



Australian Government  
Department of Industry, Science,  
Energy and Resources

National  
Measurement  
Institute

# **Proficiency Test Final Report AQA 21-12 Metals in Food**

February 2022



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

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## TABLE OF CONTENTS

1	SUMMARY	1
2	INTRODUCTION	2
2.1	NMI Proficiency Testing Program	2
2.2	Study Aims	2
2.3	Study Conduct	2
3	STUDY INFORMATION	2
3.1	Selection of Matrices and Inorganic Analytes	2
3.2	Participation	2
3.3	Test Material Specification	3
3.4	Laboratory Code	3
3.5	Sample Preparation, Analysis and Homogeneity Testing	3
3.6	Stability of Analytes	3
3.7	Sample Storage, Dispatch and Receipt	3
3.8	Instructions to Participants	3
3.9	Interim Report	4
4	PARTICIPANT LABORATORY INFORMATION	5
4.1	Test Method Summaries	5
4.2	Instruments Used for Measurements	6
4.3	Additional Information	6
4.4	Basis of Participants' Measurement Uncertainty Estimates	7
4.5	Participant Comments on this PT Study or Suggestions for Future Studies	7
5	PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS	8
5.1	Results Summary	8
5.2	Outliers and Extreme Outliers	8
5.3	Assigned Value	8
5.4	Robust Average and Robust Between-Laboratory Coefficient of Variation	8
5.5	Target Standard Deviation	8
5.6	z-Score	9
5.7	$E_n$ -Score	9
5.8	Traceability and Measurement Uncertainty	9
6	TABLES AND FIGURES	10
7	DISCUSSION OF RESULTS	116
7.1	Assigned Value and Traceability	116
7.2	$E_n$ -score	117
7.3	z-Score	117
7.4	Participants' Results and Analytical Methods for Total Elements	125
7.5	Comparison with the Previous Proficiency Studies of Metals and Nutrients in Soil	133
7.6	Reference Materials and Certified Reference Materials	133
8	REFERENCES	136
	APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING	137
	APPENDIX 2 - ASSIGNED VALUE, Z-SCORE AND $E_N$ SCORE CALCULATION	139
	APPENDIX 3 – REFERENCE VALUES	140
	APPENDIX 4 - ACRONYMS AND ABBREVIATIONS	142



## 1 SUMMARY

This report presents the results of the proficiency test AQA 21-12 Toxic and Essential Elements in Tea Leaves and Biota. The study focused on the measurement of total: Al, As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Se, Sn, Tl, U, V and Zn in tea leaves, and of total: Ag, Al, As, B, Ca, Cd, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, P, Pb, Se, Sn, Sr, V, and Zn in a freeze dried marine biota sample.

Twelve 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. However for Ni and Fe in S1 the assigned values were reference values measured using isotope dilution mass spectrometry (IDMS). An information value by IDMS was also provided for Sn in S1 (Appendix 3).

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 355  $z$ -scores, 341 (96%) were satisfactory with  $|z| \leq 2.0$ .

Of 355  $E_n$ -scores, 318 (90%) were satisfactory with  $|E_n| \leq 1.0$ .

**Laboratories 1 and 3** returned the highest number of satisfactory  $z$  scores (40 out of 40 reported).

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

Aluminium measurements presented difficulties to testing laboratories. Some participants may need to reassess their extraction method since they only recovered a fraction of Al from the tea leaves sample. 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.<sup>1</sup>

- 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;*

Of 405 numerical results, 394 (97%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 6.2% to 200% 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.

## **2 INTRODUCTION**

### **2.1 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 interlaboratory comparison."<sup>2</sup> 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;
- PFOS/PFOA in water, soil, biota and food;
- allergens in food;
- controlled drug assay; and
- folic acid in flour.

### **2.2 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; and
- develop the practical application of traceability and measurement uncertainty.
- produce materials that can be used in method validation and as control samples.

### **2.3 Study Conduct**

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

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.

## **3 STUDY INFORMATION**

### **3.1 Selection of Matrices and Inorganic Analytes**

The sixty-two 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.

### **3.2 Participation**

Twelve laboratories participated and submitted results.

The timetable of the study was:

Invitation issued: 17 August 2021

Samples dispatched: 7 September 2021  
Results due: 14 October 2021  
Interim report issued: 18 October 2021

### **3.3 Test Material Specification**

Two samples were provided for analysis:

- Sample S1 was 5 g of dried tea leaves; and
- Sample S2 was 10 g of freeze dried marine biota.

### **3.4 Laboratory Code**

All participant laboratories were assigned a confidential code number.

### **3.5 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 Na in S1 and Al in S2<sup>2</sup>. 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.

### **3.6 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.

### **3.7 Sample Storage, Dispatch and Receipt**

Samples S1 and S2 were stored at room temperature before dispatch.

The samples were dispatched by courier on 7 September 2021.

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.

### **3.8 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.
- Quantitatively analyse the samples using your normal test method.
- Participants are asked to report the results in units of **mg/kg** on as received basis for:



<b>SAMPLE S1 dried tea leaves</b>		<b>SAMPLE S2 freeze dried marine biota</b>	
<b>Test TOTAL</b>	<b>Approximate Conc. Range (as received basis) mg/kg</b>	<b>Test TOTAL</b>	<b>Approximate Conc. Range (as received basis) mg/kg</b>
Al	500-10000	Ag	0.25-5
As	0.25-5	Al	5-100
Ba	5-100	As	5-100
Be	0.025-0.5	B	0.5-10
Ca	500-10000	Ca	500-10000
Cd	0.025-0.5	Cd	0.025-0.5
Co	0.25-5	Cr	0.5-10
Cr	5-100	Cu	5-100
Cu	5-100	Fe	5-100
Cs	0.25-5	Hg	0.025-0.5
Fe	500-10000	K	500-10000
Ga	0.25-5	Li	0.025-0.5
Hg	0.025-0.5	Mg	500-10000
La	0.5-10	Mn	0.25-5
K	5000-100000	Na	500-10000
Mg	500-10000	Ni	0.25-5
Mn	50-1000	P	1000-20000
Mo	0.25-5	Pb	0.025-0.5
Na	500-10000	Se	0.5-10
Ni	0.5-10	Sn	0.025-0.5
P	500-10000	Sr	5-100
Pb	0.5-10	V	0.025-5
Rb	5-100	Zn	5-100
S	NA		
Se	0.025-0.5		
Sn	0.025-0.5		
Tl	0.025-0.5		
U	0.025-0.5		
V	5-100		
Zn	5-100		

NA-Not Available

- 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.

### 3.9 Interim Report

An interim report was e-mailed to participants on 18 October 2021.

## 4 PARTICIPANT LABORATORY INFORMATION

### 4.1 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 <sub>3</sub> (mL)	Vol. HCl (mL)	Vol. HNO <sub>3</sub> (1:1) (mL)	Vol. HCl (1:1) (mL)	Vol. H <sub>2</sub> O <sub>2</sub> (mL)	Other
1		1	95-100	120	3	1				
2	In house - referencing APHA 3125	0.4	120	60	10					
3	Inhouse	0.2	109	240	10					
4	European Standard EN 13805:2002 – Foodstuffs – Determination of trace elements – pressure digestion	0.5	170	12		0.5	7		1	
5	In-house method Microwave digestion for trace elements and Hot block digestion for major elements. Analysed by ICP-MS and ICP-OES	0.5	85-165	50	5					
6	AOAC 990.08	0.25	85	240	3	2				
7	In house, hot block digestion	1	110	60	5	1.5				
8	Not Applicable	NA	NA	NA	NA	NA	NA	NA	NA	NA
9	AOAC 990.08	1	85	240	5	5				
10	In House	1	112.5	120	10	10				
11*	In-house method	1.0471	95	120	6	NA	NA	NA	NA	NA
12	Not Applicable	NA	NA	NA	NA	NA	NA	NA	NA	NA

\*Additional information in Table 3

Table 2 Methodology for Total Elements in S2

Lab. Code	Method Reference	Sample Mass (g)	Temp. (°C)	Time (min)	Vol. HNO <sub>3</sub> (mL)	Vol. HCl (mL)	Vol. HNO <sub>3</sub> (1:1) (mL)	Vol. HCl (1:1) (mL)	Vol. H <sub>2</sub> O <sub>2</sub> (mL)	Other
1		1	95-100	120	3	1				
2	In house – referencing APHA 3125	0.4	120	60	2.5	7.5				
3	200.3 modified	0.2	120	240	6	1			2	
4*	European Standard EN 13805:2002 – Foodstuffs – Determination of trace elements – pressure digestion	0.5	144 then 210	5 then 12		0.5	7		1	
5	In-house method Microwave digestion for trace elements and Hot block digestion for major elements. Analysed by ICP-MS and ICP-OES	0.5	85-165	50	5					
6	AOAC 990.08	0.25	85	240	3	2				
7	In house, hot block digestion		110	60	5	1.5				
8*		0.515	105	60	2.5	0.5				H <sub>2</sub> O – 2mL

9	AOAC 990.08	1	85	240	5	5				
10	In House	1	112.5	120	10	10				
11	Not Applicable	NA	NA	NA	NA	NA	NA	NA	NA	NA
12	USEPA 200.2 rev 2.8	2	95	60			2		2	HCl (1:4) – 10mL

\*Additional information in Table 3

#### 4.2 Instruments Used for Measurements

The instruments and settings used by participants are presented in Appendix 5.

#### 4.3 Additional Information

Participants had the option to report additional information for each sample analysed. These are transcribed in Table 3.

Table 3 Additional Information

Lab Code	Additional Information
4	Methodology for S2: Microwave digestion
8	Sample S2: Storage: At room temperature, not stored in a desiccator. Methodology for S2: Note: Selenium were prepared using a different extraction method: sample mass = 0.511 g, extraction with 5 mL of 12.5% Tetramethylammonium hydroxide, digestion temp 115°C for 60 mins.
11	Methodology for S1: Final volume made to 50.0 mL

#### 4.4 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about the basis of their uncertainty estimates (Table 4).

Table 4 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation <sup>a</sup>		Guide Document for Estimating MU
		Precision	Method Bias	
1	Top Down - precision and estimates of the method and laboratory bias	Control Samples - RM Duplicate Analysis	CRM Recoveries of SS	Nordtest Report TR537
2	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Standard Purity	Eurachem/CITAC Guide
3	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - RM Duplicate Analysis		
4	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis	CRM	NMI Uncertainty Course
5	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - RM Duplicate Analysis	CRM Laboratory Bias from PT Studies	other please type
6	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS Duplicate Analysis	Laboratory Bias from PT Studies Recoveries of SS	
7	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis	CRM Instrument Calibration	Eurachem/CITAC Guide
8	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	Eurachem/CITAC Guide
9	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Laboratory Bias from PT Studies Recoveries of SS	NMI Uncertainty Course
10	Professional judgment	Control Samples - RM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Recoveries of SS	NATA General Accreditation, Guidance, Estimating and Reporting MU (Replace TN 33)
11	Horwitz formula	Control Samples - SS Instrument Calibration	Recoveries of SS	Eurachem/CITAC Guide
12	Top Down - precision and estimates of the method and laboratory bias	Standard deviation from PT studies only		Eurachem/CITAC Guide
		Control Samples - RM Duplicate Analysis Instrument Calibration		

<sup>a</sup>RM = Reference Material, CRM = Certified Reference Material, SS = Spiked Samples.

#### 4.5 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.

## 5 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

### 5.1 Results Summary

Participant results are listed in Tables 5 to 57 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 54. An example chart with interpretation guide is shown in Figure 1.

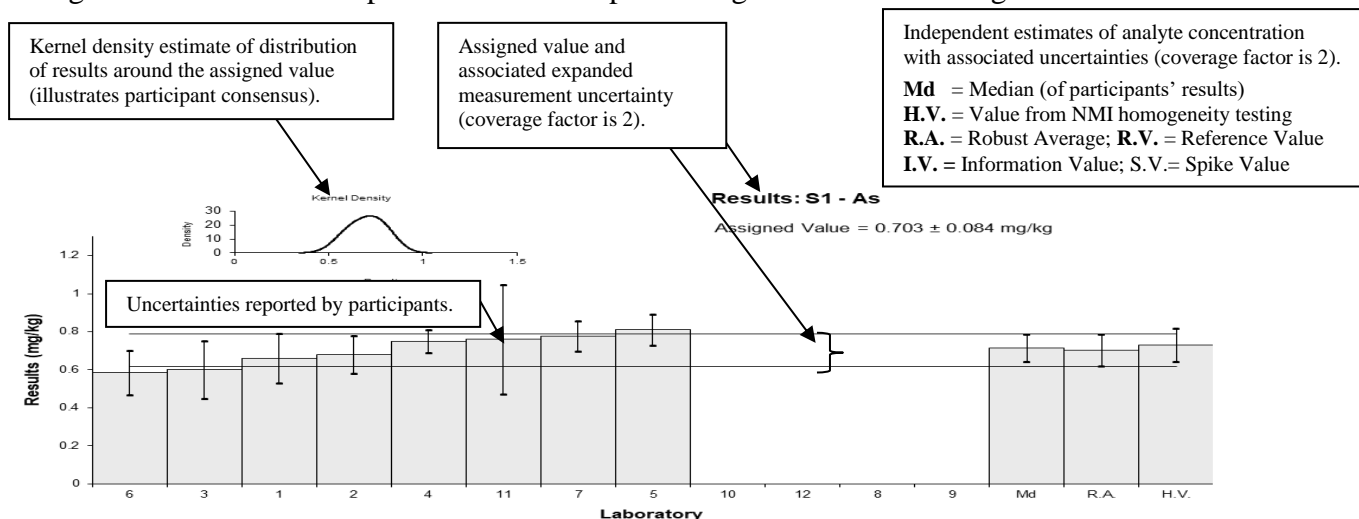


Figure 1 Guide to Presentation of Results

### 5.2 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.<sup>4,5</sup>

### 5.3 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.'<sup>2</sup> In this study the property is the mass fraction of analyte. For Fe and Ni in S1, the assigned values were reference values measured using isotope dilution mass spectrometry. For all other analytes the assigned values were the robust average of participants' results; the expanded uncertainties were estimated from associated robust standard deviation.<sup>5,6</sup>

### 5.4 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 interlaboratory comparisons, ISO13528:2015(E)'.<sup>6</sup>

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 ISO13528:2015(E).<sup>6</sup>

### 5.5 Target Standard Deviation

The target standard deviation ( $\sigma$ ) 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.

$$\sigma = (X) * PCV \quad \text{Equation 1}$$

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/or on experience from previous studies. It is backed up by mathematical models such as the Thompson Horwitz equation.<sup>7</sup>

## 5.6 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:

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

Where:

- $z$  is z-score
- $\chi$  is participant's result;
- $X$  is the assigned value;
- $\sigma$  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.

## 5.7 E<sub>n</sub>-Score

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

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

Where:

- $E_n$  is E<sub>n</sub>-score;
- $\chi$  is a participant's result;
- $X$  is the assigned value;
- $U_\chi$  is the expanded uncertainty of the participant's result;
- $U_X$  is the expanded uncertainty of the assigned value.

An E<sub>n</sub>-score with absolute value ( $|E_n|$ ):

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

## 5.8 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025:2018<sup>8</sup> must establish and demonstrate the traceability and measurement uncertainty associated with their test results. Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.<sup>1</sup>

## 6 TABLES AND FIGURES

Table 5

### Sample Details

<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Al
<b>Units</b>	mg/kg

### Participant Results

Lab Code	Result	Uncertainty
1	3850	770
2	3025	300
3	3600	700
4	6310	1350
5	5770	570
6	2697	539
7	4110	411
8	NT	NT
9	NT	NT
10	NT	NT
11	NT	NT
12	NT	NT

### Statistics

<b>Assigned Value</b>	Not Set	
<b>Homogeneity Value</b>	6200	740
<b>Robust Average</b>	4200	1500
<b>Median</b>	3900	1100
<b>Mean</b>	4200	
<b>N</b>	7	
<b>Max.</b>	6310	
<b>Min.</b>	2697	
<b>Robust SD</b>	1500	
<b>Robust CV</b>	37%	

Results: S1 - Al

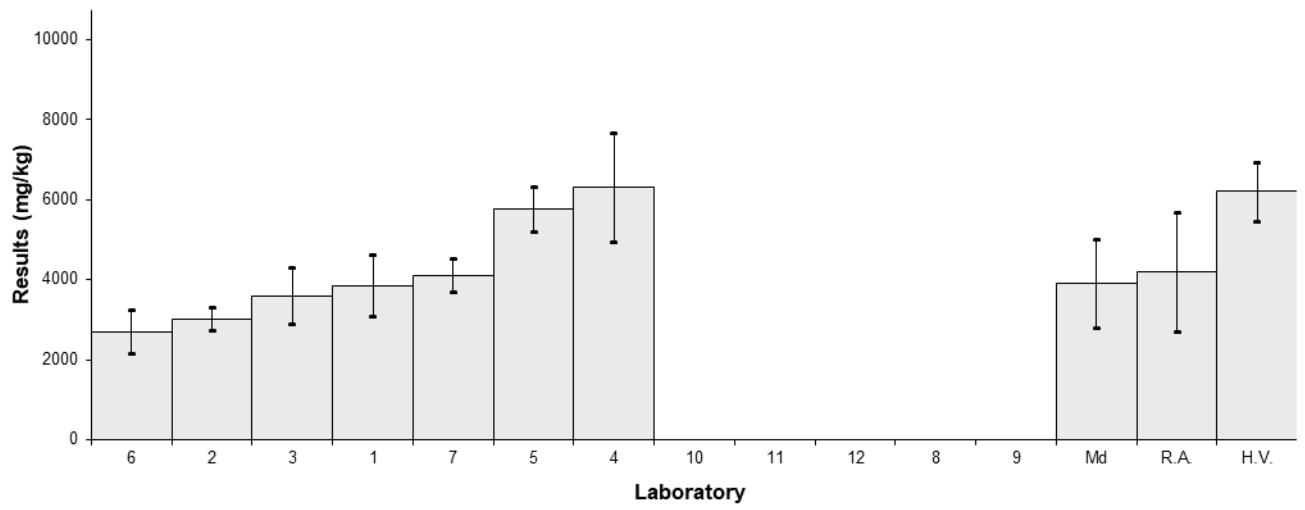


Figure 2



Table 6

**Sample Details**

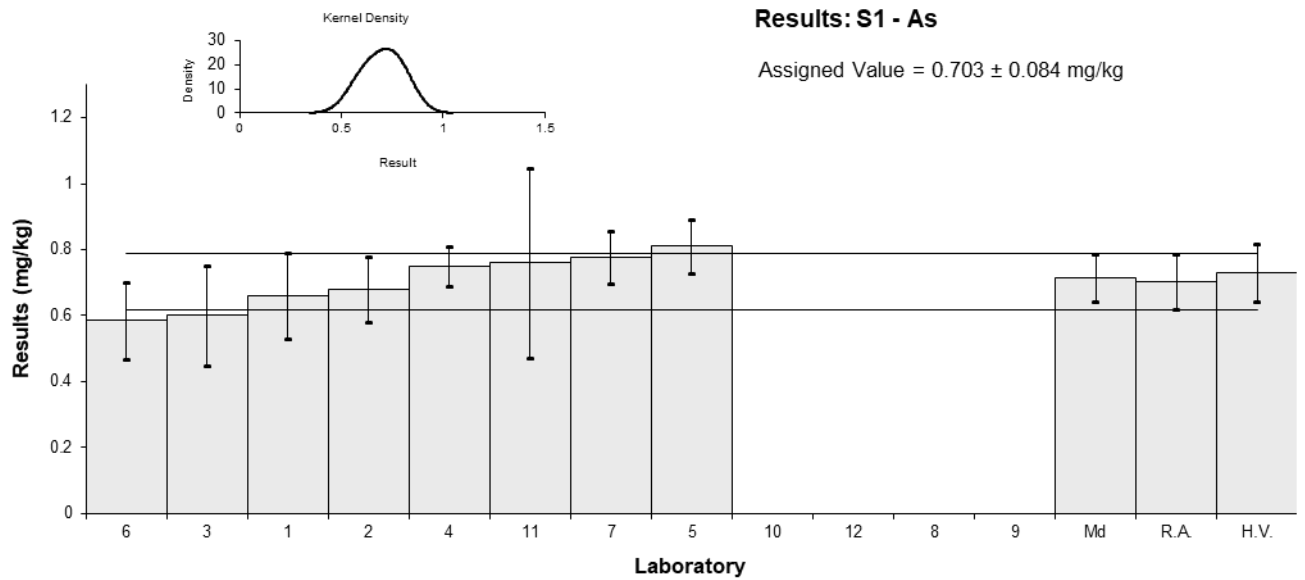
<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	As
<b>Units</b>	mg/kg

**Participant Results**

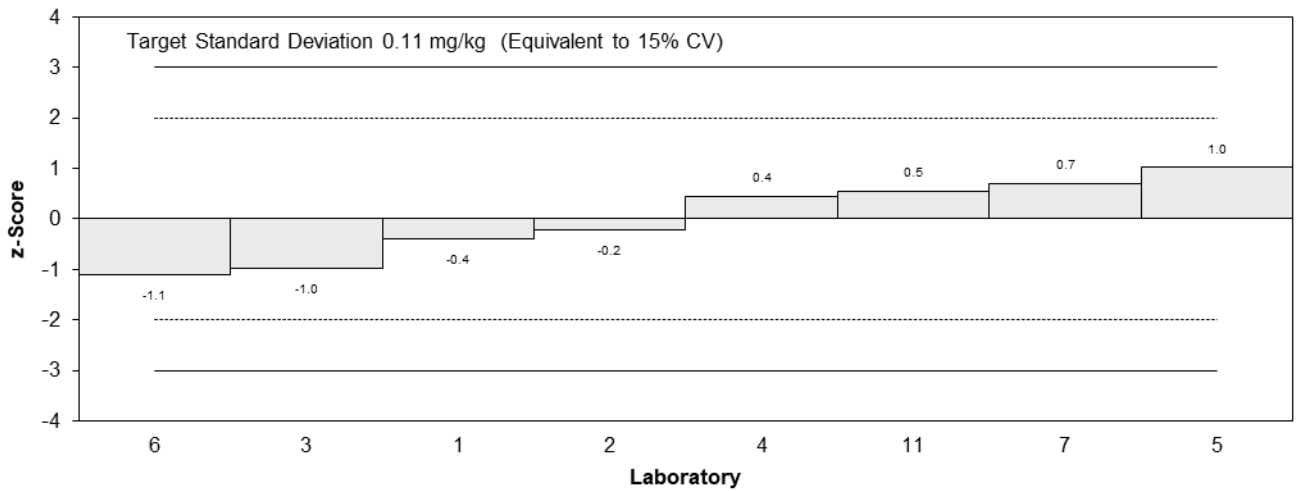
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.66	0.13	-0.41	-0.28
2	0.68	0.1	-0.22	-0.18
3	0.60	0.15	-0.98	-0.60
4	0.75	0.06	0.45	0.46
5	0.81	0.08	1.01	0.92
6	0.585	0.117	-1.12	-0.82
7	0.777	0.078	0.70	0.65
8	NT	NT		
9	NT	NT		
10	<2	NR		
11	0.76	0.287	0.54	0.19
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	0.703	0.084
<b>Homogeneity Value</b>	0.729	0.088
<b>Robust Average</b>	0.703	0.084
<b>Median</b>	0.715	0.073
<b>Mean</b>	0.703	
<b>N</b>	8	
<b>Max.</b>	0.81	
<b>Min.</b>	0.585	
<b>Robust SD</b>	0.095	
<b>Robust CV</b>	14%	



**z-Scores: S1 - As**



**En-Scores: S1 - As**

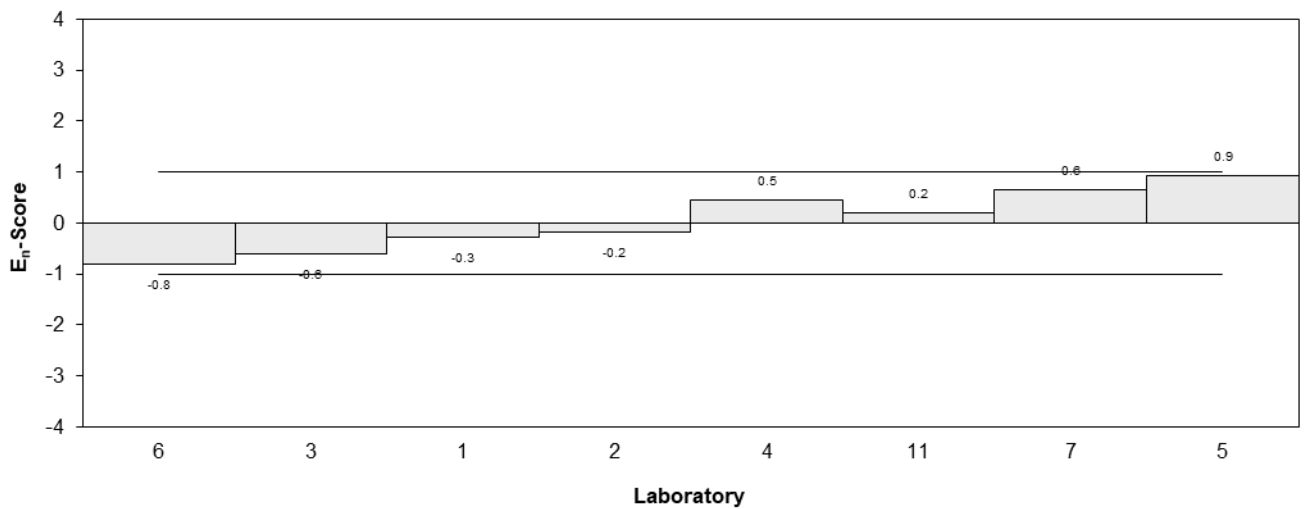


Figure 3

Table 7

**Sample Details**

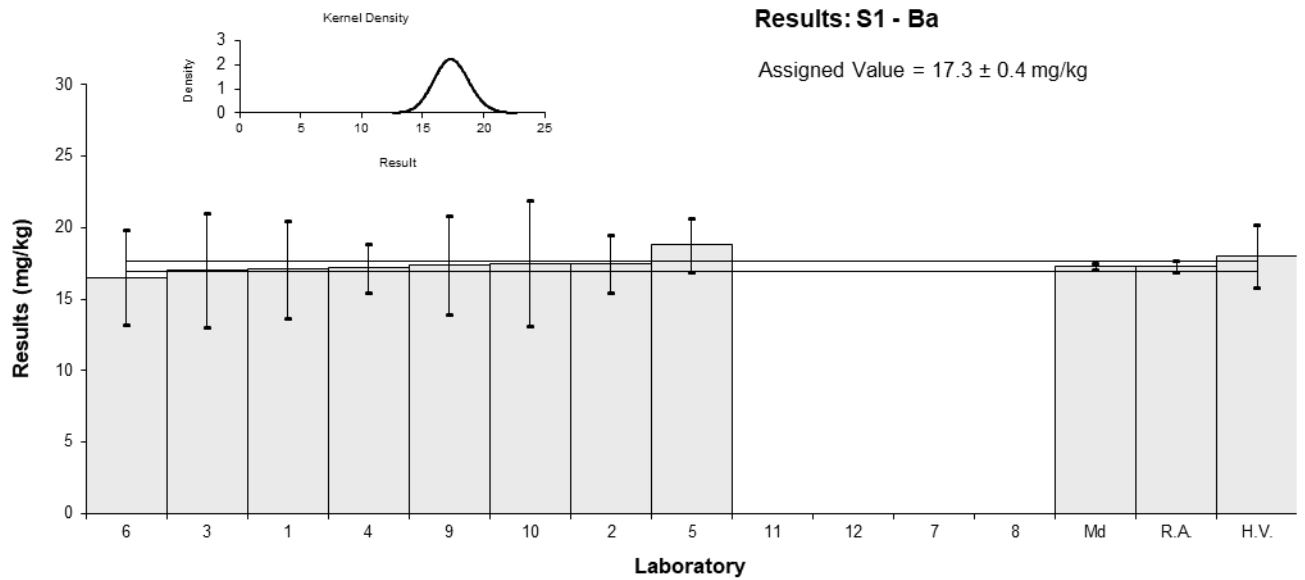
<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Ba
<b>Units</b>	mg/kg

**Participant Results**

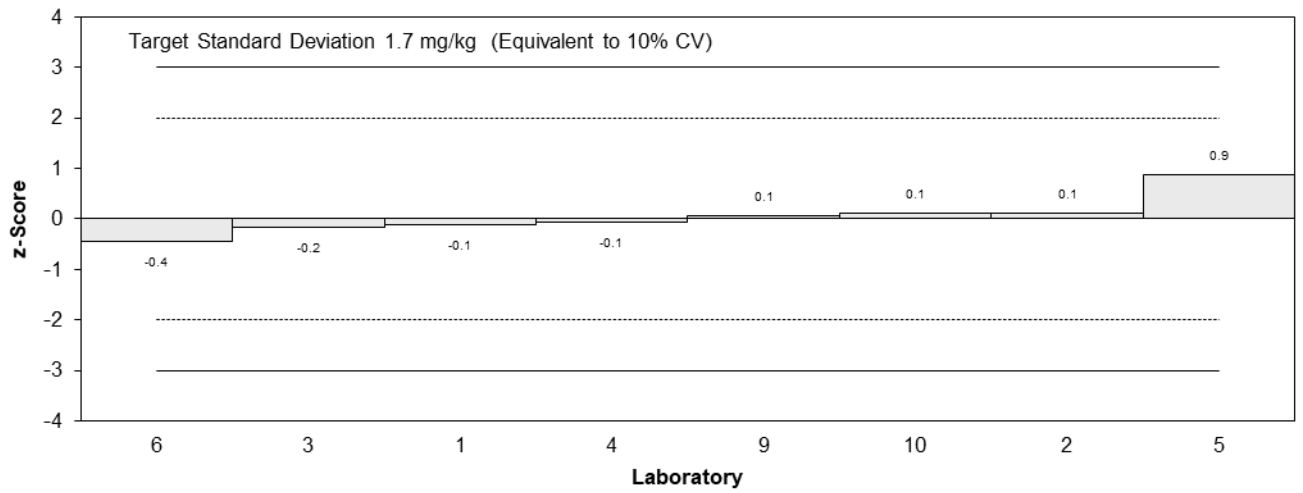
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	17.1	3.4	-0.12	-0.06
2	17.5	2.0	0.12	0.10
3	17	4	-0.17	-0.07
4	17.2	1.7	-0.06	-0.06
5	18.8	1.9	0.87	0.77
6	16.53	3.31	-0.45	-0.23
7	NT	NT		
8	NT	NT		
9	17.4	3.48	0.06	0.03
10	17.5	4.4	0.12	0.05
11	NT	NT		
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	17.3	0.4
<b>Homogeneity Value</b>	18.0	2.2
<b>Robust Average</b>	17.3	0.4
<b>Median</b>	17.3	0.2
<b>Mean</b>	17.4	
<b>N</b>	8	
<b>Max.</b>	18.8	
<b>Min.</b>	16.53	
<b>Robust SD</b>	0.49	
<b>Robust CV</b>	2.8%	



**z-Scores: S1 - Ba**



**En-Scores: S1 - Ba**

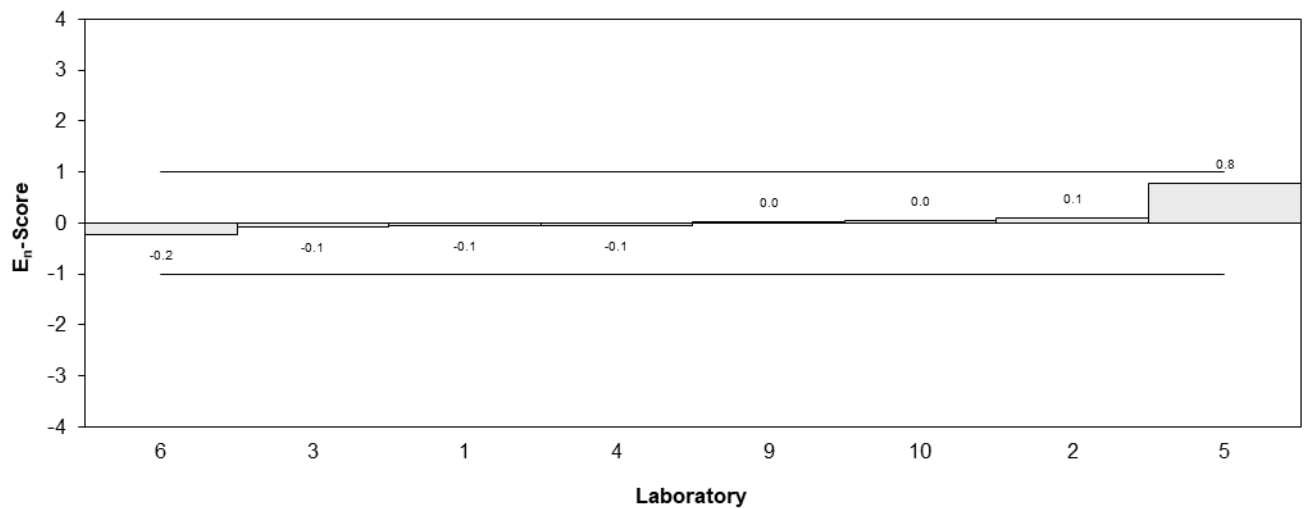


Figure 4

Table 8

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Be
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	0.038	0.01
2	<0.1	NR
3	0.03	0.01
4	0.05	0.1
5	NR	NR
6	0.025	0.005
7	NT	NT
8	NT	NT
9	NT	NT
10	<1	NR
11	NT	NT
12	NT	NT

**Statistics**

<b>Assigned Value</b>	Not Set	
<b>Homogeneity Value</b>	0.0571	0.0086
<b>Median</b>	0.034	0.015
<b>Mean</b>	0.036	
<b>N</b>	4	
<b>Max.</b>	0.05	
<b>Min.</b>	0.025	

Results: S1 - Be

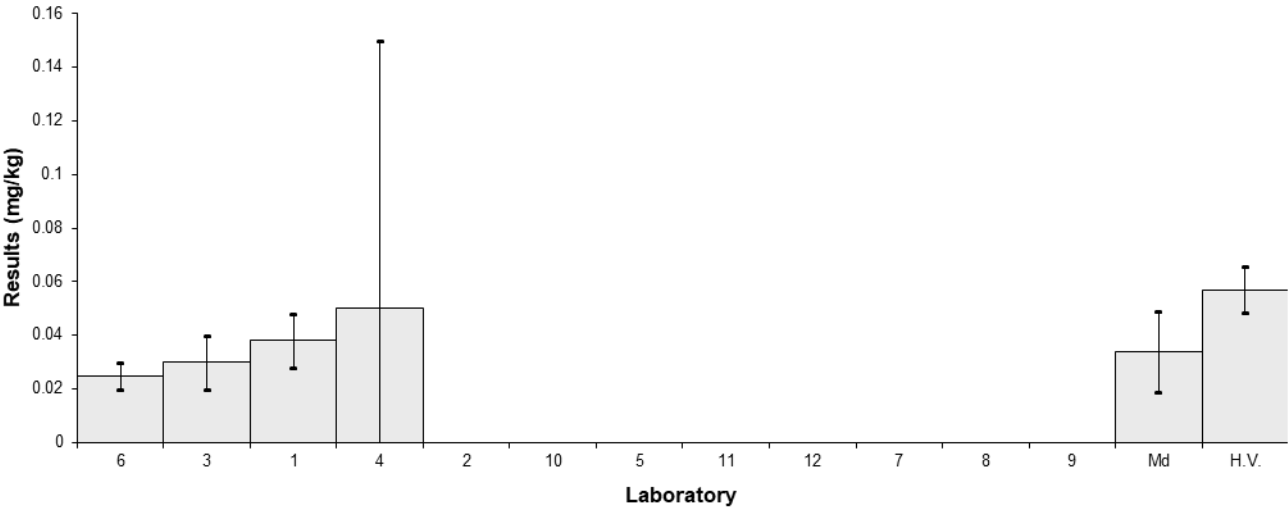


Figure 5

Table 9

**Sample Details**

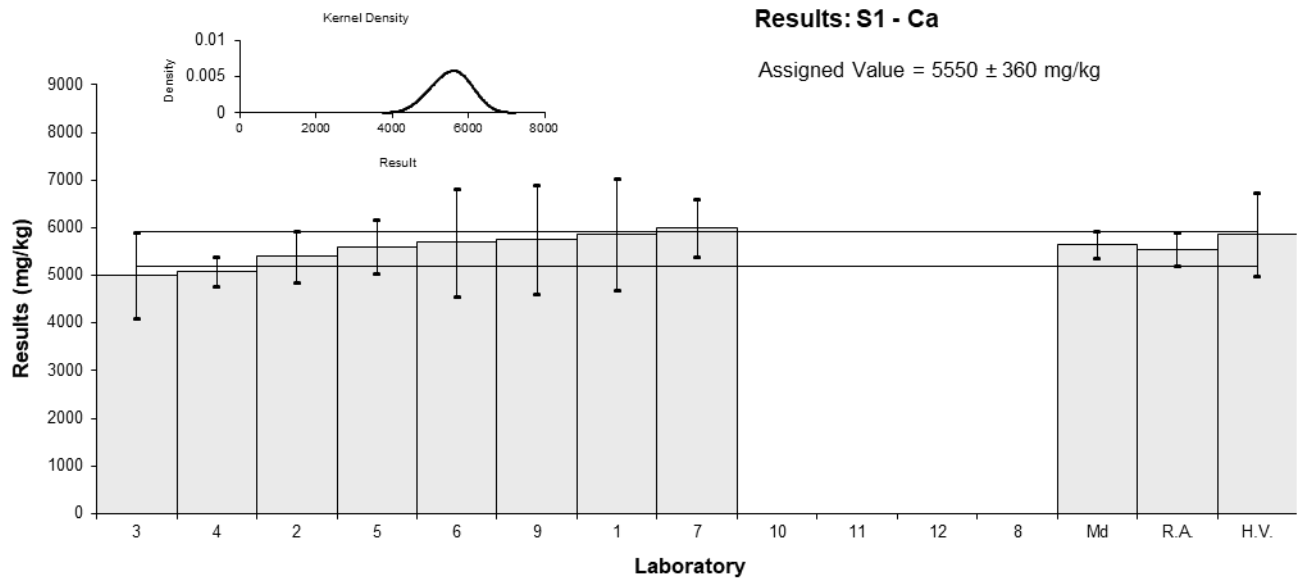
<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Ca
<b>Units</b>	mg/kg

**Participant Results**

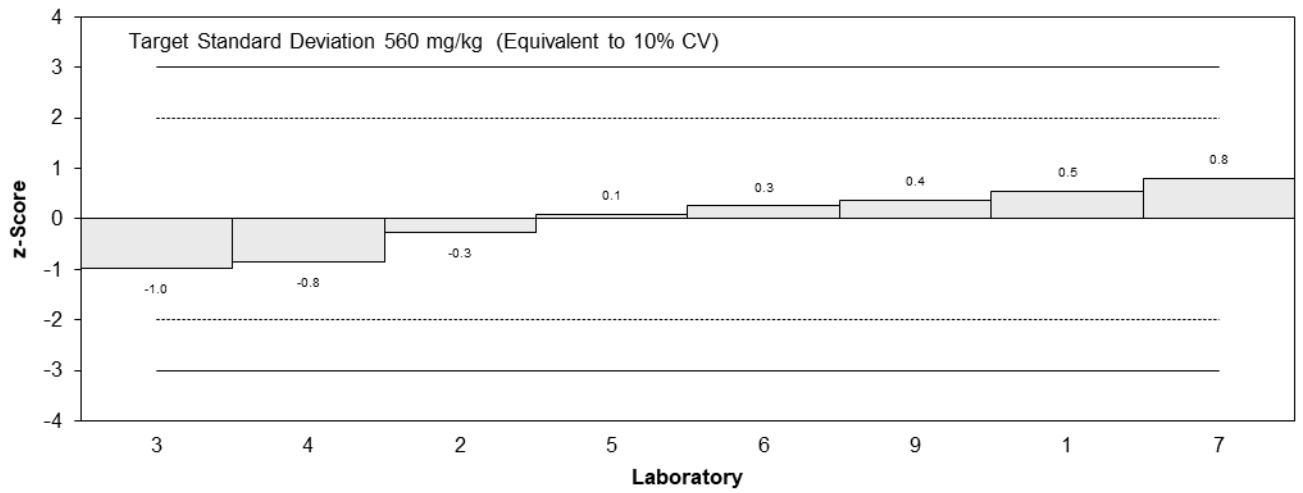
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	5850	1170	0.54	0.25
2	5400	540	-0.27	-0.23
3	5000	900	-0.99	-0.57
4	5080	315	-0.85	-0.98
5	5600	560	0.09	0.08
6	5690	1138	0.25	0.12
7	5990	599	0.79	0.63
8	NT	NT		
9	5750	1150	0.36	0.17
10	NT	NT		
11	NT	NT		
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	5550	360
<b>Homogeneity Value</b>	5860	880
<b>Robust Average</b>	5550	360
<b>Median</b>	5650	280
<b>Mean</b>	5550	
<b>N</b>	8	
<b>Max.</b>	5990	
<b>Min.</b>	5000	
<b>Robust SD</b>	400	
<b>Robust CV</b>	7.3%	



**z-Scores: S1 - Ca**



**En-Scores: S1 - Ca**

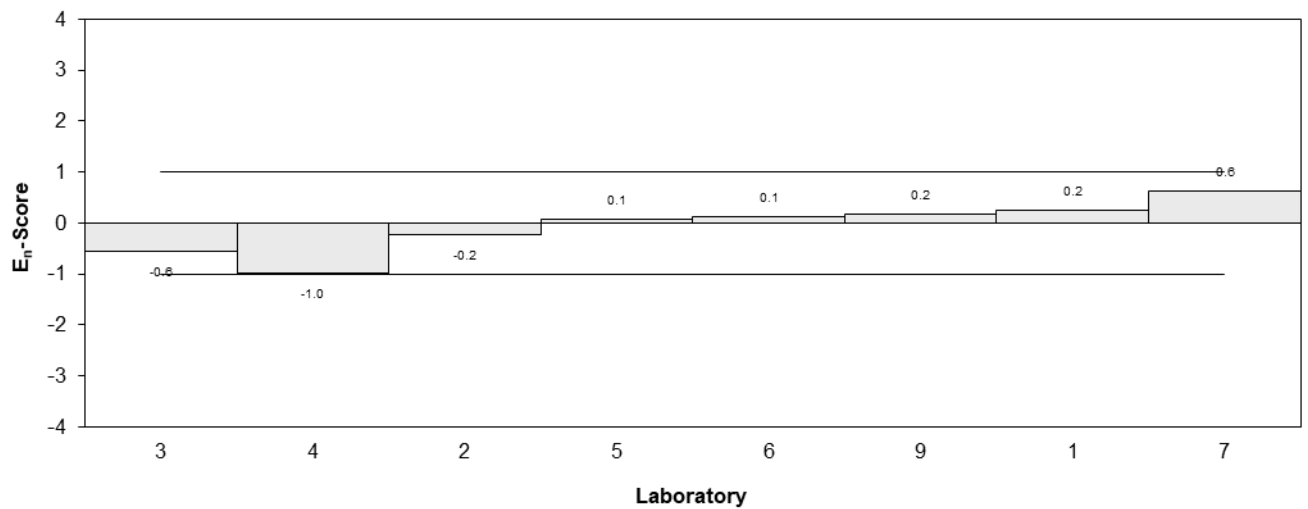


Figure 6



Table 10

**Sample Details**

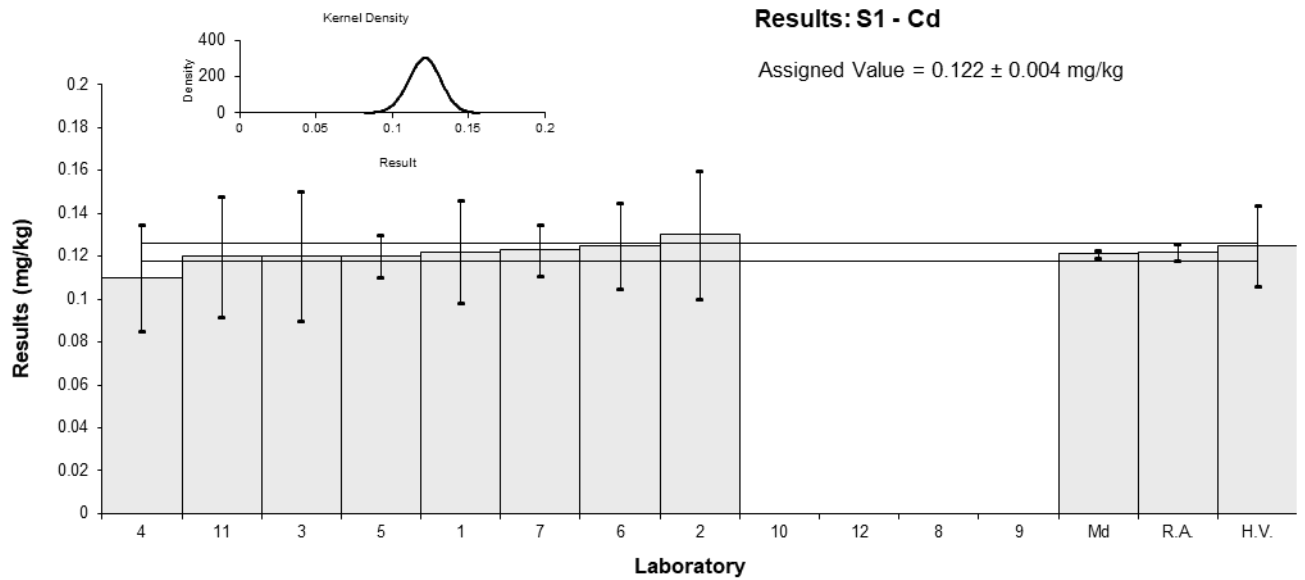
<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Cd
<b>Units</b>	mg/kg

**Participant Results**

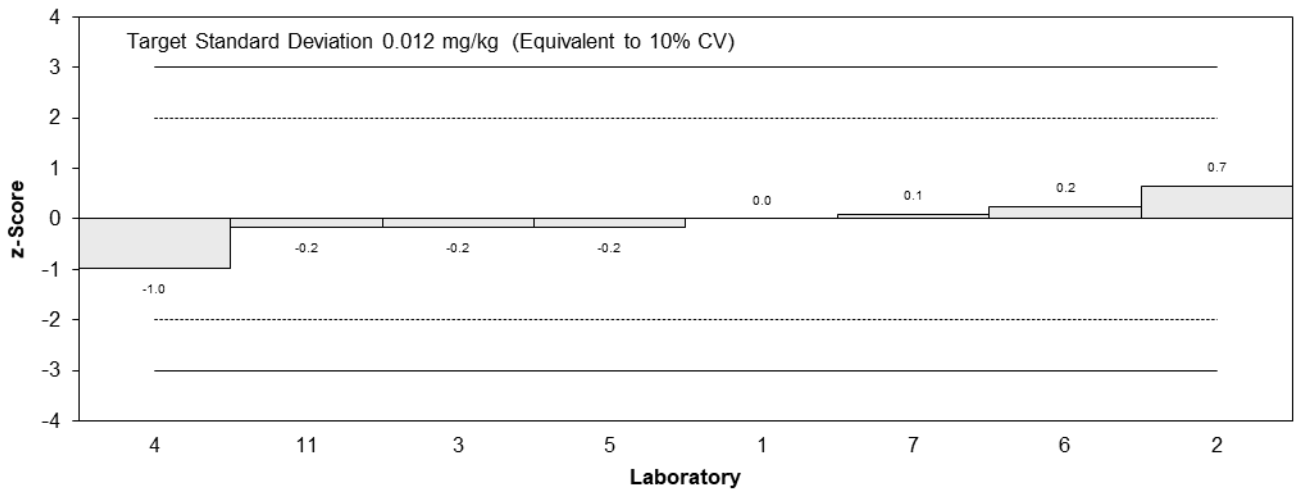
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.122	0.024	0.00	0.00
2	0.13	0.03	0.66	0.26
3	0.12	0.03	-0.16	-0.07
4	0.11	0.025	-0.98	-0.47
5	0.12	0.01	-0.16	-0.19
6	0.125	0.02	0.25	0.15
7	0.123	0.012	0.08	0.08
8	NT	NT		
9	NT	NT		
10	<1	NR		
11	0.12	0.028	-0.16	-0.07
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	0.122	0.004
<b>Homogeneity Value</b>	0.125	0.019
<b>Robust Average</b>	0.122	0.004
<b>Median</b>	0.121	0.002
<b>Mean</b>	0.121	
<b>N</b>	8	
<b>Max.</b>	0.13	
<b>Min.</b>	0.11	
<b>Robust SD</b>	0.0047	
<b>Robust CV</b>	3.9%	



**z-Scores: S1 - Cd**



**En-Scores: S1 - Cd**

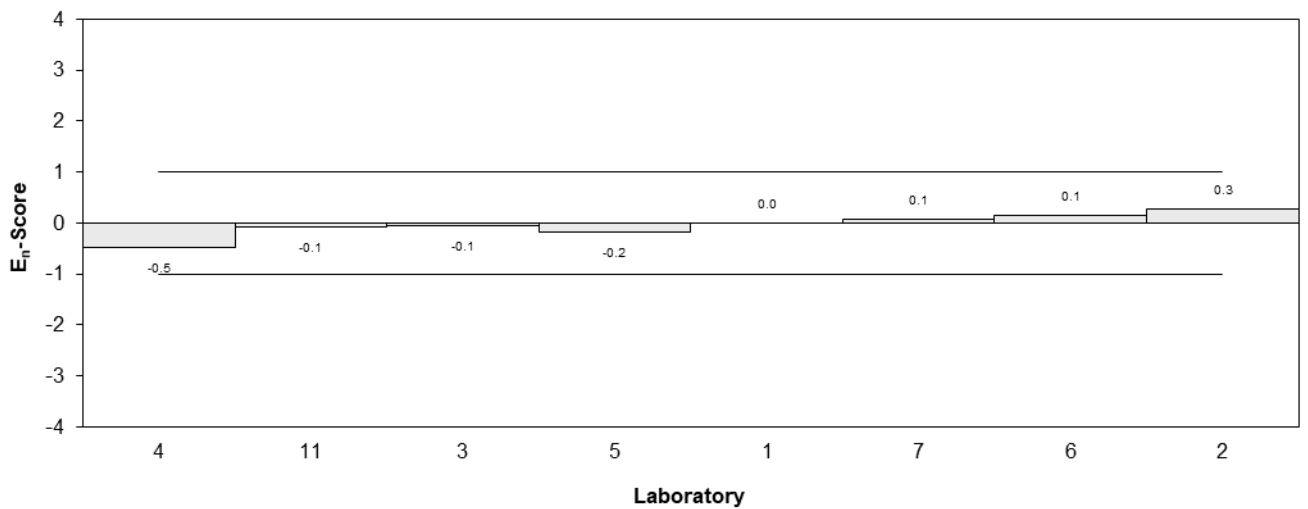


Figure 7

Table 11

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Co
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.273	0.055	-0.29	-0.21
2	0.27	0.05	-0.34	-0.26
3	0.28	0.06	-0.17	-0.12
4	0.40	0.08	1.90	1.10
5	0.34	0.03	0.86	0.75
6	0.212	0.04	-1.34	-1.08
7	0.267	0.027	-0.40	-0.35
8	NT	NT		
9	NT	NT		
10	<1	NR		
11	NT	NT		
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	0.290	0.060
<b>Homogeneity Value</b>	0.385	0.058
<b>Robust Average</b>	0.290	0.060
<b>Median</b>	0.273	0.010
<b>Mean</b>	0.292	
<b>N</b>	7	
<b>Max.</b>	0.4	
<b>Min.</b>	0.212	
<b>Robust SD</b>	0.064	
<b>Robust CV</b>	22%	

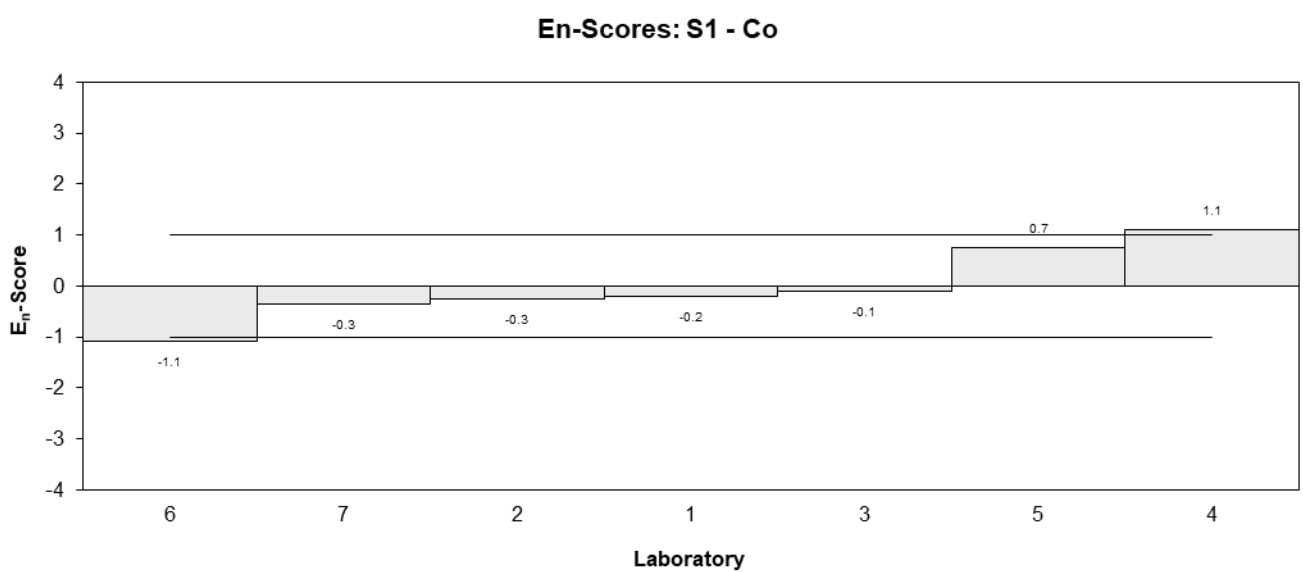
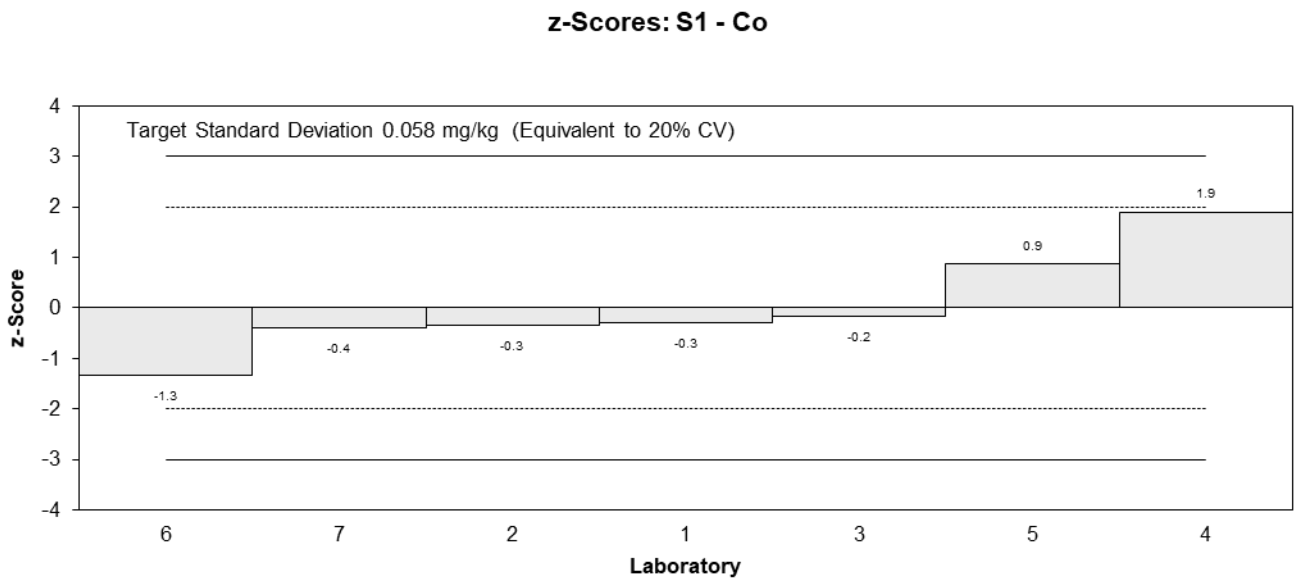
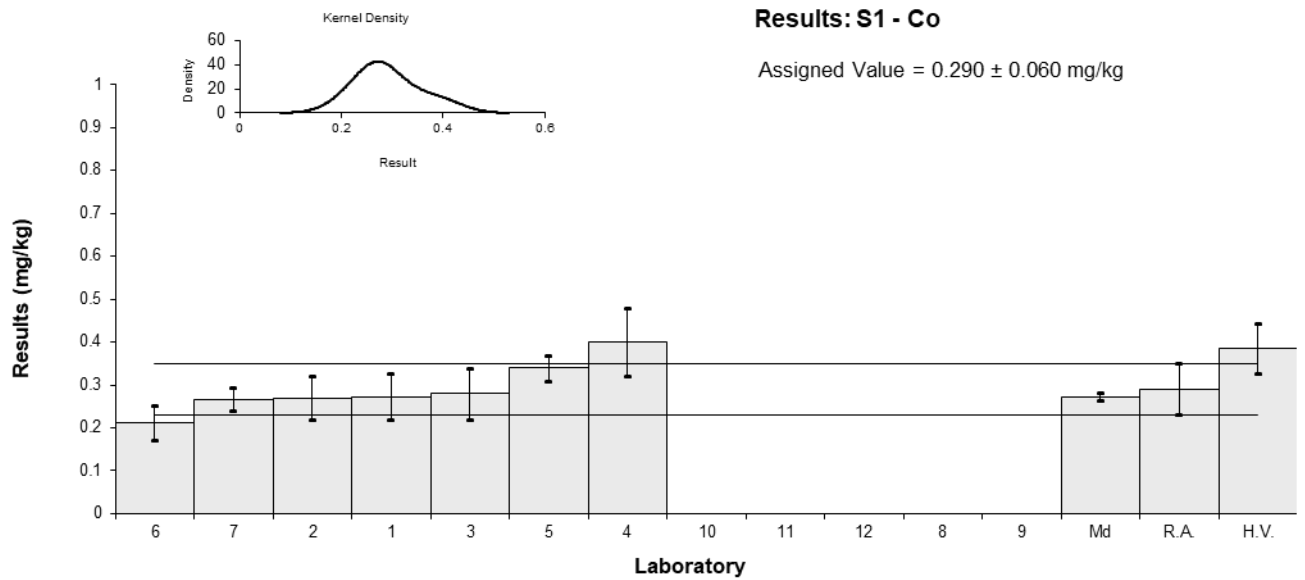


Figure 8

Table 12

**Sample Details**

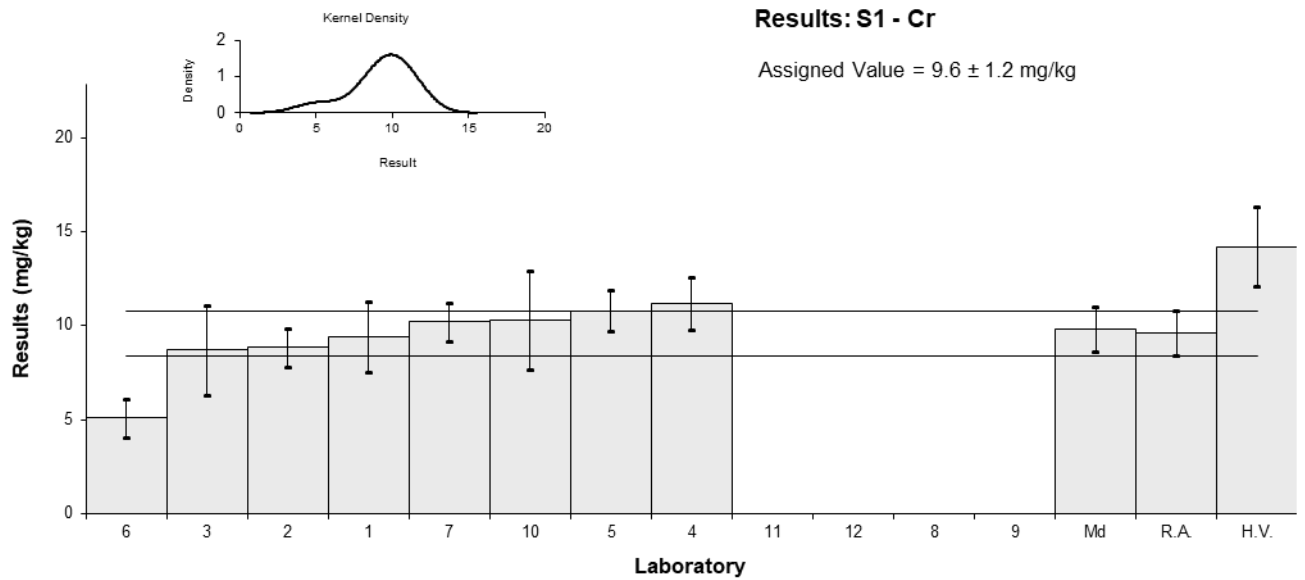
<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Cr
<b>Units</b>	mg/kg

**Participant Results**

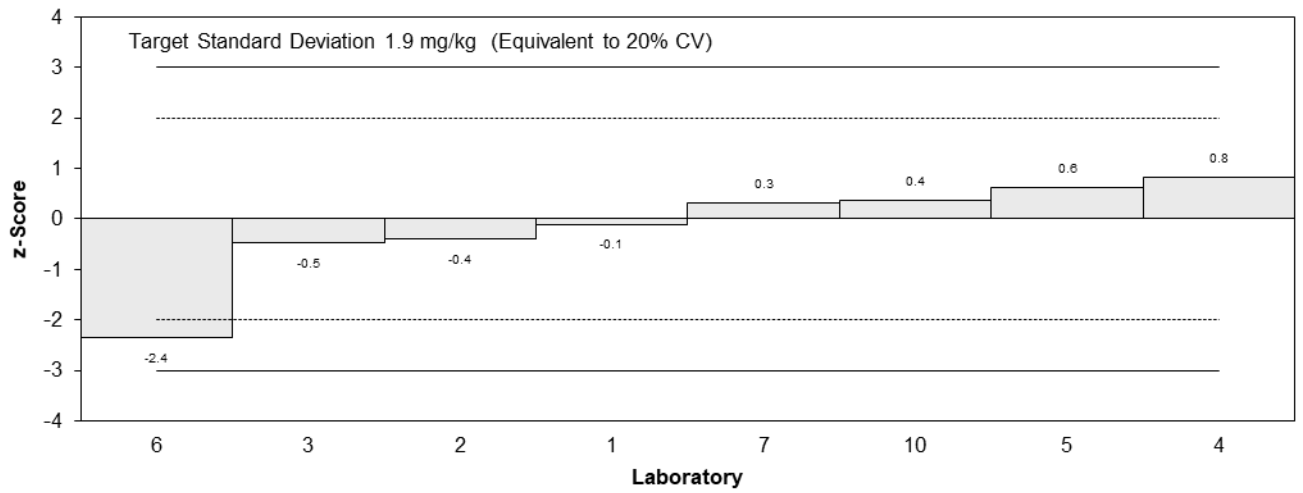
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	9.4	1.9	-0.10	-0.09
2	8.83	1.0	-0.40	-0.49
3	8.7	2.4	-0.47	-0.34
4	11.2	1.4	0.83	0.87
5	10.8	1.1	0.63	0.74
6	5.08	1.02	-2.35	-2.87
7	10.2	1.02	0.31	0.38
8	NT	NT		
9	NT	NT		
10	10.3	2.6	0.36	0.24
11	NT	NT		
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	9.6	1.2
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	14.2	2.1
<b>Robust Average</b>	9.6	1.2
<b>Median</b>	9.8	1.2
<b>Mean</b>	9.3	
<b>N</b>	8	
<b>Max.</b>	11.2	
<b>Min.</b>	5.08	
<b>Robust SD</b>	1.4	
<b>Robust CV</b>	14%	



**z-Scores: S1 - Cr**



**En-Scores: S1 - Cr**

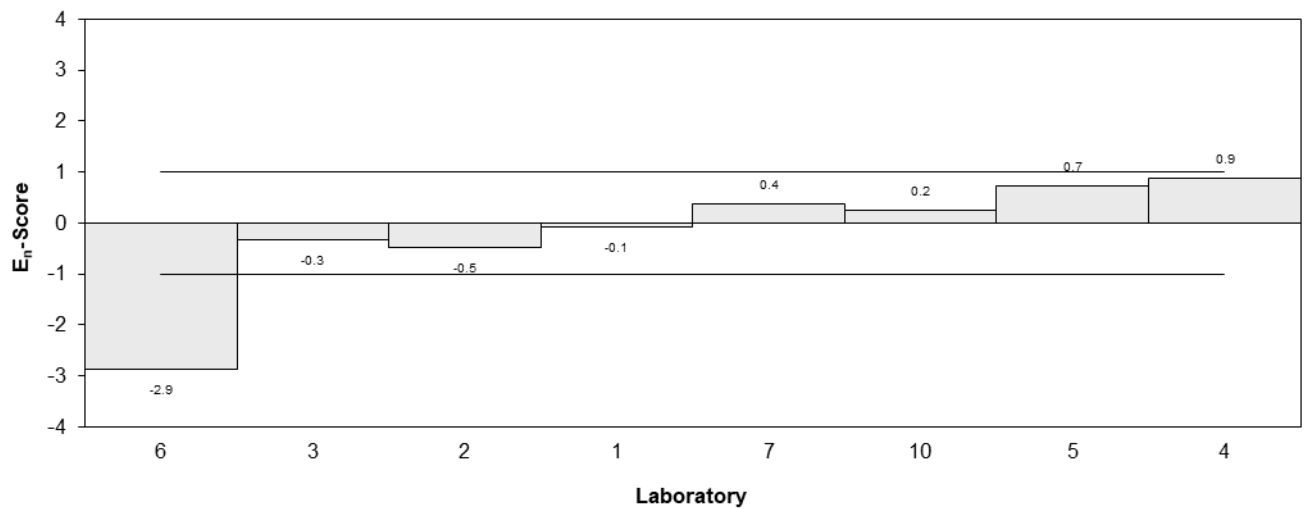


Figure 9

Table 13

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Cs
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	0.25	0.05
2	NT	NT
3	NT	NT
4	NT	NT
5	NR	NR
6	0.150	0.030
7	NT	NT
8	NT	NT
9	NT	NT
10	NT	NT
11	NT	NT
12	NT	NT

**Statistics\***

<b>Assigned Value</b>	Not Set	0.063
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.420	
<b>Mean</b>	0.200	
<b>N</b>	2	

\*Insufficient data to calculate statistics.

Results: S1 - Cs

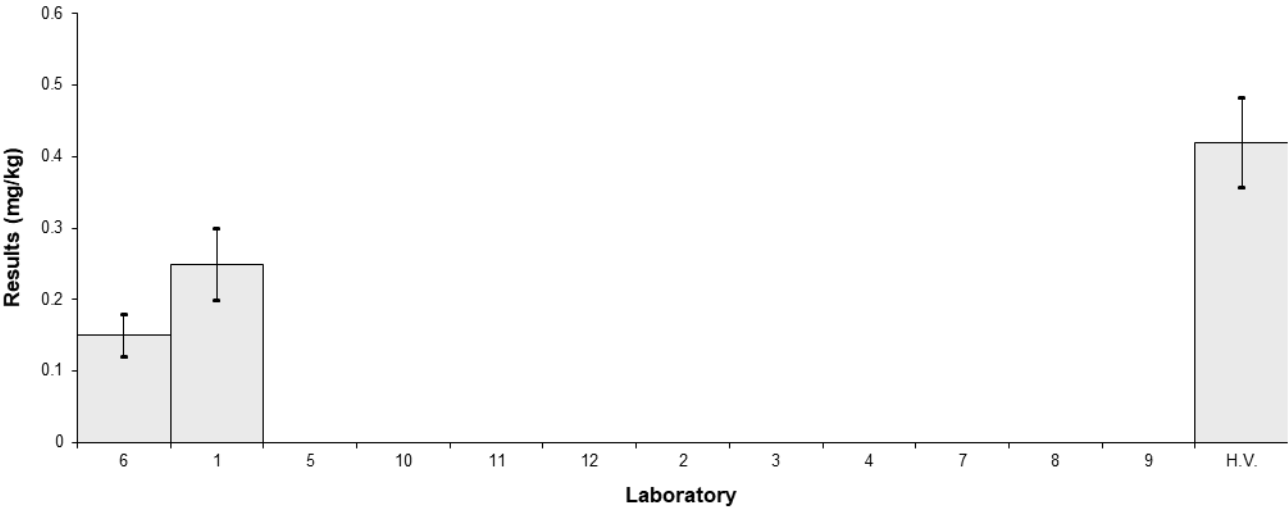


Figure 10



Table 14

**Sample Details**

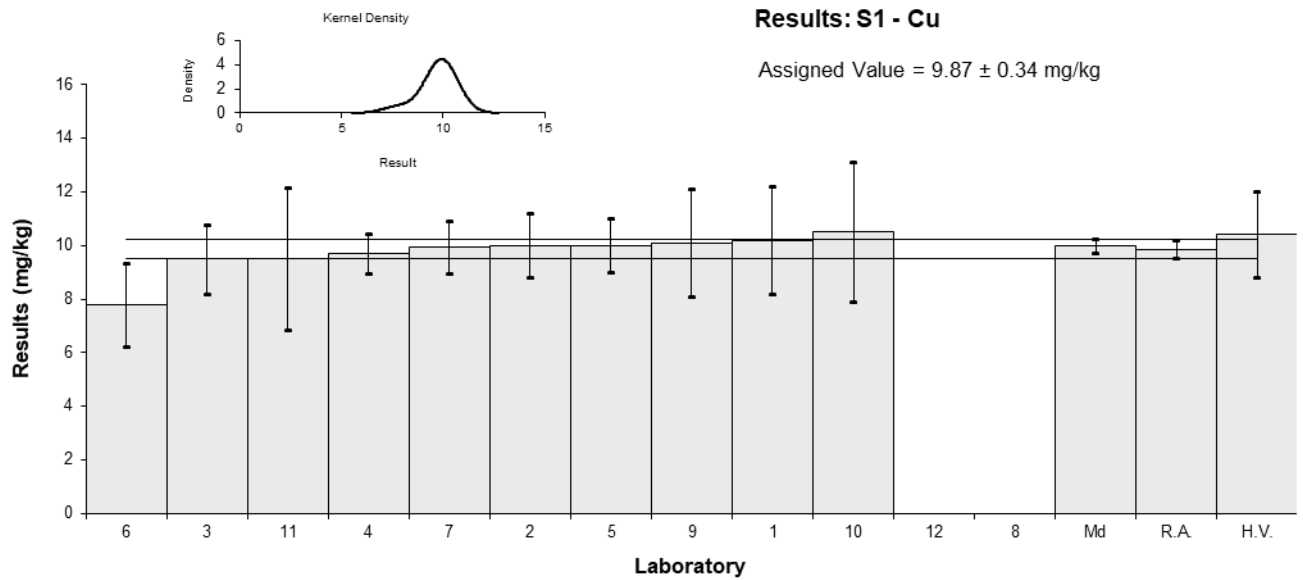
<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Cu
<b>Units</b>	mg/kg

**Participant Results**

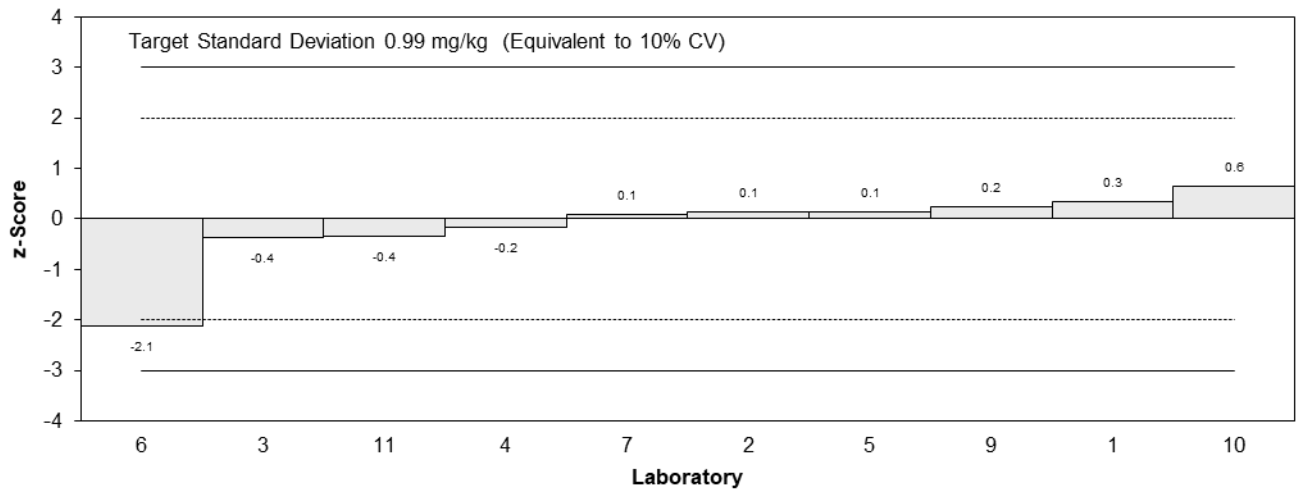
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	10.2	2.0	0.33	0.16
2	10.0	1.2	0.13	0.10
3	9.5	1.3	-0.37	-0.28
4	9.7	0.73	-0.17	-0.21
5	10.0	1.0	0.13	0.12
6	7.78	1.56	-2.12	-1.31
7	9.95	0.995	0.08	0.08
8	NT	NT		
9	10.10	2.02	0.23	0.11
10	10.5	2.6	0.64	0.24
11	9.52	2.66	-0.35	-0.13
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	9.87	0.34
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	10.4	1.6
<b>Robust Average</b>	9.87	0.34
<b>Median</b>	9.98	0.27
<b>Mean</b>	9.73	
<b>N</b>	10	
<b>Max.</b>	10.5	
<b>Min.</b>	7.78	
<b>Robust SD</b>	0.43	
<b>Robust CV</b>	4.4%	



**z-Scores: S1 - Cu**



**En-Scores: S1 - Cu**

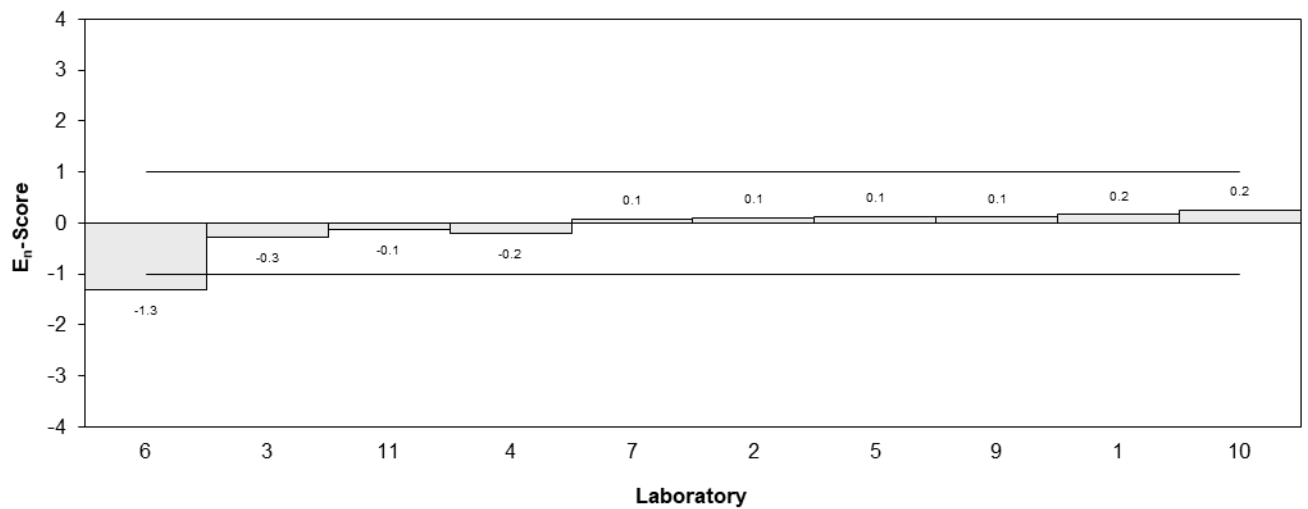


Figure 11

Table 15

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Fe
<b>Units</b>	mg/kg

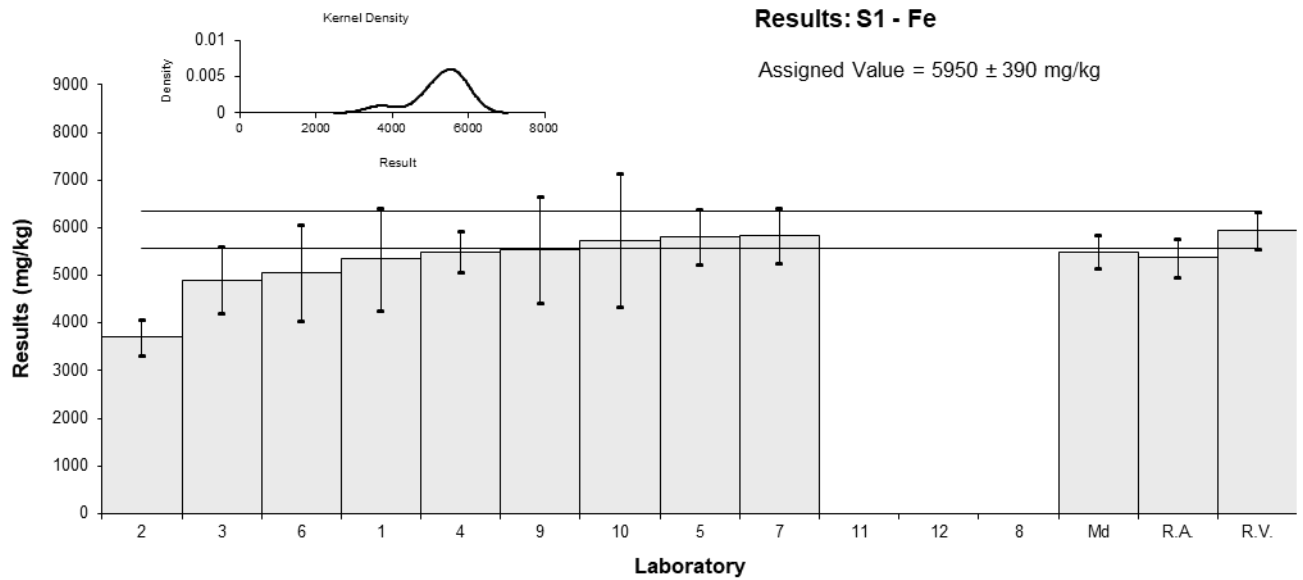
**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	5340	1070	-1.03	-0.54
2	3700	370	-3.78	-4.19
3	4900	700	-1.76	-1.31
4	5490	430	-0.77	-0.79
5	5800	580	-0.25	-0.21
6	5049	1010	-1.51	-0.83
7	5830	583	-0.20	-0.17
8	NT	NT		
9	5540	1110	-0.69	-0.35
10	5730	1400	-0.37	-0.15
11	NT	NT		
12	NT	NT		

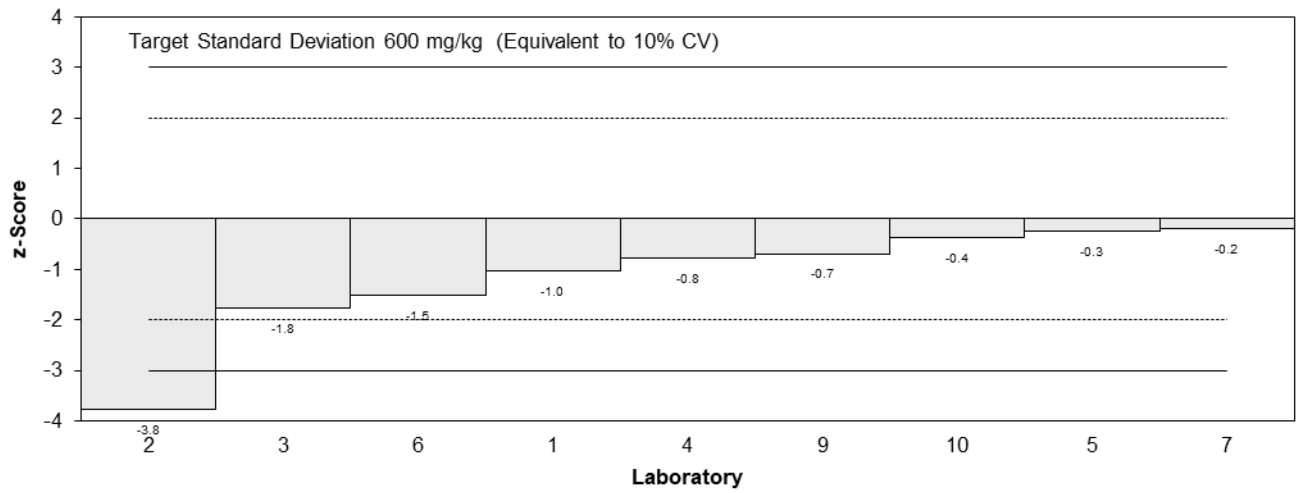
**Statistics**

<b>Assigned Value*</b>	5950	390
<b>Spike</b>	Not Spiked	
<b>Reference Value*</b>	5950	390
<b>Robust Average</b>	5370	400
<b>Median</b>	5490	350
<b>Mean</b>	5260	
<b>N</b>	9	
<b>Max.</b>	5830	
<b>Min.</b>	3700	
<b>Robust SD</b>	470	
<b>Robust CV</b>	8.8%	

\*Reference Value by IDMS



**z-Scores: S1 - Fe**



**En-Scores: S1 - Fe**

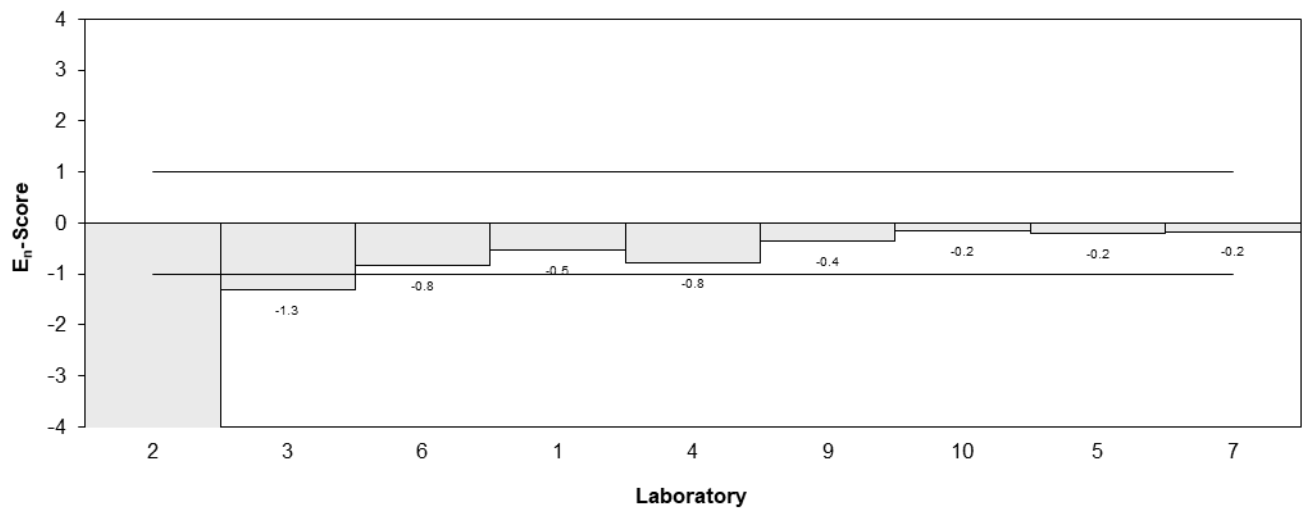


Figure 12

Table 16

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Ga
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	2.28	0.46
2	NT	NT
3	NT	NT
4	NT	NT
5	NR	NR
6	3.34	0.668
7	NT	NT
8	NT	NT
9	NT	NT
10	NT	NT
11	NT	NT
12	NT	NT

**Statistics\***

<b>Assigned Value</b>	Not Set	0.43
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	2.88	
<b>Mean</b>	2.81	
<b>N</b>	2	

\*Insufficient data to calculate statistics.

Results: S1 - Ga

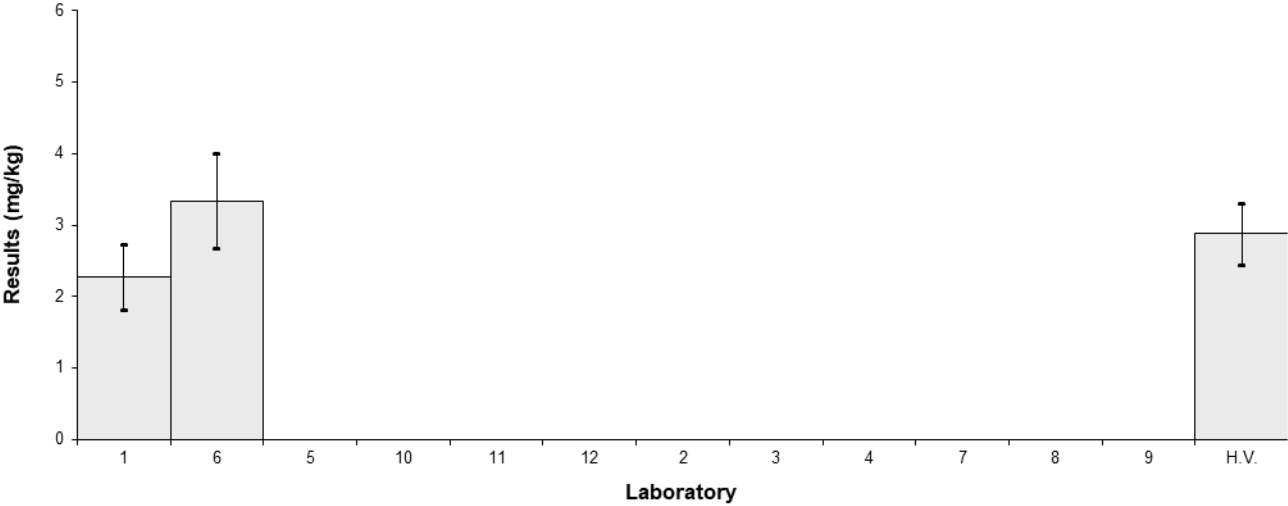


Figure 13

Table 17

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Hg
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	0.037	0.007
2	<0.1	NR
3	0.03	0.02
4	NR	NR
5	0.026	0.003
6	0.042	0.008
7	0.031	0.003
8	NT	NT
9	<0.1	NR
10	0.07	0.02
11	NT	NT
12	NT	NT

**Statistics**

<b>Assigned Value</b>	Not Set	
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.0492	0.0098
<b>Robust Average</b>	0.037	0.012
<b>Median</b>	0.0340	0.0093
<b>Mean</b>	0.0393	
<b>N</b>	6	
<b>Max.</b>	0.07	
<b>Min.</b>	0.026	
<b>Robust SD</b>	0.011	
<b>Robust CV</b>	31%	

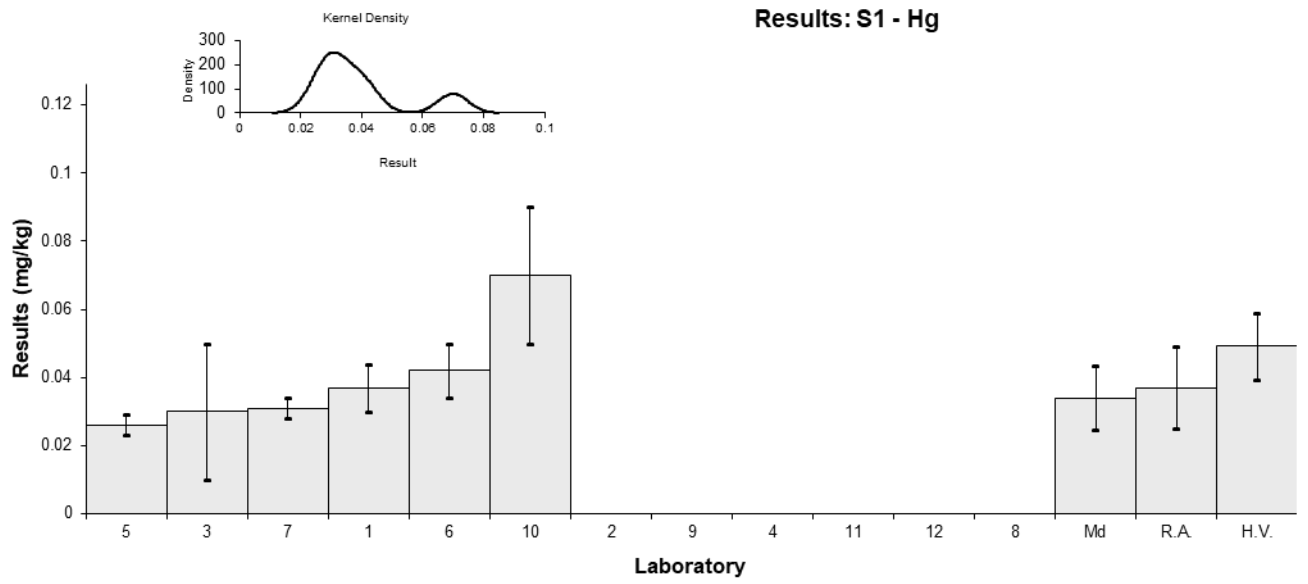


Figure 14



Table 18

**Sample Details**

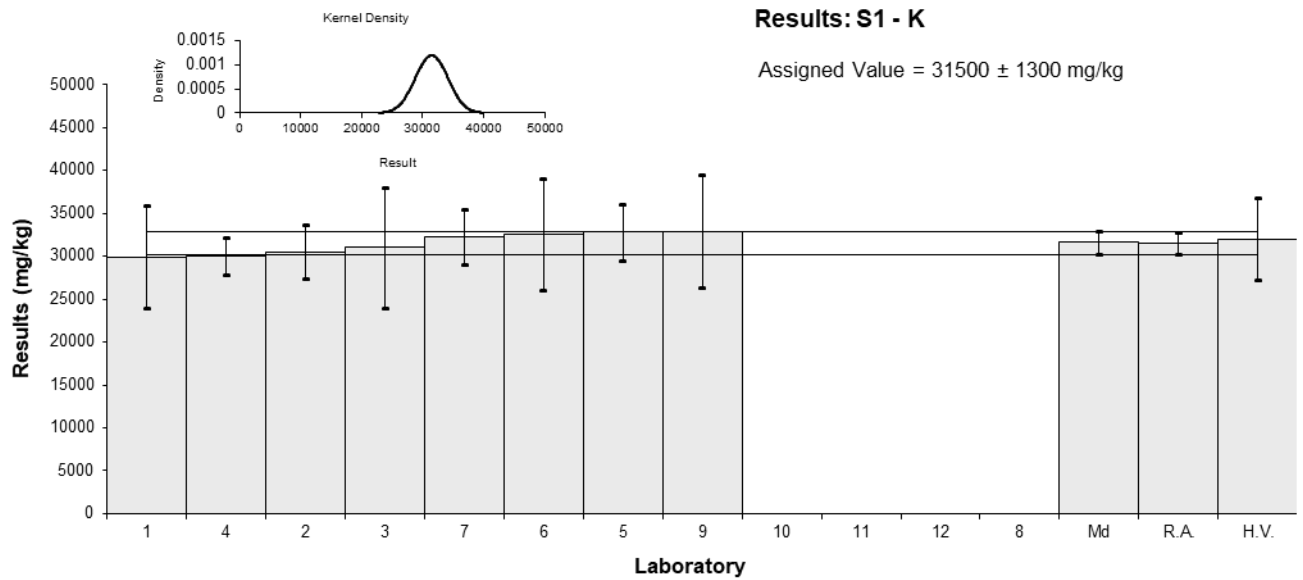
<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	K
<b>Units</b>	mg/kg

**Participant Results**

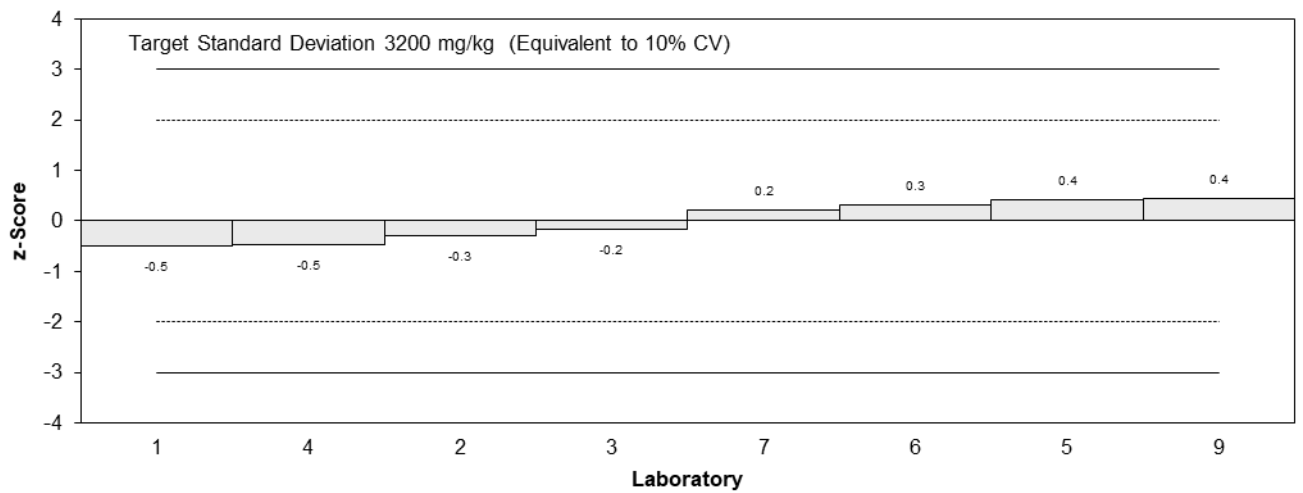
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	29900	5980	-0.51	-0.26
2	30540	3100	-0.30	-0.29
3	31000	7000	-0.16	-0.07
4	30000	2190	-0.48	-0.59
5	32800	3280	0.41	0.37
6	32518	6504	0.32	0.15
7	32200	3220	0.22	0.20
8	NT	NT		
9	32900	6590	0.44	0.21
10	NT	NT		
11	NT	NT		
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	31500	1300
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	32000	4800
<b>Robust Average</b>	31500	1300
<b>Median</b>	31600	1400
<b>Mean</b>	31500	
<b>N</b>	8	
<b>Max.</b>	32900	
<b>Min.</b>	29900	
<b>Robust SD</b>	1400	
<b>Robust CV</b>	4.6%	



**z-Scores: S1 - K**



**En-Scores: S1 - K**

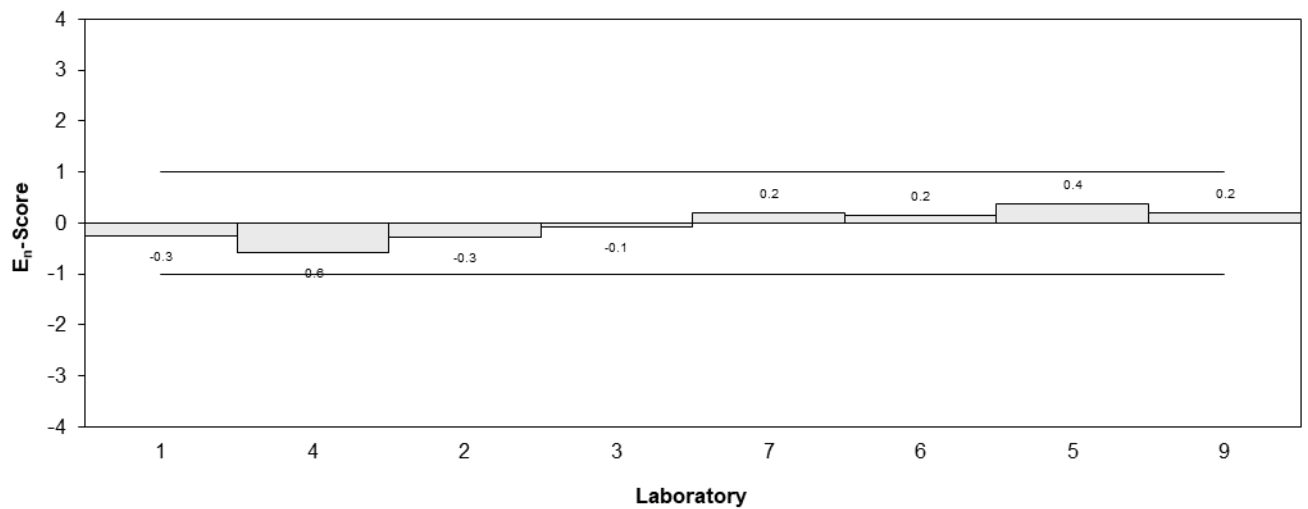


Figure 15

Table 19

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	La
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	1.87	0.37
2	NT	NT
3	NT	NT
4	NT	NT
5	NR	NR
6	0.497	0.099
7	NT	NT
8	NT	NT
9	NT	NT
10	NT	NT
11	NT	NT
12	NT	NT

**Statistics\***

<b>Assigned Value</b>	Not Set	0.36
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	2.42	
<b>Mean</b>	1.18	
<b>N</b>	2	

\*Insufficient data to calculate statistics.

Results: S1 - La

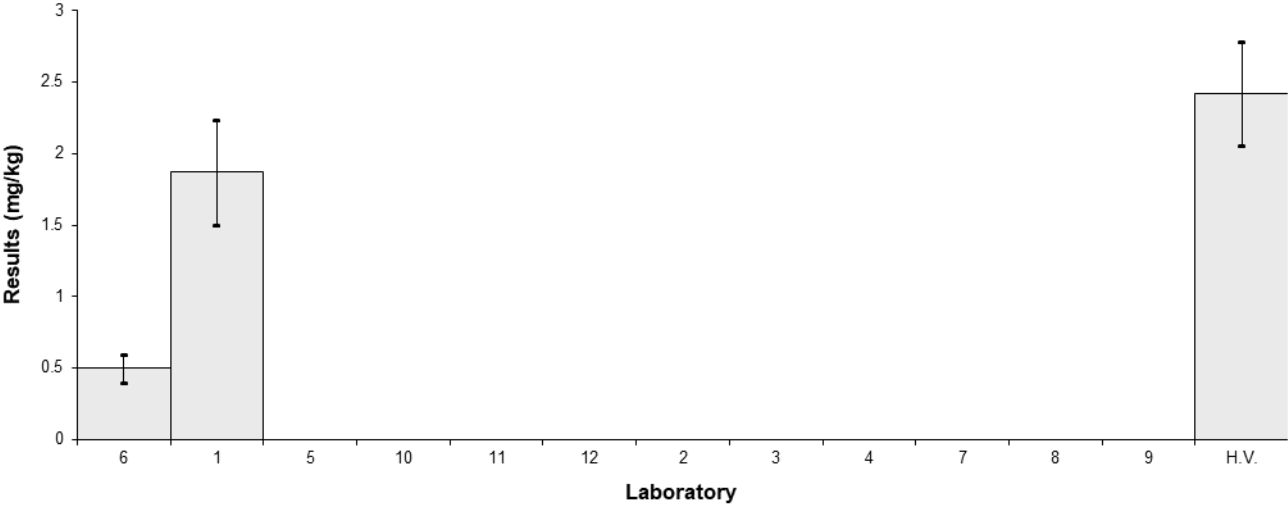


Figure 16

Table 20

**Sample Details**

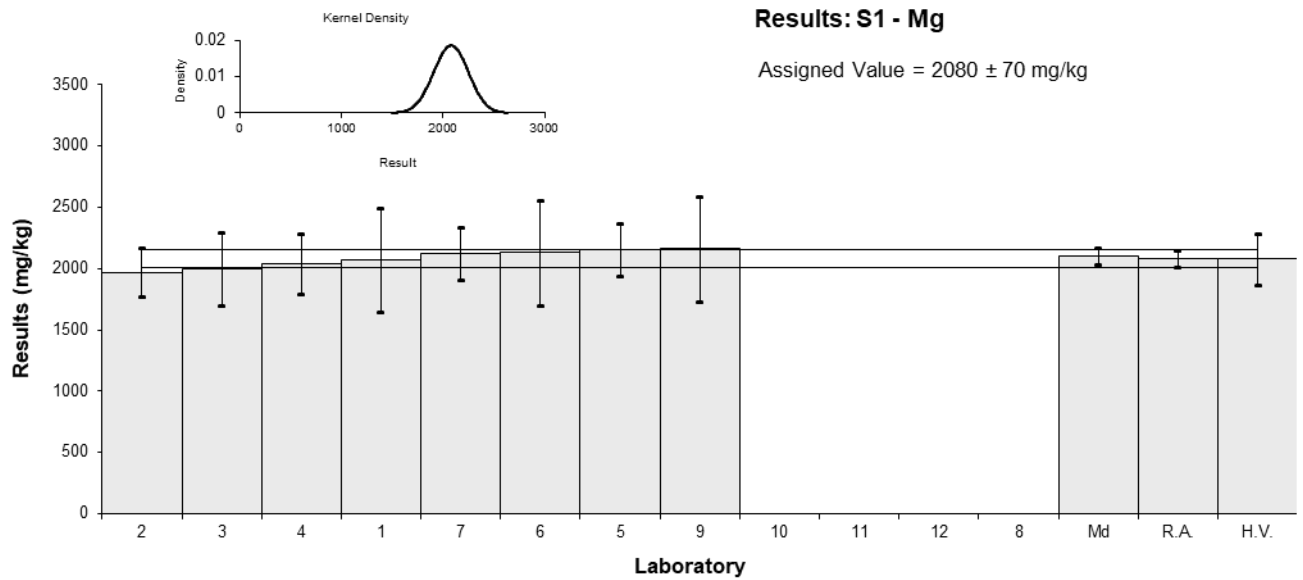
<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Mg
<b>Units</b>	mg/kg

**Participant Results**

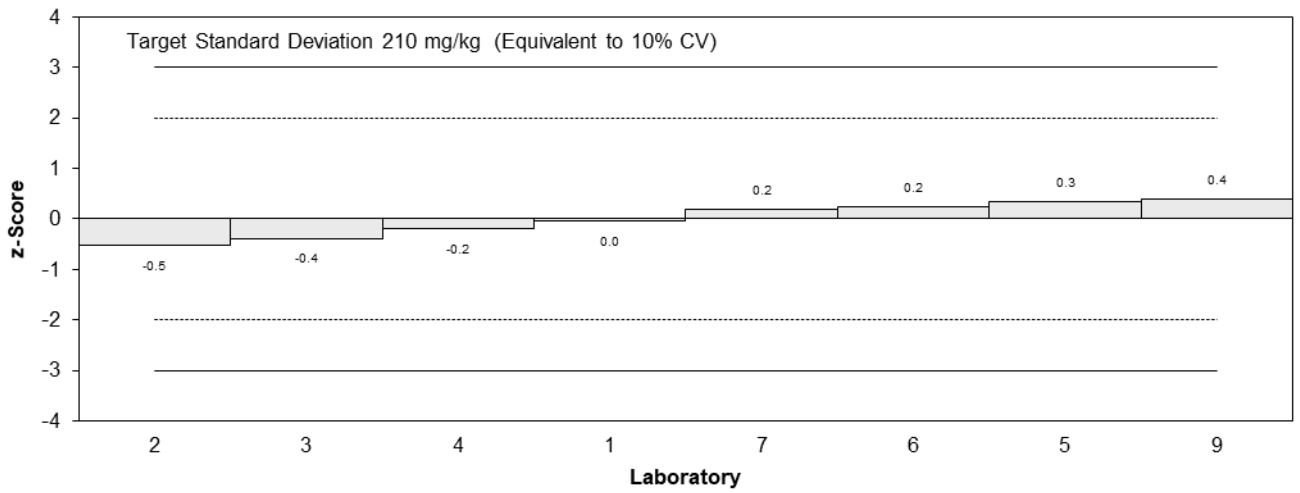
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	2070	420	-0.05	-0.02
2	1970	200	-0.53	-0.52
3	2000	300	-0.38	-0.26
4	2040	245	-0.19	-0.16
5	2150	215	0.34	0.31
6	2130	426	0.24	0.12
7	2120	212	0.19	0.18
8	NT	NT		
9	2160	431	0.38	0.18
10	NT	NT		
11	NT	NT		
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	2080	70
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	2080	210
<b>Robust Average</b>	2080	70
<b>Median</b>	2100	70
<b>Mean</b>	2080	
<b>N</b>	8	
<b>Max.</b>	2160	
<b>Min.</b>	1970	
<b>Robust SD</b>	81	
<b>Robust CV</b>	3.9%	



**z-Scores: S1 - Mg**



**En-Scores: S1 - Mg**

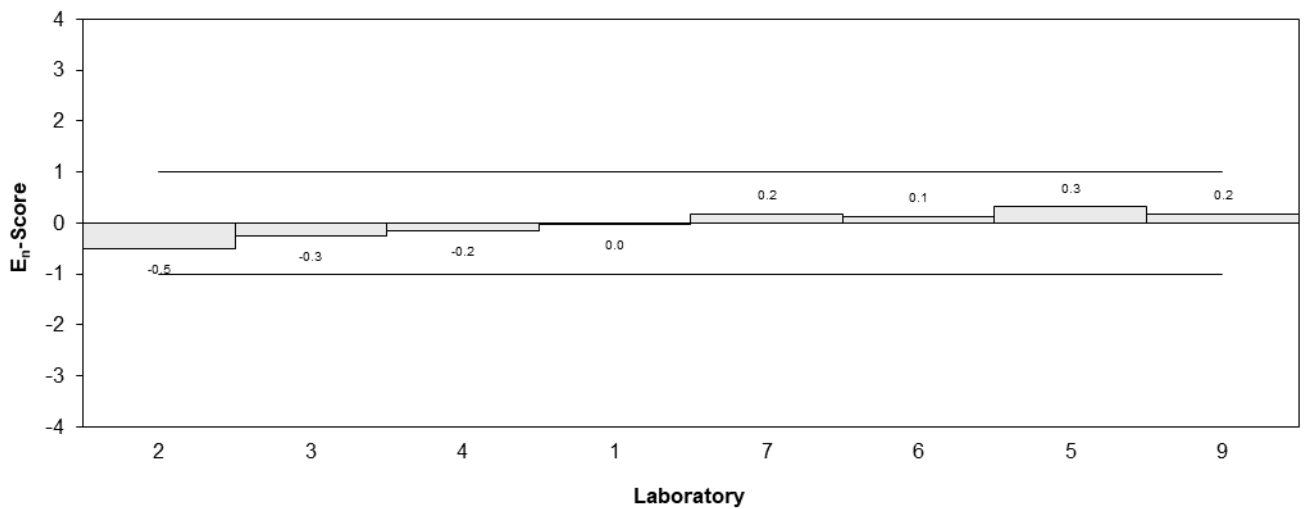


Figure 17

Table 21

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Mn
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	160	32	0.32	0.16
2	151	15	-0.26	-0.26
3	150	30	-0.32	-0.17
4	150	20	-0.32	-0.25
5	161	16	0.39	0.36
6	153	30.61	-0.13	-0.06
7	158	15.8	0.19	0.18
8	NT	NT		
9	159	31.7	0.26	0.13
10	151	38	-0.26	-0.10
11	NT	NT		
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	155	4
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	159	16
<b>Robust Average</b>	155	4
<b>Median</b>	153	3
<b>Mean</b>	155	
<b>N</b>	9	
<b>Max.</b>	161	
<b>Min.</b>	150	
<b>Robust SD</b>	5.3	
<b>Robust CV</b>	3.4%	

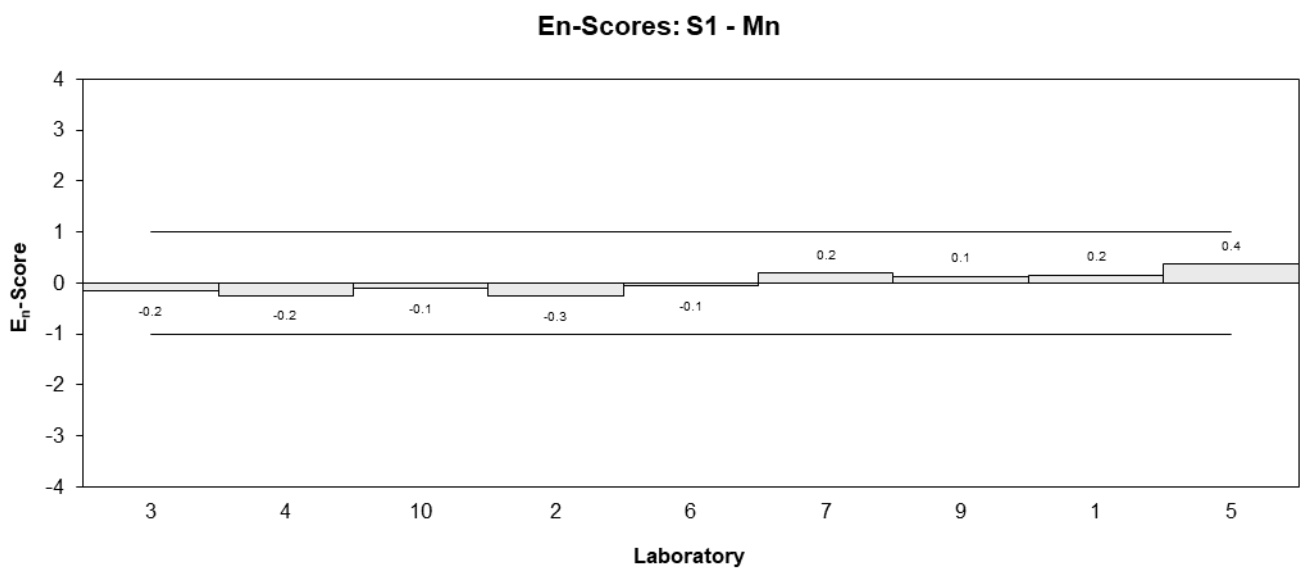
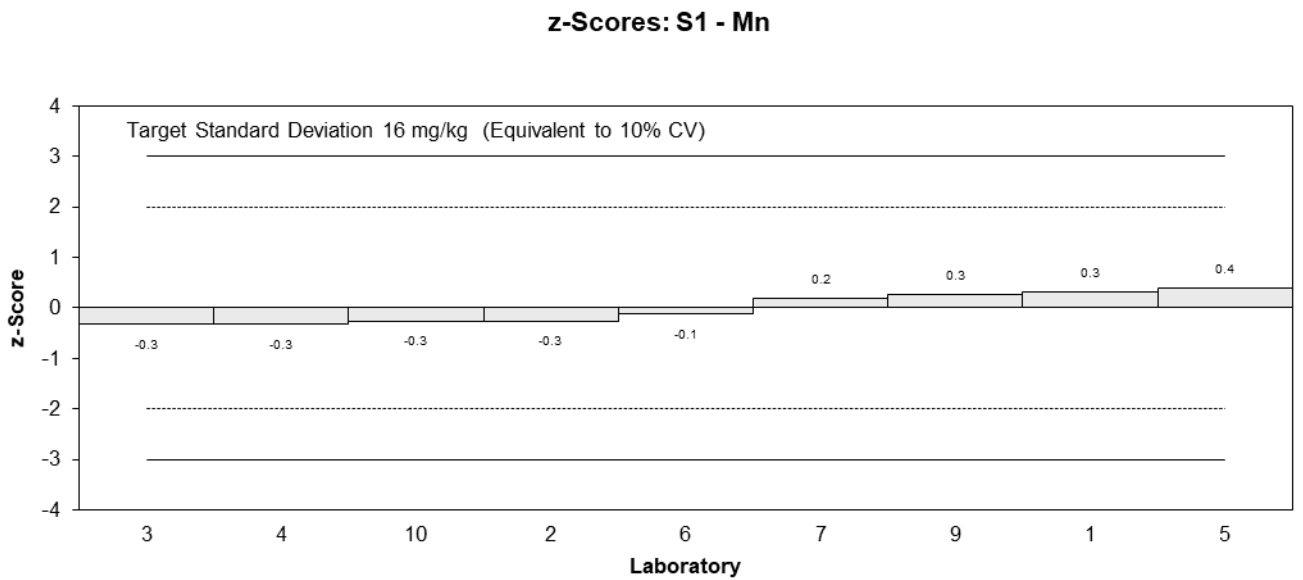
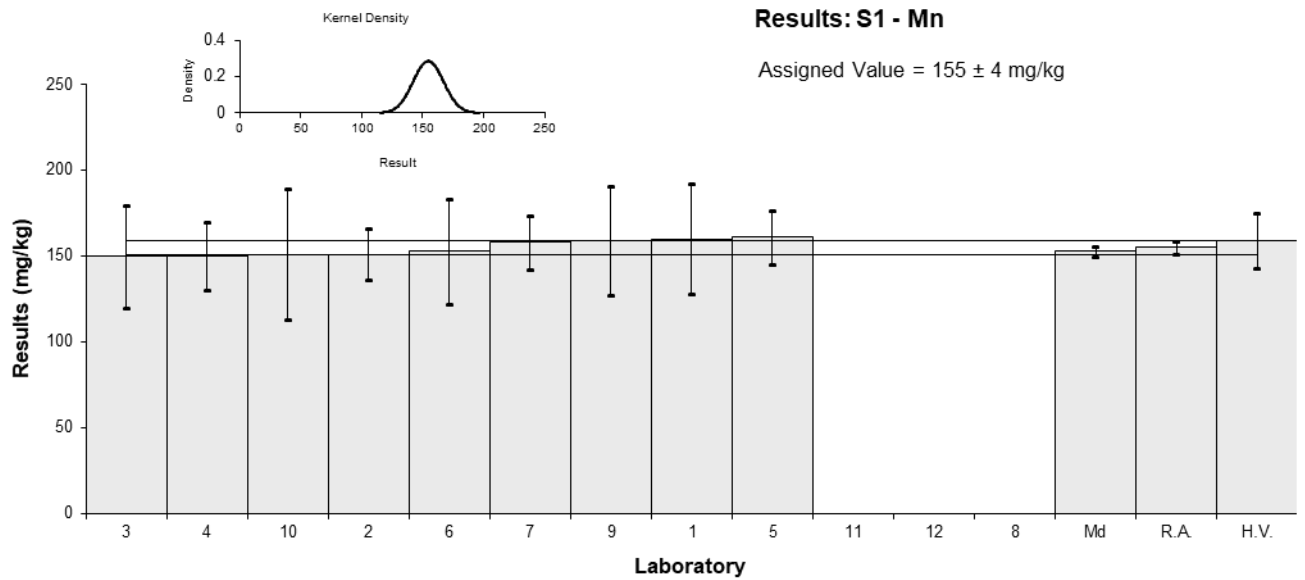


Figure 18



Table 22

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Mo
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.48	0.10	-0.06	-0.03
2	0.55	0.08	1.39	0.70
3	0.41	0.09	-1.51	-0.70
4	0.42	0.04	-1.30	-0.95
5	0.45	0.04	-0.68	-0.50
6	0.51	0.102	0.56	0.23
7	NT	NT		
8	NT	NT		
9	0.503	0.101	0.41	0.18
10	<1	NR		
11	0.54	0.169	1.18	0.32
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	0.483	0.053
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.417	0.063
<b>Robust Average</b>	0.483	0.053
<b>Median</b>	0.492	0.056
<b>Mean</b>	0.483	
<b>N</b>	8	
<b>Max.</b>	0.55	
<b>Min.</b>	0.41	
<b>Robust SD</b>	0.059	
<b>Robust CV</b>	12%	

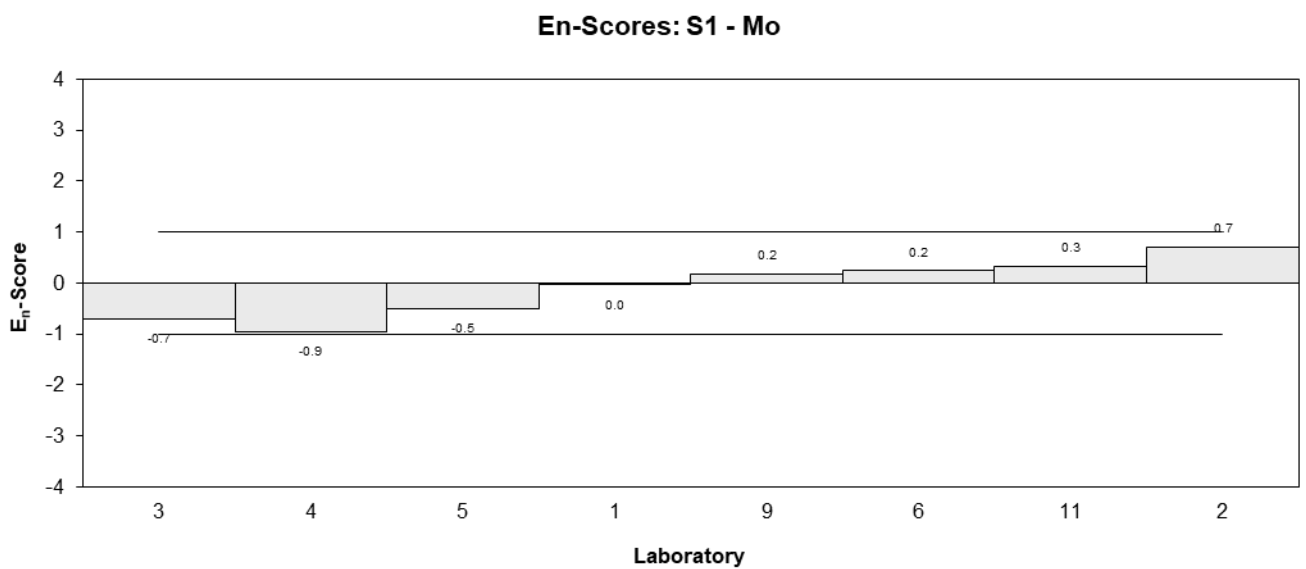
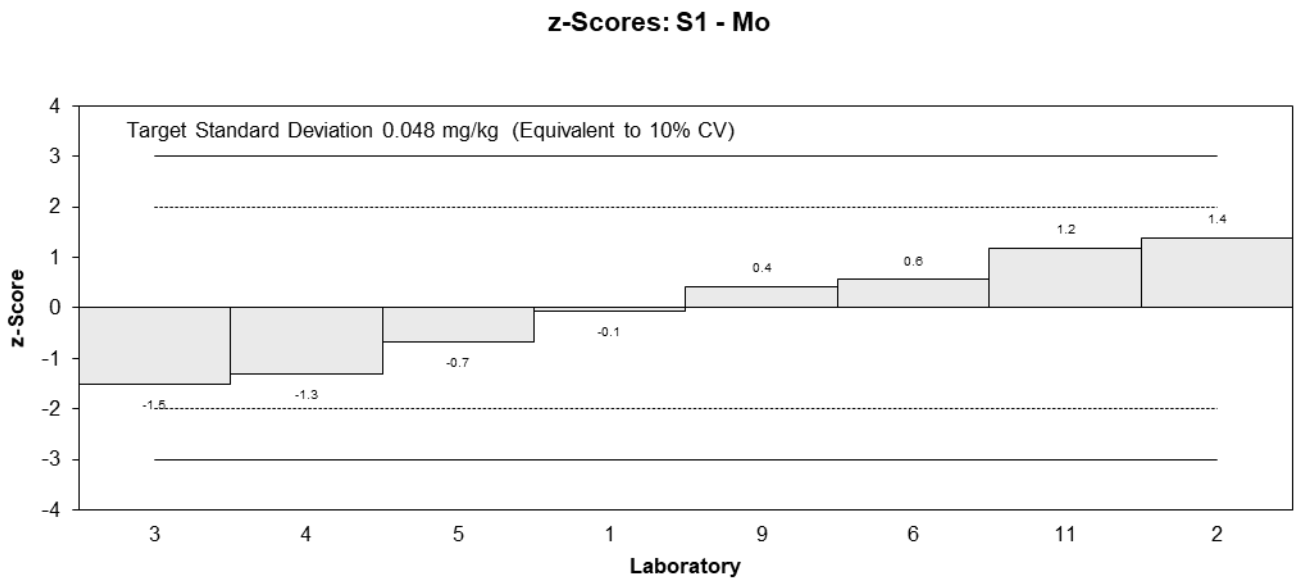
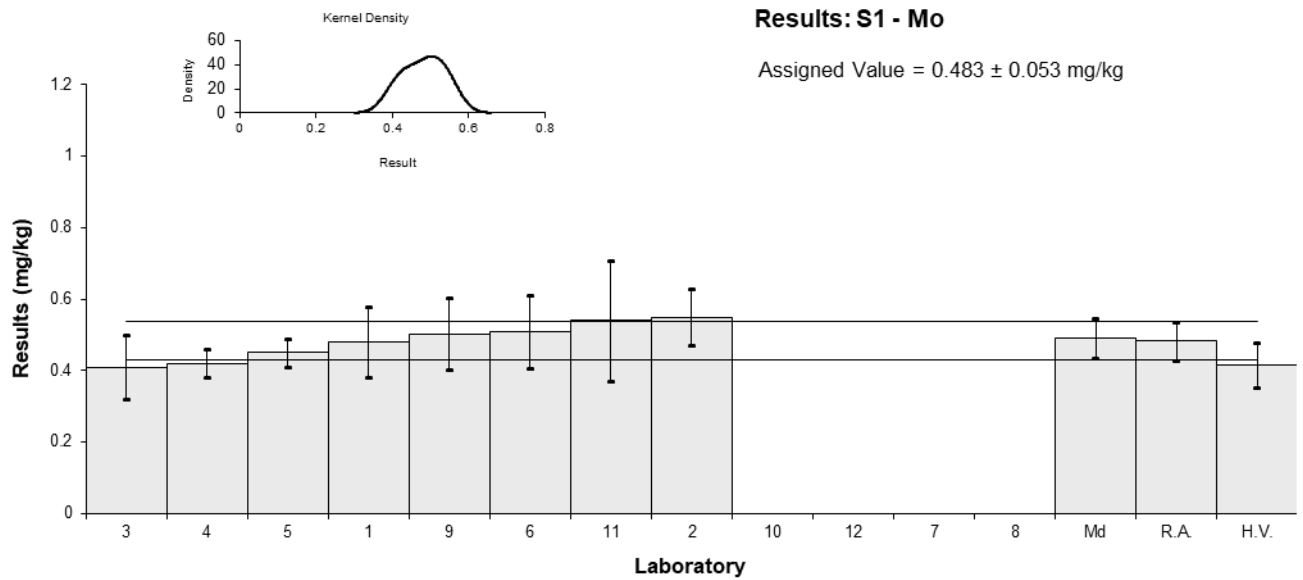


Figure 19

Table 23

**Sample Details**

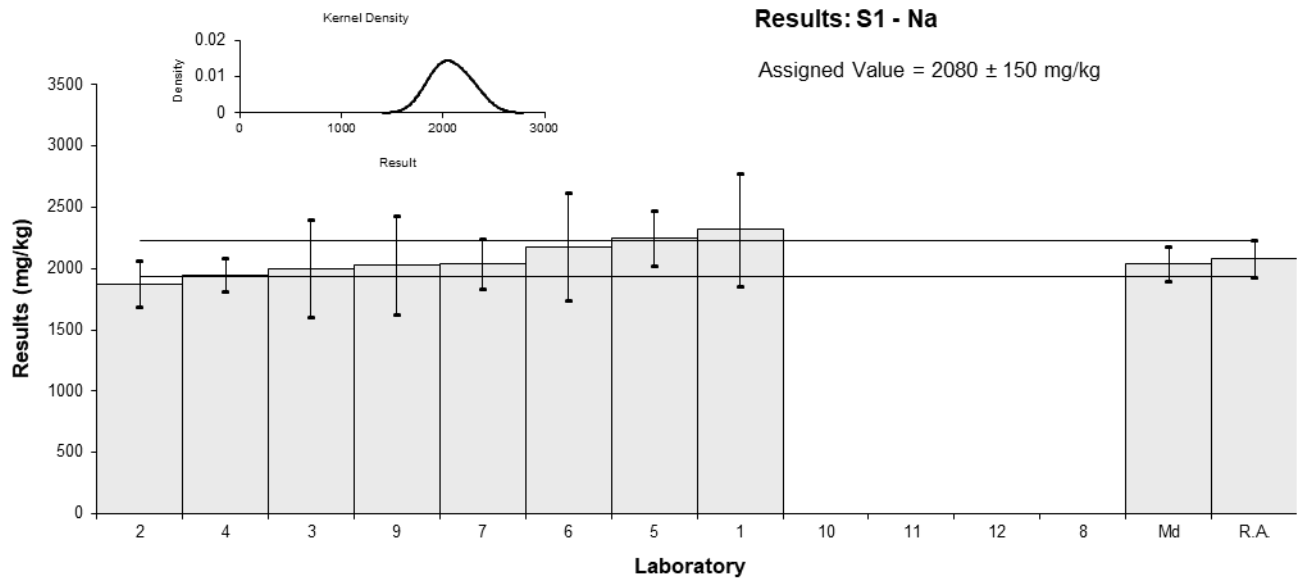
<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Na
<b>Units</b>	mg/kg

**Participant Results**

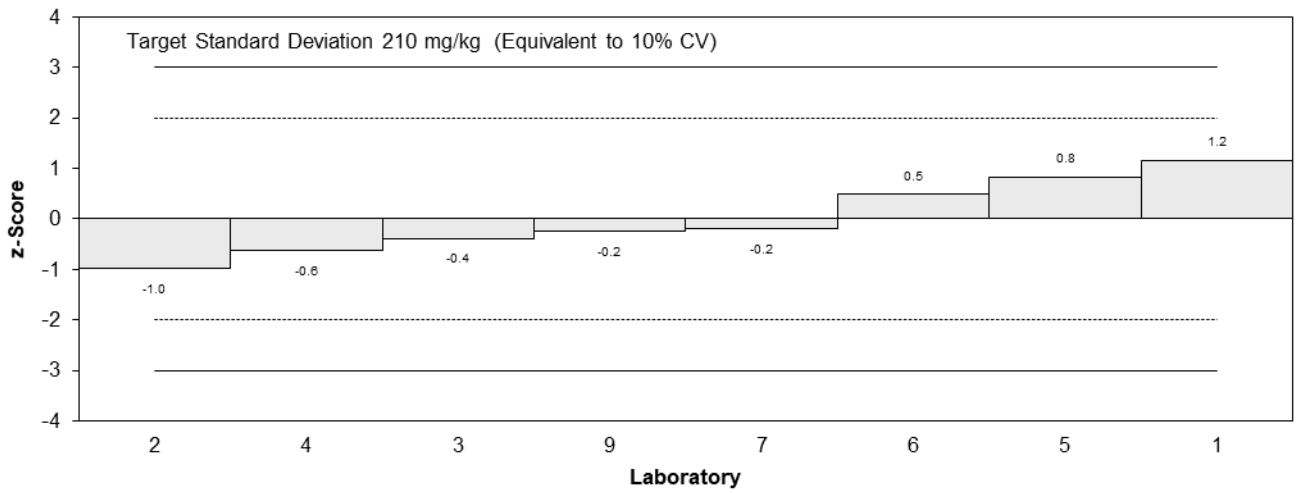
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	2320	460	1.15	0.50
2	1875	190	-0.99	-0.85
3	2000	400	-0.38	-0.19
4	1950	140	-0.62	-0.63
5	2250	225	0.82	0.63
6	2180	436	0.48	0.22
7	2040	204	-0.19	-0.16
8	NT	NT		
9	2030	405	-0.24	-0.12
10	NT	NT		
11	NT	NT		
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	2080	150
<b>Spike</b>	Not Spiked	
<b>Robust Average</b>	2080	150
<b>Median</b>	2040	140
<b>Mean</b>	2080	
<b>N</b>	8	
<b>Max.</b>	2320	
<b>Min.</b>	1875	
<b>Robust SD</b>	170	
<b>Robust CV</b>	8.4%	



**z-Scores: S1 - Na**



**En-Scores: S1 - Na**

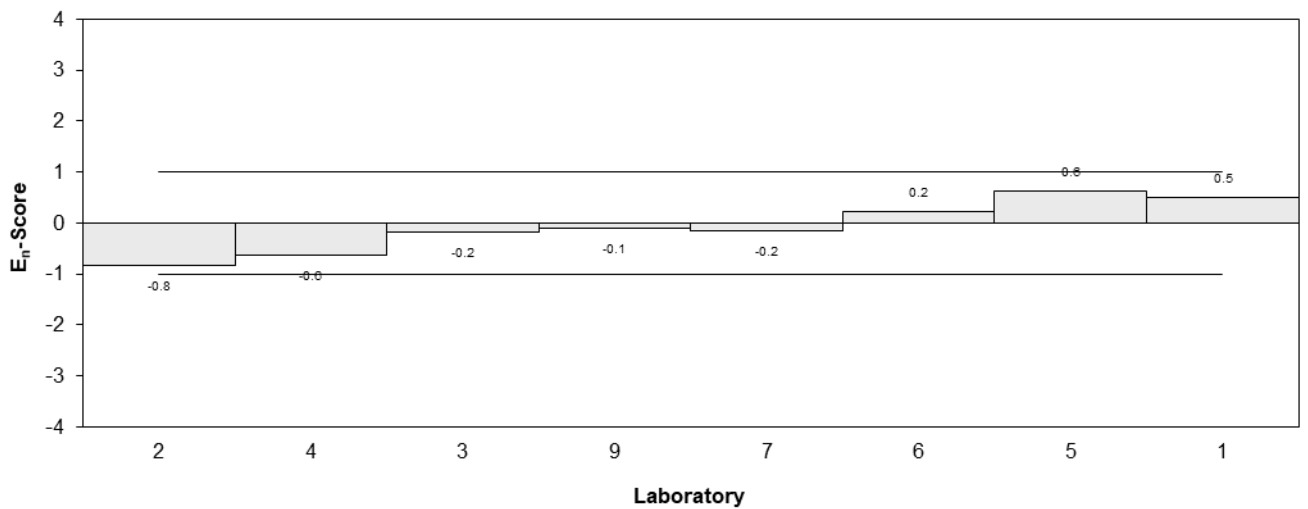


Figure 20

Table 24

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Ni
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	3.33	0.67	-1.76	-2.27
2	2.91	0.4	-2.17	-3.80
3	3.4	0.7	-1.69	-2.12
4	4.7	1.1	-0.43	-0.37
5	4.6	0.5	-0.53	-0.82
6	1.26	0.252	-3.77	-7.78
7	3.46	0.346	-1.63	-3.04
8	NT	NT		
9	NT	NT		
10	4.3	1.1	-0.82	-0.71
11	NT	NT		
12	NT	NT		

**Statistics**

<b>Assigned Value*</b>	5.14	0.43
<b>Spike</b>	Not Spiked	
<b>Reference Value*</b>	5.14	0.43
<b>Robust Average</b>	3.59	0.91
<b>Median</b>	3.43	0.86
<b>Mean</b>	3.50	
<b>N</b>	8	
<b>Max.</b>	4.7	
<b>Min.</b>	1.26	
<b>Robust SD</b>	1.0	
<b>Robust CV</b>	29%	

\*Reference Value by IDMS

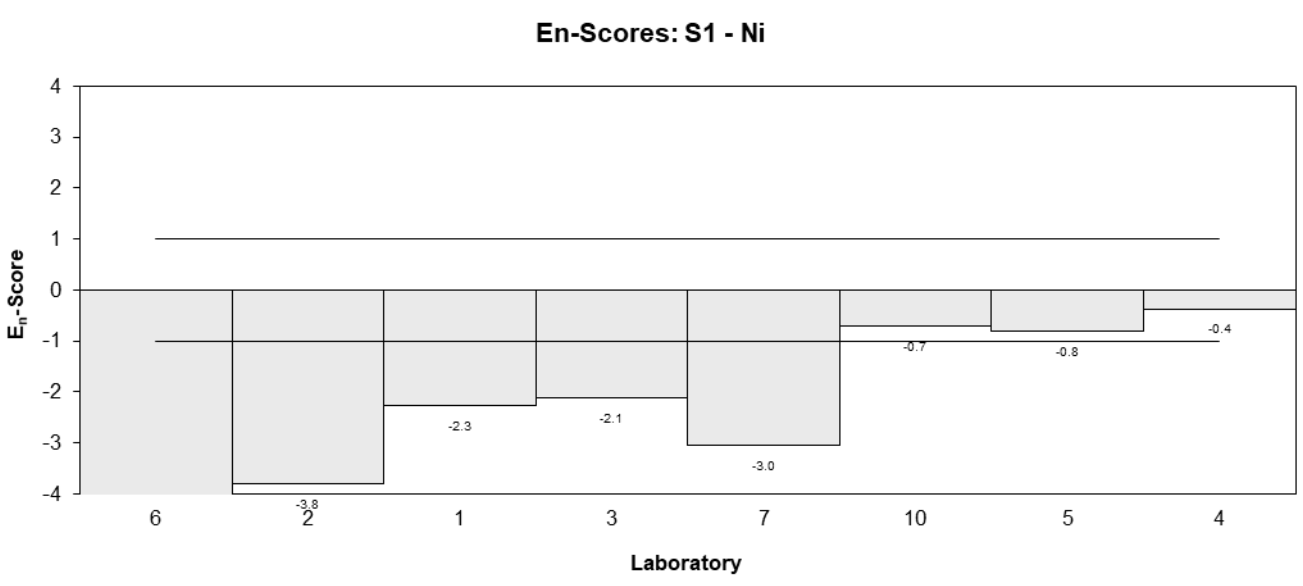
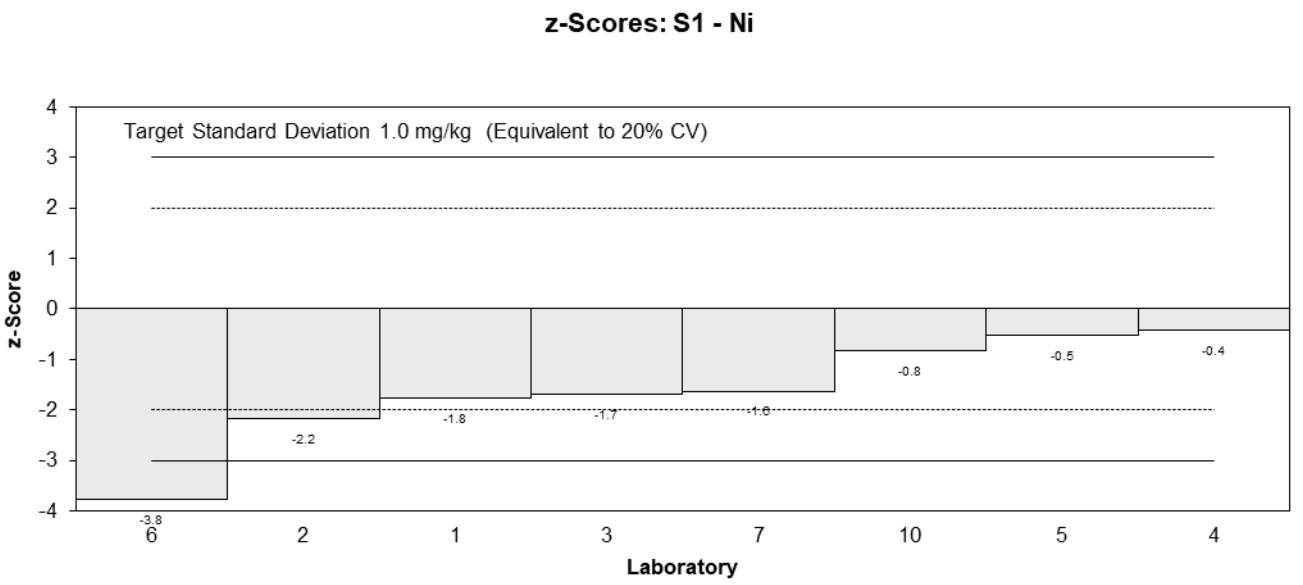
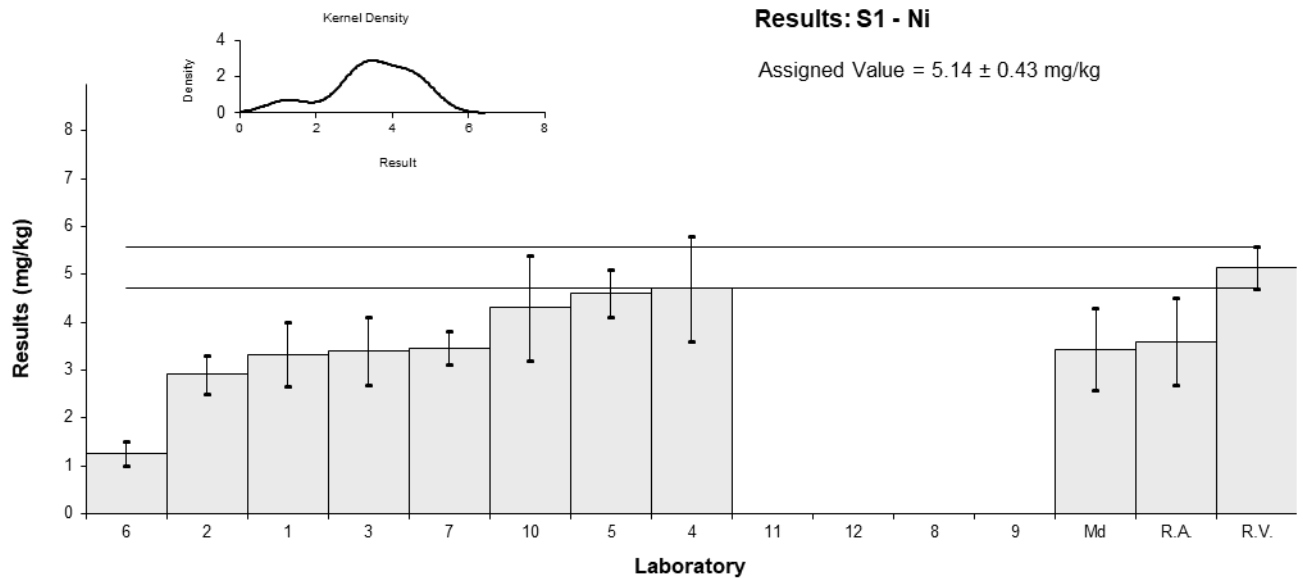


Figure 21

Table 25

**Sample Details**

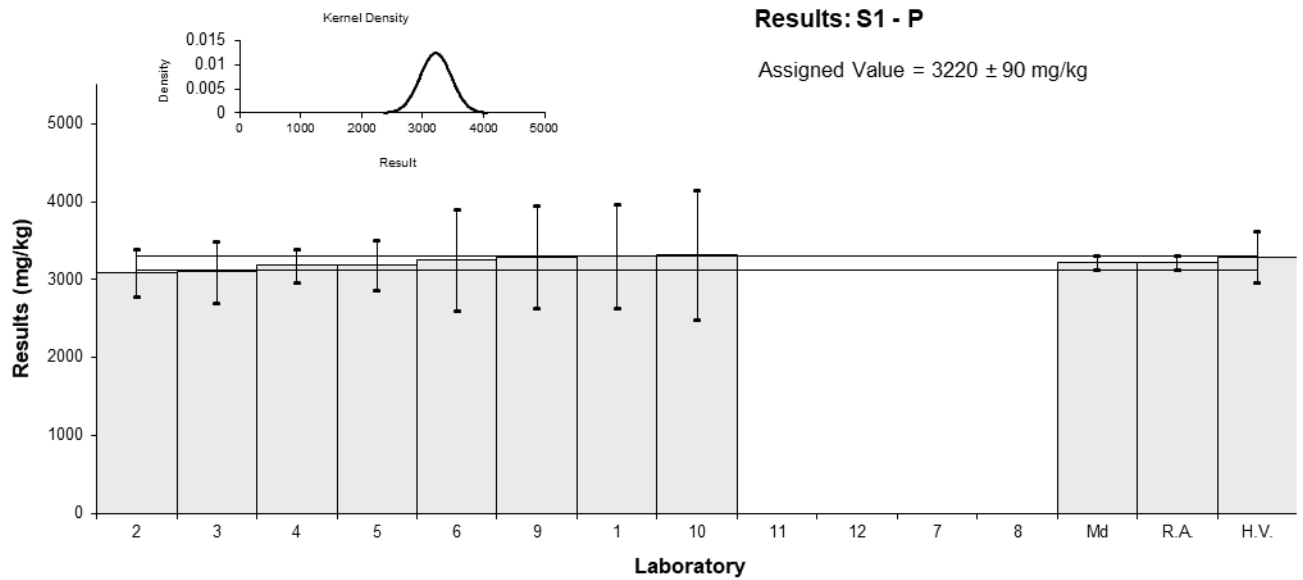
<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	P
<b>Units</b>	mg/kg

**Participant Results**

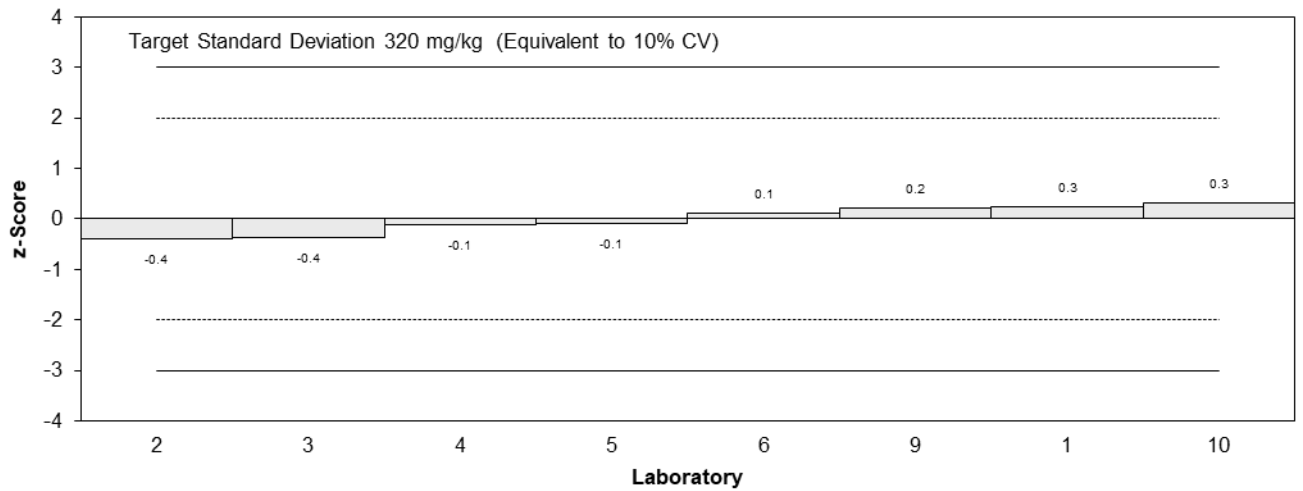
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	3301	660	0.25	0.12
2	3090	310	-0.40	-0.40
3	3100	400	-0.37	-0.29
4	3180	220	-0.12	-0.17
5	3190	319	-0.09	-0.09
6	3256	651	0.11	0.05
7	NT	NT		
8	NT	NT		
9	3290	657	0.22	0.11
10	3320	830	0.31	0.12
11	NT	NT		
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	3220	90
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	3290	330
<b>Robust Average</b>	3220	90
<b>Median</b>	3220	90
<b>Mean</b>	3220	
<b>N</b>	8	
<b>Max.</b>	3320	
<b>Min.</b>	3090	
<b>Robust SD</b>	100	
<b>Robust CV</b>	3.2%	



**z-Scores: S1 - P**



**En-Scores: S1 - P**

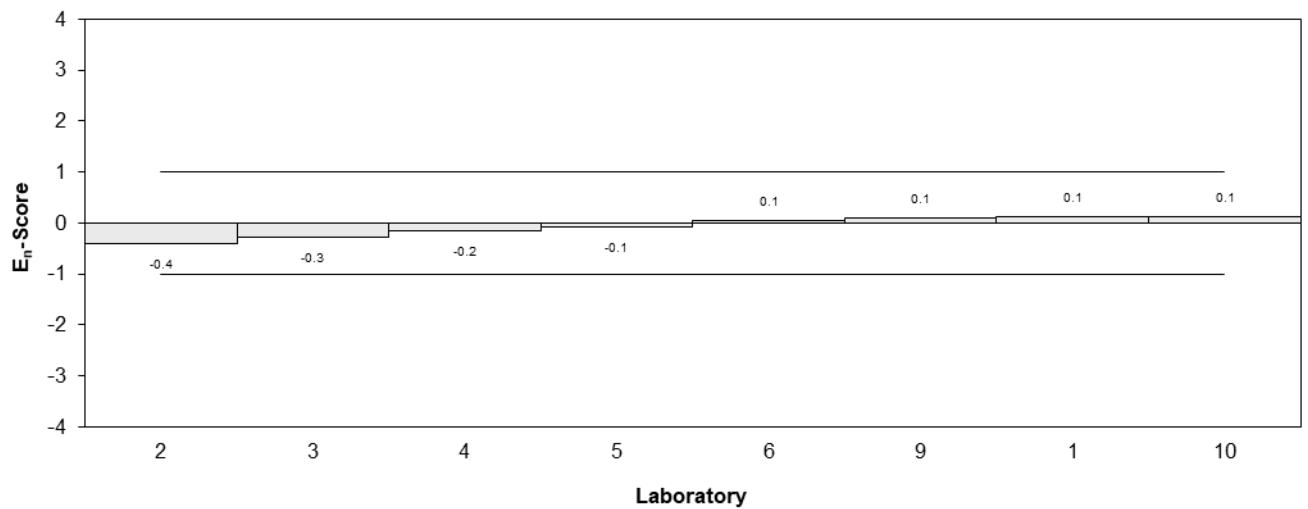


Figure 22



Table 26

**Sample Details**

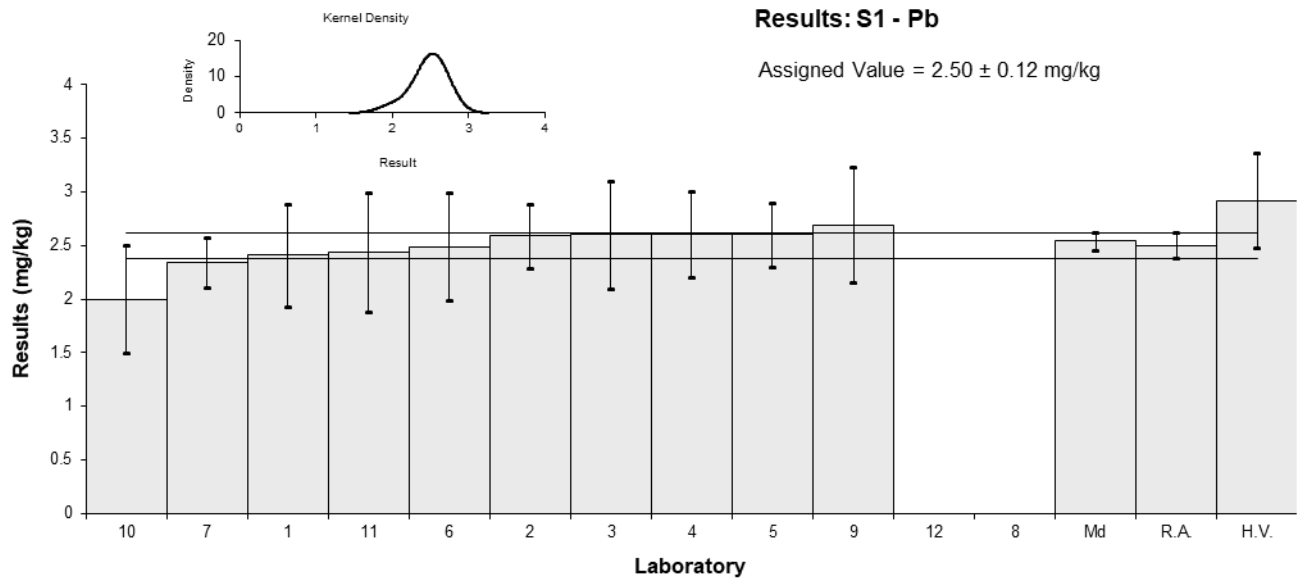
<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Pb
<b>Units</b>	mg/kg

**Participant Results**

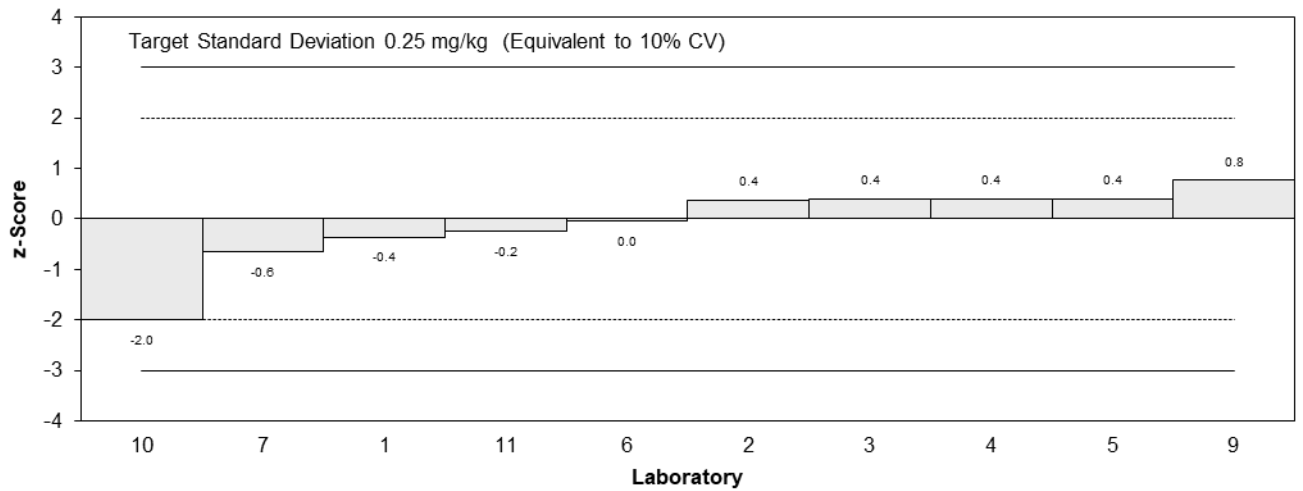
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	2.41	0.48	-0.36	-0.18
2	2.59	0.3	0.36	0.28
3	2.6	0.5	0.40	0.19
4	2.6	0.4	0.40	0.24
5	2.6	0.3	0.40	0.31
6	2.49	0.498	-0.04	-0.02
7	2.34	0.234	-0.64	-0.61
8	NT	NT		
9	2.69	0.539	0.76	0.34
10	2	0.5	-2.00	-0.97
11	2.44	0.558	-0.24	-0.11
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	2.50	0.12
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	2.92	0.44
<b>Robust Average</b>	2.50	0.12
<b>Median</b>	2.54	0.08
<b>Mean</b>	2.48	
<b>N</b>	10	
<b>Max.</b>	2.69	
<b>Min.</b>	2	
<b>Robust SD</b>	0.15	
<b>Robust CV</b>	6.1%	



**z-Scores: S1 - Pb**



**En-Scores: S1 - Pb**

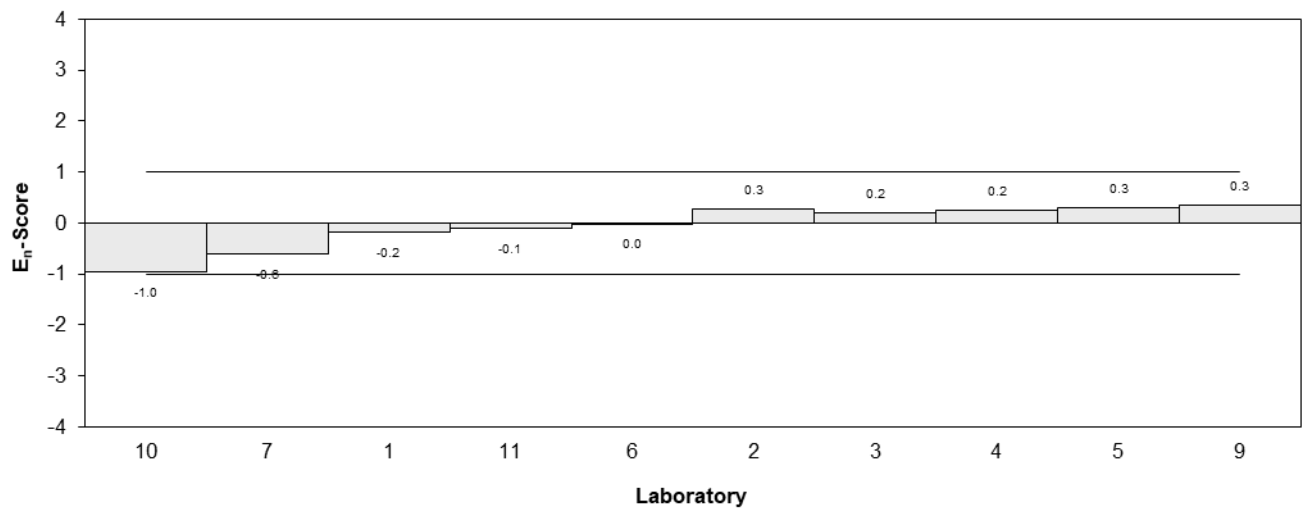


Figure 23

Table 27

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Rb
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	54.5	10.9
2	NT	NT
3	NT	NT
4	NT	NT
5	NR	NR
6	29.56	5.91
7	NT	NT
8	NT	NT
9	NT	NT
10	NT	NT
11	NT	NT
12	NT	NT

**Statistics\***

<b>Assigned Value</b>	Not Set	6.1
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	40.4	
<b>Mean</b>	42.0	
<b>N</b>	2	

\*Insufficient data to calculate statistics.

Results: S1 - Rb

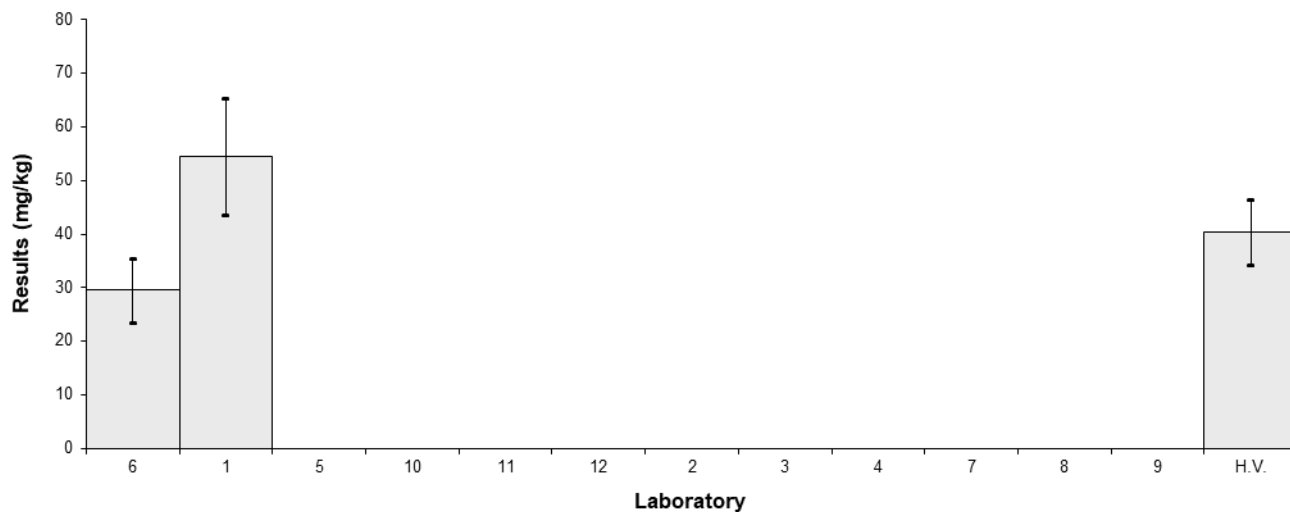


Figure 24

Table 28

**Sample Details**

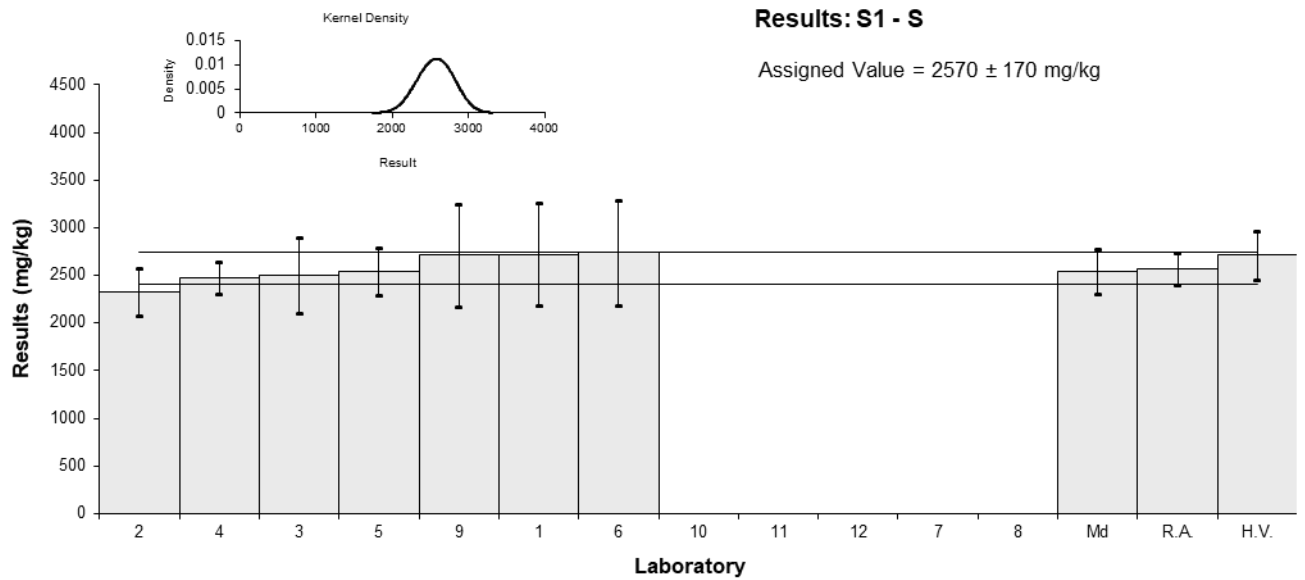
<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	S
<b>Units</b>	mg/kg

**Participant Results**

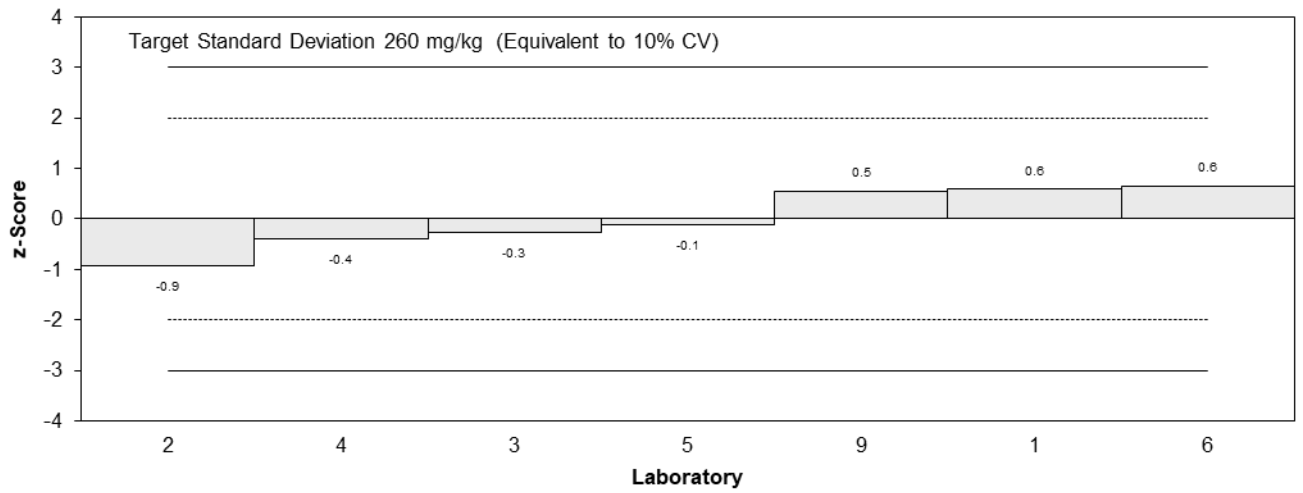
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	2720	540	0.58	0.26
2	2330	250	-0.93	-0.79
3	2500	400	-0.27	-0.16
4	2470	170	-0.39	-0.42
5	2540	254	-0.12	-0.10
6	2737	547	0.65	0.29
7	NT	NT		
8	NT	NT		
9	2710	541	0.54	0.25
10	NT	NT		
11	NT	NT		
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	2570	170
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	2710	250
<b>Robust Average</b>	2570	170
<b>Median</b>	2540	230
<b>Mean</b>	2570	
<b>N</b>	7	
<b>Max.</b>	2737	
<b>Min.</b>	2330	
<b>Robust SD</b>	180	
<b>Robust CV</b>	6.8%	



**z-Scores: S1 - S**



**En-Scores: S1 - S**

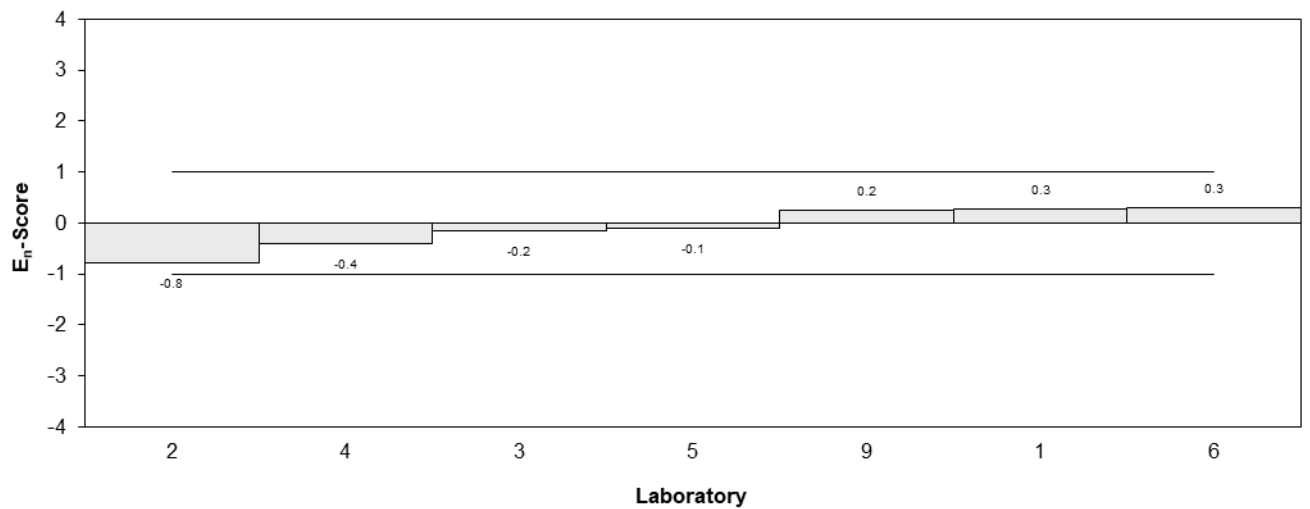


Figure 25

Table 29

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Se
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.196	0.040	-0.50	-0.35
2	0.16	0.04	-1.33	-0.92
3	0.26	0.08	0.96	0.45
4	0.20	0.03	-0.41	-0.31
5	0.27	0.03	1.19	0.91
6	0.175	0.035	-0.99	-0.71
7	0.263	0.026	1.03	0.81
8	NT	NT		
9	<1	NR		
10	<5	NR		
11	NT	NT		
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	0.218	0.049
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.217	0.033
<b>Robust Average</b>	0.218	0.049
<b>Median</b>	0.200	0.055
<b>Mean</b>	0.218	
<b>N</b>	7	
<b>Max.</b>	0.27	
<b>Min.</b>	0.16	
<b>Robust SD</b>	0.052	
<b>Robust CV</b>	24%	

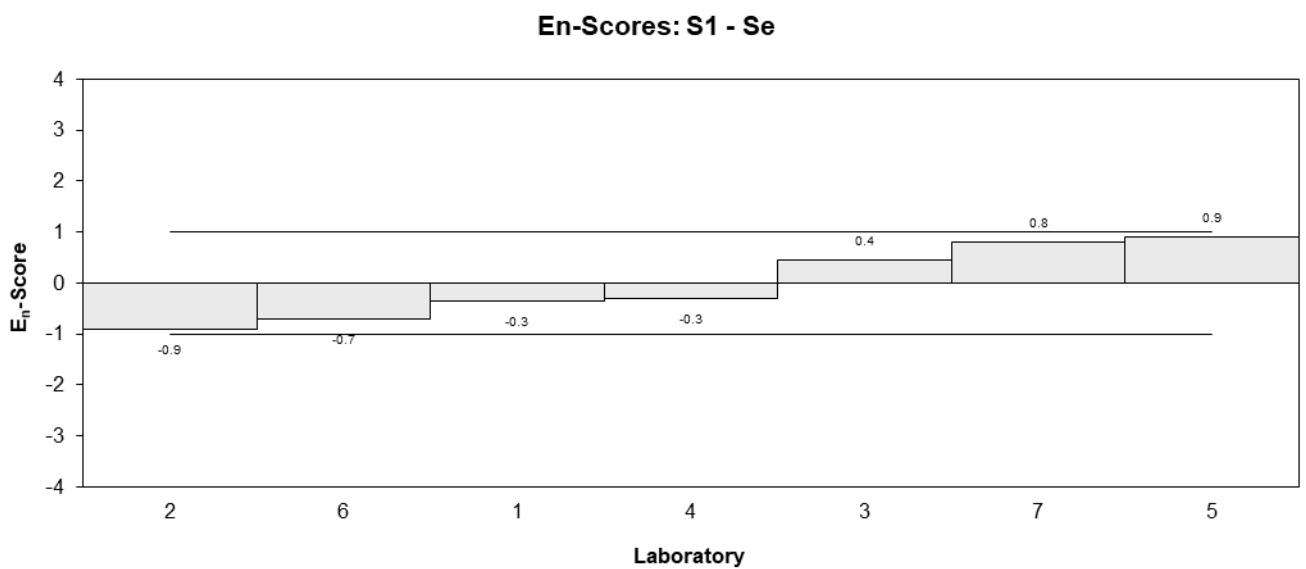
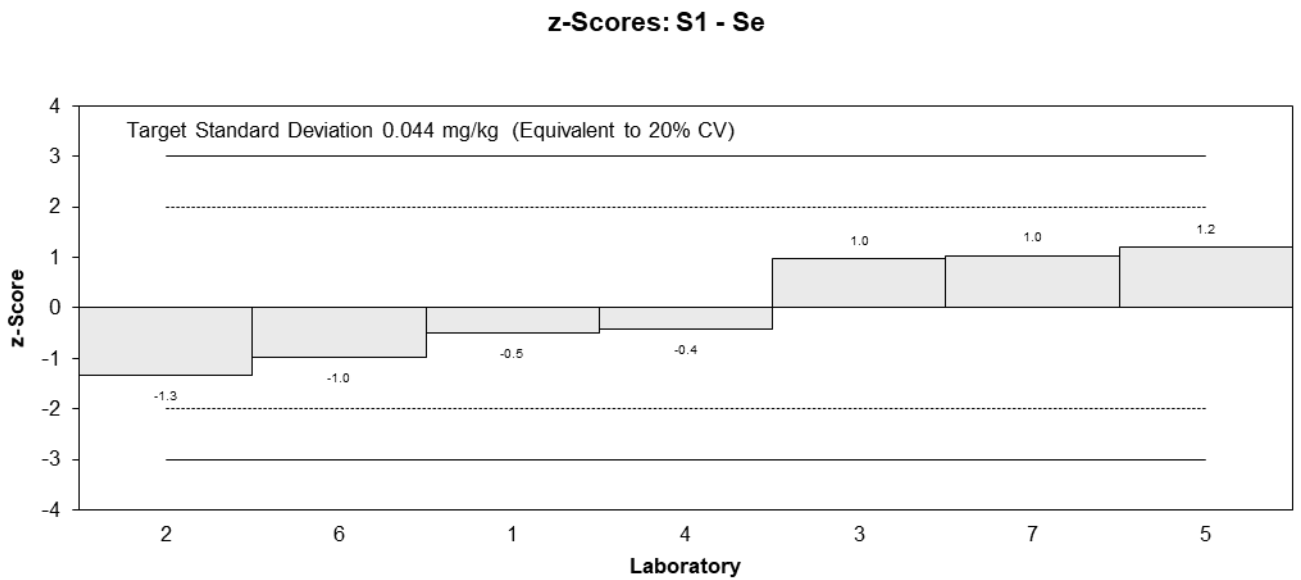
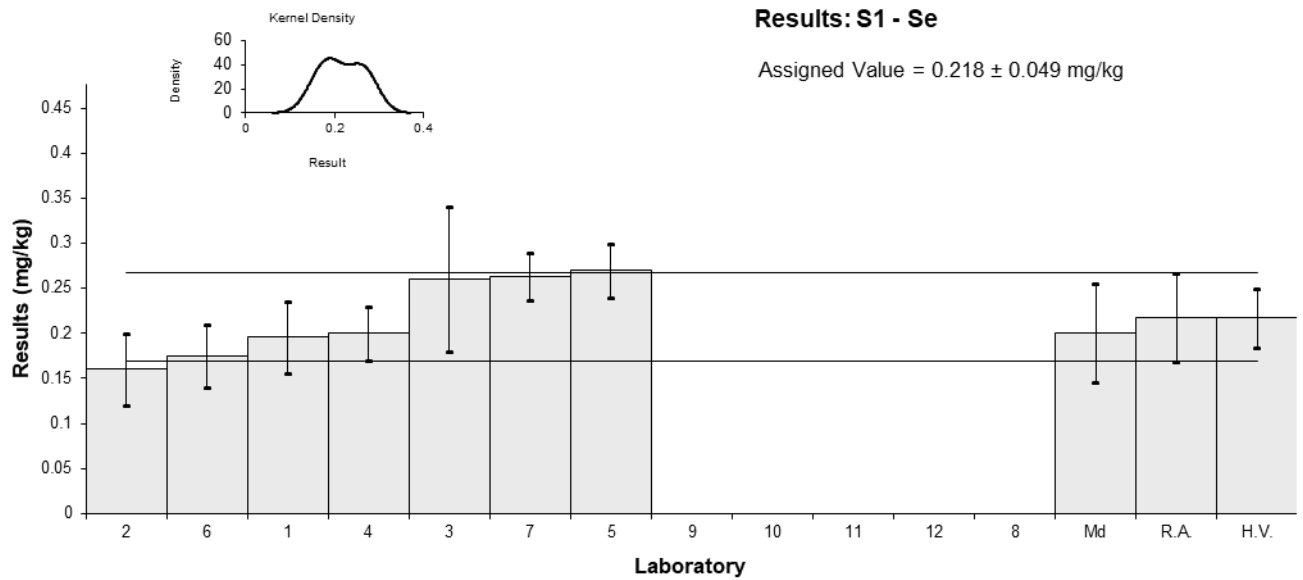


Figure 26



Table 30

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Sn
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	0.246	0.050
2	0.27	0.05
3	NT	NT
4	<1.0	1.0
5	NR	NR
6	0.394	0.079
7	NT	NT
8	NT	NT
9	NT	NT
10	NT	NT
11	0.27	0.057
12	NT	NT

**Statistics**

<b>Assigned Value</b>	Not Set	
<b>Spike</b>	Not Spiked	
<b>Information Value*</b>	0.342	0.044
<b>Robust Average</b>	0.295	0.095
<b>Median</b>	0.270	0.028
<b>Mean</b>	0.295	
<b>N</b>	4	
<b>Max.</b>	0.394	
<b>Min.</b>	0.246	
<b>Robust SD</b>	0.076	
<b>Robust CV</b>	26%	

\*Information Value by IDMS.

Results: S1 - Sn

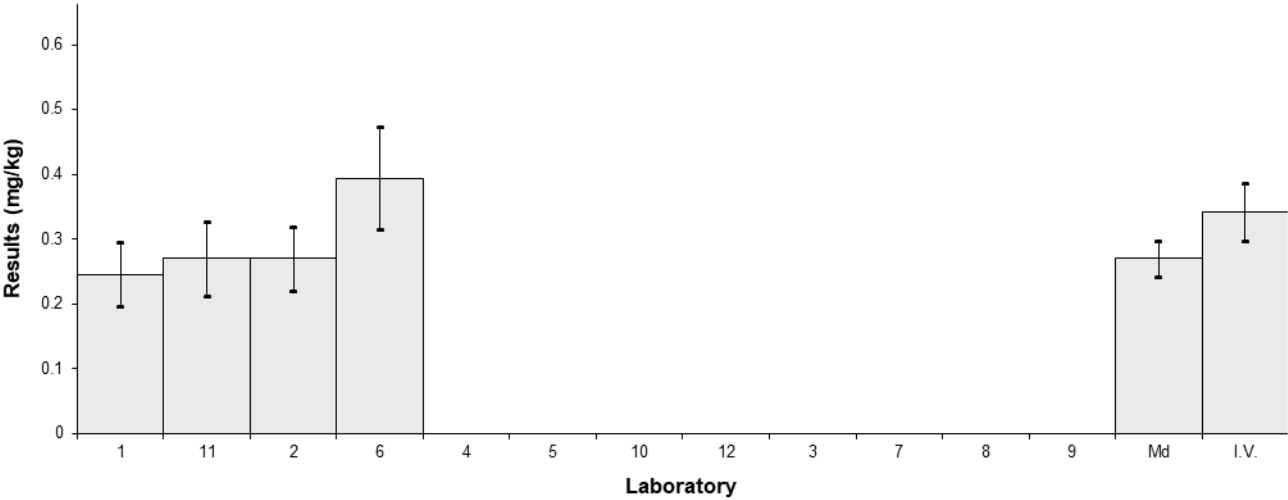


Figure 27

Table 31

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	TI
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	0.026	0.01
2	<0.1	NR
3	0.029	0.009
4	NT	NT
5	NR	NR
6	0.023	0.005
7	0.022	0.002
8	NT	NT
9	NT	NT
10	<10	NR
11	NT	NT
12	NT	NT

**Statistics\***

<b>Assigned Value</b>	Not Set	
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.0393	0.0059
<b>Median</b>	0.0245	0.0047
<b>Mean</b>	0.0250	
<b>N</b>	4	
<b>Max.</b>	0.029	
<b>Min.</b>	0.022	

\*Insufficient data to calculate statistics.

Results: S1 - TI

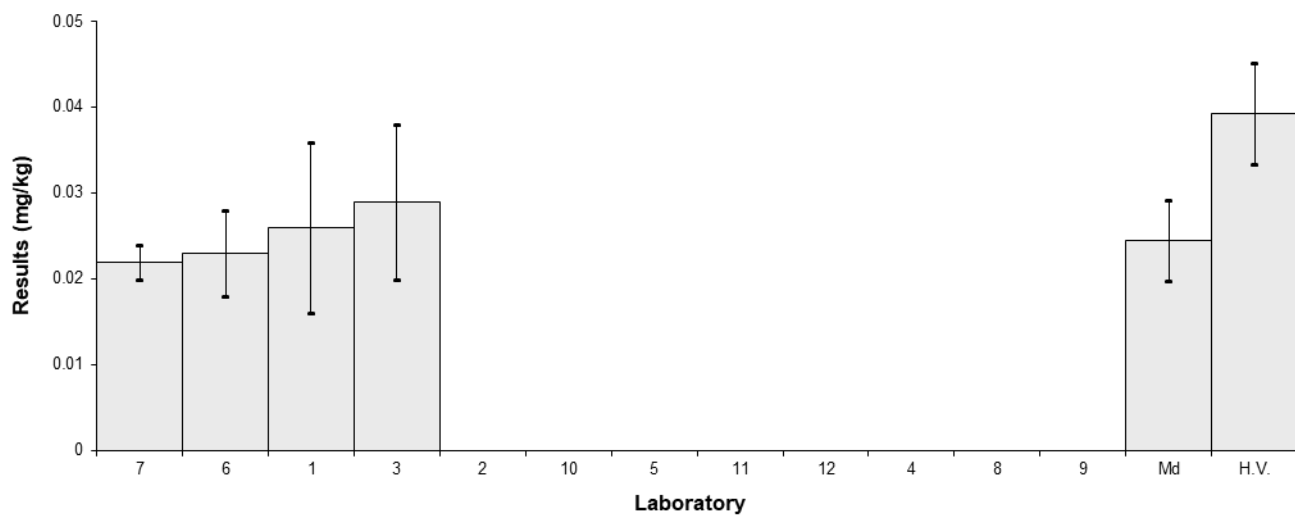


Figure 28

Table 32

**Sample Details**

<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	U
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	0.158	0.032
2	0.18	0.04
3	0.17	0.04
4	NT	NT
5	NR	NR
6	0.172	0.034
7	NT	NT
8	NT	NT
9	NT	NT
10	NT	NT
11	NT	NT
12	NT	NT

**Statistics\***

<b>Assigned Value</b>	Not Set	
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.230	0.046
<b>Median</b>	0.171	0.012
<b>Mean</b>	0.170	
<b>N</b>	4	
<b>Max.</b>	0.18	
<b>Min.</b>	0.158	

\*Insufficient data to calculate statistics.

Results: S1 - U

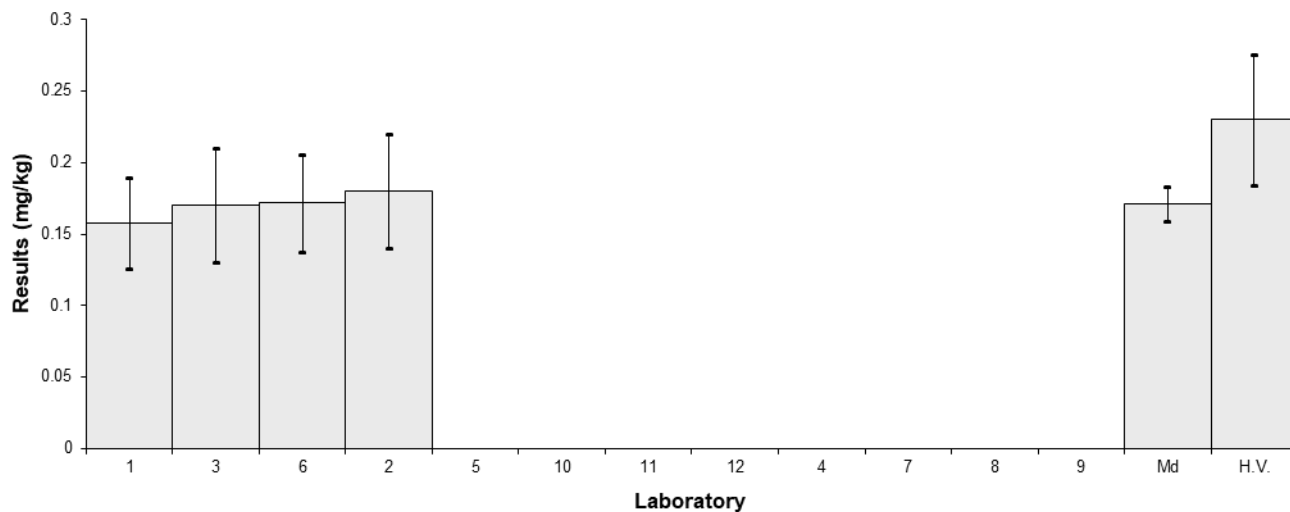


Figure 29

Table 33

**Sample Details**

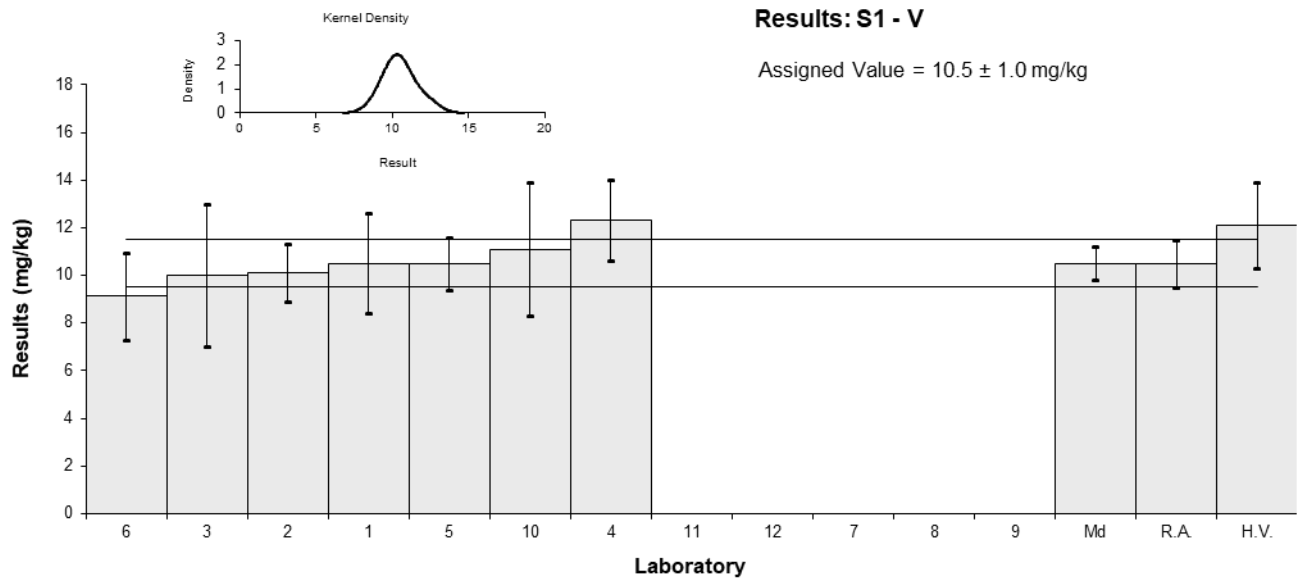
<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	V
<b>Units</b>	mg/kg

**Participant Results**

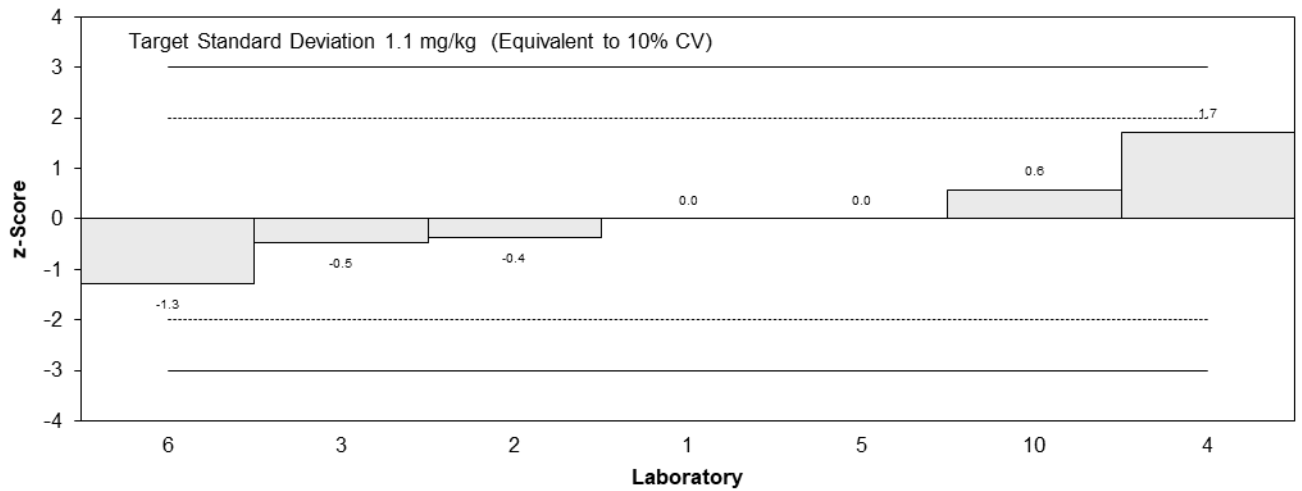
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	10.5	2.1	0.00	0.00
2	10.1	1.2	-0.38	-0.26
3	10	3	-0.48	-0.16
4	12.3	1.7	1.71	0.91
5	10.5	1.1	0.00	0.00
6	9.14	1.83	-1.30	-0.65
7	NT	NT		
8	NT	NT		
9	NT	NT		
10	11.1	2.8	0.57	0.20
11	NT	NT		
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	10.5	1.0
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	12.1	1.8
<b>Robust Average</b>	10.5	1.0
<b>Median</b>	10.5	0.7
<b>Mean</b>	10.5	
<b>N</b>	7	
<b>Max.</b>	12.3	
<b>Min.</b>	9.14	
<b>Robust SD</b>	1.0	
<b>Robust CV</b>	9.8%	



**z-Scores: S1 - V**



**En-Scores: S1 - V**

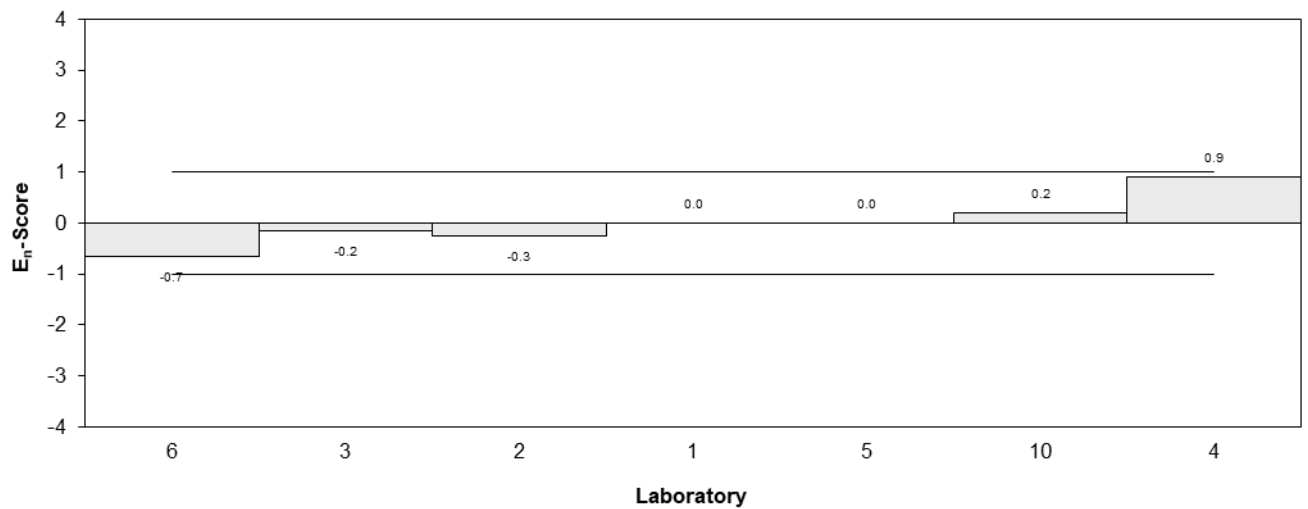


Figure 30



Table 34

**Sample Details**

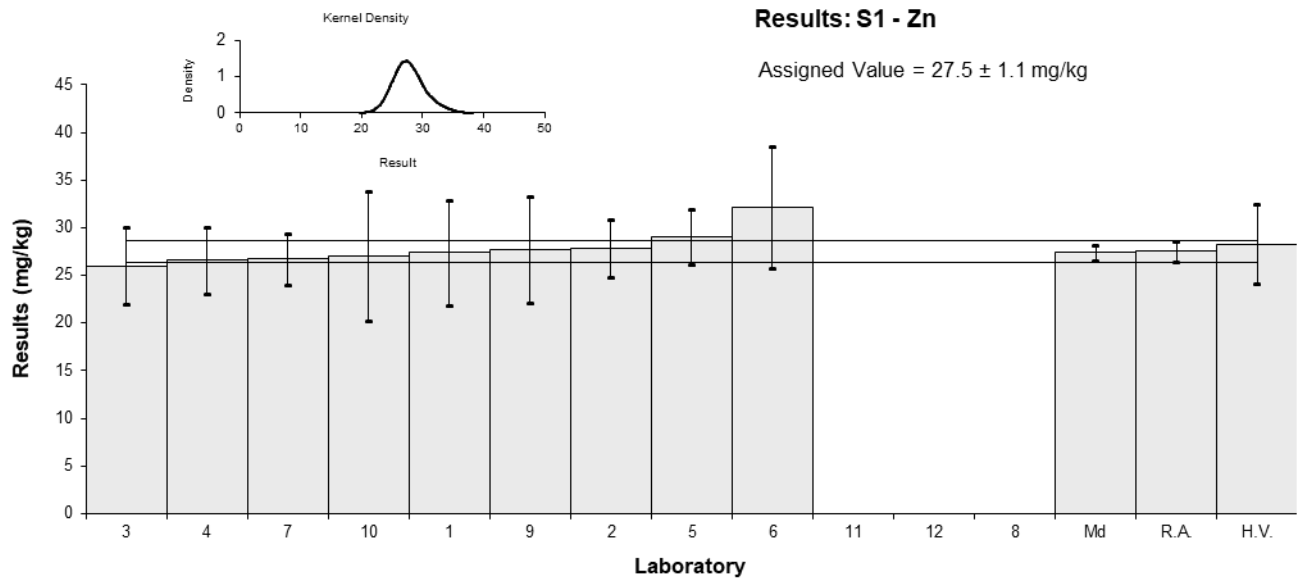
<b>Sample No.</b>	S1
<b>Matrix.</b>	Tea Leaves
<b>Analyte.</b>	Zn
<b>Units</b>	mg/kg

**Participant Results**

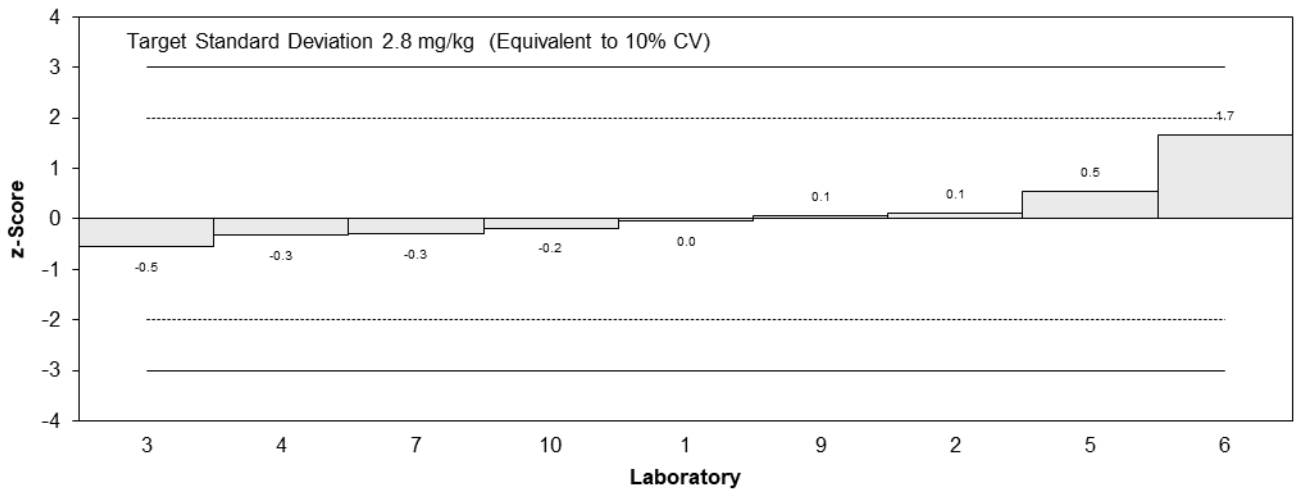
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	27.4	5.5	-0.04	-0.02
2	27.8	3.0	0.11	0.09
3	26	4	-0.55	-0.36
4	26.6	3.5	-0.33	-0.25
5	29	2.9	0.55	0.48
6	32.1	6.41	1.67	0.71
7	26.7	2.67	-0.29	-0.28
8	NT	NT		
9	27.7	5.54	0.07	0.04
10	27	6.8	-0.18	-0.07
11	NT	NT		
12	NT	NT		

**Statistics**

<b>Assigned Value</b>	27.5	1.1
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	28.3	4.2
<b>Robust Average</b>	27.5	1.1
<b>Median</b>	27.4	0.8
<b>Mean</b>	27.8	
<b>N</b>	9	
<b>Max.</b>	32.1	
<b>Min.</b>	26	
<b>Robust SD</b>	1.3	
<b>Robust CV</b>	4.6%	



**z-Scores: S1 - Zn**



**En-Scores: S1 - Zn**

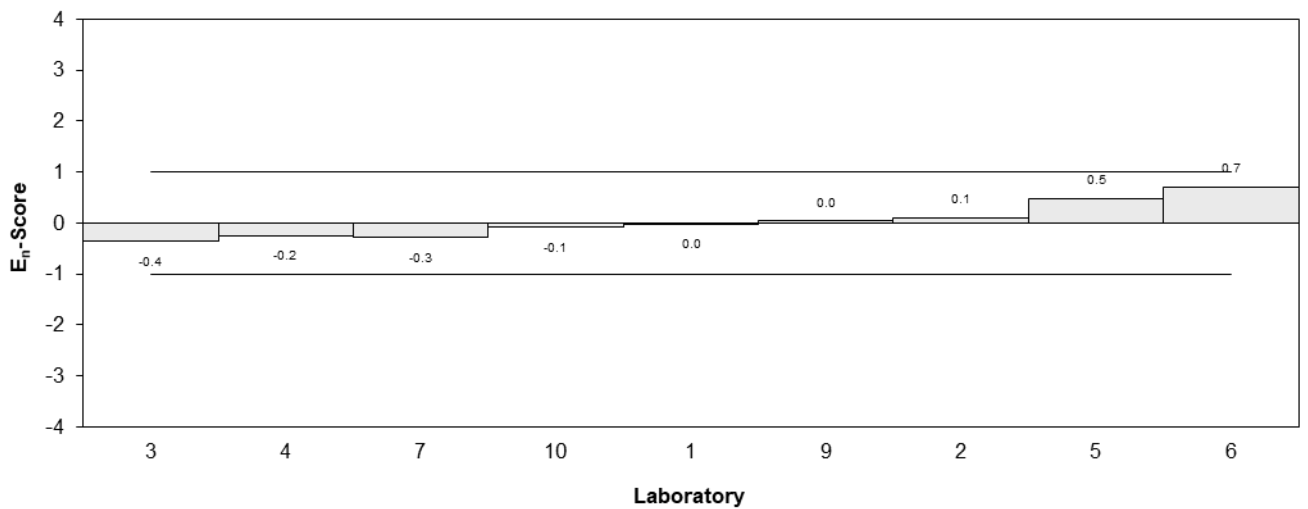


Figure 31

Table 35

**Sample Details**

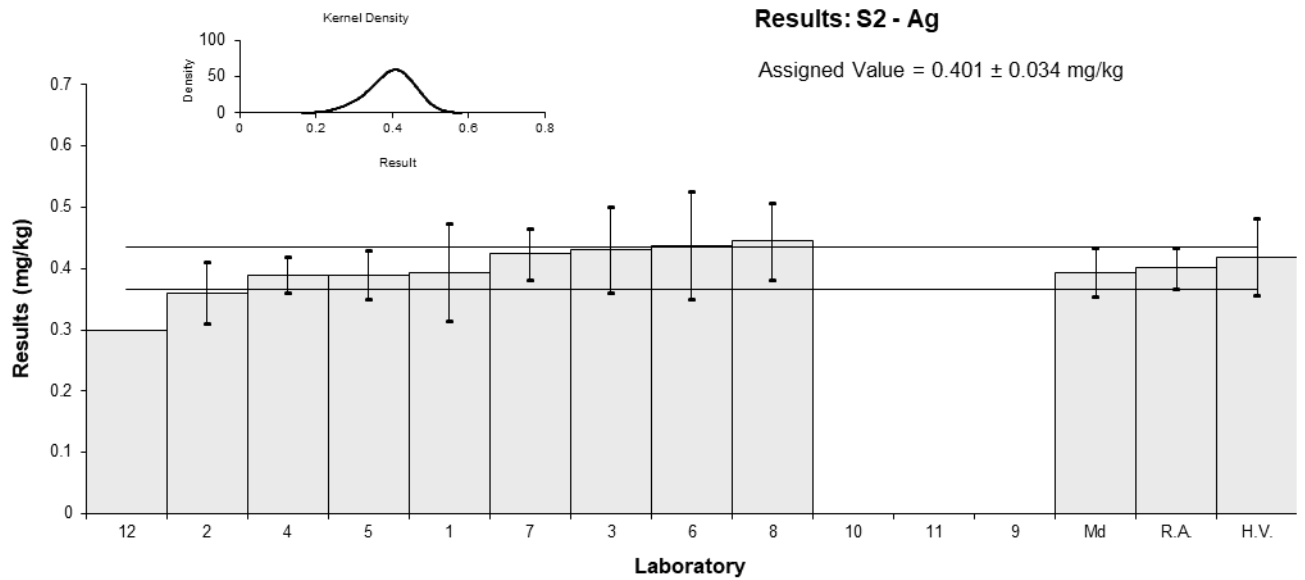
<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Ag
<b>Units</b>	mg/kg

**Participant Results**

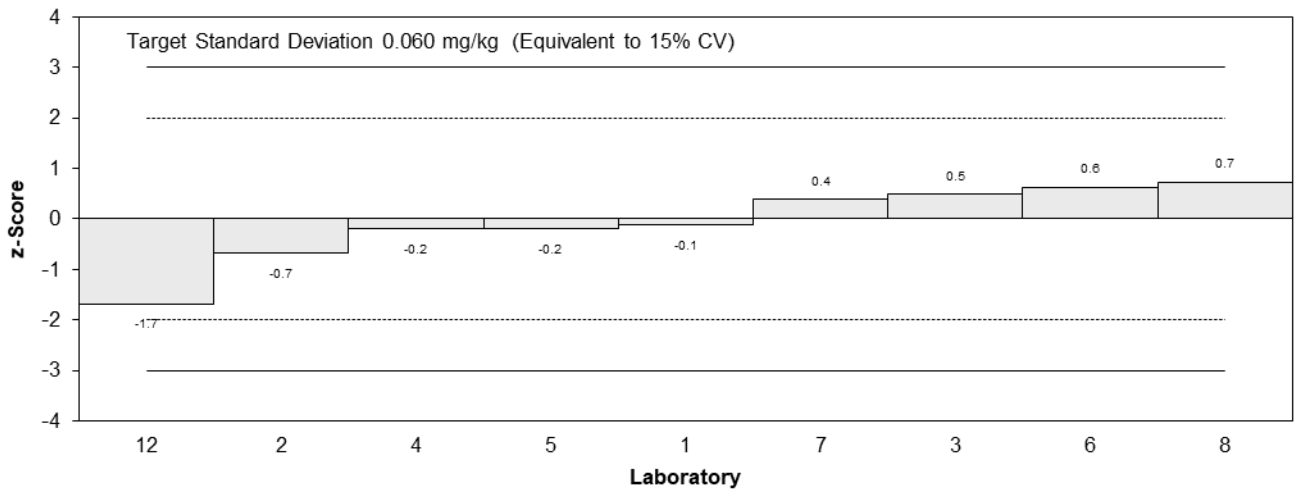
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.394	0.079	-0.12	-0.08
2	0.36	0.05	-0.68	-0.68
3	0.43	0.07	0.48	0.37
4	0.39	0.03	-0.18	-0.24
5	0.39	0.04	-0.18	-0.21
6	0.438	0.088	0.62	0.39
7	0.424	0.042	0.38	0.43
8	0.445	0.063	0.73	0.61
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	0.3	NR	-1.68	-2.97

**Statistics**

<b>Assigned Value</b>	0.401	0.034
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.419	0.063
<b>Robust Average</b>	0.401	0.034
<b>Median</b>	0.394	0.039
<b>Mean</b>	0.397	
<b>N</b>	9	
<b>Max.</b>	0.445	
<b>Min.</b>	0.3	
<b>Robust SD</b>	0.041	
<b>Robust CV</b>	10%	



**z-Scores: S2 - Ag**



**En-Scores: S2 - Ag**

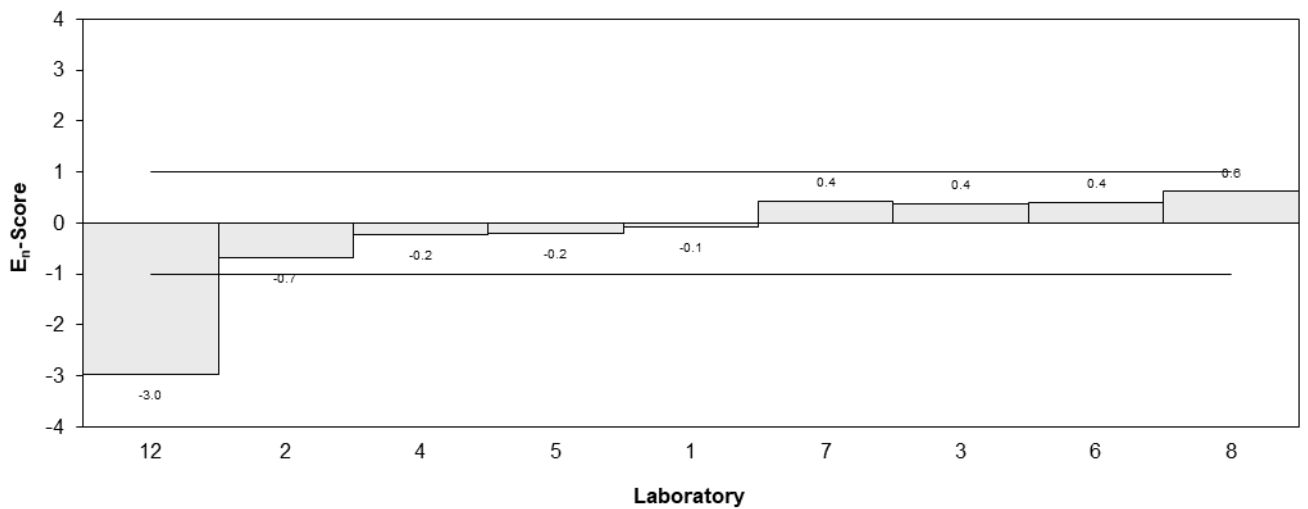


Figure 32

Table 36

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Al
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	8.9	1.8	1.27	0.75
2	23	2.5	11.20	5.36
3	7	2	-0.07	-0.04
4	8.0	1.7	0.63	0.39
5	9.5	0.9	1.69	1.31
6	5.43	1.09	-1.18	-0.86
7	5.99	0.599	-0.78	-0.65
8	6.2	1.1	-0.63	-0.46
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	5.6	NR	-1.06	-0.94

**Statistics**

<b>Assigned Value*</b>	7.1	1.6
<b>Spike</b>	Not Spiked	
<b>Robust Average</b>	7.5	1.8
<b>Median</b>	7.0	1.6
<b>Mean</b>	8.8	
<b>N</b>	9	
<b>Max.</b>	23	
<b>Min.</b>	5.43	
<b>Robust SD</b>	2.1	
<b>Robust CV</b>	29%	

\*Robust Average excluding laboratory 2.

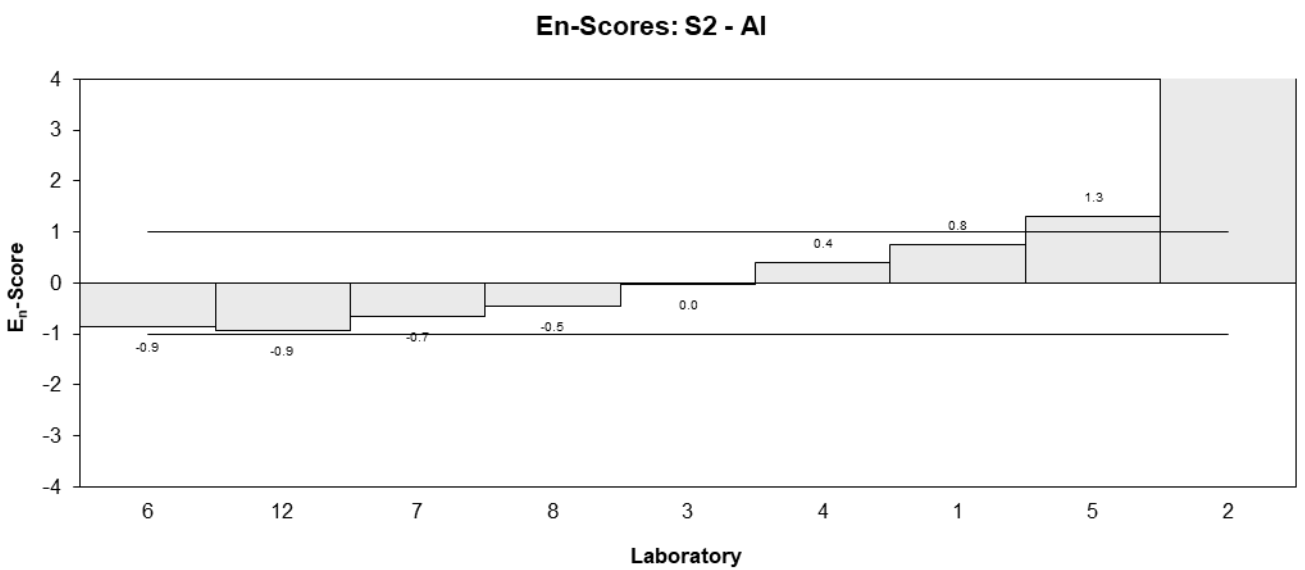
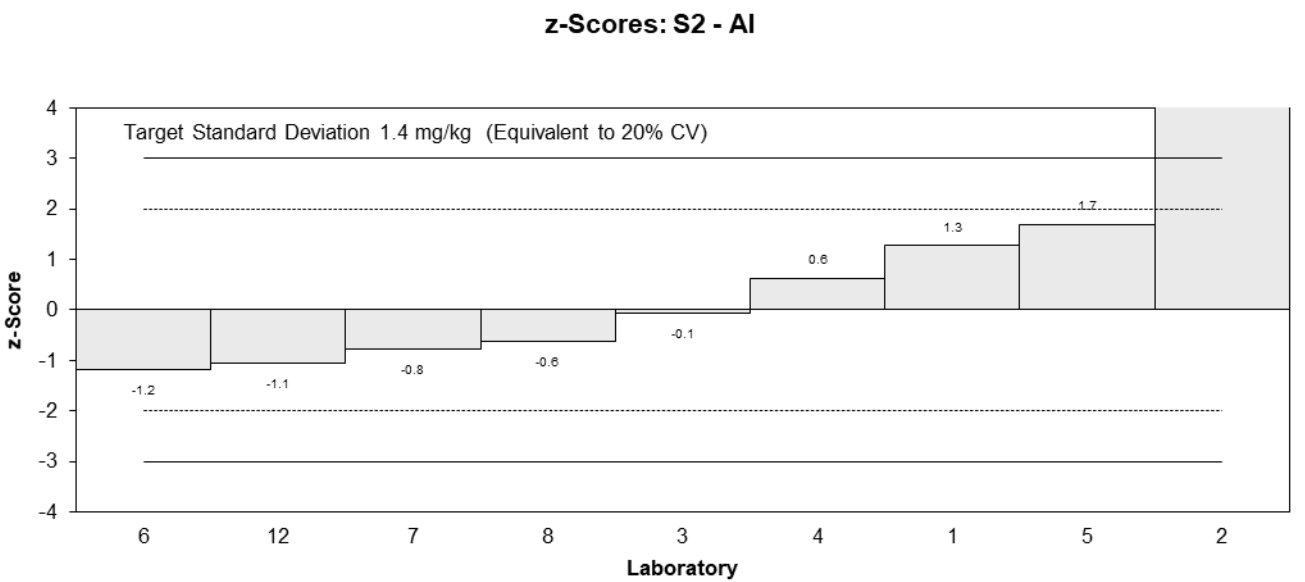
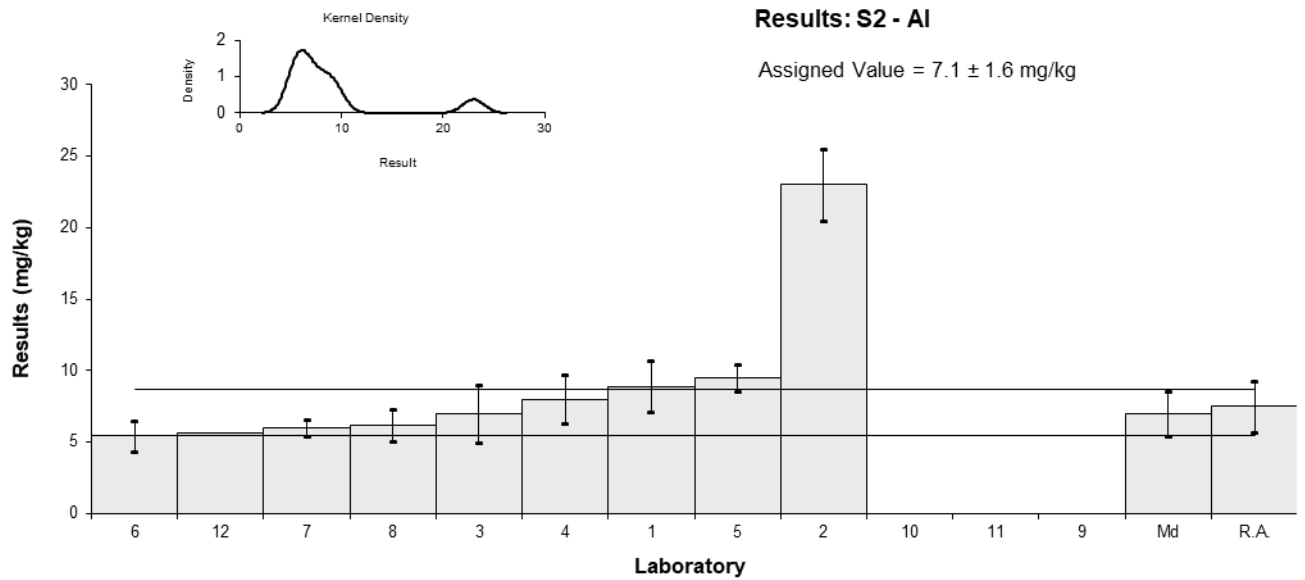


Figure 33

Table 37

**Sample Details**

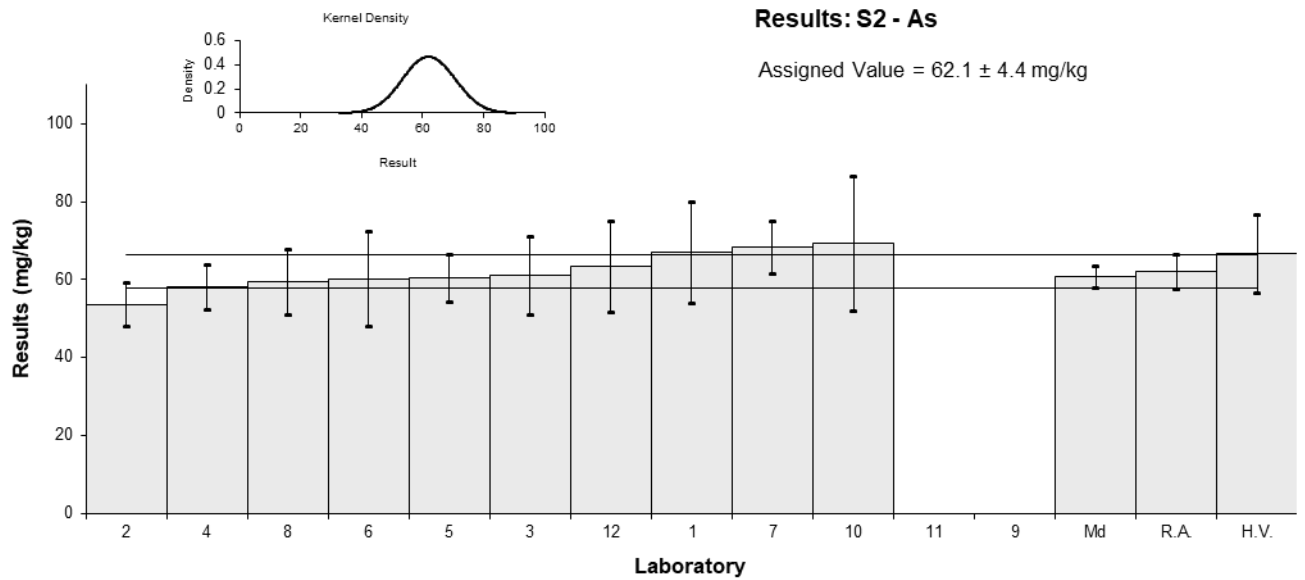
<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	As
<b>Units</b>	mg/kg

**Participant Results**

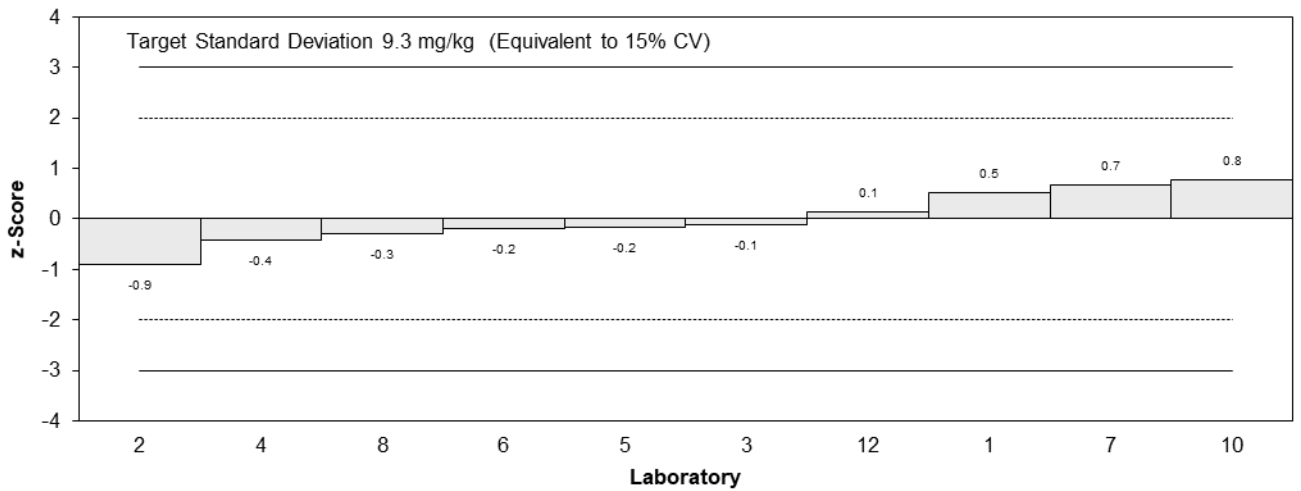
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	67	13	0.53	0.36
2	53.7	5.5	-0.90	-1.19
3	61	10	-0.12	-0.10
4	58.1	5.8	-0.43	-0.55
5	60.5	6.05	-0.17	-0.21
6	60.3	12.06	-0.19	-0.14
7	68.3	6.83	0.67	0.76
8	59.4	8.4	-0.29	-0.28
9	NT	NT		
10	69.3	17.3	0.77	0.40
11	NT	NT		
12	63.4	11.8	0.14	0.10

**Statistics**

<b>Assigned Value</b>	62.1	4.4
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	67	10
<b>Robust Average</b>	62.1	4.4
<b>Median</b>	60.8	2.8
<b>Mean</b>	62.1	
<b>N</b>	10	
<b>Max.</b>	69.3	
<b>Min.</b>	53.7	
<b>Robust SD</b>	5.5	
<b>Robust CV</b>	8.9%	



**z-Scores: S2 - As**



**En-Scores: S2 - As**

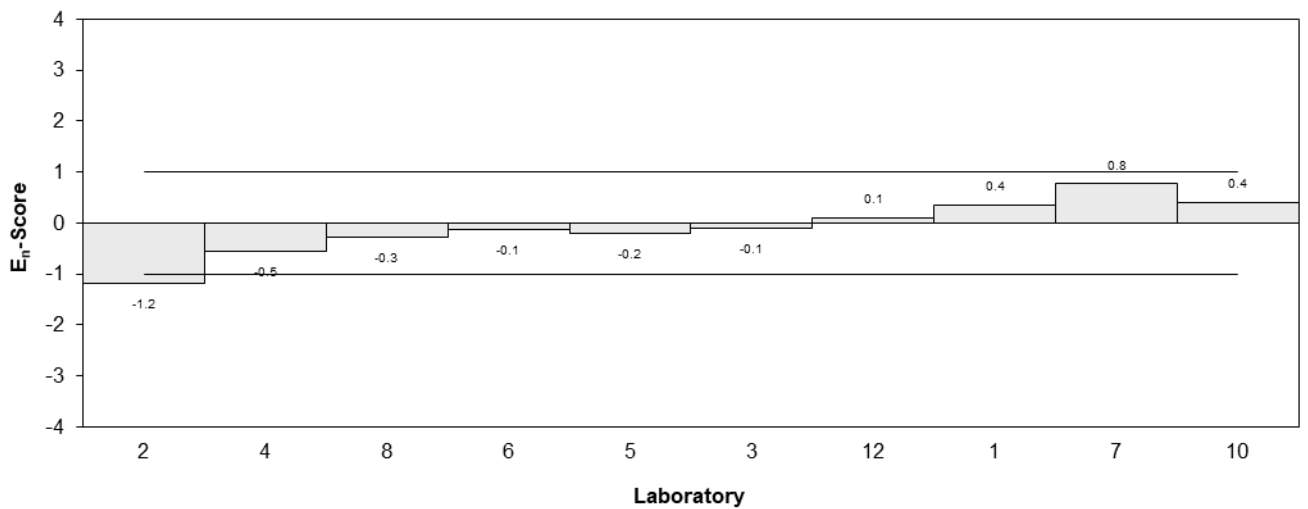


Figure 34



Table 38

**Sample Details**

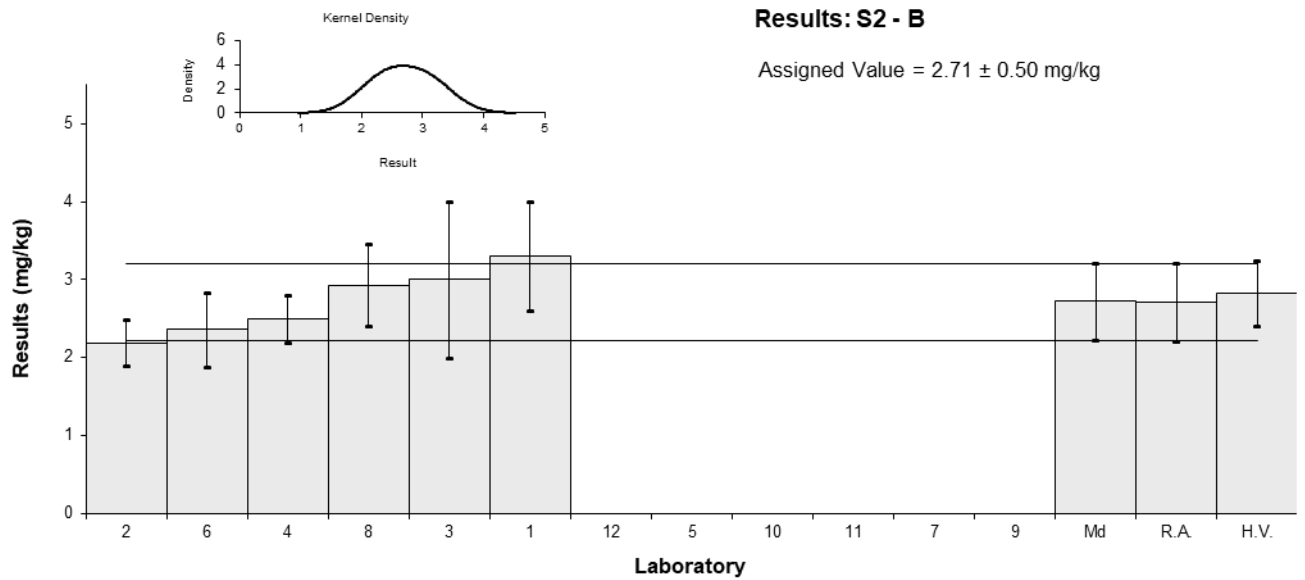
<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	B
<b>Units</b>	mg/kg

**Participant Results**

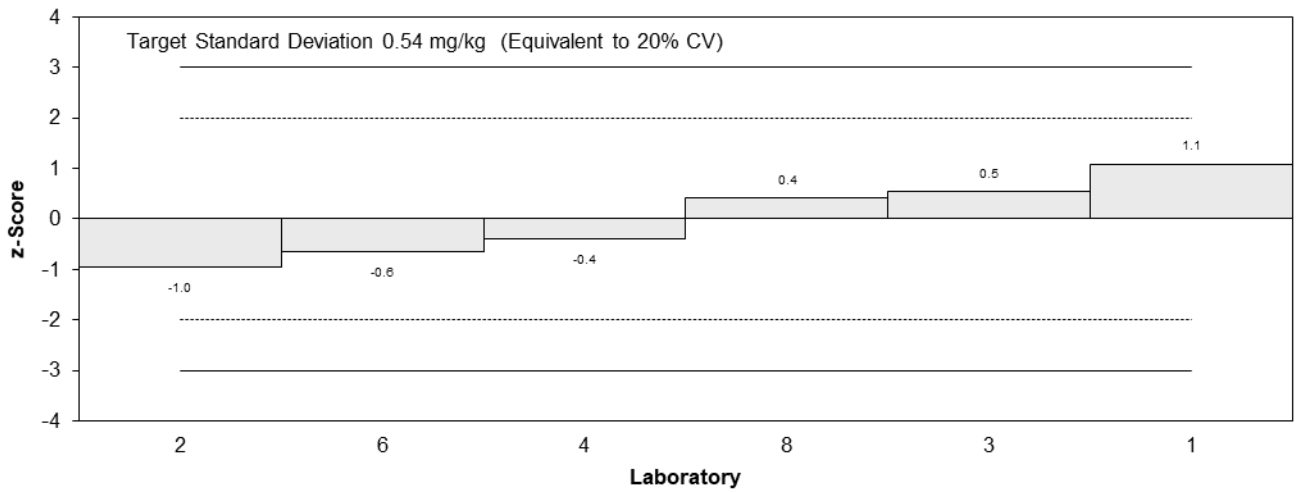
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	3.3	0.7	1.09	0.69
2	2.19	0.3	-0.96	-0.89
3	3	1	0.54	0.26
4	2.5	0.3	-0.39	-0.36
5	NR	NR		
6	2.36	0.471	-0.65	-0.51
7	NT	NT		
8	2.93	0.53	0.41	0.30
9	NT	NT		
10	NT	NT		
11	NT	NT		
12	<5	NR		

**Statistics**

<b>Assigned Value</b>	2.71	0.50
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	2.82	0.42
<b>Robust Average</b>	2.71	0.50
<b>Median</b>	2.72	0.50
<b>Mean</b>	2.71	
<b>N</b>	6	
<b>Max.</b>	3.3	
<b>Min.</b>	2.19	
<b>Robust SD</b>	0.49	
<b>Robust CV</b>	18%	



**z-Scores: S2 - B**



**En-Scores: S2 - B**

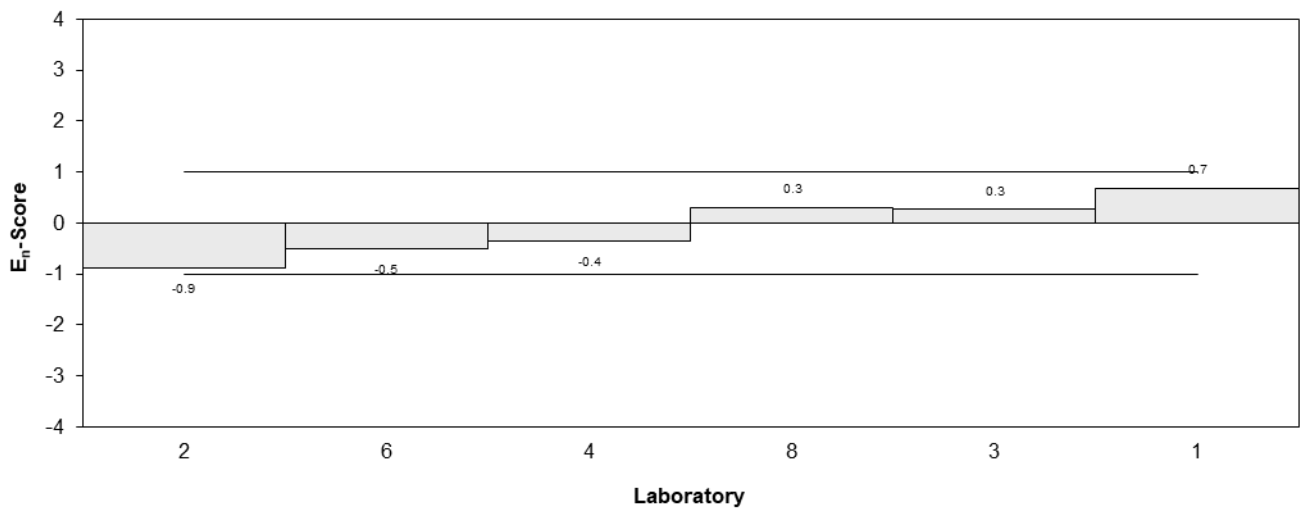


Figure 35

Table 39

**Sample Details**

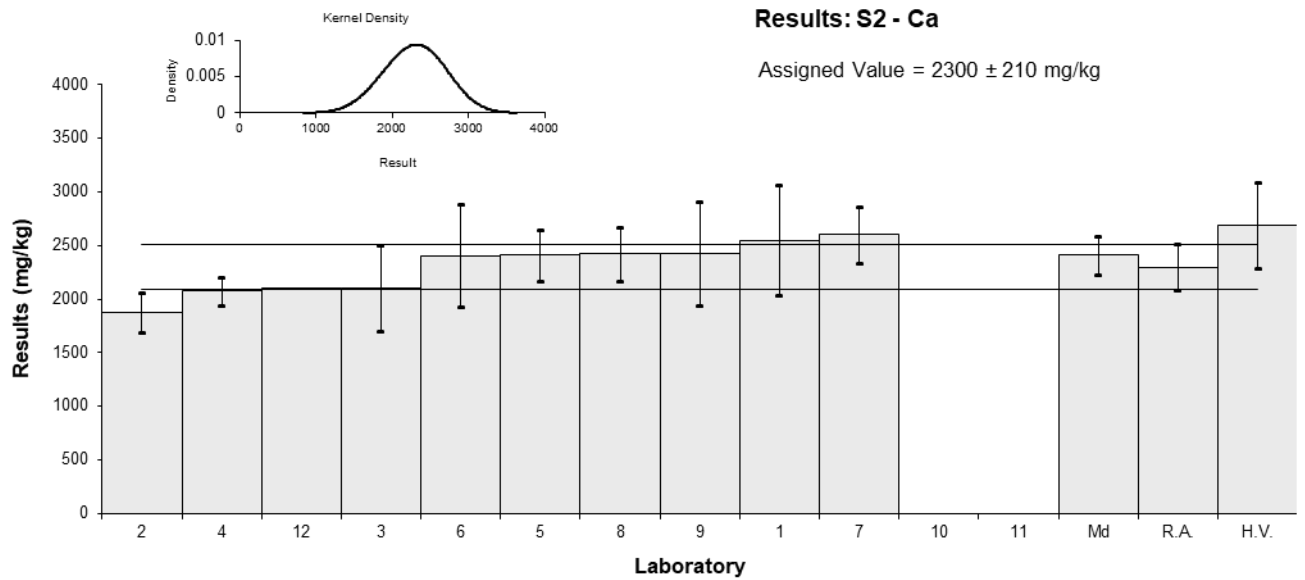
<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Ca
<b>Units</b>	mg/kg

**Participant Results**

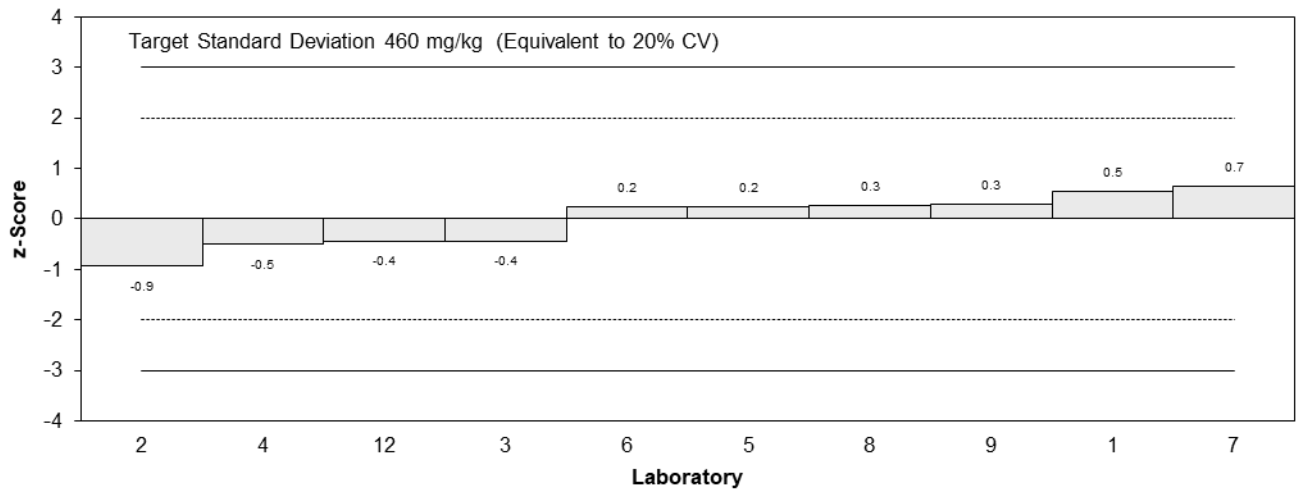
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	2550	510	0.54	0.45
2	1875	190	-0.92	-1.50
3	2100	400	-0.43	-0.44
4	2075	130	-0.49	-0.91
5	2410	241	0.24	0.34
6	2407	481	0.23	0.20
7	2600	260	0.65	0.90
8	2420	250	0.26	0.37
9	2430	485	0.28	0.25
10	NT	NT		
11	NT	NT		
12	2100	NR	-0.43	-0.95

**Statistics**

<b>Assigned Value</b>	2300	210
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	2690	400
<b>Robust Average</b>	2300	210
<b>Median</b>	2410	180
<b>Mean</b>	2300	
<b>N</b>	10	
<b>Max.</b>	2600	
<b>Min.</b>	1875	
<b>Robust SD</b>	270	
<b>Robust CV</b>	12%	



**z-Scores: S2 - Ca**



**En-Scores: S2 - Ca**

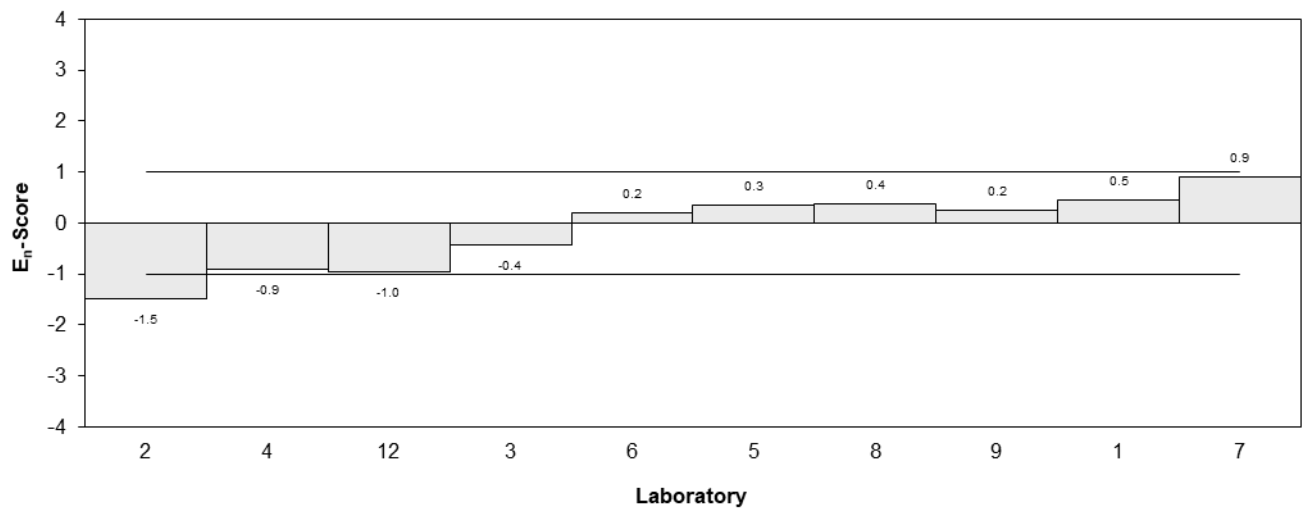


Figure 36

Table 40

**Sample Details**

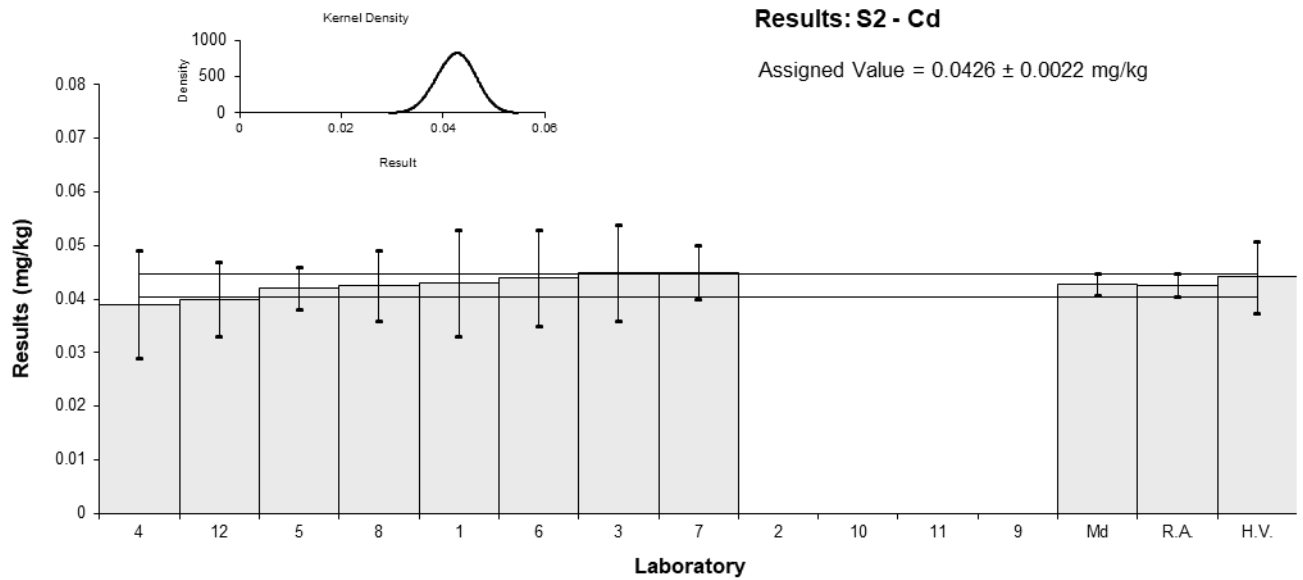
<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Cd
<b>Units</b>	mg/kg

**Participant Results**

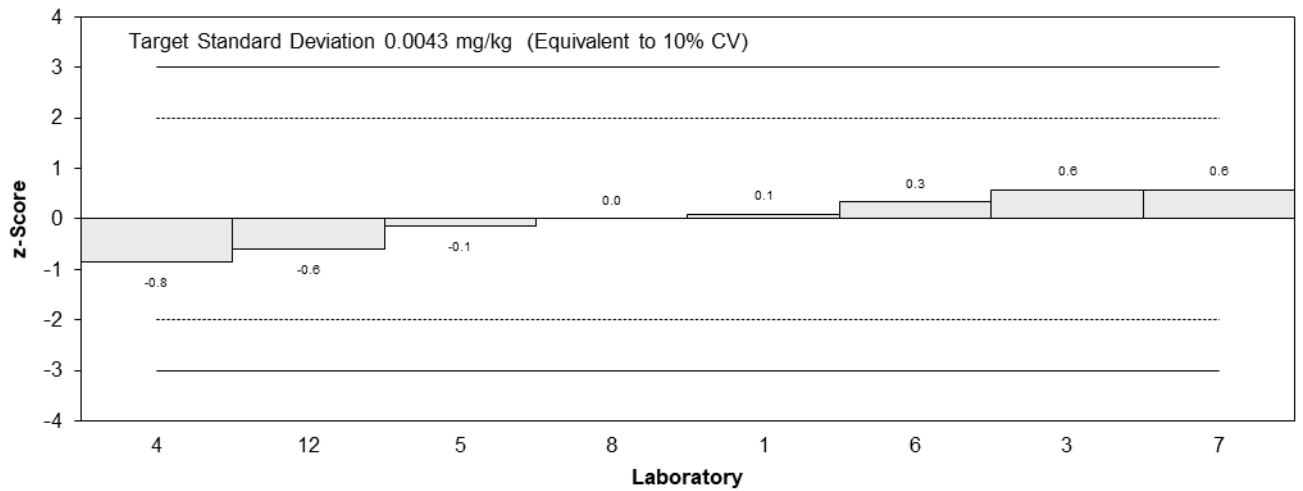
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.043	0.01	0.09	0.04
2	<0.1	NR		
3	0.045	0.009	0.56	0.26
4	0.039	0.010	-0.85	-0.35
5	0.042	0.004	-0.14	-0.13
6	0.044	0.009	0.33	0.15
7	0.045	0.005	0.56	0.44
8	0.0426	0.0066	0.00	0.00
9	NT	NT		
10	<1	NR		
11	NT	NT		
12	0.04	0.007	-0.61	-0.35

**Statistics**

<b>Assigned Value</b>	0.0426	0.0022
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.0441	0.0066
<b>Robust Average</b>	0.0426	0.0022
<b>Median</b>	0.0428	0.0021
<b>Mean</b>	0.0426	
<b>N</b>	8	
<b>Max.</b>	0.045	
<b>Min.</b>	0.039	
<b>Robust SD</b>	0.0025	
<b>Robust CV</b>	5.9%	



**z-Scores: S2 - Cd**



**En-Scores: S2 - Cd**

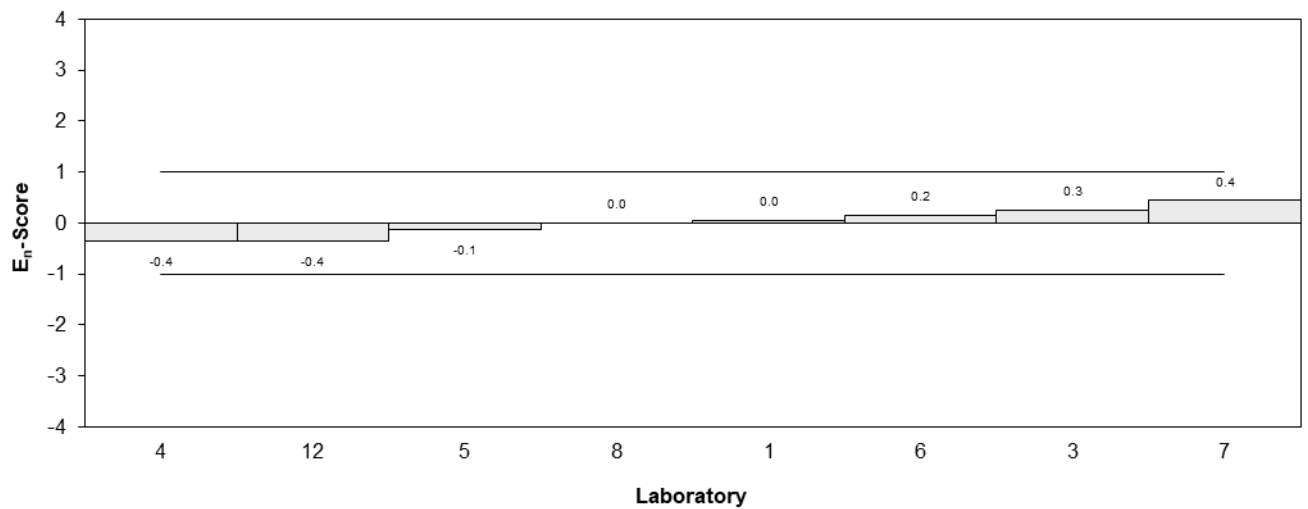


Figure 37

Table 41

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Cr
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.78	0.16	0.13	0.10
2	0.65	0.1	-0.72	-0.70
3	0.7	0.2	-0.39	-0.26
4	0.84	0.15	0.53	0.42
5	0.80	0.08	0.26	0.28
6	0.550	0.110	-1.38	-1.29
7	0.980	0.098	1.45	1.42
8	0.67	0.11	-0.59	-0.55
9	NT	NT		
10	1.5	0.4	4.87	1.77
11	NT	NT		
12	0.84	0.33	0.53	0.23

**Statistics**

<b>Assigned Value*</b>	0.76	0.12
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.77	0.12
<b>Robust Average</b>	0.78	0.13
<b>Median</b>	0.79	0.11
<b>Mean</b>	0.83	
<b>N</b>	10	
<b>Max.</b>	1.5	
<b>Min.</b>	0.55	
<b>Robust SD</b>	0.17	
<b>Robust CV</b>	22%	

\*Robust Average excluding laboratory 10.

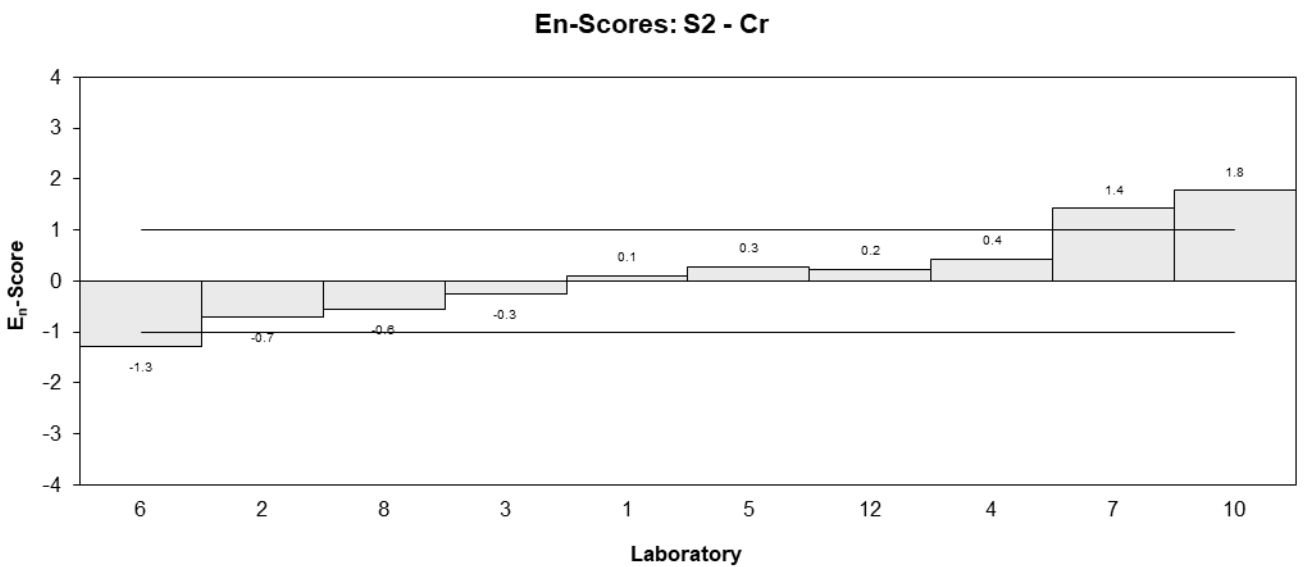
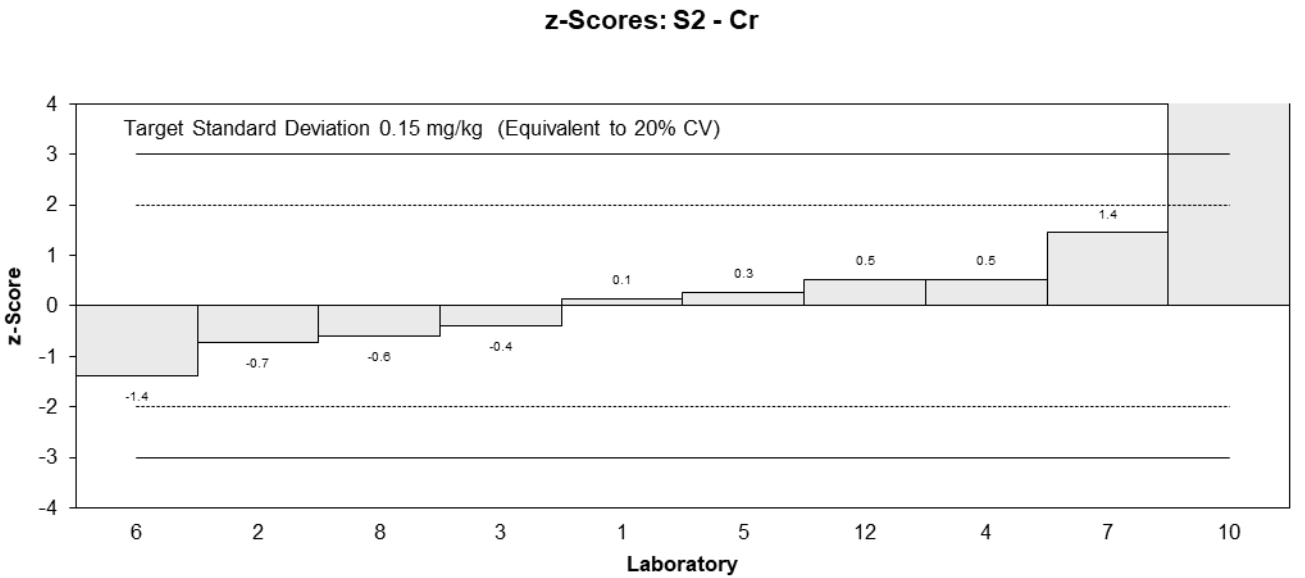
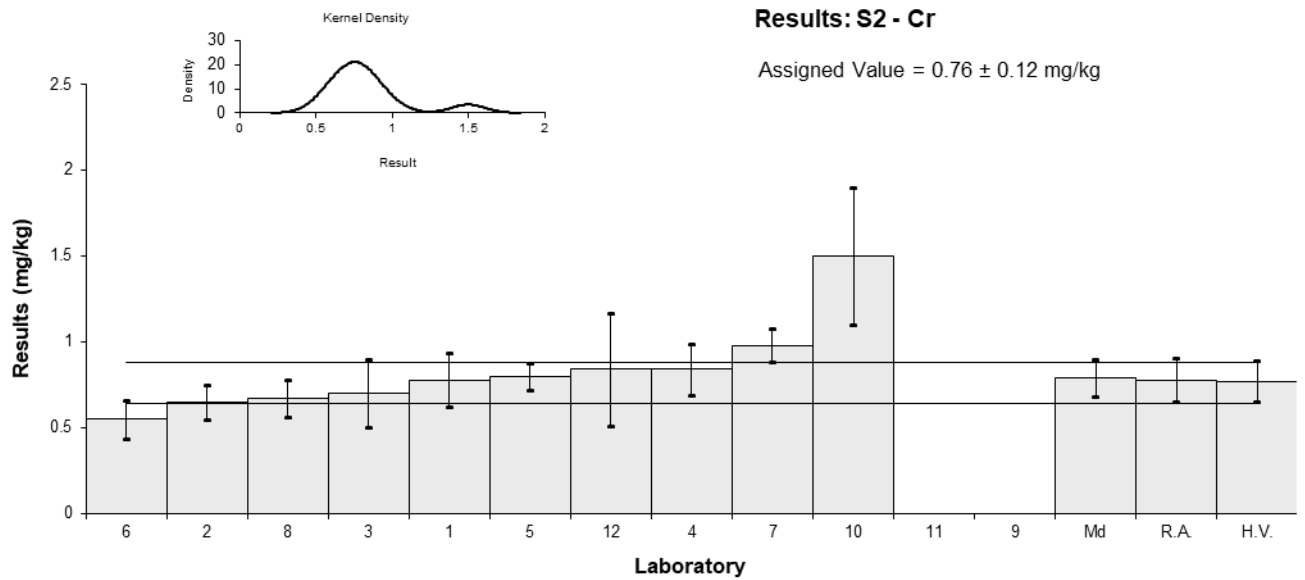


Figure 38



Table 42

**Sample Details**

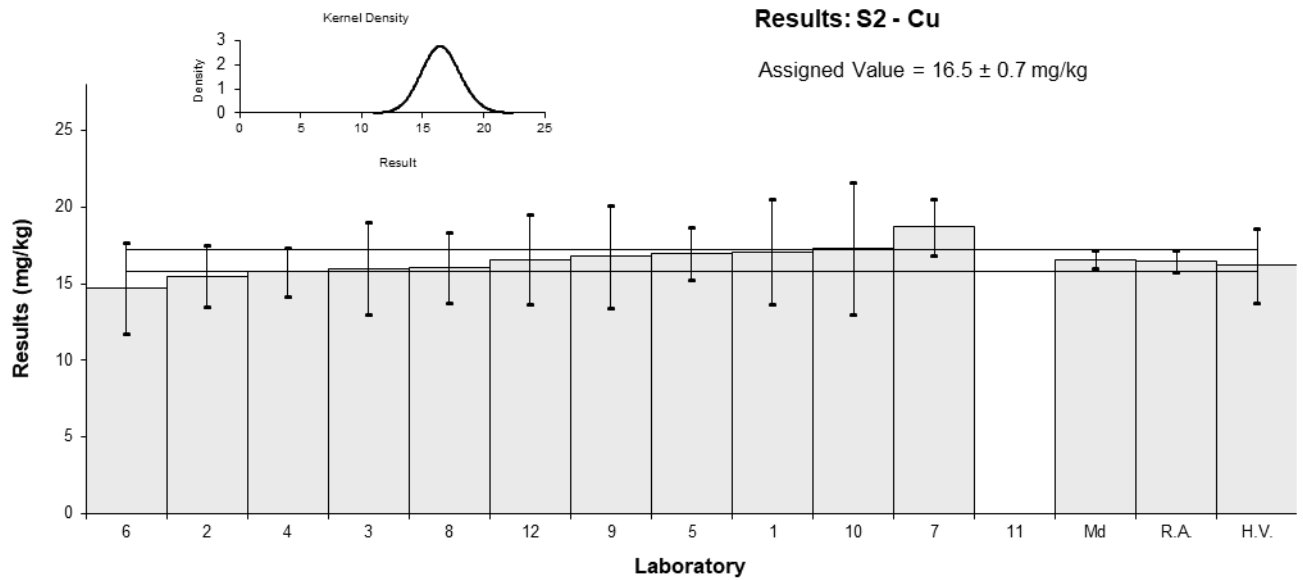
<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Cu
<b>Units</b>	mg/kg

**Participant Results**

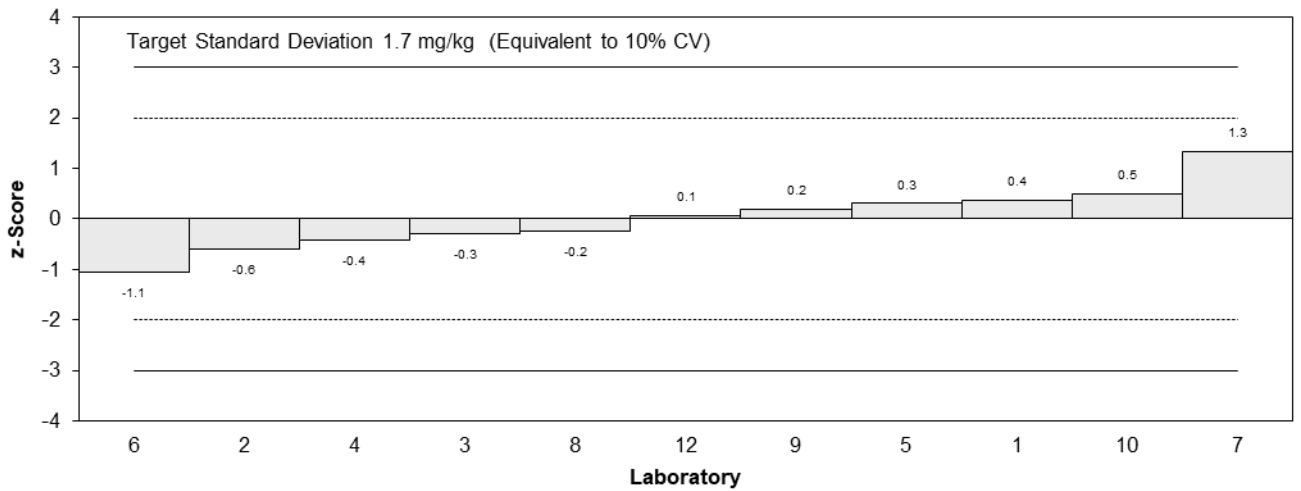
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	17.1	3.4	0.36	0.17
2	15.5	2.0	-0.61	-0.47
3	16	3	-0.30	-0.16
4	15.8	1.6	-0.42	-0.40
5	17	1.7	0.30	0.27
6	14.74	2.95	-1.07	-0.58
7	18.7	1.87	1.33	1.10
8	16.1	2.3	-0.24	-0.17
9	16.8	3.36	0.18	0.09
10	17.3	4.3	0.48	0.18
11	NT	NT		
12	16.6	2.9	0.06	0.03

**Statistics**

<b>Assigned Value</b>	16.5	0.7
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	16.2	2.4
<b>Robust Average</b>	16.5	0.7
<b>Median</b>	16.6	0.6
<b>Mean</b>	16.5	
<b>N</b>	11	
<b>Max.</b>	18.7	
<b>Min.</b>	14.74	
<b>Robust SD</b>	0.99	
<b>Robust CV</b>	6%	



**z-Scores: S2 - Cu**



**En-Scores: S2 - Cu**

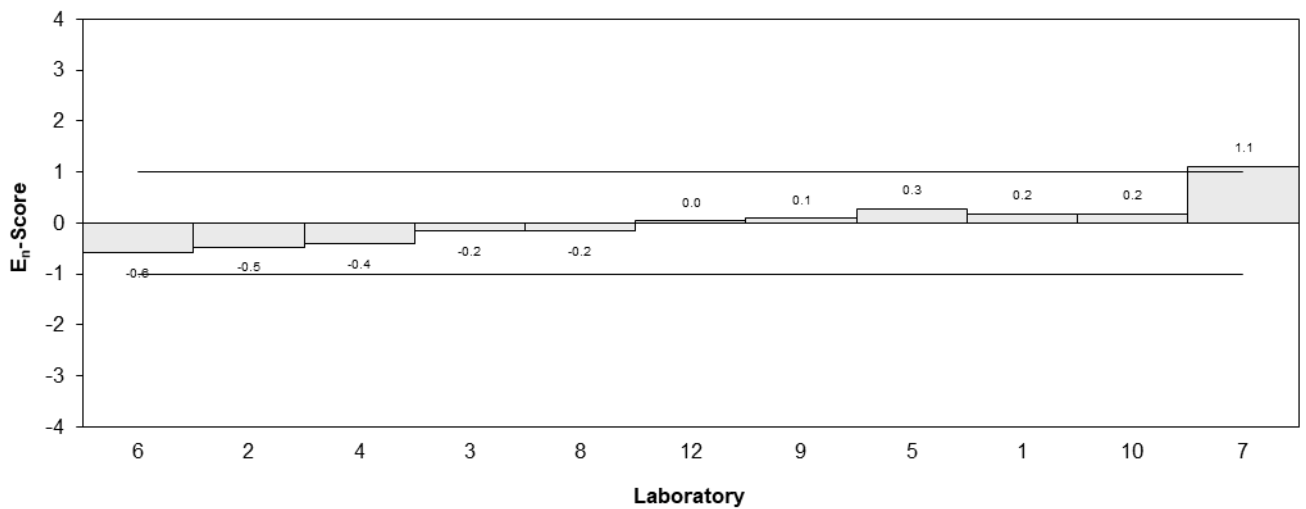


Figure 39

Table 43

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Fe
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	19.7	3.9	-0.44	-0.30
2	173	19	47.99	7.92
3	19	3	-0.66	-0.52
4	17.6	1.4	-1.11	-1.15
5	20.5	2.05	-0.19	-0.18
6	25.32	5.06	1.33	0.74
7	24.4	2.44	1.04	0.91
8	19.8	3.9	-0.41	-0.27
9	23.7	4.73	0.82	0.48
10	24.3	6.1	1.01	0.48
11	NT	NT		
12	17	5.0	-1.30	-0.72

**Statistics\***

<b>Assigned Value</b>	21.1	2.7
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	20.4	3.1
<b>Robust Average</b>	21.1	2.7
<b>Median</b>	20.2	3.0
<b>Mean</b>	21.1	
<b>N</b>	10	
<b>Max.</b>	25.32	
<b>Min.</b>	17	
<b>Robust SD</b>	3.4	
<b>Robust CV</b>	16%	

\*Laboratory 2 was excluded from statistical calculation (extreme outlier).

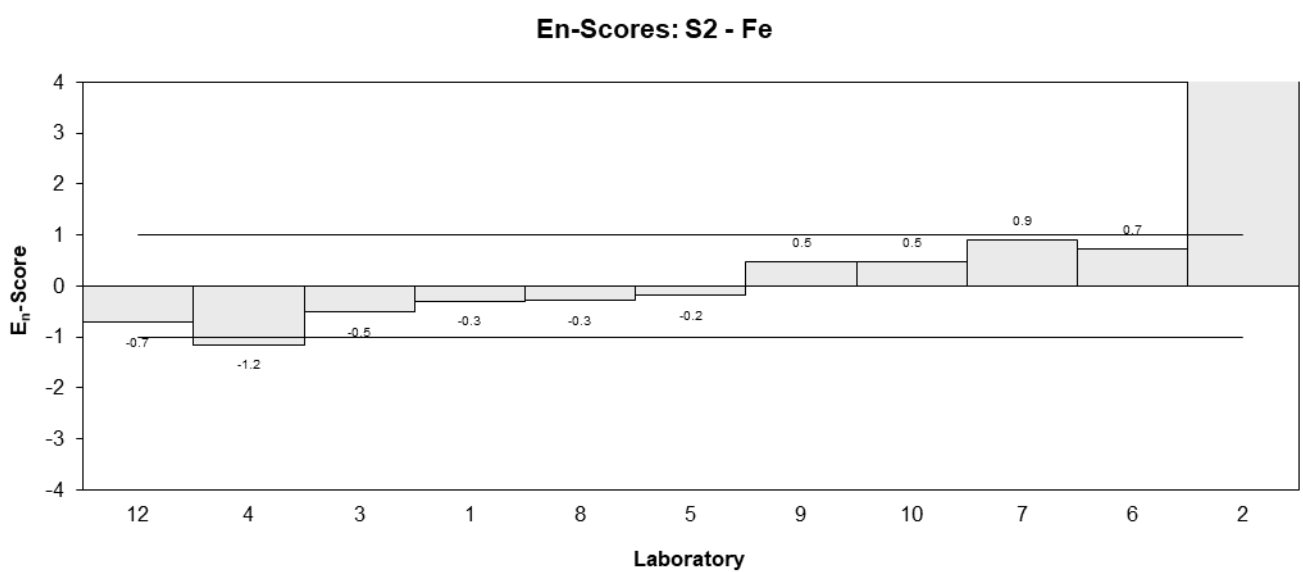
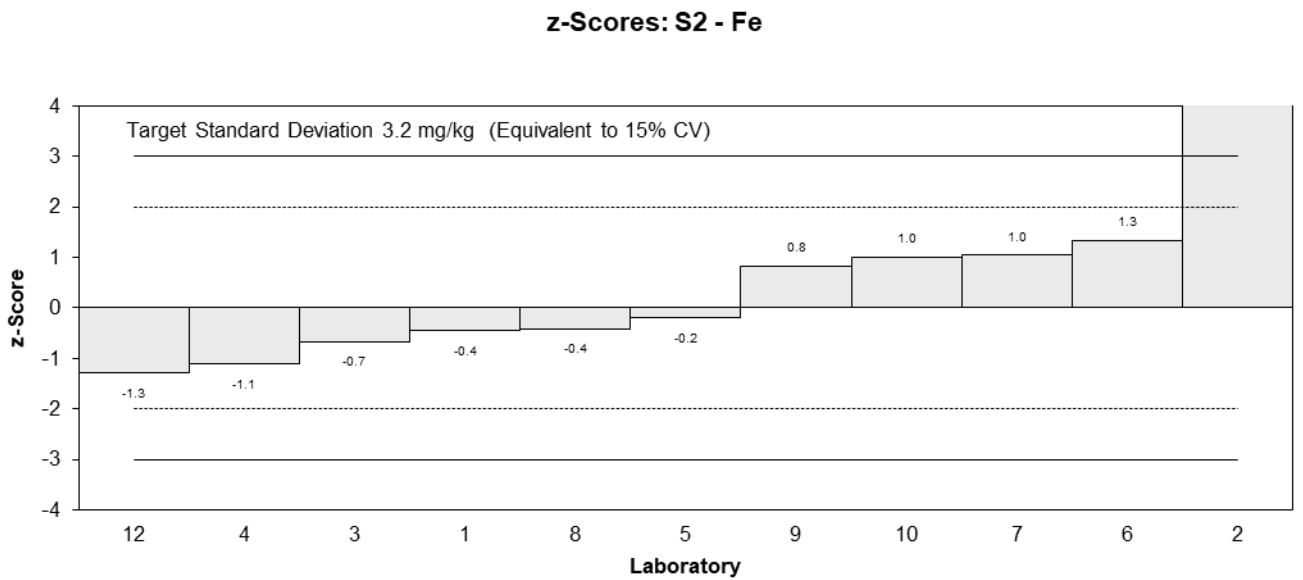
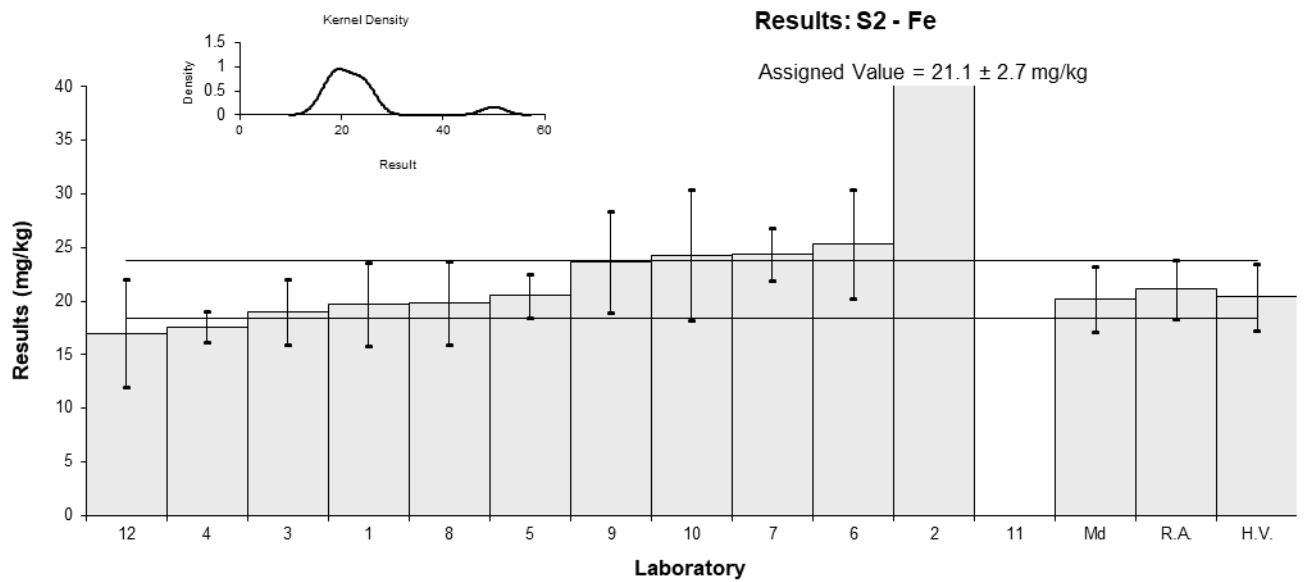


Figure 40

Table 44

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Hg
<b>Units</b>	mg/kg

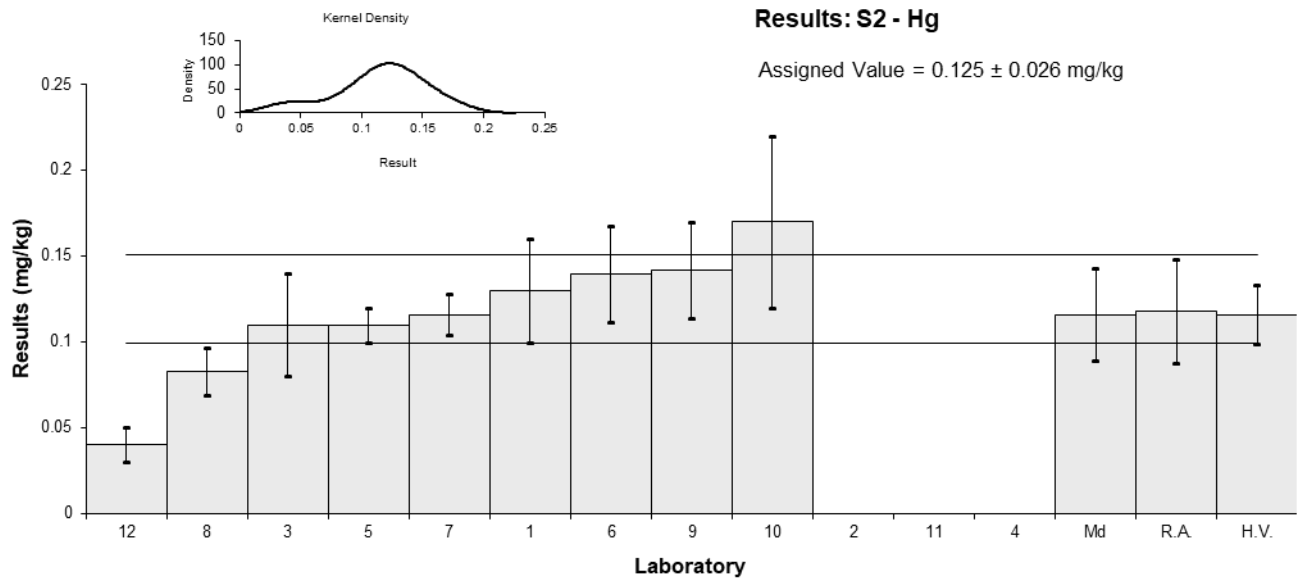
**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.13	0.03	0.20	0.13
2	<0.1	NR		
3	0.11	0.03	-0.60	-0.38
4	NT	NT		
5	0.11	0.01	-0.60	-0.54
6	0.140	0.028	0.60	0.39
7	0.116	0.012	-0.36	-0.31
8	0.083	0.014	-1.68	-1.42
9	0.142	0.028	0.68	0.44
10	0.17	0.05	1.80	0.80
11	NT	NT		
12	0.04	0.01	-3.40	-3.05

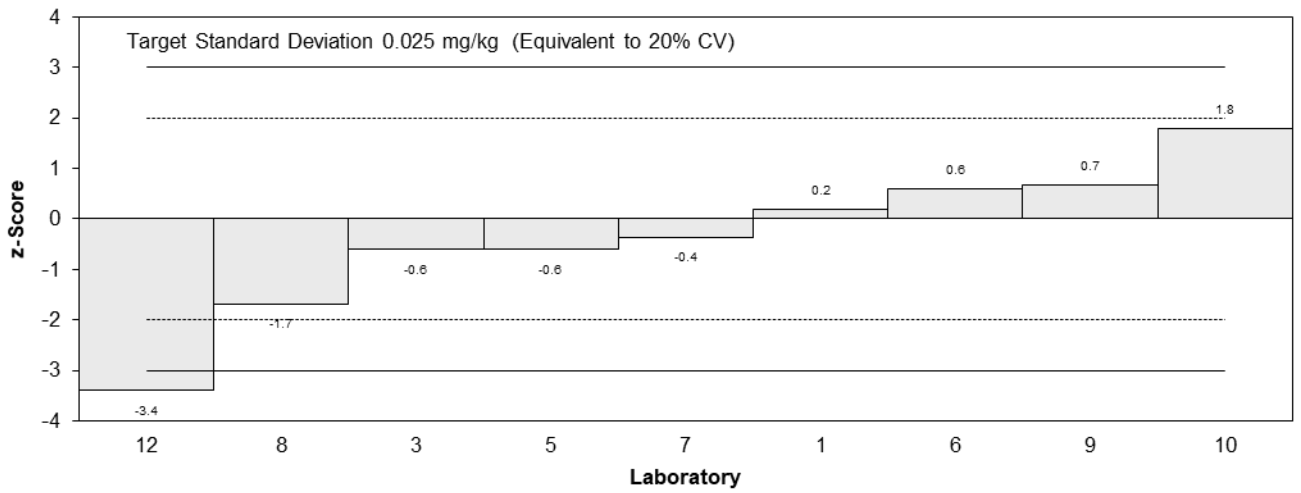
**Statistics**

<b>Assigned Value*</b>	0.125	0.026
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.116	0.017
<b>Robust Average</b>	0.118	0.030
<b>Median</b>	0.116	0.027
<b>Mean</b>	0.116	
<b>N</b>	9	
<b>Max.</b>	0.17	
<b>Min.</b>	0.04	
<b>Robust SD</b>	0.036	
<b>Robust CV</b>	31%	

\*Robust Average excluding laboratory 12.



**z-Scores: S2 - Hg**



**En-Scores: S2 - Hg**

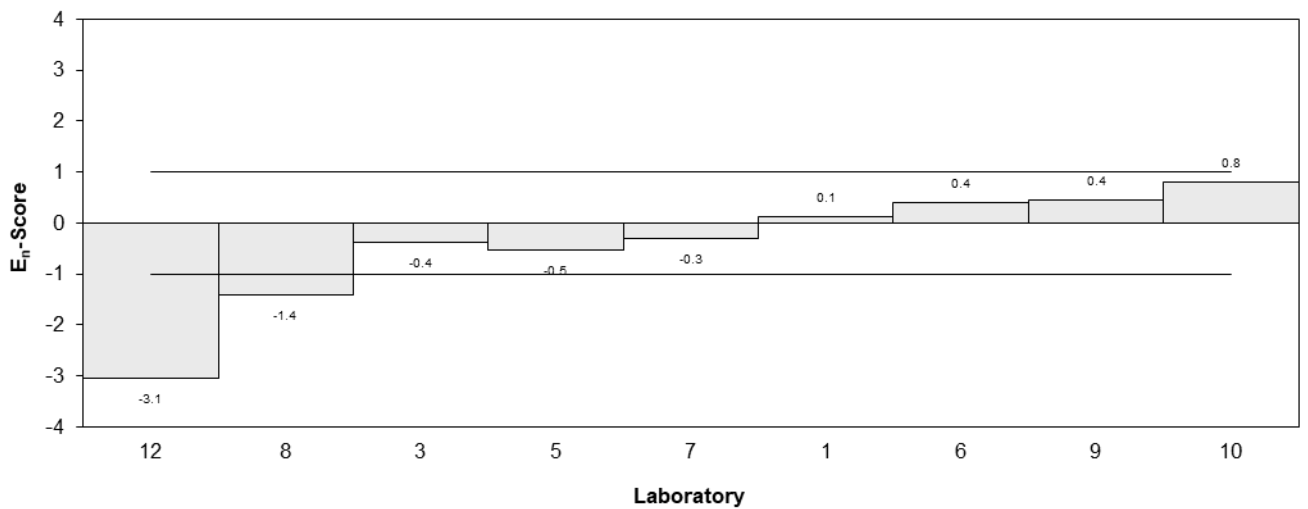


Figure 41

Table 45

**Sample Details**

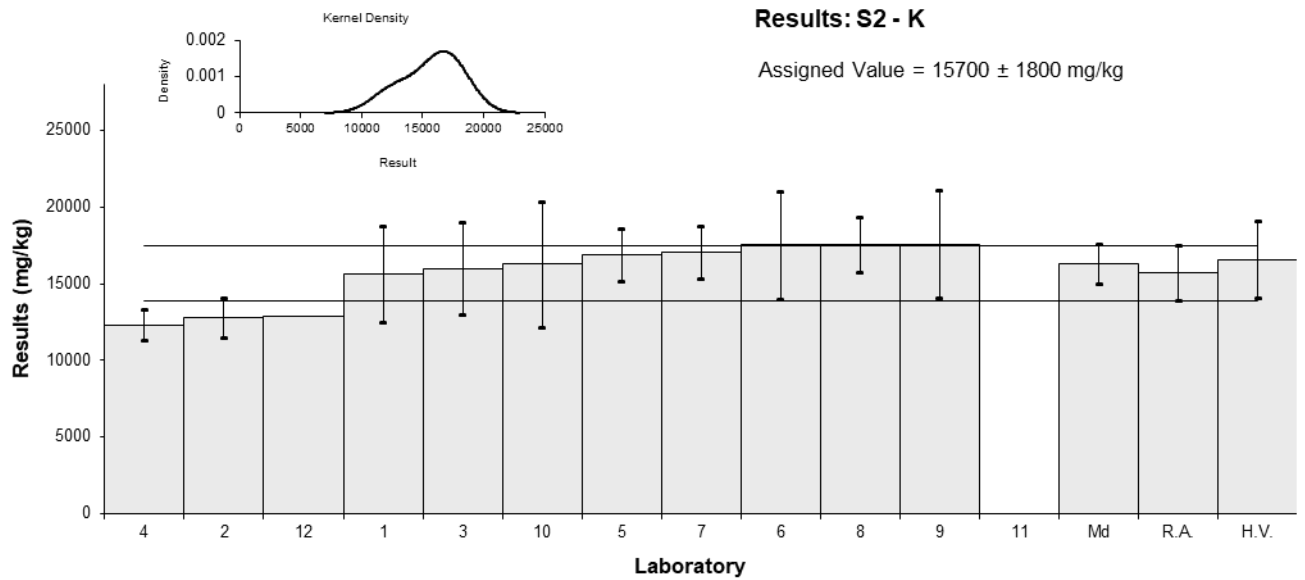
<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	K
<b>Units</b>	mg/kg

**Participant Results**

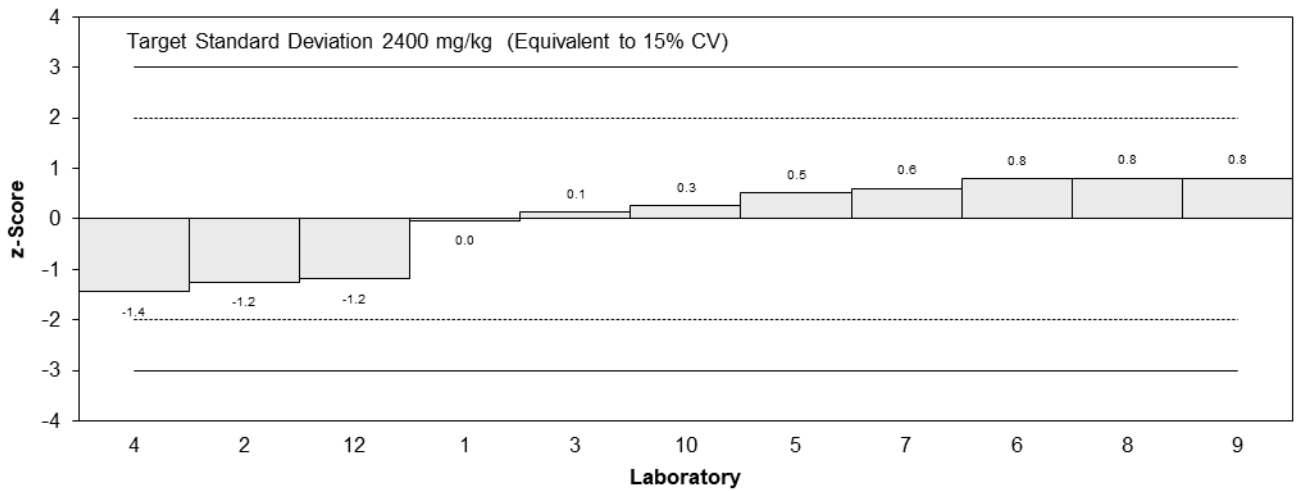
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	15630	3120	-0.03	-0.02
2	12760	1300	-1.25	-1.32
3	16000	3000	0.13	0.09
4	12300	1000	-1.44	-1.65
5	16900	1690	0.51	0.49
6	17559	3512	0.79	0.47
7	17100	1710	0.59	0.56
8	17600	1800	0.81	0.75
9	17600	3510	0.81	0.48
10	16300	4100	0.25	0.13
11	NT	NT		
12	12900	NR	-1.19	-1.56

**Statistics**

<b>Assigned Value</b>	15700	1800
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	16600	2500
<b>Robust Average</b>	15700	1800
<b>Median</b>	16300	1300
<b>Mean</b>	15700	
<b>N</b>	11	
<b>Max.</b>	17600	
<b>Min.</b>	12300	
<b>Robust SD</b>	2300	
<b>Robust CV</b>	15%	



**z-Scores: S2 - K**



**En-Scores: S2 - K**

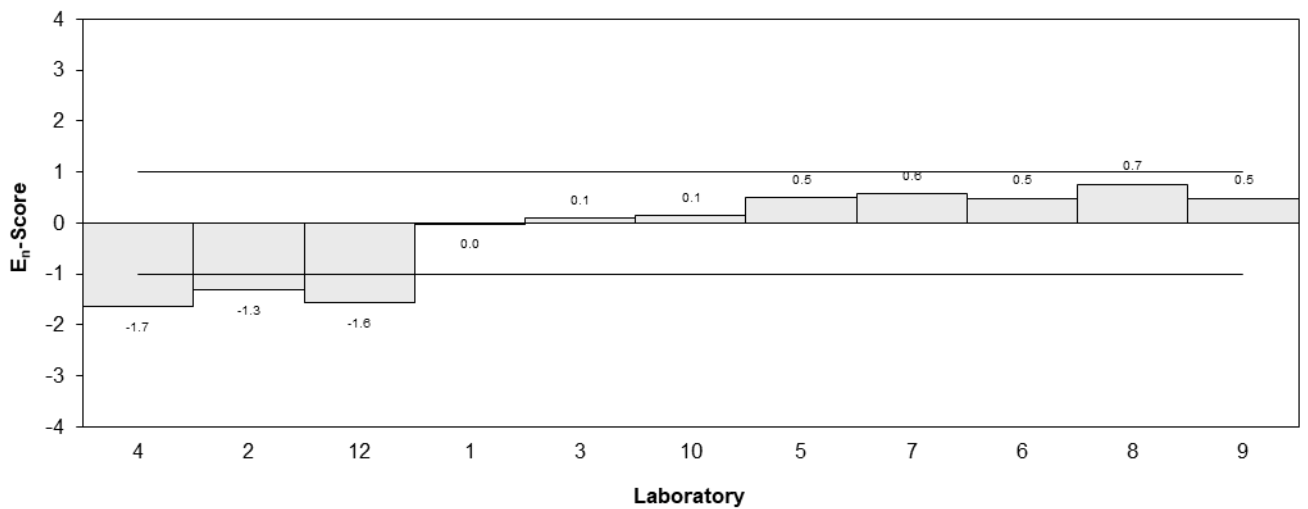


Figure 42



Table 46

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Li
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	0.26	0.05
2	0.20	0.04
3	<2	NR
4	0.16	0.03
5	NR	NR
6	0.207	0.041
7	NT	NT
8	< 0.5	0.095
9	NT	NT
10	NT	NT
11	NT	NT
12	0.1	NR

**Statistics**

<b>Assigned Value</b>	Not Set	
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.217	0.033
<b>Median</b>	0.200	0.074
<b>Mean</b>	0.185	
<b>N</b>	5	
<b>Max.</b>	0.26	
<b>Min.</b>	0.1	

Results: S2 - Li

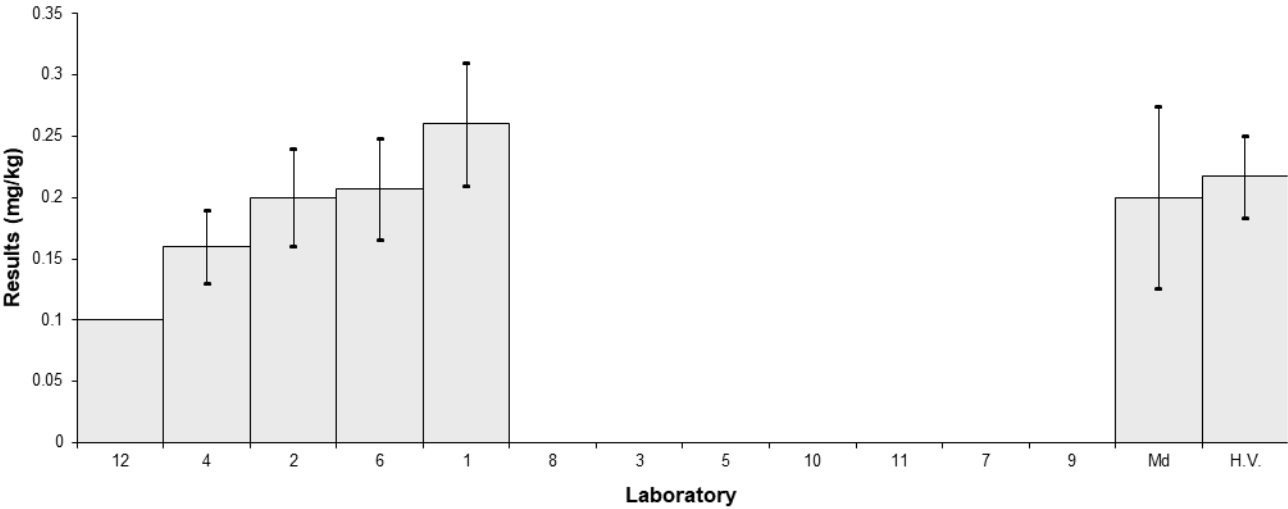


Figure 43

Table 47

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Mg
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	1458	290	-0.65	-0.32
2	1385	140	-1.12	-0.95
3	1500	200	-0.38	-0.26
4	1400	160	-1.03	-0.80
5	1650	165	0.58	0.44
6	1718	344	1.01	0.43
7	1640	164	0.51	0.39
8	1690	170	0.83	0.62
9	1660	332	0.64	0.28
10	NT	NT		
11	NT	NT		
12	1450	NR	-0.71	-0.92

**Statistics**

<b>Assigned Value</b>	1560	120
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	1810	270
<b>Robust Average</b>	1560	120
<b>Median</b>	1570	120
<b>Mean</b>	1560	
<b>N</b>	10	
<b>Max.</b>	1718	
<b>Min.</b>	1385	
<b>Robust SD</b>	150	
<b>Robust CV</b>	9.4%	

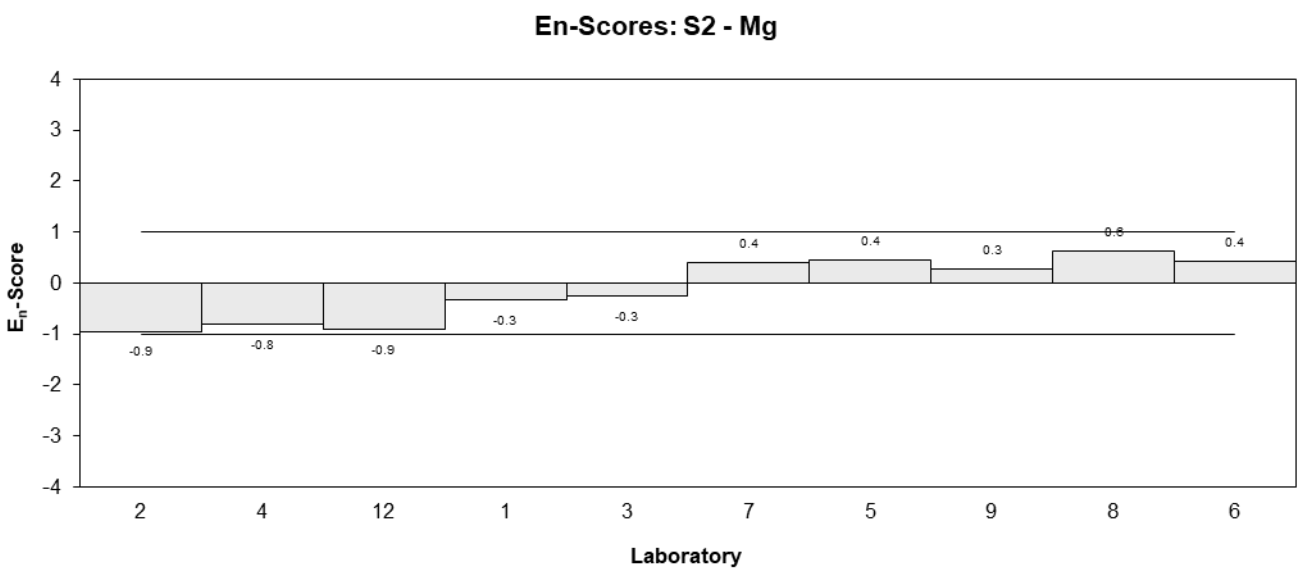
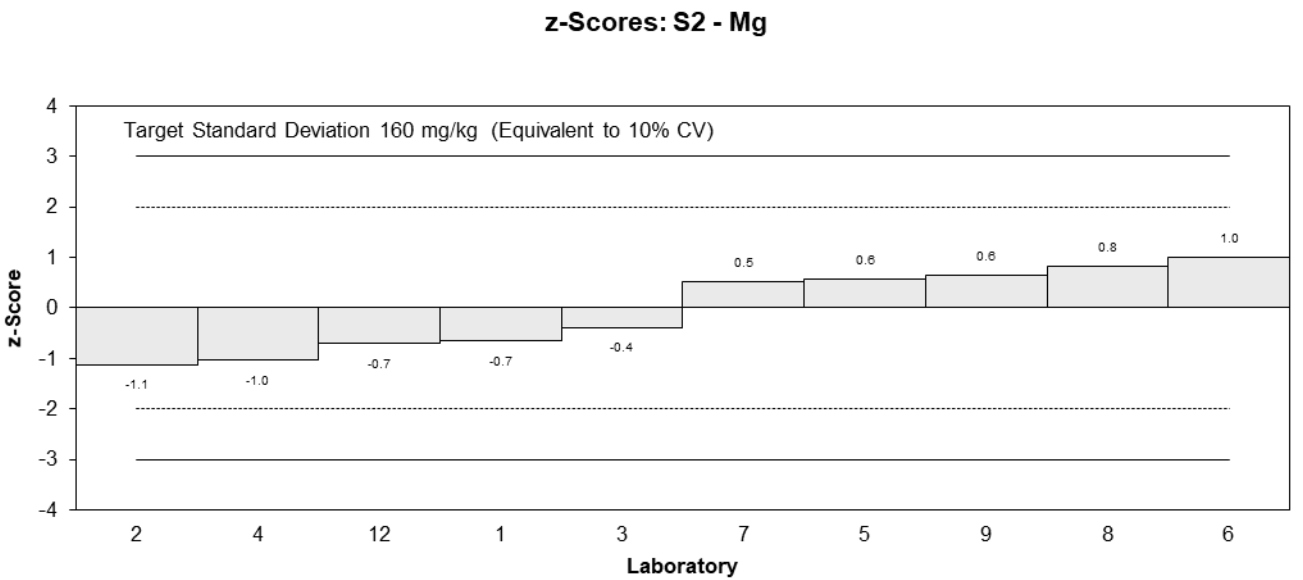
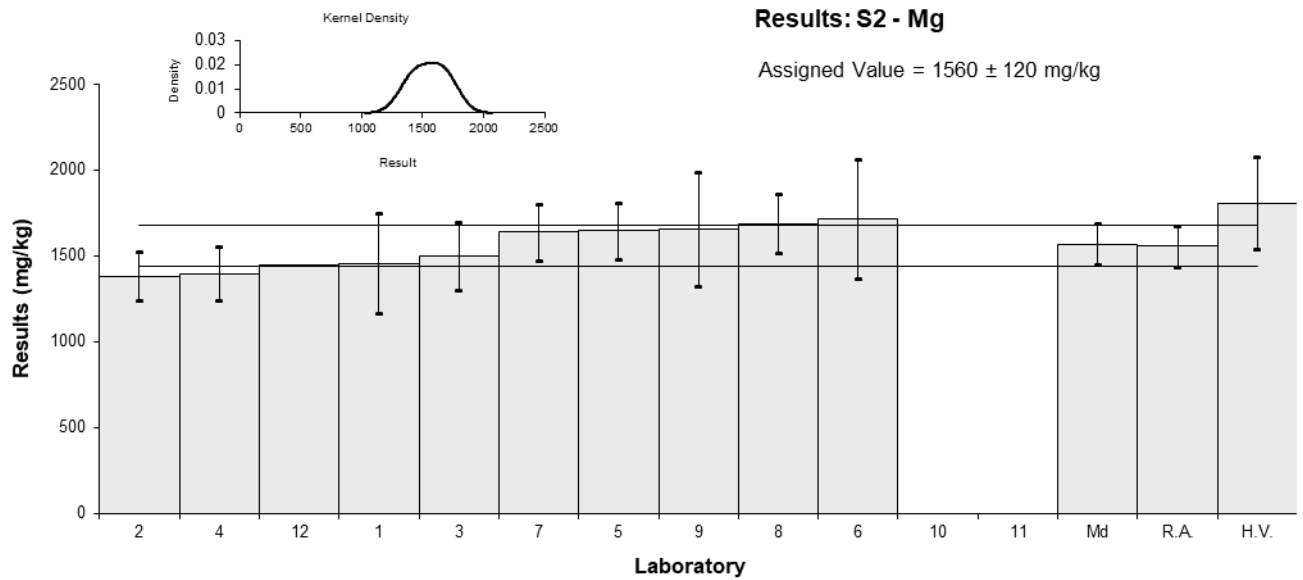


Figure 44

Table 48

**Sample Details**

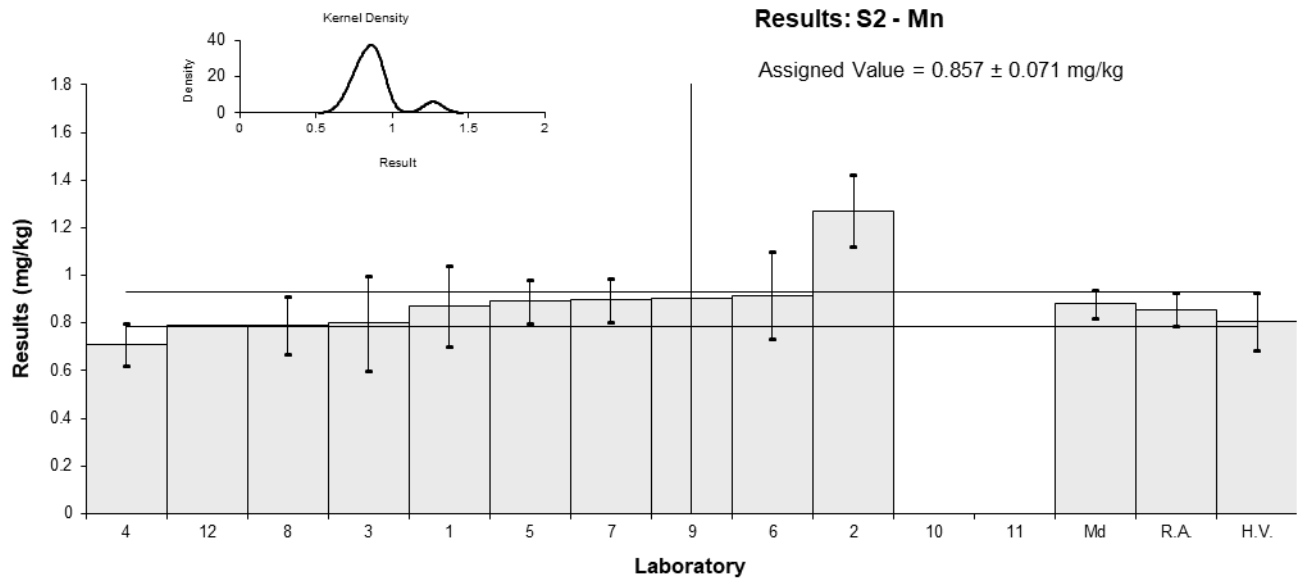
<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Mn
<b>Units</b>	mg/kg

**Participant Results**

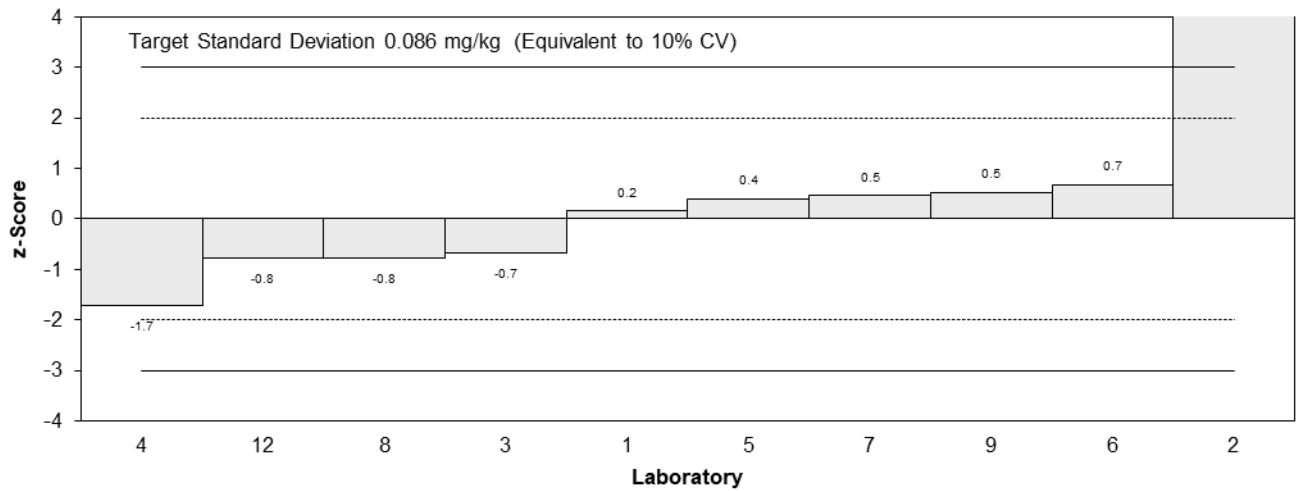
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.87	0.17	0.15	0.07
2	1.27	0.15	4.82	2.49
3	0.8	0.2	-0.67	-0.27
4	0.71	0.09	-1.72	-1.28
5	0.89	0.09	0.39	0.29
6	0.915	0.183	0.68	0.30
7	0.896	0.090	0.46	0.34
8	0.79	0.12	-0.78	-0.48
9	0.902	1.80	0.53	0.02
10	<1	NR		
11	NT	NT		
12	0.79	NR	-0.78	-0.94

**Statistics**

<b>Assigned Value</b>	0.857	0.071
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.81	0.12
<b>Robust Average</b>	0.857	0.071
<b>Median</b>	0.880	0.061
<b>Mean</b>	0.883	
<b>N</b>	10	
<b>Max.</b>	1.27	
<b>Min.</b>	0.71	
<b>Robust SD</b>	0.090	
<b>Robust CV</b>	11%	



**z-Scores: S2 - Mn**



**En-Scores: S2 - Mn**

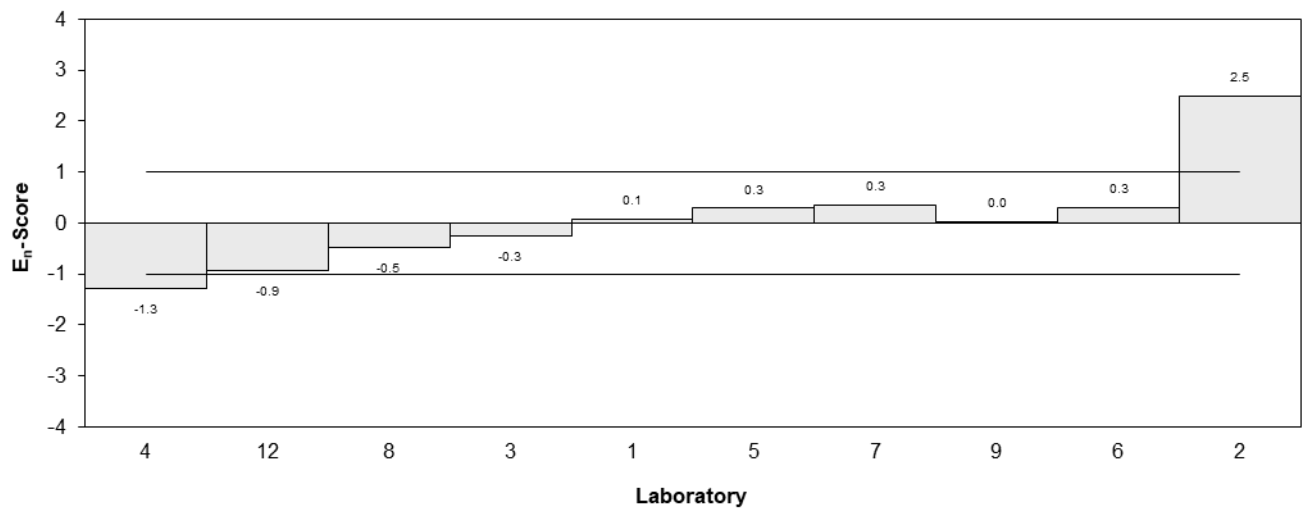


Figure 45

Table 49

**Sample Details**

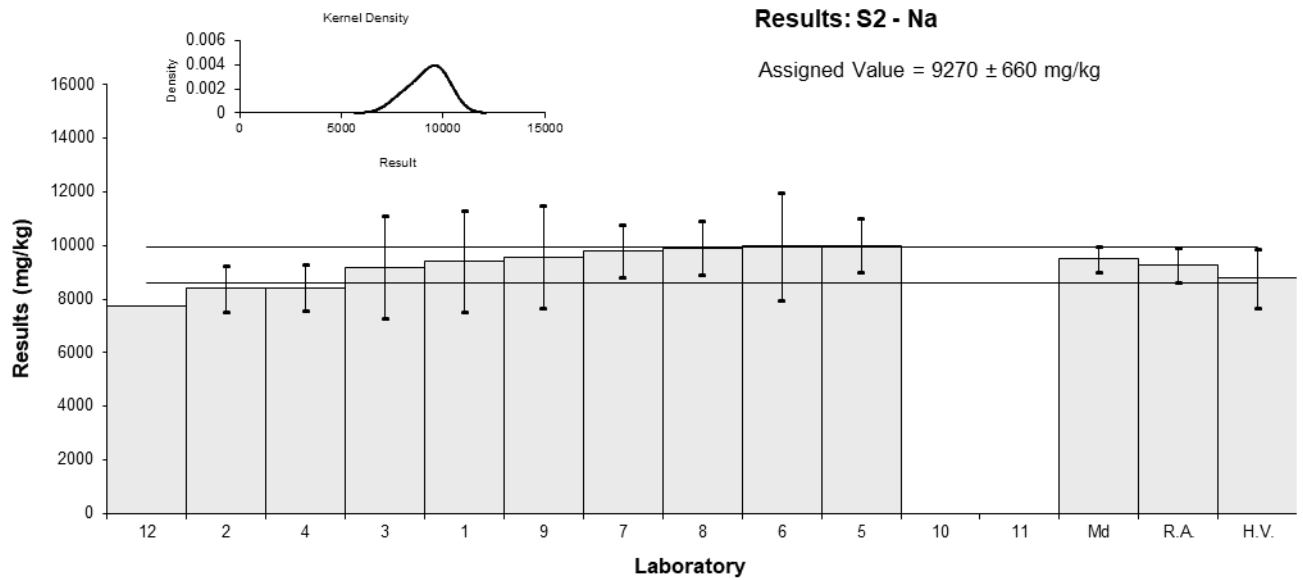
<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Na
<b>Units</b>	mg/kg

**Participant Results**

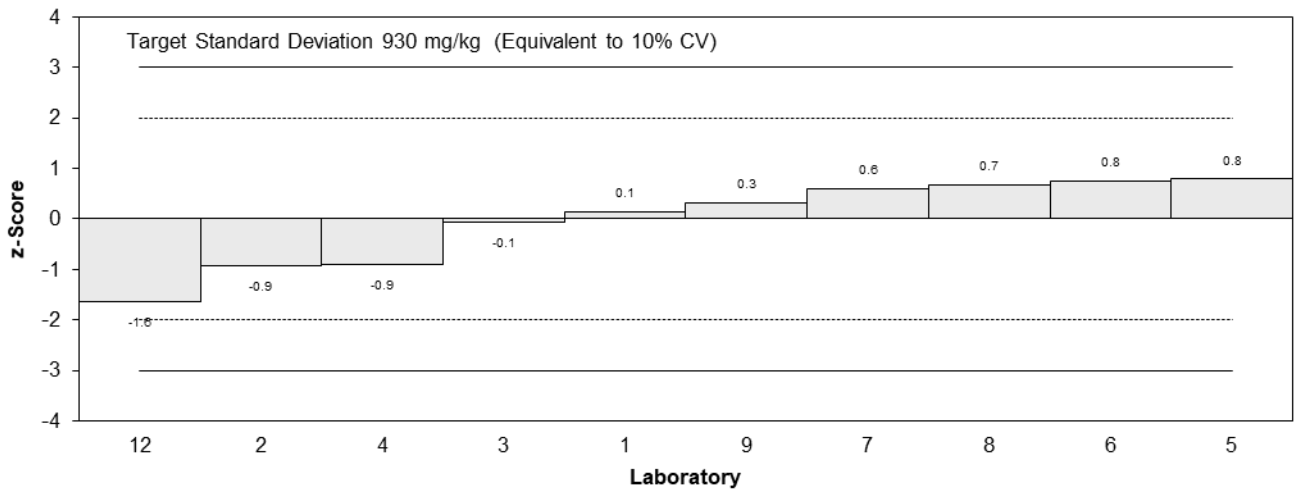
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	9404	1880	0.14	0.07
2	8400	850	-0.94	-0.81
3	9200	1900	-0.08	-0.03
4	8430	850	-0.91	-0.78
5	10000	1000	0.79	0.61
6	9969	1994	0.75	0.33
7	9820	982	0.59	0.46
8	9900	1000	0.68	0.53
9	9570	1910	0.32	0.15
10	NT	NT		
11	NT	NT		
12	7750	NR	-1.64	-2.30

**Statistics**

<b>Assigned Value</b>	9270	660
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	8800	1100
<b>Robust Average</b>	9270	660
<b>Median</b>	9490	470
<b>Mean</b>	9240	
<b>N</b>	10	
<b>Max.</b>	10000	
<b>Min.</b>	7750	
<b>Robust SD</b>	830	
<b>Robust CV</b>	9%	



**z-Scores: S2 - Na**



**En-Scores: S2 - Na**

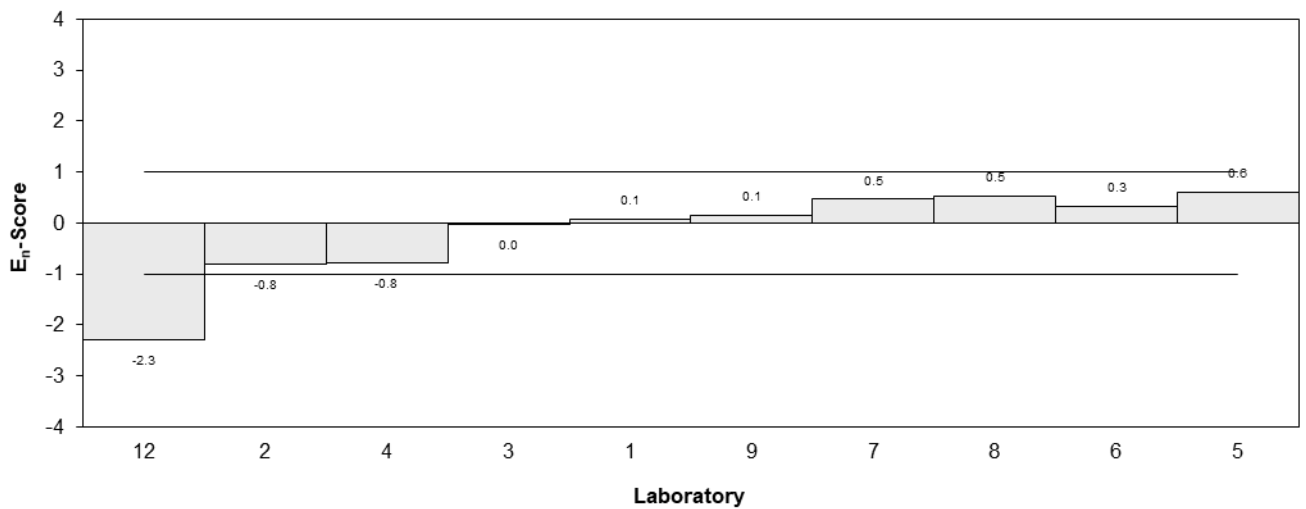


Figure 46



Table 50

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Ni
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	0.49	0.10	0.17	0.14
2	0.45	0.1	-0.25	-0.21
3	0.4	0.2	-0.78	-0.36
4	0.51	0.10	0.38	0.32
5	0.44	0.04	-0.36	-0.53
6	0.218	0.044	-2.70	-3.84
7	0.487	0.049	0.14	0.19
8	< 0.5	0.095		
9	NT	NT		
10	<1	NR		
11	NT	NT		
12	0.54	0.09	0.70	0.64

**Statistics**

<b>Assigned Value*</b>	0.474	0.050
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.533	0.080
<b>Robust Average</b>	0.459	0.060
<b>Median</b>	0.469	0.043
<b>Mean</b>	0.442	
<b>N</b>	8	
<b>Max.</b>	0.54	
<b>Min.</b>	0.218	
<b>Robust SD</b>	0.068	
<b>Robust CV</b>	15%	

\*Robust Average excluding laboratory 6.

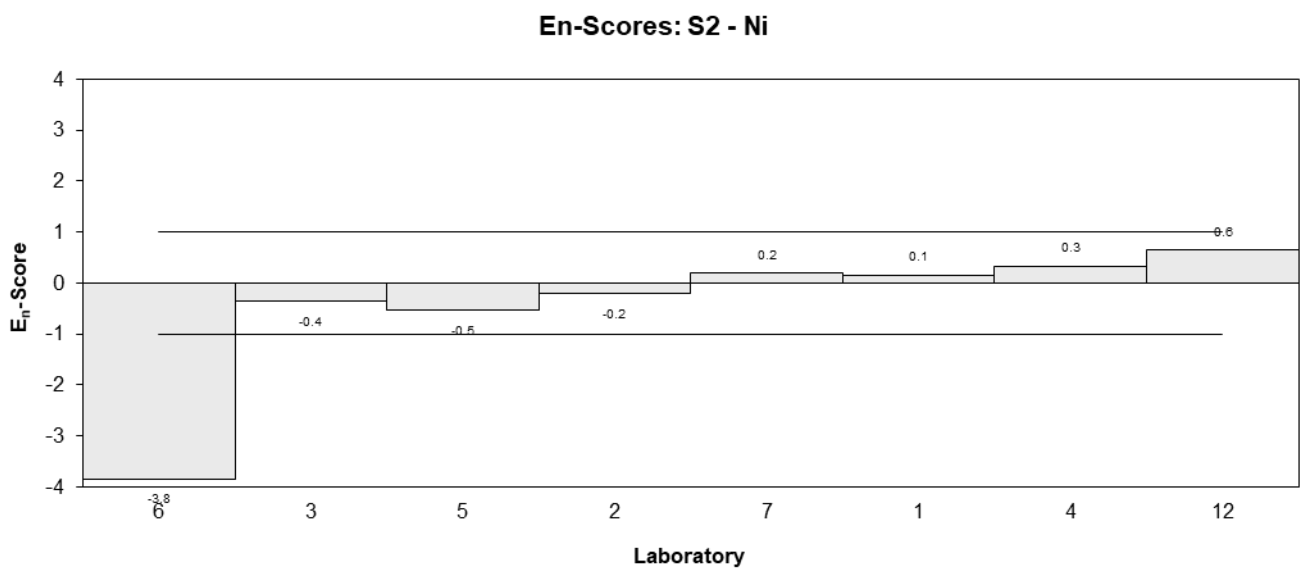
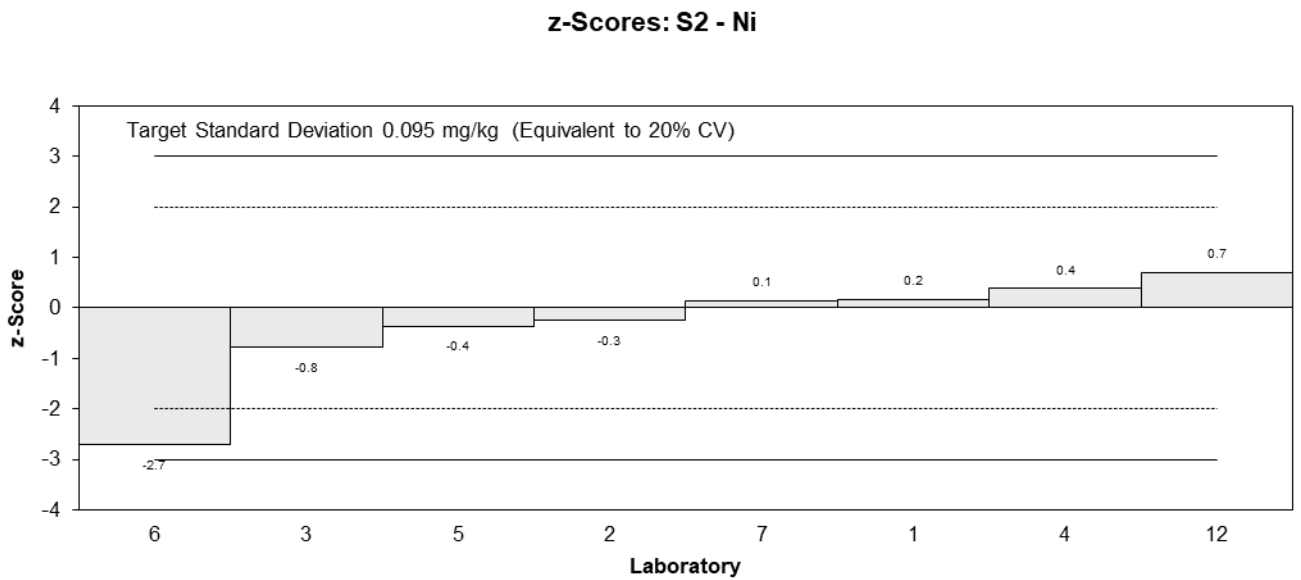
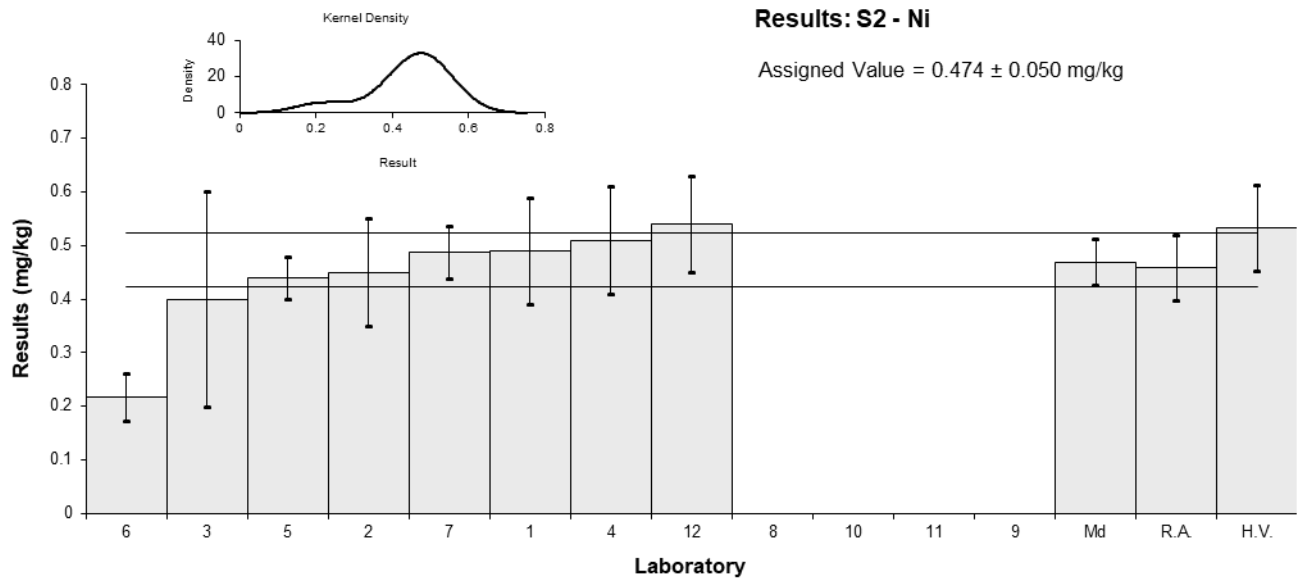


Figure 47

Table 51

**Sample Details**

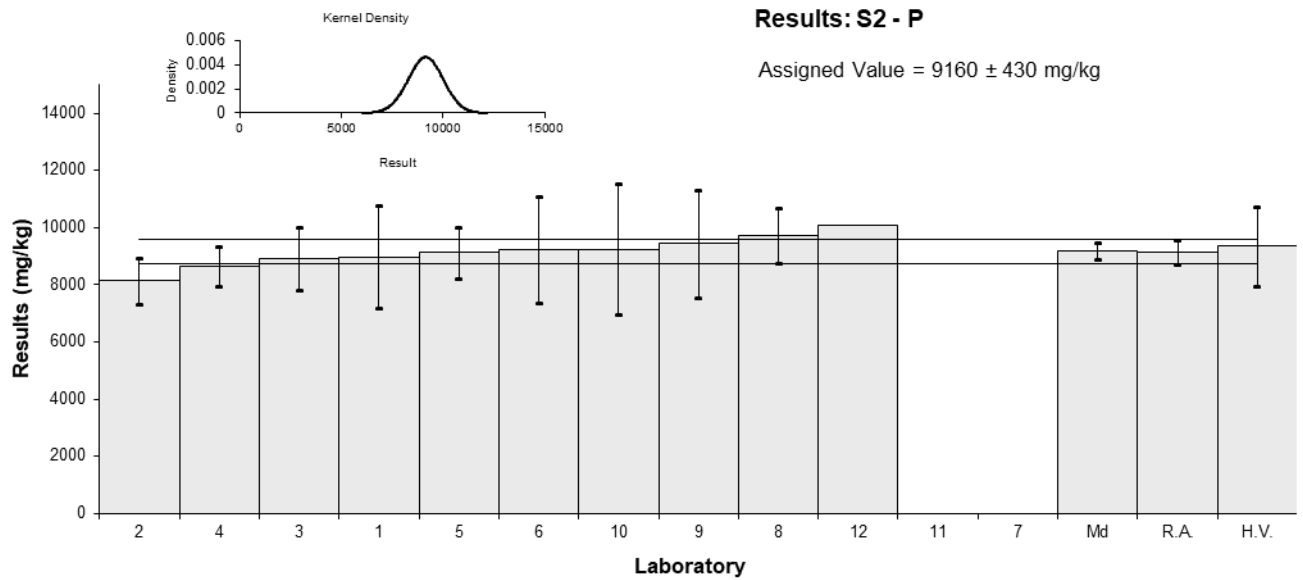
<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	P
<b>Units</b>	mg/kg

**Participant Results**

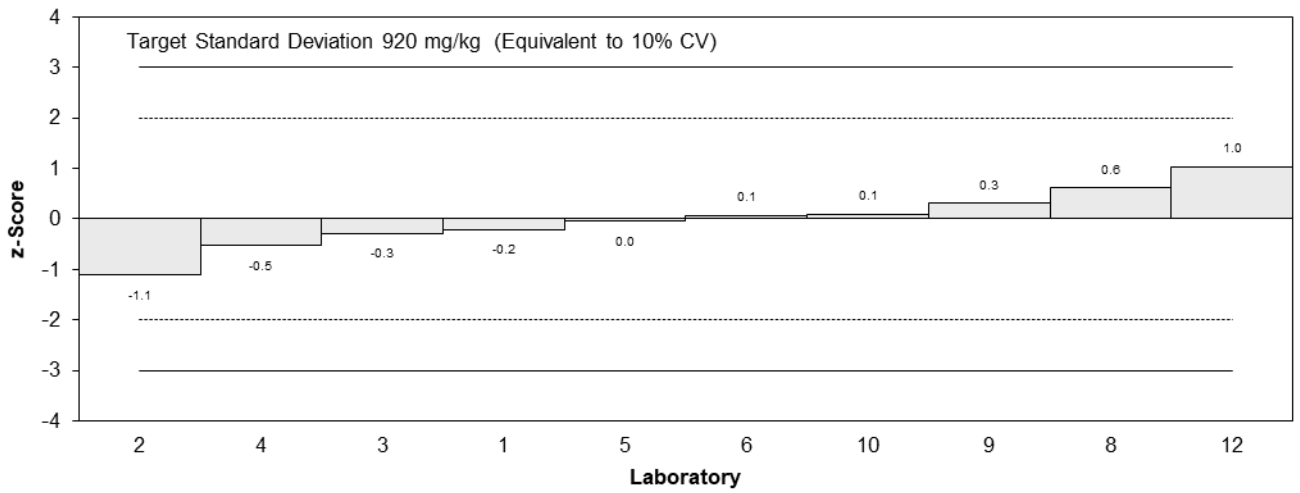
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	8970	1790	-0.21	-0.10
2	8140	820	-1.11	-1.10
3	8900	1100	-0.28	-0.22
4	8670	695	-0.53	-0.60
5	9120	912	-0.04	-0.04
6	9226	1845	0.07	0.03
7	NT	NT		
8	9720	980	0.61	0.52
9	9440	1890	0.31	0.14
10	9250	2300	0.10	0.04
11	NT	NT		
12	10100	NR	1.03	2.19

**Statistics**

<b>Assigned Value</b>	9160	430
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	9400	1400
<b>Robust Average</b>	9160	430
<b>Median</b>	9170	290
<b>Mean</b>	9150	
<b>N</b>	10	
<b>Max.</b>	10100	
<b>Min.</b>	8140	
<b>Robust SD</b>	550	
<b>Robust CV</b>	6%	



**z-Scores: S2 - P**



**En-Scores: S2 - P**

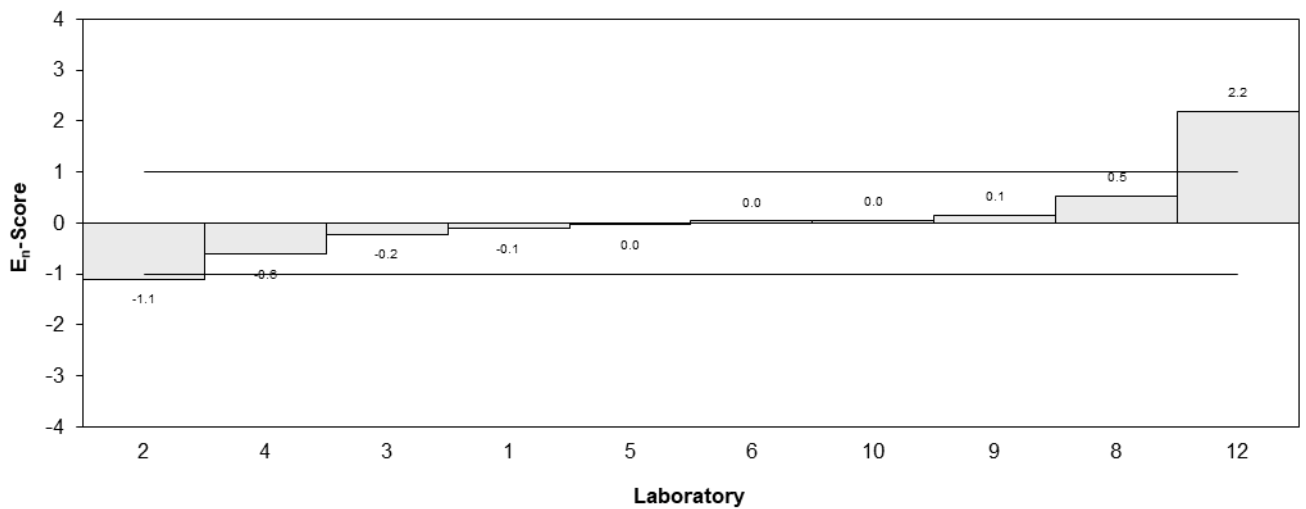


Figure 48

Table 52

## Sample Details

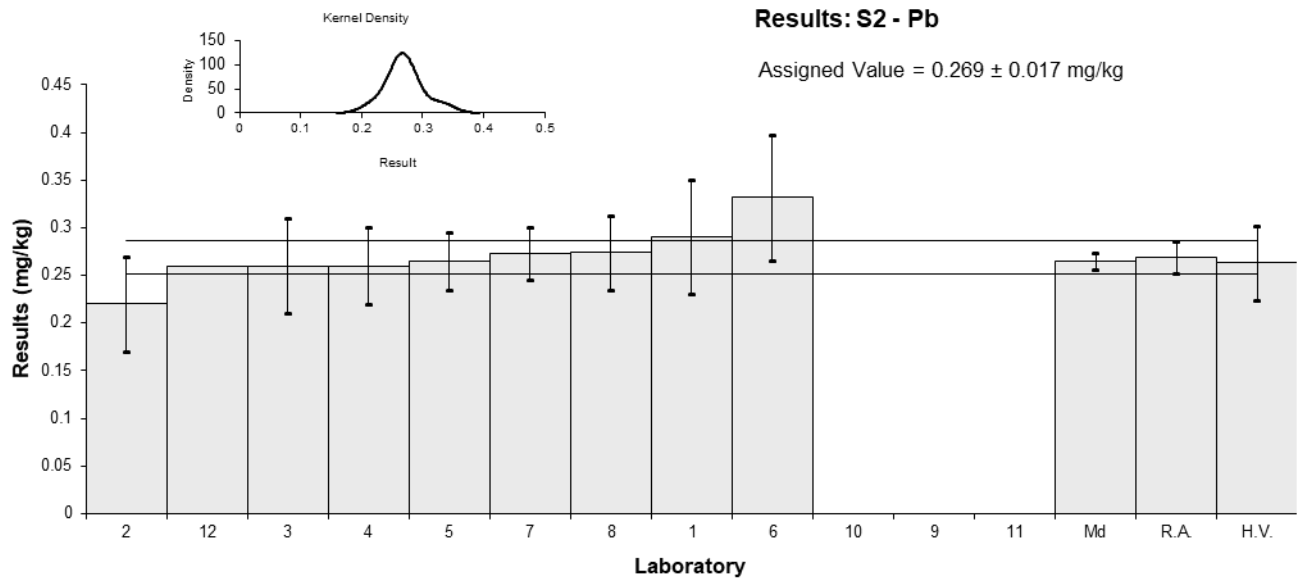
<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Pb
<b>Units</b>	mg/kg

## Participant Results

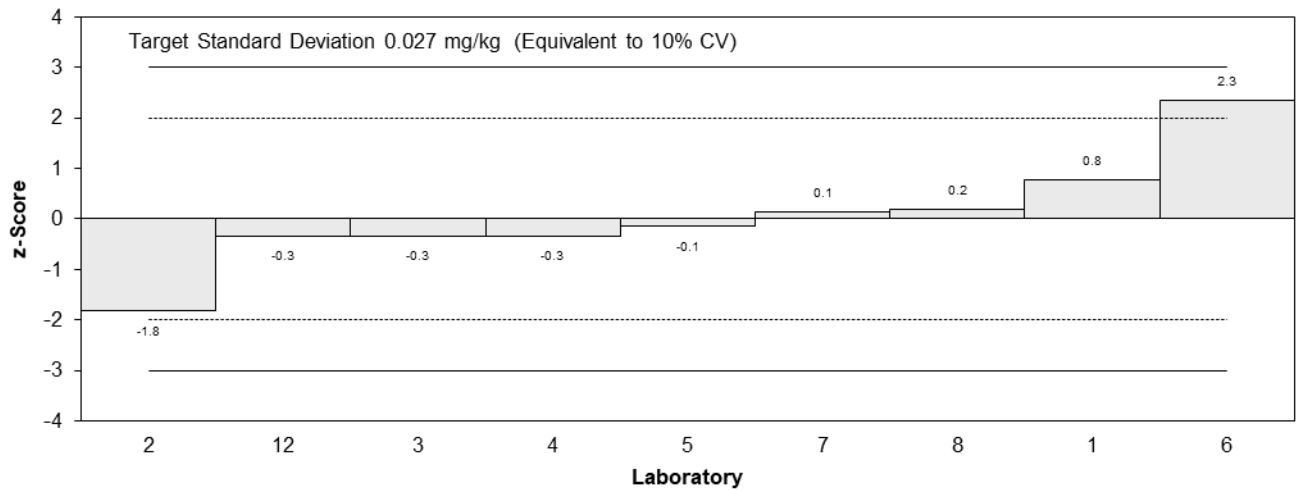
Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	0.29	0.06	0.78	0.34
2	0.22	0.05	-1.82	-0.93
3	0.26	0.05	-0.33	-0.17
4	0.26	0.04	-0.33	-0.21
5	0.265	0.03	-0.15	-0.12
6	0.332	0.066	2.34	0.92
7	0.273	0.027	0.15	0.13
8	0.274	0.039	0.19	0.12
9	<1	NR		
10	<1	NR		
11	NT	NT		
12	0.26	NR	-0.33	-0.53

## Statistics

<b>Assigned Value</b>	0.269	0.017
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.263	0.039
<b>Robust Average</b>	0.269	0.017
<b>Median</b>	0.265	0.009
<b>Mean</b>	0.270	
<b>N</b>	9	
<b>Max.</b>	0.332	
<b>Min.</b>	0.22	
<b>Robust SD</b>	0.021	
<b>Robust CV</b>	7.7%	



**z-Scores: S2 - Pb**



**En-Scores: S2 - Pb**

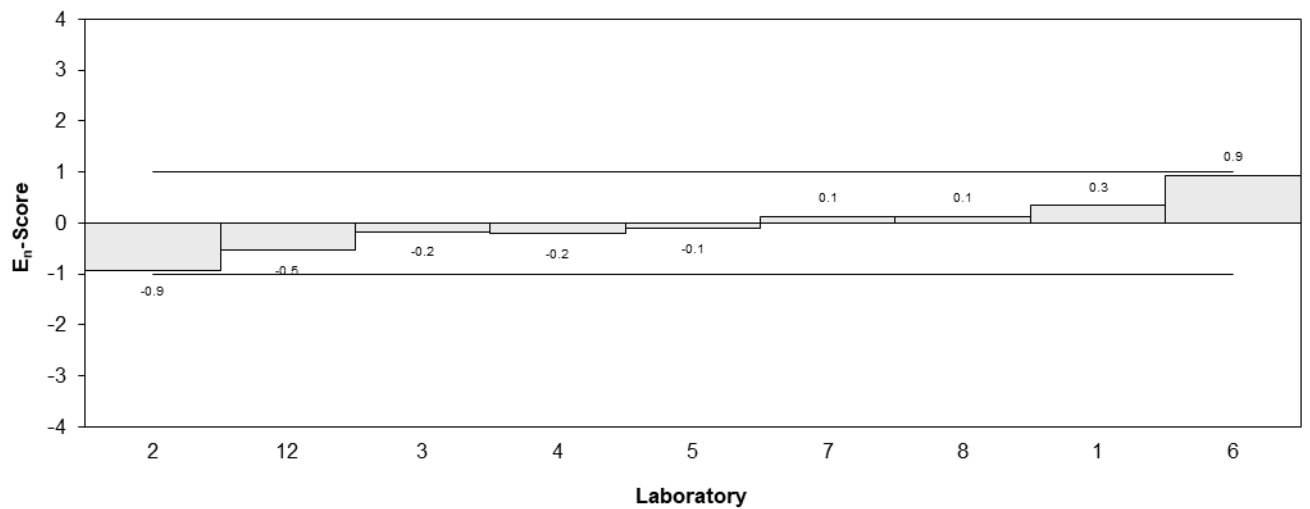


Figure 49

Table 53

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Se
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	3.9	0.78	-0.59	-0.44
2	3.89	0.5	-0.61	-0.64
3	3.8	0.9	-0.75	-0.50
4	4.28	0.54	0.00	0.00
5	4.65	0.465	0.58	0.64
6	4.17	0.834	-0.17	-0.12
7	4.88	0.488	0.93	1.00
8	4.48	0.63	0.31	0.28
9	4.46	0.891	0.28	0.19
10	7.2	1.8	4.55	1.59
11	NT	NT		
12	7.72	2.2	5.36	1.54

**Statistics**

<b>Assigned Value*</b>	4.28	0.35
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	4.80	0.72
<b>Robust Average</b>	4.51	0.52
<b>Median</b>	4.46	0.42
<b>Mean</b>	4.86	
<b>N</b>	11	
<b>Max.</b>	7.72	
<b>Min.</b>	3.8	
<b>Robust SD</b>	0.70	
<b>Robust CV</b>	15%	

\*Robust Average excluding laboratories 10 and 12.

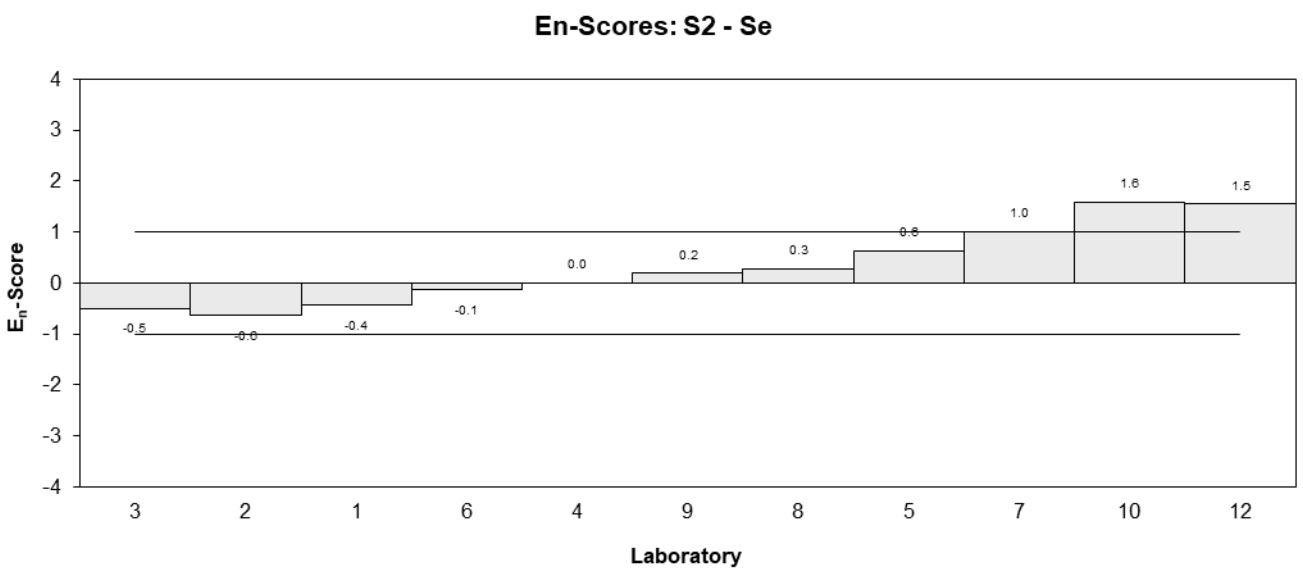
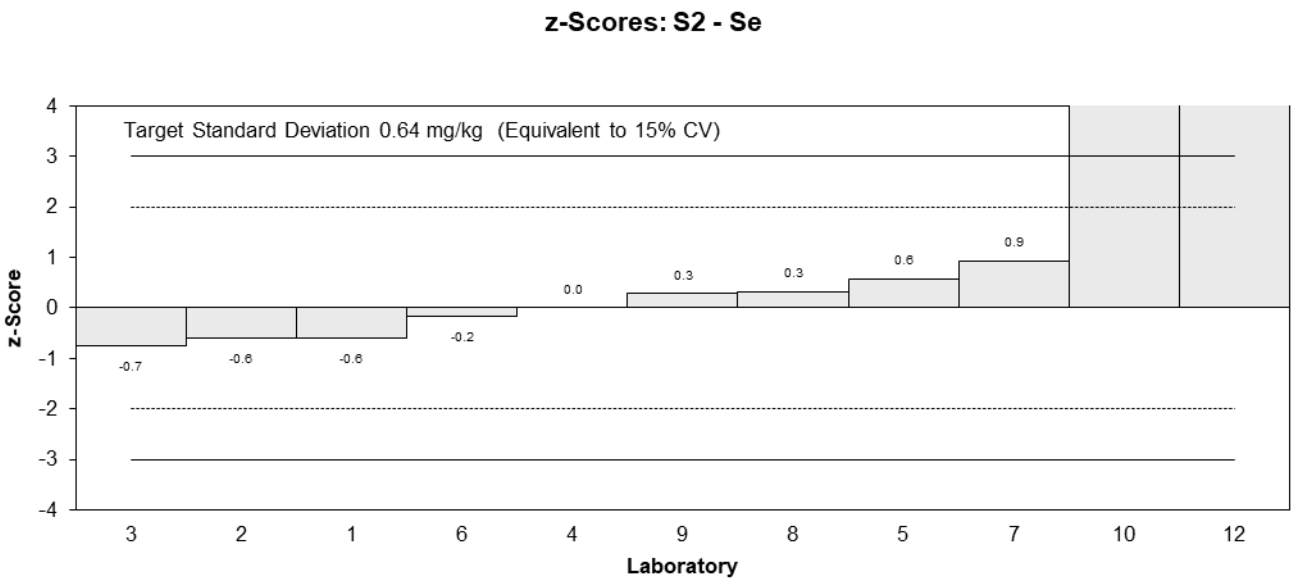
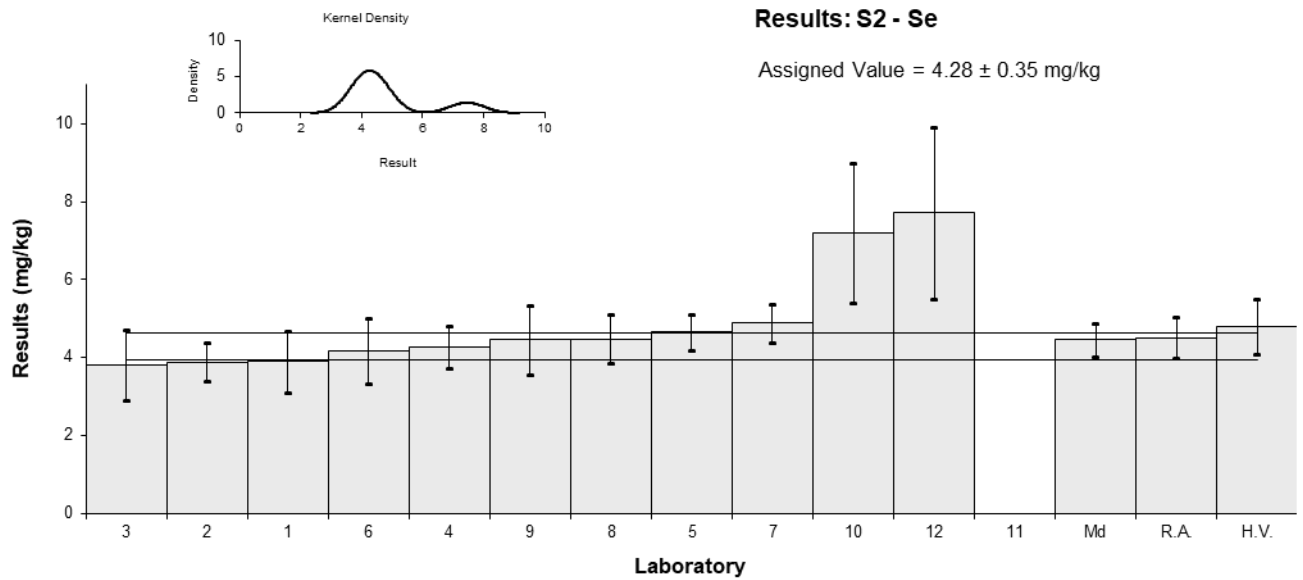


Figure 50



Table 54

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Sn
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	0.29	0.06
2	0.31	0.04
3	NT	NT
4	NT	NT
5	NR	NR
6	0.389	0.078
7	NT	NT
8	< 0.5	0.095
9	NT	NT
10	NT	NT
11	NT	NT
12	<0.5	NR

**Statistics\***

<b>Assigned Value</b>	Not Set	
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.280	0.042
<b>Median</b>	0.310	0.074
<b>Mean</b>	0.330	
<b>N</b>	3	
<b>Max.</b>	0.389	
<b>Min.</b>	0.29	

Results: S2 - Sn

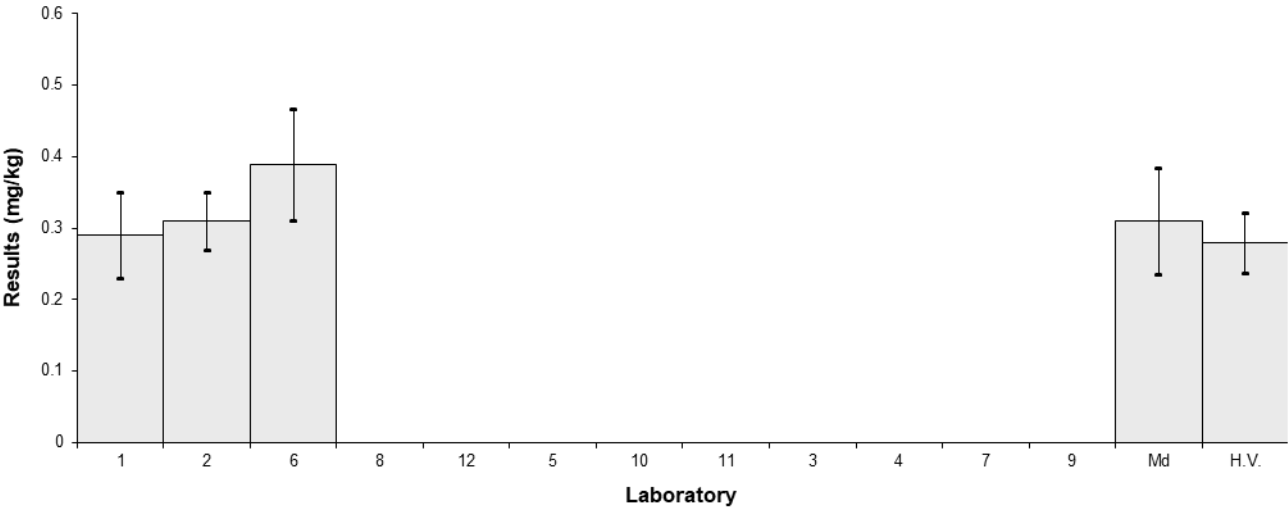


Figure 51

Table 55

## Sample Details

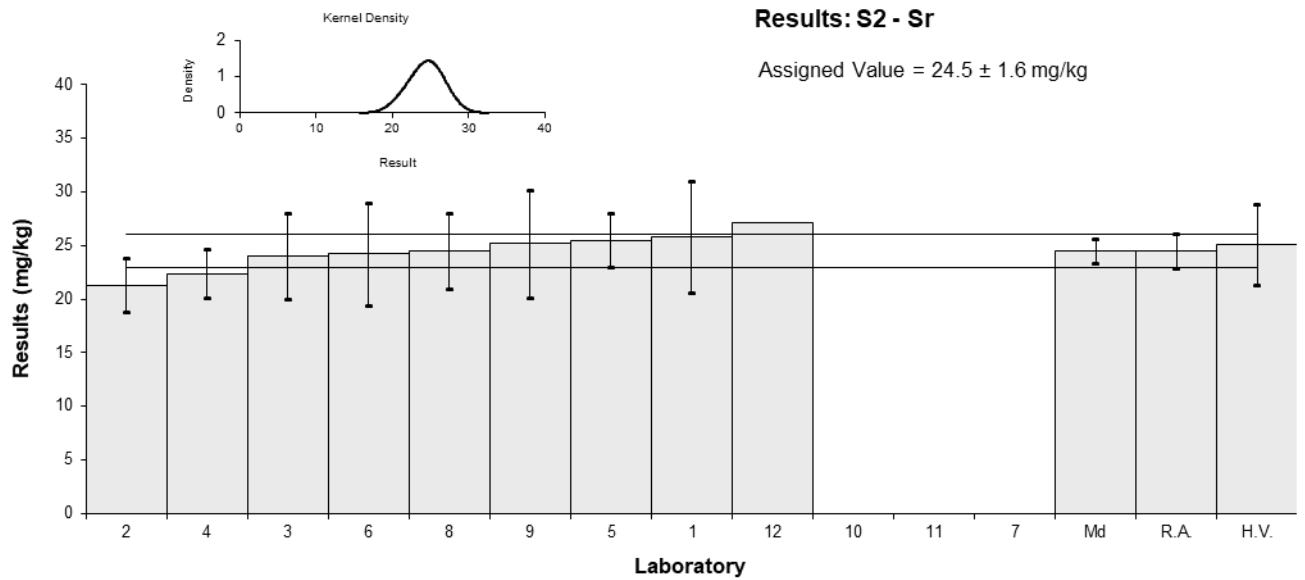
<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Sr
<b>Units</b>	mg/kg

## Participant Results

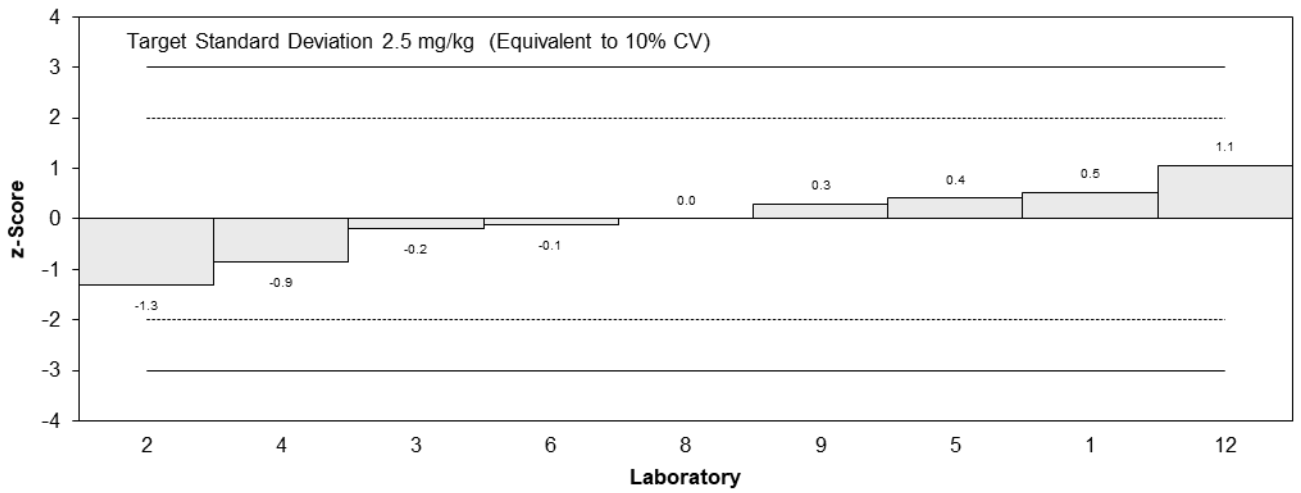
Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	25.8	5.2	0.53	0.24
2	21.3	2.5	-1.31	-1.08
3	24	4	-0.20	-0.12
4	22.4	2.25	-0.86	-0.76
5	25.5	2.55	0.41	0.33
6	24.20	4.84	-0.12	-0.06
7	NT	NT		
8	24.5	3.5	0.00	0.00
9	25.2	5.03	0.29	0.13
10	NT	NT		
11	NT	NT		
12	27.1	NR	1.06	1.63

## Statistics

<b>Assigned Value</b>	24.5	1.6
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	25.1	3.8
<b>Robust Average</b>	24.5	1.6
<b>Median</b>	24.5	1.1
<b>Mean</b>	24.4	
<b>N</b>	9	
<b>Max.</b>	27.1	
<b>Min.</b>	21.3	
<b>Robust SD</b>	1.9	
<b>Robust CV</b>	7.9%	



**z-Scores: S2 - Sr**



**En-Scores: S2 - Sr**

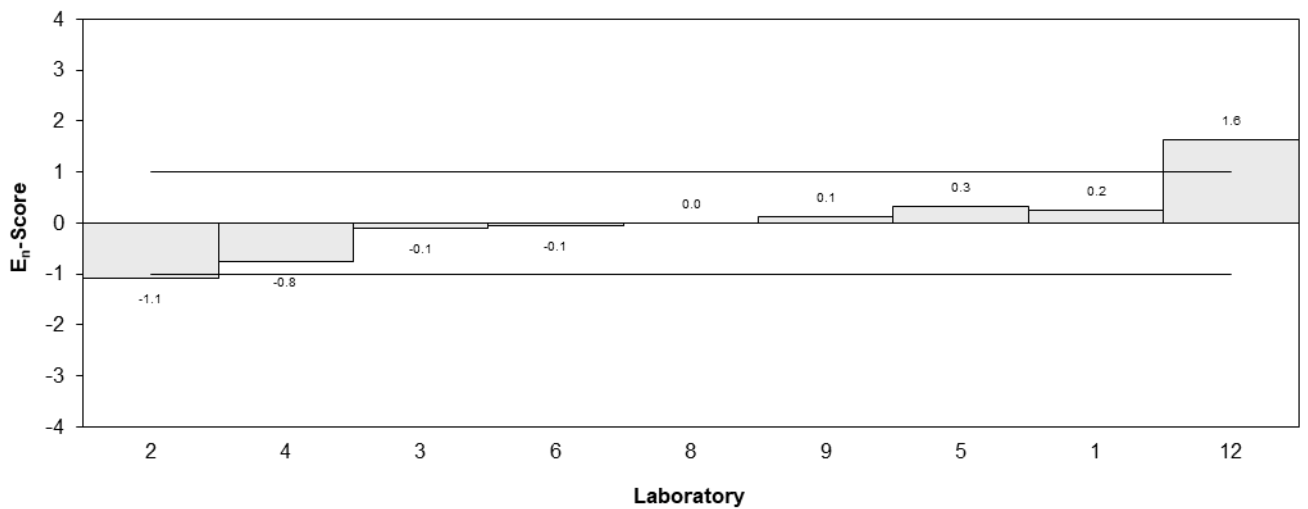


Figure 52

Table 56

**Sample Details**

<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	V
<b>Units</b>	mg/kg

**Participant Results**

<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>
1	0.046	0.01
2	0.34	0.04
3	0.04	0.02
4	0.05	0.01
5	0.044	0.004
6	<0.1	0.010
7	NT	NT
8	< 0.3	0.048
9	NT	NT
10	<1	NR
11	NT	NT
12	<0.5	NR

**Statistics\***

<b>Assigned Value</b>	Not Set	
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	0.0584	0.0088
<b>Median</b>	0.0450	0.0071
<b>Mean</b>	0.0450	
<b>N</b>	4	
<b>Max.</b>	0.05	
<b>Min.</b>	0.04	

\*Laboratory 2 was excluded from statistical calculation (extreme outlier).

Results: S2 - V

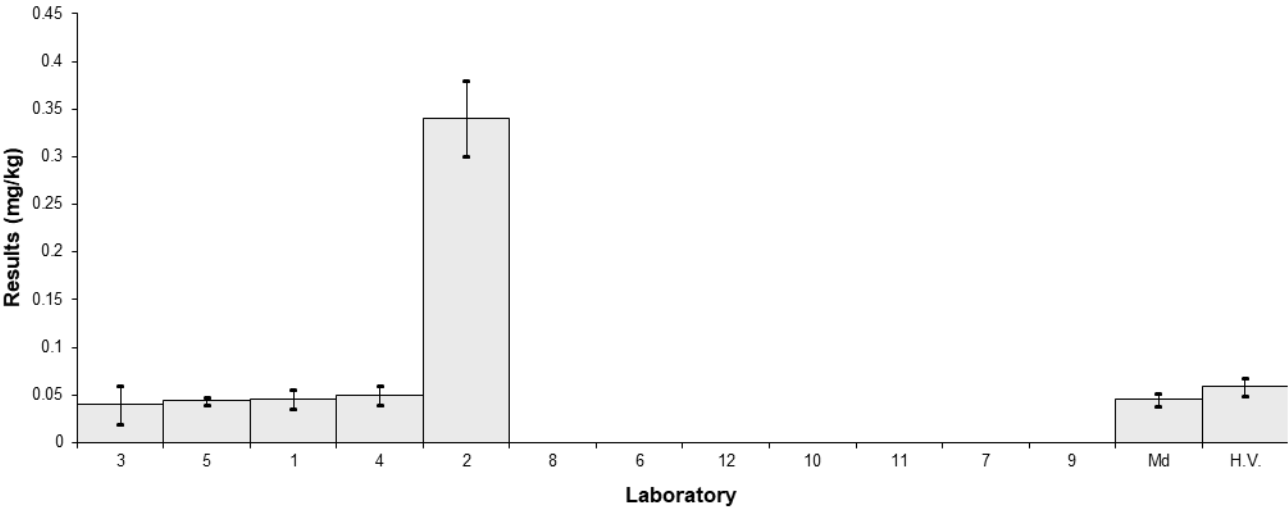


Figure 53

Table 57

**Sample Details**

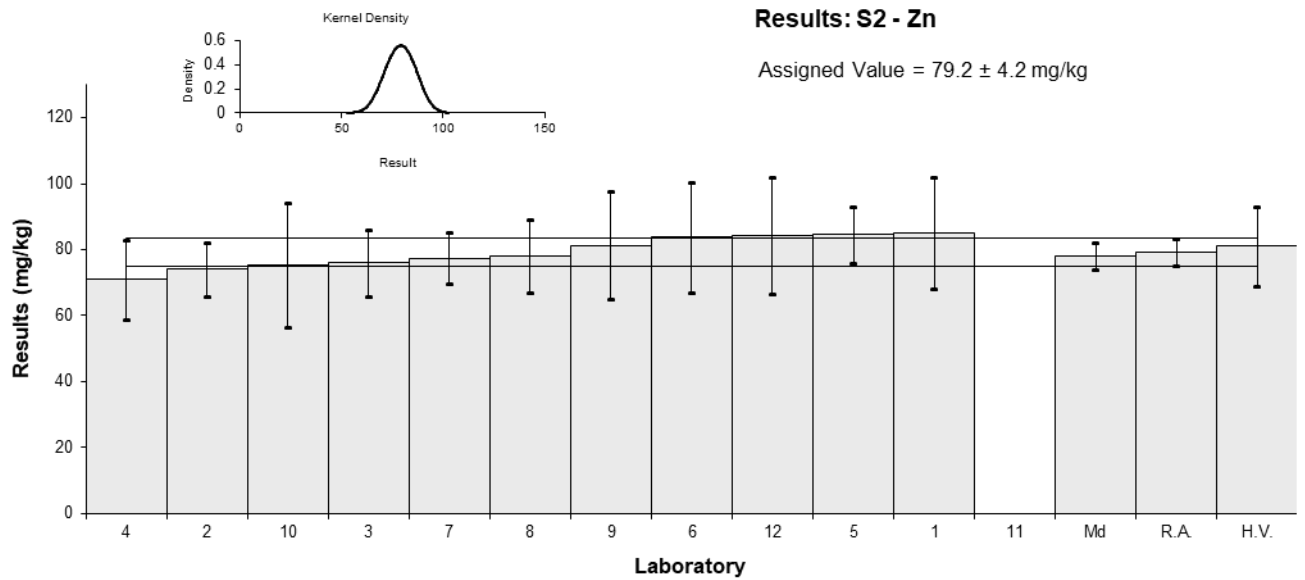
<b>Sample No.</b>	S2
<b>Matrix.</b>	Biota
<b>Analyte.</b>	Zn
<b>Units</b>	mg/kg

**Participant Results**

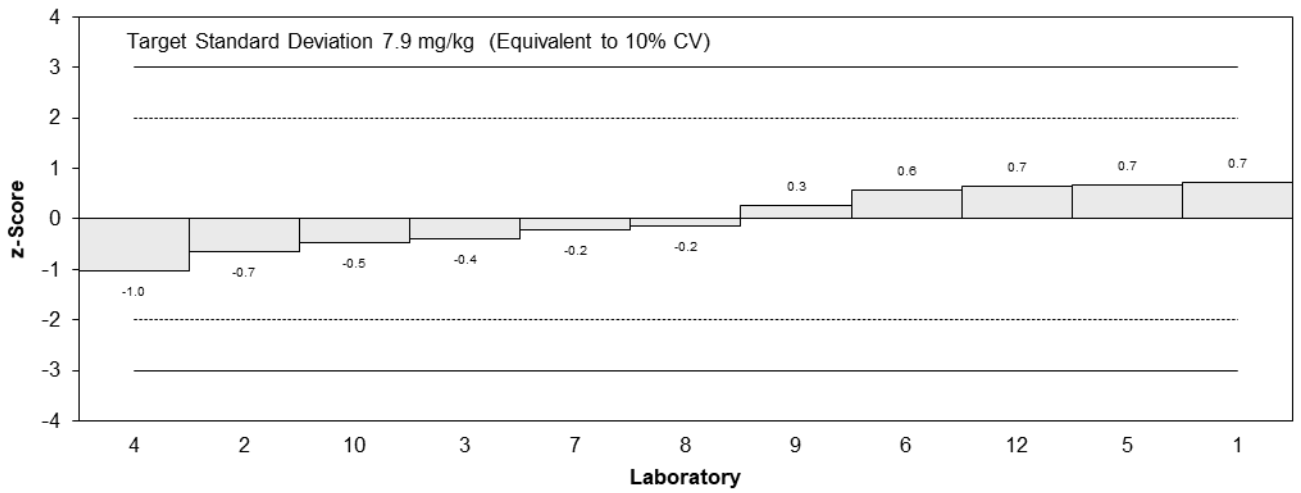
<b>Lab Code</b>	<b>Result</b>	<b>Uncertainty</b>	<b>z-Score</b>	<b>E<sub>n</sub>-Score</b>
1	85	17	0.73	0.33
2	74.0	8.0	-0.66	-0.58
3	76	10	-0.40	-0.30
4	71	12	-1.04	-0.64
5	84.5	8.45	0.67	0.56
6	83.73	16.75	0.57	0.26
7	77.4	7.74	-0.23	-0.20
8	78	11	-0.15	-0.10
9	81.3	16.3	0.27	0.12
10	75.4	18.9	-0.48	-0.20
11	NT	NT		
12	84.4	17.7	0.66	0.29

**Statistics**

<b>Assigned Value</b>	79.2	4.2
<b>Spike</b>	Not Spiked	
<b>Homogeneity Value</b>	81	12
<b>Robust Average</b>	79.2	4.2
<b>Median</b>	78.0	4.0
<b>Mean</b>	79.2	
<b>N</b>	11	
<b>Max.</b>	85	
<b>Min.</b>	71	
<b>Robust SD</b>	5.5	
<b>Robust CV</b>	7%	



**z-Scores: S2 - Zn**



**En-Scores: S2 - Zn**

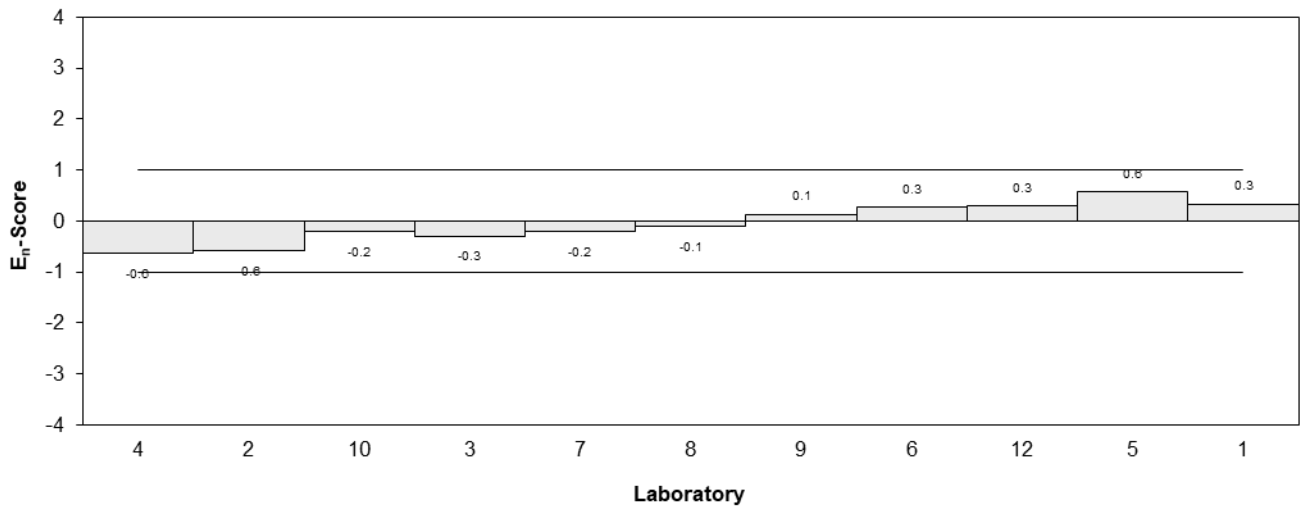


Figure 54



## 7 DISCUSSION OF RESULTS

### 7.1 Assigned Value and Traceability

**Assigned Values** were the robust average of participants' results except for Fe and Ni in S1. The robust averages used as assigned values and their associated expanded uncertainties were calculated using the procedure described in ISO13528:2015(E) 'Statistical methods for use in proficiency testing by interlaboratory comparisons'. Results less than 50% and more than 150% of the robust average were investigated and then removed before calculation of the assigned value.<sup>6</sup> Appendix 2 sets out the calculation of the robust average of As in Sample S1 and its associated uncertainty.

Assigned values for Fe and Ni in S1 were reference values from measurements made using IDMS (Appendix 3).

No assigned value was set for Be, Cs, Ga, Hg, La, Rb, Sn, Tl and U in S1 and Li, Sn and V in S2 because too few participants reported results for these elements. No assigned value was set for Al in S1 either, because the results were not compatible with each other. However, participants may still compare their reported results for these elements with the robust average of participants' results and/or the homogeneity value. Descriptive statistics for these elements are presented in Chapter 5.

**Traceability** of the reference values for Fe and Cr in S2 rely on gravimetric sample preparation and elemental quantification by ICP-MS. Gravimetric measurements were calibrated using Australian standards for mass and are traceable to the SI unit for mass (kg). ICP-MS measurements calibrated with isotope dilution are traceable to the SI units for mass (kg) through the primary calibration standard certified by NIST (USA) and the SI unit for amount of substance (mol) through data for isotopic composition and relative atomic mass. Isotopic compositions are traceable to IUPAC published data.

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. Of 405 numerical results, 394 (97%) were reported with an expanded measurement uncertainty, indicating that the majority of laboratories have addressed this requirement of ISO/IEC 17025.<sup>8</sup> The magnitude of these expanded uncertainties was within the range 6.2% to 200% of the reported value. The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 4.

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.<sup>9-14</sup>

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 (Figure 2 to 54). As a simple rule of thumb, when the uncertainty estimate is smaller than uncertainty of the assigned value, or larger than the uncertainty of the assigned value plus twice the target standard deviation, then this should be reviewed as suspect.

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies only, can also be used to estimate the

uncertainty of their measurement results.<sup>10</sup> An example of estimating measurement uncertainty using proficiency testing data only is given in Appendix 3.

Laboratories 4, 8, 10 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.<sup>1</sup>

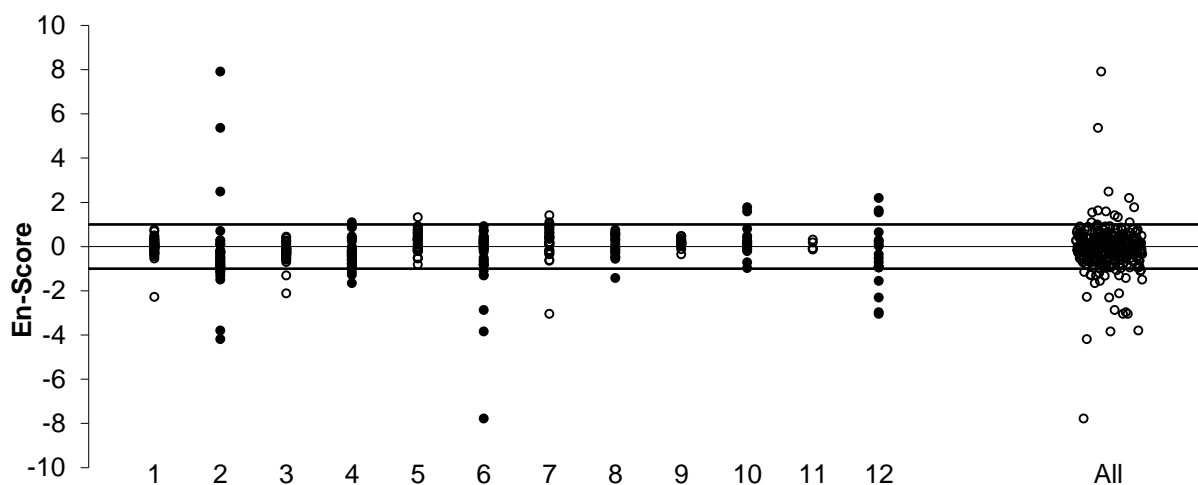
In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of  $14.74 \pm 2.95$  mg/kg, it is better to report  $14.7 \pm 3.0$  mg/kg or instead of  $5.99 \pm 0.599$  mg/kg, it is better to report  $5.99 \pm 0.60$  mg/kg.<sup>1</sup>

## 7.2 E<sub>n</sub>-score

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

The dispersal of participants' E<sub>n</sub>-scores is graphically presented in Figure 55. Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E<sub>n</sub>-score.

Of 355 results for which E<sub>n</sub>-scores were calculated, 318 (90%) 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.



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

Figure 55 E<sub>n</sub>-Score Dispersal by Laboratory

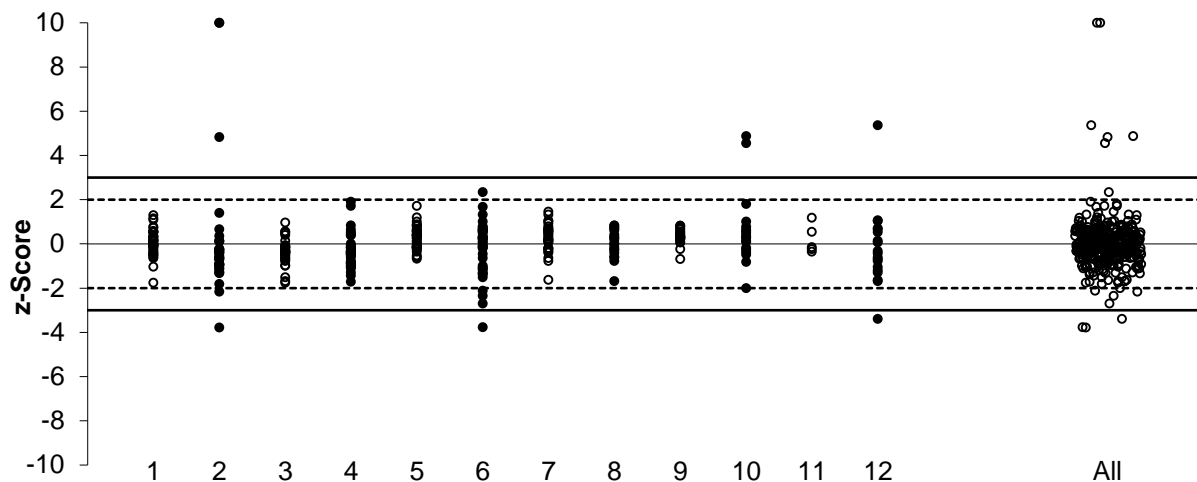
## 7.3 z-Score

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<sup>7</sup> and the between laboratory coefficient of variation resulted in this study are presented for comparison in Table 58.

The dispersal of participants' z-scores is presented in Figure 56 (by laboratory code) and in Figure 57 (by test). Of 355 results for which z-scores were calculated, 341 (96%) returned a satisfactory score of  $|z| \leq 2.0$  and 5 (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 56 z-Score Dispersal by Laboratory

Nine laboratories analysed both samples. **Laboratories 1, 3 and 6** reported results for all tests for which a z-scores were calculated (40).

Summary of participants' performance is presented in Figure 58. **Laboratories 1 and 3** returned the highest number of satisfactory z scores (40 out of 40 reported). All results reported by **laboratories 5** (39), **4** (39), **7** (32), **9** (25), **8** (19), and **11** (5) also returned satisfactory z scores.

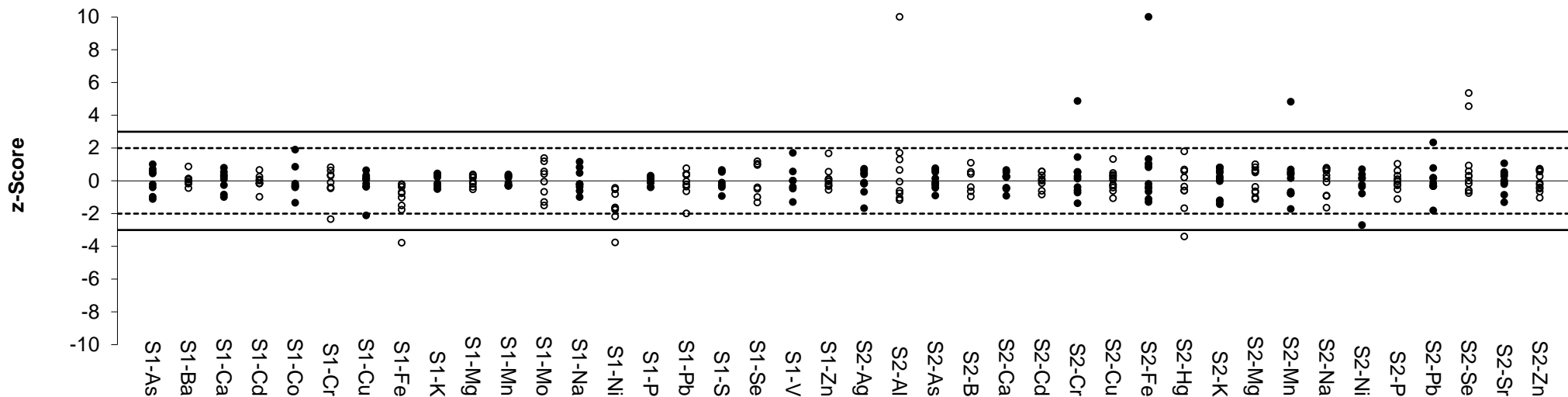
**Laboratory 1** returned the highest number of satisfactory  $E_n$  scores (39 out of 40). All results reported by **laboratories 9** (25), and **11** (5) returned satisfactory  $E_n$  scores.

Table 58 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 CV)
S1	Al	Not Set	37%	NA	Not Set
S1	As	0.703	14%	17%	15%
S1	Ba	17.3	2.8%	10%	10%
S1	Be	Not Set	35%	NA	Not Set
S1	Ca	5550	7.3%	4.4%	10%
S1	Cd	0.122	3.9%	22%	10%
S1	Co	0.290	22%	19%	20%
S1	Cr	9.6	14%	11%	20%
S1	Cs	Not Set	NA	NA	Not Set
S1	Cu	9.87	4.4%	11%	10%
S1	Fe	5950	8.8%	4.3%	10%
S1	Ga	Not Set	NA	NA	Not Set
S1	Hg	Not Set	22%	NA	Not Set
S1	K	31500	4.6%	3.4%	10%
S1	La	Not Set	NA	NA	Not Set
S1	Mg	2080	3.9%	5.1%	10%
S1	Mn	155	3.4%	7.5%	10%
S1	Mo	0.483	12%	18%	10%
S1	Na	2080	8.4%	5.1%	10%
S1	Ni	5.14	21%	13%	20%

Sample	Test	Assigned value (mg/kg)	Between Laboratories CV*	Thompson/Horwitz CV	Target SD (as CV)
S1	P	3220	3.2%	4.7%	10%
S1	Pb	2.50	6.1%	14%	10%
S1	Rb	Not Set	NA	NA	Not Set
S1	S	2570	6.8%	4.9%	10%
S1	Se	0.218	24%	20%	20%
S1	Sn	Not Set	26%	NA	Not Set
S1	Tl	Not Set	14%	NA	Not Set
S1	U	Not Set	6%	NA	Not Set
S1	V	10.5	9.8%	11%	10%
S1	Zn	27.5	4.6%	9.7%	10%
S2	Ag	0.401	10%	18%	15%
S2	Al	7.1	25%	12%	20%
S2	As	62.1	8.9%	8.6%	15%
S2	B	2.71	18%	14%	20%
S2	Ca	2300	12%	5%	20%
S2	Cd	0.0426	5.9%	22%	10%
S2	Cr	0.76	19%	17%	20%
S2	Cu	16.5	6%	10%	10%
S2	Fe	21.1	16%	10%	15%
S2	Hg	0.125	24%	22%	20%
S2	K	15700	15%	3.7%	15%
S2	Li	Not Set	36%	NA	Not Set
S2	Mg	1560	9.4%	5.3%	10%
S2	Mn	0.857	11%	16%	10%
S2	Na	9270	9%	4%	10%
S2	Ni	0.474	11%	18%	20%
S2	P	9160	6%	4.1%	10%
S2	Pb	0.269	7.7%	19%	10%
S2	Se	4.28	9.9%	13%	15%
S2	Sn	Not Set	18%	NA	Not Set
S2	Sr	24.5	7.9%	9.9%	10%
S2	V	Not Set	10%	NA	Not Set
S2	Zn	79.2	7%	8.3%	10%

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



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

Figure 57 z-Score Dispersal by Analyte

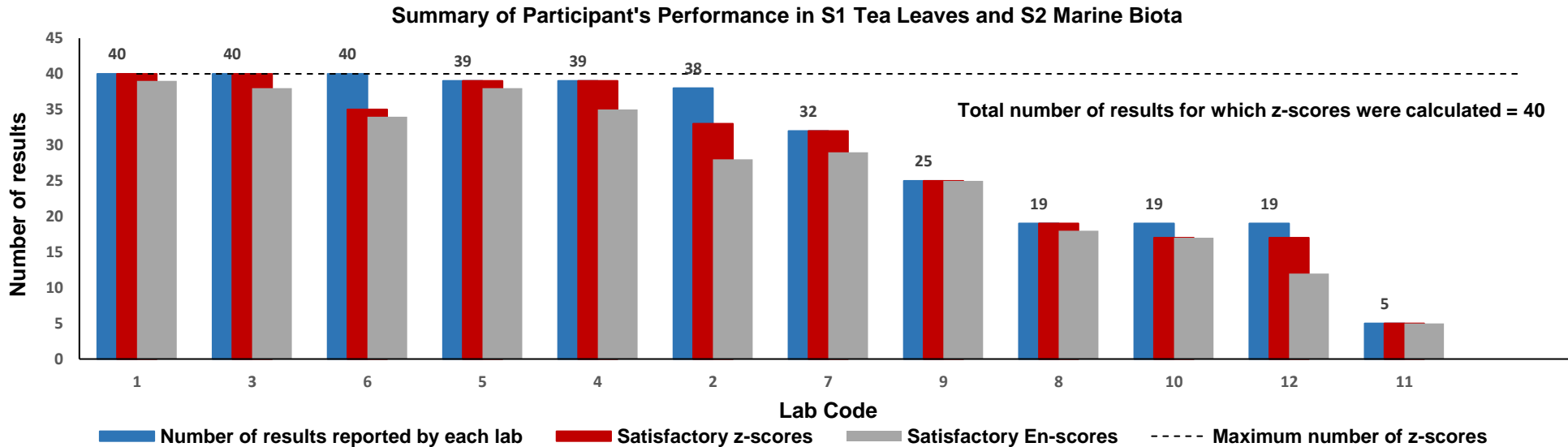


Figure 58 Summary of Participants' Performance

Table 59 Summary of Participants' Results and Performance in S1

Lab Code	Al (mg/kg)	As (mg/kg)	Ba (mg/kg)	Be (mg/kg)	Ca (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cs (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Ga (mg/kg)	Hg (mg/kg)	K (mg/kg)	La (mg/kg)
A.V.	Not Set	0.703	17.3	Not Set	5550	0.122	0.290	9.6	Not Set	9.87	5950	Not Set	Not Set	31500	Not Set
H.V./R.V.	6200	0.729	18.0	0.0571	5860	0.125	0.385	14.2	0.420	10.4	5950	2.88	0.0492	32000	2.42
1	3850	0.66	17.1	0.038	5850	0.122	0.273	9.4	0.25	10.2	5340	2.28	0.037	29900	1.87
2	3025	0.68	17.5	<0.1	5400	0.13	0.27	8.83	NT	10.0	3700	NT	<0.1	30540	NT
3	3600	0.60	17	0.03	5000	0.12	0.28	8.7	NT	9.5	4900	NT	0.03	31000	NT
4	6310	0.75	17.2	0.05	5080	0.11	0.40	11.2	NT	9.7	5490	NT	NR	30000	NT
5	5770	0.81	18.8	NR	5600	0.12	0.34	10.8	NR	10.0	5800	NR	0.026	32800	NR
6	2697	0.585	16.53	0.025	5690	0.125	0.212	5.08	0.150	7.78	5049	3.34	0.042	32518	0.497
7	4110	0.777	NT	NT	5990	0.123	0.267	10.2	NT	9.95	5830	NT	0.031	32200	NT
8	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
9	NT	NT	17.4	NT	5750	NT	NT	NT	NT	10.10	5540	NT	<0.1	32900	NT
10	NT	<2	17.5	<1	NT	<1	<1	10.3	NT	10.5	5730	NT	0.07	NT	NT
11	NT	0.76	NT	NT	NT	0.12	NT	NT	NT	9.52	NT	NT	NT	NT	NT
12	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT

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

Table 59 Summary of Participants' Results and Performance in S1 (continued)

Lab Code	Mg (mg/kg)	Mn (mg/kg)	Mo (mg/kg)	Na (mg/kg)	Ni (mg/kg)	P (mg/kg)	Pb (mg/kg)	Rb (mg/kg)	S (mg/kg)	Se (mg/kg)	Sn (mg/kg)	Tl (mg/kg)	U (mg/kg)	V (mg/kg)	Zn (mg/kg)
A.V.	2080	155	0.483	2080	5.14	3220	2.50	Not Set	2570	0.218	Not Set	Not Set	Not Set	10.5	27.5
H.V./R.V./I.V.	2080	159	0.417	NA	5.14	3290	2.92	40.4	2710	0.217	0.342	0.0393	0.230	12.1	28.3
1	2070	160	0.48	2320	3.33	3301	2.41	54.5	2720	0.196	0.246	0.026	0.158	10.5	27.4
2	1970	151	0.55	1875	2.91	3090	2.59	NT	2330	0.16	0.27	<0.1	0.18	10.1	27.8
3	2000	150	0.41	2000	3.4	3100	2.6	NT	2500	0.26	NT	0.029	0.17	10	26
4	2040	150	0.42	1950	4.7	3180	2.6	NT	2470	0.20	<1.0	NT	NT	12.3	26.6
5	2150	161	0.45	2250	4.6	3190	2.6	NR	2540	0.27	NR	NR	NR	10.5	29
6	2130	153	0.51	2180	1.26	3256	2.49	29.56	2737	0.175	0.394	0.023	0.172	9.14	32.1
7	2120	158	NT	2040	3.46	NT	2.34	NT	NT	0.263	NT	0.022	NT	NT	26.7
8	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
9	2160	159	0.503	2030	NT	3290	2.69	NT	2710	<1	NT	NT	NT	NT	27.7
10	NT	151	<1	NT	4.3	3320	2	NT	NT	<5	NT	<10	NT	11.1	27
11	NT	NT	0.54	NT	NT	NT	2.44	NT	NT	NT	0.27	NT	NT	NT	NT
12	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT

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

Table 60 Summary of Participants' Results and Performance in S2

Lab Code	Ag (mg/kg)	Al (mg/kg)	As (mg/kg)	B (mg/kg)	Ca (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Hg (mg/kg)	K (mg/kg)	Li (mg/kg)
A.V.	0.401	7.1	62.1	2.71	2300	0.0426	0.76	16.5	21.1	0.125	15700	Not Set
H.V.	0.419	NA	67	2.82	2690	0.0441	0.77	16.2	20.4	0.116	16600	0.217
1	0.394	8.9	67	3.3	2550	0.043	0.78	17.1	19.7	0.13	15630	0.26
2	0.36	23	53.7	2.19	1875	<0.1	0.65	15.5	173	<0.1	12760	0.20
3	0.43	7	61	3	2100	0.045	0.7	16	19	0.11	16000	<2
4	0.39	8.0	58.1	2.5	2075	0.039	0.84	15.8	17.6	NT	12300	0.16
5	0.39	9.5	60.5	NR	2410	0.042	0.80	17	20.5	0.11	16900	NR
6	0.438	5.43	60.3	2.36	2407	0.044	0.550	14.74	25.32	0.140	17559	0.207
7	0.424	5.99	68.3	NT	2600	0.045	0.980	18.7	24.4	0.116	17100	NT
8	0.445	6.2	59.4	2.93	2420	0.0426	0.67	16.1	19.8	0.083	17600	< 0.5
9	NT	NT	NT	NT	2430	NT	NT	16.8	23.7	0.142	17600	NT
10	NT	NT	69.3	NT	NT	<1	1.5	17.3	24.3	0.17	16300	NT
11	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
12	0.3	5.6	63.4	<5	2100	0.04	0.84	16.6	17	0.04	12900	0.1

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



Table 60 Summary of Participants' Results and Performance in S2 (continued)

Lab Code	Mg (mg/kg)	Mn (mg/kg)	Na (mg/kg)	Ni (mg/kg)	P (mg/kg)	Pb (mg/kg)	Se (mg/kg)	Sn (mg/kg)	Sr (mg/kg)	V (mg/kg)	Zn (mg/kg)
A.V.	1560	0.857	9270	0.474	9160	0.269	4.28	Not Set	24.5	Not Set	79.2
H.V	1810	0.81	8800	0.533	9400	0.263	4.80	0.280	25.1	0.0584	81
1	1458	0.87	9404	0.49	8970	0.29	3.9	0.29	25.8	0.046	85
2	1385	1.27	8400	0.45	8140	0.22	3.89	0.31	21.3	0.34	74.0
3	1500	0.8	9200	0.4	8900	0.26	3.8	NT	24	0.04	76
4	1400	0.71	8430	0.51	8670	0.26	4.28	NT	22.4	0.05	71
5	1650	0.89	10000	0.44	9120	0.265	4.65	NR	25.5	0.044	84.5
6	1718	0.915	9969	0.218	9226	0.332	4.17	0.389	24.20	<0.1	83.73
7	1640	0.896	9820	0.487	NT	0.273	4.88	NT	NT	NT	77.4
8	1690	0.79	9900	< 0.5	9720	0.274	4.48	< 0.5	24.5	< 0.3	78
9	1660	0.902	9570	NT	9440	<1	4.46	NT	25.2	NT	81.3
10	NT	<1	NT	<1	9250	<1	7.2	NT	NT	<1	75.4
11	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
12	1450	0.79	7750	0.54	10100	0.26	7.72	<0.5	27.1	<0.5	84.4

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

## 7.4 Participants' Results and Analytical Methods for Total Elements

A summary of participants' performance in the two study samples is presented in Figures 56 and 57 and Tables 59 and 60.

Measurements of total Al in S1 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.

Measurements of Be, Cs, Ga, La, Li, Rb, Sn, Tl and U also challenged participants' analytical methods. Only laboratories 1 and 6 reported results for all these analytes.

### Extraction Method

The Codex Alimentarius Commission 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.<sup>15</sup> In previous NMI PT studies participants used various extraction methods and the results produced were compatible except for 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 nitric acid, a high digestion temperature (larger than approximately 170°C) 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. It is a challenge for them to find a method/extraction regime 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 was found in this and in previous studies of the importance of using (in addition to nitric acid) a high ratio HCl (mL)/sample size (g) when a high digestion temperature (> 170°C) or when HF cannot be used for total Cr, Fe, Ni and V extraction.

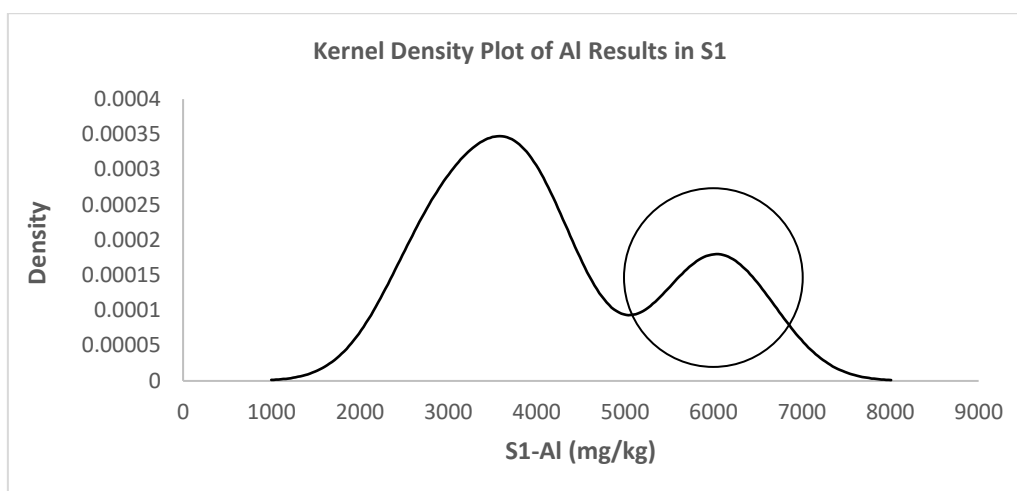
In the present study, one sample was tea leaves and one sample was freeze dried marine biota. Nine laboratories reported results for both samples and six used the same extraction regime for both samples. Laboratories 2 and 3 both used nitric acid and hydrochloric acid for digestion of the marine biota sample but nitric acid only for the tea leaves sample. Laboratory 4 extracted the tea leaves sample at 170 °C and the marine biota sample at 144°C for 5 min and then at 210°C for 12 min.

One participant used alkaline TMAH digestion for Se measurement in S2.

The method descriptions provided by participants are presented in Tables 1, 2 and 3.

**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 might explain the variability of results.

In the present study the Al results had a bimodal distribution (Figure 59). As the instruction was given to undertake "digestion until extraction was complete", the closest values to the true value are most likely to be 5570 mg/kg and 6310 mg/kg as reported by Laboratories 5 and 4 respectively. These values were also in good agreement with the homogeneity value (6200 mg/kg). Both results were produced under high digestion temperatures of 160°C to 260°C.



Lab code	S1 Al Results mg/kg	Digestion Regime						
		Sample Mass (g)	Temp °C	Time (min.)	HNO <sub>3</sub> (mL)	HCl (mL)	HNO <sub>3</sub> (1:1)(mL)	H <sub>2</sub> O <sub>2</sub> (mL)
6	2697	0.25	85	240	3	2		
2	3025	0.4	120	60	10			
3	3600	0.2	109	240	10			
1	3850	1	95-100	120	3	1		
7	4110	1	110	60	5	1.5		
5	5770	0.5	85-165	50	5			
4	6310	0.5	170	12		0.5	7	1
H.V.	6200	0.5	260	60	3	1		

H.V.= Homogeneity Value

Figure 59 Participants' Results versus Digestion Regime

The results reported for Al in the marine biota sample were in relatively good agreement with each other (CV of 25%).

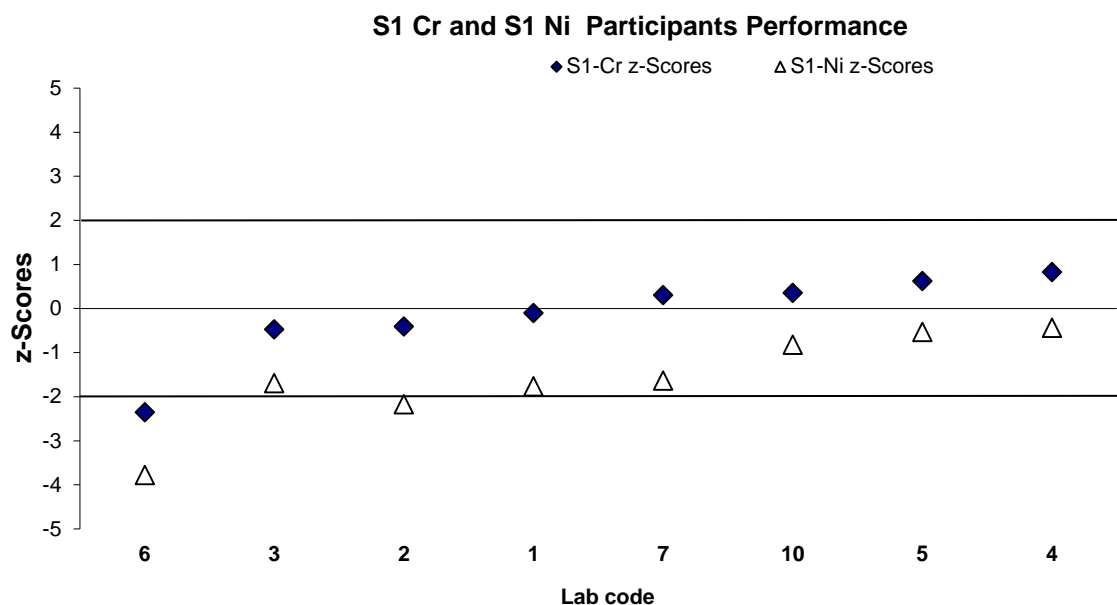
**Chromium and Nickel** are strongly dependent on digestion regime, especially when the sample has high silica content.

In the present study most of the results reported for these elements were in good agreement with each other, as well as with the assigned value/reference value or homogeneity value. The robust between-laboratory CV for these elements was between 11% and 21%.

Similar to previous studies, the results which were closest to the true values for Ni and Cr were those produced under high digestion temperatures and those produced using a high ratio of HCl to sample size (Figure 60).

Laboratories 5 and 4 used high digestion temperatures of 165°C and 170°C respectively while laboratory 10 used a digestion temperature of 112.5°C but a ratio of HCl to sample size of 10. The results reported by these laboratories for Ni and Cr in S1 were the closest to the homogeneity value for Cr and the reference value for Ni respectively. The homogeneity value and reference value were also produced under high digestion temperatures of 260°C and 200°C respectively.

Total Al, Cr and Ni are some of the most difficult elements to analyse in food samples. 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 method). Bias can be expressed as recovery and should be corrected for or included in the uncertainty estimate.<sup>1</sup>



Lab. Code	S1 Cr mg/kg	S1-Ni mg/kg	Digestion Regime				
			HCl (mL)/ sample size (g)	Temp (°C)	Time (min)	Sample Size (g)	Reagents Used
6	5.08	1.26	8	85	240	0.25	3 mL HNO <sub>3</sub> , 2 mL HCl
3	8.7	3.4	0	109	240	0.2	10 mL HNO <sub>3</sub>
2	8.83	2.91	0	120	60	0.4	10 mL HNO <sub>3</sub>
1	9.4	3.33	1	95-100	120	1	3 mL HNO <sub>3</sub> , 1 mL HCl
7	10.2	3.46	1.5	110	60	1	5 mL HNO <sub>3</sub> , 1.5 mL HCl
10	10.3	4.3	<b>10</b>	112.5	120	1	10 mL HNO <sub>3</sub> , 10 mL HCl
5	10.8	4.6	0	<b>85-165</b>	50	0.5	5 mL HNO <sub>3</sub> ,
4	11.2	4.7	1	<b>170</b>	12	0.5	7 mL HNO <sub>3</sub> (1:1), 0.5 mL HCl, 1 mL H <sub>2</sub> O <sub>2</sub>

H.V.	14.2		2	<b>260</b>	60	0.5	3 mL HNO <sub>3</sub> , 1 mL HCl
R.V		5.41		<b>200</b>	60	0.25	5 mL HNO <sub>3</sub> , 1 mL HCl, 1 mL H <sub>2</sub> O <sub>2</sub>

H.V.= Homogeneity Value; R.V. = Reference Value

Figure 60 Participants' Results/Performance versus Digestion Regime

### Instrumental Techniques

Plots of participants' results/performance against the instrumental technique used are presented in Figures 61 to 72.

**Aluminium, Chromium, Nickel** There was no apparent association between results/performance for Al, Cr, Ni in S1 and S2 and instrumental technique used (Figures 61 to 64).

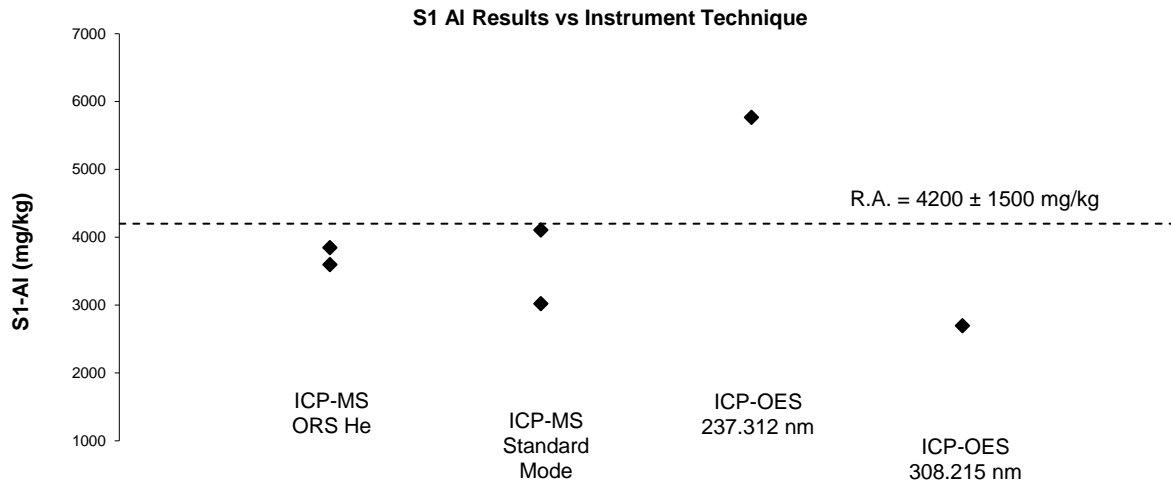


Figure 61 S1 Al Results vs. Instrumental Technique

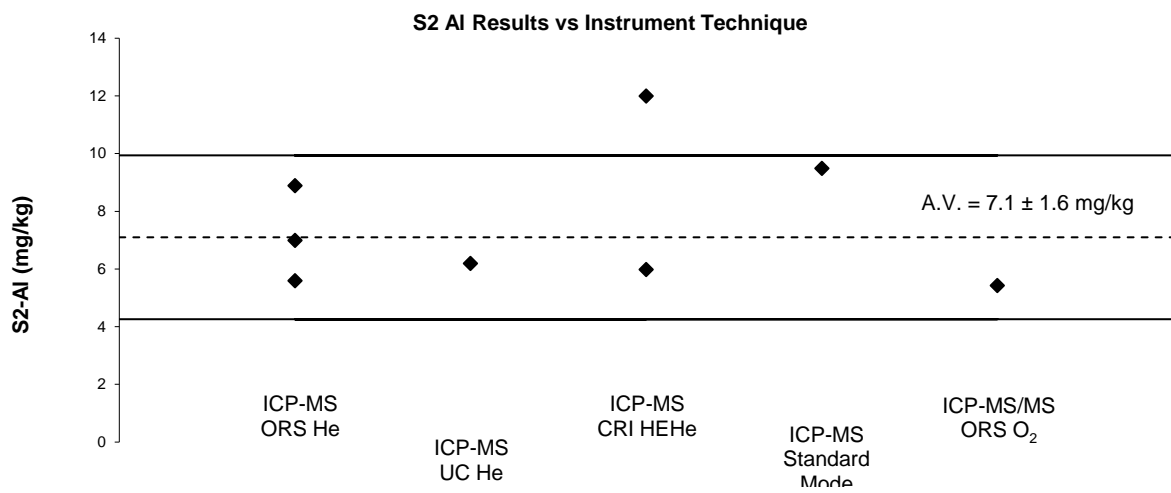


Figure 62 S2 Al Results vs. Instrumental Technique

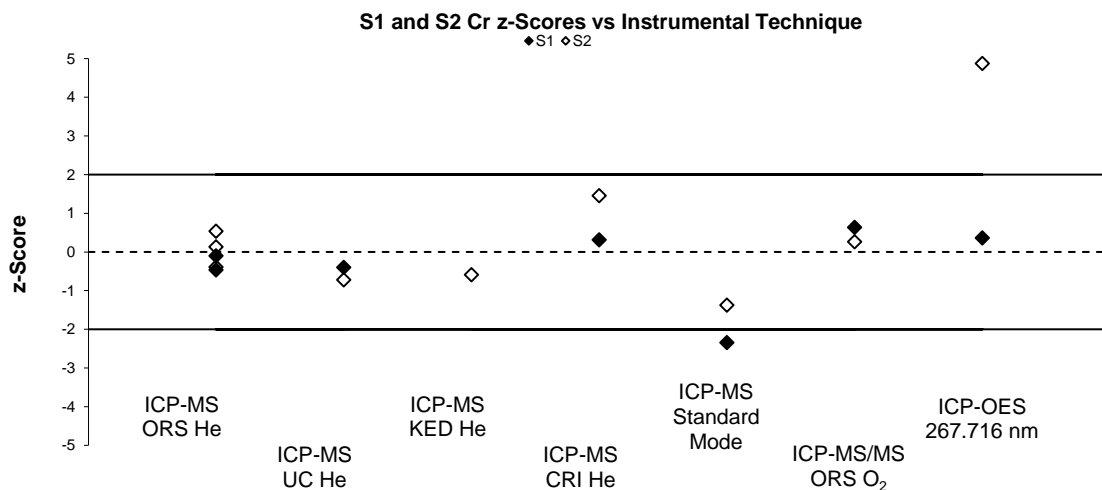


Figure 63 S1 and S2 Cr z-Scores vs. Instrumental Technique

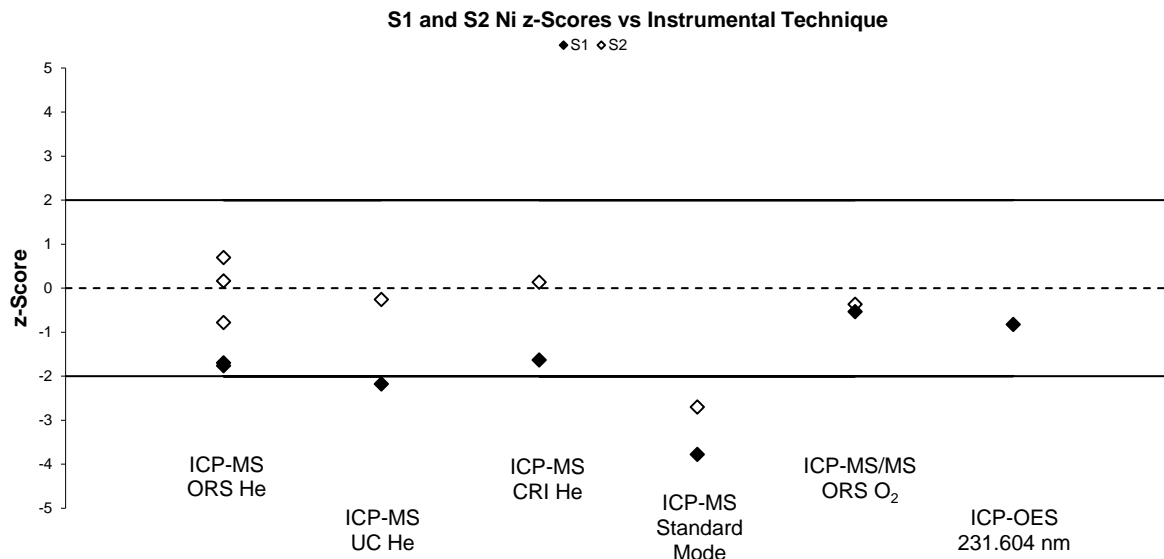


Figure 64 S1 and S2 Ni z-Scores vs. Instrumental Technique

**Arsenic** Participants used a wide variety of instrumental techniques for the measurement of As in S1 and S2 and all produced satisfactory results.

Figure 65 presents plots of participants' results reported for As in S1 versus instrumental technique.

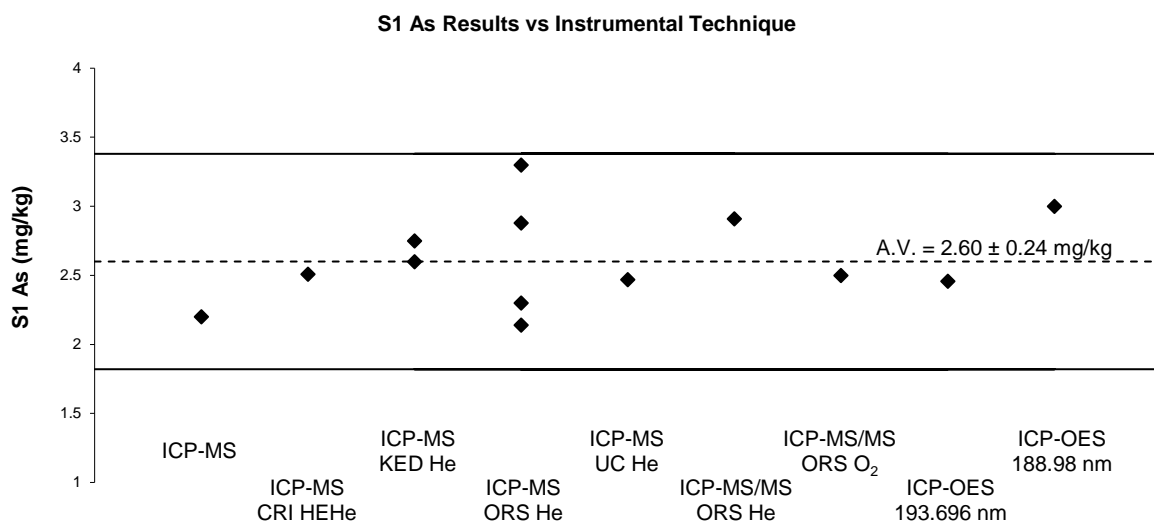


Figure 65 S1 As Results vs. Instrumental Technique

**Beryllium** level in S1 was low. Only four participants reported results for this element. The four results were in poor agreement with each other and with the homogeneity value.

**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 (0.0332 mg/kg).

Mercury level in S2 was approximately four times higher than in S1. Nine 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 66 and 67.

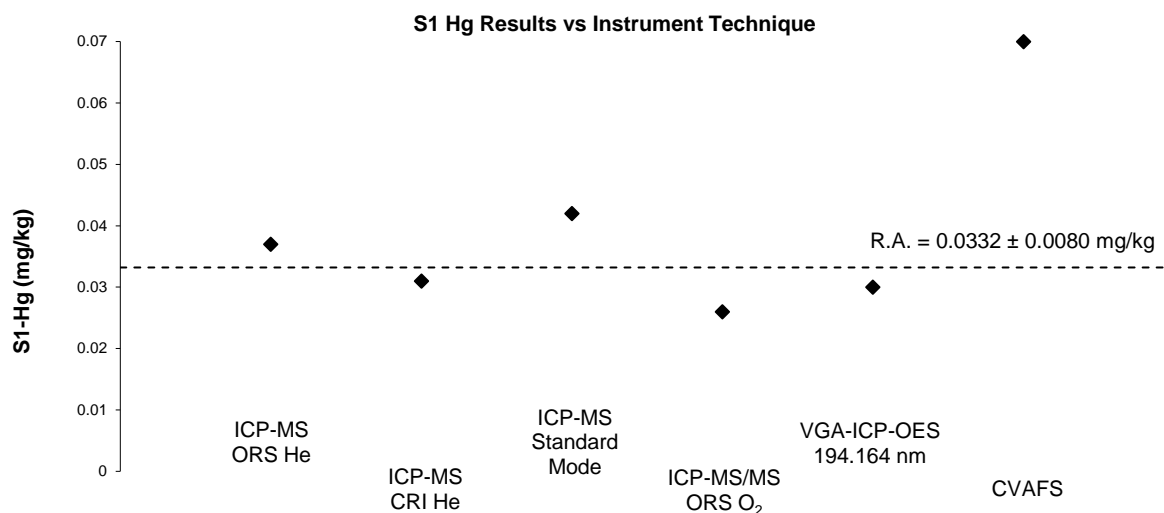


Figure 66 S1 Hg Results vs. Instrumental Technique

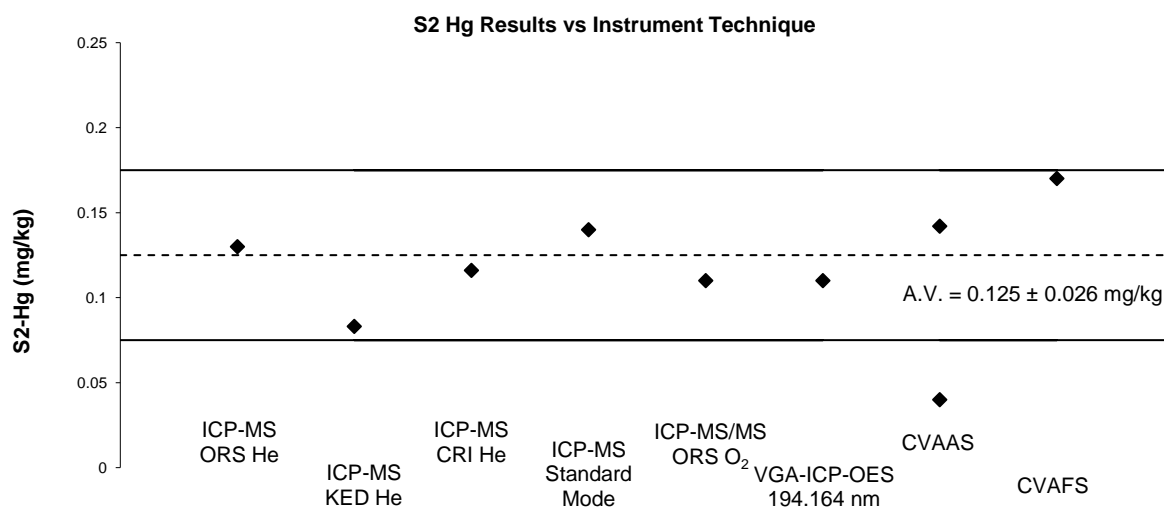


Figure 67 S2 Hg Results vs. Instrumental Technique

**Tin** Only three results were reported for Sn in S1 and four in S2. In each sample, Sn results were in good agreement with each other and with their respective information/homogeneity values (0.342 mg/kg in S1 and 0.280 mg/Kg in S2). All participants used ICP-MS for the measurement of Sn.

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

Plots of participants' performance for Na and K in the two study samples are presented in Figures 68 and 69. ICP-OES-AV with 766 nm wavelength or ICP-OES-RV with 766 nm wavelength were the preferred techniques for K measurements in S1 and S2. For the measurement of Na, most participants chose ICP-OES-AV with a wavelength of 589 nm and ICP-OES-RV with a wavelength of 590 nm.

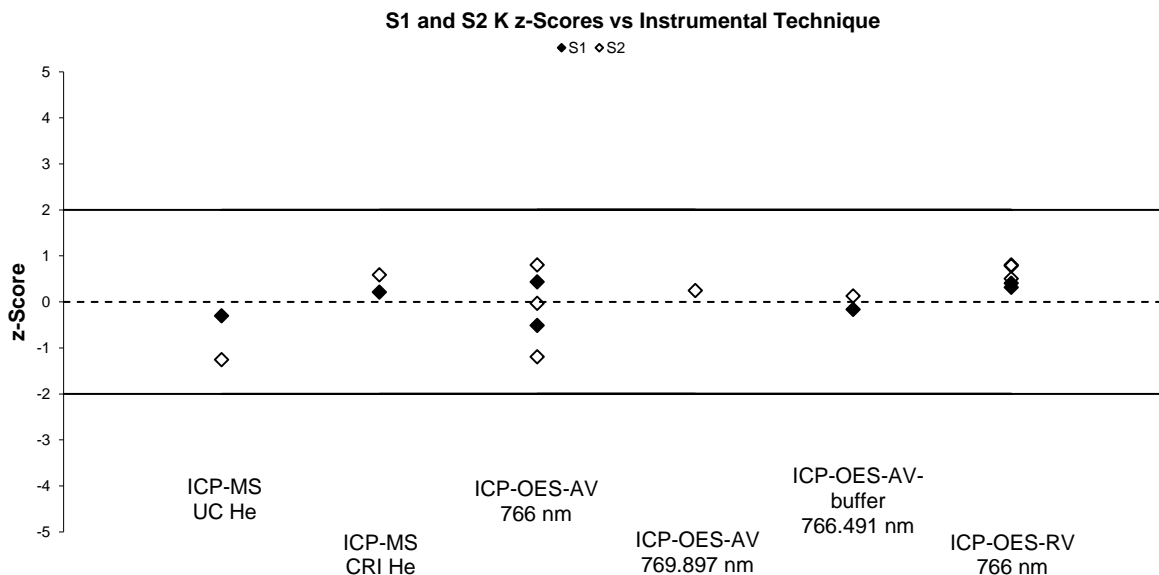


Figure 68 S1 and S2 K z-Scores vs. Instrumental Technique

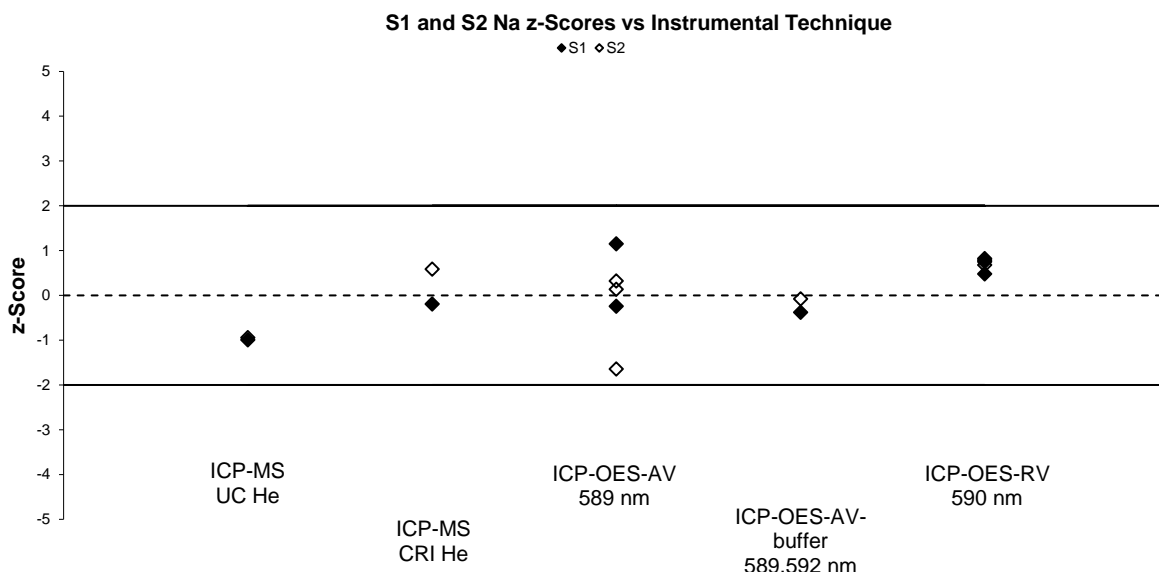


Figure 69: S2 Na Results vs. Instrumental Technique

**Selenium** Unsolved interference problems might explain the high unsatisfactory results produced by ICP-MS in S2 (Figure 70). Apart from molecular and polyatomic interferences whose effects may be reduced by using a collision reaction cell, matrix effects are another main factor that 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.<sup>16</sup>

Se level in S1 was low at 0.218 mg/kg. Seven laboratories reported results for this test in the tea leaves samples and all performed satisfactorily. All used ICP-MS in collision or standard mode, except for one. One laboratory reported using ICP-MS/MS in reaction mode with O<sub>2</sub> as reaction gas (Figure 71).



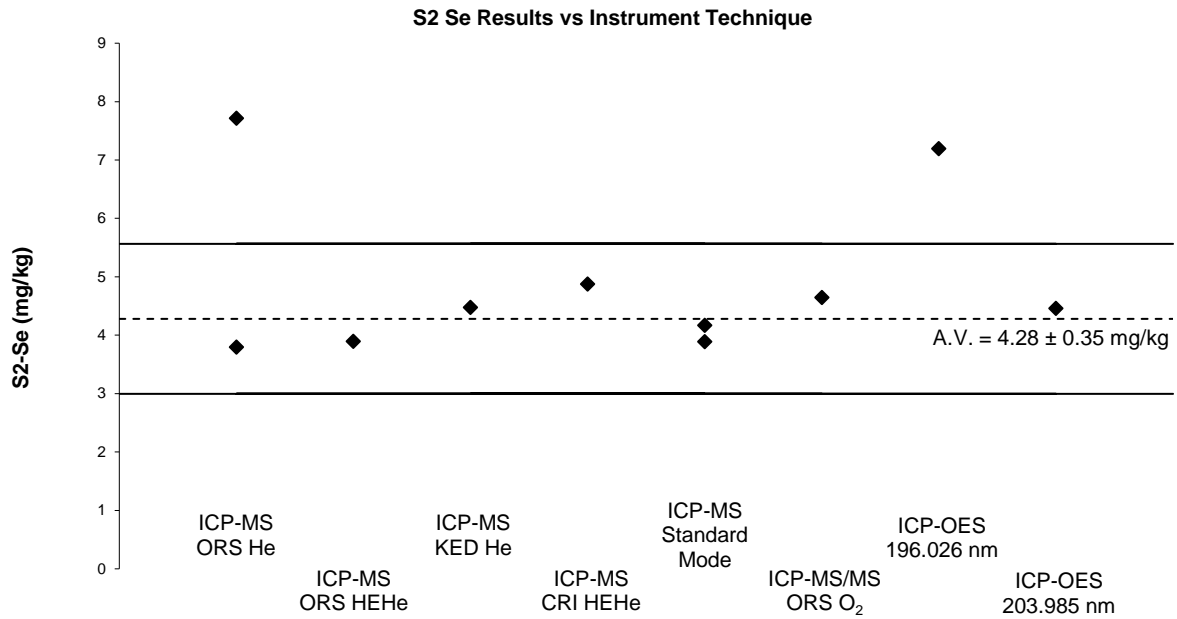


Figure 70: S2-Se Results vs. Instrumental Technique

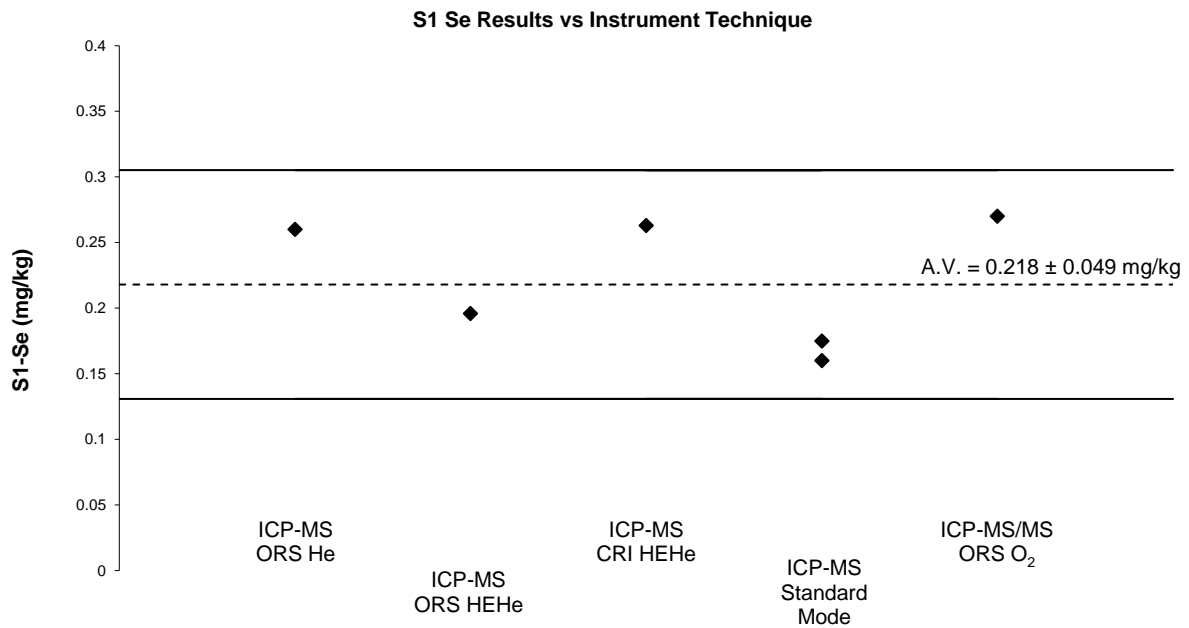
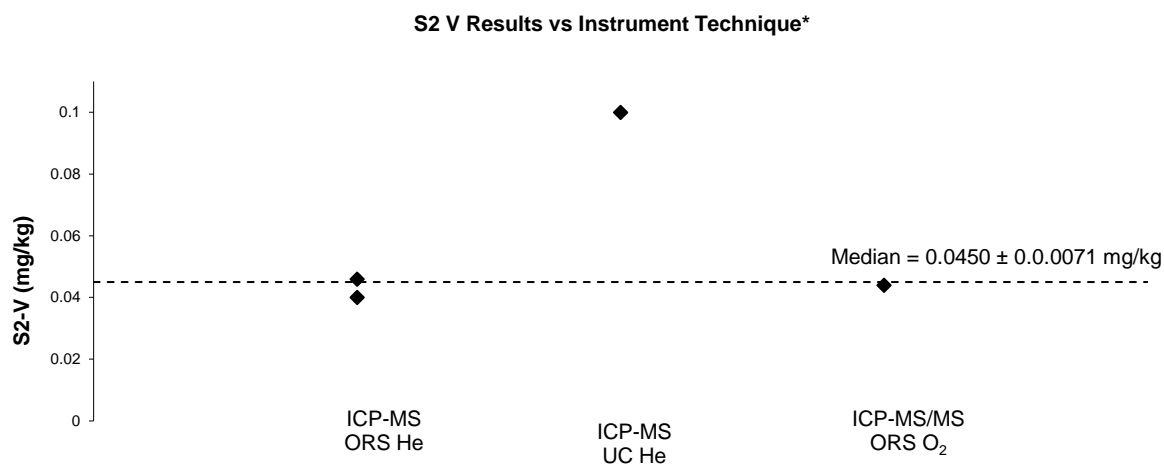


Figure 71: S1-Se Results vs. Instrumental Technique

All participants used the same digestion regime as for the other elements, with the exception of one. One participant reported: “Selenium were prepared using a different extraction method: sample mass = 0.511 g, extraction with 5 mL of 12.5% Tetramethylammonium hydroxide, digestion temp 115°C for 60 mins.”

**Vanadium** No assigned value could be set for low-level V in S2 because only five participants reported results for this test. All results but one were in good agreement with each other and with the homogeneity value (Figure 72).

Overcoming  $^{35}\text{Cl}^{16}\text{O}^+$  interferences on low-level  $^{51}\text{V}$  may have been the main challenge for participating laboratories.



\*Laboratory 2 result of 0.34 mg/kg has been plotted as 0.10 mg/kg.

Figure 72: S1-Se Results vs. Instrumental Technique

## 7.5 Comparison with the Previous Proficiency Studies of Metals and Nutrients in Soil

AQA 21-12 is the sixteenth NMI study of elements in food. Laboratories improved their performance in the measurement of Cr, Ni and Fe in food samples. The results reported for these elements in the tea leaves and marine biota samples were compatible with each other.

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 73.

## 7.6 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 61.

Table 61 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	RM
2	CRM – BRAN 1, DORM 4 and TORT 3

Lab. Code	Description of Control Samples
3	RM
5	RM – In-house reference materials (from previous PT program) and Certified reference materials (ERM and NIST)
6	SS
7	CRM – NIST SRM 1548 Typical Diet, NIST SRM 1567b Wheat Flour
8	CRM – Apple Leaves NIST 1515, Oyster Tissue NIST 1566b, Bovine Liver Powder NIST 1577c, Rice Flour NIST 1568a, Milk Powder TYG091RM FAPAS, WMP 10612-QC-PR8071 Global Proficiency, Skimmed Milk Powder ERM - BD151.
9	CRM
10	RM
11	SS
12	RM

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 ’<sup>17</sup>*

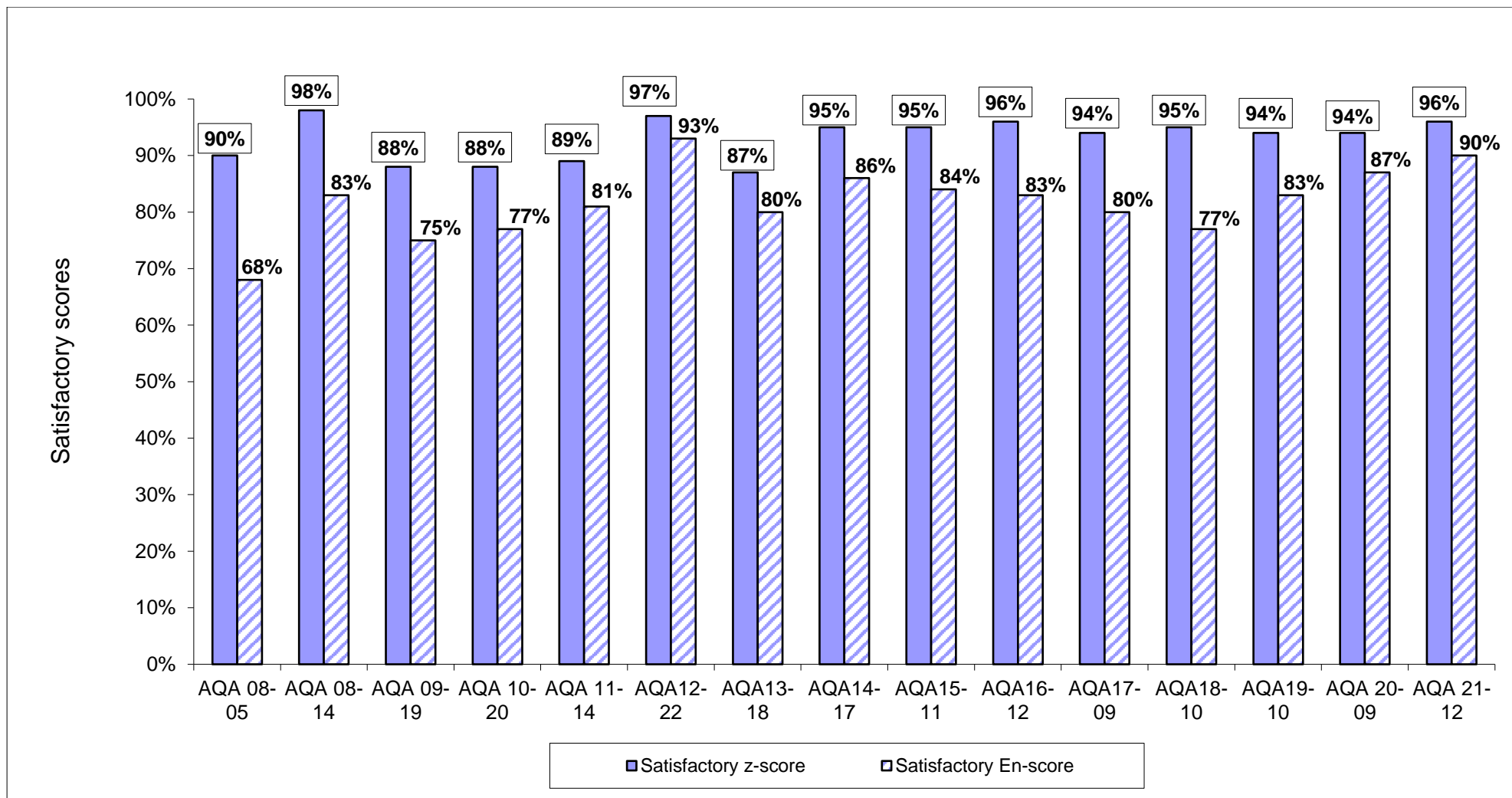


Figure 73 Participants' Performance over Time

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## APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

### A1.1 Sample Preparation

**Sample S1** – was dried tea leaves.

**Sample S2** – was freeze dried marine biota (75% finfish, 18% crab meat and 7% molluscs).

### A1.2 Sample Analysis and Homogeneity Testing

The same procedure was followed for the preparation of Samples S1 and S2 as in previous NMI PT studies. Partial homogeneity testing was conducted for elements of interest, with the exception of Na in S1 and Al 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 0.5 g of sample was weighed and digested at 260°C for 1 hour with 3 mL of HNO<sub>3</sub> 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 62.

Table 62 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	400	107 m/z
Al	ICP-OES	Y	NA	NA	400	NA	396.152 nm
As	ICP-MS	Rh	ORS	He	400	400	75 m/z
B	ICP-MS	Rh	NA	NA	NA	400	11 m/z
Ba	ICP-OES	Y	NA	NA	400	NA	493.408 nm
Be	ICP-MS	Rh	NA	NA	400	NA	9 m/z
S1: Ca	ICP-OES	Y	NA	NA	400	NA	317.933 nm
S2: Ca	ICP-MS	Rh	ORS	He	NA	400	43 m/z
Cd	ICP-MS	Rh	ORS	He	400	400	111 m/z
Co	ICP-MS	Rh	ORS	He	400	NA	59 m/z
Cr	ICP-MS	Rh	ORS	He	400	400	52 m/z
Cs	ICP-MS	Rh	ORS	He	400	NA	133 m/z
Cu	ICP-MS	Rh	ORS	He	400	400	63 m/z
S2: Fe	ICP-MS	Rh	ORS	He	NA	400	56 m/z
Ga	ICP-MS	Rh	ORS	He	400	NA	71 m/z
Hg	ICP-MS	Ir	NA	NA	400	400	202 m/z
S1: K	ICP-OES	Y	NA	NA	400	NA	766.491 nm
S2: K	ICP-MS	Rh	ORS	He	NA	400	39 m/z
La	ICP-MS	Rh	ORS	He	400	NA	139 m/z
Li	ICP-MS	Rh	ORS	He	NA	400	7 m/z
S1: Mg	ICP-OES	Y	NA	NA	400	NA	285.213 nm
S2: Mg	ICP-MS	Rh	ORS	He	NA	400	24 m/z
S1: Mn	ICP-OES	Y	NA	NA	400	NA	293.931 nm
S2: Mn	ICP-MS	Rh	ORS	He	NA	400	55 m/z
Mo	ICP-MS	Rh	ORS	He	400	NA	95 m/z
Na	ICP-MS	Rh	ORS	He	NA	400	23 m/z
S2-Ni	ICP-MS	Rh	NA	NA	400	400	60 m/z
S1: P	ICP-OES	Y	NA	NA	400	NA	213.618 nm
S2: P	ICP-MS	Rh	ORS	HEHe	NA	400	31 m/z
Pb	ICP-MS	Ir	ORS	He	400	400	Average of 206, 207, 208 m/z

Rb	ICP-MS	Rh	ORS	He	400	NA	85 m/z
S	ICP-OES	Y	NA	NA	400	NA	181.972 nm
Se	ICP-MS	Rh	ORS	HEHe	400	400	78 m/z
S2-Sn	ICP-MS	Rh	ORS	He	400	400	118 m/z
Sr	ICP-MS	Rh	ORS	He	NA	400	88 m/z
Tl	ICP-MS	Ir	ORS	He	400	NA	205 m/z
U	ICP-MS	Ir	ORS	He	400	NA	238 m/z
V	ICP-MS	Rh	ORS	He	400	400	51 m/z
Zn	ICP-MS	Rh	ORS	He	400	400	64 m/z

NA- Not Applicable

## APPENDIX 2 - ASSIGNED VALUE, Z-SCORE AND E<sub>N</sub> SCORE CALCULATION

### Assigned Value

The assigned value was calculated as the robust average using the procedure described in 'ISO13528:2015(E), Statistical methods for use in proficiency testing by inter-laboratory comparisons – Annex C'.<sup>6</sup> The uncertainty was estimated as:

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

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 63.

Table 63 Uncertainty of Assigned Value for As in Sample S1

No. results (p)	8
Robust Average	0.703 mg/kg
$S_{rob\ av}$	0.095 mg/kg
$u_{rob\ av}$	0.042 mg/kg
$k$	2
$U_{rob\ av}$	0.084 mg/kg

The assigned value for As in Sample S1 is **0.703 ± 0.084 mg/kg**.

### z-Score and E<sub>N</sub>-score

For each participant's result a z-score and E<sub>N</sub>-score are calculated according to Equation 2 and Equation 3 respectively (see page 9).

A worked example is set out below in Table 64.

Table 64 z-Score and E<sub>N</sub>-score for As result reported by Laboratory 2 in S1

As Result mg/kg	Assigned Value mg/kg	Set Target Standard Deviation	z-Score	E <sub>N</sub> -Score
0.68 ± 0.1	0.703 ± 0.084	15% as CV or 0.15 x 0.703 = 0.11 mg/kg	$z = \frac{(0.68 - 0.703)}{0.11}$  $z = -0.22$	$E_n = \frac{(0.68 - 0.703)}{\sqrt{0.1^2 + 0.084^2}}$  $E_n = -0.18$



## APPENDIX 3 – REFERENCE VALUES

### A.3.1 Description of Method of Analysis

All analytes were quantified by double isotope dilution ICP-MS. NIST 3100 series primary calibration materials were used, see table below for details, and these were diluted gravimetrically to working concentrations.

Analyte	Standard Name	Lot No.
Fe	NIST 3126a	140812
Ni	NIST 3136	120619
Sn	NIST 3161a	140917

Isotope dilution was performed by spiking calibration standards and undigested samples with isotopically enriched  $^{56}\text{Fe}$  (Oakridge),  $^{61}\text{Ni}$  (Oakridge) and  $^{117}\text{Sn}$  (Oakridge) standards.

For each analysis approximately 0.25 g of the sample was weighed into a PTFE microwave vessel along with the internal standards followed by the addition of 8 mL  $\text{HNO}_3$  (67-69%), 1 mL  $\text{H}_2\text{O}_2$  (30-32%) and 1 mL  $\text{HCl}$  (34-37%) digestion reagents. Samples were then digested in a microwave digester (Ethos UP, 220 °C, 30 min ramp, 60 min hold). Digests were then diluted to 25 mL with UHP water to produce a clear and colourless solution. This digest solution contained fine white particulates assumed to be undigested silica. For Fe analysis a further 1/100 dilution of the digest was performed again using UHP water.

Each experimental batch contained CRMs and method blanks prepared using the same procedures. Isotope ratios were measured by ICP-SF-MS (Element 2) using medium resolution (Fe, Ni) and high resolution (Sn). Confirmation analysis was performed on an ICP-MS-MS (Agilent 8800) using  $\text{H}_2$  gas at 5.5 mL/min (Fe) and He gas at 5.5 mL/min (Ni, Sn). All measurements for all samples were measured bracketed on either side by the calibration solutions.

### A.3.2 Reference Values

The reference values and associated measurement uncertainty estimates for AQA 21-12 Sample S1 are presented below. The reference values come from the analysis of 3 bottles with 5-8 subsamples taken from each. Measurement uncertainty is given as a 95% level of confidence. Measurements are based on the sample as received (wet mass), no specific correction or uncertainty for moisture content variation has been made.

Sample	Analyte	Reference Value (mg/kg)	Expanded Uncertainty (95%) (mg/kg)	Relative Expanded Uncertainty	Coverage Factor (95%)
AQA 21-12 S1	Fe	5950	390	6.6%	2.07
	Ni	5.14	0.43	8.4%	2.14

### A.3.3 Information Values

An information value and associated measurement uncertainty estimates for Sn is also provided below. This information value come from the analysis of 3 bottles with 5-8 subsamples taken from each. Measurement uncertainty is given as a 95% level of confidence. Measurements are based on the sample as received (wet mass), no specific correction or uncertainty for moisture content variation has been made.

Sample	Analyte	Information Value (mg/kg)	Expanded Uncertainty (95%) (mg/kg)	Relative Expanded Uncertainty	Coverage Factor (95%)
AQA 21-12 S1	Sn	0.342	0.044	13%	2.08

While the digestion method (see Subchapter A.3.1) likely represents a ‘practical’ total extraction (i.e. not using hydrofluoric acid), no certified Sn values were present in the CRMs analysed so it is not possible conclude whether that total extraction for Sn has been achieved, meaning that there is some chance that the information value provided is biased low.

### A.3.4 Homogeneity Assessment

Homogeneity was not explicitly assessed, but the analysis was carried out on 5-8 subsamples of 3 separate bottles and some component of this will be captured within the method precision.

### A.3.5 Stability Assessment

Stability was not assessed.

### A.3.6 Reference Value and Information Value Measurement Uncertainty

The measurement uncertainty associated with the reference values and informative values takes into account all factors that can reasonably be expected to affect the measurement result. Briefly, these include the primary calibration material, gravimetric sample preparation, homogeneity, method trueness and method precision. Some variation in moisture content is expected to be covered in the method precision term but has not been specifically considered. Measurement uncertainty is reported as a 95% level of confidence.

### A.3.7 Statement of Traceability

The reference values given in this report rely on gravimetric sample preparation and elemental quantification by ICP-MS. Gravimetric measurements were calibrated using Australian standards for mass and are traceable to the SI unit for mass (kg). ICP-MS measurements were calibrated with isotope dilution and are traceable to (i) the SI unit for mass (kg) through the primary calibration standard certified by NIST (USA) and (ii) the SI unit for amount of substance (mol) through data for isotopic composition and relative atomic mass. Isotopic composition is traceable to IUPAC published data.

## APPENDIX 4 - ACRONYMS AND ABBREVIATIONS

CRM	Certified Reference Material
CV	Coefficient of Variation
CV <sub>Rob</sub>	Robust Coefficient of Variation
DRC	Dynamic Reaction Cell
GUM	Guide to the Expression of Uncertainty in Measurement
HEHe	High energy helium
HV	Homogeneity Value
IV	Informative Value
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
SA-ICP-MS	Standard Addition – Inductively Coupled Plasma – Mass spectrometry
SV	Spiked or formulated concentration of a PT sample
SD <sub>Rob</sub>	Robust Standard Deviation
SI	The International System of Units
s <sup>2</sup> <sub>sam</sub>	Sampling variance
s <sub>a</sub> /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
VGA-ICP-OES	Vapor Generation Accessory- Inductively Coupled Plasma - Optical Emission Spectrometry

## APPENDIX 5 - INSTRUMENT DETAILS

Table 65 Instrument Conditions for Ag

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	NA	80	107
2	ICP-MS	Rh	NA	NA	NA	625	109
3	ICP-MS	103	Collision	He	NA	100	107
4					NA		
5	ICP-MS/MS	Rh 103	ORS	O2	80	80	108 m/z
6	ICP-MS	Ge 72	ORS		NA	200	107m/z
7	ICP-MS	Rh	CRI	standard mode	NA	80	
8	ICP-MS	Rh	KED	He	NA	485.45	109
9							
10					NA		
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS	Rh	ORS	He	NA	25	107

Table 66 Instrument Conditions for Al

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	80	27
2	ICP-MS	Sc	NA	NA	625	625	27
3	ICP-MS	45	Collision	He	250	100	27
4							
5	ICP-OES-AV	In 303.936			80	80	237.312
6	ICP-OES-RV	Y324	NA		200	200	308.215nm
7	ICP-MS	Sc	CRI	standard mode	380	40	
8	ICP-MS	Sc	KED	He	NA	485.45	27
9							
10							
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS	Rh	ORS	He	NA	25	27

Table 67 Instrument Conditions for As

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	80	75
2	ICP-MS	Ge	UC	He	625	625	75
3	ICP-MS	72	Collision	He	250	100	75
4							
5	ICP-MS/MS	Rh 103	ORS	O2	80	80	91 m/z
6	ICP-MS	Ge 72	ORS		4000	4000	75m/z
7	ICP-MS	Te	CRI	HEHe	80	160	
8	ICP-MS	Te	KED	He	NA	485.45	75
9							
10	ICP-OES-AV	Y 371.029			1	1	188.98
11	ICP-MS 7900	Li,Rh,In,Te, Lu	Quadrupole	He	50	NA	75
12	ICP-MS	Sc	ORS	He	NA	25	75

Table 68 Instrument Conditions for B

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	NA	80	11
2	ICP-MS	Sc	NA	NA	NA	625	10
3	ICP-OES-AV- buffer	Lu			NA	100	249.678
4					NA		
5	ICP-MS/MS	Sc 45	ORS	NA	80	80	11 m/z
6	ICP-MS	Ge 72	ORS		NA	200	11m/z
7					NA		
8	ICP-MS	Sc	KED	He	NA	485.45	10
9							
10					NA		
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS	Sc	NA	NA	NA	25	11

Table 69 Instrument Conditions for Ba

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	NA	134
2	ICP-MS	Rh	NA	NA	625	NA	138
3	ICP-MS	175	Collision	He	250	NA	138
4						NA	
5	ICP-MS/MS	Rh 103	ORS	O2	80	80	153 m/z
6	ICP-MS	Rh 103	ORS		200	NA	137m/z
7						NA	
8	NA	NA	NA	NA	NA	NA	NA
9	ICP-OES-AV	Y371 / Te214			50		233.527
10	ICP-OES-AV	Y 371.029			1	NA	233.527
11	NA	NA	NA	NA	NA	NA	NA
12	NA	NA	NA	NA	NA	NA	NA

Table 70 Instrument Conditions for Be

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	NA	9
2	ICP-MS	Sc	NA	NA	625	NA	9
3	ICP-OES-AV- buffer	Lu			250	NA	313.042
4						NA	
5	ICP-MS/MS	Sc 45	ORS	NA			9 m/z
6	ICP-MS	Ge 72	ORS		200	NA	9m/z
7						NA	
8	NA	NA	NA	NA	NA	NA	NA
9							
10	ICP-OES-AV	Y 371.029			1	NA	234.861
11	NA	NA	NA	NA	NA	NA	NA
12	NA	NA	NA	NA	NA	NA	NA

Table 71 Instrument Conditions for Ca

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV	Y	ORS	He	80	80	43
2	ICP-MS	Sc	UC	He	625	625	44
3	ICP-OES-AV- buffer	Lu			250	100	430.253
4							
5	ICP-OES-AV	Eu397.197			80	80	370.602
6	ICP-OES-RV	Y324	NA		200	200	393.366nm
7	ICP-MS	Rh	CRI	standard mode	800	800	
8	ICP-OES-RV	N/A	NA	He	NA	97.09	184
9	ICP-OES-AV	Y371 / Te214			50	50	315.887
10							
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-OES-AV	Eu	NA	NA	NA	25	315

Table 72 Instrument Conditions for Cd

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	80	111
2	ICP-MS	Rh	NA	NA	625	625	111
3	ICP-MS	103	Collision	He	250	100	114
4							
5	ICP-MS/MS	Rh 103	ORS	O2	80	80	111 m/z
6	ICP-MS	Rh 103	ORS		200	200	111m/z
7	ICP-MS	Rh	CRI	He	80	80	
8	ICP-MS	Rh	KED	He	NA	485.45	111
9							
10	ICP-OES-AV	Y 371.029			1	1	228.802
11	ICP-MS 7900	Li,Rh,In,Te, Lu	Quadrupole	He	50	NA	111
12	ICP-MS	Rh	ORS	He	NA	25	111

Table 73 Instrument Conditions for Co

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	NA	59
2	ICP-MS	Ge	UC	He	625	NA	59
3	ICP-MS	103	Collision	He	250	NA	59
4						NA	
5	ICP-MS/MS	Rh 103	ORS	O2	80	80	59 m/z
6	ICP-MS	Ge 72	ORS		200	NA	59m/z
7	ICP-MS	Rh	CRI	He	80	NA	
8	NA	NA	NA	NA	NA	NA	NA
9							
10	ICP-OES-AV	Y 371.029			1	NA	228.615
11	NA	NA	NA	NA	NA	NA	NA
12	NA	NA	NA	NA	NA	NA	NA

Table 74 Instrument Conditions for Cr

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	80	52
2	ICP-MS	Sc	UC	He	625	625	52
3	ICP-MS	72	Collision	He	250	100	52
4							
5	ICP-MS/MS	Rh 103	ORS	O2	80	80	52 m/z
6	ICP-MS	Ge 72	ORS		4000	4000	52m/z
7	ICP-MS	Rh	CRI	He	160	80	
8	ICP-MS	Sc	KED	He	NA	485.45	52
9							
10	ICP-OES-AV	Y 371.029			1	1	267.716
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS	Sc	ORS	He	NA	25	52



Table 75 Instrument Conditions for Cs

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	NA	133
2						NA	
3						NA	
4						NA	
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS	Rh 103	ORS		200	NA	133m/z
7						NA	
8	NA	NA	NA	NA	NA	NA	NA
9							
10						NA	
11	NA	NA	NA	NA	NA	NA	NA
12	NA	NA	NA	NA	NA	NA	NA

Table 76 Instrument Conditions for Cu

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	80	63
2	ICP-MS	Ge	UC	He	625	625	63
3	ICP-OES-AV- buffer	Lu			250	100	327.395
4							
5	ICP-MS/MS	Rh 103	ORS	O2	80	80	63 m/z
6	ICP-MS	Ge 72	ORS		200	4000	63m/z
7	ICP-MS	Rh	CRI	He	160	80	
8	ICP-MS	Ga	KED	He	NA	485.45	63
9	ICP-OES-AV	Y371 / Te214			50	50	324.754
10	ICP-OES-AV	Y 371.029			1	1	327.395
11	ICP-MS 7900	Li,Rh,In,Te, Lu	Quadrupole	He	50	NA	63
12	ICP-MS	Sc	ORS	He	NA	25	63

Table 77 Instrument Conditions for Fe

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	80	56
2	ICP-MS	Sc	UC	He	625	625	56
3	ICP-OES-AV- buffer	Lu			250	100	238.204
4							
5	ICP-OES-AV	Rh 103	ORS	O2	80	80	56 m/z
6	ICP-OES-AV	Y324	NA		200	200	238.204nm
7	ICP-MS	Rh	CRI	HEHe	800	80	
8	ICP-OES-RV	N/A	NA	He	NA	97.09	240
9	ICP-OES-AV	Y371 / Te214			50	50	240.489
10	ICP-OES-AV	Y 371.029			1	1	259.94
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS	Sc	ORS	He	NA	25	56

Table 78 Instrument Conditions for Ga

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	NA	71
2						NA	
3						NA	
4						NA	
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS	Rh 103	ORS		4000	NA	69m/z
7						NA	
8	NA	NA	NA	NA	NA	NA	NA
9							
10						NA	
11	NA	NA	NA	NA	NA	NA	NA
12	NA	NA	NA	NA	NA	NA	NA

Table 79 Instrument Conditions for Hg

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ir	ORS	He	80	80	202
2	ICP-MS	Ir	NA	NA	625	625	201
3	VGA-ICP-OES				100	100	194.164
4							
5	ICP-MS/MS	Ir 193	ORS	O2	80	80	202 m/z
6	ICP-MS	Ir 193	ORS		200	200	202m/z
7	ICP-MS	Ir	CRI	He	40	400	
8	ICP-MS	Tb	KED	He	NA	485.45	201
9	CVAAS				50	50	
10	CVAFS	NA			1	1	254
11	NA	NA	NA	NA	NA	NA	NA
12	CVAAS	NA	NA	NA	NA	25	153

Table 80 Instrument Conditions for K

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV	Y	ORS	He	80	80	39
2	ICP-MS	Sc	UC	He	625	625	39
3	ICP-OES-AV- buffer	Lu			1250	500	766.491
4							
5	ICP-OES-RV	In 410.176			80	80	766.491
6	ICP-OES-RV	Y324	NA		4000	200	766.49nm
7	ICP-MS	Rh	CRI	He	800	800	
8	ICP-OES-RV	N/A	NA	He	NA	97.09	766
9	ICP-OES-AV	Y371 / Te214			50	50	766.491
10							
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-OES-AV	Eu	NA	NA	NA	25	766

Table 81 Instrument Conditions for La

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	NA	139
2						NA	
3						NA	
4						NA	
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS	Rh 103	ORS		4000	NA	139m/z
7						NA	
8	NA	NA	NA	NA	NA	NA	NA
9							
10						NA	
11	NA	NA	NA	NA	NA	NA	NA
12	NA	NA	NA	NA	NA	NA	NA

Table 82 Instrument Conditions for Li

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	NA	80	7
2	ICP-MS	Sc	NA	NA	NA	625	7
3	ICP-OES-AV-buffer	Lu			NA	100	670.783
4					NA		
5	ICP-MS/MS	Sc 45	ORS	NA	80	80	7 m/z
6	ICP-MS	Ge 72	ORS		NA	200	7m/z
7					NA		
8	ICP-MS	Sc	KED	He	NA	485.45	7
9							
10					NA		
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS	Sc	NA	NA	NA	25	7

Table 83 Instrument Conditions for Mg

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV	Y	ORS	He	80	80	24
2	ICP-MS	Sc	UC	He	625	625	25
3	ICP-OES-AV- buffer	Lu			250	100	279.078
4							
5	ICP-OES-AV	Eu390.711			80	80	383.829
6	ICP-OES-RV	Y324	NA		200	200	280.270nm
7	ICP-MS	Rh	CRI	He	800	800	
8	ICP-OES-RV	N/A	NA	He	NA	97.09	285
9	ICP-OES-AV	Y371 / Te214			50	50	280.27
10							
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-OES-AV	Eu	NA	NA	NA	25	383

Table 84 Instrument Conditions for Mn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	80	55
2	ICP-MS	Sc	UC	He	625	625	55
3	ICP-OES-AV- buffer	Lu			250	100	257.61
4							
5	ICP-MS/MS	Rh 103	ORS	O2	80	80	55 m/z
6	ICP-MS	Ge 72	ORS		4000	200	55m/z
7	ICP-MS	Rh	CRI	He	800	80	
8	ICP-MS	Sc	KED	He	NA	485.45	55
9	ICP-OES-AV	Y371 / Te214			50	50	293.931
10	ICP-OES-AV	Y 371.029			1	1	293.931
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS	Sc	ORS	He	NA	25	55

Table 85 Instrument Conditions for Mo

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	NA	95
2	ICP-MS	Rh	NA	NA	625	NA	95
3	ICP-MS	103	Collision	He	250	NA	98
4						NA	
5	ICP-MS/MS	Rh 103	ORS	O2	80	80	95 m/z
6	ICP-MS	Ge 72	ORS		4000	NA	95m/z
7						NA	
8	NA	NA	NA	NA	NA	NA	NA
9	ICP-OES-AV	Y371 / Te214			50	50	202.032
10	ICP-OES-AV	Y 371.029			1	NA	202.032
11	ICP-MS 7900	Li,Rh,In,Te, Lu	Quadrupole	He	50	NA	95
12	NA	NA	NA	NA	NA	NA	NA

Table 86 Instrument Conditions for Na

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV	Y	ORS	He	80	80	23
2	ICP-MS	Sc	UC	He	625	625	23
3	ICP-OES-AV- buffer	Lu			250	500	589.592
4							
5	ICP-OES-RV	In 410.176			80	80	589.592
6	ICP-OES-RV	Y324	NA		200	4000	589.592nm
7	ICP-MS	Rh	CRI	He	160	160	
8	ICP-OES-RV	N/A	NA	He	NA	97.09	590
9	ICP-OES-AV	Y371 / Te214			50	50	588.995
10							
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-OES-AV	Eu	NA	NA	NA	25	589

Table 87 Instrument Conditions for Ni

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	80	60
2	ICP-MS	Ge	UC	He	625	625	60
3	ICP-MS	103	Collision	He	250	100	60
4							
5	ICP-MS/MS	Rh 103	ORS	O2	80	80	60 m/z
6	ICP-MS	Ge 72	ORS		200	200	60m/z
7	ICP-MS	Rh	CRI	He	80	80	
8	ICP-MS	Ga	KED	He	NA	485.45	60
9							
10	ICP-OES-AV	Y 371.029			1	1	231.604
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS	Sc	ORS	He	NA	25	60

Table 88 Instrument Conditions for P

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Y	ORS	HEHe	80	80	31
2	ICP-MS	Sc	UC	He	625	625	31
3	ICP-OES-AV- buffer	Lu			250	500	213.618
4							
5	ICP-OES-AV	In 303.936			80	80	185.878
6	ICP-OES-RV	Te214	NA		200	200	185.878nm
7							
8	ICP-OES-RV	N/A	NA	He	NA	97.09	186
9	ICP-OES-AV	Y371 / Te214			50	50	177.434
10	ICP-OES-AV	Y 371.029			10	10	213.618
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-OES-AV	Eu	NA	NA	NA	25	185

Table 89 Instrument Conditions for Pb

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ir	ORS	He	80	80	208
2	ICP-MS	Ir	NA	NA	625	625	206+207+208
3	ICP-MS	103	Collision	He	250	100	208
4							
5	ICP-MS/MS	Ir 193	ORS	O2	80	80	208 m/z
6	ICP-MS	Ir 193	ORS		200	200	208m/z
7	ICP-MS	Ir	CRI	standard mode	80	40	
8	ICP-MS	Tb	KED	He	NA	485.45	206+207+208
9	ICP-OES-AV	Y371 / Te214			50	50	220.353
10	ICP-OES-AV	Y 371.029			1	1	220.353
11	ICP-MS 7900	Li,Rh,In,Te, Lu	Quadrupole	He	50	NA	206
12	ICP-MS	Ir	ORS	He	NA	25	208

Table 90 Instrument Conditions for Rb

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	NA	85
2						NA	
3						NA	
4						NA	
5	NT	NT	NT	NT	NT	NT	NT
6	ICP-MS	Rh 103	ORS		4000	NA	85m/z
7						NA	
8	NA	NA	NA	NA	NA	NA	NA
9							
10						NA	
11	NA	NA	NA	NA	NA	NA	NA
12	NA	NA	NA	NA	NA	NA	NA



Table 91 Instrument Conditions for S

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV	Y	ORS	He	80	NA	181
2	ICP-OES-AV	Y	NA	NA	62.5	NA	181.975
3	ICP-OES-AV-buffer	Lu			250	NA	181.972
4						NA	
5	ICP-OES-AV	In 303.936			80	80	181.972 nm
6	ICP-OES-RV	Te214	NA		200	NA	180.669nm
7						NA	
8	NA	NA	NA	NA	NA	NA	NA
9	ICP-OES-AV	Y371 / Te214			500	500	180.669
10						NA	
11	NA	NA	NA	NA	NA	NA	NA
12	NA	NA	NA	NA	NA	NA	NA

Table 92 Instrument Conditions for Se

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	HEHe	80	80	78
2	ICP-MS	Rh	NA	NA	625	625	82
3	ICP-MS	72	Collision	He	250	100	78
4							
5	ICP-MS/MS	ICP-MS/MS	Rh 103	ORS	O2	80	Se 78/94(m/z)
6	ICP-MS	Rh 103	ORS		4000	4000	78m/z
7	ICP-MS	Te	CRI	HEHe	160	800	
8	ICP-MS	Te	KED	He	NA	485.45	82
9	ICP-OES-AV	Y371 / Te214				50	203.985
10	ICP-OES-AV	Y 371.029			1	1	196.026
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS	Sc	ORS	He	NA	25	78

Table 93 Instrument Conditions for Sn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	80	118
2	ICP-MS	Rh	NA	NA	625	625	118
3							
4							
5	ICP-MS/MS	ICP-MS/MS	Rh 103	ORS	O2	80	Sn 189.927(nm)
6	ICP-MS	Rh 103	ORS		4000	200	118m/z
7							
8	ICP-MS	Rh	KED	He	NA	485.45	120
9							
10							
11	ICP-MS 7900	Li,Rh,In,Te, Lu	Quadrupole	He	50	NA	118
12	ICP-MS	Rh	ORS	He	NA	25	118

Table 94 Instrument Conditions for Sr

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	NA	80	88
2	ICP-MS	Rh	NA	NA	NA	625	88
3	ICP-OES-AV- buffer	Lu			NA	100	407.771
4					NA		
5	ICP-MS/MS	Rh 103	ORS	O2	80	80	88 m/z
6	ICP-MS	Ge 72	ORS		NA	4000	88m/z
7					NA		
8	ICP-MS	Rh	KED	He	NA	485.45	88
9	ICP-OES-AV	Y371 / Te214				50	216.596
10					NA		
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS	Rh	ORS	He	NA	25	88

Table 95 Instrument Conditions for Tl

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ir	ORS	He	80	NA	232
2	ICP-MS	Ir	NA	NA	625	NA	205
3	ICP-MS	193	Collision	He	250	NA	205
4						NA	
5	ICP-MS/MS	Ir 193	ORS	O2	1600	NA	Tl 205/205(m/z)
6	ICP-MS	Ir 193	ORS		200	NA	205m/z
7	ICP-MS	Rh	CRI	standard mode	80	NA	
8	NA	NA	NA	NA	NA	NA	NA
9							
10	ICP-OES-AV	Y 371.029			1	NA	276.789
11	NA	NA	NA	NA	NA	NA	NA
12	NA	NA	NA	NA	NA	NA	NA

Table 96 Instrument Conditions for U

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Ir	ORS	He	80	NA	205
2	ICP-MS	Ir	NA	NA	625	NA	238
3	ICP-MS	103	Collision	He	250	NA	238
4						NA	
5	ICP-MS/MS	Ir 193	ORS	HEHe	80	80	238 m/z
6	ICP-MS	Ir 193	ORS		200	NA	238m/z
7						NA	
8	NA	NA	NA	NA	NA	NA	NA
9							
10						NA	
11	NA	NA	NA	NA	NA	NA	NA
12	NA	NA	NA	NA	NA	NA	NA

Table 97 Instrument Conditions for V

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	80	51
2	ICP-MS	Sc	UC	He	625	625	51
3	ICP-MS	45	Collision	He	250	100	51
4							
5	ICP-MS/MS	Rh 103	ORS	O2	80	80	67 m/z
6	ICP-MS	Ge 72	ORS		4000	200	51m/z
7							
8	ICP-MS	Sc	KED	He	NA	485.45	51
9							
10	ICP-OES-AV	Y 371.029			1	1	311.837
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS	Sc	ORS	He	NA	25	51

Table 98 Instrument Conditions for Zn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	80	80	64
2	ICP-MS	Ge	UC	He	625	625	66
3	ICP-OES-AV- buffer	Lu			250	100	206.2
4							
5	ICP-MS/MS	Rh 103	ORS	O2	80	80	66 m/z
6	ICP-OES-AV	Te214	NA		200	200	206.2nm
7	ICP-MS	Rh	CRI	He	80	800	
8	ICP-MS	Te	KED	He	NA	485.45	66
9	ICP-OES-AV	Y371 / Te214			50	50	202.548
10	ICP-OES-AV	Y 371.029			1	1	213.857
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS	Sc	ORS	He	NA	25	66

**END OF REPORT**