Australian Government
Department of Industry, Innovation and Science

National Measurement Institute

Proficiency Test Report AQA 19-16 Trace Elements in Sea Water

January 2020

ACKNOWLEDGMENTS

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

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

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

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Accredited for compliance with ISO/IEC 17043

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1 SUMMARY

This report presents the results of the proficiency test AQA 19-16, Trace Elements in Sea Water. The study focused on the measurement of dissolved: Al, Ag, As, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, P, Pb, Se, Sn, Tl, U, V and Zn and total: Al, Ag, As, Ba, Cd, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Tl, U, V and Zn.

The assigned values were the robust average 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 performance of participant laboratories and assess their accuracy;

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

Of 347 numeric results, 328 (95%) returned a satisfactory score of $|z| \leq 2.0$.

Of 347 results, 315 (91%) returned a satisfactory score of $|E_n| \leq 1.0$.

ii. evaluate the laboratories' methods used in determination of inorganic analytes in seawater;

Aluminium, nickel and phosphorus at low levels in seawater were the analytes which presented the most analytical difficulty to participating laboratories.

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

Overall, participants performed better in this study than in the previous NMI PT studies in seawater AQA 18-16 and AQA 17-16.

iv. develop the practical application of traceability and measurement uncertainty and provide participants with information that will be useful in assessing their uncertainty estimates;

Of 347 numerical results, 330 (95%) were reported with an expanded measurement uncertainty. An example of estimating measurement uncertainty using only the proficiency testing data is given in Appendix 3.

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

Surplus test samples from the present study are available for sale. The samples were assessed for homogeneity and stability and are well characterised, both by in-house testing and from the results of the proficiency round.

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;
- PFAS in water, soil, biota and food;
- allergens in food;
- controlled drug assay; and
- folic acid in flour.

AQA 19-16 is the 24th NMI proficiency study of metals in water.

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 seawater;
- compare the performance of participant laboratories with their past performance;
- develop the practical application of traceability and measurement uncertainty; and
- produce materials that can be used in method validation and as control samples.

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 Harmonized 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 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 40 tests were selected from those for which an investigation level is published in Australian and New Zealand Guidelines for Fresh and Marine Water Quality[5] and are commonly measured by water testing laboratories.

3.2 Participation

Thirteen laboratories participated and twelve submitted results.

The timetable of the study was:

Invitation issued:	01 October 2019
Samples dispatched:	28 October 2019
Results due:	15 November 2019
Interim report issued:	22 November 2019

3.3 Test Material Specification

Two samples were provided for analysis:

Sample S1 was 100 mL of filtered seawater preserved by adding 2% (v/w) nitric acid; and

Sample S2 was 100 mL of unfiltered seawater preserved by adding 2% (v/w) nitric acid.

3.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

3.5 Sample Preparation, Analysis and Homogeneity Testing

A partial homogeneity testing was conducted in this study. The same sample preparation procedure was followed as in previous studies.[2] The test samples from the previous studies were demonstrated to be sufficiently homogeneous for evaluation of participants' performance. The results from the partial homogeneity testing are reported in this study as homogeneity values. No homogeneity testing was conducted for U in S1 and S2.

The preparation and analysis are described in Appendix 1.

3.6 Stability of Analytes

No stability study was carried out for samples S1 and S2. Stability studies conducted for similar previous proficiency studies of metals in seawater found no significant changes in any of the analytes' concentration.

3.7 Sample Storage, Dispatch and Receipt

Samples S1 and S2 were refrigerated before dispatch.

The samples were dispatched by courier on 28 October 2019.

A description of the test samples, instructions for participants, and a form for participants to confirm the receipt of the test samples, were sent 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:

- Quantitatively analyse the samples using your normal test method.
- Participants are asked to report results in units of µg/L for S1 and S2

SAMPLE S1 filtered, acidified sea water		SAMPLE S2 unfiltered, acidified sea water	
Test Dissolved	Approximate Conc. Range µg/L	Test Total	Approximate Conc. Range µg/L
Al	<50	Al	>100

Ag	<10	Ag	>100
As	<10	As	>100
Be	<10	Ba	>100
Cd	<10	Cd	>100
Co	<10	Cr	>100
Cr	<10	Cu	>100
Cu	<50	Fe	>100
Fe	<50	Mn	>100
Hg	<10	Mo	>100
Mn	<10	Ni	>100
Ni	<10	P	>100
P	>100	Pb	>100
Pb	<10	Sb	>100
Se	<10	Se	>100
Sn	<10	Sn	>100
Tl	<10	Tl	>100
U	<10	U	>100
V	<10	V	>100
Zn	<50	Zn	>100

- Report results as you would report to a client. For each analyte in each sample, report the expanded measurement uncertainty associated with your analytical result (e.g. 5.23 ± 0.51 µg/L).
- Please send us the requested details regarding the test method and the basis of your uncertainty estimate.
- Return the completed results sheet by e-mail (proficiency@measurement.gov.au) by 15 November 2019. Late results cannot be included in the report.

3.9 Interim Report

An interim report was emailed to participants on 22 November 2019.

4 PARTICIPANT LABORATORY INFORMATION

4.1 Methodology for Total and Dissolved Elements

Summaries of test methods are transcribed in Tables 1 and 2. The instruments and settings reported by participants are presented in Appendix 5.

Table 1 Methodology for Total Elements

Lab. Code	Method Reference	Sample Volume (mL)	Digestion Temp. (ºC)	Digestion Time (min)	Vol. HNO_3 (mL)	Vol. HCl (mL)
1*		10	170	30	1.25	0.63
3	3051A	20	170	15	1	1
6*	200.7-8					
7		30	95-100	90	2	
8	ICP-MS:APHA (2017),3125 / ICP-OES:US EPA (1994), Method 200.7 Revision 4.4 / Hg:US EPA,Method 1631 Revision.E	10	105	2	0.5	0.25
9*	EPA 200.8	1mL of HCl was added to 50mL of the 2% HNO3 acidified sample received.				
10	USEPA6020	10	95	90	2	3
11	APHA Method 3030 E 23rd ed. 2017 (modified) APHA Method 3030 F 23rd ed. 2017 (modified)	10	100	60	0.5	0.1 (Ag Only)
12	In House W32a					
13	USEPA METHOD 3050B	50	85	120	1	1

*Additional Information in Table 2.

4.2 Additional Information

Participants had the option to report additional information for each sample analysed. These are transcribed in Table 2.

Table 2 Additional information

Lab. Code	Additional Information
1	Samples were digested 10 ml and made to 50 ml. An additional dilution of 3 ml into 15ml was made making a total dilution offline of 25x.
6	Samples not digested
9	Where O2 has been selected as the gas it is a H_2 +N_2O mix.

4.3 Basis of Participants' Measurement Uncertainty Estimates

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

Table 3 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation		Guide Document for Estimating MU
		Precision[a]	Method Bias[a]	
1	Method still in development-uncertainty not determined to date.			
2	Professional Judgement			
3	Top Down - precision and estimates of the method and laboratory bias	Control Samples-CRM Duplicate Analysis	CRM	NMI Uncertainty Course
4	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis	CRM	
6	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis Instrumental Calibration	CRM Recoveries of SS	NATA Technical Note 33
7	Top Down - precision and estimates of the method and laboratory bias	Control Samples-RM Duplicate Analysis	Recoveries of SS	Nordtest Report TR537
8	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Instrument Calibration	CRM Recoveries of SS Instrument Calibration Standard Purity	Eurachem/CITAC Guide
9	Top Down - precision and estimates of the method and laboratory bias	Control Samples-SS	CRM Laboratory bias from PT studies Recoveries of SS	NATA Technical Note 33
10	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples-SS Duplicate Analysis	CRM Recoveries of SS	Eurachem/CITAC Guide
11	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples-CRM Duplicate Analysis Instrumental Calibration	CRM Recoveries of SS Instrument Calibration	Eurachem/CITAC Guide
12	Top Down - precision and estimates of the method and laboratory bias	Control Samples-CRM Duplicate Analysis	CRM	Nordtest Report TR537
13	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples-SS Duplicate Analysis	Recoveries of SS	NATA Technical Note 33

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

4.4 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. Participants' comments are reproduced in Table 4.

Table 4 Participants' Comments

Participants' Comments	Study Co-ordinator's Response
Other elements of interest are: Li, Si, Ti, Sr, La, Pt, Bi, & Th	These elements have been included in this year program for trace elements in water

5 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

5.1 Results Summary

Participant results are listed in Tables 5 to 44 with results' summary statistics: robust average, median, maximum, minimum, robust standard deviation (SD_{rob}) and robust coefficient of variation (CV_{rob}). Bar charts of results and performance scores are presented in Figures 2 to 41.

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

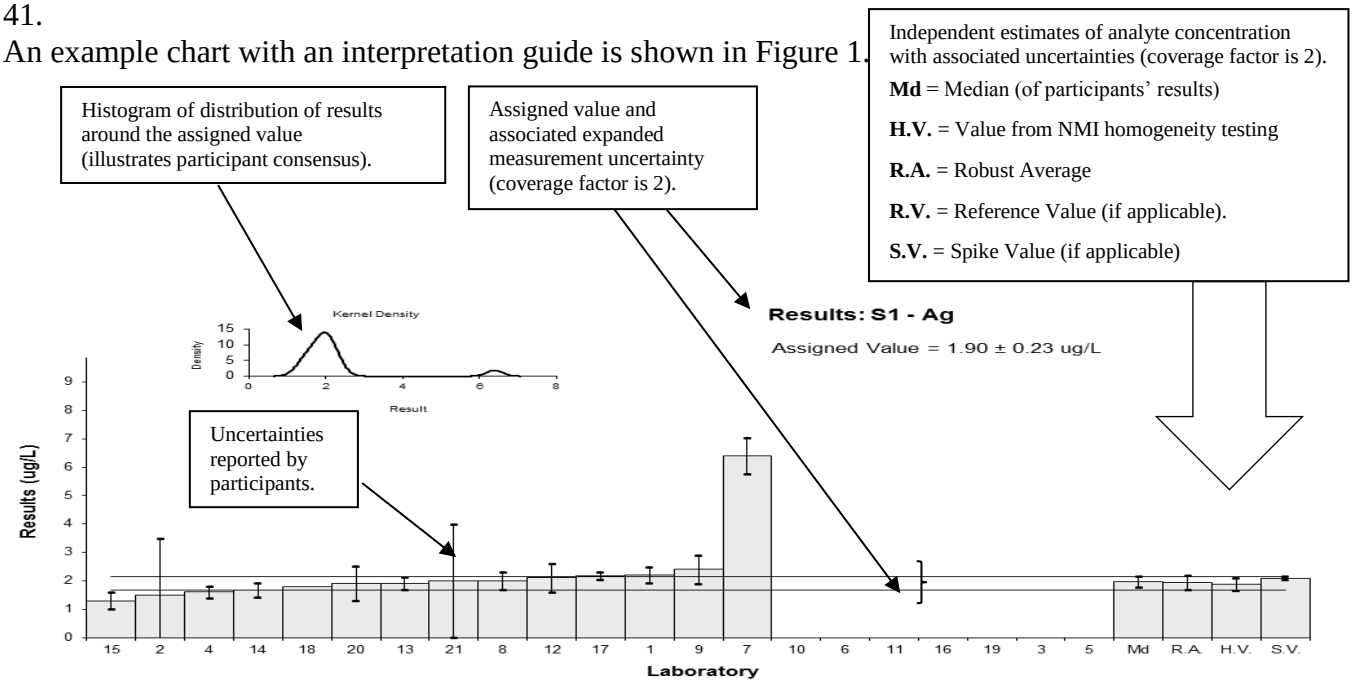


Figure 1 Guide to Presentation of Results

5.2 Assigned Value

An example of an 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 concentration of analyte. Assigned values were the robust average of participants' results; the expanded uncertainties were estimated from the associated robust standard deviations.

5.3 Robust Average

The robust averages and associated expanded measurement uncertainties were calculated using the procedure described in 'Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO13528:2015(E)'.[6]

5.4 Robust Between-Laboratory Coefficient of Variation

The robust between-laboratory coefficient of variation (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

The target standard deviation (σ) is the product of the assigned value *(X)* and the performance coefficient of variation (PCV) as presented in Equation 1. This value is used for calculation of participant z-score and provides scaling for laboratory deviation from the assigned value.

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

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 on experience from previous studies. It is backed up by mathematical models such as Thompson Horwitz equation (see Table 45).[7] By setting a fixed and realistic value for the PCV, the participants' performance does not depend on other participants' performance and can be compared from study to study and against achievable performance.

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:

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

where:

z is z-score
χ is participants' 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 3. 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:

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

where:

E_n is E_n-score
χ is participants' result
X is the assigned value
U_χ is the expanded uncertainty of the participants' 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 5

Sample Details

Sample No.	S1
Matrix.	Sea Water
Analyte.	Ag
Units	µg/L

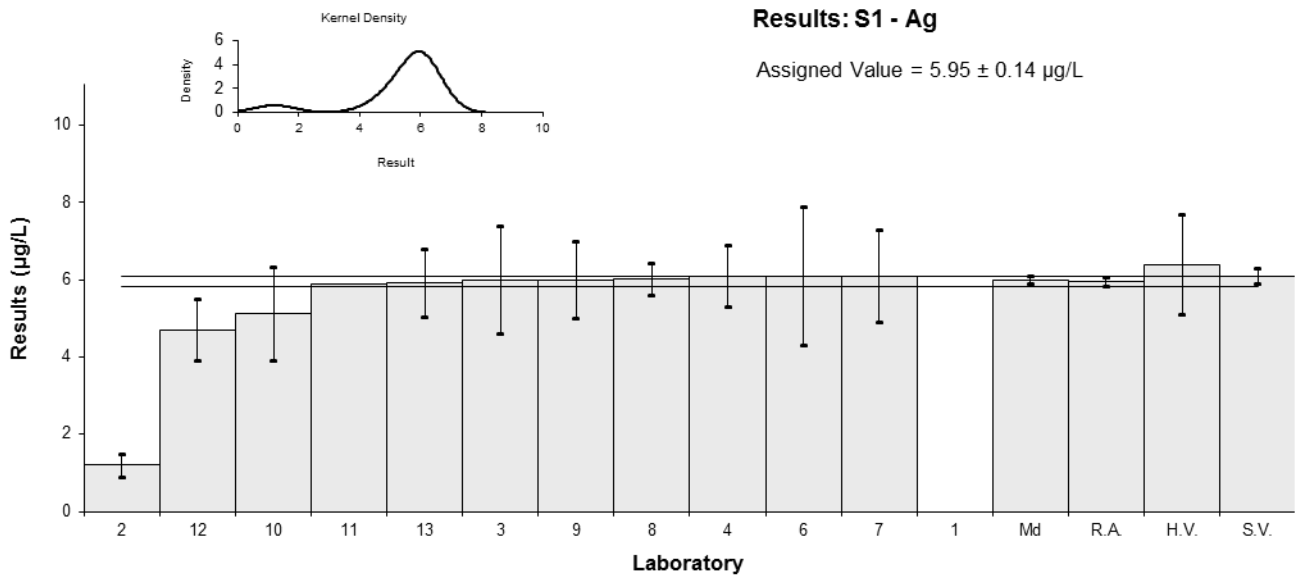
Participant Results

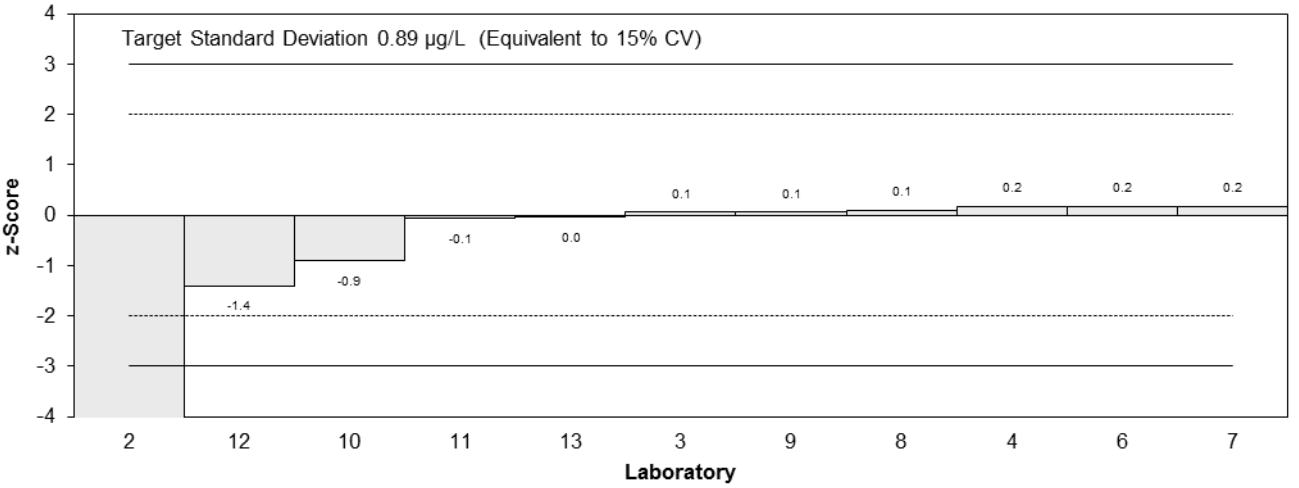
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	1.2	0.3	-5.32	-14.35
3	6.0	1.4	0.06	0.04
4	6.1	0.8	0.17	0.18
6	6.1	1.8	0.17	0.08
7	6.1	1.2	0.17	0.12
8	6.03	0.41	0.09	0.18
9	6	1	0.06	0.05
10	5.14	1.21	-0.91	-0.66
11	5.9	NR	-0.06	-0.36
12	4.7	0.8	-1.40	-1.54
13	5.92	0.89	-0.03	-0.03

Statistics

Assigned Value*	5.95	0.14
Spike	6.08	0.17
Homogeneity Value	6.4	1.3
Robust Average	5.95	0.11
Median	6.00	0.10
Mean	5.38	
N	11	
Max.	6.1	
Min.	1.2	
Robust SD	0.15	
Robust CV	2.5%	

*Robust Average excluding Laboratory 2.


Kernel Density
Density
Result
Results: S1 - Ag
Assigned Value = 5.95 ± 0.14 µg/L
Results (µg/L)
Laboratory
2 12 10 11 13 3 9 8 4 6 7 1 Md R.A. H.V. S.V.


z-Scores: S1 - Ag
Target Standard Deviation 0.89 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
2 12 10 11 13 3 9 8 4 6 7
-1.4 -0.9 -0.1 0.0 0.1 0.1 0.1 0.2 0.2 0.2

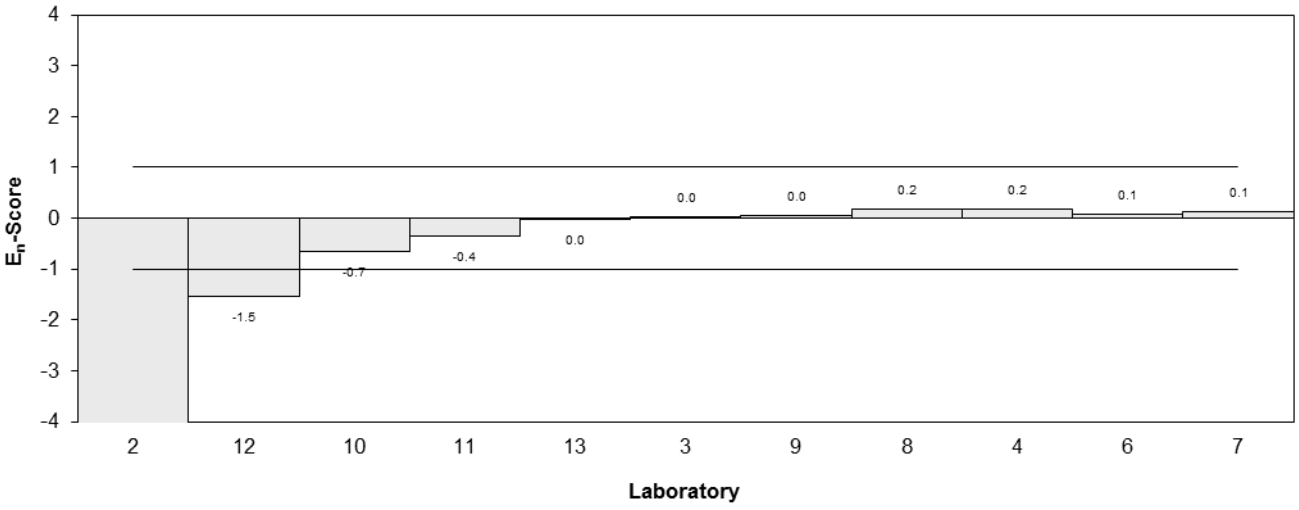

En-Scores: S1 - Ag
En-Score
Laboratory
2 12 10 11 13 3 9 8 4 6 7
-1.5 -0.7 -0.4 0.0 0.0 0.0 0.2 0.2 0.1 0.1

Figure 2

Table 6

Sample Details

Sample No.	S1
Matrix.	Sea Water
Analyte.	Al
Units	µg/L

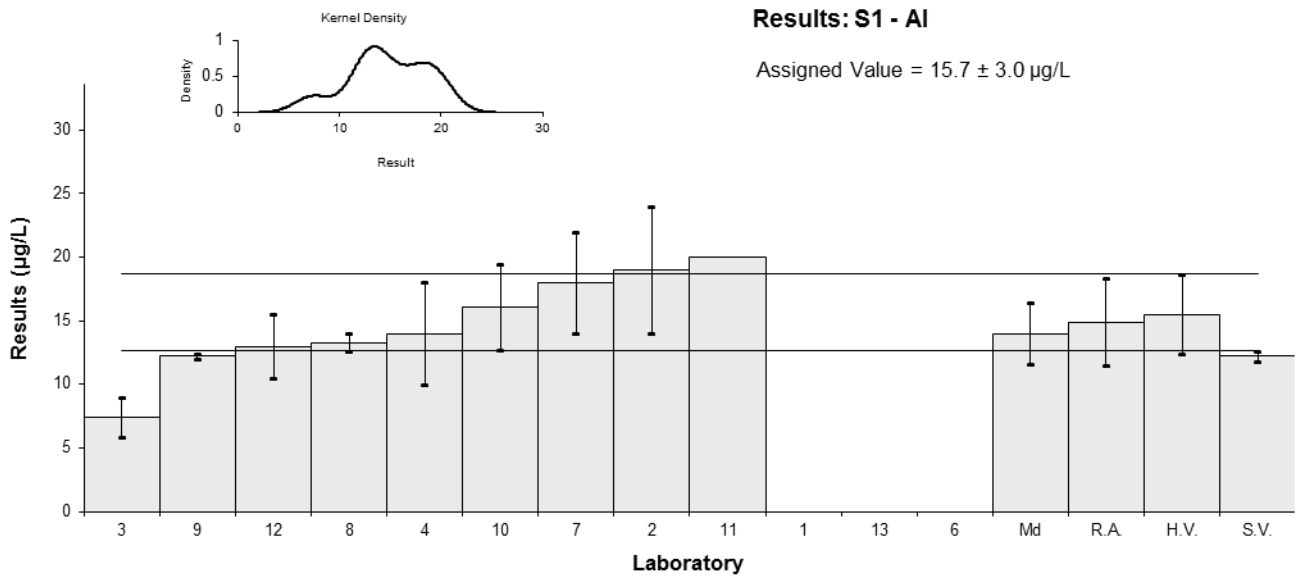
Participant Results

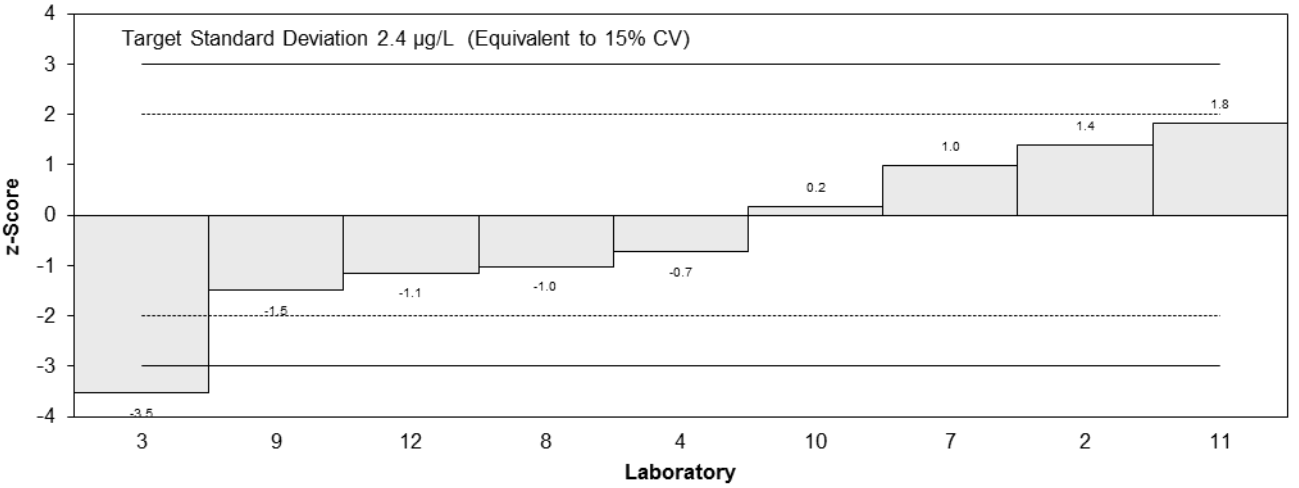
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	19	5	1.40	0.57
3	7.4	1.6	-3.52	-2.44
4	14	4	-0.72	-0.34
6	NT	NT		
7	18	4	0.98	0.46
8	13.3	0.70	-1.02	-0.78
9	12.2	0.2	-1.49	-1.16
10	16.1	3.4	0.17	0.09
11	20	NR	1.83	1.43
12	13	2.5	-1.15	-0.69
13	NT	NT		

Statistics

Assigned Value*	15.7	3.0
Spike	12.2	0.4
Homogeneity Value	15.5	3.1
Robust Average	14.9	3.4
Median	14.0	2.4
Mean	14.8	
N	9	
Max.	20	
Min.	7.4	
Robust SD	4.1	
Robust CV	28%	

*Robust Average excluding Laboratory 3.


Kernel Density
Density
Result
Results: S1 - Al
Assigned Value = 15.7 ± 3.0 µg/L
Results (µg/L)
Laboratory
3
9
12
8
4
10
7
2
11
1
13
6
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Al
Target Standard Deviation 2.4 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-3.5
-1.5
-1.1
-1.0
-0.7
0.2
1.0
1.4
1.8

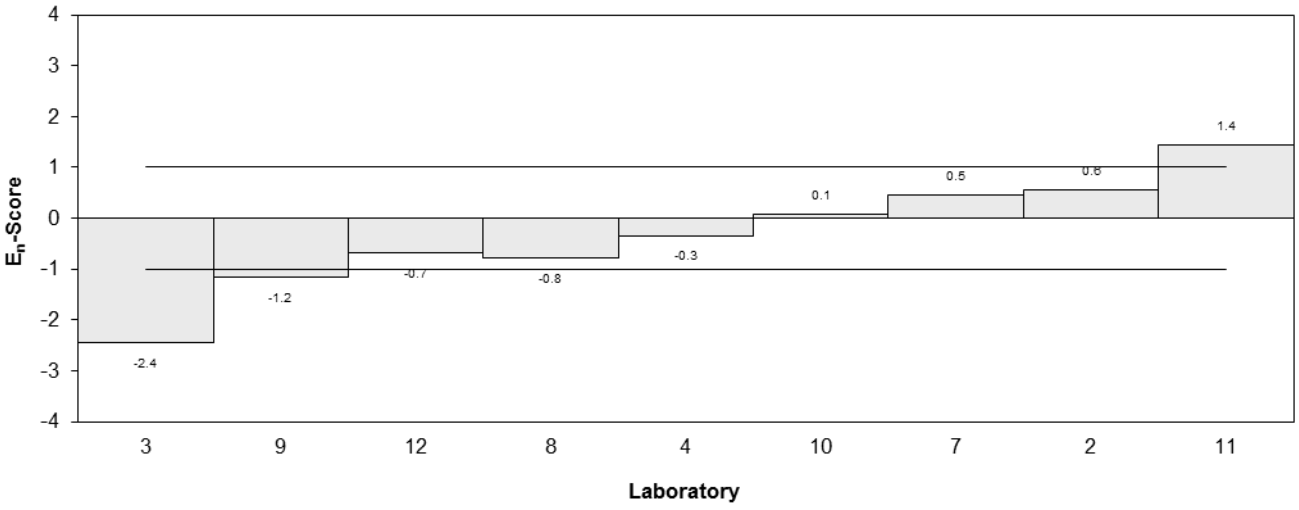

En-Scores: S1 - Al
En-Score
Laboratory
-2.4
-1.2
-0.7
-0.8
-0.3
0.1
0.5
0.6
1.4

Figure 3

Table 7

Sample Details

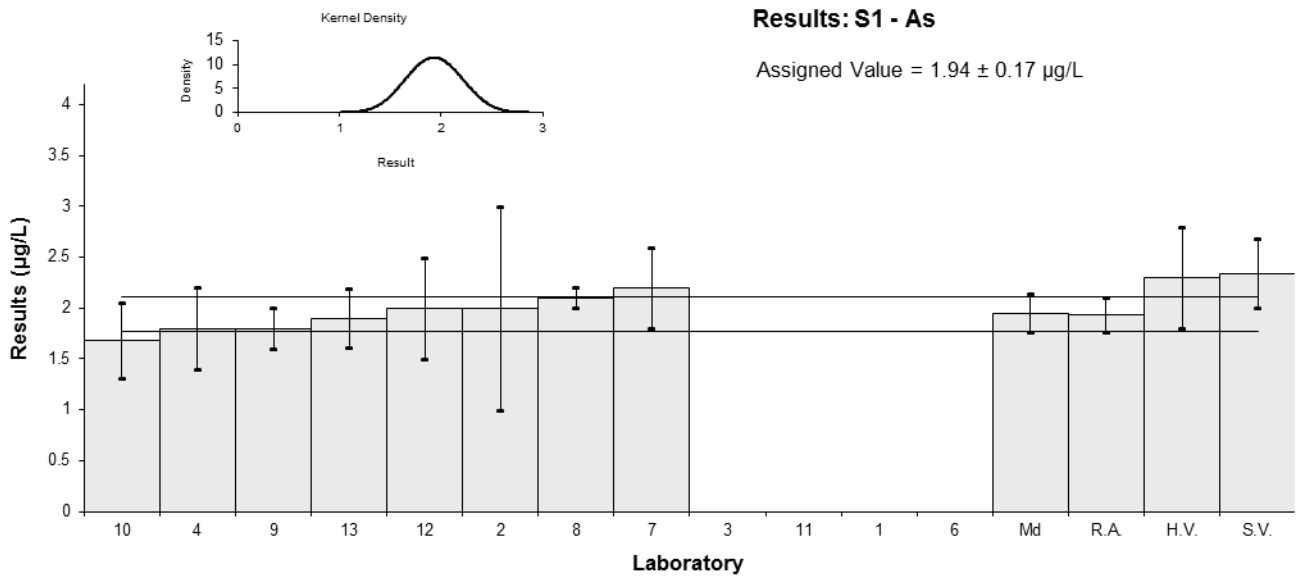
Sample No.	S1
Matrix.	Sea Water
Analyte.	As
Units	µg/L

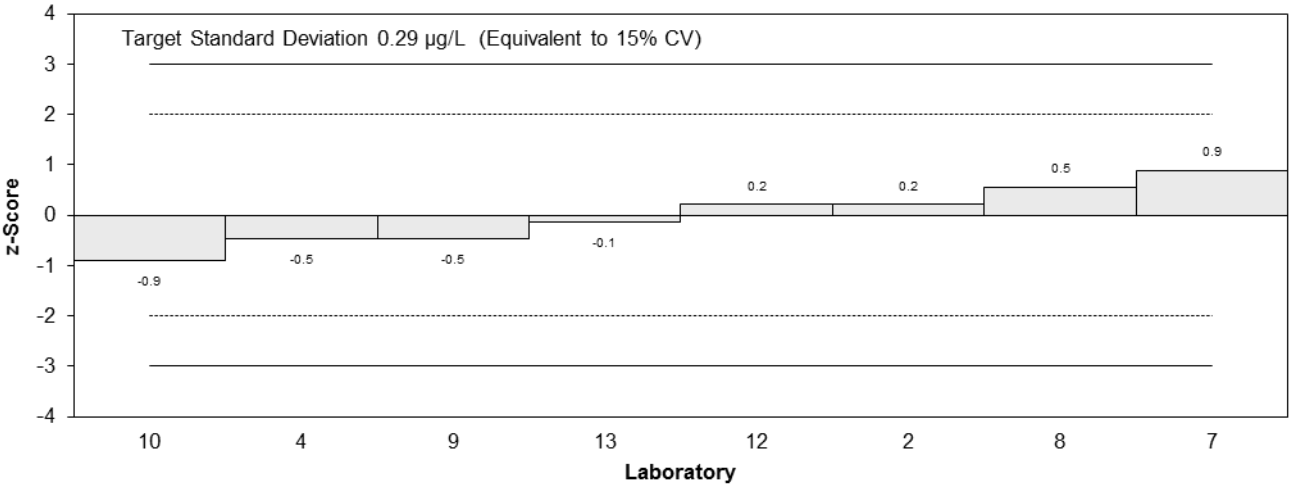
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	2	1	0.21	0.06
3	<10	NR		
4	1.8	0.4	-0.48	-0.32
6	NT	NT		
7	2.2	0.4	0.89	0.60
8	2.10	0.10	0.55	0.81
9	1.8	0.2	-0.48	-0.53
10	1.68	0.37	-0.89	-0.64
11	<4	2.7		
12	2.0	0.5	0.21	0.11
13	1.90	0.29	-0.14	-0.12

Statistics

Assigned Value	1.94	0.17
Spike	2.34	0.34
Homogeneity Value	2.25	0.45
Robust Average	1.94	0.17
Median	1.95	0.19
Mean	1.94	
N	8	
Max.	2.2	
Min.	1.68	
Robust SD	0.20	
Robust CV	10%	


Kernel Density
Density
Result
Results: S1 - As
Assigned Value = 1.94 ± 0.17 µg/L
Results (µg/L)
10 4 9 13 12 2 8 7 3 11 1 6 Md R.A. H.V. S.V.
Laboratory


z-Scores: S1 - As
Target Standard Deviation 0.29 µg/L (Equivalent to 15% CV)
z-Score
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10 4 9 13 12 2 8 7
Laboratory

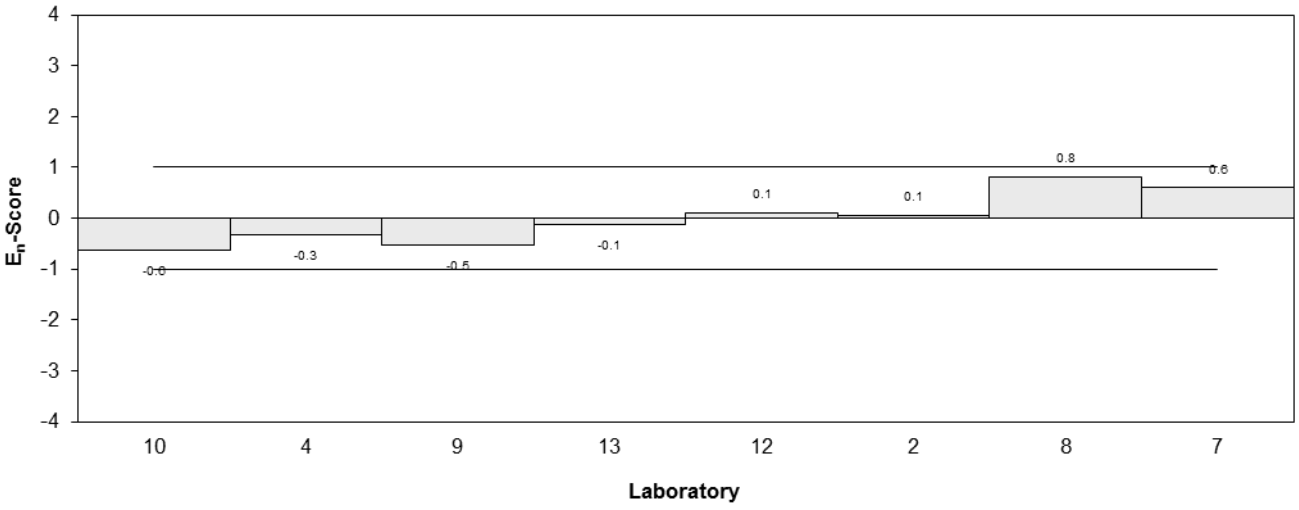

En-Scores: S1 - As
En-Score
-0.6 -0.3 -0.5 -0.1 0.1 0.1 0.8 0.6
10 4 9 13 12 2 8 7
Laboratory

Figure 4

Table 8

Sample Details

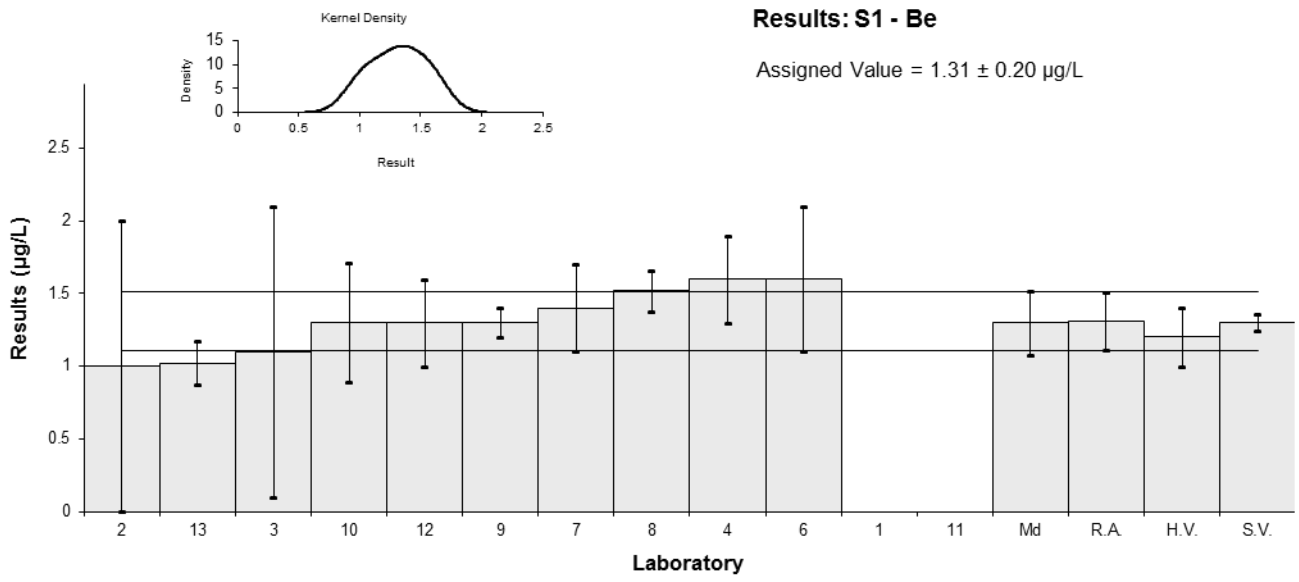
Sample No.	S1
Matrix.	Sea Water
Analyte.	Be
Units	µg/L

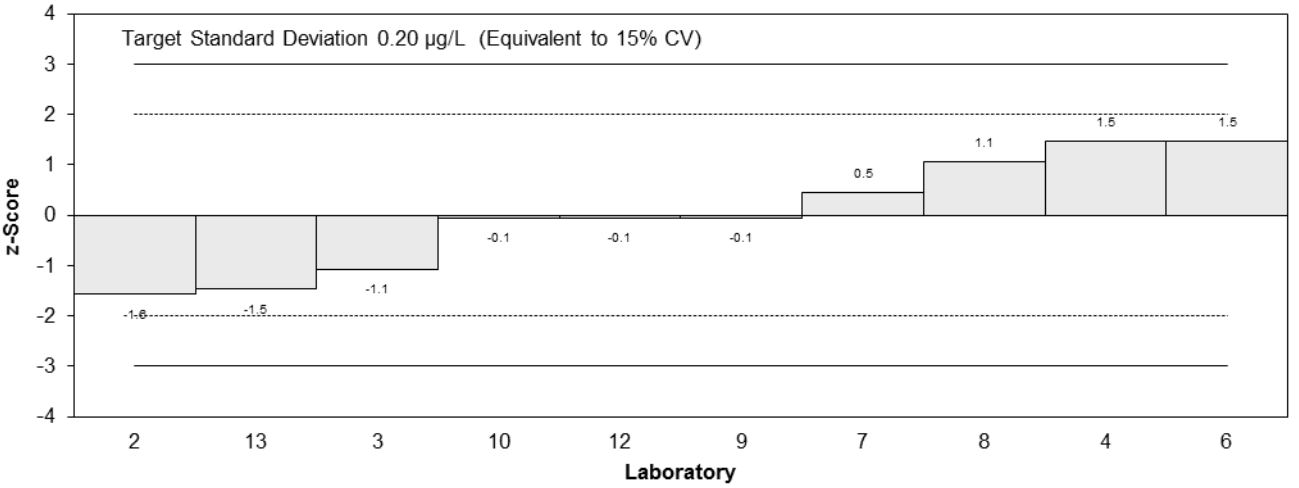
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	1	1	-1.58	-0.30
3	1.1	1	-1.07	-0.21
4	1.6	0.3	1.48	0.80
6	1.6	0.5	1.48	0.54
7	1.4	0.3	0.46	0.25
8	1.52	0.14	1.07	0.86
9	1.3	0.1	-0.05	-0.04
10	1.30	0.41	-0.05	-0.02
11	NT	NT		
12	1.3	0.3	-0.05	-0.03
13	1.02	0.15	-1.48	-1.16

Statistics

Assigned Value	1.31	0.20
Spike	1.30	0.06
Homogeneity Value	1.20	0.24
Robust Average	1.31	0.20
Median	1.30	0.22
Mean	1.31	
N	10	
Max.	1.6	
Min.	1	
Robust SD	0.25	
Robust CV	19%	


Kernel Density
Density
Result
Results: S1 - Be
Assigned Value = 1.31 ± 0.20 µg/L
Results (µg/L)
Laboratory
2
13
3
10
12
9
7
8
4
6
1
11
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Be
Target Standard Deviation 0.20 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.6
-1.5
-1.1
-0.1
-0.1
-0.1
0.5
1.1
1.5
1.5

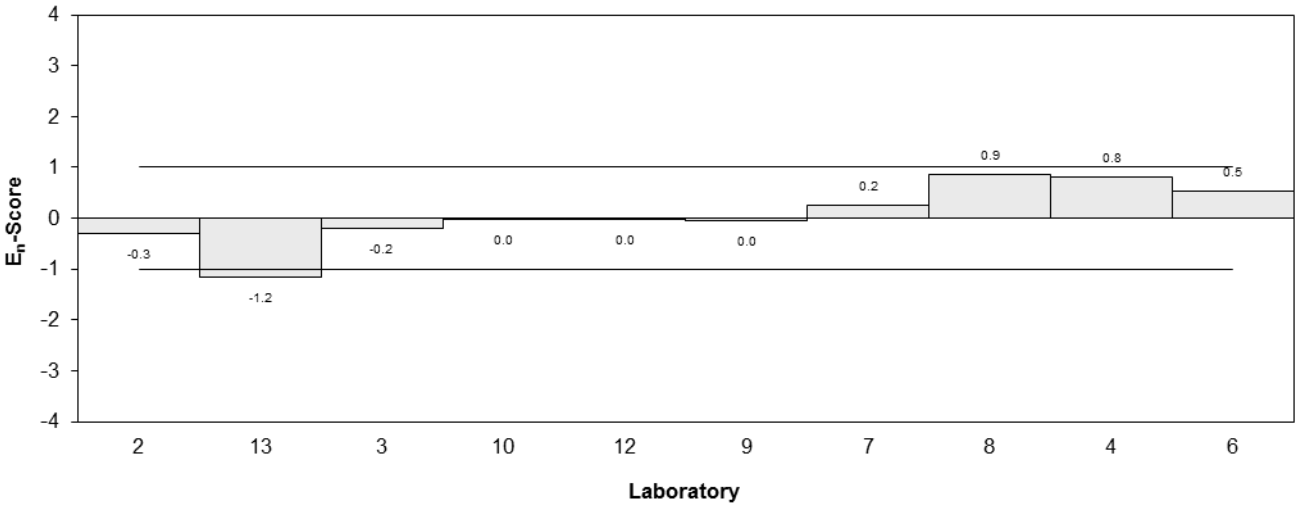

En-Scores: S1 - Be
En-Score
Laboratory
-0.3
-1.2
-0.2
0.0
0.0
0.0
0.2
0.9
0.8
0.5

Figure 5

Table 9

Sample Details

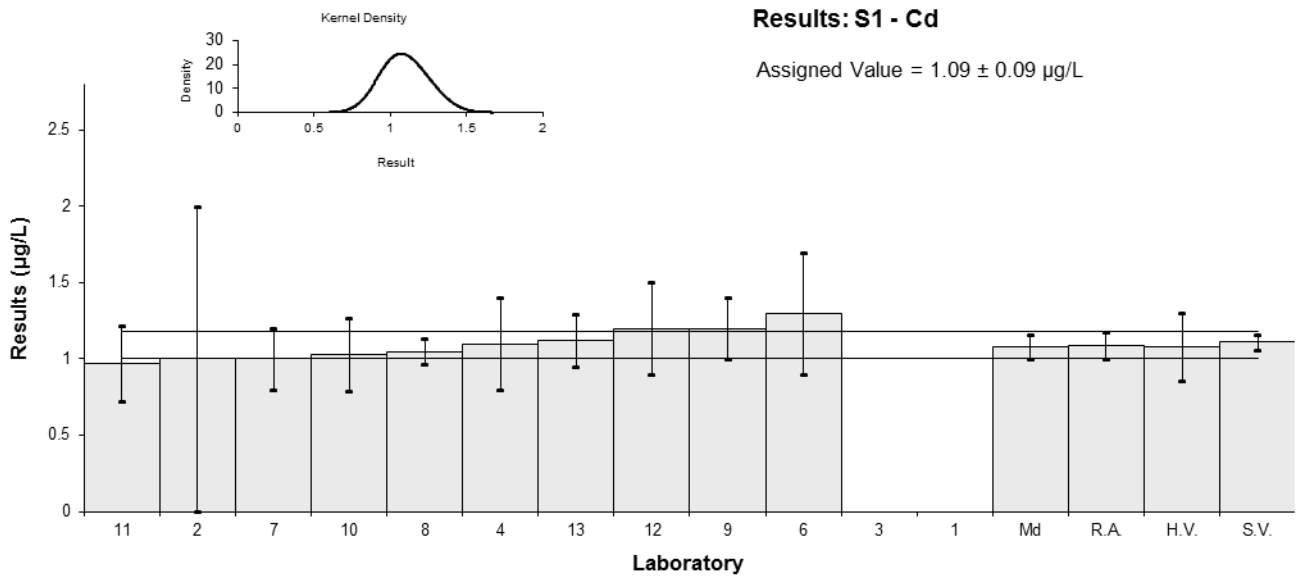
Sample No.	S1
Matrix.	Sea Water
Analyte.	Cd
Units	µg/L

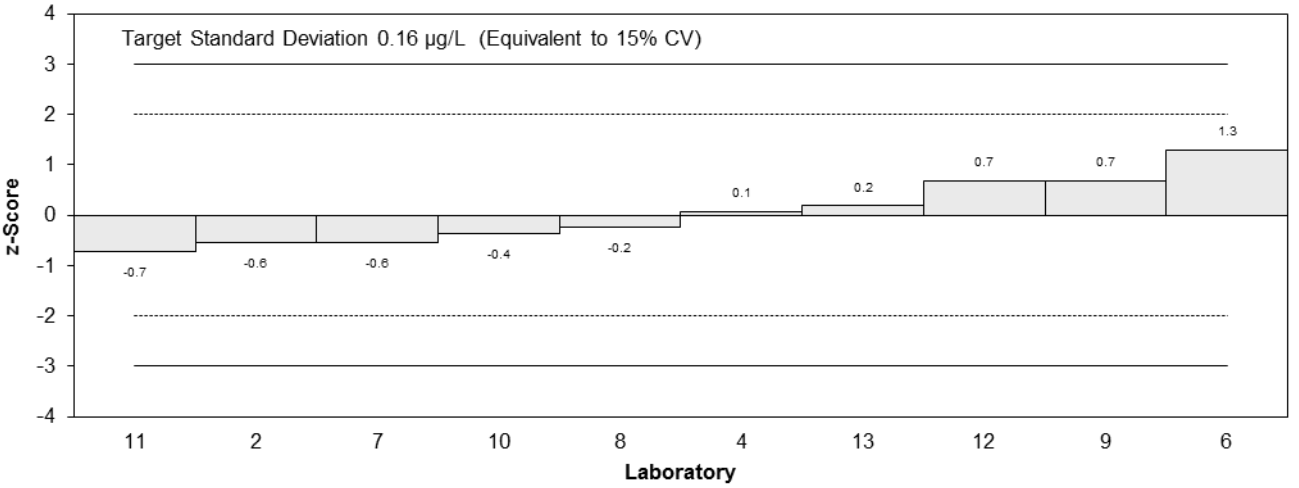
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	1	1	-0.55	-0.09
3	<1	NR		
4	1.1	0.3	0.06	0.03
6	1.3	0.4	1.28	0.51
7	1.0	0.2	-0.55	-0.41
8	1.05	0.08	-0.24	-0.33
9	1.2	0.2	0.67	0.50
10	1.03	0.24	-0.37	-0.23
11	0.97	0.25	-0.73	-0.45
12	1.2	0.3	0.67	0.35
13	1.12	0.17	0.18	0.16

Statistics

Assigned Value	1.09	0.09
Spike	1.11	0.05
Homogeneity Value	1.08	0.22
Robust Average	1.09	0.09
Median	1.08	0.08
Mean	1.10	
N	10	
Max.	1.3	
Min.	0.97	
Robust SD	0.11	
Robust CV	10%	


Kernel Density
Density
Result
Results: S1 - Cd
Assigned Value = 1.09 ± 0.09 µg/L
Results (µg/L)
Laboratory
11
2
7
10
8
4
13
12
9
6
3
1
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Cd
Target Standard Deviation 0.16 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.7
-0.6
-0.6
-0.4
-0.2
0.1
0.2
0.7
0.7
1.3

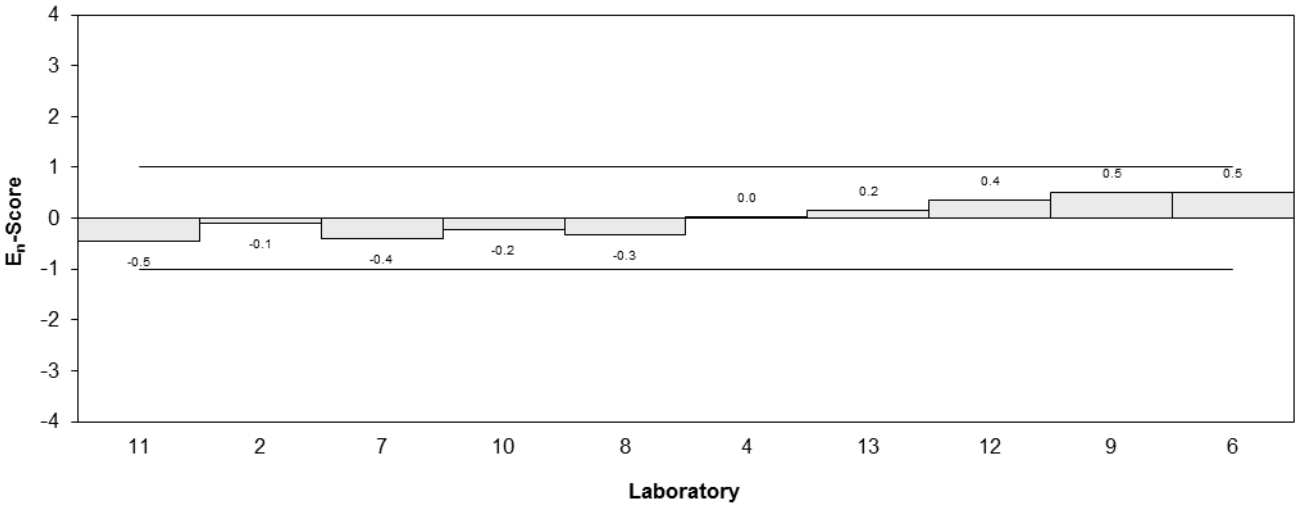

En-Scores: S1 - Cd
En-Score
Laboratory
-0.5
-0.1
-0.4
-0.2
-0.3
0.0
0.2
0.4
0.5
0.5

Figure 6

Table 10

Sample Details

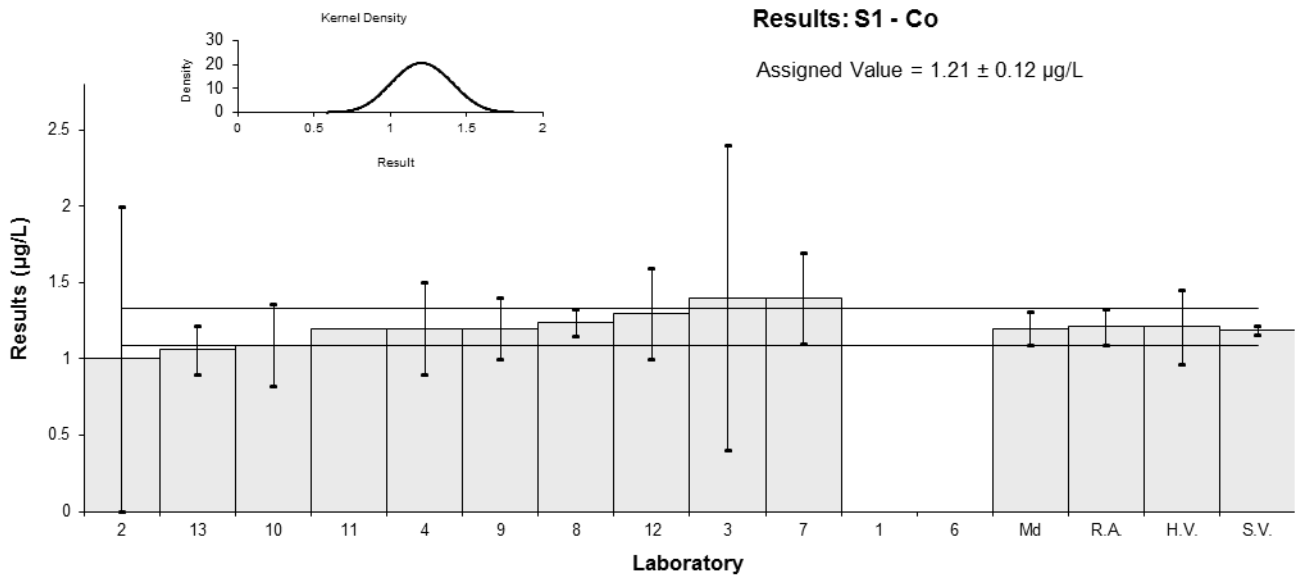
Sample No.	S1
Matrix.	Sea Water
Analyte.	Co
Units	µg/L

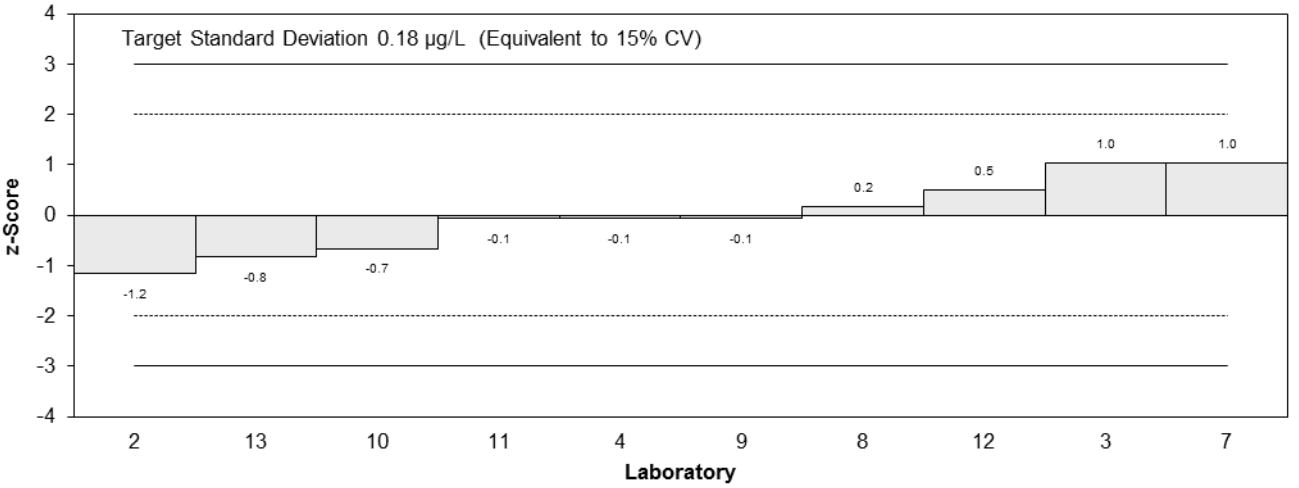
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	1	1	-1.16	-0.21
3	1.4	1	1.05	0.19
4	1.2	0.3	-0.06	-0.03
6	NT	NT		
7	1.4	0.3	1.05	0.59
8	1.24	0.09	0.17	0.20
9	1.2	0.2	-0.06	-0.04
10	1.09	0.27	-0.66	-0.41
11	1.2	NR	-0.06	-0.08
12	1.3	0.3	0.50	0.28
13	1.06	0.16	-0.83	-0.75

Statistics

Assigned Value	1.21	0.12
Spike	1.19	0.03
Homogeneity Value	1.21	0.24
Robust Average	1.21	0.12
Median	1.20	0.11
Mean	1.21	
N	10	
Max.	1.4	
Min.	1	
Robust SD	0.15	
Robust CV	12%	


Kernel Density
Density
Result
Results: S1 - Co
Assigned Value = 1.21 ± 0.12 µg/L
Results (µg/L)
Laboratory
2
13
10
11
4
9
8
12
3
7
1
6
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Co
Target Standard Deviation 0.18 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.2
-0.8
-0.7
-0.1
-0.1
-0.1
0.2
0.5
1.0
1.0

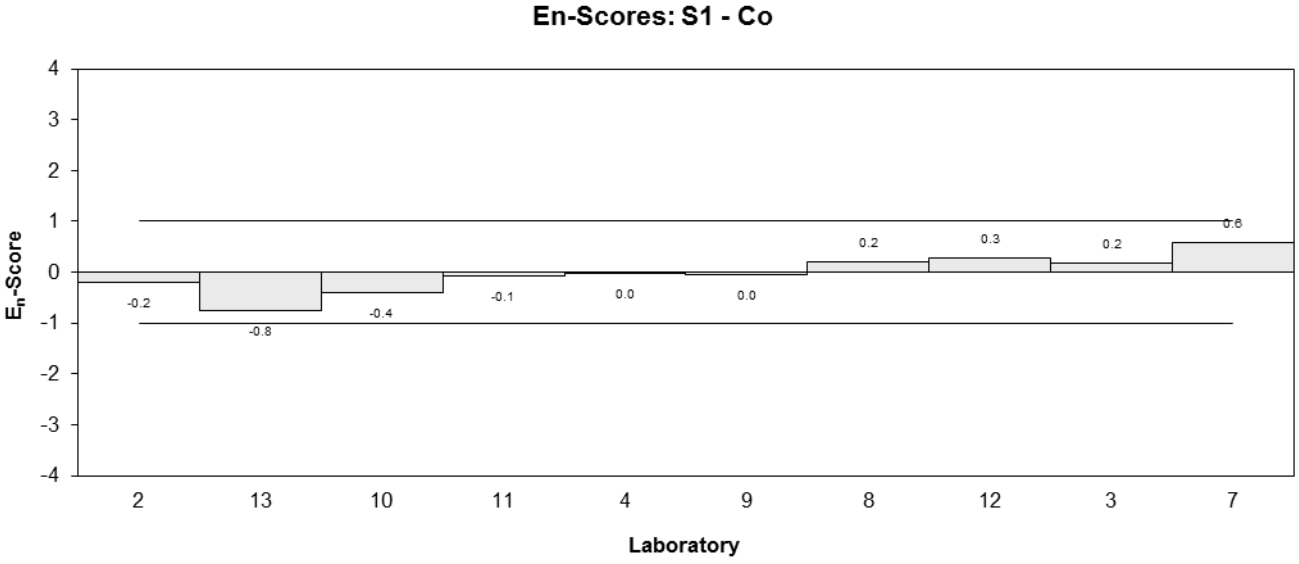

En-Scores: S1 - Co
En-Score
Laboratory
-0.2
-0.8
-0.4
-0.1
0.0
0.0
0.2
0.3
0.2
0.6

Figure 7

Table 11

Sample Details

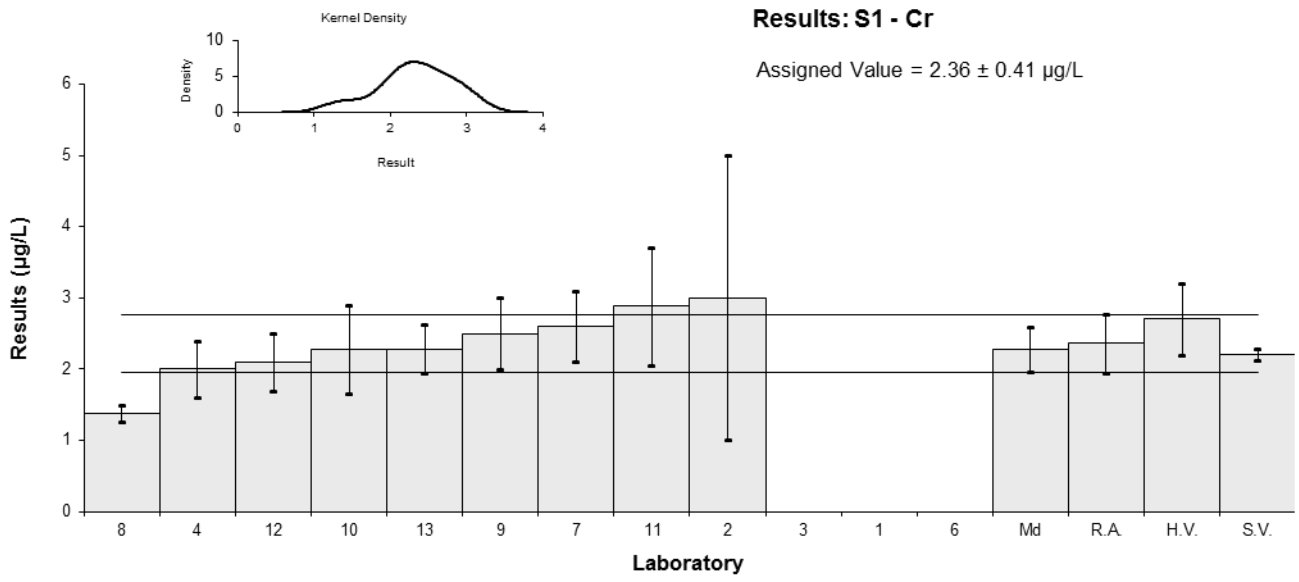
Sample No.	S1
Matrix.	Sea Water
Analyte.	Cr
Units	µg/L

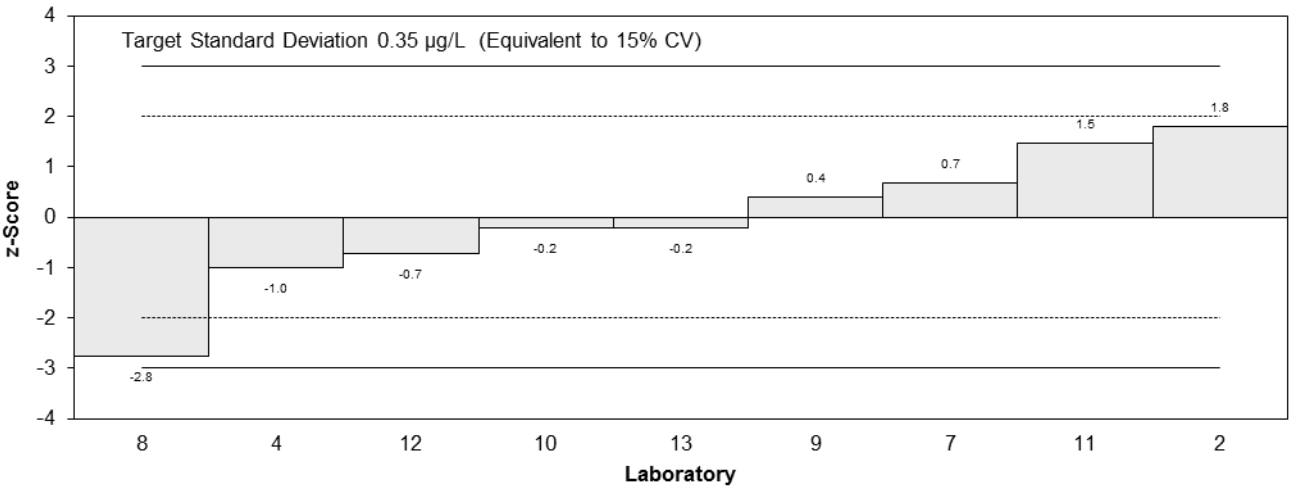
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	3	2	1.81	0.31
3	<5	NR		
4	2.0	0.4	-1.02	-0.63
6	NT	0.9		
7	2.6	0.5	0.68	0.37
8	1.38	0.12	-2.77	-2.29
9	2.5	0.5	0.40	0.22
10	2.28	0.62	-0.23	-0.11
11	2.88	0.83	1.47	0.56
12	2.1	0.4	-0.73	-0.45
13	2.28	0.34	-0.23	-0.15

Statistics

Assigned Value	2.36	0.41
Spike	2.21	0.08
Homogeneity Value	2.69	0.54
Robust Average	2.36	0.41
Median	2.28	0.32
Mean	2.34	
N	9	
Max.	3	
Min.	1.38	
Robust SD	0.49	
Robust CV	21%	


Kernel Density
Density
Result
Results: S1 - Cr
Assigned Value = 2.36 ± 0.41 µg/L
Results (µg/L)
8 4 12 10 13 9 7 11 2 3 1 6 Md R.A. H.V. S.V.
Laboratory


z-Scores: S1 - Cr
Target Standard Deviation 0.35 µg/L (Equivalent to 15% CV)
z-Score
-2.8 -1.0 -0.7 -0.2 -0.2 0.4 0.7 1.5 1.8
8 4 12 10 13 9 7 11 2
Laboratory

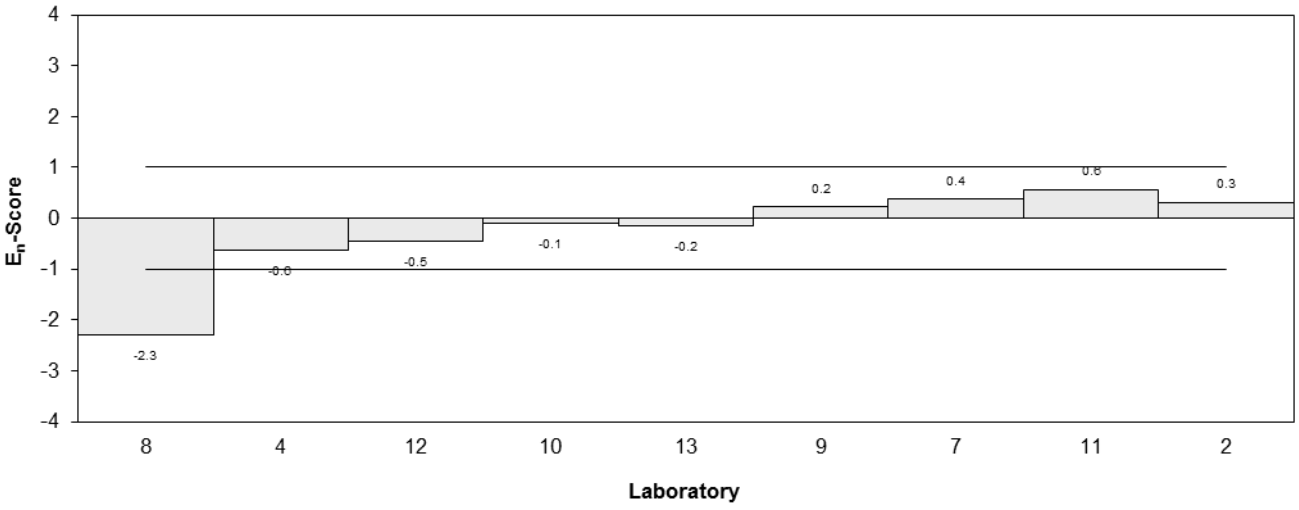

En-Scores: S1 - Cr
En-Score
-2.3 -0.6 -0.5 -0.1 -0.2 0.2 0.4 0.6 0.3
8 4 12 10 13 9 7 11 2
Laboratory

Figure 8

Table 12

Sample Details

Sample No.	S1
Matrix.	Sea Water
Analyte.	Cu
Units	µg/L

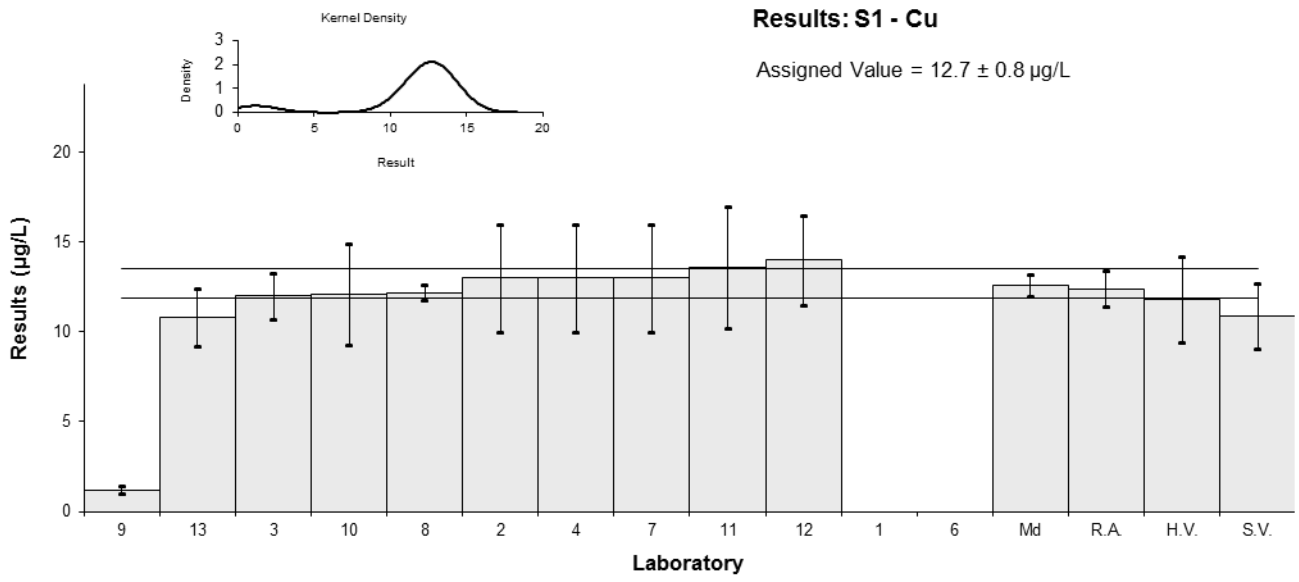
Participant Results

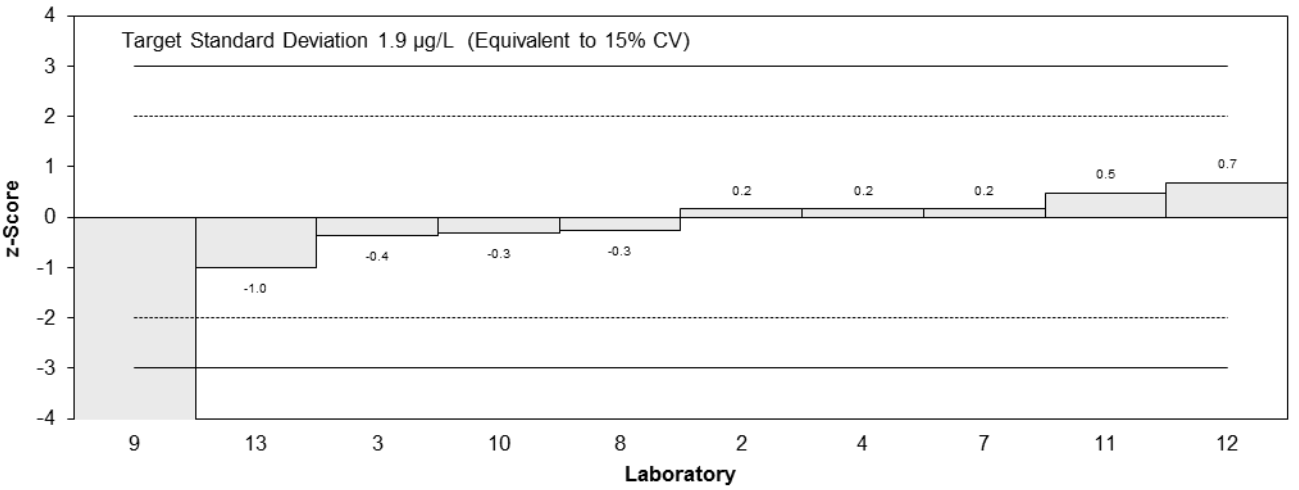
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	13	3	0.16	0.10
3	12	1.3	-0.37	-0.46
4	13	3	0.16	0.10
6	NT	NT		
7	13	3	0.16	0.10
8	12.2	0.45	-0.26	-0.54
9	1.2	0.23	-6.04	-13.82
10	12.1	2.8	-0.31	-0.21
11	13.6	3.4	0.47	0.26
12	14	2.5	0.68	0.50
13	10.8	1.62	-1.00	-1.05

Statistics

Assigned Value*	12.7	0.8
Spike	10.9	1.8
Homogeneity Value	11.8	2.4
Robust Average	12.4	1.0
Median	12.6	0.6
Mean	11.5	
N	10	
Max.	14	
Min.	1.2	
Robust SD	1.3	
Robust CV	10%	

*Robust Average excluding Laboratory 9.


Kernel Density
Density
Result
Results: S1 - Cu
Assigned Value = 12.7 ± 0.8 µg/L
Results (µg/L)
Laboratory
9
13
3
10
8
2
4
7
11
12
1
6
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Cu
Target Standard Deviation 1.9 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.0
-0.4
-0.3
-0.3
0.2
0.2
0.2
0.5
0.7

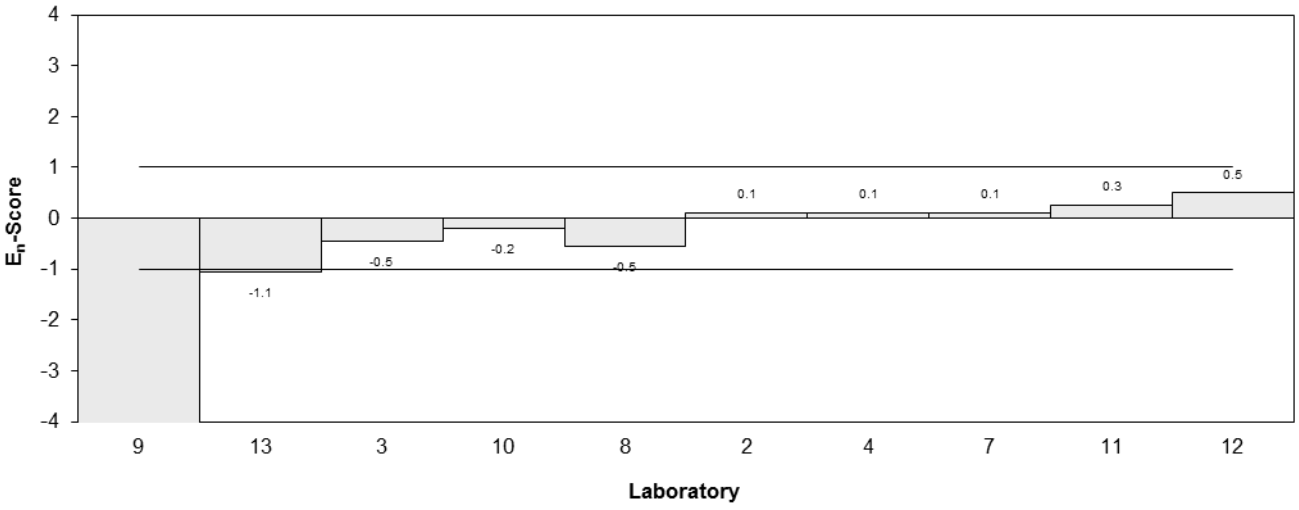

En-Scores: S1 - Cu
En-Score
Laboratory
-1.1
-0.5
-0.2
-0.5
0.1
0.1
0.1
0.3
0.5

Figure 9

Table 13

Sample Details

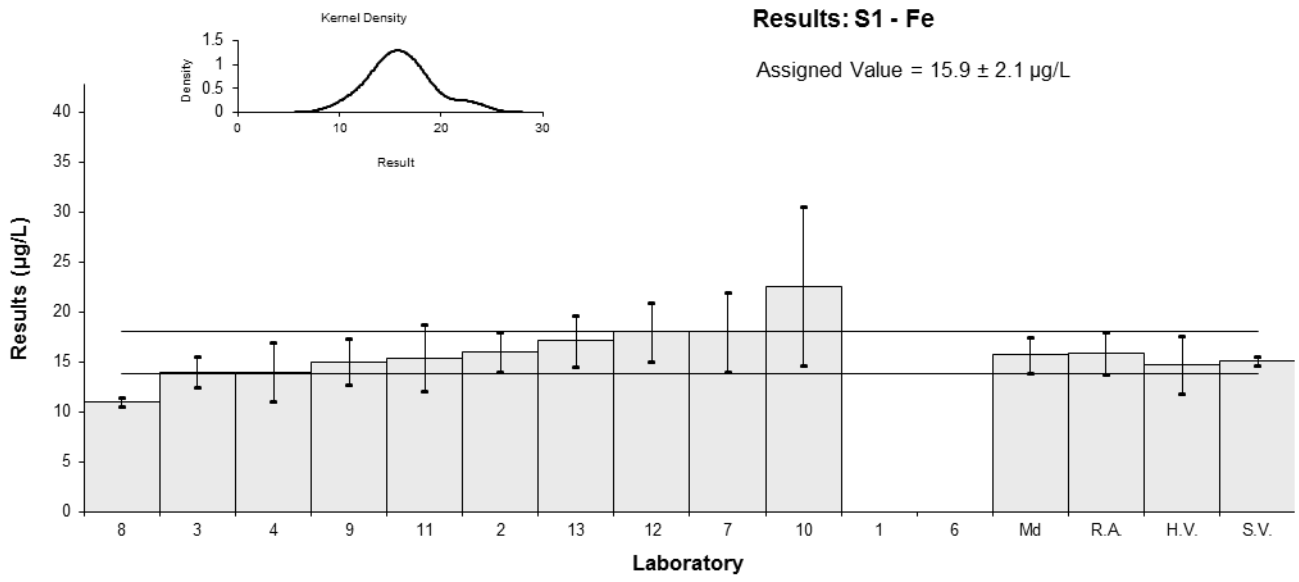
Sample No.	S1
Matrix.	Sea Water
Analyte.	Fe
Units	µg/L

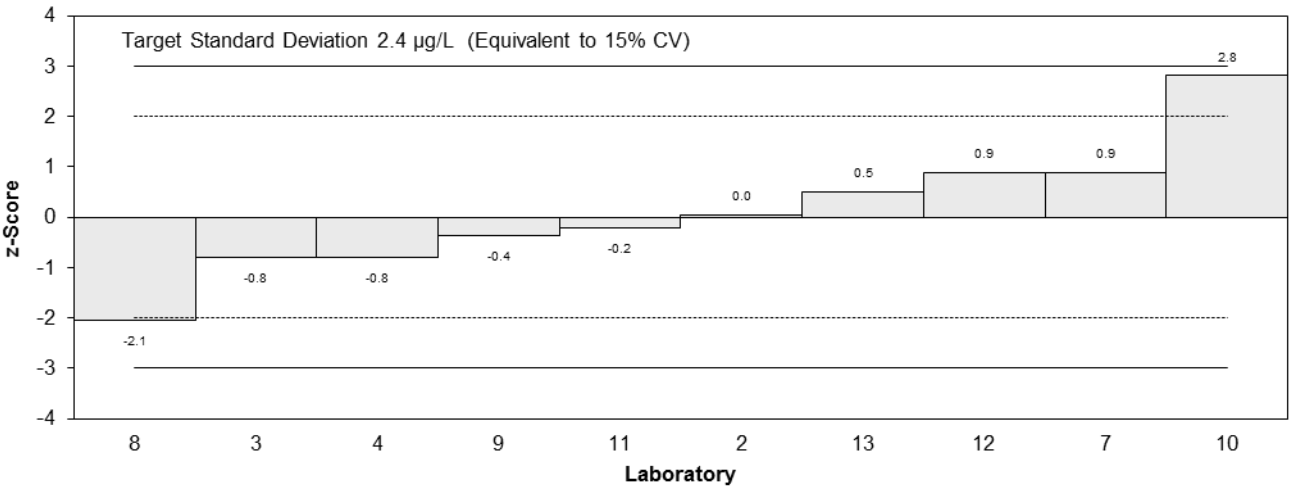
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	16	2	0.04	0.03
3	14	1.5	-0.80	-0.74
4	14	3	-0.80	-0.52
6	NT	NT		
7	18	4	0.88	0.46
8	11	0.46	-2.05	-2.28
9	15	2.3	-0.38	-0.29
10	22.6	8.0	2.81	0.81
11	15.4	3.3	-0.21	-0.13
12	18	3.0	0.88	0.57
13	17.1	2.56	0.50	0.36

Statistics

Assigned Value	15.9	2.1
Spike	15.1	0.4
Homogeneity Value	14.7	2.9
Robust Average	15.9	2.1
Median	15.7	1.8
Mean	16.1	
N	10	
Max.	22.6	
Min.	11	
Robust SD	2.7	
Robust CV	17%	


Kernel Density
Density
Result
Results: S1 - Fe
Assigned Value = 15.9 ± 2.1 µg/L
Results (µg/L)
Laboratory
8
3
4
9
11
2
13
12
7
10
1
6
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Fe
Target Standard Deviation 2.4 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-2.1
-0.8
-0.8
-0.4
-0.2
0.0
0.5
0.9
0.9
2.8

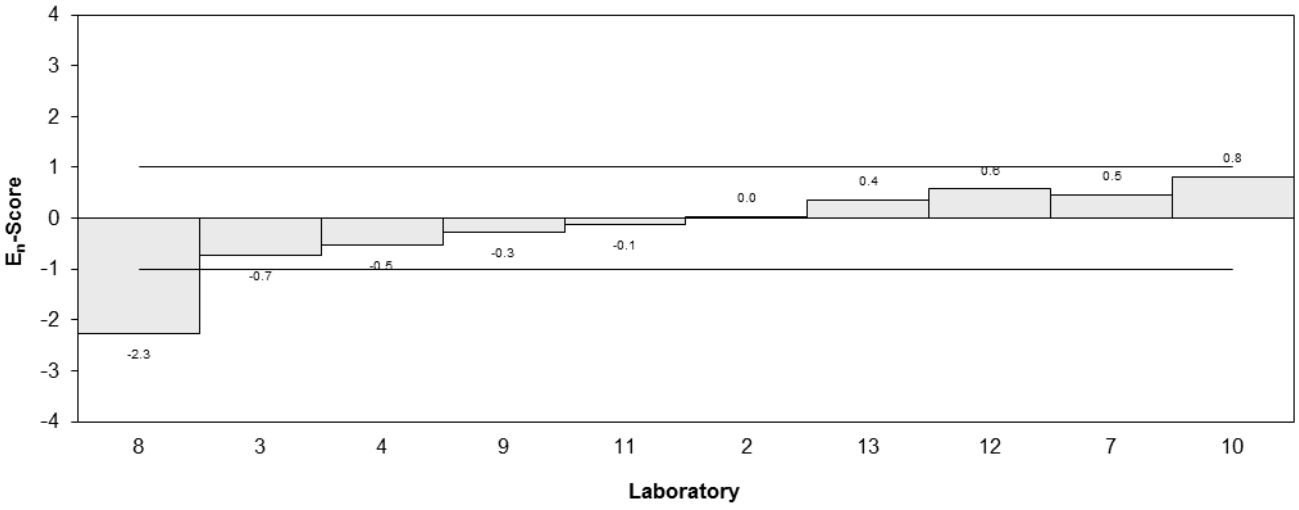

En-Scores: S1 - Fe
En-Score
Laboratory
-2.3
-0.7
-0.5
-0.3
-0.1
0.0
0.4
0.6
0.5
0.8

Figure 10

Table 14

Sample Details

Sample No.	S1
Matrix.	Sea Water
Analyte.	Hg
Units	µg/L

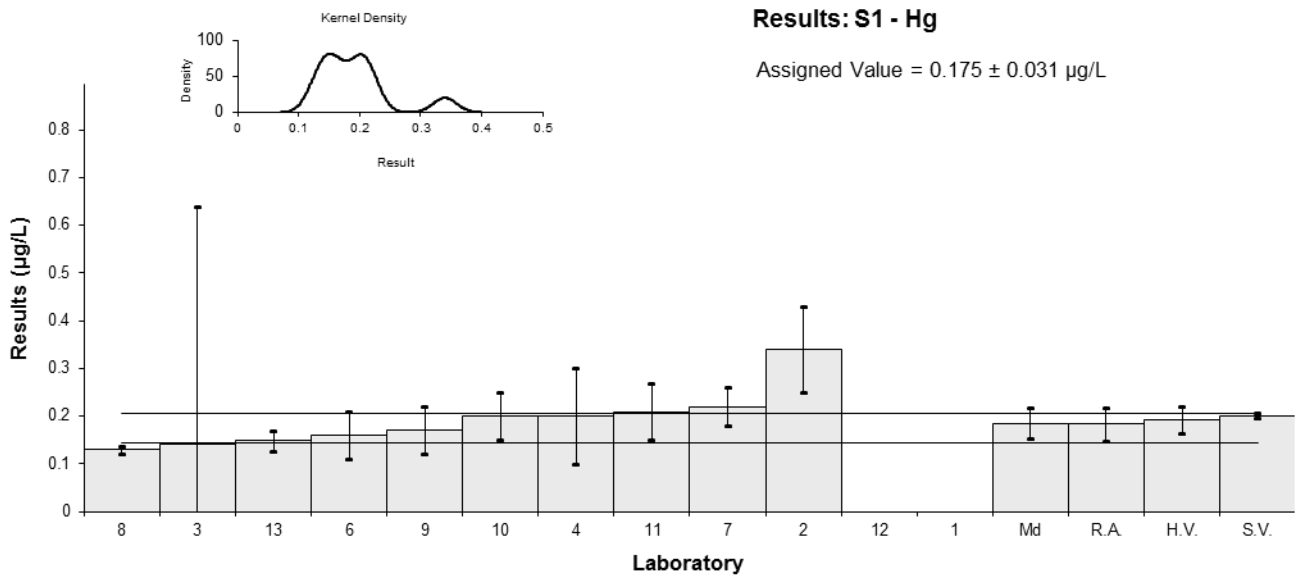
Participant Results

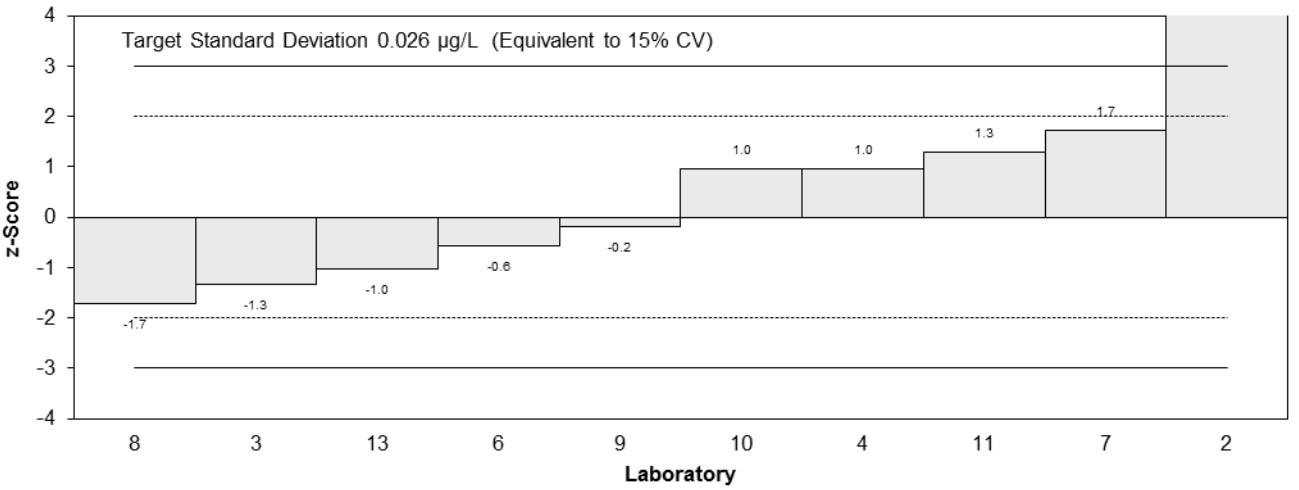
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	0.34	0.09	6.29	1.73
3	0.14	0.5	-1.33	-0.07
4	0.2	0.1	0.95	0.24
6	0.16	0.05	-0.57	-0.25
7	0.22	0.04	1.71	0.89
8	0.13	0.008	-1.71	-1.41
9	0.17	0.05	-0.19	-0.08
10	0.20	0.05	0.95	0.42
11	0.209	0.059	1.30	0.51
12	<0.5	NR		
13	0.148	0.022	-1.03	-0.71

Statistics

Assigned Value*	0.175	0.031
Spike	0.201	0.006
Homogeneity Value	0.192	0.029
Robust Average	0.183	0.035
Median	0.185	0.032
Mean	0.192	
N	10	
Max.	0.34	
Min.	0.13	
Robust SD	0.044	
Robust CV	24%	

*Robust Average excluding Laboratory 2.


Kernel Density
Density
Result
Results: S1 - Hg
Assigned Value = 0.175 ± 0.031 µg/L
Results (µg/L)
Laboratory
8 3 13 6 9 10 4 11 7 2 12 1 Md R.A. H.V. S.V.


z-Scores: S1 - Hg
Target Standard Deviation 0.026 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
8 3 13 6 9 10 4 11 7 2
-1.7 -1.3 -1.0 -0.6 -0.2 1.0 1.0 1.3 1.7

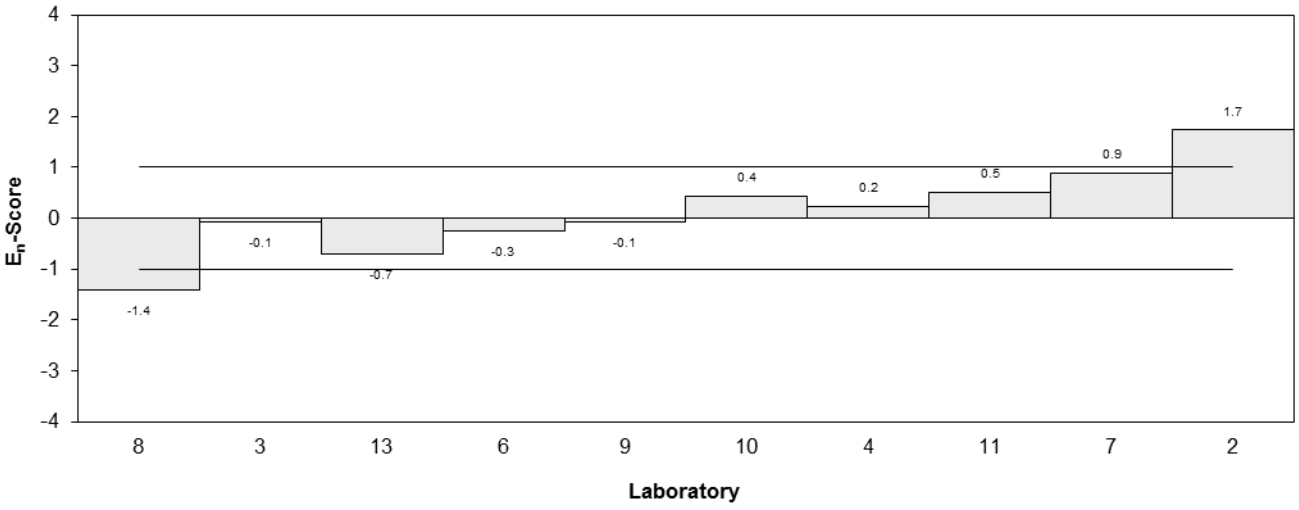

En-Scores: S1 - Hg
En-Score
Laboratory
8 3 13 6 9 10 4 11 7 2
-1.4 -0.1 -0.7 -0.3 -0.1 0.4 0.2 0.5 0.9 1.7

Figure 11

Table 15

Sample Details

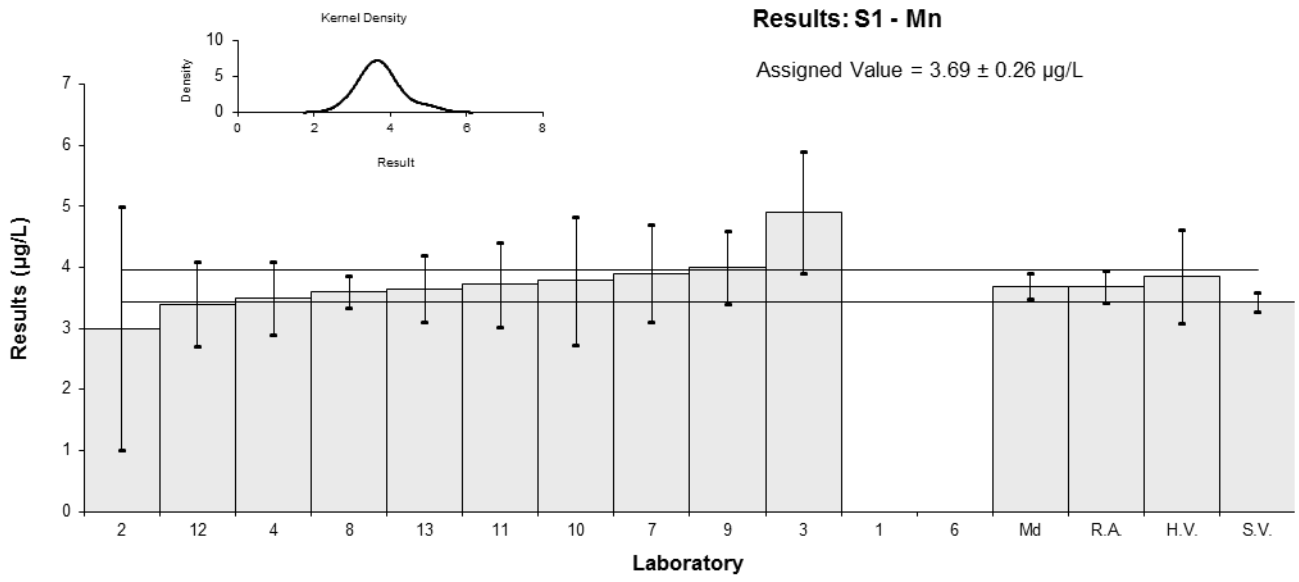
Sample No.	S1
Matrix.	Sea Water
Analyte.	Mn
Units	µg/L

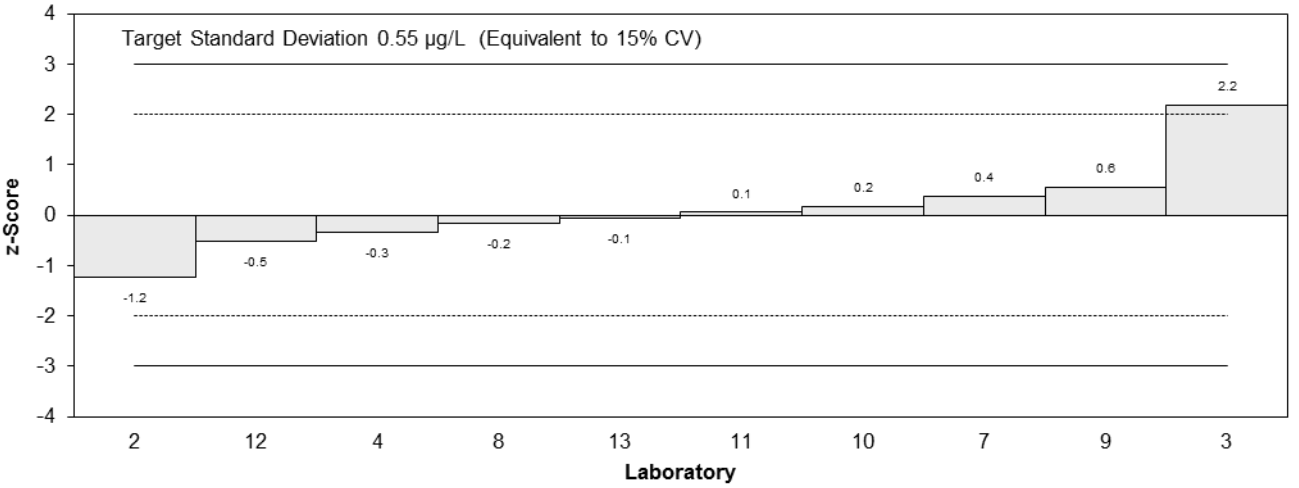
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	3	2	-1.25	-0.34
3	4.9	1	2.19	1.17
4	3.5	0.6	-0.34	-0.29
6	NT	NT		
7	3.9	0.8	0.38	0.25
8	3.6	0.26	-0.16	-0.24
9	4	0.6	0.56	0.47
10	3.78	1.04	0.16	0.08
11	3.72	0.69	0.05	0.04
12	3.4	0.7	-0.52	-0.39
13	3.65	0.55	-0.07	-0.07

Statistics

Assigned Value	3.69	0.26
Spike	3.44	0.16
Homogeneity Value	3.85	0.77
Robust Average	3.69	0.26
Median	3.69	0.21
Mean	3.75	
N	10	
Max.	4.9	
Min.	3	
Robust SD	0.33	
Robust CV	8.9%	


Kernel Density
Density
Result
Results: S1 - Mn
Assigned Value = 3.69 ± 0.26 µg/L
Results (µg/L)
Laboratory
2
12
4
8
13
11
10
7
9
3
1
6
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Mn
Target Standard Deviation 0.55 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.2
-0.5
-0.3
-0.2
-0.1
0.1
0.2
0.4
0.6
2.2

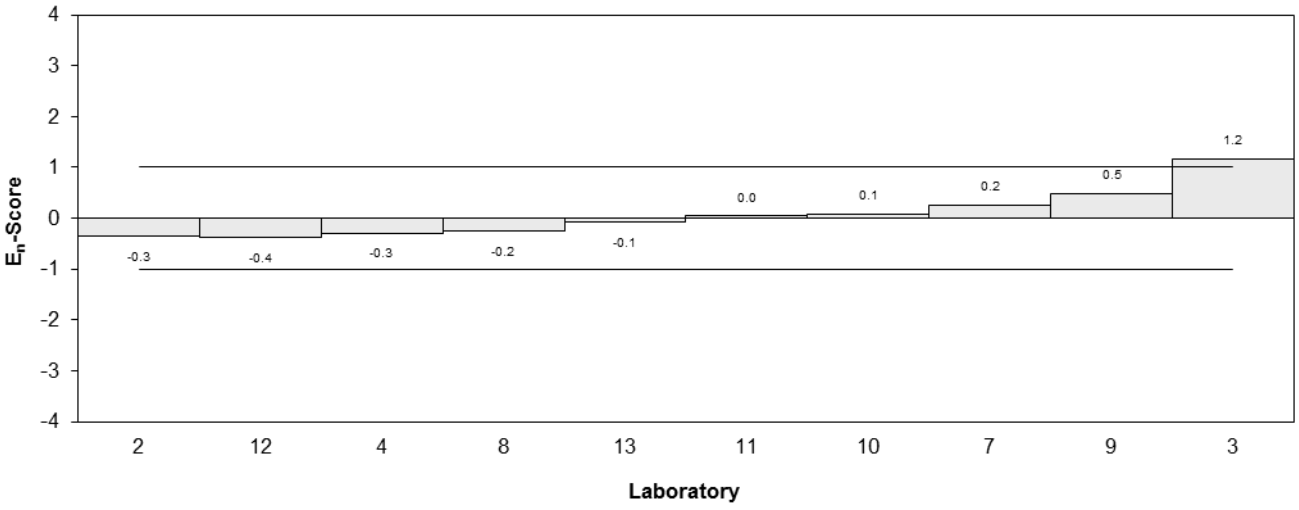

En-Scores: S1 - Mn
En-Score
Laboratory
-0.3
-0.4
-0.3
-0.2
-0.1
0.0
0.1
0.2
0.5
1.2

Figure 12

Table 16

Sample Details

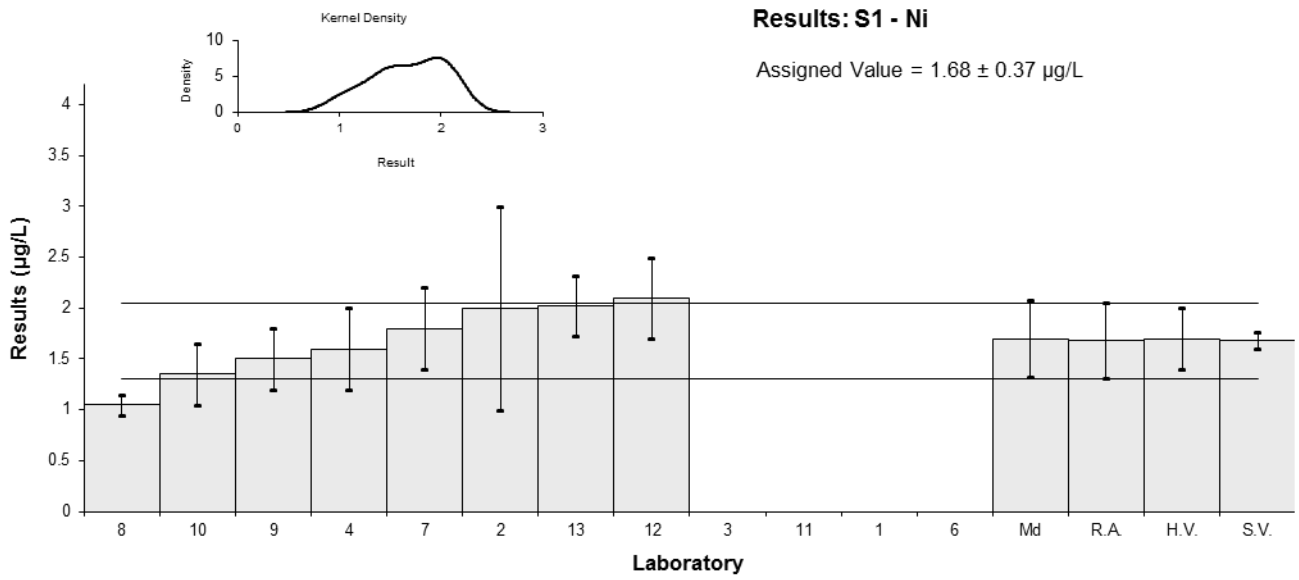
Sample No.	S1
Matrix.	Sea Water
Analyte.	Ni
Units	µg/L

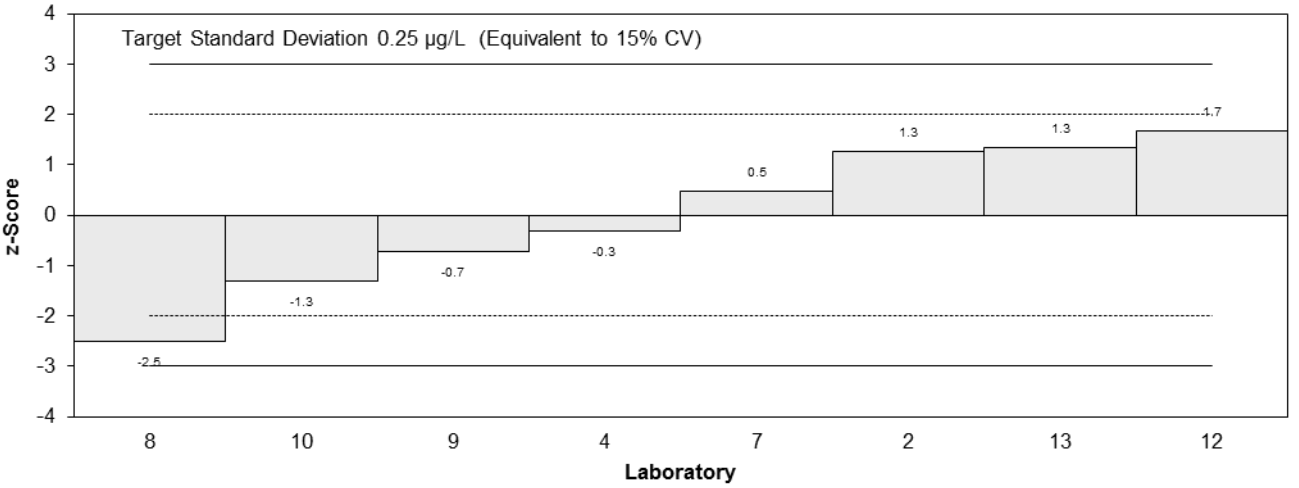
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	2	1	1.27	0.30
3	<10	NR		
4	1.6	0.4	-0.32	-0.15
6	NT	NT		
7	1.8	0.4	0.48	0.22
8	1.05	0.1	-2.50	-1.64
9	1.5	0.3	-0.71	-0.38
10	1.35	0.30	-1.31	-0.69
11	<7	NR		
12	2.1	0.4	1.67	0.77
13	2.02	0.30	1.35	0.71

Statistics

Assigned Value	1.68	0.37
Spike	1.68	0.08
Homogeneity Value	1.69	0.34
Robust Average	1.68	0.37
Median	1.70	0.38
Mean	1.68	
N	8	
Max.	2.1	
Min.	1.05	
Robust SD	0.42	
Robust CV	25%	


Results: S1 - Ni
Assigned Value = 1.68 ± 0.37 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
8
10
9
4
7
2
13
12
3
11
1
6
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Ni
Target Standard Deviation 0.25 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-2.5
-1.3
-0.7
-0.3
0.5
1.3
1.3
1.7

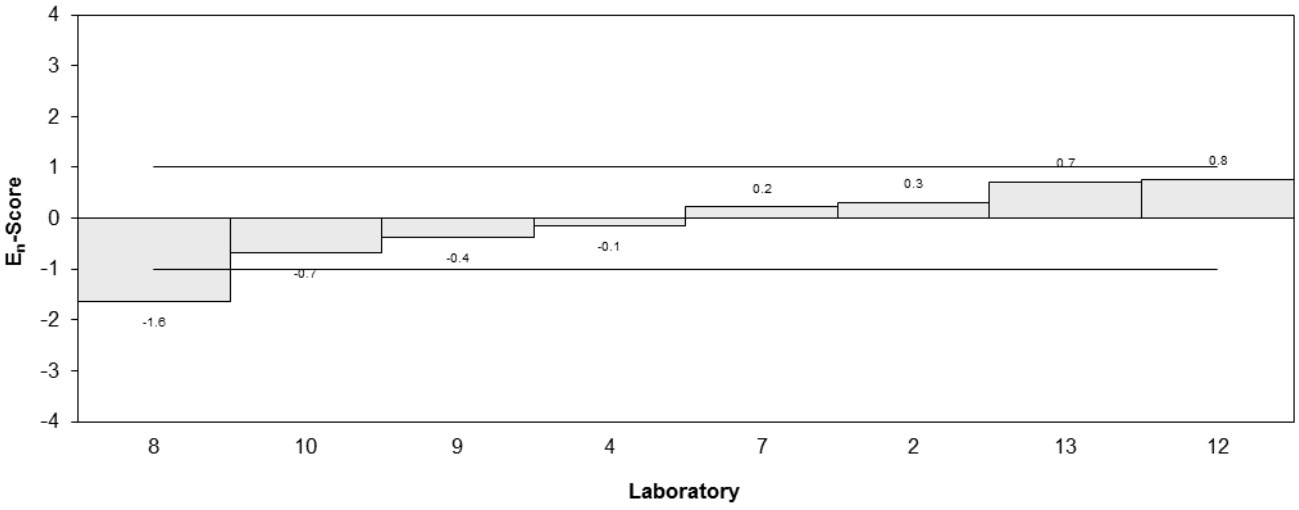

En-Scores: S1 - Ni
En-Score
Laboratory
-1.6
-0.7
-0.4
-0.1
0.2
0.3
0.7
0.8

Figure 13

Table 17

Sample Details

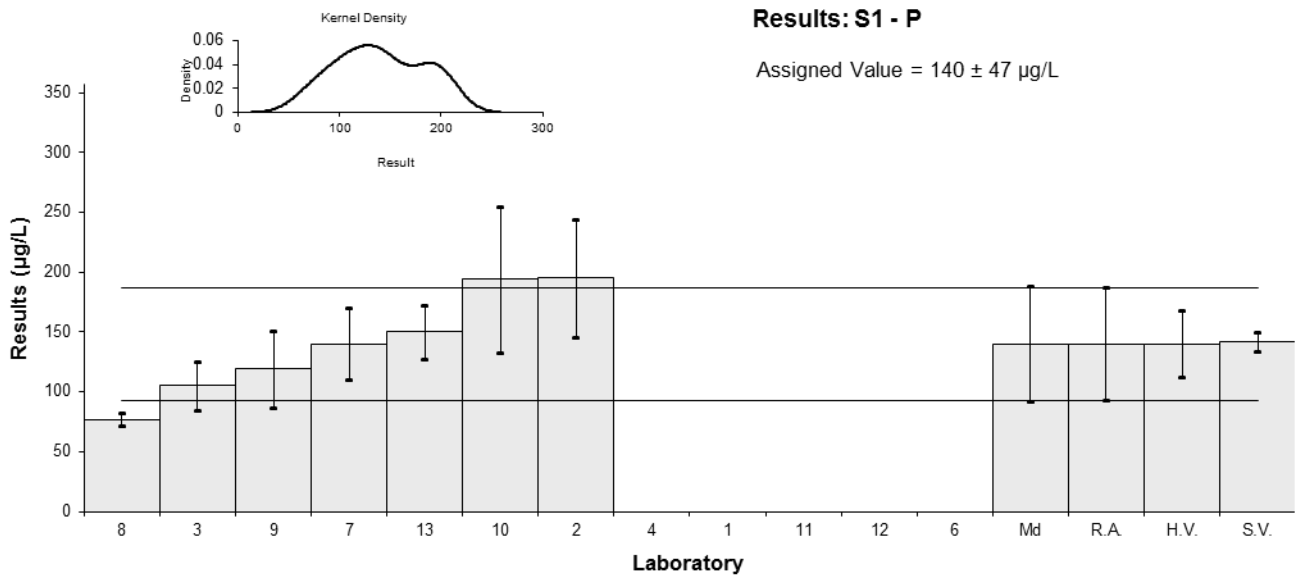
Sample No.	S1
Matrix.	Sea Water
Analyte.	P
Units	µg/L

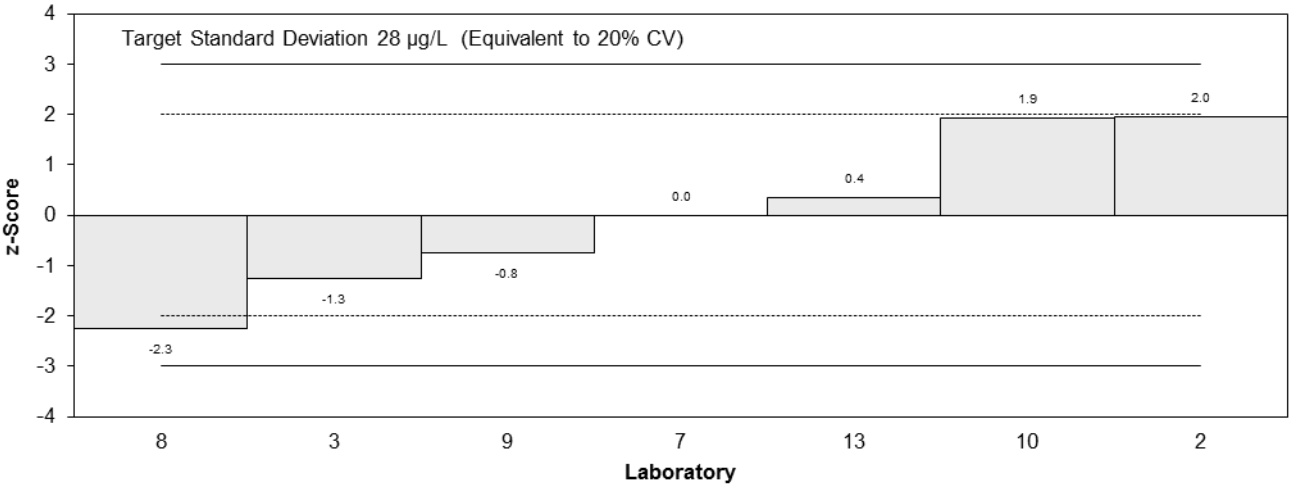
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	195	49	1.96	0.81
3	105	20	-1.25	-0.69
4	NR	NR		
6	NT	NT		
7	140	30	0.00	0.00
8	76.8	5.21	-2.26	-1.34
9	119	32	-0.75	-0.37
10	194	61	1.93	0.70
11	NT	NT		
12	NT	NT		
13	150	22.5	0.36	0.19

Statistics

Assigned Value	140	47
Spike	142	8
Homogeneity Value	140	28
Robust Average	140	47
Median	140	48
Mean	140	
N	7	
Max.	195	
Min.	76.8	
Robust SD	50	
Robust CV	36%	


Kernel Density
Density
0.06
0.04
0.02
0
0
100
200
300
Result
Results: S1 - P
Assigned Value = 140 ± 47 µg/L
Results (µg/L)
350
300
250
200
150
100
50
0
8
3
9
7
13
10
2
4
1
11
12
6
Md
R.A.
H.V.
S.V.
Laboratory


z-Scores: S1 - P
Target Standard Deviation 28 µg/L (Equivalent to 20% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-2.3
-1.3
-0.8
0.0
0.4
1.9
2.0
8
3
9
7
13
10
2
Laboratory

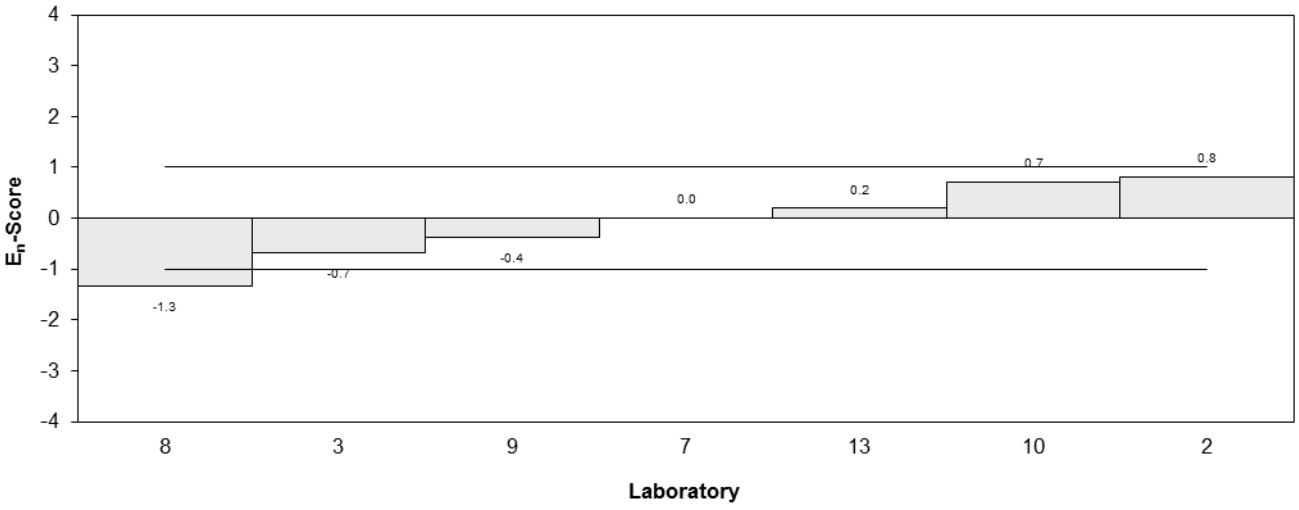

En-Scores: S1 - P
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.3
-0.7
-0.4
0.0
0.2
0.7
0.8
8
3
9
7
13
10
2
Laboratory

Figure 14

Table 18

Sample Details

Sample No.	S1
Matrix.	Sea Water
Analyte.	Pb
Units	µg/L

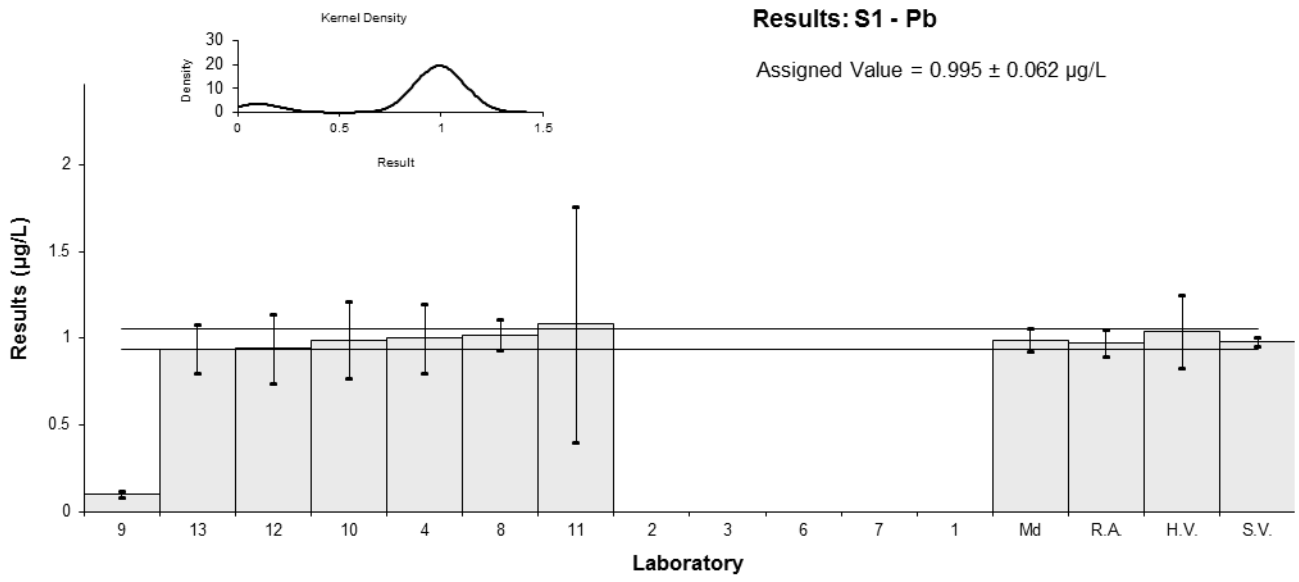
Participant Results

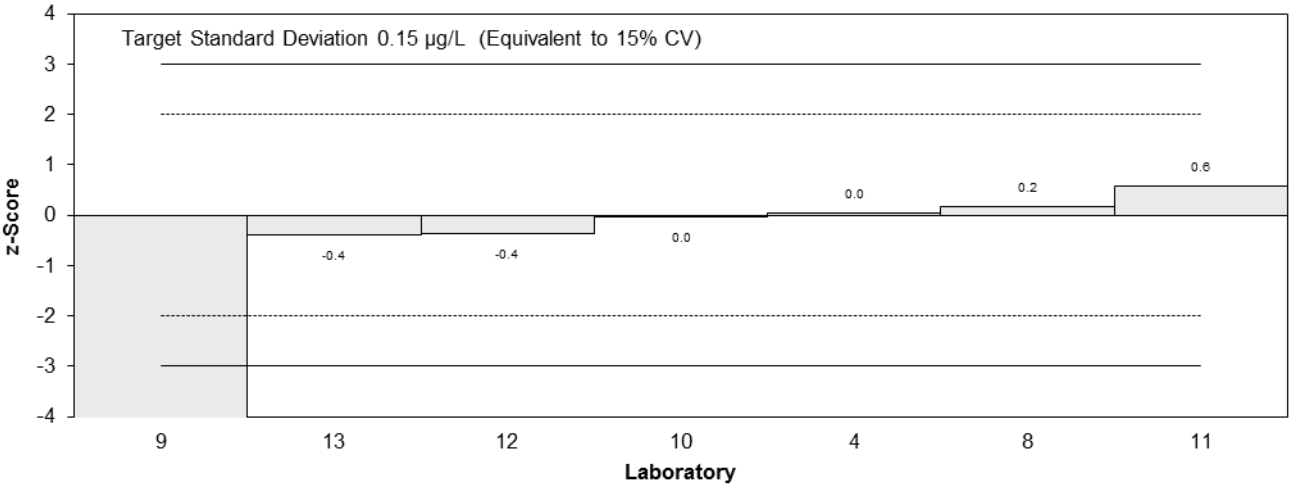
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	<1	1		
3	<1	NR		
4	1.0	0.2	0.03	0.02
6	<1	NR		
7	<1	NR		
8	1.02	0.09	0.17	0.23
9	0.1	0.02	-6.00	-13.74
10	0.99	0.22	-0.03	-0.02
11	1.08	0.68	0.57	0.12
12	0.94	0.2	-0.37	-0.26
13	0.937	0.14	-0.39	-0.38

Statistics

Assigned Value*	0.995	0.062
Spike	0.979	0.028
Homogeneity Value	1.04	0.21
Robust Average	0.974	0.079
Median	0.990	0.069
Mean	0.867	
N	7	
Max.	1.08	
Min.	0.1	
Robust SD	0.084	
Robust CV	8.6%	

*Robust Average excluding Laboratory 9.


Kernel Density
Density
Result
Results: S1 - Pb
Assigned Value = 0.995 ± 0.062 µg/L
Results (µg/L)
Laboratory
9
13
12
10
4
8
11
2
3
6
7
1
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Pb
Target Standard Deviation 0.15 µg/L (Equivalent to 15% CV)
z-Score
-0.4
-0.4
0.0
0.0
0.2
0.6
Laboratory
9
13
12
10
4
8
11

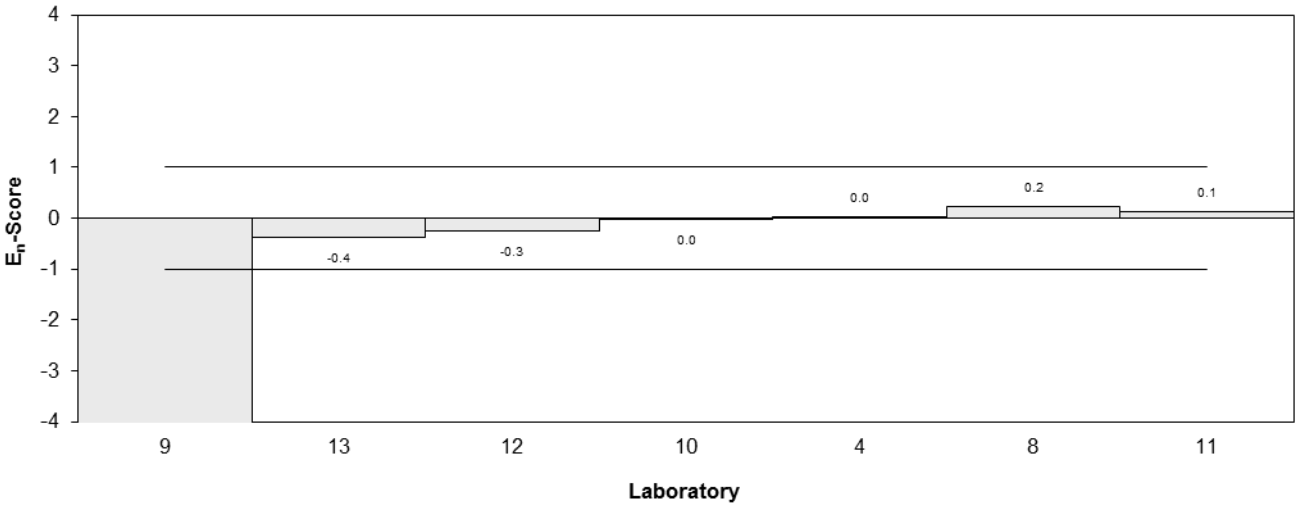

En-Scores: S1 - Pb
En-Score
-0.4
-0.3
0.0
0.0
0.2
0.1
Laboratory
9
13
12
10
4
8
11

Figure 15

Table 19

Sample Details

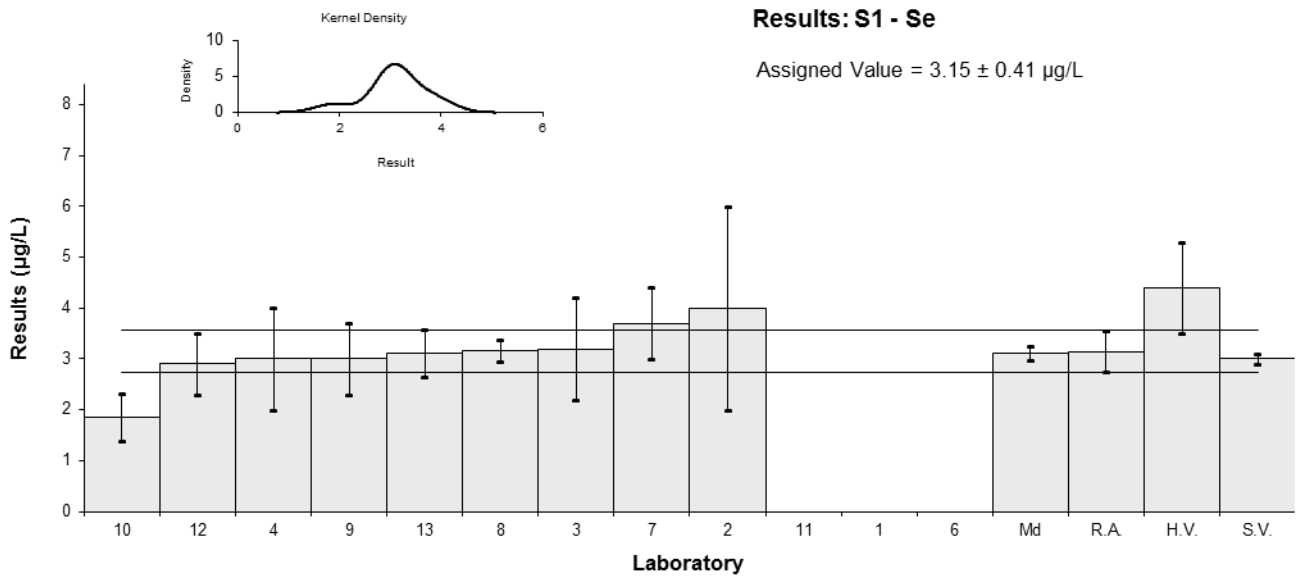
Sample No.	S1
Matrix.	Sea Water
Analyte.	Se
Units	µg/L

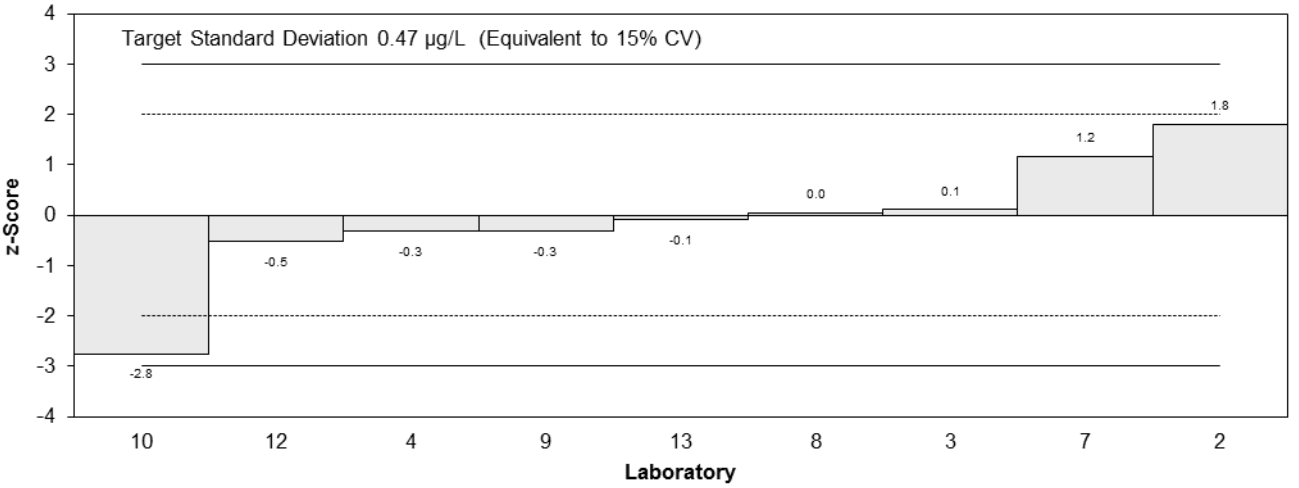
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	4	2	1.80	0.42
3	3.2	1	0.11	0.05
4	3	1	-0.32	-0.14
6	NT	NT		
7	3.7	0.7	1.16	0.68
8	3.17	0.21	0.04	0.04
9	3	0.7	-0.32	-0.18
10	1.85	0.46	-2.75	-2.11
11	<4	2.7		
12	2.9	0.6	-0.53	-0.34
13	3.11	0.47	-0.08	-0.06

Statistics

Assigned Value	3.15	0.41
Spike	3.01	0.10
Homogeneity Value	4.42	0.88
Robust Average	3.15	0.41
Median	3.11	0.13
Mean	3.10	
N	9	
Max.	4	
Min.	1.85	
Robust SD	0.49	
Robust CV	16%	


Kernel Density
Density
Result
Results: S1 - Se
Assigned Value = 3.15 ± 0.41 µg/L
Results (µg/L)
10
12
4
9
13
8
3
7
2
11
1
6
Md
R.A.
H.V.
S.V.
Laboratory


z-Scores: S1 - Se
Target Standard Deviation 0.47 µg/L (Equivalent to 15% CV)
z-Score
-2.8
-0.5
-0.3
-0.3
-0.1
0.0
0.1
1.2
1.8
10
12
4
9
13
8
3
7
2
Laboratory

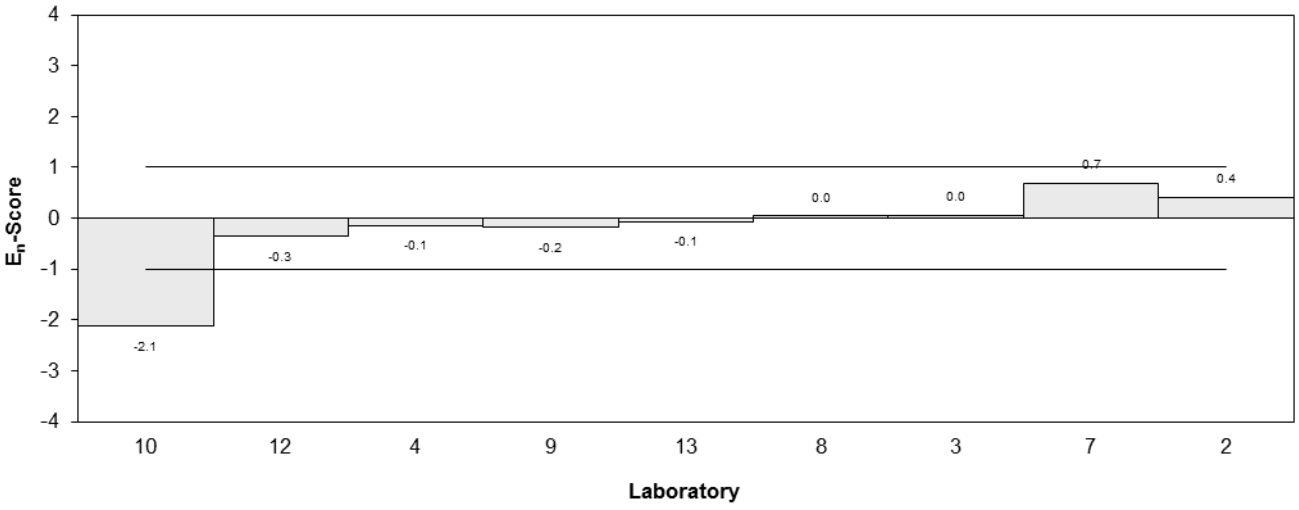

En-Scores: S1 - Se
En-Score
-2.1
-0.3
-0.1
-0.2
-0.1
0.0
0.0
0.7
0.4
10
12
4
9
13
8
3
7
2
Laboratory

Figure 16

Table 20

Sample Details

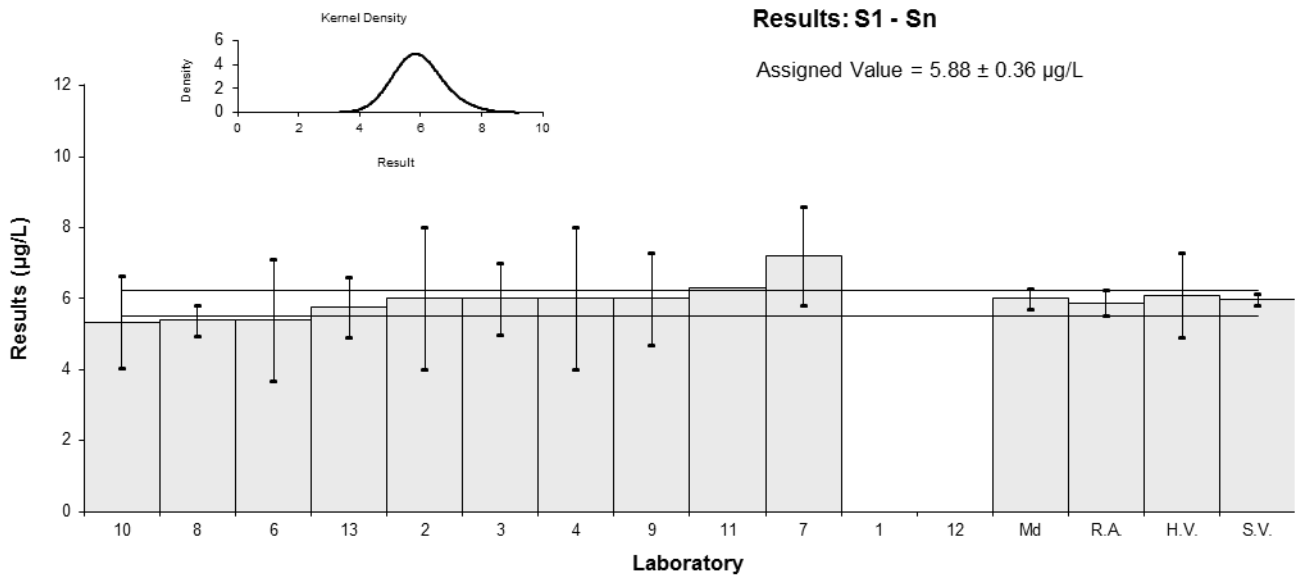
Sample No.	S1
Matrix.	Sea Water
Analyte.	Sn
Units	µg/L

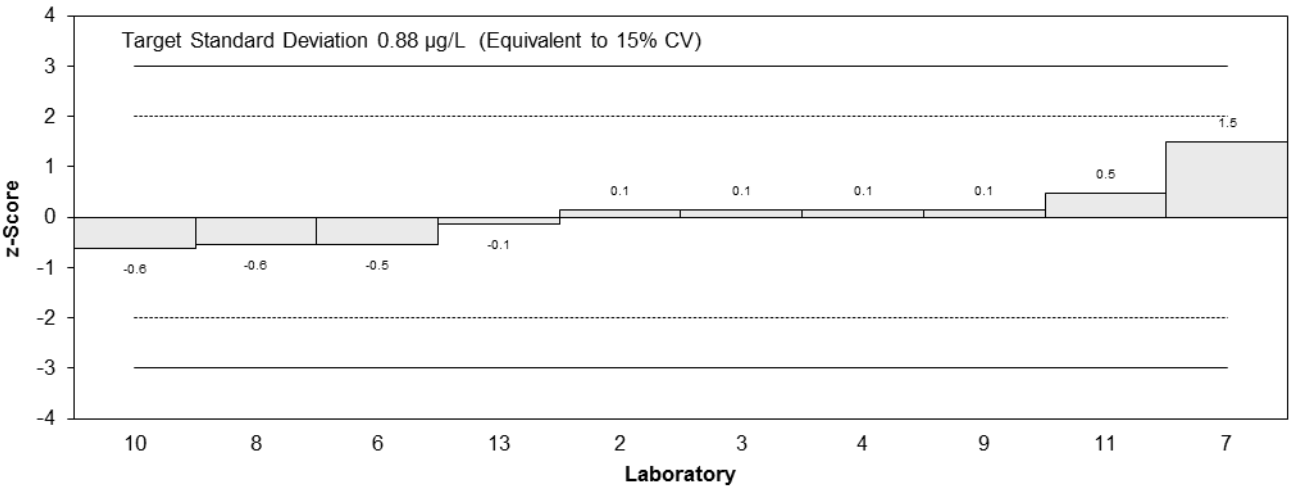
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	6	2	0.14	0.06
3	6.0	1	0.14	0.11
4	6	2	0.14	0.06
6	5.4	1.7	-0.54	-0.28
7	7.2	1.4	1.50	0.91
8	5.39	0.44	-0.56	-0.86
9	6	1.3	0.14	0.09
10	5.34	1.31	-0.61	-0.40
11	6.3	NR	0.48	1.17
12	NT	NT		
13	5.76	0.86	-0.14	-0.13

Statistics

Assigned Value	5.88	0.36
Spike	5.98	0.17
Homogeneity Value	6.1	1.2
Robust Average	5.88	0.36
Median	6.00	0.29
Mean	5.94	
N	10	
Max.	7.2	
Min.	5.34	
Robust SD	0.46	
Robust CV	7.8%	


Kernel Density
Density
Result
Results: S1 - Sn
Assigned Value = 5.88 ± 0.36 µg/L
Results (µg/L)
10 8 6 13 2 3 4 9 11 7 1 12 Md R.A. H.V. S.V.
Laboratory


z-Scores: S1 - Sn
Target Standard Deviation 0.88 µg/L (Equivalent to 15% CV)
z-Score
-0.6 -0.6 -0.5 -0.1 0.1 0.1 0.1 0.1 0.5 1.5
10 8 6 13 2 3 4 9 11 7
Laboratory

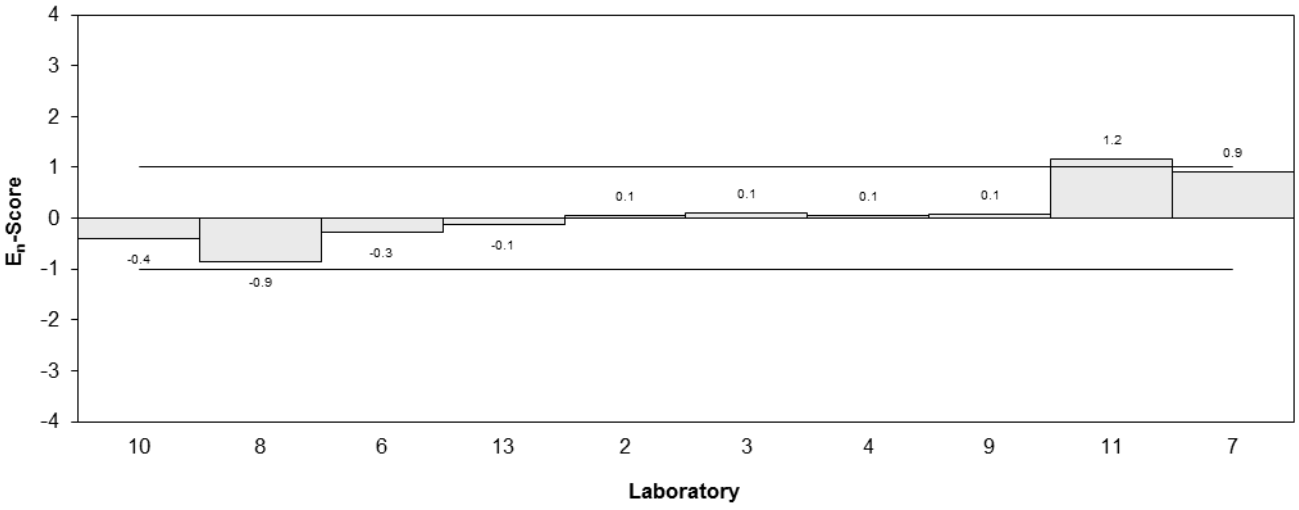

En-Scores: S1 - Sn
En-Score
-0.4 -0.9 -0.3 -0.1 0.1 0.1 0.1 0.1 1.2 0.9
10 8 6 13 2 3 4 9 11 7
Laboratory

Figure 17

Table 21

Sample Details

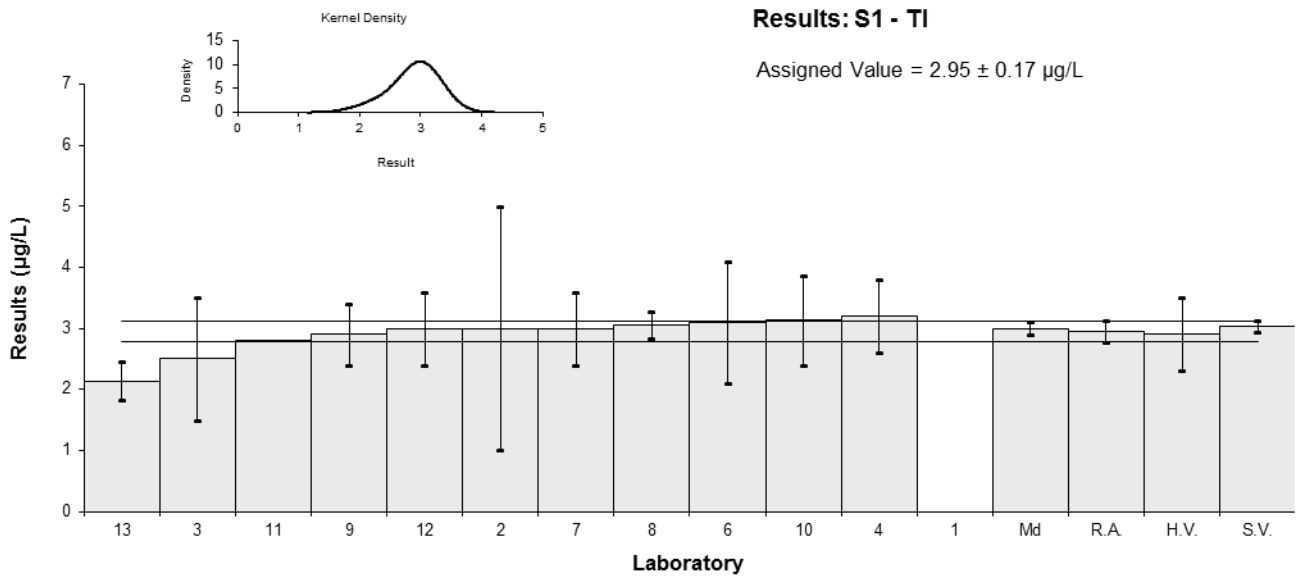
Sample No.	S1
Matrix.	Sea Water
Analyte.	Tl
Units	µg/L

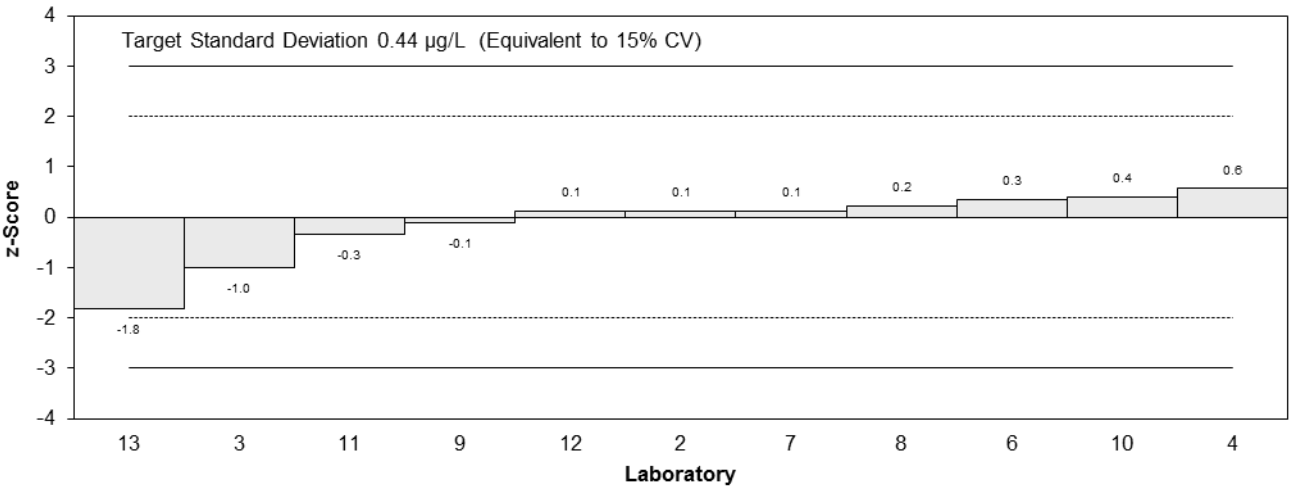
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	3	2	0.11	0.02
3	2.5	1	-1.02	-0.44
4	3.2	0.6	0.56	0.40
6	3.1	1	0.34	0.15
7	3.0	0.6	0.11	0.08
8	3.05	0.22	0.23	0.36
9	2.9	0.5	-0.11	-0.09
10	3.13	0.73	0.41	0.24
11	2.8	NR	-0.34	-0.88
12	3.0	0.6	0.11	0.08
13	2.14	0.32	-1.83	-2.24

Statistics

Assigned Value	2.95	0.17
Spike	3.03	0.09
Homogeneity Value	2.94	0.59
Robust Average	2.95	0.17
Median	3.00	0.10
Mean	2.89	
N	11	
Max.	3.2	
Min.	2.14	
Robust SD	0.22	
Robust CV	7.5%	


Kernel Density
Density
Result
Results: S1 - Tl
Assigned Value = 2.95 ± 0.17 µg/L
Results (µg/L)
13 3 11 9 12 2 7 8 6 10 4 1 Md R.A. H.V. S.V.
Laboratory


z-Scores: S1 - Tl
Target Standard Deviation 0.44 µg/L (Equivalent to 15% CV)
z-Score
-1.8 -1.0 -0.3 -0.1 0.1 0.1 0.1 0.2 0.3 0.4 0.6
13 3 11 9 12 2 7 8 6 10 4
Laboratory

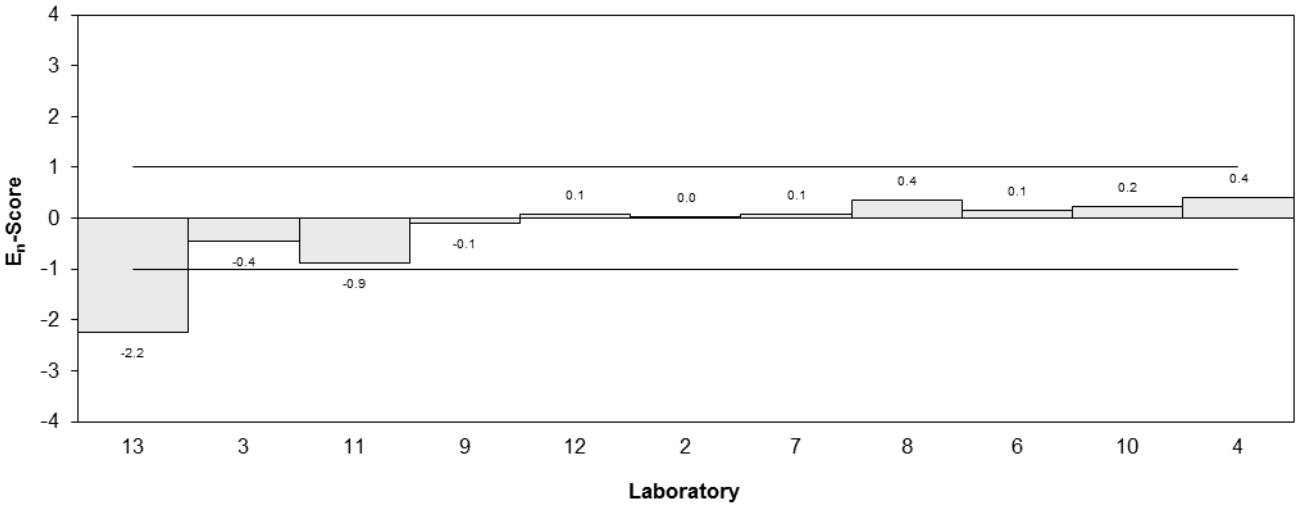

En-Scores: S1 - Tl
En-Score
-2.2 -0.4 -0.9 -0.1 0.1 0.0 0.1 0.4 0.1 0.2 0.4
13 3 11 9 12 2 7 8 6 10 4
Laboratory

Figure 18

Table 22

Sample Details

Sample No.	S1
Matrix.	Sea Water
Analyte.	U
Units	µg/L

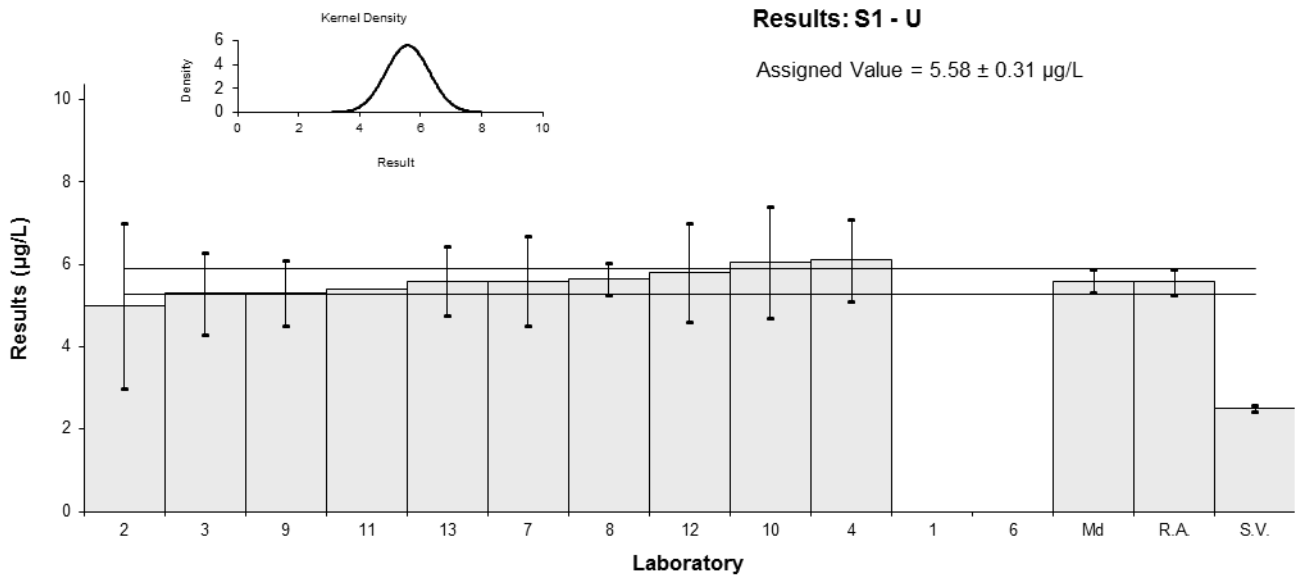
Participant Results

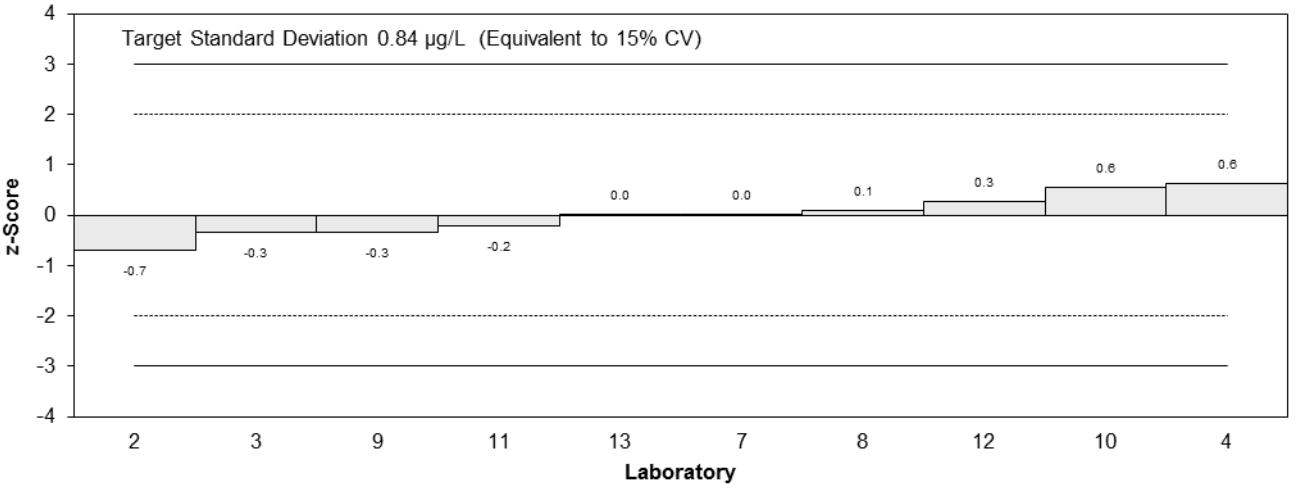
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	5	2	-0.69	-0.29
3	5.3	1	-0.33	-0.27
4	6.1	1.0	0.62	0.50
6	NT	NT		
7	5.6	1.1	0.02	0.02
8	5.65	0.38	0.08	0.14
9	5.3	0.8	-0.33	-0.33
10	6.05	1.36	0.56	0.34
11	5.4	NR	-0.22	-0.58
12	5.8	1.2	0.26	0.18
13	5.59	0.84	0.01	0.01

Statistics

Assigned Value	5.58	0.31
Spike*	2.50	0.07
Robust Average	5.58	0.31
Median	5.60	0.27
Mean	5.58	
N	10	
Max.	6.1	
Min.	5	
Robust SD	0.39	
Robust CV	7%	

*Incurred value not included


Results: S1 - U
Assigned Value = 5.58 ± 0.31 µg/L
Kernel Density
Density
Result
Results (µg/L)
Laboratory
2
3
9
11
13
7
8
12
10
4
1
6
Md
R.A.
S.V.


z-Scores: S1 - U
Target Standard Deviation 0.84 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-0.7
-0.3
-0.3
-0.2
0.0
0.0
0.1
0.3
0.6
0.6

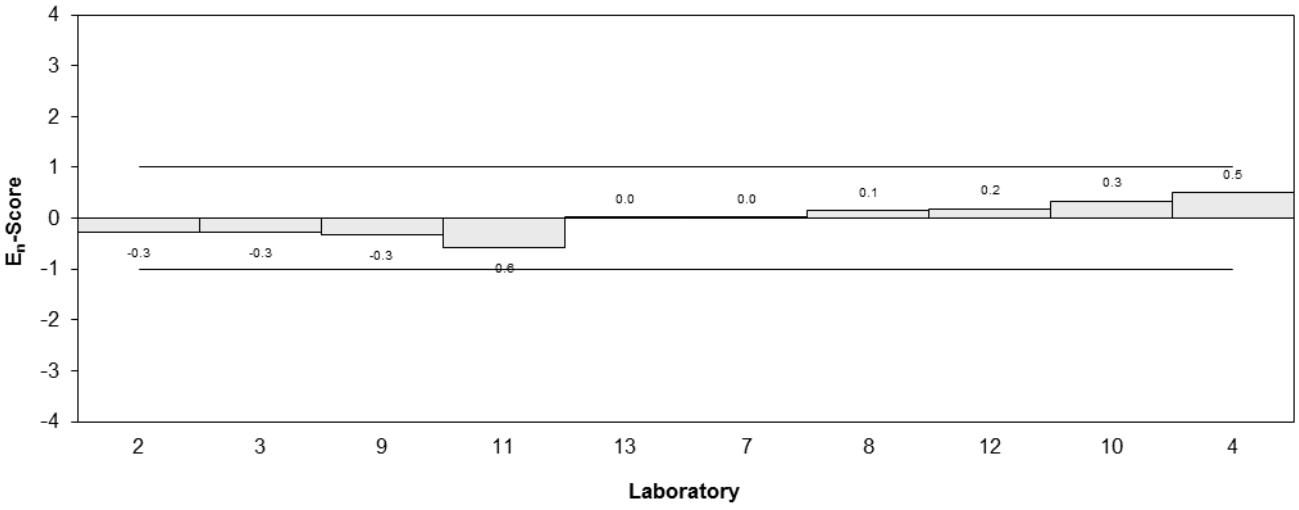

En-Scores: S1 - U
En-Score
Laboratory
-0.3
-0.3
-0.3
-0.6
0.0
0.0
0.1
0.2
0.3
0.5

Figure 19

Table 23

Sample Details

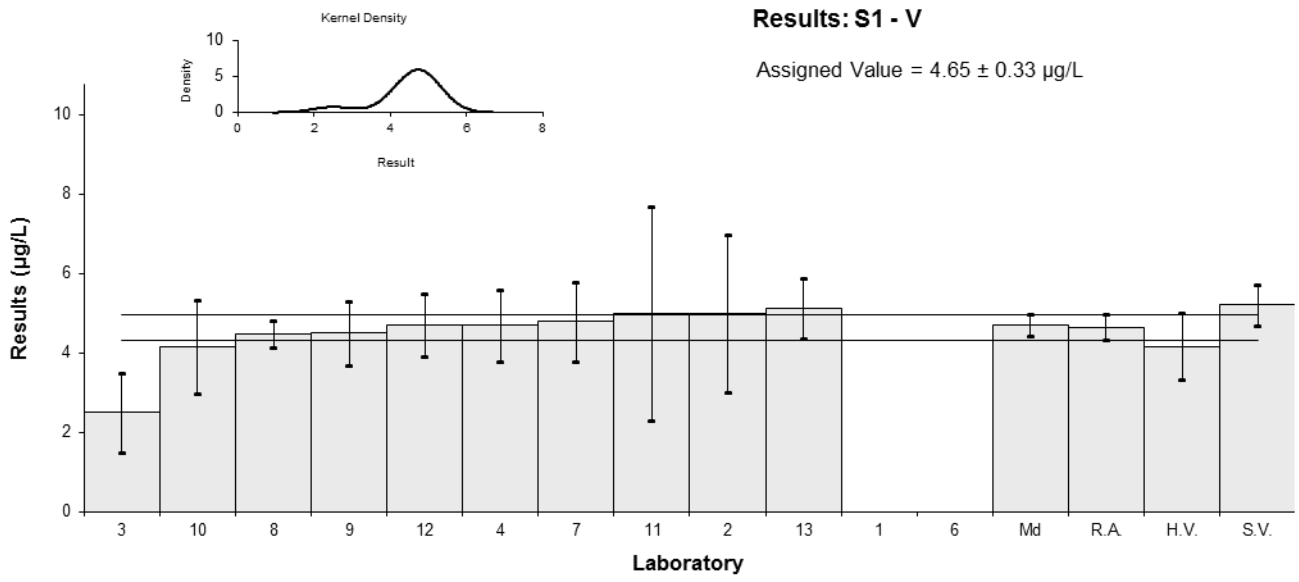
Sample No.	S1
Matrix.	Sea Water
Analyte.	V
Units	µg/L

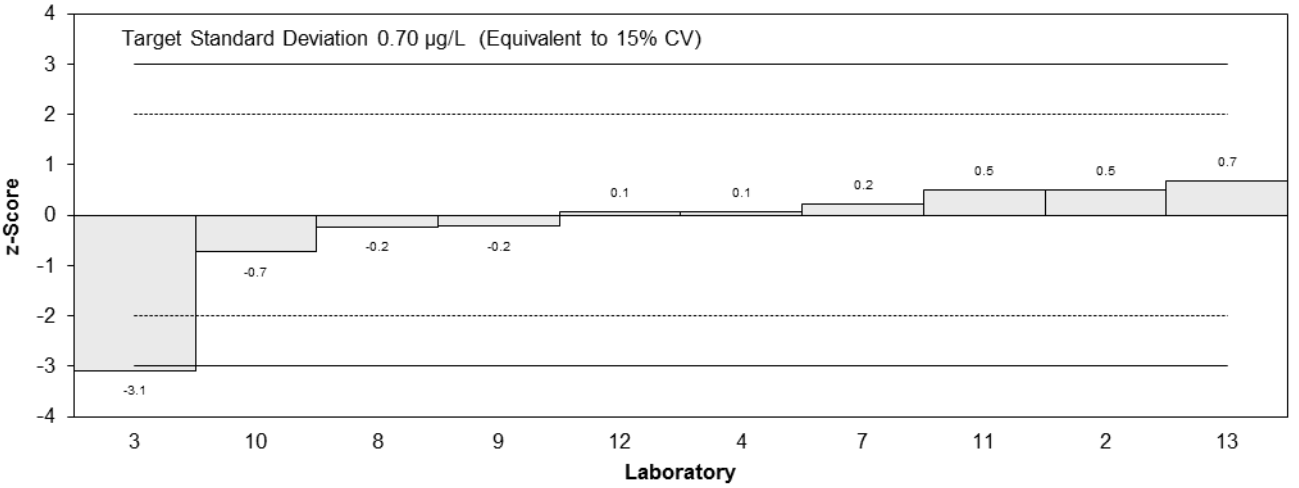
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	5	2	0.50	0.17
3	2.5	1	-3.08	-2.04
4	4.7	0.9	0.07	0.05
6	NT	NT		
7	4.8	1.0	0.22	0.14
8	4.49	0.34	-0.23	-0.34
9	4.5	0.8	-0.22	-0.17
10	4.14	1.18	-0.73	-0.42
11	5.0	2.7	0.50	0.13
12	4.7	0.8	0.07	0.06
13	5.12	0.77	0.67	0.56

Statistics

Assigned Value	4.65	0.33
Spike	5.21	0.51
Homogeneity Value	4.17	0.83
Robust Average	4.65	0.33
Median	4.70	0.27
Mean	4.50	
N	10	
Max.	5.12	
Min.	2.5	
Robust SD	0.41	
Robust CV	8.8%	


Kernel Density
Density
Result
Results: S1 - V
Assigned Value = 4.65 ± 0.33 µg/L
Results (µg/L)
Laboratory
3
10
8
9
12
4
7
11
2
13
1
6
Md
R.A.
H.V.
S.V.


z-Scores: S1 - V
Target Standard Deviation 0.70 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-3.1
-0.7
-0.2
-0.2
0.1
0.1
0.2
0.5
0.5
0.7

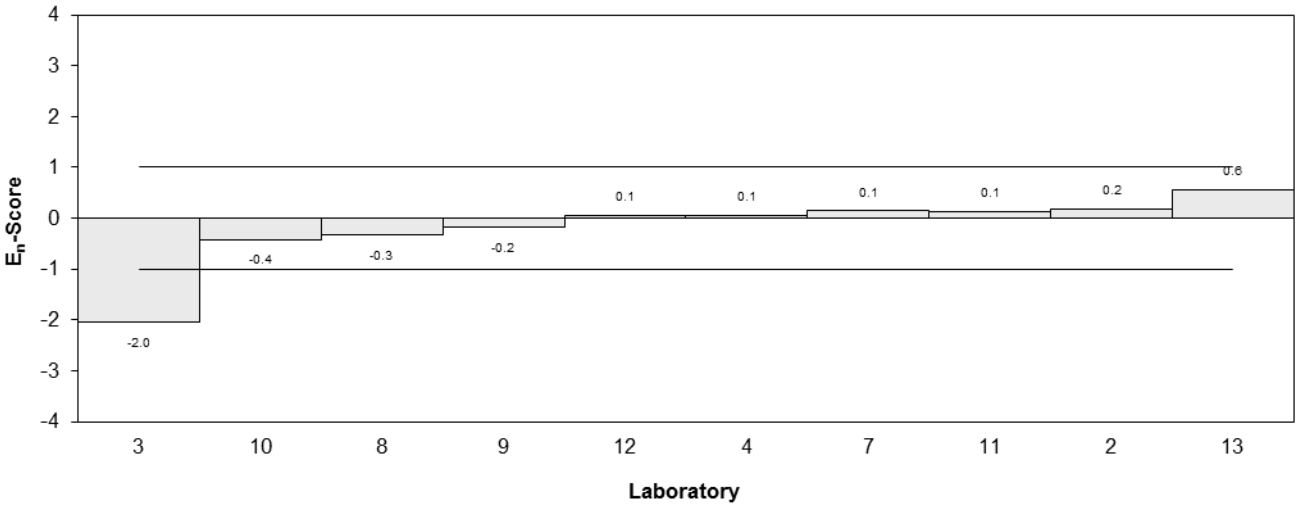

En-Scores: S1 - V
En-Score
Laboratory
-2.0
-0.4
-0.3
-0.2
0.1
0.1
0.1
0.1
0.2
0.6

Figure 20

Table 24

Sample Details

Sample No.	S1
Matrix.	Sea Water
Analyte.	Zn
Units	µg/L

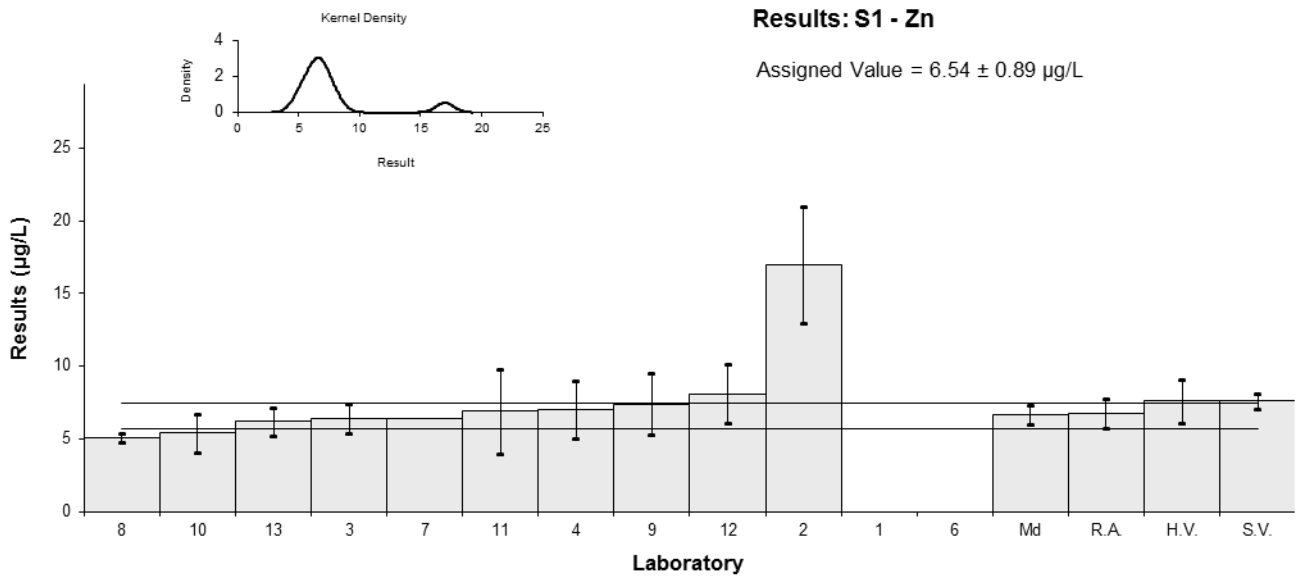
Participant Results

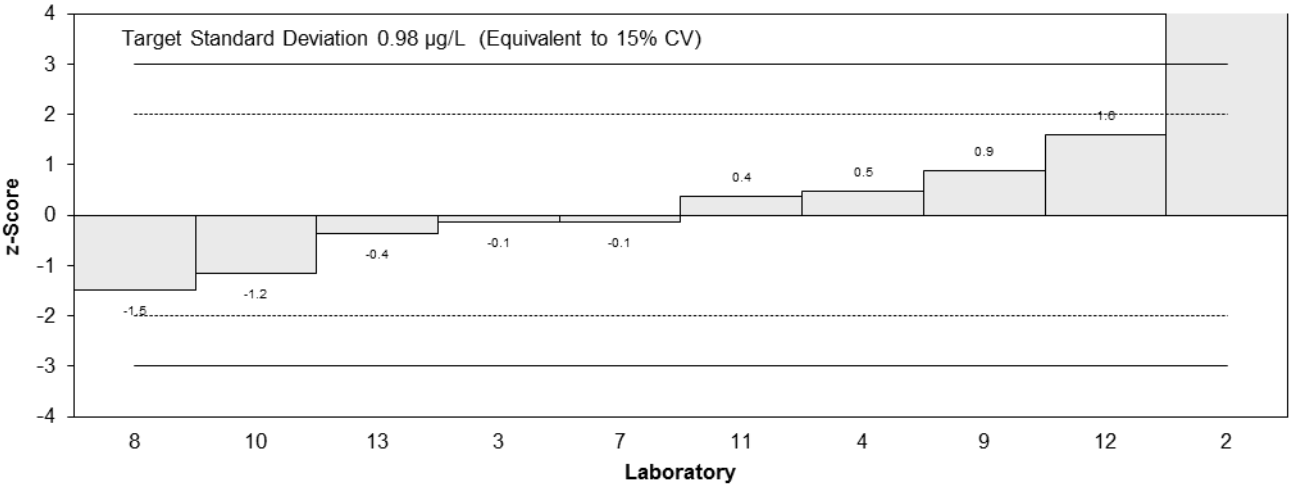
Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NT	NT		
2	17	4	10.66	2.55
3	6.4	1	-0.14	-0.10
4	7	2	0.47	0.21
6	NT	NT		
7	6.4	NR	-0.14	-0.16
8	5.07	0.34	-1.50	-1.54
9	7.4	2.1	0.88	0.38
10	5.40	1.31	-1.16	-0.72
11	6.9	2.9	0.37	0.12
12	8.1	2.0	1.59	0.71
13	6.18	0.93	-0.37	-0.28

Statistics

Assigned Value*	6.54	0.89
Spike	7.59	0.49
Homogeneity Value	7.6	1.5
Robust Average	6.75	0.99
Median	6.65	0.65
Mean	7.59	
N	10	
Max.	17	
Min.	5.07	
Robust SD	1.26	
Robust CV	19%	

*Robust Average excluding Laboratory 2.


Kernel Density
Density
Result
Results: S1 - Zn
Assigned Value = 6.54 ± 0.89 µg/L
Results (µg/L)
Laboratory
8
10
13
3
7
11
4
9
12
2
1
6
Md
R.A.
H.V.
S.V.


z-Scores: S1 - Zn
Target Standard Deviation 0.98 µg/L (Equivalent to 15% CV)
z-Score
Laboratory
-1.5
-1.2
-0.4
-0.1
-0.1
0.4
0.5
0.9
1.6

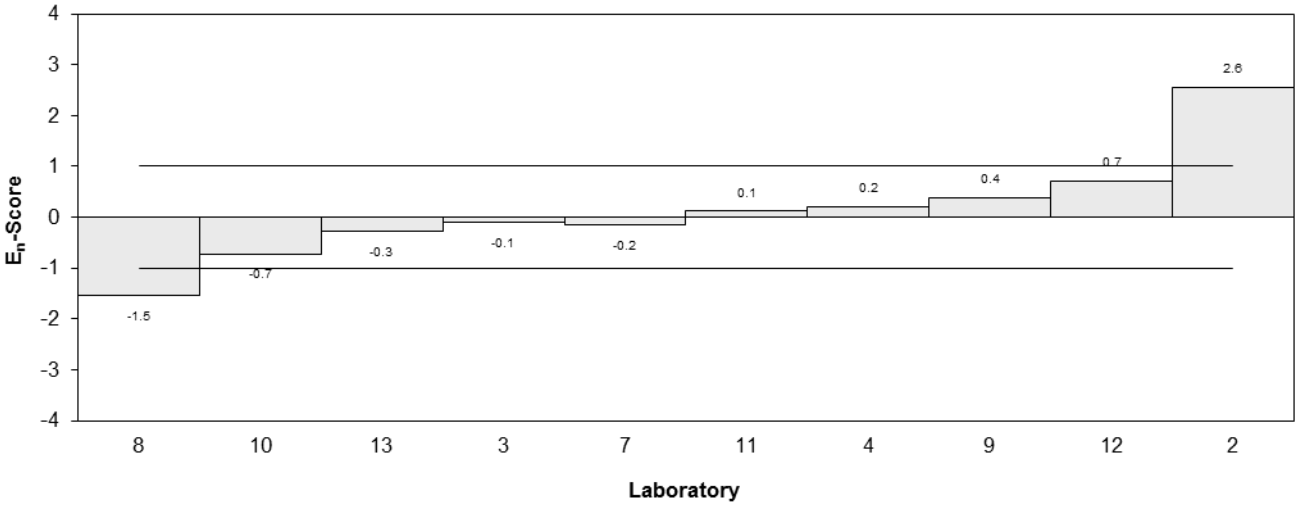

En-Scores: S1 - Zn
En-Score
Laboratory
-1.5
-0.7
-0.3
-0.1
-0.2
0.1
0.2
0.4
0.7
2.6

Figure 21

Table 25

Sample Details

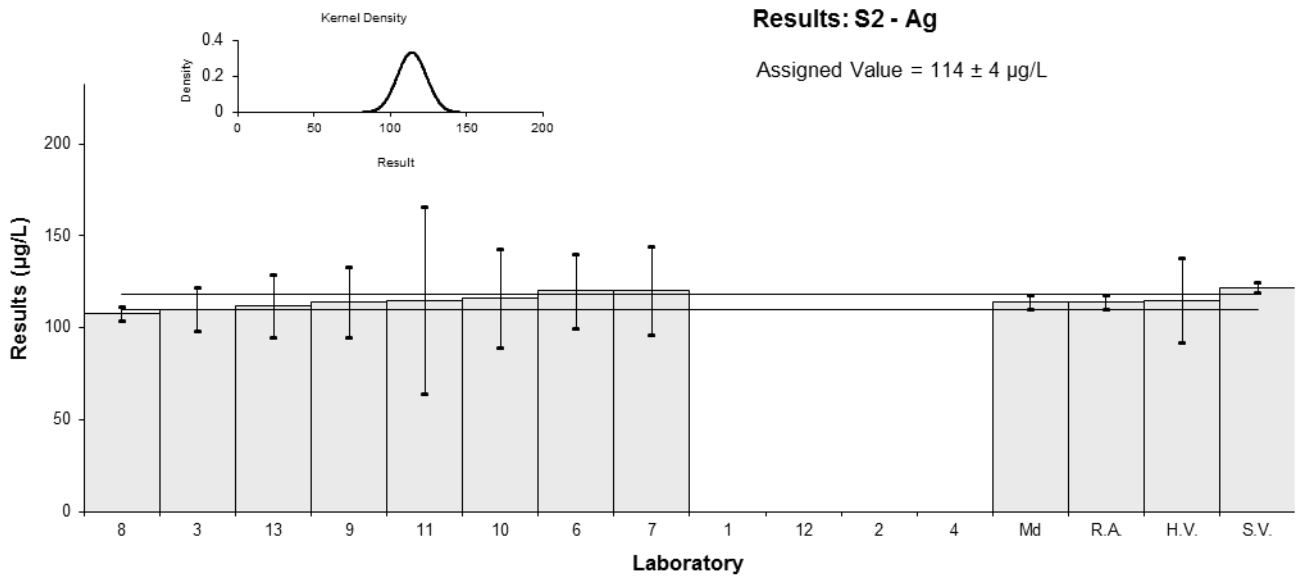
Sample No.	S2
Matrix.	Sea Water
Analyte.	Ag
Units	µg/L

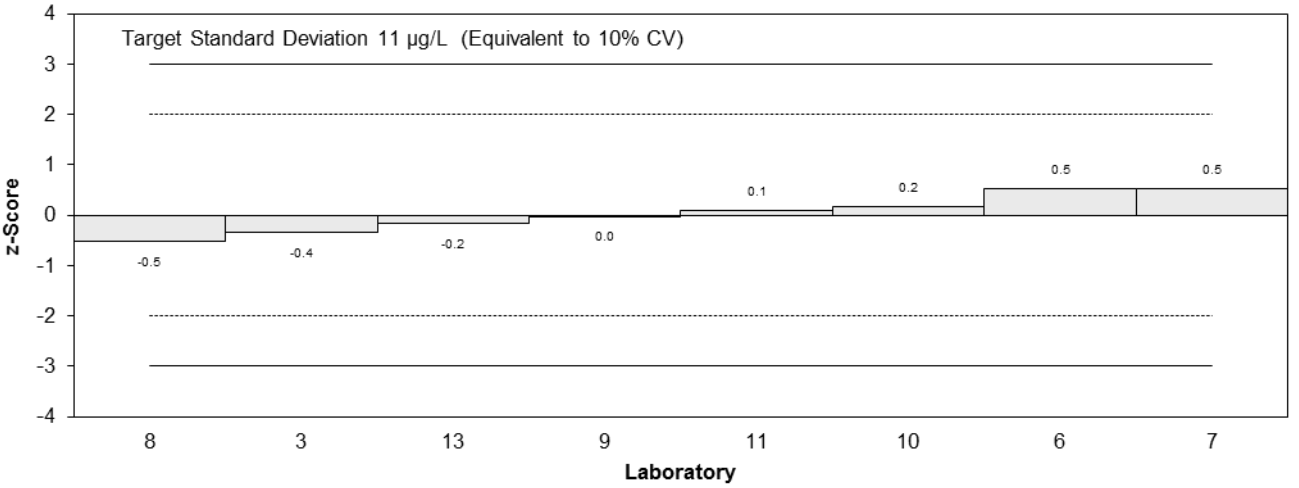
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	NT	NT		
3	110	12	-0.35	-0.32
4	NT	NT		
6	120	20	0.53	0.29
7	120	24	0.53	0.25
8	108	3.83	-0.53	-1.08
9	113.8	19.3	-0.02	-0.01
10	116	27	0.18	0.07
11	115	51	0.09	0.02
12	NT	NT		
13	112	17	-0.18	-0.11

Statistics

Assigned Value	114	4
Spike	122	3
Homogeneity Value	115	23
Robust Average	114	4
Median	114	4
Mean	114	
N	8	
Max.	120	
Min.	108	
Robust SD	5	
Robust CV	4.4%	


Kernel Density
Density
Result
Results: S2 - Ag
Assigned Value = 114 ± 4 µg/L
Results (µg/L)
Laboratory
8
3
13
9
11
10
6
7
1
12
2
4
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Ag
Target Standard Deviation 11 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-0.5
-0.4
-0.2
0.0
0.1
0.2
0.5
0.5

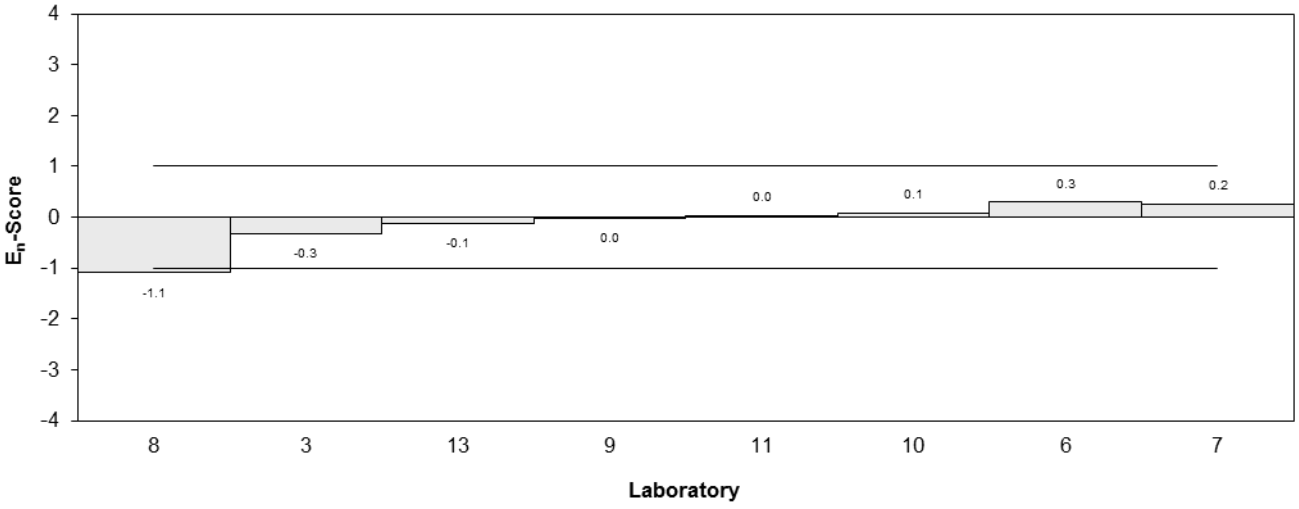

En-Scores: S2 - Ag
En-Score
Laboratory
-1.1
-0.3
-0.1
0.0
0.0
0.1
0.3
0.2

Figure 22

Table 26

Sample Details

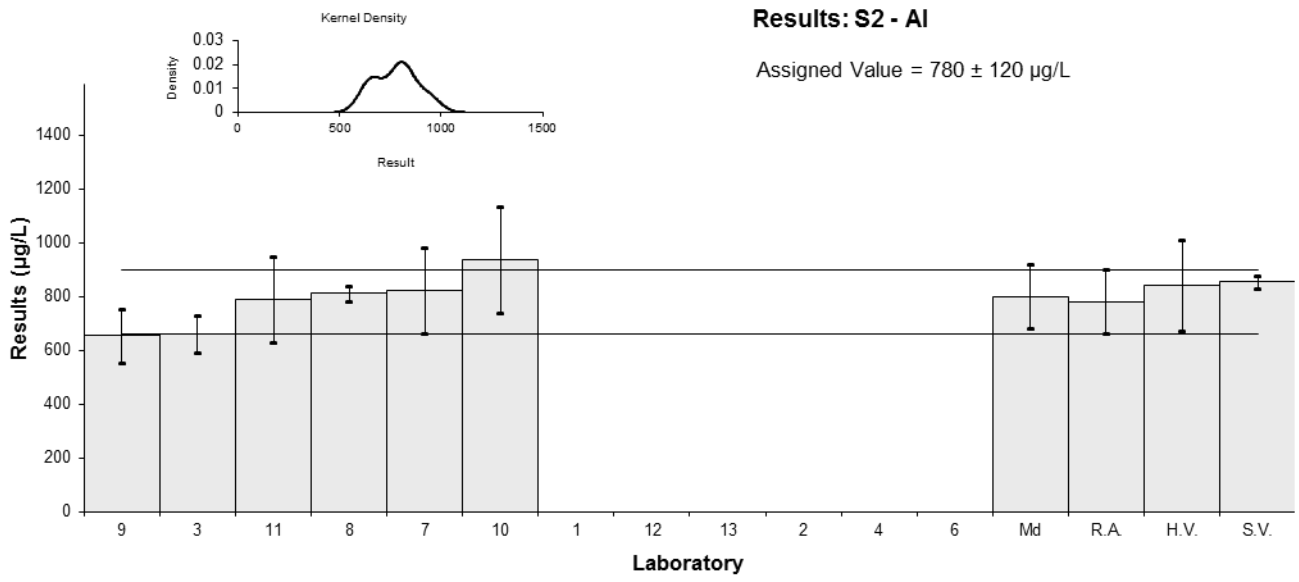
Sample No.	S2
Matrix.	Sea Water
Analyte.	Al
Units	µg/L

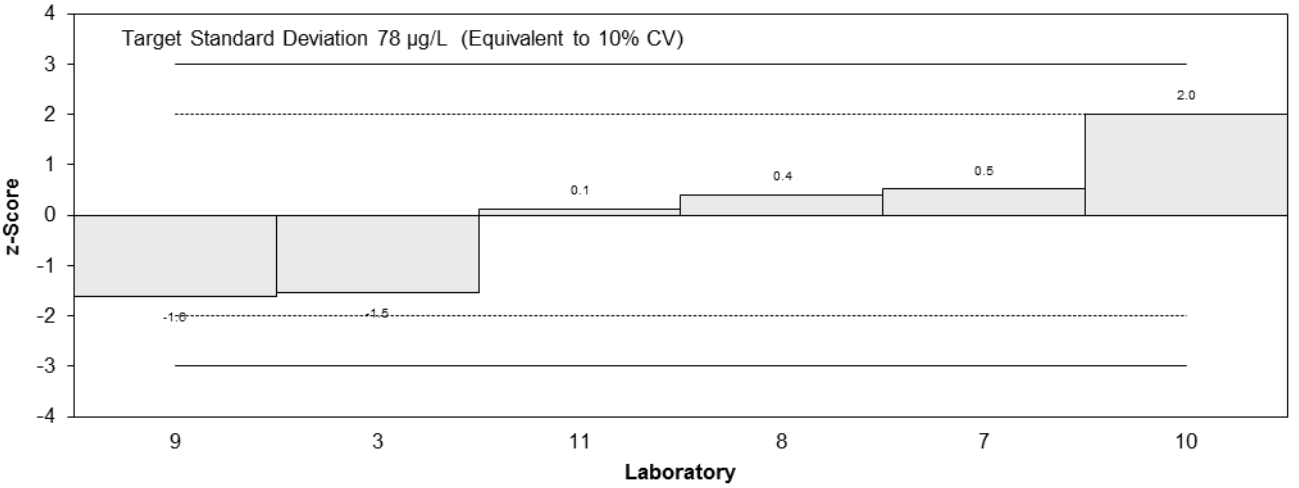
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	NT	NT		
3	660	70	-1.54	-0.86
4	NT	NT		
6	NT	NT		
7	820	160	0.51	0.20
8	811	28.6	0.40	0.25
9	654	100	-1.62	-0.81
10	937	197	2.01	0.68
11	790	160	0.13	0.05
12	NT	NT		
13	NT	NT		

Statistics

Assigned Value	780	120
Spike	853	24
Homogeneity Value	840	170
Robust Average	780	120
Median	800	120
Mean	779	
N	6	
Max.	937	
Min.	654	
Robust SD	122	
Robust CV	16%	


Kernel Density
Density
0.03
0.02
0.01
0
0
500
1000
1500
Result
Results: S2 - Al
Assigned Value = 780 ± 120 µg/L
Results (µg/L)
1400
1200
1000
800
600
400
200
0
9
3
11
8
7
10
1
12
13
2
4
6
Md
R.A.
H.V.
S.V.
Laboratory


z-Scores: S2 - Al
Target Standard Deviation 78 µg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
2.0
0.5
0.4
0.1
-1.6
-1.5
9
3
11
8
7
10
Laboratory

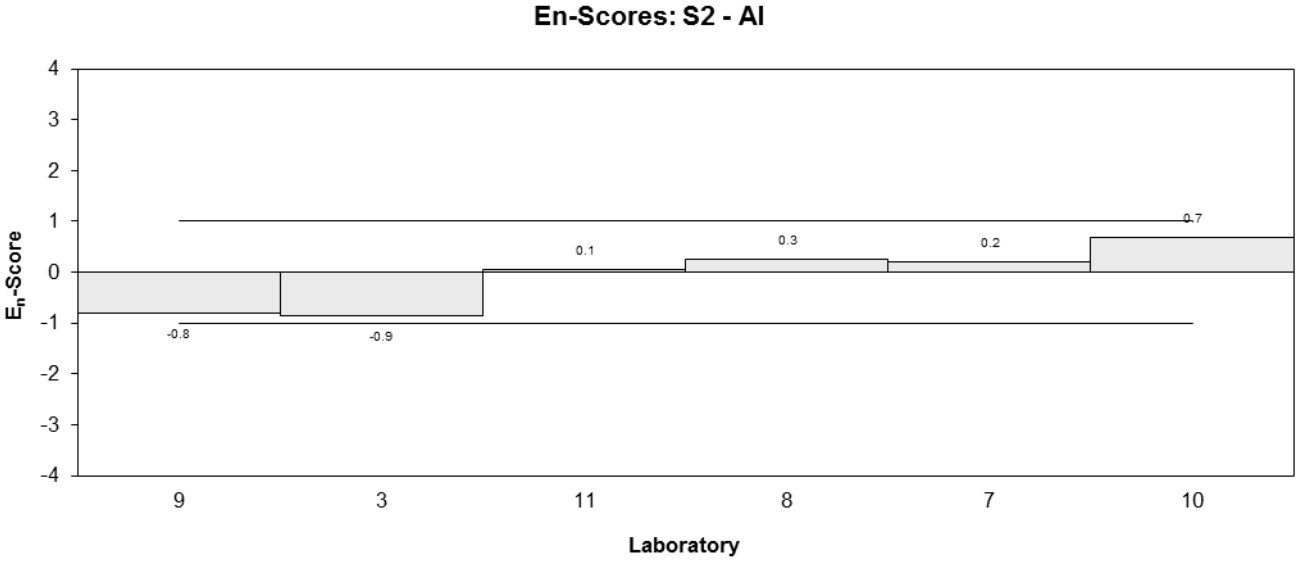

En-Scores: S2 - Al
En-Score
4
3
2
1
0
-1
-2
-3
-4
0.7
0.3
0.2
0.1
-0.8
-0.9
9
3
11
8
7
10
Laboratory

Figure 23

Table 27

Sample Details

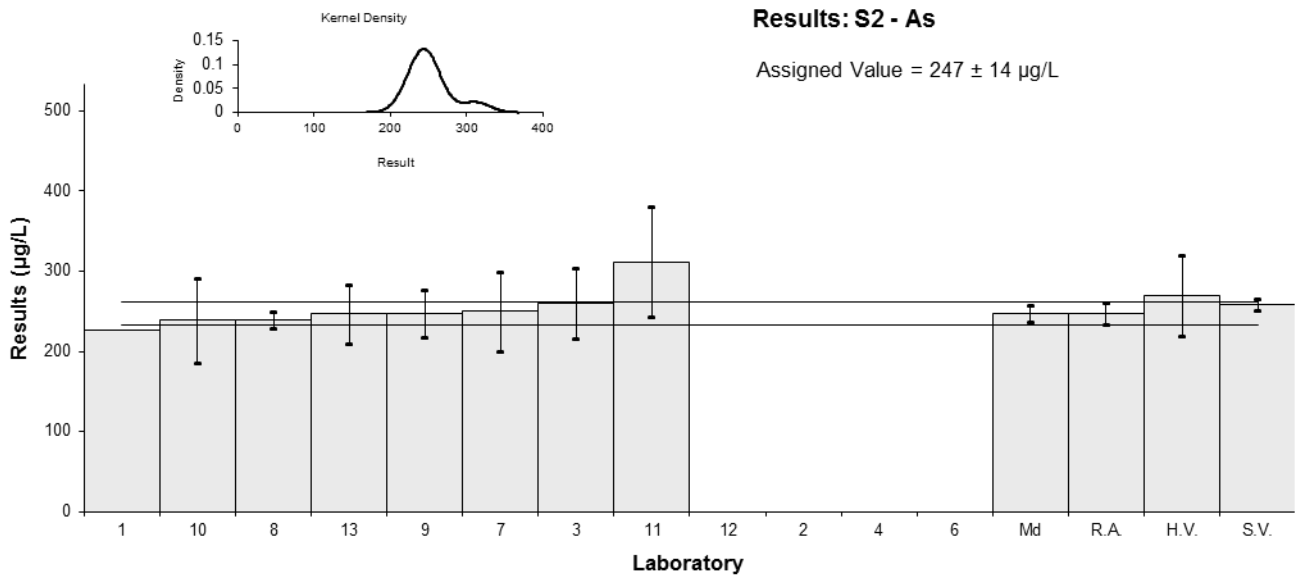
Sample No.	S2
Matrix.	Sea Water
Analyte.	As
Units	µg/L

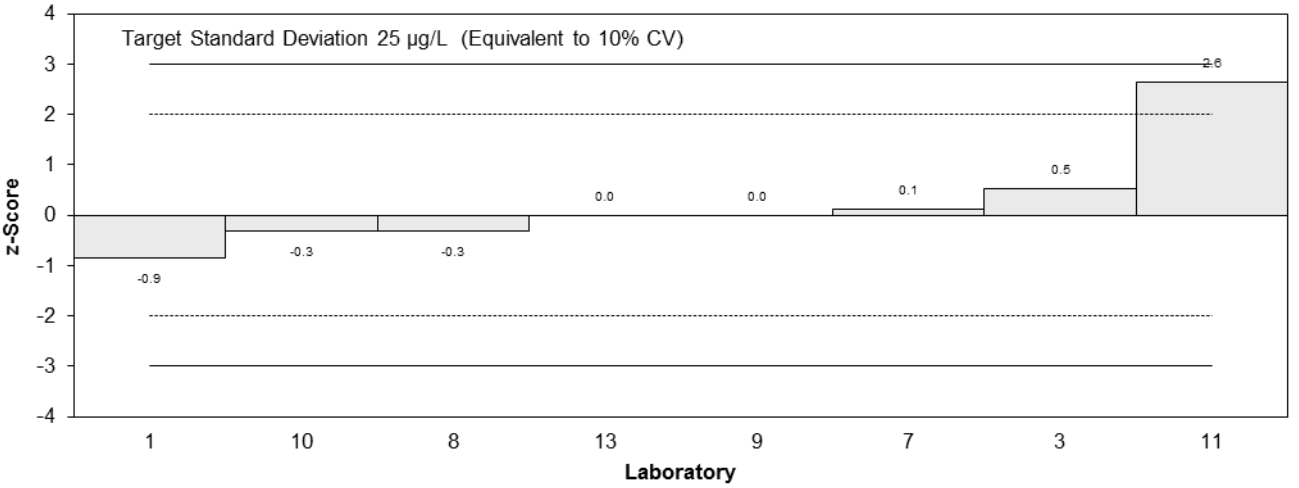
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	226	NR	-0.85	-1.50
2	NT	NT		
3	260	44	0.53	0.28
4	NT	NT		
6	NT	NT		
7	250	50	0.12	0.06
8	239	10	-0.32	-0.46
9	247	30	0.00	0.00
10	239	53	-0.32	-0.15
11	312	69	2.63	0.92
12	NT	NT		
13	247	37	0.00	0.00

Statistics

Assigned Value	247	14
Spike	258	7
Homogeneity Value	270	50
Robust Average	247	14
Median	247	10
Mean	253	
N	8	
Max.	312	
Min.	226	
Robust SD	15	
Robust CV	6.1%	


Kernel Density
Density
Result
Results: S2 - As
Assigned Value = 247 ± 14 µg/L
Results (µg/L)
Laboratory
1
10
8
13
9
7
3
11
12
2
4
6
Md
R.A.
H.V.
S.V.


z-Scores: S2 - As
Target Standard Deviation 25 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-0.9
-0.3
-0.3
0.0
0.0
0.1
0.5
2.6

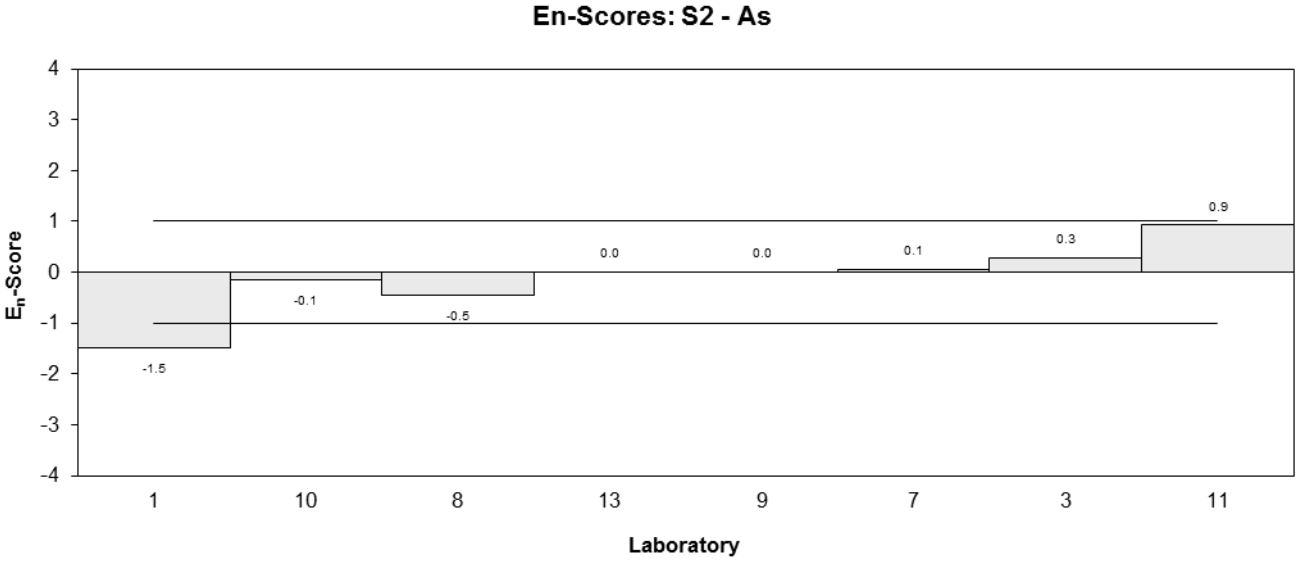

En-Scores: S2 - As
En-Score
Laboratory
-1.5
-0.1
-0.5
0.0
0.0
0.1
0.3
0.9

Figure 24

Table 28

Sample Details

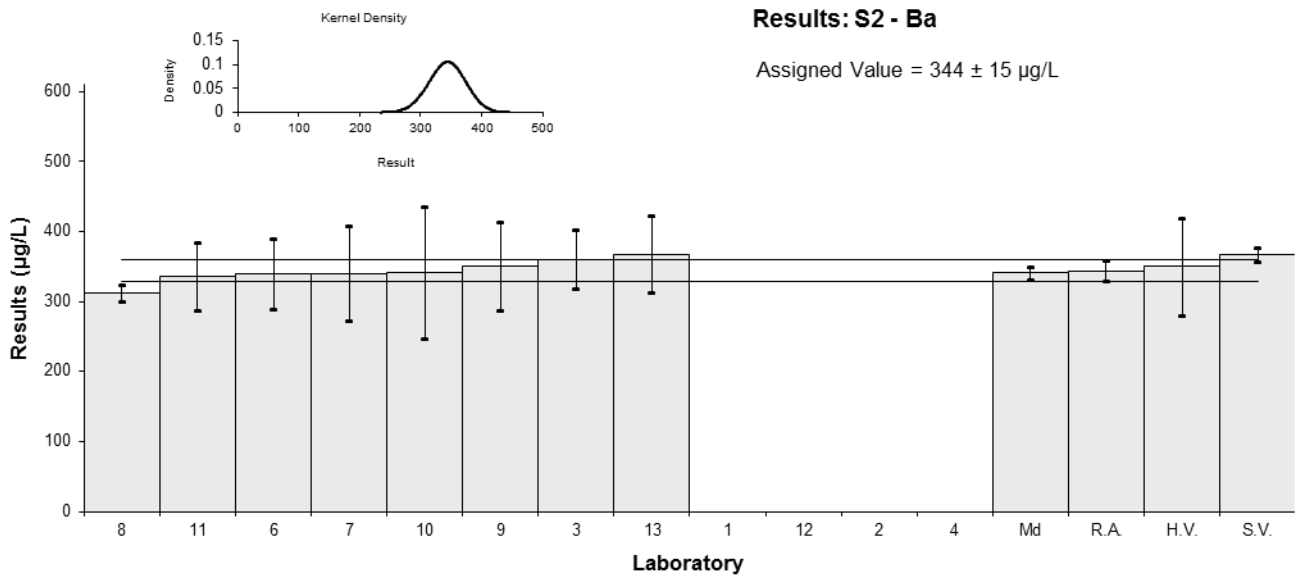
Sample No.	S2
Matrix.	Sea Water
Analyte.	Ba
Units	µg/L

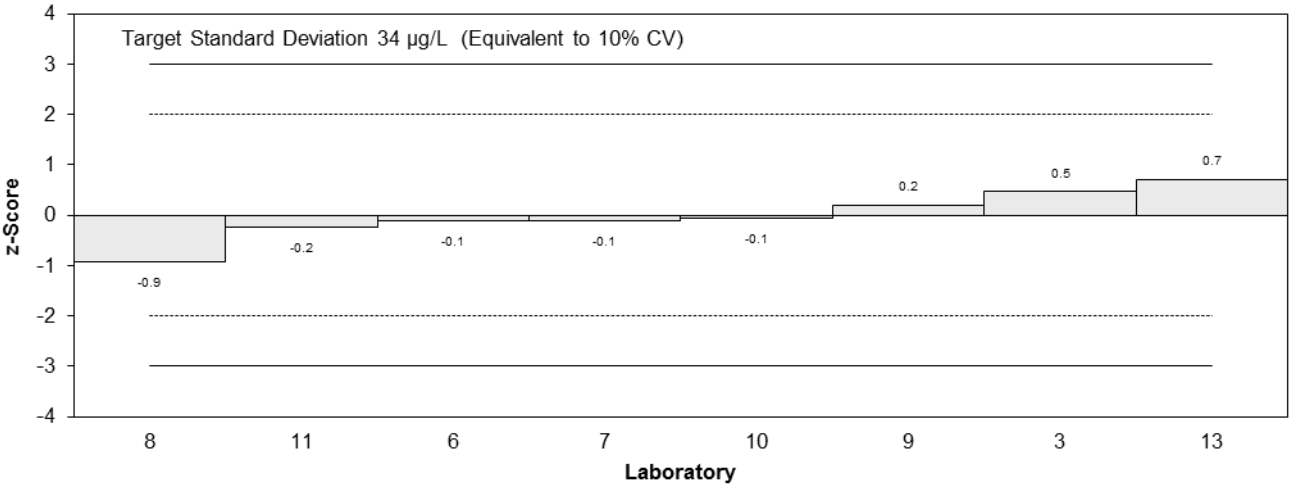
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	NT	NT		
3	360	42	0.47	0.36
4	NT	NT		
6	340	50	-0.12	-0.08
7	340	68	-0.12	-0.06
8	312	11.3	-0.93	-1.70
9	351	63	0.20	0.11
10	342	94	-0.06	-0.02
11	336	48	-0.23	-0.16
12	NT	NT		
13	368	55	0.70	0.42

Statistics

Assigned Value	344	15
Spike	367	10
Homogeneity Value	350	70
Robust Average	344	15
Median	341	9
Mean	344	
N	8	
Max.	368	
Min.	312	
Robust SD	17	
Robust CV	4.9%	


Kernel Density
Density
0.15
0.1
0.05
0
0
100
200
300
400
500
Result
Results: S2 - Ba
Assigned Value = 344 ± 15 µg/L
Results (µg/L)
600
500
400
300
200
100
0
8
11
6
7
10
9
3
13
1
12
2
4
Md
R.A.
H.V.
S.V.
Laboratory


z-Scores: S2 - Ba
Target Standard Deviation 34 µg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.9
-0.2
-0.1
-0.1
-0.1
0.2
0.5
0.7
8
11
6
7
10
9
3
13
Laboratory

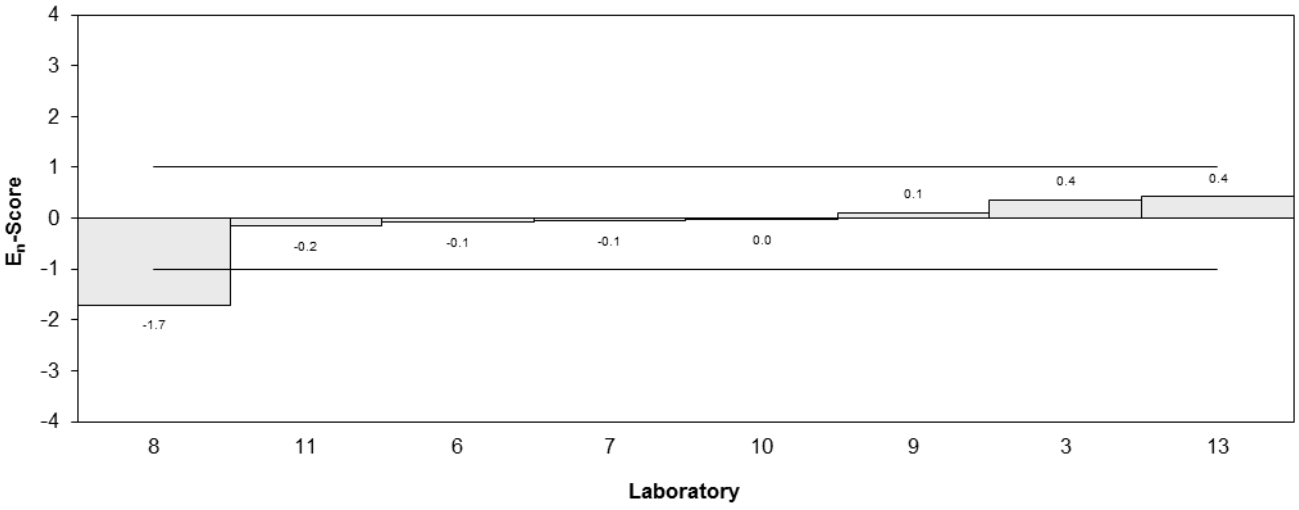

En-Scores: S2 - Ba
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.7
-0.2
-0.1
-0.1
0.0
0.1
0.4
0.4
8
11
6
7
10
9
3
13
Laboratory

Figure 25

Table 29

Sample Details

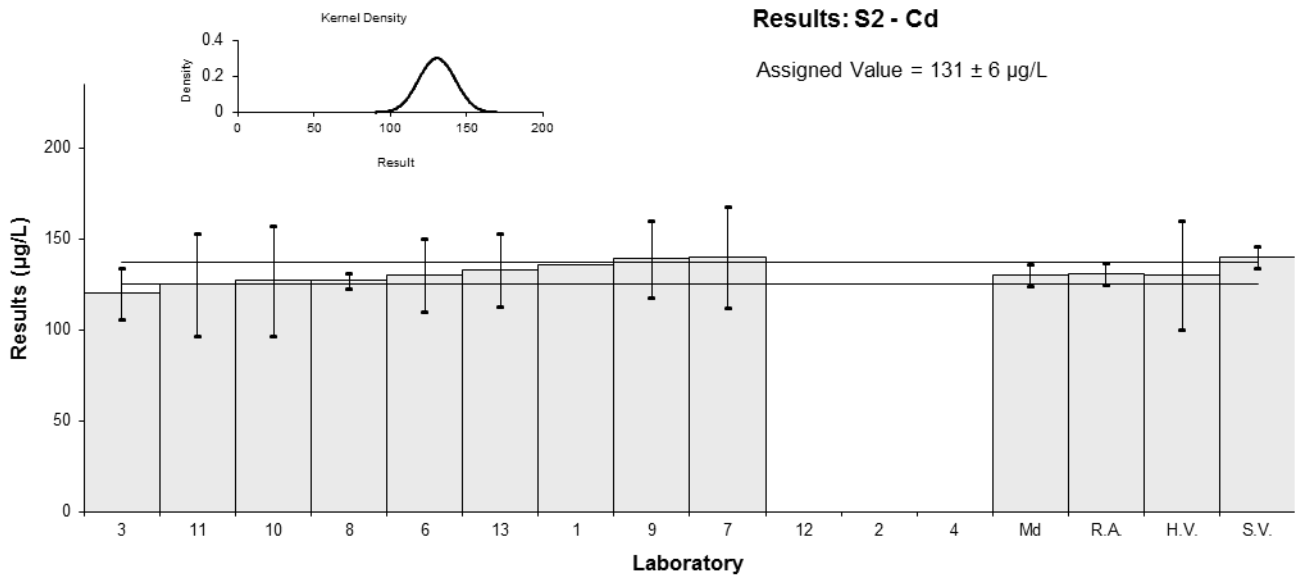
Sample No.	S2
Matrix.	Sea Water
Analyte.	Cd
Units	µg/L

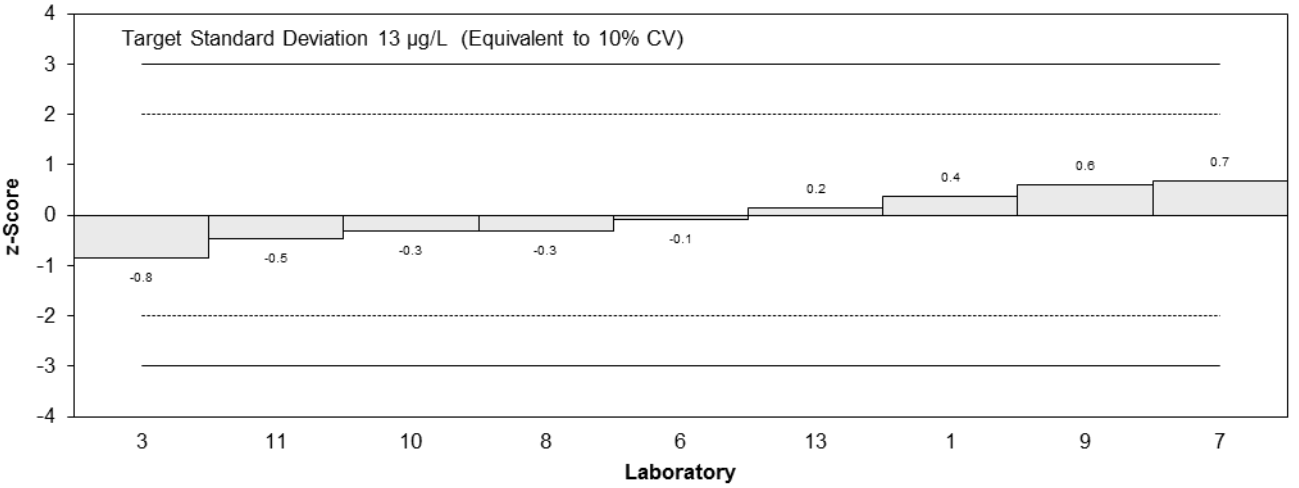
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	136	NR	0.38	0.83
2	NT	NT		
3	120	14	-0.84	-0.72
4	NT	NT		
6	130	20	-0.08	-0.05
7	140	28	0.69	0.31
8	127	4.46	-0.31	-0.54
9	139	21	0.61	0.37
10	127	30	-0.31	-0.13
11	125	28	-0.46	-0.21
12	NT	NT		
13	133	20	0.15	0.10

Statistics

Assigned Value	131	6
Spike	141	6
Homogeneity Value	130	30
Robust Average	131	6
Median	130	6
Mean	131	
N	9	
Max.	140	
Min.	120	
Robust SD	8	
Robust CV	6.1%	


Kernel Density
Density
Result
Results: S2 - Cd
Assigned Value = 131 ± 6 µg/L
Results (µg/L)
Laboratory
3
11
10
8
6
13
1
9
7
12
2
4
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Cd
Target Standard Deviation 13 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-0.8
-0.5
-0.3
-0.3
-0.1
0.2
0.4
0.6
0.7

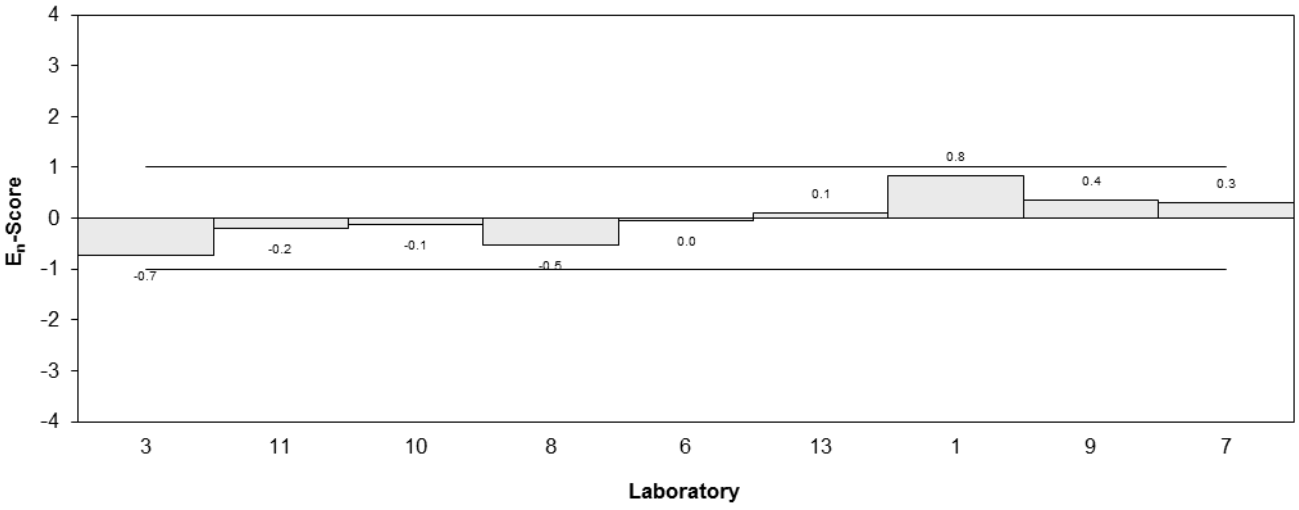

En-Scores: S2 - Cd
En-Score
Laboratory
-0.7
-0.2
-0.1
-0.5
0.0
0.1
0.8
0.4
0.3

Figure 26

Table 30

Sample Details

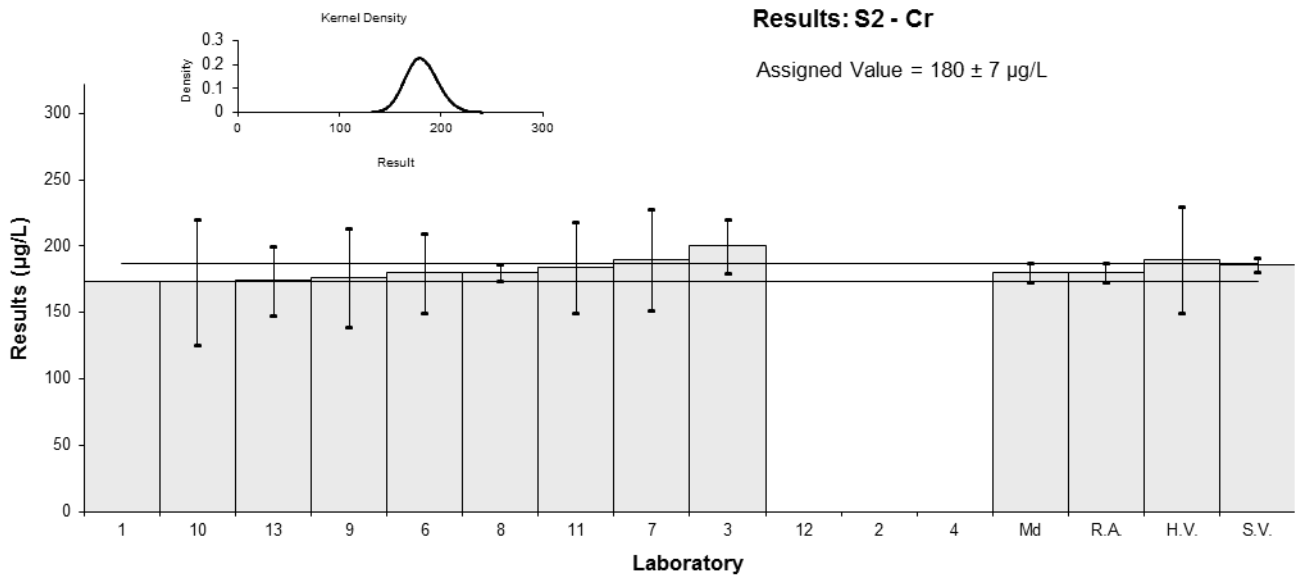
Sample No.	S2
Matrix.	Sea Water
Analyte.	Cr
Units	µg/L

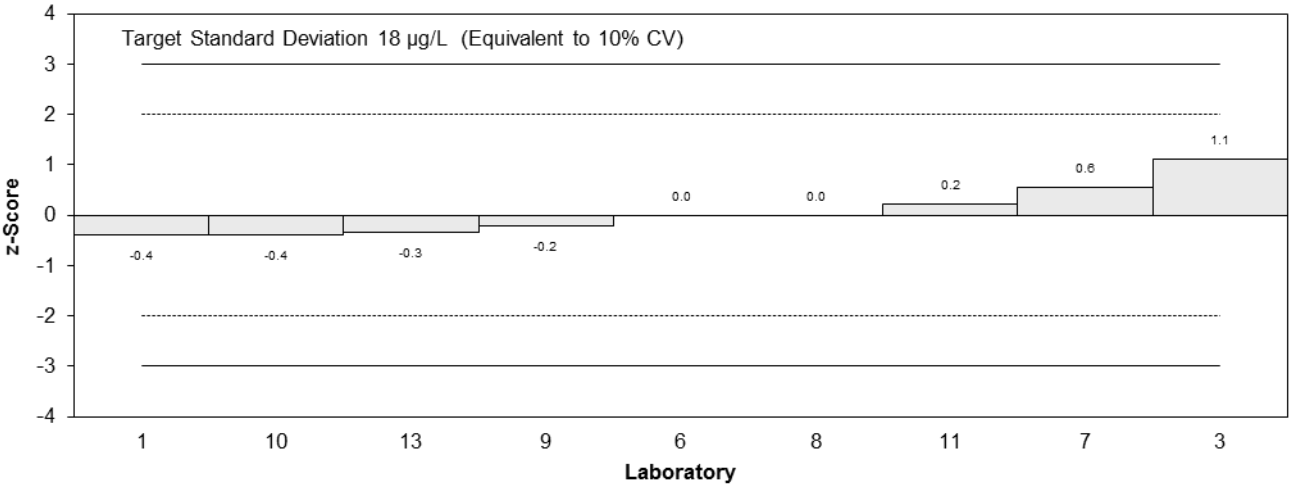
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	173	NR	-0.39	-1.00
2	NT	NT		
3	200	20	1.11	0.94
4	NT	NT		
6	180	30	0.00	0.00
7	190	38	0.56	0.26
8	180	6.34	0.00	0.00
9	176	37	-0.22	-0.11
10	173	47	-0.39	-0.15
11	184	34	0.22	0.12
12	NT	NT		
13	174	26	-0.33	-0.22

Statistics

Assigned Value	180	7
Spike	186	5
Homogeneity Value	190	40
Robust Average	180	7
Median	180	7
Mean	181	
N	9	
Max.	200	
Min.	173	
Robust SD	8	
Robust CV	4.4%	


Kernel Density
Density
Result
Results: S2 - Cr
Assigned Value = 180 ± 7 µg/L
Results (µg/L)
Laboratory
1
10
13
9
6
8
11
7
3
12
2
4
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Cr
Target Standard Deviation 18 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-0.4
-0.4
-0.3
-0.2
0.0
0.0
0.2
0.6
1.1

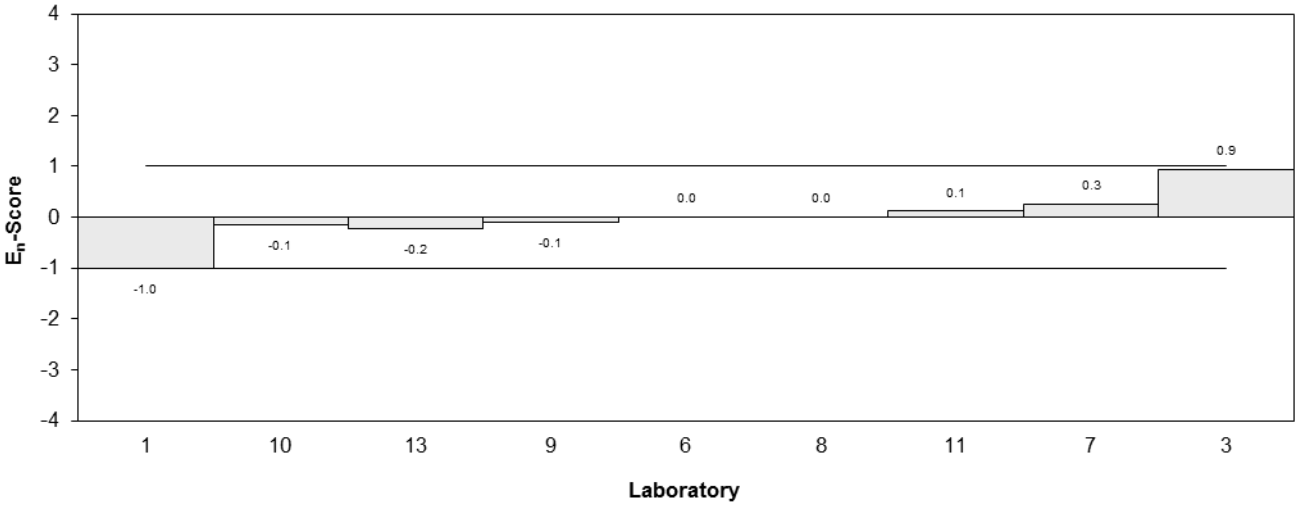

En-Scores: S2 - Cr
En-Score
Laboratory
-1.0
-0.1
-0.2
-0.1
0.0
0.0
0.1
0.3
0.9

Figure 27

Table 31

Sample Details

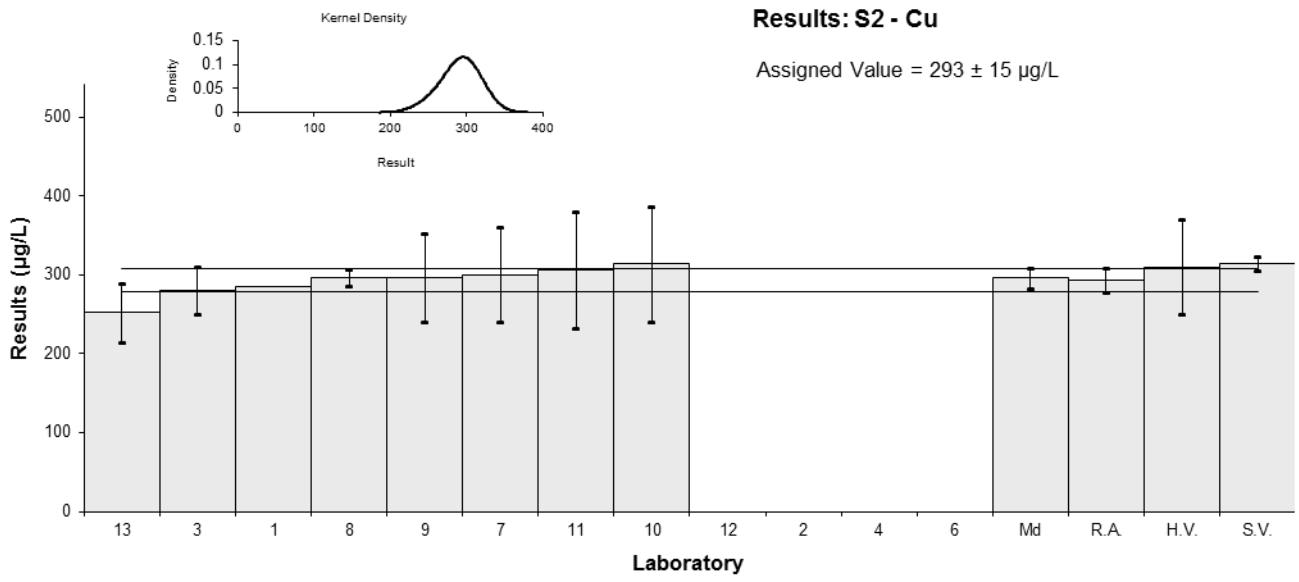
Sample No.	S2
Matrix.	Sea Water
Analyte.	Cu
Units	µg/L

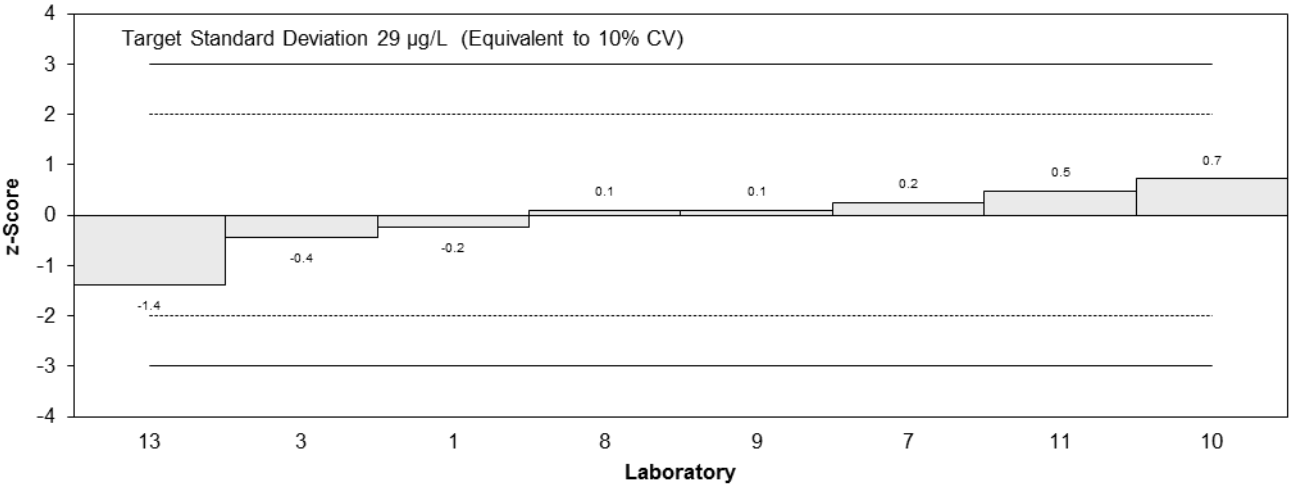
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	286	NR	-0.24	-0.47
2	NT	NT		
3	280	30	-0.44	-0.39
4	NT	NT		
6	NT	NT		
7	300	60	0.24	0.11
8	296	10.4	0.10	0.16
9	296	56	0.10	0.05
10	314	73	0.72	0.28
11	307	74	0.48	0.19
12	NT	NT		
13	252	38	-1.40	-1.00

Statistics

Assigned Value	293	15
Spike	314	9
Homogeneity Value	310	60
Robust Average	293	15
Median	296	13
Mean	291	
N	8	
Max.	314	
Min.	252	
Robust SD	17	
Robust CV	5.8%	


Kernel Density
Density
0.15
0.1
0.05
0
0
100
200
300
400
Result
Results: S2 - Cu
Assigned Value = 293 ± 15 µg/L
Results (µg/L)
500
400
300
200
100
0
13
3
1
8
9
7
11
10
12
2
4
6
Md
R.A.
H.V.
S.V.
Laboratory


z-Scores: S2 - Cu
Target Standard Deviation 29 µg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.4
-0.4
-0.2
0.1
0.1
0.2
0.5
0.7
13
3
1
8
9
7
11
10
Laboratory

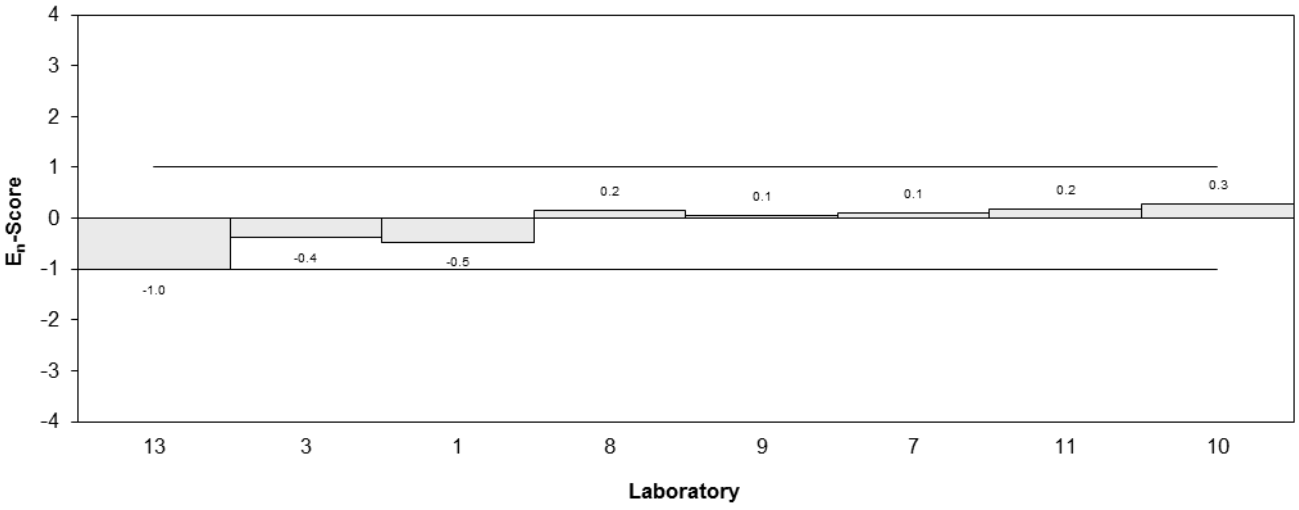

En-Scores: S2 - Cu
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.0
-0.4
-0.5
0.2
0.1
0.1
0.2
0.3
13
3
1
8
9
7
11
10
Laboratory

Figure 28

Table 32

Sample Details

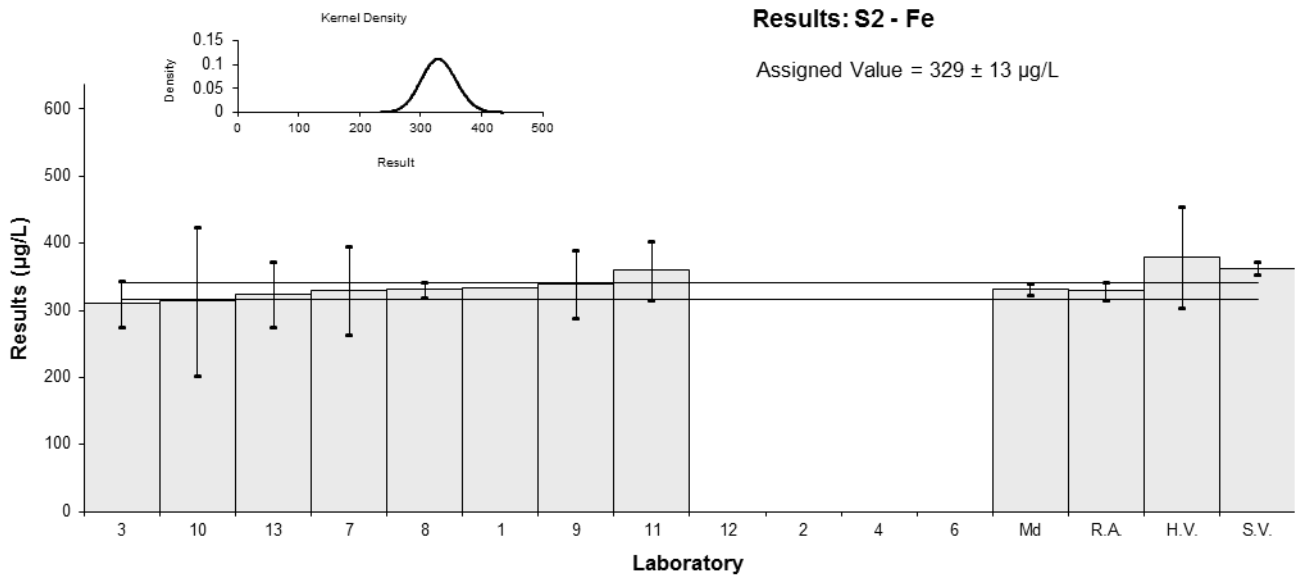
Sample No.	S2
Matrix.	Sea Water
Analyte.	Fe
Units	µg/L

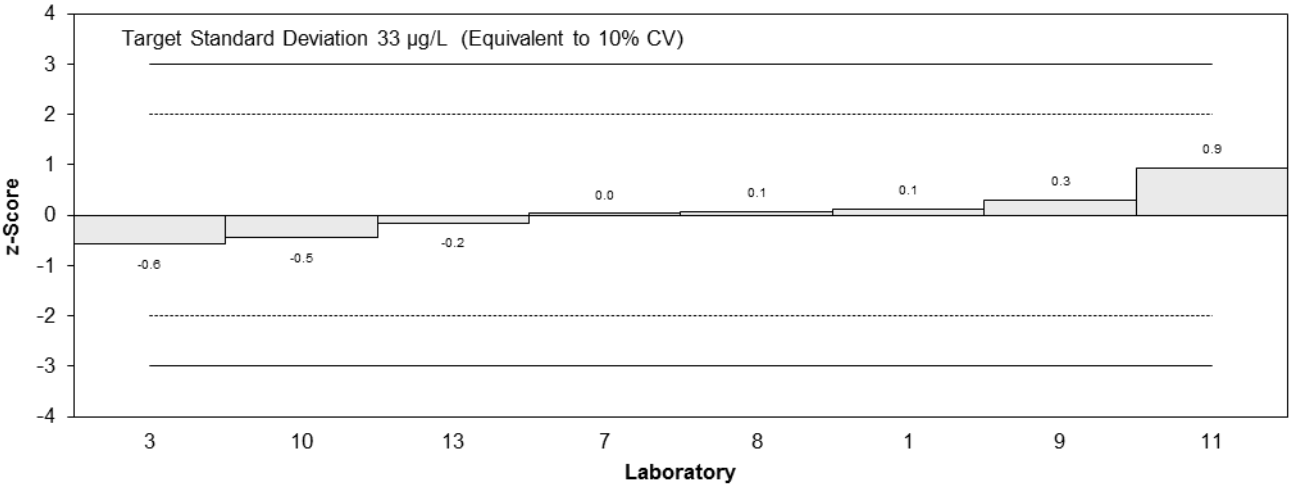
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	333	NR	0.12	0.31
2	NT	NT		
3	310	34	-0.58	-0.52
4	NT	NT		
6	NT	NT		
7	330	66	0.03	0.01
8	331	11.7	0.06	0.11
9	339	51	0.30	0.19
10	314	111	-0.46	-0.13
11	360	44	0.94	0.68
12	NT	NT		
13	324	49	-0.15	-0.10

Statistics

Assigned Value	329	13
Spike	363	10
Homogeneity Value	379	76
Robust Average	329	13
Median	331	9
Mean	330	
N	8	
Max.	360	
Min.	310	
Robust SD	15	
Robust CV	4.6%	


Kernel Density
Density
0.15
0.1
0.05
0
0
100
200
300
400
500
Result
Results: S2 - Fe
Assigned Value = 329 ± 13 µg/L
Results (µg/L)
600
500
400
300
200
100
0
3
10
13
7
8
1
9
11
12
2
4
6
Md
R.A.
H.V.
S.V.
Laboratory


z-Scores: S2 - Fe
Target Standard Deviation 33 µg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.6
-0.5
-0.2
0.0
0.1
0.1
0.3
0.9
3
10
13
7
8
1
9
11
Laboratory

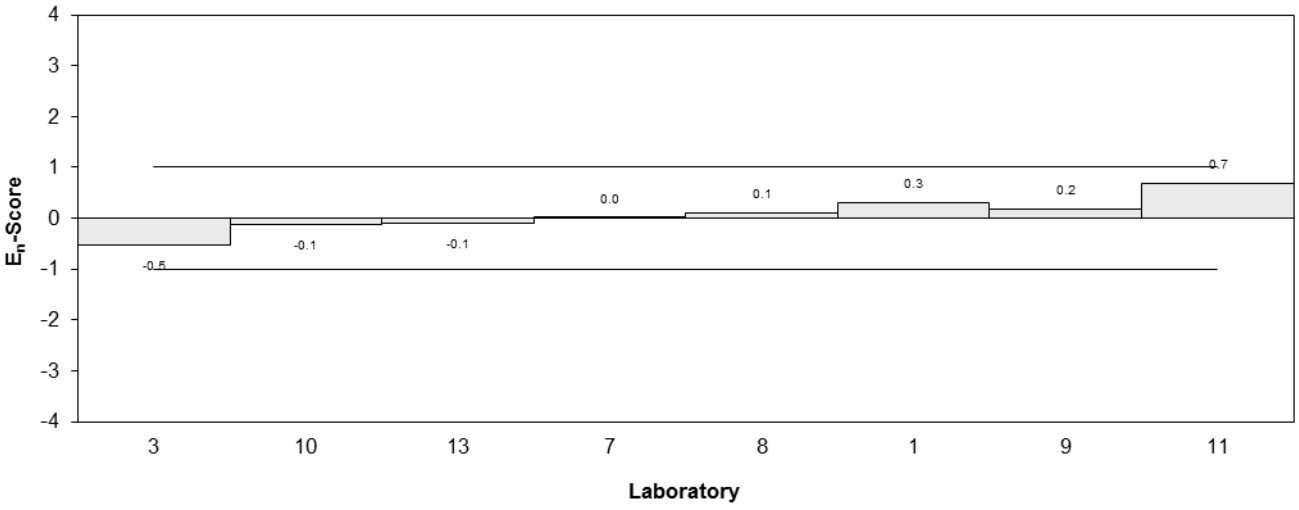

En-Scores: S2 - Fe
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.5
-0.1
-0.1
0.0
0.1
0.3
0.2
0.7
3
10
13
7
8
1
9
11
Laboratory

Figure 29

Table 33

Sample Details

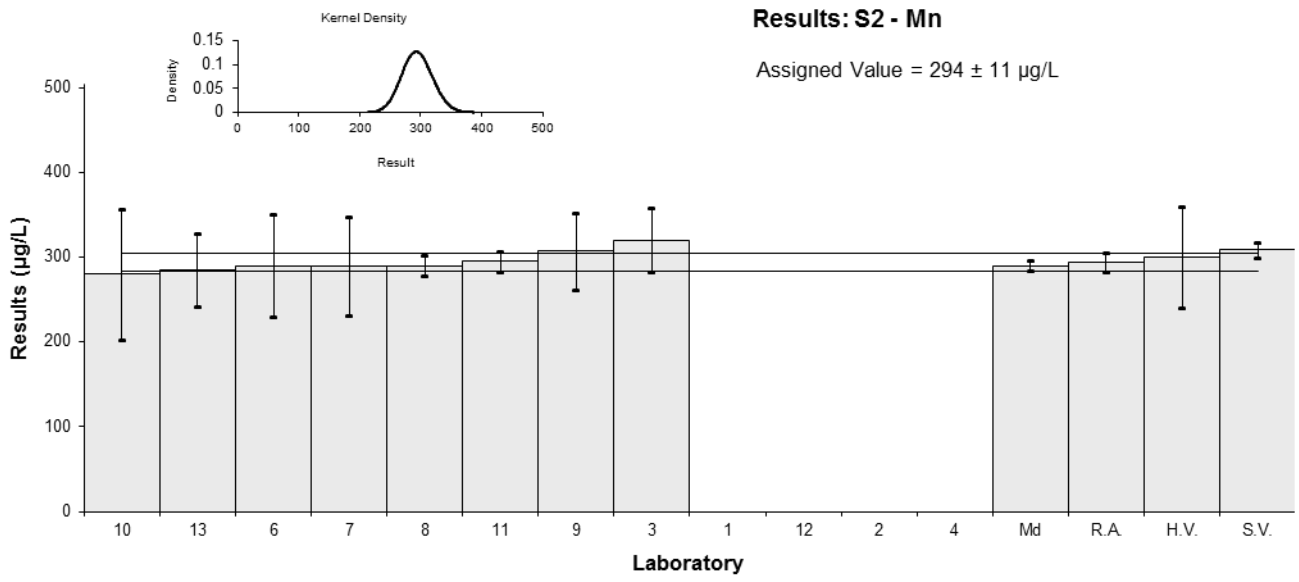
Sample No.	S2
Matrix.	Sea Water
Analyte.	Mn
Units	µg/L

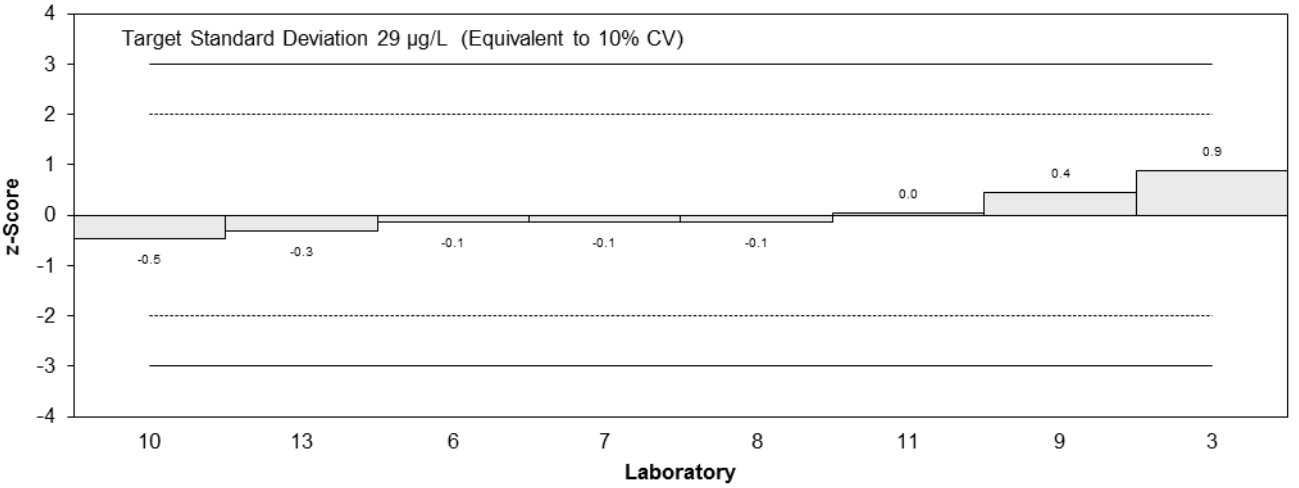
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	NT	NT		
3	320	38	0.88	0.66
4	NT	NT		
6	290	60	-0.14	-0.07
7	290	58	-0.14	-0.07
8	290	12.1	-0.14	-0.24
9	307	46	0.44	0.27
10	280	77	-0.48	-0.18
11	295	12	0.03	0.06
12	NT	NT		
13	285	43	-0.31	-0.20

Statistics

Assigned Value	294	11
Spike	309	9
Homogeneity Value	300	60
Robust Average	294	11
Median	290	6
Mean	295	
N	8	
Max.	320	
Min.	280	
Robust SD	12	
Robust CV	4.1%	


Kernel Density
Density
Result
Results: S2 - Mn
Assigned Value = 294 ± 11 µg/L
Results (µg/L)
Laboratory
10
13
6
7
8
11
9
3
1
12
2
4
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Mn
Target Standard Deviation 29 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-0.5
-0.3
-0.1
-0.1
-0.1
0.0
0.4
0.9

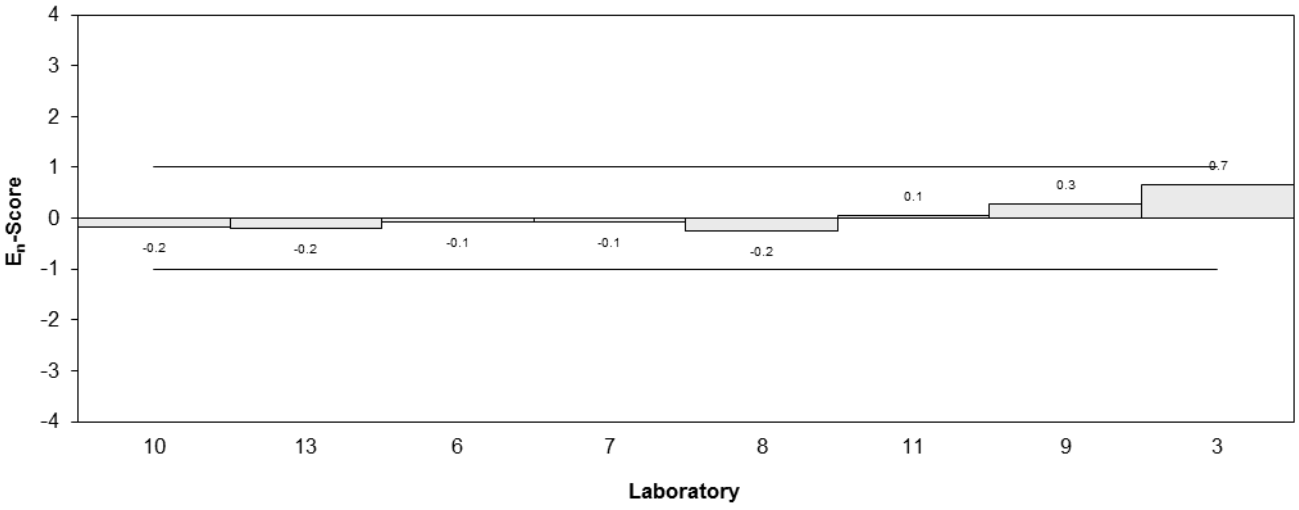

En-Scores: S2 - Mn
En-Score
Laboratory
-0.2
-0.2
-0.1
-0.1
-0.2
0.1
0.3
0.7

Figure 30

Table 34

Sample Details

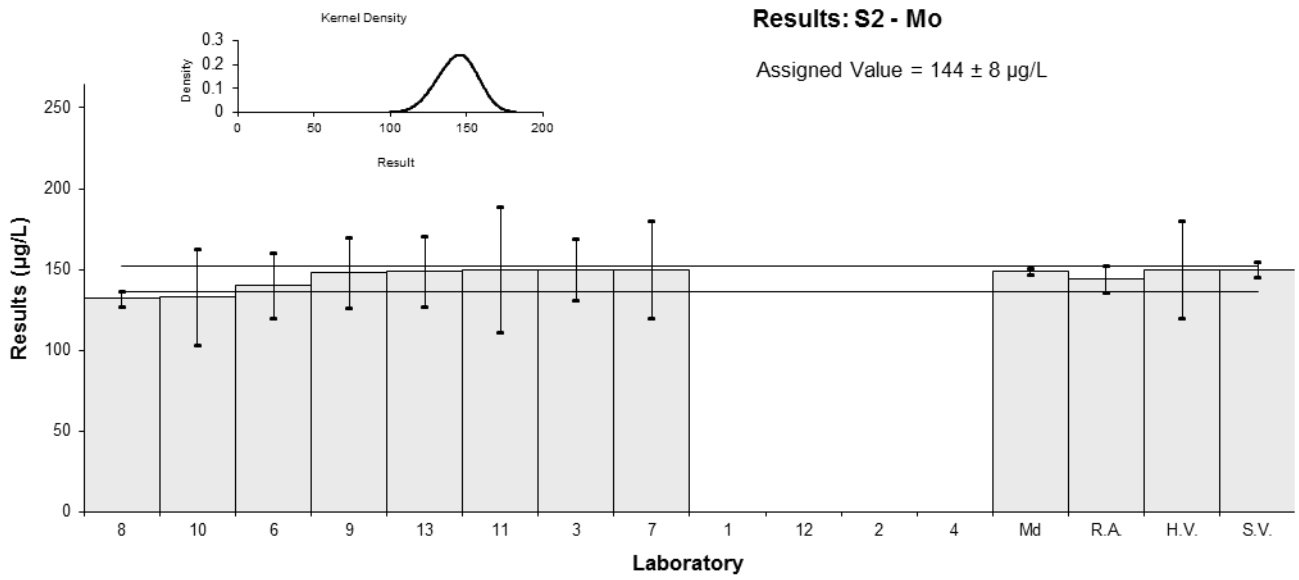
Sample No.	S2
Matrix.	Sea Water
Analyte.	Mo
Units	µg/L

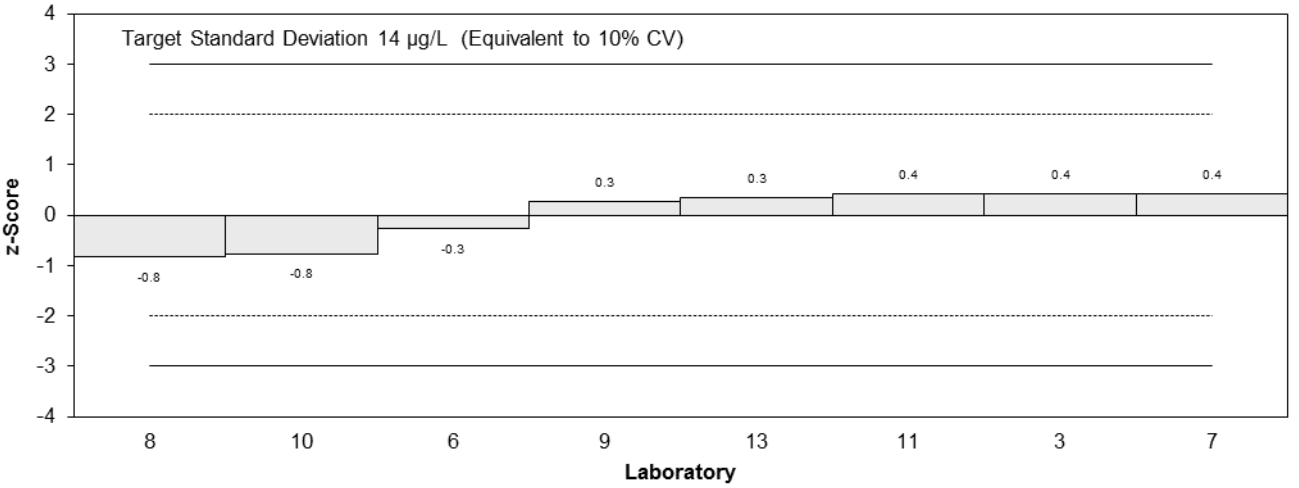
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	NT	NT		
3	150	19	0.42	0.29
4	NT	NT		
6	140	20	-0.28	-0.19
7	150	30	0.42	0.19
8	132	4.80	-0.83	-1.29
9	148	22	0.28	0.17
10	133	30	-0.76	-0.35
11	150	39	0.42	0.15
12	NT	NT		
13	149	22	0.35	0.21

Statistics

Assigned Value	144	8
Spike	150	5
Homogeneity Value	150	30
Robust Average	144	8
Median	149	2
Mean	144	
N	8	
Max.	150	
Min.	132	
Robust SD	9	
Robust CV	6.3%	


Kernel Density
Density
Result
Results: S2 - Mo
Assigned Value = 144 ± 8 µg/L
Results (µg/L)
Laboratory
8
10
6
9
13
11
3
7
1
12
2
4
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Mo
Target Standard Deviation 14 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-0.8
-0.8
-0.3
0.3
0.3
0.4
0.4
0.4

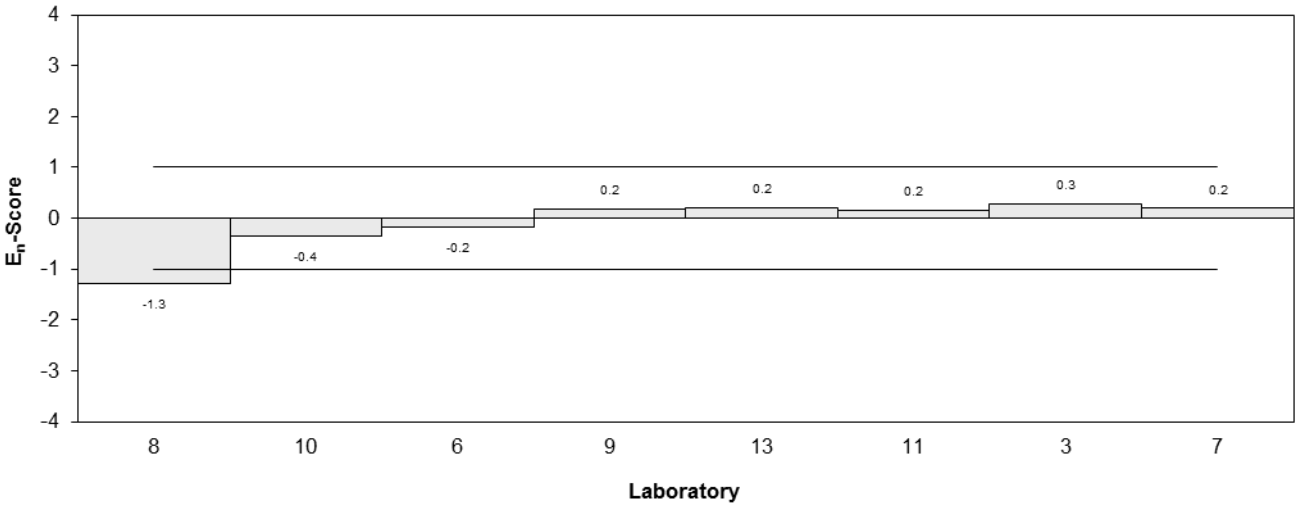

En-Scores: S2 - Mo
En-Score
Laboratory
-1.3
-0.4
-0.2
0.2
0.2
0.2
0.3
0.2

Figure 31

Table 35

Sample Details

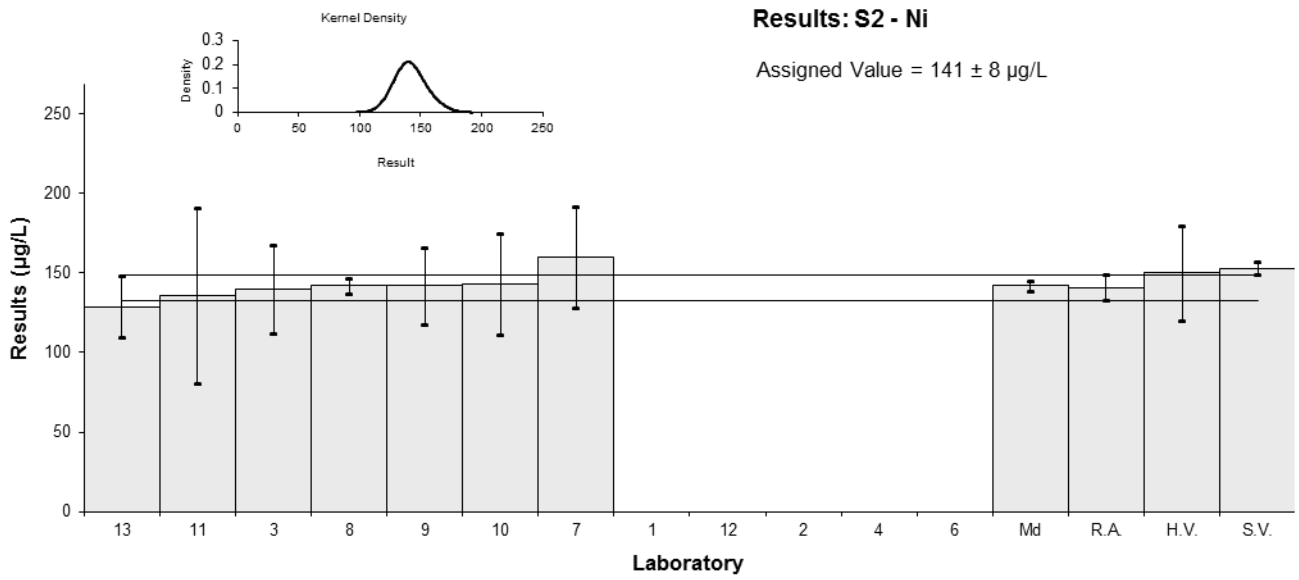
Sample No.	S2
Matrix.	Sea Water
Analyte.	Ni
Units	µg/L

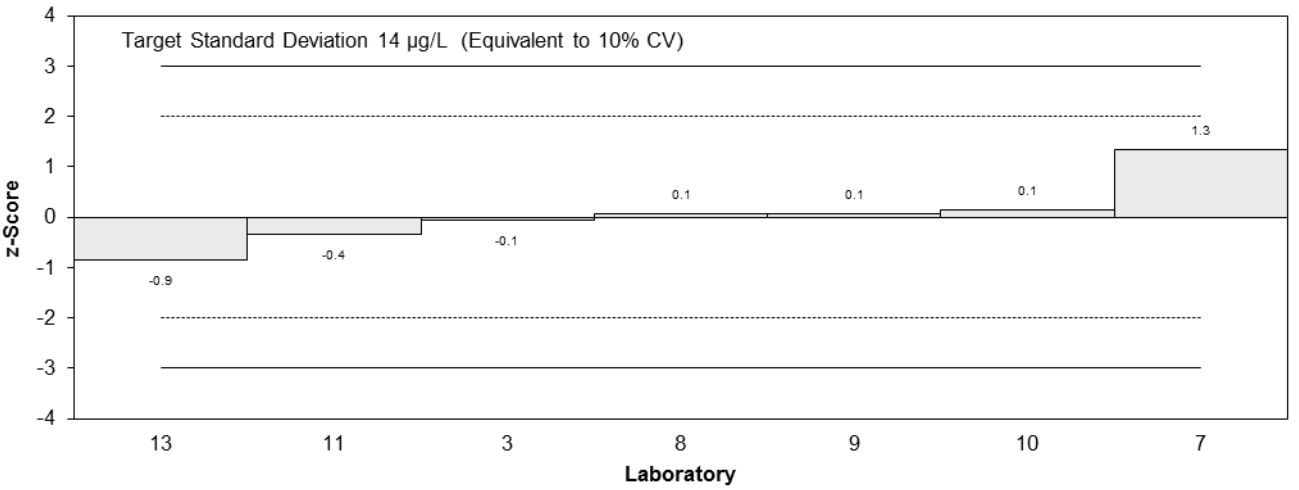
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	NT	NT		
3	140	28	-0.07	-0.03
4	NT	NT		
6	NT	NT		
7	160	32	1.35	0.58
8	142	5.00	0.07	0.11
9	142	24	0.07	0.04
10	143	32	0.14	0.06
11	136	55	-0.35	-0.09
12	NT	NT		
13	129	19	-0.85	-0.58

Statistics

Assigned Value	141	8
Spike	154	4
Homogeneity Value	150	30
Robust Average	141	8
Median	142	3
Mean	142	
N	7	
Max.	160	
Min.	129	
Robust SD	8	
Robust CV	5.7%	


Kernel Density
Density
Result
Results: S2 - Ni
Assigned Value = 141 ± 8 µg/L
Results (µg/L)
Laboratory
13
11
3
8
9
10
7
1
12
2
4
6
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Ni
Target Standard Deviation 14 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-0.9
-0.4
-0.1
0.1
0.1
0.1
1.3

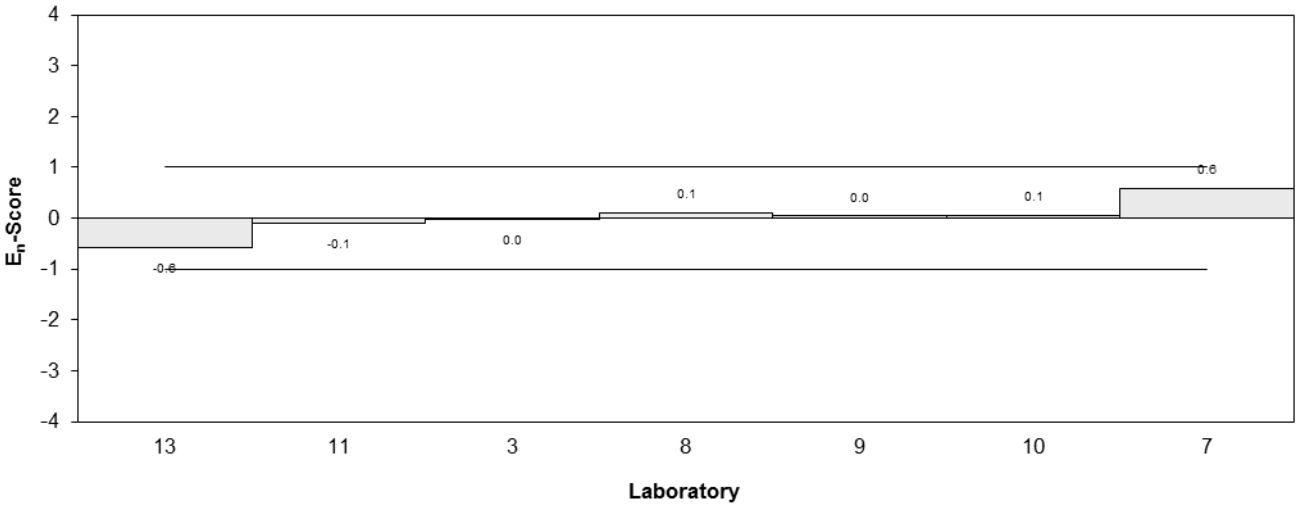

En-Scores: S2 - Ni
En-Score
Laboratory
-0.6
-0.1
0.0
0.1
0.0
0.1
0.6

Figure 32

Table 36

Sample Details

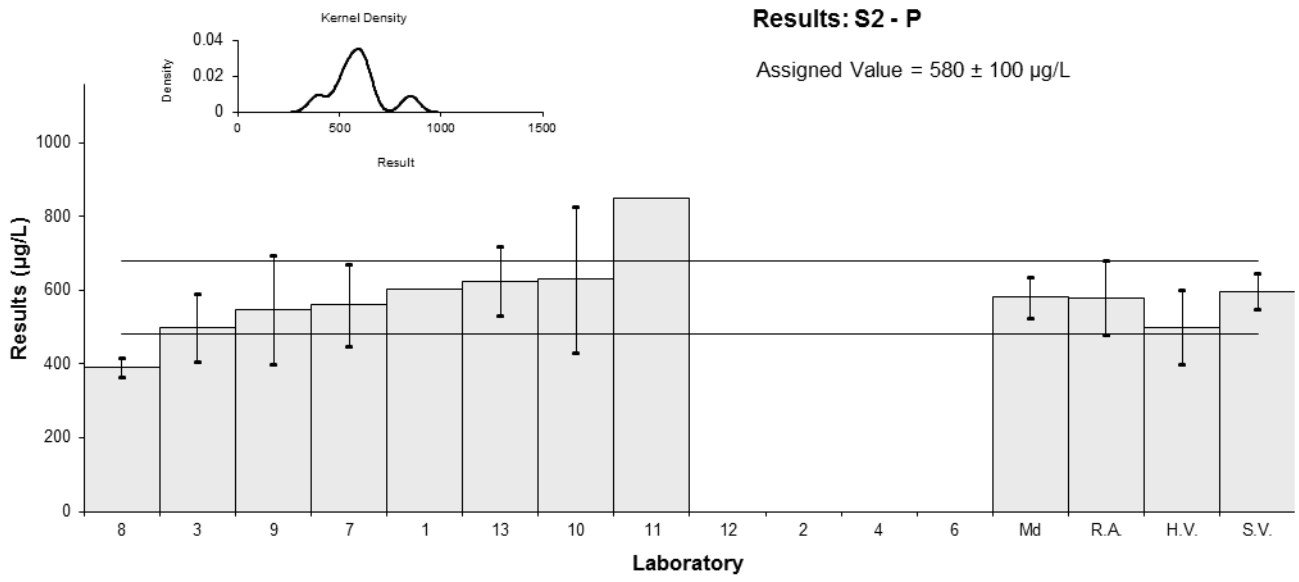
Sample No.	S2
Matrix.	Sea Water
Analyte.	P
Units	µg/L

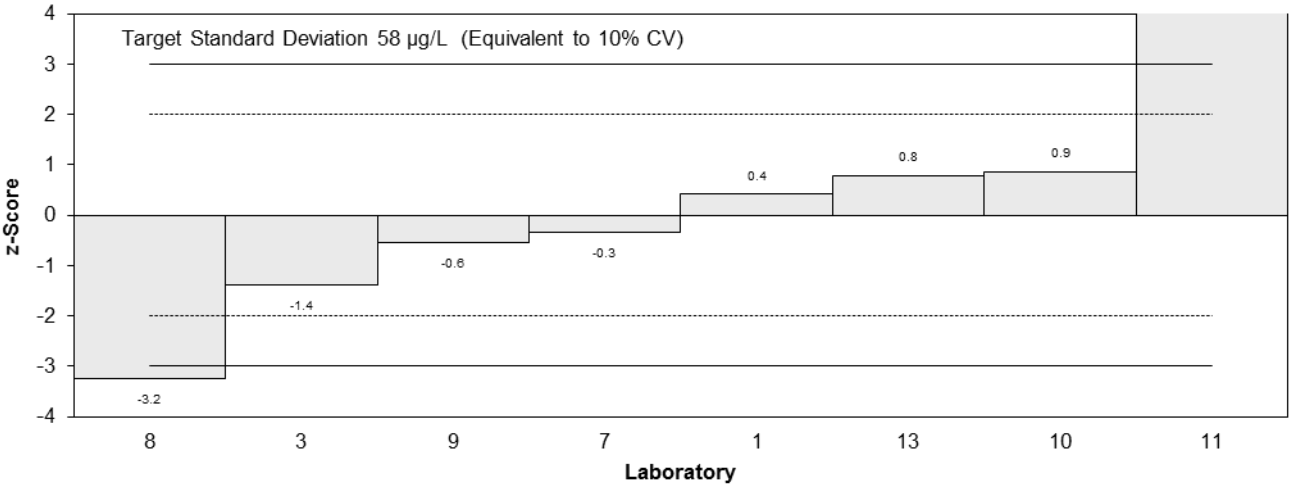
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	604	NR	0.41	0.24
2	NT	NT		
3	500	92	-1.38	-0.59
4	NT	NT		
6	NT	NT		
7	560	110	-0.34	-0.13
8	392	26.6	-3.24	-1.82
9	548	148	-0.55	-0.18
10	630	198	0.86	0.23
11	850	NR	4.66	2.70
12	NT	NT		
13	625	94	0.78	0.33

Statistics

Assigned Value	580	100
Spike	598	50
Homogeneity Value	500	100
Robust Average	580	100
Median	582	56
Mean	589	
N	8	
Max.	850	
Min.	392	
Robust SD	120	
Robust CV	21%	


Kernel Density
Density
0.04
0.02
0
0
500
1000
1500
Result
Results: S2 - P
Assigned Value = 580 ± 100 µg/L
Results (µg/L)
1000
800
600
400
200
0
8
3
9
7
1
13
10
11
12
2
4
6
Md
R.A.
H.V.
S.V.
Laboratory


z-Scores: S2 - P
Target Standard Deviation 58 µg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-3.2
-1.4
-0.6
-0.3
0.4
0.8
0.9
8
3
9
7
1
13
10
11
Laboratory

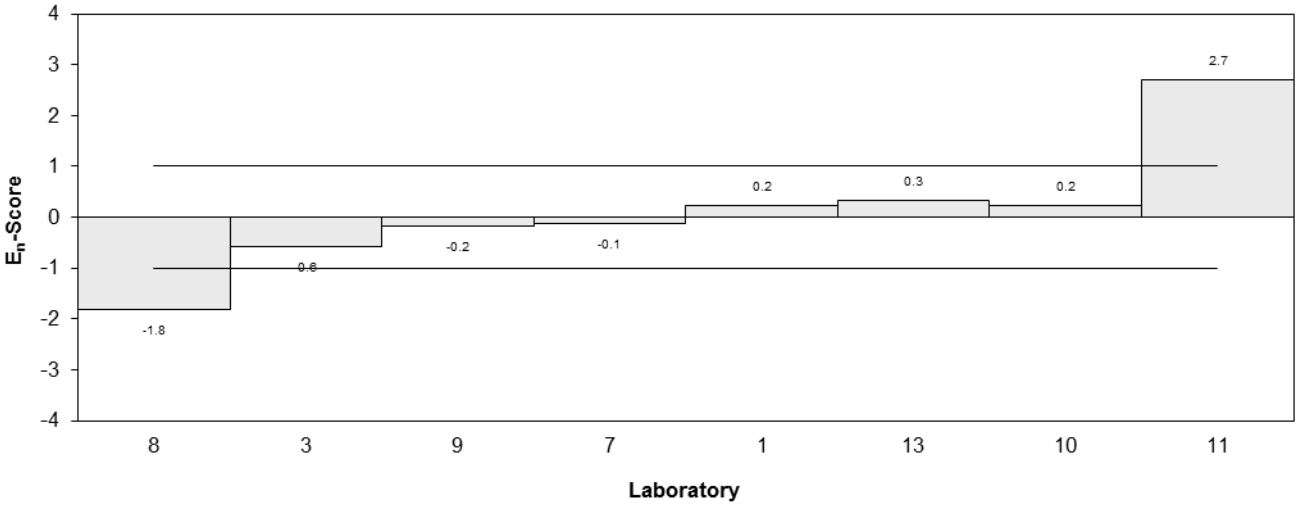

En-Scores: S2 - P
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.8
-0.6
-0.2
-0.1
0.2
0.3
0.2
2.7
8
3
9
7
1
13
10
11
Laboratory

Figure 33

Table 37

Sample Details

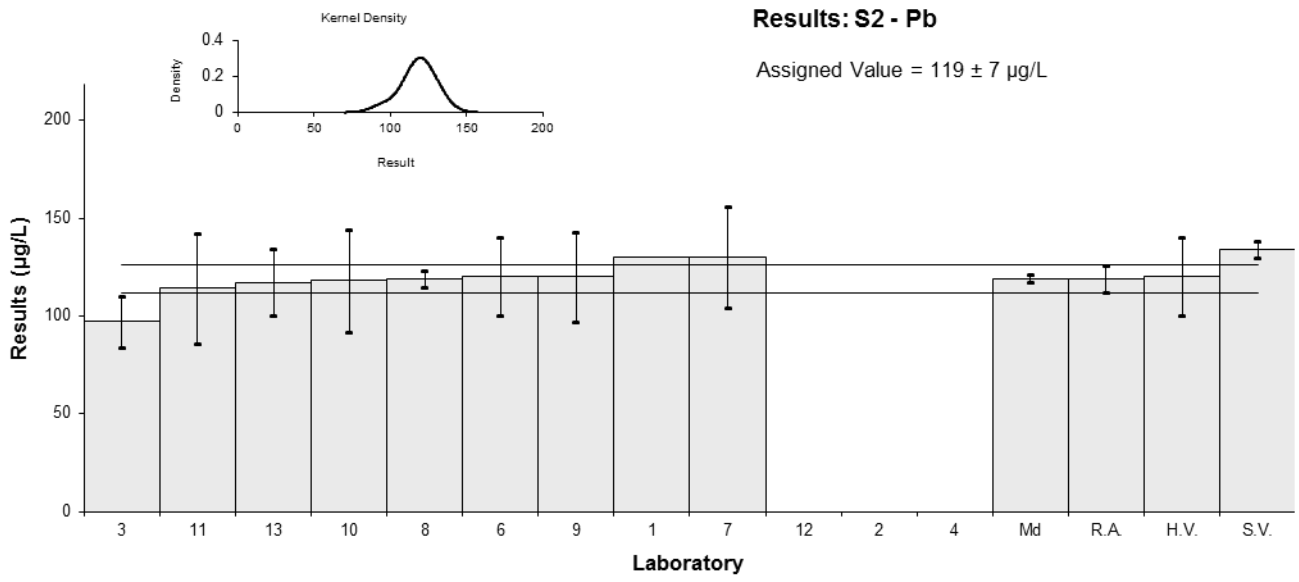
Sample No.	S2
Matrix.	Sea Water
Analyte.	Pb
Units	µg/L

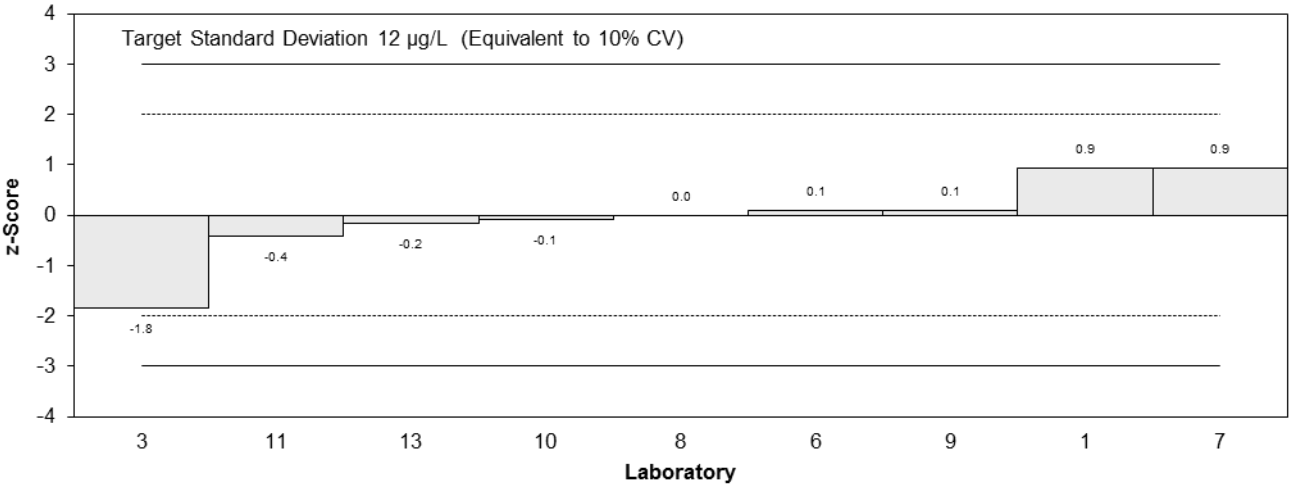
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	130	NR	0.92	1.57
2	NT	NT		
3	97	13	-1.85	-1.49
4	NT	NT		
6	120	20	0.08	0.05
7	130	26	0.92	0.41
8	119	4.31	0.00	0.00
9	120	23	0.08	0.04
10	118	26	-0.08	-0.04
11	114	28	-0.42	-0.17
12	NT	NT		
13	117	17	-0.17	-0.11

Statistics

Assigned Value	119	7
Spike	134	4
Homogeneity Value	120	20
Robust Average	119	7
Median	119	2
Mean	118	
N	9	
Max.	130	
Min.	97	
Robust SD	8	
Robust CV	6.7%	


Kernel Density
Density
Result
Results: S2 - Pb
Assigned Value = 119 ± 7 µg/L
Results (µg/L)
Laboratory
3
11
13
10
8
6
9
1
7
12
2
4
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Pb
Target Standard Deviation 12 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-1.8
-0.4
-0.2
-0.1
0.0
0.1
0.1
0.9
0.9

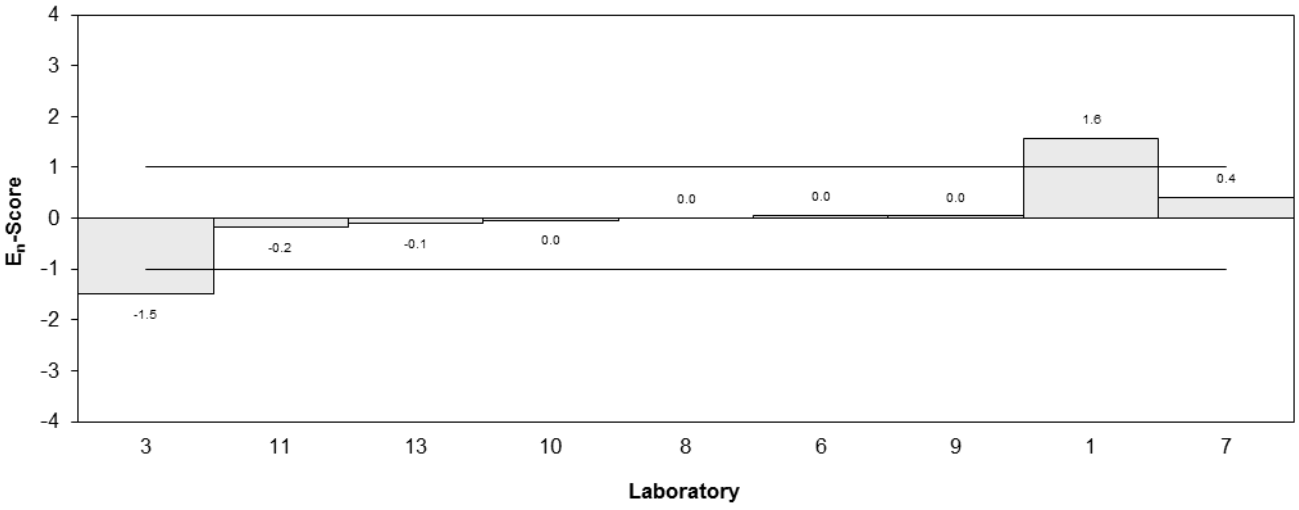

En-Scores: S2 - Pb
En-Score
Laboratory
-1.5
-0.2
-0.1
0.0
0.0
0.0
0.0
1.6
0.4

Figure 34

Table 38

Sample Details

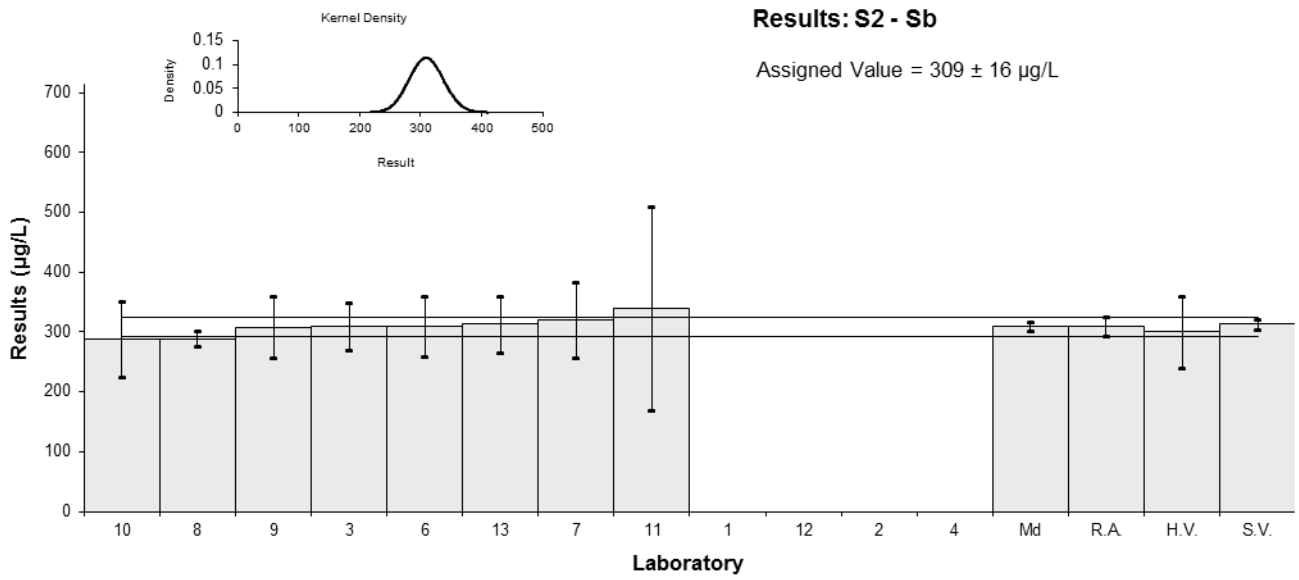
Sample No.	S2
Matrix.	Sea Water
Analyte.	Sb
Units	µg/L

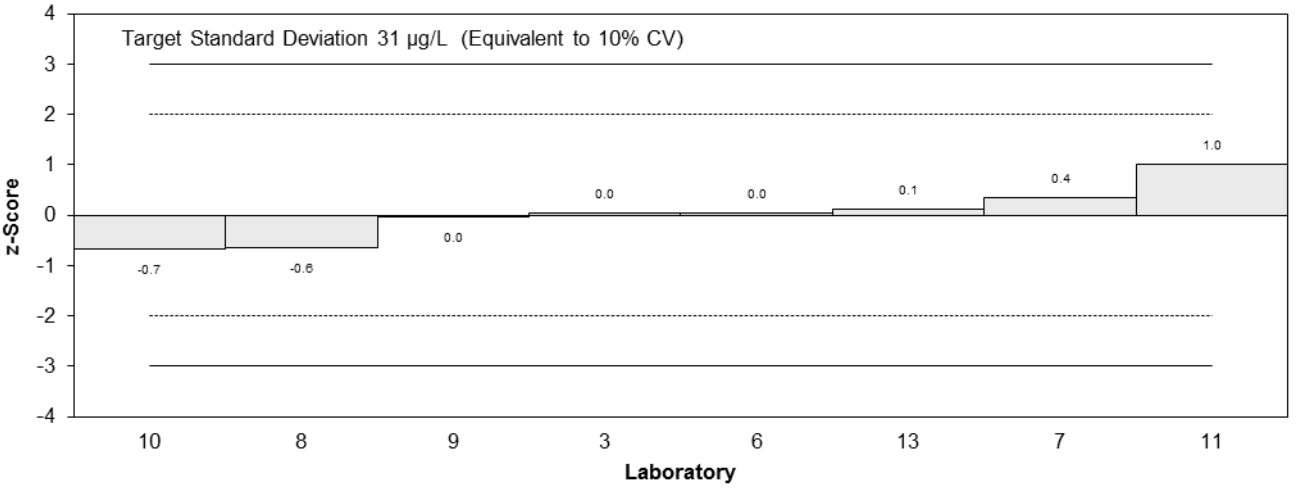
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	NT	NT		
3	310	40	0.03	0.02
4	NT	NT		
6	310	50	0.03	0.02
7	320	64	0.36	0.17
8	289	12.4	-0.65	-0.99
9	308	52	-0.03	-0.02
10	288	64	-0.68	-0.32
11	340	170	1.00	0.18
12	NT	NT		
13	313	47	0.13	0.08

Statistics

Assigned Value	309	16
Spike	314	9
Homogeneity Value	300	60
Robust Average	309	16
Median	310	8
Mean	310	
N	8	
Max.	340	
Min.	288	
Robust SD	18	
Robust CV	5.8%	


Kernel Density
Density
Result
Results: S2 - Sb
Assigned Value = 309 ± 16 µg/L
Results (µg/L)
Laboratory
10
8
9
3
6
13
7
11
1
12
2
4
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Sb
Target Standard Deviation 31 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-0.7
-0.6
0.0
0.0
0.0
0.1
0.4
1.0

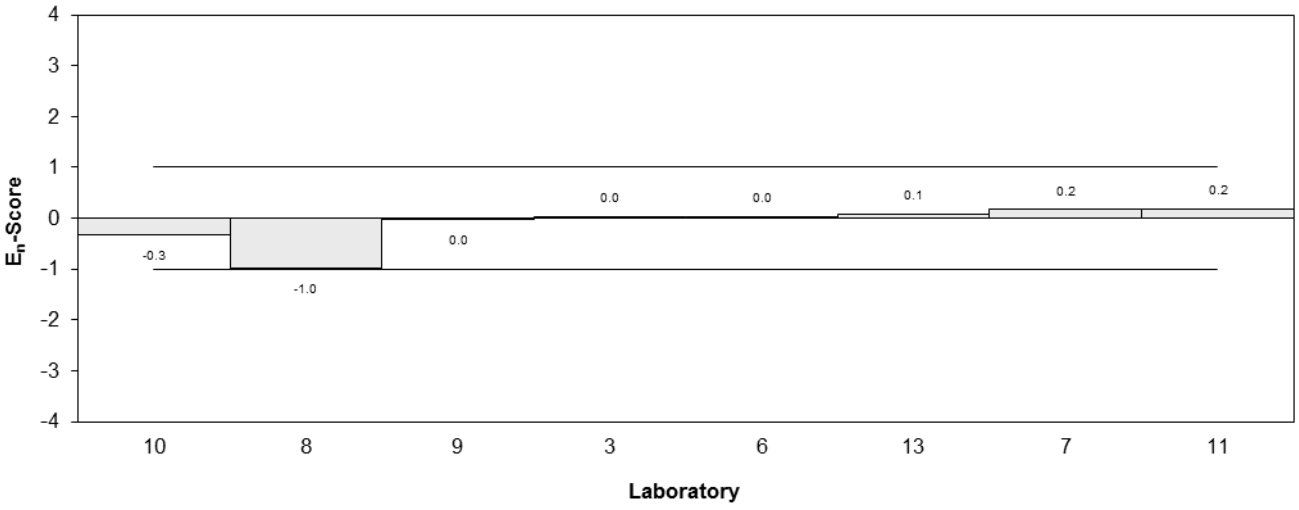

En-Scores: S2 - Sb
En-Score
Laboratory
-0.3
-1.0
0.0
0.0
0.0
0.1
0.2
0.2

Figure 35

Table 39

Sample Details

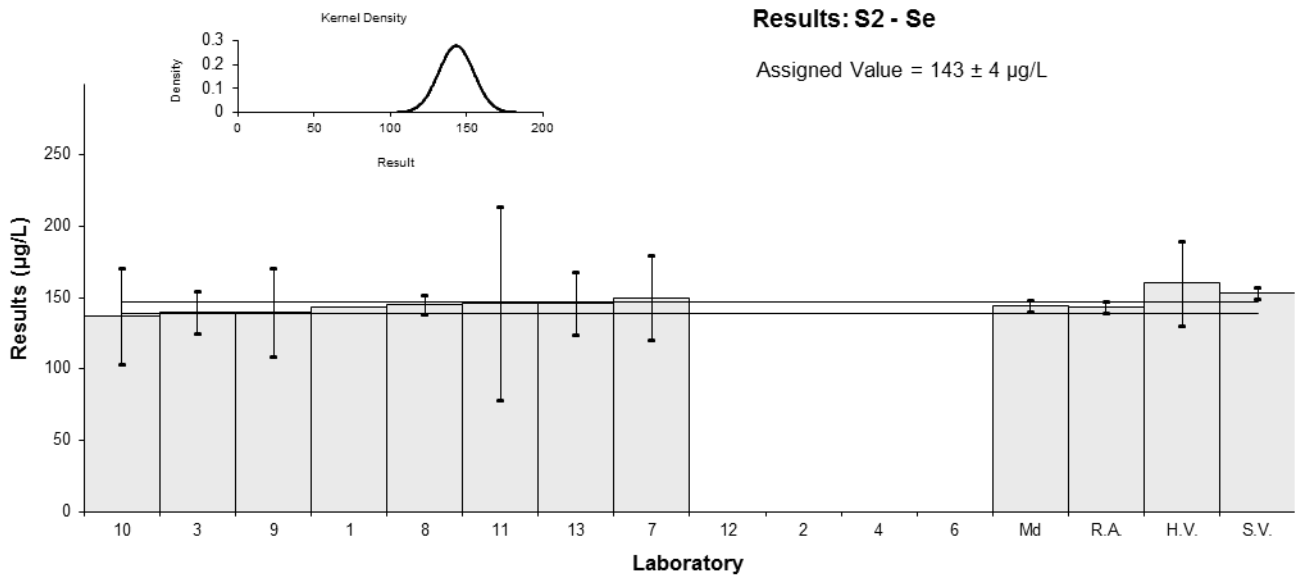
Sample No.	S2
Matrix.	Sea Water
Analyte.	Se
Units	µg/L

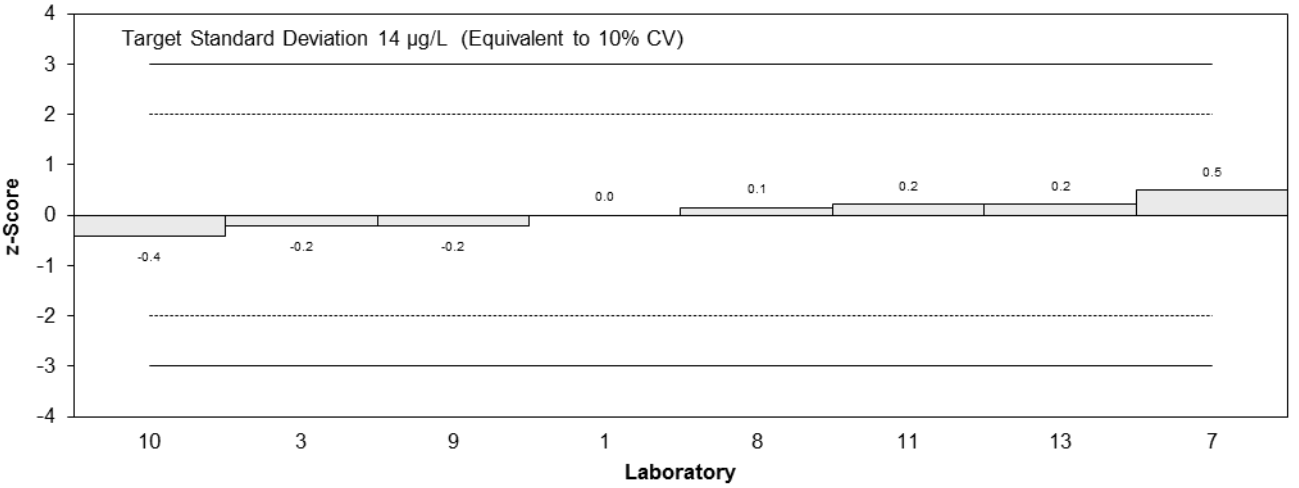
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	143	NR	0.00	0.00
2	NT	NT		
3	140	15	-0.21	-0.19
4	NT	NT		
6	NT	NT		
7	150	30	0.49	0.23
8	145	6.58	0.14	0.26
9	140	31	-0.21	-0.10
10	137	34	-0.42	-0.18
11	146	68	0.21	0.04
12	NT	NT		
13	146	22	0.21	0.13

Statistics

Assigned Value	143	4
Spike	153	4
Homogeneity Value	160	30
Robust Average	143	4
Median	144	4
Mean	143	
N	8	
Max.	150	
Min.	137	
Robust SD	5	
Robust CV	3.5%	


Kernel Density
Density
Result
Results: S2 - Se
Assigned Value = 143 ± 4 µg/L
Results (µg/L)
Laboratory
10
3
9
1
8
11
13
7
12
2
4
6
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Se
Target Standard Deviation 14 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-0.4
-0.2
-0.2
0.0
0.1
0.2
0.2
0.5

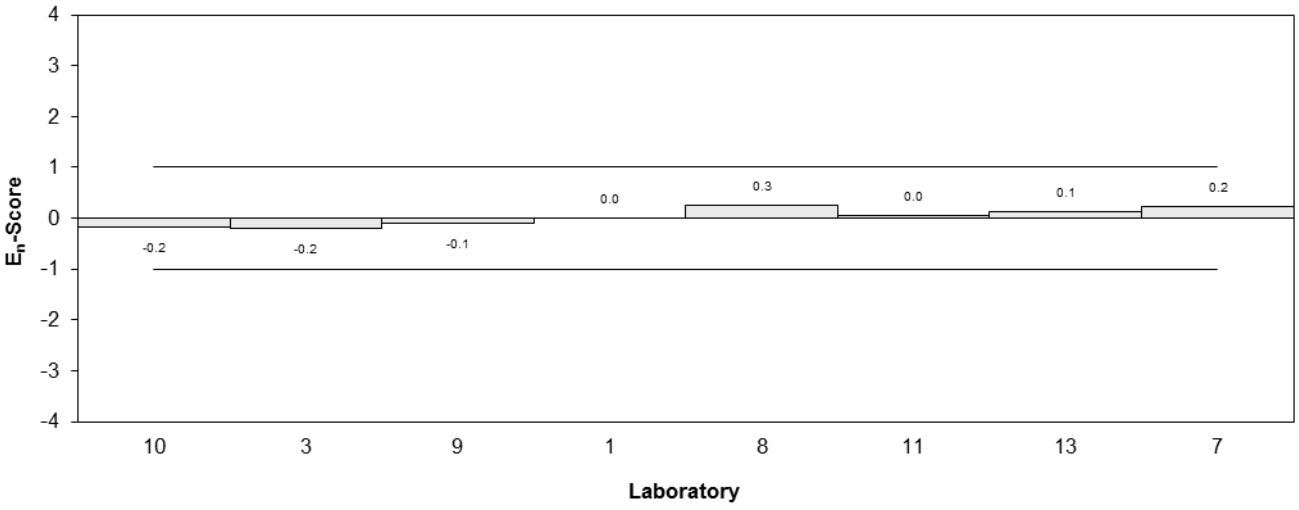

En-Scores: S2 - Se
En-Score
Laboratory
-0.2
-0.2
-0.1
0.0
0.3
0.0
0.1
0.2

Figure 36

Table 40

Sample Details

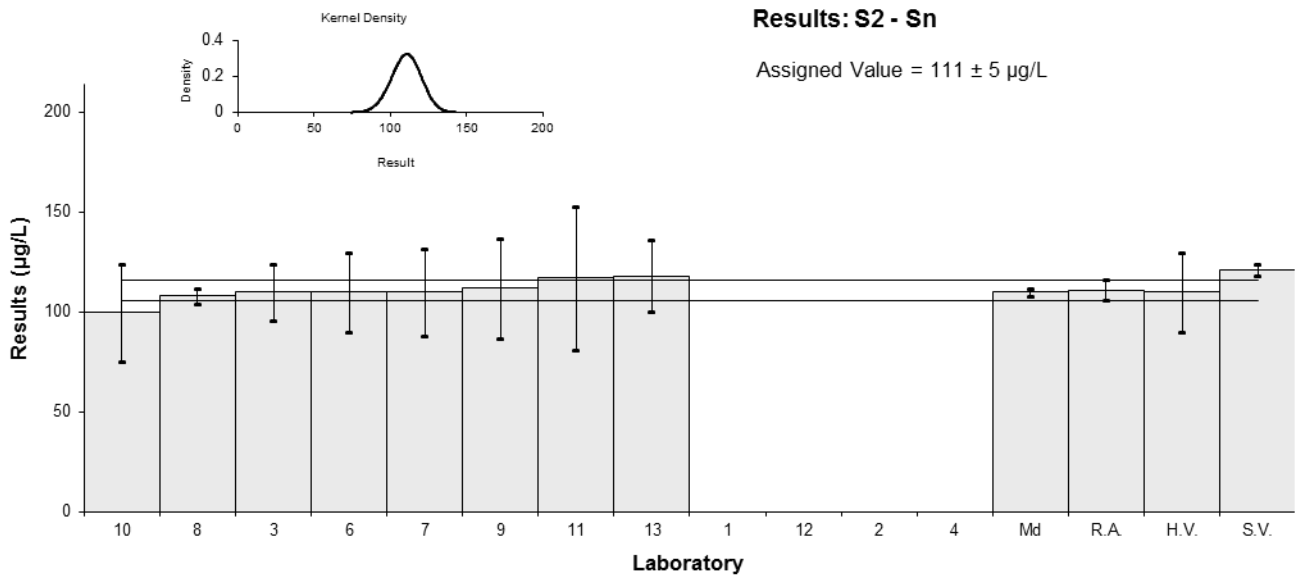
Sample No.	S2
Matrix.	Sea Water
Analyte.	Sn
Units	µg/L

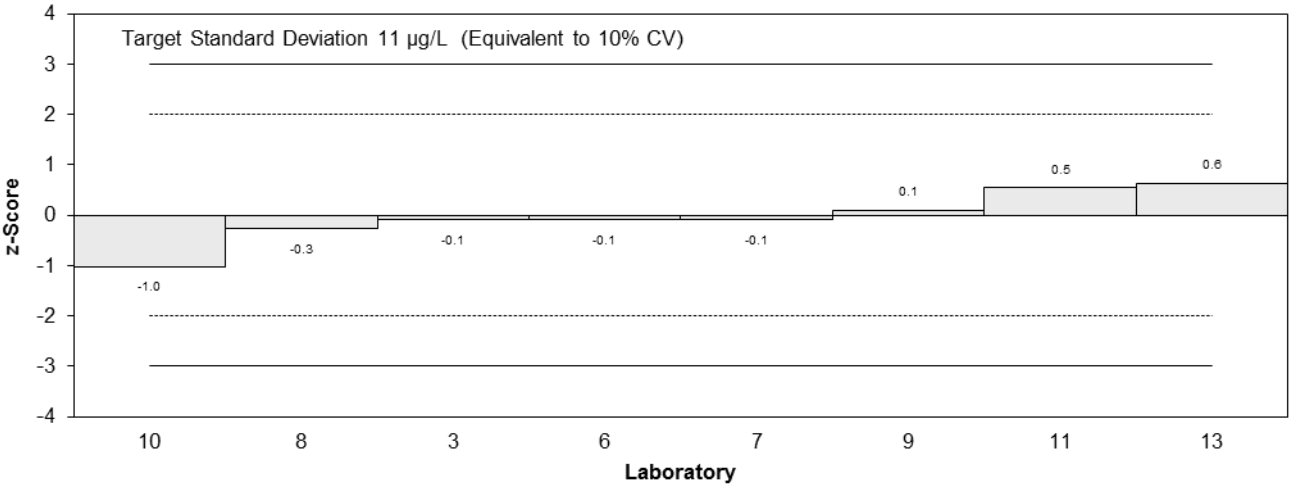
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	NT	NT		
3	110	14	-0.09	-0.07
4	NT	NT		
6	110	20	-0.09	-0.05
7	110	22	-0.09	-0.04
8	108	4.02	-0.27	-0.47
9	112	25	0.09	0.04
10	99.7	24.5	-1.02	-0.45
11	117	36	0.54	0.17
12	NT	NT		
13	118	18	0.63	0.37

Statistics

Assigned Value	111	5
Spike	121	3
Homogeneity Value	110	20
Robust Average	111	5
Median	110	2
Mean	111	
N	8	
Max.	118	
Min.	99.7	
Robust SD	6	
Robust CV	5.4%	


Kernel Density
Density
Result
Results: S2 - Sn
Assigned Value = 111 ± 5 µg/L
Results (µg/L)
Laboratory
10
8
3
6
7
9
11
13
1
12
2
4
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Sn
Target Standard Deviation 11 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-1.0
-0.3
-0.1
-0.1
-0.1
0.1
0.5
0.6

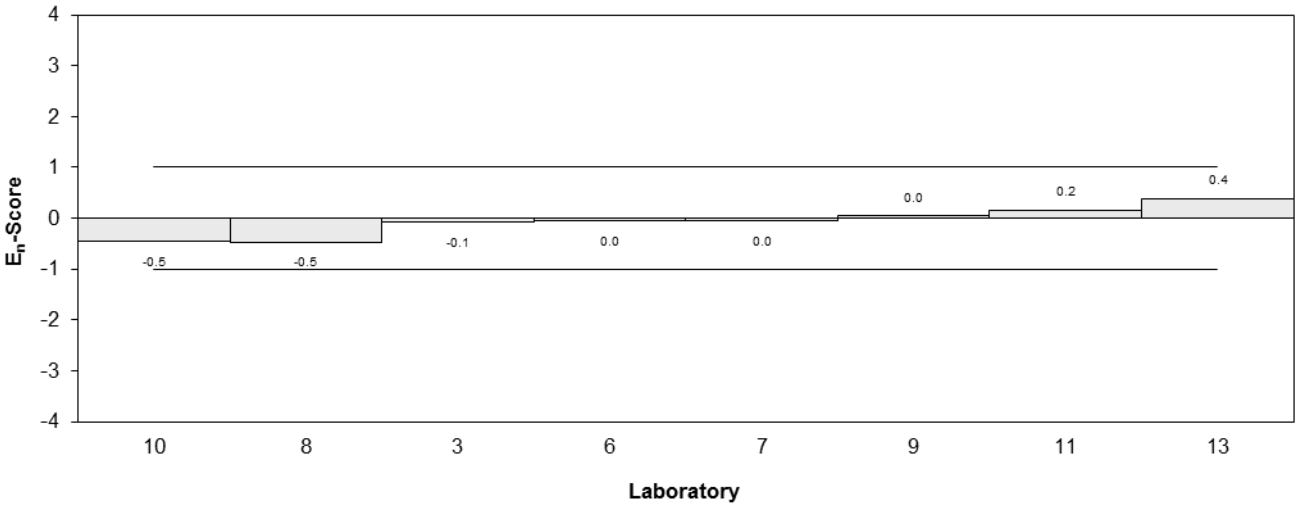

En-Scores: S2 - Sn
En-Score
Laboratory
-0.5
-0.5
-0.1
0.0
0.0
0.0
0.2
0.4

Figure 37

Table 41

Sample Details

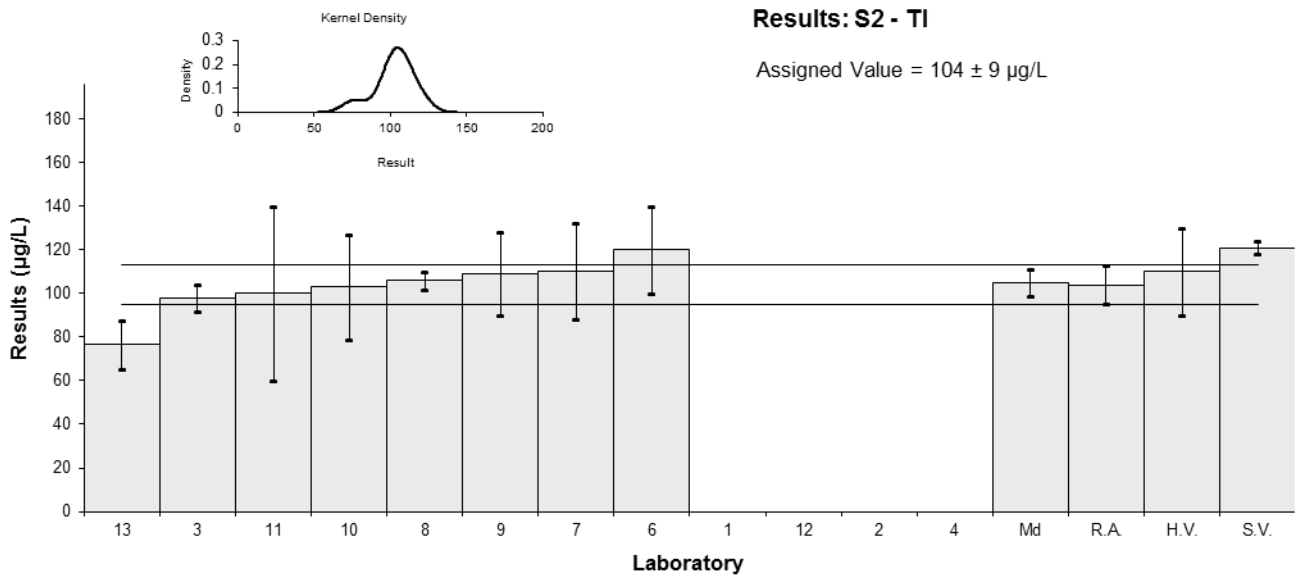
Sample No.	S2
Matrix.	Sea Water
Analyte.	Tl
Units	µg/L

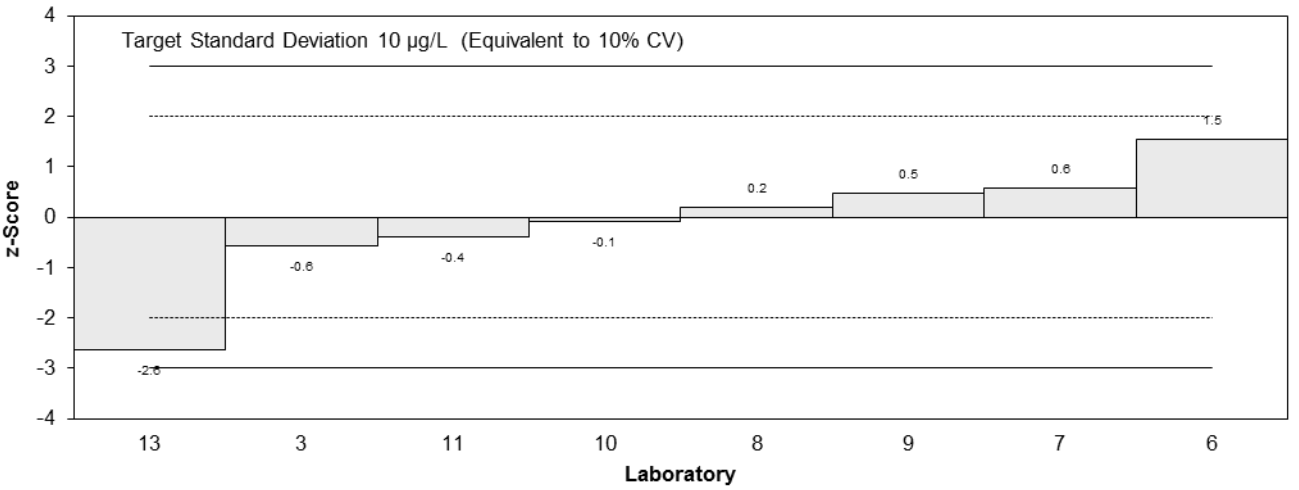
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	NT	NT		
3	98	6	-0.58	-0.55
4	NT	NT		
6	120	20	1.54	0.73
7	110	22	0.58	0.25
8	106	4.02	0.19	0.20
9	109	19	0.48	0.24
10	103	24	-0.10	-0.04
11	100	40	-0.38	-0.10
12	NT	NT		
13	76.5	11	-2.64	-1.93

Statistics

Assigned Value	104	9
Spike	121	3
Homogeneity Value	110	20
Robust Average	104	9
Median	105	6
Mean	103	
N	8	
Max.	120	
Min.	76.5	
Robust SD	11	
Robust CV	11%	


Kernel Density
Density
Result
Results: S2 - Tl
Assigned Value = 104 ± 9 µg/L
Results (µg/L)
Laboratory
13
3
11
10
8
9
7
6
1
12
2
4
Md
R.A.
H.V.
S.V.


z-Scores: S2 - Tl
Target Standard Deviation 10 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-2.6
-0.6
-0.4
-0.1
0.2
0.5
0.6
1.5

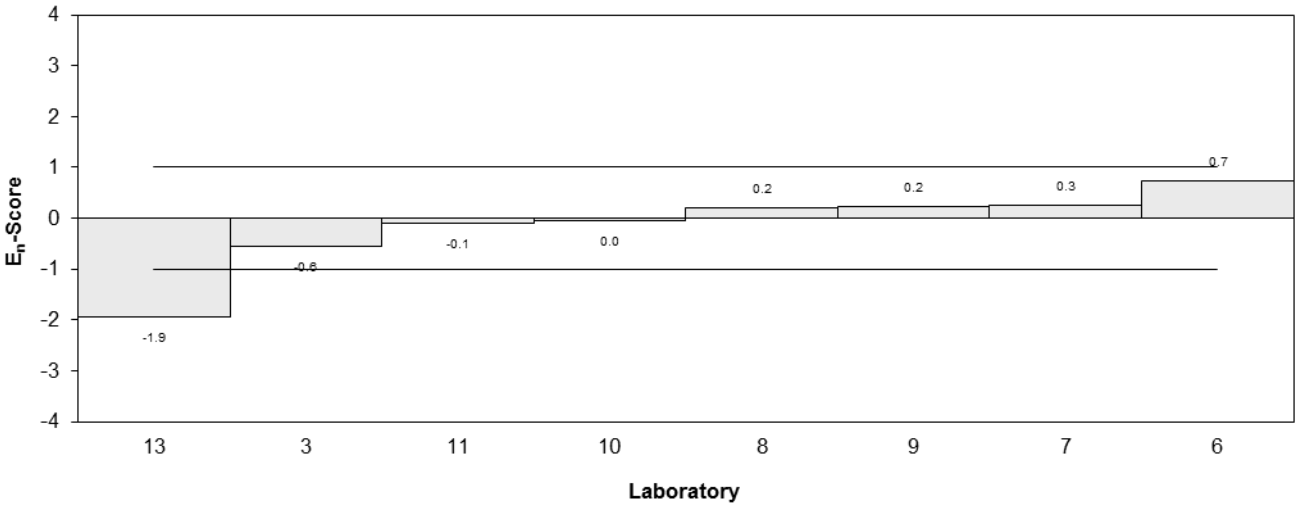

En-Scores: S2 - Tl
En-Score
Laboratory
-1.9
-0.6
-0.1
0.0
0.2
0.2
0.3
0.7

Figure 38

Table 42

Sample Details

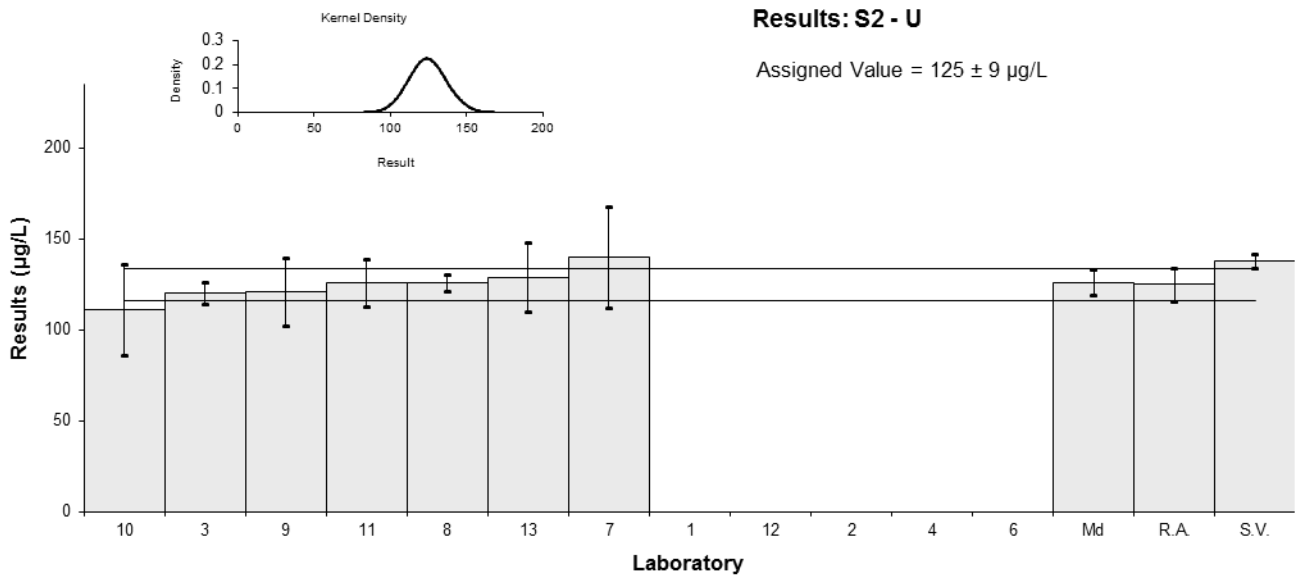
Sample No.	S2
Matrix.	Sea Water
Analyte.	U
Units	µg/L

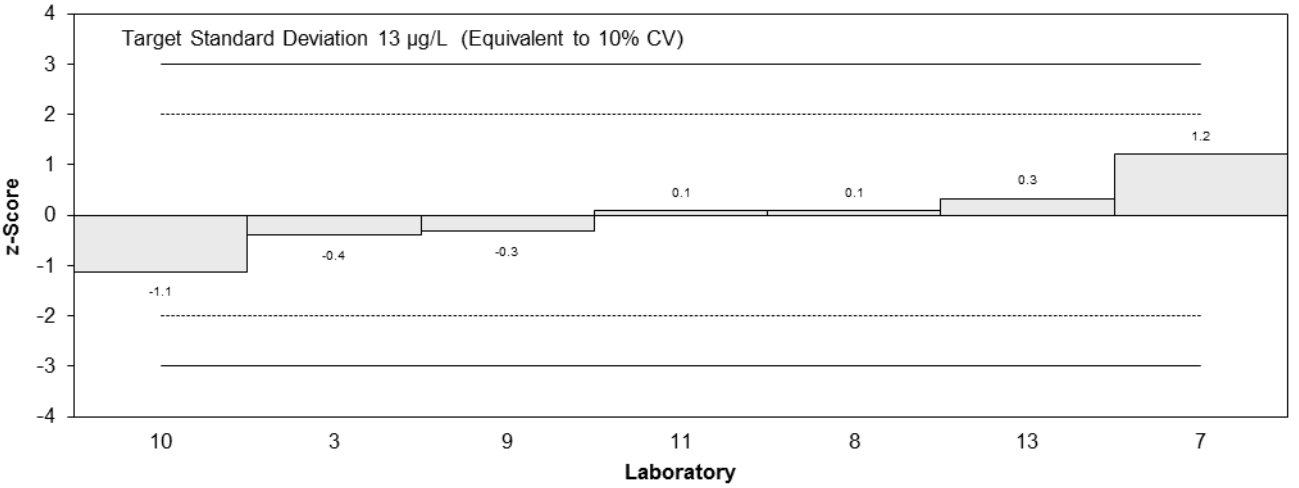
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	NT	NT		
3	120	6	-0.40	-0.46
4	NT	NT		
6	NT	NT		
7	140	28	1.20	0.51
8	126	4.45	0.08	0.10
9	121	19	-0.32	-0.19
10	111	25	-1.12	-0.53
11	126	13	0.08	0.06
12	NT	NT		
13	129	19	0.32	0.19

Statistics

Assigned Value	125	9
Spike	138	4
Robust Average	125	9
Median	126	7
Mean	125	
N	7	
Max.	140	
Min.	111	
Robust SD	10	
Robust CV	8%	


Kernel Density
Density
Result
Results: S2 - U
Assigned Value = 125 ± 9 µg/L
Results (µg/L)
Laboratory
10
3
9
11
8
13
7
1
12
2
4
6
Md
R.A.
S.V.


z-Scores: S2 - U
Target Standard Deviation 13 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-1.1
-0.4
-0.3
0.1
0.1
0.3
1.2

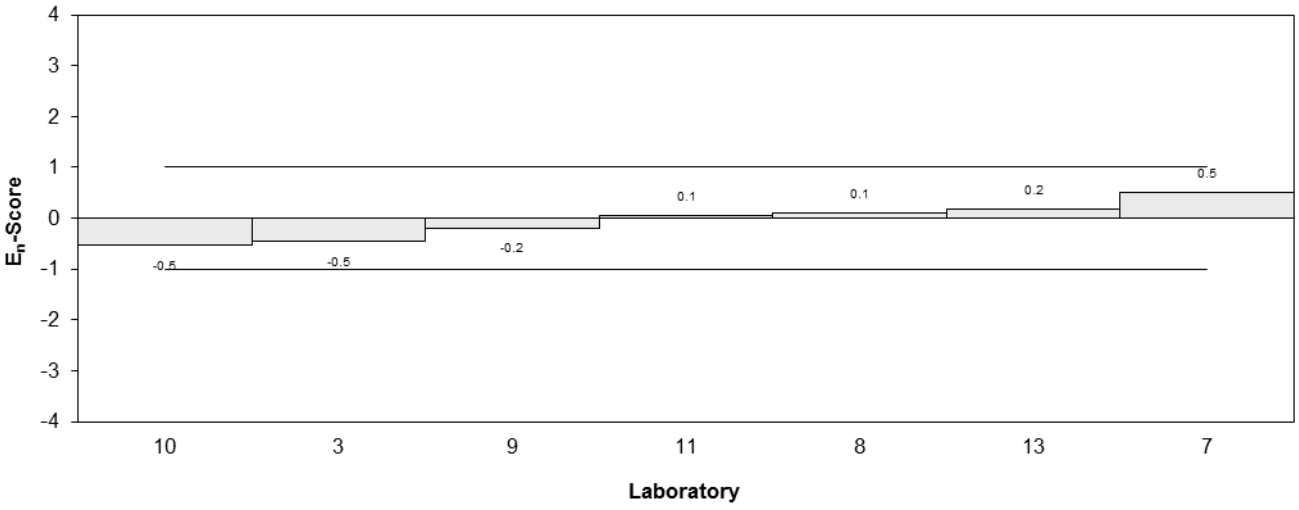

En-Scores: S2 - U
En-Score
Laboratory
-0.5
-0.5
-0.2
0.1
0.1
0.2
0.5

Figure 39

Table 43

Sample Details

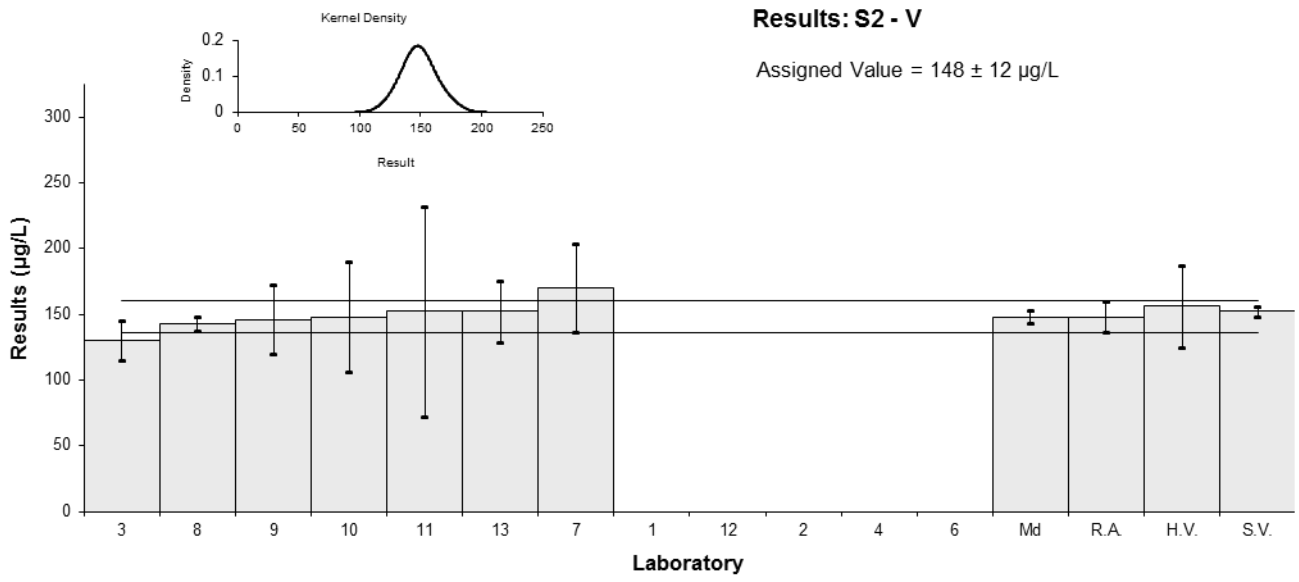
Sample No.	S2
Matrix.	Sea Water
Analyte.	V
Units	µg/L

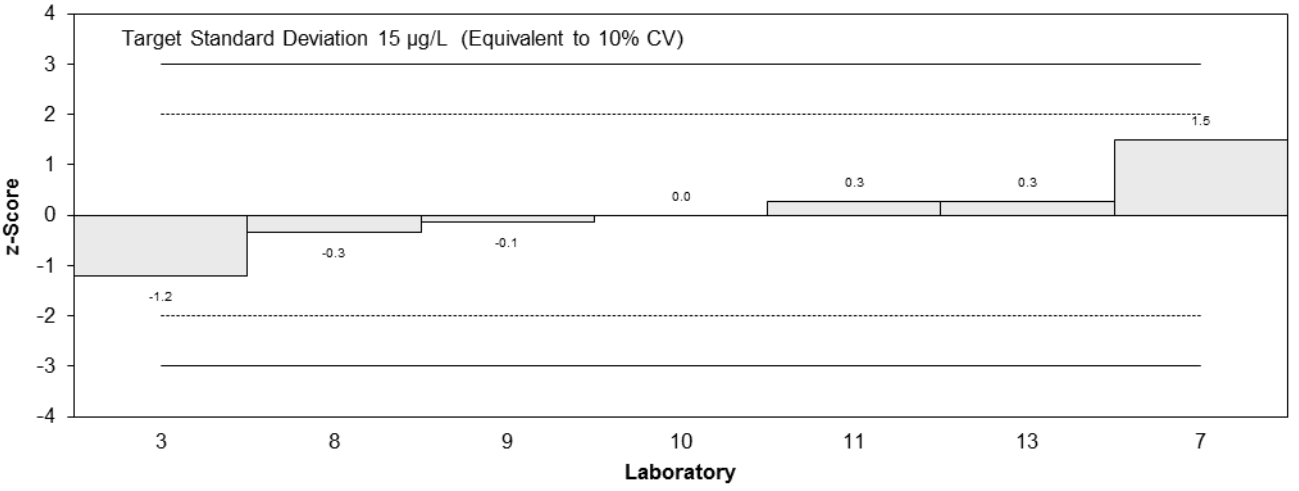
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	NR	NR		
2	NT	NT		
3	130	15	-1.22	-0.94
4	NT	NT		
6	NT	NT		
7	170	34	1.49	0.61
8	143	5.21	-0.34	-0.38
9	146	26	-0.14	-0.07
10	148	42	0.00	0.00
11	152	80	0.27	0.05
12	NT	NT		
13	152	23	0.27	0.15

Statistics

Assigned Value	148	12
Spike	153	4
Homogeneity Value	156	31
Robust Average	148	12
Median	148	5
Mean	149	
N	7	
Max.	170	
Min.	130	
Robust SD	13	
Robust CV	8.8%	


Kernel Density
Density
Result
Results: S2 - V
Assigned Value = 148 ± 12 µg/L
Results (µg/L)
Laboratory
3
8
9
10
11
13
7
1
12
2
4
6
Md
R.A.
H.V.
S.V.


z-Scores: S2 - V
Target Standard Deviation 15 µg/L (Equivalent to 10% CV)
z-Score
Laboratory
-1.2
-0.3
-0.1
0.0
0.3
0.3
1.5

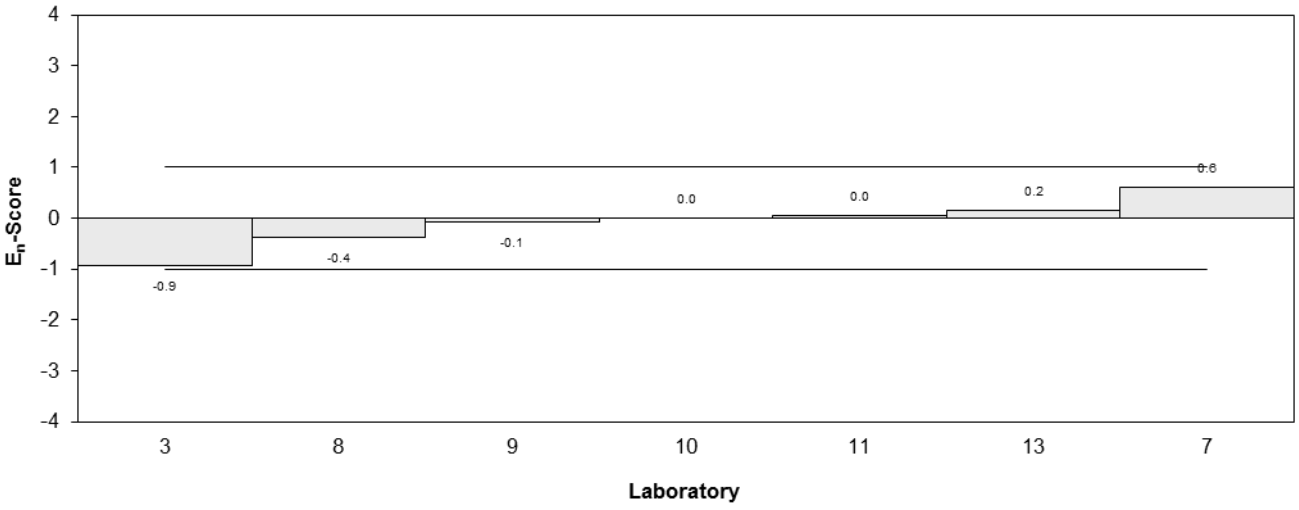

En-Scores: S2 - V
En-Score
Laboratory
-0.9
-0.4
-0.1
0.0
0.0
0.2
0.6

Figure 40

Table 44

Sample Details

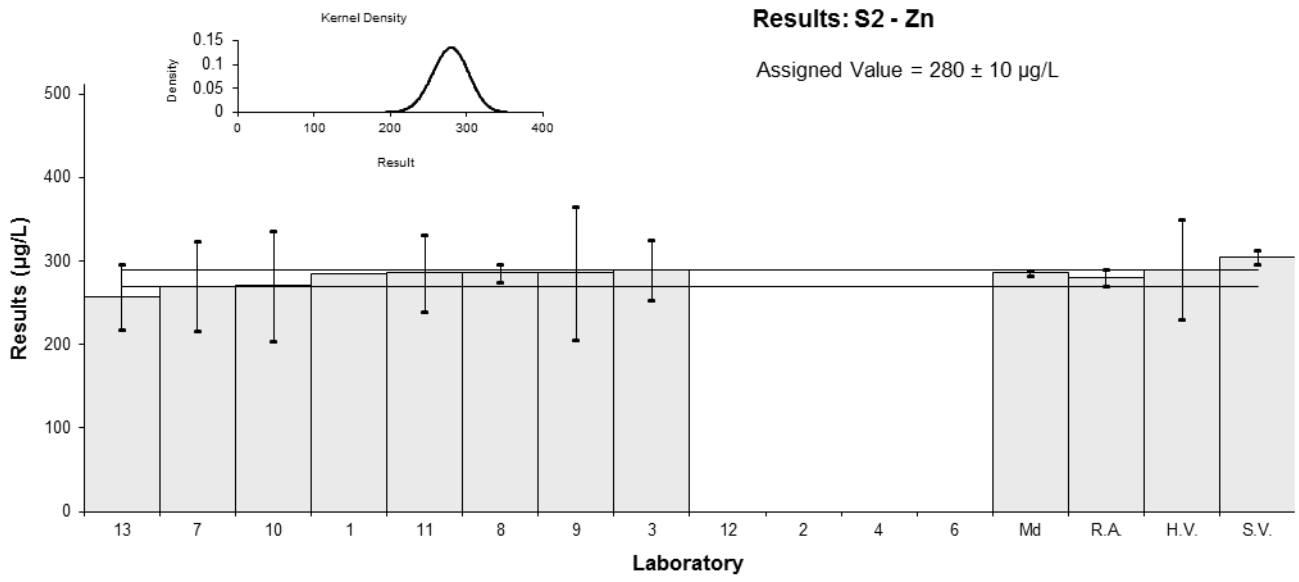
Sample No.	S2
Matrix.	Sea Water
Analyte.	Zn
Units	µg/L

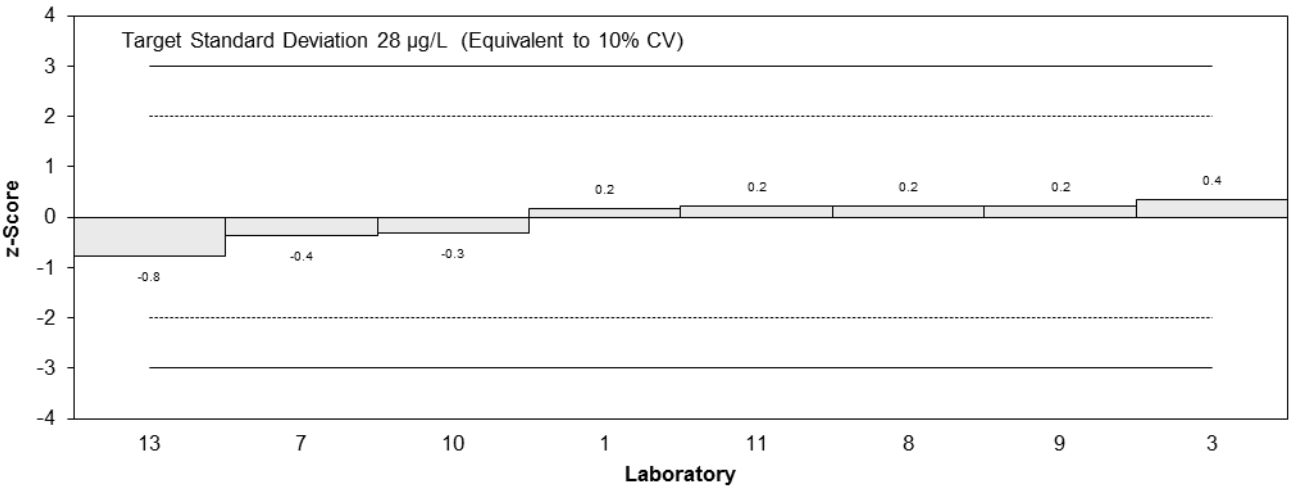
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	285	NR	0.18	0.50
2	NT	NT		
3	290	36	0.36	0.27
4	NT	NT		
6	NT	NT		
7	270	54	-0.36	-0.18
8	286	10.3	0.21	0.42
9	286	80	0.21	0.07
10	271	66	-0.32	-0.13
11	286	46	0.21	0.13
12	NT	NT		
13	258	39	-0.79	-0.55

Statistics

Assigned Value	280	10
Spike	305	9
Homogeneity Value	290	60
Robust Average	280	10
Median	286	3
Mean	279	
N	8	
Max.	290	
Min.	258	
Robust SD	12	
Robust CV	4.3%	


Kernel Density
Density
0.15
0.1
0.05
0
0
100
200
300
400
Result
Results: S2 - Zn
Assigned Value = 280 ± 10 µg/L
Results (µg/L)
500
400
300
200
100
0
13
7
10
1
11
8
9
3
12
2
4
6
Md
R.A.
H.V.
S.V.
Laboratory


z-Scores: S2 - Zn
Target Standard Deviation 28 µg/L (Equivalent to 10% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-0.8
-0.4
-0.3
0.2
0.2
0.2
0.2
0.4
13
7
10
1
11
8
9
3
Laboratory

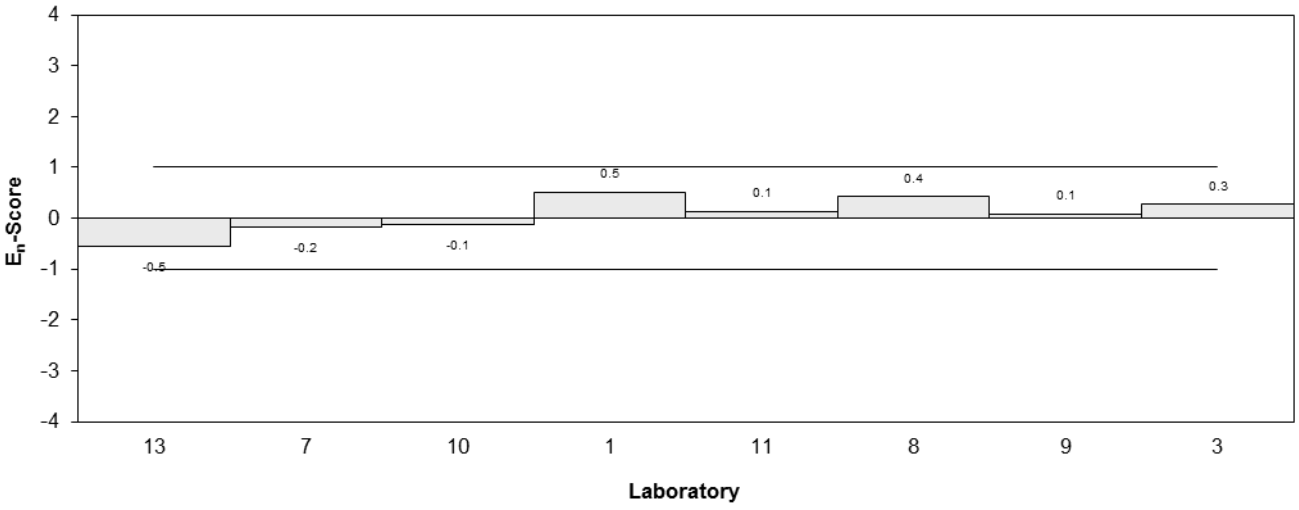

En-Scores: S2 - Zn
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.5
-0.2
-0.1
0.5
0.1
0.4
0.1
0.3
13
7
10
1
11
8
9
3
Laboratory

Figure 41

7 DISCUSSION OF RESULTS

7.1 Assigned Value

Sample S1 was filtered seawater while **Sample S2** was the same seawater unfiltered. A known amount of single element standard solutions was added to the two study samples.

Assigned Values were the robust average of participants' results. The robust averages 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 removed before calculation of each assigned value.[6] Appendix 2 sets out the calculation for the robust average of V in Sample S1 and its associated uncertainty.

Spike Value includes both the incurred and the fortified value with the exception of U in S1.

Assigned values, spike values and homogeneity values were in agreement with each other within their estimates of uncertainty for all elements of interest with the exception of spike value for U in S1.

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

7.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. Of 347 numerical results, 330 (95%) were reported with an expanded measurement uncertainty, indicating that the majority of laboratories have addressed this requirement of ISO 17025.[8] The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 3.

Approaches to estimating measurement uncertainty include: standard deviation of replicate analysis, Horwitz formula, 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 comparisons studies.[9 – 15]

Proficiency tests allow a check of the reasonableness of uncertainty estimates. Results and the expanded MU are presented in the bar charts for each analyte (Figure 2 to 41). In this study, the reported expanded measurement uncertainty has been over-estimated in some cases (e.g. Labs 13, 6, 7 for Ag in S1, Lab 3 for Be in S1 or Lab 2 for Cd in S1) or under-estimated (e.g. Lab 8 for P in S1 and Al in S2 or Lab 9 for Al in S1). As a simple rule of thumb, when the uncertainty estimate is smaller than the assigned uncertainty value or larger than the uncertainty of the assigned value plus twice the target standard deviation then this should be viewed as suspect.

Stable control samples that cover the whole analytical process (including extraction) and **have a matrix similar** to the samples; **or**

- Stable control samples **and** duplicate analyses if control samples do not cover whole analytical process (e.g. the control sample is a synthetic sample- we have to take into consideration uncertainties arising from different matrices); **or**
- When control samples are not stable, from analysis of natural duplicates (gives within-day variation for sampling and measurement) and long-term uncertainty component from the variation in the instrument calibration; **or**

- Replicate analyses performed on the same sample at different times to obtain estimates of intermediate precision; within-batch replication provides estimates of repeatability only.

The most common sources for estimating the method bias component for the measurement uncertainty calculation are from:

- Certified reference material recoveries; **or**
- Participation in PT studies (laboratory bias from at least 6 successful PT studies); **or**
- From sample spike recoveries.

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.[10, 12] An example of estimating measurement uncertainty using proficiency testing data only is given in Appendix 3.

Some laboratories attached estimates of the expanded measurement uncertainty to 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.

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 16.2 ± 1.701 µg/L, it is better to report 16.2 ± 1.7 µg/L or instead of 10.75 ± 1.20 µg/L, it is better to report 10.8 ± 1.2 µg/L.[9]

7.3 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 42. 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 347 results for which E_n-scores were calculated, 315 (91%) 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.

7.4 z-Score

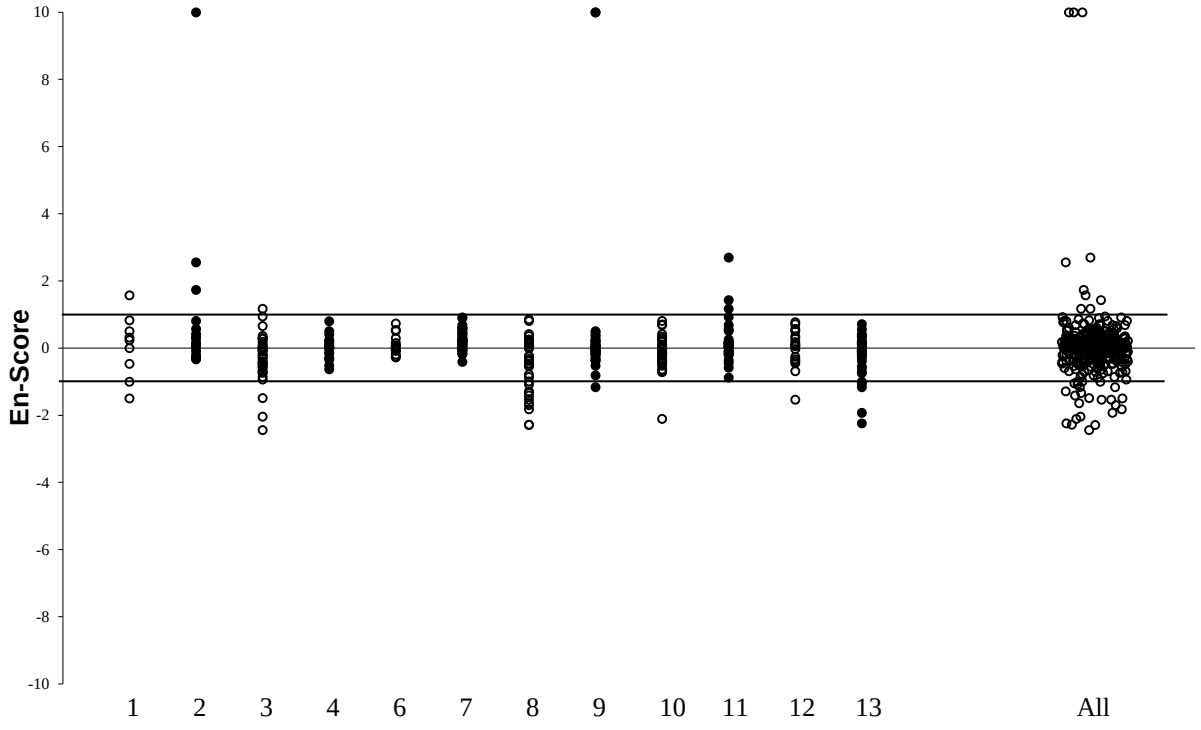
The z-score compares the participant's deviation from the assigned value with the target standard deviation set for proficiency assessment.

The target standard deviation defines satisfactory performance in a proficiency test. Target standard deviations equivalent to 10% to 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 fixed reference value points for assessment of laboratory performance, independent of group performance.

The between laboratory coefficient of variation predicted by the Thompson equation[7] and the participants' coefficient of variation resulted in this study are presented for comparison in Table 45.

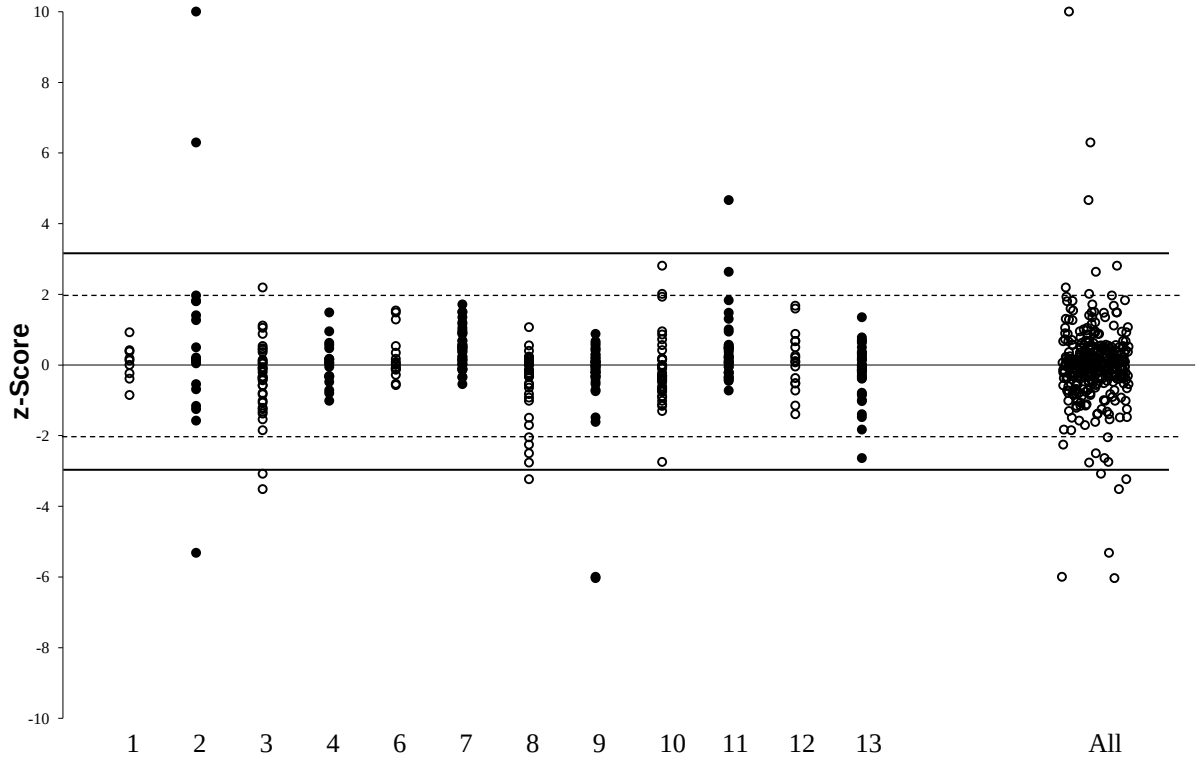
The dispersal of participants' z-scores is presented in Figure 43 (by laboratory code) and in Figure 44 (by test). Of 347 results for which z-scores were calculated, 328 (95%) returned a satisfactory score of $|z| \leq 2.0$ and 10 (3%) were questionable of $2.0 < |z| < 3.0$. Participants with multiple z-scores larger than 2 or smaller than -2 should check for laboratory bias.

Laboratories 1, 4, 6, 7, and 12 returned satisfactory z-scores for all analytes reported.



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

Figure 42 E_n-Score Dispersal by Laboratory



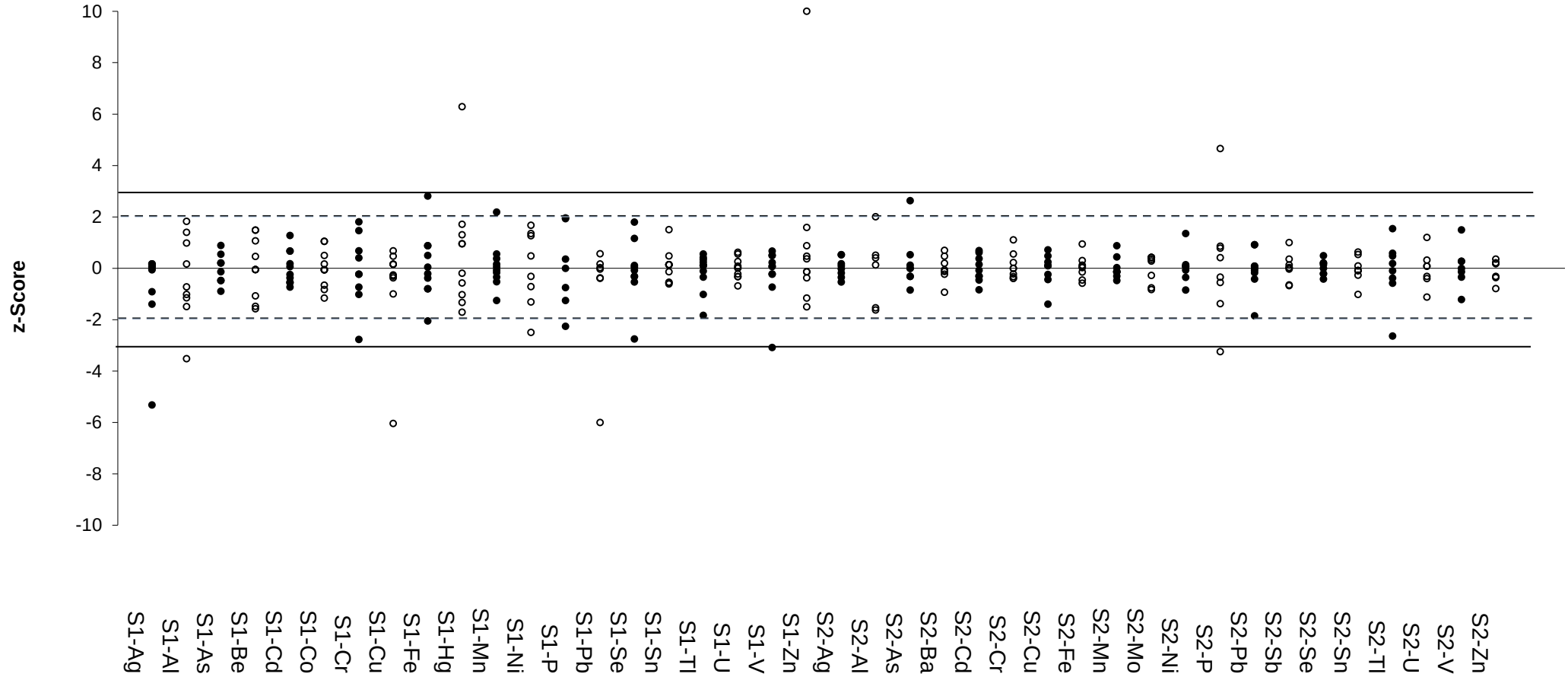
Scores of >10 or <-10 have been plotted as 10 or -10.

Figure 43 z-Score Dispersal by Laboratory

Table 45 Between Laboratory CV of this Study, Thompson CV and Set Target CV

Sample	Analyte	Assigned value	Between Laboratory CV*	Thompson/ Horwitz CV	Target SD (as PCV)
S1	Ag	5.95 µg/L	3%	22%	15%
S1	Al	15.7 µg/L	22%	22%	15%
S1	As	1.94 µg/L	10%	22%	15%
S1	Be	1.31 µg/L	19%	22%	15%
S1	Cd	1.09 µg/L	10%	22%	15%
S1	Co	1.21 µg/L	13%	22%	15%
S1	Cr	2.36 µg/L	21%	22%	15%
S1	Cu	12.7 µg/L	7.9%	22%	15%
S1	Fe	15.9 µg/L	17%	22%	15%
S1	Hg	0.175 µg/L	21%	22%	15%
S1	Mn	3.69 µg/L	9%	22%	15%
S1	Ni	1.68 µg/L	25%	22%	15%
S1	P	140 µg/L	36%	22%	20%
S1	Pb	0.995 µg/L	6.1%	22%	15%
S1	Se	3.15 µg/L	16%	22%	15%
S1	Sn	5.88 µg/L	7.8%	22%	15%
S1	Tl	2.95 µg/L	7.6%	22%	15%
S1	U	5.58 µg/L	7%	22%	15%
S1	V	4.65 µg/L	8.9%	22%	15%
S1	Zn	6.54 µg/L	16%	22%	15%
S2	Ag	114 µg/L	4.3%	22%	10%
S2	Al	780 µg/L	16%	17%	10%
S2	As	247 µg/L	6.2%	20%	10%
S2	Ba	344 µg/L	5%	19%	10%
S2	Cd	131 µg/L	5.9%	22%	10%
S2	Cr	180 µg/L	4.6%	21%	10%
S2	Cu	293 µg/L	5.7%	19%	10%
S2	Fe	329 µg/L	4.6%	19%	10%
S2	Mn	294 µg/L	4.2%	19%	10%
S2	Mo	144 µg/L	6.2%	21%	10%
S2	Ni	141 µg/L	6%	21%	10%
S2	P	580 µg/L	20%	17%	10%
S2	Pb	119 µg/L	6.8%	22%	10%
S2	Sb	309 µg/L	5.7%	19%	10%
S2	Se	143 µg/L	3.3%	21%	10%
S2	Sn	111 µg/L	5%	22%	10%
S2	Tl	104 µg/L	10%	22%	10%
S2	U	125 µg/L	8%	22%	10%
S2	V	148 µg/L	8.6%	21%	10%
S2	Zn	280 µg/L	4.1%	19%	10%

* Robust between Laboratories CV with outliers removed



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

Figure 44 z-Score Dispersal by Analyte

Table 46 Summary of Participants' Results and Performance for Total and Dissolved Elements

Lab Code	S1 - Al µg/L	S2 - Al µg/L	S1 - Ag µg/L	S2 - Ag µg/L	S1 - As µg/L	S2 - As µg/L	S2 - Ba µg/L	S1 - Be µg/L	S1 - Cd µg/L	S2 - Cd µg/L	S1 - Co µg/L	S1 - Cr µg/L	S2 - Cr µg/L	S1 - Cu µg/L	S2 - Cu µg/L
AV	15.7	780	5.95	114	1.94	247	344	1.31	1.09	131	1.21	2.36	180	12.7	293
HV	15.5	840	6.4	115	2.25	270	350	1.20	1.08	130	1.21	2.69	190	11.8	310
SV	12.2	853	6.08	122	2.34	258	367	1.30	1.11	141	1.19	2.21	186	10.9	314
1	NT	NR	NT	NR	NT	226	NR	NT	NT	136	NT	NT	173	NT	286
2	19	NT	1.2	NT	2	NT	NT	1	1	NT	1	3	NT	13	NT
3	7.4	660	6	110	<10	260	360	1.1	<1	120	1.4	<5	200	12	280
4	14	NT	6.1	NT	1.8	NT	NT	1.6	1.1	NT	1.2	2	NT	13	NT
6	NT	NT	6.1	120	NT	NT	340	1.6	1.3	130	NT	NT	180	NT	NT
7	18	820	6.1	120	2.2	250	340	1.4	1	140	1.4	2.6	190	13	300
8	13.3	811	6.03	108	2.1	239	312	1.52	1.05	127	1.24	1.38	180	12.2	296
9	12.2	654	6	113.8	1.8	247	351	1.3	1.2	139	1.2	2.5	176	1.2	296
10	16.1	937	5.14	116	1.68	239	342	1.3	1.03	127	1.09	2.28	173	12.1	314
11	20	790	5.9	115	<4	312	336	NT	0.97	125	1.2	2.88	184	13.6	307
12	13	NT	4.7	NT	2	NT	NT	1.3	1.2	NT	1.3	2.1	NT	14	NT
13	NT	NT	5.92	112	1.9	247	368	1.02	1.12	133	1.06	2.28	174	10.8	252

Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value, H.V. = Homogeneity Value, S.V. = Spike Value

Table 46 Summary of Participants' Results and Performance for Total and Dissolved Elements (continued)

Lab Code	S1 - Fe µg/L	S2 - Fe µg/L	S1 - Hg µg/L	S1 - Mn µg/L	S2 - Mn µg/L	S2 - Mo µg/L	S1 - Ni µg/L	S2 - Ni µg/L	S1 - P µg/L	S2 - P µg/L	S1 - Pb µg/L	S2 - Pb µg/L	S2 - Sb µg/L	S1 - Se µg/L	S2 - Se µg/L
AV	15.9	329	0.175	3.69	294	144	1.68	141	140	580	0.995	119	309	3.15	143
HV	14.7	379	0.192	3.85	300	150	1.69	150	140	500	1.04	120	300	4.42	160
SV	15.1	363	0.201	3.44	309	150	1.68	154	142	598	0.979	134	314	3.01	153
1	NT	333	NT	NT	NR	NR	NT	NR	NT	604	NT	130	NR	NT	143
2	16	NT	0.34	3	NT	NT	2	NT	195	NT	<1	NT	NT	4	NT
3	14	310	0.14	4.9	320	150	<10	140	105	500	<1	97	310	3.2	140
4	14	NT	0.2	3.5	NT	NT	1.6	NT	NR	NT	1	NT	NT	3	NT
6	NT	NT	0.16	NT	290	140	NT	NT	NT	NT	<1	120	310	NT	NT
7	18	330	0.22	3.9	290	150	1.8	160	140	560	<1	130	320	3.7	150
8	11	331	0.13	3.6	290	132	1.05	142	76.8	392	1.02	119	289	3.17	145
9	15	339	0.17	4	307	148	1.5	142	119	548	0.1	120	308	3	140
10	22.6	314	0.2	3.78	280	133	1.35	143	194	630	0.99	118	288	1.85	137
11	15.4	360	0.209	3.72	295	150	<7	136	NT	850	1.08	114	340	<4	146
12	18	NT	<0.5	3.4	NT	NT	2.1	NT	NT	NT	0.94	NT	NT	2.9	NT
13	17.1	324	0.148	3.65	285	149	2.02	129	150	625	0.937	117	313	3.11	146

Shaded cells are results which returned a questionable or unsatisfactory z-score. A.V. = Assigned Value, H.V.= Homogeneity Value, S.V. = Spike Value

Table 46 Summary of Participants' Results and Performance for Total and Dissolved Elements (continued)

Lab Code	S1 - Sn µg/L	S2 - Sn µg/L	S1 - Tl µg/L	S2 - Tl µg/L	S1 - U µg/L	S2 - U µg/L	S1 - V µg/L	S2 - V µg/L	S1 - Zn µg/L	S2 - Zn µg/L
AV	5.88	111	2.95	104	5.58	125	4.65	148	6.54	280
HV	6.1	110	2.94	110	NA	NA	4.17	156	7.6	290
SV	5.98	121	3.03	121	2.50	138	5.21	153	7.59	305
1	NT	NR	NT	NR	NT	NR	NT	NR	NT	285
2	6	NT	3	NT	5	NT	5	NT	17	NT
3	6	110	2.5	98	5.3	120	2.5	130	6.4	290
4	6	NT	3.2	NT	6.1	NT	4.7	NT	7	NT
6	5.4	110	3.1	120	NT	NT	NT	NT	NT	NT
7	7.2	110	3	110	5.6	140	4.8	170	6.4	270
8	5.39	108	3.05	106	5.65	126	4.49	143	5.07	286
9	6	112	2.9	109	5.3	121	4.5	146	7.4	286
10	5.34	99.7	3.13	103	6.05	111	4.14	148	5.4	271
11	6.3	117	2.8	100	5.4	126	5	152	6.9	286
12	NT	NT	3	NT	5.8	NT	4.7	NT	8.1	NT
13	5.76	118	2.14	76.5	5.59	129	5.12	152	6.18	258

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

7.5 Participants' Results and Analytical Methods for Total and Dissolved Elements

Sample S1 was filtered seawater. The analytes' concentration in this sample ranged from 0.175 to 140 µg/L. **Sample S2** was unfiltered seawater and participants were asked to report results for total elements. Analytes' concentration in this sample was 2 to 7 times higher than in Sample S1. A summary of participants' results and performance in the two study samples is presented in Table 46 and in Figures 43 and 44.

Low level Al, Ni and P in S1 were the tests which had the highest coefficient of variation, ranging from 22% to 36%.

Individual Element Commentary

Participants were requested to analyse the samples using their normal test method and to report a single result as they would normally report to a client. With the exception of one participant, all who reported results for total elements in S2 performed digestion. Most used a digestion temperature of 85°C to 100°C and two digested their samples at 170°C. Six laboratories used nitric acid and hydrochloric acid for extraction and two used only nitric acid. Laboratory 11 reported using only hydrochloric acid for Ag extraction. No relationship was evident between the results reported for total elements in S2 and the digestion method employed.

Instrumental measurement was one of the main factors that influenced the results for total and dissolved elements in the seawater samples. However, participants' performance does not reflect only instrumental performance, but also the performance of the analyst and of the analytical method used by the testing laboratory. Thus, these results should not be construed as an evaluation of a particular instrument.

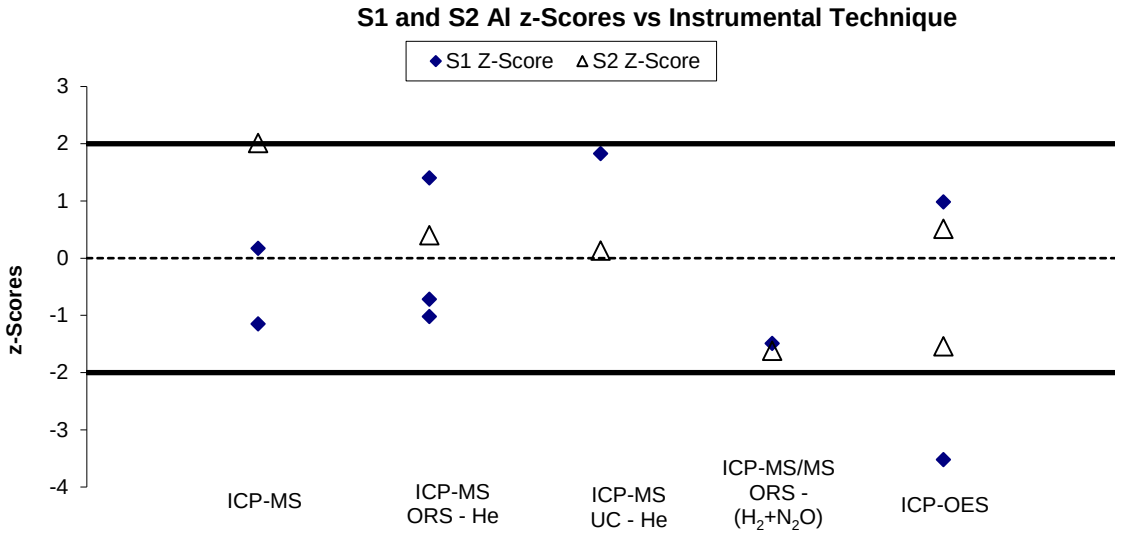
Participants used a wide variety of instrumental techniques, collision/reaction cells and cell gases. Most laboratories reported using ICP-MS with a collision/reaction cell; some used ICP-OES, and some only ICP-MS. One participant used ICP-MS measurements with a preconcentration and matrix separation step (seaFAST-ICP-MS) and one reported using ICP-MS/MS in collision mode or reaction mode with a H_2 and N_2O mix. Plots of participants' results and performance versus instrumental techniques used are presented in Figure 45.

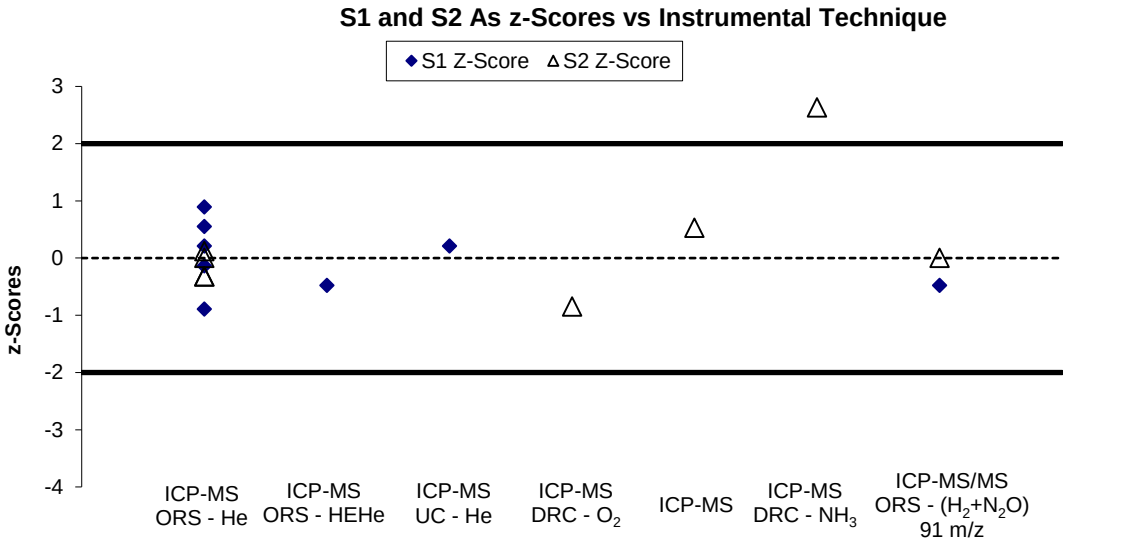
Aluminium level in S1 was low at 15.7 µg/L and this posed significant problems for laboratories. The between laboratory CV for Al in S1 was 22%.

Laboratory 9 should check the method used for Al measurements as their reported results for S1 and S2 were both low, with z-scores close to -2, which is an indication of laboratory and/or method bias.

Arsenic measurements at low levels posed no significant problems for laboratories. The between-laboratory CV for As in S1 was 10%. The unsatisfactory z-score is high, likely indicating unsolved interference problems (Figure 45).

Ammonia as reaction gas is not effective in removing $^{40}Ar^{35}Cl^+$ interferences on As. ICP-MS with H_2 or O_2 as reaction gas may be a better option. When testing As in seawater, the largest and most common interference to overcome in analysis by ICP-MS is $^{40}Ar^{35}Cl^+$. Hydrogen as reaction gas has been proven to reduce Ar-based interferences while the mass shifting of $^{75}As^+$ to m/z 91 as $^{75}AsO^{16+}$, by O_2 is also considered an effective solution for overcoming As interferences in seawater.[16]





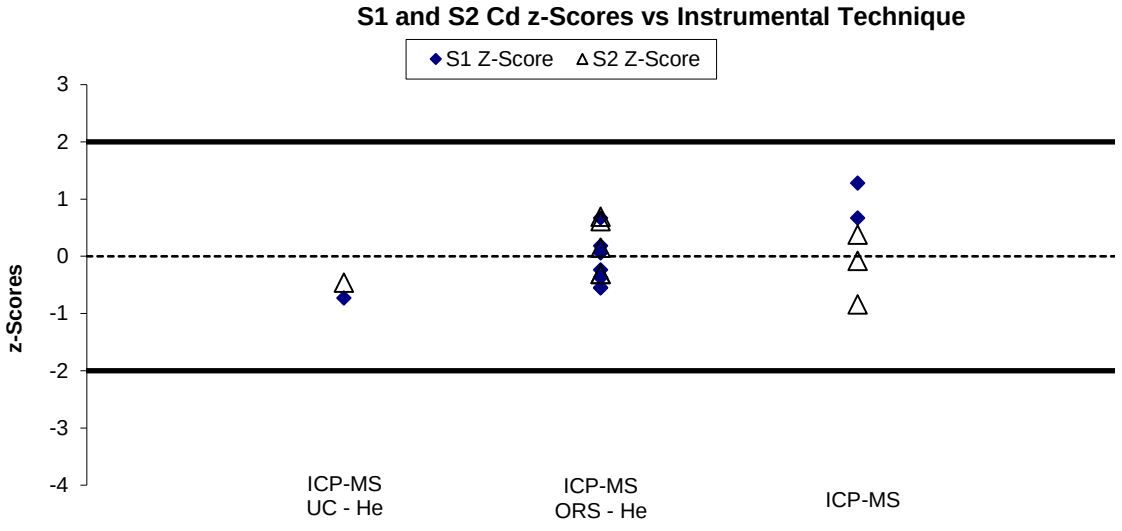
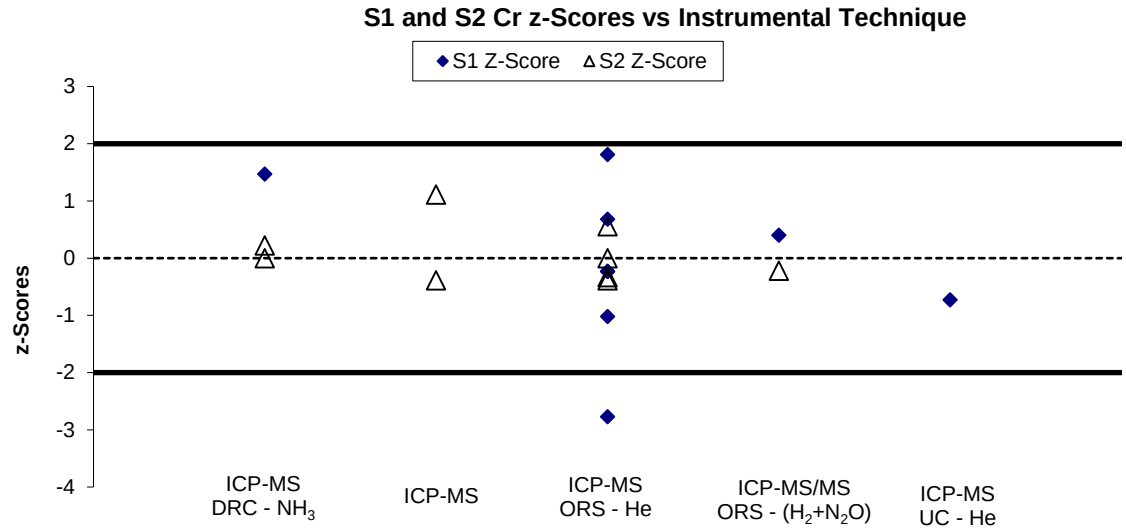
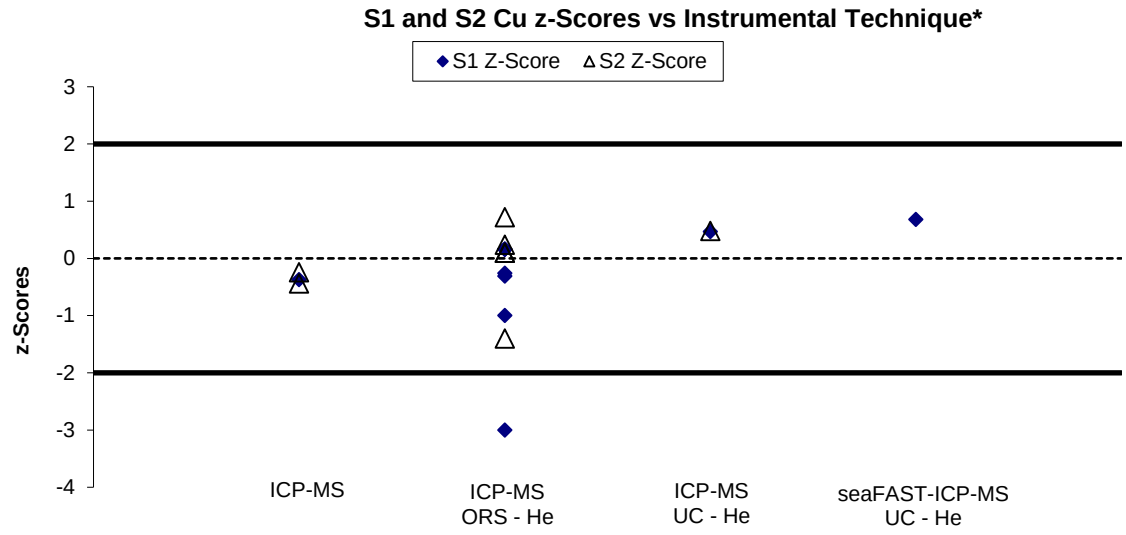
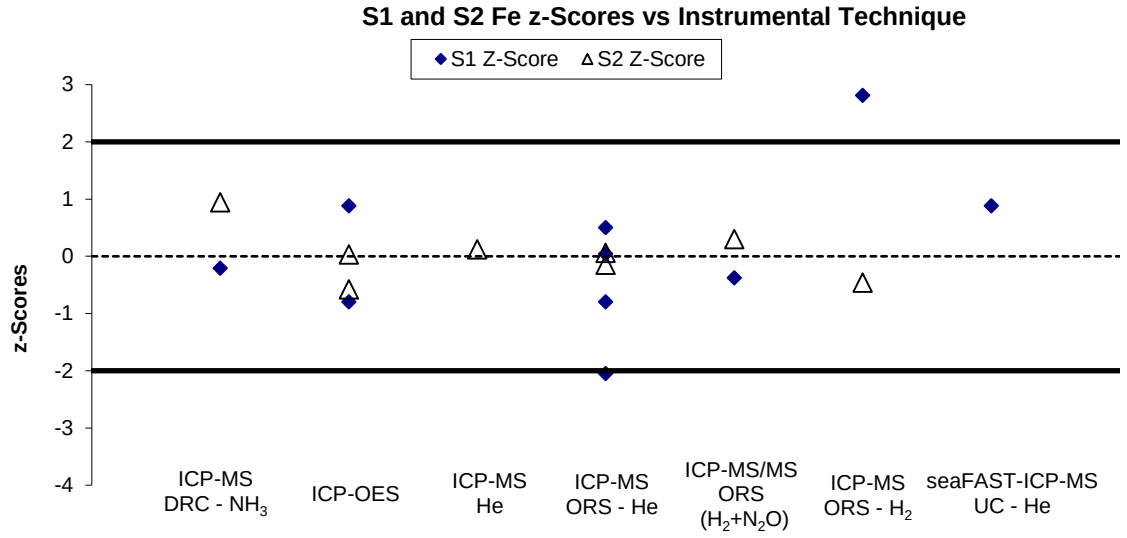


Figure 45 Participants' Results and Performance vs Instrumental Technique

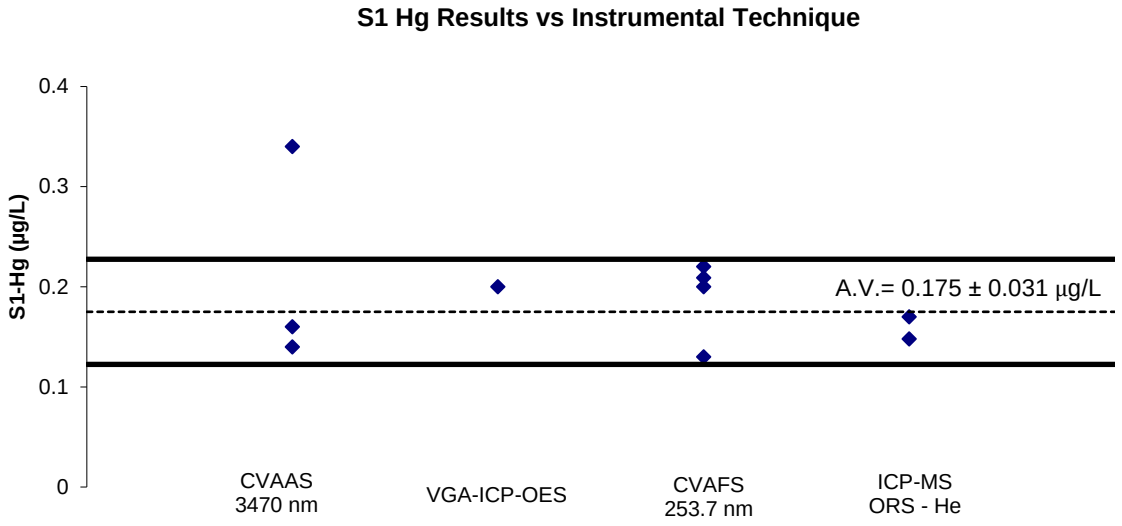


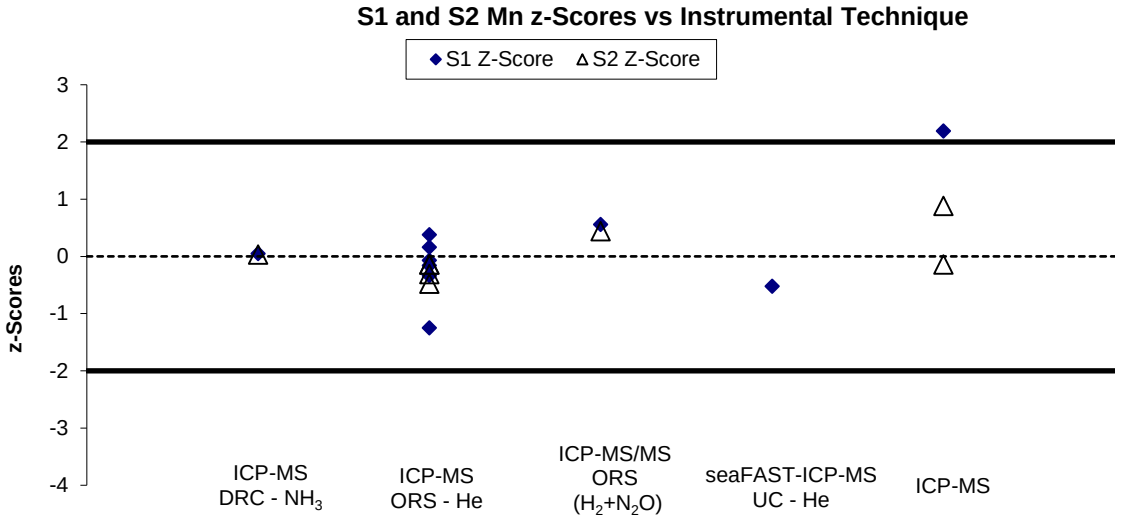




*Scores of <-3 have been plotted as -3.

Figure 45 Participants' Results and Performance vs Instrumental Technique (continued)





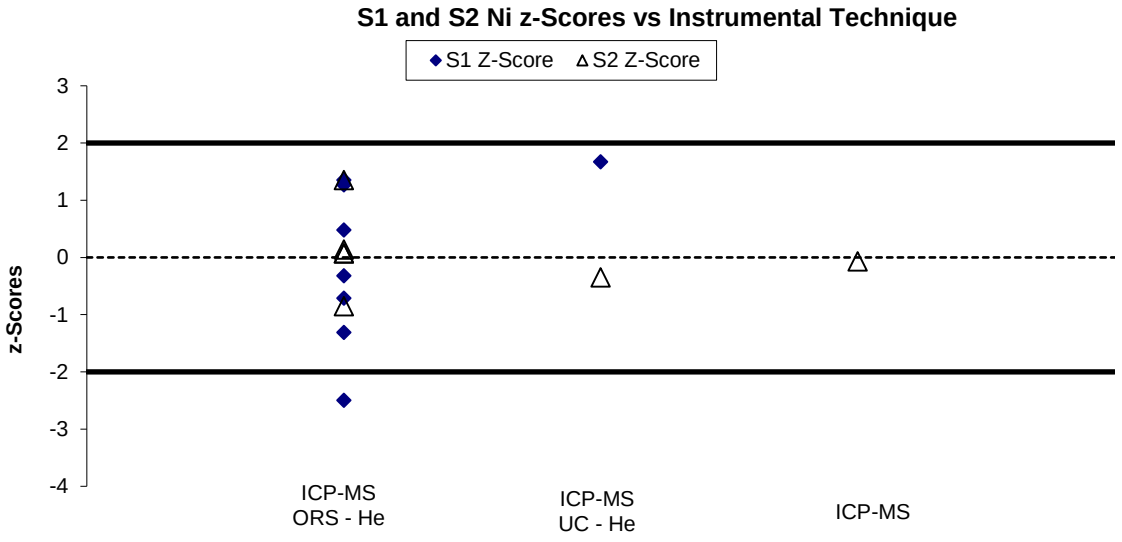
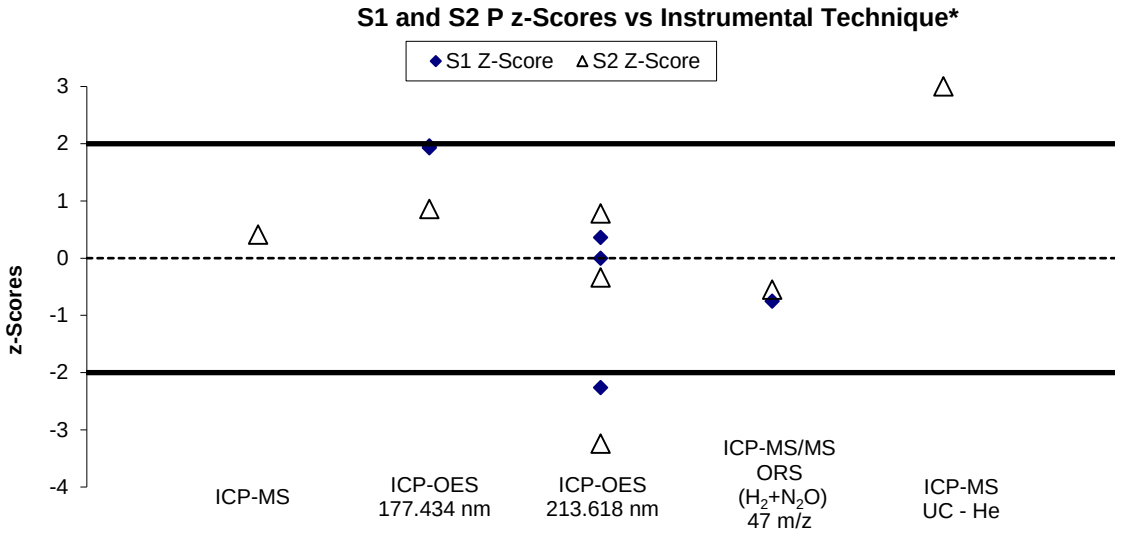
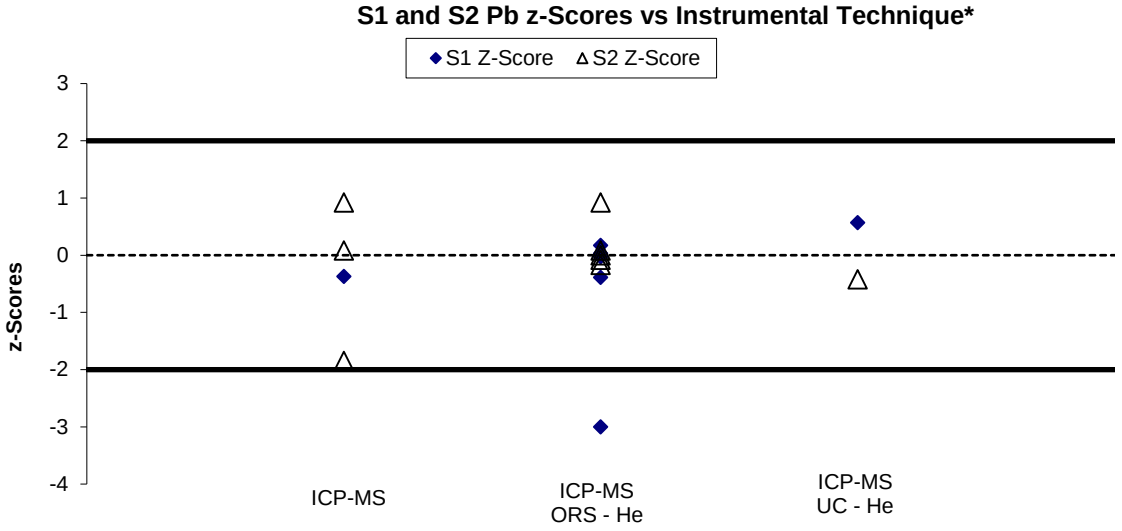
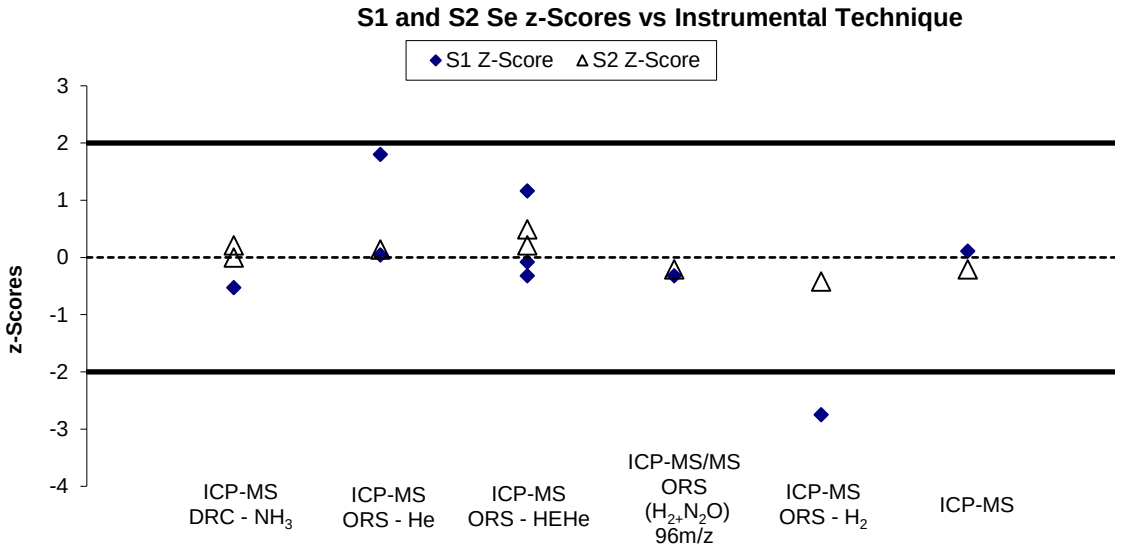


Figure 45 Participants' Results and Performance vs Instrumental Technique (continued)

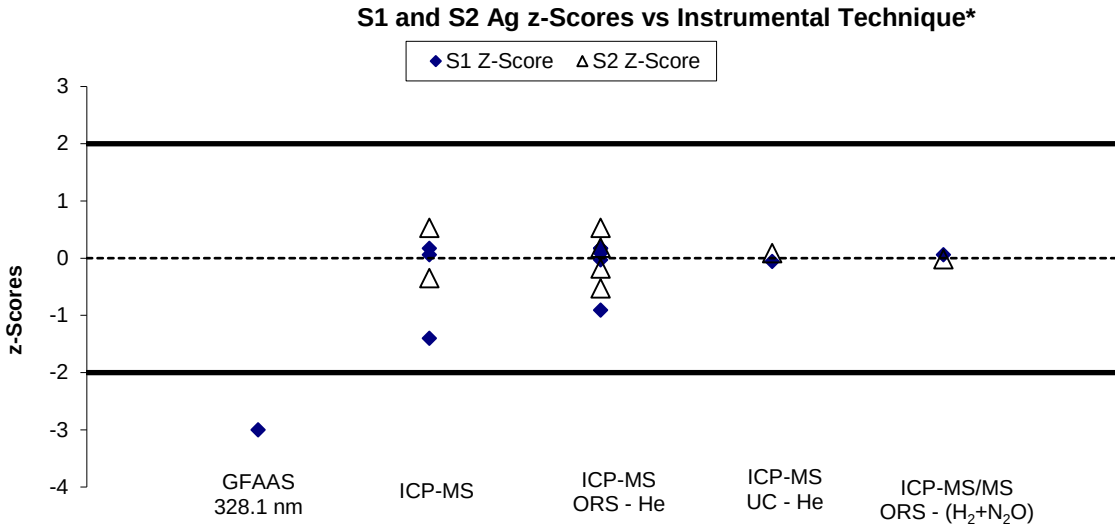


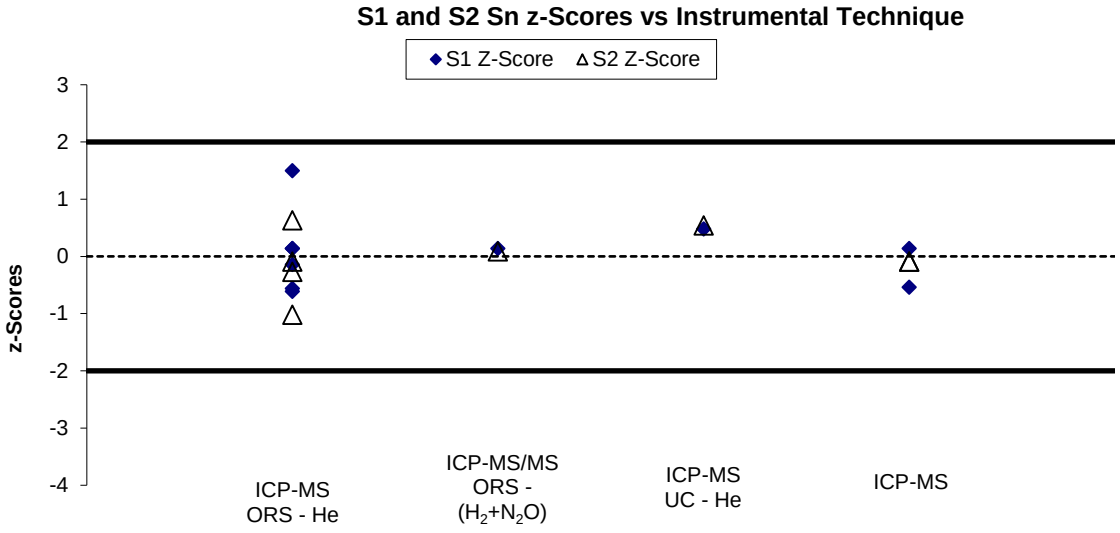




Scores of >3 or <-3 have been plotted as 3 or -3

Figure 45 Participants' Results and Performance vs Instrumental Technique (continued)





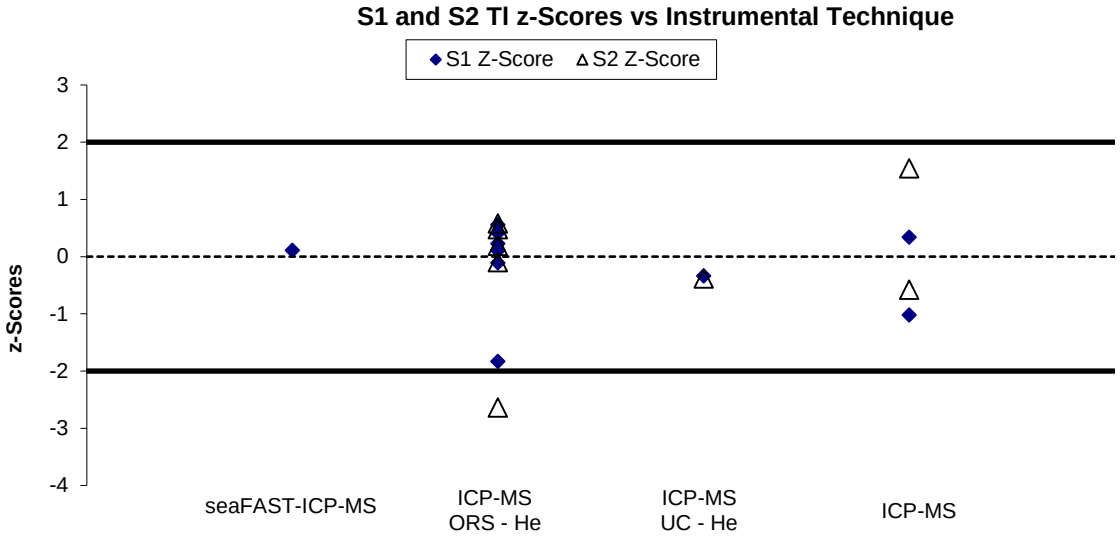


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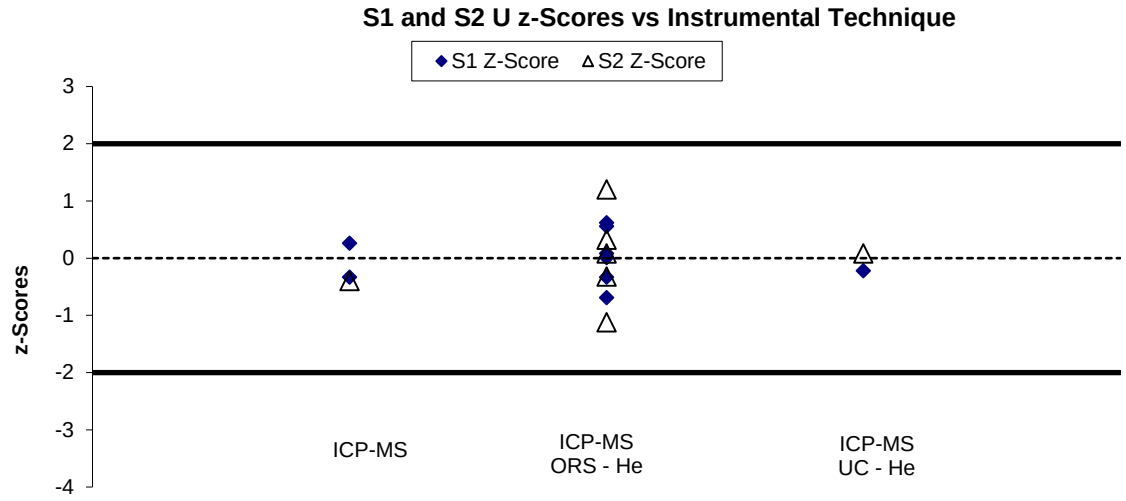
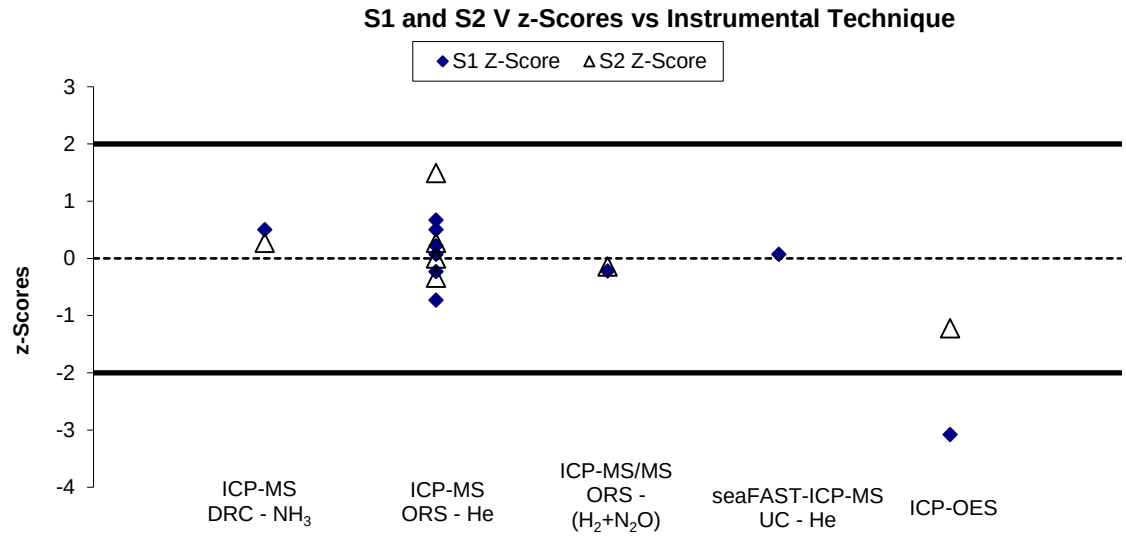
Figure 45 Participants' Results and Performance vs Instrumental Technique (continued)





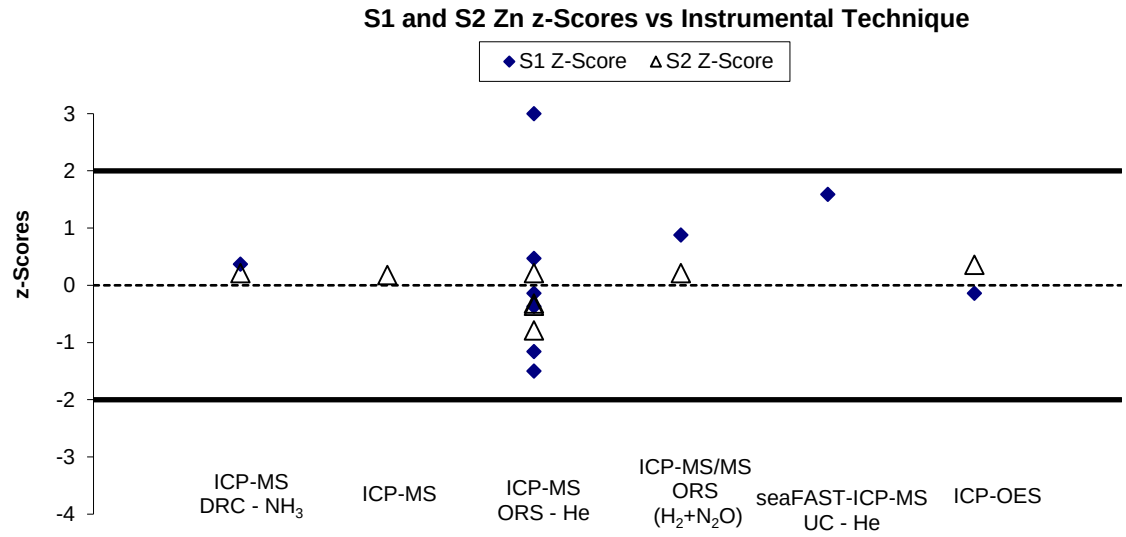


Figure 45 Participants' Results and Performance vs Instrumental Technique (continued)

Chromium and Nickel measurements at the low level in S1 challenged participating laboratories: the between laboratories CV was high, at 21% and 25% respectively.

Participants used a wide variety of instrumental techniques to overcome the interference problems with Cr in the seawater sample while with the exception of one all laboratories used ICP-MS in collision mode for Ni measurements (Figure 45).

Iron and Zinc The coefficient of variation in S1 for Fe and Zn was 16% and 17% respectively. These elements are known to be ubiquitous in the environment and controlling Fe or Zn contamination is a challenge for laboratories. No relationship between the results reported for these elements and the instrumental technique used was evident.

Mercury Use of expired standards or those not prepared fresh from standard stock solutions before measurement could be a cause of high Hg results.

Phosphorus assigned value in S1 was 140 µg/L and the between laboratory coefficient of variation was high at 36%. Most laboratories used ICP-OES with a wavelength of 213.618 nm or 177.4 nm for P measurements in S1. One laboratory reported a satisfactory P result from ICP-MS/MS measurements in reaction mode using a mixture of H_2 and N_2O as reaction gases (Figure 45).

Selenium Participants reported using 6 different instrumental techniques: ICP-MS in collision, reaction or MS/MS mode and with various collision/reaction gases: He, HEHe, NH_3, H_2+N_2O and H_2. With the exception of one, all results reported for Se were in good agreement with each other and with the assigned value.

Vanadium level in S1 was low at 4.65 µg/L, and ICP-OES might not be the right technique for V measurements below 5 ppb level in the solution.

Comparisons of Participants' Performance in Samples S1 and S2

Plots of participants' performance in Samples S1 and S2 are presented in Figure 46. Plots of z-scores that are close to the zero axes are an indication of excellent accuracy.

Laboratories whose z-scores for an element in both samples S1 and S2 lie on the same side of the centre line may need to monitor their procedure as may be an indication of method bias.

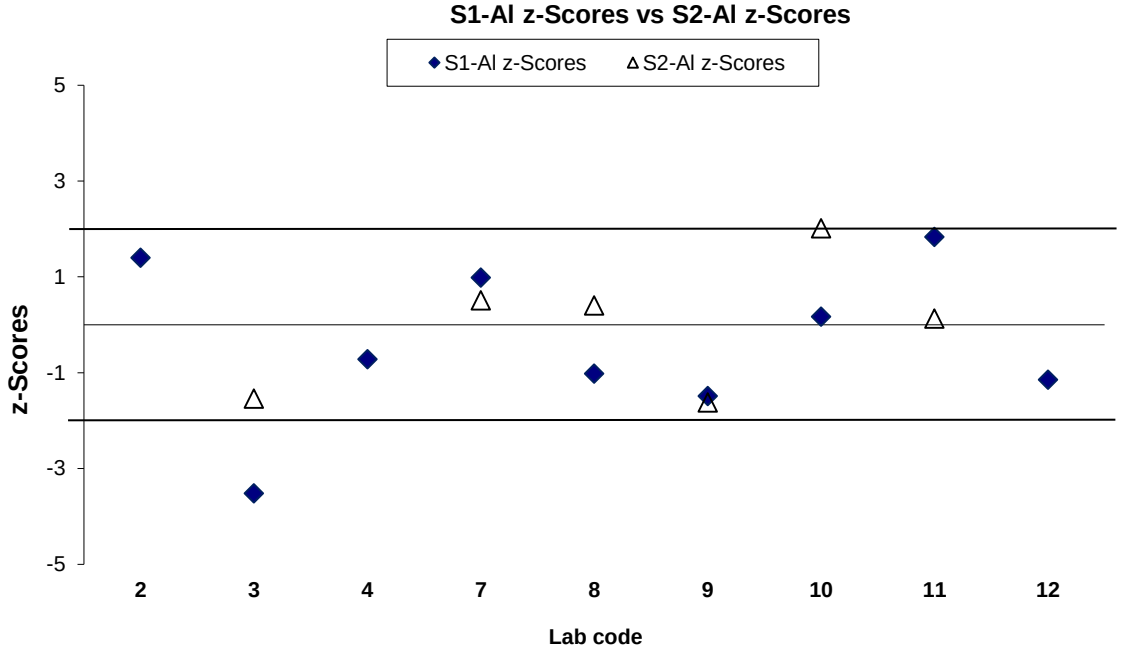
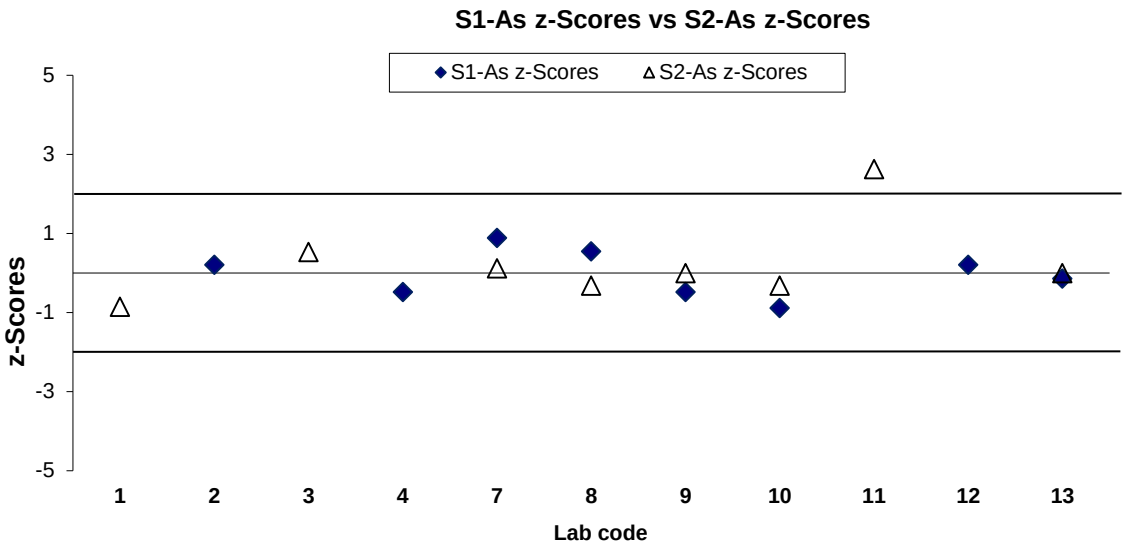
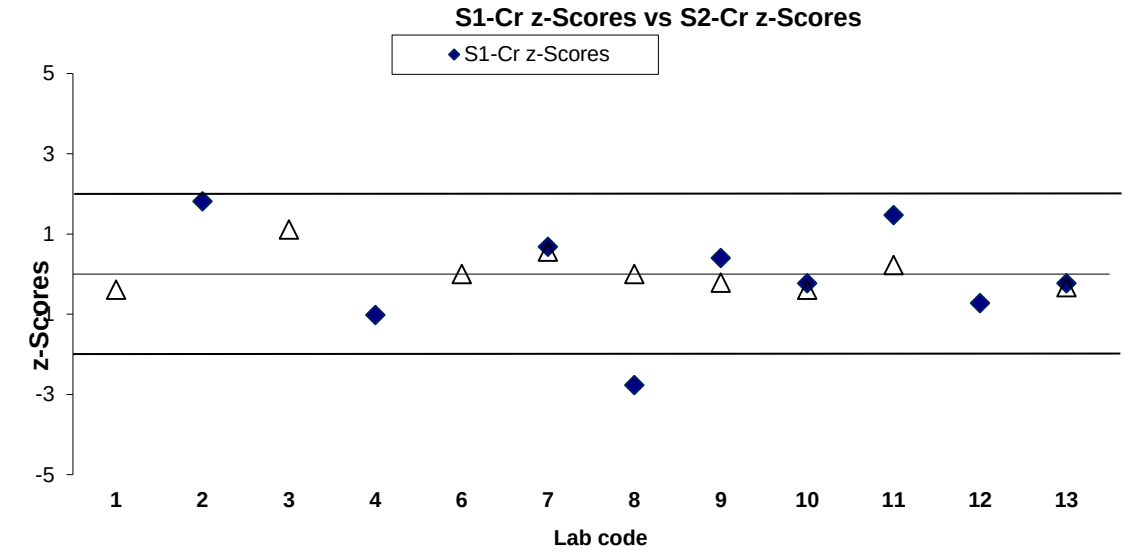


Figure 46 Comparisons of Participants' Performance in S1 and S2





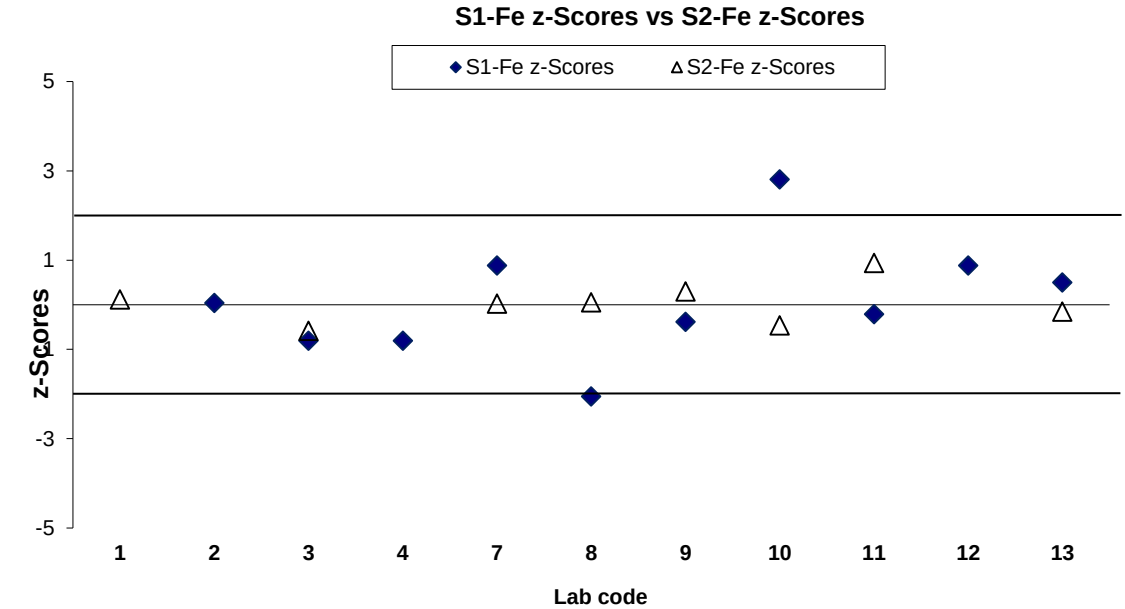
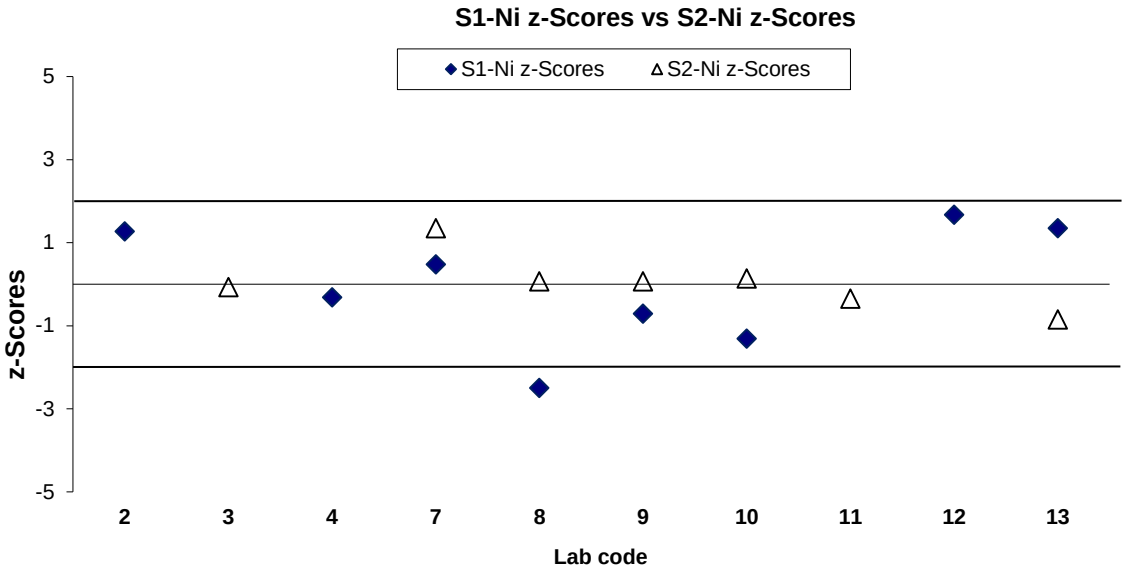
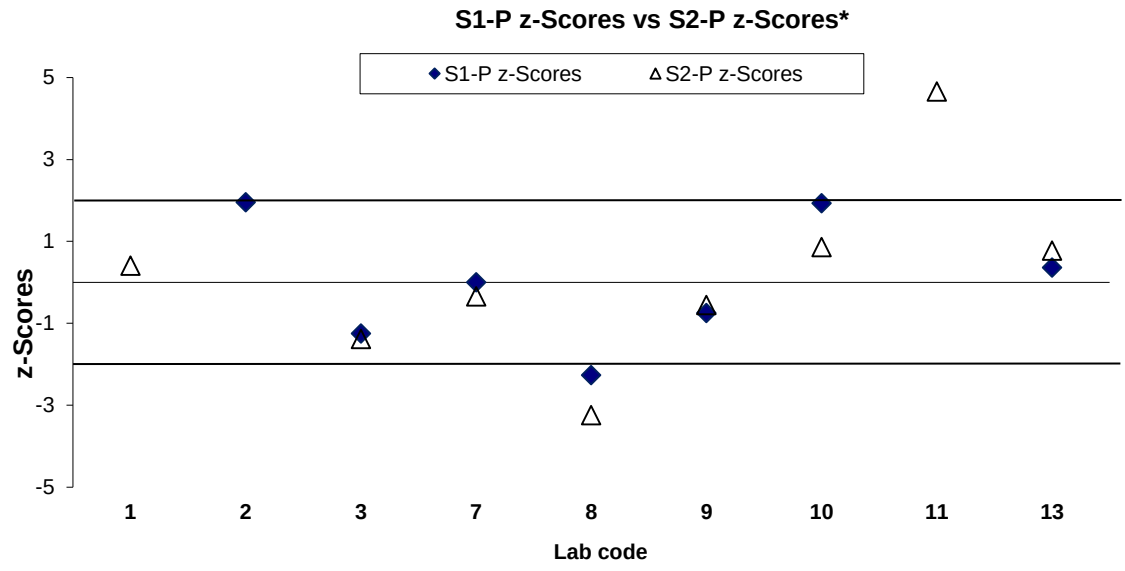
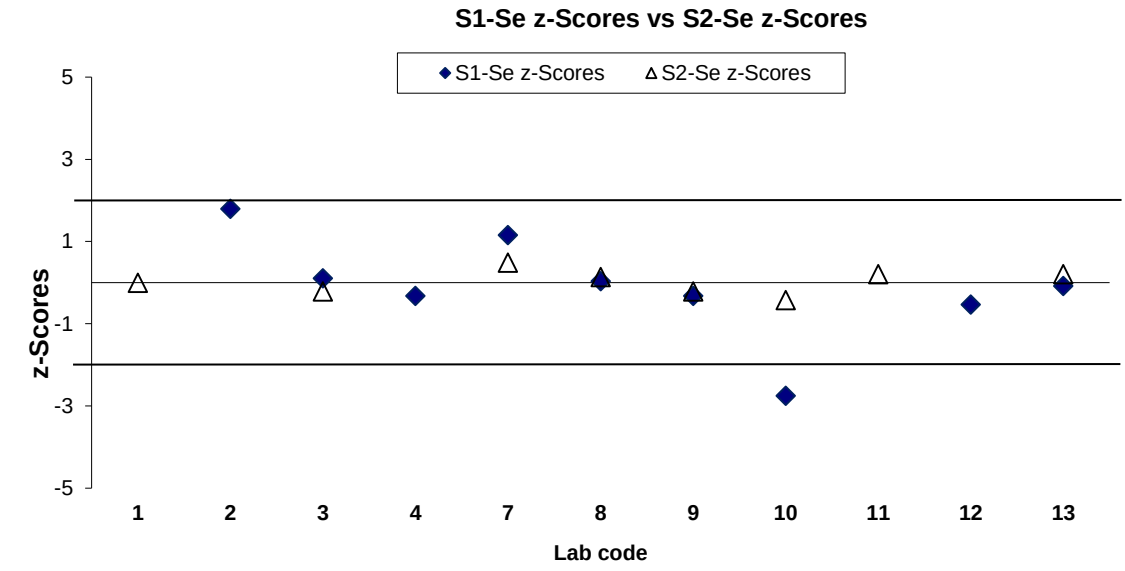


Figure 46 Comparisons of Participants' Performance in S1 and S2 (continued)







Scores of <-3 have been plotted as -3.

Figure 46 Comparisons of Participants' Performance in S1 and S2 (continued)

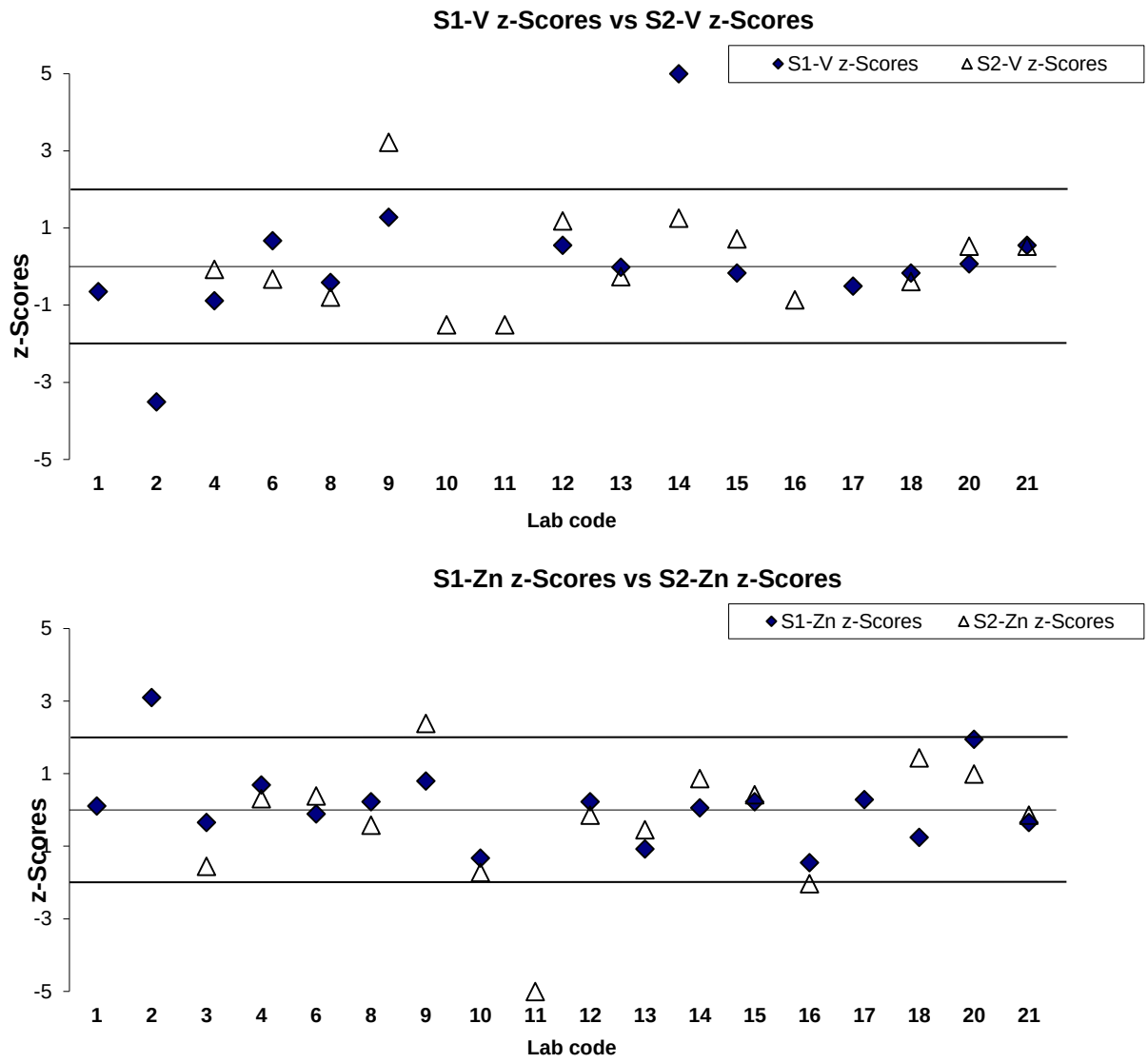


Figure 46 Comparisons of Participants' Performance in S1 and S2 (continued)

7.6 Comparison with Previous NMI Proficiency Tests of Metals in Water

AQA 19-16 is the 24th NMI proficiency test of metals in water and the 18th study in seawater.

Participants' performance in measurement of metals in seawater over last ten years is presented in Figure 47. Despite differences in the analytes' concentrations, on average participants' performance has improved over time.

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.

Over time, laboratories should expect at least 95% of their scores to lie within the range $|z| \leq 2$. Scores in the range $2 < |z| < 3$ can occasionally 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 is an indication of method or laboratory bias.

7.7 Reference Materials and Certified Reference Materials

Participants reported whether control samples (spiked samples, certified reference materials-CRMs or matrix specific reference materials-RMs) had been used (Table 47).

Table 47 Control Samples Used by Participants

Lab. Code	RMs or CRMs identity
3	NMIA MX014
7	MX014
9	TM-25.5, TM-26.3, TMDA-52.4, TMDA-52.3, CASS-6
10	HPS (CRMSW), saline water CRM
11	Nass-7 Seawater Certified Reference Material for Trace Metals and other constituents Cass-6 Nearshore Seawater ceritifed Reference Material for Trace Metals and other constituents
12	NASS 7, CASS 6, NMI MX014
13	SS

A certified reference material for trace elements in seawater (MX014) is available from NMI.

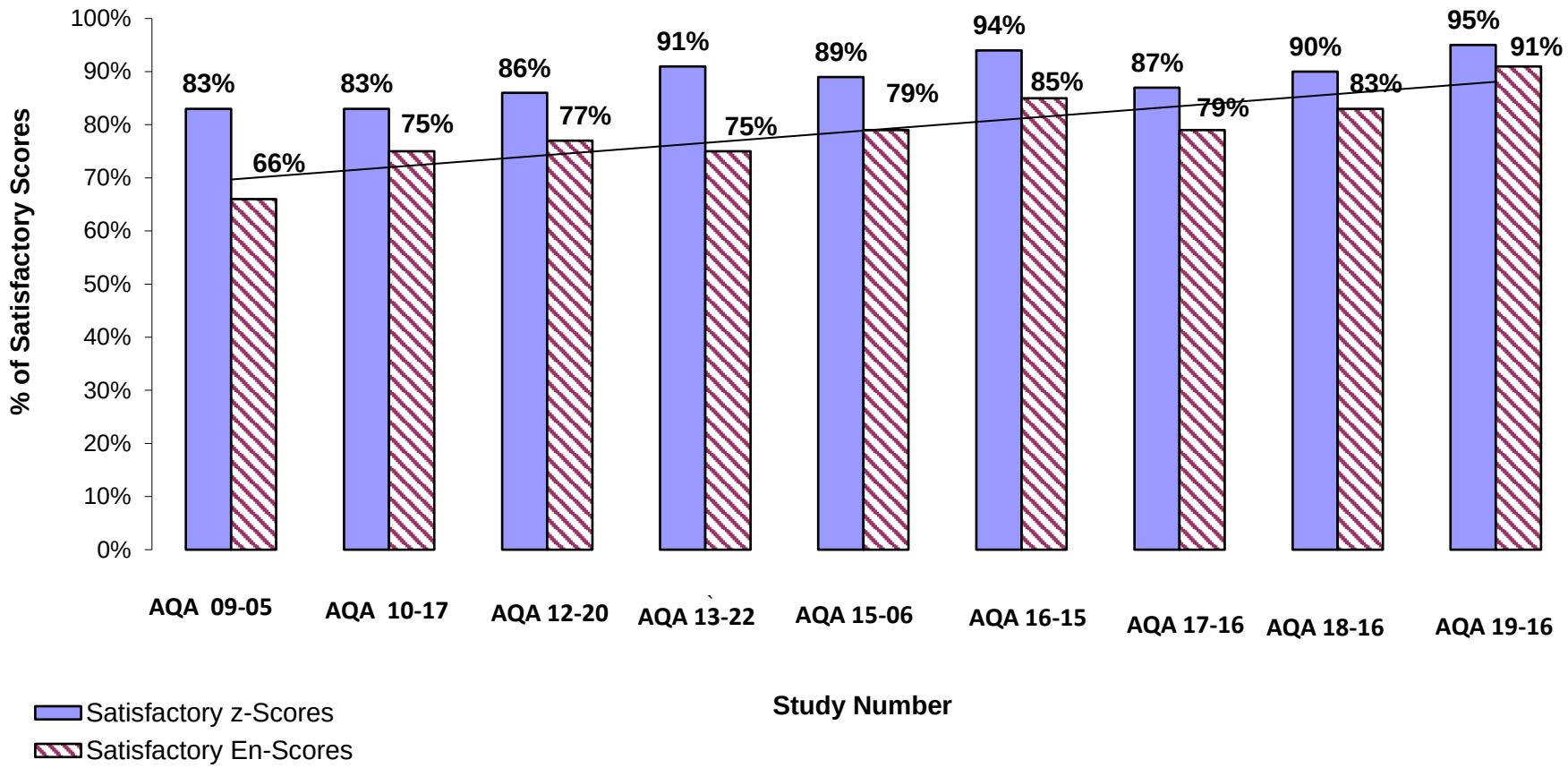


Figure 47 Participants' Performance in Metals in Seawater PT Studies over Last Ten Years

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APPENDIX 1 – SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

Sample Preparation

Sample S1 was prepared from seawater. Approximately 10 L of seawater from Sydney harbour was filtered through a 0.45 µm pore size filter, stabilised by adding 2% (v/w) nitric acid and further fortified with 20 elements.

Sample S2 was unfiltered seawater stabilised by adding 2% (v/w) nitric acid and further fortified for 20 elements.

Sample Analysis and Homogeneity Testing

With the exception of U in S1 and S2, a partial homogeneity test was conducted for all analytes of interest. Three bottles were analysed in duplicate and the average of the results was reported as the homogeneity value.

Sample Analysis for Dissolved and Total Elements

For analyses of total elements in Sample S2, a test portion of 30 mL was transferred to a 50 mL graduated polypropylene centrifuge tube. The samples were digested using 2 mL of nitric acid and 1 mL of hydrochloric acid on a hot block at 95±5^{o}C for 120 min.

Testing involved measurements using ICP-MS or ICP-OES. The measurement instrument was calibrated using external standards for targeted analytes. A set of quality control samples consisting of blanks, a blank matrix spike, duplicates, sample matrix spikes and a certified reference material (MX014) was carried through the same set of procedures and analysed simultaneously with the samples. A summary of the ion/wavelength and instrument conditions used for each analyte is given in Table 48.

Table 48 Instrumental Technique used for Dissolved Elements

Analyte	Instrument	Internal Standard	Reaction/ Collision Cell (if applicable)	Cell Mode/Gas (if applicable)	S1 Final Dilution Factor	S2 Final Dilution Factor	Ion/Wavelength
Ag	ICP-MS	Rh	ORS	He	10	10	107 m/z
Al	ICP-OES	Lu	NA	NA	2	2	167.019 nm
As	ICP-MS	Rh	ORS	He	10	10	75 m/z
Ba	ICP-MS	Rh	ORS	He	NA	10	134 m/z
Be	ICP-MS	Rh	NA	NA	10	NA	9 m/z
Cd	ICP-MS	Rh	ORS	He	10	10	111 m/z
Co	ICP-MS	Rh	ORS	He	10	NA	59 m/z
Cr	ICP-MS	Rh	ORS	He	10	10	52 m/z
Cu	ICP-MS	Rh	ORS	He	10	10	63 m/z
Fe	ICP-OES	Lu	NA	NA	2	2	238.204 nm
Hg	ICP-MS	Rh	ORS	He	10	NA	201 m/z
Mn	ICP-MS	Rh	ORS	He	10	10	55 m/z
Mo	ICP-MS	Rh	ORS	He	NA	10	60 m/z
Ni	ICP-MS	Rh	ORS	He	10	10	60 m/z
P	ICP-MS	Rh	ORS	HEHe	10	10	31 m/z
Pb	ICP-MS	Ir	NA	NA	10	10	Average of 206, 207, 208 m/z
Sb	ICP-MS	Rh	ORS	He	NA	10	78 m/z
Se	ICP-MS	Rh	ORS	HEHe	10	10	78 m/z
Sn	ICP-MS	Rh	NA	NA	10	10	118 m/z
Tl	ICP-MS	Rh	ORS	He	10	10	205m/z
V	ICP-MS	Rh	ORS	He	10	10	51 m/z
Zn	ICP-MS	Rh	ORS	He	10	10	66 m/z

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

The assigned value was calculated as the robust average using the procedure described in 'ISO13258:2015, Statistical methods for use in proficiency testing by interlaboratory 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 49.

Table 49 Uncertainty of Assigned Value for V in Sample S1

No. results (p)	10
Robust Average	4.65 µg/L
$S_{rob\ av}$	0.41 µg/L
$u_{rob\ av}$	0.17 µg/L
k	2
$U_{rob\ av}$	0.33 µg/L

The assigned value for **V** in Sample S1 is **4.65 ± 0.33 µg/L.**

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 11).

A worked example is set out below in Table 50.

Table 50 z-Score and E_n-score for V result reported by Laboratory 8 in S1

V Result µg/L	Assigned Value µg/L	Set Target Standard Deviation	z-Score	E_n-Score
4.49±0.34	4.65±0.33	15% as CV or 0.15x4.65= =0.6975 µg/L	$z = \frac{(4.49 - 4.65)}{0.6975}$ z = -0.23	$En = \frac{(4.49 - 4.65)}{\sqrt{0.34^2 + 0.33^2}}$ E_n= -0.34

APPENDIX 3 - USING PT DATA FOR UNCERTAINTY ESTIMATION

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies can also be used to estimate the uncertainty of their measurement results.[10, 12] An example is given below.

Between 2007 and 2019, NMI carried out 24 proficiency tests for metals in water. These studies involved analyses of dissolved or total elements at low and high levels in potable, fresh (river), saline water, ground water and waste water. Laboratory X participated and submitted satisfactory Ni results in 12 of these PTs.

Table 51 Ni Results for Laboratory X From Proficiency Testing Studies of Metals in Water

Study No.	Sample	Laboratory result* µg/L	Assigned value µg/L	Robust CV of all results (%)	Number of Results
AQA 08-02	Fresh	51 ± 7.2	52.0 ± 3.1	9.9	18
AQA 08-10	Fresh	20 ± 3	18.9 ± 0.6	7.8	26
	Fresh	200 ± 20	191 ± 5	5.5	26
AQA 09-05	Saline	5.0 ± 1.2	5.5 ± 0.6	13.3	14
	Saline	43 ± 5	44.7 ± 3.3	10.8	18
AQA 09-18	Fresh	5.3 ± 0.5	5.04 ± 0.27	7.4	14
	Fresh	49 ± 4	48.9 ± 1.2	3.3	16
AQA 10-06	Potable	49 ± 4	50 ± 1	5.9	20
	Potable	48 ± 4	50 ± 1	3	20
AQA 11-17	Waste water	97 ± 9	99 ± 1	1.5	15
	Waste water	97 ± 9	98 ± 1	1.5	15
AQA 12-09	Fresh	43 ± 6	45 ± 2	6.6	19
	Fresh	51 ± 7	53 ± 2	7.5	19
AQA 12-20	Sea water	40 ± 4.4	38.4 ± 2.1	11	22
AQA 13-09	Fresh	4.3 ± 0.5	4.09 ± 0.17	8.5	15
	Fresh	36 ± 4	36.1 ± 1.0	4.5	16
AQA 14-08	Ground water	18.0 ± 2.0	19.1 ± 0.7	7.9	13
AQA 15-18	S2	32	33.6	4.9	6.2
AQA 16-15	S1	7.2	6.52	9.9	10
	S2	46	40.9	11.7	13
Average				7.3**	

* Expanded uncertainty at approximately 95% confidence. ** The mean value of Robust CV was used.

Taking the average of the robust CV over these PT samples gives an estimate of the relative standard uncertainty of 7.3%. Using a coverage factor of 2 gives a relative expanded uncertainty of 15%, at a level of confidence of approximately 95%. Table 51 sets out the expanded uncertainty for results of the measurement of Ni in fresh, saline, waste or potable water over the range 5 – 200 µg/L.

Table 52 Uncertainty of Ni results estimated using PT data

Results µg/L	Uncertainty µg/L
5.0	0.75
20	3
50	7.5
200	30

The MU estimates made using PT data is close to Laboratory X's own uncertainty estimates reported with their PT results. The estimate of 15% passes the test of being reasonable, and the analysis of the 6 different matrices over 9 years can safely be assumed to include all the

relevant uncertainty components (different operators, reagents, calibrants etc), and so complies with ISO 17025.[8]

APPENDIX 4 - ACRONYMS AND ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
CRI	Collision Reaction Interface
CRM	Certified Reference Material
CV	Coefficient of Variation
CVAAS	Cold Vapour Atomic Absorption Spectrometry
CVAFS	Cold Vapour Atomic Fluorescence Spectrometry
AFS	Atomic fluorescence spectroscopy
DRC	Dynamic Reaction Cell
FIA	Flow Injection Analyser
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
HEHe	High energy He mode
ICP-OES-AV	Inductively Coupled Plasma – Optical Emission Spectrometry- axial view
ICP-OES-RV	Inductively Coupled Plasma – Optical Emission Spectrometry- radial view
Max	Maximum value in a set of results
Md	Median
Min	Minimum value in a set of results
NMI	National Measurement Institute (of Australia)
NR	Not Reported
NT	Not Tested
ORS	Octopole Reaction System
PT	Proficiency Test
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
RM	Reference Material
Robust CV	Robust Coefficient of Variation
Robust SD	Robust Standard Deviation
S	Spiked or formulated concentration of a PT sample
SS	Spiked sample
sea*FAST*-ICP-MS	Automated inductively coupled plasma spectrometry preconcentration system for undiluted seawater
SI	The International System of Units
s^2_{sam}	Sampling variance
s_a/σ	Analytical standard deviation divided by the target standard deviation
SRM	Standard Reference Material (Trademark of NIST)
Target SD	Target standard deviation
σ	Target standard deviation
UC	Universal Cell
VGA	Vapour Generator Accessory

APPENDIX 5 - INSTRUMENT DETAILS FOR DISSOLVED ELEMENTS

Table 53 Instrument Conditions Al

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NA	NA	NA	NA	NA	NA	NA
2	ICP-MS		ORS		10	NA	
3	ICP-OES-AV						
4	ICP-MS	45	ORS	He	1	NA	27
6							
7	ICP-OES-AV	Y	NA	NA	2	2	167.019
8	ICP-MS	Ge	ORS	He	1	10	27
9	ICP-MS/MS	Sc	ORS	H2-N2O	1	1	27
10	ICP-MS	Li6	NA	NA	1.05	21	27
11	ICP-MS	Sc	UC	He	20	20	27
12	ICP-MS	Sc	NA	NA	1	NA	27
13							

Table 54 Instrument Conditions Ag

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NA	NA	NA	NA	NA	NA	NA
2	GFAAS		NA		10	NA	328.1
3	ICP-MS						
4	ICP-MS	103	ORS	He	1	NA	107
6	ICP-MS	In			10	10	107
7	ICP-MS	Rh	ORS	He	10	50	107
8	ICP-MS	Ge	ORS	He	1	10	107
9	ICP-MS/MS	Te	ORS	H2-N2O	1	1	107
10	ICP-MS	Ir	ORS	He	1.05	21	107
11	ICP-MS	Rh	UC	He	20	20	109
12	ICP-MS	Rh	NA	NA	1	NA	109
13	ICP-MS	Rh	ORS	He	10	10	

Table 55 Instrument Conditions As

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	Ga71	DRC	O2	NA	25	91
2	ICP-MS	Y	ORS	He	10	NA	75
3	ICP-MS						
4	ICP-MS	72	ORS	HEHe	1	NA	75
6							
7	ICP-MS	Rh	ORS	He	10	50	75
8	ICP-MS	Ge	ORS	He	1	10	75
9	ICP-MS/MS	Ge	ORS	H2-N2O	1	1	75→91
10	ICP-MS	Ge	ORS	He	1.05	21	75
11	ICP-MS	Te	DRC	NH3	20	20	75
12	ICP-MS	Rh	UC	He	1	NA	75
13	ICP-MS	Ge	ORS	He	10	10	

Table 56 Instrument Conditions Ba

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NA	NA	NA	NA	NA	NA	NA
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS				NA		
4	NA	NA	NA	NA	NA	NA	NA
6	ICP-MS	In			NA	10	137
7	ICP-OES-AV	Y	NA	NA	NA	2	455.403
8	ICP-MS	Ge	ORS	He	NA	10	137
9	ICP-MS	Tb	ORS	He	NA	1	137
10	ICP-MS	Ir	ORS	He	NA	21	137
11	ICP-MS	Tb	UC	He	NA	20	137
12	NA	NA	NA	NA	NA	NA	NA
13	ICP-MS	Rh	ORS	He	NA	10	

Table 57 Instrument Conditions Be

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NA	NA	NA	NA	NA	NA	NA
2	ICP-MS	Li	ORS		10	NA	9
3	ICP-MS					NA	
4	ICP-OES-AV	Lu			1	NA	313.107
6	ICP-MS	Sc			10	NA	9
7	ICP-MS	Sc	NA	NA	10	NA	9
8	ICP-MS	Ge	ORS	He	1	NA	9
9	ICP-MS	Sc	ORS	NA	1	NA	9
10	ICP-MS	Li6	NA	NA	1.05	NA	9
11	NA	NA	NA	NA	NA	NA	NA
12	ICP-MS	Sc	NA	NA	1	NA	9
13	ICP-MS	Ge	ORS	He	10	NA	

Table 58 Instrument Conditions Cd

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	Rh103	NA	NA	NA	25	111
2	ICP-MS	In	ORS		10	NA	111
3	ICP-MS						
4	ICP-MS	103	ORS	He	1	NA	114
6	ICP-MS	In			10	10	111
7	ICP-MS	Rh	ORS	He	10	50	111
8	ICP-MS	Ge	ORS	He	1	10	111
9	ICP-MS	Te	ORS	He	1	1	111
10	ICP-MS	Ir	ORS	He	1.05	21	114
11	ICP-MS	Rh	UC	He	20	20	111
12	ICP-MS	Rh	NA	NA	1	NA	111
13	ICP-MS	Rh	ORS	He	10	10	

Table 59 Instrument Conditions Co

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NA	NA	NA	NA	NA	NA	NA
2	ICP-MS	Sc	ORS		10	NA	59
3	ICP-MS					NA	
4	ICP-MS	115	ORS	He	1	NA	59
6						NA	
7	ICP-MS	Rh	ORS	He	10	NA	59
8	ICP-MS	Ge	ORS	He	1	NA	59
9	ICP-MS	Ge	ORS	He	1	NA	59
10	ICP-MS	In	ORS	He	1.05	NA	59
11	ICP-MS	Ga	UC	He	20	NA	59
12	ICP-MS	Rh	UC	He	1	NA	59
13	ICP-MS	Ge	ORS	He	10	NA	

Table 60 Instrument Conditions Cr

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	Ga71	NA	He	NA	25	52
2	ICP-MS	Sc	ORS		10	NA	52
3	ICP-MS						
4	ICP-MS	72	ORS	He	1	NA	52
6	ICP-MS	Ga	DRC	NH3	10	10	52
7	ICP-MS	Rh	ORS	He	10	50	52
8	ICP-MS	Ge	ORS	He	1	10	52
9	ICP-MS/MS	Ge	ORS	H2-N2O	1	1	52
10	ICP-MS	Ge	ORS	He	1.05	21	52
11	ICP-MS	Ga	DRC	NH3	20	20	52
12	ICP-MS	Sc	UC	He	1	NA	52
13	ICP-MS	Ge	ORS	He	10	10	

Table 61 Instrument Conditions Cu

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	Ga71	NA	He	NA	25	63
2	ICP-MS	Y	ORS		10	NA	65
3	ICP-MS						
4	ICP-MS	103	ORS	He	1	NA	65
6							
7	ICP-MS	Rh	ORS	He	10	50	63
8	ICP-MS	Ge	ORS	He	1	10	63
9	ICP-MS	Ge	ORS	He	1	1	63
10	ICP-MS	Rh	ORS	He	1.05	21	63
11	ICP-MS	Ga	UC	He	20	20	63
12	seaFAST-ICP-MS	NA	UC	He	1	NA	63
13	ICP-MS	Ge	ORS	He	10	10	

Table 62 Instrument Conditions Fe

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	Ga71	NA	He	NA	25	56
2	ICP-MS	Sc	ORS		10	NA	56
3	ICP-OES-AV						
4	ICP-MS	72	ORS	He	1	NA	56
6							
7	ICP-OES-AV	Y	NA	NA	2	2	238.204
8	ICP-MS	Ge	ORS	He	1	10	56
9	ICP-MS/MS	Ge	ORS	H2-N2O	1	1	56
10	ICP-MS	Ge	ORS	H2	1.05	21	56
11	ICP-MS	Ga	DRC	NH3	20	20	54
12	seaFAST-ICP-MS	NA	UC	He	1	NA	56
13	ICP-MS	Ge	ORS	He	10	10	

Table 63 Instrument Conditions Hg

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NA	NA	NA	NA	NA	NA	NA
2	CVAAS	SnCl2	NA		10	NA	3470
3	CVAAS					NA	
4	VGA-ICP-OES				1	NA	194.164
6	CVAAS				2.5	NA	
7	CVAFS	NA	NA	NA	2	NA	NA
8	CVAFS				1	NA	253.7
9	ICP-MS	Ir	ORS	He	1	NA	202
10	CVAFS		NA	NA	3	NA	253.7
11	Fluorescence	NA	NA	NA	5	NA	254
12	ICP-MS	Ir	NA	NA	1	NA	201
13	ICP-MS	Ir	ORS	He	10	NA	

Table 64 Instrument Conditions Mn

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NA	NA	NA	NA	NA	NA	NA
2	ICP-MS	Sc	ORS		10	NA	55
3	ICP-MS						
4	ICP-MS	72	ORS	He	1	NT	55
6	ICP-MS	Ga			10	10	55
7	ICP-MS	Rh	ORS	He	10	50	55
8	ICP-MS	Ge	ORS	He	1	10	55
9	ICP-MS/MS	Sc	ORS	H2-N2O	1	1	55
10	ICP-MS	Ge	ORS	He	1.05	21	55
11	ICP-MS	Ga	DRC	NH3	20	20	55
12	seaFAST-ICP-MS	NA	UC	He	1	NA	55
13	ICP-MS	Ge	ORS	He	10	10	

Table 65 Instrument Conditions Mo

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NA	NA	NA	NA	NA	NA	NA
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS				NA		
4	NA	NA	NA	NA	NA	NA	NA
6	ICP-MS	In			NA	10	95
7	ICP-MS	Rh	ORS	He	NA	50	95
8	ICP-MS	Ge	ORS	He	NA	10	95
9	ICP-MS/MS	In	ORS	H2-N2O	NA	1	98→130
10	ICP-MS	In	ORS	He	NA	21	95
11	ICP-MS	Rh	UC	He	NA	20	98
12	NA	NA	NA	NA	NA	NA	NA
13	ICP-MS	Rh	ORS	He	NA	10	

Table 66 Instrument Conditions Ni

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NA	NA	NA	NA	NA	NA	NA
2	ICP-MS	Sc	ORS	He	10	NA	60
3	ICP-MS						
4	ICP-MS	103	ORS	He	1	NT	60
6							
7	ICP-MS	Rh	ORS	He	10	50	60
8	ICP-MS	Ge	ORS	He	1	10	60
9	ICP-MS	Ge	ORS	He	1	1	60
10	ICP-MS	Ge	ORS	He	1.05	21	60
11	ICP-MS	Ga	UC	He	20	20	60
12	ICP-MS	Rh	UC	He	1	NA	60
13	ICP-MS	Ge	ORS	He	10	10	

Table 67 Instrument Conditions P

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	Be9	NA	NA	NA	25	31
2	ICP-OES-AV	Yb	NA		10	NA	177.4343
3	ICP-OES-AV						
4						NA	
6							
7	ICP-OES-AV	Y	NA	NA	2	2	213.618
8	ICP-OES-AV				1	10	213.618
9	ICP-MS/MS	Ge	ORS	H2-N2O	1	1	31→47
10	ICP-OES-AV	Lu	NA	NA	1.05	10.5	177.434
11	ICP-MS	Sc	UC	He	NA	20	31
12						NA	
13	ICP-OES-AV	Te	ORS	NA	1	1	213.618

Table 68 Instrument Conditions Pb

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	Lu175	NA	NA	NA	25	208
2	ICP-MS	Ir	ORS		10	NA	206
3	ICP-MS						
4	ICP-MS	103	ORS	He	1	NT	208
6	ICP-MS	Ir			10	10	207
7	ICP-MS	Ir	ORS	He	10	50	207
8	ICP-MS	Ge	ORS	He	1	10	208
9	ICP-MS	Ir	ORS	He	1	1	208
10	ICP-MS	Ir	ORS	He	1.05	21	208
11	ICP-MS	Tb	UC	He	20	20	206+207+208
12	ICP-MS	Ir	NA	NA	1	NA	206+207+208
13	ICP-MS	Ir	ORS	He	10	10	

Table 69 Instrument Conditions Sb

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NA	NA	NA	NA	NA	NA	NA
2	NA	NA	NA	NA	NA	NA	NA
3	ICP-MS				NA		
4	NA	NA	NA	NA	NA	NA	NA
6	ICP-MS	In			NA	10	121
7	ICP-MS	Rh	ORS	He	NA	50	121
8	ICP-MS	Ge	ORS	He	NA	10	121
9	ICP-MS/MS	Te	ORS	H2-N2O	NA	1	121
10	ICP-MS	In	ORS	He	NA	21	121
11	ICP-MS	Rh	UC	He	NA	20	121
12	NA	NA	NA	NA	NA	NA	NA
13	ICP-MS	Rh	ORS	He	NA	10	

Table 70 Instrument Conditions Se

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	Ga71	DRC	NH3	NA	25	82
2	ICP-MS	Y	ORS	He	10	NA	78
3	ICP-MS						
4	ICP-MS	103	ORS	HEHe	1	NT	78
6							
7	ICP-MS	Rh	ORS	HEHe	10	50	78
8	ICP-MS	Ge	ORS	He	1	10	78
9	ICP-MS/MS	Ge	ORS	H2-N2O	1	1	80→96
10	ICP-MS	In	ORS	H2	1.05	21	78
11	ICP-MS	Te	DRC	NH3	20	20	82
12	ICP-MS	Rh	DRC	NH3	1	NA	82
13	ICP-MS	Rh	ORS	HEHe	10	10	

Table 71 Instrument Conditions Sn

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NA	NA	NA	NA	NA	NA	NA
2	ICP-MS	In	ORS	He	10	NA	118
3	ICP-MS						
4	ICP-MS	115	ORS	He	1	NT	118
6	ICP-MS	In			10	10	118
7	ICP-MS	Rh	ORS	He	10	50	118
8	ICP-MS	Ge	ORS	He	1	10	118
9	ICP-MS/MS	In	ORS	H2-N2O	1	1	118
10	ICP-MS	In	ORS	He	1.05	21	118
11	ICP-MS	Rh	UC	He	20	20	120
12						NA	
13	ICP-MS	Rh	ORS	He	10	10	

Table 72 Instrument Conditions Tl

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NA	NA	NA	NA	NA	NA	NA
2	ICP-MS	Ir	ORS		10	NA	205
3	ICP-MS						
4	ICP-MS	193	ORS	He	1	NA	205
6	ICP-MS	Ir			10	10	203
7	ICP-MS	Ir	ORS	He	10	50	205
8	ICP-MS	Ge	ORS	He	1	10	205
9	ICP-MS	Ir	ORS	He	1	1	205
10	ICP-MS	Ir	ORS	He	1.05	21	205
11	ICP-MS	Tb	UC	He	20	20	205
12	seaFAST-ICP-MS	NA	NA	NA	1	NA	205
13	ICP-MS	Ir	ORS	He	10	10	

Table 73 Instrument Conditions U

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NA	NA	NA	NA	NA	NA	NA
2	ICP-MS	Ir	ORS		10	NA	238
3	ICP-MS						
4	ICP-MS	103	ORS	He	1	NA	238
6							
7	ICP-MS	Ir	ORS	He	10	50	238
8	ICP-MS	Ge	ORS	He	1	10	238
9	ICP-MS	Tb	ORS	He	1	1	238
10	ICP-MS	Ir	ORS	He	1.05	21	238
11	ICP-MS	Tb	UC	He	20	20	238
12	ICP-MS	Ir	NA	NA	1	NA	238
13	ICP-MS	Ir	ORS	He	10	10	

Table 74 Instrument Conditions V

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	NA	NA	NA	NA	NA	NA	NA
2	ICP-MS	Sc	ORS		10	NA	51
3	ICP-OES-AV						
4	ICP-MS	45	ORS	He	1	NT	51
6							
7	ICP-MS	Rh	ORS	He	10	50	51
8	ICP-MS	Ge	ORS	He	1	10	51
9	ICP-MS/MS	Sc	ORS	H2-N2O	1	1	80→96
10	ICP-MS	Ge	ORS	He	1.05	21	51
11	ICP-MS	Ga	DRC	NH3	20	20	51
12	seaFAST-ICP-MS	NA	UC	He	1	NA	51
13	ICP-MS	Ge	ORS	He	10	10	

Table 75 Instrument Conditions Zn

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion(m/z)
1	ICP-MS	Ga71	NA	He	NA	25	66
2	ICP-MS	Y	ORS		10	NA	66
3	ICP-OES-AV						
4	ICP-MS	103	ORS	He	1	NT	66
6							
7	ICP-MS	Rh	ORS	He	10	50	64
8	ICP-MS	Ge	ORS	He	1	10	66
9	ICP-MS/MS	Te	ORS	O2	1	1	66
10	ICP-MS	Ge	ORS	He	1.05	21	68
11	ICP-MS	Te	DRC	NH3	20	20	66
12	seaFAST-ICP-MS	NA	UC	He	1	NA	66
13	ICP-MS	Ge	ORS	He	10	10	

END OF REPORT