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

Proficiency Test Final Report AQA 23-01 Toxic and Essential Elements in Food

April 2023

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ACKNOWLEDGMENTS

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

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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Accredited for compliance with ISO/IEC 17043

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SUMMARY

This report presents the results of the proficiency test AQA 23-01 Toxic and Essential Elements in Food. The study focused on the measurement of total: Ag, As, B, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Se, Sn, Tl, U, V and Zn in celery puree, and of total: Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, Sb, Se, Sn, U, V, and Zn in a freeze-dried bovine liver sample.

Eight laboratories registered to participate and all submitted results.

The assigned values were the robust averages of participants' results. The associated uncertainties were estimated from the robust standard deviation of the participants' results.

The outcomes of the study were assessed against the aims as follows, to:

i. compare the performances of participant laboratories and assess their accuracy;

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

Of 288 z-scores, 284 (99%) were satisfactory with $|z| \leq 2.0$.

Of 288 E_n-scores, 274 (95%) were satisfactory with $|E_n| \leq 1.0$.

Laboratories 1, 3, 4 and **7** returned the highest number of satisfactory z-scores (43 out of 43 reported).

Laboratories 4 and **7** returned the highest number of satisfactory E_n scores (43 out of 43).

ii. evaluate the laboratories' methods used in determination of total elements in food;

Aluminium measurements presented difficulty to testing laboratories. Some participants may need to reassess their extraction methods. According to Eurachem/CITAC Guide CG 4, laboratories should consider using matrix-matched control samples to assess their extraction efficiency (the bias of their analytical methods). Bias can be expressed as recovery and should be corrected for or included in the uncertainty estimate.[1]

Selenium measurements in the more complex matrix, freeze dried liver, challenged participants' analytical techniques. ICP-MS with high-energy He was the preferred measurement technique.

iii. compare the performance of participant laboratories with their past performance;

Participants have improved their performance in the measurement of Cr and Ni in matrices with high silica content.

iv. develop the practical application of traceability and measurement uncertainty;

All results were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 1% to 400% of the reported value.

v. produce materials that can be used in method validation and as control samples.

The test samples of this study were checked for homogeneity and are well characterised, both by in-house testing and from the results of the proficiency round. Surplus of these test samples is available for purchase from NMI.

1 INTRODUCTION

1.1 NMI Proficiency Testing Program

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

Proficiency testing (PT): "is evaluation of participant performance against pre-established criteria by means of inter-laboratory comparison."[2] NMI PT studies target chemical testing in areas of high public significance such as trade, environment and food safety. NMI offers studies in:

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

AQA 23-01 is the sixteenth NMI proficiency test on inorganic contaminants and nutrients in food.

1.2 Study Aims

The aims of the study were to:

- compare the performance of participant laboratories and assess their accuracy;
- evaluate the laboratories' methods used in determination of inorganic analytes in food;
- compare the performance of participant laboratories with their past performance;
- develop the practical application of traceability and measurement uncertainty; and
- produce materials that can be used in method validation and as control samples.

1.3 Study Conduct

The conduct of NMI proficiency tests is described in the NMI Chemical Proficiency Testing Study Protocol.[3] The statistical methods used are described in the NMI Chemical Proficiency Statistical Manual.[4] These documents have been prepared with reference to ISO Standard 17043[2] and The International Harmonised Protocol for Proficiency Testing of (Chemical) Analytical Laboratories.[5]

NMI is accredited by National Association of Testing Authorities, Australia (NATA) to ISO/IEC 17043 as a provider of proficiency testing schemes. This proficiency test is within the scope of NMI's accreditation.

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

2 STUDY INFORMATION

2.1 Selection of Matrices and Inorganic Analytes

The fifty tests in the study samples were representative of those commonly measured in food, and included toxic elements such as Cd and Pb and nutrient elements such as Na, P and Mg.

2.2 Participation

Eight laboratories participated and submitted results.

The timetable of the study was:

Invitation issued:	12 January 2023
Samples dispatched:	7 February 2023
Results due:	3 March 2023
Interim report issued:	9 March 2023
Preliminary report issued	13 March 2023

The results due date was extended to accommodate sample delivery delays to some international participants.

2.3 Test Material Specification

Two samples were provided for analysis:

- Sample S1 was 40 g of frozen celery puree; and
- Sample S2 was 15 g of freeze dried bovine liver.

2.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

2.5 Sample Preparation, Analysis and Homogeneity Testing

Test samples from previous studies have been demonstrated to be sufficiently homogeneous for the evaluation of participants' performance. Therefore, only a partial homogeneity test was conducted for all analytes, with the exception of Ag, B, Na, Sn, Tl and U in Sample S1 and Al in Sample S2. The results from the partial homogeneity test for these samples are reported in the present study as the homogeneity value.

The preparation, analysis and homogeneity testing of the study samples are described in Appendix 1.

2.6 Stability of Analytes

No stability study was carried out during the period of the present study. Stability studies conducted for the previous proficiency tests of metals and nutrients in food found no significant changes in any of the analytes' concentration over the study period. Results of this study gave no reason to question the stability of the test samples.

2.7 Sample Storage, Dispatch and Receipt

Sample S1 was stored frozen and sample S2 was stored at room temperature before dispatch.

The samples were dispatched by courier on 7 February 2023.

A description of the test samples, instructions for participants, and a form for participants to confirm the receipt of the test samples, were included with the samples.

An Excel spreadsheet for the electronic reporting of results was e-mailed to participants.

2.8 Instructions to Participants

Participants were instructed as follows:

- The samples should be stored during analysis at room temperature in a dry place e.g. desiccator with anhydrous calcium sulphate.
- These samples are an attempt to mime the real samples encountered by a laboratory in its routine activities. Please use appropriate Good Laboratory Practice when handling them.
- Quantitatively analyse the samples using your normal test method.
- Report the results in units of **mg/kg** on as received basis for:

SAMPLE S1 Celery puree		SAMPLE S2 Frieze dried bovine liver (AGAL 20)	
TOTAL	**Approximate Conc. Range mg/kg**	**TOTAL**	**Approximate Conc. Range mg/kg**
Ag	0.01-0.4	Ag	0.025-1
As	0.025-1	Al	0.5-20
B	0.5-20	As	0.25-10
Ca	25-1000	Ba	0.25-10
Cd	0.01-0.4	Cd	0.25-10
Cr	0.025-1	Ca	25-1000
Co	0.025-1	Co	0.25-10
Cu	0.5-20	Cr	0.25-10
Fe	0.5-20	Cu	25-1000
Pb	0.01-0.4	Fe	25-1000
Mg	25-1000	Hg	0.25-10
Mn	0.5-20	K	500-20000
Hg	0.01-0.4	Mg	25-1000
Mo	0.025-1	Mn	0.5-20
Ni	0.01-0.4	Mo	0.5-20
P	25-1000	Na	250-10000
K	125-5000	Ni	0.25-10
Se	0.025-1	P	500-20000
Na	25-1000	Pb	0.25-10
Tl	0.005-0.2	Rb	0.25-10
Sn	0.025-1	Sb	0.25-10
U	0.025-1	Se	0.25-10
V	0.025-1	Sn	0.025-1
Zn	0.5-20	U	0.25-10
		V	0.25-10
		Zn	25-1000

- Report results using the electronic results sheet emailed to you.
- Report results as you would report to a client.
- Please send the requested details regarding the test method and the basis of your uncertainty estimate.

2.9 Interim and Preliminary Reports

An interim report was e-mailed to participants on 9 March 2023.

A preliminary report was issued on 13 March 2023. This report included: a summary of the results reported by laboratories, assigned values, performance coefficient of variations, z-scores and En-scores for each analyte tested by participants.

No data from the preliminary report has been changed in the present final report.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Test Method Summaries

Summaries of test methods are transcribed in Tables 1 to 2.

Table 1 Methodology for Total Elements in S1

Lab. Code	Method Reference	Sample Mass (g)	Temp. (°C)	Time (min)	Vol. HNO_3 (mL)	Vol. HCl (mL)
1	AOAC 990.08	5	85	240	3	2
3	EPA Method 3050B Acid Digestion of Sediments, Sludges and Soils	5	85	240	5	5
4		1	100	120	3	1
5	In-house method. Microwave digestion for trace elements and Hot block digestion for major elements. Analysed by ICP-MS and ICP-OES	3	85-165		5	
6	S394	2	200	45	10	2
7		1	100	120	3	1
8	In House S6 - referencing APHA 3125	2	120	60	5	

Table 2 Methodology for Total Elements in S2

Lab. Code	Method Reference	Sample Mass (g)	Temp. (°C)	Time (min)	Vol. HNO_3 (mL)	Vol. HCl (mL)	Vol. H_2O_2 (mL)
1	AOAC 990.08	0.5	85	240	3	2	
2		0.5	190	30	2		1
3	EPA Method 3050B Acid Digestion of Sediments, Sludges and Soils	0.25	85	240	5	5	
4		1	100	120	3	1	
5	In-house method. Microwave digestion for trace elements and Hot block digestion for major elements. Analysed by ICP-MS and ICP-OES	0.3	85-165		5		
7		1	100	120	3	1	
8	In House S6 - referencing APHA 3125	0.2	120	60	5		

3.2 Instruments Used for Measurements

The instruments and settings used by participants are presented in Appendix 4.

3.3 Additional Information

Participants had the option to report additional information for each sample analysed. No laboratories supplied additional information.

3.4 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about the basis of their uncertainty estimates (Table 3).

Table 3 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
1	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - SS Duplicate Analysis	Laboratory Bias from PT Studies Recoveries of SS	In-house method
2	Standard deviation of replicate analyses multiplied by 2 or 3	Standard deviation from PT studies only		NMI Uncertainty Course
		Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Variation in Sample Moisture Content	
3	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - SS Duplicate Analysis	Laboratory Bias from PT Studies Recoveries of SS	ISO/GUM
4	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis Instrument Calibration		Nordtest Report TR537
5	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - RM Duplicate Analysis	CRM Laboratory Bias from PT Studies	Eurachem Guide on the Fitness for Purpose of Analytical methods, First edition 2019
6	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS Duplicate Analysis Instrument Calibration	CRM Recoveries of SS	Eurachem/CITAC Guide
7	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis Instrument Calibration		Nordtest Report TR537
8	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM	Nordtest Report TR537

[a]RM = Reference Material, CRM = Certified Reference Material, SS = Spiked Samples.

3.5 Participant Comments on this PT Study or Suggestions for Future Studies

The study co-ordinator welcomes comments or suggestions from participants about this study or possible future studies. Such feedback may be useful in improving future studies.

There were no comments from participants on this study.

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 4 to 52 with resultant summary statistics: robust average, median, maximum, minimum, robust standard deviation (SD_{rob}) and robust coefficient of variation (CV_{rob}). Bar charts of the results and performance scores are presented in Figures 2 to 50. An example chart with interpretation guide is shown in Figure 1.

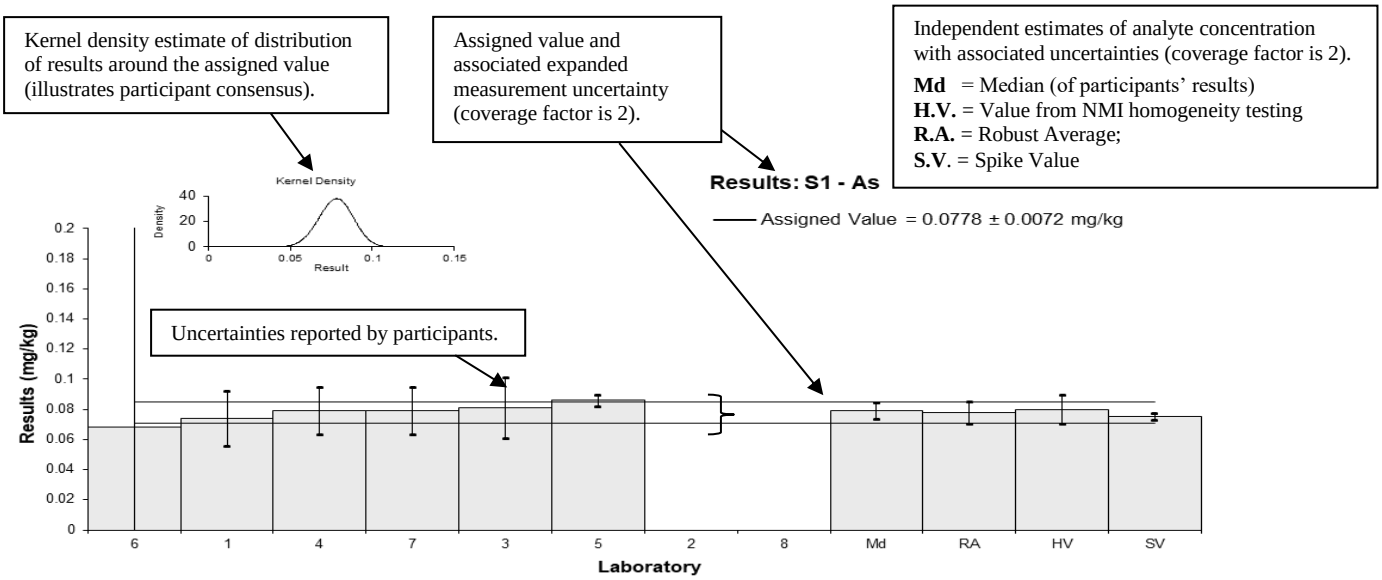


Figure 1 Guide to Presentation of Results

4.2 Outliers and Extreme Outliers

Outliers were results less than 50% and greater than 150% of the robust average and were removed before assigned value calculation. Extreme outliers were obvious blunders, such as those with incorrect units, decimal errors, or results from a different proficiency test item (gross errors) and were removed for calculation of summary statistics.[4, 5, 6]

4.3 Assigned Value

An example of the assigned value calculation using data from the present study is given in Appendix 2. The assigned value is defined as: 'the value attributed to a particular property of a proficiency test item.[2] In this study the property is the mass fraction of analyte. Assigned values were the robust average of participants' results, outliers removed; the expanded uncertainties were estimated from associated robust standard deviation.[5, 6]

4.4 Robust Average and Robust Between-Laboratory Coefficient of Variation

The robust averages and associated expanded measurement uncertainties were calculated using the procedure described in 'Statistical methods for use in proficiency testing by inter-laboratory comparisons, ISO 13528.[6]

The robust between-laboratory coefficient of variation (robust CV) is a measure of the variability of participants' results and was calculated using the procedure described in ISO 13528. [6]

4.5 Target Standard Deviation for Proficiency Assessment

The target standard deviation for proficiency assessment (σ) is the product of the assigned value *(X)* and the performance coefficient of variation (PCV). This value is used for calculation of participant z-score and provides scaling for laboratory deviation from the assigned value.

$\sigma = (X) * PCV$ Equation 1

It is important to note that the PCV is a fixed value and is not the standard deviation of participants' results. The fixed value set for PCV is based on the existing regulation, the acceptance criteria indicated by the methods, the matrix, the concentration level of analyte and on experience from previous studies. It is backed up by mathematical models such as the Thompson Horwitz equation.[7]

4.6 z-Score

An example of z-score calculation using data from the present study is given in Appendix 2. For each participant's result a z-score is calculated according to Equation 2 below:

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

Where:

z is z-score
χ is participant's result;
X is the assigned value;
σ is the target standard deviation.

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

- $|z| \leq 2.0$ is satisfactory;
- $2.0 < |z| < 3.0$ is questionable;
- $|z| \geq 3.0$ is unsatisfactory.

4.7 E_n-Score

An example of E_n-score calculation using data from the present study is given in Appendix 2. The E_n-score is complementary to the z-score in assessment of laboratory performance. E_n-score includes measurement uncertainty and is calculated according to Equation 3 below:

$$E_n = \frac{(\chi - X)}{\sqrt{U_\chi^2 + U_X^2}}$$ 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 uncertainty of the participant's result;
U_X is the expanded uncertainty of the assigned value.

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

- $|E_n| \leq 1.0$ is satisfactory;
- $|E_n| > 1.0$ is unsatisfactory.

4.8 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025 must establish and demonstrate the traceability and measurement uncertainty associated with their test results.[8] Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.[1]

5 TABLES AND FIGURES

Table 4

Sample Details

Sample No.	S1
Matrix	Celery
Analyte	Ag
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty
1	0.029	0.007
2	NT	NT
3	0.027	0.007
4	0.028	0.0056
5	0.026	0.003
6	NT	NT
7	0.029	0.0058
8	<0.1	NR

Statistics

Assigned Value	Not Set	
Spike Value	0.0351	0.0010
Median	0.0280	0.0017
Mean	0.0278	
N	5	
Max	0.029	
Min	0.026	

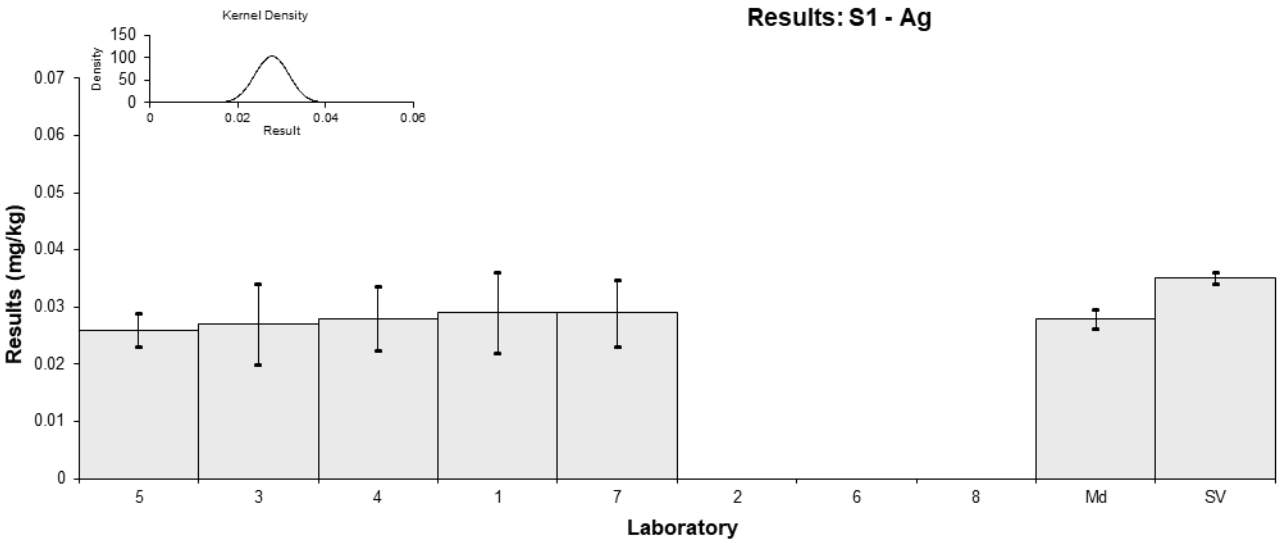

Results: S1 - Ag
Kernel Density
Density
150
100
50
0
0
0.02
0.04
0.06
Result
Results (mg/kg)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
5
3
4
1
7
2
6
8
Md
SV
Laboratory

Figure 2

Table 5

Sample Details

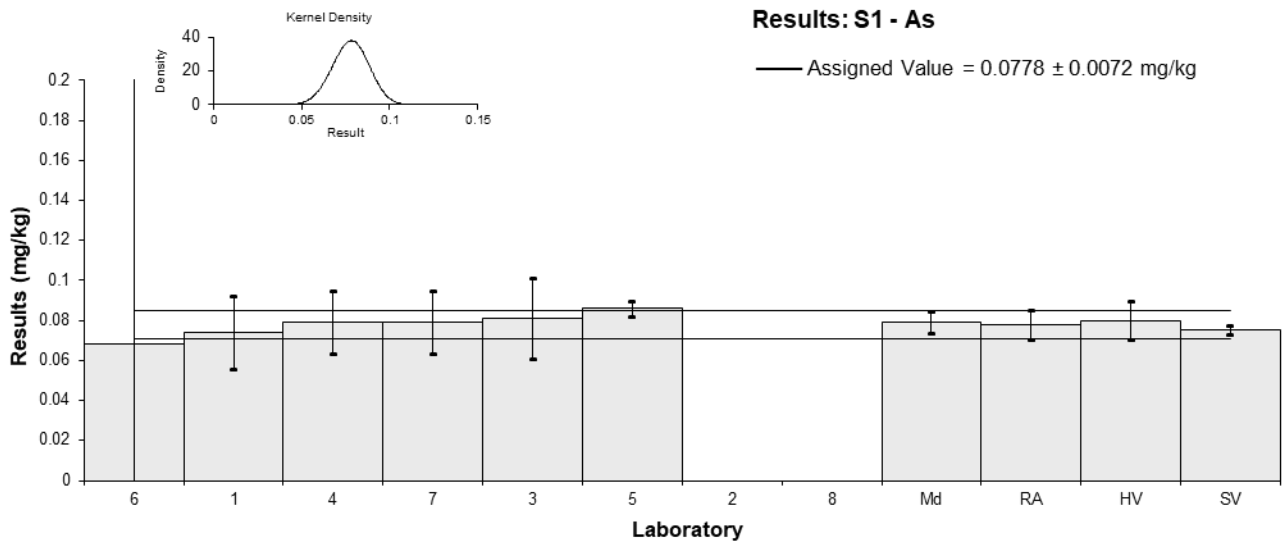
Sample No.	S1
Matrix	Celery
Analyte	As
Unit	mg/kg

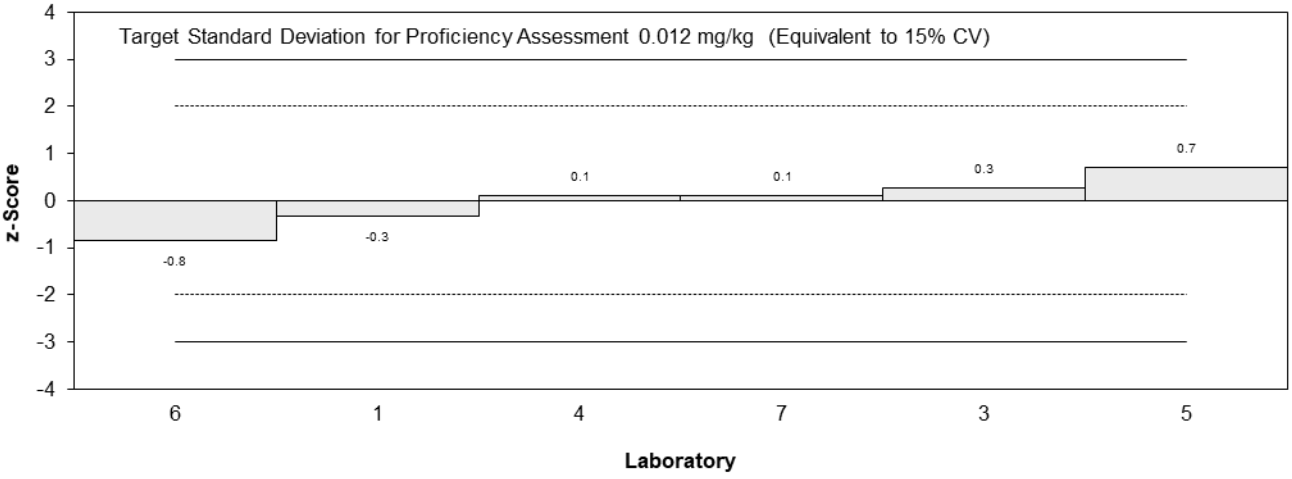
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.074	0.018	-0.33	-0.20
2	NT	NT		
3	0.081	0.020	0.27	0.15
4	0.079	0.0158	0.10	0.07
5	0.086	0.004	0.70	1.00
6	0.068	17.3	-0.84	0.00
7	0.079	0.0158	0.10	0.07
8	<0.1	NR		

Statistics

Assigned Value	0.0778	0.0072
Spike Value	0.0754	0.0021
Homogeneity Value	0.0799	0.0096
Robust Average	0.0778	0.0072
Median	0.0790	0.0053
Mean	0.0778	
N	6	
Max	0.086	
Min	0.068	
Robust SD	0.007	
Robust CV	9%	


Results: S1 - As
Assigned Value = 0.0778 ± 0.0072 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
6
1
4
7
3
5
2
8
Md
RA
HV
SV


z-Scores: S1 - As
Target Standard Deviation for Proficiency Assessment 0.012 mg/kg (Equivalent to 15% CV)
z-Score
-0.8
-0.3
0.1
0.1
0.3
0.7
Laboratory
6
1
4
7
3
5

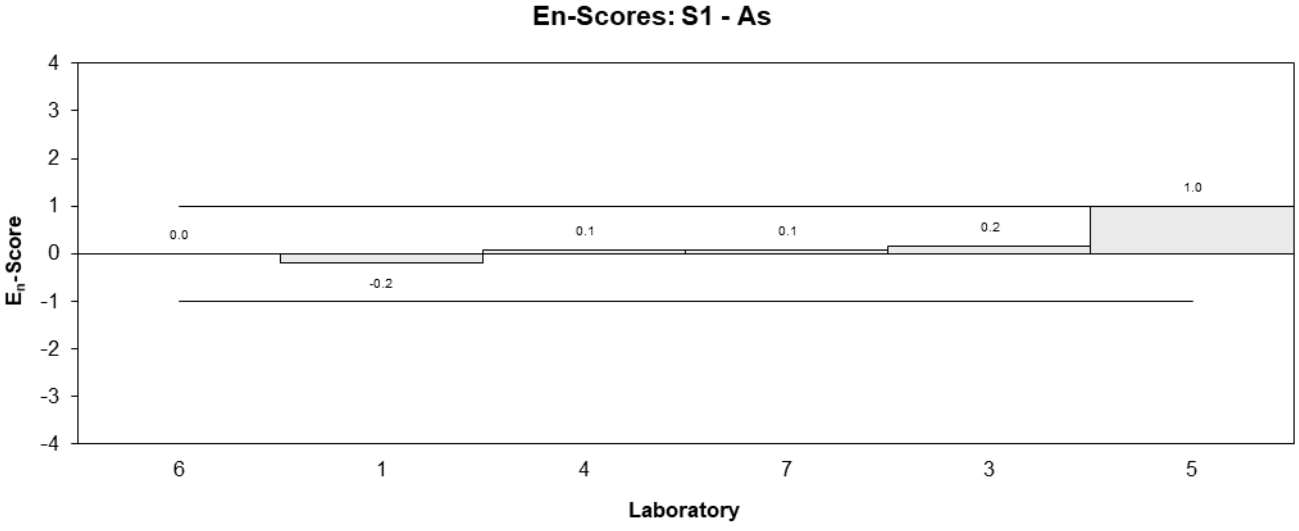

En-Scores: S1 - As
En-Score
0.0
-0.2
0.1
0.1
0.2
1.0
Laboratory
6
1
4
7
3
5

Figure 3

Table 6

Sample Details

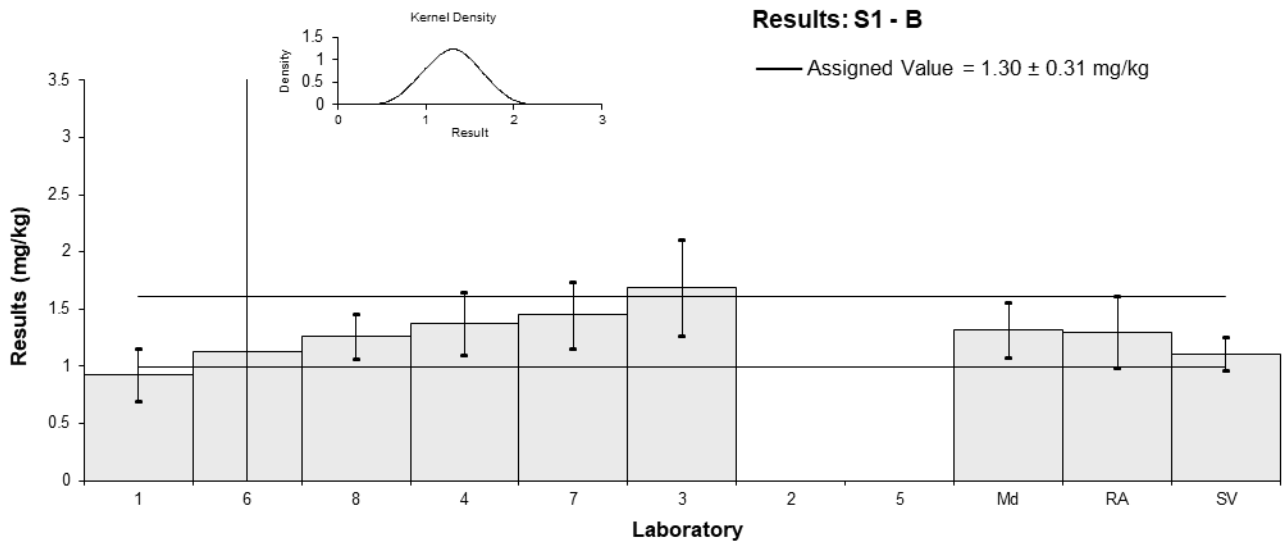
Sample No.	S1
Matrix	Celery
Analyte	B
Unit	mg/kg

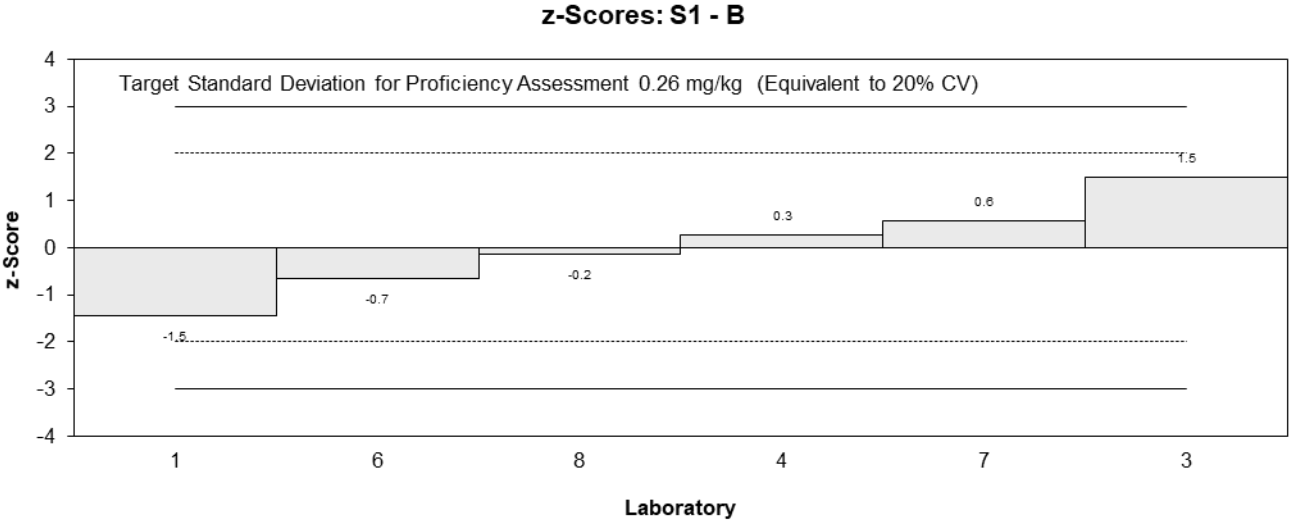
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.92	0.23	-1.46	-0.98
2	NT	NT		
3	1.69	0.4225	1.50	0.74
4	1.37	0.274	0.27	0.17
5	NR	NR		
6	1.13	18.3	-0.65	-0.01
7	1.45	0.29	0.58	0.35
8	1.26	0.20	-0.15	-0.11

Statistics

Assigned Value	1.30	0.31
Spike Value	1.11	0.15
Robust Average	1.30	0.31
Median	1.32	0.24
Mean	1.30	
N	6	
Max	1.69	
Min	0.92	
Robust SD	0.3	
Robust CV	23%	


Kernel Density
Density
Result
Results: S1 - B
Assigned Value = 1.30 ± 0.31 mg/kg
Results (mg/kg)
Laboratory
1
6
8
4
7
3
2
5
Md
RA
SV


z-Scores: S1 - B
Target Standard Deviation for Proficiency Assessment 0.26 mg/kg (Equivalent to 20% CV)
z-Score
Laboratory
-1.5
-0.7
-0.2
0.3
0.6
1.5

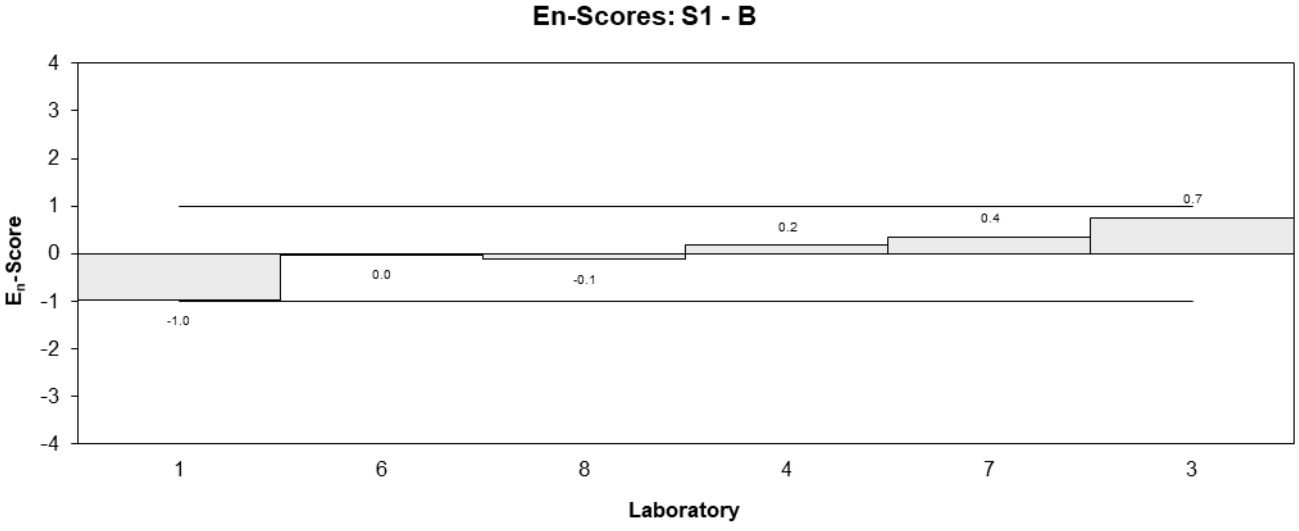

En-Scores: S1 - B
En-Score
Laboratory
-1.0
0.0
-0.1
0.2
0.4
0.7

Figure 4

Table 7

Sample Details

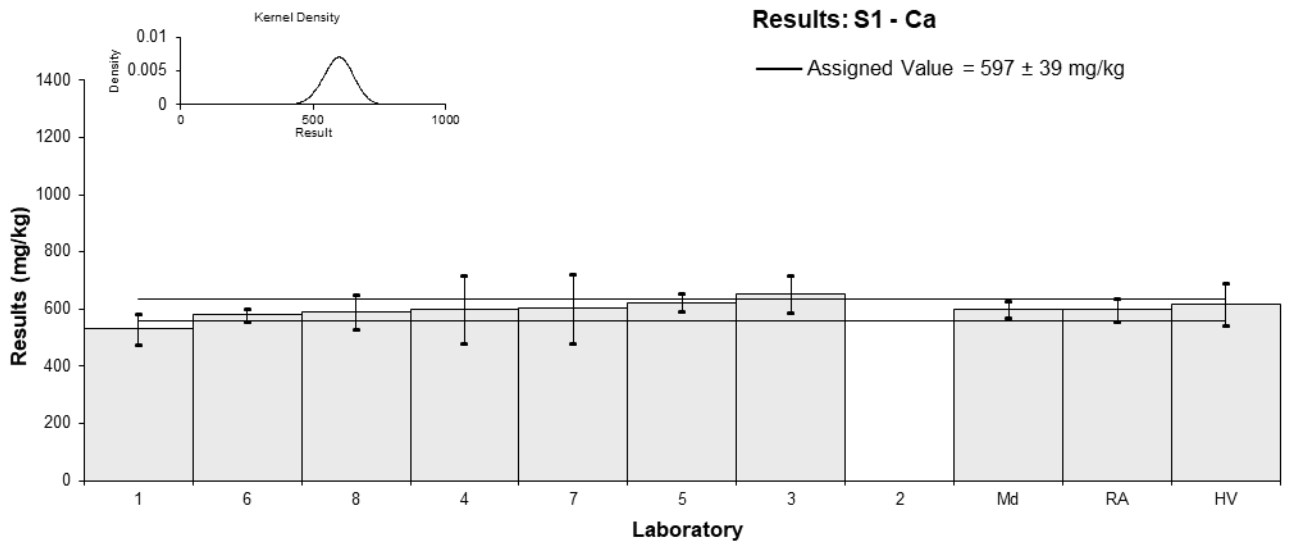
Sample No.	S1
Matrix	Celery
Analyte	Ca
Unit	mg/kg

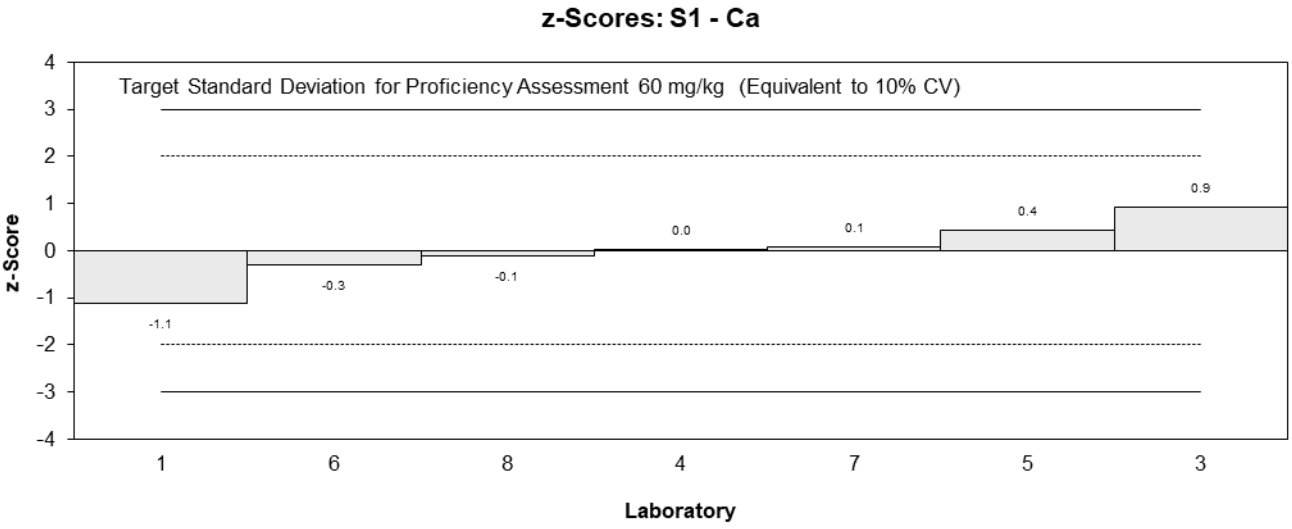
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	530	53	-1.12	-1.02
2	NT	NT		
3	652	65.2	0.92	0.72
4	599	119.8	0.03	0.02
5	623	30	0.44	0.53
6	579.02	21.3	-0.30	-0.40
7	602	120.4	0.08	0.04
8	590	60	-0.12	-0.10

Statistics

Assigned Value	597	39
Spike Value	Not Spiked	
Homogeneity Value	617	74
Robust Average	597	39
Median	599	28
Mean	596	
N	7	
Max	652	
Min	530	
Robust SD	41	
Robust CV	6.9%	


Kernel Density
Density
0.01
0.005
0
0
500
1000
Result
Results: S1 - Ca
Assigned Value = 597 ± 39 mg/kg
Results (mg/kg)
1400
1200
1000
800
600
400
200
0
1
6
8
4
7
5
3
2
Md
RA
HV
Laboratory


z-Scores: S1 - Ca
Target Standard Deviation for Proficiency Assessment 60 mg/kg (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.1
-0.3
-0.1
0.0
0.1
0.4
0.9
1
6
8
4
7
5
3
Laboratory

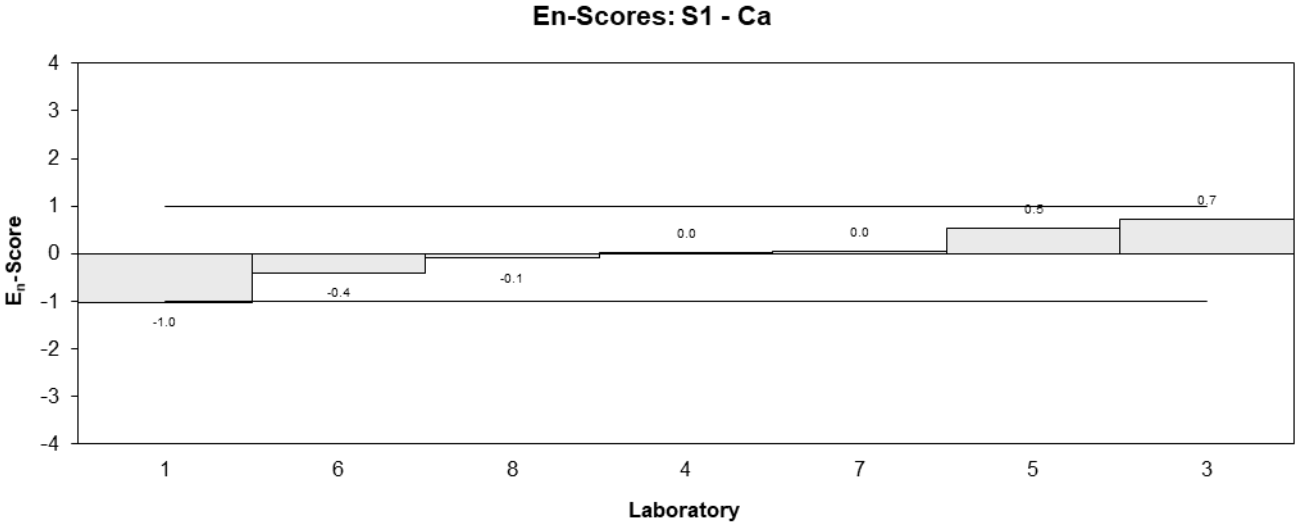

En-Scores: S1 - Ca
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.0
-0.4
-0.1
0.0
0.0
0.5
0.7
1
6
8
4
7
5
3
Laboratory

Figure 5

Table 8

Sample Details

Sample No.	S1
Matrix	Celery
Analyte	Cd
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.019	0.005	-0.59	-0.23
2	NT	NT		
3	0.020	0.005	-0.10	-0.04
4	0.020	0.004	-0.10	-0.05
5	0.022	0.002	0.89	0.74
6	0.019	22.4	-0.59	0.00
7	0.021	0.0042	0.40	0.18
8	<0.1	NR		

Statistics

Assigned Value	0.0202	0.0014
Spike Value	0.0208	0.0008
Homogeneity Value	0.0222	0.0027
Robust Average	0.0202	0.0014
Median	0.0200	0.0015
Mean	0.0202	
N	6	
Max	0.022	
Min	0.019	
Robust SD	0.0013	
Robust CV	6.6%	

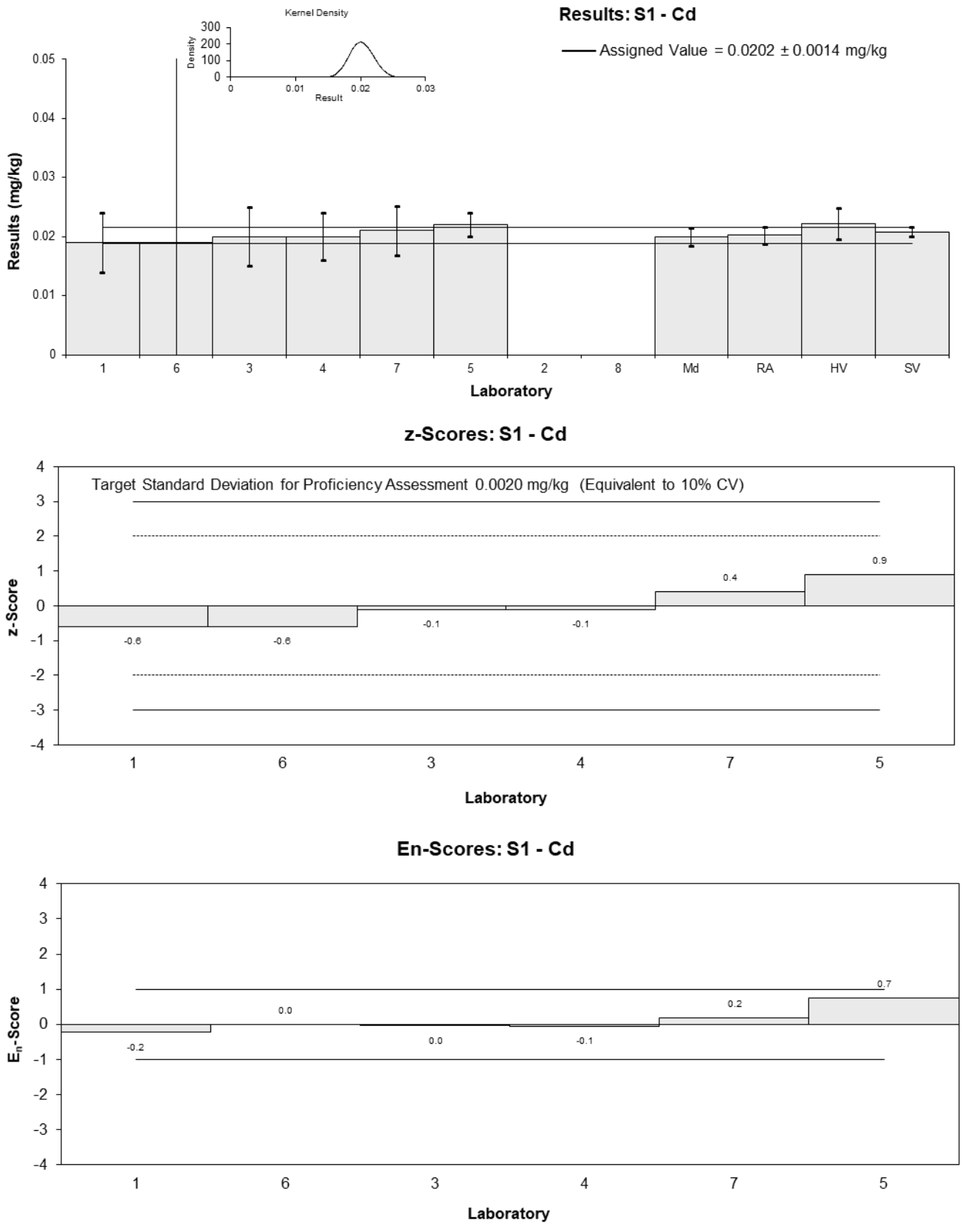

Kernel Density
Density
Result
Results: S1 - Cd
Assigned Value = 0.0202 ± 0.0014 mg/kg
Results (mg/kg)
Laboratory
1
6
3
4
7
5
2
8
Md
RA
HV
SV
z-Scores: S1 - Cd
Target Standard Deviation for Proficiency Assessment 0.0020 mg/kg (Equivalent to 10% CV)
z-Score
-0.6
-0.6
-0.1
-0.1
0.4
0.9
En-Scores: S1 - Cd
En-Score
-0.2
0.0
0.0
-0.1
0.2
0.7

Figure 6

Table 9

Sample Details

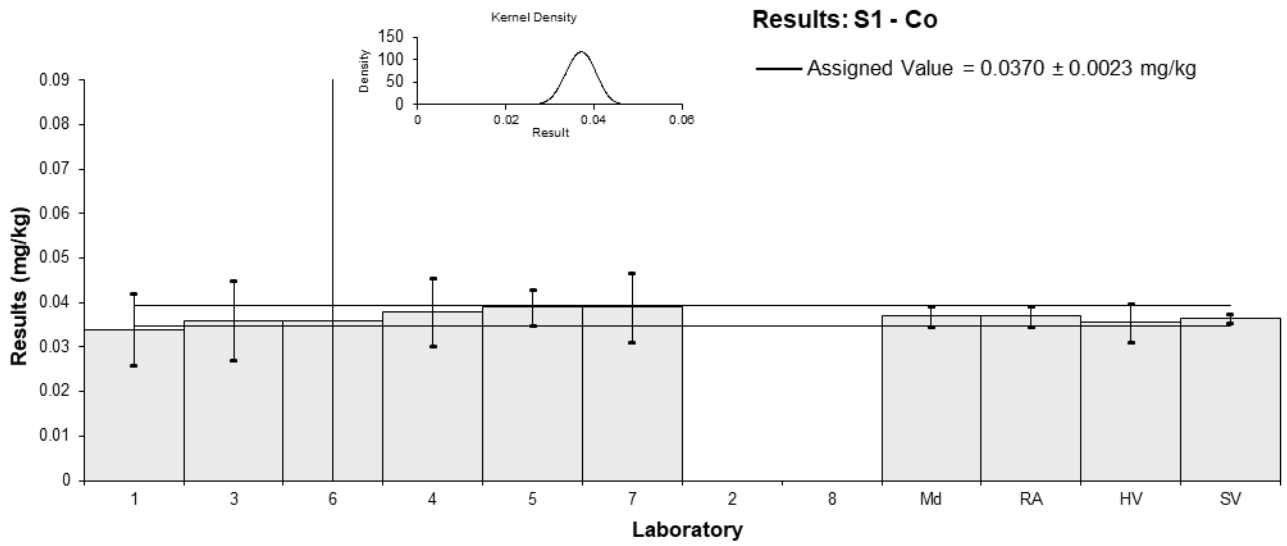
Sample No.	S1
Matrix	Celery
Analyte	Co
Unit	mg/kg

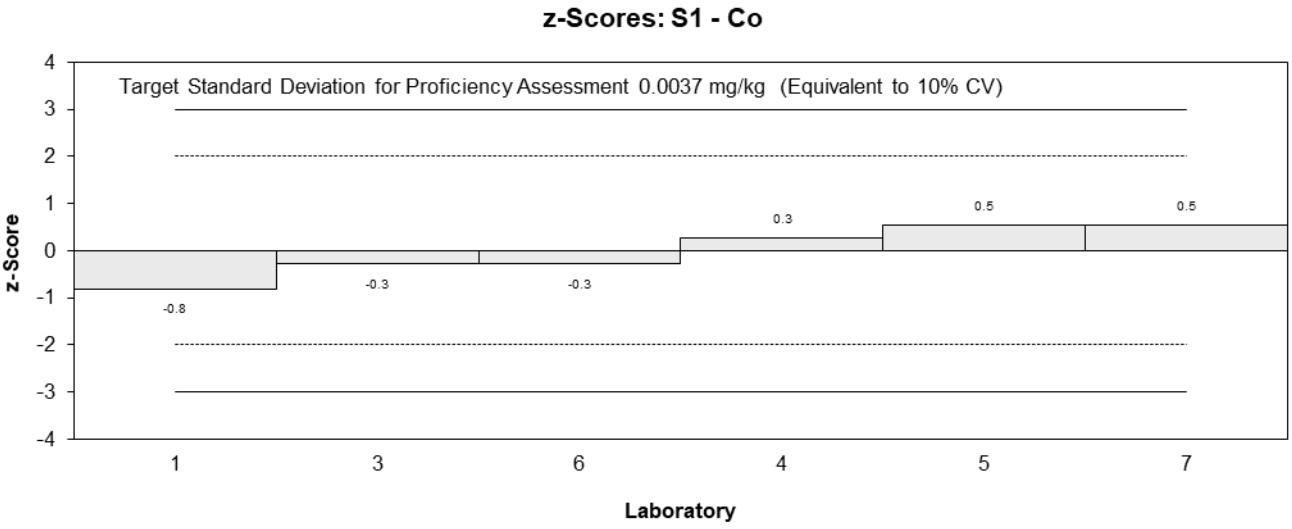
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.034	0.008	-0.81	-0.36
2	NT	NT		
3	0.036	0.009	-0.27	-0.11
4	0.038	0.0076	0.27	0.13
5	0.039	0.004	0.54	0.43
6	0.036	22.2	-0.27	0.00
7	0.039	0.0078	0.54	0.25
8	<0.1	NR		

Statistics

Assigned Value	0.0370	0.0023
Spike Value	0.0365	0.0011
Homogeneity Value	0.0355	0.0043
Robust Average	0.0370	0.0023
Median	0.0370	0.0023
Mean	0.0370	
N	6	
Max	0.039	
Min	0.034	
Robust SD	0.0023	
Robust CV	6.1%	


Kernel Density
Density
Result
Results: S1 - Co
Assigned Value = 0.0370 ± 0.0023 mg/kg
Results (mg/kg)
Laboratory
1
3
6
4
5
7
2
8
Md
RA
HV
SV


z-Scores: S1 - Co
Target Standard Deviation for Proficiency Assessment 0.0037 mg/kg (Equivalent to 10% CV)
z-Score
-0.8
-0.3
-0.3
0.3
0.5
0.5
Laboratory

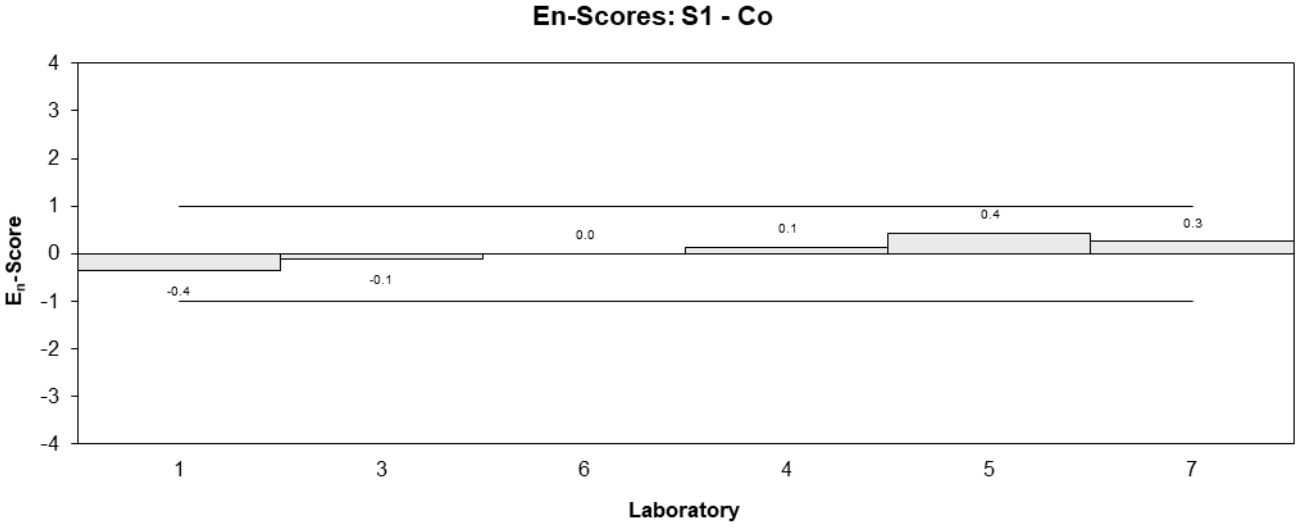

En-Scores: S1 - Co
En-Score
-0.4
-0.1
0.0
0.1
0.4
0.3
Laboratory

Figure 7

Table 10

Sample Details

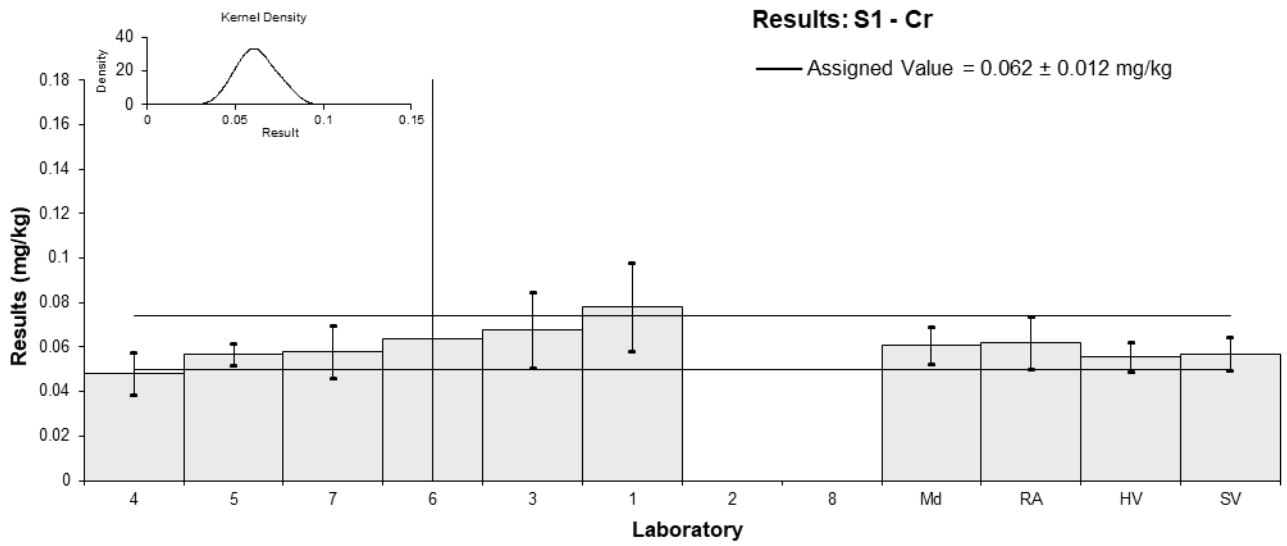
Sample No.	S1
Matrix	Celery
Analyte	Cr
Unit	mg/kg

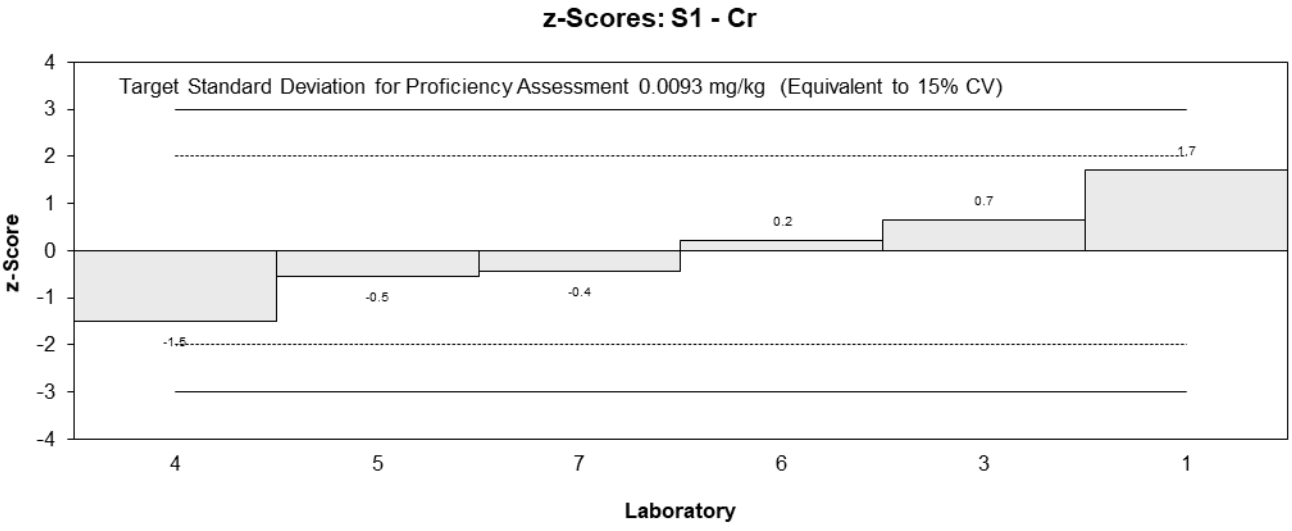
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.078	0.020	1.72	0.69
2	NT	NT		
3	0.068	0.017	0.65	0.29
4	0.048	0.0096	-1.51	-0.91
5	0.057	0.005	-0.54	-0.38
6	0.064	22.0	0.22	0.00
7	0.058	0.0116	-0.43	-0.24
8	<0.1	NR		

Statistics

Assigned Value	0.062	0.012
Spike Value	0.0571	0.0076
Homogeneity Value	0.0558	0.0067
Robust Average	0.062	0.012
Median	0.0610	0.0083
Mean	0.0622	
N	6	
Max	0.078	
Min	0.048	
Robust SD	0.012	
Robust CV	19%	


Kernel Density
Density
Result
Results: S1 - Cr
Assigned Value = 0.062 ± 0.012 mg/kg
Results (mg/kg)
Laboratory
4
5
7
6
3
1
2
8
Md
RA
HV
SV


z-Scores: S1 - Cr
Target Standard Deviation for Proficiency Assessment 0.0093 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
-1.5
-0.5
-0.4
0.2
0.7
1.7

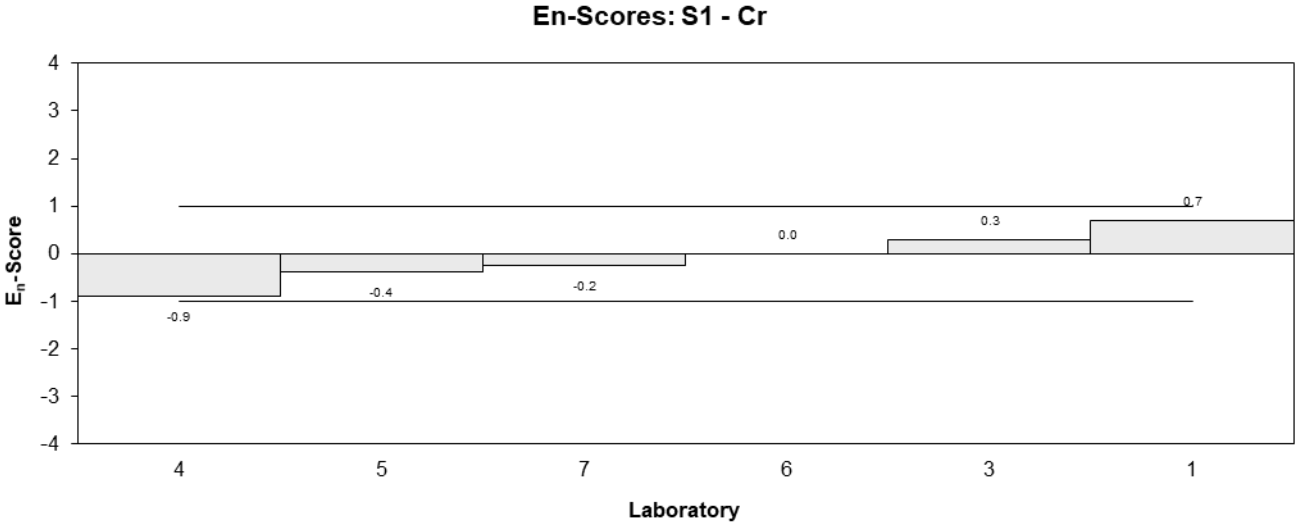

En-Scores: S1 - Cr
En-Score
Laboratory
-0.9
-0.4
-0.2
0.0
0.3
0.7

Figure 8

Table 11

Sample Details

Sample No.	S1
Matrix	Celery
Analyte	Cu
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.57	0.39	-1.28	-0.58
2	NT	NT		
3	1.82	0.455	0.11	0.04
4	1.81	0.362	0.06	0.03
5	1.80	0.09	0.00	0.00
6	1.77	11.1	-0.17	0.00
7	1.87	0.374	0.39	0.19
8	1.84	0.30	0.22	0.13

Statistics

Assigned Value	1.80	0.05
Spike Value	Not Spiked	
Homogeneity Value	1.80	0.22
Robust Average	1.80	0.05
Median	1.81	0.04
Mean	1.78	
N	7	
Max	1.87	
Min	1.57	
Robust SD	0.054	
Robust CV	3%	

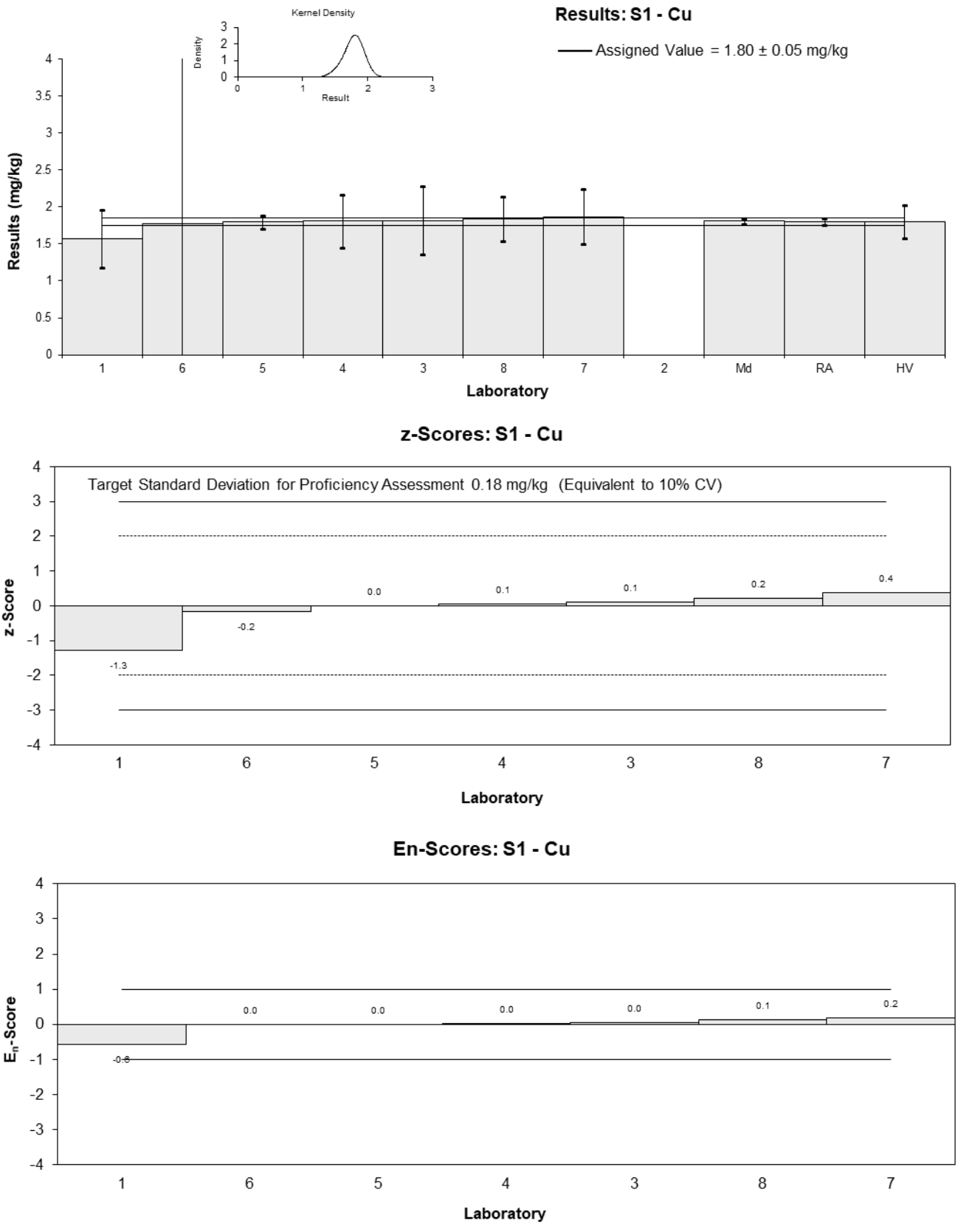

Kernel Density
Density
Result
Results: S1 - Cu
Assigned Value = 1.80 ± 0.05 mg/kg
Results (mg/kg)
Laboratory
1
6
5
4
3
8
7
2
Md
RA
HV
z-Scores: S1 - Cu
Target Standard Deviation for Proficiency Assessment 0.18 mg/kg (Equivalent to 10% CV)
z-Score
-1.3
-0.2
0.0
0.1
0.1
0.2
0.4
Laboratory
En-Scores: S1 - Cu
En-Score
-0.6
0.0
0.0
0.0
0.0
0.1
0.2
Laboratory

Figure 9

Table 12

Sample Details

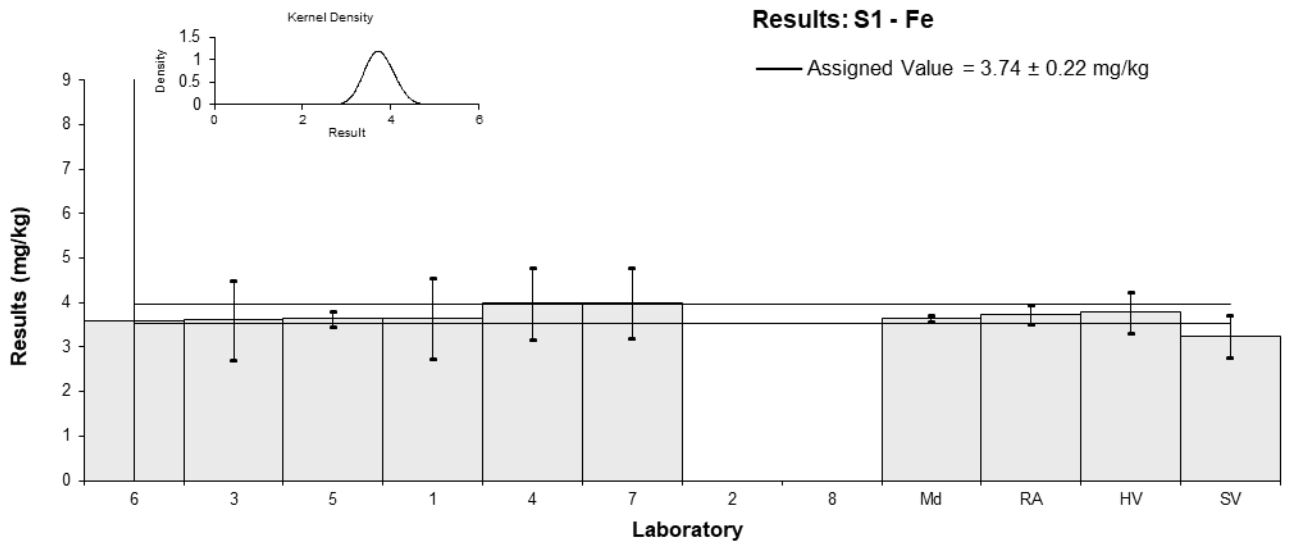
Sample No.	S1
Matrix	Celery
Analyte	Fe
Unit	mg/kg

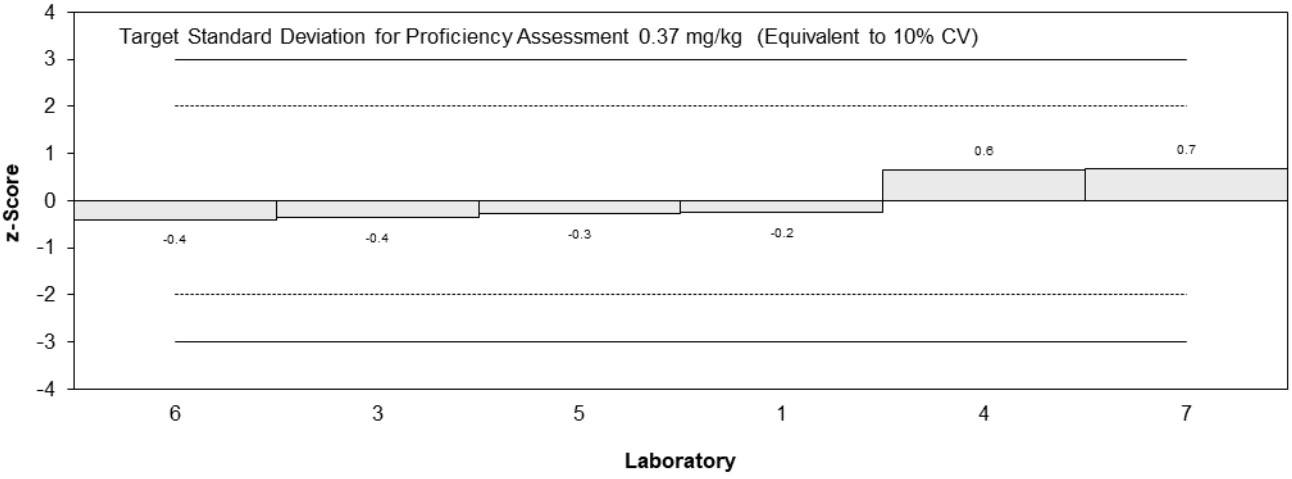
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	3.65	0.90	-0.24	-0.10
2	NT	NT		
3	3.61	0.903	-0.35	-0.14
4	3.98	0.796	0.64	0.29
5	3.64	0.18	-0.27	-0.35
6	3.59	17.7	-0.40	-0.01
7	3.99	0.798	0.67	0.30
8	NT	NT		

Statistics

Assigned Value	3.74	0.22
Spike Value	3.25	0.48
Homogeneity Value	3.78	0.45
Robust Average	3.74	0.22
Median	3.65	0.07
Mean	3.74	
N	6	
Max	3.99	
Min	3.59	
Robust SD	0.21	
Robust CV	5.7%	


Kernel Density
Density
Result
Results: S1 - Fe
Assigned Value = 3.74 ± 0.22 mg/kg
Results (mg/kg)
Laboratory
6
3
5
1
4
7
2
8
Md
RA
HV
SV


z-Scores: S1 - Fe
Target Standard Deviation for Proficiency Assessment 0.37 mg/kg (Equivalent to 10% CV)
z-Score
-0.4
-0.4
-0.3
-0.2
0.6
0.7
Laboratory
6
3
5
1
4
7

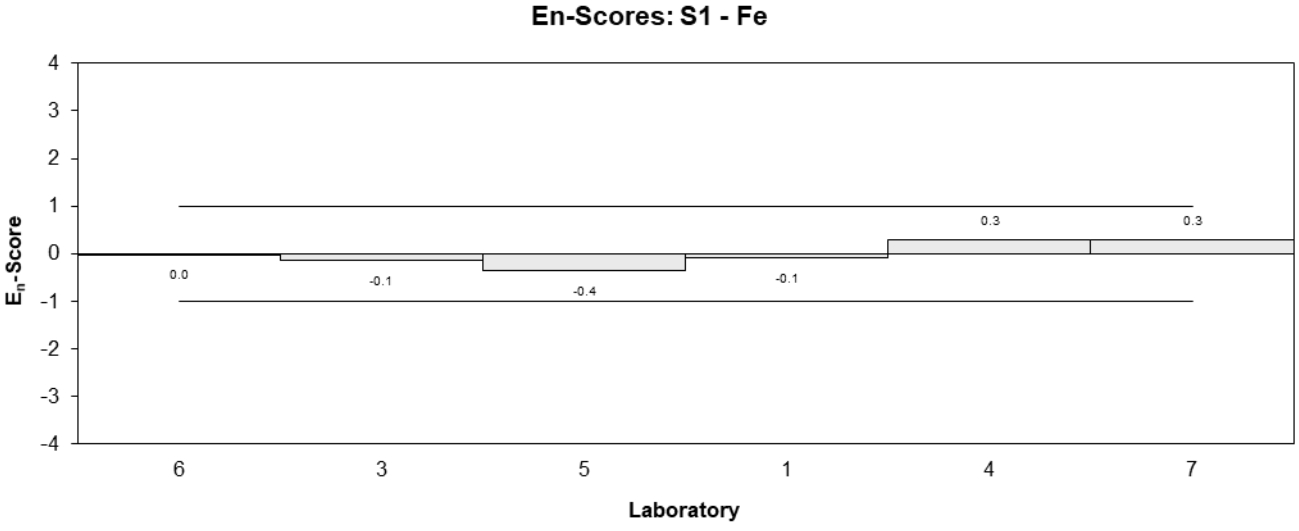

En-Scores: S1 - Fe
En-Score
0.0
-0.1
-0.4
-0.1
0.3
0.3
Laboratory
6
3
5
1
4
7

Figure 10

Table 13

Sample Details

Sample No.	S1
Matrix	Celery
Analyte	Hg
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty
1	0.022	0.005
2	NT	NT
3	<0.100	0.025
4	0.026	0.0052
5	0.022	0.002
6	0.019964	27.2
7	0.027	0.0054
8	0.05	0.01

Statistics

Assigned Value	Not Set	
Spike Value	0.0262	0.0008
Homogeneity Value	0.0257	0.0031
Robust Average	0.0250	0.0056
Median	0.0240	0.0038
Mean	0.0278	
N	6	
Max	0.05	
Min	0.019964	
Robust SD	0.0054	
Robust CV	22%	

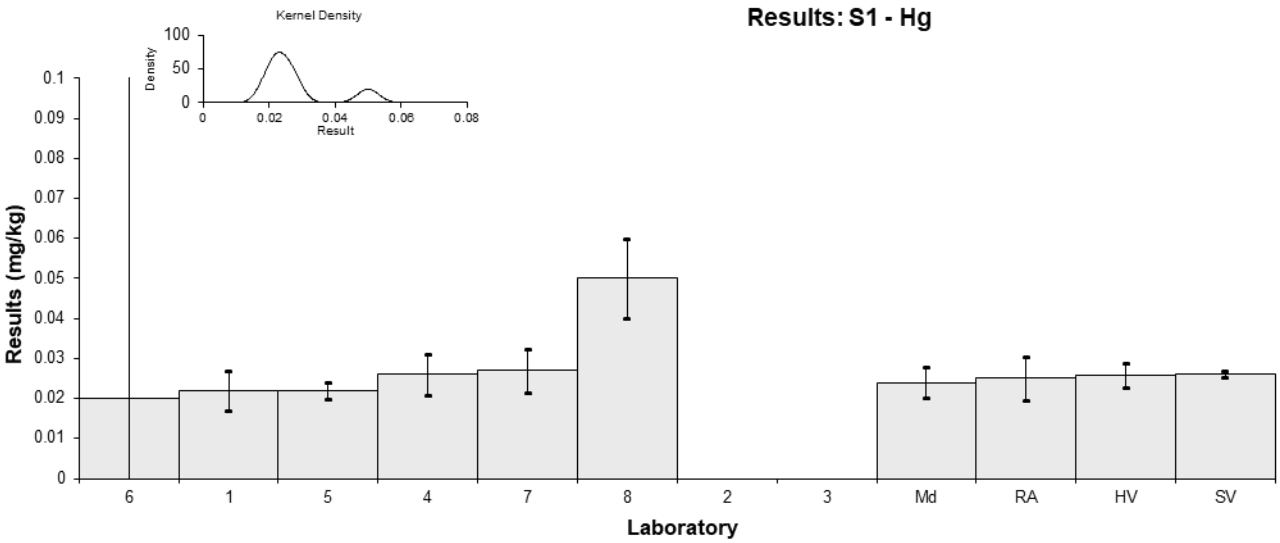

Results: S1 - Hg
Kernel Density
Density
100
50
0
0
0.02
0.04
0.06
0.08
Result
Results (mg/kg)
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
6
1
5
4
7
8
2
3
Md
RA
HV
SV
Laboratory

Figure 11

Table 14

Sample Details

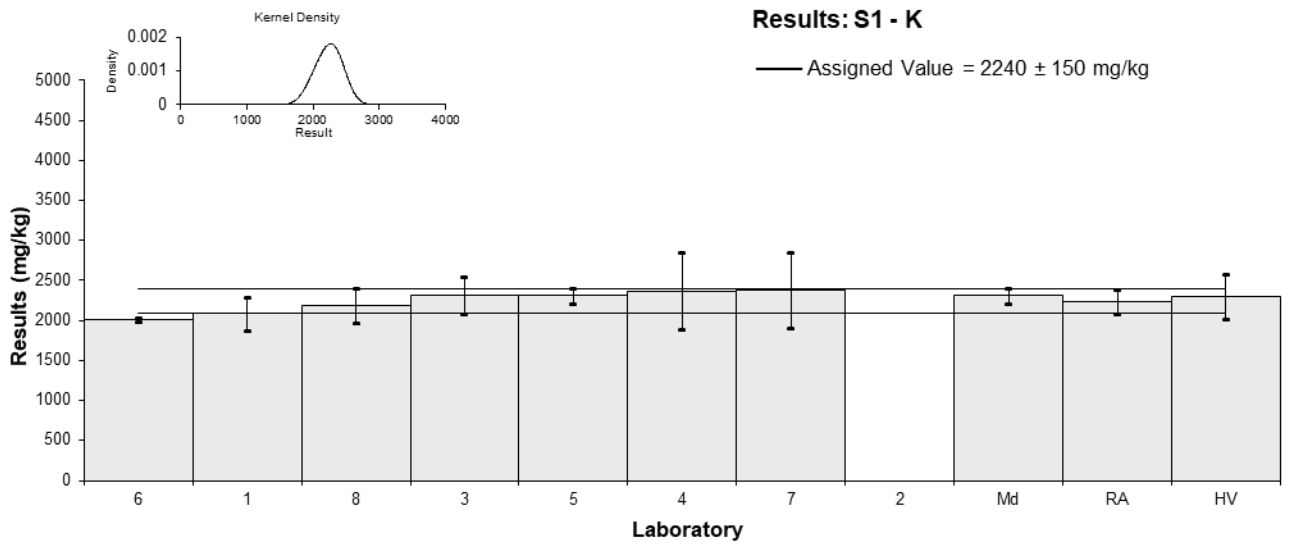
Sample No.	S1
Matrix	Celery
Analyte	K
Unit	mg/kg

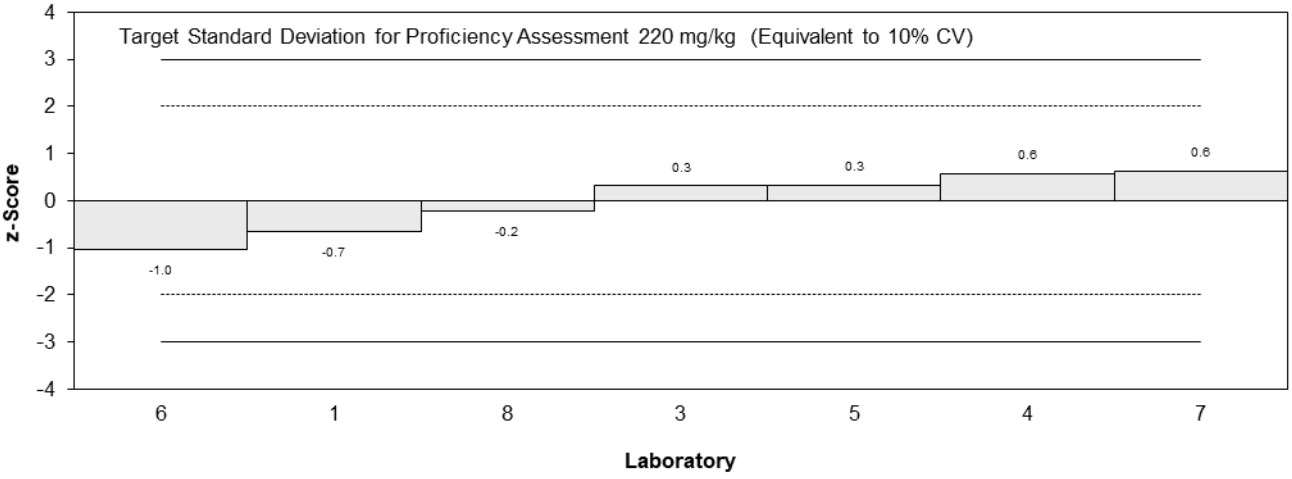
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2090	209	-0.67	-0.58
2	NT	NT		
3	2310	231	0.31	0.25
4	2370	474	0.58	0.26
5	2311	100	0.32	0.39
6	2009.59	25.6	-1.03	-1.51
7	2380	476	0.62	0.28
8	2190	220	-0.22	-0.19

Statistics

Assigned Value	2240	150
Spike Value	Not Spiked	
Homogeneity Value	2300	280
Robust Average	2240	150
Median	2310	100
Mean	2240	
N	7	
Max	2380	
Min	2009.59	
Robust SD	160	
Robust CV	7.3%	


Kernel Density
Density
0.002
0.001
0
0
1000
2000
3000
4000
Result
Results: S1 - K
Assigned Value = 2240 ± 150 mg/kg
Results (mg/kg)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
6
1
8
3
5
4
7
2
Md
RA
HV
Laboratory


z-Scores: S1 - K
Target Standard Deviation for Proficiency Assessment 220 mg/kg (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.0
-0.7
-0.2
0.3
0.3
0.6
0.6
6
1
8
3
5
4
7
Laboratory

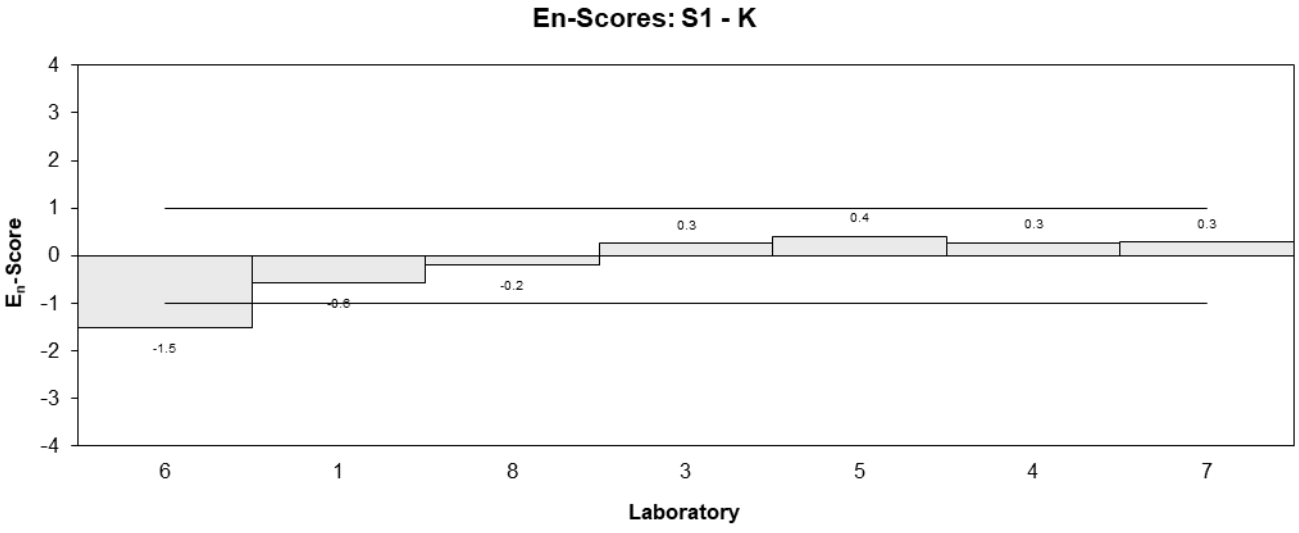

En-Scores: S1 - K
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.5
-0.6
-0.2
0.3
0.4
0.3
0.3
6
1
8
3
5
4
7
Laboratory

Figure 12

Table 15

Sample Details

Sample No.	S1
Matrix	Celery
Analyte	Mg
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	91.8	9.2	-1.26	-1.08
2	NT	NT		
3	113	11.3	0.76	0.58
4	101	20.2	-0.38	-0.18
5	114	5	0.86	0.95
6	103.18	19.2	-0.17	-0.09
7	104	20.8	-0.10	-0.04
8	109	11	0.38	0.29

Statistics

Assigned Value	105	8
Spike Value	Not Spiked	
Homogeneity Value	105	13
Robust Average	105	8
Median	104	7
Mean	105	
N	7	
Max	114	
Min	91.8	
Robust SD	8.5	
Robust CV	8.1%	

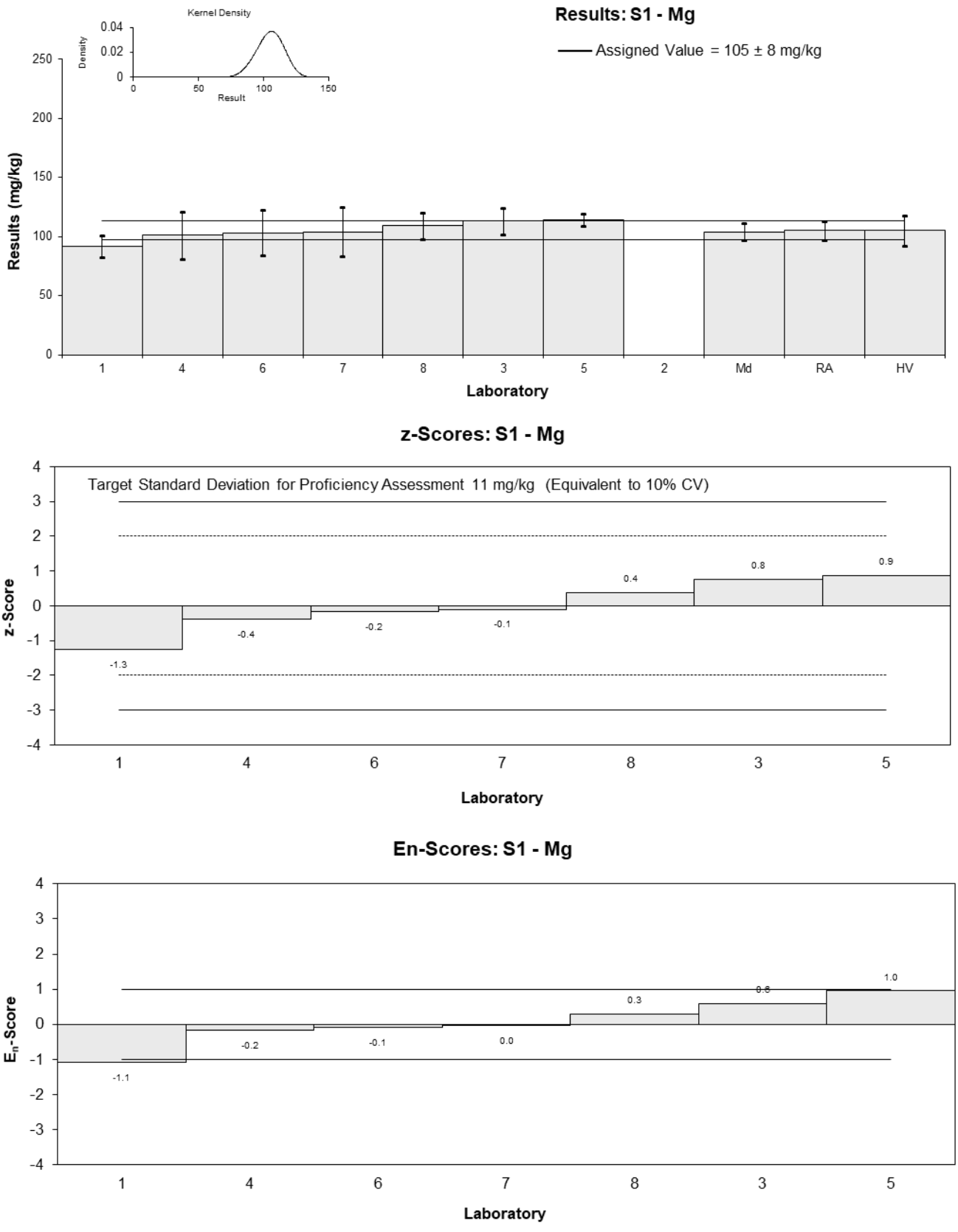

Kernel Density
Density
0.04
0.02
0
0
50
100
150
Result
Results: S1 - Mg
Assigned Value = 105 ± 8 mg/kg
Results (mg/kg)
250
200
150
100
50
0
1
4
6
7
8
3
5
2
Md
RA
HV
Laboratory
z-Scores: S1 - Mg
Target Standard Deviation for Proficiency Assessment 11 mg/kg (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.3
-0.4
-0.2
-0.1
0.4
0.8
0.9
1
4
6
7
8
3
5
Laboratory
En-Scores: S1 - Mg
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.1
-0.2
-0.1
0.0
0.3
0.6
1.0
1
4
6
7
8
3
5
Laboratory

Figure 13

Table 16

Sample Details

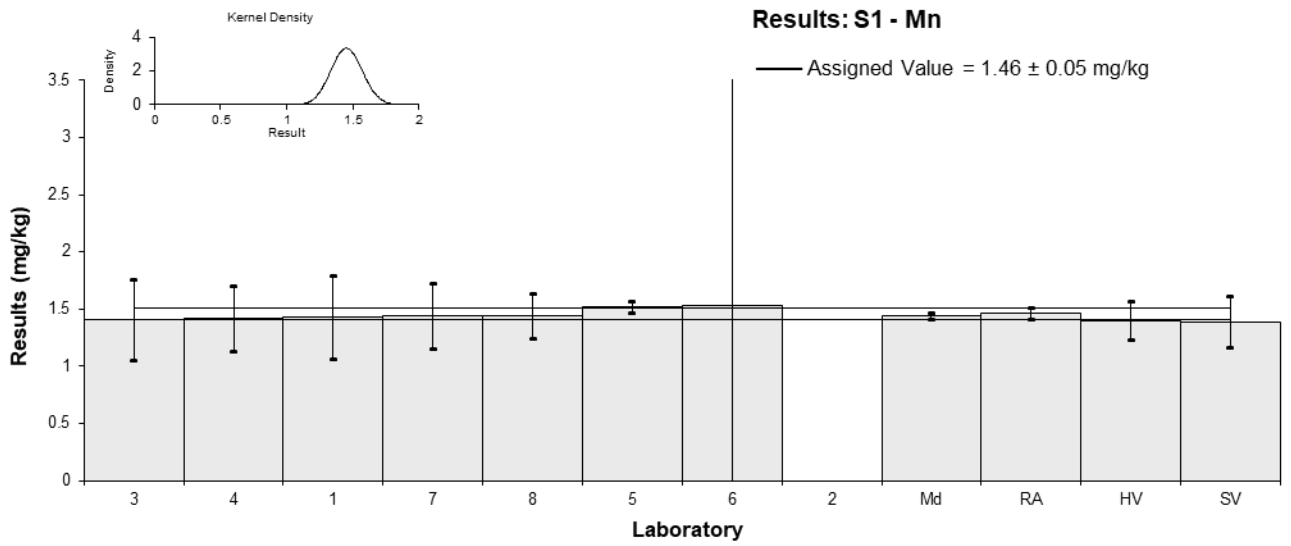
Sample No.	S1
Matrix	Celery
Analyte	Mn
Unit	mg/kg

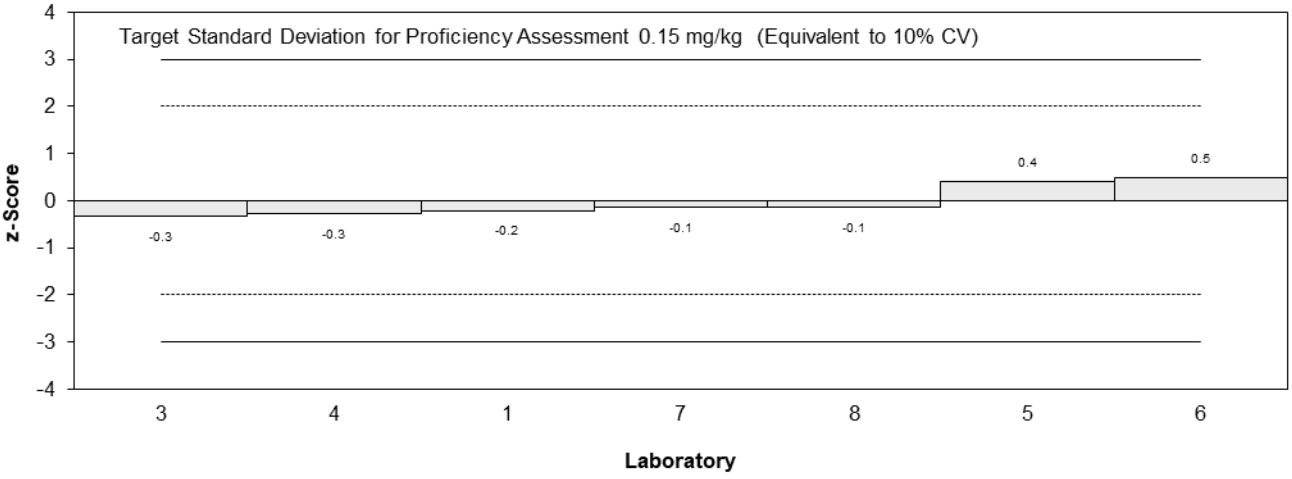
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.43	0.36	-0.21	-0.08
2	NT	NT		
3	1.41	0.353	-0.34	-0.14
4	1.42	0.284	-0.27	-0.14
5	1.52	0.05	0.41	0.85
6	1.53	16.6	0.48	0.00
7	1.44	0.288	-0.14	-0.07
8	1.44	0.20	-0.14	-0.10

Statistics

Assigned Value	1.46	0.05
Spike Value	1.39	0.22
Homogeneity Value	1.40	0.17
Robust Average	1.46	0.05
Median	1.44	0.03
Mean	1.46	
N	7	
Max	1.53	
Min	1.41	
Robust SD	0.055	
Robust CV	3.8%	


Kernel Density
Density
Result
Results: S1 - Mn
Assigned Value = 1.46 ± 0.05 mg/kg
Results (mg/kg)
Laboratory
3
4
1
7
8
5
6
2
Md
RA
HV
SV


z-Scores: S1 - Mn
Target Standard Deviation for Proficiency Assessment 0.15 mg/kg (Equivalent to 10% CV)
z-Score
Laboratory
-0.3
-0.3
-0.2
-0.1
-0.1
0.4
0.5

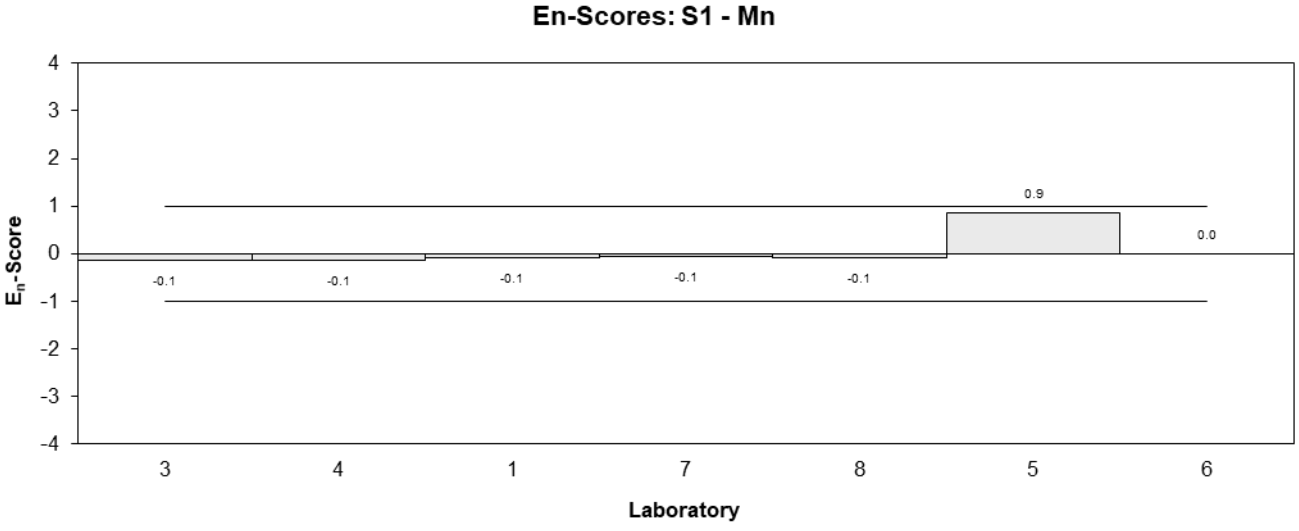

En-Scores: S1 - Mn
En-Score
Laboratory
-0.1
-0.1
-0.1
-0.1
-0.1
0.9
0.0

Figure 14

Table 17

Sample Details

Sample No.	S1
Matrix	Celery
Analyte	Mo
Unit	mg/kg

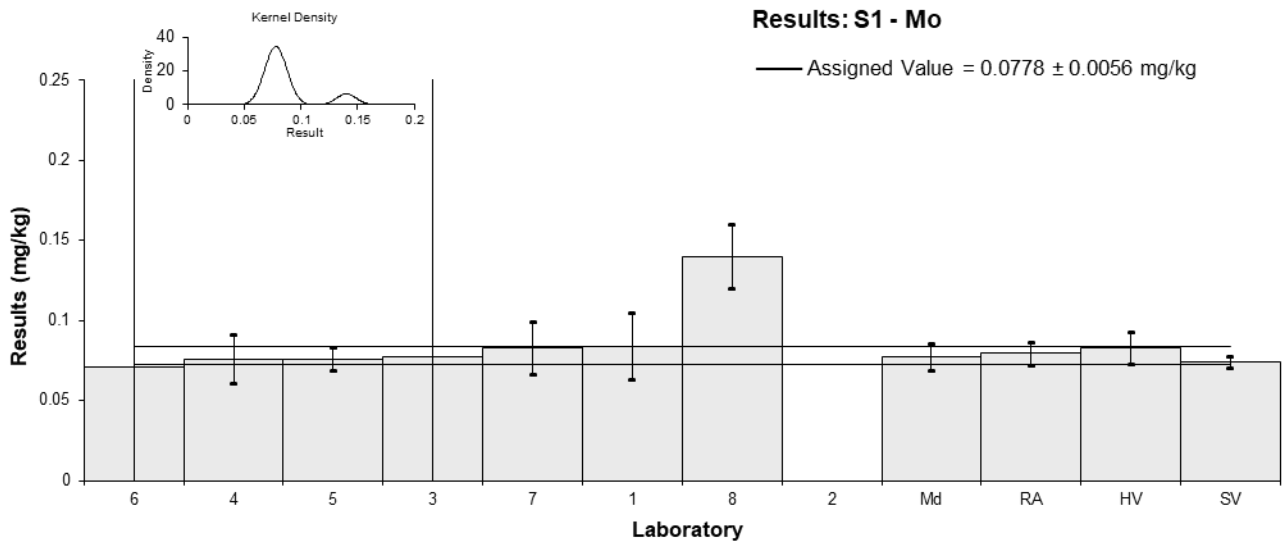
Participant Results

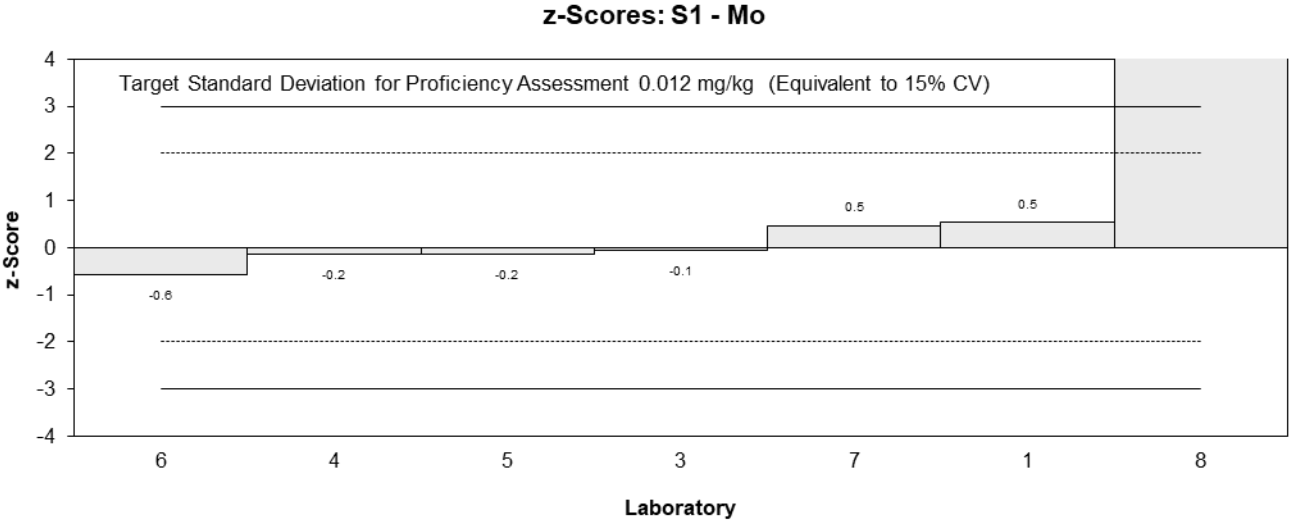
Lab. Code	Result	Uncertainty	z	E_n
1	0.084	0.021	0.53	0.29
2	NT	NT		
3	0.077	0.308	-0.07	0.00
4	0.076	0.0152	-0.15	-0.11
5	0.076	0.007	-0.15	-0.20
6	0.071	16.2	-0.58	0.00
7	0.083	0.0166	0.45	0.30
8*	0.14	0.02	5.33	2.99

* Outlier, see Section 4.2

Statistics

Assigned Value	0.0778	0.0056
Spike Value	0.0740	0.0035
Homogeneity Value	0.0827	0.0099
Robust Average	0.0797	0.0072
Median	0.0770	0.0084
Mean	0.087	
N	7	
Max	0.14	
Min	0.071	
Robust SD	0.0076	
Robust CV	9.6%	


Results: S1 - Mo
Assigned Value = 0.0778 ± 0.0056 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
6
4
5
3
7
1
8
2
Md
RA
HV
SV


z-Scores: S1 - Mo
Target Standard Deviation for Proficiency Assessment 0.012 mg/kg (Equivalent to 15% CV)
z-Score
-0.6
-0.2
-0.2
-0.1
0.5
0.5
Laboratory

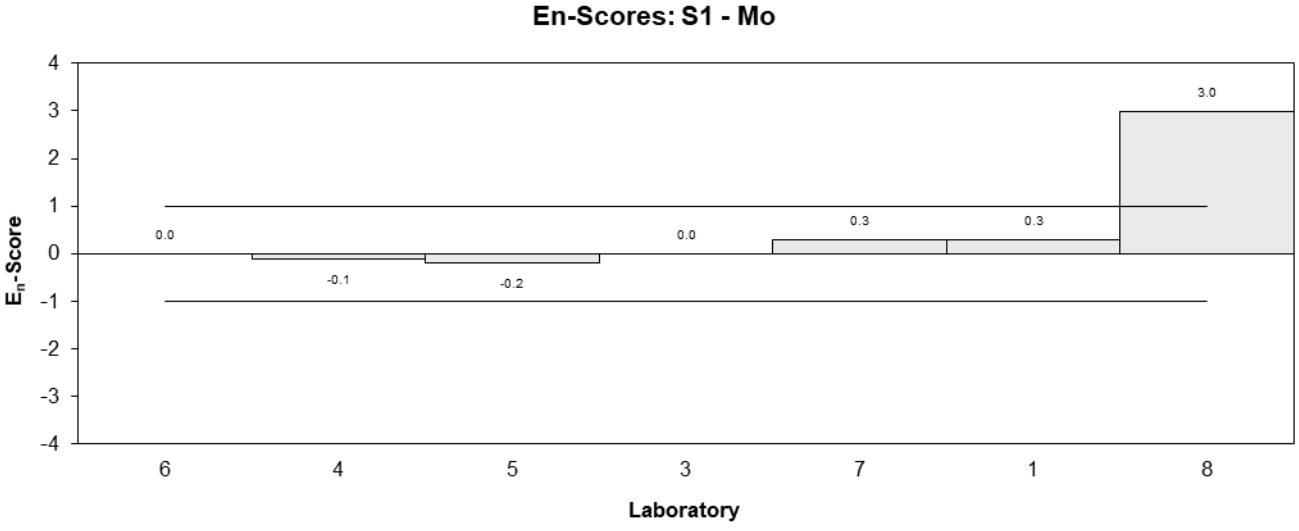

En-Scores: S1 - Mo
En-Score
0.0
-0.1
-0.2
0.0
0.3
0.3
3.0
Laboratory

Figure 15

Table 18

Sample Details

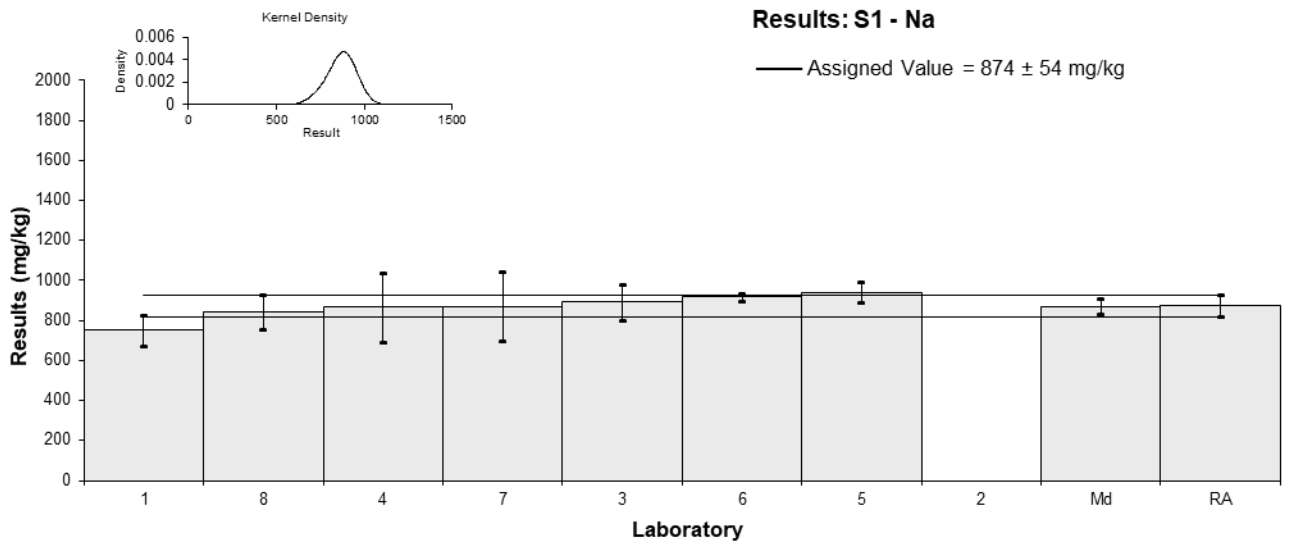
Sample No.	S1
Matrix	Celery
Analyte	Na
Unit	mg/kg

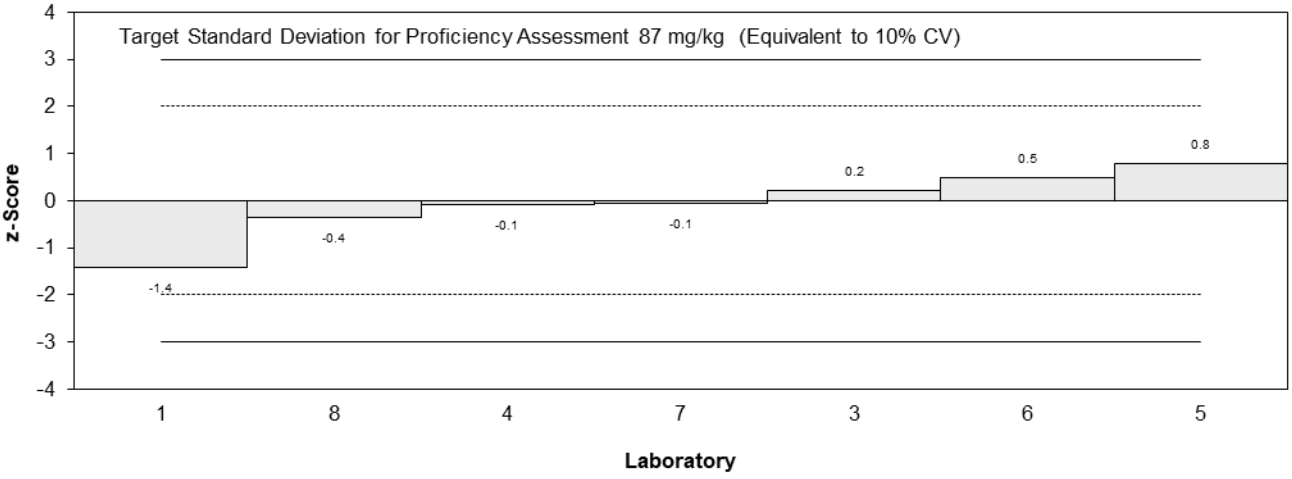
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	750	75	-1.42	-1.34
2	NT	NT		
3	892	89.2	0.21	0.17
4	867	173.4	-0.08	-0.04
5	942	50	0.78	0.92
6	916.46	18.7	0.49	0.74
7	870	174	-0.05	-0.02
8	842	85	-0.37	-0.32

Statistics

Assigned Value	874	54
Spike Value	Not Spiked	
Robust Average	874	54
Median	870	39
Mean	868	
N	7	
Max	942	
Min	750	
Robust SD	57	
Robust CV	6.5%	


Kernel Density
Density
0.006
0.004
0.002
0
0
500
1000
1500
Result
Results: S1 - Na
Assigned Value = 874 ± 54 mg/kg
Results (mg/kg)
2000
1800
1600
1400
1200
1000
800
600
400
200
0
1
8
4
7
3
6
5
2
Md
RA
Laboratory


z-Scores: S1 - Na
Target Standard Deviation for Proficiency Assessment 87 mg/kg (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.4
-0.4
-0.1
-0.1
0.2
0.5
0.8
1
8
4
7
3
6
5
Laboratory

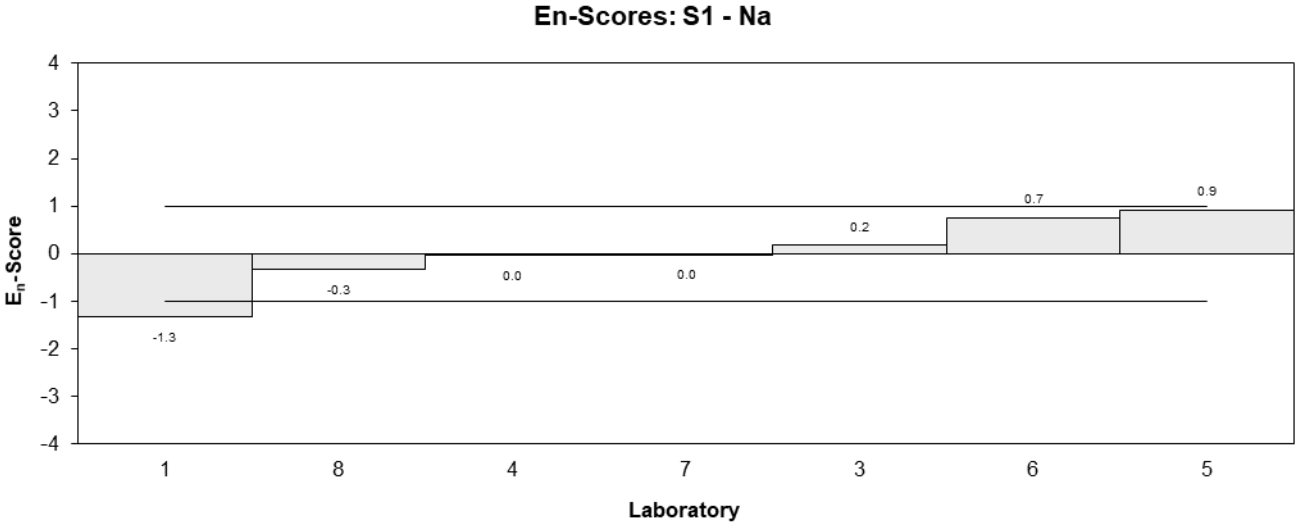

En-Scores: S1 - Na
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.3
-0.3
0.0
0.0
0.2
0.7
0.9
1
8
4
7
3
6
5
Laboratory

Figure 16

Table 19

Sample Details

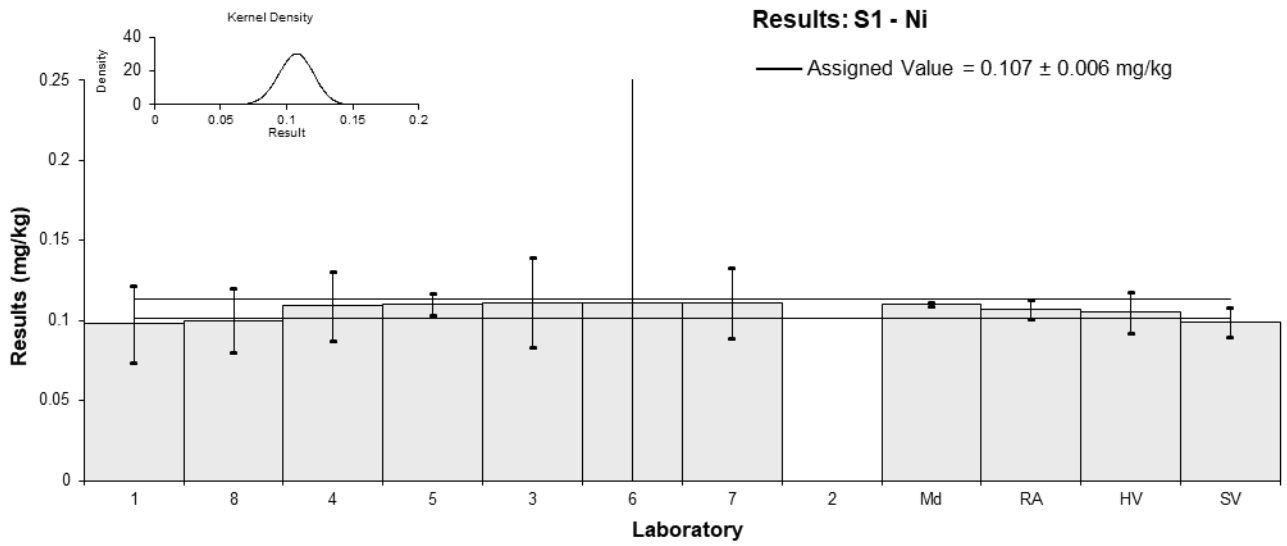
Sample No.	S1
Matrix	Celery
Analyte	Ni
Unit	mg/kg

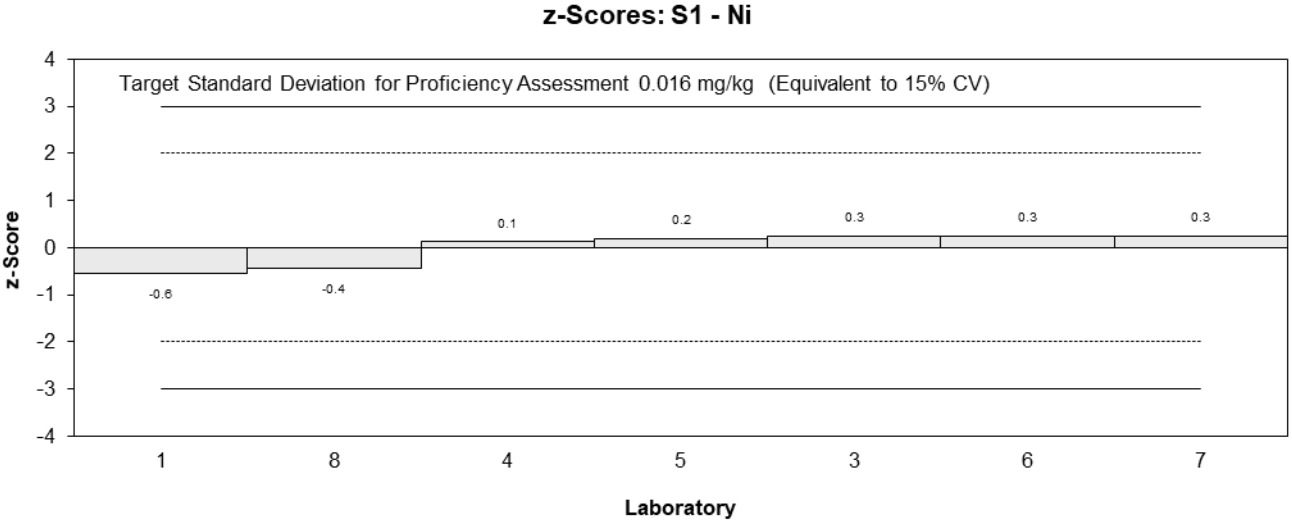
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.098	0.024	-0.56	-0.36
2	NT	NT		
3	0.111	0.028	0.25	0.14
4	0.109	0.0218	0.12	0.09
5	0.110	0.007	0.19	0.33
6	0.111	23.8	0.25	0.00
7	0.111	0.0222	0.25	0.17
8	0.10	0.02	-0.44	-0.34

Statistics

Assigned Value	0.107	0.006
Spike Value	0.0989	0.0092
Homogeneity Value	0.105	0.013
Robust Average	0.107	0.006
Median	0.110	0.001
Mean	0.107	
N	7	
Max	0.111	
Min	0.098	
Robust SD	0.0064	
Robust CV	6%	


Kernel Density
Density
Result
Results: S1 - Ni
Assigned Value = 0.107 ± 0.006 mg/kg
Results (mg/kg)
Laboratory
1
8
4
5
3
6
7
2
Md
RA
HV
SV


z-Scores: S1 - Ni
Target Standard Deviation for Proficiency Assessment 0.016 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
-0.6
-0.4
0.1
0.2
0.3
0.3
0.3

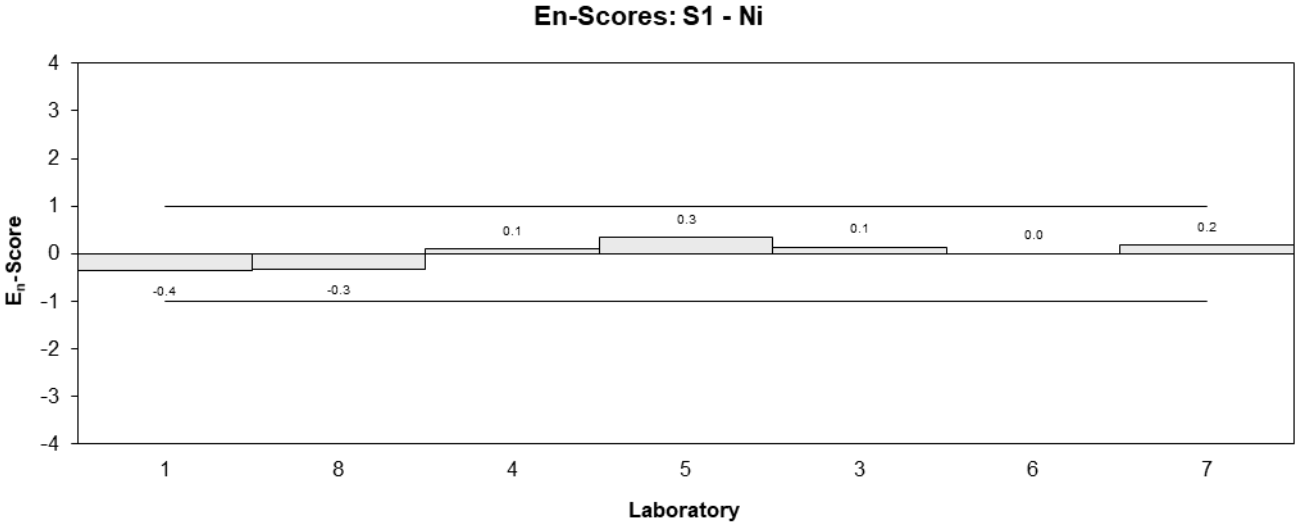

En-Scores: S1 - Ni
En-Score
Laboratory
-0.4
-0.3
0.1
0.3
0.1
0.0
0.2

Figure 17

Table 20

Sample Details

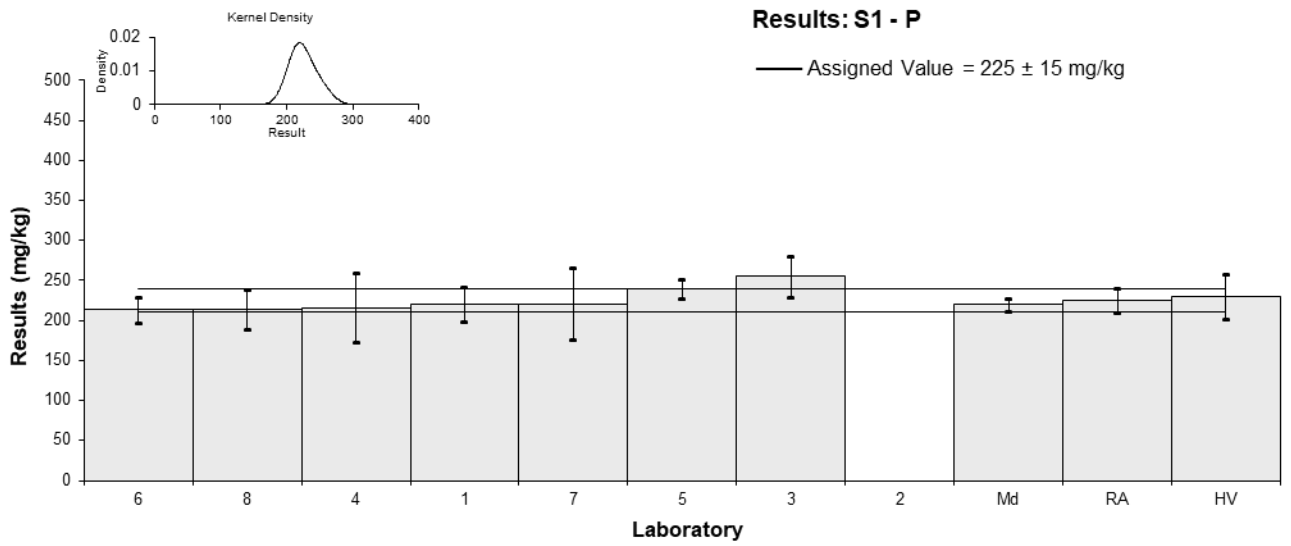
Sample No.	S1
Matrix	Celery
Analyte	P
Unit	mg/kg

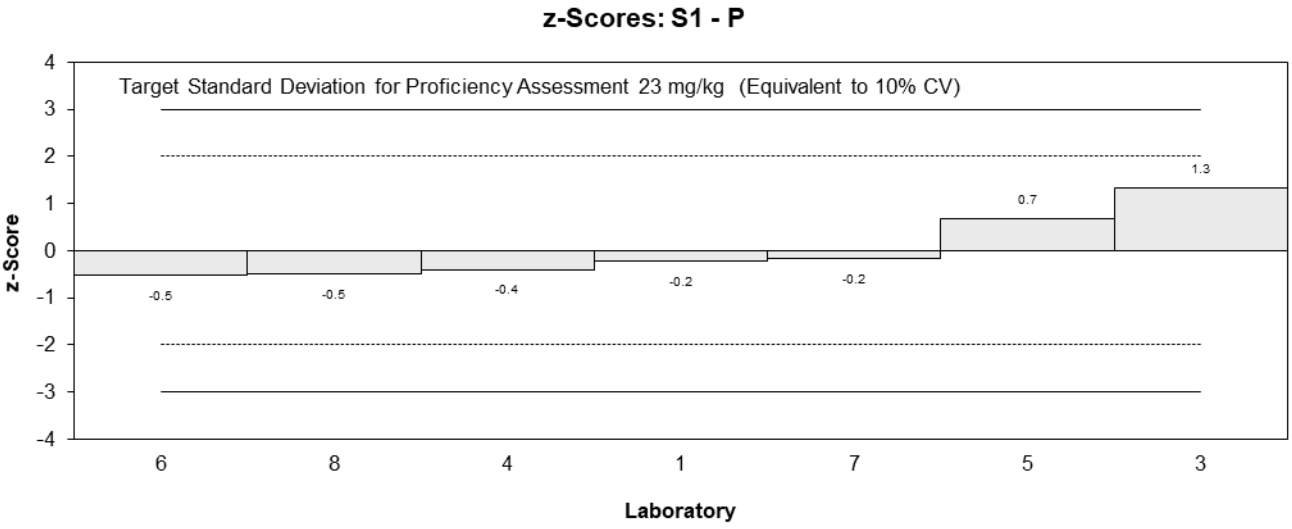
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	220	22	-0.22	-0.19
2	NT	NT		
3	255	25.5	1.33	1.01
4	216	43.2	-0.40	-0.20
5	240	12	0.67	0.78
6	213.30	15.9	-0.52	-0.54
7	221	44.2	-0.18	-0.09
8	214	25	-0.49	-0.38

Statistics

Assigned Value	225	15
Spike Value	Not Spiked	
Homogeneity Value	230	28
Robust Average	225	15
Median	220	8
Mean	226	
N	7	
Max	255	
Min	213.3	
Robust SD	16	
Robust CV	6.9%	


Kernel Density
Density
0.02
0.01
0
0
100
200
300
400
Result
Results: S1 - P
Assigned Value = 225 ± 15 mg/kg
Results (mg/kg)
500
450
400
350
300
250
200
150
100
50
0
6
8
4
1
7
5
3
2
Md
RA
HV
Laboratory


z-Scores: S1 - P
Target Standard Deviation for Proficiency Assessment 23 mg/kg (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.5
-0.5
-0.4
-0.2
-0.2
0.7
1.3
6
8
4
1
7
5
3
Laboratory

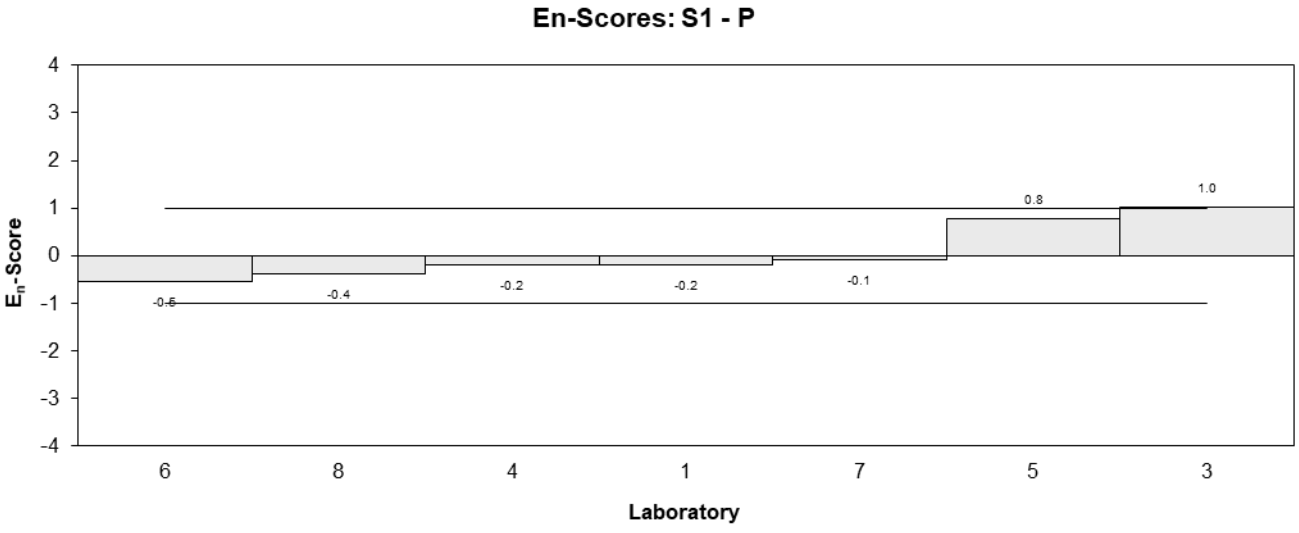

En-Scores: S1 - P
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.5
-0.4
-0.2
-0.2
-0.1
0.8
1.0
6
8
4
1
7
5
3
Laboratory

Figure 18

Table 21

Sample Details

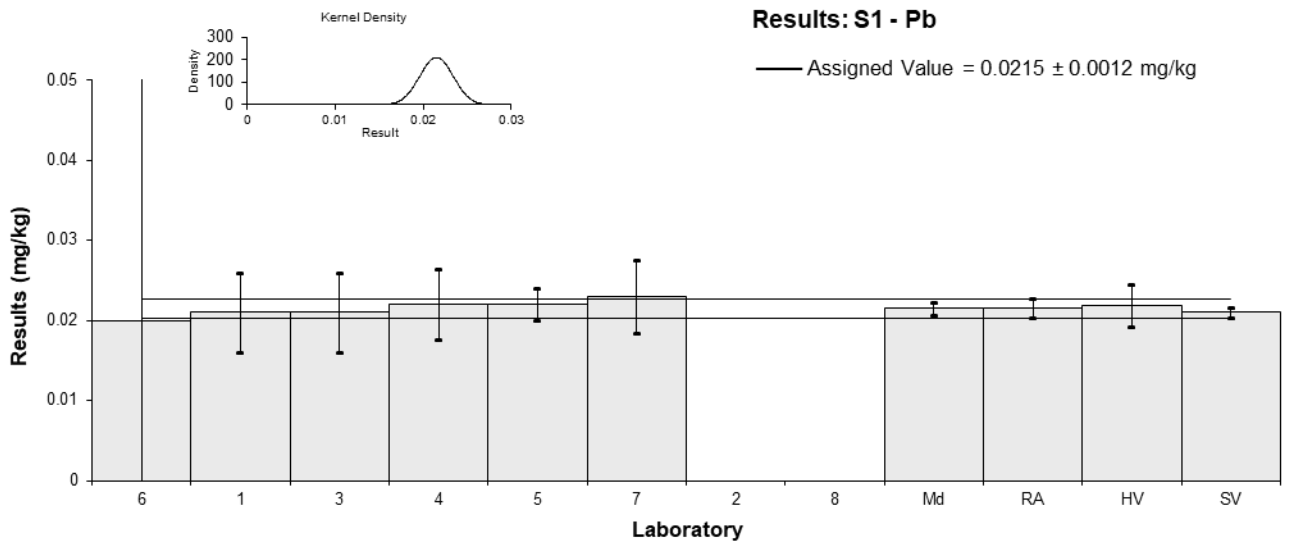
Sample No.	S1
Matrix	Celery
Analyte	Pb
Unit	mg/kg

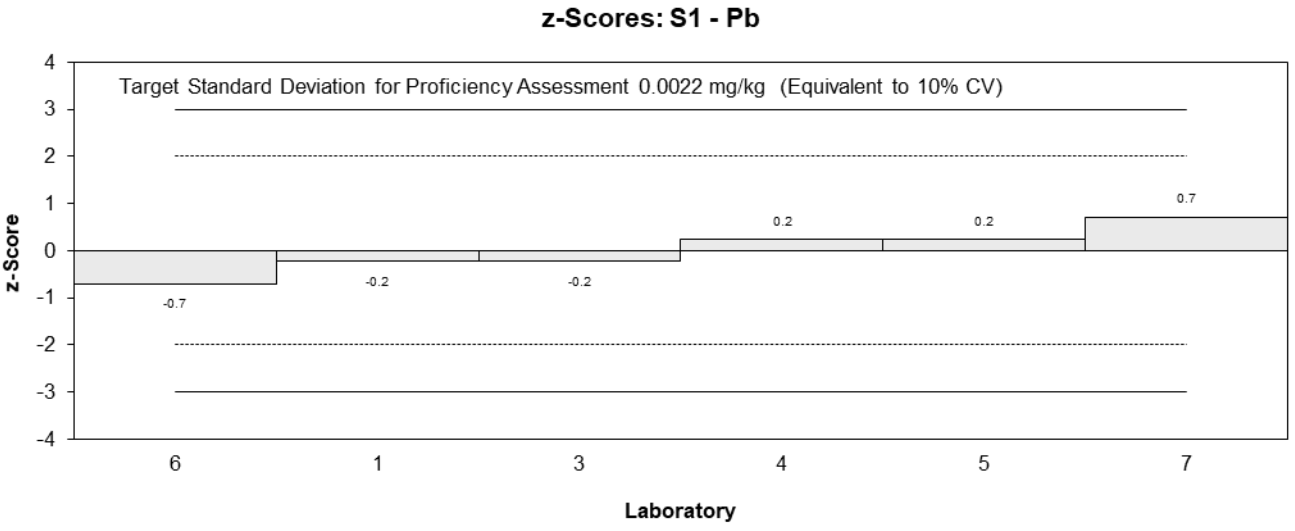
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.021	0.005	-0.23	-0.10
2	NT	NT		
3	0.021	0.005	-0.23	-0.10
4	0.022	0.0044	0.23	0.11
5	0.022	0.002	0.23	0.21
6	0.02	16.3	-0.70	0.00
7	0.023	0.0046	0.70	0.32
8	<0.1	NR		

Statistics

Assigned Value	0.0215	0.0012
Spike Value	0.0210	0.0006
Homogeneity Value	0.0219	0.0026
Robust Average	0.0215	0.0012
Median	0.0215	0.0008
Mean	0.0215	
N	6	
Max	0.023	
Min	0.02	
Robust SD	0.0012	
Robust CV	5.5%	


Kernel Density
Density
300
200
100
0
0
0.01
0.02
0.03
Result
Results: S1 - Pb
Assigned Value = 0.0215 ± 0.0012 mg/kg
Results (mg/kg)
0.05
0.04
0.03
0.02
0.01
0
6
1
3
4
5
7
2
8
Md
RA
HV
SV
Laboratory


z-Scores: S1 - Pb
Target Standard Deviation for Proficiency Assessment 0.0022 mg/kg (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.7
-0.2
-0.2
0.2
0.2
0.7
6
1
3
4
5
7
Laboratory

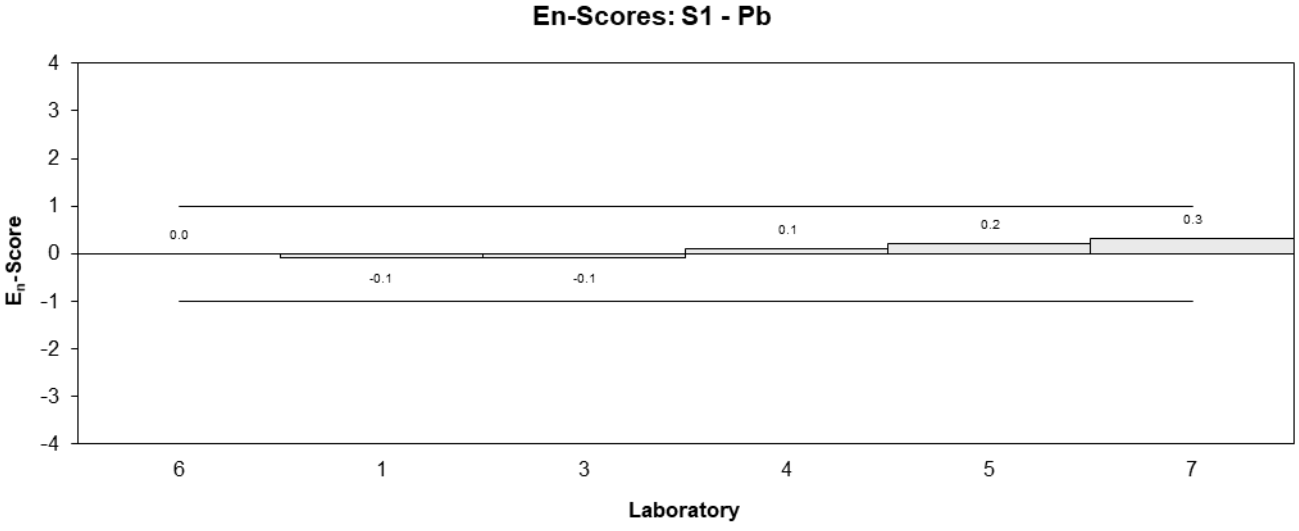

En-Scores: S1 - Pb
En-Score
4
3
2
1
0
-1
-2
-3
-4
0.0
-0.1
-0.1
0.1
0.2
0.3
6
1
3
4
5
7
Laboratory

Figure 19

Table 22

Sample Details

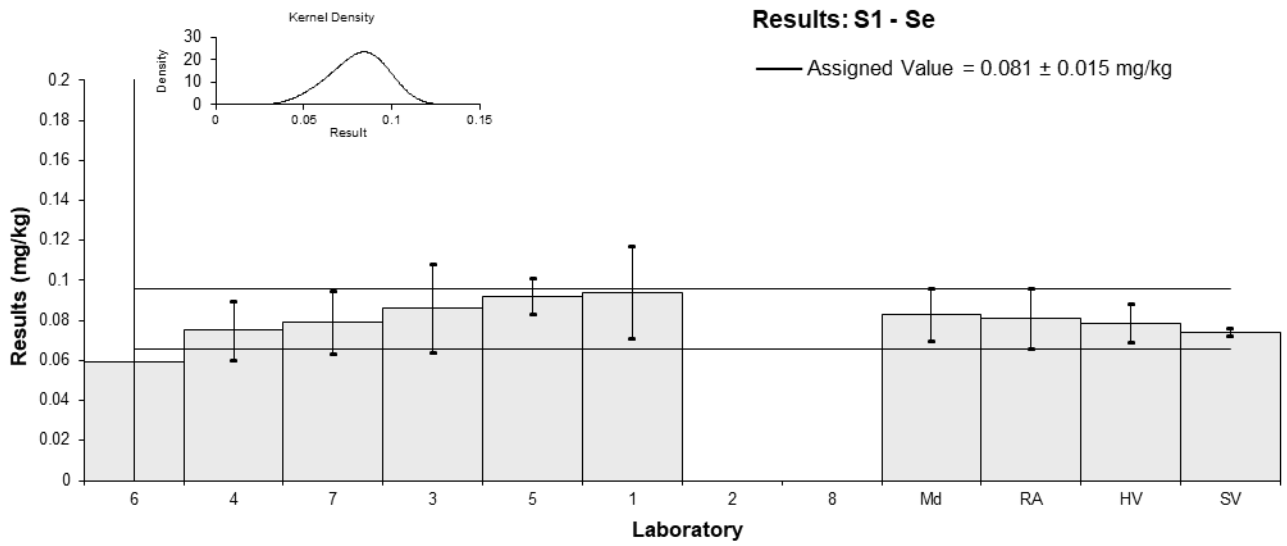
Sample No.	S1
Matrix	Celery
Analyte	Se
Unit	mg/kg

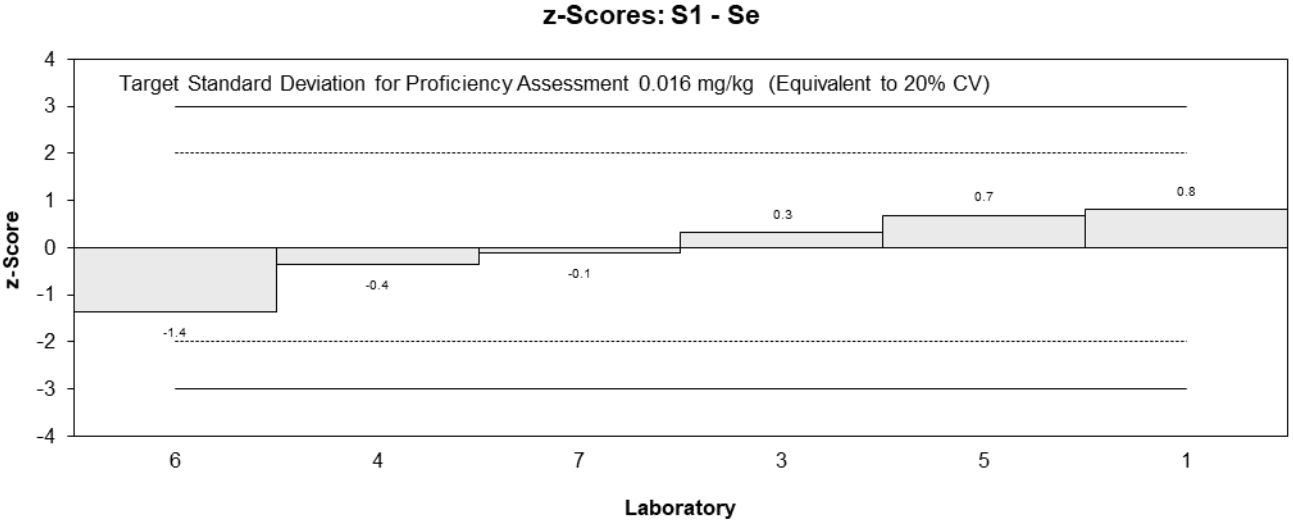
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.094	0.023	0.80	0.47
2	NT	NT		
3	0.086	0.022	0.31	0.19
4	0.075	0.015	-0.37	-0.28
5	0.092	0.009	0.68	0.63
6	0.059	14.8	-1.36	0.00
7	0.079	0.0158	-0.12	-0.09
8	NT	NT		

Statistics

Assigned Value	0.081	0.015
Spike Value	0.0743	0.0021
Homogeneity Value	0.0788	0.0095
Robust Average	0.081	0.015
Median	0.083	0.013
Mean	0.081	
N	6	
Max	0.094	
Min	0.059	
Robust SD	0.015	
Robust CV	18%	


Results: S1 - Se
Assigned Value = 0.081 ± 0.015 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
6
4
7
3
5
1
2
8
Md
RA
HV
SV


z-Scores: S1 - Se
Target Standard Deviation for Proficiency Assessment 0.016 mg/kg (Equivalent to 20% CV)
z-Score
-1.4
-0.4
-0.1
0.3
0.7
0.8
Laboratory
6
4
7
3
5
1

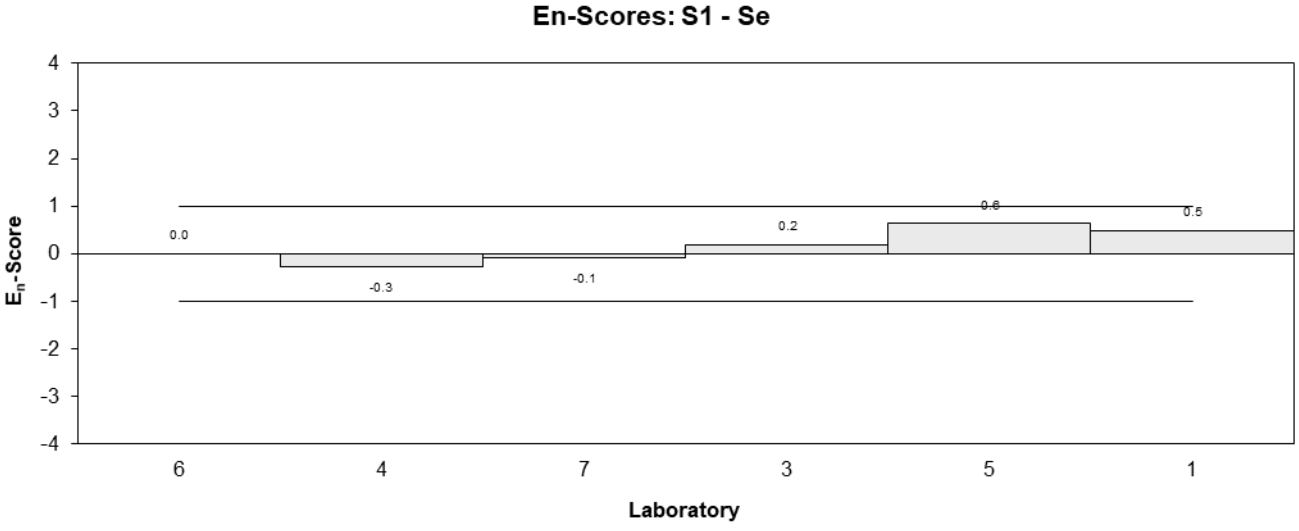

En-Scores: S1 - Se
En-Score
0.0
-0.3
-0.1
0.2
0.6
0.5
Laboratory
6
4
7
3
5
1

Figure 20

Table 23

Sample Details

Sample No.	S1
Matrix	Celery
Analyte	Sn
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.056	0.014	0.83	0.52
2	NT	NT		
3	0.052	0.013	0.42	0.28
4	0.047	0.0094	-0.10	-0.09
5	0.041	0.004	-0.73	-0.92
6	0.043	16.7	-0.52	0.00
7	0.049	0.0098	0.10	0.09
8	NT	NT		

Statistics

Assigned Value	0.0480	0.0065
Spike Value	Not Spiked	
Robust Average	0.0480	0.0065
Median	0.0480	0.0068
Mean	0.0480	
N	6	
Max	0.056	
Min	0.041	
Robust SD	0.0063	
Robust CV	13%	

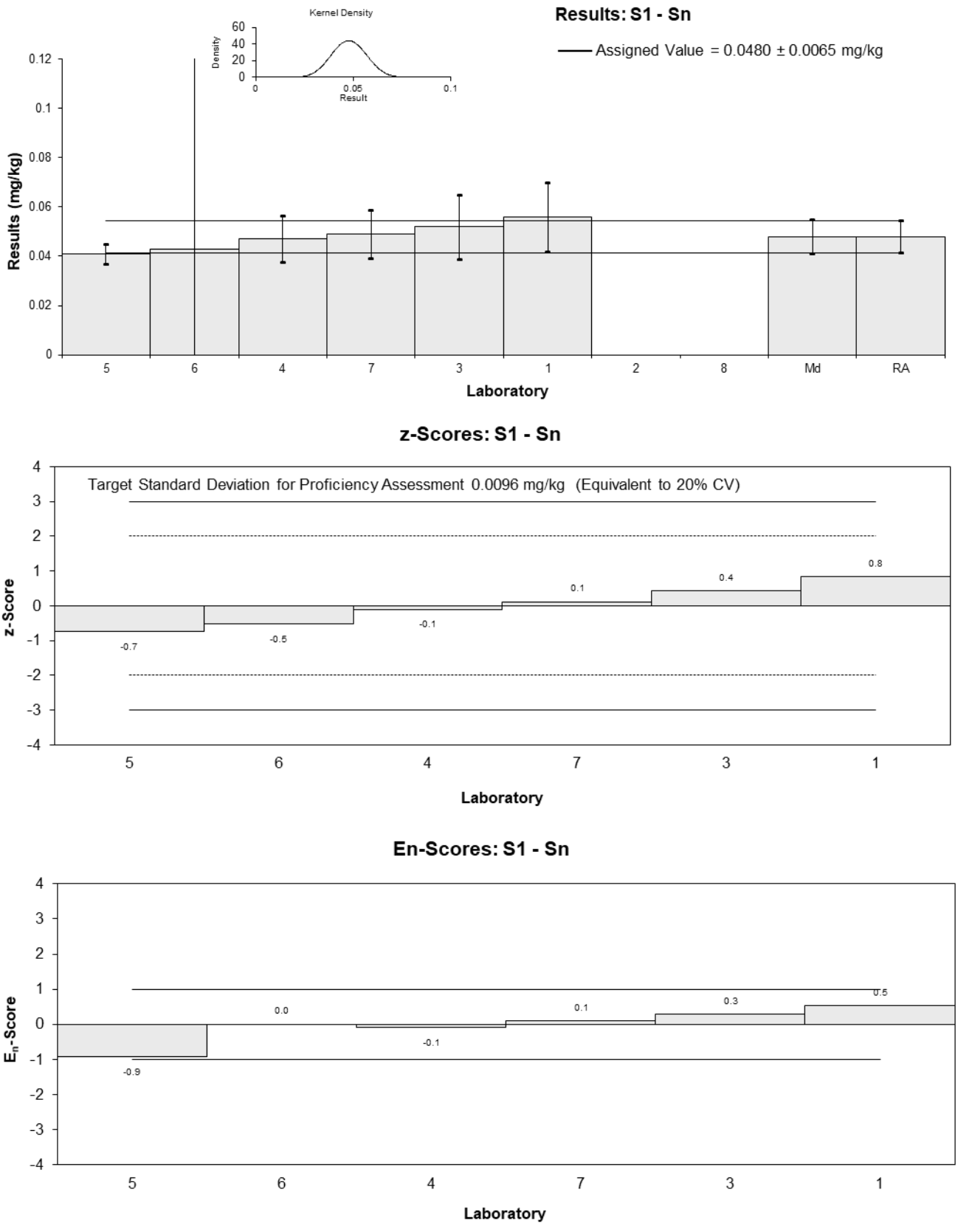

Kernel Density
Density
Result
Results: S1 - Sn
Assigned Value = 0.0480 ± 0.0065 mg/kg
Results (mg/kg)
Laboratory
5
6
4
7
3
1
2
8
Md
RA
z-Scores: S1 - Sn
Target Standard Deviation for Proficiency Assessment 0.0096 mg/kg (Equivalent to 20% CV)
z-Score
-0.7
-0.5
-0.1
0.1
0.4
0.8
En-Scores: S1 - Sn
En-Score
-0.9
0.0
-0.1
0.1
0.3
0.5

Figure 21

Table 24

Sample Details

Sample No.	S1
Matrix	Celery
Analyte	Tl
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty
1	0.007	0.002
2	NT	NT
3	<0.100	0.025
4	<0.01	NR
5	NR	NR
6	NT	NT
7	<0.01	NR
8	<0.1	NR

Statistics*

Assigned Value	Not Set	
Spike Value	0.0100	0.0003
N	1	

*Insufficient data to calculate statistics

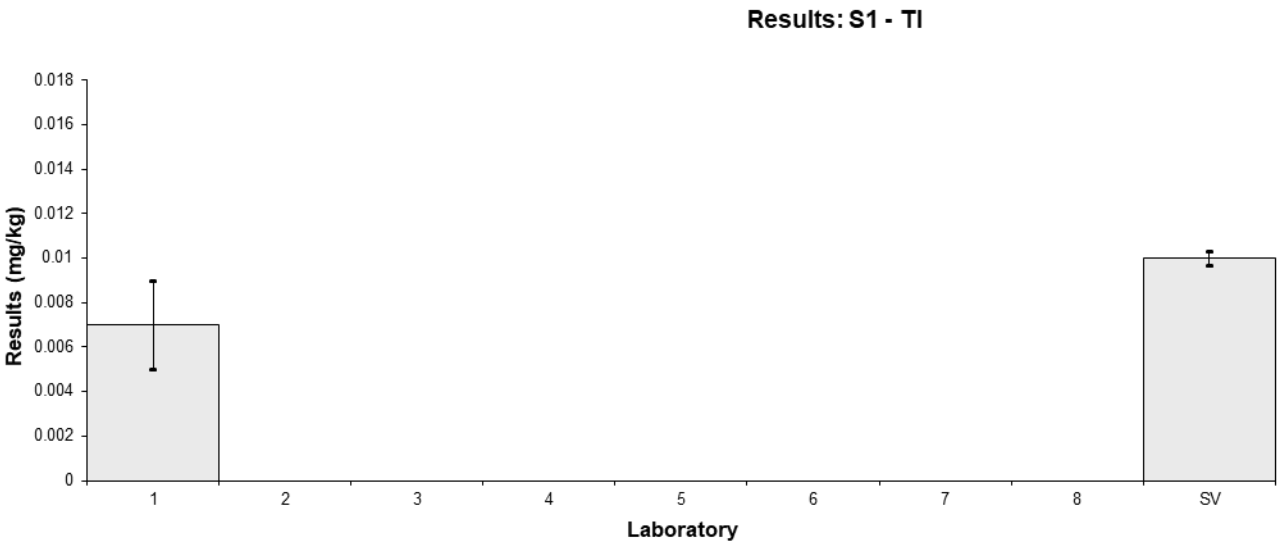

Results: S1 - Tl
Results (mg/kg)
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
1
2
3
4
5
6
7
8
SV
Laboratory

Figure 22

Table 25

Sample Details

Sample No.	S1
Matrix	Celery
Analyte	U
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty
1	0.055	0.014
2	NT	NT
3	<0.100	0.025
4	0.065	0.013
5	NR	NR
6	NT	NT
7	0.067	0.0134
8	0.11	0.02

Statistics

Assigned Value	Not Set	
Spike Value	0.0646	0.0018
Median	0.066	0.011
Mean	0.074	
N	4	
Max	0.11	
Min	0.055	

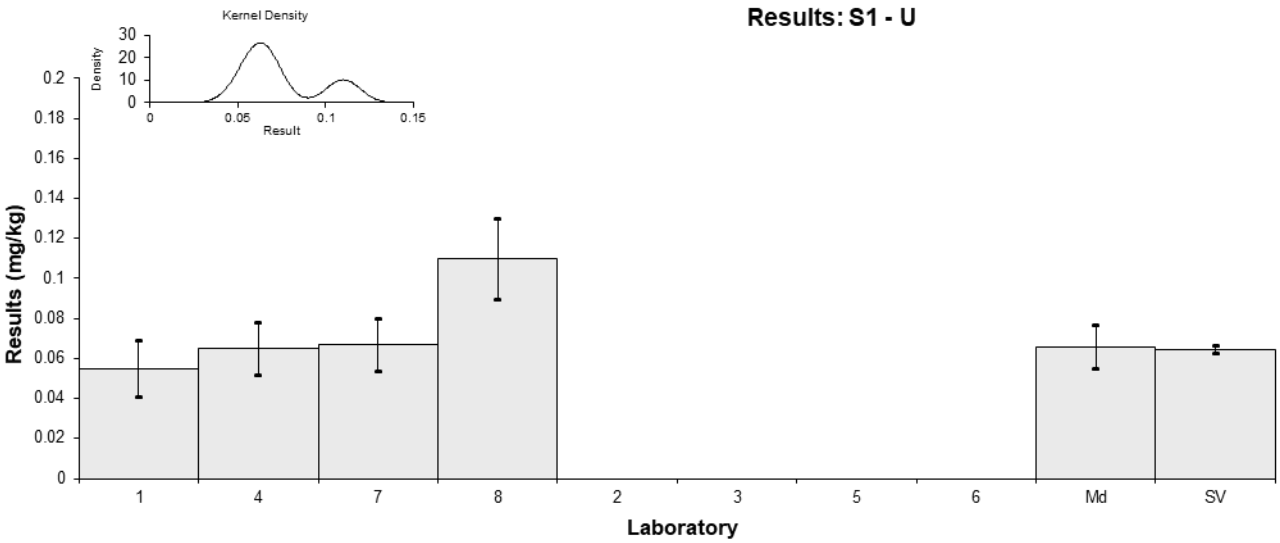

Results: S1 - U
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
1
4
7
8
2
3
5
6
Md
SV

Figure 23

Table 26

Sample Details

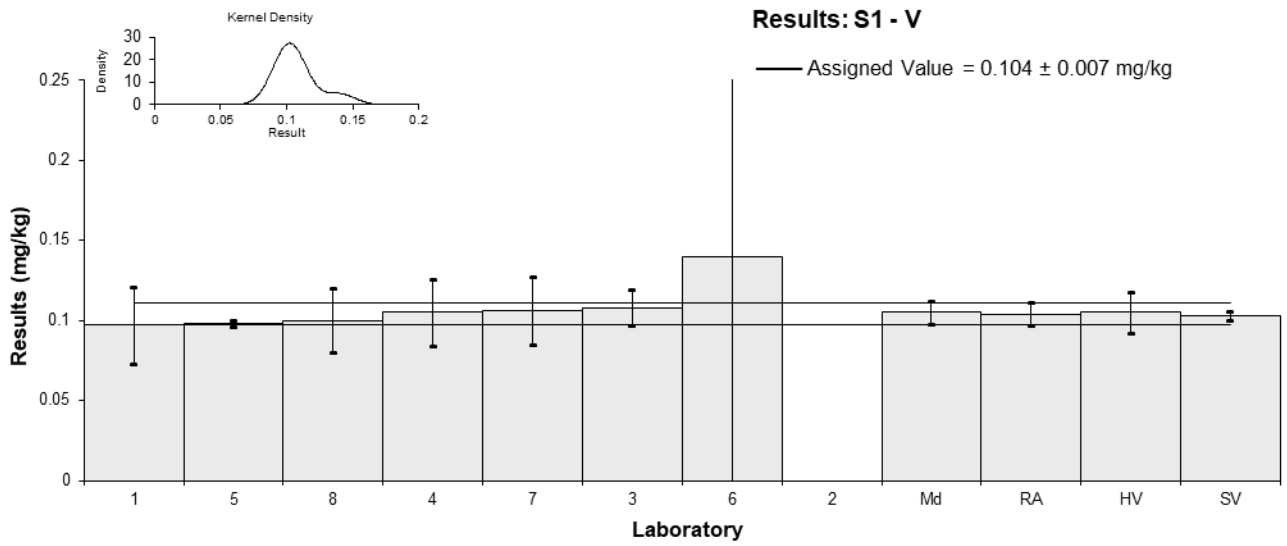
Sample No.	S1
Matrix	Celery
Analyte	V
Unit	mg/kg

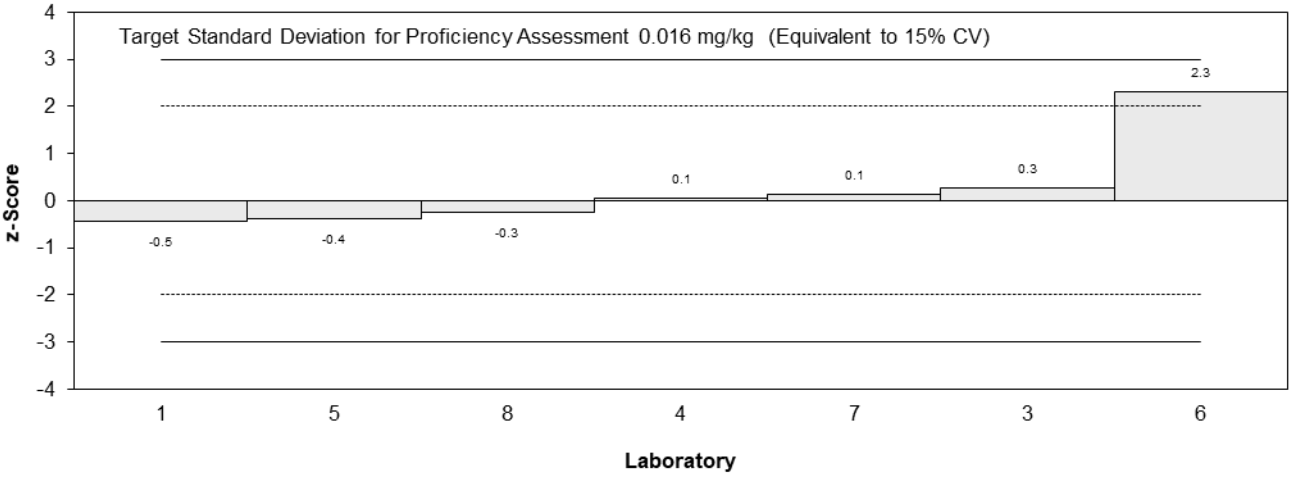
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.097	0.024	-0.45	-0.28
2	NT	NT		
3	0.108	0.011	0.26	0.31
4	0.105	0.021	0.06	0.05
5	0.098	0.002	-0.38	-0.82
6	0.14	17.0	2.31	0.00
7	0.106	0.0212	0.13	0.09
8	0.10	0.02	-0.26	-0.19

Statistics

Assigned Value	0.104	0.007
Spike Value	0.103	0.003
Homogeneity Value	0.105	0.013
Robust Average	0.104	0.007
Median	0.105	0.007
Mean	0.108	
N	7	
Max	0.14	
Min	0.097	
Robust SD	0.0072	
Robust CV	6.9%	


Kernel Density
Density
Result
Results: S1 - V
Assigned Value = 0.104 ± 0.007 mg/kg
Results (mg/kg)
Laboratory
1
5
8
4
7
3
6
2
Md
RA
HV
SV


z-Scores: S1 - V
Target Standard Deviation for Proficiency Assessment 0.016 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
-0.5
-0.4
-0.3
0.1
0.1
0.3
2.3

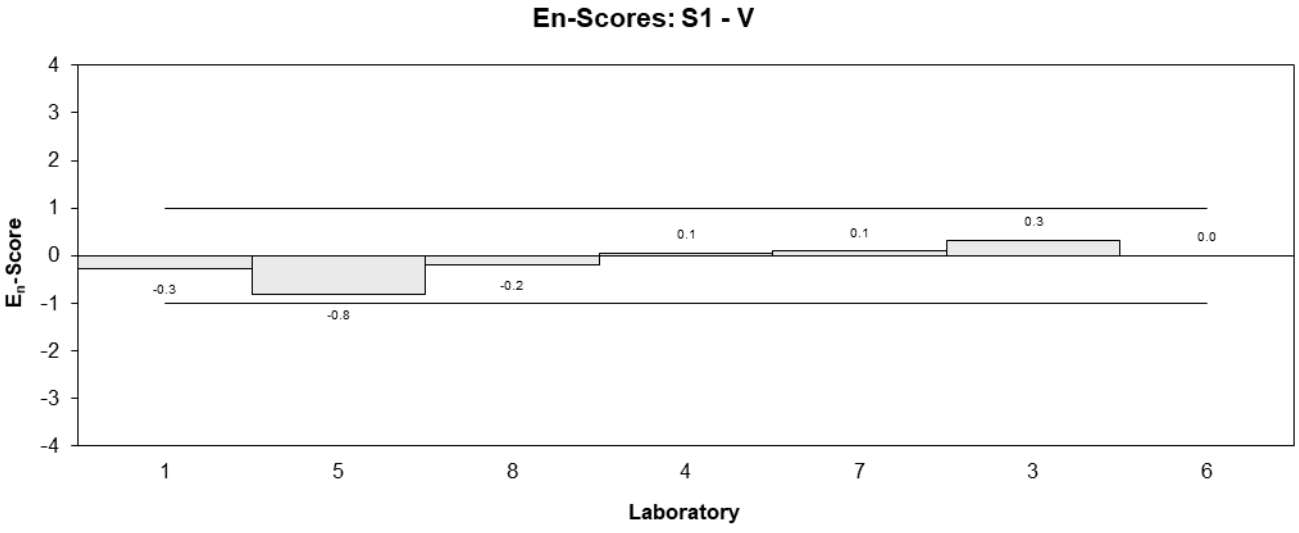

En-Scores: S1 - V
En-Score
Laboratory
-0.3
-0.8
-0.2
0.1
0.1
0.3
0.0

Figure 24

Table 27

Sample Details

Sample No.	S1
Matrix	Celery
Analyte	Zn
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.70	0.42	1.20	0.61
2	NT	NT		
3	1.407	0.352	-0.15	-0.09
4	1.36	0.272	-0.37	-0.28
5	1.50	0.07	0.28	0.53
6	1.4695	11.9	0.14	0.00
7	1.35	0.27	-0.42	-0.32
8	1.41	0.20	-0.14	-0.14

Statistics

Assigned Value	1.44	0.09
Spike Value	1.39	0.23
Homogeneity Value	1.41	0.17
Robust Average	1.44	0.09
Median	1.41	0.08
Mean	1.46	
N	7	
Max	1.7	
Min	1.35	
Robust SD	0.093	
Robust CV	6.4%	

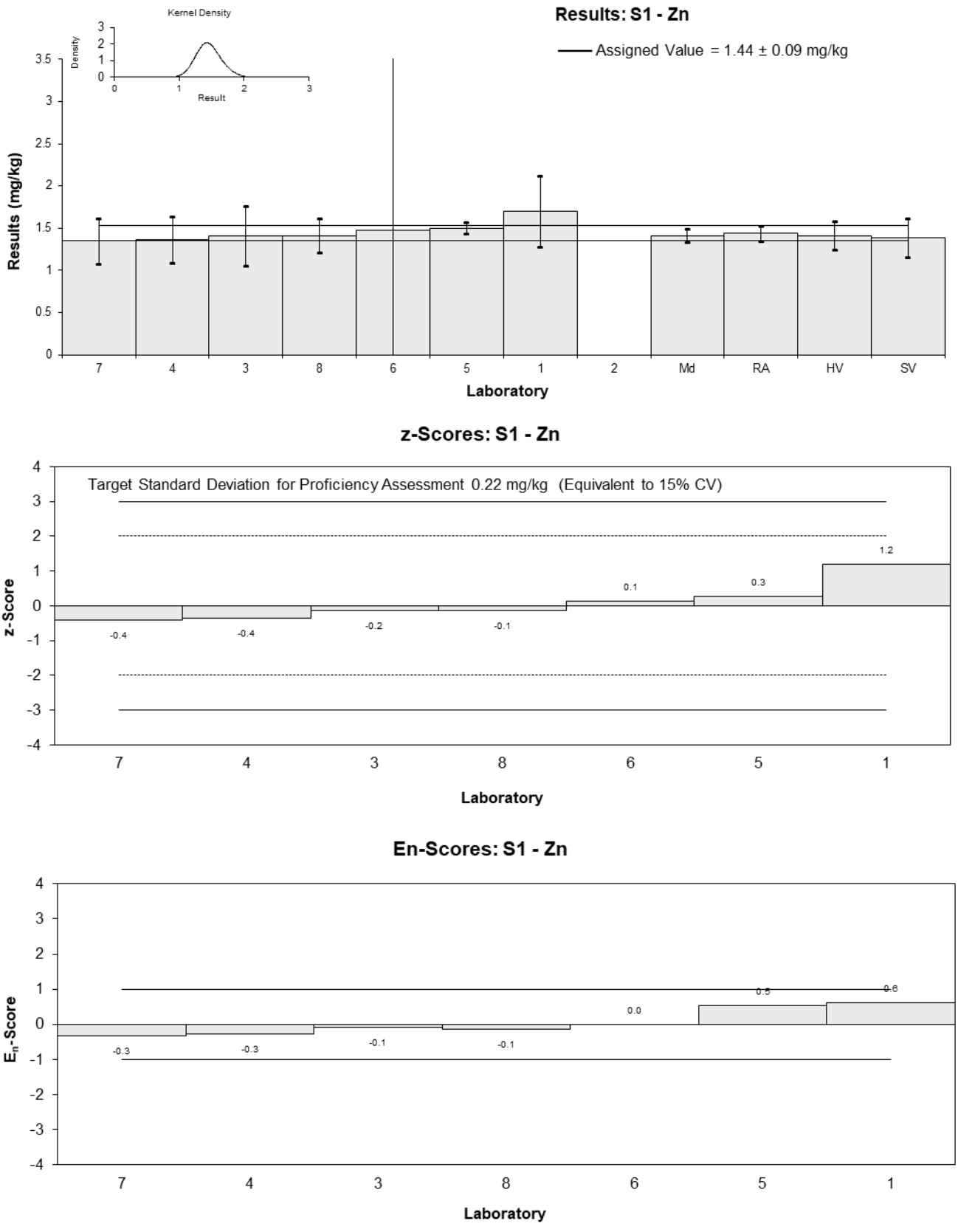

Results: S1 - Zn
Assigned Value = 1.44 ± 0.09 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
7
4
3
8
6
5
1
2
Md
RA
HV
SV
z-Scores: S1 - Zn
Target Standard Deviation for Proficiency Assessment 0.22 mg/kg (Equivalent to 15% CV)
z-Score
-0.4
-0.4
-0.2
-0.1
0.1
0.3
1.2
En-Scores: S1 - Zn
En-Score
-0.3
-0.3
-0.1
-0.1
0.0
0.5
0.6

Figure 25

Table 28

Sample Details

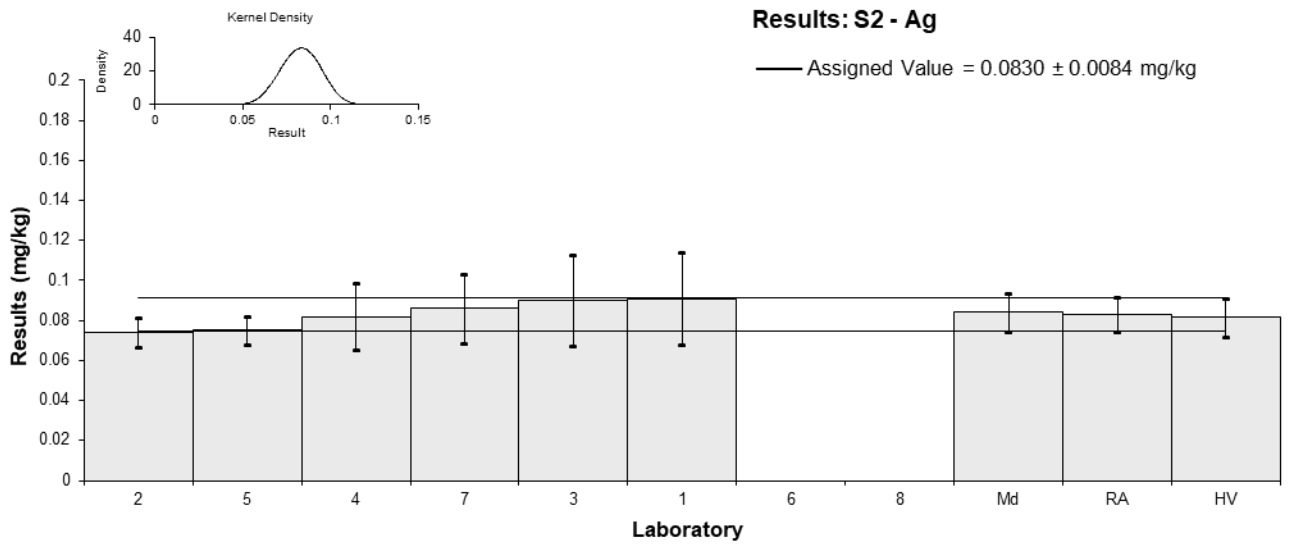
Sample No.	S2
Matrix	Bovine Liver
Analyte	Ag
Unit	mg/kg

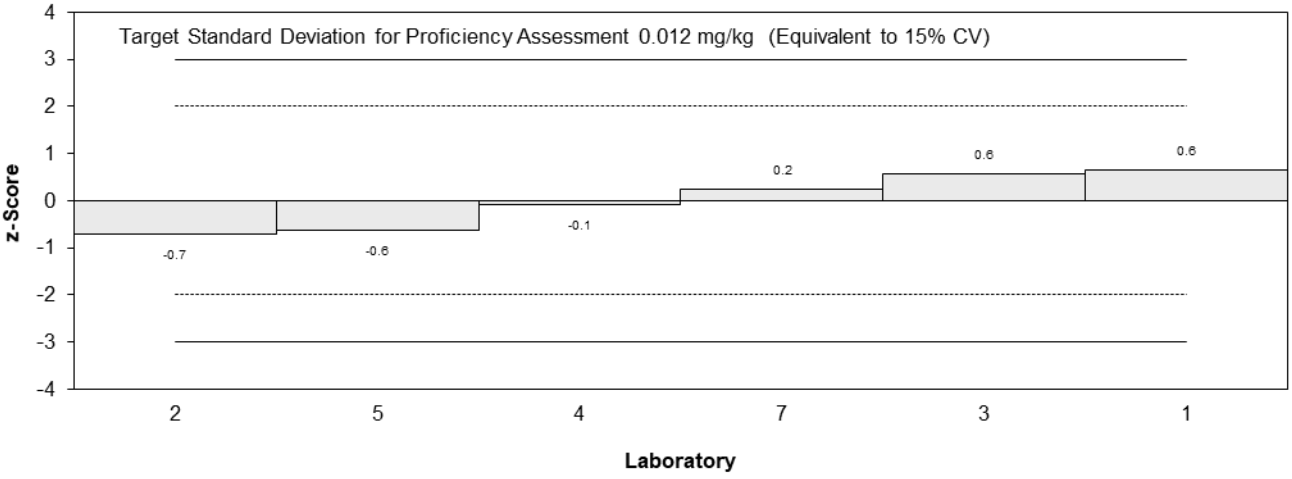
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.091	0.023	0.64	0.33
2	0.074187539816	0.007418753981	-0.71	-0.79
3	0.090	0.023	0.56	0.29
4	0.082	0.0164	-0.08	-0.05
5	0.075	0.007	-0.64	-0.73
6	NT	NT		
7	0.086	0.0172	0.24	0.16
8	<0.5	NR		

Statistics

Assigned Value	0.0830	0.0084
Spike Value	Not Spiked	
Homogeneity Value	0.0815	0.0098
Robust Average	0.0830	0.0084
Median	0.0840	0.0098
Mean	0.0830	
N	6	
Max	0.091	
Min	0.074187539816	
Robust SD	0.0083	
Robust CV	9.9%	


Results: S2 - Ag
Assigned Value = 0.0830 ± 0.0084 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
2
5
4
7
3
1
6
8
Md
RA
HV


z-Scores: S2 - Ag
Target Standard Deviation for Proficiency Assessment 0.012 mg/kg (Equivalent to 15% CV)
z-Score
-0.7
-0.6
-0.1
0.2
0.6
0.6
Laboratory
2
5
4
7
3
1

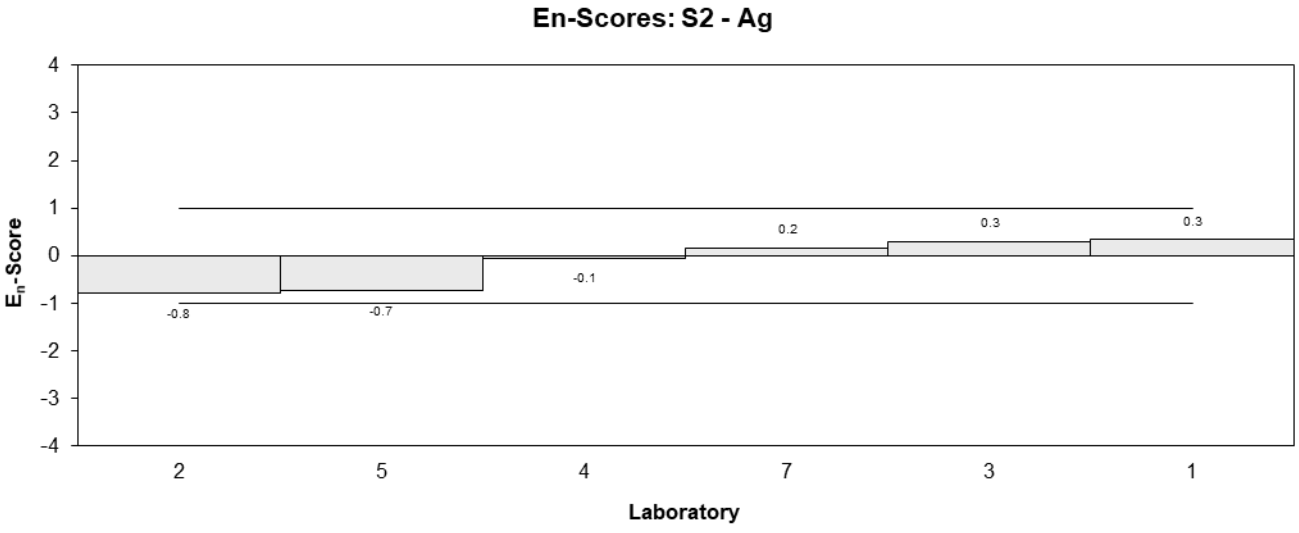

En-Scores: S2 - Ag
En-Score
-0.8
-0.7
-0.1
0.2
0.3
0.3
Laboratory
2
5
4
7
3
1

Figure 26

Table 29

Sample Details

Sample No.	S2
Matrix	Bovine Liver
Analyte	Al
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty
1	3.76	0.94
2	3.880817396864	0.388081739686
3	7.24	1.81
4	4.06	0.812
5	6.5	0.7
6	NT	NT
7	3.78	0.756
8	10	1.5

Statistics

Assigned Value	Not Set	
Spike Value	Not Spiked	
Robust Average	5.5	2.3
Median	4.1	0.42
Mean	5.6	
N	7	
Max	10	
Min	3.76	
Robust SD	2.5	
Robust CV	45%	

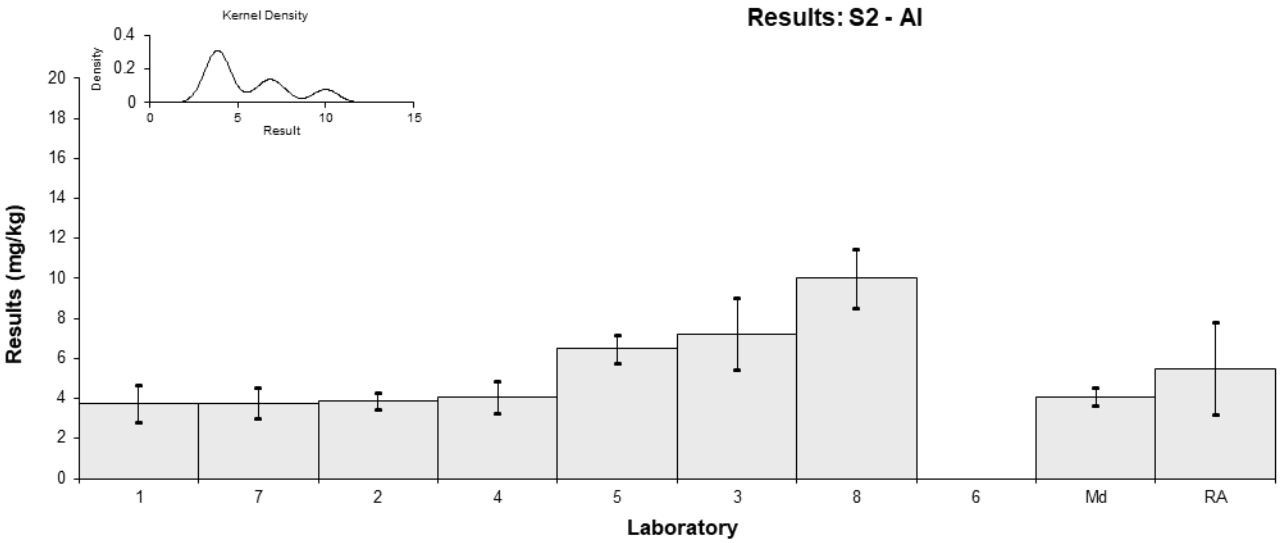

Results: S2 - Al
Kernel Density
Density
0.4
0.2
0
0
5
10
15
Result
Results (mg/kg)
20
18
16
14
12
10
8
6
4
2
0
1
7
2
4
5
3
8
6
Md
RA
Laboratory

Figure 27

Table 30

Sample Details

Sample No.	S2
Matrix	Bovine Liver
Analyte	As
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.94	0.23	0.12	0.07
2	0.965447632070	0.096544763207	0.30	0.32
3	0.926	0.092	0.01	0.02
4	0.826	0.1652	-0.71	-0.53
5	0.92	0.04	-0.03	-0.04
6	NT	NT		
7	0.833	0.1666	-0.66	-0.49
8	1.10	0.20	1.27	0.81

Statistics

Assigned Value	0.924	0.086
Spike Value	Not Spiked	
Homogeneity Value	0.84	0.10
Robust Average	0.924	0.086
Median	0.926	0.055
Mean	0.930	
N	7	
Max	1.1	
Min	0.826	
Robust SD	0.091	
Robust CV	9.8%	

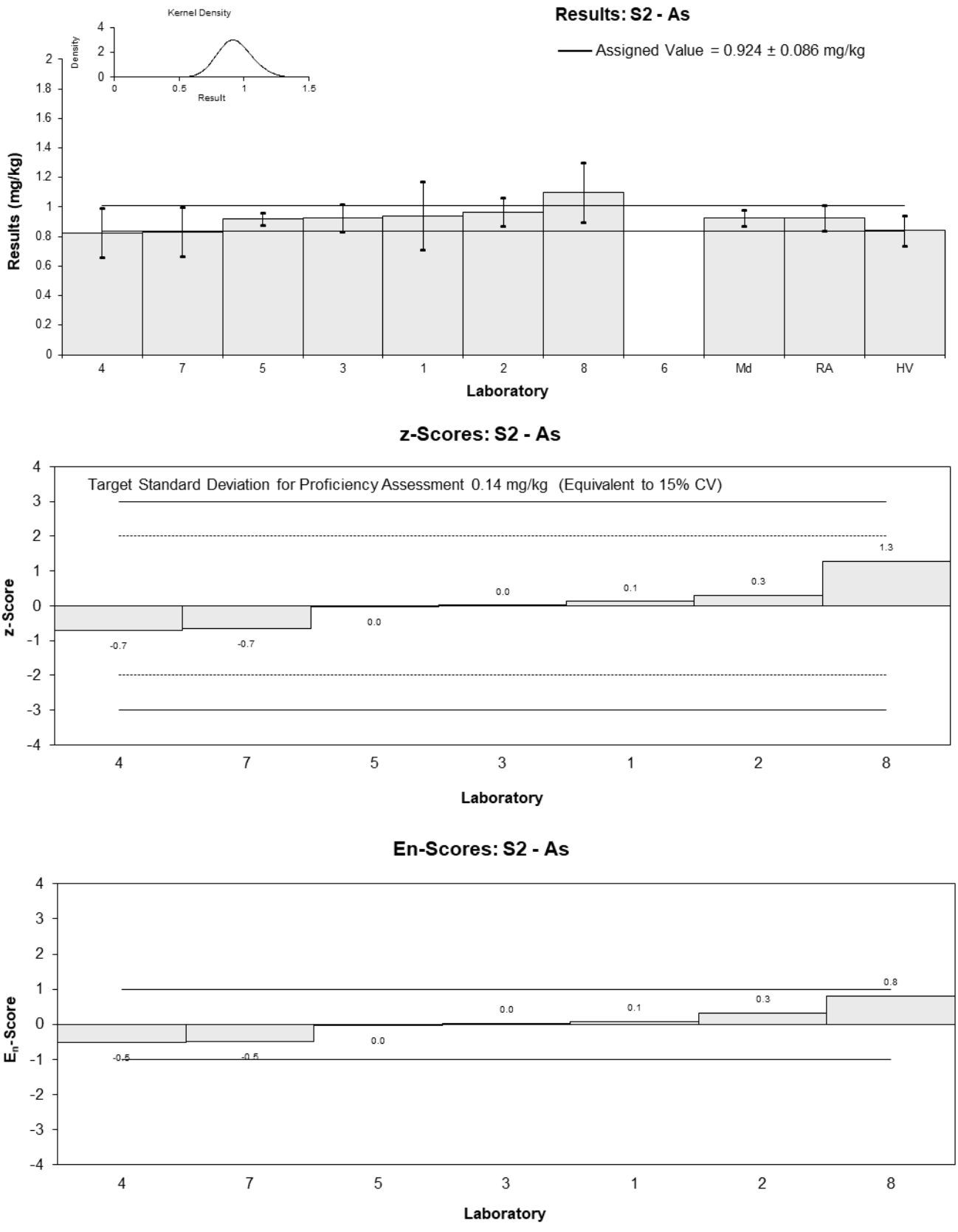

Results: S2 - As
Assigned Value = 0.924 ± 0.086 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
4 7 5 3 1 2 8 6 Md RA HV
z-Scores: S2 - As
Target Standard Deviation for Proficiency Assessment 0.14 mg/kg (Equivalent to 15% CV)
z-Score
-0.7 -0.7 0.0 0.0 0.1 0.3 1.3
Laboratory
4 7 5 3 1 2 8
En-Scores: S2 - As
En-Score
-0.5 -0.5 0.0 0.0 0.1 0.3 0.8
Laboratory
4 7 5 3 1 2 8

Figure 28

Table 31

Sample Details

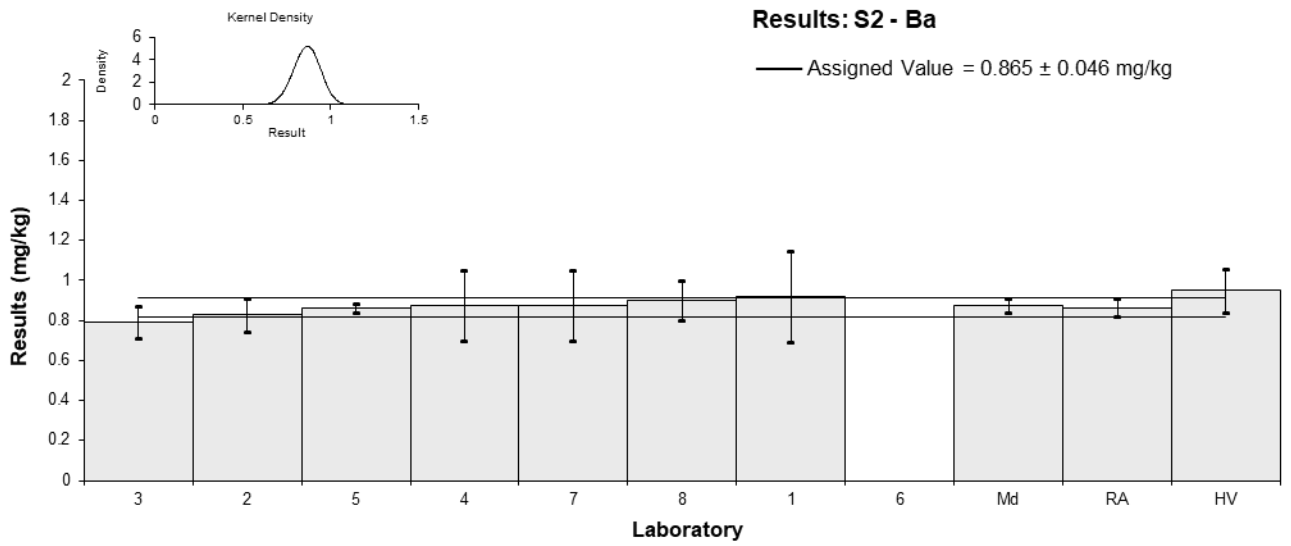
Sample No.	S2
Matrix	Bovine Liver
Analyte	Ba
Unit	mg/kg

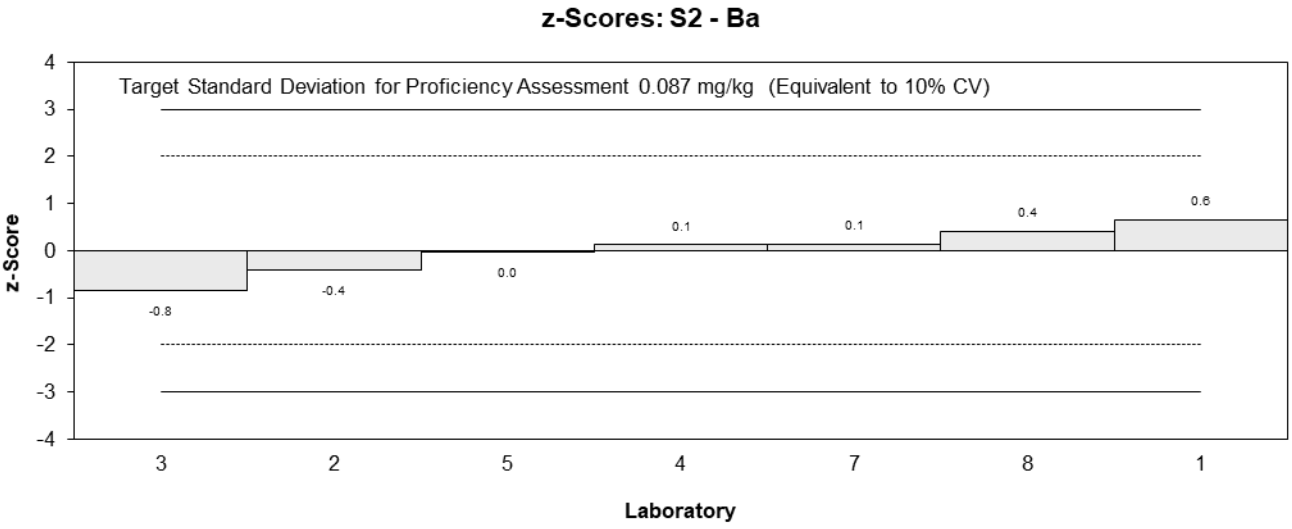
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.92	0.23	0.64	0.23
2	0.828936489524	0.082893648952	-0.42	-0.38
3	0.792	0.079	-0.84	-0.80
4	0.875	0.175	0.12	0.06
5	0.862	0.020	-0.03	-0.06
6	NT	NT		
7	0.876	0.1752	0.13	0.06
8	0.90	0.10	0.40	0.32

Statistics

Assigned Value	0.865	0.046
Spike Value	Not Spiked	
Homogeneity Value	0.95	0.11
Robust Average	0.865	0.046
Median	0.875	0.035
Mean	0.865	
N	7	
Max	0.92	
Min	0.792	
Robust SD	0.049	
Robust CV	5.6%	


Kernel Density
Density
Result
Results: S2 - Ba
Assigned Value = 0.865 ± 0.046 mg/kg
Results (mg/kg)
Laboratory
3
2
5
4
7
8
1
6
Md
RA
HV


z-Scores: S2 - Ba
Target Standard Deviation for Proficiency Assessment 0.087 mg/kg (Equivalent to 10% CV)
z-Score
-0.8
-0.4
0.0
0.1
0.1
0.4
0.6
Laboratory

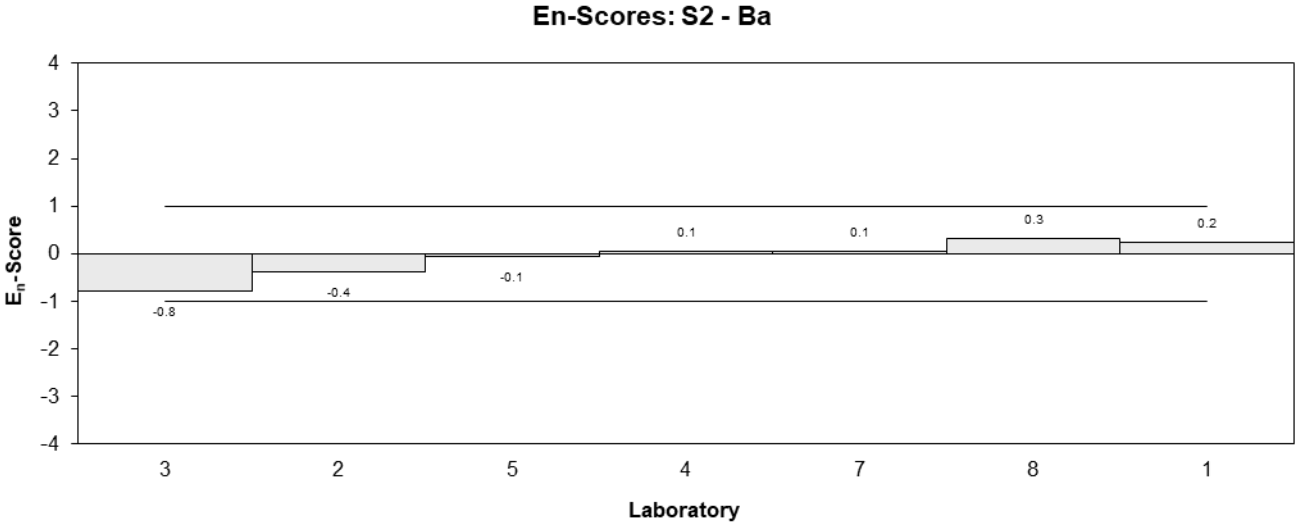

En-Scores: S2 - Ba
En-Score
-0.8
-0.4
-0.1
0.1
0.1
0.3
0.2
Laboratory

Figure 29

Table 32

Sample Details

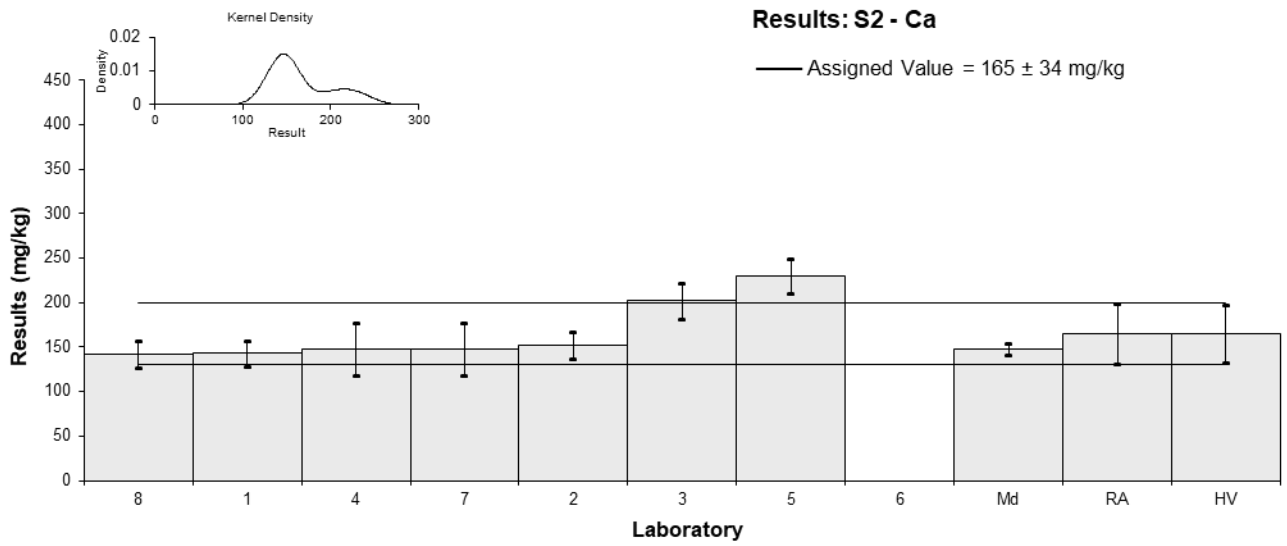
Sample No.	S2
Matrix	Bovine Liver
Analyte	Ca
Unit	mg/kg

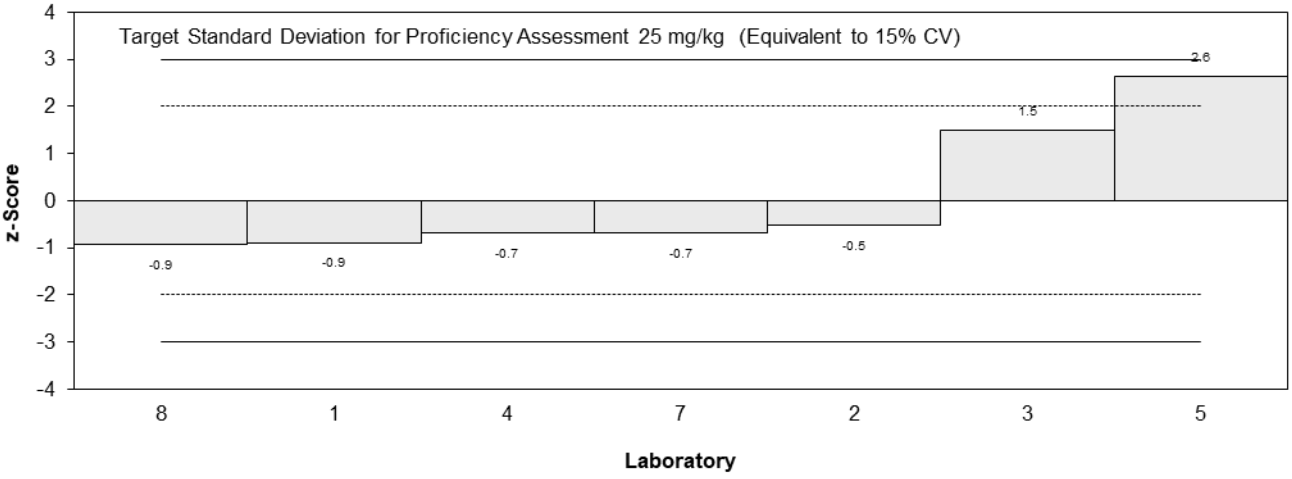
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	143	14	-0.89	-0.60
2	152.2429625806	15.22429625806	-0.52	-0.34
3	202	20.2	1.49	0.94
4	148	29.6	-0.69	-0.38
5	230	20	2.63	1.65
6	NT	NT		
7	148	29.6	-0.69	-0.38
8	142	15	-0.93	-0.62

Statistics

Assigned Value	165	34
Spike Value	Not Spiked	
Homogeneity Value	165	33
Robust Average	165	34
Median	148	7
Mean	166	
N	7	
Max	230	
Min	142	
Robust SD	36	
Robust CV	22%	


Kernel Density
Density
Result
Results: S2 - Ca
Assigned Value = 165 ± 34 mg/kg
Results (mg/kg)
Laboratory
8
1
4
7
2
3
5
6
Md
RA
HV


z-Scores: S2 - Ca
Target Standard Deviation for Proficiency Assessment 25 mg/kg (Equivalent to 15% CV)
z-Score
Laboratory
-0.9
-0.9
-0.7
-0.7
-0.5
1.5
2.6

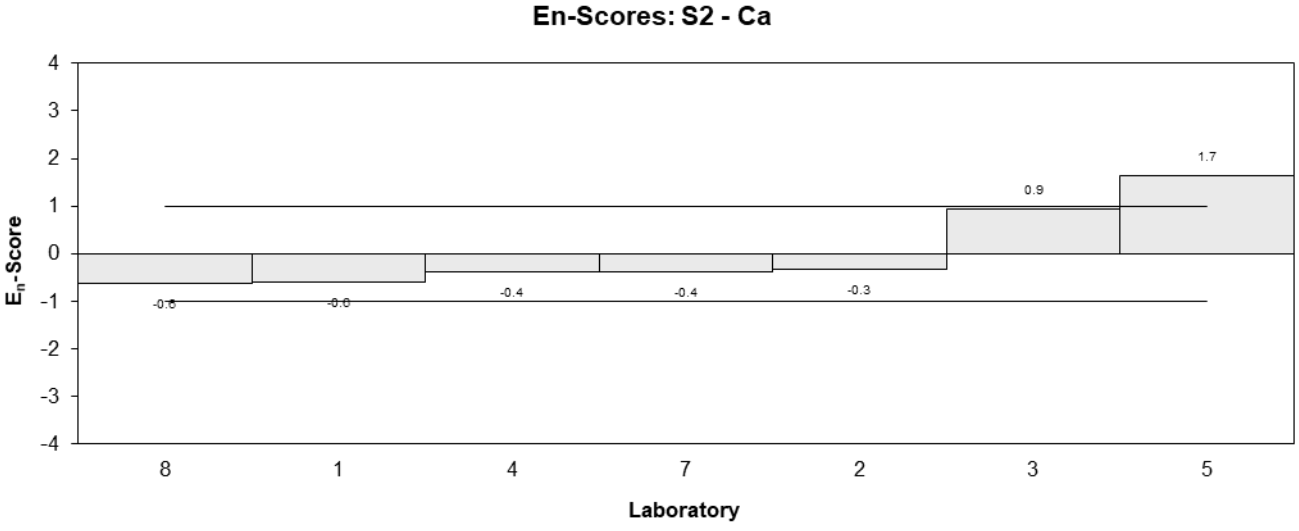

En-Scores: S2 - Ca
En-Score
Laboratory
-0.6
-0.6
-0.4
-0.4
-0.3
0.9
1.7

Figure 30

Table 33

Sample Details

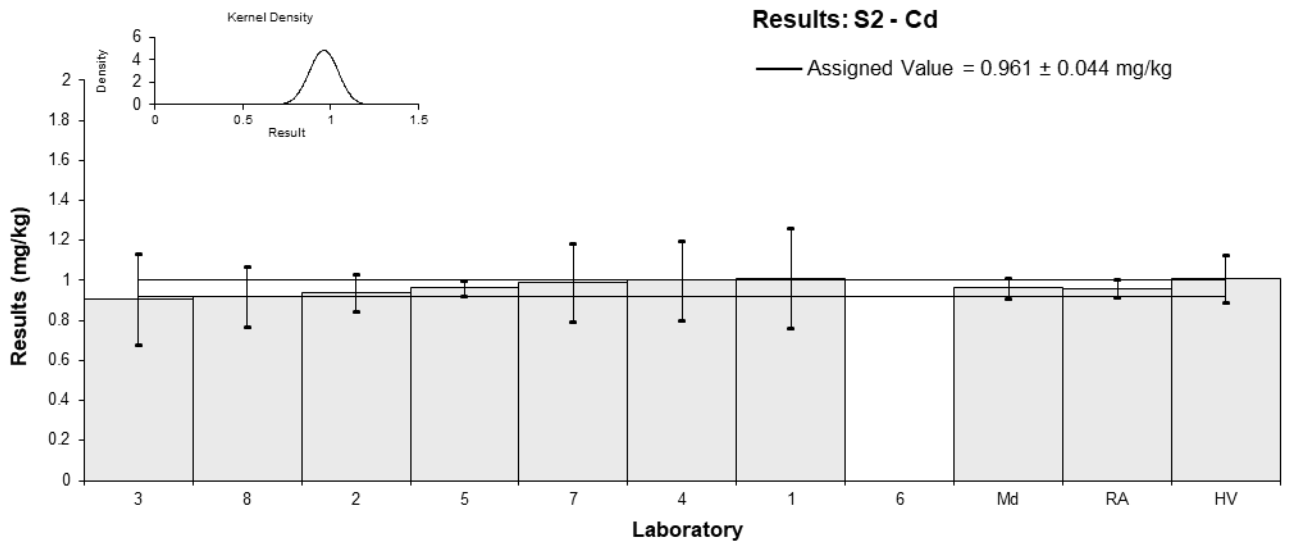
Sample No.	S2
Matrix	Bovine Liver
Analyte	Cd
Unit	mg/kg

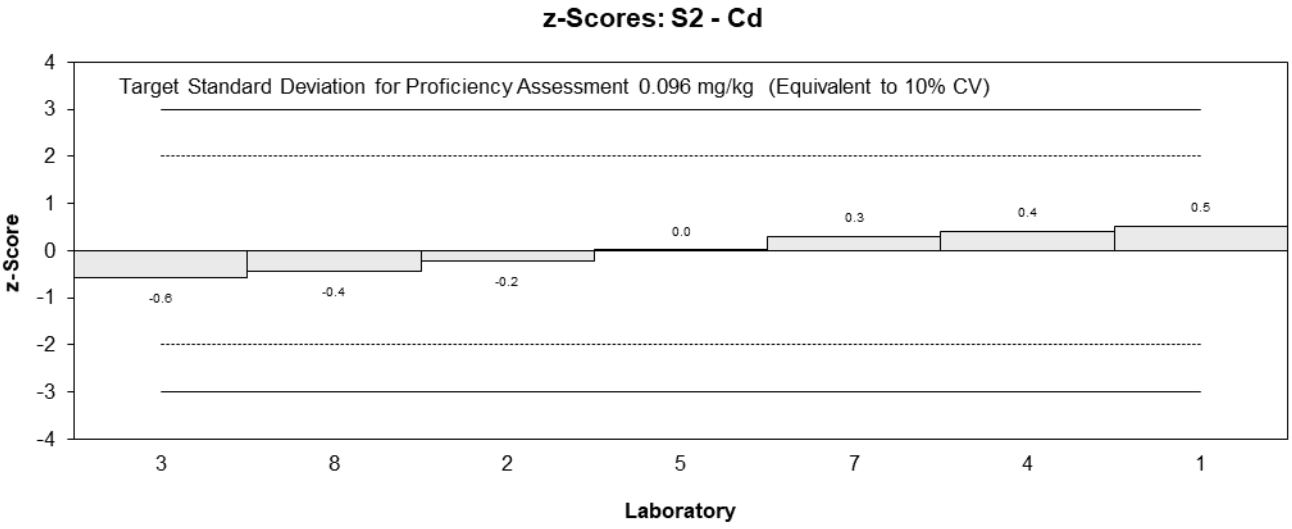
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.01	0.25	0.51	0.19
2	0.939893172676	0.093989317267	-0.22	-0.20
3	0.906	0.227	-0.57	-0.24
4	1.00	0.2	0.41	0.19
5	0.962	0.040	0.01	0.02
6	NT	NT		
7	0.990	0.198	0.30	0.14
8	0.92	0.15	-0.43	-0.26

Statistics

Assigned Value	0.961	0.044
Spike Value	Not Spiked	
Homogeneity Value	1.01	0.12
Robust Average	0.961	0.044
Median	0.962	0.053
Mean	0.961	
N	7	
Max	1.01	
Min	0.906	
Robust SD	0.046	
Robust CV	4.8%	


Kernel Density
Density
Result
Results: S2 - Cd
Assigned Value = 0.961 ± 0.044 mg/kg
Results (mg/kg)
Laboratory
3
8
2
5
7
4
1
6
Md
RA
HV


z-Scores: S2 - Cd
Target Standard Deviation for Proficiency Assessment 0.096 mg/kg (Equivalent to 10% CV)
z-Score
-0.6
-0.4
-0.2
0.0
0.3
0.4
0.5
Laboratory

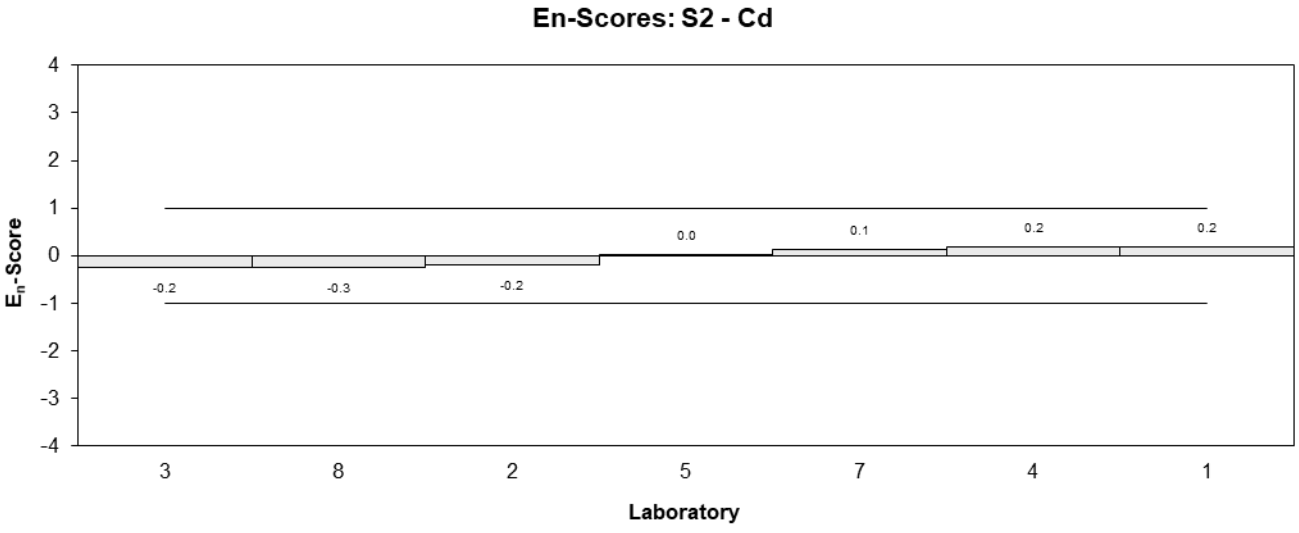

En-Scores: S2 - Cd
En-Score
-0.2
-0.3
-0.2
0.0
0.1
0.2
0.2
Laboratory

Figure 31

Table 34

Sample Details

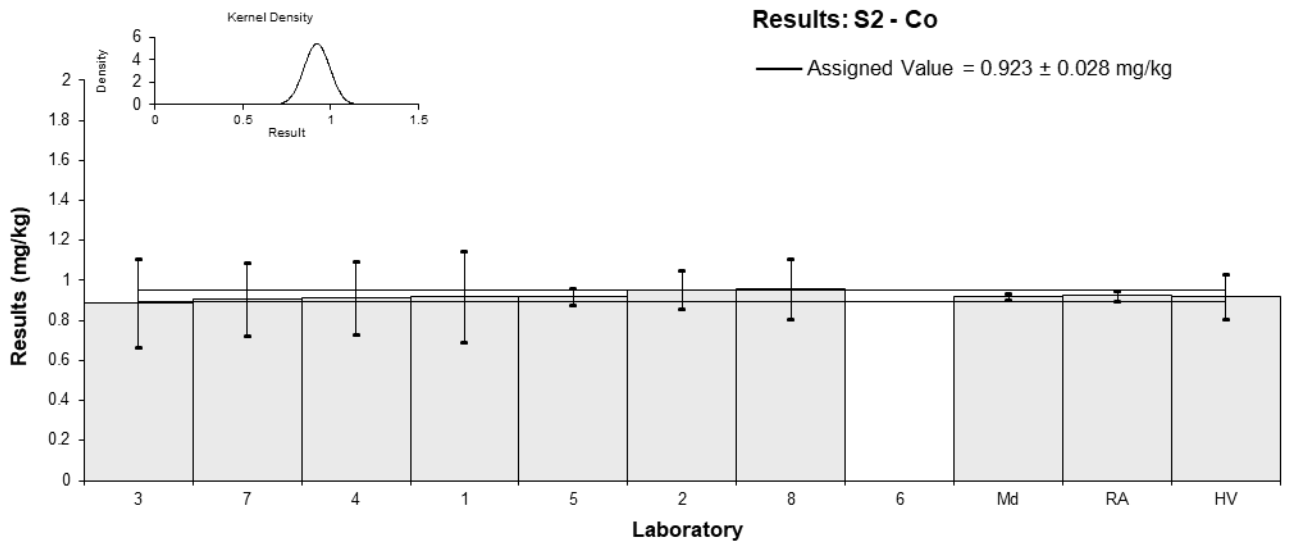
Sample No.	S2
Matrix	Bovine Liver
Analyte	Co
Unit	mg/kg

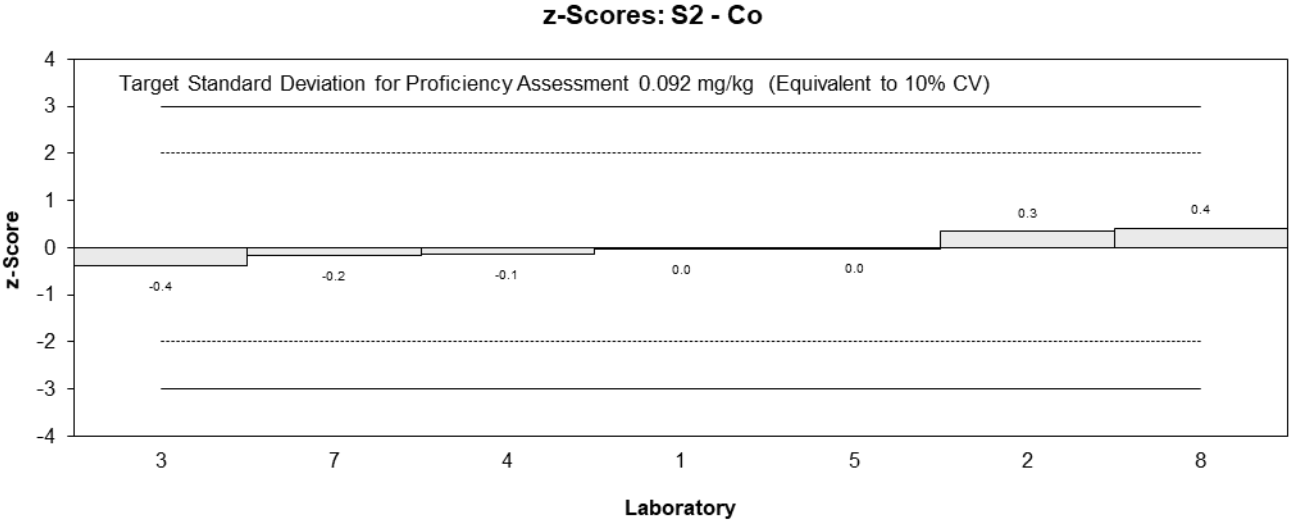
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.92	0.23	-0.03	-0.01
2	0.954550803513	0.095455080351	0.34	0.32
3	0.887	0.223	-0.39	-0.16
4	0.911	0.1822	-0.13	-0.07
5	0.921	0.040	-0.02	-0.04
6	NT	NT		
7	0.908	0.1816	-0.16	-0.08
8	0.96	0.15	0.40	0.24

Statistics

Assigned Value	0.923	0.028
Spike Value	Not Spiked	
Homogeneity Value	0.92	0.11
Robust Average	0.923	0.028
Median	0.920	0.017
Mean	0.923	
N	7	
Max	0.96	
Min	0.887	
Robust SD	0.029	
Robust CV	3.2%	


Kernel Density
Density
Result
Results: S2 - Co
Assigned Value = 0.923 ± 0.028 mg/kg
Results (mg/kg)
Laboratory
3
7
4
1
5
2
8
6
Md
RA
HV


z-Scores: S2 - Co
Target Standard Deviation for Proficiency Assessment 0.092 mg/kg (Equivalent to 10% CV)
z-Score
-0.4
-0.2
-0.1
0.0
0.0
0.3
0.4
Laboratory

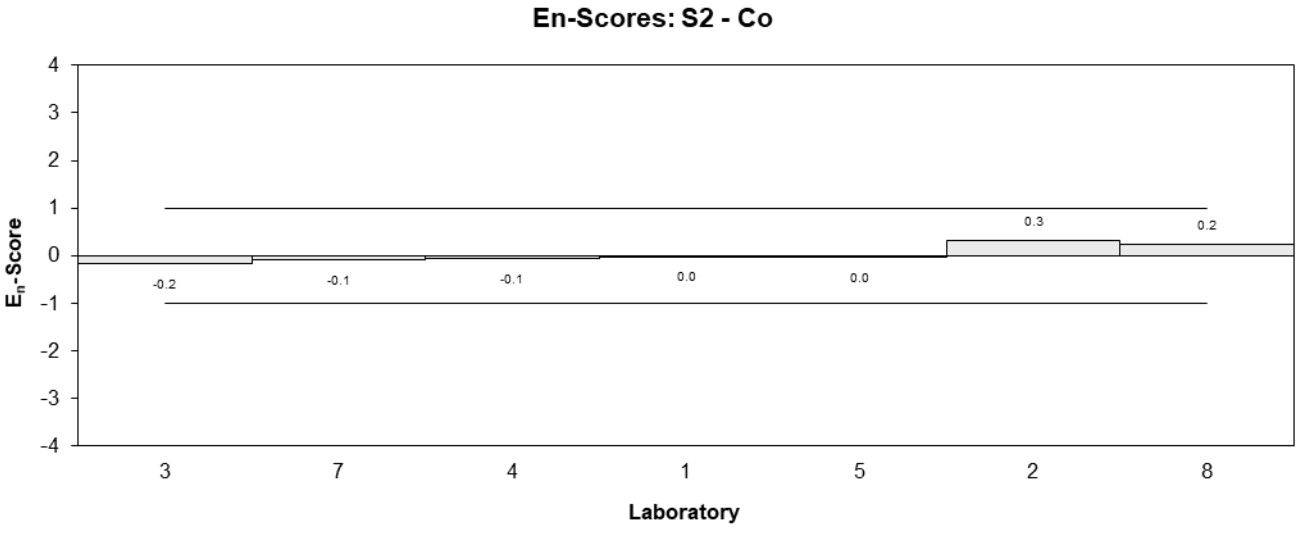

En-Scores: S2 - Co
En-Score
-0.2
-0.1
-0.1
0.0
0.0
0.3
0.2
Laboratory

Figure 32

Table 35

Sample Details

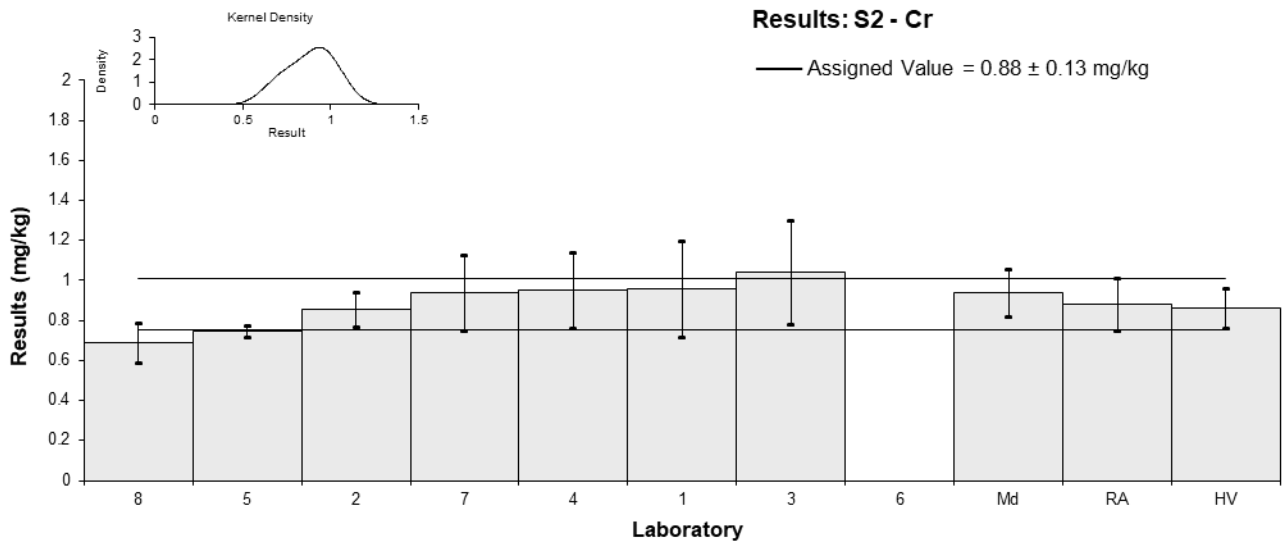
Sample No.	S2
Matrix	Bovine Liver
Analyte	Cr
Unit	mg/kg

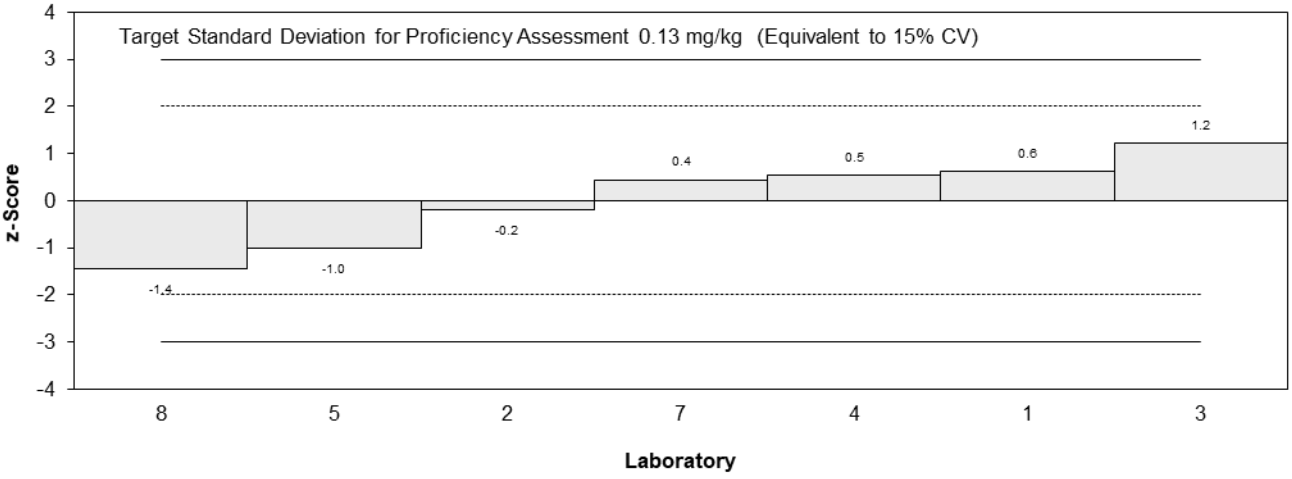
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.96	0.24	0.61	0.29
2	0.853792761601	0.085379276160	-0.20	-0.17
3	1.04	0.260	1.21	0.55
4	0.950	0.19	0.53	0.30
5	0.746	0.030	-1.02	-1.00
6	NT	NT		
7	0.938	0.1876	0.44	0.25
8	0.69	0.10	-1.44	-1.16

Statistics

Assigned Value	0.88	0.13
Spike Value	Not Spiked	
Homogeneity Value	0.86	0.10
Robust Average	0.88	0.13
Median	0.94	0.12
Mean	0.883	
N	7	
Max	1.04	
Min	0.69	
Robust SD	0.14	
Robust CV	16%	


Kernel Density
Density
Result
Results: S2 - Cr
Assigned Value = 0.88 ± 0.13 mg/kg
Results (mg/kg)
Laboratory
8
5
2
7
4
1
3
6
Md
RA
HV


z-Scores: S2 - Cr
Target Standard Deviation for Proficiency Assessment 0.13 mg/kg (Equivalent to 15% CV)
z-Score
-1.4
-1.0
-0.2
0.4
0.5
0.6
1.2
Laboratory

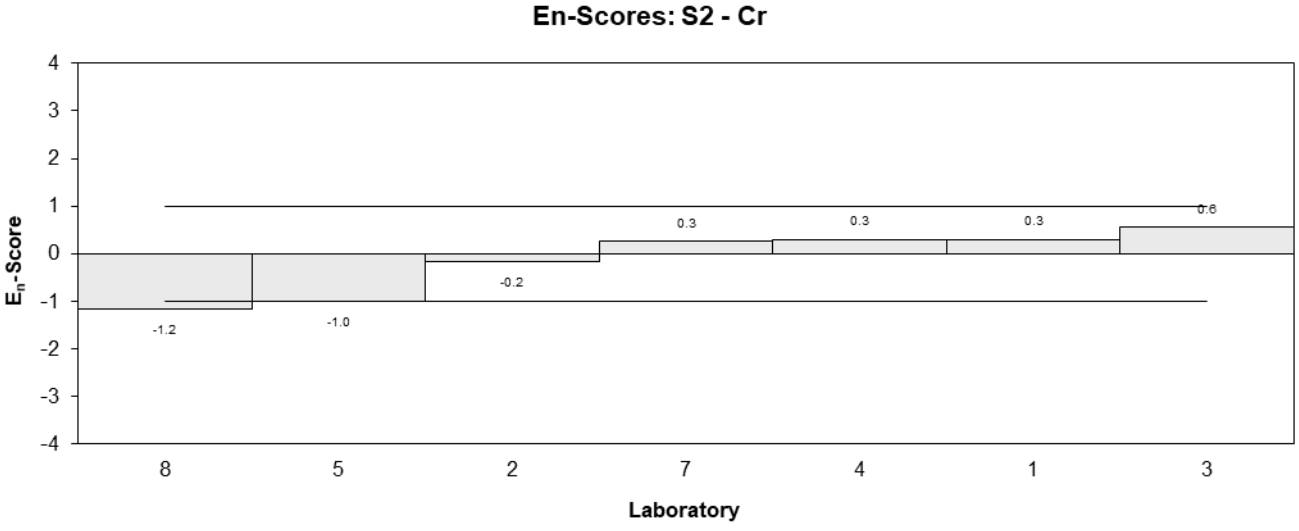

En-Scores: S2 - Cr
En-Score
-1.2
-1.0
-0.2
0.3
0.3
0.3
0.6
Laboratory

Figure 33

Table 36

Sample Details

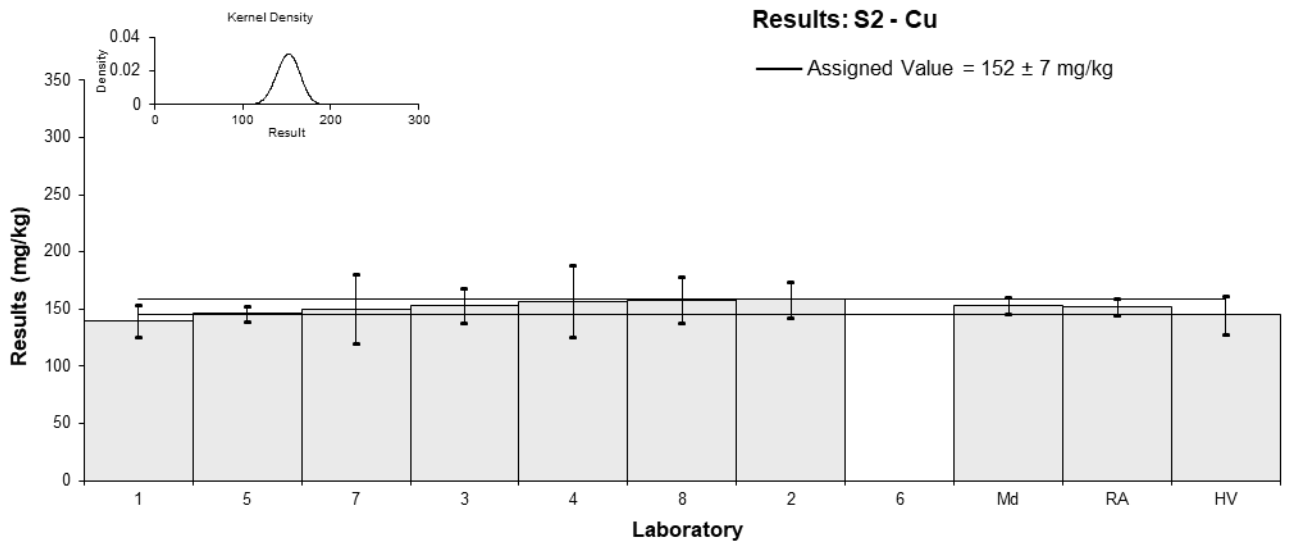
Sample No.	S2
Matrix	Bovine Liver
Analyte	Cu
Unit	mg/kg

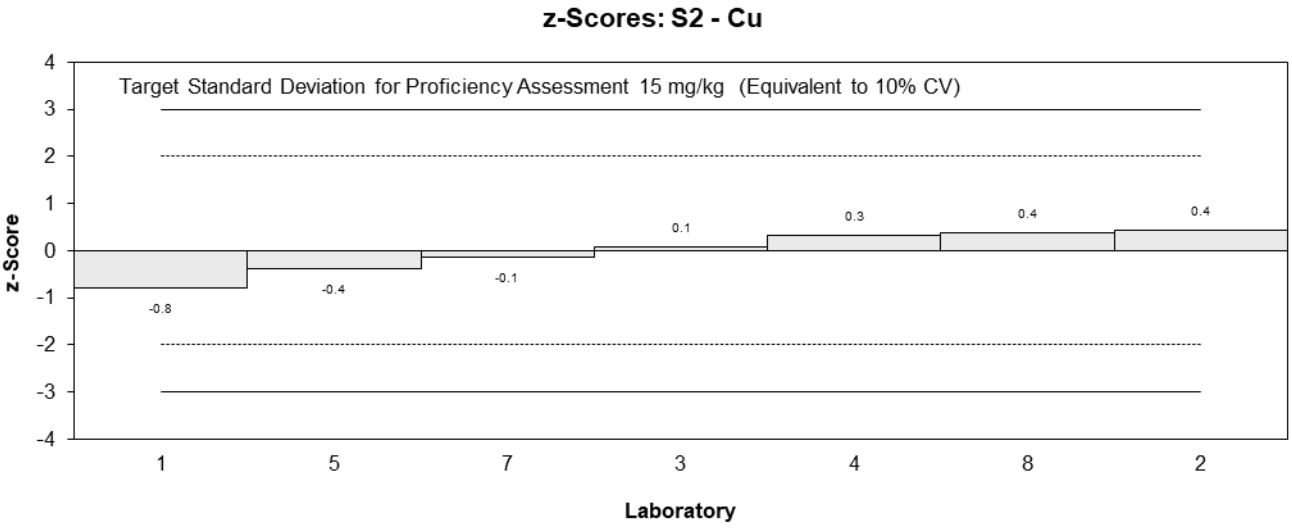
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	140	14	-0.79	-0.77
2	158.5068551756	15.85068551756	0.43	0.38
3	153	15.3	0.07	0.06
4	157	31.4	0.33	0.16
5	146	7	-0.39	-0.61
6	NT	NT		
7	150	30	-0.13	-0.06
8	158	20	0.39	0.28

Statistics

Assigned Value	152	7
Spike Value	Not Spiked	
Homogeneity Value	145	17
Robust Average	152	7
Median	153	7
Mean	152	
N	7	
Max	158.5068551756	
Min	140	
Robust SD	7.8	
Robust CV	5.2%	


Kernel Density
Density
0.04
0.02
0
0
100
200
300
Result
Results: S2 - Cu
Assigned Value = 152 ± 7 mg/kg
Results (mg/kg)
350
300
250
200
150
100
50
0
1
5
7
3
4
8
2
6
Md
RA
HV
Laboratory


z-Scores: S2 - Cu
Target Standard Deviation for Proficiency Assessment 15 mg/kg (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.8
-0.4
-0.1
0.1
0.3
0.4
0.4
1
5
7
3
4
8
2
Laboratory

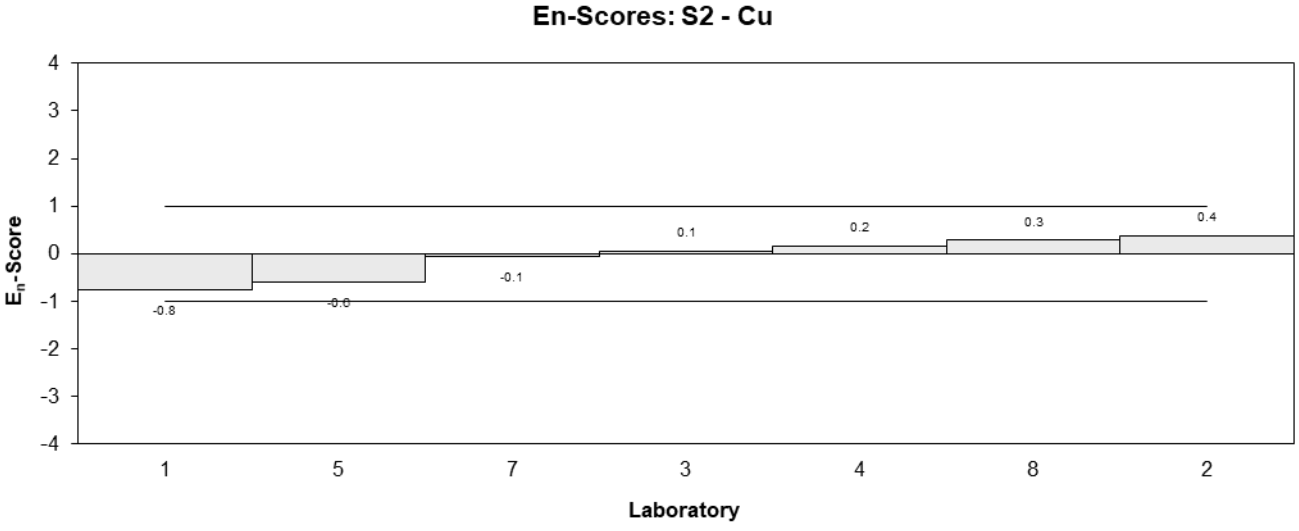

En-Scores: S2 - Cu
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.8
-0.0
-0.1
0.1
0.2
0.3
0.4
1
5
7
3
4
8
2
Laboratory

Figure 34

Table 37

Sample Details

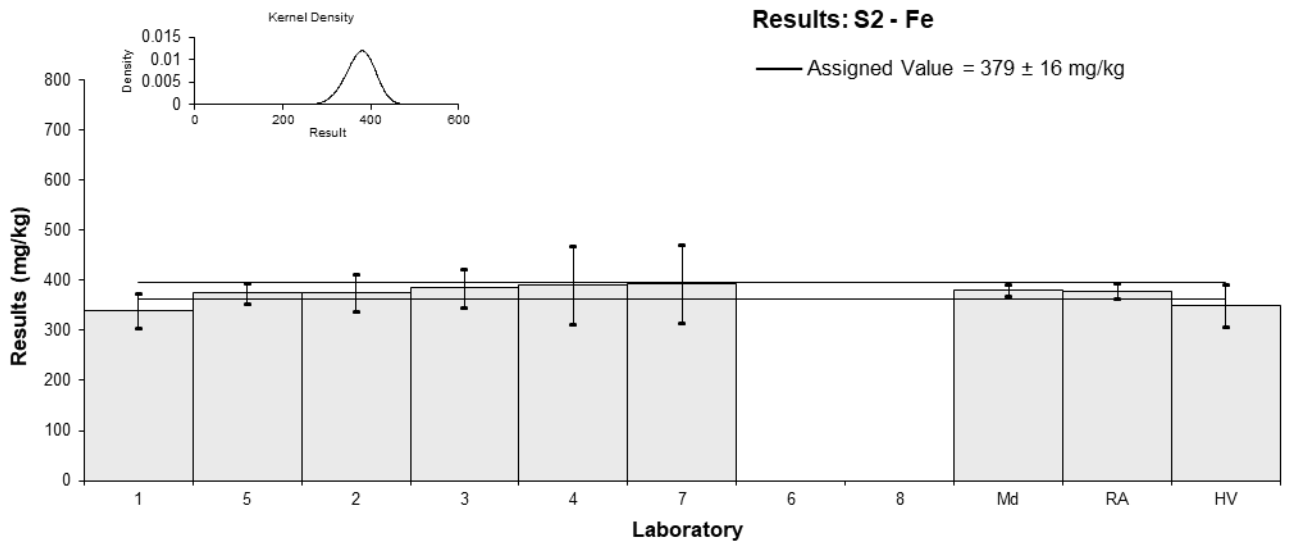
Sample No.	S2
Matrix	Bovine Liver
Analyte	Fe
Unit	mg/kg

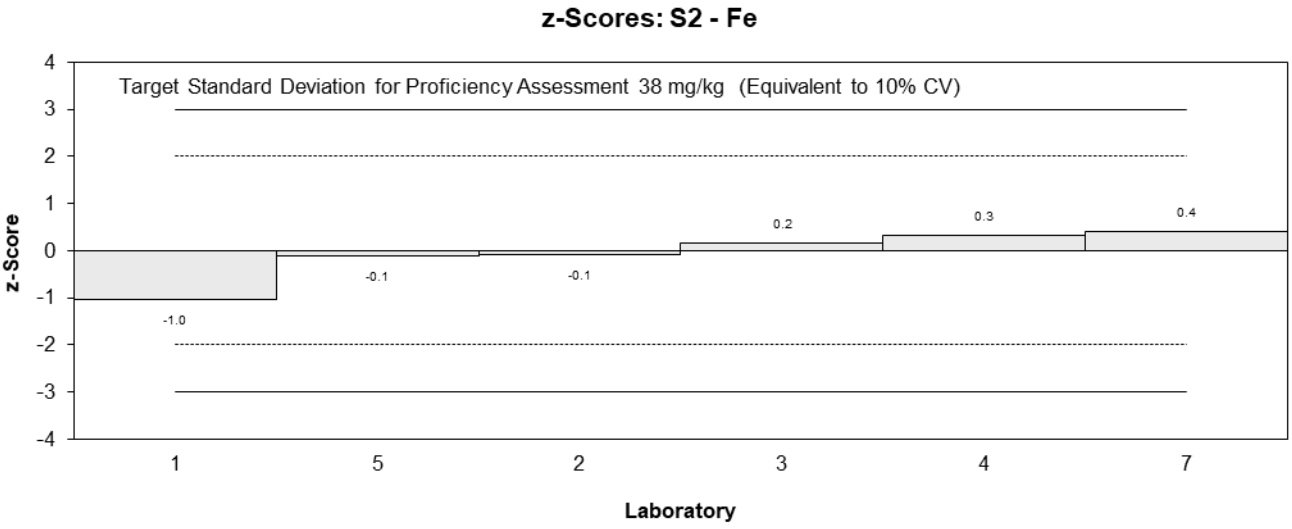
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	340	34	-1.03	-1.04
2	375.7404915319	37.57404915319	-0.09	-0.08
3	385	38.5	0.16	0.14
4	391	78.2	0.32	0.15
5	375	20	-0.11	-0.16
6	NT	NT		
7	394	78.8	0.40	0.19
8	NT	NT		

Statistics

Assigned Value	379	16
Spike Value	Not Spiked	
Homogeneity Value	349	42
Robust Average	379	16
Median	380	12
Mean	377	
N	6	
Max	394	
Min	340	
Robust SD	16	
Robust CV	4.1%	


Kernel Density
Density
0.015
0.01
0.005
0
0
200
400
600
Result
Results: S2 - Fe
Assigned Value = 379 ± 16 mg/kg
Results (mg/kg)
800
700
600
500
400
300
200
100
0
1
5
2
3
4
7
6
8
Md
RA
HV
Laboratory


z-Scores: S2 - Fe
Target Standard Deviation for Proficiency Assessment 38 mg/kg (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.0
-0.1
-0.1
0.2
0.3
0.4
1
5
2
3
4
7
Laboratory

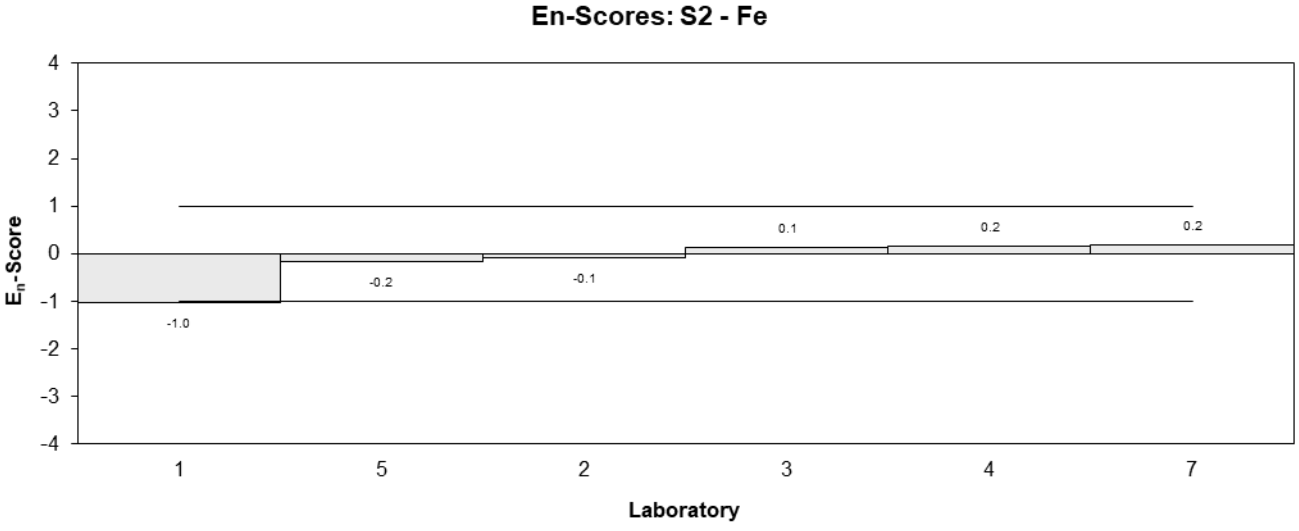

En-Scores: S2 - Fe
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.0
-0.2
-0.1
0.1
0.2
0.2
1
5
2
3
4
7
Laboratory

Figure 35

Table 38

Sample Details

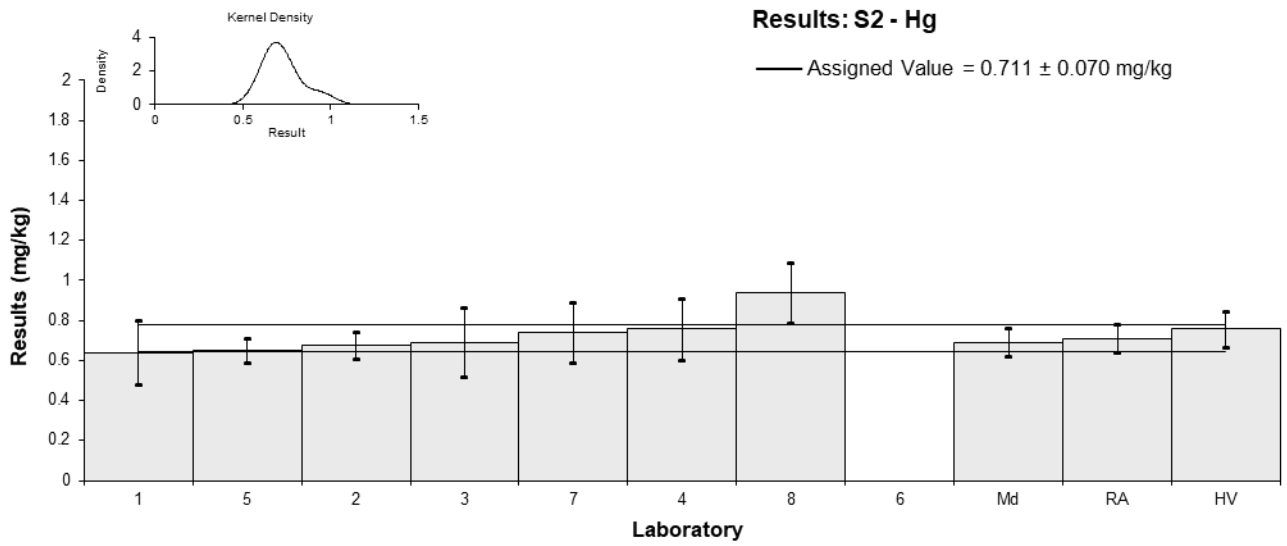
Sample No.	S2
Matrix	Bovine Liver
Analyte	Hg
Unit	mg/kg

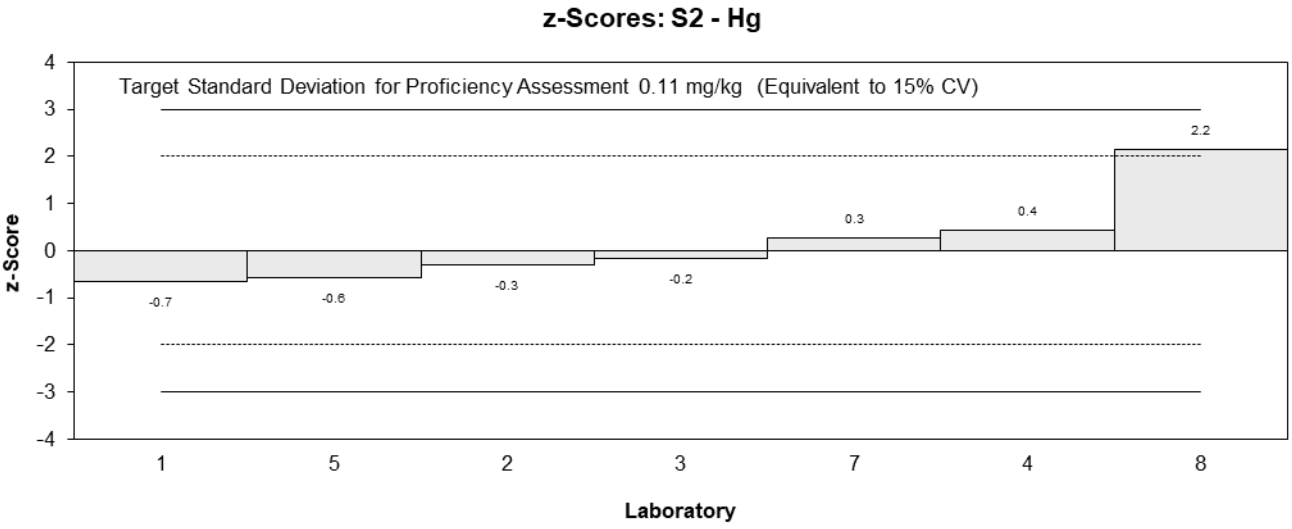
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.64	0.16	-0.67	-0.41
2	0.677505628563	0.067750562856	-0.31	-0.34
3	0.692	0.173	-0.18	-0.10
4	0.757	0.1514	0.43	0.28
5	0.65	0.06	-0.57	-0.66
6	NT	NT		
7	0.741	0.1482	0.28	0.18
8	0.94	0.15	2.15	1.38

Statistics

Assigned Value	0.711	0.070
Spike Value	Not Spiked	
Homogeneity Value	0.758	0.091
Robust Average	0.711	0.070
Median	0.692	0.069
Mean	0.728	
N	7	
Max	0.94	
Min	0.64	
Robust SD	0.074	
Robust CV	10%	


Kernel Density
Density
Result
Results: S2 - Hg
Assigned Value = 0.711 ± 0.070 mg/kg
Results (mg/kg)
Laboratory
1
5
2
3
7
4
8
6
Md
RA
HV


z-Scores: S2 - Hg
Target Standard Deviation for Proficiency Assessment 0.11 mg/kg (Equivalent to 15% CV)
z-Score
-0.7
-0.6
-0.3
-0.2
0.3
0.4
2.2
Laboratory

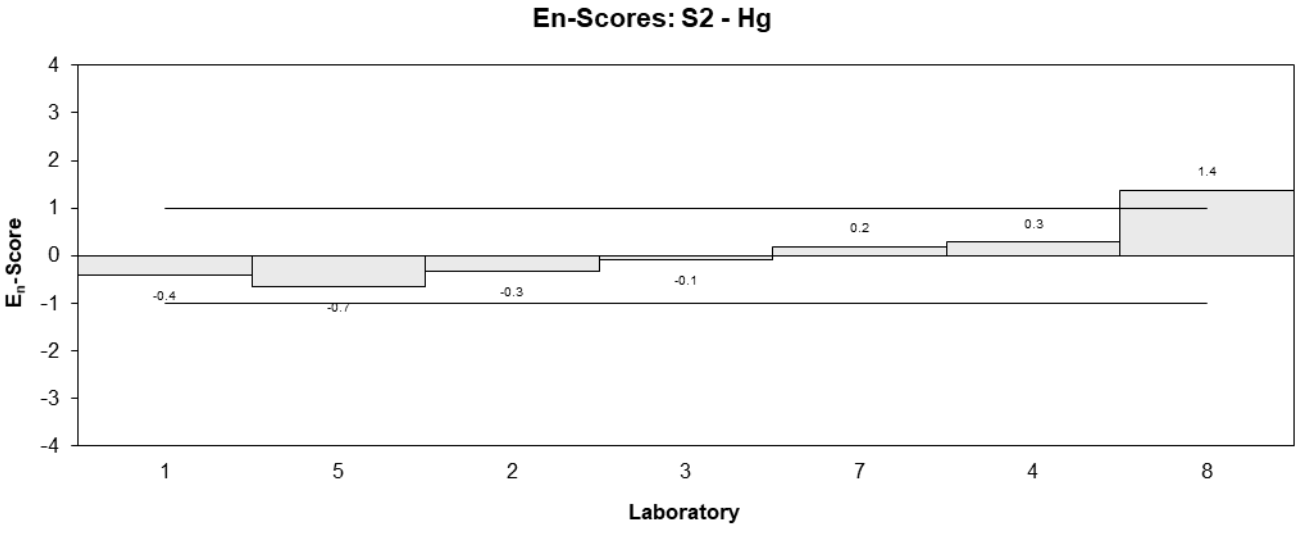

En-Scores: S2 - Hg
En-Score
-0.4
-0.7
-0.3
-0.1
0.2
0.3
1.4
Laboratory

Figure 36

Table 39

Sample Details

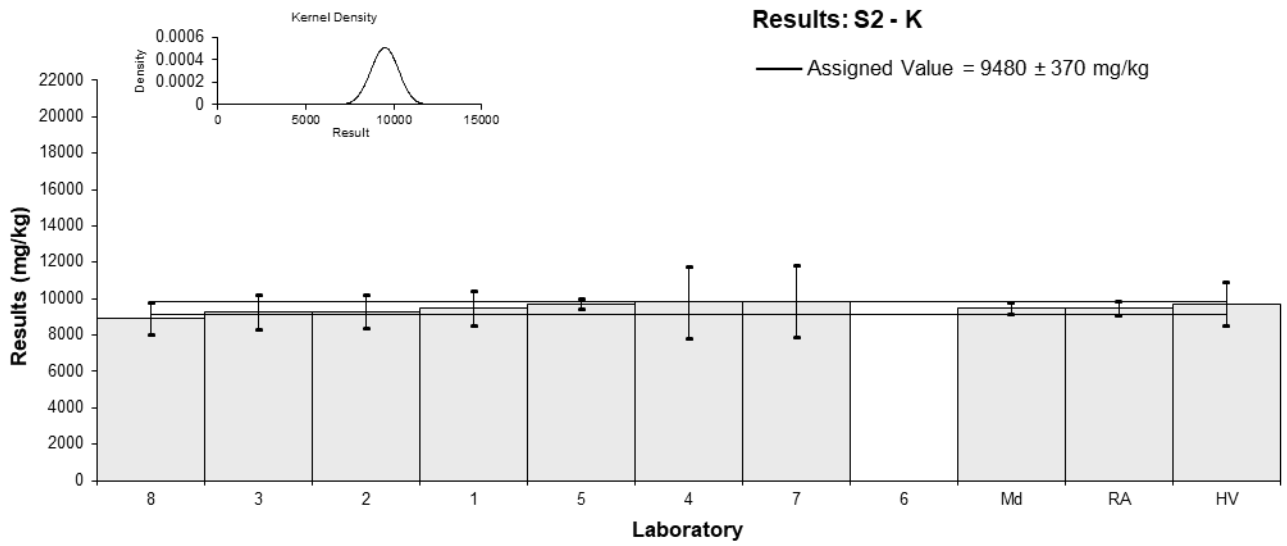
Sample No.	S2
Matrix	Bovine Liver
Analyte	K
Unit	mg/kg

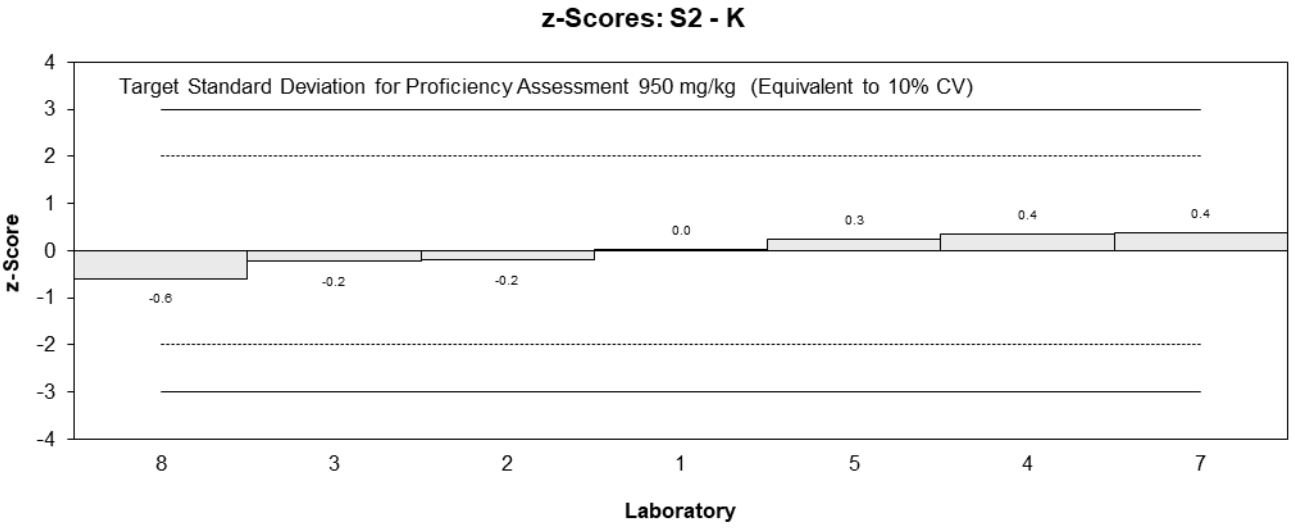
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	9500	950	0.02	0.02
2	9297.448603252	929.7448603252	-0.19	-0.18
3	9270	927	-0.22	-0.21
4	9820	1964	0.36	0.17
5	9720	300	0.25	0.50
6	NT	NT		
7	9850	1970	0.39	0.18
8	8921	900	-0.59	-0.57

Statistics

Assigned Value	9480	370
Spike Value	Not Spiked	
Homogeneity Value	9700	1200
Robust Average	9480	370
Median	9500	320
Mean	9480	
N	7	
Max	9850	
Min	8921	
Robust SD	390	
Robust CV	4.1%	


Kernel Density
Density
0.0006
0.0004
0.0002
0
0
5000
10000
15000
Result
Results: S2 - K
Assigned Value = 9480 ± 370 mg/kg
Results (mg/kg)
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
8
3
2
1
5
4
7
6
Md
RA
HV
Laboratory


z-Scores: S2 - K
Target Standard Deviation for Proficiency Assessment 950 mg/kg (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.6
-0.2
-0.2
0.0
0.3
0.4
0.4
8
3
2
1
5
4
7
Laboratory

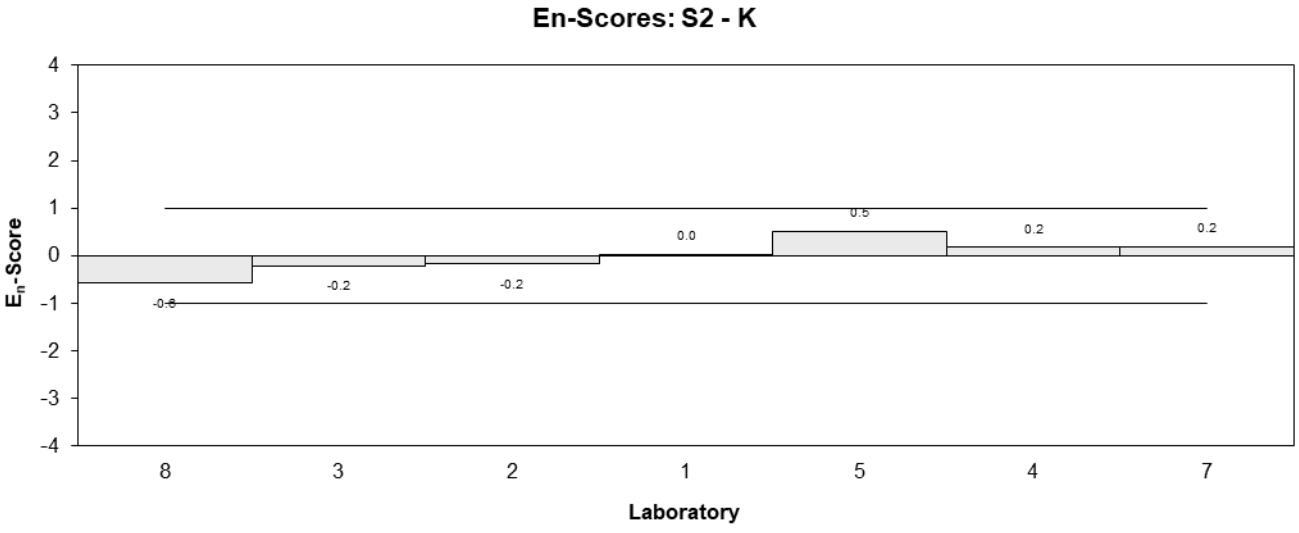

En-Scores: S2 - K
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.6
-0.2
-0.2
0.0
0.5
0.2
0.2
8
3
2
1
5
4
7
Laboratory

Figure 37

Table 40

Sample Details

Sample No.	S2
Matrix	Bovine Liver
Analyte	Mg
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	560	56	-0.36	-0.33
2	541.0725097455	54.10725097455	-0.69	-0.65
3	605	60.5	0.41	0.36
4	576	115.2	-0.09	-0.04
5	622	30	0.71	0.98
6	NT	NT		
7	578	115.6	-0.05	-0.03
8	583	60	0.03	0.03

Statistics

Assigned Value	581	29
Spike Value	Not Spiked	
Homogeneity Value	570	68
Robust Average	581	29
Median	578	25
Mean	581	
N	7	
Max	622	
Min	541.0725097455	
Robust SD	30	
Robust CV	5.2%	

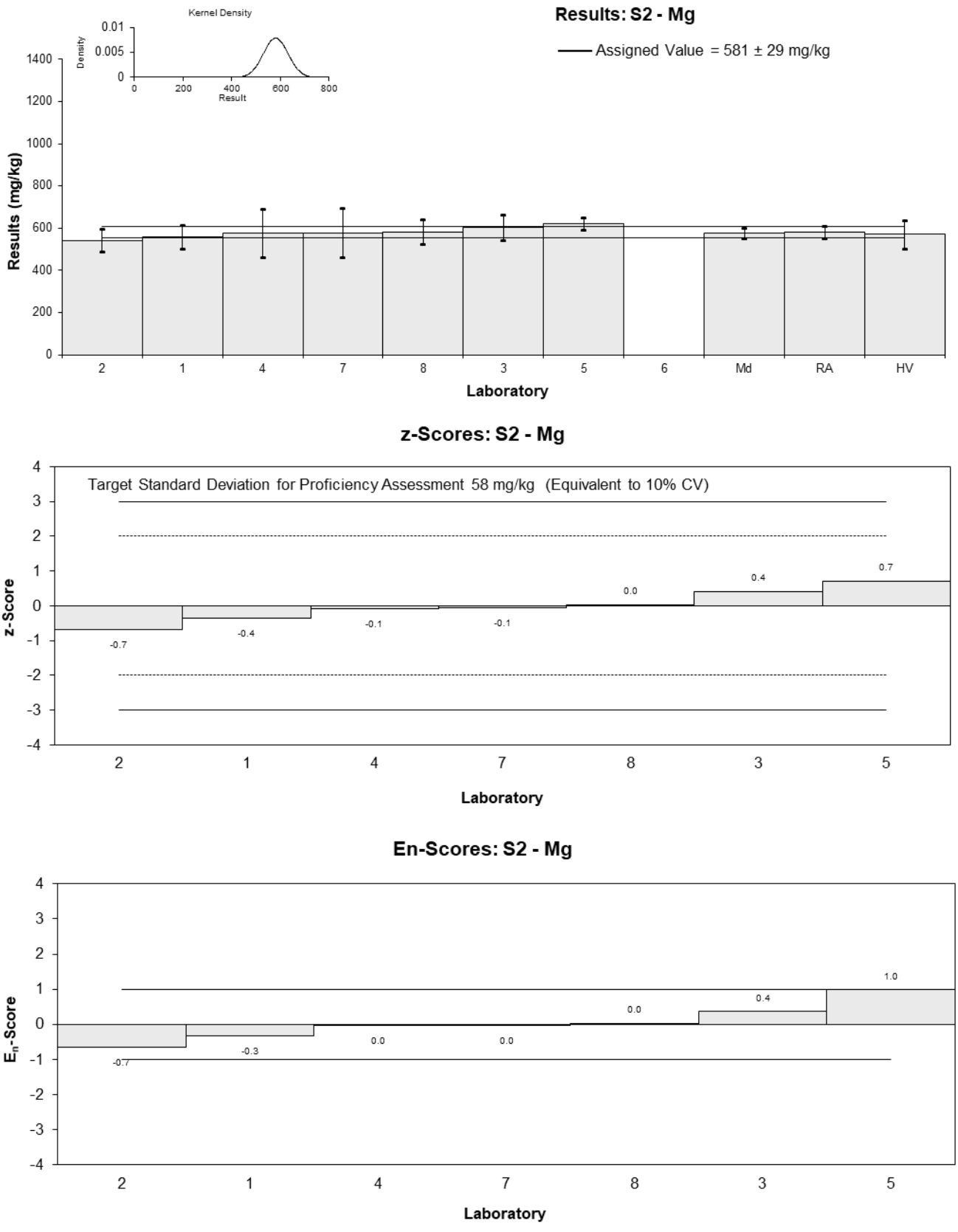

Kernel Density
Density
Result
Results: S2 - Mg
Assigned Value = 581 ± 29 mg/kg
Results (mg/kg)
Laboratory
2
1
4
7
8
3
5
6
Md
RA
HV
z-Scores: S2 - Mg
Target Standard Deviation for Proficiency Assessment 58 mg/kg (Equivalent to 10% CV)
z-Score
-0.7
-0.4
-0.1
-0.1
0.0
0.4
0.7
En-Scores: S2 - Mg
En-Score
-0.7
-0.3
0.0
0.0
0.0
0.4
1.0

Figure 38

Table 41

Sample Details

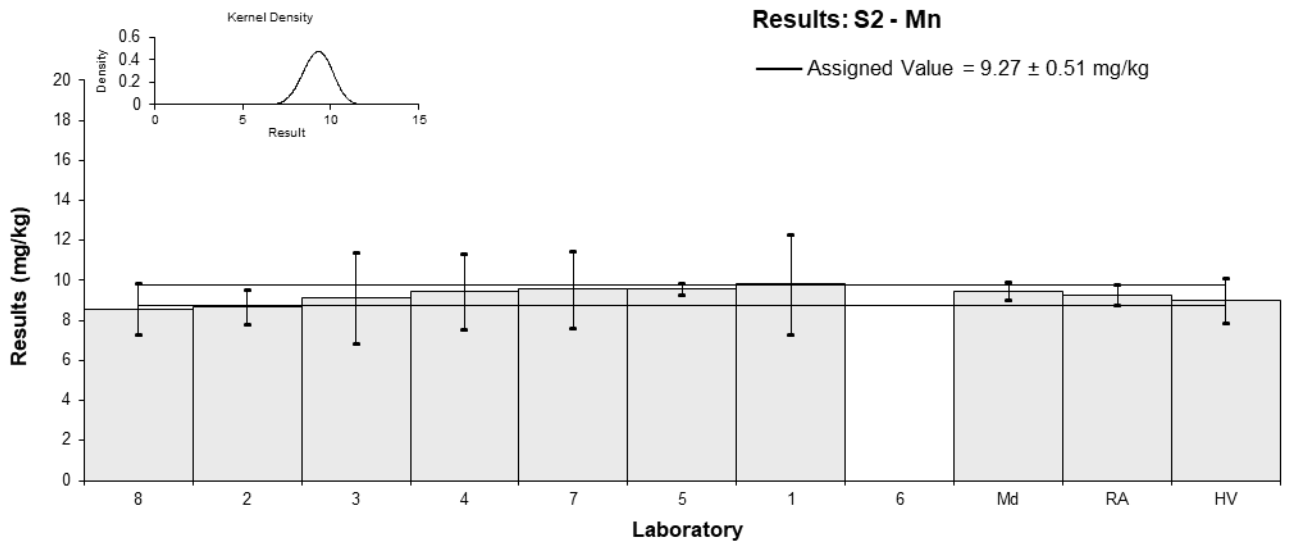
Sample No.	S2
Matrix	Bovine Liver
Analyte	Mn
Unit	mg/kg

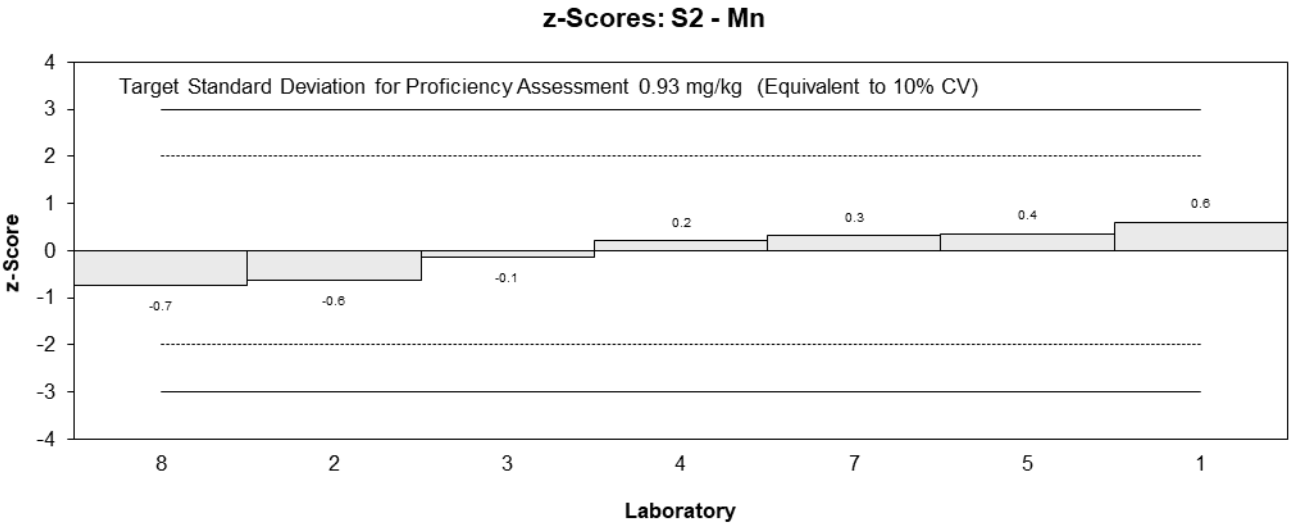
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	9.82	2.5	0.59	0.22
2	8.696187913720	0.869618791372	-0.62	-0.57
3	9.14	2.29	-0.14	-0.06
4	9.46	1.892	0.20	0.10
5	9.6	0.3	0.36	0.56
6	NT	NT		
7	9.56	1.912	0.31	0.15
8	8.58	1.3	-0.74	-0.49

Statistics

Assigned Value	9.27	0.51
Spike Value	Not Spiked	
Homogeneity Value	9.0	1.1
Robust Average	9.27	0.51
Median	9.46	0.45
Mean	9.27	
N	7	
Max	9.82	
Min	8.58	
Robust SD	0.54	
Robust CV	5.8%	


Kernel Density
Density
Result
Results: S2 - Mn
Assigned Value = 9.27 ± 0.51 mg/kg
Results (mg/kg)
Laboratory
8
2
3
4
7
5
1
6
Md
RA
HV


z-Scores: S2 - Mn
Target Standard Deviation for Proficiency Assessment 0.93 mg/kg (Equivalent to 10% CV)
z-Score
-0.7
-0.6
-0.1
0.2
0.3
0.4
0.6
Laboratory

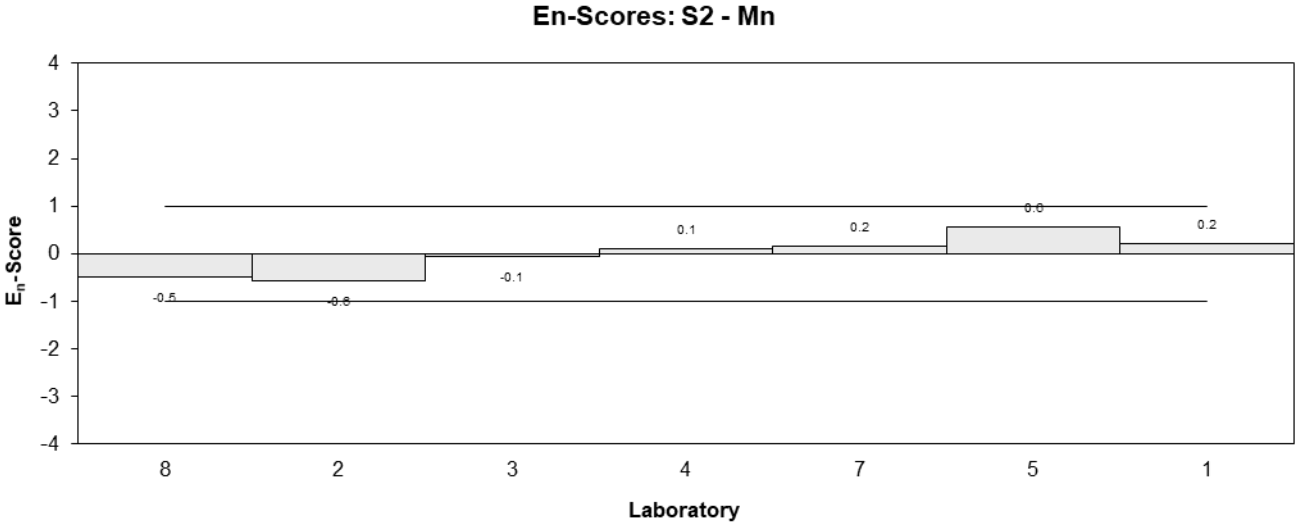

En-Scores: S2 - Mn
En-Score
-0.5
-0.6
-0.1
0.1
0.2
0.6
0.2
Laboratory

Figure 39

Table 42

Sample Details

Sample No.	S2
Matrix	Bovine Liver
Analyte	Mo
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	3.87	0.97	0.29	0.11
2	3.770105970506	0.377010597050	0.03	0.03
3	3.52	0.880	-0.64	-0.27
4	3.73	0.746	-0.08	-0.04
5	3.81	0.10	0.13	0.32
6	NT	NT		
7	3.67	0.734	-0.24	-0.12
8	3.88	0.6	0.32	0.20

Statistics

Assigned Value	3.76	0.12
Spike Value	Not Spiked	
Homogeneity Value	3.88	0.47
Robust Average	3.76	0.12
Median	3.77	0.14
Mean	3.75	
N	7	
Max	3.88	
Min	3.52	
Robust SD	0.13	
Robust CV	3.4%	

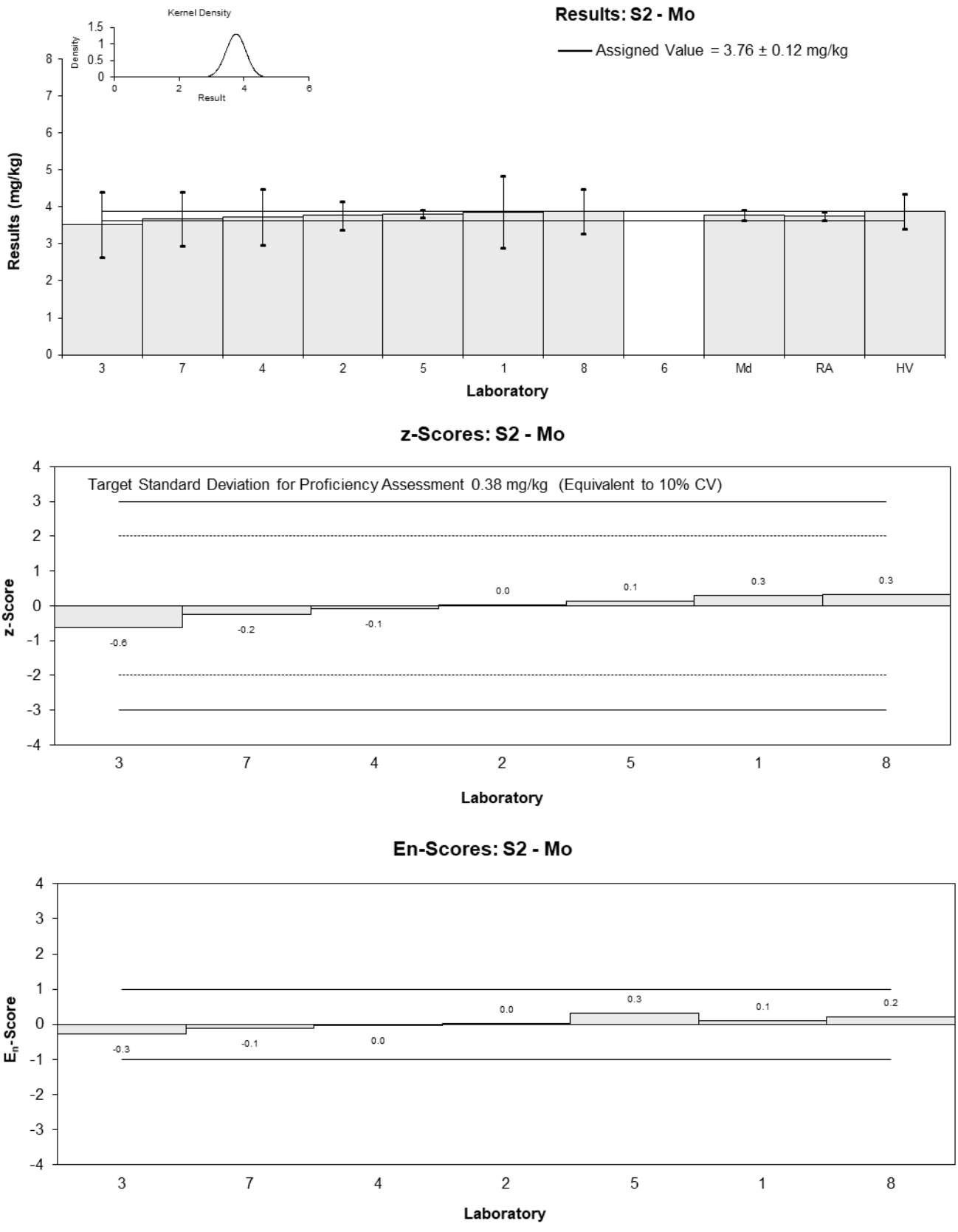

Kernel Density
Density
Result
Results: S2 - Mo
Assigned Value = 3.76 ± 0.12 mg/kg
Results (mg/kg)
Laboratory
3
7
4
2
5
1
8
6
Md
RA
HV
z-Scores: S2 - Mo
Target Standard Deviation for Proficiency Assessment 0.38 mg/kg (Equivalent to 10% CV)
z-Score
-0.6
-0.2
-0.1
0.0
0.1
0.3
0.3
Laboratory
En-Scores: S2 - Mo
En-Score
-0.3
-0.1
0.0
0.0
0.3
0.1
0.2
Laboratory

Figure 40

Table 43

Sample Details

Sample No.	S2
Matrix	Bovine Liver
Analyte	Na
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2100	210	-0.19	-0.16
2	1942.219434847	194.2219434847	-0.92	-0.85
3	2220	222	0.37	0.31
4	2150	430	0.05	0.02
5	2330	100	0.89	1.16
6	NT	NT		
7	2160	432	0.09	0.04
8	2060	220	-0.37	-0.31

Statistics

Assigned Value	2140	130
Spike Value	Not Spiked	
Homogeneity Value	2250	270
Robust Average	2140	130
Median	2150	100
Mean	2140	
N	7	
Max	2330	
Min	1942.219434847	
Robust SD	140	
Robust CV	6.5%	

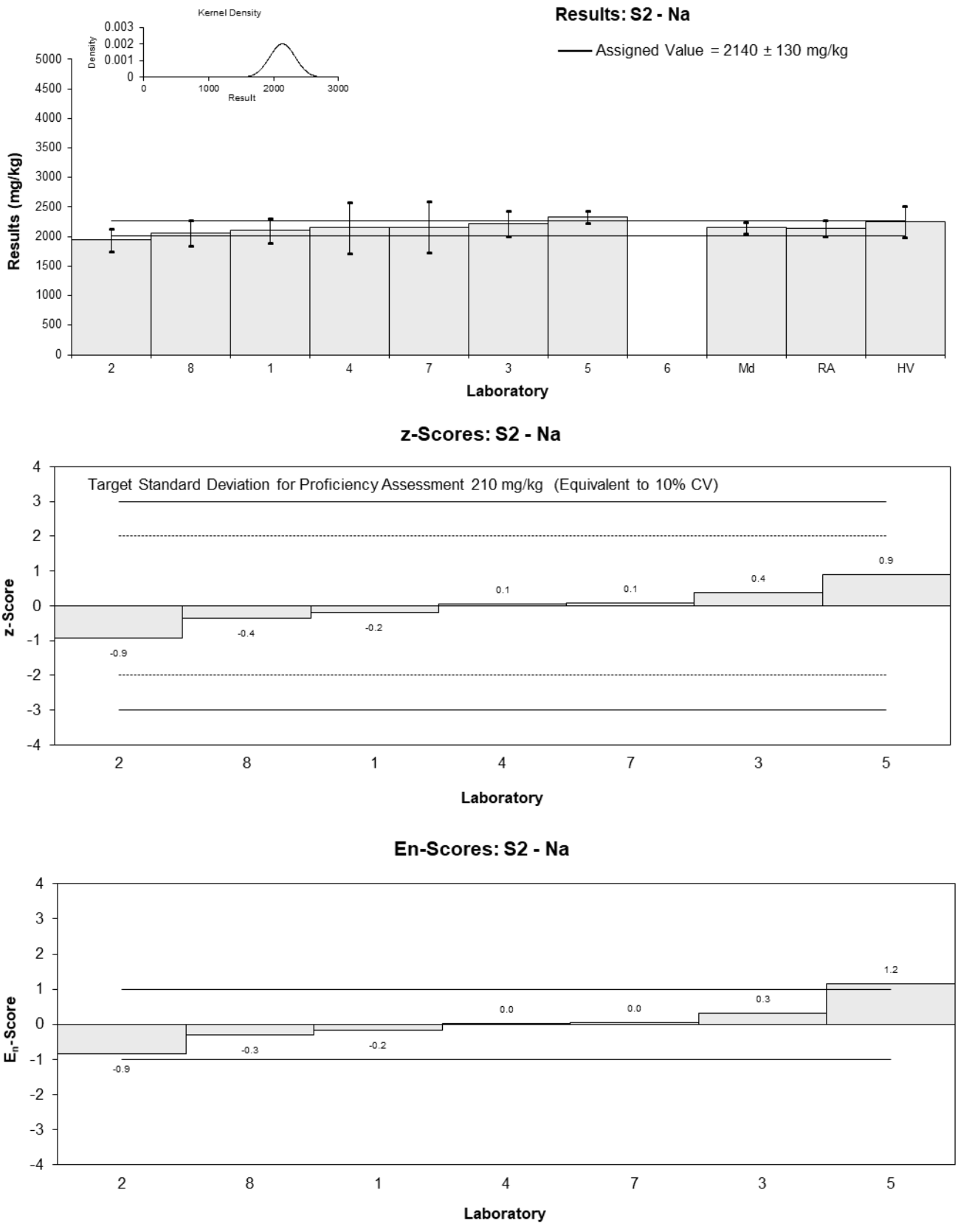

Results: S2 - Na
Assigned Value = 2140 ± 130 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
2
8
1
4
7
3
5
6
Md
RA
HV
z-Scores: S2 - Na
Target Standard Deviation for Proficiency Assessment 210 mg/kg (Equivalent to 10% CV)
z-Score
-0.9
-0.4
-0.2
0.1
0.1
0.4
0.9
Laboratory
En-Scores: S2 - Na
En-Score
-0.9
-0.3
-0.2
0.0
0.0
0.3
1.2
Laboratory

Figure 41

Table 44

Sample Details

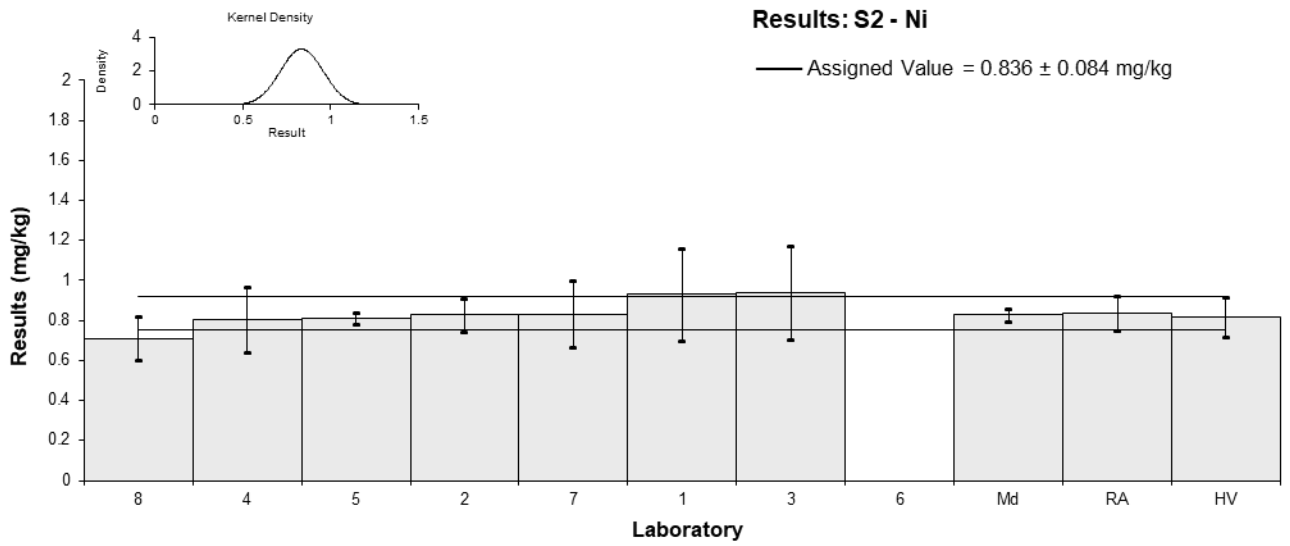
Sample No.	S2
Matrix	Bovine Liver
Analyte	Ni
Unit	mg/kg

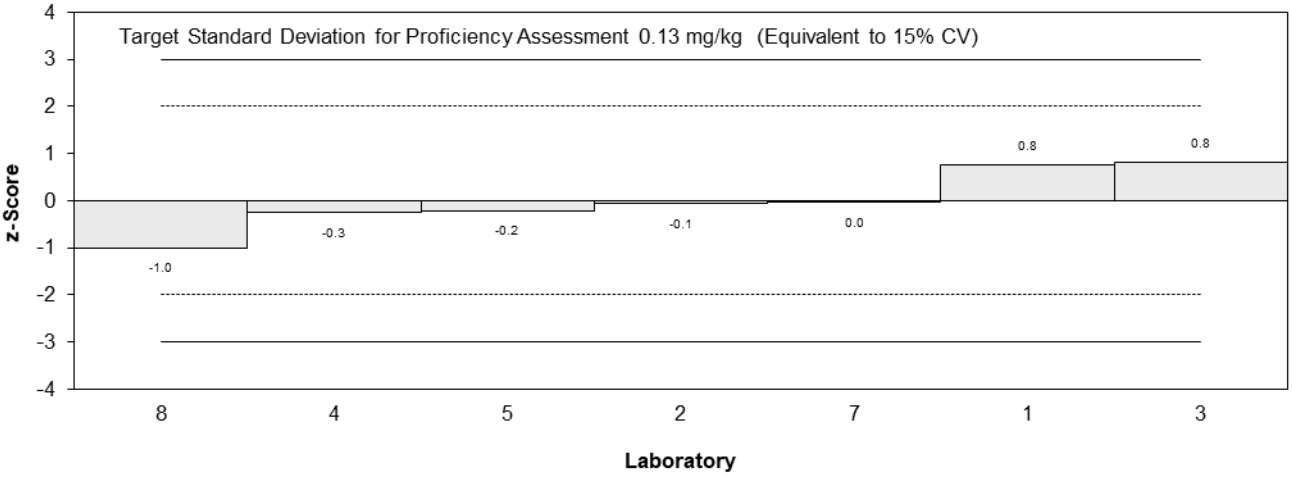
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.93	0.23	0.75	0.38
2	0.827557772152	0.082755777215	-0.07	-0.07
3	0.939	0.235	0.82	0.41
4	0.804	0.1608	-0.26	-0.18
5	0.81	0.03	-0.21	-0.29
6	NT	NT		
7	0.832	0.1664	-0.03	-0.02
8	0.71	0.11	-1.00	-0.91

Statistics

Assigned Value	0.836	0.084
Spike Value	Not Spiked	
Homogeneity Value	0.817	0.098
Robust Average	0.836	0.084
Median	0.828	0.033
Mean	0.836	
N	7	
Max	0.939	
Min	0.71	
Robust SD	0.089	
Robust CV	11%	


Kernel Density
Density
Result
Results: S2 - Ni
Assigned Value = 0.836 ± 0.084 mg/kg
Results (mg/kg)
Laboratory
8
4
5
2
7
1
3
6
Md
RA
HV


z-Scores: S2 - Ni
Target Standard Deviation for Proficiency Assessment 0.13 mg/kg (Equivalent to 15% CV)
z-Score
-1.0
-0.3
-0.2
-0.1
0.0
0.8
0.8
Laboratory

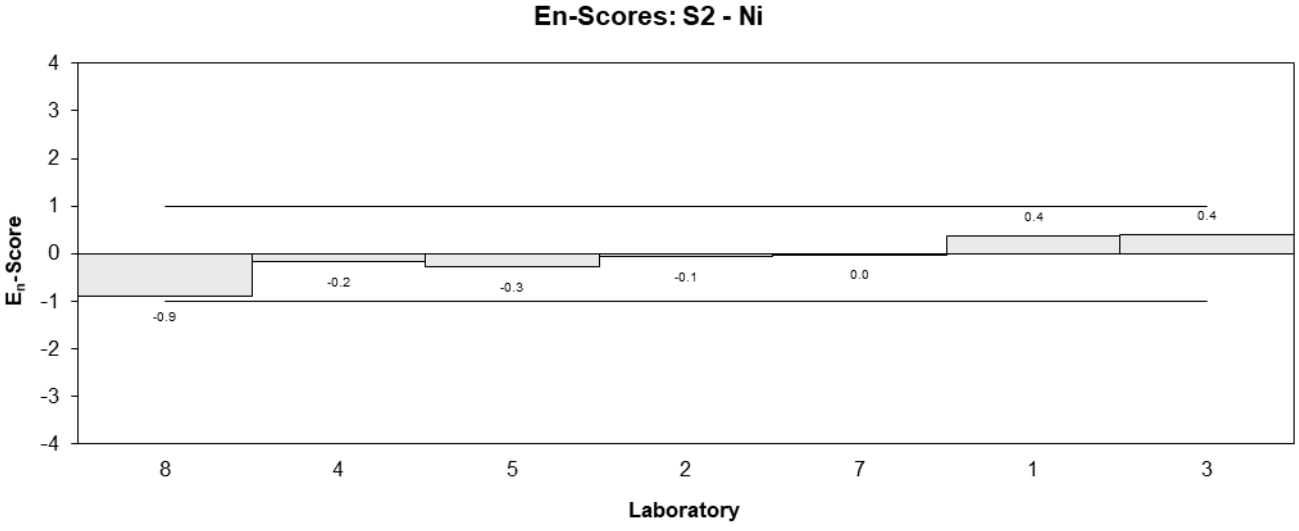

En-Scores: S2 - Ni
En-Score
-0.9
-0.2
-0.3
-0.1
0.0
0.4
0.4
Laboratory

Figure 42

Table 45

Sample Details

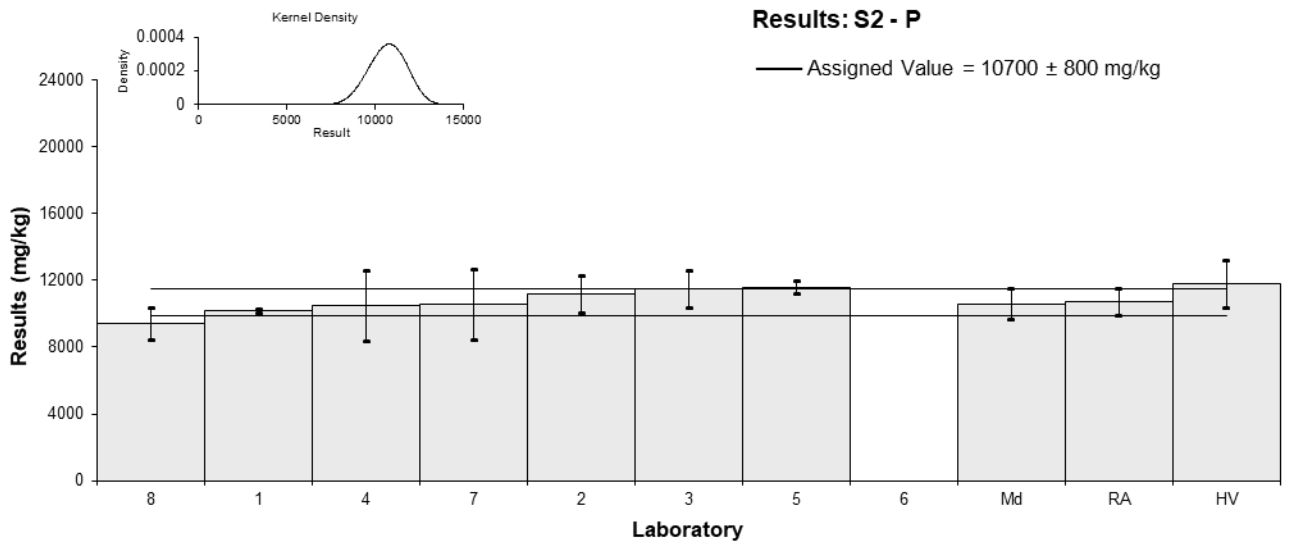
Sample No.	S2
Matrix	Bovine Liver
Analyte	P
Unit	mg/kg

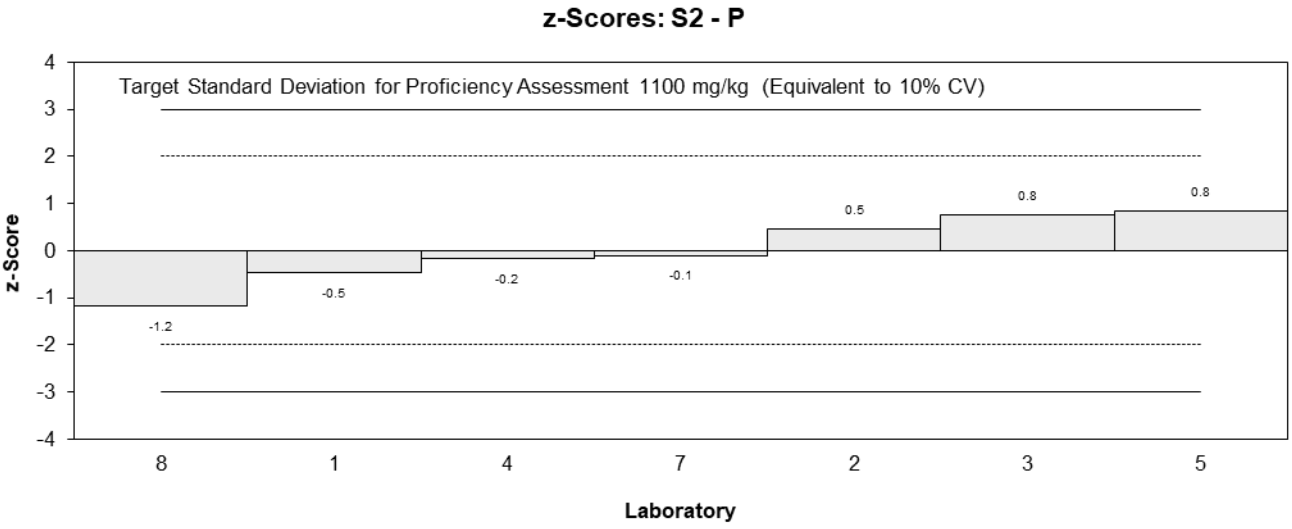
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	10200	102	-0.47	-0.62
2	11206.24011242	1120.624011242	0.47	0.37
3	11500	1150	0.75	0.57
4	10520	2104	-0.17	-0.08
5	11600	400	0.84	1.01
6	NT	NT		
7	10590	2118	-0.10	-0.05
8	9441	950	-1.18	-1.01

Statistics

Assigned Value	10700	800
Spike Value	Not Spiked	
Homogeneity Value	11800	1400
Robust Average	10700	800
Median	10600	900
Mean	10700	
N	7	
Max	11600	
Min	9441	
Robust SD	880	
Robust CV	8.2%	


Kernel Density
Density
0.0004
0.0002
0
0
5000
10000
15000
Result
Results: S2 - P
Assigned Value = 10700 ± 800 mg/kg
Results (mg/kg)
24000
20000
16000
12000
8000
4000
0
8
1
4
7
2
3
5
6
Md
RA
HV
Laboratory


z-Scores: S2 - P
Target Standard Deviation for Proficiency Assessment 1100 mg/kg (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.2
-0.5
-0.2
-0.1
0.5
0.8
0.8
8
1
4
7
2
3
5
Laboratory

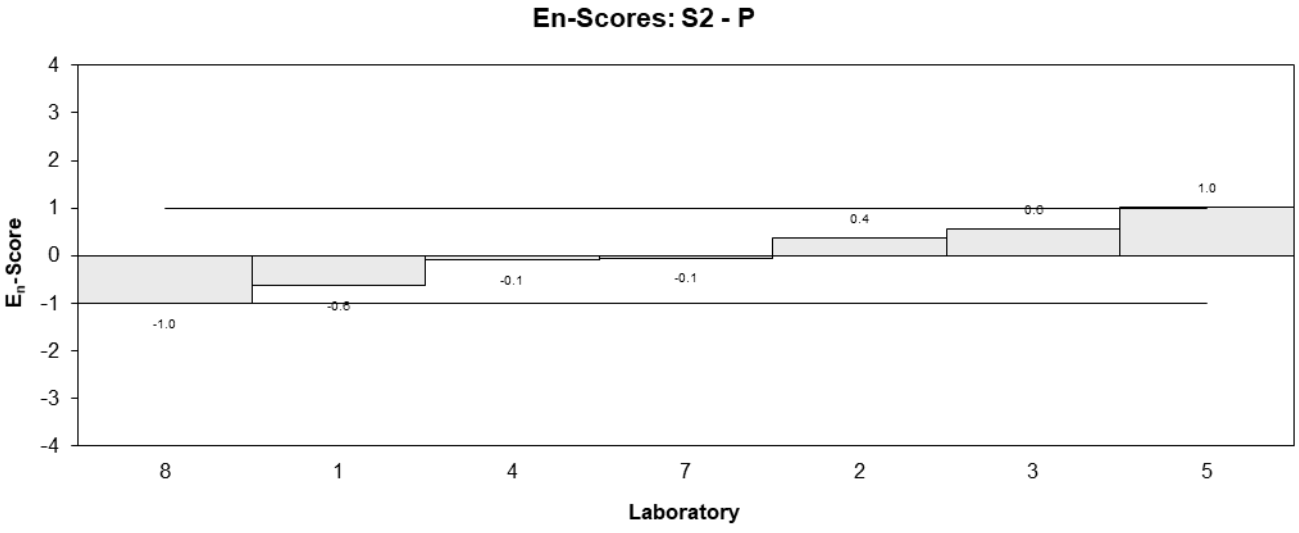

En-Scores: S2 - P
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.0
-0.6
-0.1
-0.1
0.4
0.6
1.0
8
1
4
7
2
3
5
Laboratory

Figure 43

Table 46

Sample Details

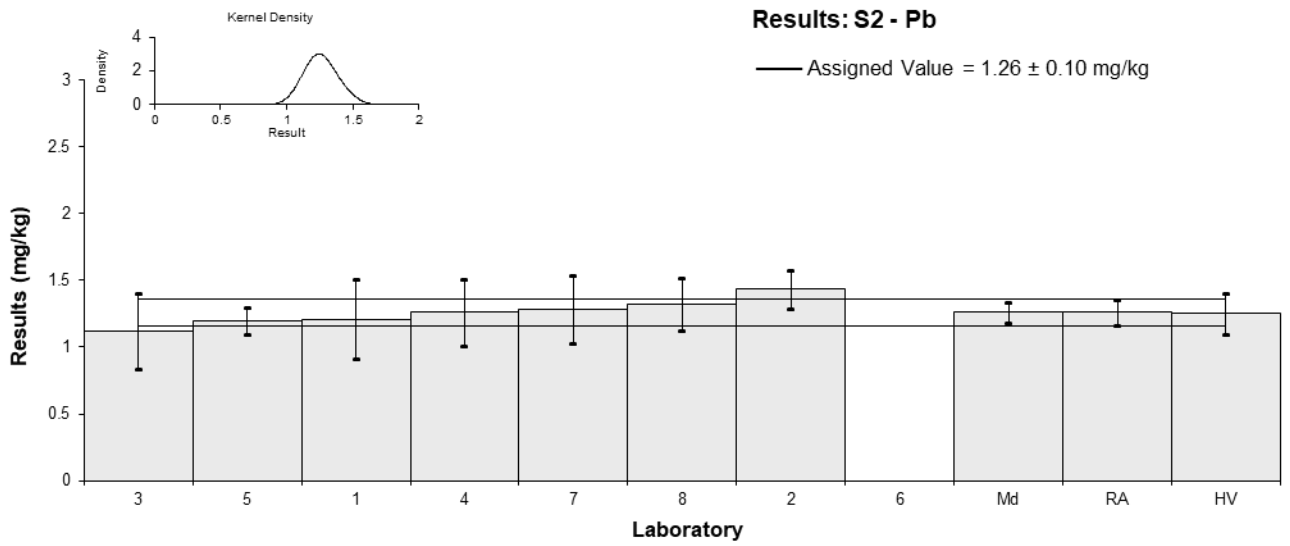
Sample No.	S2
Matrix	Bovine Liver
Analyte	Pb
Unit	mg/kg

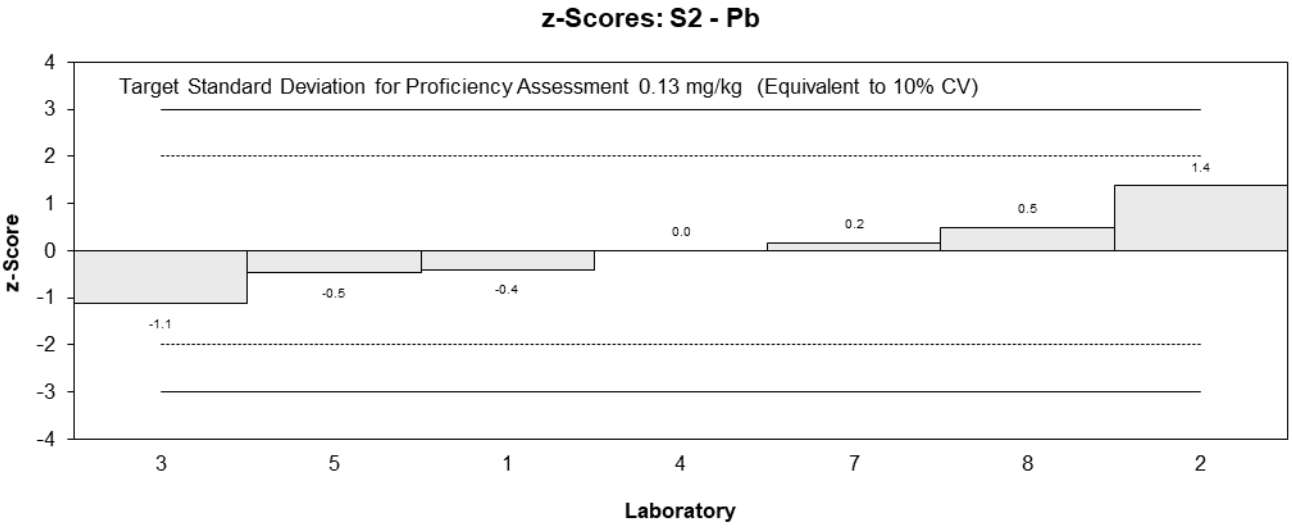
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.21	0.30	-0.40	-0.16
2	1.432854306359	0.143285430635	1.37	0.99
3	1.12	0.280	-1.11	-0.47
4	1.26	0.252	0.00	0.00
5	1.2	0.1	-0.48	-0.42
6	NT	NT		
7	1.28	0.256	0.16	0.07
8	1.32	0.20	0.48	0.27

Statistics

Assigned Value	1.26	0.10
Spike Value	Not Spiked	
Homogeneity Value	1.25	0.15
Robust Average	1.26	0.10
Median	1.26	0.08
Mean	1.26	
N	7	
Max	1.432854306359	
Min	1.12	
Robust SD	0.11	
Robust CV	8.7%	


Kernel Density
Density
Result
Results: S2 - Pb
Assigned Value = 1.26 ± 0.10 mg/kg
Results (mg/kg)
Laboratory
3
5
1
4
7
8
2
6
Md
RA
HV


z-Scores: S2 - Pb
Target Standard Deviation for Proficiency Assessment 0.13 mg/kg (Equivalent to 10% CV)
z-Score
-1.1
-0.5
-0.4
0.0
0.2
0.5
1.4
Laboratory

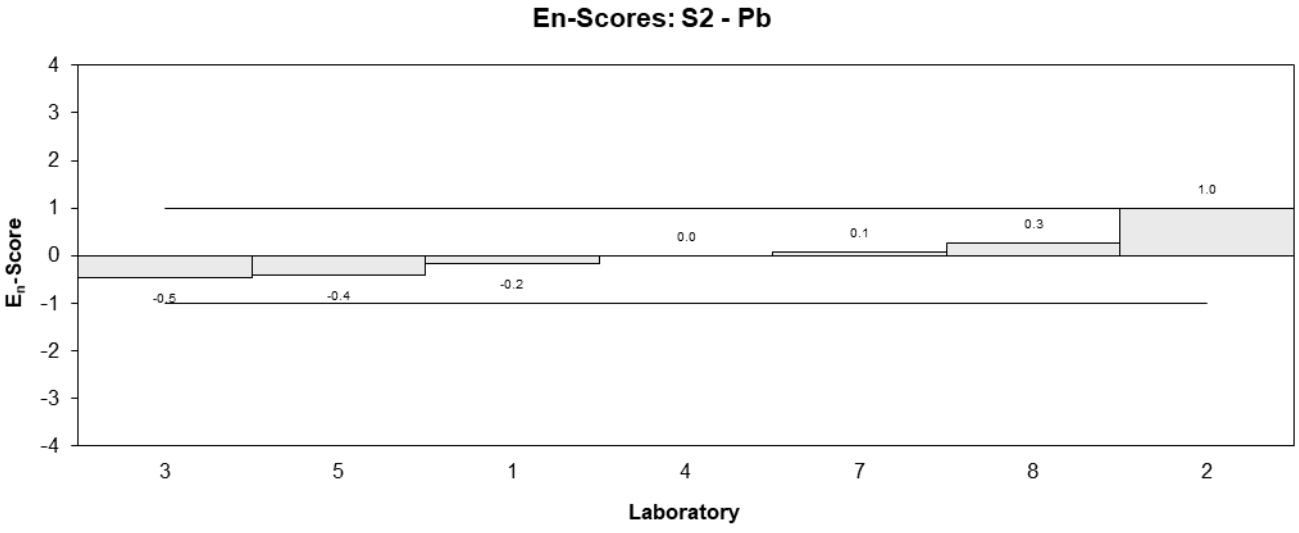

En-Scores: S2 - Pb
En-Score
-0.5
-0.4
-0.2
0.0
0.1
0.3
1.0
Laboratory

Figure 44

Table 47

Sample Details

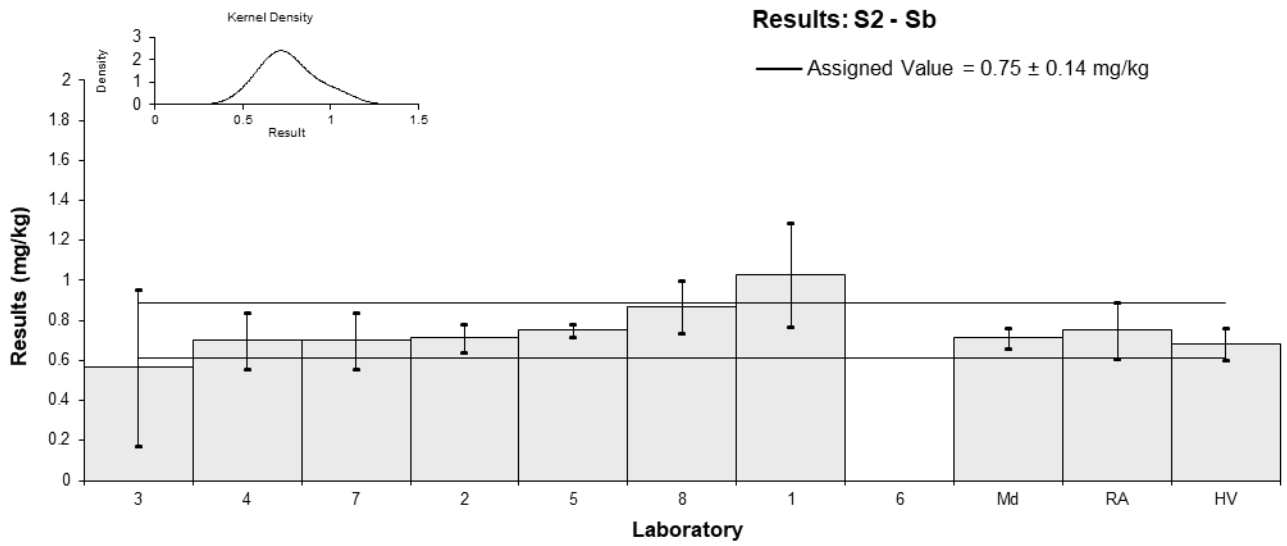
Sample No.	S2
Matrix	Bovine Liver
Analyte	Sb
Unit	mg/kg

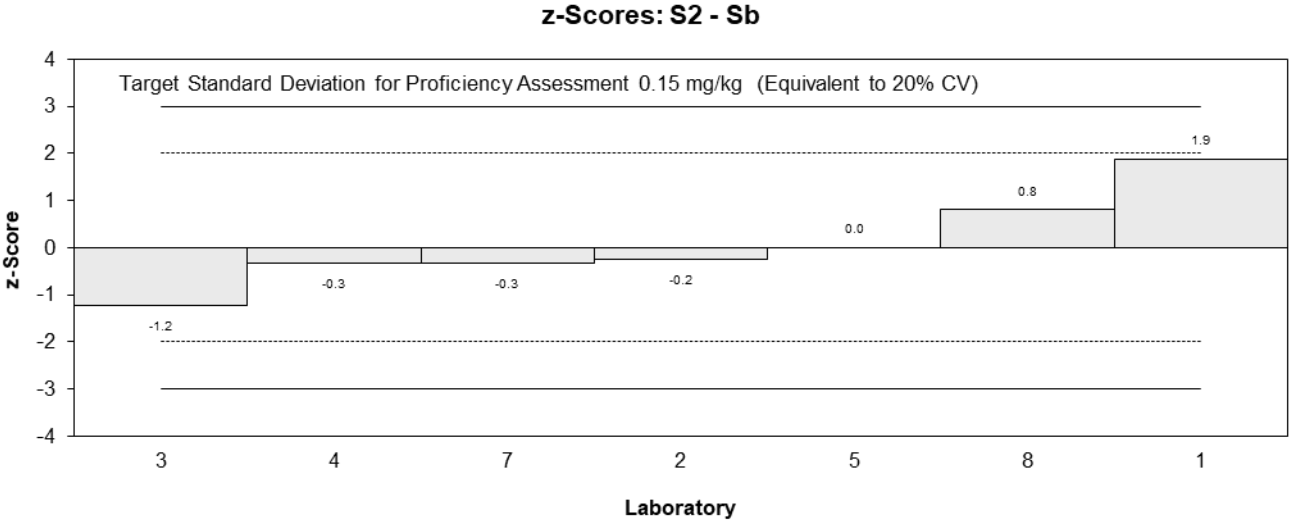
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	1.03	0.26	1.87	0.95
2	0.713592513374	0.071359251337	-0.24	-0.23
3	0.565	0.391	-1.23	-0.45
4	0.699	0.1398	-0.34	-0.26
5	0.75	0.03	0.00	0.00
6	NT	NT		
7	0.701	0.1402	-0.33	-0.25
8	0.87	0.13	0.80	0.63

Statistics

Assigned Value	0.75	0.14
Spike Value	Not Spiked	
Homogeneity Value	0.683	0.082
Robust Average	0.75	0.14
Median	0.714	0.051
Mean	0.76	
N	7	
Max	1.03	
Min	0.565	
Robust SD	0.15	
Robust CV	20%	


Kernel Density
Density
Result
Results: S2 - Sb
Assigned Value = 0.75 ± 0.14 mg/kg
Results (mg/kg)
Laboratory
3
4
7
2
5
8
1
6
Md
RA
HV


z-Scores: S2 - Sb
Target Standard Deviation for Proficiency Assessment 0.15 mg/kg (Equivalent to 20% CV)
z-Score
Laboratory
-1.2
-0.3
-0.3
-0.2
0.0
0.8
1.9

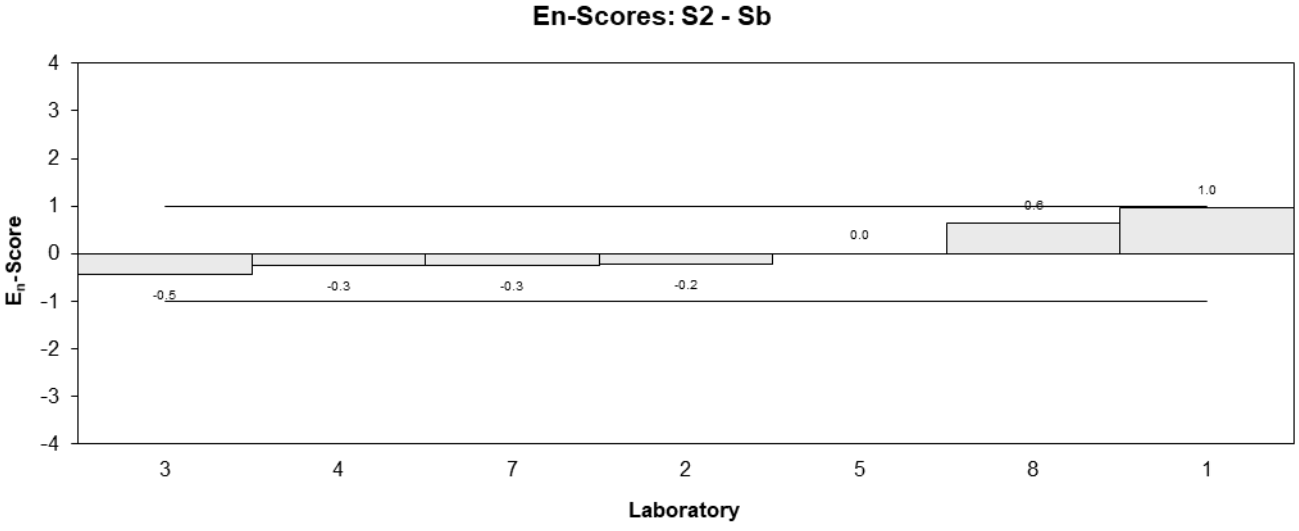

En-Scores: S2 - Sb
En-Score
Laboratory
-0.5
-0.3
-0.3
-0.2
0.0
0.6
1.0

Figure 45

Table 48

Sample Details

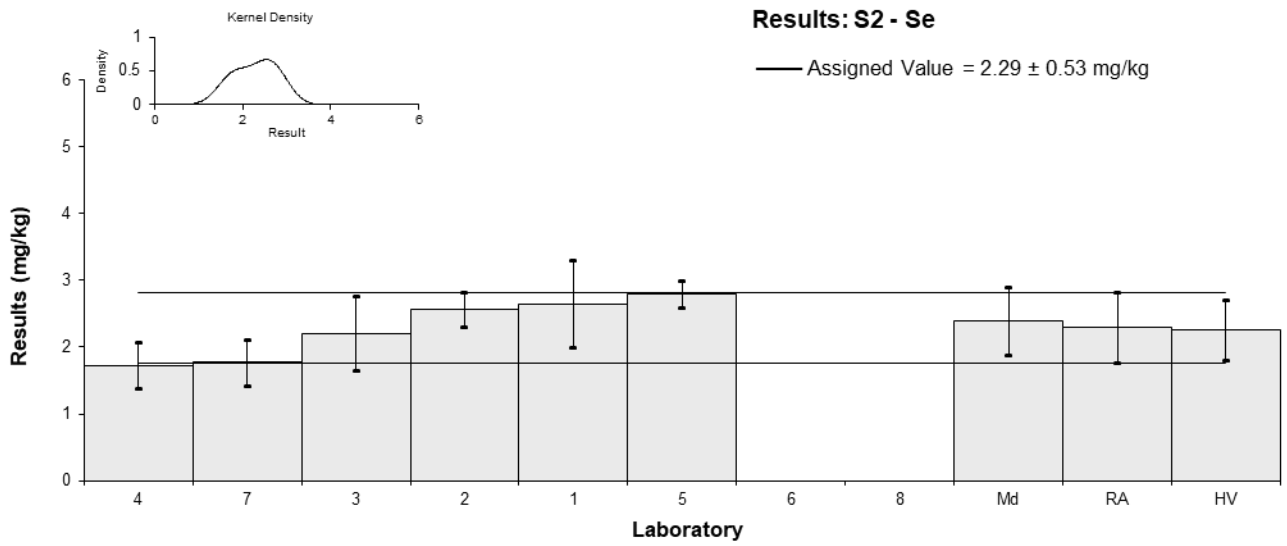
Sample No.	S2
Matrix	Bovine Liver
Analyte	Se
Unit	mg/kg

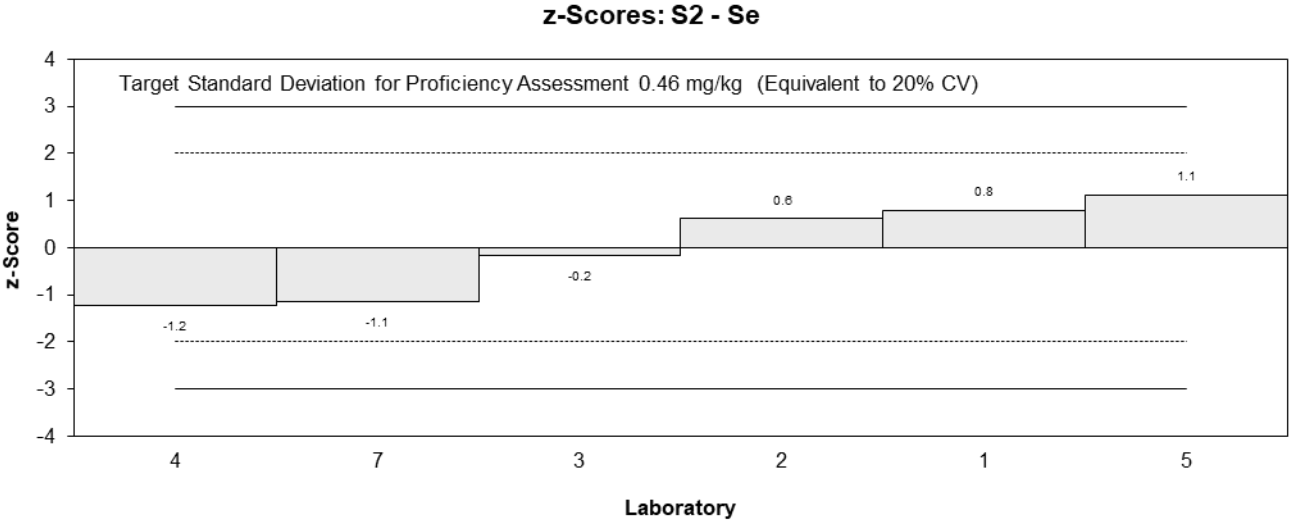
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	2.65	0.66	0.79	0.43
2	2.571032807928	0.257103280792	0.61	0.48
3	2.21	0.553	-0.17	-0.10
4	1.73	0.346	-1.22	-0.88
5	2.8	0.2	1.11	0.90
6	NT	NT		
7	1.77	0.354	-1.14	-0.82
8	NT	NT		

Statistics

Assigned Value	2.29	0.53
Spike Value	Not Spiked	
Homogeneity Value	2.26	0.45
Robust Average	2.29	0.53
Median	2.39	0.51
Mean	2.29	
N	6	
Max	2.8	
Min	1.73	
Robust SD	0.52	
Robust CV	23%	


Kernel Density
Density
Result
Results: S2 - Se
Assigned Value = 2.29 ± 0.53 mg/kg
Results (mg/kg)
Laboratory
4
7
3
2
1
5
6
8
Md
RA
HV


z-Scores: S2 - Se
Target Standard Deviation for Proficiency Assessment 0.46 mg/kg (Equivalent to 20% CV)
z-Score
-1.2
-1.1
-0.2
0.6
0.8
1.1
Laboratory

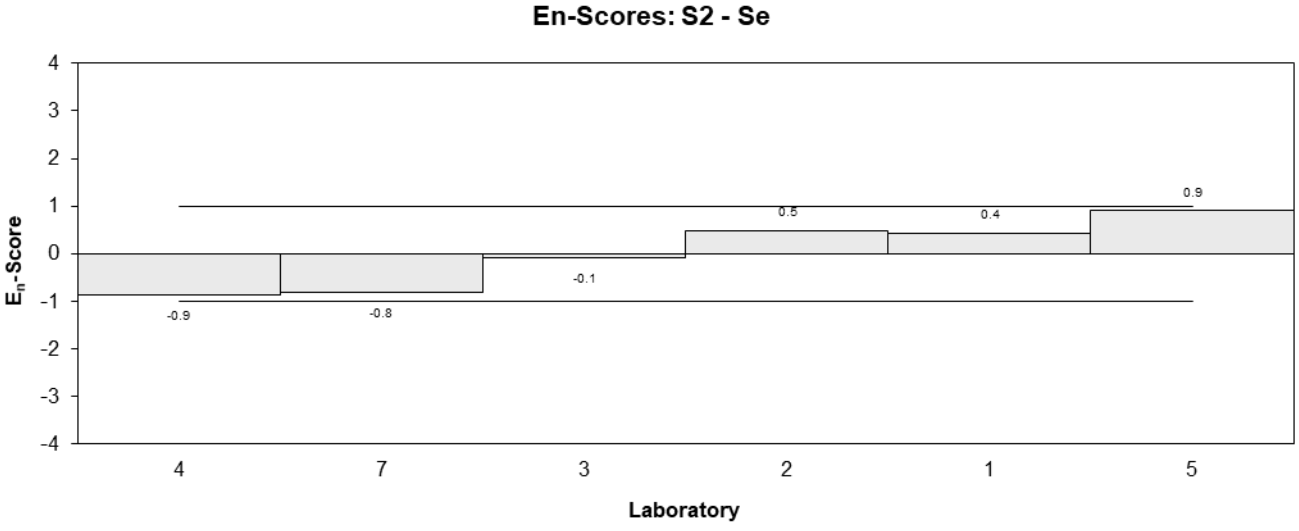

En-Scores: S2 - Se
En-Score
-0.9
-0.8
-0.1
0.5
0.4
0.9
Laboratory

Figure 46

Table 49

Sample Details

Sample No.	S2
Matrix	Bovine Liver
Analyte	Sn
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty
1	0.88	0.22
2	0.464886596570	0.046488659657
3	0.767	0.077
4	NR	0
5	0.35	0.03
6	NT	NT
7	NR	0
8	NT	NT

Statistics

Assigned Value	Not Set	
Spike Value	Not Spiked	
Homogeneity Value	0.698	0.084
Median	0.62	0.38
Mean	0.62	
N	4	
Max	0.88	
Min	0.35	

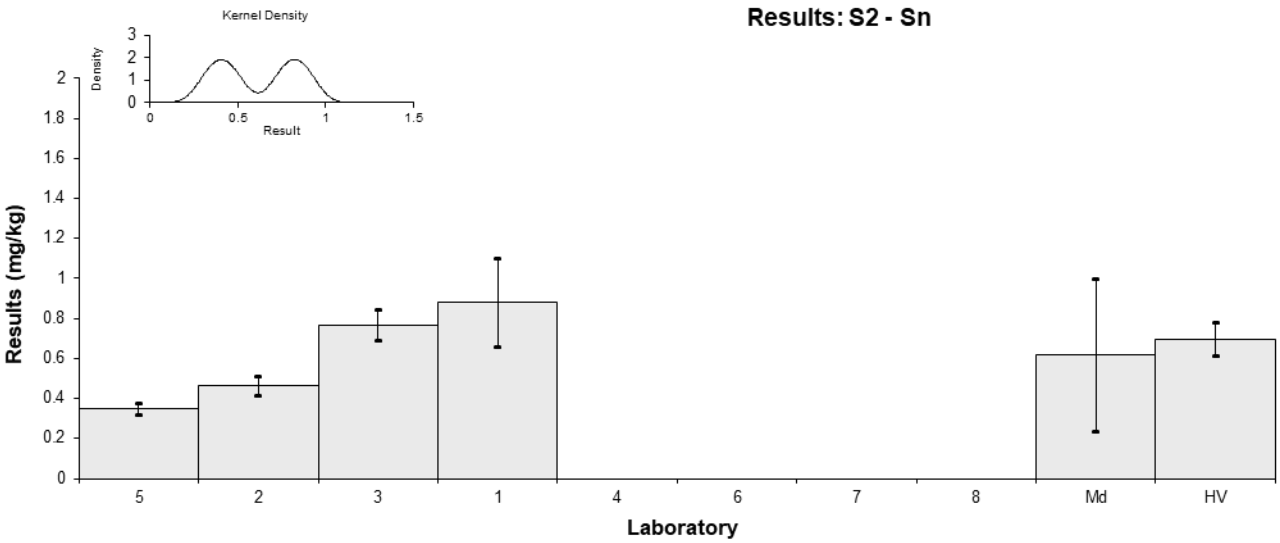

Results: S2 - Sn
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
5
2
3
1
4
6
7
8
Md
HV

Figure 47

Table 50

Sample Details

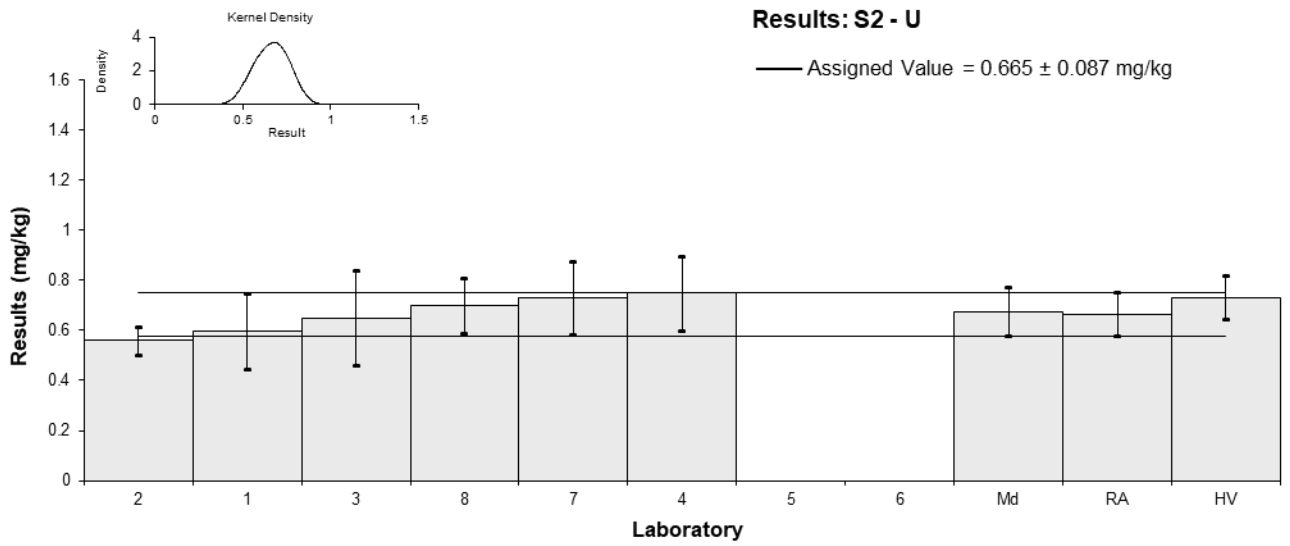
Sample No.	S2
Matrix	Bovine Liver
Analyte	U
Unit	mg/kg

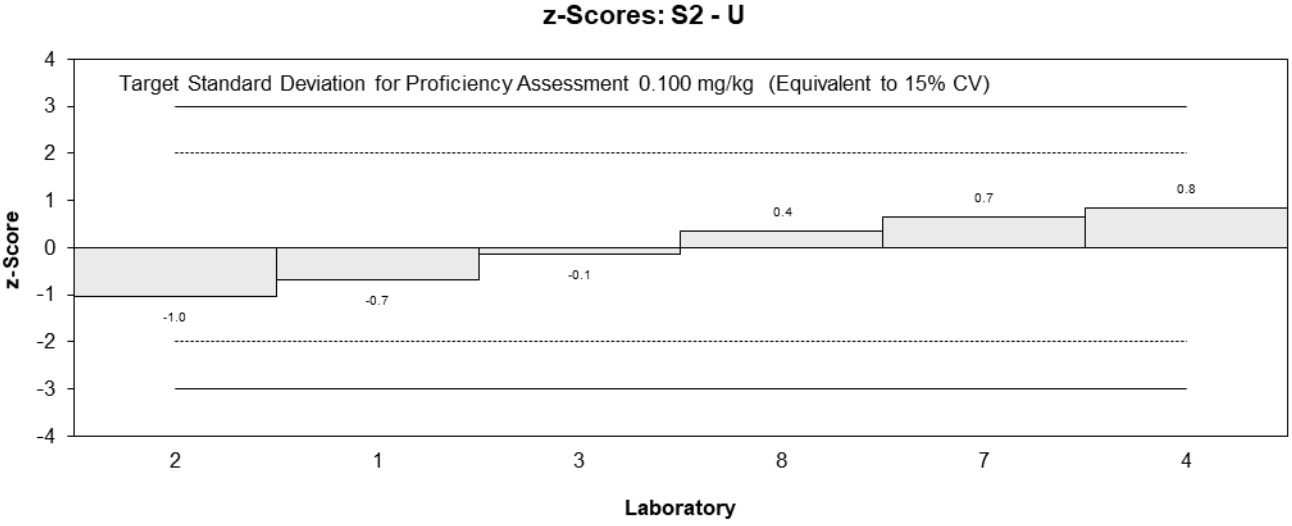
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.596	0.15	-0.69	-0.40
2	0.561140882725	0.056114088272	-1.04	-1.00
3	0.651	0.192	-0.14	-0.07
4	0.749	0.1498	0.84	0.48
5	NR	NR		
6	NT	NT		
7	0.731	0.1462	0.66	0.39
8	0.70	0.11	0.35	0.25

Statistics

Assigned Value	0.665	0.087
Spike Value	Not Spiked	
Homogeneity Value	0.732	0.088
Robust Average	0.665	0.087
Median	0.676	0.098
Mean	0.665	
N	6	
Max	0.749	
Min	0.561140882725	
Robust SD	0.085	
Robust CV	13%	


Kernel Density
Density
Result
Results: S2 - U
Assigned Value = 0.665 ± 0.087 mg/kg
Results (mg/kg)
Laboratory
2
1
3
8
7
4
5
6
Md
RA
HV


z-Scores: S2 - U
Target Standard Deviation for Proficiency Assessment 0.100 mg/kg (Equivalent to 15% CV)
z-Score
-1.0
-0.7
-0.1
0.4
0.7
0.8
Laboratory
2
1
3
8
7
4

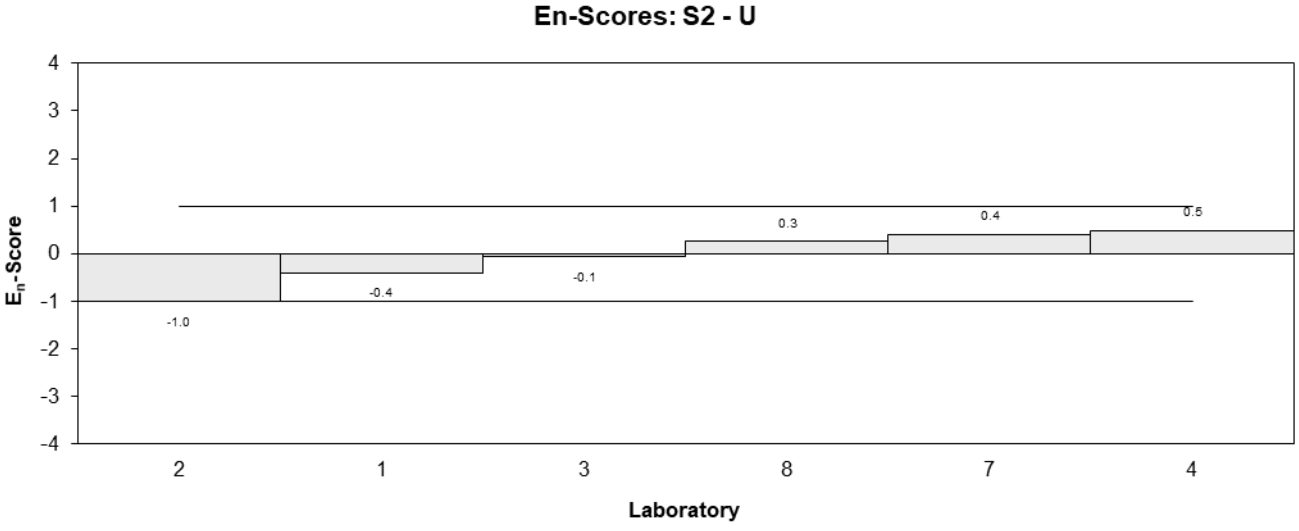

En-Scores: S2 - U
En-Score
-1.0
-0.4
-0.1
0.3
0.4
0.5
Laboratory
2
1
3
8
7
4

Figure 48

Table 51

Sample Details

Sample No.	S2
Matrix	Bovine Liver
Analyte	V
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	0.80	0.20	0.62	0.32
2	0.663813427275	0.066381342727	-0.62	-0.74
3	0.812	0.203	0.73	0.38
4	0.744	0.1488	0.11	0.07
5	0.717	0.020	-0.14	-0.22
6	NT	NT		
7	0.724	0.1448	-0.07	-0.05
8	0.66	0.10	-0.66	-0.61

Statistics

Assigned Value	0.732	0.064
Spike Value	Not Spiked	
Homogeneity Value	0.732	0.088
Robust Average	0.732	0.064
Median	0.724	0.084
Mean	0.732	
N	7	
Max	0.812	
Min	0.66	
Robust SD	0.068	
Robust CV	9.2%	

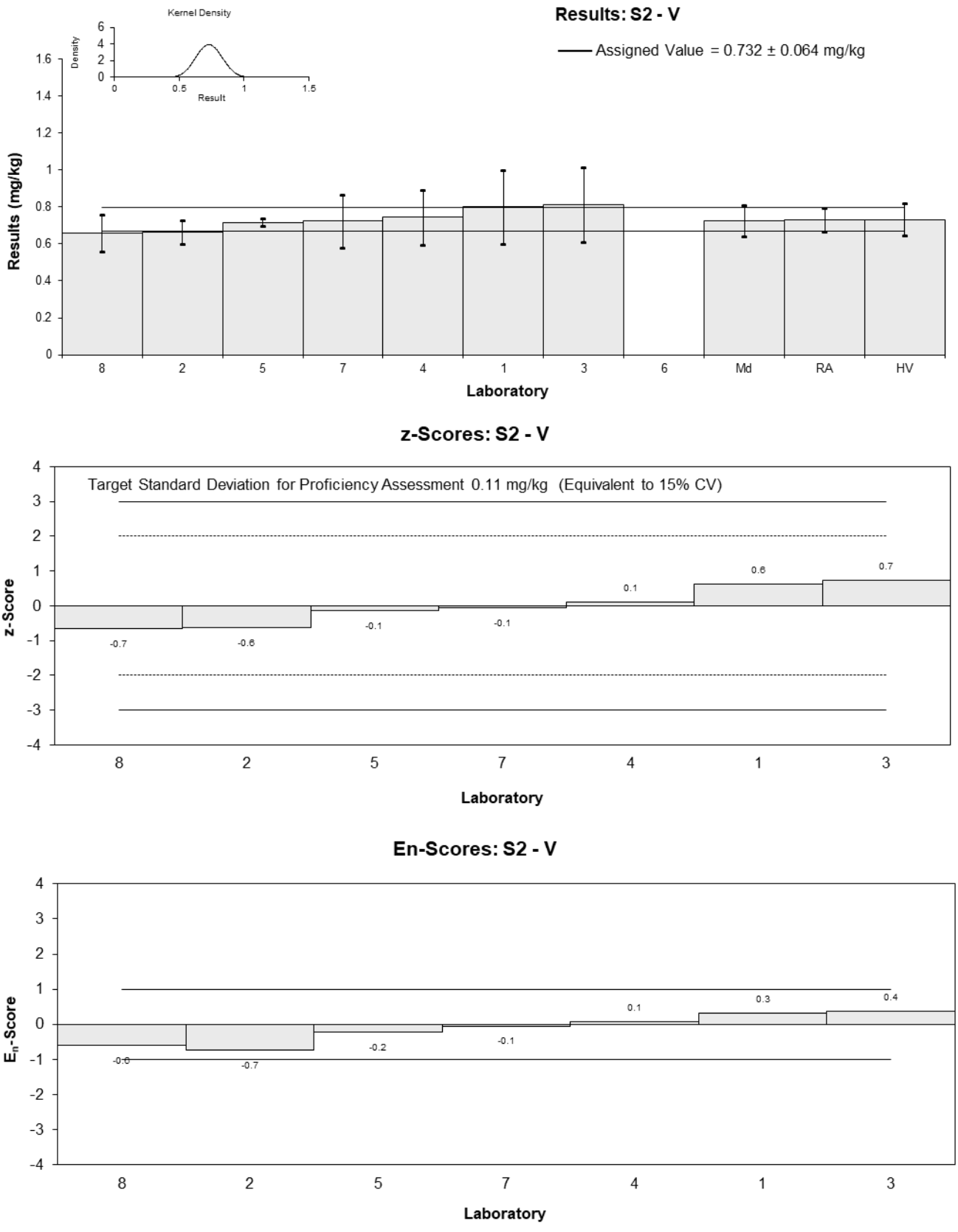

Results: S2 - V
Assigned Value = 0.732 ± 0.064 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
8
2
5
7
4
1
3
6
Md
RA
HV
z-Scores: S2 - V
Target Standard Deviation for Proficiency Assessment 0.11 mg/kg (Equivalent to 15% CV)
z-Score
-0.7
-0.6
-0.1
-0.1
0.1
0.6
0.7
En-Scores: S2 - V
En-Score
-0.6
-0.7
-0.2
-0.1
0.1
0.3
0.4

Figure 49

Table 52

Sample Details

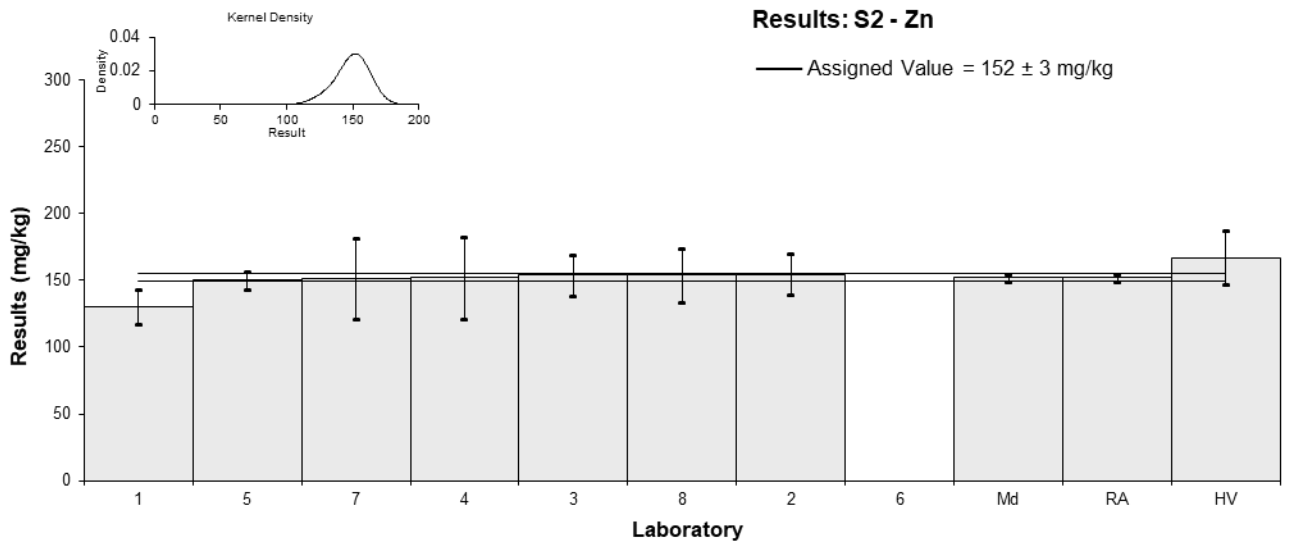
Sample No.	S2
Matrix	Bovine Liver
Analyte	Zn
Unit	mg/kg

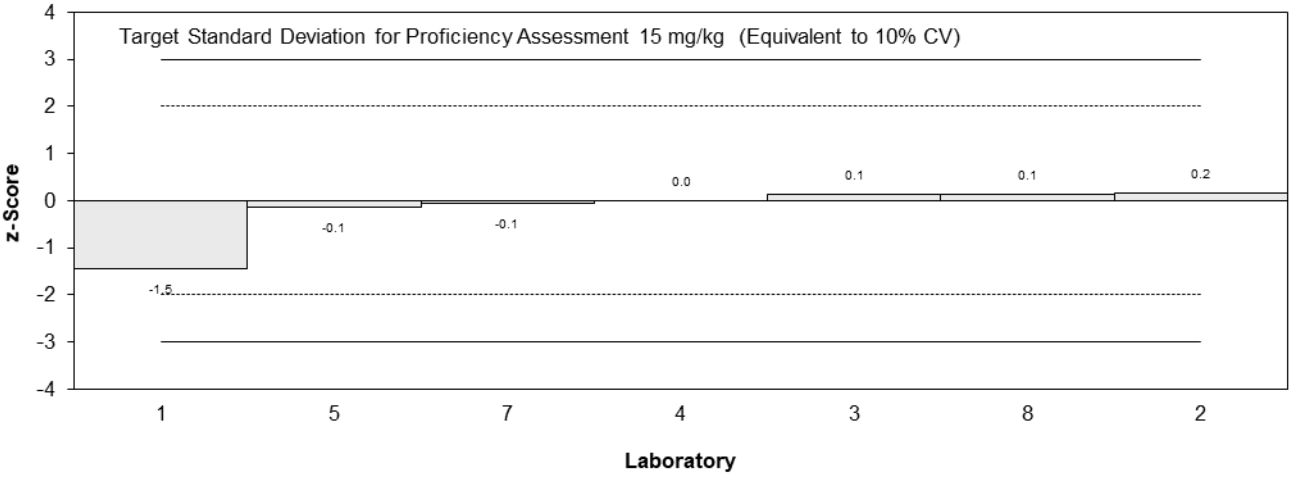
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	130	13	-1.45	-1.65
2	154.5797421669	15.45797421669	0.17	0.16
3	154	15.4	0.13	0.13
4	152	30.4	0.00	0.00
5	150	7	-0.13	-0.26
6	NT	NT		
7	151	30.2	-0.07	-0.03
8	154	20	0.13	0.10

Statistics

Assigned Value	152	3
Spike Value	Not Spiked	
Homogeneity Value	167	20
Robust Average	152	3
Median	152	3
Mean	149	
N	7	
Max	154.5797421669	
Min	130	
Robust SD	2.9	
Robust CV	1.9%	


Kernel Density
Density
Result
Results: S2 - Zn
Assigned Value = 152 ± 3 mg/kg
Results (mg/kg)
Laboratory
1
5
7
4
3
8
2
6
Md
RA
HV


z-Scores: S2 - Zn
Target Standard Deviation for Proficiency Assessment 15 mg/kg (Equivalent to 10% CV)
z-Score
-1.5
-0.1
-0.1
0.0
0.1
0.1
0.2
Laboratory

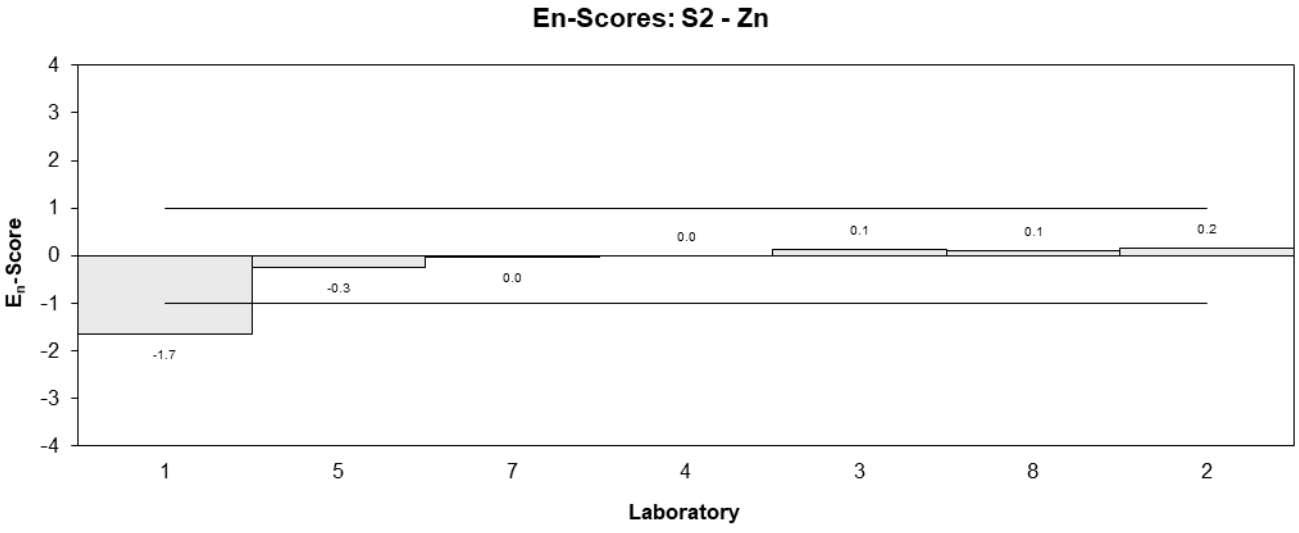

En-Scores: S2 - Zn
En-Score
-1.7
-0.3
0.0
0.0
0.1
0.1
0.2
Laboratory

Figure 50

6 DISCUSSION OF RESULTS

6.1 Assigned Value and Traceability

Assigned Values were the robust average of participants' results. The robust averages used as assigned values and their associated expanded uncertainties were calculated using the procedure described in ISO13528 'Statistical methods for use in proficiency testing by inter-laboratory comparisons'. Results less than 50% and more than 150% of the robust average were investigated and then removed before calculation of the assigned value.[6] Appendix 2 sets out the calculation of the robust average of As in Sample S1 and its associated uncertainty.

Rb in Sample S2 was omitted from Tables and Figures in Chapter 5 because no laboratories reported results for this test.

No assigned value was set for Ag, Hg, Tl and U in Sample S1 and Al and Sn in Sample S2 because the results were either too variable or because too few participants reported results for these elements. However, participants may still compare their reported results for these elements with the robust average of participants' results, homogeneity value and/or spike value. Descriptive statistics for these elements are presented in Chapter 5.

Traceability. The consensus of participants' results (robust average) is not traceable to any external reference. So although expressed in SI units, the metrological traceability of these assigned values has not been established.

Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. All results were reported with an expanded measurement uncertainty, indicating that the majority of laboratories have addressed this requirement of ISO/IEC 17025.[8] The magnitude of these expanded uncertainties was within the range 1% to 400% of the reported value. The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 3.

Approaches to estimating measurement uncertainty include: standard deviation of replicate analysis, Horwitz formula, long term reproducibility, professional judgement, bottom up approach, top down approach using precision and estimates of method and laboratory bias, and top down approach using only the reproducibility from inter-laboratory comparison studies.[9 – 14]

Participation in proficiency testing programs allows participants to check how reasonable their estimates of uncertainty are. Results and the expanded MU are presented in the bar charts for each analyte (Figures 2 to 50).

Laboratory 3 attached an estimate of the expanded measurement uncertainty for results reported as less than their limit of detection. An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.[1]

In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write 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 14.74 ± 2.95 mg/kg, it is better to report 14.7 ± 3.0 mg/kg or instead of 5.99 ± 0.599 mg/kg, it is better to report 5.99 ± 0.60 mg/kg.[1]

Laboratory 2 reported results and uncertainties with up to 15 significant figures. Although all significant figures were used in the assessment of results (z and En- score calculation), the last 2 to 5 digits were omitted for some of these results presented in Tables and Figures Chapter 6.

Laboratory 6 may have reported the uncertainty for some of its measurement results as relative uncertainty (expressed as percentage) not as absolute uncertainty (in units of mg/kg)

as instructed. The expanded uncertainty reported by them was within the range 1.3% to 136245% of the reported value.

6.2 E_n-score

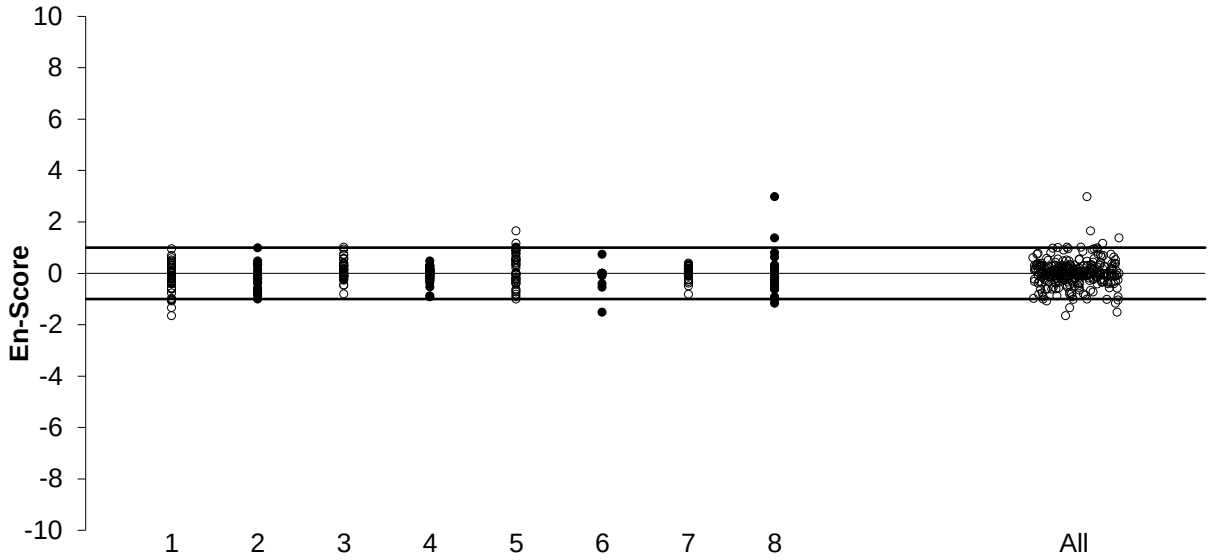
E_n-score can be interpreted in conjunction with z-scores. The E_n-score indicates how closely a result agrees with the assigned value taking into account the respective uncertainties. An unsatisfactory E_n score for an analyte can either be caused by an inappropriate measurement, an inappropriate estimation of measurement uncertainty, or both.

If a participant did not report any uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the En-score.

The dispersal of participants' En-scores is graphically presented in Figure 51.

Of 288 results for which E_n-scores were calculated, 274 (95%) returned a satisfactory score of $|E_n| \leq 1.0$ indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.

Laboratories 4 and **7** returned the highest number of satisfactory E_n scores (43 out of 43). All results reported by **laboratory 2** (23) also returned satisfactory E_n scores.



Scores of >10 or < -10 have been plotted as 10 or -10.

Figure 51 E_n-Score Dispersal by Laboratory

6.3 z-Score

The z-score compares participants' deviation from the assigned value with the target standard deviation set for proficiency assessment.

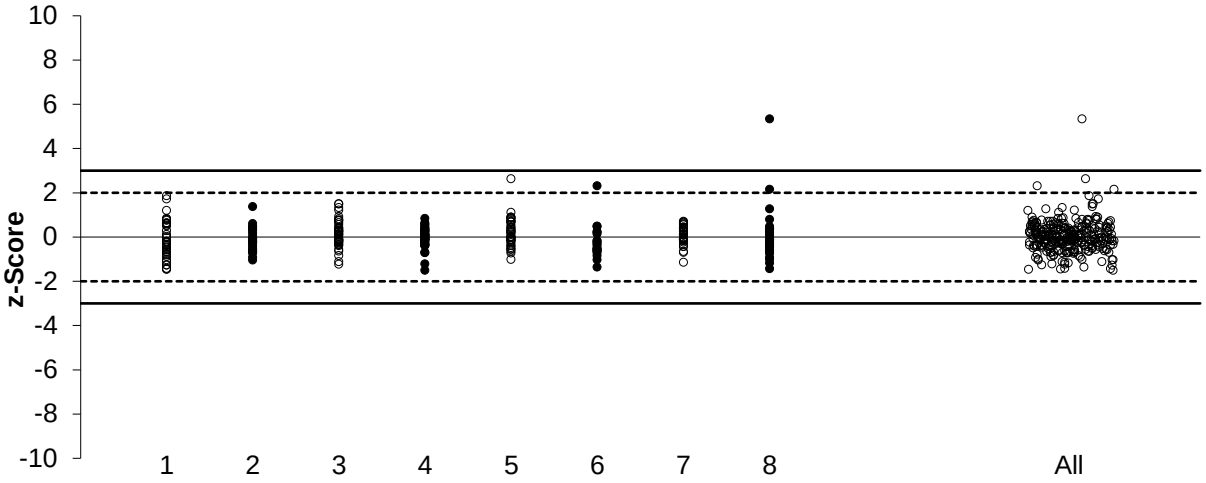
The target standard deviation defines satisfactory performance in a proficiency test. Target standard deviations equivalent to 10%, 15% and 20% PCV were used to calculate z-scores. Unlike the standard deviation based on between laboratories CV, setting the target standard deviation as a realistic set value enables z-scores to be used as a fixed reference value point for assessment of laboratory performance, independent of group performance.

The between laboratory coefficient of variation predicted by the Thompson equation and the between laboratory coefficient of variation resulted in this study are presented for comparison in Table 53.

The dispersal of participants' z-scores is presented in Figure 52 (by laboratory code) and in Figure 53 (by test).

Of 288 results for which z-scores were calculated, 284 (99%) returned a satisfactory score of $|z| \leq 2.0$ and 3 (1%) were questionable of $2.0 < |z| < 3.0$.

Participants with multiple z-scores larger than 2 or smaller than -2 should check for laboratory bias.



Scores of >10 or < -10 have been plotted as 10 or -10.

Figure 52 z-Score Dispersal by Laboratory

Summary of participants' performance is presented in Figure 54.

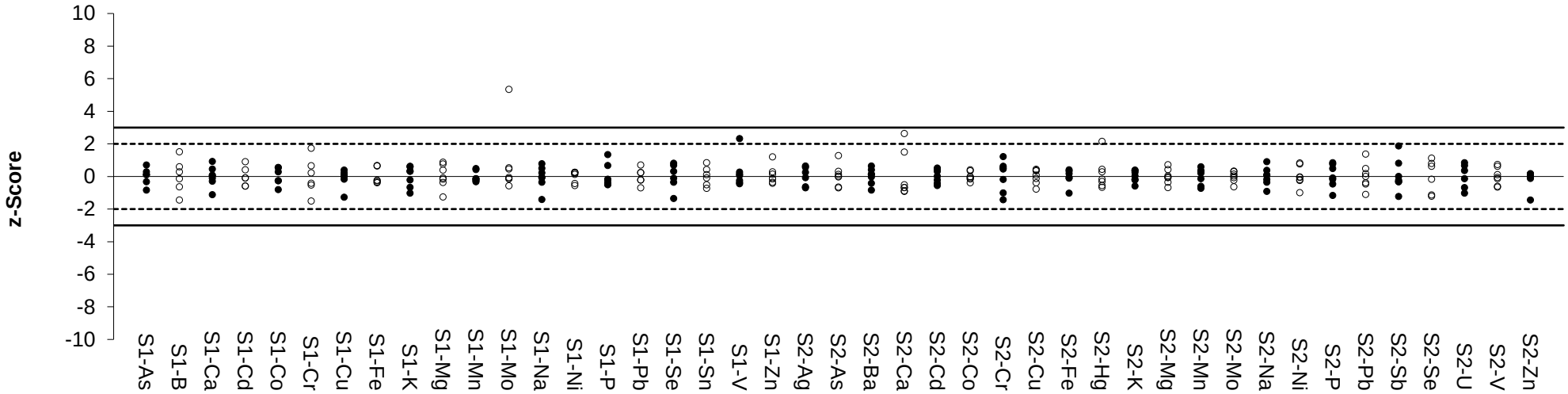
Laboratories 1, 3, 4 and **7** returned the highest number of satisfactory z scores (43 out of 43 reported). All results reported by **laboratory 2** (23) also returned satisfactory z scores.

Table 53 Between Laboratory CV of this study, Thompson CV and Set Target PCV

Sample	Test	Assigned value (mg/kg)	Between Laboratories CV*	Thompson/ Horwitz CV	Target SD (as PCV)
S1	Ag	Not Set	NA	NA	Not Set
S1	As	0.0778	9%	22%	15%
S1	B	1.30	23%	15%	20%
S1	Ca	597	6.9%	6.1%	10%
S1	Cd	0.0202	6.6%	22%	10%
S1	Co	0.0370	6.1%	22%	10%
S1	Cr	0.062	19%	22%	15%
S1	Cu	1.80	3%	15%	10%
S1	Fe	3.74	5.7%	13%	10%
S1	Hg	Not Set	22%	NA	Not Set
S1	K	2240	7.3%	5%	10%
S1	Mg	105	8.1%	7.9%	10%
S1	Mn	1.46	3.8%	15%	10%
S1	Mo	0.0778	7.1%	22%	15%
S1	Na	874	6.5%	5.8%	10%
S1	Ni	0.107	6%	22%	15%
S1	P	225	6.9%	7.1%	10%
S1	Pb	0.0215	5.5%	22%	10%
S1	Se	0.081	18%	22%	20%
S1	Sn	0.0480	13%	22%	20%
S1	Tl	Not Set	NA	NA	Not Set
S1	U	Not Set	NA	NA	Not Set
S1	V	0.104	6.9%	22%	15%
S1	Zn	1.44	6.4%	15%	15%
S2	Ag	0.0830	9.9%	22%	15%
S2	Al	Not Set	45%	NA	Not Set

Sample	Test	Assigned value (mg/kg)	Between Laboratories CV*	Thompson/ Horwitz CV	Target SD (as PCV)
S2	As	0.924	9.8%	16%	15%
S2	Ba	0.865	5.6%	16%	10%
S2	Ca	165	22%	7.4%	15%
S2	Cd	0.961	4.8%	16%	10%
S2	Co	0.923	3.2%	16%	10%
S2	Cr	0.88	16%	16%	15%
S2	Cu	152	5.2%	7.5%	10%
S2	Fe	379	4.1%	6.5%	10%
S2	Hg	0.711	10%	17%	15%
S2	K	9480	4.1%	4%	10%
S2	Mg	581	5.2%	6.1%	10%
S2	Mn	9.27	5.8%	11%	10%
S2	Mo	3.76	3.4%	13%	10%
S2	Na	2140	6.5%	5%	10%
S2	Ni	0.836	11%	16%	15%
S2	P	10700	8.2%	4%	10%
S2	Pb	1.26	8.7%	15%	10%
S2	Sb	0.75	20%	17%	20%
S2	Se	2.29	23%	14%	20%
S2	Sn	Not Set	NA	NA	Not Set
S2	U	0.665	13%	17%	15%
S2	V	0.732	9.2%	17%	15%
S2	Zn	152	1.9%	7.5%	10%

NA= Not Available, *Robust between Laboratories CV with outliers removed;



Scores of >10 or < -10 have been plotted as 10 or -10.

Figure 53 z-Score Dispersal by Analyte

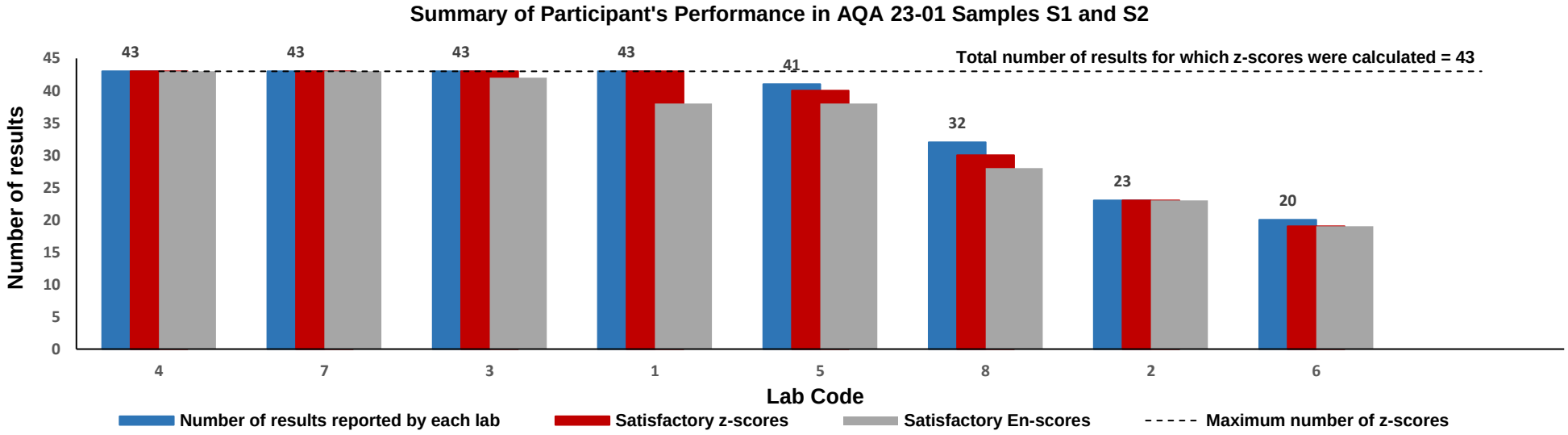


Figure 54 Summary of Participants' Performance

Table 54 Summary of Participants' Results and Performance in S1

Lab Code	Ag (mg/kg)	As (mg/kg)	B (mg/kg)	Ca (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Hg (mg/kg)	K (mg/kg)	Mg (mg/kg)
A.V.	Not Set	0.0778	1.30	597	0.0202	0.0370	0.062	1.80	3.74	Not Set	2240	105
H.V.	NA	0.0754	NA	617	0.0222	0.0355	0.0558	1.80	3.78	0.0257	2300	105
1	0.029	0.074	0.92	530	0.019	0.034	0.078	1.57	3.65	0.022	2090	91.8
2	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
3	0.027	0.081	1.69	652	0.020	0.036	0.068	1.82	3.61	<0.100	2310	113
4	0.028	0.079	1.37	599	0.020	0.038	0.048	1.81	3.98	0.026	2370	101
5	0.026	0.086	NR	623	0.022	0.039	0.057	1.80	3.64	0.022	2311	114
6	NT	0.068	1.13	579.02	0.019	0.036	0.064	1.77	3.59	0.019964	2009.59	103.18
7	0.029	0.079	1.45	602	0.021	0.039	0.058	1.87	3.99	0.027	2380	104
8	<0.1	<0.1	1.26	590	<0.1	<0.1	<0.1	1.84	NT	0.05	2190	109

Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value, H.V. = Homogeneity Value, NA = Not Available

Table 54 Summary of Participants' Results and Performance in S1 (continued)

Lab Code	Mn (mg/kg)	Mo (mg/kg)	Na (mg/kg)	Ni (mg/kg)	P (mg/kg)	Pb (mg/kg)	Se (mg/kg)	Sn (mg/kg)	Tl (mg/kg)	U (mg/kg)	V (mg/kg)	Zn (mg/kg)
A.V.	1.46	0.0778	874	0.107	225	0.0215	0.081	0.0480	Not Set	Not Set	0.104	1.44
H.V.	1.40	0.0827	NA	0.105	230	0.0219	0.0788	NA	NA	NA	0.105	1.41
1	1.43	0.084	750	0.098	220	0.021	0.094	0.056	0.007	0.055	0.097	1.70
2	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
3	1.41	0.077	892	0.111	255	0.021	0.086	0.052	<0.100	<0.100	0.108	1.407
4	1.42	0.076	867	0.109	216	0.022	0.075	0.047	<0.01	0.065	0.105	1.36
5	1.52	0.076	942	0.110	240	0.022	0.092	0.041	NR	NR	0.098	1.50
6	1.53	0.071	916.46	0.111	213.30	0.02	0.059	0.043	NT	NT	0.14	1.4695
7	1.44	0.083	870	0.111	221	0.023	0.079	0.049	<0.01	0.067	0.106	1.35
8	1.44	0.14	842	0.10	214	<0.1	NT	NT	<0.1	0.11	0.10	1.41

Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value, H.V. = Homogeneity Value, NA = Not Available

Table 55 Summary of Participants' Results and Performance in S2

Lab Code	Ag (mg/kg)	Al (mg/kg)	As (mg/kg)	Ba (mg/kg)	Ca (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Hg (mg/kg)	K (mg/kg)	Mg (mg/kg)
A.V.	0.0830	Not Set	0.924	0.865	165	0.961	0.923	0.88	152	379	0.711	9480	581
H.V.	0.0815	NA	0.84	0.95	165	1.01	0.92	0.86	145	349	0.758	9700	570
1	0.091	3.76	0.94	0.92	143	1.01	0.92	0.96	140	340	0.64	9500	560
2	0.074187539 8165179	3.880817396 86436	0.965447632 070884	0.828936489 524805	152.2429625 80603	0.939893172 676869	0.954550803 513873	0.853792761 601218	158.5068551 75627	375.7404915 3196	0.677505628 563151	9297.448603 25219	541.0725097 45508
3	0.090	7.24	0.926	0.792	202	0.906	0.887	1.04	153	385	0.692	9270	605
4	0.082	4.06	0.826	0.875	148	1.00	0.911	0.950	157	391	0.757	9820	576
5	0.075	6.5	0.92	0.862	230	0.962	0.921	0.746	146	375	0.65	9720	622
6	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
7	0.086	3.78	0.833	0.876	148	0.990	0.908	0.938	150	394	0.741	9850	578
8	<0.5	10	1.10	0.90	142	0.92	0.96	0.69	158	NT	0.94	8921	583

Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value, H.V. = Homogeneity Value, NA = Not Available

Table 55 Summary of Participants' Results and Performance in S2 (continued)

Lab Code	Mn (mg/kg)	Mo (mg/kg)	Na (mg/kg)	Ni (mg/kg)	P (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	Se (mg/kg)	Sn (mg/kg)	U (mg/kg)	V (mg/kg)	Zn (mg/kg)
A.V.	9.27	3.76	2140	0.836	10700	1.26	0.75	2.29	Not Set	0.665	0.732	152
H.V.	9.0	3.88	2250	0.817	11800	1.25	0.683	2.26	0.698	0.732	0.732	167
1	9.82	3.87	2100	0.93	10200	1.21	1.03	2.65	0.88	0.596	0.80	130
2	8.6961879137 2091	3.7701059705 0605	1942.2194348 4735	0.8275577721 52792	11206.240112 4283	1.4328543063 5924	0.7135925133 74339	2.5710328079 2843	0.4648865965 70691	0.5611408827 25211	0.6638134272 75877	154.57974216 6976
3	9.14	3.52	2220	0.939	11500	1.12	0.565	2.21	0.767	0.651	0.812	154
4	9.46	3.73	2150	0.804	10520	1.26	0.699	1.73	NR	0.749	0.744	152
5	9.6	3.81	2330	0.81	11600	1.2	0.75	2.8	0.35	NR	0.717	150
6	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
7	9.56	3.67	2160	0.832	10590	1.28	0.701	1.77	NR	0.731	0.724	151
8	8.58	3.88	2060	0.71	9441	1.32	0.87	NT	NT	0.70	0.66	154

Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value, H.V. = Homogeneity Value, NA = Not Available

6.4 Participants' Results and Analytical Methods for Total Elements

A summary of participants' performance in the two study samples is presented in Figures 51 to 54 and Tables 54 and 55. Overall measurements of total elements in celery puree and freeze-dried liver did not challenge participants results, with 99% of the reported results returning satisfactory z-scores.

Sample S1 was celery puree and did not challenge participants' subsampling procedures. The between laboratory-CV's in S1 were comparable to those of S2.

Measurements of total Al in S2 presented the most analytical difficulty to participants. No assigned value could be set for this test in the present and previous studies because the reported results were not compatible with each other.

Selenium measurements in complex matrices such as freeze-dried liver challenged participants' analytical techniques. The between laboratory-CV in S2 was 23%.

The method descriptions provided by participants are presented in Tables 1 and 2; instrumental conditions are presented in Appendix 4.

Extraction Method

The Codex Alimentarius Commission's recommendation for the measurement of elemental impurities in food samples by ICP is "digestion until extraction is complete". Laboratories are expected to report total elements in food samples.[15] In previous NMI PT studies, participants used various extraction methods and the results produced were compatible, with the exception of Al, Cr, Fe, Ni and V in some types of food.

The extraction of these elements is strongly dependent on digestion regime, especially when the food material has high silica content. An aggressive digestion regime involving nitric acid, a high digestion temperature (higher than approximately 170ºC) and/or hydrofluoric acid is usually recommended for the complete extraction of these elements.

Food laboratories are required to test for a number of total elements in a variety of food samples, and it is often challenging to find a method/extraction regime which is suitable for all of them. The use of HF is banned in many laboratories and microwave digesters allow only a limited number of samples to be digested at a time. Evidence has been found in previous studies of the importance of using (in addition to nitric acid) a high ratio of HCl (mL) to sample size (g) when the digestion temperature is high (> 170ºC) or when HF cannot be used for total Cr, Fe, Ni and V extraction.

In the present study, one sample was celery puree and one sample was freeze dried bovine liver. Six laboratories reported results for both samples and all used the same extraction regime for both samples.

The amount of celery puree sample taken for analysis by participants varied from 1 g to 5 g, while the amount of freeze dried bovine liver sample used for analysis varied from 0.2 g to 1 g. Caution should be exercised when a small sample size is taken for analysis as this may not be representative of the whole sample. Caution should also be exercised when using too much sample mass and not enough digestion acid for the sample mass.

Of three participants who used only nitric acid for extraction, one used a digestion temperature of 190°C and one used a digestion temperature of 165°C. Laboratory 8 extracted the freeze-dried liver sample at 100ºC and used a large ratio of nitric acid to sample size (25).

Laboratories 1 and 3 extracted their sample at 85ºC and used a large ratio of hydrochloric acid to sample size, of 4 and 20 respectively.

Laboratory 5 reported using: “microwave digestion for trace elements (165ºC) and hot block digestion for major elements (85ºC).”

Although participants used a wide variety of extraction methods the results reported for total elements in the two study samples were compatible with each other with the exception of aluminium.

Aluminium is one of the most difficult elements to analyse in food samples. In previous PT studies, no assigned value could be set in the wheat, oyster tissue, freeze dried liver, biota, freeze dried prawn and hemp samples because the reported results were not compatible with each other. Incomplete dissolution of silicate compounds may explain the variability of results.

As in previous studies, Al results in freeze dried liver sample, had a multi modal distribution (Figure 55) and no assigned value could be set. Due to the limited amount of data and the wide variety of analytical methods used, no significant trends in extraction or sample preparation procedures could be identified.

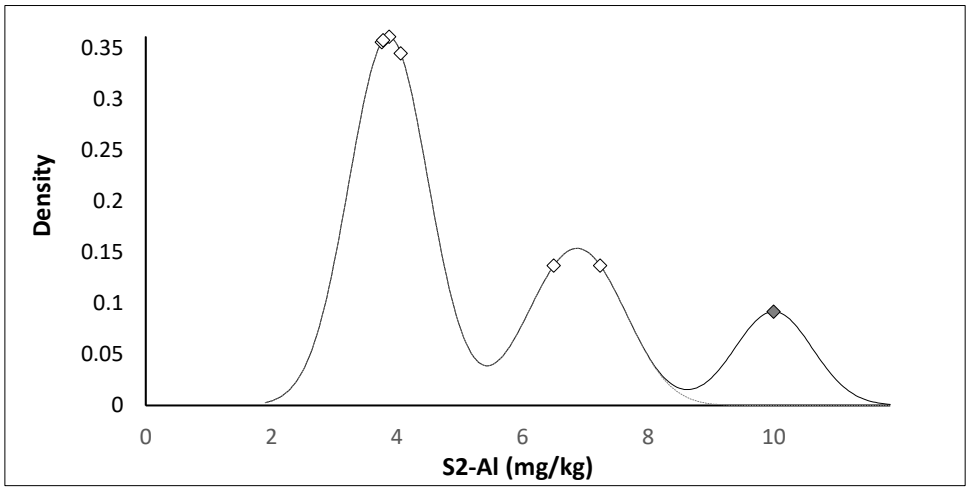


Figure 55 S2-Al Kernel Density Plot of Participants’ Results

Aluminium extraction is highly dependent on digestion temperature, and as such, sufficiently high temperatures (typically > 200 °C) should be employed to ensure complete extraction.

According to Eurachem/CITAC Guide CG 4, laboratories should consider using matrix-matched control samples to assess their extraction efficiency (the bias of their analytical methods). Bias can be expressed as recovery and should be corrected for or included in the uncertainty estimate.[1]

Chromium and Nickel are two elements which are also strongly dependent on digestion regime, especially when the sample has high silica content. Evidence has been found in previous studies that a high ratio of HCl to sample size is essential for complete extraction of Cr and Ni in food samples when high digestion temperatures cannot be employed.

In the present study, participants used various extraction methods, high digestion temperatures and/or a high ratio of hydrochloric acid or nitric acid to sample size and the results reported for these elements were in good agreement with each other, as well as with the assigned value or homogeneity value. The robust between-laboratory CV for these elements was between 6% and 19% (Figure 56).

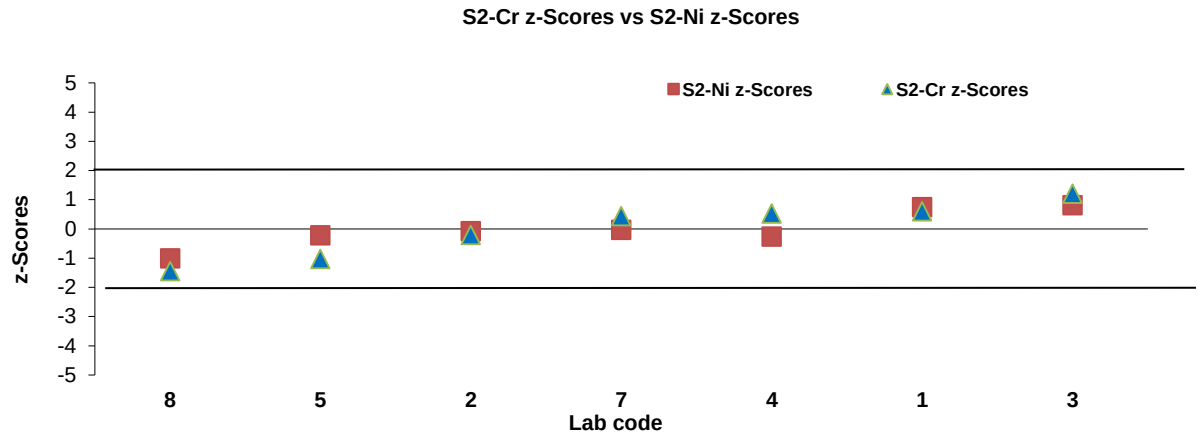


Figure 56 Participants' Performance for Ni and Cr in S2

Instrumental Techniques

Plots of participants' results/performance against the instrumental technique used are presented in Figures 57 to 65.

Aluminium, Chromium, Nickel There was no trend between results/performance for Al, Cr, Ni in S1 and S2 and instrumental technique used (Figures 57 to 59).

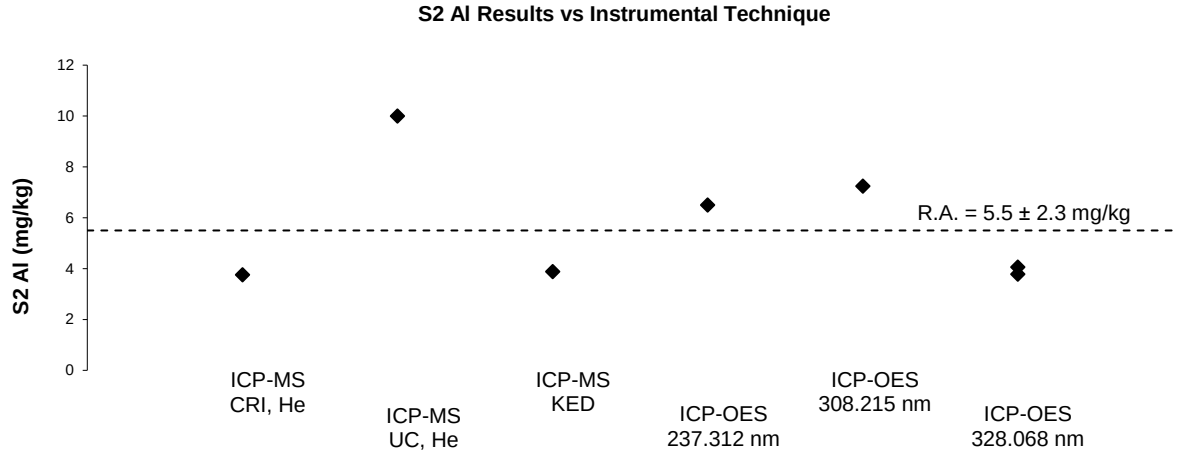


Figure 57 S1 Al Results vs. Instrumental Technique

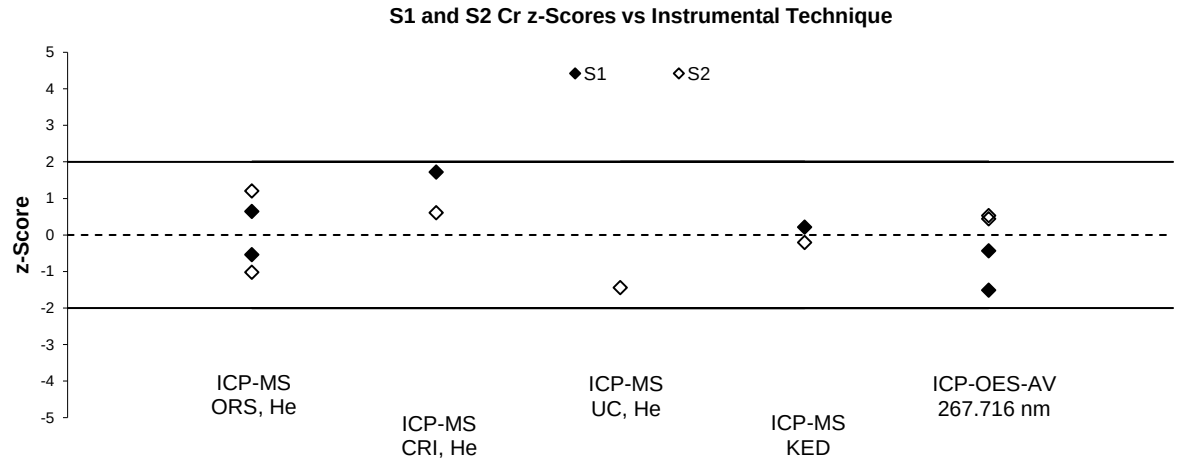


Figure 58 S1 and S2 Cr z-Scores vs. Instrumental Technique

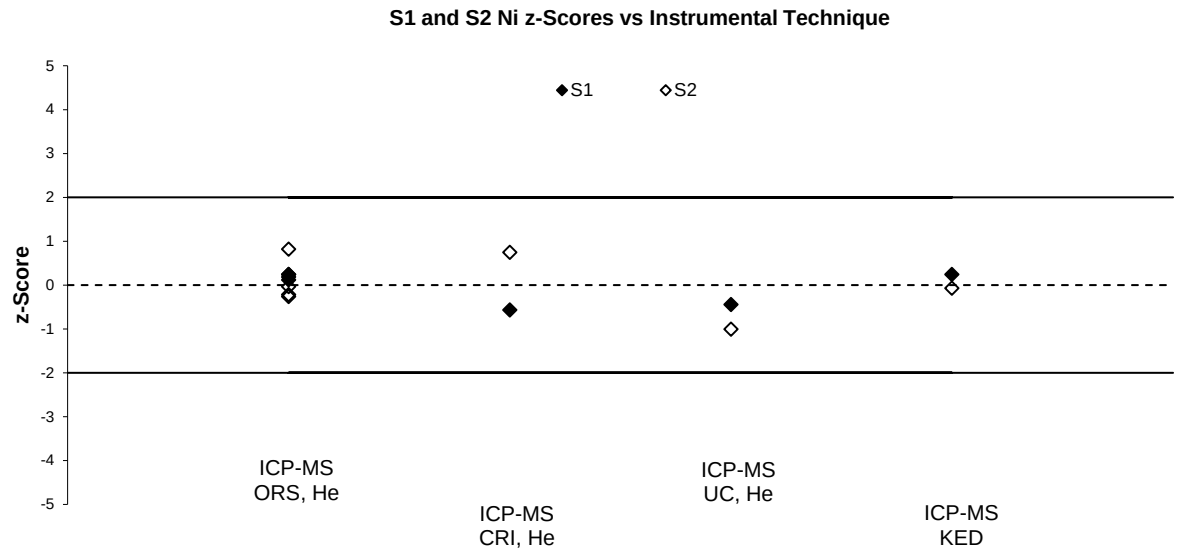


Figure 59 S1 and S2 Ni z-Scores vs. Instrumental Technique

Arsenic For As measurements in the two study samples all participants used ICP-MS in collision mode. Figure 60 presents plots of participants' results reported for As in S1 versus instrumental technique.

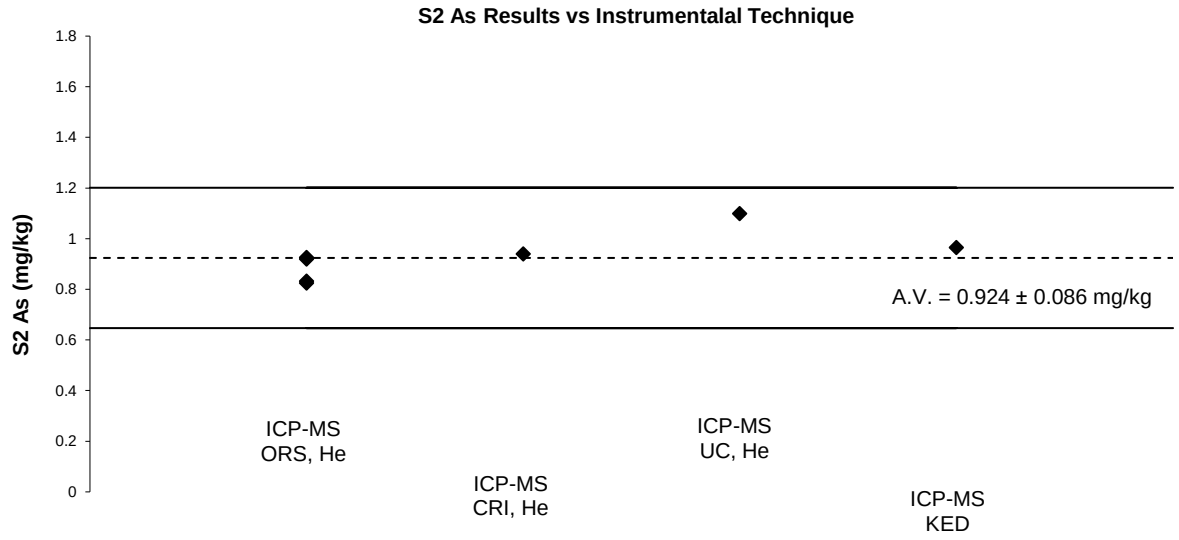


Figure 60 S1 As Results vs. Instrumental Technique

Boron was one of the elements which challenged participants' analytical techniques, resulting in a large between laboratory-CV of 23%. All participants reported using ICP-MS in collision mode.

Mercury level in S1 was low and challenged participants' instrumental techniques. Only six results were reported for this test in S1, of which five were compatible with each other and with the robust average (0.025 mg/kg).

Mercury level in S2 was approximately thirty times higher than in S1. Seven participants reported results and all but one performed satisfactorily.

Plots of participants' results for Hg in S1 and S2 versus instrumental technique used are presented in Figures 61 and 62.

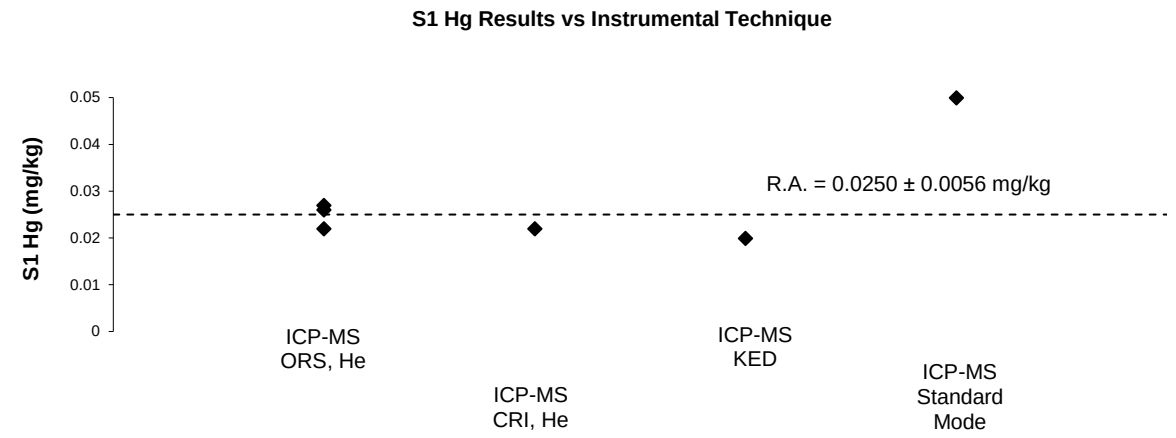


Figure 61 S1 Hg Results vs. Instrumental Technique

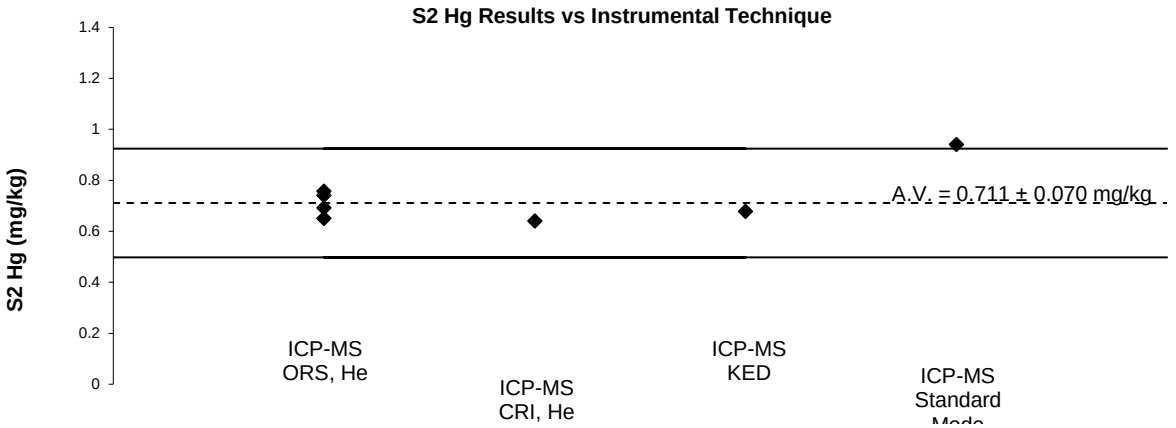


Figure 62 S2 Hg Results vs. Instrumental Technique

Uranium level in S1 was low. Only four results were reported for U in S1. Three of the four reported results were in excellent agreement with each other, centred on a value of 0.062 mg/kg. All participants used ICP-MS for the measurement of U.

Calcium, Magnesium, Potassium and Sodium measurements in S1 and S2 did not challenge participants' analytical techniques. All reported results but one returned satisfactory z-scores for these tests.

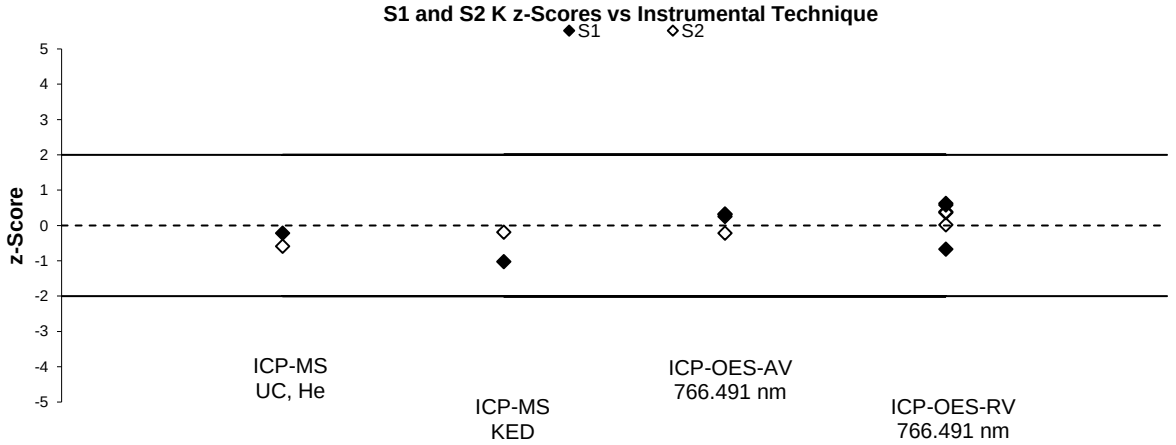


Figure 63 S1 and S2 K z-Scores vs. Instrumental Technique

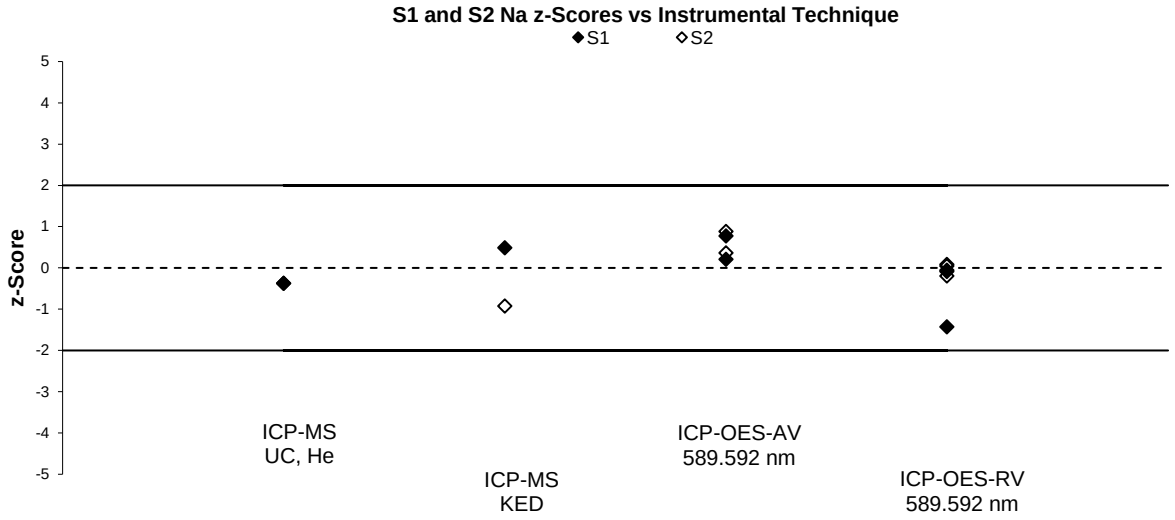


Figure 64: S2 Na Results vs. Instrumental Technique

Plots of participants' performance for Na and K in the two study samples are presented in Figures 63 and 64. ICP-OES with 766 nm wavelength was the preferred techniques for K measurements in S1 and S2. For the measurement of Na, most participants chose ICP-OES with a wavelength of 589.

Selenium measurements in the more complex matrix, freeze dried liver, challenged participants' analytical techniques. Selenium levels in the celery puree sample were approximately 30 times lower than in the freeze-dried liver sample, however the between-laboratory CV was lower.

Complete digestion is more challenging to achieve in the freeze-dried liver sample than in the celery puree sample, which may explain the discrepancy in the variability of Se results between the two samples. Matrix effects can hamper accurate measurement of elements in food samples when complete digestion cannot be achieved. Matrix effects are common in food analyses using ICP-MS; they take place in the plasma and consist of signal enhancement caused by charge transfer reactions from charged carbon species to atoms like Se with a lower ionization potential.[16]

Six laboratories reported results for Se in S2. ICP-MS with high energy He was the preferred measurement technique. One laboratory reported using ICP-MS in reaction mode with H_2 as reaction gas (Figure 65).

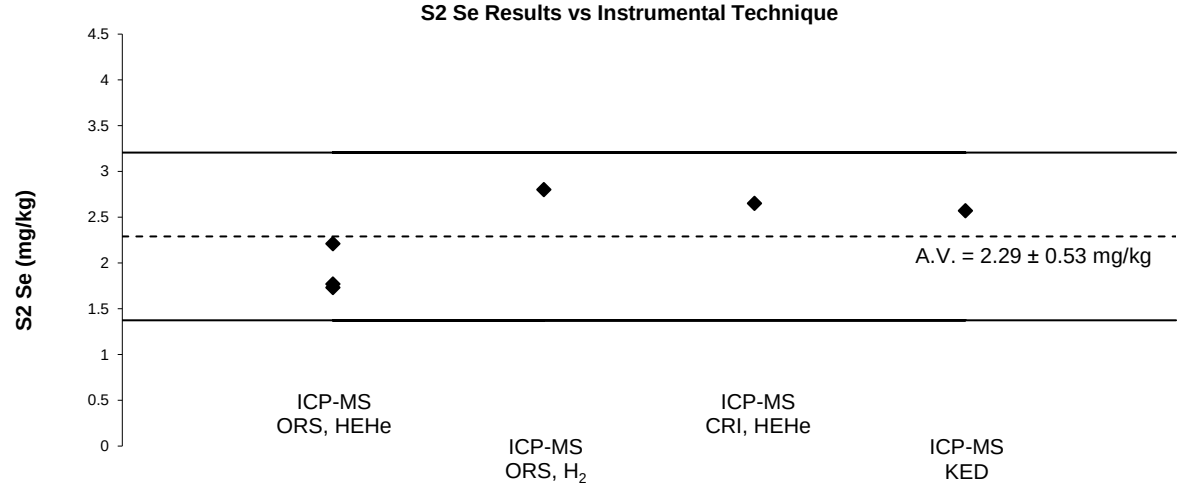


Figure 65: S2-Se Results vs. Instrumental Technique

6.5 Comparison with the Previous Proficiency Studies of Toxic and Essential Elements in Food

AQA 23-01 is the sixteenth NMI study of elements in food. Laboratories improved their performance in the measurement of elements in food samples. Only four questionable or unsatisfactory z-scores were given in this study, in comparison, AQA 21-12 had 14 and AQA 20-09 had 29.

Over time laboratories should expect at least 95% of their scores to be $|z| \leq 2.0$. Scores in the range $2.0 < |z| \leq 3.0$ occasionally can occur, however these should be interpreted in conjunction with the other scores obtained by that laboratory. For example, a trend of z-scores on one side of the zero line are an indication of method or laboratory bias.

Individual performance history reports are emailed to each participant at the end of the study; the consideration of z-scores for an analyte over time provides much more useful information than a single z-score.

Participants' performance in measurements of trace elements in food over time is presented in Figure 66.

6.6 Reference Materials and Certified Reference Materials

Proficiency testing and matrix matched control samples taken through all steps of the analytical process are highly valuable quality control tools for assessing extraction efficiency. Control samples used by participants in this study are presented in Table 56.

Table 56 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	SS
2	CRM – NMIA MX009
3	SS
4	RM
5	RM – In-house reference materials (from previous PT program) and Certified reference materials (ERM and NIST)
6	SS
7	RM
8	CRM – BRAN 1

Some laboratories reported using certified reference materials. These materials may not meet the internationally recognised definition of a Certified Reference Material:

> *'a 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'*[17]

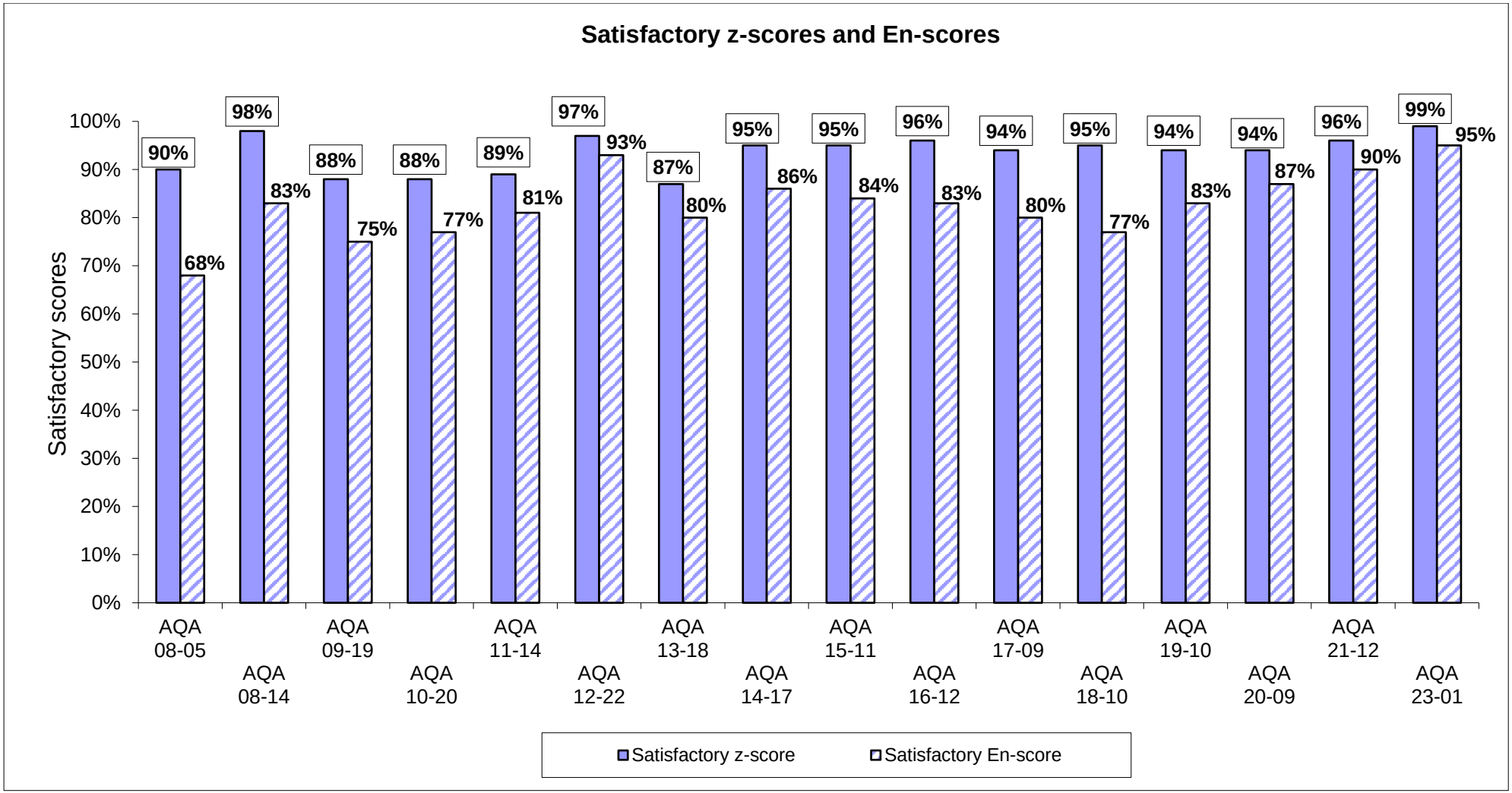


Figure 66 Participants' Performance over Time

7 REFERENCES

Note: For all undated references, the latest edition of the referenced document (including any amendments) applies.

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[3] NMI Chemical Proficiency Testing Study Protocol, viewed 30 March 2023, < https://www.industry.gov.au/sites/default/files/2020-10/cpt_study_protocol.pdf>.

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[14] ASTM E2554-13, *Standard Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques.*

[15] Codex Alimetarius Comission, *Codex Standards* -viewed 30 March 2023 < http: //www.fao.org/fao-who-codexalimentarius/en/>.

[16] Erik, H & Sturup, L 1994, "Carbon-enhanced Inductively Coupled Plasma Mass Spectrometric Detection of Arsenic and Selenium and its Application to Arsenic" *Speciation Journal of Analytical Spectrometry*, vol 9, pp 1099-1105.

[17] JCGM 200:2012, *International vocabulary of metrology – Basic and General Concepts and Associated Terms (VIM)*, 3rd edition.

APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

A1.1 Sample Preparation

Sample S1 – was celery puree fortified with 17 analytes.

Sample S2 – was freeze dried bovine liver reference material (AGAL 20) previous prepared by NMI.

A1.2 Sample Analysis and Homogeneity Testing

Partial homogeneity testing was conducted for elements of interest, with the exception of Ag, B, Na, Sn, Tl, and U in S1 and Al and Rb in S2. Three bottles were analysed in duplicate and the average of the results was reported as the homogeneity value. Measurements were made under repeatability conditions in random order.

Sample Analysis for Total Elements in S1 and S2

Approximately 1.6 g of sample S1 and 0.5 g of sample S2 were weighed and digested at 260ºC for 1 hour with 3 mL of HNO_3 and 1 mL of HCl. After digestion, each sample was diluted to 40 mL with ultra-high purity water and then further diluted as necessary for ICP-MS determination. A summary of the instruments used and the ion monitored for each analyte is given in Table 57.

Table 57 Instrumental Techniques Used for Total Elements in S1 and S2

Analyte	Instrument	Internal Standard	Reaction/ Collision Cell (if applicable)	Cell Mode/ Gas (if applicable)	S1 Final Dilution Factor	S2 Final Dilution Factor	Ion
Ag	ICP-MS	Rh	ORS	He	NA	80	107 m/z
As	ICP-MS	Rh	ORS	He	80	80	75 m/z
Ba	ICP-MS	Rh	ORS	He	NA	80	137 m/z
Ca	ICP-MS	Rh	ORS	He	80	80	43 m/z
Cd	ICP-MS	Rh	ORS	He	80	80	111 m/z
Co	ICP-MS	Rh	ORS	He	80	80	59 m/z
Cr	ICP-MS	Rh	ORS	He	80	80	52 m/z
Cu	ICP-MS	Rh	ORS	He	80	80	63 m/z
Fe	ICP-MS	Rh	ORS	He	80	80	56 m/z
Hg	ICP-MS	Ir	NA	NA	80	80	202 m/z
K	ICP-MS	Rh	ORS	He	80	80	39 m/z
Mg	ICP-MS	Rh	ORS	He	80	80	24 m/z
Mn	ICP-MS	Rh	ORS	He	80	80	55 m/z
Mo	ICP-MS	Rh	ORS	He	80	80	95 m/z
Na	ICP-MS	Rh	ORS	He	NA	80	23 m/z
Ni	ICP-MS	Rh	NA	NA	80	80	60 m/z
P	ICP-MS	Rh	ORS	HEHe	80	80	31 m/z
Pb	ICP-MS	Ir	ORS	He	80	80	Average of 206, 207, 208 m/z
Sb	ICP-MS	Rh	ORS	He	NA	80	121 m/z
Se	ICP-MS	Rh	ORS	HEHe	80	80	78 m/z
Sn	ICP-MS	Rh	ORS	He	NA	80	118 m/z
U	ICP-MS	Ir	ORS	He	NA	80	238 m/z
V	ICP-MS	Rh	ORS	He	80	80	51 m/z
Zn	ICP-MS	Rh	ORS	He	80	80	64 m/z

NA- Not Applicable

APPENDIX 2 - ASSIGNED VALUE, Z-SCORE AND E_N SCORE CALCULATION

Assigned Value

The assigned value was calculated as the robust average using the procedure described in 'ISO13528, Statistical methods for use in proficiency testing by inter-laboratory comparisons – Annex C'.[6] 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 58.

Table 58 Uncertainty of Assigned Value for As in Sample S1

No. results (p)	6
Robust Average	0.0778 mg/kg
$S_{rob\ av}$	0.0070 mg/kg
$u_{rob\ av}$	0.0036 mg/kg
k	2
$U_{rob\ av}$	0.0072 mg/kg

The assigned value for **As** in Sample S1 is **0.0778 ± 0.0072 mg/kg**.

z-Score and E_n-score

For each participant's result a z-score and E_n-score are calculated according to Equation 2 and Equation 3 respectively (see page 8).

A worked example is set out below in Table 59.

Table 59 z-Score and E_n-score for As result reported by Laboratory 1 in S1

As Result mg/kg	Assigned Value mg/kg	Set Target Standard Deviation	z-Score	E_n-Score
0.074 ± 0.018	0.0778 ± 0.0072	15% as CV or 0.15 x 0.0778= 0.012 mg/kg	$z = \frac{(0.074 - 0.0778)}{0.012}$ z = -0.33	$En = \frac{(0.074 - 0.0778)}{\sqrt{0.018^2 + 0.0072^2}}$ E_n = -0.20

APPENDIX 3 - ACRONYMS AND ABBREVIATIONS

CRM	Certified Reference Material
CRI	Collision Reaction Interface
CV	Coefficient of Variation
CV_{Rob}	Robust Coefficient of Variation
GUM	Guide to the Expression of Uncertainty in Measurement
HEHe	High energy helium
HV	Homogeneity Value
KED	Kinetic Energy Discrimination
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ICP-MS/MS	Inductively Coupled Plasma – Tandem Mass Spectrometry
ICP-OES-AV	Inductively Coupled Plasma – Optical Emission Spectrometry- axial view
ICP-OES-AV-buffer	Inductively Coupled Plasma – Optical Emission Spectrometry- axial view with buffer
ICP-OES-RV	Inductively Coupled Plasma – Optical Emission Spectrometry- radial view
IDMS	Isotope Dilution Mass Spectrometry
ISO/IEC	International Organisation for Standardisation / International Electrotechnical Commission
IUPAC	International Union of Pure and Applied Chemists
Max	Maximum value in a set of results
Md	Median
Min	Minimum value in a set of results
MU	Measurement Uncertainty
N	Number of Participants
NIST	National Institute of Standards and Technology
NMI	National Measurement Institute (Australia)
NR	Not Reported
NT	Not Tested
ORS	Octopole Reaction System
PCV	Performance Coefficient of Variation
PFAS	Polyfluoroalkyl Substances
PT	Proficiency Test
RM	Reference Material
RV	Reference Value
SV	Spiked or formulated concentration of a PT sample
SD_{Rob}	Robust Standard Deviation
SI	The International System of Units
s^2_{sam}	Sampling variance
s_a/σ	Analytical standard deviation divided by the target standard deviation
SRM	Standard Reference Material (Trademark of NIST)
Target SD	Target standard deviation (symbol: σ)
UC	Universal Cell

APPENDIX 4 - INSTRUMENT DETAILS

Table 60 Instrument Conditions for Ag in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	CRI	He	10	107
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	107
4	ICP-MS	Rh	ORS	He	2	107
5	ICP-MS	Rh 103	ORS	He	80	108 m/z
7	ICP-MS	Rh	ORS	He	2	107
8	ICP-MS	Rh	NA	NA	125	109

Table 61 Instrument Conditions for As in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	10	75
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	75
4	ICP-MS	Rh	ORS	He	2	75
5	ICP-MS	Rh 103	ORS	He	80	91 m/z
6	ICP-MS	73Ge	KED	Argon	50	75As
7	ICP-MS	Rh	ORS	He	2	75
8	ICP-MS	Ge	UC	He	125	75

Table 62 Instrument Conditions for B in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	10	11
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	11
4	ICP-MS	Sc	NA	NA	2	11
5	ICP-MS	Sc 45	ORS	He	80	11 m/z
6	ICP-MS	45Sc	KED	Argon	50	11B
7	ICP-MS	Sc	NA	NA	2	11
8	ICP-MS	Sc	NA	NA	125	10

Table 63 Instrument Conditions for Ca in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-RV	Y			10	317.933
3	ICP-OES-AV	214.282 Te/371.029 Y	NA	NA	200	315.887
4	ICP-OES-RV	Y	NA	NA	2	422.673
5	ICP-OES-AV	Eu397.197			80	370.602
6	ICP-MS	45Sc	KED	Argon	50	42Ca
7	ICP-OES-RV	Y	NA	NA	2	422.673
8	ICP-MS	Sc	UC	He	125	44

Table 64 Instrument Conditions for Cd in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	CRI	He	10	111
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	111
4	ICP-MS	Rh	ORS	He	2	111
5	ICP-MS	Rh 103	ORS	He	80	111 m/z
6	ICP-MS	115In	KED	Argon	50	111Cd
7	ICP-MS	Rh	ORS	He	2	111
8	ICP-MS	Rh	NA	NA	125	111

Table 65 Instrument Conditions for Co in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	10	59
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	59
4	ICP-MS	Rh	ORS	He	2	59
5	ICP-MS	Rh 103	ORS		80	59 m/z
6	ICP-MS	45Sc	KED	Argon	50	59Co
7	ICP-MS	Rh	ORS	He	2	59
8	ICP-MS	Ge	UC	He	125	59

Table 66 Instrument Conditions for Cr in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	10	52
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	52
4	ICP-OES-AV	Y	NA	NA	2	267.716
5	ICP-MS	Rh 103	ORS	He	80	52 m/z
6	ICP-MS	45Sc	KED	Argon	50	52Cr
7	ICP-OES-AV	Y	NA	NA	2	267.716
8	ICP-MS	Sc	UC	He	125	52

Table 67 Instrument Conditions for Cu in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	10	63
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	63
4	ICP-MS	Rh	ORS	He	2	63/65
5	ICP-MS	Rh 103	ORS	He	80	63 m/z
6	ICP-MS	73Ge	KED	Argon	50	65Cu
7	ICP-MS	Rh	ORS	He	2	63/65
8	ICP-MS	Ge	UC	He	125	63

Table 68 Instrument Conditions for Fe in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	100	56
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	56
4	ICP-OES-RV	Y	NA	NA	2	238.204
5	ICP-MS	Rh 103	ORS	He	80	56 m/z
6	ICP-MS	45Sc	KED	Argon	50	57Fe
7	ICP-OES-RV	Y	NA	NA	2	238.204
8	ICP-MS	Ge	CRI	He	100	56

Table 69 Instrument Conditions for Hg in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ir	CRI	He	10	202
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	202
4	ICP-MS	Rh	ORS	He	2	202
5	ICP-MS	Ir 193	ORS	He	80	202 m/z
6	ICP-MS	193Ir	KED	Argon	50	202Hg
7	ICP-MS	Rh	ORS	He	2	202
8	ICP-MS	Ir	NA	NA	125	201

Table 70 Instrument Conditions for K in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-RV	Y			100	766.491
3	ICP-OES-AV	214.282 Te/371.029 Y	NA	NA	200	766.491
4	ICP-OES-RV	Y	NA	NA	2	766.491
5	ICP-OES-AV	In 410.176			80	766.491
6	ICP-MS	45Sc	KED	Argon	50	39K
7	ICP-OES-RV	Y	NA	NA	2	766.491
8	ICP-MS	Sc	UC	He	125	39

Table 71 Instrument Conditions for Mg in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-RV	Y			10	383.829
3	ICP-OES-AV	214.282 Te/371.029 Y	NA	NA	200	383.829
4	ICP-OES-RV	Y	NA	NA	2	285.213
5	ICP-OES-AV	Eu390.711			80	285.213
6	ICP-MS	45Sc	KED	Argon	50	25Mg
7	ICP-OES-RV	Y	NA	NA	2	285.213
8	ICP-MS	Sc	UC	He	125	25

Table 72 Instrument Conditions for Mn in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	100	55
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	55
4	ICP-OES-AV	Y	NA	NA	2	257.61
5	ICP-MS	Rh 103	ORS	He	80	55 m/z
6	ICP-MS	45Sc	KED	Argon	50	55Mn
7	ICP-OES-AV	Y	NA	NA	2	257.61
8	ICP-MS	Sc	UC	He	125	55

Table 73 Instrument Conditions for Mo in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	CRI	He	10	95
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	95
4	ICP-MS	Rh	ORS	He	2	95
5	ICP-MS	Rh 103	ORS	He	80	95 m/z
6	ICP-MS	115In	KED	Argon	50	95Mo
7	ICP-MS	Rh	ORS	He	2	95
8	ICP-MS	Rh	NA	NA	125	95

Table 74 Instrument Conditions for Na in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-RV	Y	CRI	He	10	589.592
3	ICP-OES-AV	214.282 Te/371.029 Y	NA	NA	200	589.592
4	ICP-OES-RV	Y	NA	NA	2	589.592
5	ICP-OES-AV	In 410.176			80	589.592
6	ICP-MS	45Sc	KED	Argon	50	23Na
7	ICP-OES-RV	Y	NA	NA	2	589.592
8	ICP-MS	Sc	UC	He	125	23

Table 75 Instrument Conditions for Ni in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	10	60
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	60
4	ICP-MS	Rh	ORS	He	2	60
5	ICP-MS	Rh 103	ORS	He	80	60 m/z
6	ICP-MS	73Ge	KED	Argon	50	62Ni
7	ICP-MS	Rh	ORS	He	2	60
8	ICP-MS	Ge	UC	He	125	60

Table 76 Instrument Conditions for P in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-RV	Te			10	178.222
3	ICP-OES-AV	214.282 Te/371.029 Y	NA	NA	200	213.618
4	ICP-OES-AV	Y	NA	NA	2	213.618
5	ICP-OES-AV	In 303.936			80	185.878
6	ICP-MS	45Sc	KED	Argon	50	31P
7	ICP-OES-AV	Y	NA	NA	2	213.618
8	ICP-MS	Sc	UC	He	125	31

Table 77 Instrument Conditions for Pb in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ir	CRI	He	10	208
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	208
4	ICP-MS	Rh	ORS	He	2	206+207+208
5	ICP-MS	Ir 193	ORS	He	80	208 m/z
6	ICP-MS	193Ir	KED	Argon	50	208Pb
7	ICP-MS	Rh	ORS	He	2	206+207+208
8	ICP-MS	Ir	NA	NA	125	206+207+208

Table 78 Instrument Conditions for Se in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	HEHe	10	78
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	HEHe	200	78
4	ICP-MS	Rh	ORS	HEHe	2	78
5	ICP-MS	Rh 103	ORS	H2	80	94 m/z
6	ICP-MS	73Ge	KED	Argon	50	78Se
7	ICP-MS	Rh	ORS	HEHe	2	78

Table 79 Instrument Conditions for Sn in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	CRI	He	10	118
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	118
4	ICP-MS	Rh	ORS	He	2	118
5	ICP-MS	Rh 103	ORS	He	80	134 m/z
6	ICP-MS	115In	KED	Argon	50	118Sn
7	ICP-MS	Rh	ORS	He	2	118

Table 80 Instrument Conditions for Tl in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ir	CRI	He	10	205
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	205
4	ICP-MS	Rh	ORS	He	2	205
5	ICP-MS	Ir 193	ORS	He	80	205 m/z
7	ICP-MS	Rh	ORS	He	2	205
8	ICP-MS	Ir	NA	NA	125	205

Table 81 Instrument Conditions for U in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ir	CRI	He	10	238
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	238
4	ICP-MS	Ir	ORS	He	2	238
5	ICP-MS	Ir 193	ORS	He	80	238 m/z
7	ICP-MS	Ir	ORS	He	2	238
8	ICP-MS	Ir	NA	NA	125	238

Table 82 Instrument Conditions for V in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	10	51
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	51
4	ICP-MS	Rh	ORS	He	2	51
5	ICP-MS	Rh 103	ORS	He	80	67 m/z
6	ICP-MS	45Sc	KED	Argon	50	51V
7	ICP-MS	Rh	ORS	He	2	51
8	ICP-MS	Sc	UC	He	125	51

Table 83 Instrument Conditions for Zn in S1

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	100	66
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	66
4	ICP-OES-AV	Y	NA	NA	2	213.857
5	ICP-MS	Rh 103	ORS	He	80	66 m/z
6	ICP-MS	73Ge	KED	Argon	50	66Zn
7	ICP-OES-AV	Y	NA	NA	2	213.857
8	ICP-MS	Ge	UC	He	125	66

Table 84 Instrument Conditions for Ag in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	CRI	He	100	107
2	ICP-MS	Rh	KED	He	100	106.905
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	107
4	ICP-MS	Rh	ORS	He	2	107
5	ICP-MS	Rh 103	ORS	He	80	107 m/z
7	ICP-MS	Rh	ORS	He	2	107
8	ICP-MS	Rh	NA	NA	1240	109

Table 85 Instrument Conditions for Al in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	100	27
2	ICP-MS	Sc	KED	He	100	26.9815
3	ICP-OES-AV	214.282 Te/371.029 Y	NA	NA	200	308.215
4	ICP-OES-AV	Y	NA	NA	2	328.068
5	ICP-OES-AV	In 303.936			80	237.312
7	ICP-OES-AV	Y	NA	NA	2	328.068
8	ICP-MS	Sc	UC	He	1240	27

Table 86 Instrument Conditions for As in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	100	75
2	ICP-MS	Ge	KED	He	100	74.9216
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	75
4	ICP-MS	Rh	ORS	He	2	75
5	ICP-MS	Rh 103	ORS	He	80	91 m/z
7	ICP-MS	Rh	ORS	He	2	75
8	ICP-MS	Ge	UC	He	1240	75

Table 87 Instrument Conditions for Ba in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	CRI	He	100	137
2	ICP-MS	In	KED	He	100	137.905
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	137
4	ICP-OES-AV	Y	NA	NA	2	233.527
5	ICP-MS	Rh 103	ORS	He	80	153 m/z
7	ICP-OES-AV	Y	NA	NA	2	233.527
8	ICP-MS	Rh	NA	NA	1240	138

Table 88 Instrument Conditions for Ca in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-RV	Y			100	317.933
2	ICP-MS	Sc	KED	He	100	43.9555
3	ICP-OES-AV	214.282 Te/371.029 Y	NA	NA	200	315.887
4	ICP-OES-RV	Y	NA	NA	2	422.673
5	ICP-OES-AV	Eu397.197			80	370.602
7	ICP-OES-RV	Y	NA	NA	2	422.673
8	ICP-MS	Sc	UC	He	1240	44

Table 89 Instrument Conditions for Cd in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	CRI	He	100	111
2	ICP-MS	In	KED	He	100	110.904
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	111
4	ICP-MS	Rh	ORS	He	2	111
5	ICP-MS	Rh 103	ORS	He	80	111 m/z
7	ICP-MS	Rh	ORS	He	2	111
8	ICP-MS	Rh	NA	NA	1240	111

Table 90 Instrument Conditions for Co in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	100	59
2	ICP-MS	Ge	KED	He	100	58.9332
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	59
4	ICP-MS	Rh	ORS	He	2	59
5	ICP-MS	Rh 103	ORS	He	80	59 m/z
7	ICP-MS	Rh	ORS	He	2	59
8	ICP-MS	Ge	UC	He	1240	59

Table 91 Instrument Conditions for Cr in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	100	52
2	ICP-MS	Sc	KED	He	100	51.9405
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	52
4	ICP-OES-AV	Y	NA	NA	2	267.716
5	ICP-MS	Rh 103	ORS	He	80	52 m/z
7	ICP-OES-AV	Y	NA	NA	2	267.716
8	ICP-MS	Sc	UC	He	1240	52

Table 92 Instrument Conditions for Cu in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV	Te			100	327.395
2	ICP-MS	Ge	KED	He	500	62.9298
3	ICP-OES-AV	214.282 Te/371.029 Y	ORS	He	200	324.754
4	ICP-MS	Rh	ORS	He	2	63/65
5	ICP-MS	Rh 103	ORS	He	80	63 m/z
7	ICP-MS	Rh	ORS	He	2	63/65
8	ICP-MS	Ge	UC	He	1240	63

Table 93 Instrument Conditions for Fe in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV	Te			100	259.94
2	ICP-MS	Ge	KED	He	100	55.9349
3	ICP-OES-AV	214.282 Te/371.029 Y	NA	NA	200	240.489
4	ICP-OES-RV	Y	NA	NA	2	238.204
5	ICP-MS	Rh 103	ORS	He	80	56 m/z
7	ICP-OES-RV	Y	NA	NA	2	238.204
8	ICP-OES-AV	Te			100	259.94

Table 94 Instrument Conditions for Hg in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ir	CRI	He	100	202
2	ICP-MS	Ir	KED	He	100	201.971
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	202
4	ICP-MS	Rh	ORS	He	2	202
5	ICP-MS	Ir 193	ORS	He	80	202 m/z
7	ICP-MS	Rh	ORS	He	2	202
8	ICP-MS	Ir	NA	NA	1240	201

Table 95 Instrument Conditions for K in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-RV	Y			100	766.491
2	ICP-MS	Sc	KED	He	100	38.9637
3	ICP-OES-AV	214.282 Te/371.029 Y	NA	NA	200	766.491
4	ICP-OES-RV	Y	NA	NA	2	766.491
5	ICP-OES-AV	In 410.176			80	766.491
7	ICP-OES-RV	Y	NA	NA	2	766.491
8	ICP-MS	Sc	UC	He	1240	39

Table 96 Instrument Conditions for Mg in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-RV	Y			100	383.829
2	ICP-MS	Sc	KED	He	100	23.985
3	ICP-OES-AV	214.282 Te/371.029 Y	NA	NA	200	383.829
4	ICP-OES-RV	Y	NA	NA	2	285.213
5	ICP-OES-AV	Eu390.711			80	285.213
7	ICP-OES-RV	Y	NA	NA	2	285.213
8	ICP-MS	Sc	UC	He	1240	25

Table 97 Instrument Conditions for Mn in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	2000	55
2	ICP-MS	Ge	KED	He	100	54.9381
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	55
4	ICP-OES-AV	Y	NA	NA	2	257.61
5	ICP-MS	Rh 103	ORS	He	80	55 m/z
7	ICP-OES-AV	Y	NA	NA	2	257.61
8	ICP-MS	Sc	UC	He	1240	55

Table 98 Instrument Conditions for Mo in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	100	95
2	ICP-MS	Rh	KED	He	100	94.9058
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	95
4	ICP-MS	Rh	ORS	He	2	95
5	ICP-MS	Rh 103	ORS	He	80	95 m/z
7	ICP-MS	Rh	ORS	He	2	95
8	ICP-MS	Rh	NA	NA	1240	95

Table 99 Instrument Conditions for Na in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-RV	Y			100	589.592
2	ICP-MS	Sc	KED	He	100	22.9898
3	ICP-OES-AV	214.282 Te/371.029 Y	NA	NA	200	589.592
4	ICP-OES-RV	Y	NA	NA	2	589.592
5	ICP-OES-AV	In 410.176			80	589.592
7	ICP-OES-RV	Y	NA	NA	2	589.592
8	ICP-MS	Sc	UC	He	1240	23

Table 100 Instrument Conditions for Ni in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	100	60
2	ICP-MS	Ge	KED	He	100	59.9332
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	60
4	ICP-MS	Rh	ORS	He	2	60
5	ICP-MS	Rh 103	ORS	He	80	60 m/z
7	ICP-MS	Rh	ORS	He	2	60
8	ICP-MS	Ge	UC	He	1240	60

Table 101 Instrument Conditions for P in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-RV	Te			1000	178.222
2	ICP-MS	Sc	KED	He	5000	30.9938
3	ICP-OES-AV	214.282 Te/371.029 Y	NA	NA	200	213.618
4	ICP-OES-AV	Y	NA	NA	2	213.618
5	ICP-OES-AV	In 303.936			80	185.878
7	ICP-OES-AV	Y	NA	NA	2	213.618
8	ICP-MS	Sc	NA	NA	1240	31

Table 102 Instrument Conditions for Pb in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ir	CRI	He	100	208
2	ICP-MS	Ir	KED	He	100	205.975
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	208
4	ICP-MS	Rh	ORS	He	2	206+207+208
5	ICP-MS	Ir 193	ORS	He	80	208 m/z
7	ICP-MS	Rh	ORS	He	2	206+207+208
8	ICP-MS	Ir	NA	NA	1240	206+207+208

Table 103 Instrument Conditions for Rb in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
4	ICP-MS	Rh	ORS	He	2	85
7	ICP-MS	Rh	ORS	He	2	85

Table 104 Instrument Conditions for Sb in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	CRI	He	100	121
2	ICP-MS	In	KED	He	100	120.904
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	121
4	ICP-MS	Rh	ORS	He	2	121
5	ICP-MS	Rh 103	ORS	He	80	121 m/z
7	ICP-MS	Rh	ORS	He	2	121
8	ICP-MS	Rh	NA	NA	1240	121

Table 105 Instrument Conditions for Se in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	HEHe	100	78
2	ICP-MS	Ge	KED	He	100	77.9173
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	HEHe	200	78
4	ICP-MS	Rh	ORS	HEHe	2	78
5	ICP-MS	Rh 103	ORS	H2	80	94 m/z
7	ICP-MS	Rh	ORS	HEHe	2	78

Table 106 Instrument Conditions for Sn in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	CRI	He	100	118
2	ICP-MS	In	KED	He	100	117.902
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	118
4	ICP-MS	Rh	ORS	He	2	118
5	ICP-MS	Rh 103	ORS	He	80	134 m/z
7	ICP-MS	Rh	ORS	He	2	118

Table 107 Instrument Conditions for U in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ir	CRI	He	100	238
2	ICP-MS	Ir	KED	He	100	238.05
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	238
4	ICP-MS	Ir	ORS	He	2	238
5	ICP-MS	Ir 193	ORS	He	80	238 m/z
7	ICP-MS	Ir	ORS	He	2	238
8	ICP-MS	Ir	NA	NA	1240	238

Table 108 Instrument Conditions for V in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ge	CRI	He	100	51
2	ICP-MS	Sc	KED	He	100	50.944
3	ICP-MS	72 Ge/103 Rh/193 Ir	ORS	He	200	51
4	ICP-MS	Rh	ORS	He	2	51
5	ICP-MS	Rh 103	ORS	He	80	67 m/z
7	ICP-MS	Rh	ORS	He	2	51
8	ICP-MS	Sc	UC	He	1240	51

Table 109 Instrument Conditions for Zn in S2

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV	Te			100	206.2
2	ICP-MS	Ge	KED	He	500	65.926
3	ICP-OES-AV	214.282 Te/371.029 Y	NA	NA	200	202.548
4	ICP-OES-AV	Y	NA	NA	2	213.857
5	ICP-MS	Rh 103	ORS	He	80	66 m/z
7	ICP-OES-AV	Y	NA	NA	2	213.857
8	ICP-MS	Ge	UC	He	1240	66

END OF REPORT