Australian Government
Department of Industry, Science, Energy and Resources

National Measurement Institute

Proficiency Test Final Report AQA 22-01 Nutrition Information Panel

June 2022

ACKNOWLEDGMENTS

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

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

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

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1 SUMMARY

This report presents the results of the proficiency test AQA 22-01 Nutrition Information Panel. The study focused on the measurement of moisture content, protein, saturated fat, total fat, total sugars, total dietary fibre, total nitrogen and total ash in bread crumb. The measurement of total: Ca, Fe, K, Mg and Na were also included in the program.

Nine laboratories registered to participate and all submitted results.

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

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

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

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

Of 83 z-scores, 78 (94%) were satisfactory with $|z| \leq 2.0$.

Of 83 E_n-scores, 73 (88%) were satisfactory with $|E_n| \leq 1.0$.

Laboratories 1 and **3** returned the highest number of satisfactory z scores (11 out of 11 reported).

ii. evaluate the laboratories' methods used in determination of nutrition information panel in food;

A limited number of laboratories have the capability to measure total dietary fibre in food.

The methods used by participants for TN measurement in S1 produced accurate results. The results reported were in excellent agreement with each-other, with a between laboratory CV of 2.2%.

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

Of 91 numerical results, 84 (92%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 1.5% to 27% of the reported value.

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

The test samples of this study were checked for homogeneity for some tests 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."[1] 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 nutrition information panel;
- develop the practical application of traceability and measurement uncertainty; and
- 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.[2] The statistical methods used are described in the NMI Chemical Proficiency Statistical Manual.[3] These documents have been prepared with reference to ISO Standard 17043[1] and The International Harmonised Protocol for Proficiency Testing of (Chemical) Analytical Laboratories.[4]

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 NOT 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 thirteen tests in the study samples were representative of those published in Australia New Zealand Food Standards Code.[5]

3.2 Participation

Nine laboratories participated and submitted results.

The timetable of the study was:

Invitation issued:	24 January 2022
Samples dispatched:	14 February 2022
Results due:	8 April 2022
Interim report issued:	11 April 2022

3.3 Test Material Specification

One sample was provided for analysis:

- Sample S1 was 100 g of dried bread crumbs.

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 Ca, Fe, K, Mg and Na, as the same preparation procedure was followed in previous studies.[1] The results from the partial homogeneity test for these samples are reported in the present study as the homogeneity value.

No homogeneity test was conducted for ash, moisture content, protein, total nitrogen, total fat, saturated fat, total sugars and total dietary fibre.

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. Results of this study gave no reason to question the stability of the test samples.

3.7 Sample Storage, Dispatch and Receipt

Sample S1 was stored at room temperature before dispatch.

The sample was dispatched by courier on 14 February 2022.

A description of the test sample, instructions for participants, and a form for participants to confirm the receipt of the test sample, was 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 sample should be stored during analysis at room temperature in a dry place e.g. desiccator with anhydrous calcium sulphate.
- Quantitatively analyse the sample using your normal test method.
- Participants are asked to report the results on as received basis for:

SAMPLE S1 bread crumbs	
Test	Units
Ca	mg/kg
Fe	mg/kg
K	mg/kg
Mg	mg/kg
Na	mg/kg
Ash at 550 +/- 25 ºC	g/100 g
Moisture at 102 +/- 2 ºC	g/100 g
Protein (use protein factor 6.25)	g/100 g
Total Nitrogen	g/100 g
Total Fat	g/100 g
Saturated Fat	g/100 g
Total Sugars	g/100 g
*Total Dietary Fibre (by AOAC 985.29 or 991.43)	g/100 g

*Association of Official Analytical Chemists 985.29 Total Dietary in Foods, Enzymatic – Gravimetric Method; Association of Official Analytical Chemists 991.43 Total, Insoluble and Soluble Dietary Fibre in Food- Enzymatic-Gravimetric Method

- 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.
- Please return the completed results sheet by e-mail (proficiency@measurement.gov.au) by **14 March 2022**.

The results due date was extended to 8 April 2022 due to exceptional circumstances.

3.9 Interim Report

An interim report was e-mailed to participants on 11 April 2022.

4 PARTICIPANT LABORATORY INFORMATION

4.1 Test Method Summaries

Summaries of test methods are transcribed in Tables 1 to 9.

Table 1 Methodology for Total Elements

Lab. Code	Method Reference	Sample Mass (g)	Temp. (°C)	Time (min)	Vol. HNO_3 (mL)	Vol. HCl (mL)	Vol. HNO_3 (1:1) (mL)	Vol. HCl (1:1) (mL)	Vol. H_2O_2 (mL)	Other
1	In-house	0.5	103	90	3	1				
2		0.5				0.5			1	
3	In-house	0.5	103	90	3	1				
4	In-house TP394	2	200	45	10	2				
5		0.5	100	120	3	1				
6*										
7	In-house	0.5	95-105	45	3.5					
8										
9	AOAC 985.35, AOAC 2011.14	1.0073	110	100	7					

*Additional information in Table 9

Table 2 Methodology for Moisture Content and Ash

Lab Code	Methodology for Moisture Content and Ash
1	In house method .Moisture- sample weight - 1-2g , oven temperature 102+/-2ºC. Ash - sample weight - 1-2g, Ash furnace temperature - 550 degree, Time in ash furnace (hours) 24 - <48 hrs.
2	Loss on drying at 100C & Loss on Ignition at 550C
3	In house method .Moisture- sample weight - 1-2g , oven temperature 102+/-2ºC. Ash - sample weight - 1-2g, Ash furnace temperature - 550 degree, Time in ash furnace (hours) 24 - <48 hrs.
4	Ash AACC 08-01 Moisture - Gravimetric air oven
5	in-house method
6	Air oven and muffle, in house
8	Fan forced oven at 103° C/Furnace AACC 08-01
9	Air oven drying 102ºC for 90mins

Table 3 Methodology for Protein

Lab Code	Methodology for Protein
1	In house method - Kjeldahl , Sample weight - 1-2g ,sulphuric acid digestion with catalyst copper (cu).
2	Calculation = TN x 6.25
3	In house method - Kjeldahl , Sample weight - 1-2g ,sulphuric acid digestion with catalyst copper (cu).
4	AACC 46-12; 70-20a Kjeldhal
6	Kjeldahl, in house
8	Kjeldahl AACC 46-12
9	Dumas combustion

Table 4 Methodology for Total Nitrogen

Lab Code	Methodology for Total Nitrogen
1	In house method - Keldahl, Sample weight - 1-2g, sulphuric acid didestion with catalyst copper (cu).
2	Total Nitrogen by high temperature combustion
3	In house method - Kjeldahl , Sample weight - 1-2g ,sulphuric acid digestion with catalyst copper (cu).
4	AACC 46-12; 70-20a kjeldhal
6	Kjeldahl, in house
8	Kjeldahl AACC 46-12
9	NT

Table 5 Methodology for Total Fat

Lab Code	Methodology for Total Fat
1	HCl Hydrolysis followed by Mojonnier extraction with diethyl ether and petroleum spirits.
2	Soxhlet extraction and Gravimetric determination of fat
3	HCl Hydrolysis followed by Mojonnier extraction with diethyl ether and petroleum spirits.
4	AOAC 922.06 - acid hydrolysis
6	Mojonnier acid hydrolysis, in house
8	Acid hydrolysis - AOAC 922.06
9	Acid Hydrolysis AOAC 992.06

Table 6 Methodology for Saturated Fat

Lab Code	Methodology for Saturated Fat
1	Fat extraction using CEM EDGE followed by esterification using 2M methanolic KOH and hexane.
3	Fat extraction using CEM EDGE followed by esterification using 2M methanolic KOH and hexane.
4	AOAC 969.33
6	Derivitisation then GC-FID, in house
8	Gas chromatography: AOAC 969.33
9	NT

Table 7 Methodology for Total Sugars

Lab Code	Methodology for Total Sugars
1	Water extraction, HPLC determination with refractive index detector
2	Simple Sugars by HPLC-RI
3	Water extraction, HPLC determination with refractive index detector
4	In house - LCMS
6	LCMS
8	In house HPLC
9	Water extraction, HPLC

Table 8 Methodology for Total Dietary Fibre

Lab Code	Methodology for Total Dietary Fibre
4	AOAC 985.29
6	AOAC 985.29
8	NT
9	AOAC 991.43

4.2 Instruments Used for Measurements

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

4.3 Additional Information

Participants had the option to report additional information for each sample analysed. These are transcribed in Table 9.

Table 9 Additional Information

Lab Code	Additional Information
6	Methodology for Total Elements - 4g Sample ashed then boiled in HCl for AAS (final 10% acid). 2.5g sample ashed then boiled in HNO_3 for ICPMS (final 5% acid).

4.4 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about the basis of their uncertainty estimates (Table 10).

Table 10 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
1	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples Duplicate Analysis Instrument Calibration	Laboratory Bias from PT Studies Recoveries of SS	ISO/GUM
2	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis	CRM	NMI Uncertainty Course
3	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples Duplicate Analysis Instrument Calibration	Laboratory Bias from PT Studies Recoveries of SS	ISO/GUM
4	Top Down - precision and estimates of the method and laboratory bias	Standard deviation from PT studies only		NATA technical note
		Duplicate Analysis	Laboratory Bias from PT Studies Recoveries of SS	
5	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis	Instrument Calibration Recoveries of SS	Nordtest Report TR537
6	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate Analysis	Variation in Sample Moisture Content Laboratory Bias from PT Studies Recoveries of SS	
7	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples - RM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	Control charts from LCS
8	Top Down - precision and estimates of the method and laboratory bias	Standard deviation from PT studies only		NATA technical Note
		Duplicate Analysis	Laboratory Bias from PT Studies	
9	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis	Laboratory Bias from PT Studies Recoveries of SS	ISO/GUM

[a]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 11 to 23 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 14. An example chart with interpretation guide is shown in Figure 1.

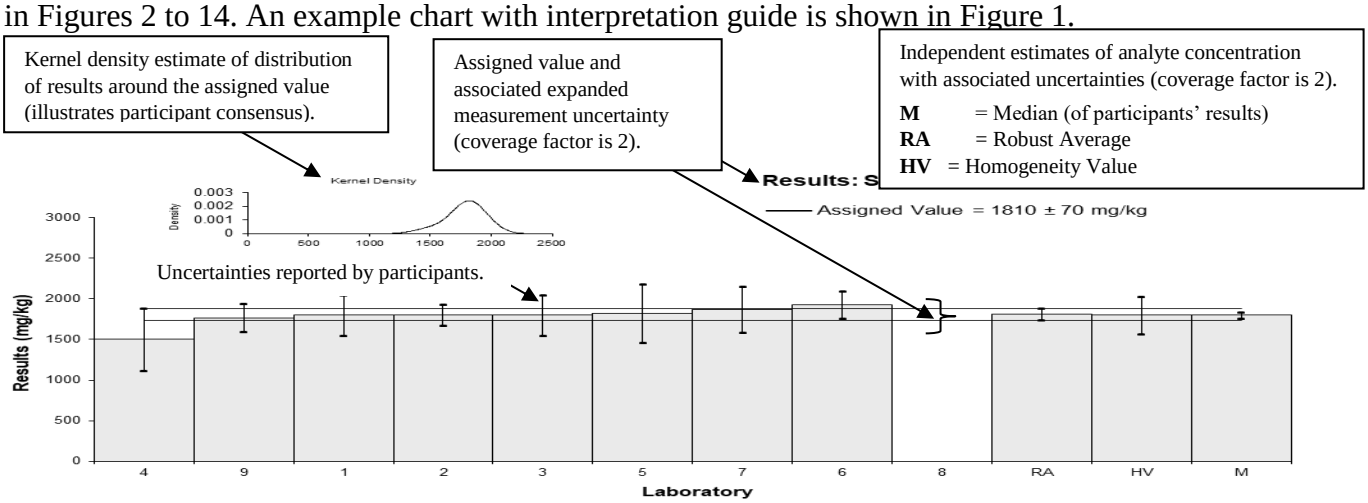


Figure 1 Guide to Presentation of Results

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.[3, 4]

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.'[1] In this study the property is the mass fraction of analyte. Assigned values were the robust average of participants' results; the expanded uncertainties were estimated from the associated robust standard deviations.[4, 6]

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)'.[6]

The robust between-laboratory coefficient of variation (robust CV) is a measure of the variability of participants' results and was calculated using the procedure described in ISO13528:2015(E).[6]

5.5 Target Standard Deviation for Proficiency Assessment

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

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

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

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:

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

Where:

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

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

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

5.7 E_n-Score

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

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

Where:

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

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

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

5.8 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025:2018[8] must establish and demonstrate the traceability and measurement uncertainty associated with their test results. Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.[9]

6 TABLES AND FIGURES

Table 11

Sample Details

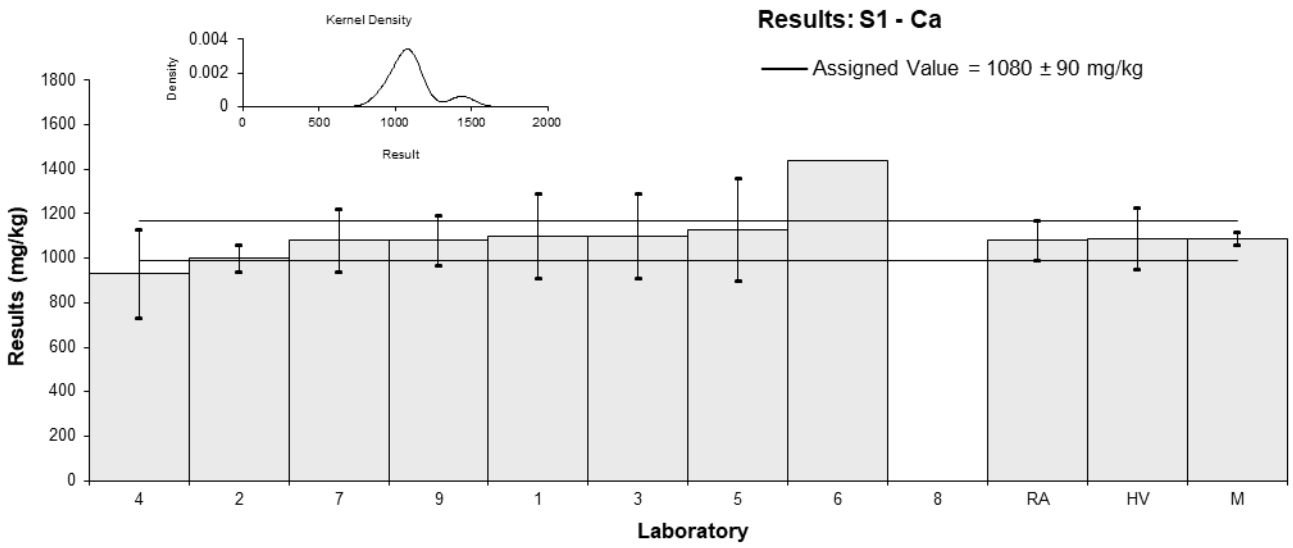
Sample	S1
Analyte	Ca
Matrix	Bread Crumbs
Unit	mg/kg

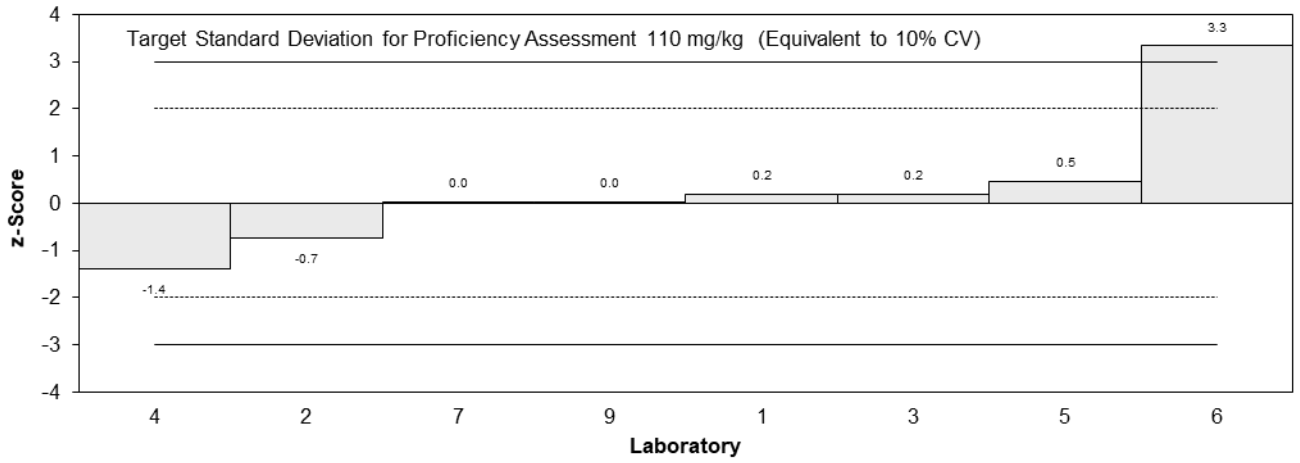
Participant Results

Lab. Code	Result	U	z	E_n
1	1100	190	0.19	0.10
2	1000	60	-0.74	-0.74
3	1100	190	0.19	0.10
4	930	200	-1.39	-0.68
5	1130	230	0.46	0.20
6	1440	NR	3.33	4.00
7	1082	141	0.02	0.01
8	NT	NT		
9	1082	113.6	0.02	0.01

Statistics

Assigned Value	1080	90
Homogeneity Value	1090	140
Robust Average	1080	90
Median	1090	30
Mean	1110	110
N	8	
Max	1440	
Min	930	
Robust SD	100	
Robust CV (%)	9.3	


Results: S1 - Ca
Assigned Value = 1080 ± 90 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
4
2
7
9
1
3
5
6
8
RA
HV
M


z-Scores: S1 - Ca
Target Standard Deviation for Proficiency Assessment 110 mg/kg (Equivalent to 10% CV)
z-Score
Laboratory
-1.4
-0.7
0.0
0.0
0.2
0.2
0.5
3.3

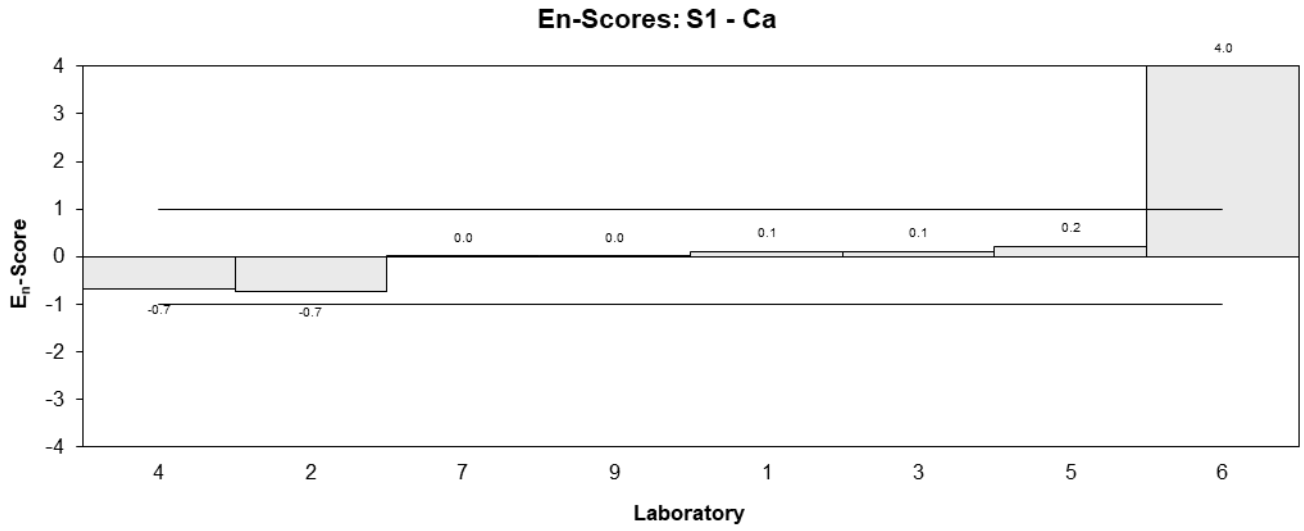

En-Scores: S1 - Ca
En-Score
Laboratory
-0.7
-0.7
0.0
0.0
0.1
0.1
0.2
4.0

Figure 2

Table 12

Sample Details

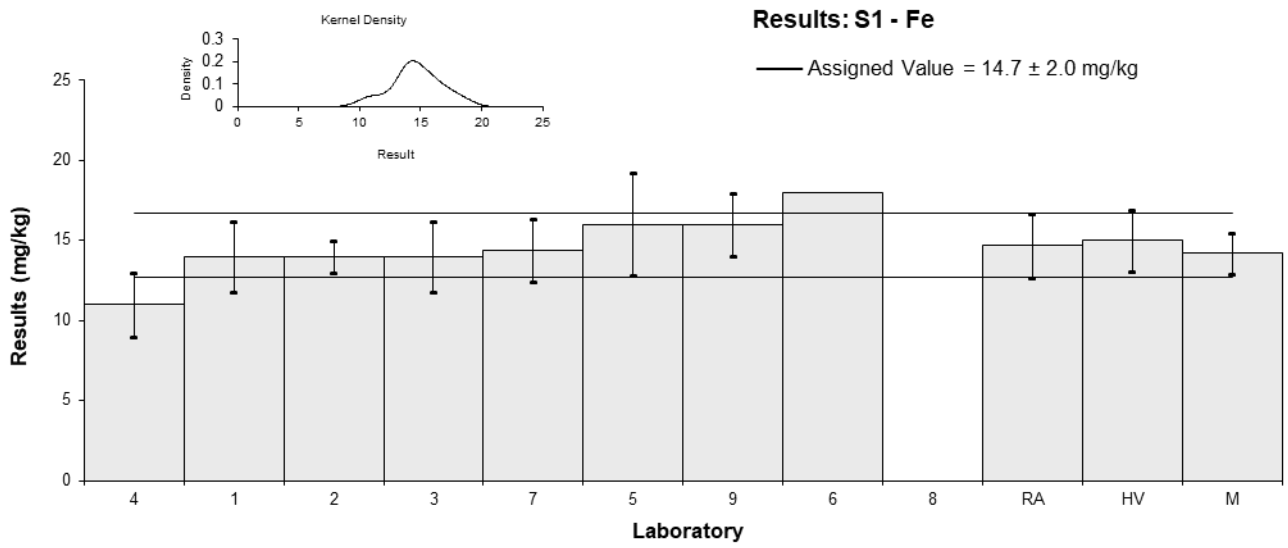
Sample	S1
Analyte	Fe
Matrix	Bread Crumbs
Unit	mg/kg

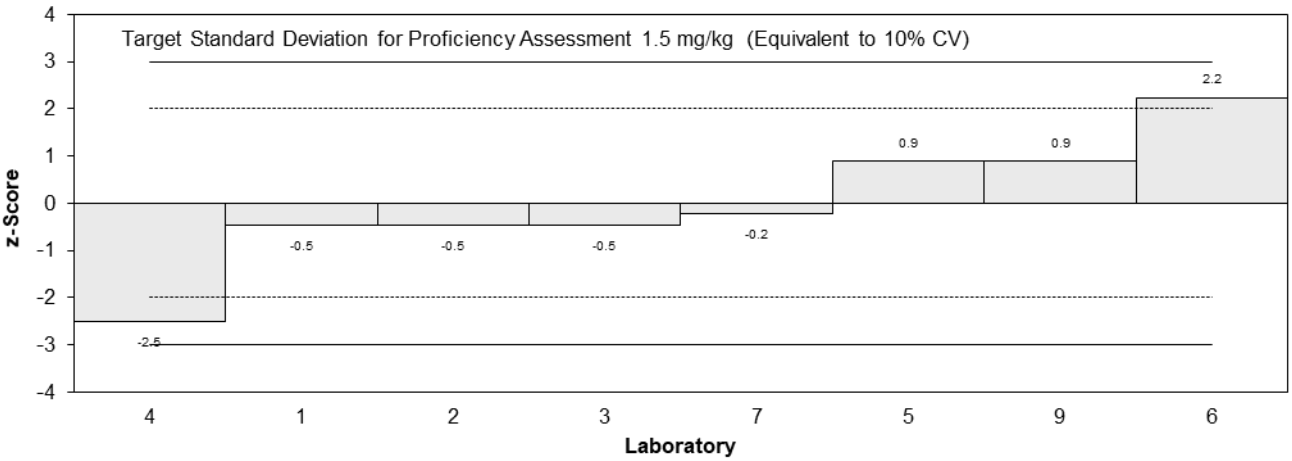
Participant Results

Lab. Code	Result	U	z	E_n
1	14	2.2	-0.48	-0.24
2	14	1	-0.48	-0.31
3	14	2.2	-0.48	-0.24
4	11	2.0	-2.52	-1.31
5	16	3.2	0.88	0.34
6	18.0	NR	2.24	1.65
7	14.38	1.94	-0.22	-0.11
8	NT	NT		
9	16	1.98	0.88	0.46

Statistics

Assigned Value	14.7	2.0
Homogeneity Value	15.0	1.9
Robust Average	14.7	2.0
Median	14.2	1.3
Mean	14.7	1.5
N	8	
Max	18	
Min	11	
Robust SD	2.2	
Robust CV (%)	15	


Kernel Density
Density
Result
Results: S1 - Fe
Assigned Value = 14.7 ± 2.0 mg/kg
Results (mg/kg)
Laboratory
4
1
2
3
7
5
9
6
8
RA
HV
M


z-Scores: S1 - Fe
Target Standard Deviation for Proficiency Assessment 1.5 mg/kg (Equivalent to 10% CV)
z-Score
Laboratory
-2.5
-0.5
-0.5
-0.5
-0.2
0.9
0.9
2.2

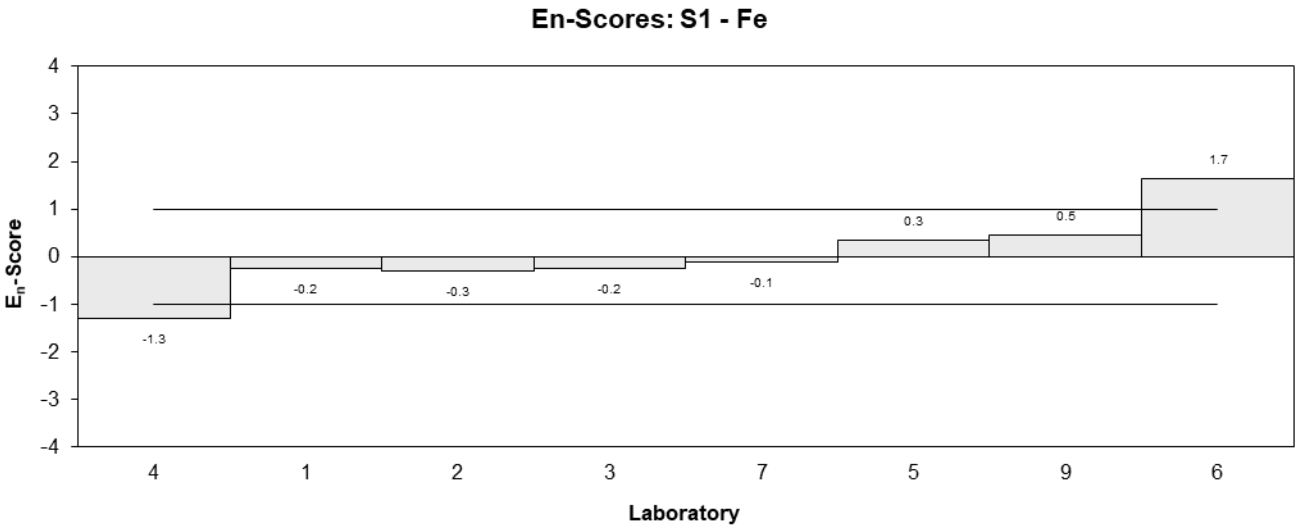

En-Scores: S1 - Fe
En-Score
Laboratory
-1.3
-0.2
-0.3
-0.2
-0.1
0.3
0.5
1.7

Figure 3

Table 13

Sample Details

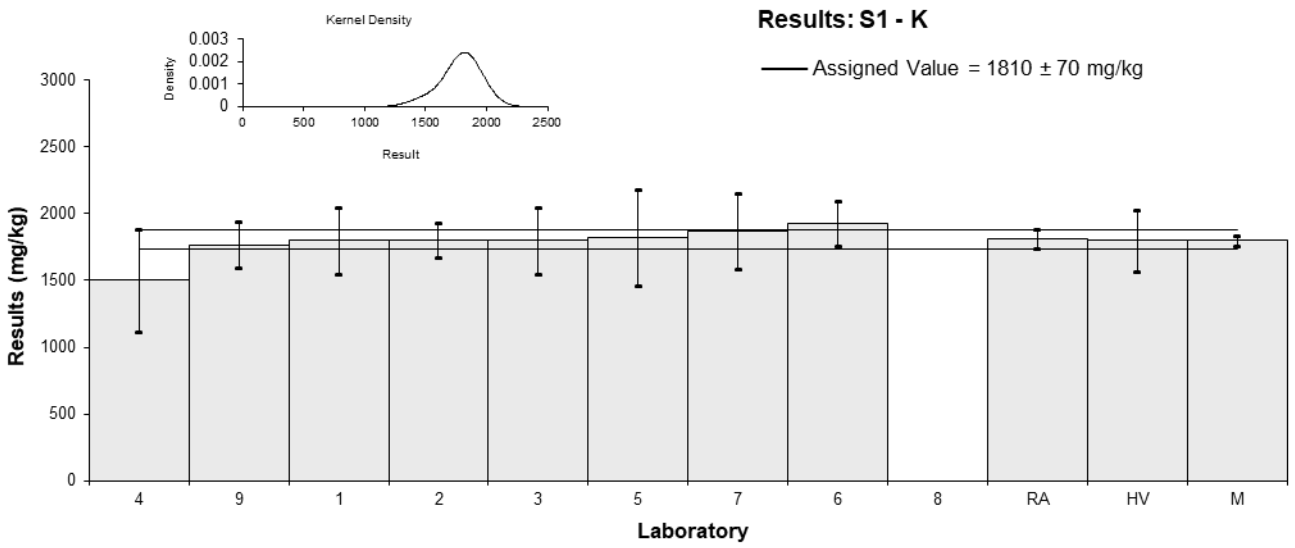
Sample	S1
Analyte	K
Matrix	Bread Crumbs
Unit	mg/kg

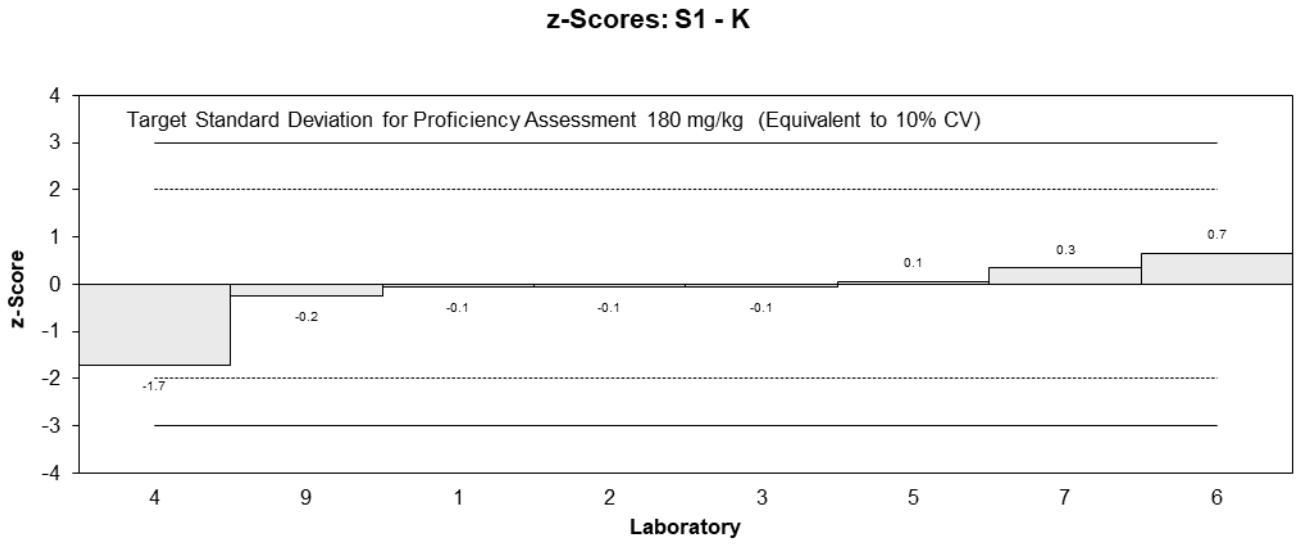
Participant Results

Lab. Code	Result	U	z	E_n
1	1800	250	-0.06	-0.04
2	1800	130	-0.06	-0.07
3	1800	250	-0.06	-0.04
4	1500	380	-1.71	-0.80
5	1820	360	0.06	0.03
6	1930	170	0.66	0.65
7	1872	281	0.34	0.21
8	NT	NT		
9	1766	173	-0.24	-0.24

Statistics

Assigned Value	1810	70
Homogeneity Value	1800	230
Robust Average	1810	70
Median	1800	40
Mean	1790	90
N	8	
Max	1930	
Min	1500	
Robust SD	80	
Robust CV (%)	4.4	


Kernel Density
Density
0.003
0.002
0.001
0
0
500
1000
1500
2000
2500
Result
Results: S1 - K
Assigned Value = 1810 ± 70 mg/kg
Results (mg/kg)
3000
2500
2000
1500
1000
500
0
4
9
1
2
3
5
7
6
8
RA
HV
M
Laboratory


z-Scores: S1 - K
Target Standard Deviation for Proficiency Assessment 180 mg/kg (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.7
-0.2
-0.1
-0.1
-0.1
0.1
0.3
0.7
4
9
1
2
3
5
7
6
Laboratory

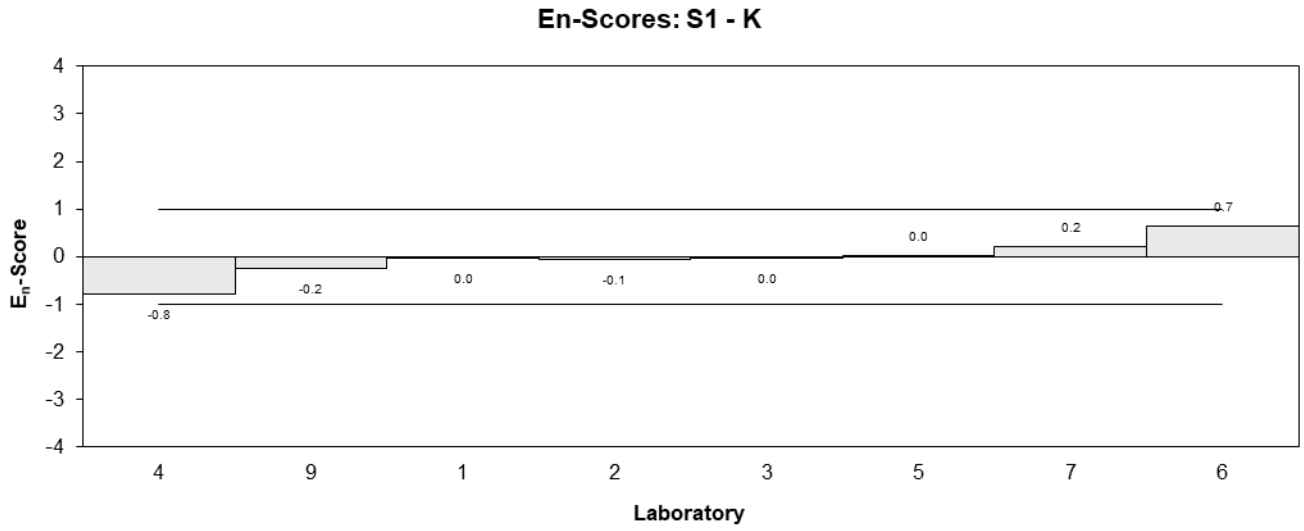

En-Scores: S1 - K
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.8
-0.2
0.0
-0.1
0.0
0.0
0.2
0.7
4
9
1
2
3
5
7
6
Laboratory

Figure 4

Table 14

Sample Details

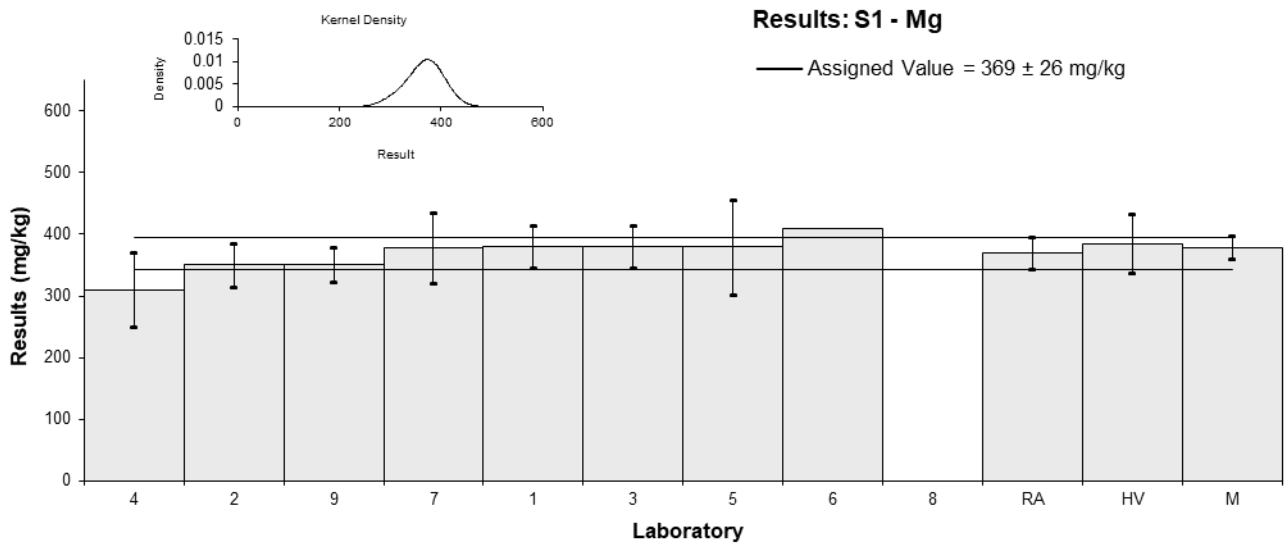
Sample	S1
Analyte	Mg
Matrix	Bread Crumbs
Unit	mg/kg

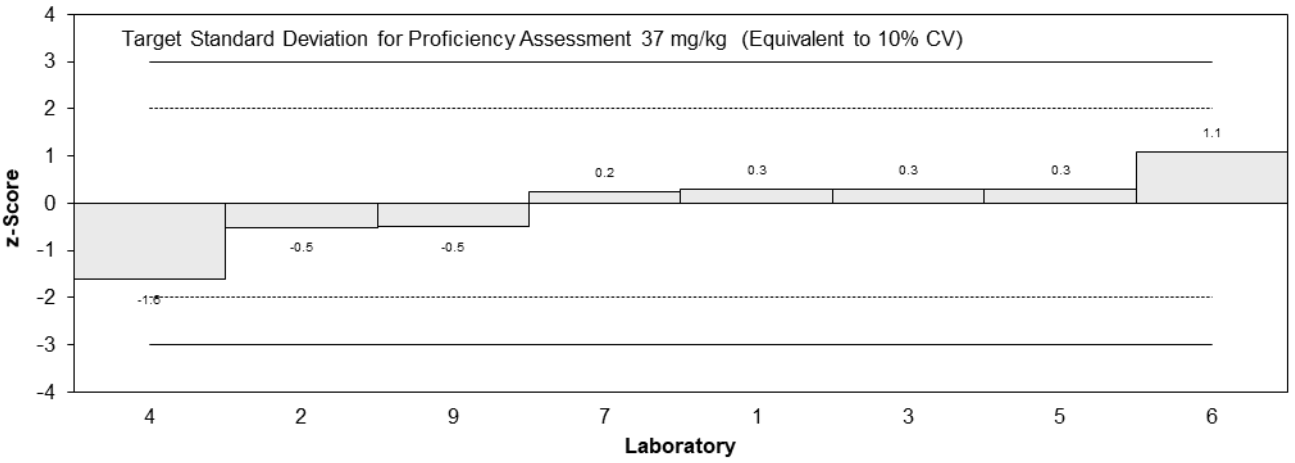
Participant Results

Lab. Code	Result	U	z	E_n
1	380	34	0.30	0.26
2	350	35	-0.51	-0.44
3	380	34	0.30	0.26
4	310	60	-1.60	-0.90
5	380	77	0.30	0.14
6	409	NR	1.08	1.54
7	378	57	0.24	0.14
8	NT	NT		
9	351	28.8	-0.49	-0.46

Statistics

Assigned Value	369	26
Homogeneity Value	385	48
Robust Average	369	26
Median	379	19
Mean	367	21
N	8	
Max	409	
Min	310	
Robust SD	29	
Robust CV (%)	7.9	


Kernel Density
Density
0.015
0.01
0.005
0
0
200
400
600
Result
Results: S1 - Mg
Assigned Value = 369 ± 26 mg/kg
Results (mg/kg)
600
500
400
300
200
100
0
4
2
9
7
1
3
5
6
8
RA
HV
M
Laboratory


z-Scores: S1 - Mg
Target Standard Deviation for Proficiency Assessment 37 mg/kg (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.6
-0.5
-0.5
0.2
0.3
0.3
0.3
1.1
4
2
9
7
1
3
5
6
Laboratory

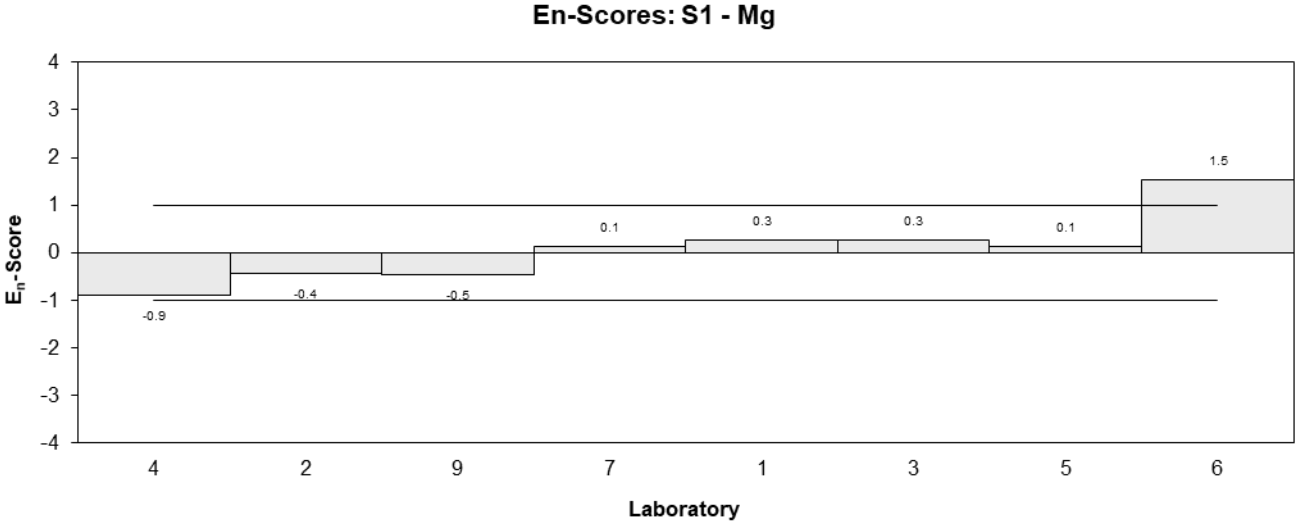

En-Scores: S1 - Mg
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.9
-0.4
-0.5
0.1
0.3
0.3
0.1
1.5
4
2
9
7
1
3
5
6
Laboratory

Figure 5

Table 15

Sample Details

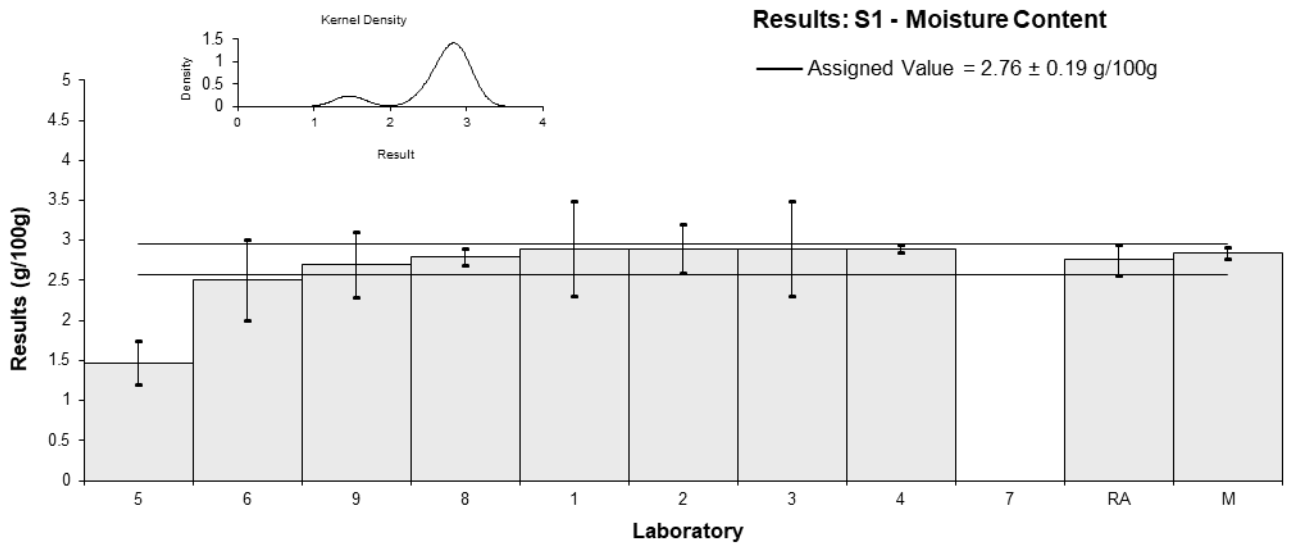
Sample	S1
Analyte	Moisture Content
Matrix	Bread Crumbs
Unit	g/100g

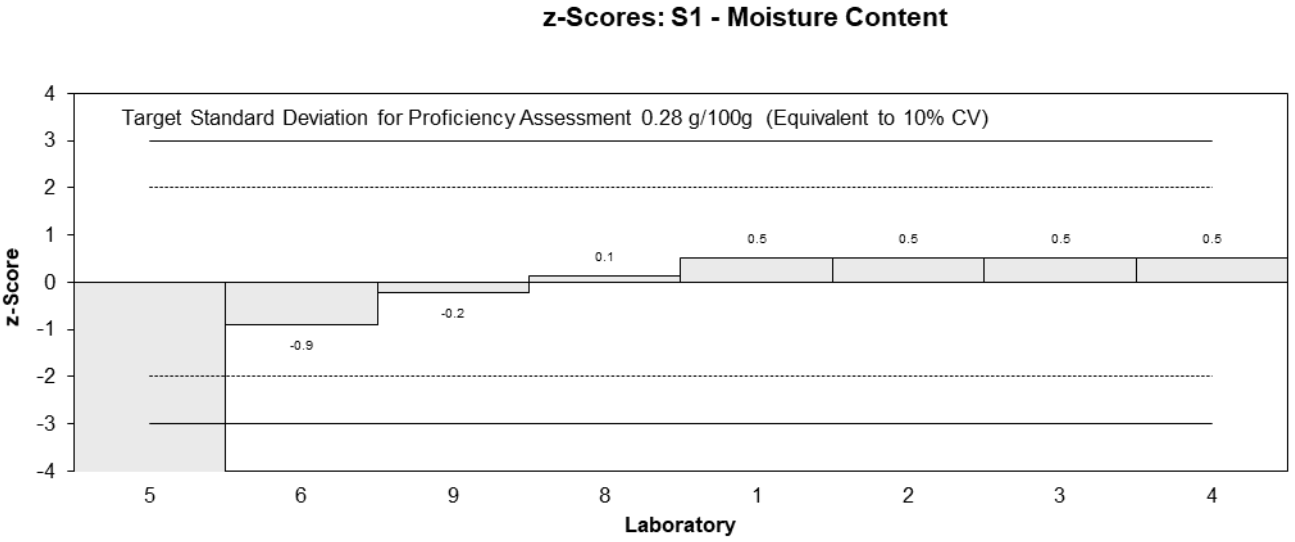
Participant Results

Lab. Code	Result	U	z	E_n
1	2.9	0.6	0.51	0.22
2	2.9	0.3	0.51	0.39
3	2.9	0.6	0.51	0.22
4	2.9	0.05	0.51	0.71
5	1.47	0.27	-4.67	-3.91
6	2.51	0.5	-0.91	-0.47
7	NT	NT		
8	2.8	0.1	0.14	0.19
9	2.7	0.41	-0.22	-0.13

Statistics

Assigned Value	2.76	0.19
Robust Average	2.76	0.19
Median	2.85	0.07
Mean	2.64	0.35
N	8	
Max	2.9	
Min	1.47	
Robust SD	0.22	
Robust CV (%)	7.8	


Kernel Density
Density
Result
Results: S1 - Moisture Content
Assigned Value = 2.76 ± 0.19 g/100g
Results (g/100g)
Laboratory
5
6
9
8
1
2
3
4
7
RA
M


z-Scores: S1 - Moisture Content
Target Standard Deviation for Proficiency Assessment 0.28 g/100g (Equivalent to 10% CV)
z-Score
Laboratory
-0.9
-0.2
0.1
0.5
0.5
0.5
0.5

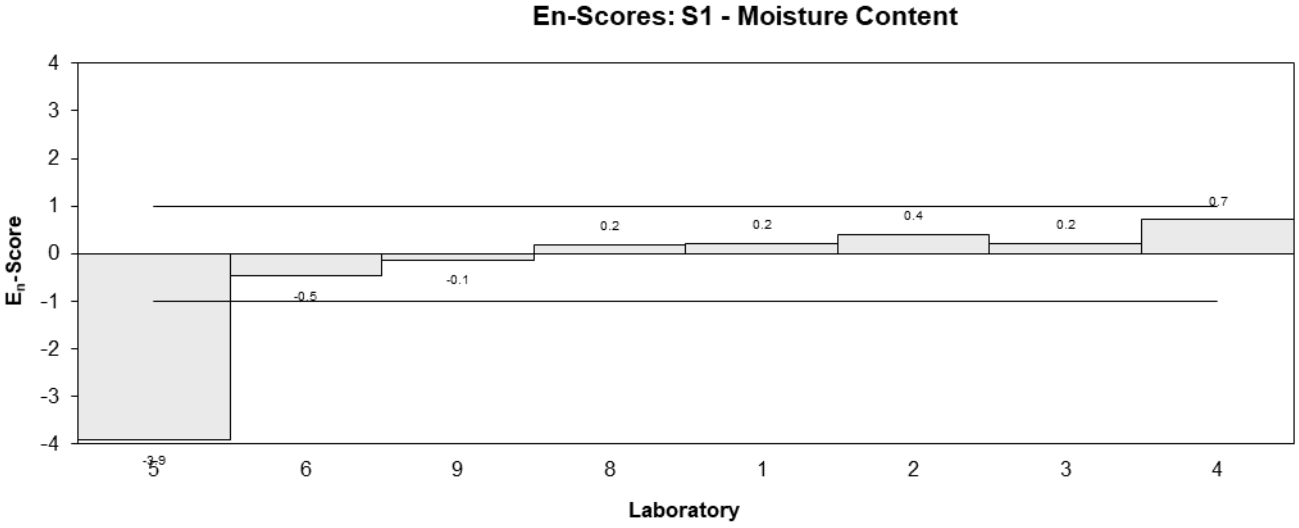

En-Scores: S1 - Moisture Content
En-Score
Laboratory
-0.5
-0.1
0.2
0.2
0.4
0.2
0.7

Figure 6

Table 16

Sample Details

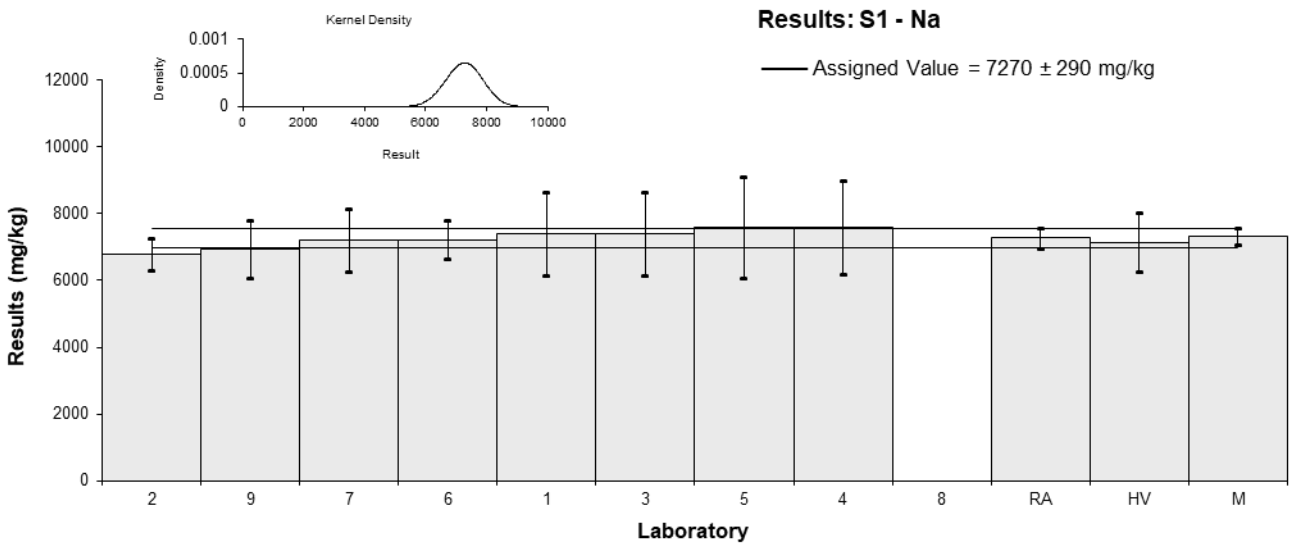
Sample	S1
Analyte	Na
Matrix	Bread Crumbs
Unit	mg/kg

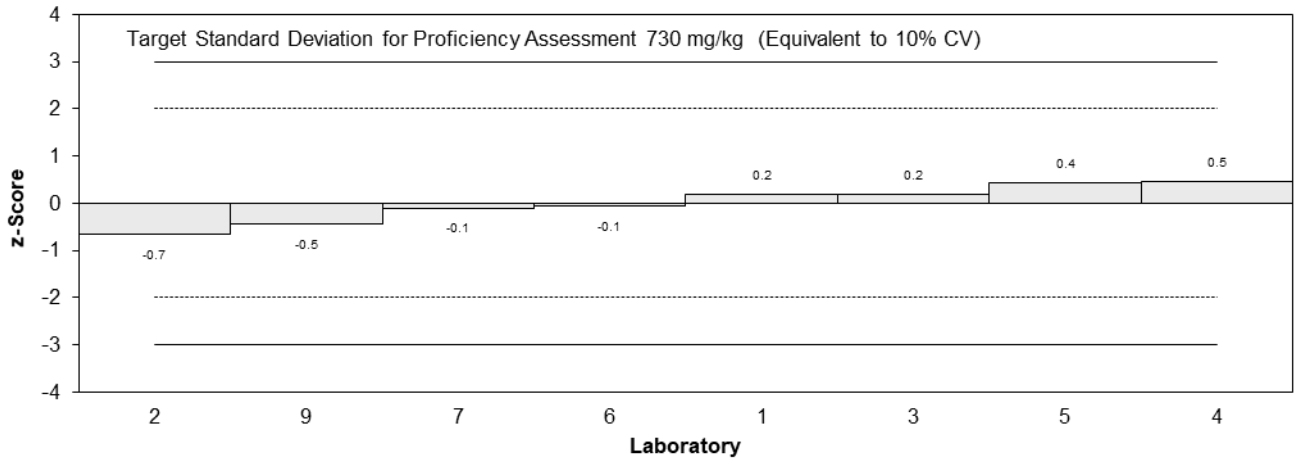
Participant Results

Lab. Code	Result	U	z	E_n
1	7400	1260	0.18	0.10
2	6800	480	-0.65	-0.84
3	7400	1260	0.18	0.10
4	7600	1400	0.45	0.23
5	7580	1520	0.43	0.20
6	7230	580	-0.06	-0.06
7	7198	936	-0.10	-0.07
8	NT	NT		
9	6946	854	-0.45	-0.36

Statistics

Assigned Value	7270	290
Homogeneity Value	7150	890
Robust Average	7270	290
Median	7320	250
Mean	7270	200
N	8	
Max	7600	
Min	6800	
Robust SD	320	
Robust CV (%)	4.5	


Kernel Density
Density
0.001
0.0005
0
0
2000
4000
6000
8000
10000
Result
Results: S1 - Na
Assigned Value = 7270 ± 290 mg/kg
Results (mg/kg)
12000
10000
8000
6000
4000
2000
0
2
9
7
6
1
3
5
4
8
RA
HV
M
Laboratory


z-Scores: S1 - Na
Target Standard Deviation for Proficiency Assessment 730 mg/kg (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.7
-0.5
-0.1
-0.1
0.2
0.2
0.4
0.5
2
9
7
6
1
3
5
4
Laboratory

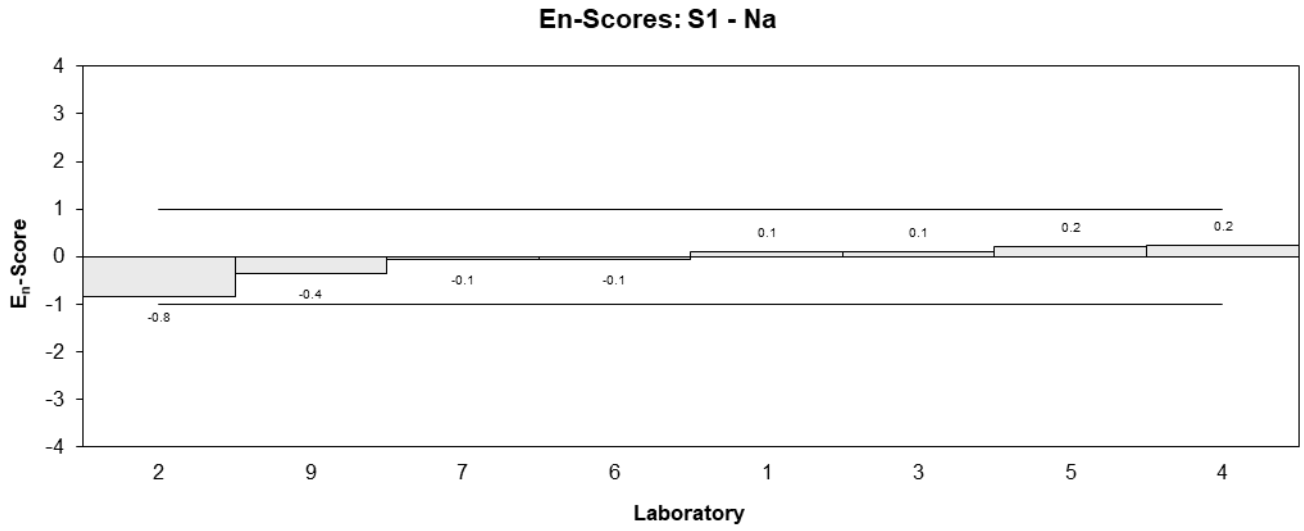

En-Scores: S1 - Na
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.8
-0.4
-0.1
-0.1
0.1
0.1
0.2
0.2
2
9
7
6
1
3
5
4
Laboratory

Figure 7

Table 17

Sample Details

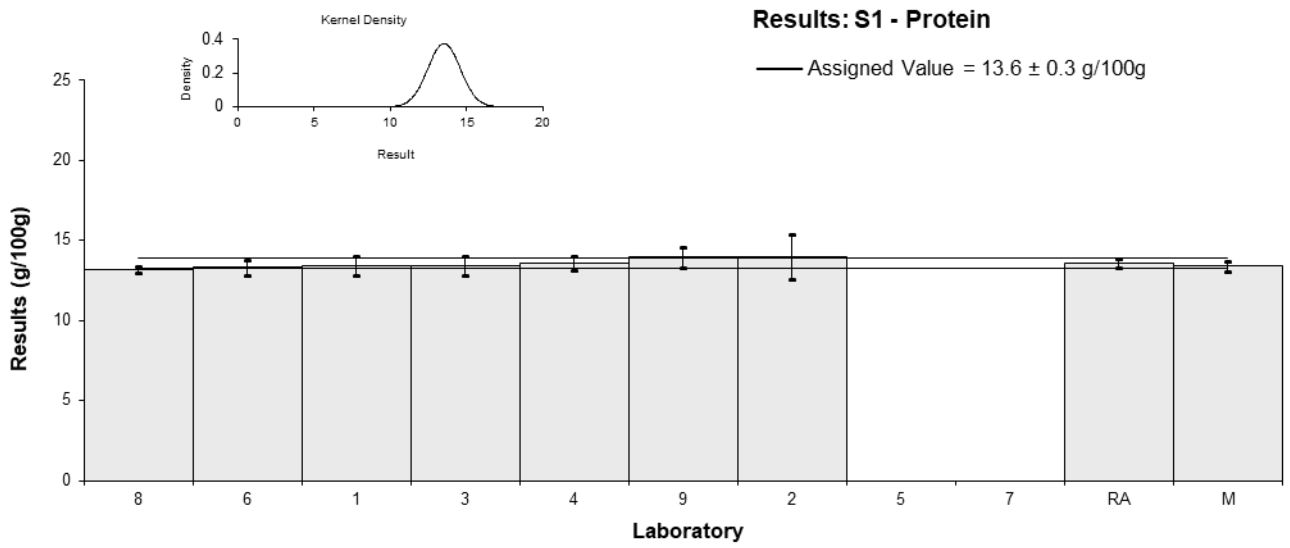
Sample	S1
Analyte	Protein
Matrix	Bread Crumbs
Unit	g/100g

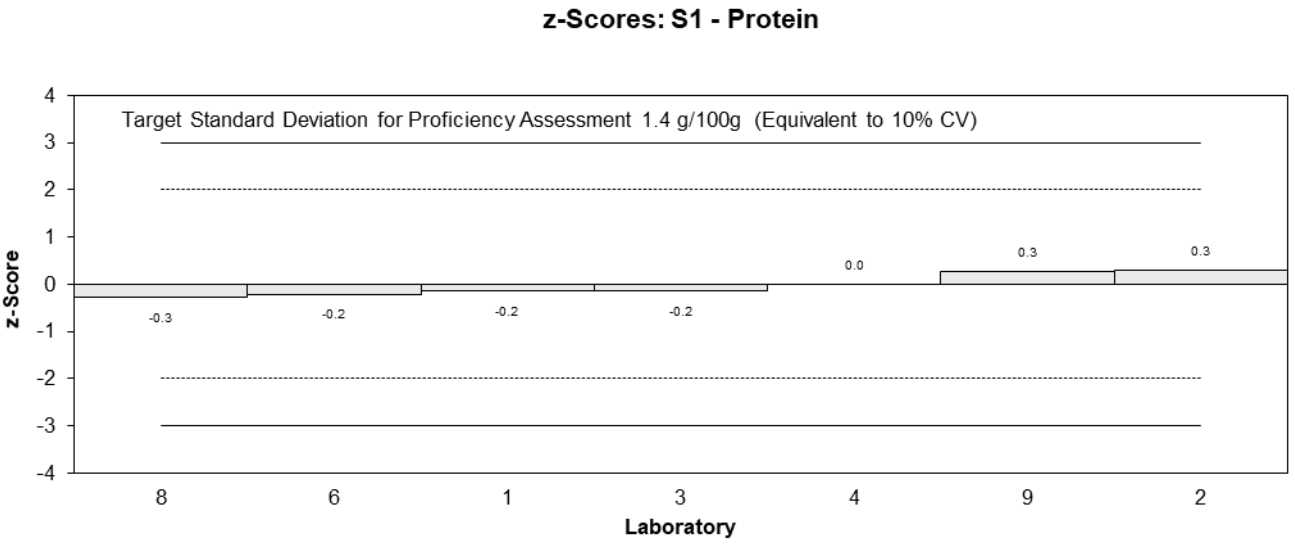
Participant Results

Lab. Code	Result	U	z	E_n
1	13.4	0.6	-0.15	-0.30
2	14.0	1.4	0.29	0.28
3	13.4	0.6	-0.15	-0.30
4	13.60	0.44	0.00	0.00
5	NR	NR		
6	13.31	0.5	-0.21	-0.50
7	NT	NT		
8	13.2	0.2	-0.29	-1.11
9	13.95	0.61	0.26	0.51

Statistics

Assigned Value	13.6	0.3
Robust Average	13.6	0.3
Median	13.4	0.3
Mean	13.6	0.2
N	7	
Max	14	
Min	13.2	
Robust SD	0.36	
Robust CV (%)	2.6	


Kernel Density
Density
Result
Results: S1 - Protein
Assigned Value = 13.6 ± 0.3 g/100g
Results (g/100g)
Laboratory
8
6
1
3
4
9
2
5
7
RA
M


z-Scores: S1 - Protein
Target Standard Deviation for Proficiency Assessment 1.4 g/100g (Equivalent to 10% CV)
z-Score
-0.3
-0.2
-0.2
-0.2
0.0
0.3
0.3
Laboratory
8
6
1
3
4
9
2

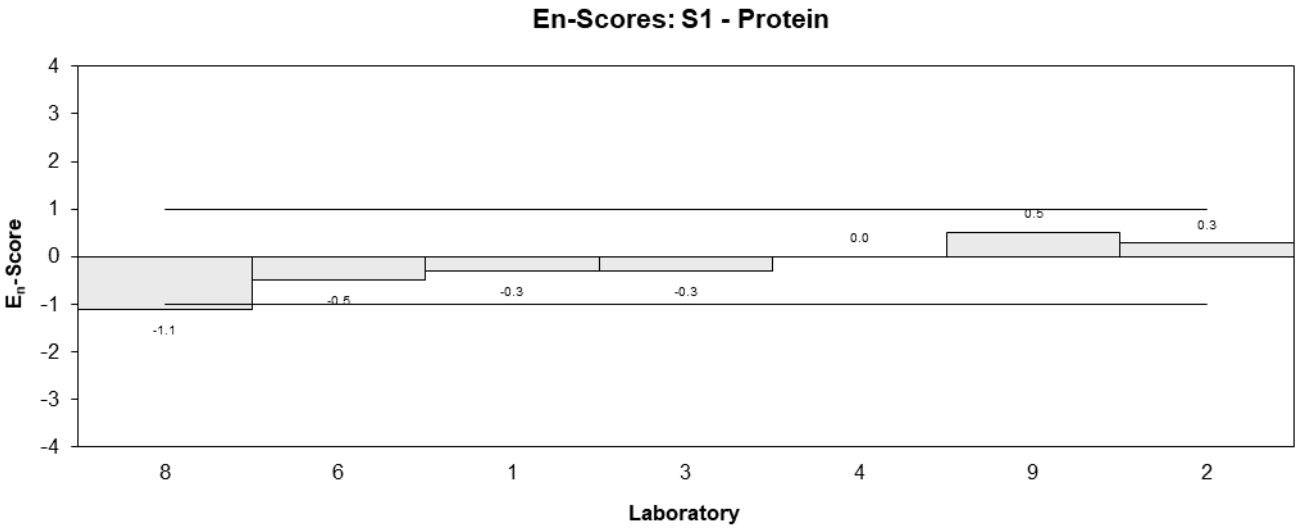

En-Scores: S1 - Protein
En-Score
-1.1
-0.5
-0.3
-0.3
0.0
0.5
0.3
Laboratory
8
6
1
3
4
9
2

Figure 8

Table 18

Sample Details

Sample	S1
Analyte	Saturated Fat
Matrix	Bread Crumbs
Unit	g/100g

Participant Results

Lab. Code	Result	U
1	1.3	0.1
2	NT	NT
3	1.4	0.1
4	1.21	0.10
5	NR	NR
6	0.46	NR
7	NT	NT
8	0.9	0.1
9	NT	NT

Statistics

Assigned Value	Not Set	
Median	1.21	0.32
Mean	1.05	0.34
N	5	
Max	1.4	
Min	0.46	
Robust SD	0.43	
Robust CV (%)	41	

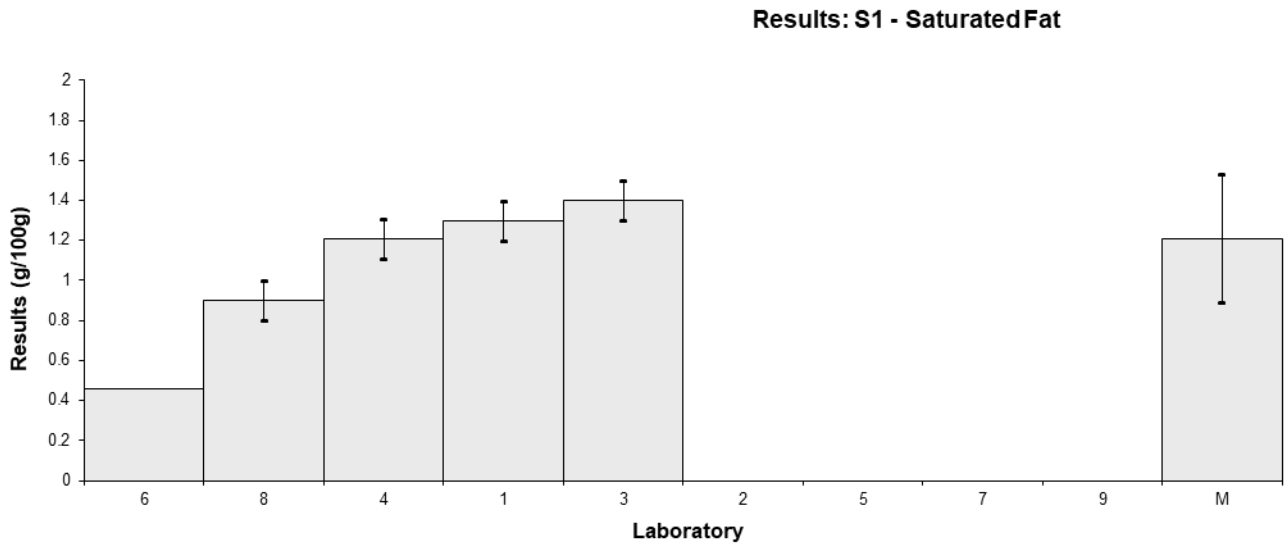

Results: S1 - Saturated Fat
Results (g/100g)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
6
8
4
1
3
2
5
7
9
M
Laboratory

Figure 9

Table 19

Sample Details

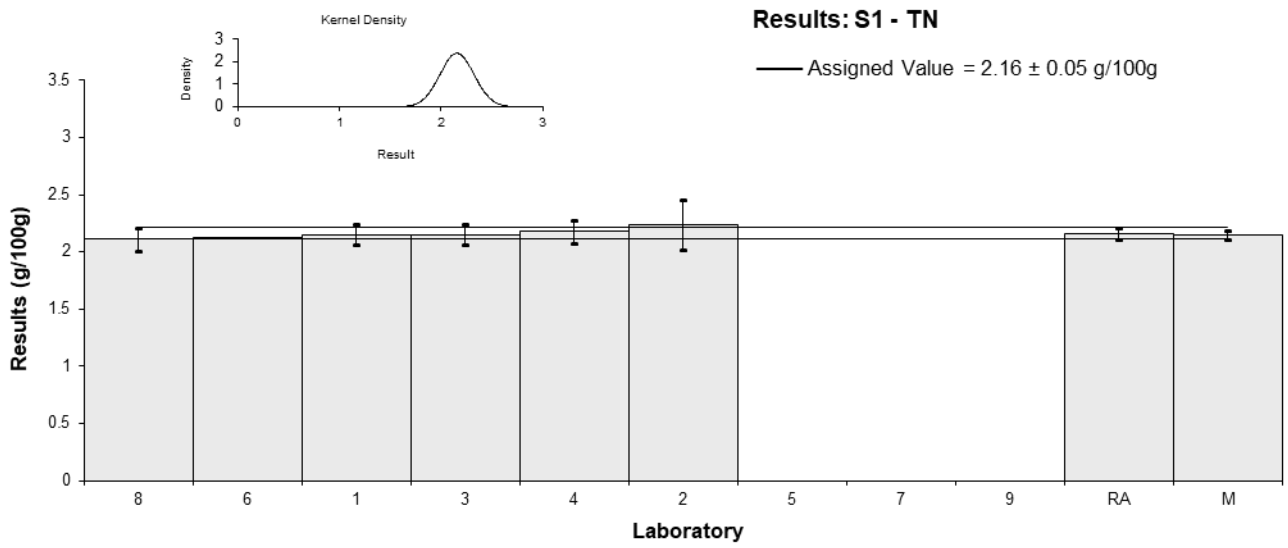
Sample	S1
Analyte	TN
Matrix	Bread Crumbs
Unit	g/100g

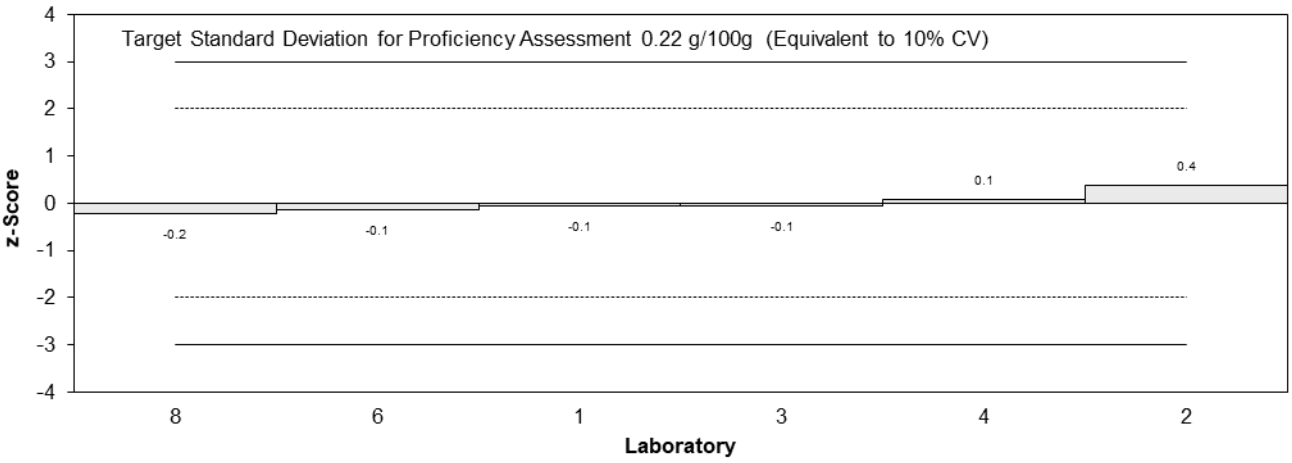
Participant Results

Lab. Code	Result	U	z	E_n
1	2.15	0.09	-0.05	-0.10
2	2.24	0.22	0.37	0.35
3	2.15	0.09	-0.05	-0.10
4	2.18	0.10	0.09	0.18
5	NR	NR		
6	2.130	NR	-0.14	-0.60
7	NT	NT		
8	2.11	0.1	-0.23	-0.45
9	NT	NT		

Statistics

Assigned Value	2.16	0.05
Robust Average	2.16	0.05
Median	2.15	0.04
Mean	2.16	0.04
N	6	
Max	2.24	
Min	2.11	
Robust SD	0.048	
Robust CV (%)	2.2	


Kernel Density
Density
Result
Results: S1 - TN
Assigned Value = 2.16 ± 0.05 g/100g
Results (g/100g)
Laboratory
8
6
1
3
4
2
5
7
9
RA
M


z-Scores: S1 - TN
Target Standard Deviation for Proficiency Assessment 0.22 g/100g (Equivalent to 10% CV)
z-Score
-0.2
-0.1
-0.1
-0.1
0.1
0.4
Laboratory
8
6
1
3
4
2

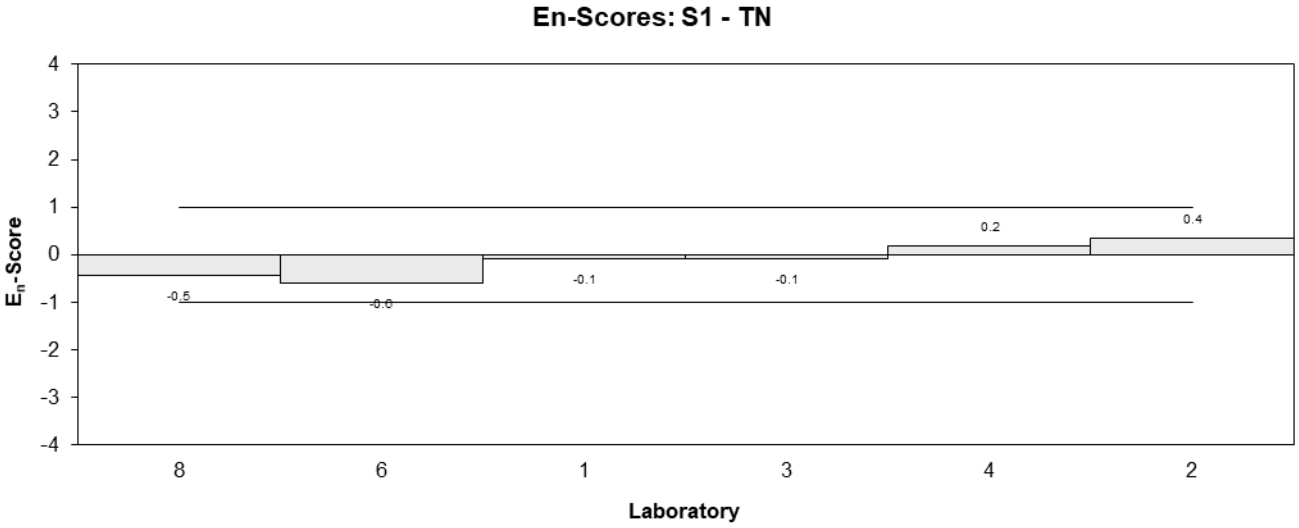

En-Scores: S1 - TN
En-Score
-0.5
-0.6
-0.1
-0.1
0.2
0.4
Laboratory
8
6
1
3
4
2

Figure 10

Table 20

Sample Details

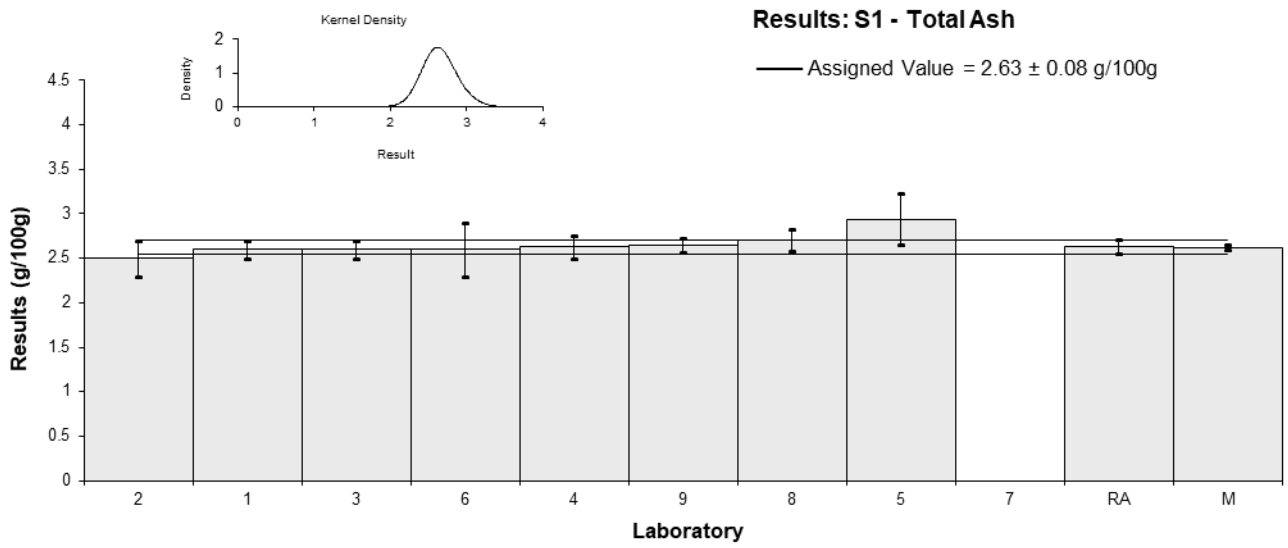
Sample	S1
Analyte	Total Ash
Matrix	Bread Crumbs
Unit	g/100g

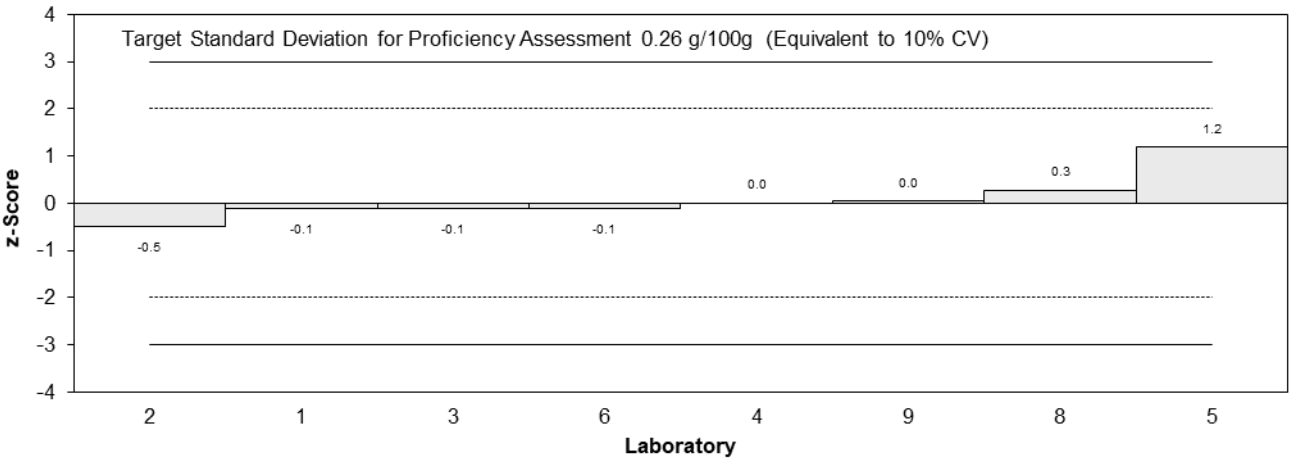
Participant Results

Lab. Code	Result	U	z	E_n
1	2.6	0.1	-0.11	-0.23
2	2.5	0.2	-0.49	-0.60
3	2.6	0.1	-0.11	-0.23
4	2.63	0.13	0.00	0.00
5	2.94	0.29	1.18	1.03
6	2.60	0.3	-0.11	-0.10
7	NT	NT		
8	2.7	0.12	0.27	0.49
9	2.64	0.08	0.04	0.09

Statistics

Assigned Value	2.63	0.08
Robust Average	2.63	0.08
Median	2.62	0.03
Mean	2.65	0.09
N	8	
Max	2.94	
Min	2.5	
Robust SD	0.087	
Robust CV (%)	3.3	


Kernel Density
Density
Result
Results: S1 - Total Ash
Assigned Value = 2.63 ± 0.08 g/100g
Results (g/100g)
Laboratory
2
1
3
6
4
9
8
5
7
RA
M


z-Scores: S1 - Total Ash
Target Standard Deviation for Proficiency Assessment 0.26 g/100g (Equivalent to 10% CV)
z-Score
Laboratory
-0.5
-0.1
-0.1
-0.1
0.0
0.0
0.3
1.2

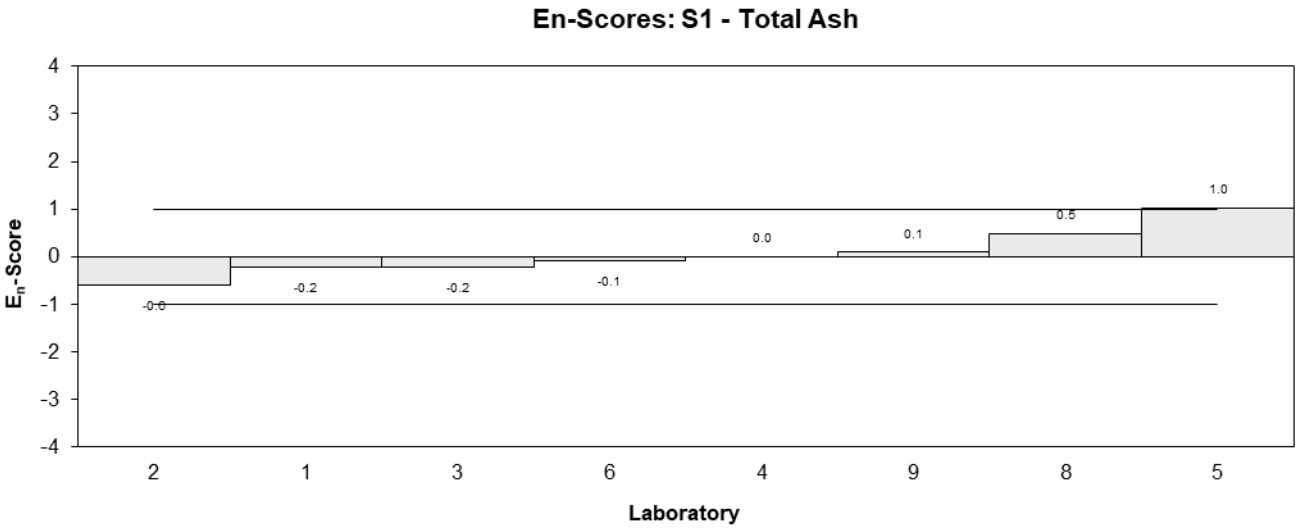

En-Scores: S1 - Total Ash
En-Score
Laboratory
-0.6
-0.2
-0.2
-0.1
0.0
0.1
0.5
1.0

Figure 11

Table 21

Sample Details

Sample	S1
Analyte	Total Dietary Fibre
Matrix	Bread Crumbs
Unit	g/100g

Participant Results

Lab. Code	Result	U
1	NT	NT
2	NT	NT
3	NT	NT
4	4.81	1.31
5	NR	NR
6	4.66	NR
7	NT	NT
8	NT	NT
9	4.3	0.60

Statistics

Assigned Value	Not Set	
Median	4.66	0.32
Mean	4.59	0.30
N	3	
Max	4.81	
Min	4.3	
Robust SD	0.30	
Robust CV (%)	6.5	

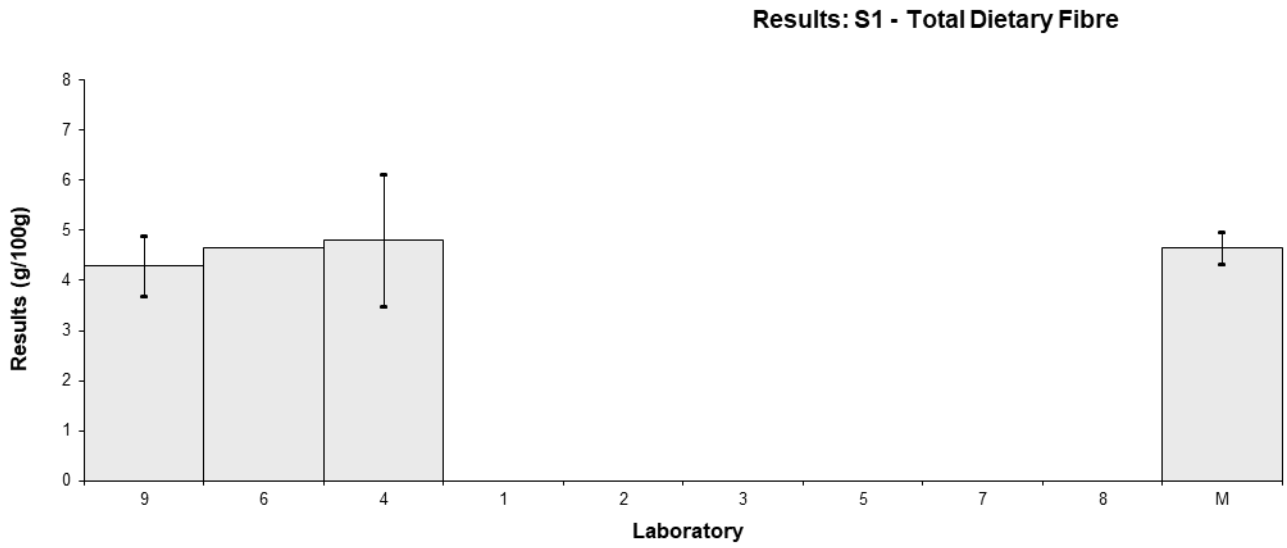

Results: S1 - Total Dietary Fibre
Results (g/100g)
0
1
2
3
4
5
6
7
8
9
6
4
1
2
3
5
7
8
M
Laboratory

Figure 12

Table 22

Sample Details

Sample	S1
Analyte	Total Fat
Matrix	Bread Crumbs
Unit	g/100g

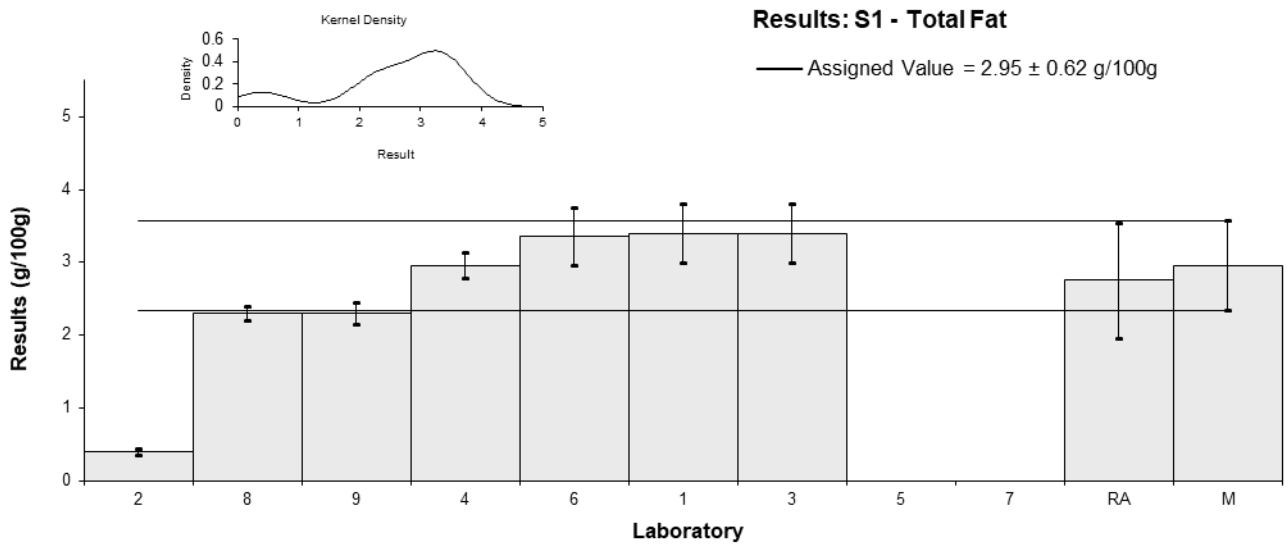
Participant Results

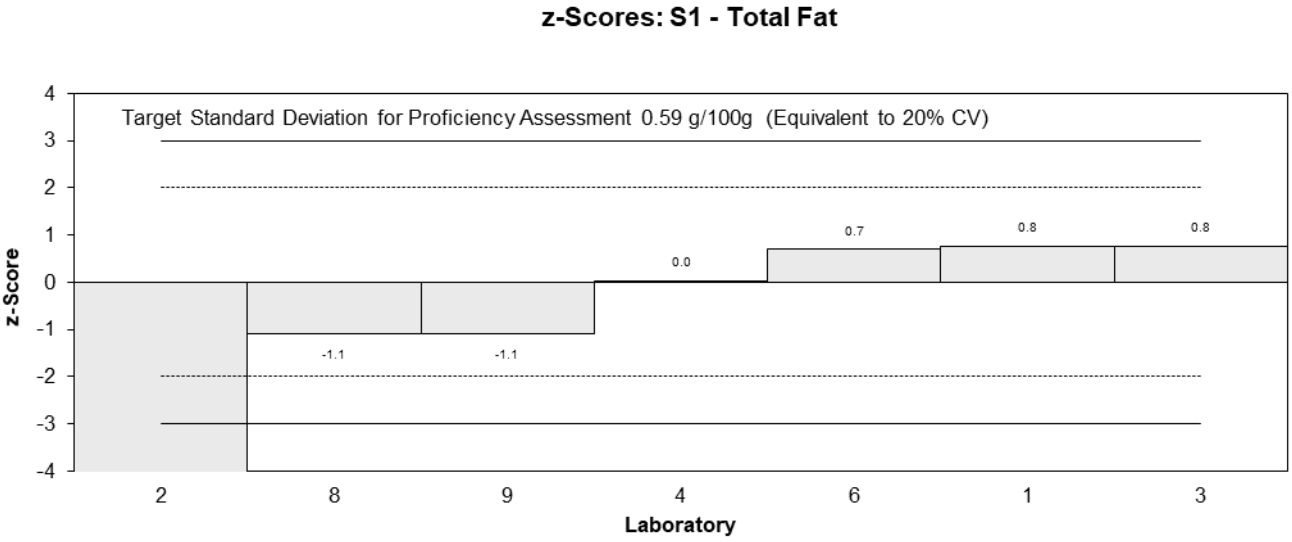
Lab. Code	Result	U	z	E_n
1	3.4	0.4	0.76	0.61
2*	0.4	0.05	-4.32	-4.10
3	3.4	0.4	0.76	0.61
4	2.96	0.18	0.02	0.02
5	NR	NR		
6	3.36	0.4	0.69	0.56
7	NT	NT		
8	2.3	0.1	-1.10	-1.04
9	2.3	0.15	-1.10	-1.02

* Outlier

Statistics

Assigned Value	2.95	0.62
Robust Average	2.75	0.79
Median	2.96	0.62
Mean	2.59	0.82
N	7	
Max	3.4	
Min	0.4	
Robust SD	0.83	
Robust CV (%)	30	


Kernel Density
Density
Result
Results: S1 - Total Fat
Assigned Value = 2.95 ± 0.62 g/100g
Results (g/100g)
Laboratory
2
8
9
4
6
1
3
5
7
RA
M


z-Scores: S1 - Total Fat
Target Standard Deviation for Proficiency Assessment 0.59 g/100g (Equivalent to 20% CV)
z-Score
0.0
0.7
0.8
0.8
-1.1
-1.1
Laboratory
2
8
9
4
6
1
3

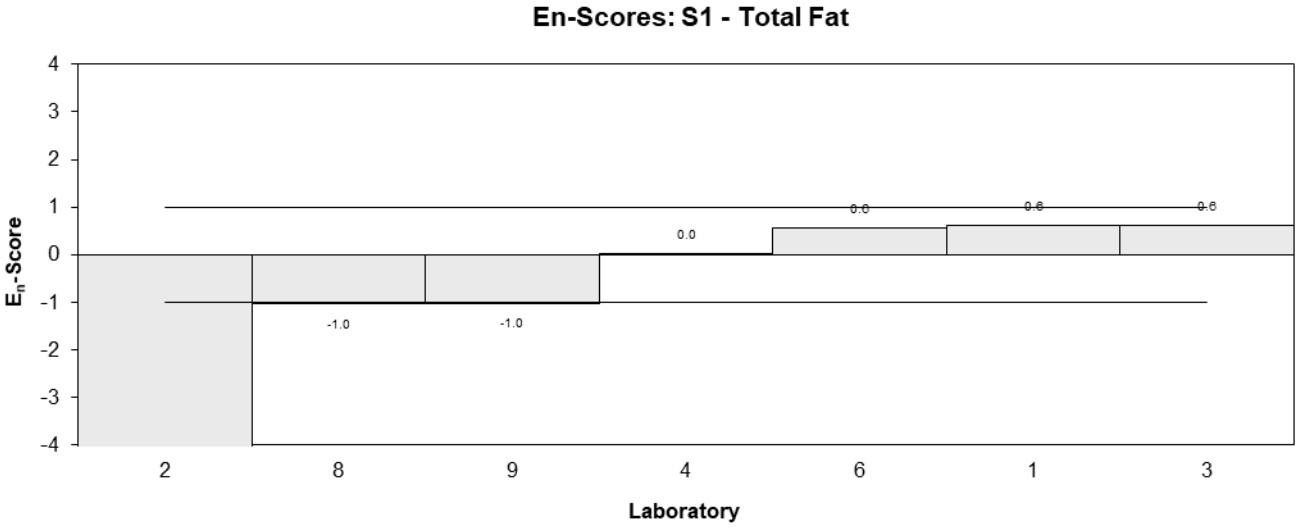

En-Scores: S1 - Total Fat
En-Score
0.0
0.6
0.6
0.6
-1.0
-1.0
Laboratory
2
8
9
4
6
1
3

Figure 13

Table 23

Sample Details

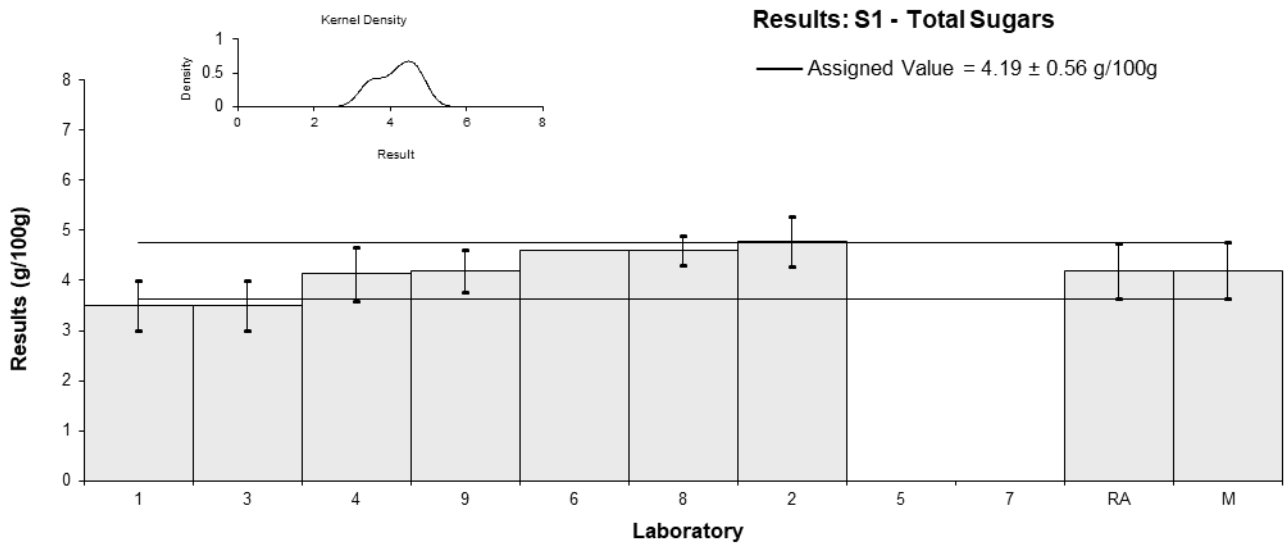
Sample	S1
Analyte	Total Sugars
Matrix	Bread Crumbs
Unit	g/100g

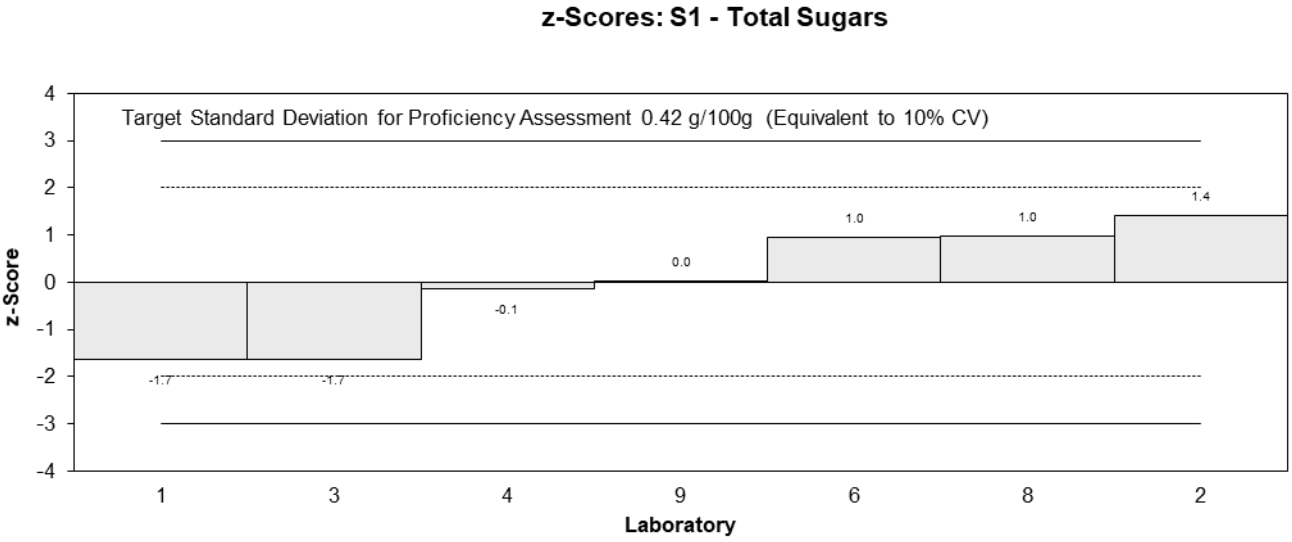
Participant Results

Lab. Code	Result	U	z	E_n
1	3.5	0.5	-1.65	-0.92
2	4.78	0.5	1.41	0.79
3	3.5	0.5	-1.65	-0.92
4	4.13	0.54	-0.14	-0.08
5	NR	NR		
6	4.59	NR	0.95	0.71
7	NT	NT		
8	4.6	0.3	0.98	0.65
9	4.2	0.42	0.02	0.01

Statistics

Assigned Value	4.19	0.56
Robust Average	4.19	0.56
Median	4.20	0.56
Mean	4.19	0.39
N	7	
Max	4.78	
Min	3.5	
Robust SD	0.59	
Robust CV (%)	14	


Kernel Density
Density
Result
Results: S1 - Total Sugars
Assigned Value = 4.19 ± 0.56 g/100g
Results (g/100g)
Laboratory
1
3
4
9
6
8
2
5
7
RA
M


z-Scores: S1 - Total Sugars
Target Standard Deviation for Proficiency Assessment 0.42 g/100g (Equivalent to 10% CV)
z-Score
Laboratory
-1.7
-1.7
-0.1
0.0
1.0
1.0
1.4

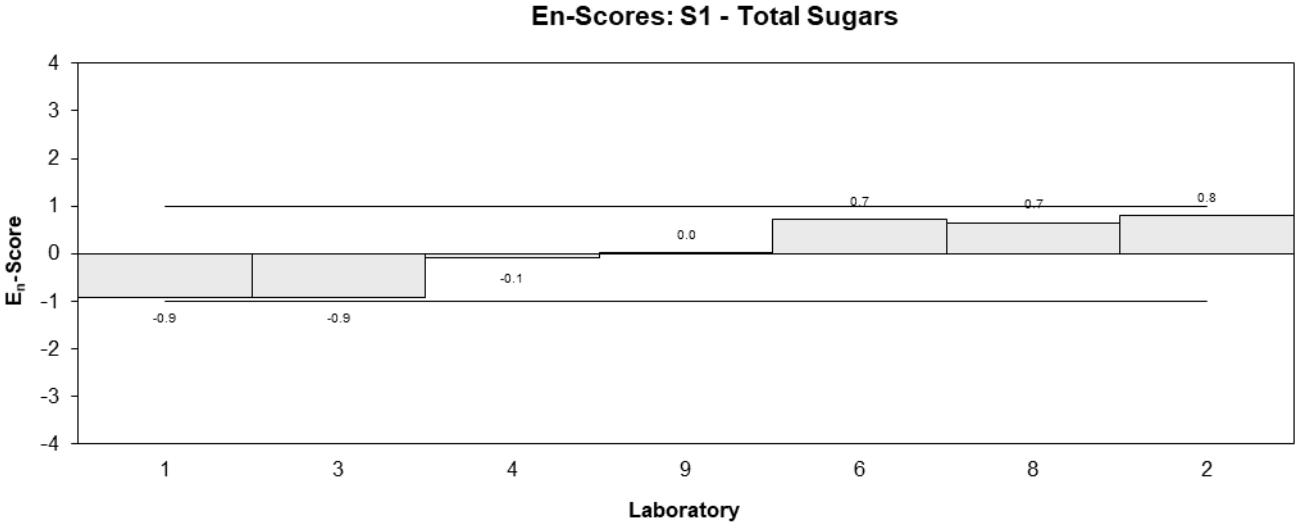

En-Scores: S1 - Total Sugars
En-Score
Laboratory
-0.9
-0.9
-0.1
0.0
0.7
0.7
0.8

Figure 14

7 DISCUSSION OF RESULTS

7.1 Assigned Value and Traceability

Assigned Values were the robust average of participants' results. The robust averages used as assigned values and their associated expanded uncertainties were calculated using the procedure described in ISO13528:2015(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.[6] Appendix 2 sets out the calculation of the robust average of K in Sample S1 and its associated uncertainty.

No assigned value was set for saturated fat and dietary fibre because not enough participants reported results for these tests. However, participants may still compare their reported results for these tests with the median of participants' results. Descriptive statistics for these tests are presented in Chapter 6.

Traceability The assigned values are not traceable to any external reference; they are traceable to the consensus of participants' results derived from a variety of measurement methods and (presumably) a variety of calibrators. So although expressed in SI units, the metrological traceability of the 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 91 numerical results, 84 (92%) were reported with an expanded measurement uncertainty, indicating that the majority of laboratories have addressed this requirement of ISO/IEC 17025.[8] The magnitude of these expanded uncertainties was within the range 1.5% to 27% of the reported value. The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 10.

Approaches to estimating measurement uncertainty include: standard deviation of replicate analysis, Horwitz formula, long term reproducibility, professional judgement, bottom up approach, top down approach using precision and estimates of method and laboratory bias, and top down approach using only the reproducibility from inter-laboratory comparison studies.[9 – 15]

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 14). 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.

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 14.38 ± 1.94 mg/kg, it is better to report 14.4 ± 1.9 mg/kg or instead of 1082 ± 113.6 mg/kg, it is better to report 1080 ± 114 mg/kg.[9]

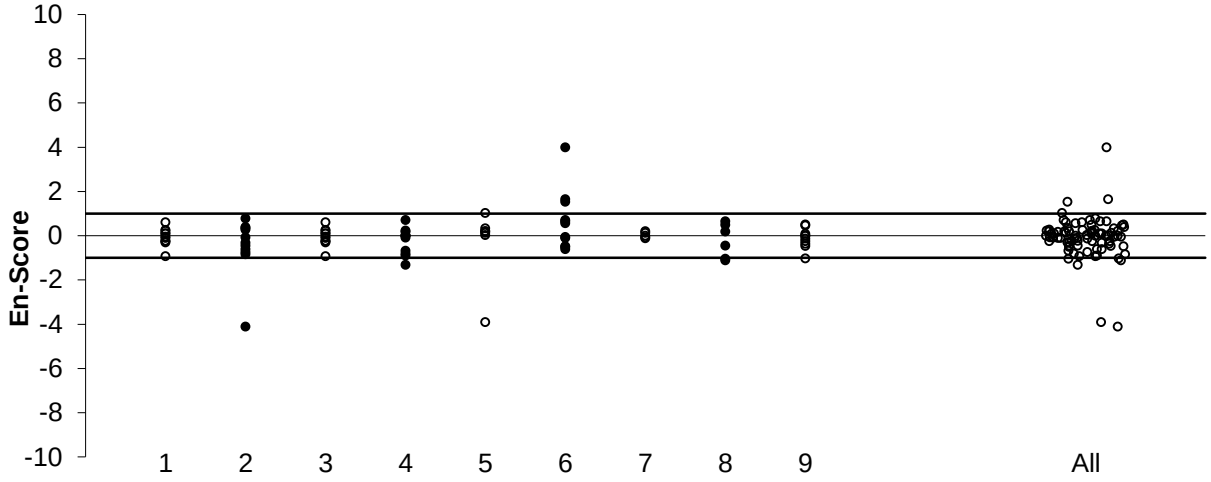
7.2 E_n-score

E_n-score should be interpreted only in conjunction with z-scores. The E_n-score indicates how closely a result agrees with the assigned value taking into account the respective uncertainties.

An unsatisfactory E_n score for an analyte can either be caused by an inappropriate measurement, an inappropriate estimation of measurement uncertainty, or both.

The dispersal of participants' E_n-scores is graphically presented in Figure 15. Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n-score.

Of 83 results for which E_n-scores were calculated, 73 (88%) 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 15 E_n-Score Dispersal by Laboratory

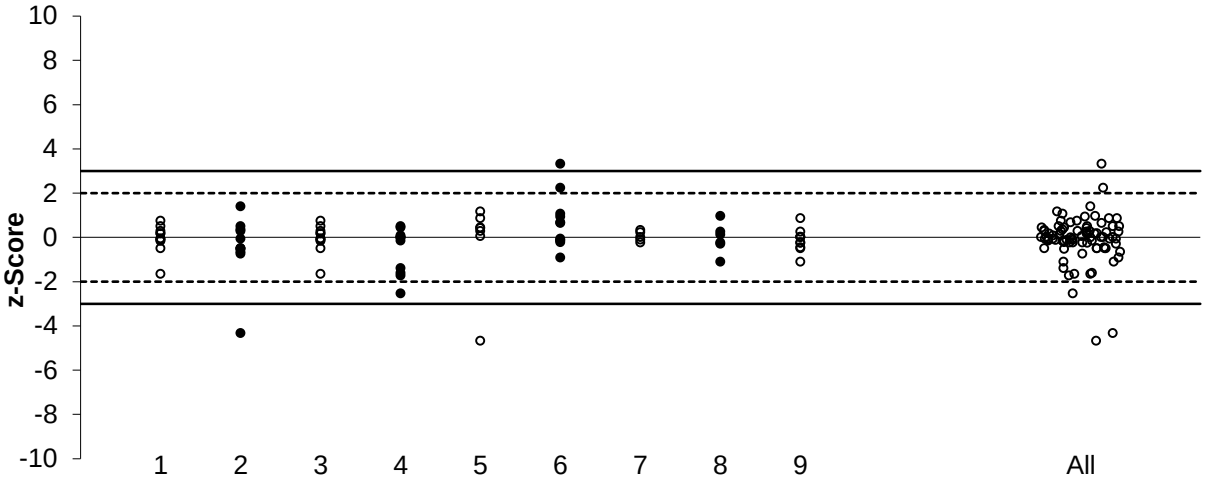
7.3 z-Score

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% 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[7] and the between laboratory coefficient of variation resulted in this study are presented for comparison in Table 24.

The dispersal of participants' z-scores is presented in Figure 16 (by laboratory code) and in Figure 17 (by test). Of 83 results for which z-scores were calculated, 78 (94%) returned a satisfactory score of $|z| \leq 2.0$ and 2 (2%) 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 16 z-Score Dispersal by Laboratory

Laboratories 1, 2, 3, 4 and **6** reported results for all tests for which z-scores were calculated (11).

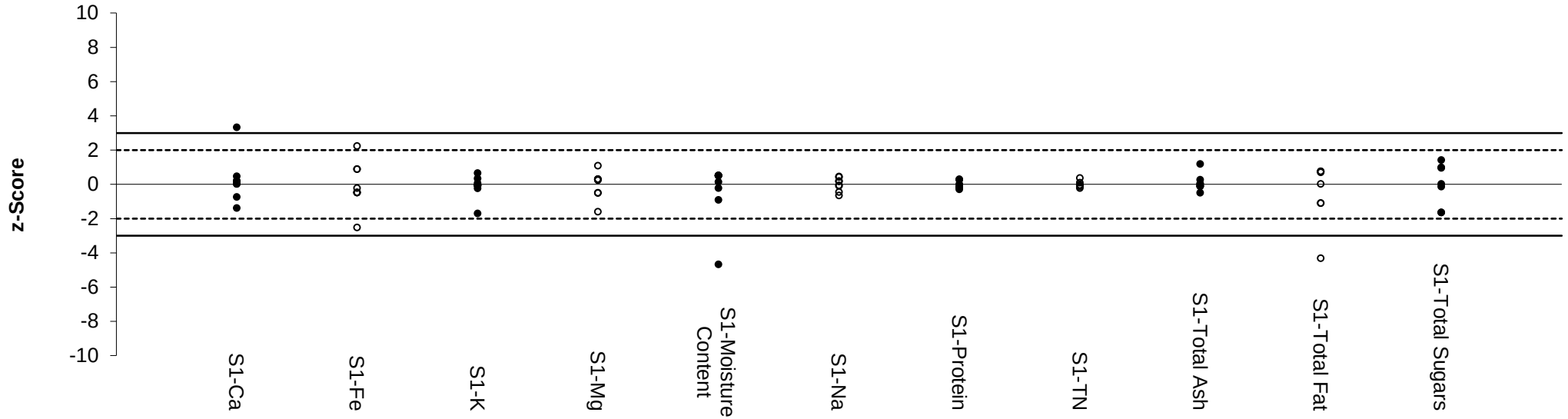
Laboratories 1 and **3** returned the highest number of satisfactory z scores (11 out of 11 reported). All results reported by **laboratories 9** (10), **8** (6) and **7** (5) also returned satisfactory z scores.

Laboratories 1 and **3** returned the highest number of satisfactory E_n scores (11 out of 11). All results reported by **laboratory 7** (5) returned satisfactory E_n scores.

Table 24 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	Ca	1080	9.3%	5.6%	10%
S1	Fe	14.7	15%	11%	10%
S1	K	1810	4.4%	5.2%	10%
S1	Mg	369	7.9%	6.6%	10%
S1	Na	7270	4.5%	4.2%	10%
S1	Ash	2.63	3.3%	3.5%	10%
S1	Moisture	2.76	7.8%	3.4%	10%
S1	Protein	13.6	2.6%	2.7%	10%
S1	Total Nitrogen	2.16	2.2%	3.6%	10%
S1	Total Fat	2.95	20%	3.4%	20%
S1	Saturated Fat	Not Set	41%	NA	Not Set
S1	Total Sugars	4.19	14%	3.2%	10%
S1	Total Dietary Fibre	Not Set	6.5%	NA	Not Set

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



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

Figure 17 z-Score Dispersal by Test

Table 25 Summary of Participants' Results and Performance in S1

Lab Code	Ca (mg/kg)	Fe (mg/kg)	K (mg/kg)	Mg (mg/kg)	Na (mg/kg)	Ash (%)	Moisture (%)	Protein (%)	Total Nitrogen (%)	Total Fat (%)	Saturated Fat (%)	Total Sugars (%)	Total Dietary Fibres (%)
A.V.	1080	14.7	1810	369	7270	2.63	2.76	13.6	2.16	2.95	Not Set	4.19	Not Set
H.V.	1090	15.0	1800	385	7150	NA	NA	NA	NA	NA	NA	NA	NA
1	1100	14	1800	380	7400	2.6	2.9	13.4	2.15	3.4	1.3	3.5	NT
2	1000	14	1800	350	6800	2.5	2.9	14	2.24	0.4	NT	4.78	NT
3	1100	14	1800	380	7400	2.6	2.9	13.4	2.15	3.4	1.4	3.5	NT
4	930	11	1500	310	7600	2.63	2.9	13.6	2.18	2.96	1.21	4.13	4.81
5	1130	16	1820	380	7580	2.94	1.47	NR	NR	NR	NR	NR	NR
6	1440	18	1930	409	7230	2.6	2.51	13.31	2.13	3.36	0.46	4.59	4.66
7	1082	14.38	1872	378	7198	NT	NT	NT	NT	NT	NT	NT	NT
8	NT	NT	NT	NT	NT	2.7	2.8	13.2	2.11	2.3	0.9	4.6	NT
9	1082	16	1766	351	6946	2.64	2.7	13.95	NT	2.3	NT	4.2	4.3

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 is presented in Figures 16 and 17 and Table 25.

Measurement of total dietary fibre presented the most analytical difficulty to participants. No assigned value could be set for this test because only three participants reported results.

Individual Test Commentary

Protein Seven participants reported results for protein. Of these, five used the Kjeldahl method and two used the Dumas method. Results produced by both methods were compatible with each other (Figure 18)**.**

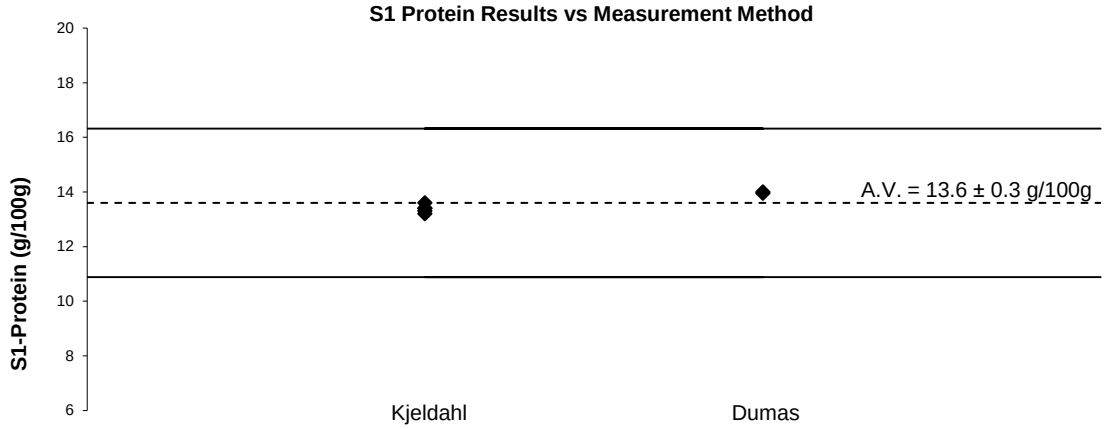


Figure 18 S1 Protein Results vs. Instrumental Technique

Total Nitrogen measurement did not present difficulty to participating laboratories. Reported results were in excellent agreement with each other, with a between-laboratory CV of 2.2%.

Total Fat There are two gravimetric methods used for total fat determination, acid hydrolysis and Soxhlet extraction (without hydrolysis). With the exception of one, all participants used the Association of Official Analytical Chemists (AOAC) Method 922.06 - Mojonnier technique (Figure 19). This method involves the separation of fat from the food matrix by hydrolysis with hot acid, followed by extraction with organic solvents. The extract is evaporated and the fat is then determined by weighing the dry fatty extract.

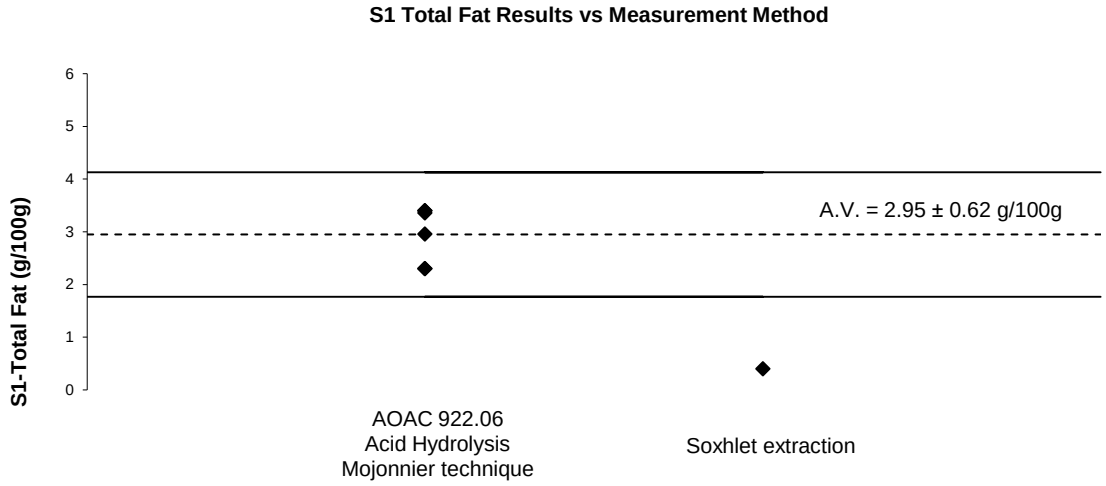


Figure 19 S1 Total Fat Results vs. Instrumental Technique

Laboratory 6 reported using the Kjeldahl method. Caution should be exercised when the Kjeldahl method is used as the results may vary with reflux rate and extraction time.

Plots of participants' results versus method used are presented in Figure 19. The Soxhlet method measures crude fat including free fat while the acid hydrolysis method measures total fat including free and bounded, which may explain the low result reported by Laboratory 6.[16]

Total Sugars Seven participants reported results for total sugars. Five used HPLC with refractive index detector and two used LCMS (Figure 20). The results were compatible with each other.

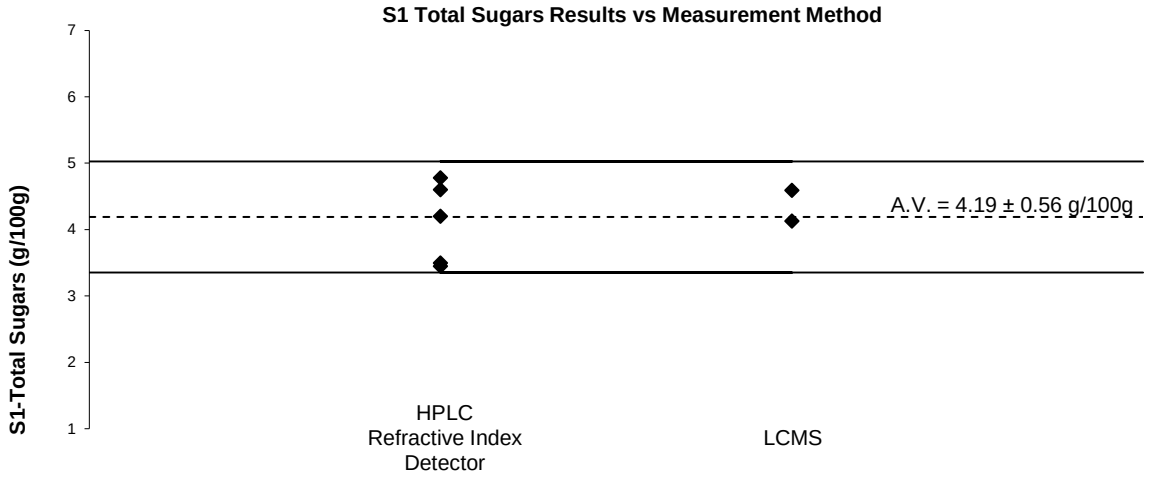


Figure 20 S1 Total Fat Results vs. Instrumental Technique

Total Dietary Fibre Measurement of total dietary fibre in food is an empirical measurement – where the method defines the measurand. With testing laboratories using different methods, each could be considered to be measuring a different measurand that is their version of 'total dietary fibre'. This lack of uniformity in procedures can make it difficult to compare participants' results.

The participating laboratories were instructed to use AOAC Method 985.29 *Total Dietary in Foods, Enzymatic – Gravimetric Method* or the AOAC Method 991.43 *Total, Insoluble and Soluble Dietary Fibre in Food- Enzymatic-Gravimetric Method*

Of nine participants only 3 reported results for dietary fibre. The results were compatible with each other centered on 4.66 g/100g value (Figure 21).

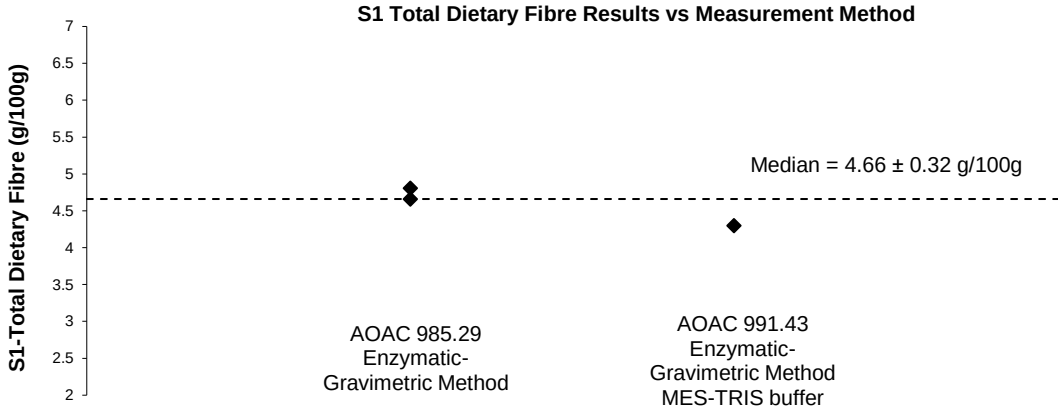


Figure 21 S1 Total Fat Results vs. Instrumental Technique

Ca, Fe, K, Mg, Na Eight laboratories reported results for Ca, Fe, K, Mg, Na in the bread crumbs sample. The amount of sample taken for analysis by most participants was 0.5 g. One reported using 1 g of sample and one used 2 g. Two participants used only nitric acid for extraction, and one used only 0.5 mL of HCl and 1 mL of H_2O_2. All laboratories except for two conducted their extraction at 95-110ºC. Laboratory 4 extracted their sample at 200ºC for 45 min while laboratory 6 reported: "4g Sample ashed then boiled in HCl for AAS (final 10% acid). 2.5g sample ashed then boiled in HNO_3 for ICPMS (final 5% acid)".

Plots of participants' results versus instrumental technique used are presented in Figures 22 to 26.

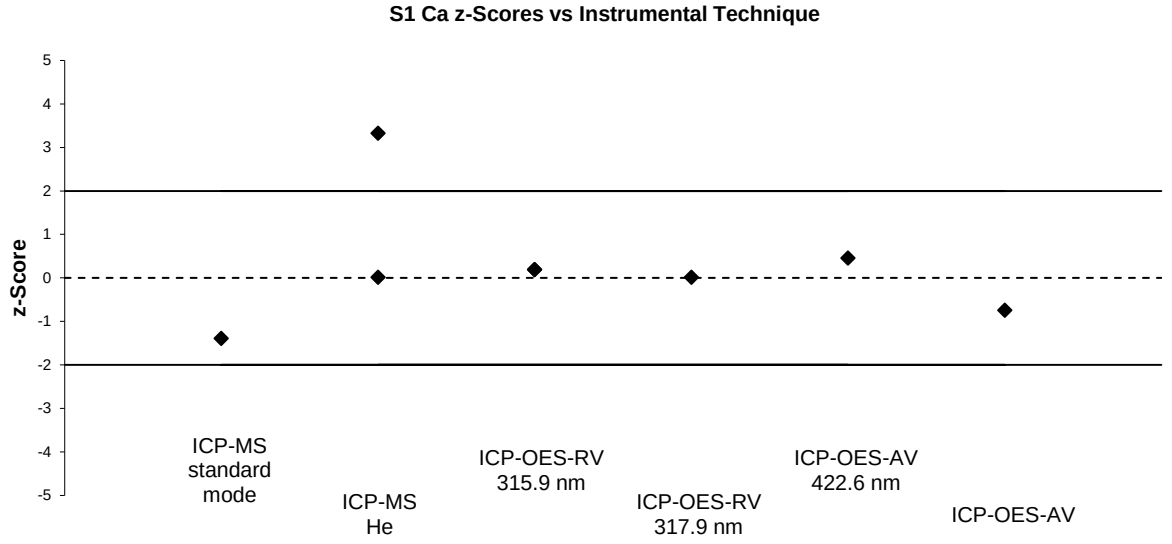


Figure 22 S1 Ca z-Scores vs. Instrumental Technique

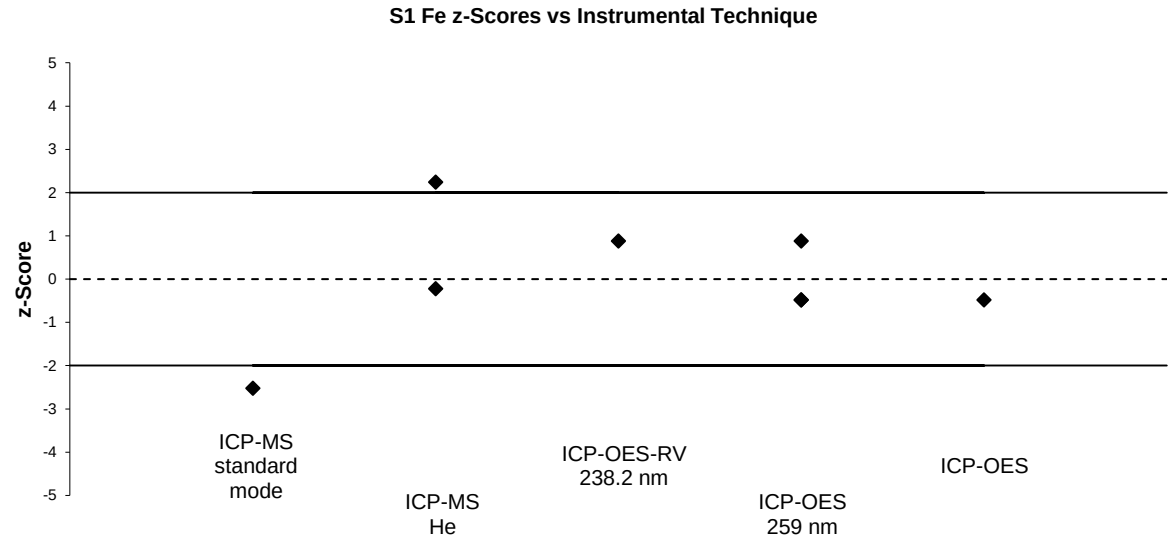


Figure 23 S1 Fe z-Scores vs. Instrumental Technique

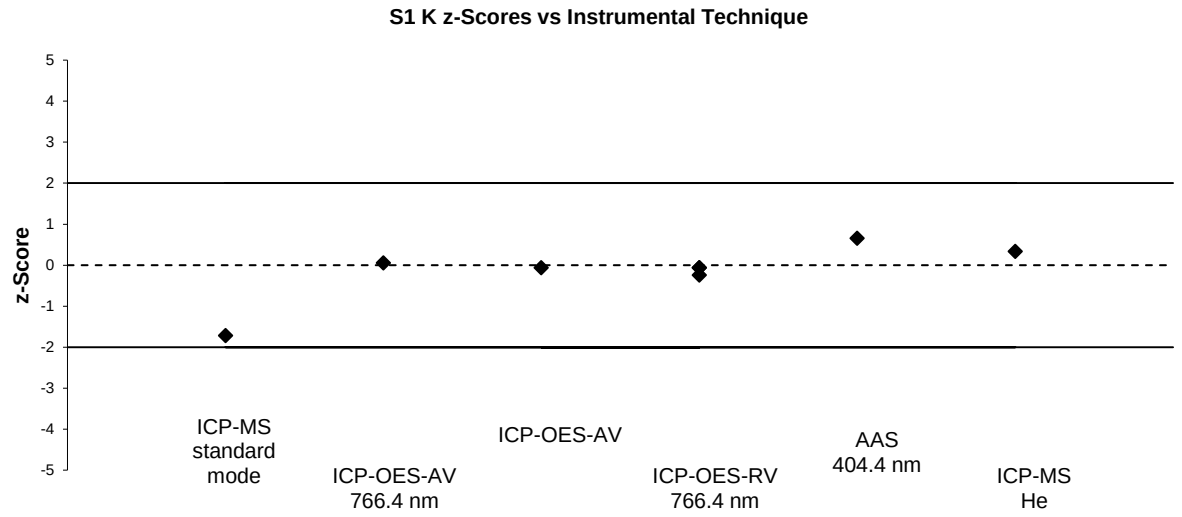


Figure 24 S1 K z-Scores vs. Instrumental Technique

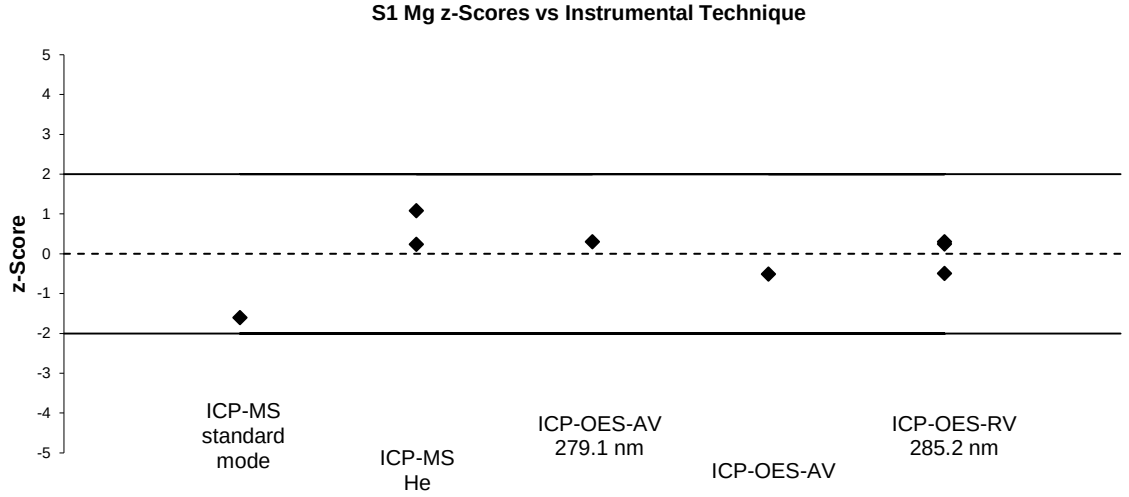


Figure 25 S1 Mg z-Scores vs. Instrumental Technique

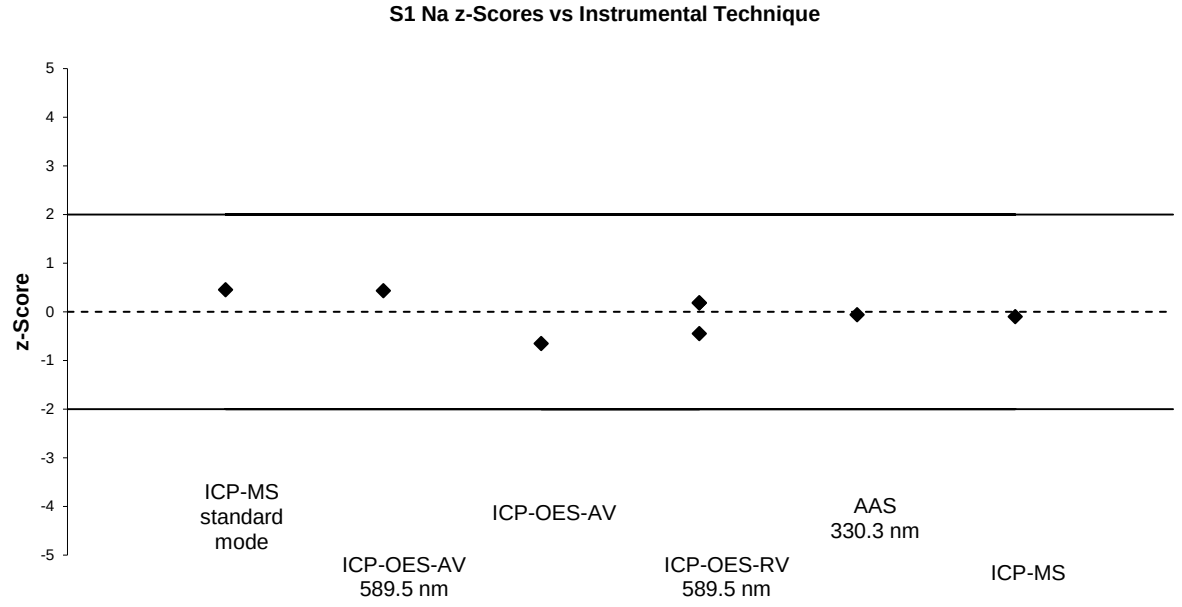


Figure 26 S1 Na z-Scores vs. Instrumental Technique

7.5 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.

Only one laboratory reported using a reference material as control samples.

The test samples of this study were checked for homogeneity for some tests 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.

8 REFERENCES

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APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

A1.1 Sample Preparation

Sample S1 – was 100 g of dried bread crumbs bought from a local grocer.

A1.2 Sample Analysis and Homogeneity Testing

The same procedure was followed for the preparation of Samples S1 as in previous NMI PT studies of toxic and essential elelemnts in food. Therefore, only a partial homogeneity test was conducted for some of the tests of interest : Ca, Fe, K, Mg and Na. 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 100ºC for 2 hour with 3 mL of HNO_3 and 1 mL of HCl. After digestion, each sample was diluted to 40 mL with ultra-high purity water and then further diluted as necessary for ICP-MS determination. A summary of the instruments used and the ion monitored for each analyte is given in Table 27.

Table 26 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	Ion
Ca	ICP-OES-AV	Lu	NA	NA	400	422.673 nm
Fe	ICP-OES-RV	Lu	NA	NA	80	238.204 nm
K	ICP-OES-AV	Lu	NA	NA	400	766.491 nm
Mg	ICP-OES-AV	Lu	NA	NA	400	279.078 nm
Na	ICP-OES-AV	Lu	NA	NA	400	589.592 nm

NA- Not Applicable

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

Assigned Value

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

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

where:

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

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

A worked example is set out below in Table 27.

Table 27 Uncertainty of Assigned Value for K in Sample S1

No. results (p)	8
Robust Average	1810 mg/kg
$S_{rob\ av}$	80 mg/kg
$u_{rob\ av}$	35 mg/kg
k	2
$U_{rob\ av}$	70 mg/kg

The assigned value for **K** in Sample S1 is **1810 ± 70 mg/kg**.

z-Score and E_n-score

For each participant's result a z-score and E_n-score are calculated according to Equation 2 and Equation 3 respectively (see page 9).

A worked example is set out below in Table 30.

Table 28 z-Score and E_n-score for K result reported by Laboratory 1 in S1

K Result mg/kg	Assigned Value mg/kg	Set Target Standard Deviation	z-Score	E_n-Score
1800 ± 250	1810 ± 70	10% as CV or 0.10 x 1810= 180 mg/kg	$z = \frac{(1800 - 1810)}{180}$ z = -0.06	$En = \frac{(1800 - 1810)}{\sqrt{250^2 + 70^2}}$ E_n = -0.04

APPENDIX 3 - ACRONYMS AND ABBREVIATIONS

AOAC	Association of Official Analytical Chemists
CRM	Certified Reference Material
CV	Coefficient of Variation
CV_{Rob}	Robust Coefficient of Variation
GUM	Guide to the Expression of Uncertainty in Measurement
HV	Homogeneity Value
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ICP-OES-AV	Inductively Coupled Plasma – Optical Emission Spectrometry- axial view
ICP-OES-RV	Inductively Coupled Plasma – Optical Emission Spectrometry- radial view
ISO/IEC	International Organisation for Standardisation / International Electrotechnical Commission
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
NMI	National Measurement Institute (Australia)
NR	Not Reported
NT	Not Tested
PCV	Performance Coefficient of Variation
PT	Proficiency Test
RM	Reference Material
SD_{Rob}	Robust Standard Deviation
SI	The International System of Units
s^2_{sam}	Sampling variance
s_a/σ	Analytical standard deviation divided by the target standard deviation
Target SD	Target standard deviation (symbol: σ)

APPENDIX 4 - INSTRUMENT DETAILS

Table 29 Instrument Conditions for Ca

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-RV	Lutetium 2mg/L			28	315.887
2	ICP-OES-AV					
3	ICP-OES-RV	Lutetium 2mg/L			28	315.887
4	ICP MS	45Sc,73Ge	KED	ARGON	50	42Ca
5	ICP-OES-AV	Y			10	422.673
6	ICP-MS	Yes	He	He	40	44 ion
7	ICP-MS	72 Ge	KED	H2	80	40 Ca
9	ICP-OES-RV	Yttrium			1	317.933

Table 30 Instrument Conditions for Fe

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV	Lutetium 2mg/L			28	259ax
2	ICP-OES-AV					
3	ICP-OES-AV	Lutetium 2mg/L			28	259ax
4	ICP MS	45Sc,73Ge	KED	ARGON	50	57Fe
5	ICP-OES-RV	Y			2	238.204
6	ICP-MS	Yes	He	He	40	56 ion
7	ICP-MS	45 Sc	KED	He	80	56 Fe
9	ICP-OES-AV	Yttrium			1	238.204

Table 31 Instrument Conditions for K

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-RV	Lutetium 2mg/L			28	766.49
2	ICP-OES-AV					
3	ICP-OES-RV	Lutetium 2mg/L			28	766.49
4	ICP MS	45Sc,73Ge	KED	ARGON	50	39K
5	ICP-OES-AV	Y			10	766.491
6	AAS	No	NA	NA	25	404.4 nm
7	ICP-MS	72 Ge	KED	He	80	39 K
9	ICP-OES-RV	Yttrium			1	766.49

Table 32 Instrument Conditions for Mg

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-RV	Lutetium 2mg/L			28	285.213
2	ICP-OES-AV					
3	ICP-OES-RV	Lutetium 2mg/L			28	285.213
4	ICP MS	45Sc,73Ge	KED	ARGON	50	25Mg
5	ICP-OES-AV	Y			10	279.078
6	ICP-MS	Yes	He	He	400	24 ion
7	ICP-MS	103 Rh	KED	He	80	24 Mg
9	ICP-OES-RV	Yttrium			1	285.213

Table 33 Instrument Conditions for Na

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-RV	Lutetium 2mg/L			280	589.592
2	ICP-OES-AV					
3	ICP-OES-RV	Lutetium 2mg/L			280	589.592
4	ICP MS	45Sc,73Ge	KED	ARGON	50	23Na
5	ICP-OES-AV	Y			10	589.592
6	AAS	No	NA	NA	25	330.3 nm
7	ICP-MS	103 Rh	KED	He	80	23 Na
9	ICP-OES-RV	Yttrium			1	589.592

END OF REPORT