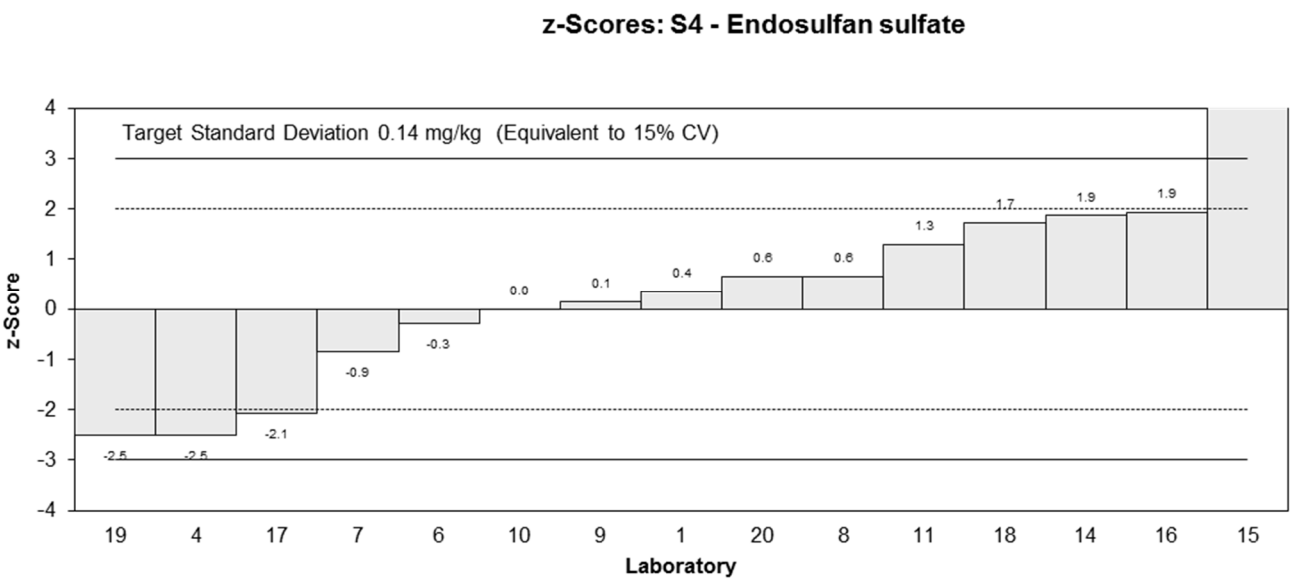
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.98	0.002	88	0.36	0.31
4	0.58	0.27	95	-2.51	-1.12
6	0.89	0.27	112	-0.29	-0.13
7	0.81	0.21	80	-0.86	-0.45
8	1.02	0.011	NR	0.65	0.56
9	0.95	33.11	95.6	0.14	0.00
10	0.93	NR	NR	0.00	0.00
11	1.11	0.333	87	1.29	0.49
12	NT	NT	NT		
13	NT	NT	NT		
14	1.19	0.36	64	1.86	0.66
15	1.57	NR	107	4.59	4.00
16	1.2	0.19	96	1.94	1.09
17	0.64	0.23	111	-2.08	-1.04
18	1.17	0.03	62	1.72	1.47
19	0.58	0.33	102	-2.51	-0.95
20	1.02	30	NR	0.65	0.00

Statistics

Assigned Value	0.93	0.16
Spike	1.21	0.06
Robust Average	0.96	0.17
Median	0.98	0.14
Mean	0.98	
N	15	
Max.	1.57	
Min.	0.58	
Robust SD	0.24	
Robust CV	25%	


Kernel Density
Density
Result
Results: S4 - Endosulfan sulfate
Assigned Value = 0.93 ± 0.16 mg/kg
Results (mg/kg)
Laboratory
19 4 17 7 6 10 9 1 20 8 11 18 14 16 15 12 13 Md R.A. S.V.


z-Scores: S4 - Endosulfan sulfate
Target Standard Deviation 0.14 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
19 4 17 7 6 10 9 1 20 8 11 18 14 16 15
-2.5 -2.5 -2.1 -0.9 -0.3 0.0 0.1 0.4 0.6 0.6 1.3 1.7 1.9 1.9

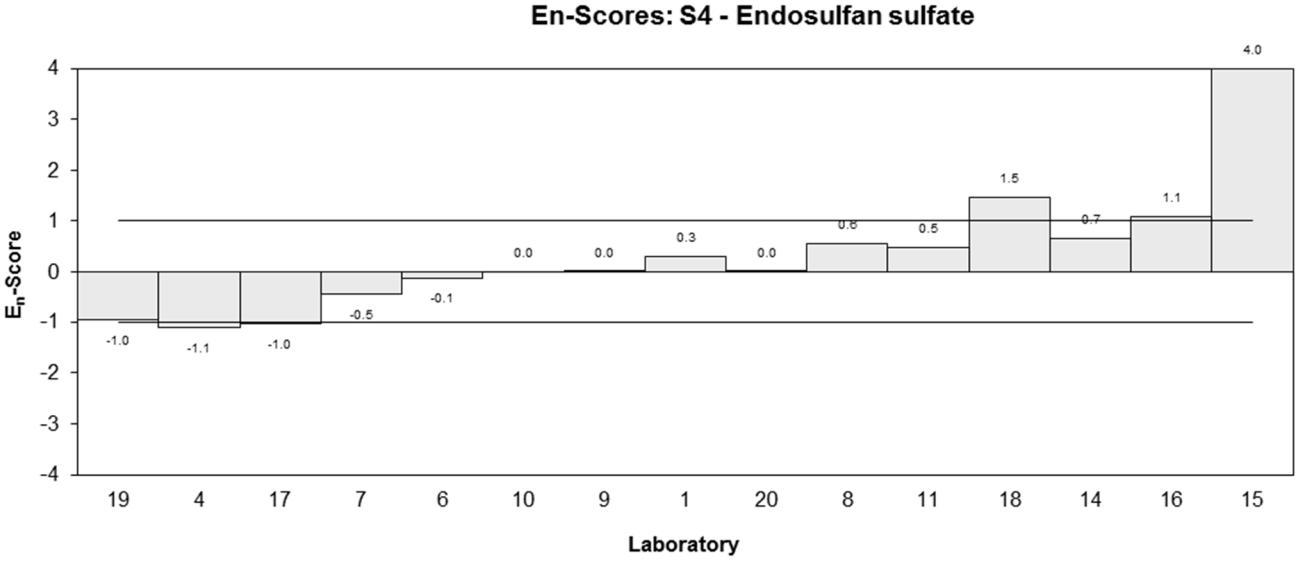

En-Scores: S4 - Endosulfan sulfate
En-Score
Laboratory
19 4 17 7 6 10 9 1 20 8 11 18 14 16 15
-1.0 -1.1 -1.0 -0.5 -0.1 0.0 0.0 0.3 0.0 0.6 0.5 1.5 0.7 1.1 4.0

Figure 13

Table 16

Sample Details

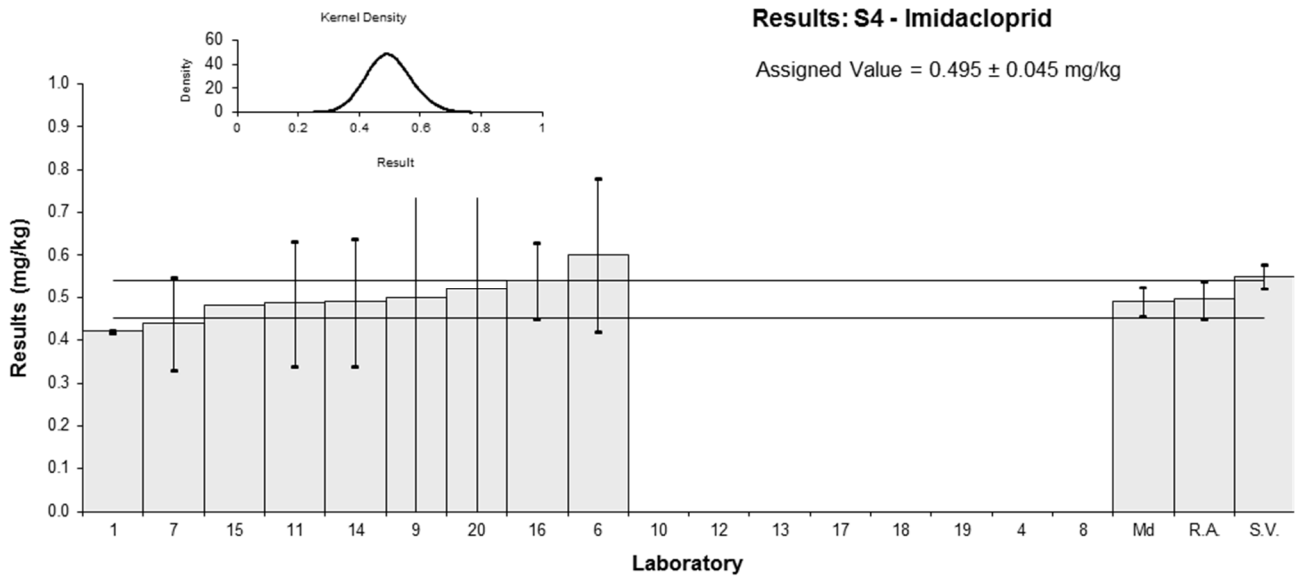
Sample No.	S4
Matrix.	Potato
Analyte.	Imidacloprid
Units	mg/kg

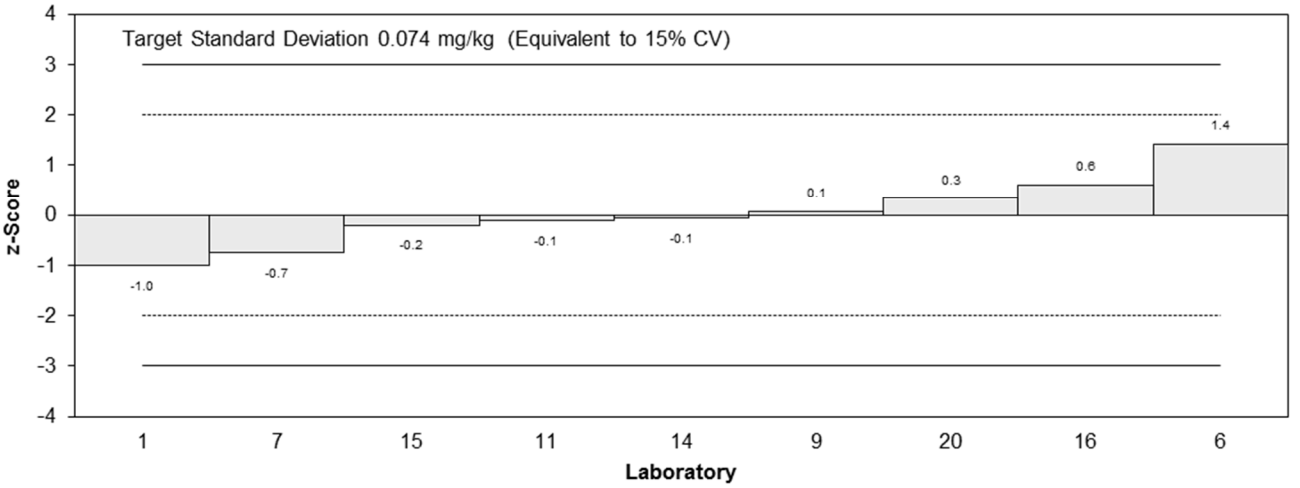
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	0.42	.002	90	-1.01	-1.67
4	NT	NT	NT		
6	0.60	0.18	98	1.41	0.57
7	0.44	0.11	108	-0.74	-0.46
8	NT	NT	NT		
9	0.50	21.54	105.5	0.07	0.00
10	NT	NT	NT		
11	0.486	0.146	119	-0.12	-0.06
12	NT	NT	NT		
13	NT	NT	NT		
14	0.49	0.15	101	-0.07	-0.03
15	0.48	NR	89	-0.20	-0.33
16	0.54	0.09	95	0.61	0.45
17	NT	NT	NT		
18	NT	NT	NT		
19	NT	NT	NT		
20	0.52	30	NR	0.34	0.00

Statistics

Assigned Value	0.495	0.045
Spike	0.551	0.028
Robust Average	0.495	0.045
Median	0.490	0.034
Mean	0.497	
N	9	
Max.	0.6	
Min.	0.42	
Robust SD	0.054	
Robust CV	11%	


Kernel Density
Density
Result
Results: S4 - Imidacloprid
Assigned Value = 0.495 ± 0.045 mg/kg
Results (mg/kg)
Laboratory
1 7 15 11 14 9 20 16 6 10 12 13 17 18 19 4 8 Md R.A. S.V.


z-Scores: S4 - Imidacloprid
Target Standard Deviation 0.074 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
1 7 15 11 14 9 20 16 6
-1.0 -0.7 -0.2 -0.1 -0.1 0.1 0.3 0.6 1.4

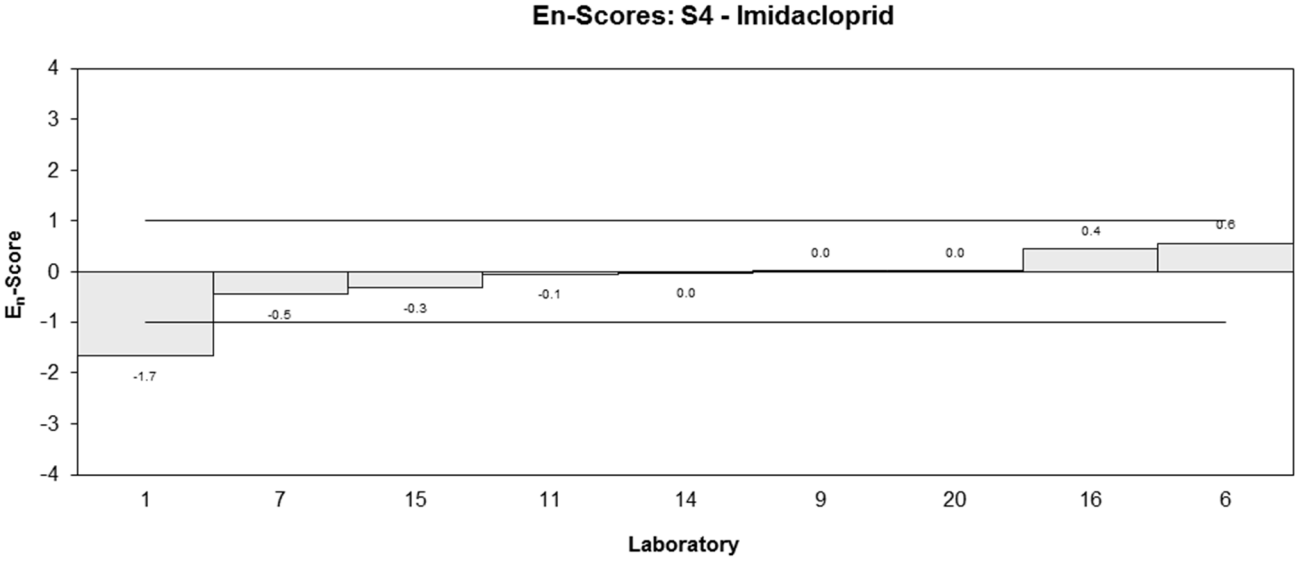

En-Scores: S4 - Imidacloprid
En-Score
Laboratory
1 7 15 11 14 9 20 16 6
-1.7 -0.5 -0.3 -0.1 0.0 0.0 0.0 0.4 0.6

Figure 14

Table 17

Sample Details

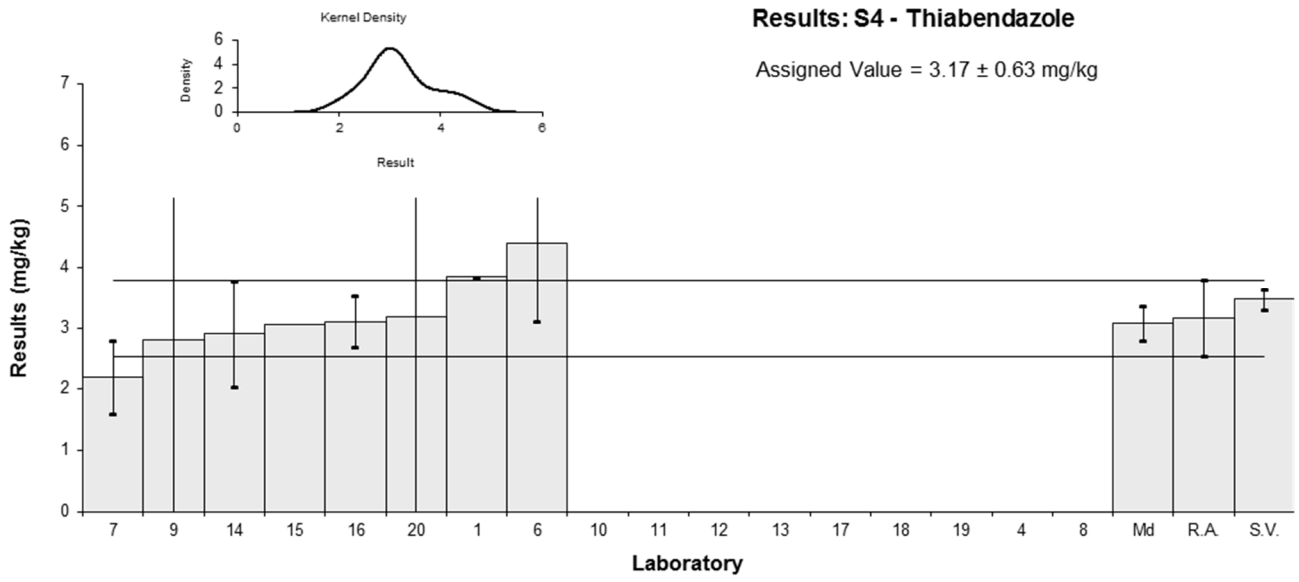
Sample No.	S4
Matrix.	Potato
Analyte.	Thiabendazole
Units	mg/kg

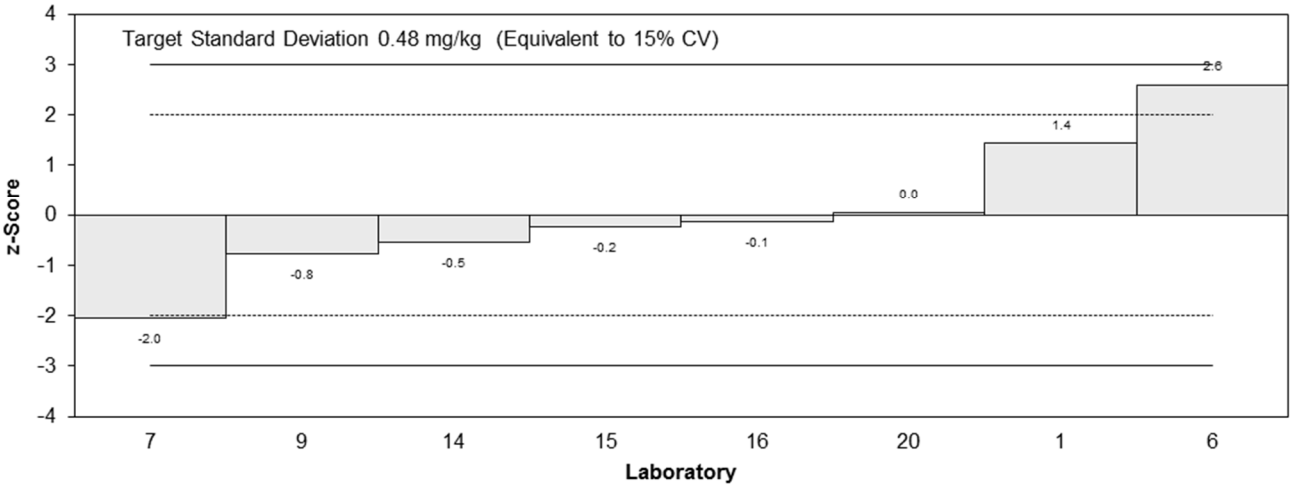
Participant Results

Lab Code	Result	Uncertainty	Recovery	z-Score	E_n-Score
1	3.85	.002	89	1.43	1.08
4	NT	NT	NT		
6	4.4	1.3	86	2.59	0.85
7	2.2	0.6	90	-2.04	-1.11
8	NT	NT	NT		
9	2.8	20.73	106.8	-0.78	-0.02
10	NT	NT	NT		
11	NT	NT	NT		
12	NT	NT	NT		
13	NT	NT	NT		
14	2.91	0.87	98	-0.55	-0.24
15	3.06	NR	70	-0.23	-0.17
16	3.1	0.42	84	-0.15	-0.09
17	NT	NT	NT		
18	NT	NT	NT		
19	NT	NT	NT		
20	3.19	30	NR	0.04	0.00

Statistics

Assigned Value	3.17	0.63
Spike	3.47	0.17
Robust Average	3.17	0.63
Median	3.08	0.28
Mean	3.19	
N	8	
Max.	4.4	
Min.	2.2	
Robust SD	0.71	
Robust CV	22%	


Kernel Density
Density
Result
Results: S4 - Thiabendazole
Assigned Value = 3.17 ± 0.63 mg/kg
Results (mg/kg)
Laboratory
7 9 14 15 16 20 1 6 10 11 12 13 17 18 19 4 8 Md R.A. S.V.


z-Scores: S4 - Thiabendazole
Target Standard Deviation 0.48 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
7 9 14 15 16 20 1 6
-2.0
-0.8
-0.5
-0.2
-0.1
0.0
1.4
2.6

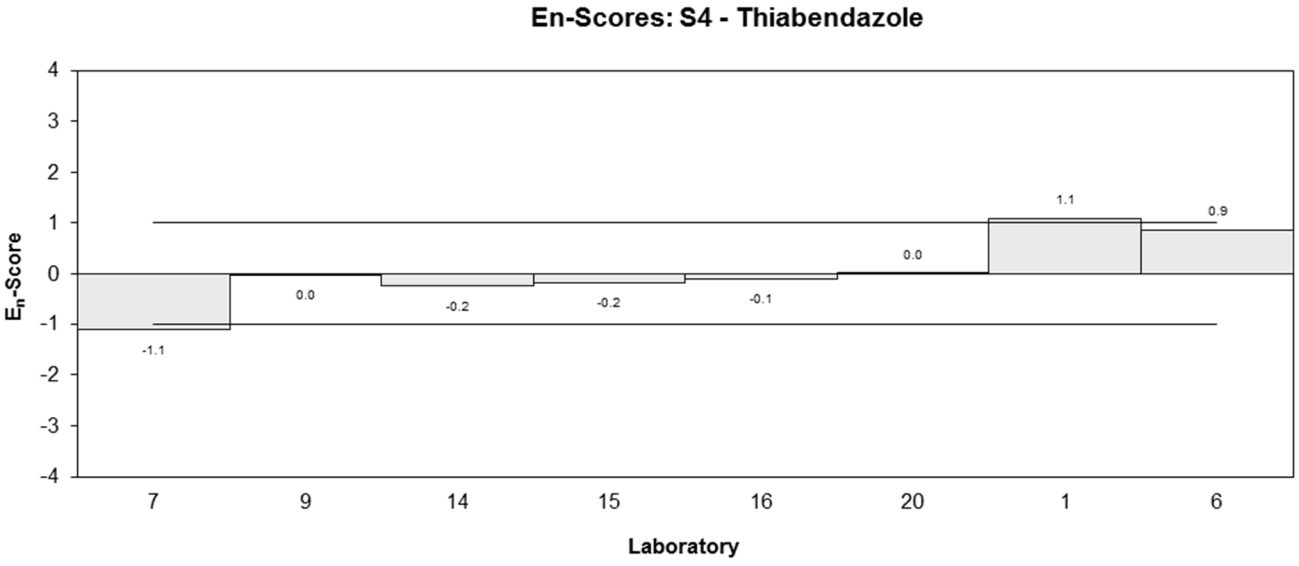

En-Scores: S4 - Thiabendazole
En-Score
Laboratory
7 9 14 15 16 20 1 6
-1.1
0.0
-0.2
-0.2
-0.1
0.0
1.1
0.9

Figure 15

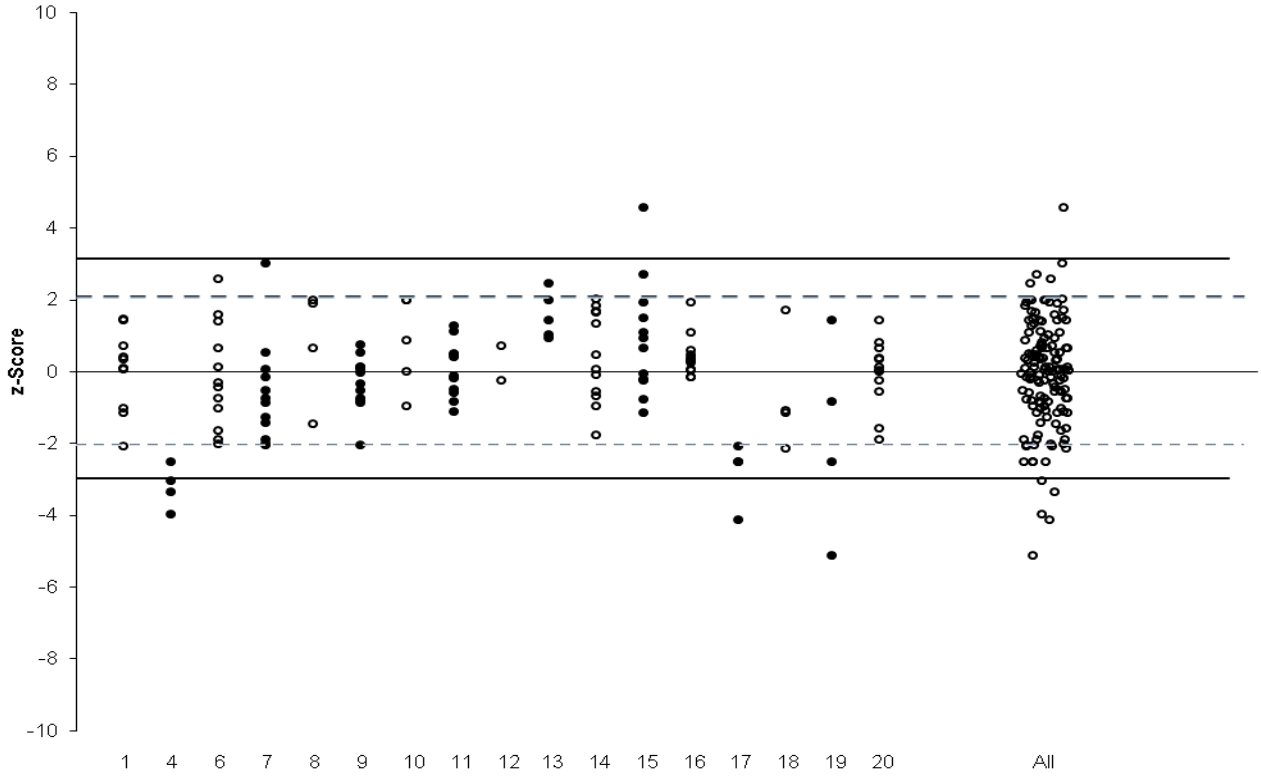


Figure 16 z-Score by laboratory

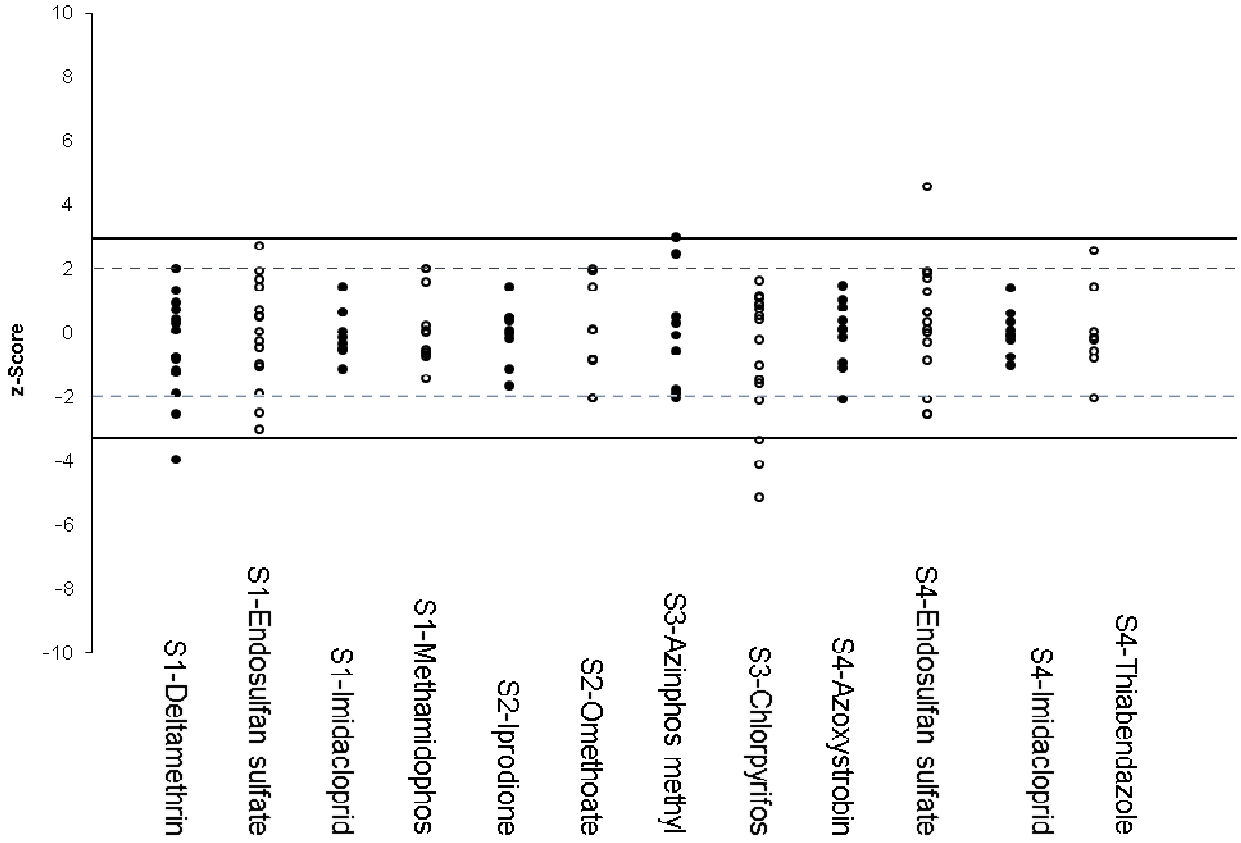


Figure 17 z-Score by analyte

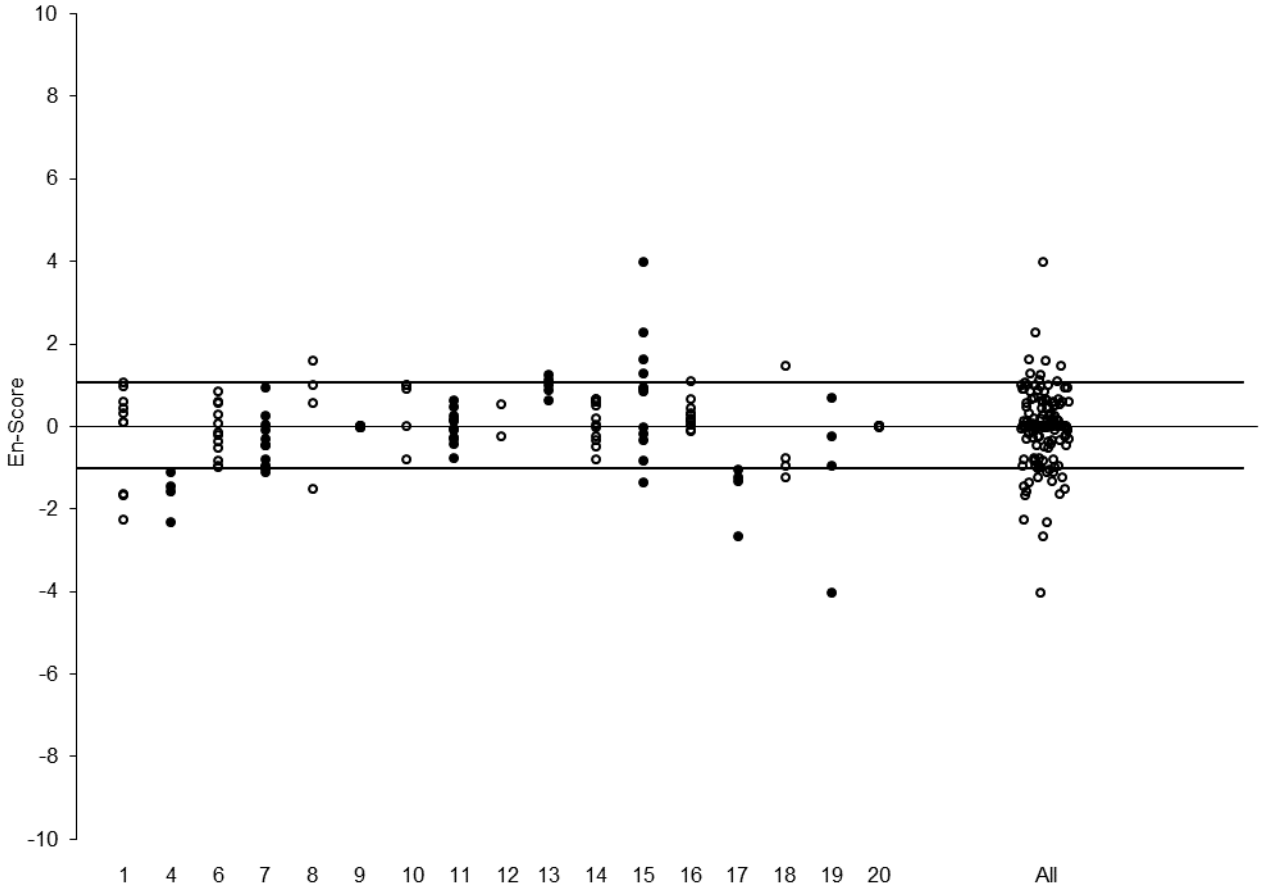


Figure 18 Summary of E_n-scores by laboratory

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'.[9] Appendix 3 sets out the calculation for the expanded uncertainty of the robust average of chlorpyrifos in Sample S3.

Sample S1 was tomato puree. This sample has been previously issued as Sample S1 in AQA 18-07.

With the exception of methamidophos in Sample S1, the robust average was within the range 77% - 96% of the spiked level, providing additional support for the assigned values (Table 18). The robust average for methamidophos was 54% of the spike level. There was reasonable consensus amongst participants and the recovery vs spiked value was similar (58%) with what was obtained for this analyte in AQA 18-07 and an assigned value was calculated. However z-scores for methamidophos should be interpreted with caution.

No assigned value was set for methomyl in Sample S2 and diazinon in Sample S3. For methomyl, the robust average was significantly lower (13%) than the spiked concentration and for diazinon there was no consensus among the 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.

Table 18 Spiked and Assigned Values

Sample	Pesticide	Assigned Value (mg/kg)	Spiked concentration (mg/kg)	Assigned/spiked (%)
S1	Deltamethrin	0.64	0.748	86
S1	Endosulfan sulfate	1.39	1.47	95
S1	Imidacloprid	0.337	0.352	96
S1	Methamidophos	0.079	0.151	54
S2	Iprodione	0.663	0.802	83
S2	Omethoate	2.87	3.10	93
S3	Azinphos methyl	1.24	1.40	89
S3	Chlorpyrifos	0.601	0.701	86
S4	Azoxystrobin	2.55	2.79	91
S4	Endosulfan sulfate	0.93	1.21	77
S4	Imidacloprid	0.495	0.551	90
S4	Thiabendazole	3.17	3.47	91

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[9] there is a requirement for the evaluation of the measurement uncertainty of chemical measurements.

Of 162 numerical results, 142 (88%) were reported with an associated expanded measurement uncertainty. Laboratories **10**, **12** and **15** did not report an estimate of measurement uncertainty for all or some analytes. Laboratory **10** was not accredited. Laboratories **9** and **20** reported

very large measurement uncertainties, very likely they reported relative uncertainties instead of absolute values.

The magnitude of these uncertainties was within the range 0.05 – 86% relative. This does not include the measurement uncertainty estimates from laboratories **9** and **20** (assumed blunders). Of the 142 expanded uncertainties reported, 30 were less than 15% relative and 5 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 1.78 ± 0.356 mg/kg the recommended format is 1.78 ± 0.36 mg/kg.[11]

6.3 z-Scores

Based on practical experience and published models the performance coefficient of variation (PCV) should be approximately 15% for the concentrations of pesticides in the study samples. A target standard deviation equivalent to 15% PCV was used to calculate z-scores for all analytes. The between laboratory coefficient of variation predicted by the modified Horwitz equation[12] is presented for comparison in Table 19.

Table 19 Target standard deviations and modified Horwitz values

Sample	Pesticide	Assigned value (mg/kg)	Modified Horwitz CV (%)	Target SD (as PCV) (%)	Participants' SD (as CV) (%)
S1	Deltamethrin	0.64	17	15	26
S1	Endosulfan sulfate	1.39	15	15	27
S1	Imidacloprid	0.337	19	15	12
S1	Methamidophos	0.079	23	15	17
S2	Iprodione	0.663	17	15	15
S2	Omethoate	2.87	14	15	26
S3	Azinphos methyl	1.24	15	15	31
S3	Chlorpyrifos	0.601	17	15	23
S4	Azoxystrobin	2.55	14	15	17
S4	Endosulfan sulfate	0.93	16	15	25
S4	Imidacloprid	0.495	18	15	11
S4	Thiabendazole	3.17	13	15	22

To account for possible bias in the consensus value due to laboratories using inefficient extraction techniques, z-scores were adjusted for deltamethrin and methamidophos in Sample S1 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 137 results for which z-scores were calculated, 115 (84%) returned $|z| \leq 2$ indicating a satisfactory performance.

The dispersal of participants' z-scores is presented in Figure 16. The dispersal of z-scores for each analyte is presented in Figure 17.

Six laboratories reported results for all analytes spiked into the samples. Laboratories **16** and **20** returned satisfactory z-scores for all twelve 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 137 results for which E_n-scores were calculated, 111 (81%) 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 18.

Laboratories **6**, **9**, **14** and **20** returned satisfactory E_n-scores for all twelve analytes for which E_n-scores were calculated.

6.5 False Negatives

Five laboratories reported a false negative – a pesticide present for which they tested but did not report a result. These are listed in Table 20.

Table 20 False negatives

Sample	Analyte	Lab Code
S1	Methamidophos	12, 18
S2	Omethoate	12
S3	Azinophos-methyl	1
	Diazinon	4, 17

6.6 Reporting of Pesticides not spiked in the PT samples

Two 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 21.

Table 21 Pesticides not added in the test materials

Lab. Code	Sample	Pesticide	Concentration (mg/kg)	Uncertainty (mg/kg)	Recovery (%)
6	S1	Triclopyr	0.12	NR	NR
6	S1	Picloram	0.096	NR	NR
6	S1	Mecoprop (MCPP)	0.13	NR	NR
6	S1	MCPA	0.15	NR	NR
6	S1	Dichlorprop	0.12	NR	NR
6	S1	Dicamba	0.14	NR	NR
6	S1	2,4-DB	0.16	NR	NR
6	S1	2,4-D	0.12	0.04	NR
6	S1	2,4,5-T	0.12	NR	NR
7	S2	Dimethoate	2.2	0.4	115

Laboratories 9, 11, 19 and 20 reported traces of beta-endosulfan in Sample S1. 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 4. 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, SPE, florisil, silica gel and primary/secondary amines (PSA). Most methods used by participants were based around the QuEChERS[13] extraction and clean-up procedure. Participants reported using GC-ECD/FPD, GC-MS(MS) and LC-MS(MS). No trends with the analytical methods were observed.

Recoveries were reported within the range 53% to 128%. 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. Twelve laboratories reported using 'certified standards' from:

- Dr Ehrenstorfer
- AccuStandards

These materials may not meet the internationally-recognised definition of a CRM:

> ***'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'* [14]

6.9 Effect of Sample Matrix

Sample S1 was tomato puree, Sample S2 was cauliflower puree, Sample S3 was apple puree and Sample S4 was potato puree. Despite the samples being different matrices, and the different pesticides spiked into each sample, the proportion of satisfactory z-scores was around 83% for all except Sample S3 Apple for which participants' received the lowest number of satisfactory scores (Table 22). A high number of Not Tested analytes were recorded for Samples S2 Cauliflower and S4 Potato.

Table 22 Satisfactory z-scores for each matrix

Sample	Expected number of z-scores	Actual number of z-scores	Satisfactory	% satisfactory	% Not tested (NT)
S1 Tomato	68	51 (75%)	42	82	22
S2 Cauliflower	34	18 (53%)	15	83	43
S3 Apple	34	25 (74%)	19	76	14
S4 Potato	68	42 (61%)	35	83	38

6.10 Long Term Reproducibility of Participants' Results

Sample S1 tomato puree was previously used as Sample S1 in AQA 18-07. It was prepared in April 2018 and had been stored in a freezer at approximately -20°C. Stability of the spiked pesticides was demonstrated.[6,8]

The long term reproducibility of analytical results can be examined for the 14 participants that returned results in both studies. These results are detailed in Table 23. All non-numerical results have been removed and values are only shown when results were available for both studies.

Table 23 Participant results for identical Sample S1 AQA 11-03 and S1 AQA 10-03

Study no	Lab. Code	S1-Tomato Deltamethrin (mg/kg	S1-Tomato Endosulfan Sulfate (mg/kg)	S1-Tomato Imidacloprid (mg/kg)	S1-Tomato Methamidophos (mg/kg)
AQA 19-08	**1**	0.65 ± 0.002	1.54 ± 0.002	0.28 ± 0.002	0.08 ± 0.002
AQA 18-07		0.65 ± 0.008	0.82 ± 0.002	0.13 ± 0.008	0.12 ± 0.002
AQA 19-08	**4**	0.26 ± 0.13	0.76 ± 0.35		
AQA 18-07		2.86 ± 0.44	1.11 ± 0.22		
AQA 19-08	**6**	0.57 ± 0.17	1.3 ± 0.39	0.37 ± 0.11	0.098 ± 0.029
AQA 18-07		0.59 ± 0.18	0.56 ± 0.17	0.32 ± 0.10	0.090 ± 0.030
AQA 19-08	**7**	0.52 ± 0.08	1.0 ± 0.3	0.31 ± 0.08	0.062 ± 0.018
AQA 18-07		0.52 ± 0.10	1.36 ± 0.27	0.39 ± 0.08	0.070 ± 0.014
AQA 19-08	**8**	0.90 ± 0.015	1.79 ± 0.015		
AQA 18-07		0.82 ± 0.03	1.48 ± 0.16		
AQA 19-08	**10**	0.89	1.19		0.11
AQA 18-07		1.74	1.48		0.12
AQA 19-08	**11**	0.679 ± 0.203	1.494 ± 0.299	0.312 ± 0.09	0.072 ± 0.02
AQA 18-07		0.86 ± 0.21	1.6 ± 0.512	0.35 ± 0.102	0.054 ± 0.019
AQA 19-08	**12**	0.71 ± 0.08			
AQA 18-07		1.36			
AQA 19-08	**13**				0.134 ± 0.03
AQA 18-07					0.141 ± 0.042
AQA 19-08	**14**	0.77 ± 0.23	1.74 ± 0.52	0.34 ± 0.10	0.071± 0.021
AQA 18-07		0.43 ± 0.13	1.51 ± 0.45	0.33 ± 0.10	0.071 ± 0.021
AQA 19-08	**16**	0.67 ± 0.12	1.4 ± 0.21	0.33 ± 0.06	0.082 ± 0.020
AQA 18-07		0.77 ± 0.2	1.5 ± 0.2	0.38 ± 0.07	0.083 ± 0.02
AQA 19-08	**17**	0.40 ± 0.17	0.87 ± 0.31		
AQA 18-07		0.29 ± 0.05	1.10 ± 0.05		
AQA 19-08	**18**	0.53 ± 0.06	1.17 ± 0.14		
AQA 18-07		0.426 ± 0.0016	0.688 ± 0.0998		
AQA 19-08	**19**	0.56 ± 0.30	1.69 ± 0.34		
AQA 18-07		0.56 ± 0.34	1.54 ± 0.14		
AQA 19-08	RA	0.62 ± 0.11	1.39 ± 0.25	0.337 ± 0.035	0.082 ± 0.014
AQA 18-07	RA	0.64 ± 0.17	1.22 ± 0.25	0.304 ± 0.090	0.088 ± 0.025
Spiked Value		0.748 ± 0.037	1.47 ± 0.07	0.352 ± 0.018	0.151 ± 0.008

Note: - White background - results that are in agreement with each other (within stated uncertainties)
- Grey background - results that are not in agreement with each other (within stated uncertainties).

Laboratories **7**, **11**, **14** and **16** reported results for all the analytes spiked in the tomato sample and have all the duplicate results in agreement (within stated uncertainties).

Thirty-three percent of the paired laboratories results are not in agreement, some with a relative percent difference of over 50% (eg. laboratories 1, 4, 6, 12 and 18).

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APPENDIX 1 - SAMPLE PREPARATION, HOMOGENEITY AND STABILITY CHECK

Test Sample Preparation

Preparation of Samples S1 (Tomato)

Sample S1 tomato was prepared in March 2018 (details of the preparation are presented in AQA 18-07) and previously used as Sample S1 in AQA 18-07. The unused samples were re-labelled, shrink wrapped and sent out as Sample S1.

Preparation of Sample S2 (Cauliflower)

The cauliflower heads were rinsed using tap water and allowed to air dry. 15416.6 g of cauliflower heads were placed into a stainless steel drum and blended using a stick mixer to form a puree. During blending 8610.5g of Milli-Q water was added to the puree to enable the sieving through an 850 µm sieve. The 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, shrink-wrapped and placed in a freezer.

Preparation of Sample S3 (Apple)

The apples were rinsed with tap water and allowed to dry. The apples were placed into a stainless steel drum and blended using a stick mixer to form a puree which was passed through an 850 µm sieve. The 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, shrink-wrapped and placed in a freezer.

Preparation of Sample S4 (Potatoes)

The potatoes were washed to remove the dirt. They were allowed to dry overnight. 18908.9 g of potatoes were cut, placed in a stainless steel drum and blended using a stick mixer. 2873.1g of Milli-Q water was added to create a puree which was sieved through an 850 µm sieve. The sieved potatoes were stirred and unspiked samples were dispensed into 200 mL amber bottles. The remaining potato was then spiked, stirred for one and a half hours and dispensed into bottles which were then labelled, shrink-wrapped and placed in a freezer.

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.

Stability Check

Sample S1 from this study was previously issued as Sample S1 in AQA 18-07. Stability was demonstrated by comparing the robust average of participants' results from both studies, with each other and with the spiked value (Figure 19). Methamidophos had the robust average from both studies in good agreement with each other, but less than 60% of the spiked value.

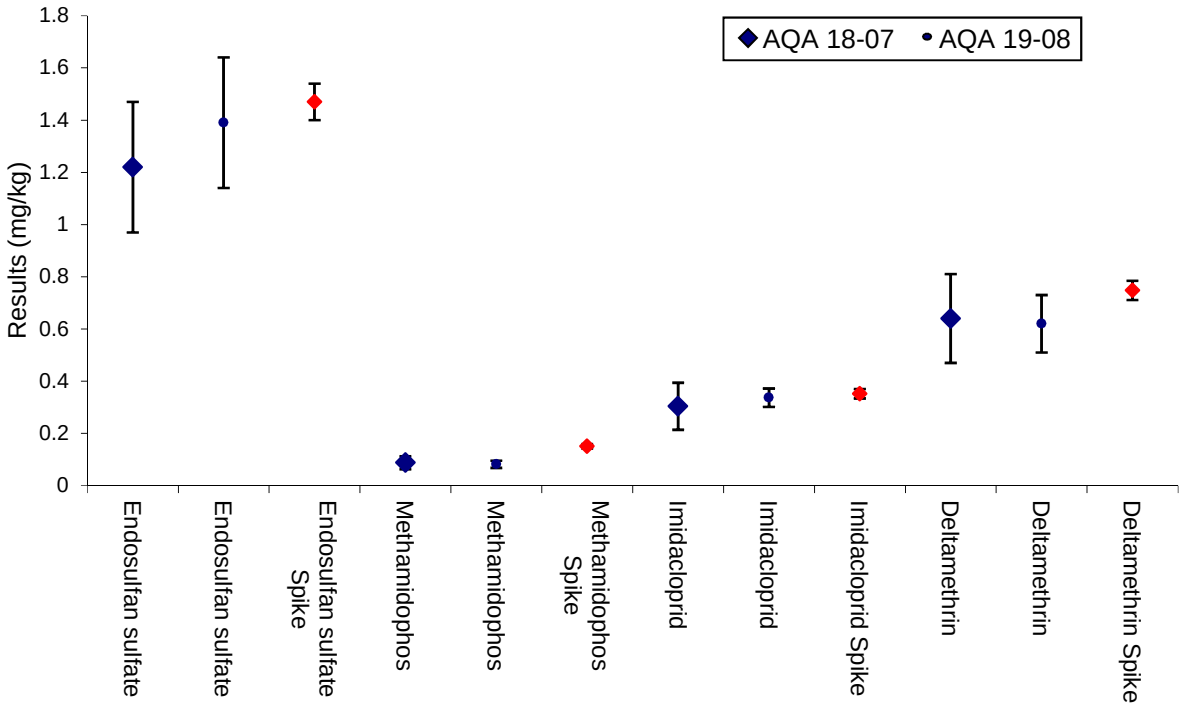

Figure 19 Robust average of participant results from AQA 18-07 and AQA 19-08 and spiked value for analytes in tomato sample

APPENDIX 2 - 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.'[11] 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 24.

Table 24 Uncertainty of robust average for Chlorpyrifos in Sample S3

No. results (p)	17
Robust Average	0.5575 mg/kg
$S_{rob\ av}$	0.1829 mg/kg
$u_{rob\ av}$	0.055mg/kg
k	2
$U_{rob\ av}$	0.11 mg/kg

The robust average for Chlorpyrifos in Sample S3 is 0.56 ± 0.11 mg/kg.

APPENDIX 3 - ACRONYMS AND ABBREVIATIONS

CITAC	Co-operation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
DCM	Dichloromethane
$\lvert E_n \rvert$	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
PCV	Performance Coefficient of Variation
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.V.	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 4- PARTICIPANTS' TEST METHODS

Table 25 Test methods Sample S1 Tomato Deltamethrin

Lab. Code	Sample Weight (g)	Extraction	Clean-up	Extraction solvent	Measurement technique
1	10	Liquid-Liquid		Ethyl acetate	GC
4	15	QuEChERS	SPE: C18, GCB/PSA	Acetonitrile	GCECD
6	10	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ
7	10	QuEChERS	PSA	Acetonitrile	GCMSMS
8					
9	10	QuEChERS	SPE	Acetonitrile	GC-MSMS
10	10	QuEChERS	QuEChERS	1%acetic acid in acetonitrile	GCECD
11	10	QuEChERS		Acetonitrile	LCMSMS
12	25	Liquid-Liquid		Acetone+DCM	GC-FPD
13					
14	10	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	GC-MS
15	25	Liquid-Liquid	silica	DCM+Acetone+Hexane	GCECD
16	20	Liquid-Liquid		Acetone,DCM,Hexane	GCMS,GC ECD
17	10	SPE	C18/Envicarb/Florisil	acetonitrile	GCECD
18	10	Acetonitrile	ODS-Carbon-Florisil	Acetone-Hexane	GCECD
19	10	SPE	C18,carbon, florisil	Acetonitrile	GCECD
20	10.0015	Liquid-Liquid	QuEChERS	Ethyl Acetate	GCMSMS/LCMSMS

Table 26 Test methods Sample S1 Tomato Endosulfan Sulfate

Lab. Code	Extraction	Clean-up	Extraction solvent	Measurement technique
1	Liquid-Liquid		Ethyl acetate	GC
4	QuEChERS	SPE: C18, GCB/PSA	Acetonitrile	GCECD
6	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ
7	QuEChERS	PSA	Acetonitrile	GCMSMS
8				
9	QuEChERS	SPE	Acetonitrile	GC-MSMS
10	QuEChERS	QuEChERS	1%acetic acid in acetonitrile	GCECD
11	QuEChERS	PSA	Acetonitrile	GCMSMS
12				
13				
14	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	GC-ECD
15	Liquid-Liquid	silica	DCM+Acetone+Hexane	GCECD
16	Liquid-Liquid		Acetone,DCM,Hexane	GCMS,GC ECD
17	SPE	C18/Envicarb/Florisil	acetonitrile	GCECD
18	Acetonitrile	ODS-Carbon-Florisil	Acetone-Hexane	GCECD
19	SPE	C18,carbon, florisil	Acetonitrile	GCECD
20	Liquid-Liquid	QuEChERS	Ethyl Acetate	GCMSMS/LCMSMS

Table 27 Test methods Sample S1 Tomato Methamidophos

Lab. Code	Extraction	Clean-up	Extraction solvent	Measurement technique
1	Liquid-Liquid		Ethyl acetate	GC
4				
6	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ
7	QuEChERS	PSA	Acetonitrile	LCMSMS
8				
9	QuEChERS	SPE	Acetonitrile	LC-MSMS
10	QuEChERS	QuEChERS	1%acetic acid in acetonitrile	GCFPD
11	QuEChERS		Acetonitrile	LCMSMS
12	Liquid-Liquid		Acetone+DCM	GC-FPD
13	QuEChERS	PSA	Acetonitrile	LC-QQQ
14	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	GC-FPD
15	Liquid-Liquid	PSA+GCB+C18	DCM+Acetone+MeCN	LC-MSMS
16	Liquid-Liquid		Acetone,DCM,Hexane	GCMS,LCMS
17				
18				
19				
20	Liquid-Liquid	QuEChERS	Ethyl Acetate	GCMSMS/LCMSMS

Table 28 Test methods Sample S1 Tomato Imidacloprid

Lab. Code	Extraction	Clean-up	Extraction solvent	Measurement technique
1	Liquid-Liquid		Ethyl acetate	LC
4				
6	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ
7	QuEChERS	PSA	Acetonitrile	LCMSMS
8				
9	QuEChERS	SPE	Acetonitrile	LC-MSMS
10				
11	QuEChERS		Acetonitrile	LCMSMS
12				
13				
14	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	LC-MS/MS
15	Liquid-Liquid	PSA+GCB+C18	DCM+Acetone+MeCN	LC-MSMS
16	Liquid-Liquid		Acetone,DCM,Hexane	LCMS
17				
18				
19				
20	Liquid-Liquid	QuEChERS	Ethyl Acetate	GCMSMS/LCMSMS

Table 29 Test methods Sample S2 Cauliflower Iprodione

Lab. Code	Sample Weight (g)	Extraction	Clean-up	Extraction solvent	Measurement technique
1					
4					
6	10	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ
7	10	QuEChERS	PSA	Acetonitrile	GCMSMS
8					
9	10	QuEChERS	SPE	Acetonitrile	GC-MSMS
10					
11	10	QuEChERS	PSA	Acetonitrile	GCMSMS
12					
13	15	QuEChERS	PSA	Acetonitrile	LC-QQQ
14	10	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	GC-MS
15	25	Liquid-Liquid	PSA+GCB+C18	DCM+Acetone+MeCN	LC-MSMS
16	20	Liquid-Liquid		Acetone,DCM,Hexane	GCMS,LCMS
17					
18					
19					
20	9.9943	Liquid-Liquid	QuEChERS	Ethyl Acetate	GCMSMS/LCMSMS

Table 30 Test methods Sample S2 Cauliflower Methomyl

Lab. Code	Extraction	Clean-up	Extraction solvent	Measurement technique
1	Liquid-Liquid		Ethyl acetate	LC
4				
6	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ
7	QuEChERS	PSA	Acetonitrile	LCMSMS
8				
9	QuEChERS	SPE	Acetonitrile	LC-MSMS
10				
11	QuEChERS		Acetonitrile	LCMSMS
12				
13	QuEChERS	PSA	Acetonitrile	LC-QQQ
14	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	LC-MS/MS
15	Liquid-Liquid	PSA+GCB+C18	DCM+Acetone+MeCN	LC-MSMS
16	Liquid-Liquid		Acetone,DCM,Hexane	LCMS
17				
18				
19				
20	Liquid-Liquid	QuEChERS	Ethyl Acetate	GCMSMS/LCMSMS

Table 31 Test methods Sample S2 Cauliflower Omethoate

Lab. Code	Extraction	Clean-up	Extraction solvent	Measurement technique
1	Liquid-Liquid		Ethyl acetate	GC
4				
6	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ
7	QuEChERS	PSA	Acetonitrile	LCMSMS
8				
9	QuEChERS	SPE	Acetonitrile	LC-MSMS
10				
11	QuEChERS		Acetonitrile	LCMSMS
12				
13				
14	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	LC-MS/MS
15	Liquid-Liquid		DCM+Acetone+EA	GCFPD
16	Liquid-Liquid		Acetone,DCM,Hexane	GCMS,LCMS
17				
18				
19				
20	Liquid-Liquid	QuEChERS	Ethyl Acetate	GCMSMS/LCMSMS

Table 32 Test methods Sample S3 Apple Azinophos-methyl

Lab. Code	Sample Weight (g)	Extraction	Clean-up	Extraction solvent	Measurement technique
1	10	Liquid-Liquid		Ethyl acetate	GC
4					
6	10	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ
7	10	QuEChERS	PSA	Acetonitrile	LCMSMS
8					
9	10	QuEChERS	SPE	Acetonitrile	GC-MSMS
10					
11	10	QuEChERS		Acetonitrile	LCMSMS
12					
13	15	QuEChERS	PSA	Acetonitrile	LC-QQQ
14	10	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	GC-FPD
15	25	Liquid-Liquid	PSA+GCB+C18	DCM+Acetone+MeCN	LC-MSMS
16	20	Liquid-Liquid		Acetone,DCM,Hexane	GCMS,LCMS
17					
18					
19					
20	10.0225	Liquid-Liquid	QuEChERS	Ethyl Acetate	GCMSMS/LCMSMS

Table 33 Test methods Sample S3 Apple Chlorpyrifos

Lab. Code	Clean-up	Extraction	Extraction solvent	Measurement technique
1	Liquid-Liquid		Ethyl acetate	GC
4	QuEChERS	SPE: C18, GCB/PSA	Acetonitrile	GCFPD
6	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ
7	QuEChERS	PSA	Acetonitrile	GCMSMS
8				
9	QuEChERS	SPE	Acetonitrile	GC-MSMS
10	QuEChERS	QuEChERS	1%acetic acid in acetonitrile	GCFPD
11	QuEChERS	PSA	Acetonitrile	GCMSMS
12				
13	QuEChERS	PSA	Acetonitrile	LC-QQQ
14	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	GC-FPD
15	Liquid-Liquid		DCM+Acetone+EA	GCFPD
16	Liquid-Liquid		Acetone,DCM,Hexane	GCMS,LCMS
17	SPE	C18/Envicarb/Florisil	acetonitrile	GCNPD
18	Acetonitrile	ODS-Carbon-Florisil	Acetone-Hexane	GC-FPD
19	SPE	C18,carbon, florisil	Acetonitrile	GCNPD
20	Liquid-Liquid	QuEChERS	Ethyl Acetate	GCMSMS/LCMSMS

Table 34 Test methods Sample S3 Apple Diazinon

Lab. Code	Clean-up	Extraction	Extraction solvent	Measurement technique
1	Liquid-Liquid		Ethyl acetate	GC
4	QuEChERS	SPE: C18, GCB/PSA	Acetonitrile	GCFPD
6	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ
7	QuEChERS	PSA	Acetonitrile	GCMSMS
8				
9	QuEChERS	SPE	Acetonitrile	GC-MSMS
10	QuEChERS	QuEChERS	1%acetic acid in acetonitrile	GCFPD
11	QuEChERS		Acetonitrile	LCMSMS
12				
13	QuEChERS	PSA	Acetonitrile	LC-QQQ
14	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	GC-FPD
15	Liquid-Liquid		DCM+Acetone+EA	GCFPD
16	Liquid-Liquid		Acetone,DCM,Hexane	GCMS,LCMS
17	SPE	C18/Envicarb/Florisil	acetonitrile	GCNPD
18	Acetonitrile	ODS-Carbon-Florisil	Acetone-Hexane	GC-FPD
19	SPE	C18,carbon, florisil	Acetonitrile	GCNPD
20	Liquid-Liquid	QuEChERS	Ethyl Acetate	GCMSMS/LCMSMS

Table 35 Test methods Sample S4 Potato Azoxystrobin

Lab. Code	Sample Weight (g)	Extraction	Clean-up	Extraction solvent	Measurement technique
1	10	Liquid-Liquid		Ethel acetate	LC
4					
6	5	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ
7	10	QuEChERS	PSA	Acetonitrile	LCMSMS
8					
9	10	QuEChERS	SPE	Acetonitrile	LC-MSMS
10					
11	10	QuEChERS		Acetonitrile	LCMSMS
12					
13	15	QuEChERS	PSA	Acetonitrile	LC-QQQ
14	10	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	GC-MS
15	25	Liquid-Liquid	PSA+GCB+C18	DCM+Acetone+MeCN	LC-MSMS
16	20	Liquid-Liquid		Acetone,DCM,Hexane	GCMS,LCMS
17					
18					
19					
20	10.0054	Liquid-Liquid	QuEChERS	Ethyl Acetate	GCMSMS/LCMSMS

Table 36 Test methods Sample S4 Potato Endosulfan Sulfate

Lab. Code	Extraction	Clean-up	Extraction solvent	Measurement technique
1	Liquid-Liquid		Ethyl acetate	GC
4	QuEChERS	SPE: C18, GCB/PSA	Acetonitrile	GCECD
6	Liquid-Liquid	ChemElut	Methanol/Water	GC-QQQ
7	QuEChERS	PSA	Acetonitrile	GCMSMS
8				
9	QuEChERS	SPE	Acetonitrile	GS-MSMS
10	QuEChERS	QuEChERS	1%acetic acid in acetonitrile	GCECD
11	QuEChERS	PSA	Acetonitrile	GCMSMS
12				
13				
14	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	GC-ECD
15	Liquid-Liquid	silica	DCM+Acetone+Hexane	GCECD
16	Liquid-Liquid		Acetone,DCM,Hexane	GCMS,GC ECD
17	SPE	C18/Envicarb/Florisil	acetonitrile	GCECD
18	Acetonitrile	ODS-Carbon-Florisil	Acetone-Hexane	GCECD
19	SPE	C18, florisil	Acetonitrile	GCECD
20	Liquid-Liquid	QuEChERS	Ethyl Acetate	GCMSMS/LCMSMS

Table 37 Test methods Sample S4 Potato Imidacloprid

Lab. Code	Extraction	Clean-up	Extraction solvent	Measurement technique
1	Liquid-Liquid		Ethyl acetate	LC
4				
6	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ
7	QuEChERS	PSA	Acetonitrile	LCMSMS
8				
9	QuEChERS	SPE	Acetonitrile	LC-MSMS
10				
11	QuEChERS		Acetonitrile	LCMSMS
12				
13				
14	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	LC-MS/MS
15	Liquid-Liquid	PSA+GCB+C18	DCM+Acetone+MeCN	LC-MSMS
16	Liquid-Liquid		Acetone,DCM,Hexane	LCMS
17				
18				
19				
20	Liquid-Liquid	QuEChERS	Ethyl Acetate	GCMSMS/LCMSMS

Table 38 Test methods Sample S4 Potato Thiabendazole

Lab. Code	Extraction	Clean-up	Extraction solvent	Measurement technique
1	Liquid-Liquid		Ethyl acetate	LC
4				
6	Liquid-Liquid	ChemElut	Methanol/Water	LC-QQQ
7	QuEChERS	PSA	Acetonitrile	LCMSMS
8				
9	QuEChERS	SPE	Acetonitrile	LC-MSMS
10				
11	QuEChERS		Acetonitrile	
12				
13				
14	QuEChERS: ACN, NaCl, MgSO4, Citrate buffer	Dispersive SPE:- PSA, C18, MgSO4.	Acetonitrile	LC-MS/MS
15	Liquid-Liquid	PSA+GCB+C18	DCM+Acetone+MeCN	LC-MSMS
16	Liquid-Liquid		Acetone,DCM,Hexane	LCMS
17				
18				
19				
20	Liquid-Liquid	QuEChERS	Ethyl Acetate	GCMSMS/LCMSMS

END OF REPORT