

Proficiency Test Report AQA 18-05 Water Characteristics

July 2018

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, conducting and reporting of the study is acknowledged.

Luminita Antin Dr Andrew Evans Wei Huang Alexander Sadler

Paul Armishaw Manager, Chemical Reference Values North Ryde 1670 Phone: 61-2-9449 0149

proficiency@measurement.gov.au



Accredited for compliance with ISO/IEC 17043

TABLE OF CONTENTS

1	S	UMMARY	5
2		NTRODUCTION	6
		NMI Proficiency Testing Program	6
		Study Aims	6
		Study Conduct	6
3		TUDY INFORMATION	6
	3.1	Selection of Matrices and Inorganic Analytes	6
	3.2	Participation	7
	3.3	Test Material Specification	7
	3.4	Laboratory Code	7
	3.5	Sample Preparation, Analysis and Homogeneity Testing	7
	3.6	Stability of Analytes	7
	3.7	Sample Storage, Dispatch and Receipt	7
	3.8	Instructions to Participants	7
	3.9	Interim Report	8
4	Р	ARTICIPANT LABORATORY INFORMATION	9
	4.1	Methodology for Total Elements	9
	4.2	Methodology for S3	10
	4.3	Basis of Participants' Measurement Uncertainty Estimates	10
	4.4	Participant Comments on this PT Study or Suggestions for Future Studies	11
5	Р	RESENTATION OF RESULTS AND STATISTICAL ANALYSIS	12
	5.1	Results Summary	12
6	T.	ABLES AND FIGURES	14
7	D	ISCUSSION OF RESULTS	114
	7.1	Assigned Value	114
	7.2	Measurement Uncertainty Reported by Participants	114
	7.3	E _n -score	115
	7.4	z-Score	116
	7.5	Participants' Results and Analytical Methods for Total Elements	125
		Participants' Results and Analytical Methods for Tests in Samples S2 and S3 Oth	
		Total Elements	130
		Comparison with Previous NMI Proficiency Tests of Metals in Water	135
_		Reference Materials and Certified Reference Materials	135
8		EFERENCES	137
А		NDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING	138
		nple Preparation	138
^		nple Analysis and Homogeneity Testing	138
А		NDIX 2 - STABILITY STUDY	141
^		ility Study	141
		NDIX 3 - ASSIGNED VALUE, Z-SCORE AND E _N SCORE CALCULATION	143
		NDIX 4 - USING PT DATA FOR UNCERTAINTY ESTIMATION	145
		NDIX 5 - ACRONYMS AND ABBREVIATIONS	146
А	ヒヒロ	NDIX 6 - INSTRUMENT DETAILS FOR DISSOLVED ELEMENTS	148

1 SUMMARY

This report presents the results of the proficiency test AQA 18-05, Water Characteristics. The study focused on the measurement of total: Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Sn, Sr, Tl, U, V and Zn. Bromide, chloride, dissolved organic carbon (as dNPOC), fluoride, ammonia-N, nitrate-N, total dissolved nitrogen, total dissolved phosphorus, free reactive phosphorus, sulfate, alkalinity to pH 4.5 (as CaCO₃), colour (apparent), total hardness (as CaCO₃), pH at 25°C, silica (as SiO₂), total solids at 103-105°C, turbidity (NTU), total Kjeldahl nitrogen, total nitrogen, total organic carbon (as NPOC) were also included in the program.

The sample set consisted of three water samples.

Twenty-two laboratories registered to participate and twenty-one submitted 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 728 z-scores, 656 (90%) returned a satisfactory score of $|z| \le 2$. Of 728 E_n-scores, 579 (80%) returned a satisfactory score of $|E_n| \le 1$

ii. evaluate the laboratories' methods used in determination of total elements in potable water and river water;

Rounding of results and reporting results with an insufficient number of significant figures was one of the main causes for variability of the reported results.

- iii. compare the performance of participant laboratories with their past performance; On average participants' performance has remained consistent over time.
 - 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 737 numerical results, 693 (94%) were reported with an expanded measurement uncertainty. An example of estimating measurement uncertainty using the proficiency testing data only is given in Appendix 4.

v. produce materials that can be used in method validation and as control samples. The study samples were checked for homogeneity and stability and are well characterised, both by in-house testing and from the results of the proficiency round. Surplus test samples are available for sale.

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 inter-laboratory comparison." NMI PT studies target chemical testing in areas of high public significance such as trade, environment and food safety. NMI offers studies in:

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

AQA 18-05 is the 22nd NMI proficiency study of inorganic analytes in water.

2.2 Study Aims

The aims of the study were to:

- compare the performance of participant laboratories and assess their accuracy in the performance of 50 tests in potable/river water;
- evaluate the laboratories' methods used in determination of total elements in unfiltered potable/river water;
- 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 17043¹ 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.

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

3 STUDY INFORMATION

3.1 Selection of Matrices and Inorganic Analytes

The fifty tests were selected from those for which an investigation level is published in the Australian and New Zealand Guidelines for Sewerage Systems - Effluent Management⁵ and are commonly measured by water testing laboratories.

3.2 Participation

Twenty-two laboratories participated and twenty-one submitted results.

The timetable of the study was:

Invitation issued: 19 March 2018 Results due: 18 May 2018 Samples dispatched: 16 April 2018 Interim report issued 23 May 2018

3.3 Test Material Specification

Three samples were provided for analysis:

Sample S1 was 100 mL of unfiltered potable water preserved by adding 2% (v/w) HNO₃ and 0.01% (v/w) HCl;

Sample S2 was 200 mL of filtered and autoclaved, frozen river water; and

Sample S3 consisted of two bottles labelled A and B. The bottle A was 750 mL of unfiltered, chilled river water, while the container labelled B contained 200 mL of unfiltered and autoclaved frozen river water.

3.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

3.5 Sample Preparation, Analysis and Homogeneity Testing

The same preparation procedure was followed as in previous studies. A partial homogeneity test was conducted for all elements in Samples S1, S2 and S3 except for TDP in S2.¹ The test samples from previous studies were demonstrated to be sufficiently homogeneous for evaluation of participants' performance. ^{6,7}

The preparation, analysis and homogeneity testing of the study samples are described in Appendix 1. In the present study, the test samples were demonstrated to be sufficiently homogeneous for all of the analytes assessed.

3.6 Stability of Analytes

No stability study was carried out for Samples S1. Stability studies conducted for the previous similar proficiency studies of metals in water found no significant changes in any of the analytes' concentration. ^{6, 7}

For Sample S2 and S3, to address the issues with the holding time and holding conditions, a stability study was conducted. The stability study was conducted over the entire period of PT study and was carried out to simulate conditions encountered by the samples during storage. Details of the study and results are given in Appendix 2. The test samples were stable for the period of the proficiency test.

3.7 Sample Storage, Dispatch and Receipt

Samples S1 and S3A were refrigerated before dispatch, while samples S2 and S3B were frozen.

The samples were dispatched by courier on 16 April 2018. A description of the test samples and instructions for participants, and a samples received 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.
- If analyses cannot be commenced on the day of receipt, please store the sample labelled S3A chilled and the samples S2 and S3B frozen.
- Prior to testing thaw samples S2 and S3B completely.
- The bottles labelled S3A and S3B are NOT to be composited. The samples should be tested for the analytes of interest as indicated in the table below.
- Participants are asked to report results in units of mg/L except for turbidity and colour. Report turbidity result in nephelometric turbidity units (NTU) and the result for colour in Pt-Co units

SAMPLE S1		SAMPLE S2			
unfiltered, acidified		filtered,		SAMPLE S3	
potable water		frozen river water			
Test	Approximate	Test Approximate		Test	Approximate
total	Conc. Range		Conc. Range		Conc. Range
	mg/L		mg/L		mg/L
Al	0.05-1	Bromide	0.5-50	Sample S3 A unfiltered	d river water
As	0.001-0.08	Chloride	20-400	B (total)	0.020-2
Ba	0.005-0.1	Fluoride	0.2-5	Ca (total)	10-400
Be	0.001-0.08	Dissolved Organic Carbon as (dNPOC)	1-50	K (total)	1-40
Bi	0.001-0.08	Ammonia-N	0.01-2	Mg (total)	1-40
Cd	0.0005-0.04	Nitrate-N	0.01-2	Na (total)	10-400
Co	0.001-0.08	Total Dissolved Nitrogen	0.02-4	P (total)	0.020-2.0
Cr	0.001-0.08	Total Dissolved Phosphorus	0.01-2	Alkalinity to pH 4.5 as CaCO ₃	>10
Cu	0.100-1	Free Reactive Phosphorus	0.01-2	Colour, apparent (Pt-Co units)	>10
Fe	0.100-1	Sulfate	0.2-50	Hardness, total (CaCO ₃)	10-400
Hg	0.00005-0.005			pH (at 25°C)	>3
Li	0.001-0.08			Silica (as SiO ₂)	1-20
Mn	0.05-4			Total Solids at 103-105°C	>50
Mo	0.005-0.4			Turbidity (NTU)	>0.1
Ni	0.005-0.2			Sample S3 B unfiltered, from	ozen river water
Pb	0.005-0.4			Total Kjeldahl Nitrogen	0.2-50
Sb	0.0005-0.04			Total Nitrogen	0.2-50
Se	0.001-0.08			Total Organic Carbon (as NPOC)	0.2-50
Sn	0.0005-0.04				
Sr	0.005-0.4				
Tl	0.0005-0.04				
U	0.001-0.08				
V	0.001-0.08				
Zn	0.5-40				

- Report results as you would report to a client. Report the expanded measurement uncertainty associated with your analytical result.
- Please send us the requested details regarding the test method and the basis of your uncertainty estimate.

3.9 Interim Report

An interim report was emailed to participants on 23 May 2018.

4 PARTICIPANT LABORATORY INFORMATION

4.1 Methodology for Total Elements

Summaries of test methods for total elements are transcribed in Tables 1 and 2. The instruments and settings reported by participants are presented in Appendix 6.

Table 1 Methodology for Total Elements (Part 1)

Lab Code	Method Reference			
1	In House W32 - referencing APHA 3125			
2	USEPA6020 (ICP_MS) and APHA3120 (ICP_OES)			
3	3005			
4	APHA 3030E			
5	APHA 3125			
6	USEPA6020			
8	USEPA6020			
9	US EPA 200.8, APHA 3125B 22nd Edition 2012			
10	US EPA 200.8			
11	EPA6020A			
12	200.7-6			
13	APHA 3030E			
18	3051A			
19	APHA 3125 B			
20	Standard Methods for the examination of water and waste water. 20th ED. 3030F			
21	USEPA METHOD 3050B			
22	APHA 3030E			

Table 2 Methodology for Total Elements (Part 2)

Lab.	Sample	Digestion	Digestion	Vol.	Vol.	Additional
Code	Volume	Temp.	Time	HNO_3	HCl	Information
Code	(mL)	(°C)	(min)	(mL)	(mL)	
3	10	95	120	0.5		
5	5	95	60	2	1	
6	40	95	60	1	1	
8	40	95	60	1	1	
9	10	100	60	0.5		
10	100	95	240	1		
11	25	105	120	1.5		
12	50	85	420	1	2.5	
13	20	97	120	2		
18	20	170	15	1	1	
20	50	95	180	6	1	2 mL H ₂ O ₂
21	50	85	120	1	1	
22	30	1.5	120	0.6	0.6	0.6 mL H ₂ O ₂

4.2 Methodology for S3

Measurement methods and instrumental techniques used for the tests other than total elements in Samples S3A/S3B are presented in Appendix 7.

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.	Approach to Estimating MU	Information Sour	Guide Document for	
Code	ripprouch to Estimating ivid	Precision ^a	Method Bias ^a	Estimating MU
1	Top Down - precision and estimates of the method and laboratory bias	Control Samples-CRM Duplicate analyses	CRM Instrument calibration	Nordtest Report TR537
2	Professional judgment			
3	Top Down - precision and estimates of the method and laboratory bias	Control Samples-SS Duplicate analyses	CRM Instrument calibration	Eurachem/CITAC Guide
4	Top Down - precision and estimates of the method and laboratory bias	Control Samples		Nata Technical Note 33
5	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples Duplicate analyses Instrument calibration	CRM Recoveries of SS Instrument calibration	Nata Technical Note 33
6	Estimation of MU from within- laboratory data on bias and precision has been calculated by using the procedures outlined in ASTM E2554-13 Standard Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques	Control Samples-CRM	CRM Instrument calibration Laboratory bias from PT studies Recoveries of SS	ASTM E2554-13 Standard Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques
8	Top Down - precision and estimates of the method and laboratory bias	Control Samples-CRM Duplicate analysis Instrument calibration	CRM Instrument Calibration Laboratory bias from PT studies Recoveries of SS	ASTM E2554-13 Standard Practice for Estimating and Monitoring the Uncertainty of Test Results of a Test Method Using Control Chart Techniques
9	Top Down - precision and estimates of the method and laboratory bias	Duplicate analysis	Laboratory bias from PT studies	Eurachem/CITAC Guide
10	Top Down - precision and estimates of the method and laboratory bias	Control Samples-CRM Duplicate analyses	CRM Recoveries of SS	Nata Technical Note 33
11	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate analyses Instrument Calibration	CRM Recoveries of SS	Nata Technical Note 33
12	Top Down - precision and estimates of the method and laboratory bias	Control Samples-SS Duplicate analyses Instrument Calibration	CRM Recoveries of SS	Nata Technical Note 33

13	Calculated from Standard deviation and concentration of long term in house QC samples	Control Samples-SS Duplicate analyses Instrument Calibration	CRM Recoveries of SS Laboratory bias from PT studies Instrument calibration Standard purity	Nata Technical Note 33
14	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples-CRM Duplicate analyses	CRM	ISO/GUM
15	Standard deviation of replicate analyses multiplied by 2 or 3			NMI Uncertainty Course
16	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate analyses	Recoveries of SS	
17	Top Down - reproducibility (standard deviation) from PT studies used directly	Control Samples-RM Duplicate analyses	CRM	NATA Technical Note 33
18	Top Down - precision and estimates of the method and laboratory bias	Control Samples-CRM Duplicate analyses	CRM	NMI Uncertainty Course
20	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples-SS Duplicate analyses Instrument Calibration	Recoveries of SS Instrument Calibration	NMI Uncertainty Course
21	Standard deviation of replicate analyses multiplied by 2 or 3	Control Samples-SS Duplicate analyses	Recoveries of SS	Nata Technical Note 33
22	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Duplicate analyses	Recoveries of SS	ISO/GUM

^{*} 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	
Sample was insufficient for Total Solids, Total hardness and minerals. Two bottle of S3 samples will be sufficient to carry out all the analysis.	Thank you for your feedback, other participants are invited to comment.	
Sample [S2] was extremely limited.		
More fresh/river water PT	Thank you for your feedback!	

5 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

5.1 Results Summary

Participant results are listed in Tables 5 to 54 with resultant 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 51.

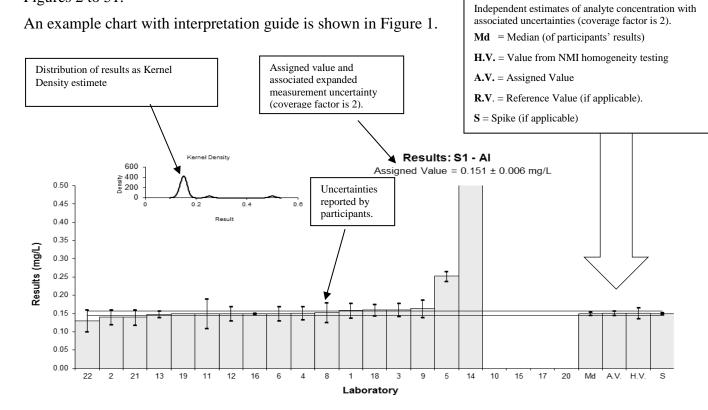


Figure 1 Guide to Presentation of Results

5.2 Assigned Value

An example of the assigned value calculation using data from the present study is given in Appendix 3. The assigned value is defined as: 'the value attributed to a particular property of a proficiency test item.' ¹ In this study the property is the mass fraction of analyte. Assigned values were the robust average of participants' results; the expanded uncertainties were estimated from the associated robust standard deviations.

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)'.8

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).⁸

5.5 Target Standard Deviation

The target standard deviation (σ) is used in the calculation of z-scores and provides scaling for laboratory deviation from the assigned value. It is important to note that the target standard deviation for this study is a fixed value established by the study coordinator and is not the standard deviation of participants' results. The fixed value set for the target standard deviation

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, and is backed up by mathematical models such as the Thompson Horwitz equation. By setting a fixed and realistic value for the performance standard deviation, the participants performance (z-score) can be compared from study to study and against achievable performance. This provides a benchmark for progressive improvement.

5.6 z-Score

An example of z-score calculation using data from the present study is given in Appendix 3.

For each participant's result a z-score is calculated according to Equation 1 below:

$$z = \frac{(\chi - X)}{\sigma}$$
 Equation 1

where:

z is z-score

 χ is participant result

X is the study assigned value

 σ is the target standard deviation from Equation 1

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

• $|z| \le 2$ is satisfactory;

• $2 < |z| \le 3$ is questionable;

• |z| > 3 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 2 below:

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

where:

 E_n is E_n -score

 χ is participant result

X is the study assigned value

 U_{χ} is the expanded uncertainty of the participant's result

 U_{x} is the expanded uncertainty of the assigned value

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

- $|E_n| \le 1$ is satisfactory;
- $|E_n| > 1$ is unsatisfactory.

5.8 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025:2005¹⁰ must establish and demonstrate the traceability and measurement uncertainty associated with their test results. Guidelines for quantifying uncertainty in analytical measurement are described in the Eurachem/CITAC Guide.¹¹

6 TABLES AND FIGURES

Table 5

Sample Details

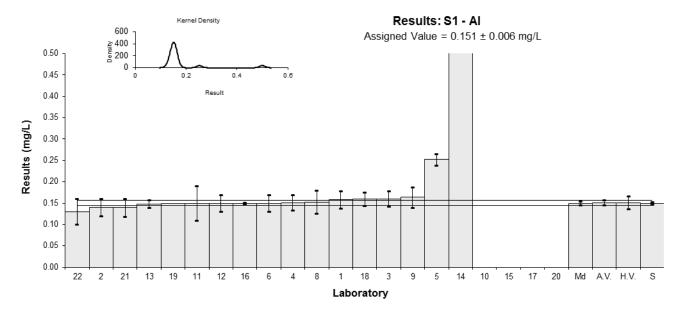
Sample No.	S1
Matrix.	Water
Analyte.	Al
Units	mg/L

Participant Results

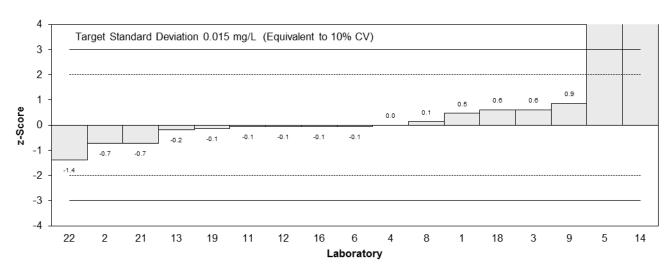
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.158	0.02	0.46	0.34
2	0.14	0.02	-0.73	-0.53
3	0.16	0.018	0.60	0.47
4	0.151	0.018	0.00	0.00
5	0.252	0.014	6.69	6.63
6	0.150	0.02	-0.07	-0.05
8	0.153	0.0264	0.13	0.07
9	0.164	0.024	0.86	0.53
10	NT	NT		
11	0.15	0.04	-0.07	-0.02
12	0.15	0.02	-0.07	-0.05
13	0.148	0.009	-0.20	-0.28
14	159	16	10519.80	9.93
15	NT	NT		
16	0.15	0.002	-0.07	-0.16
17	NT	NT		
18	0.16	0.016	0.60	0.53
19	0.1490	NR	-0.13	-0.33
20	NT	NT		
21	0.14	0.021	-0.73	-0.50
22	0.13	0.03	-1.39	-0.69

Assigned Value**	0.151	0.006
Spike	0.150	0.003
Homogeneity Value	0.151	0.015
Robust Average	0.152	0.006
Median	0.150	0.004
Mean	0.157	
N	16	
Max.	159	
Min.	0.13	
Robust SD	0.0086	
Robust CV	5.7%	

^{*}Laboratory 14 results were omitted from statistical calculation. **Robust Average excluding Laboratory 5.



z-Scores: S1 - AI



En-Scores: S1 - Al

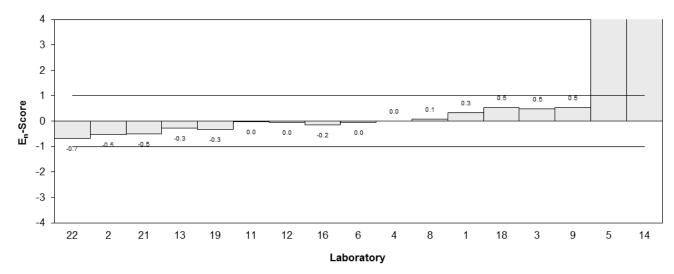


Figure 2

Table 6

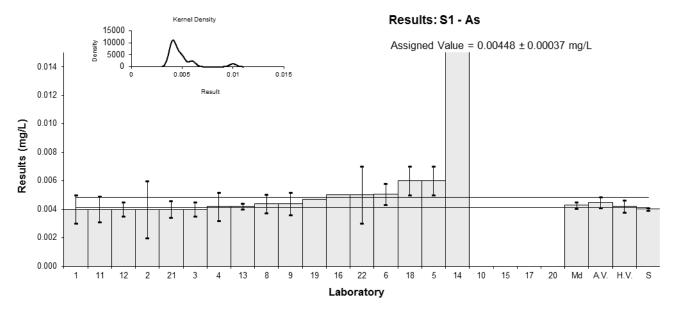
Sample No.	S1
Matrix.	Water
Analyte.	As
Units	mg/L

Participant Results

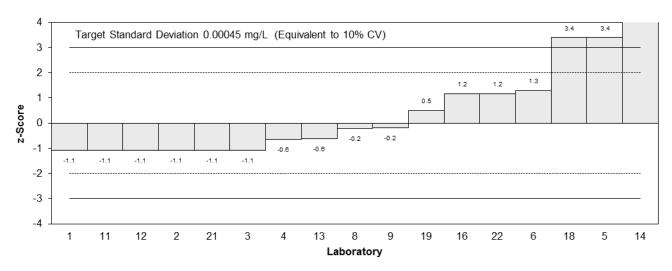
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.004	0.001	-1.07	-0.45
2	0.004	0.002	-1.07	-0.24
3	0.004	0.0005	-1.07	-0.77
4	0.00419	0.001	-0.65	-0.27
5	0.006	0.001	3.39	1.43
6	0.00506	0.00075	1.29	0.69
8	0.00438	0.000656	-0.22	-0.13
9	0.00439	0.00078	-0.20	-0.10
10	NT	NT		
11	0.004	0.0009	-1.07	-0.49
12	0.004	0.0005	-1.07	-0.77
13	0.0042	0.0002	-0.62	-0.67
14	4.32	0.5	9632.86	8.63
15	NT	NT		
16	0.005	NR	1.16	1.41
17	NT	NT		
18	0.006	0.001	3.39	1.43
19	0.0047	NR	0.49	0.59
20	NT	NT		
21	0.0040	0.0006	-1.07	-0.68
22	0.005	0.002	1.16	0.26

Assigned Value	0.00448	0.00037
Spike	0.00401	0.00008
Homogeneity Value	0.00421	0.00042
Robust Average	0.00448	0.00037
Median	0.00429	0.00023
Mean	0.00456	
N	16	
Max.	4.32	
Min.	0.004	
Robust SD	0.00058	
Robust CV	13%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - As



En-Scores: S1 - As

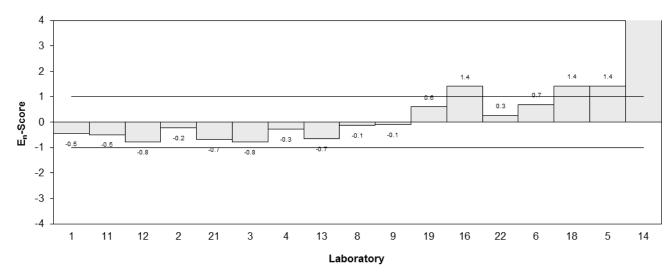


Figure 3

Table 7

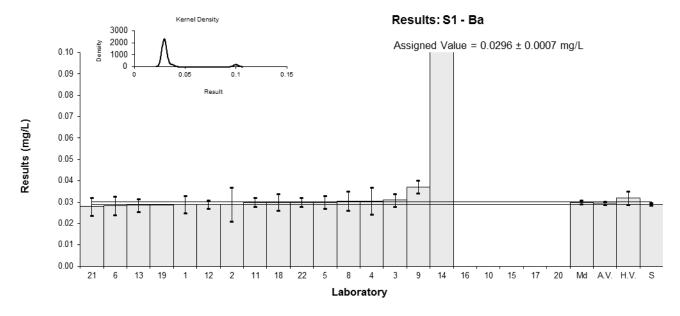
Sample No.	S1
Matrix.	Water
Analyte.	Ва
Units	mg/L

Participant Results

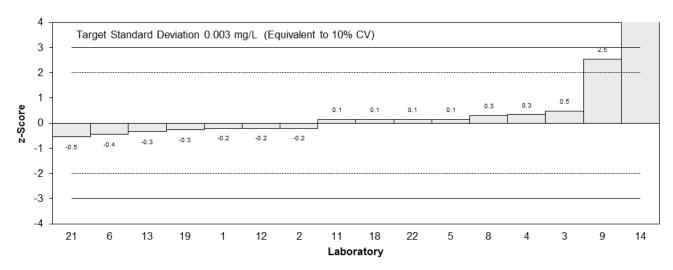
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.029	0.004	-0.20	-0.15
2	0.029	0.008	-0.20	-0.07
3	0.031	0.003	0.47	0.45
4	0.0306	0.0064	0.34	0.16
5	0.03	0.003	0.14	0.13
6	0.0283	0.0044	-0.44	-0.29
8	0.0305	0.00449	0.30	0.20
9	0.0371	0.0030	2.53	2.43
10	NT	NT		
11	0.03	0.002	0.14	0.19
12	0.029	0.002	-0.20	-0.28
13	0.0286	0.0030	-0.34	-0.32
14	31.3	3.5	10564.32	8.93
15	NT	NT		
16	<0.05	0.001		
17	NT	NT		
18	0.03	0.004	0.14	0.10
19	0.0288	NR	-0.27	-1.14
20	NT	NT		
21	0.028	0.0042	-0.54	-0.38
22	0.03	0.002	0.14	0.19

Assigned Value	0.0296	0.0007
Spike	0.0291	0.0006
Homogeneity Value	0.0319	0.0032
Robust Average	0.0296	0.0007
Median	0.0300	0.0008
Mean	0.0300	
N	15	
Max.	31.3	
Min.	0.028	
Robust SD	0.00012	
Robust CV	0.4%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Ba



En-Scores: S1 - Ba

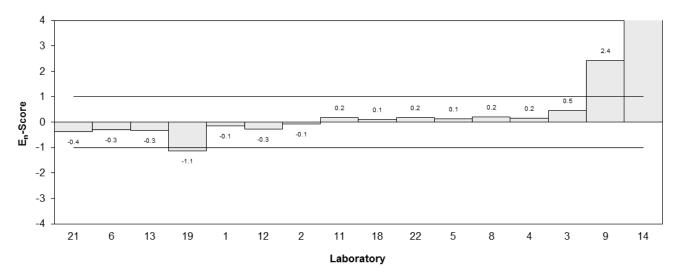


Figure 4

Table 8

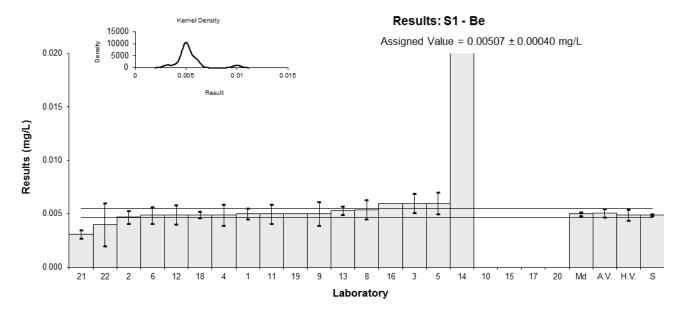
Sample No.	S1
Matrix.	Water
Analyte.	Be
Units	mg/L

Participant Results

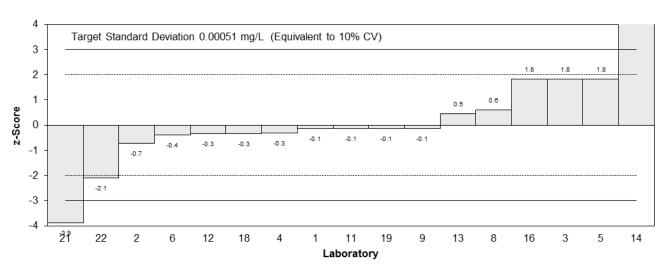
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.005	0.0005	-0.14	-0.11
2	0.0047	0.0006	-0.73	-0.51
3	0.006	0.0009	1.83	0.94
4	0.00491	0.001	-0.32	-0.15
5	0.006	0.001	1.83	0.86
6	0.00487	0.00076	-0.39	-0.23
8	0.00538	0.000896	0.61	0.32
9	0.0050	0.0011	-0.14	-0.06
10	NT	NT		
11	0.005	0.0009	-0.14	-0.07
12	0.0049	0.0009	-0.34	-0.17
13	0.0053	0.0004	0.45	0.41
14	5.04	0.5	9930.83	10.07
15	NT	NT		
16	0.006	NR	1.83	2.33
17	NT	NT		
18	0.0049	0.0003	-0.34	-0.34
19	0.0050	NR	-0.14	-0.17
20	NT	NT		
21	0.0031	0.0004	-3.89	-3.48
22	0.004	0.002	-2.11	-0.52

Assigned Value	0.00507	0.00040
Spike	0.00488	0.00010
Homogeneity Value	0.00490	0.00049
Robust Average	0.00507	0.00040
Median	0.00500	0.00017
Mean	0.00500	
N	16	
Max.	5.04	
Min.	0.0031	
Robust SD	0.0006	
Robust CV	12%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Be



En-Scores: S1 - Be

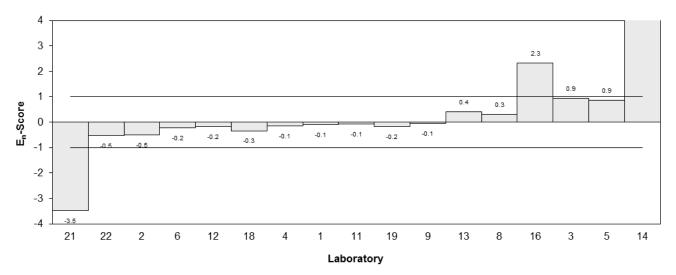


Figure 5

Table 9

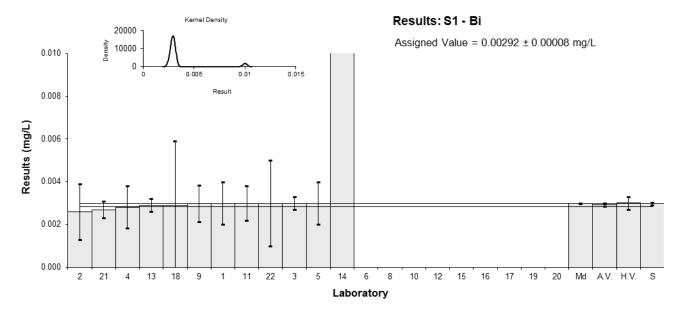
Sample No.	S1
Matrix.	Water
Analyte.	Bi
Units	mg/L

Participant Results

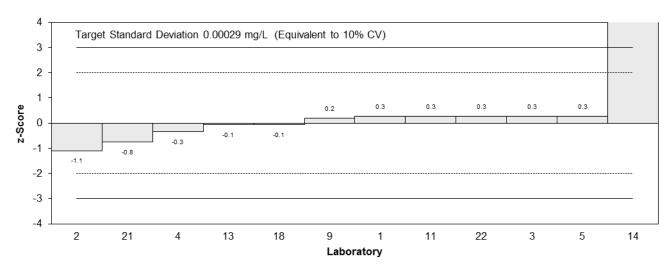
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.003	0.001	0.27	0.08
2	0.0026	0.0013	-1.10	-0.25
3	0.003	0.0003	0.27	0.26
4	0.00282	0.001	-0.34	-0.10
5	0.003	0.001	0.27	0.08
6	< 0.005	0.001		
8	<0.005	0.001		
9	0.00298	0.00085	0.21	0.07
10	NT	NT		
11	0.003	0.0008	0.27	0.10
12	NT	NT		
13	0.0029	0.0003	-0.07	-0.06
14	3.06	0.5	10469.45	6.11
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	0.0029	0.003	-0.07	-0.01
19	NT	NT		
20	NT	NT		
21	0.0027	0.0004	-0.75	-0.54
22	0.003	0.002	0.27	0.04

Assigned Value	0.00292	80000.0
Spike	0.00298	0.00006
Homogeneity Value	0.00301	0.00030
Robust Average	0.00292	0.00008
Median	0.00298	0.00002
Mean	0.00290	
N	11	
Max.	3.06	
Min.	0.0026	
Robust SD	0.00011	
Robust CV	3.8%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Bi



En-Scores: S1 - Bi

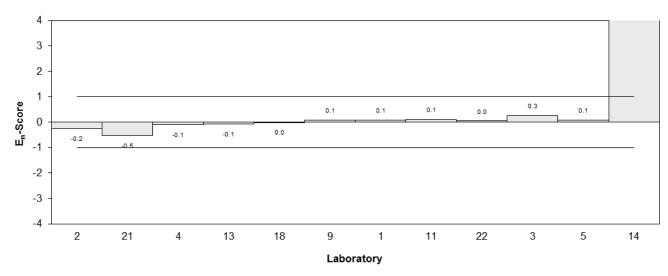


Figure 6

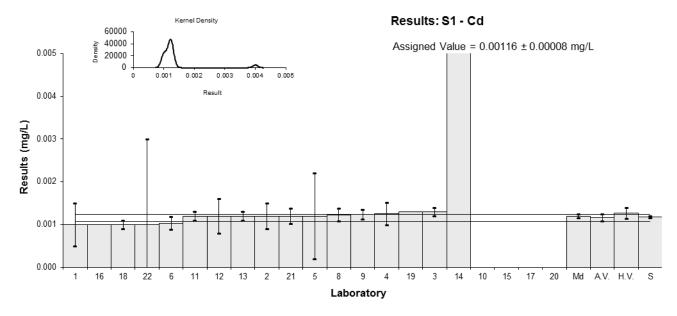
Sample No.	S1
Matrix.	Water
Analyte.	Cd
Units	mg/L

Participant Results

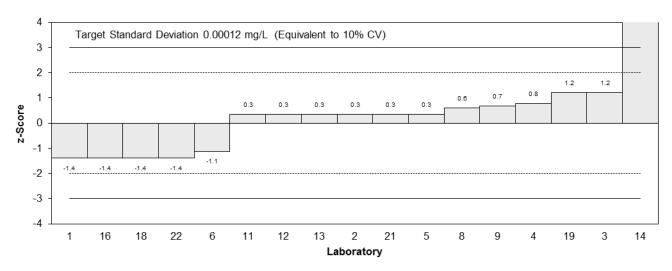
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.001	0.0005	-1.38	-0.32
2	0.0012	0.0003	0.34	0.13
3	0.0013	0.0001	1.21	1.09
4	0.00125	0.00026	0.78	0.33
5	0.0012	0.001	0.34	0.04
6	0.00103	0.00015	-1.12	-0.76
8	0.00123	0.000154	0.60	0.40
9	0.00124	0.00011	0.69	0.59
10	NT	NT		
11	0.0012	0.0001	0.34	0.31
12	0.0012	0.0004	0.34	0.10
13	0.0012	0.0001	0.34	0.31
14	1.26	0.2	10852.07	6.29
15	NT	NT		
16	0.001	NR	-1.38	-2.00
17	NT	NT		
18	0.001	0.0001	-1.38	-1.25
19	0.0013	NR	1.21	1.75
20	NT	NT		
21	0.0012	0.00018	0.34	0.20
22	0.001	0.002	-1.38	-0.08

Assigned Value	0.00116	0.00008
Spike	0.00118	0.00002
Homogeneity Value	0.00127	0.00013
Robust Average	0.00116	0.00008
Median	0.00120	0.00004
Mean	0.00116	
N	16	
Max.	1.26	
Min.	0.001	
Robust SD	0.00013	
Robust CV	11%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Cd



En-Scores: S1 - Cd

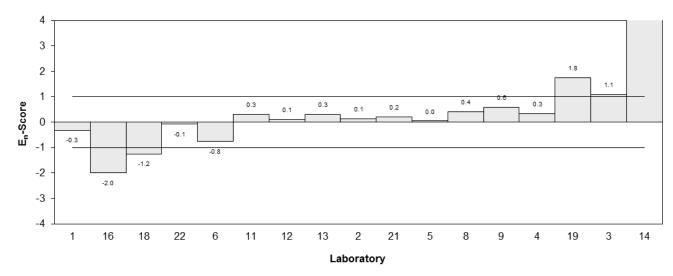


Figure 7

Table 11

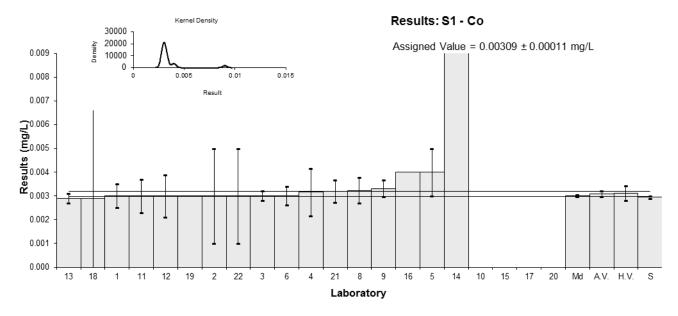
Sample No.	S1
Matrix.	Water
Analyte.	Co
Units	mg/L

Participant Results

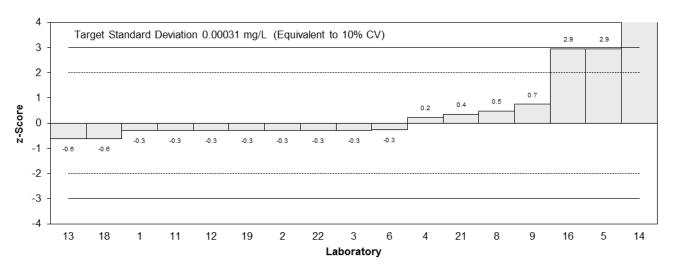
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.003	0.0005	-0.29	-0.18
2	0.003	0.002	-0.29	-0.04
3	0.003	0.0002	-0.29	-0.39
4	0.00316	0.001	0.23	0.07
5	0.004	0.001	2.94	0.90
6	0.00301	0.0004	-0.26	-0.19
8	0.00324	0.000540	0.49	0.27
9	0.00332	0.00036	0.74	0.61
10	NT	NT		
11	0.003	0.0007	-0.29	-0.13
12	0.0030	0.0009	-0.29	-0.10
13	0.0029	0.0002	-0.61	-0.83
14	3.32	0.5	10734.34	6.63
15	NT	NT		
16	0.004	NR	2.94	8.27
17	NT	NT		
18	0.0029	0.004	-0.61	-0.05
19	0.0030	NR	-0.29	-0.82
20	NT	NT		
21	0.0032	0.00048	0.36	0.22
22	0.003	0.002	-0.29	-0.04

Assigned Value	0.00309	0.00011
Spike	0.00295	0.00006
Homogeneity Value	0.00312	0.00031
Robust Average	0.00309	0.00011
Median	0.00300	0.00004
Mean	0.00317	
N	13	
Max.	3.32	
Min.	0.0029	
Robust SD	0.00017	
Robust CV	5.5%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Co



En-Scores: S1 - Co

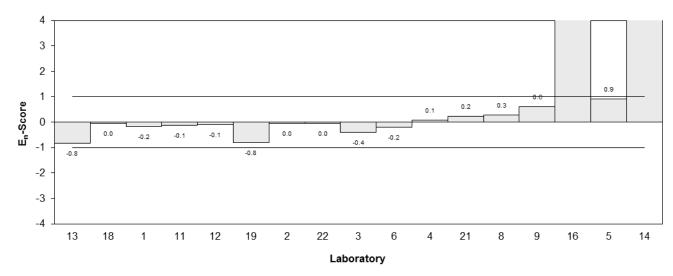


Figure 8

Table 12

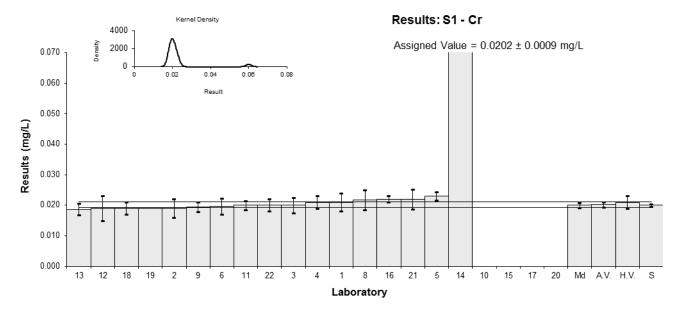
Sample No.	S1
Matrix.	Water
Analyte.	Cr
Units	mg/L

Participant Results

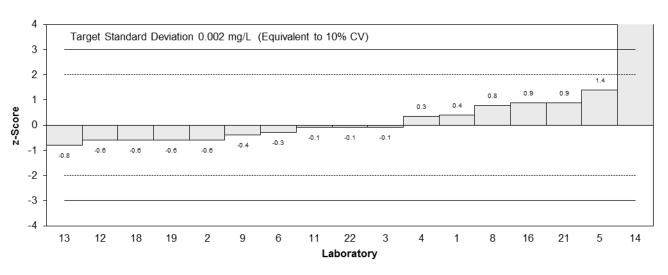
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.021	0.003	0.40	0.26
2	0.019	0.003	-0.59	-0.38
3	0.02	0.0025	-0.10	-0.08
4	0.0209	0.0021	0.35	0.31
5	0.023	0.0014	1.39	1.68
6	0.0196	0.0026	-0.30	-0.22
8	0.0218	0.00329	0.79	0.47
9	0.0194	0.0016	-0.40	-0.44
10	NT	NT		
11	0.02	0.0015	-0.10	-0.11
12	0.019	0.004	-0.59	-0.29
13	0.0186	0.0019	-0.79	-0.76
14	21.4	2.5	10584.06	8.55
15	NT	NT		
16	0.022	0.001	0.89	1.34
17	NT	NT		
18	0.019	0.002	-0.59	-0.55
19	0.0190	NR	-0.59	-1.33
20	NT	NT		
21	0.022	0.0033	0.89	0.53
22	0.02	0.002	-0.10	-0.09

Assigned Value	0.0202	0.0009
Spike	0.0200	0.0004
Homogeneity Value	0.0209	0.0021
Robust Average	0.0202	0.0009
Median	0.0200	0.0008
Mean	0.0203	
N	17	
Max.	21.4	
Min.	0.0186	
Robust SD	0.0014	
Robust CV	6.9%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Cr



En-Scores: S1 - Cr

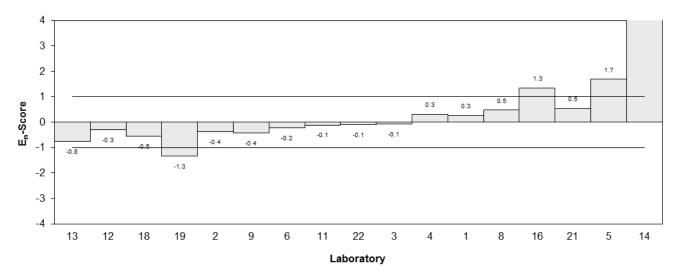


Figure 9

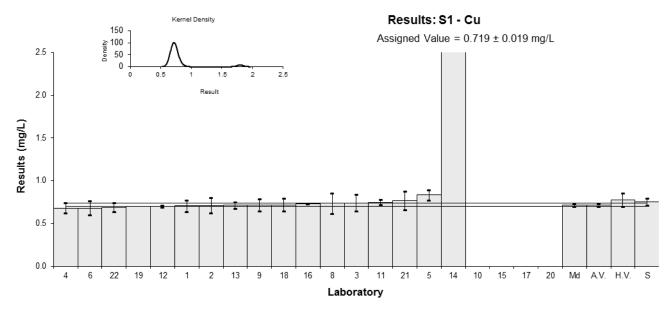
Sample No.	S1
Matrix.	Water
Analyte.	Cu
Units	mg/L

Participant Results

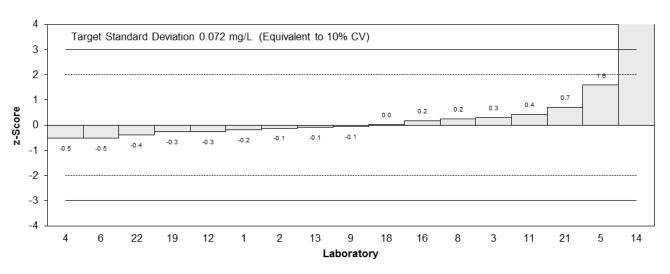
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.706	0.07	-0.18	-0.18
2	0.71	0.09	-0.13	-0.10
3	0.741	0.097	0.31	0.22
4	0.682	0.061	-0.51	-0.58
5	0.833	0.057	1.59	1.90
6	0.682	0.084	-0.51	-0.43
8	0.736	0.121	0.24	0.14
9	0.714	0.072	-0.07	-0.07
10	NT	NT		
11	0.750	0.028	0.43	0.92
12	0.70	0.01	-0.26	-0.88
13	0.713	0.040	-0.08	-0.14
14	759	80	10546.33	9.48
15	NT	NT		
16	0.732	0.002	0.18	0.68
17	NT	NT		
18	0.72	0.076	0.01	0.01
19	0.6992	NR	-0.28	-1.04
20	NT	NT		
21	0.77	0.11	0.71	0.46
22	0.69	0.05	-0.40	-0.54

Assigned Value	0.719	0.019
Spike	0.754	0.038
Homogeneity Value	0.778	0.078
Robust Average	0.719	0.019
Median	0.714	0.016
Mean	0.724	
N	16	
Max.	759	
Min.	0.682	
Robust SD	0.03	
Robust CV	4.2%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Cu



En-Scores: S1 - Cu

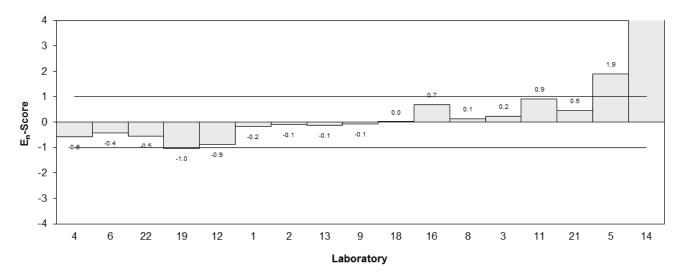


Figure 10

Table 14

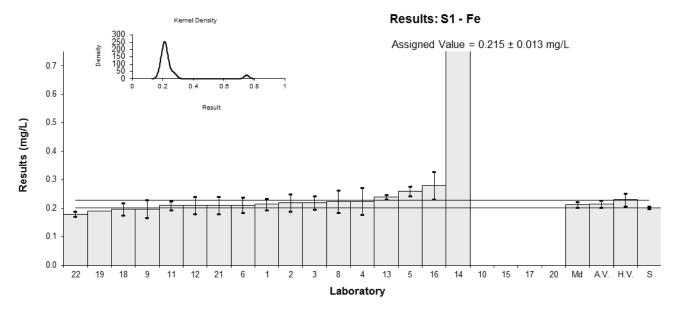
Sample No.	S1
Matrix.	Water
Analyte.	Fe
Units	mg/L

Participant Results

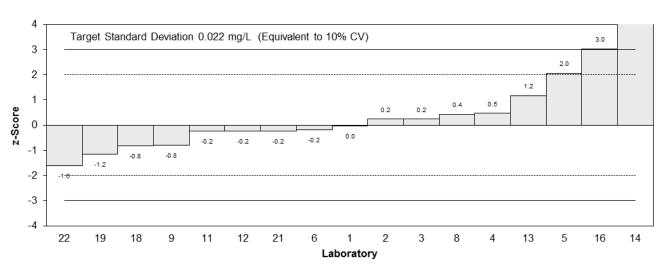
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.214	0.02	-0.05	-0.04
2	0.22	0.03	0.23	0.15
3	0.22	0.024	0.23	0.18
4	0.225	0.047	0.47	0.21
5	0.259	0.017	2.05	2.06
6	0.211	0.027	-0.19	-0.13
8	0.224	0.040	0.42	0.21
9	0.198	0.031	-0.79	-0.51
10	NT	NT		
11	0.210	0.016	-0.23	-0.24
12	0.21	0.03	-0.23	-0.15
13	0.240	0.008	1.16	1.64
14	214	25	9943.49	8.55
15	NT	NT		
16	0.28	0.048	3.02	1.31
17	NT	NT		
18	0.197	0.021	-0.84	-0.73
19	0.1899	NR	-1.17	-1.93
20	NT	NT		
21	0.21	0.031	-0.23	-0.15
22	0.18	0.01	-1.63	-2.13

Assigned Value	0.215	0.013
Spike	0.202	0.004
Homogeneity Value	0.230	0.023
Robust Average	0.215	0.013
Median	0.213	0.010
Mean	0.218	
N	17	
Max.	214	
Min.	0.18	
Robust SD	0.021	
Robust CV	9.8%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Fe



En-Scores: S1 - Fe

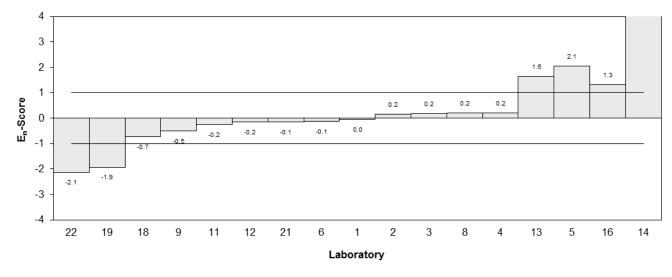


Figure 11

Table 15

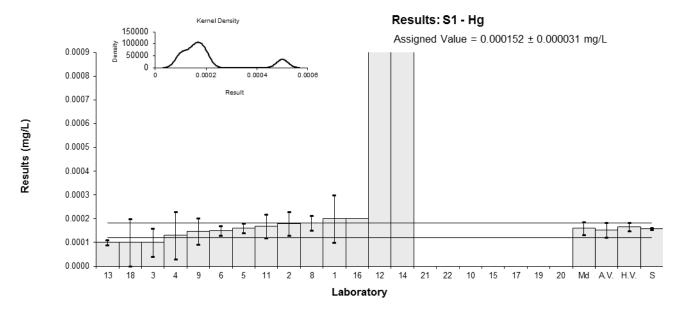
Sample No.	S1
Matrix.	Water
Analyte.	Hg
Units	mg/L

Participant Results

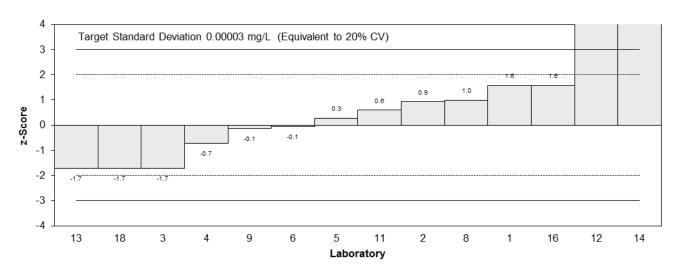
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.0002	0.0001	1.58	0.46
2	0.00018	0.00005	0.92	0.48
3	0.0001	0.00006	-1.71	-0.77
4	0.00013	0.0001	-0.72	-0.21
5	0.00016	0.00002	0.26	0.22
6	0.00015	0.00002	-0.07	-0.05
8	0.000182	0.0000311	0.99	0.68
9	0.000148	0.000055	-0.13	-0.06
10	NT	NT		
11	0.00017	0.00005	0.59	0.31
12	0.16	0.05	5258.16	3.20
13	0.0001	0.00001	-1.71	-1.60
14	0.18	0.04	5916.05	4.50
15	NT	NT		
16	0.0002	NR	1.58	1.55
17	NT	NT		
18	0.0001	0.0001	-1.71	-0.50
19	NT	NT		
20	NT	NT		
21	<0.0005	0.00007		
22	<0.0005	0.0005		

Assigned Value**	0.000152	0.000031
Spike	0.000158	0.000003
Homogeneity Value	0.000166	0.000017
Robust Average	0.000158	0.000033
Median	0.000160	0.000027
Mean	0.0124	
N	13	
Max.	0.18	
Min.	0.0001	
Robust SD	0.000047	
Robust CV	30%	

^{*}Laboratory 14 results were omitted from statistical calculation. **Robust Average excluding Laboratory 12.



z-Scores: S1 - Hg



En-Scores: S1 - Hg

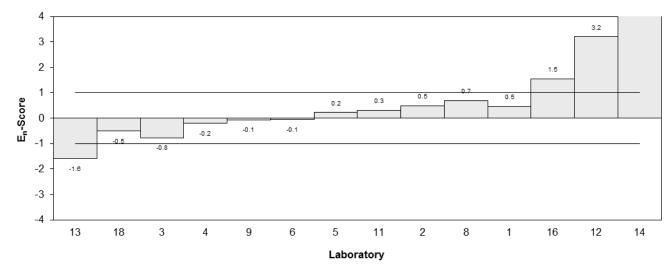


Figure 12

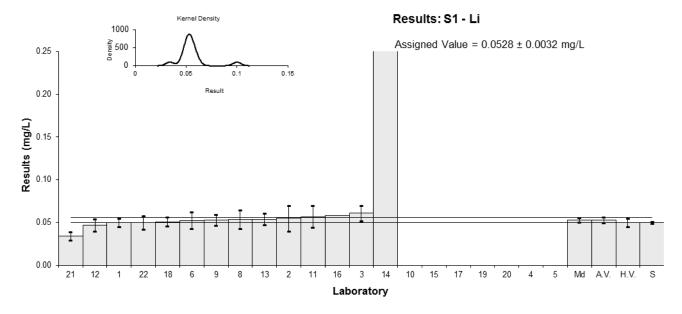
Sample No.	S1
Matrix.	Water
Analyte.	Li
Units	mg/L

Participant Results

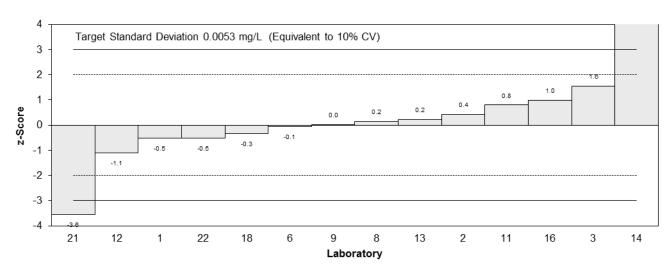
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.050	0.005	-0.53	-0.47
2	0.055	0.015	0.42	0.14
3	0.061	0.009	1.55	0.86
4	NT	NT		
5	NT	NT		
6	0.0525	0.0096	-0.06	-0.03
8	0.0536	0.0107	0.15	0.07
9	0.0529	0.0064	0.02	0.01
10	NT	NT		
11	0.057	0.0128	0.80	0.32
12	0.047	0.007	-1.10	-0.75
13	0.0540	0.0069	0.23	0.16
14	55.4	6	10482.42	9.22
15	NT	NT		
16	0.058	NR	0.98	1.63
17	NT	NT		
18	0.051	0.005	-0.34	-0.30
19	NT	NT		
20	NT	NT		
21	0.034	0.0051	-3.56	-3.12
22	0.05	0.008	-0.53	-0.32

Assigned Value	0.0528	0.0032
Spike	0.0500	0.0010
Homogeneity Value	0.0497	0.0050
Robust Average	0.0528	0.0032
Median	0.0529	0.0026
Mean	0.0520	
N	13	
Max.	55.4	
Min.	0.034	
Robust SD	0.0046	
Robust CV	8.7%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Li



En-Scores: S1 - Li

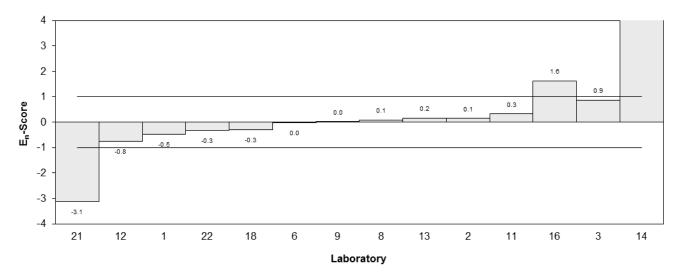


Figure 13

Table 17

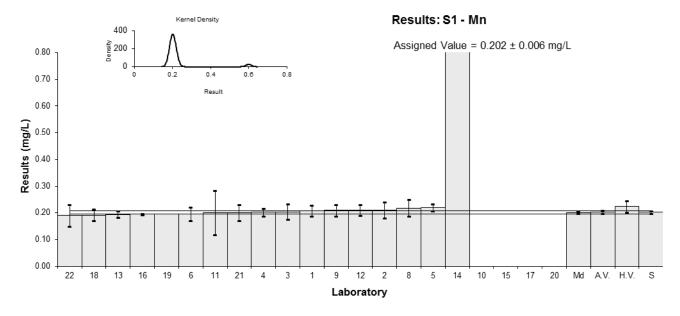
Sample No.	S1
Matrix.	Water
Analyte.	Mn
Units	mg/L

Participant Results

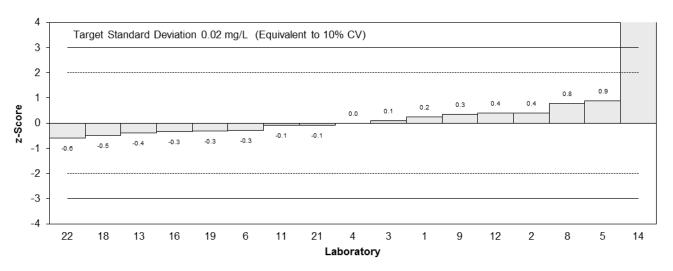
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.207	0.02	0.25	0.24
2	0.21	0.03	0.40	0.26
3	0.204	0.028	0.10	0.07
4	0.202	0.014	0.00	0.00
5	0.220	0.013	0.89	1.26
6	0.196	0.026	-0.30	-0.22
8	0.218	0.0308	0.79	0.51
9	0.209	0.021	0.35	0.32
10	NT	NT		
11	0.20	0.0834	-0.10	-0.02
12	0.21	0.02	0.40	0.38
13	0.194	0.012	-0.40	-0.60
14	211	25	10435.54	8.43
15	NT	NT		
16	0.195	0.002	-0.35	-1.11
17	NT	NT		
18	0.192	0.022	-0.50	-0.44
19	0.1958	NR	-0.31	-1.03
20	NT	NT		
21	0.20	0.03	-0.10	-0.07
22	0.19	0.04	-0.59	-0.30

Assigned Value	0.202	0.006
Spike	0.202	0.004
Homogeneity Value	0.224	0.022
Robust Average	0.202	0.006
Median	0.201	0.005
Mean	0.203	
N	17	
Max.	211	
Min.	0.19	
Robust SD	0.0096	
Robust CV	4.8%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Mn



En-Scores: S1 - Mn

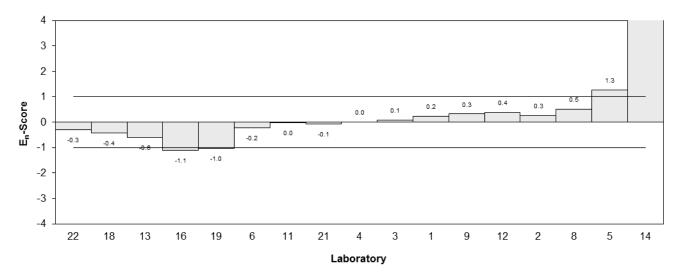


Figure 14

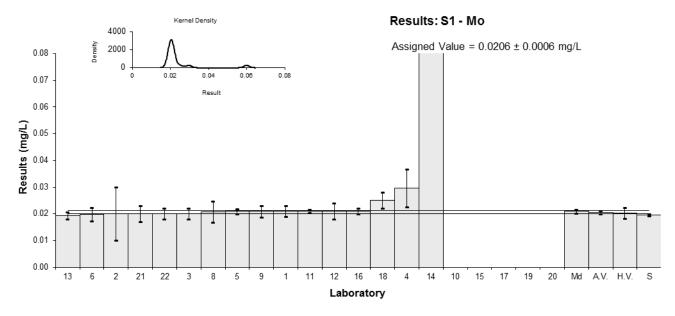
Sample No.	S1
Matrix.	Water
Analyte.	Мо
Units	mg/L

Participant Results

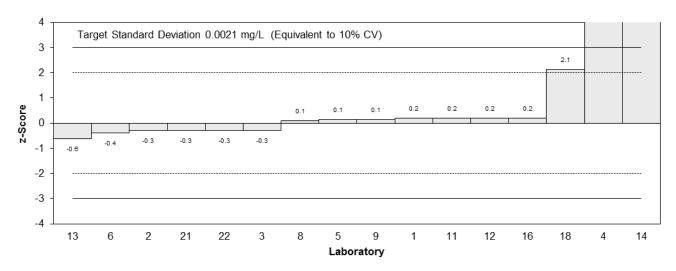
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.021	0.002	0.19	0.19
2	0.02	0.01	-0.29	-0.06
3	0.02	0.002	-0.29	-0.29
4	0.0297	0.0071	4.42	1.28
5	0.0209	0.001	0.15	0.26
6	0.0198	0.0025	-0.39	-0.31
8	0.0208	0.00389	0.10	0.05
9	0.0209	0.0021	0.15	0.14
10	NT	NT		
11	0.021	0.00063	0.19	0.46
12	0.021	0.003	0.19	0.13
13	0.0193	0.0013	-0.63	-0.91
14	19.3	2	9358.93	9.64
15	NT	NT		
16	0.021	0.001	0.19	0.34
17	NT	NT		
18	0.025	0.003	2.14	1.44
19	NT	NT		
20	NT	NT		
21	0.020	0.003	-0.29	-0.20
22	0.02	0.002	-0.29	-0.29

Assigned Value	0.0206	0.0006
Spike	0.0196	0.0004
Homogeneity Value	0.0203	0.0020
Robust Average	0.0206	0.0006
Median	0.0209	0.0007
Mean	0.0214	
N	15	
Max.	19.3	
Min.	0.0193	
Robust SD	0.0009	
Robust CV	4.4%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Mo



En-Scores: S1 - Mo

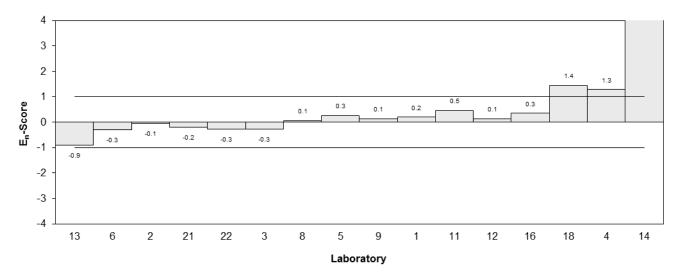


Figure 15

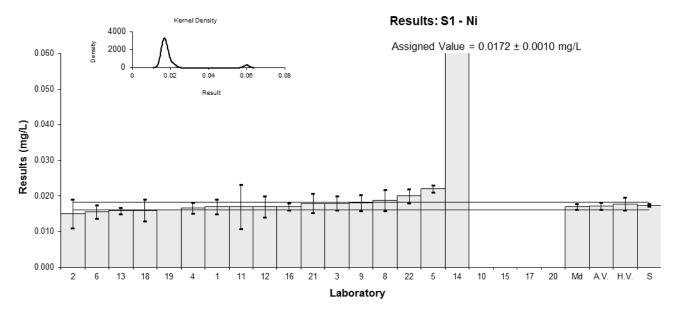
Sample No.	S1
Matrix.	Water
Analyte.	Ni
Units	mg/L

Participant Results

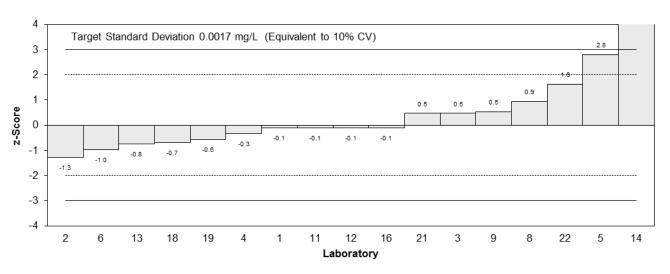
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.017	0.002	-0.12	-0.09
2	0.015	0.004	-1.28	-0.53
3	0.018	0.002	0.47	0.36
4	0.0166	0.0015	-0.35	-0.33
5	0.022	0.001	2.79	3.39
6	0.0155	0.0019	-0.99	-0.79
8	0.0188	0.00298	0.93	0.51
9	0.0181	0.0022	0.52	0.37
10	NT	NT		
11	0.017	0.0062	-0.12	-0.03
12	0.017	0.003	-0.12	-0.06
13	0.0159	0.0009	-0.76	-0.97
14	17.3	2	10048.14	8.64
15	NT	NT		
16	0.017	0.001	-0.12	-0.14
17	NT	NT		
18	0.016	0.003	-0.70	-0.38
19	0.0162	NR	-0.58	-1.00
20	NT	NT		
21	0.018	0.0027	0.47	0.28
22	0.02	0.002	1.63	1.25

Assigned Value	0.0172	0.0010
Spike	0.0174	0.0004
Homogeneity Value	0.0178	0.0018
Robust Average	0.0172	0.0010
Median	0.0170	0.0008
Mean	0.0174	
N	16	
Max.	17.3	
Min.	0.015	
Robust SD	0.0015	
Robust CV	8.7%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Ni



En-Scores: S1 - Ni

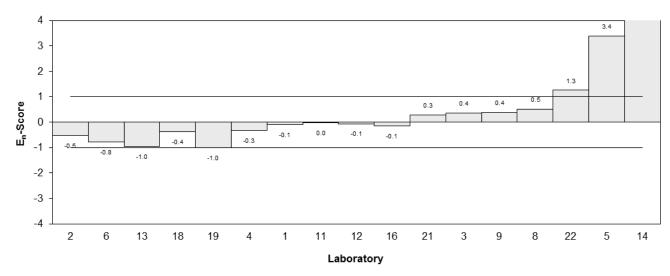


Figure 16

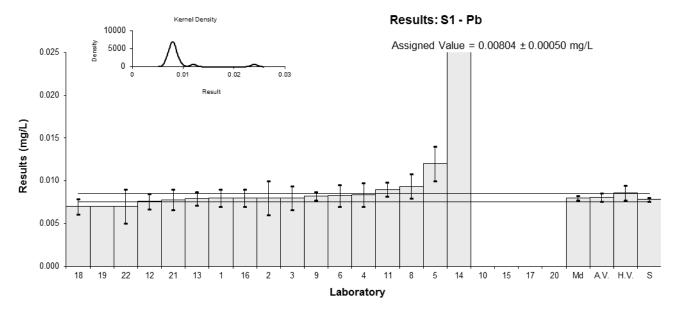
Sample No.	S1
Matrix.	Water
Analyte.	Pb
Units	mg/L

Participant Results

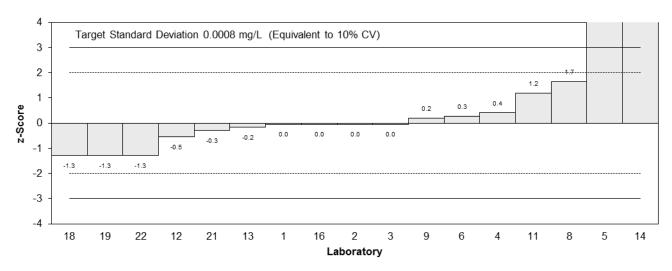
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.008	0.001	-0.05	-0.04
2	0.008	0.002	-0.05	-0.02
3	0.008	0.0014	-0.05	-0.03
4	0.00837	0.0014	0.41	0.22
5	0.012	0.002	4.93	1.92
6	0.00826	0.00128	0.27	0.16
8	0.00937	0.00143	1.65	0.88
9	0.00819	0.00050	0.19	0.21
10	NT	NT		
11	0.009	0.0008	1.19	1.02
12	0.0076	0.0009	-0.55	-0.43
13	0.0079	0.0008	-0.17	-0.15
14	8.37	1	10400.45	8.36
15	NT	NT		
16	0.008	0.001	-0.05	-0.04
17	NT	NT		
18	0.007	0.0009	-1.29	-1.01
19	0.0070	NR	-1.29	-2.08
20	NT	NT		
21	0.0078	0.0012	-0.30	-0.18
22	0.007	0.002	-1.29	-0.50

Assigned Value	0.00804	0.00050
Spike	0.00782	0.00024
Homogeneity Value	0.00856	0.00086
Robust Average	0.00804	0.00050
Median	0.00800	0.00025
Mean	0.00823	
N	16	
Max.	8.37	
Min.	0.007	
Robust SD	0.0008	
Robust CV	10%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Pb



En-Scores: S1 - Pb

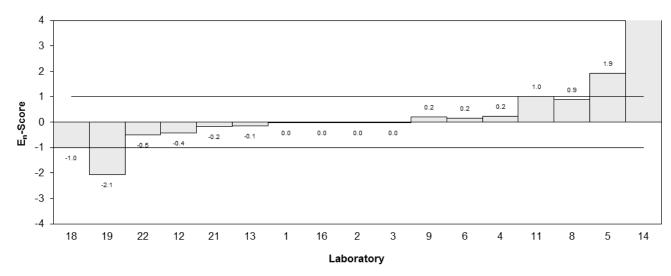


Figure 17

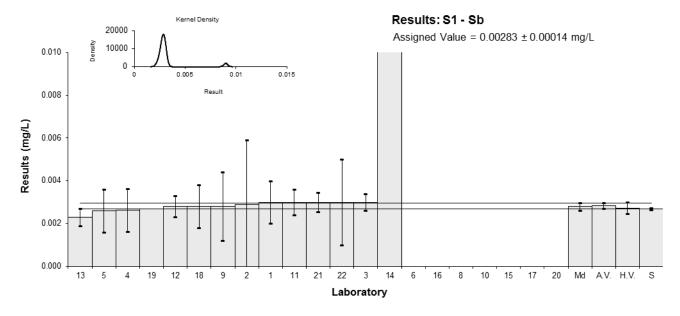
Sample No.	S1
Matrix.	Water
Analyte.	Sb
Units	mg/L

Participant Results

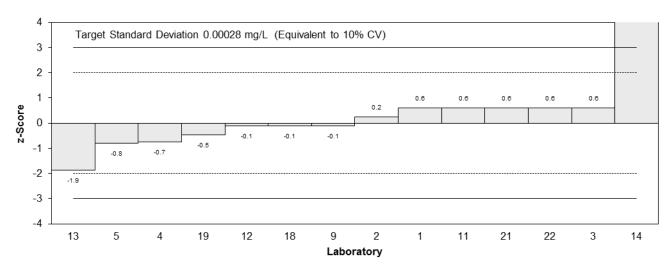
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.003	0.001	0.60	0.17
2	0.0029	0.003	0.25	0.02
3	0.003	0.0004	0.60	0.40
4	0.00262	0.001	-0.74	-0.21
5	0.0026	0.001	-0.81	-0.23
6	< 0.005	0.001		
8	<0.005	0.001		
9	0.0028	0.0016	-0.11	-0.02
10	NT	NT		
11	0.003	0.0006	0.60	0.28
12	0.0028	0.0005	-0.11	-0.06
13	0.0023	0.0004	-1.87	-1.25
14	3.14	0.5	11085.41	6.27
15	NT	NT		
16	<0.005	NR		
17	NT	NT		
18	0.0028	0.001	-0.11	-0.03
19	0.0027	NR	-0.46	-0.93
20	NT	NT		
21	0.0030	0.00045	0.60	0.36
22	0.003	0.002	0.60	0.08

Assigned Value	0.00283	0.00014
Spike	0.00269	0.00005
Homogeneity Value	0.00272	0.00027
Robust Average	0.00283	0.00014
Median	0.00280	0.00018
Mean	0.00281	
N	13	
Max.	3.14	
Min.	0.0023	
Robust SD	0.0002	
Robust CV	7.1%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Sb



En-Scores: S1 - Sb

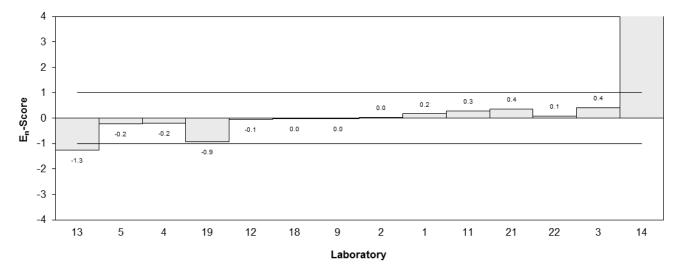


Figure 18

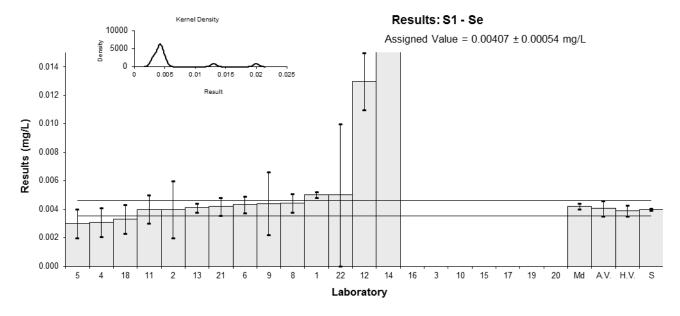
Sample No.	S1
Matrix.	Water
Analyte.	Se
Units	mg/L

Participant Results

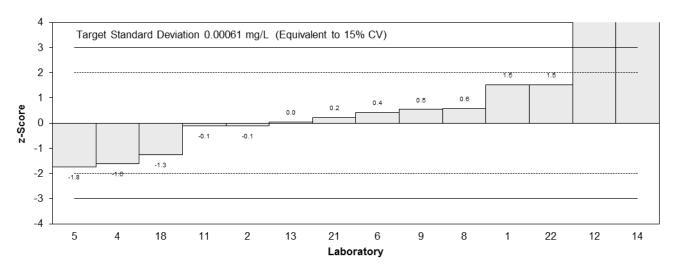
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.005	0.0002	1.52	1.62
2	0.004	0.002	-0.11	-0.03
3	<0.01	NR		
4	0.00308	0.001	-1.62	-0.87
5	0.003	0.001	-1.75	-0.94
6	0.00433	0.00059	0.43	0.33
8	0.00442	0.000656	0.57	0.41
9	0.0044	0.0022	0.54	0.15
10	NT	NT		
11	0.004	0.0010	-0.11	-0.06
12	0.013	0.002	14.63	4.31
13	0.0041	0.0003	0.05	0.05
14	4.0	0.5	6545.34	7.99
15	NT	NT		
16	<0.005	NR		
17	NT	NT		
18	0.0033	0.001	-1.26	-0.68
19	NT	NT		
20	NT	NT		
21	0.0042	0.00063	0.21	0.16
22	0.005	0.005	1.52	0.18

Assigned Value**	0.00407	0.00054
Spike	0.00398	0.00008
Homogeneity Value	0.00389	0.00039
Robust Average	0.00417	0.00058
Median	0.00420	0.00020
Mean	0.00476	
N	13	
Max.	4	
Min.	0.003	
Robust SD	0.00075	
Robust CV	18%	

^{*}Laboratory 14 results were omitted from statistical calculation. **Robust Average excluding Laboratory 12.



z-Scores: S1 - Se



En-Scores: S1 - Se

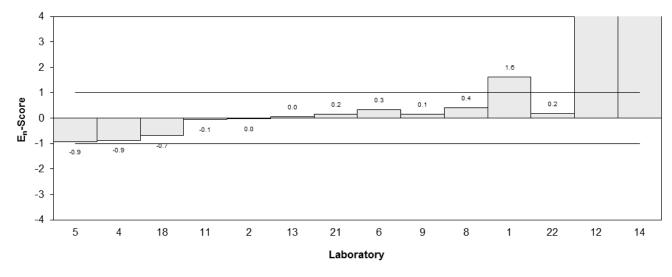


Figure 19

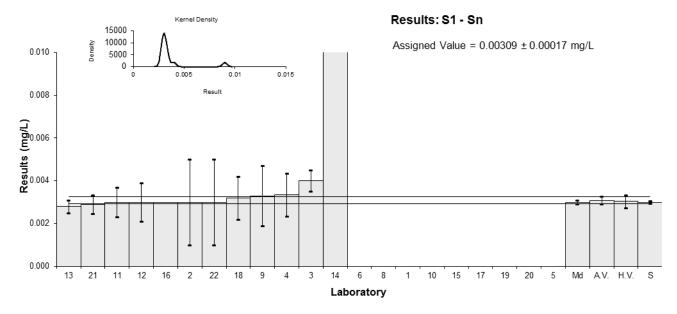
Sample No.	S1
Matrix.	Water
Analyte.	Sn
Units	mg/L

Participant Results

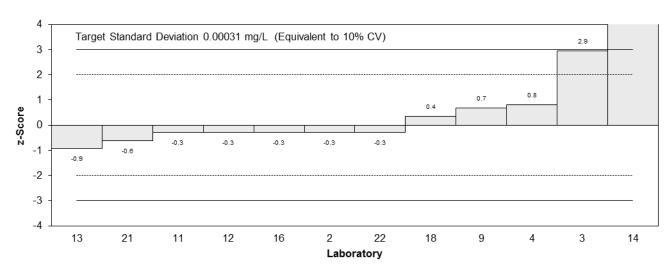
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	NT	NT		
2	0.003	0.002	-0.29	-0.04
3	0.004	0.0005	2.94	1.72
4	0.00334	0.001	0.81	0.25
5	NT	NT		
6	< 0.005	0.001		
8	<0.005	0.000732		
9	0.0033	0.0014	0.68	0.15
10	NT	NT		
11	0.003	0.0007	-0.29	-0.12
12	0.0030	0.0009	-0.29	-0.10
13	0.0028	0.0003	-0.94	-0.84
14	2.9	0.5	9375.11	5.79
15	NT	NT		
16	0.003	NR	-0.29	-0.53
17	NT	NT		
18	0.0032	0.001	0.36	0.11
19	NT	NT		
20	NT	NT		
21	0.0029	0.00043	-0.61	-0.41
22	0.003	0.002	-0.29	-0.04

A ' I \ / - I	0.00000	0.00047
Assigned Value	0.00309	0.00017
Spike	0.00299	0.00006
Homogeneity Value	0.00304	0.00030
Robust Average	0.00309	0.00017
Median	0.00314	0.00010
Mean	0.00310	
N	11	
Max.	2.9	
Min.	0.0028	
Robust SD	0.00022	
Robust CV	7.1%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Sn



En-Scores: S1 - Sn

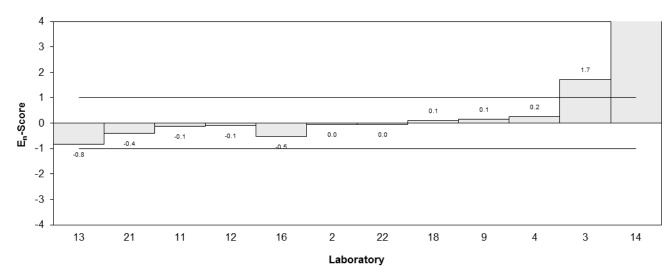


Figure 20

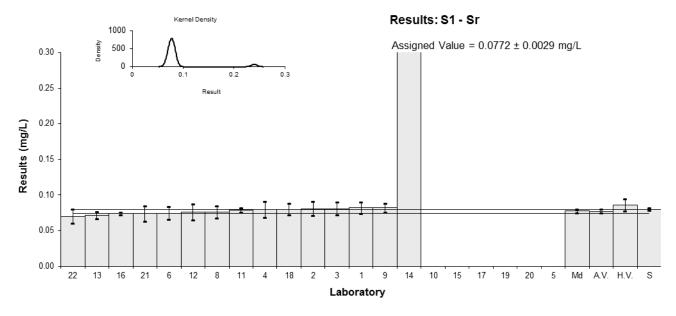
Sample No.	S1
Matrix.	Water
Analyte.	Sr
Units	mg/L

Participant Results

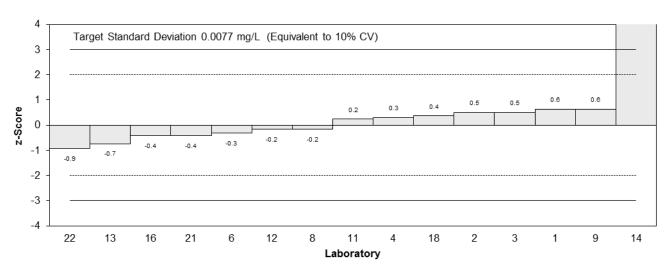
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.082	0.008	0.62	0.56
2	0.081	0.010	0.49	0.36
3	0.081	0.009	0.49	0.40
4	0.0795	0.011	0.30	0.20
5	NT	NT		
6	0.0747	0.0093	-0.32	-0.26
8	0.0760	0.00836	-0.16	-0.14
9	0.0820	0.0066	0.62	0.67
10	NT	NT		
11	0.079	0.003	0.23	0.43
12	0.076	0.011	-0.16	-0.11
13	0.0715	0.0046	-0.74	-1.05
14	82.2	10	10637.67	8.21
15	NT	NT		
16	0.074	0.002	-0.41	-0.91
17	NT	NT		
18	0.08	0.008	0.36	0.33
19	NT	NT		
20	NT	NT		
21	0.074	0.011	-0.41	-0.28
22	0.07	0.01	-0.93	-0.69

Assigned Value	0.0772	0.0029
Spike	0.0800	0.0016
Homogeneity Value	0.0863	0.0086
Robust Average	0.0772	0.0029
Median	0.0775	0.0030
Mean	0.0772	
N	15	
Max.	82.2	
Min.	0.07	
Robust SD	0.0044	
Robust CV	5.7%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Sr



En-Scores: S1 - Sr

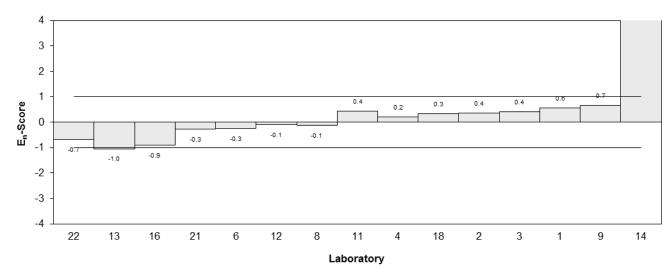


Figure 21

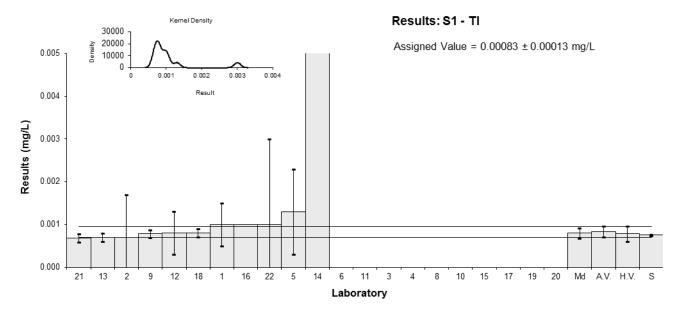
Sample No.	S1
Matrix.	Water
Analyte.	ТІ
Units	mg/L

Participant Results

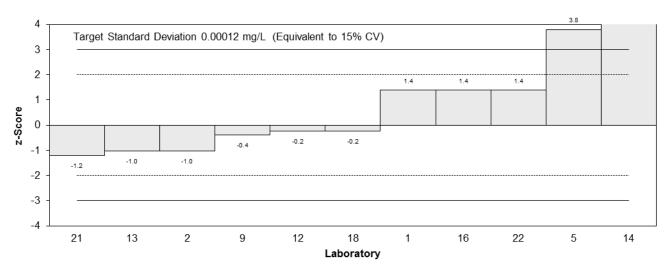
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.001	0.0005	1.38	0.33
2	0.0007	0.001	-1.04	-0.13
3	<0.001	NR		
4	<0.001	0.001		
5	0.0013	0.001	3.79	0.47
6	< 0.005	0.001		
8	< 0.005	0.000487		
9	0.000781	0.000086	-0.39	-0.31
10	NT	NT		
11	<0.001	NR		
12	0.0008	0.0005	-0.23	-0.06
13	0.0007	0.0001	-1.04	-0.79
14	0.74	0.1	5944.28	7.39
15	NT	NT		
16	0.001	NR	1.38	1.34
17	NT	NT		
18	0.0008	0.0001	-0.23	-0.18
19	NT	NT		
20	NT	NT		
21	0.00068	0.0001	-1.20	-0.92
22	0.001	0.002	1.38	0.09

Assigned Value**	0.00083	0.00013
Spike	0.00075	0.00002
Homogeneity Value	0.00079	0.00018
Robust Average	0.00085	0.00013
Median	0.00080	0.00012
Mean	0.00088	
N	10	
Max.	0.74	
Min.	0.00068	
Robust SD	0.00015	
Robust CV	18%	

^{*}Laboratory 14 results were omitted from statistical calculation. **Robust Average excluding Laboratory 5.



z-Scores: S1 - TI



En-Scores: S1 - TI

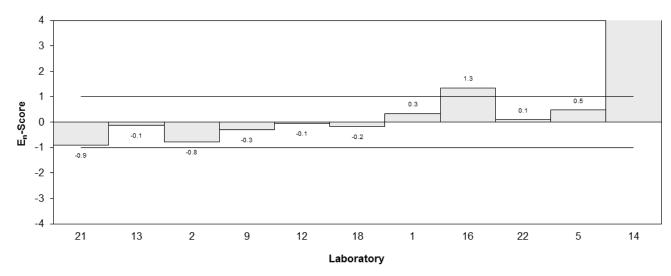


Figure 22

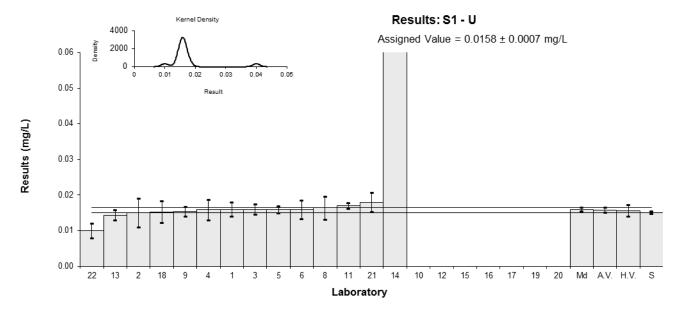
Sample No.	S1
Matrix.	Water
Analyte.	U
Units	mg/L

Participant Results

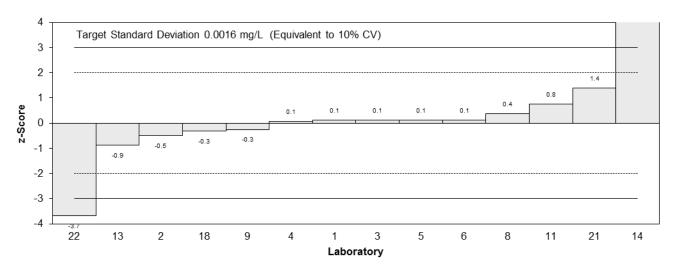
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.016	0.002	0.13	0.09
2	0.015	0.004	-0.51	-0.20
3	0.016	0.0014	0.13	0.13
4	0.0159	0.0029	0.06	0.03
5	0.016	0.001	0.13	0.16
6	0.0160	0.0026	0.13	0.07
8	0.0164	0.00328	0.38	0.18
9	0.0154	0.0013	-0.25	-0.27
10	NT	NT		
11	0.017	0.0008	0.76	1.13
12	NT	NT		
13	0.0144	0.0014	-0.89	-0.89
14	15.6	2	9863.42	7.79
15	NT	NT		
16	NT	NT		
17	NT	NT		
18	0.0153	0.003	-0.32	-0.16
19	NT	NT		
20	NT	NT		
21	0.018	0.0027	1.39	0.79
22	0.01	0.002	-3.67	-2.74

Assigned Value	0.0158	0.0007
Spike	0.0151	0.0003
Homogeneity Value	0.0156	0.0016
Robust Average	0.0158	0.0007
Median	0.0160	0.0006
Mean	0.0155	
N	14	
Max.	15.6	
Min.	0.01	
Robust SD	0.001	
Robust CV	6.3%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - U



En-Scores: S1 - U

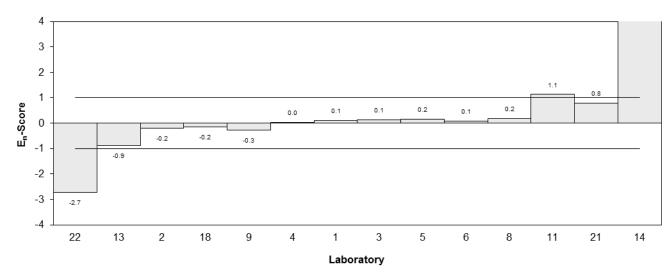


Figure 23

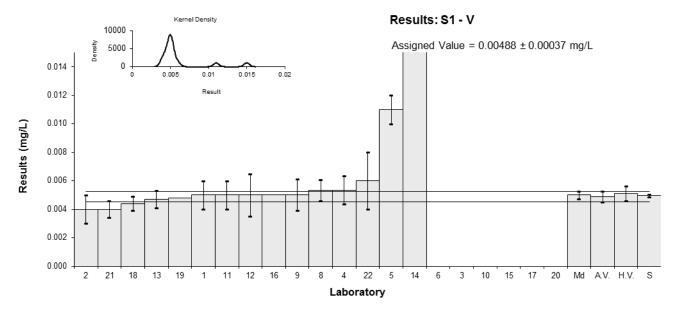
Sample No.	S1
Matrix.	Water
Analyte.	V
Units	mg/L

Participant Results

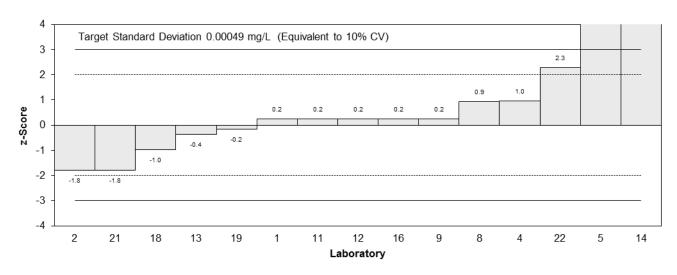
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.005	0.001	0.25	0.11
2	0.004	0.001	-1.80	-0.83
3	<0.01	NR		
4	0.00535	0.001	0.96	0.44
5	0.011	0.001	12.54	5.74
6	< 0.005	0.001		
8	0.00534	0.000753	0.94	0.55
9	0.0050	0.0011	0.25	0.10
10	NT	NT		
11	0.005	0.0010	0.25	0.11
12	0.0050	0.0015	0.25	0.08
13	0.0047	0.0006	-0.37	-0.26
14	5.5	1.0	11260.49	5.50
15	NT	NT		
16	0.005	NR	0.25	0.32
17	NT	NT		
18	0.0044	0.0005	-0.98	-0.77
19	0.0048	NR	-0.16	-0.22
20	NT	NT		
21	0.0040	0.0006	-1.80	-1.25
22	0.006	0.002	2.30	0.55

Assigned Value**	0.00488	0.00037
Spike	0.00496	0.00010
Homogeneity Value	0.00510	0.00051
Robust Average	0.00497	0.00045
Median	0.00500	0.00027
Mean	0.00533	
N	14	
Max.	5.5	
Min.	0.004	
Robust SD	0.00054	
Robust CV	11%	

^{*}Laboratory 14 results were omitted from statistical calculation. **Robust Average excluding Laboratory 5.



z-Scores: S1 - V



En-Scores: S1 - V

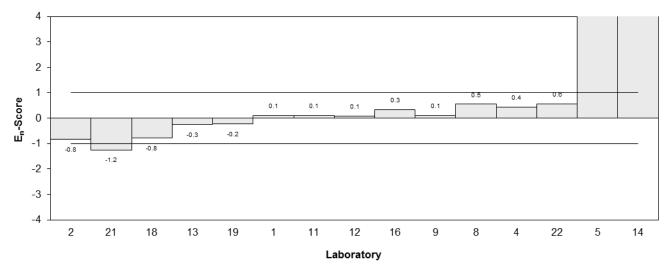


Figure 24

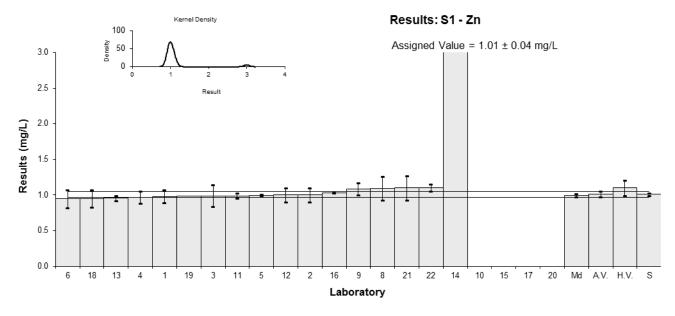
Sample No.	S1
Matrix.	Water
Analyte.	Zn
Units	mg/L

Participant Results

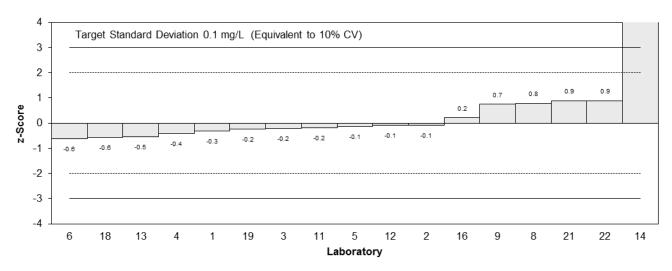
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.978	0.090	-0.32	-0.32
2	1.0	0.1	-0.10	-0.09
3	0.989	0.155	-0.21	-0.13
4	0.968	0.087	-0.42	-0.44
5	0.996	0.012	-0.14	-0.34
6	0.947	0.124	-0.62	-0.48
8	1.09	0.166	0.79	0.47
9	1.085	0.087	0.74	0.78
10	NT	NT		
11	0.990	0.0376	-0.20	-0.36
12	1.0	0.1	-0.10	-0.09
13	0.955	0.038	-0.54	-1.00
14	1050	100	10386.04	10.49
15	NT	NT		
16	1.031	0.003	0.21	0.52
17	NT	NT		
18	0.9511	0.12	-0.58	-0.47
19	0.9859	NR	-0.24	-0.60
20	NT	NT		
21	1.1	0.17	0.89	0.52
22	1.1	0.05	0.89	1.41

Assigned Value	1.01	0.04
Spike	1.01	0.02
Homogeneity Value	1.10	0.11
Robust Average	1.01	0.04
Median	0.99	0.03
Mean	1.01	
N	16	
Max.	1050	
Min.	0.947	
Robust SD	0.061	
Robust CV	6%	

^{*}Laboratory 14 results were omitted from statistical calculation.



z-Scores: S1 - Zn



En-Scores: S1 - Zn

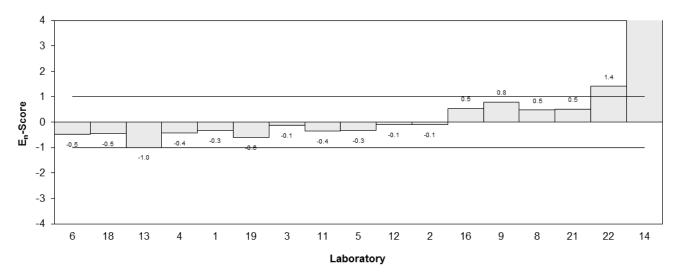


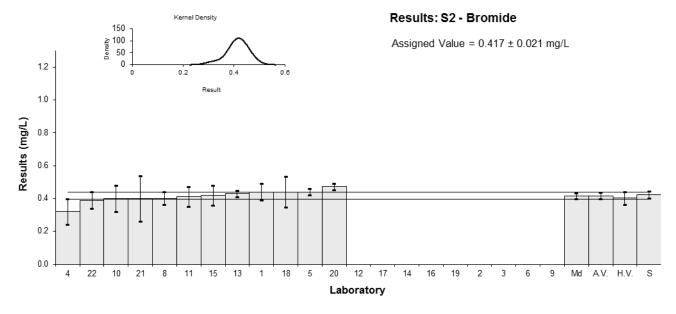
Figure 25

Sample No.	S2
Matrix.	Water
Analyte.	Bromide
Units	mg/L

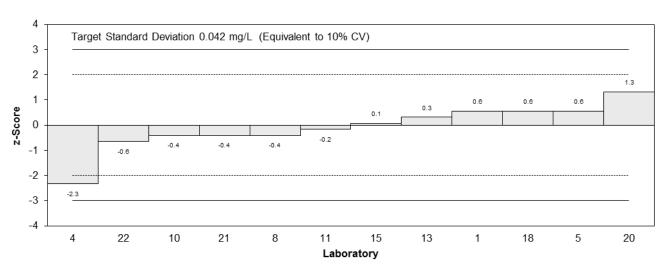
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.44	0.05	0.55	0.42
2	NT	NT		
3	NT	NT		
4	0.32	0.077	-2.33	-1.22
5	0.44	0.02	0.55	0.79
6	NT	NT		
8	0.40	0.039	-0.41	-0.38
9	NT	NT		
10	0.4	80.0	-0.41	-0.21
11	0.41	0.06	-0.17	-0.11
12	<0.50	NR		
13	0.43	0.02	0.31	0.45
14	NT	NT		
15	0.42	0.06	0.07	0.05
16	NT	NT		
17	NR	NR		
18	0.44	0.093	0.55	0.24
19	NT	NT		
20	0.472	0.02	1.32	1.90
21	0.40	0.14	-0.41	-0.12
22	0.39	0.05	-0.65	-0.50

Assigned Value	0.417	0.021
Spike	0.422	0.021
Homogeneity Value	0.402	0.040
Robust Average	0.417	0.021
Median	0.415	0.019
Mean	0.414	
N	12	
Max.	0.472	
Min.	0.32	
Robust SD	0.029	
Robust CV	7%	



z-Scores: \$2 - Bromide



En-Scores: S2 - Bromide

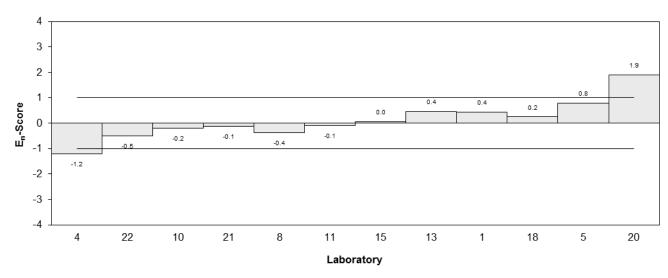


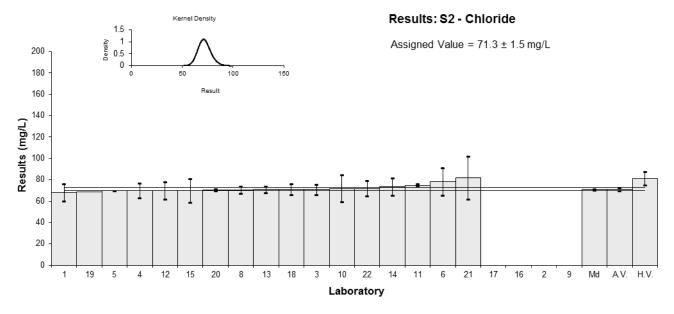
Figure 26

Sample No.	S2
Matrix.	Water
Analyte.	Chloride
Units	mg/L

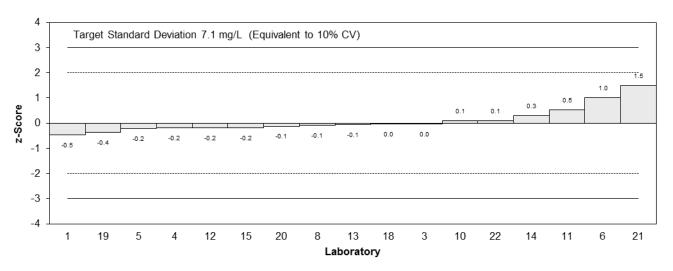
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	68	8.0	-0.46	-0.41
2	NT	NT		
3	71	4.8	-0.04	-0.06
4	69.9	7	-0.20	-0.20
5	69.7	0.025	-0.22	-1.07
6	78.45	12.91	1.00	0.55
8	70.72	3.23	-0.08	-0.16
9	NT	NT		
10	72	12.7	0.10	0.05
11	75	1.05	0.52	2.02
12	70	8	-0.18	-0.16
13	70.9	2.9	-0.06	-0.12
14	73.4	8	0.29	0.26
15	70	11	-0.18	-0.12
16	NT	NT		
17	NR	NR		
18	71	5	-0.04	-0.06
19	68.7	NR	-0.36	-1.73
20	70.4	1	-0.13	-0.50
21	82	20	1.50	0.53
22	72	7	0.10	0.10

Assigned Value	71.3	1.5
Spike	Not Spiked	
Homogeneity Value	81.3	6.4
Robust Average	71.3	1.5
Median	70.9	0.8
Mean	72	
N	17	
Max.	82	
Min.	68	
Robust SD	2.4	
Robust CV	3.4%	



z-Scores: S2 - Chloride



En-Scores: S2 - Chloride

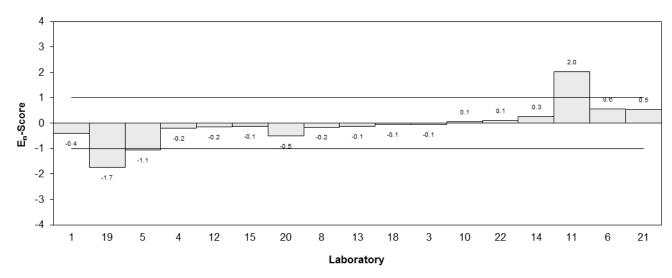


Figure 27

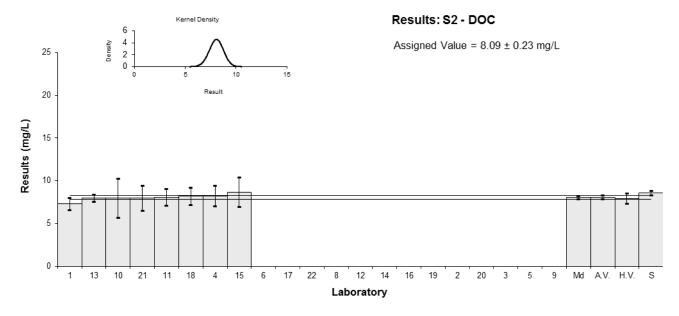
Table 31

Sample No.	S2
Matrix.	Water
Analyte.	DOC
Units	mg/L

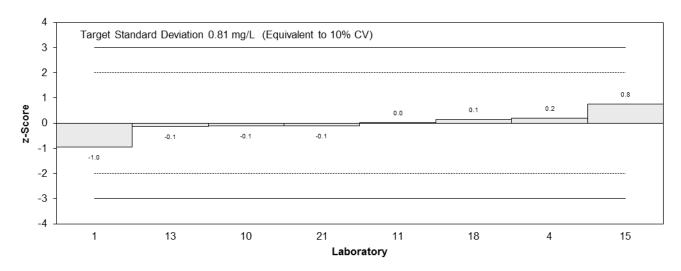
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	7.32	0.7	-0.95	-1.05
2	NT	NT		
3	NT	NT		
4	8.25	1.2	0.20	0.13
5	NT	NT		
6	<5	NR		
8	NR	NR		
9	NT	NT		
10	8	2.3	-0.11	-0.04
11	8.1	1	0.01	0.01
12	NT	NT		
13	7.98	0.4	-0.14	-0.24
14	NT	NT		
15	8.7	1.7	0.75	0.36
16	NT	NT		
17	NR	NR		
18	8.2	1	0.14	0.11
19	NT	NT		
20	NT	NT		
21	8.0	1.44	-0.11	-0.06
22	NR	NR		

Assigned Value	8.09	0.23
Spike	8.60	0.24
Homogeneity Value	7.93	0.59
Robust Average	8.09	0.23
Median	8.05	0.14
Mean	8.07	
N	8	
Max.	8.7	
Min.	7.32	
Robust SD	0.26	
Robust CV	3.2%	



z-Scores: S2 - DOC



En-Scores: S2 - DOC

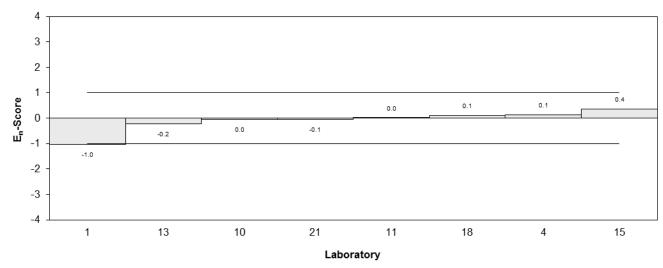


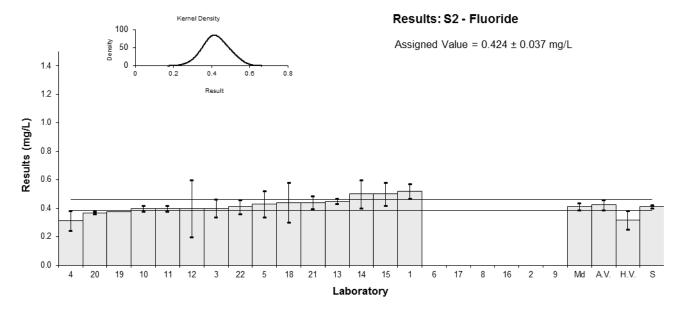
Figure 28

Sample No.	S2
Matrix.	Water
Analyte.	Fluoride
Units	mg/L

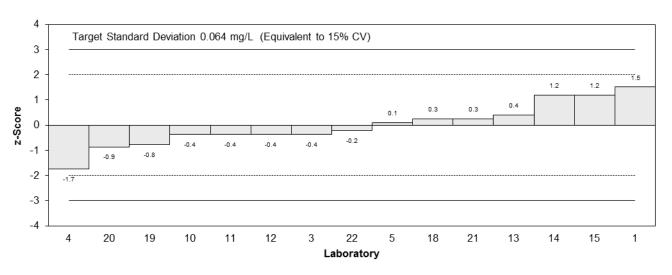
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.52	0.05	1.51	1.54
2	NT	NT		
3	0.4	0.062	-0.38	-0.33
4	0.313	0.07	-1.75	-1.40
5	0.43	0.091	0.09	0.06
6	<0.5	NR		
8	NR	NR		
9	NT	NT		
10	0.4	0.02	-0.38	-0.57
11	0.4	0.02	-0.38	-0.57
12	0.40	0.2	-0.38	-0.12
13	0.45	0.02	0.41	0.62
14	0.5	0.1	1.19	0.71
15	0.5	0.08	1.19	0.86
16	NT	NT		
17	NR	NR		
18	0.44	0.14	0.25	0.11
19	0.3752	NR	-0.77	-1.32
20	0.369	0.01	-0.86	-1.43
21	0.44	0.044	0.25	0.28
22	0.41	0.05	-0.22	-0.23

Assigned Value	0.424	0.037
Spike	0.411	0.012
Homogeneity Value	0.318	0.064
Robust Average	0.424	0.037
Median	0.410	0.025
Mean	0.423	
N	15	
Max.	0.52	
Min.	0.313	
Robust SD	0.057	
Robust CV	13%	



z-Scores: S2 - Fluoride



En-Scores: S2 - Fluoride

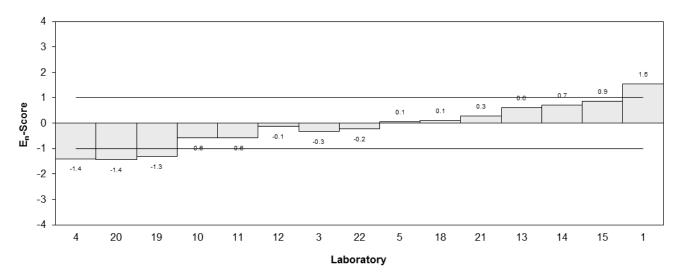


Figure 29

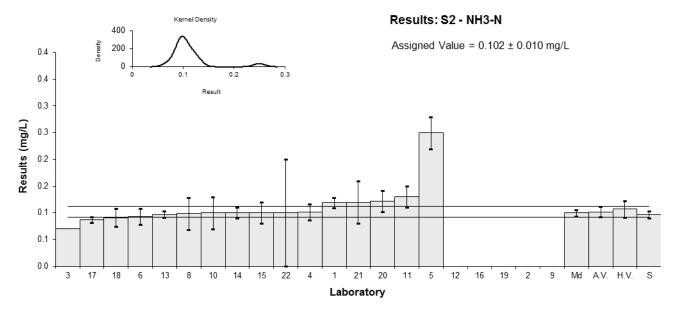
Sample No.	S2
Matrix.	Water
Analyte.	NH3-N
Units	mg/L

Participant Results

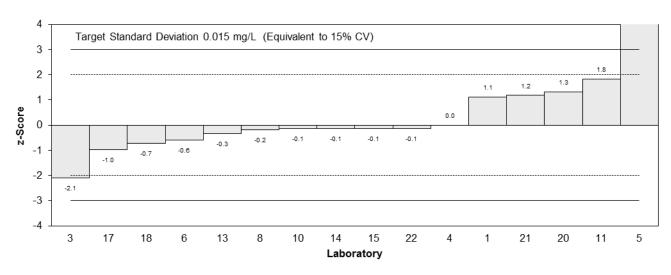
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.119	0.01	1.11	1.20
2	NT	NT		
3	0.07	NR	-2.09	-3.20
4	0.102	0.015	0.00	0.00
5	0.25	0.03	9.67	4.68
6	0.093	0.015	-0.59	-0.50
8	0.099	0.03	-0.20	-0.09
9	NT	NT		
10	0.1	0.03	-0.13	-0.06
11	0.13	0.02	1.83	1.25
12	NT	NT		
13	0.0968	0.006	-0.34	-0.45
14	0.100	0.01	-0.13	-0.14
15	0.10	0.02	-0.13	-0.09
16	NT	NT		
17	0.087	0.005	-0.98	-1.34
18	0.091	0.017	-0.72	-0.56
19	NT	NT		
20	0.122	0.02	1.31	0.89
21	0.12	0.04	1.18	0.44
22	0.1	0.1	-0.13	-0.02

Assigned Value*	0.102	0.010
Spike	0.097	0.006
Homogeneity Value	0.107	0.016
Robust Average	0.104	0.011
Median	0.100	0.006
Mean	0.111	
N	16	
Max.	0.25	
Min.	0.07	
Robust SD	0.015	
Robust CV	14%	

^{*}Robust Average excluding Laboratory 5.



z-Scores: S2 - NH3-N



En-Scores: S2 - NH3-N

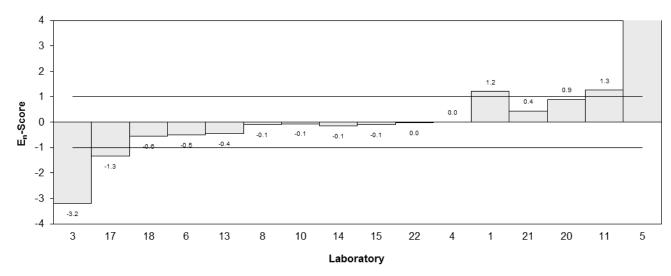


Figure 30

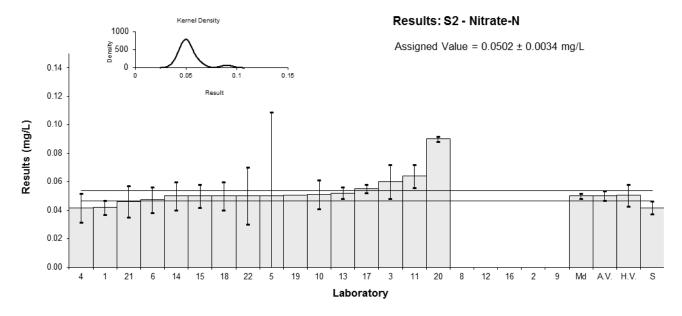
Sample No.	S2
Matrix.	Water
Analyte.	Nitrate-N
Units	mg/L

Participant Results

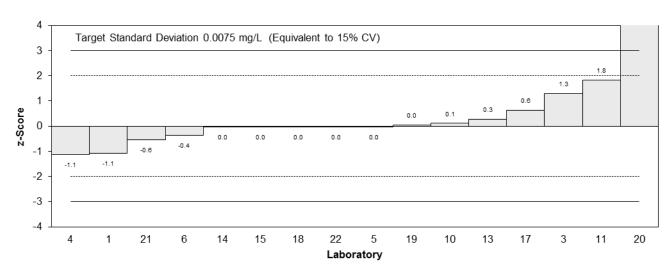
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.042	0.005	-1.09	-1.36
2	NT	NT		
3	0.06	0.012	1.30	0.79
4	0.0416	0.01	-1.14	-0.81
5	0.05	0.059	-0.03	0.00
6	0.0474	0.009	-0.37	-0.29
8	NR	NR		
9	NT	NT		
10	0.051	0.01	0.11	0.08
11	0.064	0.0082	1.83	1.55
12	NT	NT		
13	0.0522	0.004	0.27	0.38
14	0.050	0.01	-0.03	-0.02
15	0.050	800.0	-0.03	-0.02
16	NT	NT		
17	0.055	0.003	0.64	1.06
18	0.05	0.01	-0.03	-0.02
19	0.0505	NR	0.04	0.09
20	0.090	0.002	5.29	10.09
21	0.046	0.011	-0.56	-0.36
22	0.05	0.02	-0.03	-0.01

Assigned Value*	0.0502	0.0034
Spike	0.0417	0.0045
Homogeneity Value	0.0505	0.0076
Robust Average	0.0511	0.0041
Median	0.0500	0.0019
Mean	0.0531	
N	16	
Max.	0.09	
Min.	0.0416	
Robust SD	0.0053	
Robust CV	10%	

^{*}Robust Average excluding Laboratory 20.



z-Scores: S2 - Nitrate-N



En-Scores: S2 - Nitrate-N

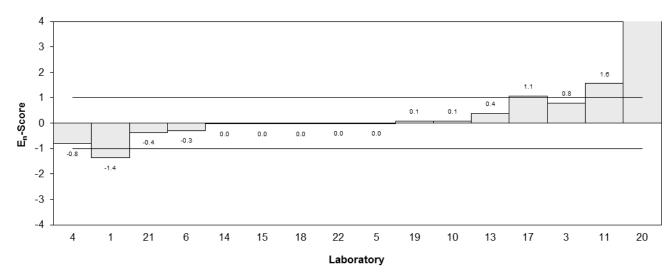


Figure 31

Sample No.	S2
Matrix.	Water
Analyte.	Orthophosphate-P
Units	mg/L

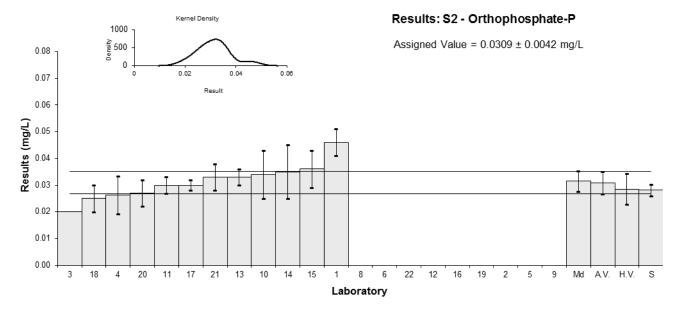
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.046	0.005	2.44	2.31
2	NT	NT		
3	0.02	NR	-1.76	-2.6
4	0.0263	0.007	-0.74	-0.56
5	NT	NT		
6	<0.05	NR		
8	< 0.1	0.005		
9	NT	NT		
10	0.034	0.009	0.5	0.31
11	0.03	0.003	-0.15	-0.17
12	NT	NT		
13	0.0331	0.003	0.36	0.43
14	0.035	0.01	0.66	0.38
15	0.036	0.007	0.83	0.62
16	NT	NT		
17	0.03	0.002	-0.15	-0.19
18	0.025	0.005	-0.95	-0.9
19	NT	NT		
20	0.027	0.005	-0.63	-0.6
21	0.033	0.005	0.34	0.32
22	NR	NR		

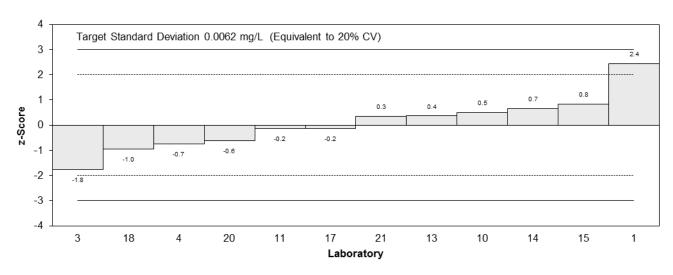
Statistics

74

Clationoc		
Assigned Value	0.0309	0.0042
Spike	0.0281	0.0021
Homogeneity Value	0.0285	0.0057
Robust Average	0.0309	0.0042
Median	0.0315	0.0038
Mean	0.0313	
N	12	
Max.	0.046	
Min.	0.02	
Robust SD	0.0058	
Robust CV	19%	



z-Scores: S2 - Orthophosphate-P



En-Scores: S2 - Orthophosphate-P

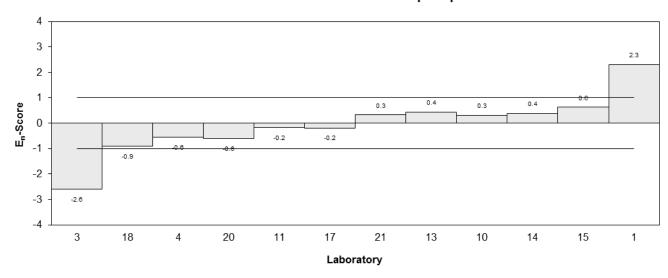


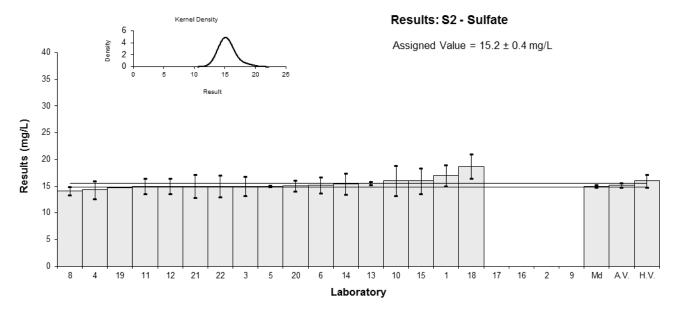
Figure 32

Sample No.	S2
Matrix.	Water
Analyte.	Sulfate
Units	mg/L

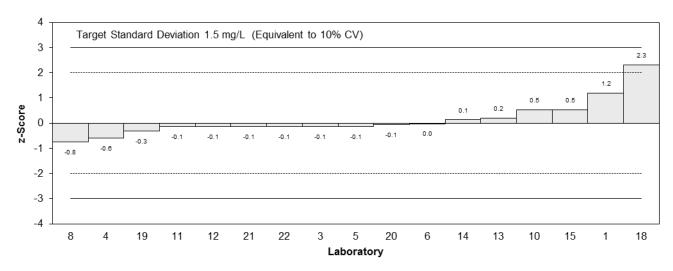
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	17	2.0	1.18	0.88
2	NT	NT		
3	15	1.78	-0.13	-0.11
4	14.3	1.7	-0.59	-0.52
5	15.0	0.07	-0.13	-0.49
6	15.18	1.52	-0.01	-0.01
8	14.056	0.79	-0.75	-1.29
9	NT	NT		
10	16	2.8	0.53	0.28
11	15	1.4	-0.13	-0.14
12	15	1.4	-0.13	-0.14
13	15.5	0.3	0.20	0.60
14	15.4	2	0.13	0.10
15	16	2.4	0.53	0.33
16	NT	NT		
17	NR	NR		
18	18.7	2.24	2.30	1.54
19	14.7	NR	-0.33	-1.25
20	15.1	1	-0.07	-0.09
21	15	2.2	-0.13	-0.09
22	15	2	-0.13	-0.10

Clationoc		
Assigned Value	15.2	0.4
Spike	Not Spiked	
Homogeneity Value	16.0	1.2
Robust Average	15.2	0.4
Median	15.0	0.2
Mean	15.4	
N	17	
Max.	18.7	
Min.	14.056	
Robust SD	0.7	
Robust CV	4.6%	



z-Scores: S2 - Sulfate



En-Scores: S2 - Sulfate

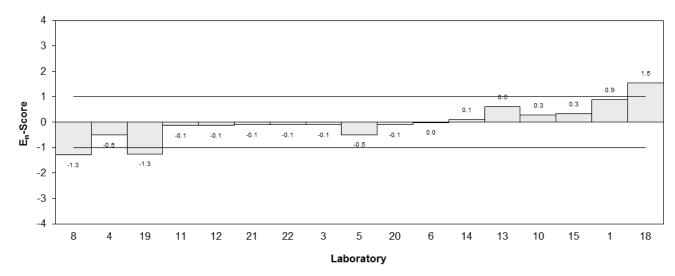


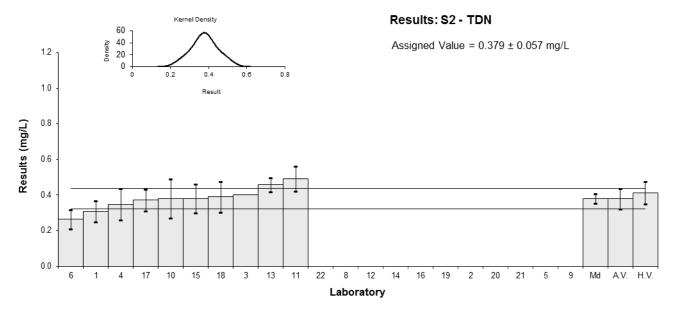
Figure 33

Sample No.	S2
Matrix.	Water
Analyte.	TDN
Units	mg/L

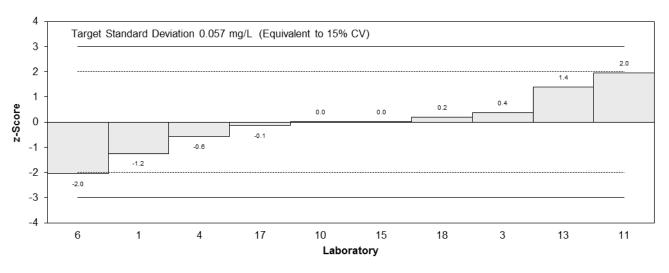
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.308	0.06	-1.25	-0.86
2	NT	NT		
3	0.4	NR	0.37	0.37
4	0.347	0.087	-0.56	-0.31
5	NT	NT		
6	0.263	0.053	-2.04	-1.49
8	NR	NR		
9	NT	NT		
10	0.38	0.11	0.02	0.01
11	0.49	0.07	1.95	1.23
12	NT	NT		
13	0.458	0.04	1.39	1.13
14	NT	NT		
15	0.38	0.08	0.02	0.01
16	NT	NT		
17	0.371	0.060	-0.14	-0.10
18	0.39	0.086	0.19	0.11
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	NR	NR		

Assigned Value	0.379	0.057
Spike	Not Spiked	
Homogeneity Value	0.413	0.062
Robust Average	0.379	0.057
Median	0.380	0.028
Mean	0.379	
N	10	
Max.	0.49	
Min.	0.263	
Robust SD	0.072	
Robust CV	19%	



z-Scores: S2 - TDN



En-Scores: S2 - TDN

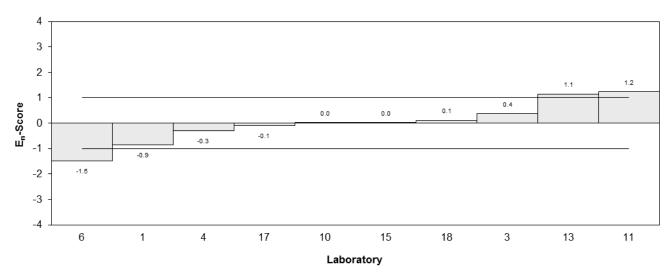


Figure 34

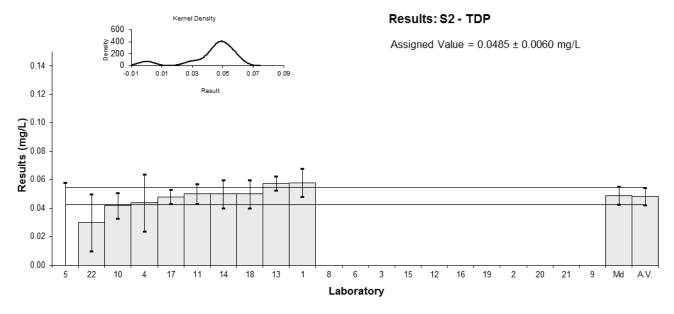
Sample No.	S2
Matrix.	Water
Analyte.	TDP
Units	mg/L

Participant Results

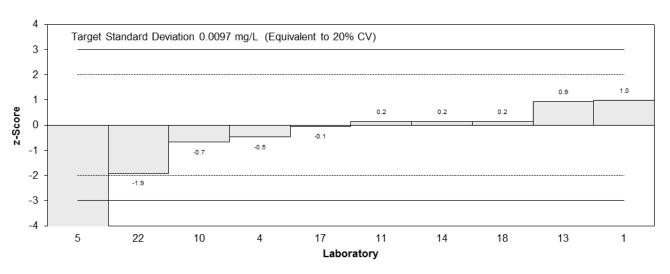
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.058	0.01	0.98	0.81
2	NT	NT		
3	<0.01	NR		
4	0.044	0.02	-0.46	-0.22
5	0.00	0.058	-5	-0.83
6	< 0.5	0.1		
8	< 0.1	0.01		
9	NT	NT		
10	0.042	0.009	-0.67	-0.6
11	0.05	0.007	0.15	0.16
12	NT	NT		
13	0.0575	0.005	0.93	1.15
14	0.05	0.01	0.15	0.13
15	NR	NR		
16	NT	NT		
17	0.048	0.005	-0.05	-0.06
18	0.05	0.01	0.15	0.13
19	NT	NT		
20	NT	NT		
21	NT	NT		
22	0.03	0.02	-1.91	-0.89

Assigned Value*	0.0485	0.0060
Spike	Not Spiked	
Robust Average	0.0458	0.0089
Median	0.0490	0.0064
Mean	0.0430	
N	10	
Max.	0.058	
Min.	0	
Robust SD	0.0078	
Robust CV	17%	

^{*}Robust Average excluding Laboratory 5.



z-Scores: S2 - TDP



En-Scores: S2 - TDP

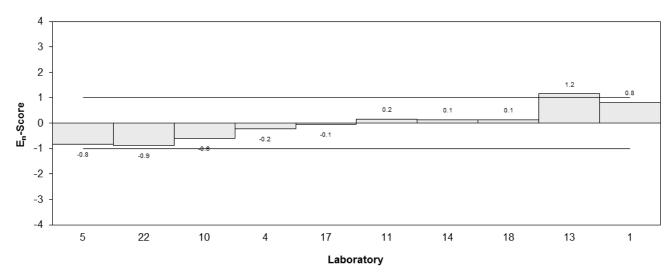


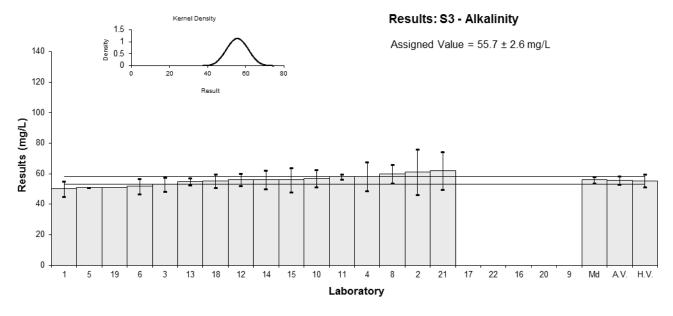
Figure 35

Sample No.	S3
Matrix.	Water
Analyte.	Alkalinity
Units	mg/L

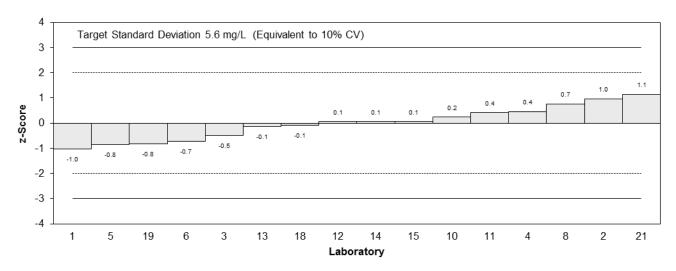
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	50	5	-1.02	-1.01
2	61	15	0.95	0.35
3	53	4.5	-0.48	-0.52
4	58.2	9.3	0.45	0.26
5	51	0.026	-0.84	-1.81
6	51.67	5.17	-0.72	-0.70
8	59.87	5.99	0.75	0.64
9	NT	NT		
10	57	5.6	0.23	0.21
11	58	1.6	0.41	0.75
12	56	4	0.05	0.06
13	54.9	2.2	-0.14	-0.23
14	56	6	0.05	0.05
15	56	8	0.05	0.04
16	NT	NT		
17	NR	NR		
18	55.2	4.4	-0.09	-0.10
19	51.12	NR	-0.82	-1.76
20	NT	NT		
21	62	12.4	1.13	0.50
22	NR	NR		

Clationoc		
Assigned Value	55.7	2.6
Spike	Not Spiked	
Homogeneity Value	55.3	4.2
Robust Average	55.7	2.6
Median	56.0	2.1
Mean	55.7	
N	16	
Max.	62	
Min.	50	
Robust SD	4.1	
Robust CV	7.4%	



z-Scores: \$3 - Alkalinity



En-Scores: S3 - Alkalinity

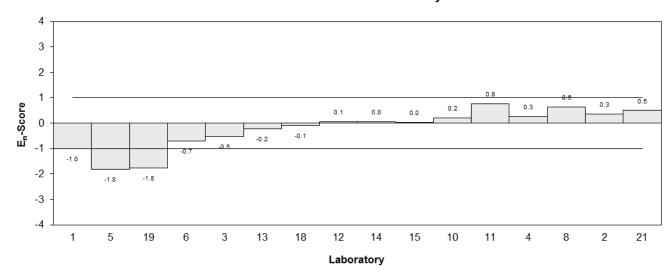


Figure 36

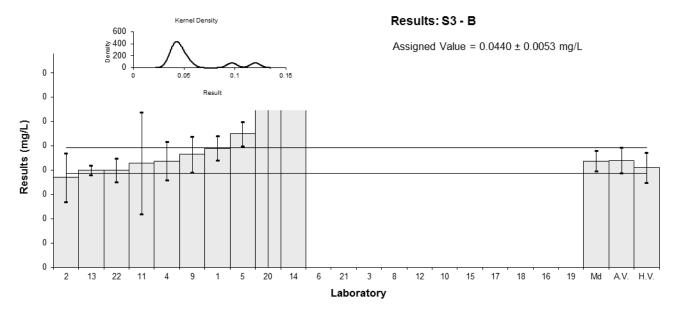
Sample No.	S3
Matrix.	Water
Analyte.	В
Units	mg/L

Participant Results

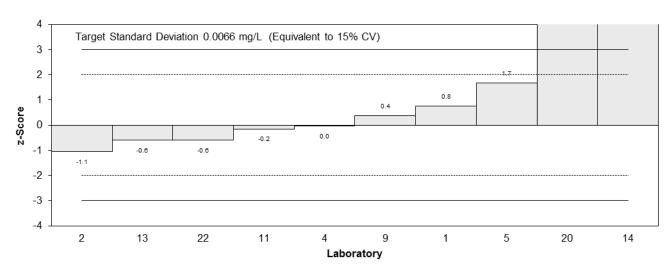
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.049	0.005	0.76	0.69
2	0.037	0.010	-1.06	-0.62
3	< 0.05	NR		
4	0.0438	800.0	-0.03	-0.02
5	0.055	0.005	1.67	1.51
6	< 0.05	0.01		
8	< 0.05	0.01		
9	0.0465	0.0074	0.38	0.27
10	<0.20	NR		
11	0.043	0.021	-0.15	-0.05
12	<0.1	NR		
13	0.04	0.002	-0.61	-0.71
14	41.3	5	6250.91	8.25
15	NR	NR		
16	NT	NT		
17	NR	NR		
18	NR	NR		
19	NT	NT		
20	0.097	0.1	8.03	0.53
21	<0.05	0.008		
22	0.04	0.005	-0.61	-0.55

0.0440	0.0053
Not Spiked	
0.0411	0.0062
0.0458	0.0066
0.0438	0.0043
0.0501	
10	
41.3	
0.037	
0.006	
13%	
	Not Spiked 0.0411 0.0458 0.0438 0.0501 10 41.3 0.037 0.006

^{*}Laboratory 14 results were omitted from statistical calculation. *Robust Average excluding Laboratory 20.



z-Scores: S3 - B



En-Scores: S3 - B

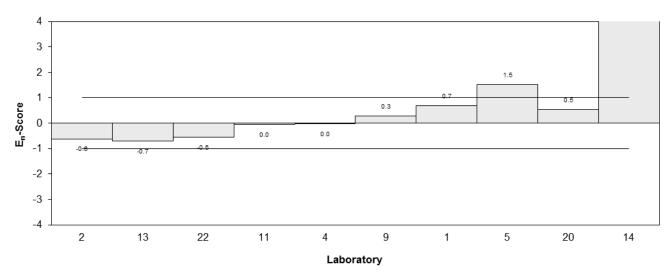


Figure 37

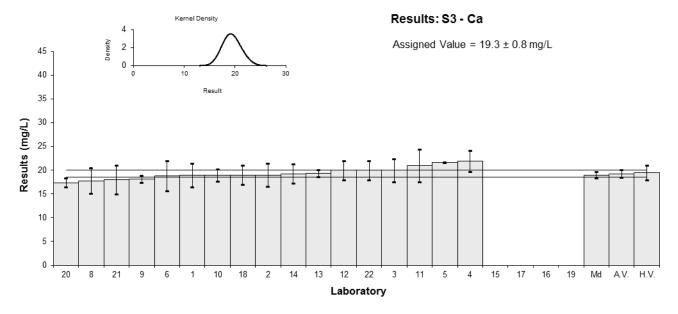
Table 41

Sample No.	S3
Matrix.	Water
Analyte.	Ca
Units	mg/L

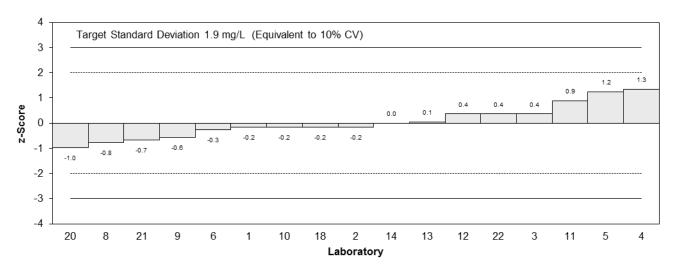
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	19	2.5	-0.16	-0.11
2	19	2.4	-0.16	-0.12
3	20	2.42	0.36	0.27
4	21.9	2.2	1.35	1.11
5	21.7	0.064	1.24	2.99
6	18.8	3.2	-0.26	-0.15
8	17.8	2.68	-0.78	-0.54
9	18.18	0.73	-0.58	-1.03
10	19	1.3	-0.16	-0.20
11	21	3.5	0.88	0.47
12	20	2	0.36	0.32
13	19.4	0.78	0.05	0.09
14	19.3	2.0	0.00	0.00
15	NR	NR		
16	NT	NT		
17	NR	NR		
18	19	2	-0.16	-0.14
19	NT	NT		
20	17.4	0.9	-0.98	-1.58
21	18	3	-0.67	-0.42
22	20	2	0.36	0.32

Assigned Value	19.3	0.8
Spike	Not Spiked	
Homogeneity Value	19.5	1.5
Robust Average	19.3	0.8
Median	19.0	0.7
Mean	19.4	
N	17	
Max.	21.9	
Min.	17.4	
Robust SD	1.3	
Robust CV	6.7%	



z-Scores: S3 - Ca



En-Scores: S3 - Ca

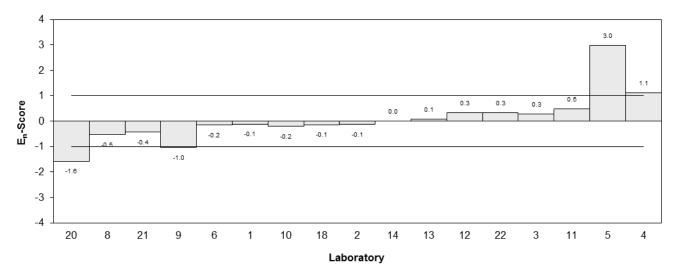


Figure 38

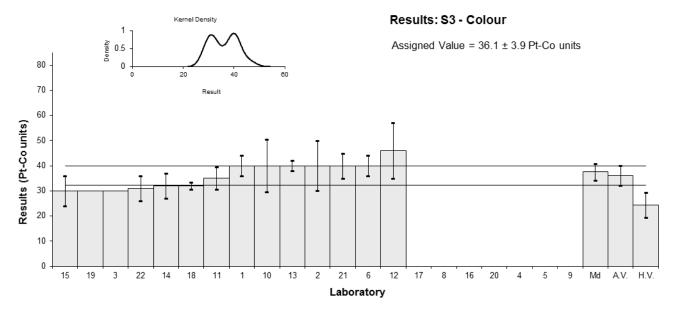
Table 42

Sample No.	S3
Matrix.	Water
Analyte.	Colour
Units	Pt-Co units

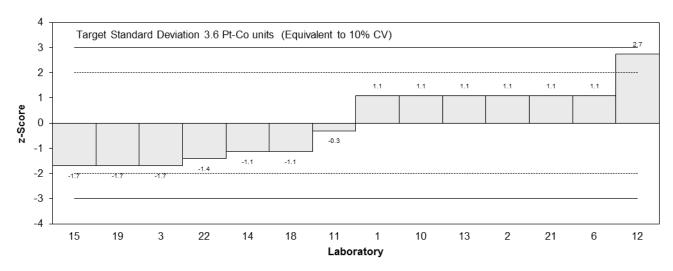
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	40	4	1.08	0.70
2	40	10	1.08	0.36
3	30	NR	-1.69	-1.56
4	NT	NT		
5	NT	NT		
6	40	4	1.08	0.70
8	NR	NR		
9	NT	NT		
10	40	10.5	1.08	0.35
11	35	4.4	-0.30	-0.19
12	46	11	2.74	0.85
13	40	2	1.08	0.89
14	32	5	-1.14	-0.65
15	30	6	-1.69	-0.85
16	NT	NT		
17	NR	NR		
18	32	1.4	-1.14	-0.99
19	30	NR	-1.69	-1.56
20	NT	NT		
21	40	5	1.08	0.62
22	31	5	-1.41	-0.80

Assigned Value	36.1	3.9
Spike	Not Spiked	
Homogeneity Value	24.3	4.9
Robust Average	36.1	3.9
Median	37.5	3.4
Mean	36.1	
N	14	
Max.	46	
Min.	30	
Robust SD	5.8	
Robust CV	16%	



z-Scores: S3 - Colour



En-Scores: \$3 - Colour

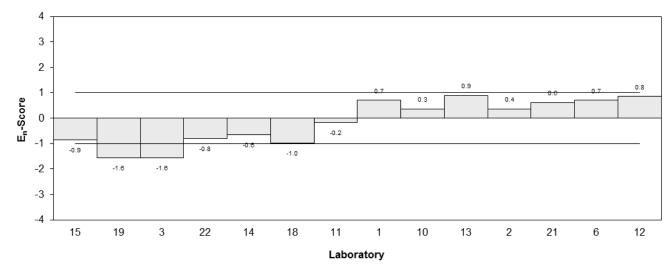


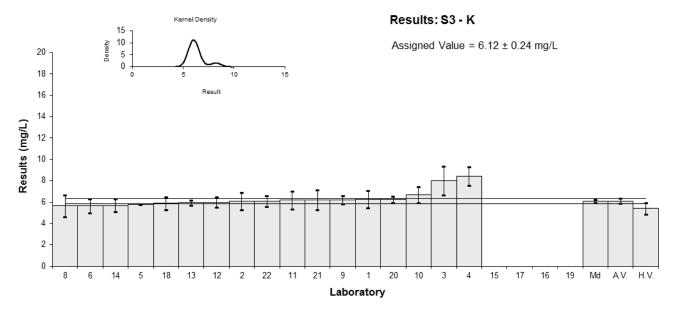
Figure 39

Sample No.	S3
Matrix.	Water
Analyte.	K
Units	mg/L

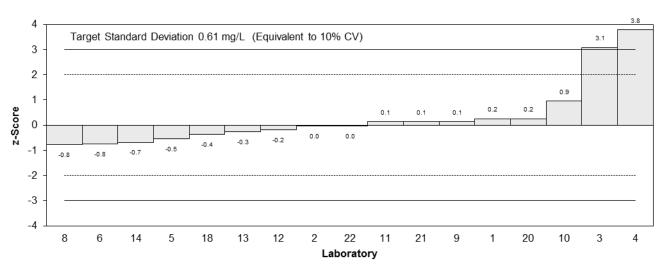
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	6.27	0.8	0.25	0.18
2	6.1	0.8	-0.03	-0.02
3	8	1.33	3.07	1.39
4	8.43	0.84	3.77	2.64
5	5.79	0.058	-0.54	-1.34
6	5.66	0.66	-0.75	-0.66
8	5.65	1.01	-0.77	-0.45
9	6.20	0.38	0.13	0.18
10	6.7	0.74	0.95	0.75
11	6.2	0.84	0.13	0.09
12	6.0	0.5	-0.20	-0.22
13	5.95	0.24	-0.28	-0.50
14	5.7	0.6	-0.69	-0.65
15	NR	NR		
16	NT	NT		
17	NR	NR		
18	5.9	0.6	-0.36	-0.34
19	NT	NT		
20	6.27	0.3	0.25	0.39
21	6.2	0.93	0.13	0.08
22	6.1	0.5	-0.03	-0.04

Clationou		
Assigned Value	6.12	0.24
Spike	Not Spiked	
Homogeneity Value	5.43	0.54
Robust Average	6.12	0.24
Median	6.10	0.13
Mean	6.31	
N	17	
Max.	8.43	
Min.	5.65	
Robust SD	0.39	
Robust CV	6.4%	



z-Scores: S3 - K



En-Scores: S3 - K

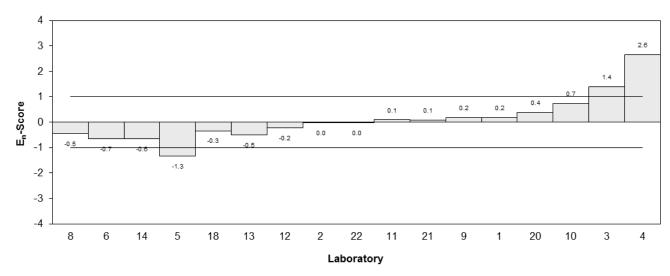


Figure 40

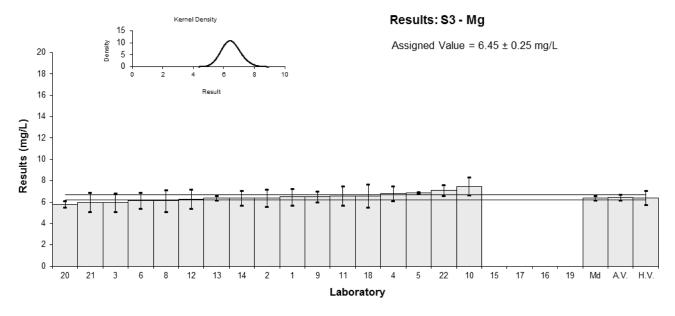
Table 44

Sample No.	S3
Matrix.	Water
Analyte.	Mg
Units	mg/L

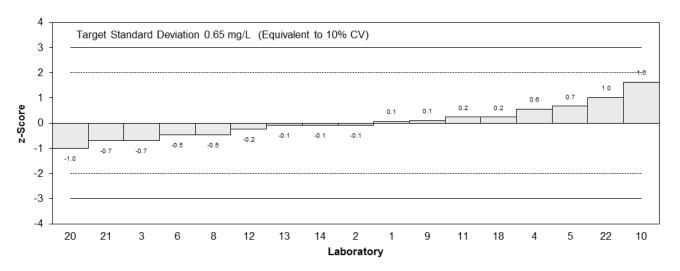
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	6.49	0.8	0.06	0.05
2	6.4	0.8	-0.08	-0.06
3	6	0.87	-0.70	-0.50
4	6.81	0.68	0.56	0.50
5	6.88	0.059	0.67	1.67
6	6.15	0.75	-0.47	-0.38
8	6.15	1.02	-0.47	-0.29
9	6.51	0.53	0.09	0.10
10	7.5	0.83	1.63	1.21
11	6.6	0.91	0.23	0.16
12	6.3	0.9	-0.23	-0.16
13	6.39	0.20	-0.09	-0.19
14	6.4	0.7	-0.08	-0.07
15	NR	NR		
16	NT	NT		
17	NR	NR		
18	6.6	1.1	0.23	0.13
19	NT	NT		
20	5.80	0.3	-1.01	-1.66
21	6.0	0.9	-0.70	-0.48
22	7.1	0.5	1.01	1.16

Assigned Value	6.45	0.25
Spike	Not Spiked	
Homogeneity Value	6.42	0.64
Robust Average	6.45	0.25
Median	6.40	0.19
Mean	6.48	
N	17	
Max.	7.5	
Min.	5.8	
Robust SD	0.40	
Robust CV	6.4%	



z-Scores: S3 - Mg



En-Scores: S3 - Mg

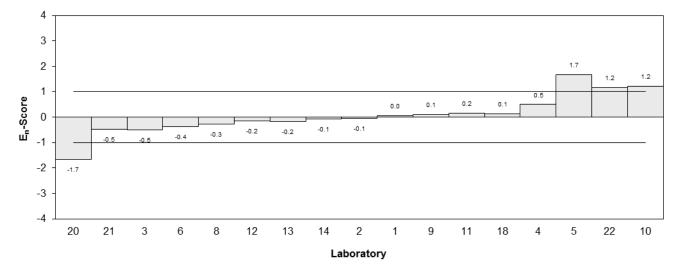


Figure 41

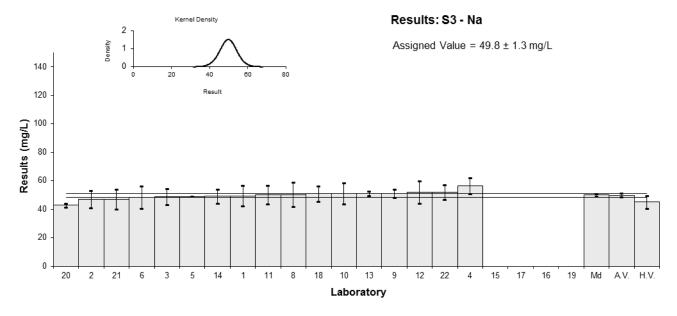
Table 45

Sample No.	S3
Matrix.	Water
Analyte.	Na
Units	mg/L

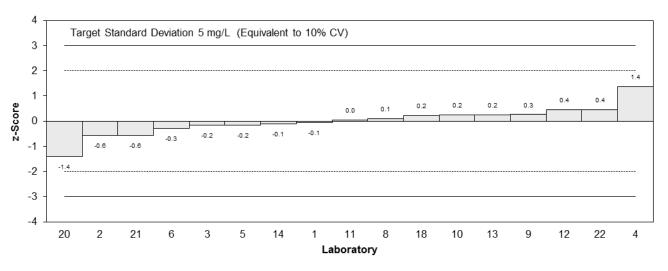
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	49.5	7.0	-0.06	-0.04
2	47	6	-0.56	-0.46
3	49	5.58	-0.16	-0.14
4	56.6	5.7	1.37	1.16
5	49.0	0.059	-0.16	-0.61
6	48.3	8.0	-0.30	-0.19
8	50.3	8.54	0.10	0.06
9	51.1	3.1	0.26	0.39
10	51	7.4	0.24	0.16
11	50	6.5	0.04	0.03
12	52	8	0.44	0.27
13	51.0	1.5	0.24	0.60
14	49.2	5	-0.12	-0.12
15	NR	NR		
16	NT	NT		
17	NR	NR		
18	50.9	5.3	0.22	0.20
19	NT	NT		
20	42.8	1.5	-1.41	-3.53
21	47	7.1	-0.56	-0.39
22	52	5	0.44	0.43

Assigned Value	49.8	1.3
Spike	Not Spiked	
Homogeneity Value	45.2	4.5
Robust Average	49.8	1.3
Median	50.0	0.8
Mean	49.8	
N	17	
Max.	56.6	
Min.	42.8	
Robust SD	2.1	
Robust CV	4.2%	



z-Scores: S3 - Na



En-Scores: S3 - Na

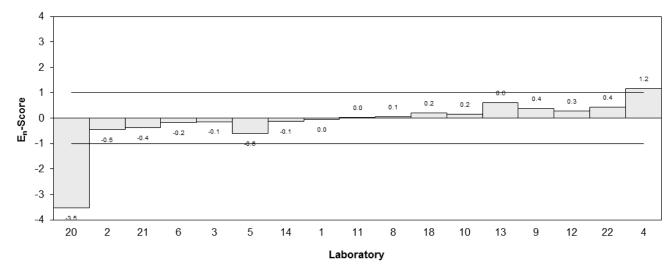


Figure 42

Sample No.	S3
Matrix.	Water
Analyte.	P
Units	mg/L

Participant Results

Lab Code	Result	Uncertainty
1	0.03	0.01
2	0.028	0.05
3	<1	NR
4	<0.1	0.1
5	<0.4	NT
6	< 0.5	0.1
8	<0.5	0.1
9	0.030	0.015
10	0.017	0.003
11	<0.05	NR
12	<0.04	NR
13	< 0.1	NR
14	NT	NT
15	NR	NR
16	NT	NT
17	0.0235	0.005
18	0.026	0.005
19	NT	NT
20	0.153	0.1
21	0.037	0.007
22	0.37	0.01

Clationico		
Assigned Value	Not Set	
Spike	Not Spiked	
Homogeneity Value	0.0291	0.0058
Robust Average	0.0368	0.0185
Median	0.0300	0.0074
Mean	0.0794	
N	9	
Max.	0.37	
Min.	0.017	
Robust SD	0.0051	
Robust CV	32%	

Results: S3 - P

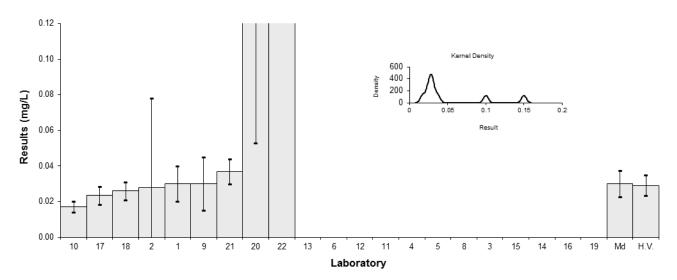


Figure 43

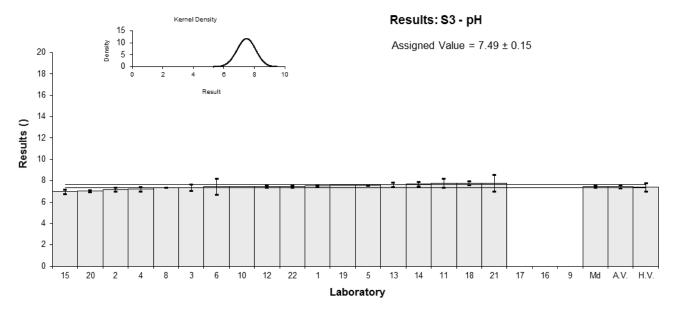
Table 47

Sample No.	S3
Matrix.	Water
Analyte.	pH

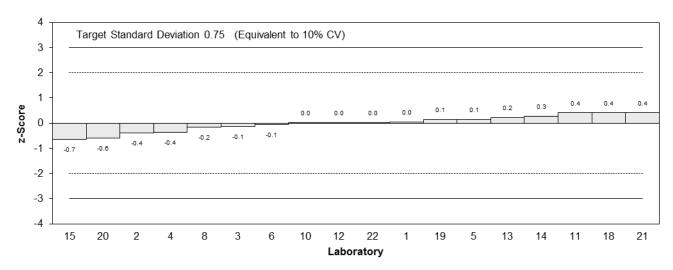
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	7.52	0.1	0.04	0.17
2	7.2	0.2	-0.39	-1.16
3	7.38	0.298	-0.15	-0.33
4	7.22	0.2	-0.36	-1.08
5	7.6	0.02	0.15	0.73
6	7.45	0.75	-0.05	-0.05
8	7.37	0.01	-0.16	-0.80
9	NT	NT		
10	7.5	NR	0.01	0.07
11	7.8	0.4	0.41	0.73
12	7.5	0.1	0.01	0.06
13	7.65	0.23	0.21	0.58
14	7.7	0.2	0.28	0.84
15	7.0	0.2	-0.65	-1.96
16	NT	NT		
17	NR	NR		
18	7.8	0.2	0.41	1.24
19	7.6	NR	0.15	0.73
20	7.05	0.1	-0.59	-2.44
21	7.8	0.8	0.41	0.38
22	7.5	0.1	0.01	0.06

Assigned Value	7.49	0.15
Assigned Value		0.15
Spike	Not Spiked	
Homogeneity Value	7.40	0.38
Robust Average	7.49	0.15
Median	7.50	0.10
Mean	7.48	
N	18	
Max.	7.8	
Min.	7	
Robust SD	0.26	
Robust CV	3.5%	



z-Scores: S3 - pH



En-Scores: S3 - pH

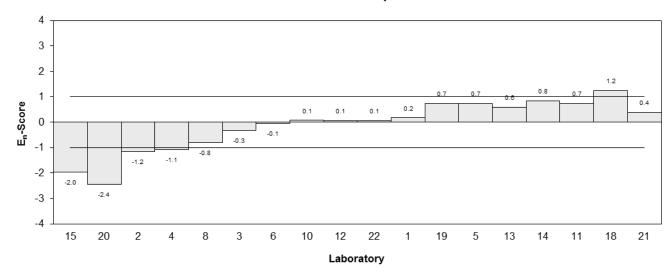


Figure 44

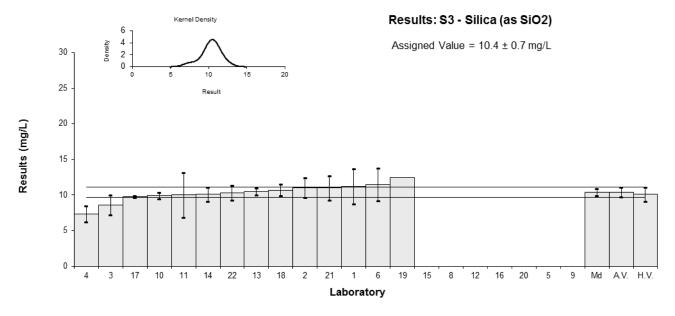
Table 48

Sample No.	S3
Matrix.	Water
Analyte.	Silica (as SiO ₂)
Units	mg/L

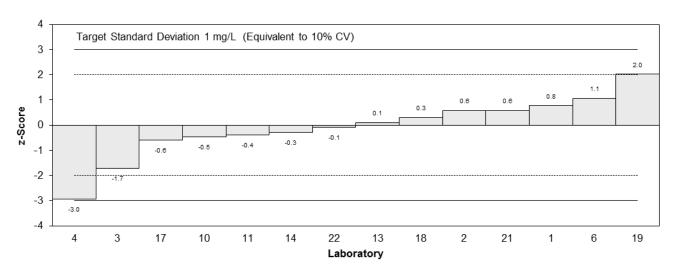
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	11.2	2.5	0.77	0.31
2	11	1.4	0.58	0.38
3	8.61	1.41	-1.72	-1.14
4	7.33	1.1	-2.95	-2.35
5	NT	NT		
6	11.5	2.3	1.06	0.46
8	NR	NR		
9	NT	NT		
10	9.92	0.45	-0.46	-0.58
11	10	3.15	-0.38	-0.12
12	NT	NT		
13	10.5	0.47	0.10	0.12
14	10.1	1	-0.29	-0.25
15	NR	NR		
16	NT	NT		
17	9.79	0.118	-0.59	-0.86
18	10.7	0.8	0.29	0.28
19	12.5	NR	2.02	3.00
20	NT	NT		
21	11	1.7	0.58	0.33
22	10.3	1	-0.10	-0.08

Clationio		
Assigned Value	10.4	0.7
Spike	10.5	0.2
Homogeneity Value	10.1	1.0
Robust Average	10.7	0.7
Median	10.4	0.5
Mean	10.3	
N	14	
Max.	12.5	
Min.	7.33	
Robust SD	1	
Robust CV	9.3%	



z-Scores: \$3 - Silica (as SiO2)



En-Scores: \$3 - Silica (as SiO2)

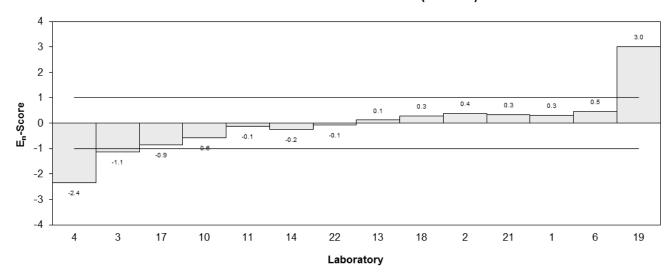


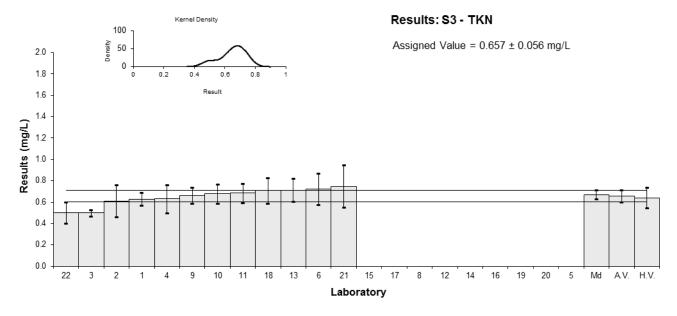
Figure 45

Sample No.	S3
Matrix.	Water
Analyte.	TKN
Units	mg/L

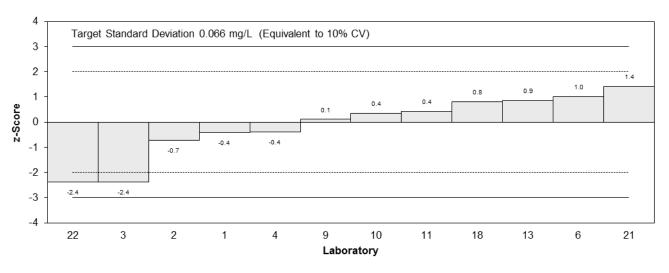
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.63	0.06	-0.41	-0.33
2	0.61	0.15	-0.72	-0.29
3	0.5	0.03	-2.39	-2.47
4	0.631	0.13	-0.40	-0.18
5	NT	NT		
6	0.723	0.145	1.00	0.42
8	NR	NR		
9	0.664	0.075	0.11	0.07
10	0.68	0.09	0.35	0.22
11	0.685	0.09	0.43	0.26
12	NT	NT		
13	0.714	0.11	0.87	0.46
14	NT	NT		
15	NR	NR		
16	NT	NT		
17	NR	NR		
18	0.71	0.12	0.81	0.40
19	NT	NT		
20	NT	NT		
21	0.75	0.2	1.42	0.45
22	0.5	0.1	-2.39	-1.37

Assigned Value	0.657	0.056
Spike	Not Spiked	
Homogeneity Value	0.640	0.096
Robust Average	0.657	0.056
Median	0.672	0.040
Mean	0.650	
N	12	
Max.	0.75	
Min.	0.5	
Robust SD	0.077	
Robust CV	12%	



z-Scores: S3 - TKN



En-Scores: S3 - TKN

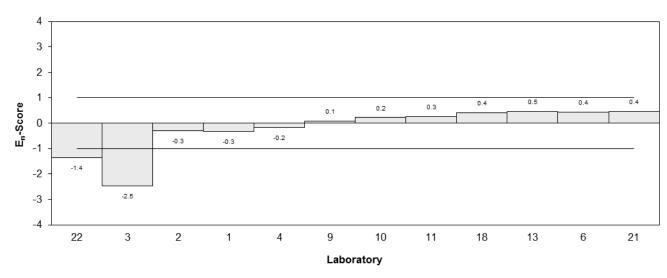


Figure 46

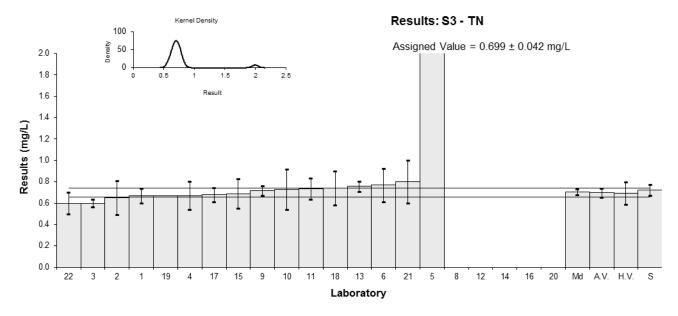
Sample No.	S3
Matrix.	Water
Analyte.	TN
Units	mg/L

Participant Results

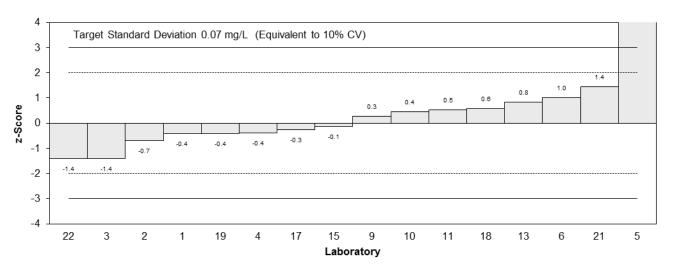
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.67	0.07	-0.41	-0.36
2	0.65	0.16	-0.70	-0.30
3	0.6	0.036	-1.42	-1.79
4	0.672	0.13	-0.39	-0.20
5	3.3	0.059	37.21	35.91
6	0.769	0.154	1.00	0.44
8	NR	NR		
9	0.718	0.043	0.27	0.32
10	0.73	0.19	0.44	0.16
11	0.736	0.1	0.53	0.34
12	NT	NT		
13	0.757	0.05	0.83	0.89
14	NT	NT		
15	0.69	0.14	-0.13	-0.06
16	NT	NT		
17	0.680	0.066	-0.27	-0.24
18	0.74	0.16	0.59	0.25
19	0.67	NR	-0.41	-0.69
20	NT	NT		
21	0.80	0.2	1.44	0.49
22	0.6	0.1	-1.42	-0.91

Assigned Value*	0.699	0.042
Spike	0.726	0.051
Homogeneity Value	0.695	0.104
Robust Average	0.706	0.045
Median	0.704	0.028
Mean	0.861	
N	16	
Max.	3.3	
Min.	0.6	
Robust SD	0.066	
Robust CV	9.3%	

^{*}Robust Average excluding Laboratory 5.



z-Scores: S3 - TN



En-Scores: S3 - TN

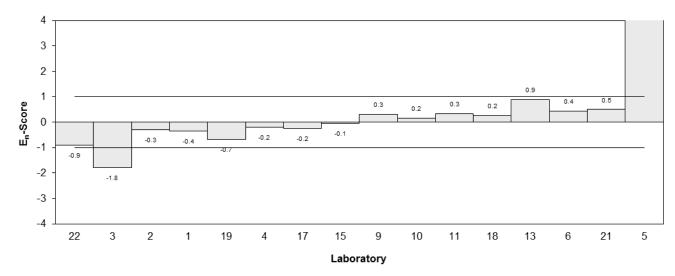


Figure 47

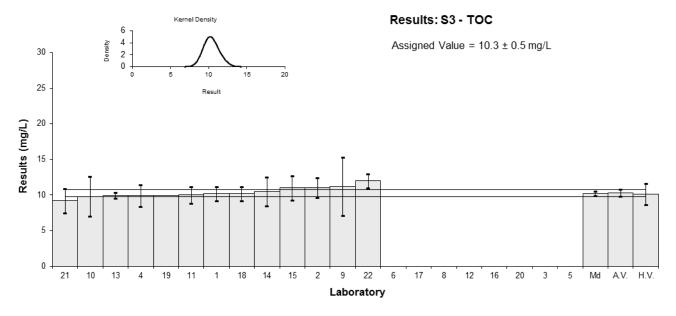
Table 51

Sample No.	S3
Matrix.	Water
Analyte.	TOC
Units	mg/L

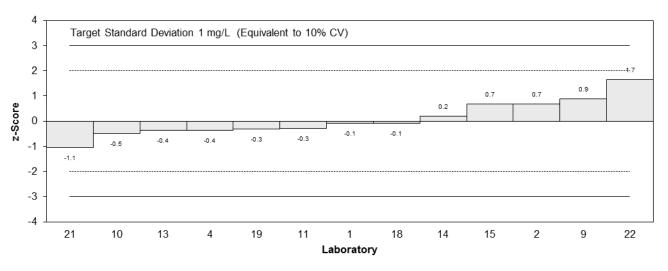
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	10.2	1	-0.10	-0.09
2	11	1.4	0.68	0.47
3	NT	NT		
4	9.91	1.5	-0.38	-0.25
5	NT	NT		
6	<5	NR		
8	NR	NR		
9	11.2	4.1	0.87	0.22
10	9.8	2.8	-0.49	-0.18
11	10	1.2	-0.29	-0.23
12	NT	NT		
13	9.91	0.4	-0.38	-0.61
14	10.5	2	0.19	0.10
15	11	1.7	0.68	0.40
16	NT	NT		
17	NR	NR		
18	10.2	1	-0.10	-0.09
19	9.98	NR	-0.31	-0.64
20	NT	NT		
21	9.2	1.7	-1.07	-0.62
22	12	1	1.65	1.52

Clandido		
Assigned Value	10.3	0.5
Spike	Not Spiked	
Homogeneity Value	10.1	1.5
Robust Average	10.3	0.5
Median	10.2	0.3
Mean	10.4	
N	13	
Max.	12	
Min.	9.2	
Robust SD	0.73	
Robust CV	7.1%	



z-Scores: S3 - TOC



En-Scores: S3 - TOC

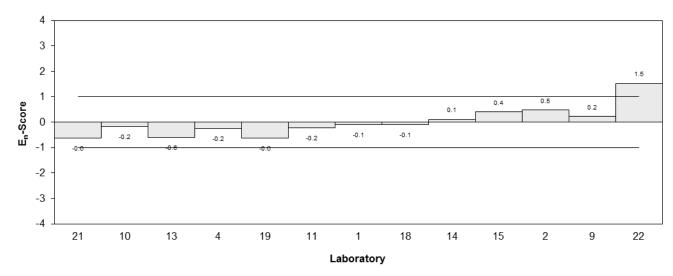


Figure 48

Table 52

Sample Details

Sample No.	S3
Matrix.	Water
Analyte.	Total Hardness
Units	mg/L

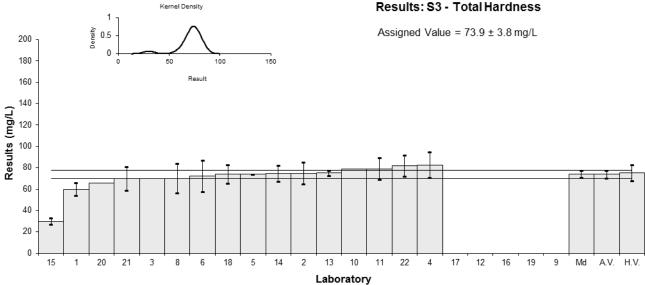
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	60	6	-1.88	-1.96
2	75	10	0.15	0.10
3	70	NR	-0.53	-1.03
4	82.7	12	1.19	0.70
5	74	0.059	0.01	0.03
6	72.3	14.5	-0.22	-0.11
8	70.2	14.0	-0.50	-0.26
9	NT	NT		
10	79	NR	0.69	1.34
11	79	10.1	0.69	0.47
12	NT	NT		
13	75.1	2.3	0.16	0.27
14	74.6	7.5	0.09	0.08
15	30	3	-5.94	-9.07
16	NT	NT		
17	NR	NR		
18	74	8.5	0.01	0.01
19	NT	NT		
20	66	NR	-1.07	-2.08
21	70	11	-0.53	-0.34
22	82	10	1.10	0.76

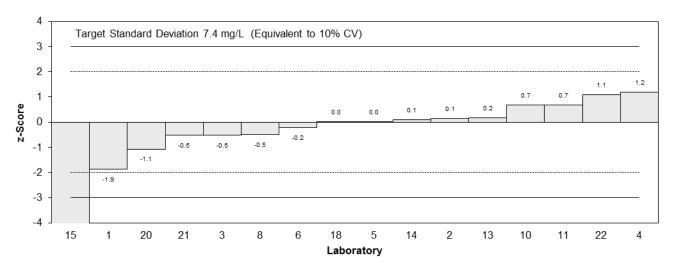
Statistics

Clationoc	, idea of the second of the se							
Assigned Value	73.9	3.8						
Spike	Not Spiked							
Homogeneity Value	75.1	7.5						
Robust Average	73.1	4.2						
Median	74.0	3.2						
Mean	70.9							
N	16							
Max.	82.7							
Min.	30							
Robust SD	6							
Robust CV	8.2%							





z-Scores: \$3 - Total Hardness



En-Scores: \$3 - Total Hardness

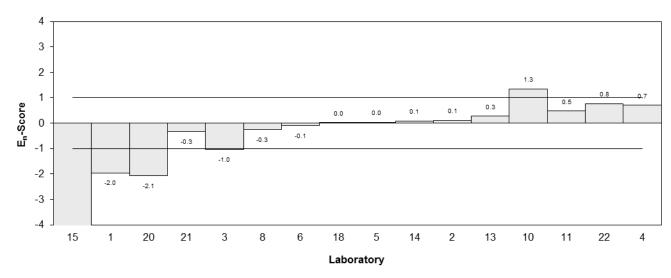


Figure 49

Sample Details

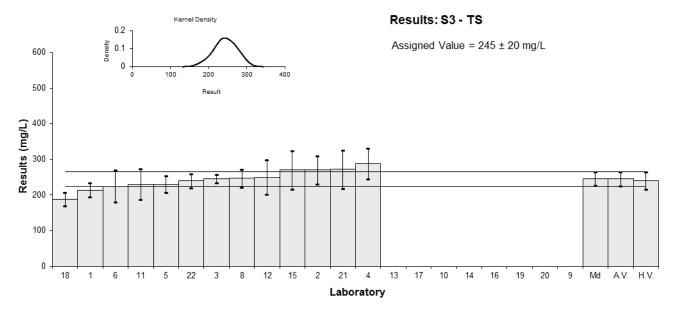
Sample No.	S3
Matrix.	Water
Analyte.	TS
Units	mg/L

Participant Results

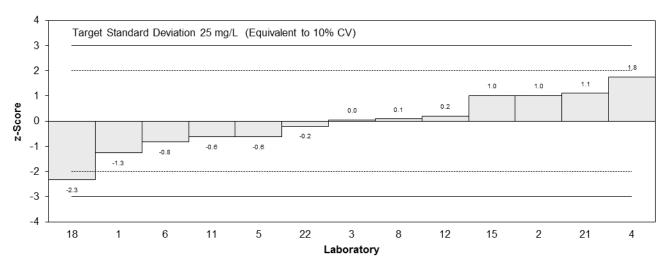
Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	214	20	-1.27	-1.10
2	270	40	1.02	0.56
3	246	11.87	0.04	0.04
4	288	43	1.76	0.91
5	230	23	-0.61	-0.49
6	225	45	-0.82	-0.41
8	247	24.7	0.08	0.06
9	NT	NT		
10	NT	NT		
11	230	43	-0.61	-0.32
12	250	48	0.20	0.10
13	NR	NR		
14	NT	NT		
15	270	54	1.02	0.43
16	NT	NT		
17	NR	NR		
18	188	18.8	-2.33	-2.08
19	NT	NT		
20	NT	NT		
21	272	54	1.10	0.47
22	240	20	-0.20	-0.18

Statistics

• 101.101.00		
Assigned Value	245	20
Spike	Not Spiked	
Homogeneity Value	240	24
Robust Average	245	20
Median	246	19
Mean	244	
N	13	
Max.	288	
Min.	188	
Robust SD	28	
Robust CV	11%	



z-Scores: S3 - TS



En-Scores: S3 - TS

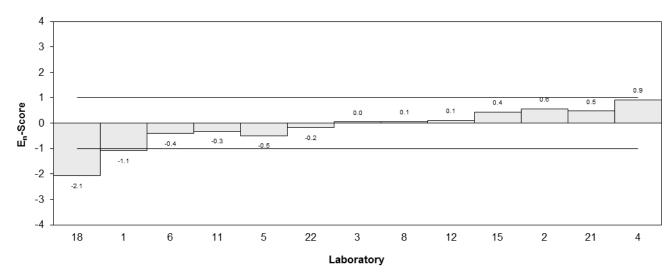


Figure 50

Table 54

Sample Details

Sample No.	S3
Matrix.	Water
Analyte.	Turbidity
Units	NTU

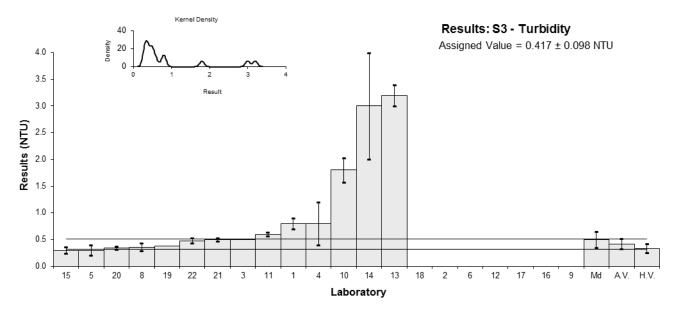
Participant Results

Lab Code	Result	Uncertainty	z-Score	E _n -Score
1	0.8	0.1	4.59	2.74
2	<0.5	0.5		
3	0.5	NR	1.00	0.85
4	0.8	0.4	4.59	0.93
5	0.3	0.1	-1.40	-0.84
6	<1	NR		
8	0.36	0.07	-0.68	-0.47
9	NT	NT		
10	1.8	0.23	16.58	5.53
11	0.6	0.04	2.19	1.73
12	<3	NR		
13	3.2	0.2	33.37	12.50
14	3	1	30.97	2.57
15	0.3	0.06	-1.40	-1.02
16	NT	NT		
17	NR	NR		
18	<0.5	0.5		
19	0.379	NR	-0.46	-0.39
20	0.343	0.03	-0.89	-0.72
21	0.50	0.03	1.00	0.81
22	0.48	0.05	0.76	0.57

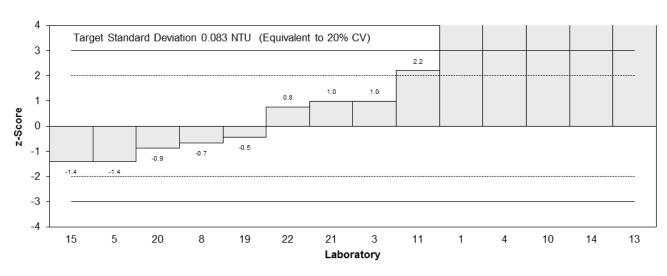
Statistics

Assigned Value*	0.417	0.098
Spike	Not Spiked	
Homogeneity Value	0.333	0.083
Robust Average	0.676	0.308
Median	0.500	0.153
Mean	0.954	
N	14	
Max.	3.2	
Min.	0.3	
Robust SD	0.12	
Robust CV	18%	

^{*}Robust Average excluding Laboratories 1, 4, 10, 13 and 14.



z-Scores: \$3 - Turbidity



En-Scores: S3 - Turbidity

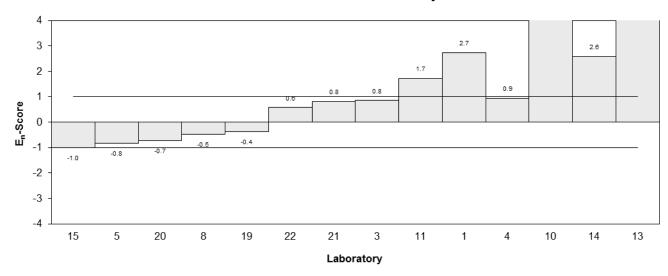


Figure 51

7 DISCUSSION OF RESULTS

7.1 Assigned Value

Sample S1 was 100 mL of unfiltered, acidified potable water. Participants were asked to report for this sample results for total: Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Tl, U, V and Zn. The sample was chilled before dispatch.

Sample S2 was 200 mL of frozen, filtered and autoclaved river water collected from Brown's Waterhole Turramurra on which analyses of ammonia-N (NH₃-N), bromide (Br⁻), chloride (Cl⁻), dissolved organic carbon (DOC as dNPOC), fluoride (F⁻), free reactive phosphorus (FRP), nitrate-N (NO₃-N), total dissolved nitrogen (TDN), total dissolved phosphorus (TDP) and sulfate (SO₄²⁻) were to be performed.

Sample S3 consisted of two containers labelled A and B with the same river water. Participants were instructed not to composite the contents of the two containers prior to analyses. The container labelled S3A contained 750 mL of unfiltered, unpreserved chilled river water to be analysed for total: B, Ca, K, Mg, Na and P and for alkalinity to pH 4.5 (as CaCO₃), apparent colour (units Pt/Co), pH (at 25°C), silica (as SiO₂), total hardness (as CaCO₃), total solid (dried at 103-105°C) and turbidity. The container labelled S3B consisted of 200 mL of frozen unfiltered river water to be analysed for total Kjeldahl nitrogen (TKN), total nitrogen (TN) and total organic carbon (TOC as NPOC). Sample S3A was chilled before dispatch while Sample S3B was frozen.

Assigned Value for the 49 tests were the robust average of participants' results. The robust averages used as assigned values and their associated expanded uncertainties were calculated using the procedure described in 'ISO13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparisons'. Results less than 50% and more than 150% of the robust average were removed before calculation of each assigned value. No assigned value was set for total P in S3, the reported results for this test were too variable. The results reported for Hg in S1 were also variable however an assigned value was set for this test because the robust average of participants' results was found to be in good agreement with the spike value. Appendix 3 sets out the calculation of the robust average and assigned value for As in Sample S1 and its associated uncertainty.

Spike Values for each test of interest includes both the incurred value and the fortified value.

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 737 numerical results, 693 (94%) were reported with an expanded measurement uncertainty, indicating that the majority of laboratories have addressed this requirement of ISO 17025. ¹⁰ 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, bottom up approach, top down approach using precision and estimates of method and laboratory bias and top down approach using only the reproducibility from inter-laboratory comparison studies. $^{11-17}$

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 51). In this study in some cases, the reported expanded measurement uncertainty has been over (e.g. Lab 22 for Al, Bi in S1) or under-estimated (e.g. Lab 16 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.

For estimating the laboratory precision three participants used only the data from duplicate analyses. This gives an estimate of within-run precision (repeatability), the intermediate precision (reproducibility) should be considered too.

Double counting the precision uncertainty components and overestimation of the laboratory or method bias are the most common errors seen in the laboratories' estimated uncertainty budgets. According to NATA Technical Note 33¹⁴ and to NORDTEST TR 537 ¹² the most common experimental data used for estimating the precision component for the measurement uncertainty calculation in the top down approach are from:

- Stable <u>control samples</u> that cover the whole analytical process (including extraction) and **have a matrix similar** to the samples; **or**
- Stable <u>control samples</u> and <u>duplicate analyses</u> 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 <u>natural duplicates</u> (gives withinday 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. ^{12, 14} An example of estimating measurement uncertainty using proficiency testing data only is given in Appendix 4.

Some laboratories estimated uncertainties for measurement results larger than the reported results themselves. Measurement uncertainty is the range estimated by laboratories that contain the true value. The reported result should be within the estimated range.

Two 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 numerical value cannot be attached to a result expressed as a range.¹¹

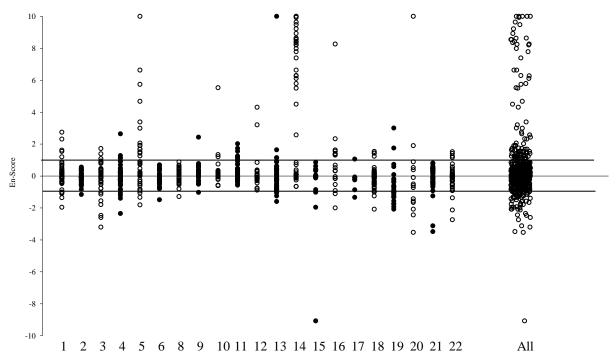
In some cases the results were reported with an inappropriate number of significant figures. The recommended format is to write uncertainty to no more than two significant figures and then to write the result with the corresponding number of decimal places. For example, instead of 18.44 ± 3.4 mg/L, it is better to report 18.4 ± 3.4 mg/L or instead of 0.0023 ± 0.00048 mg/L, it is better to report 0.0023 ± 0.0005 mg/L. ¹¹

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.

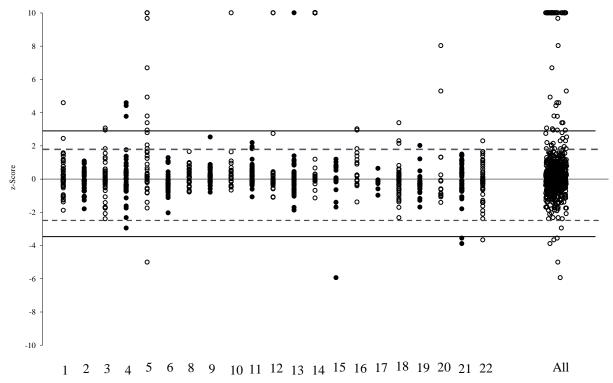
The dispersal of participants' E_n -scores is graphically presented in Figure 52. Where a laboratory did not report an expanded uncertainty with a result, an expanded uncertainty of zero (0) was used to calculate the E_n -score.

Of 728 results for which E_n -scores were calculated, 579 (80%) returned a satisfactory score of $|E_n| \le 1$ indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.



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

Figure 52 E_n-Score Dispersal by Laboratory



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

Figure 53 z-Score Dispersal by Laboratory

7.4 z-Score

The z-score compares 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%, 15% and 20% CV were used to calculate z-scores. Unlike the standard deviation based on between laboratories CV, setting the target standard deviation as a realistic, set value enables z-scores to be used as a fixed reference value point for assessment of laboratory performance, independent of group performance.

The between laboratories coefficient of variation predicted by the Thompson equation⁹ and the between laboratories coefficient of variation resulted in this study are presented for comparison in Table 55.

The dispersal of participants' z-scores is presented in Figure 53 (by laboratory code) and in Figure 54 (by test). Of 728 results for which z-scores were calculated, 656 (90%) returned a satisfactory score of $|z| \le 2$ and 21 (3%) were questionable with a score of $2 < |z| \le 3$. Participants with multiple z-scores larger than 2 or smaller than -2 should check for laboratory bias.

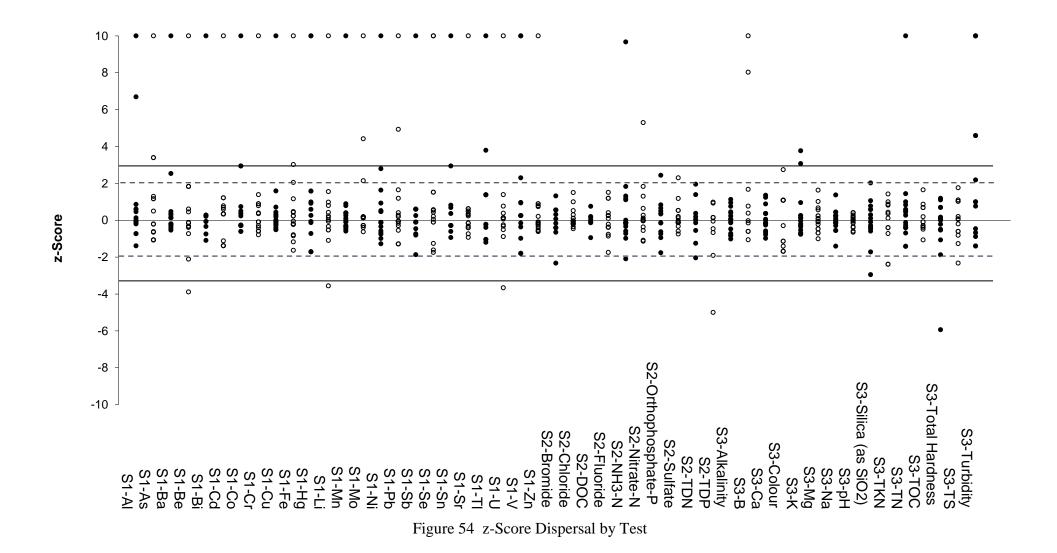
Laboratories 2, 8 and 17 returned satisfactory z-scores for all inorganic analytes reported.

Table 55 Between Laboratories CV of this study, Thompson CV and Set Target CV

Sample	Assigned va		Between Laboratories CV	Thompson/ Horwitz CV	Target SD (as CV)
S1	Al	0.151	5.7%	21%	10%
S1	As	0.00448	13%	22%	10%
S1	Ba	0.0296	0.4%	22%	10%
S1	Be	0.00507	12%	22%	10%
S1	Bi	0.00292	3.8%	22%	10%
S1	Cd	0.00116	11%	22%	10%
S1	Co	0.00309	5.5%	22%	10%
S1	Cr	0.0202	6.9%	22%	10%
S1	Cu	0.719	4.2%	17%	10%
S1	Fe	0.215	9.8%	20%	10%
S1	Hg	0.00015	30%	22%	20%
S1	Li	0.0528	8.7%	22%	10%
S1	Mn	0.202	4.8%	20%	10%
S1	Mo	0.02	4.4%	22%	10%
S1	Ni	0.0172	8.7%	22%	10%
S1	Pb	0.00804	10%	22%	10%
S1	Sb	0.00283	7.1%	22%	10%
S1	Se	0.00407	18%	22%	15%
S1	Sn	0.00309	7.1%	22%	10%
S1	Sr	0.0772	5.7%	22%	10%
S1	Tl	0.00083	18%	22%	15%
S1	U	0.0158	6.3%	22%	10%
S1	V	0.00488	11%	22%	10%
S1	Zn	1.01	6%	16%	10%
S2	Bromide	0.417	7%	18%	10%
S2	Chloride	71.3	3.4%	8%	10%
S2	DOC	8.09	3.2%	12%	10%

Table 55 Between Laboratories CV of this study, Thompson CV and Set Target CV (continued)

Sample	Analyte	Assigned value	Between Laboratories CV	Thompson/ Horwitz CV	Target SD (as CV)
S2	Fluoride	0.424	13%	18%	15%
S2	NH3-N	0.102	14%	22%	15%
S2	Nitrate-N	0.0502	10%	22%	15%
S2	Orthophosphate-P	0.0309	19%	19%	20%
S2	Sulfate	15.2	4.6%	4.6%	10%
S2	TDN	0.379	19%	19%	15%
S2	TDP	0.0485	17%	16%	20%
S3	Alkalinity	55.7	7.4%	7%	10%
S3	В	0.044	13%	14%	15%
S3	Ca	19.3	6.7%	6.7%	10%
S3	Colour	36.1	16%	16%	10%
S 3	K	6.12	6.4%	3.4%	10%
S 3	Mg	6.45	6.4%	6.4%	10%
S 3	Na	49.8	4.2%	4.2%	10%
S 3	P	Not Set	32%	18%	Not Set
S3	pН	7.49	3.5%	10%	10%
S3	Silica (as SiO ₂)	10.4	9.3%	9.6%	10%
S3	TKN	0.657	12%	12%	10%
S3	TN	0.699	9.3%	9.4%	10%
S 3	TOC	10.3	7.1%	7.1%	10%
S 3	Total Hardness	73.9	8.2%	8.1%	10%
S3	TS	245	11%	11%	10%
S3	Turbidity	0.417	18%	29%	20%



AQA 18-05 Water Characteristics

Table 56 Summary of Participants' Results and Performance for S1

Lab Code	S1-Al mg/L	S1-As mg/L	S1-Ba mg/L	S1-Be mg/L	S1-Bi mg/L	S1-Cd mg/L	S1-Co mg/L	S1-Cr mg/L	S1-Cu mg/L	S1-Fe mg/L	S1-Hg mg/L	S1-Li mg/L
H.V.	0.151	0.00421	0.0319	0.0049	0.00301	0.00127	0.00312	0.0209	0.778	0.23	0.000166	0.0497
A.V.	0.151	0.00448	0.0296	0.00507	0.00292	0.00116	0.00309	0.0202	0.719	0.215	0.000152	0.0528
1	0.158	0.004	0.029	0.005	0.003	0.001	0.003	0.021	0.706	0.214	0.0002	0.05
2	0.14	0.004	0.029	0.0047	0.0026	0.0012	0.003	0.019	0.71	0.22	0.00018	0.055
3	0.16	0.004	0.031	0.006	0.003	0.0013	0.003	0.02	0.741	0.22	0.0001	0.061
4	0.151	0.00419	0.0306	0.00491	0.00282	0.00125	0.00316	0.0209	0.682	0.225	0.00013	NT
5	0.252	0.006	0.03	0.006	0.003	0.0012	0.004	0.023	0.833	0.259	0.00016	NT
6	0.15	0.00506	0.0283	0.00487	< 0.005	0.00103	0.00301	0.0196	0.682	0.211	0.00015	0.0525
8	0.153	0.00438	0.0305	0.00538	< 0.005	0.00123	0.00324	0.0218	0.736	0.224	0.000182	0.0536
9	0.164	0.00439	0.0371	0.005	0.00298	0.00124	0.00332	0.0194	0.714	0.198	0.000148	0.0529
10	NT											
11	0.15	0.004	0.03	0.005	0.003	0.0012	0.003	0.02	0.75	0.21	0.00017	0.057
12	0.15	0.004	0.029	0.0049	NT	0.0012	0.003	0.019	0.7	0.21	0.16	0.047
13	0.148	0.0042	0.0286	0.0053	0.0029	0.0012	0.0029	0.0186	0.713	0.24	0.0001	0.054
14	159	4.32	31.3	5.04	3.06	1.26	3.32	21.4	759	214	0.18	55.4
15	NT											
16	0.15	0.005	< 0.05	0.006	NT	0.001	0.004	0.022	0.732	0.28	0.0002	0.058
17	NT											
18	0.16	0.006	0.03	0.0049	0.0029	0.001	0.0029	0.019	0.72	0.197	0.0001	0.051
19	0.149	0.0047	0.0288	0.005	NT	0.0013	0.003	0.019	0.6992	0.1899	NT	NT
20	NT											
21	0.14	0.004	0.028	0.0031	0.0027	0.0012	0.0032	0.022	0.77	0.21	< 0.0005	0.034
22	0.13	0.005	0.03	0.004	0.003	0.001	0.003	0.02	0.69	0.18	< 0.0005	0.05

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

Table 56 Summary of Participants' Results and Performance for S1 (continued)

Lab Code	S1-Mn mg/L	S1-Mo mg/L	S1-Ni	S1-Pb	S1-Sb mg/L	S1-Se	S1-Sn	S1-Sr	S1-Tl	S1-U	S1-V	S1-Zn
H.V.	0.224	0.0203	mg/L 0.0178	mg/L 0.00856	0.00272	mg/L 0.00389	mg/L 0.00304	mg/L 0.0863	mg/L 0.000786	mg/L 0.0156	mg/L 0.0051	mg/L 1.1
A.V.	0.224	0.0206	0.0172	0.00804	0.00283	0.00407	0.00309	0.0772	0.00083	0.0158	0.00488	1.01
1	0.207	0.021	0.017	0.008	0.003	0.005	NT	0.082	0.001	0.016	0.005	0.978
2	0.21	0.02	0.015	0.008	0.0029	0.004	0.003	0.081	0.0007	0.015	0.004	1
3	0.204	0.02	0.018	0.008	0.003	< 0.01	0.004	0.081	< 0.001	0.016	< 0.01	0.989
4	0.202	0.0297	0.0166	0.00837	0.00262	0.00308	0.00334	0.0795	< 0.001	0.0159	0.00535	0.968
5	0.22	0.0209	0.022	0.012	0.0026	0.003	NT	NT	0.0013	0.016	0.011	0.996
6	0.196	0.0198	0.0155	0.00826	< 0.005	0.00433	< 0.005	0.0747	< 0.005	0.016	< 0.005	0.947
8	0.218	0.0208	0.0188	0.00937	< 0.005	0.00442	< 0.005	0.076	< 0.005	0.0164	0.00534	1.09
9	0.209	0.0209	0.0181	0.00819	0.0028	0.0044	0.0033	0.082	0.000781	0.0154	0.005	1.085
10	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
11	0.2	0.021	0.017	0.009	0.003	0.004	0.003	0.079	< 0.001	0.017	0.005	0.99
12	0.21	0.021	0.017	0.0076	0.0028	0.013	0.003	0.076	0.0008	NT	0.005	1
13	0.194	0.0193	0.0159	0.0079	0.0023	0.0041	0.0028	0.0715	0.0007	0.0144	0.0047	0.955
14	211	19.3	17.3	8.37	3.14	4	2.9	82.2	0.74	15.6	5.5	1050
15	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
16	0.195	0.021	0.017	0.008	< 0.005	< 0.005	0.003	0.074	0.001	NT	0.005	1.031
17	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
18	0.192	0.025	0.016	0.007	0.0028	0.0033	0.0032	0.08	0.0008	0.0153	0.0044	0.9511
19	0.1958	NT	0.0162	0.007	0.0027	NT	NT	NT	NT	NT	0.0048	0.9859
20	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
21	0.2	0.02	0.018	0.0078	0.003	0.0042	0.0029	0.074	0.00068	0.018	0.004	1.1
22	0.19	0.02	0.02	0.007	0.003	0.005	0.003	0.07	0.001	0.01	0.006	1.1

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

Table 57 Summary of Participants' Results and Performance for S2

Lab Code	S2-NH ₃ -N mg/L	S2-Bromide mg/L	S2-Chloride mg/L	S2-DOC mg/L	S2-Fluoride mg/L	S2-PO ₄ -P mg/L	S2-NO ₃ -N mg/L	S2-Sulfate mg/L	S2-TDN mg/L	S2-TDP mg/L
H.V.	0.107	0.402	81.3	7.93	0.318	0.0285	0.0505	16	0.413	0
A.V.	0.102	0.417	71.3	8.09	0.424	0.0309	0.0502	15.2	0.379	0.0485
1	0.119	0.44	68	7.32	0.52	0.046	0.042	17	0.308	0.058
2	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
3	0.07	NT	71	NT	0.4	0.02	0.06	15	0.4	< 0.01
4	0.102	0.32	69.9	8.25	0.313	0.0263	0.0416	14.3	0.347	0.044
5	0.25	0.44	69.7	NT	0.43	NT	0.05	15	NT	0
6	0.093	NT	78.45	<5	< 0.5	< 0.05	0.0474	15.18	0.263	< 0.5
8	0.099	0.4	70.72	NR	NR	< 0.1	NR	14.056	NR	< 0.1
9	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
10	0.1	0.4	72	8	0.4	0.034	0.051	16	0.38	0.042
11	0.13	0.41	75	8.1	0.4	0.03	0.064	15	0.49	0.05
12	NT	< 0.50	70	NT	0.4	NT	NT	15	NT	NT
13	0.0968	0.43	70.9	7.98	0.45	0.0331	0.0522	15.5	0.458	0.0575
14	0.1	NT	73.4	NT	0.5	0.035	0.05	15.4	NT	0.05
15	0.1	0.42	70	8.7	0.5	0.036	0.05	16	0.38	NR
16	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
17	0.087	NR	NR	NR	NR	0.03	0.055	NR	0.371	0.048
18	0.091	0.44	71	8.2	0.44	0.025	0.05	18.7	0.39	0.05
19	NT	NT	68.7	NT	0.3752	NT	0.0505	14.7	NT	NT
20	0.122	0.472	70.4	NT	0.369	0.027	0.09	15.1	NT	NT
21	0.12	0.4	82	8	0.44	0.033	0.046	15	NT	NT
22	0.1	0.39	72	NR	0.41	NR	0.05	15	NR	0.03

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

Table 58 Summary of Participants' Results and Performance for S3

Lab Code	S3-Alkalinity mg/L	S3-B mg/L	S3-Ca mg/L	S3-Colour, apparent Pt-Co units	S3-K mg/L	S3-Mg mg/L	S3-Na mg/L	S3-P mg/L
H.V.	55.3	0.0411	19.5	24.3	5.43	6.42	45.2	0.0291
A.V.	55.7	0.044	19.3	36.1	6.12	6.45	49.8	0.029
1	50	0.049	19	40	6.27	6.49	49.5	0.03
2	61	0.037	19	40	6.1	6.4	47	0.028
3	53	< 0.05	20	30	8	6	49	<1
4	58.2	0.0438	21.9	NT	8.43	6.81	56.6	< 0.1
5	51	0.055	21.7	NT	5.79	6.88	49	< 0.4
6	51.67	< 0.05	18.8	40	5.66	6.15	48.3	< 0.5
8	59.87	< 0.05	17.8	NR	5.65	6.15	50.3	< 0.5
9	NT	0.0465	18.18	NT	6.2	6.51	51.1	0.03
10	57	< 0.20	19	40	6.7	7.5	51	0.017
11	58	0.043	21	35	6.2	6.6	50	< 0.05
12	56	< 0.1	20	46	6	6.3	52	< 0.04
13	54.9	0.04	19.4	40	5.95	6.39	51	< 0.1
14	56	41.3	19.3	32	5.7	6.4	49.2	NT
15	56	NR	NR	30	NR	NR	NR	NR
16	NT	NT	NT	NT	NT	NT	NT	NT
17	NR	NR	NR	NR	NR	NR	NR	0.0235
18	55.2	NR	19	32	5.9	6.6	50.9	0.026
19	51.12	NT	NT	30	NT	NT	NT	NT
20	NT	0.097	17.4	NT	6.27	5.8	42.8	0.153
21	62	< 0.05	18	40	6.2	6	47	0.037
22	NR	0.04	20	31	6.1	7.1	52	0.37

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

Table 58 Summary of Participants' Results and Performance for S3 (continued)

Lab Code	S3-pH	S3Silica (as SiO ₂) mg/L	S3-Total Hardness mg/L	S3-Total Solids mg/L	S3-Turbidity NTU	S3-TKN mg/L	S3-TN mg/L	S3-TOC mg/L
H.V.	7.4	10.1	75.1	240	0.333	0.64	0.695	10.1
A.V.	7.49	10.4	73.9	245	0.417	0.657	0.699	10.3
1	7.52	11.2	60	214	0.8	0.63	0.67	10.2
2	7.2	11	75	270	<0.5	0.61	0.65	11
3	7.38	8.61	70	246	0.5	0.5	0.6	NT
4	7.22	7.33	82.7	288	0.8	0.631	0.672	9.91
5	7.6	NT	74	230	0.3	NT	3.3	NT
6	7.45	11.5	72.3	225	<1	0.723	0.769	<5
8	7.37	NR	70.2	247	0.36	NR	NR	NR
9	NT	NT	NT	NT	NT	0.664	0.718	11.2
10	7.5	9.92	79	NT	1.8	0.68	0.73	9.8
11	7.8	10	79	230	0.6	0.685	0.736	10
12	7.5	NT	NT	250	<3	NT	NT	NT
13	7.65	10.5	75.1	NR	3.2	0.714	0.757	9.91
14	7.7	10.1	74.6	NT	3	NT	NT	10.5
15	7	NR	30	270	0.3	NR	0.69	11
16	NT	NT	NT	NT	NT	NT	NT	NT
17	NR	9.79	NR	NR	NR	NR	0.68	NR
18	7.8	10.7	74	188	<0.5	0.71	0.74	10.2
19	7.6	12.5	NT	NT	0.379	NT	0.67	9.98
20	7.05	NT	66	NT	0.343	NT	NT	NT
21	7.8	11	70	272	0.5	0.75	0.8	9.2
22	7.5	10.3	82	240	0.48	0.5	0.6	12

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

7.5 Participants' Results and Analytical Methods for Total Elements

The Australian Drinking Water Guidelines for parameters in water are expressed in units of mg/L.⁵ In the present study participants were requested to analyse samples using their normal test method and to report a single result in units of mg/L. A summary of participants' results and performance is presented in Tables 56 to 58 and in Figures 53 and 54.

The results reported by participants for elements in drinking water sample S1 were variable, the between laboratories coefficient of variation was high. Rounding of results and reporting results with an insufficient number of significant figures was one of the main causes for variability of the reported results. The recommended format for reporting results is to write uncertainty with no more than two significant figures and then to write the result with the corresponding number of decimal places.¹¹

Boron, Mercury, Selenium and Thallium in S1 and Phosphorus in S3 were the elements with the highest coefficient of variation, between 18% and 32%.

A systematic error was noticed for Laboratory 5 with all its unsatisfactory results in S1 higher than the assigned value. This laboratory should check for laboratory/method bias.

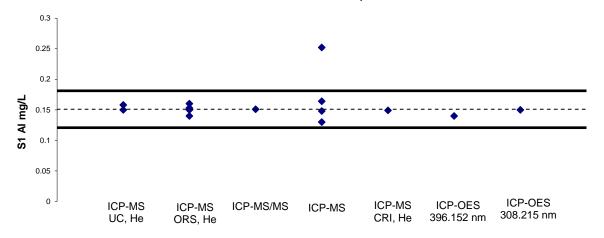
Laboratory 12 correctly measured Hg in S1 but reported results in units of $\mu g/L$ and not in units of mg/L. Laboratory 14 correctly measured all analytes in Samples S1 but reported results in different units ($\mu g/L$). The z-score results from these laboratories are not a reflection of their analytical performance and were not taken into consideration when assessing the effects of analyte on participants' performance.

Participants were requested to analyse the drinking water sample S1 for total elements. The method descriptions provided by participants are presented in Tables 1 and 2 and the instrumental conditions are presented in Appendix 6.

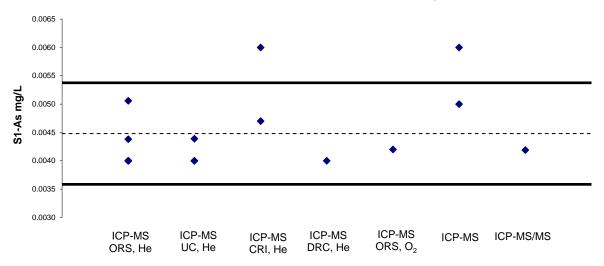
No significant differences have been noticed between the performances of participants who performed digestion and the ones who did not conduct a digestion procedure for this test sample. The instrumental measurement was one of the main factors that influenced the results. However, participants' performance does not reflect only the instrument 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 reported using ICP-MS in MS/MS mode. Plots of participants' results versus instrumental techniques used are presented in Figure 55 (Laboratory 14 not included).

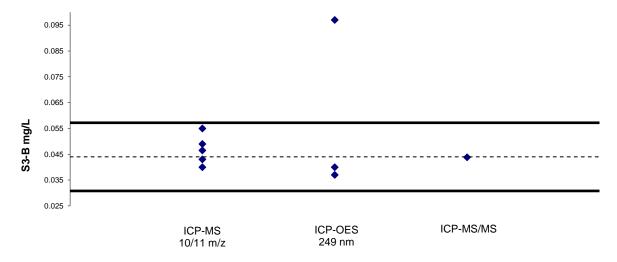
S1 Al Results vs Instrumental Technique



S1 As Results vs Instrumental Technique



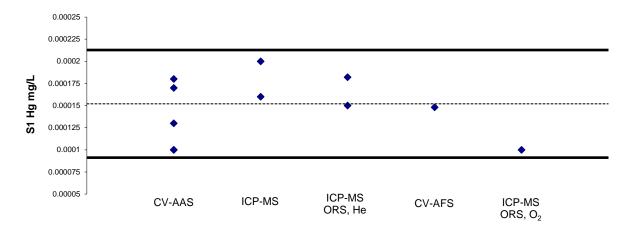
S3 B Results vs Instrumental Technique



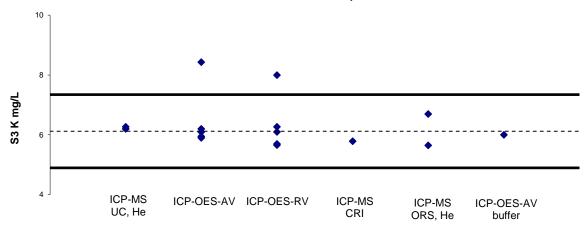
Horizontal lines on charts correspond to z-scores of 2 and -2.

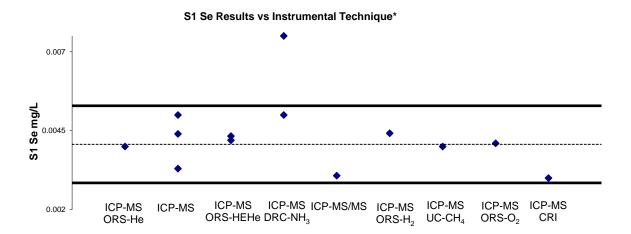
Figure 55 Participants' Results and Performance vs Instrumental Technique

S1 Hg Results vs Instrumental Technique



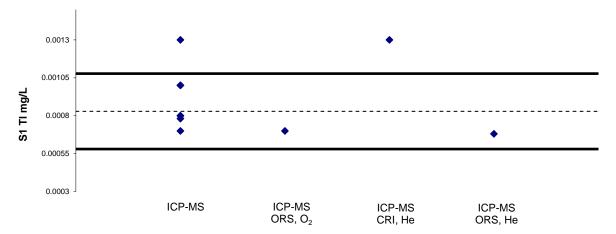
S3 K Results vs Instrumental Technique





^{*}Selenium result larger than 0.0075 mg/L has been plotted as 0.0075 mg/L Figure 55 Participants' Results vs Instrumental Technique (continued)

S1 TI Results vs Instrumental Technique



*Thallium result larger than 0.0013 mg/L has been plotted as 0.0013 mg/L Horizontal lines on charts correspond to z-scores of 2 and -2.

Figure 55 Participants' Results vs Instrumental Technique (continued)

Individual Element Commentary

Aluminium measurements at low level have not posed significant problems for laboratories. The between laboratories CV for Al in S1 was 6%.

Arsenic Participants used a wide variety of instrumental techniques for As measurements in S1. Unsolved interference problems might explain the high, unsatisfactory z-scores.

Boron level in sample S3 was low (0.0440 mg/L) and this might have presented difficulties to some laboratories; the between laboratory coefficient of variation was high (26%).

Boron measured at 249.7 nm can have significant interferences from Fe 249.771 nm if on-line inter-element correction is not used. Plots of participants' results versus instrumental technique used are presented in Figure 55.

Mercury level in S1 (0.000152 mg/L) challenged participants' analytical technique. The results reported were variable, the between coefficient of variation was large, 30%. Rounding up results and reporting Hg results with an inappropriate number of significant figures was another cause of results variability.

Selenium level in S1 in the present study was 0.00407 mg/L and in S1 of the PT study AQA 17-16 Metals in Seawater was 0.00378 mg/L. In the present study, the between coefficient of variation was 18% while in the previous one was two times lower, 9.8%.⁶

Using the right instrumental technique is still the main challenge for laboratories attempting to measure Se at low level. In the present study participants reported using 9 different instrumental techniques: ICP-MS in collision, reaction or MS/MS mode and with various collision/reaction gases: He, NH₃, H₂, CH₄ and O₂ (see Figure 55).

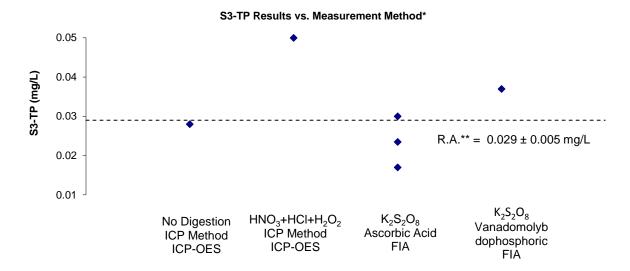
Phosphorus Caution should be exercised when low level P is measured by ICP-OES with wavelengths 213.617 nm or 214.914 nm because these wavelengths have interferences from Cu 213.598 nm and 214.898 nm respectively.

Total Phosphorus level in the test sample S3 was low, below the reporting level of many participants. Laboratories used a wide variety of measurement methods and only 9 reported results. No assigned value could be set for this test because the results were too variable. A

summary of participants' results and methods is presented in Table 59. Figure 56 presents plots of participants results versus the method used.

Table 59 Summary of Participants' Results and Methods for TP in S3

Measurement Method	TP (mg/L)					
K ₂ S ₂ O ₈ digestion Ascorbic Acid Colorimetric Method FIA determination	0.03	0.017	<0.1	0.0235		
H ₂ SO ₄ +K ₂ SO ₄ digestion Ascorbic Acid Colorimetric Method DA determination	<0.1	<0.05				
H ₂ SO ₄ +K ₂ SO ₄ digestion Vanadomolybdophosphoric Colorimetric Method DA determination FIA	0.037					
K ₂ S ₂ O ₈ digestion IC determination	<0.4					
No digestion ICP-Method ICP-OES determination	0.028	<0.5	0.37			
No digestion ICP-Method ICP-MS determination	<0.5					
Nitric/hydrochloric + peroxide ICP-Method ICP-OES determination	0.153					



^{*}Result larger than 0.05 mg/L has been plotted as 0.05 mg/L. $R.A^{**}=$ Robust average excluding results from laboratories 10, 20 and 22.

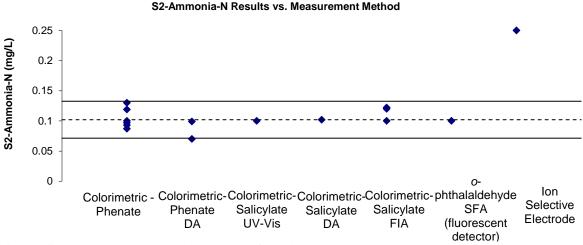
Figure 56 S3-TP Results vs. Measurement Method

7.6 Participants' Results and Analytical Methods for Tests in Samples S2 and S3 Other than Total Elements

Participants were asked to analyse samples S2 and S3 using their normal test method. Stability studies were conducted and these samples were found to be sufficiently stable for evaluation of participants' performance (See Appendix 2). The measurement methods and instrumental techniques used for S2 and S3 analyses are presented in Appendix 7.

Sample S2-Individual Test Commentary

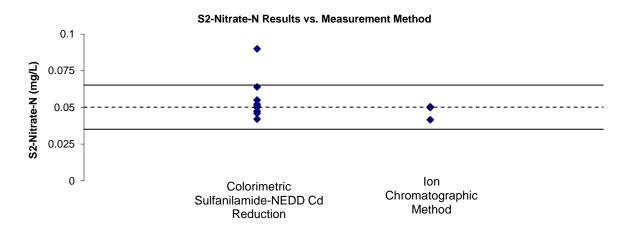
Ammonia-Nitrogen Most participants used the colorimetric-phenate or colorimetric-salicylate methods with FIA or DA determination. One laboratory reported using ion selective electrode method and one the *o*-phthalaldehyde method with SFA with fluorescent detector (Figure 57).



Horizontal lines on charts correspond to z-scores of 2 and -2

Figure 57 S2-NH₃-N Results vs. Measurement Method

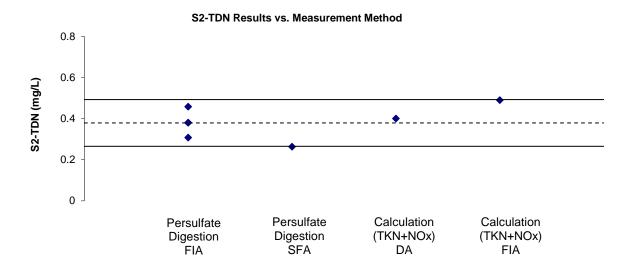
Nitrate-Nitrogen Ten participants used colorimetric-sulfanilamide-NEDD Cd reduction with FIA and four used the ion chromatographic method. Except for one, all the results reported for nitrate-N in S3 were in good agreement with each other and returned satisfactory z-scores. A plot of participants' results versus analytical method and instrumental technique used is presented in Figure 58.



Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 58 S2-Nitrate-N Results vs. Measurement Method

Total Dissolved Nitrogen Ten laboratories reported results for TDN and except for one all were in agreement with each other and with the robust average of 0.379 ± 0.057 mg/L. Figure 59 presents plots of participants' results vs the measurement method used for TDN determination in S2.



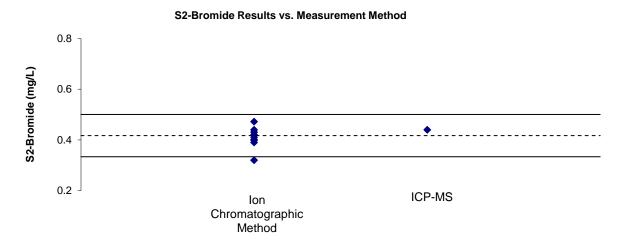
Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 59 S2-TDN Results vs. Measurement Method

Bromide Ion chromatography was the method chosen by most laboratories for bromide measurements. One participant reported using ICP method for bromide measurements in S2 (Figure 60).

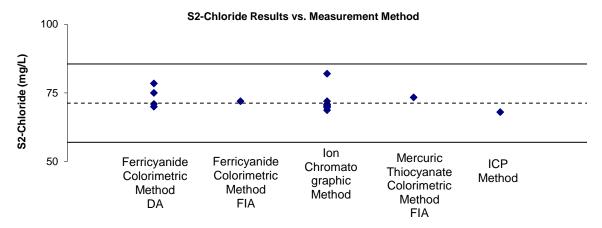
Chloride Participants used a wide variety of methods for chloride analysis in S2 and all produced comparable results (Figure 61).

Fluoride Most participants used ion selective electrode method or ion chromatographic method. One laboratory used SPADNS colorimetric method with UV-Vis determination (Figure 62). Fluoride by colorimetric method has interference from chlorides and SPANDS might not be the best choice for fluoride measurements at low level in water.



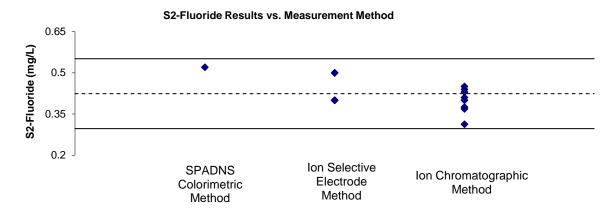
Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 60 S2-Bromide Results vs. Measurement Method



Horizontal lines on charts are the results correspond to z-scores of 2 and -2

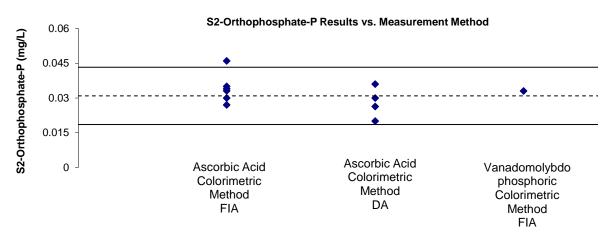
Figure 61 S2-Chloride Results vs. Measurement Method



Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 62 S2-Fluoride Results vs. Measurement Method **Dissolved Organic Carbon as dNPOC.** Participants used high temperature oxidation with NIR or FI detector and all performed satisfactorily.

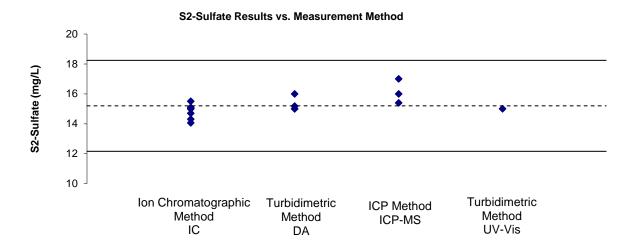
Orthophosphate-P One participant reported using a vanadomolybdophosphoric method for orthophosphate-P measurements in S2; all other participants used ascorbic acid colorimetric method with FIA or DA determination (Figure 63).



Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 63 S2-Orthophosphate-P Results vs. Measurement

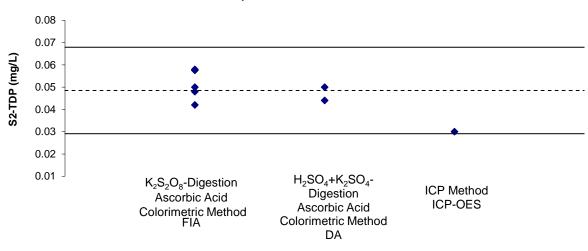
Sulfate Three participants reported using ICP-MS for sulfate measurements in S2; caution should be exercised when the ICP method is used because it measures total S and not only S from sulfate compounds (Figure 64).



Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 64 S2-Sulphate Results vs. Measurement Method

Total dissolved phosphorus level in S2 was low (0.0485 mg/L) and this might have presented difficulties to some laboratories. Only 9 participants reported results for TDP in S2. The reported results were variable with a between laboratories coefficient of variation high, 17%. Most laboratories used potassium persulfate for digestion and then measured the liberated orthophosphate colorimetrically by FIA. No digestion was performed by one participant they reported measuring TDP in the sample by ICP-OES (Figure 65).



S2-Total Dissolved Phosphorus Results vs. Measurement Method

Horizontal lines on charts are the results correspond to z-scores of 2 and -2

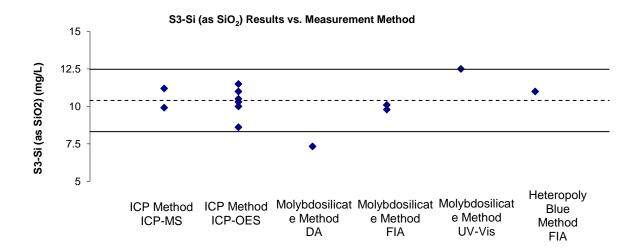
Figure 65 S2-TDP Results vs. Measurement Method

Sample S3-Individual Test Commentary

Alkalinity to pH 4.5 as (CaCO₃) did not present analytical difficulty to participants. All reported results returned satisfactory z-scores.

Colour Participating laboratories used both visual comparison method and spectrophotometric method and except for one all performed satisfactorily.

Silica (as SiO₂) Plots of participants' results versus measurement technique used are presented in Figure 66.

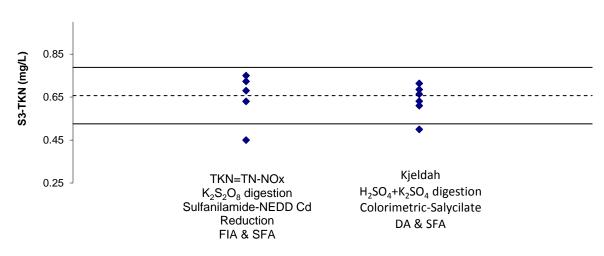


Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 66 S3-Si (as SiO₂) Results vs. Measurement Method

Total Hardness Of 16 results reported for Total Hardness, 15 returned satisfactory z-score. Most participants performed mineral analyses and reported hardness by calculation.

Total Kjeldahl Nitrogen assigned value was 0.657 mg/L. Twelve participants reported results for TKN and ten performed satisfactorily. Plots of participants' results versus analytical method and measurement technique used are presented in Figure 67.



S3-TKN Results vs. Measurement Method

Horizontal lines on charts are the results correspond to z-scores of 2 and -2

Figure 67 S3-TKN Results vs. Measurement Method

Total Nitrogen Eleven participants used persulfate digestion for TN measurements in S3 and 4 reported TN as TKN+NOx. Except for one all reported results returned satisfactory z-scores.

Turbidity level in S3 (0.417 NTU) challenged participants' analytical technique. Of 14 reported results only 8 returned satisfactory z-score.

7.7 Comparison with Previous NMI Proficiency Tests of Metals in Water

AQA 18-05 is the twenty-second NMI proficiency test of metals in water. For most of the analytes the same fixed target standard deviation was used in the present study as in the previous studies of metals in water. This allowed a comparison of participants' performance (z-score) over time and provided a benchmark for progressive improvement.

Despite different matrices, analytes and analytes' concentrations, on average participants' performance has remained consistent with the percentage of satisfactory z-scores ranging from 83% to 97% and satisfactory E_n -scores from 72% to 89% (Figure 68).

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 its scores to lie within the range $|z| \le 2$. Scores in the range $2 < |z| \le 3$ occasionally can occur, however these should be interpreted in conjunction with the other scores obtained by that laboratory. For example, a trend of z-scores on one side of the zero line are an indication of method or laboratory bias.

7.8 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 60).

Lab. Code	RMs or CRMs identity
1	CWW-TM-A, B and C (metals)
3	CRM
5	HPS CRMs
6	ICV1, ICV3, Hg CRM, Ref, CRM 26, CRM 27
8	AGAL 10 & AGAL 12, Anions-QC, pH 7 buffer, Primary multi-anion standard solution, Alkalinity- Waste water QC, TDS 1500 mg/L Calibration Standard, ICV 1, ICV 3
10	BT2000 Trace Metal in Drinking Water Standard, CA-HPS-0288 - Na, Ca, S, K,Mg, QC1195-20 Simple Nutrients, QC1051-2 Complex Nutrients, WC-TOC-10X-1 Total Organic Carbon, IC-NO2-N-10X-1 IC Standard , ASTRAL-65 IC Stock Standard
12	USEPA solution 200.7-6
17	ENCT Round 22 Bot No1-8

Table 60 Control Samples Used by Participants

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

'a reference material, accompanied by documentation issued by an authoritative body and providing one or more specified property values with associated uncertainties and traceabilities, using valid procedures' ¹⁸

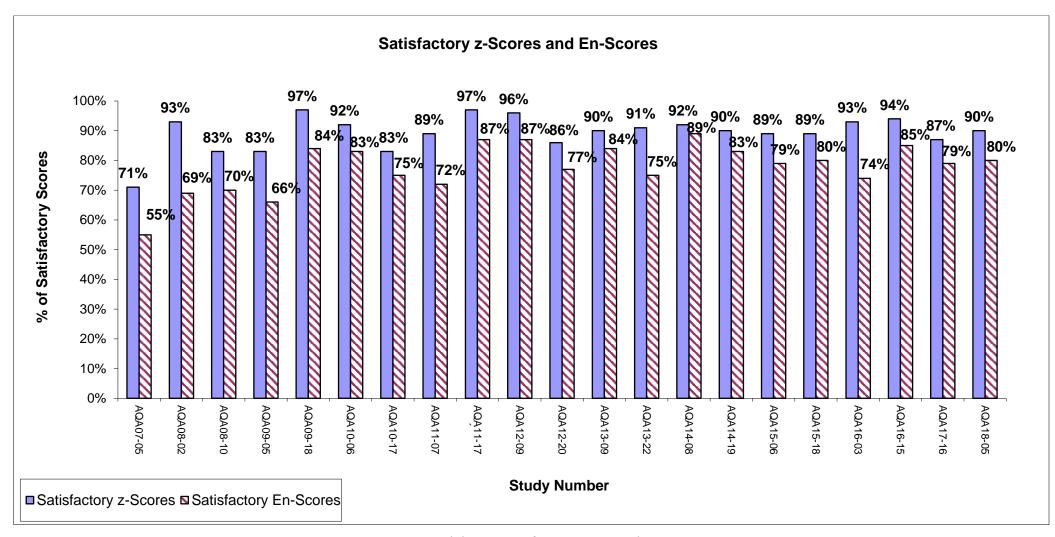


Figure 68 Participants' Performance over Time

8 REFERENCES

- [1] ISO17043:2010, Conformity assessment General requirements for proficiency testing.
- [2] NMI 2016, NMI Chemical Proficiency Testing Study Protocol, viewed 22 March 2017, http://www.measurement.gov.au>.
- [3] NMI 2016, NMI Chemical Proficiency Testing Statistical Manual, viewed 22 March 2017, http://www.measurement.gov.au.
- [4] Thompson, M, Ellison, S & Wood, R 2006, 'The international harmonized protocol for proficiency testing of (chemical) analytical laboratories', *Pure Appl. Chem*, vol 78, pp 145-196.
- [5] National Health and Medical Research Council *Australian Drinking Water Guidelines, viewed* November 2017, http://www.nhmrc.gov.au/_files_nhmrc/file/publications/synopses/adwg_11_06.pdf
- [6] NMI, (2013), AQA 13-22 Metals in Water, http://www.measurement.gov.au.
- [7] NMI (2014), AQA 14-19 Metals in Water, http://www.measurement.gov.au.
- [8] ISO13528:2015(E), Statistical methods for use in proficiency testing by interlaboratory comparisons.
- [9] Thompson, M 2000, Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing, *Analyst*, vol 125, pp 385-386.
- [10] ISO/IEC 17025:2017, General requirements for the competence of testing and calibration laboratories
- [11] Eurachem 2012, Quantifying uncertainty in Analytical Measurement, 3rd edition, viewed 10 May 2017,
 - http://www.eurachem.org/images/stories/Guides/pdf/QUAM2012_P1.pdf.
- [12] Betil, M, Naykki, T, Hovind, H & Krysell, M 2004, Nordtest Report Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories, Nordest Tekniikantie, Finland, Esopo.
- [13] Hibbert, B 2007, *Quality Assurance for the Analytical Chemistry Laboratory*, Oxford University Press.
- [14] NATA 2009, Technical Note 33.
- [15] ISO (2008), Guide to the Expression of Uncertainty in Measurement (GUM), Geneva, Switzerland.
- [16] Eurolab 2002, Technical Report No 1/2002 Measurement Uncertainty in Testing.
- [17] NMI, Estimating Measurement Uncertainty for Chemists viewed March 2017, <www.measurement.gov.au>.
- [18] JCGM 200:2008, International vocabulary of metrology Basic and general concepts and associated terms (VIM), 3rd edition.

APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING Sample Preparation

Samples S1– was unfiltered tap water further fortified for the elements of interest.

Samples S2— was prepared from river water collected from Brown's Waterhole Turramurra. Approximately 10 L of water were filtered through 0.45 µm pore size filter, autoclaved and further fortified for orthophosphate-P, ammonia-N, nitrate-N, dissolved organic carbon, bromide and fluoride. The prepared material was dispensed in units of 200 mL each and stored frozen.

Sample S3 – consisted of two containers labelled SA and S3B. The bottle S3A contained 750 mL of unfiltered, chilled, river water. Except for silicon the analytes' levels in this sample were the incurred level. The container labelled S3B consisted of 200 mL of unfiltered, autoclaved, frozen river water. This sample was spiked with sucrose and glutamic acid. Participants were instructed not to composite the contents of the two containers prior to analyses.

Sample Analysis and Homogeneity Testing

Excepting TDP in S2, a partial homogeneity test was conducted for all the analytes of interest in Samples S1, S2 and S3.^{1, 6, 7} Three bottles were analysed in duplicate and the average of the results was reported as the homogeneity value.

Methodology for Total Elements

Measurements for total elements were made using NMI Method: NT2.47.²³ NMI holds third party (NATA) accreditation for this method. 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 on a hot block at 90±100°C for 90 min.

Testing using NMI Method NT2.47 involved measurements using inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES). The measurement instrument was calibrated using external standards for targeted analytes. A set of quality control samples consisting of blanks, blank matrix spike, duplicates and sample matrix spikes, was carried through the same set of procedures and analysed at the same time as the samples. CRM NMI MX014 and Sample S1 from PT study AQA 14-19 were also used as check samples. A summary of the ion/s and wavelength used for each analyte is given in Table 61.

		1 autc 01	mstrumenta	i i ceimique t	1800 101 10	Jiai Licili	Citts
Analyte	Instrument	Internal Standard	Reaction/ Collision Cell (if applicable)	Cell Mode/Gas (if applicable)	S1 Final Dilution Factor	S3 Final Dilution Factor	Ion/Wavelength
Al	ICP-MS	Rh	NA	NA	1.1	NA	27 m/z
As	ICP-MS	Rh	ORS	Не	1.1	NA	75 m/z
В	ICP-OES	Y	NA	NA	NA	1.1	208.956 nm
Ba	ICP-MS	Rh	ORS	Не	1.1	NA	137 m/z
Be	ICP-MS	Rh	NA	NA	1.1	NA	9 m/z
Bi	ICP-MS	Ir	ORS	Не	1.1	NA	209 m/z
Ca	ICP-OES	Y	NA	NA	NA	1.1	422.491 nm
Cd	ICP-MS	Rh	ORS	Не	1.1	NA	111 m/z
Co	ICP-MS	Rh	ORS	Не	1.1	NA	59 m/z
Cr	ICP-MS	Rh	ORS	Не	1.1	NA	52 m/z
Cu	ICP-MS	Rh	ORS	Не	1.1	NA	63 m/z
Fe	ICP-MS	Rh	ORS	He	1.1	NA	56 m/z

Table 61 Instrumental Technique used for Total Elements

Hg	CVAFS	NA	NA	NA	1.1	NA	253.7 nm nm
K	ICP-MS	Rh	ORS	Не	NA	1.1	39 m/z
Li	ICP-MS	Rh	NA	NA	1.1	NA	7 m/z
Mg	ICP-OES	Y	NA	NA	NA	1.1	279.8 nm
Mn	ICP-MS	Rh	ORS	Не	1.1	NA	55 m/z
Mo	ICP-MS	Rh	ORS	Не	1.1	NA	95 m/z
Na	ICP-OES	Y	NA	NA	NA	1.1	588.995 nm
Ni	ICP-MS	Rh	ORS	Не	1.1	NA	60 m/z
P	ICP-OES	Y	NA	NA	NA	1.1	177.434 nm
Pb	ICP-MS	Ir	ORS	Не	1.1	NA	Average of 206, 207, 208 m/z
Sb	ICP-MS	Ir	ORS	Не	1.1	NA	121 m/z
Se	ICP-MS	Rh	ORS	НЕНе	1.1	NA	78 m/z
Si	ICP-OES	Y	NA	NA	NA	1.1	251.611 nm
Sn	ICP-MS	Rh	ORS	Не	1.1	NA	118 m/z
Sr	ICP-MS	Rh	ORS	Не	1.1	NA	88 m/z
Tl	ICP-MS	Rh	ORS	Не	1.1	NA	205 m/z
U	ICP-MS	Ir	ORS	Не	1.1	NA	238 m/z
V	ICP-MS	Rh	ORS	Не	1.1	NA	51 m/z
Zn	ICP-MS	Rh	ORS	Не	1.1	NA	64 m/z

Methodology for Tests Other Than Total Elements in S2 and S3

Measurements were made using NMI Methods: NW_B1, NW_D4, NW_B23_B19, NW_S15, NW_B10, NW_B11, NW_S11, NW_B14, NW_D3_B14, NW_D17, NW_S15, NW_B23, NW_D9, NW_D10_B14, NW_B3_B14 and NW_B19. NMI holds third party (NATA) accreditation for these methods. A summary of the measurement methods and instrumental techniques is presented in Tables 62 and 63.

Table 62 Methodology for S2

Test	Measurement Method	Instrument
Ammonia-N	Fluorometric Determination - OPA Method	SFA
Bromide	Ion Chromatographic Method	IC
Chloride	Ferricyanide Colorimetric Method	DA
Dissolved Organic Carbon	High-Temperature Oxidation	NIR-detector
Fluoride	Ion Selective Electrode Method	Ion Selective Electrode
Orthophosphate-P (FRP)	Ascorbic Acid Colorimetric Method	DA
Nitrate-N	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA
Sulfate	Turbidimetric Method	DA
Total Dissolved Nitrogen	Persulfate digestion	FIA

Table 63 Methodology for S3

Test	Measurement Method	Instrument
Alkalinity to pH 4.5 (as CaCO3)	Titration	Auto Titration
Colour, apparent	Spectrophotometric method	DA

Silica (as SiO2)	ICP Method	ICP-OES
Total Hardness (as CaCO3)	Calculation	ICP-OES
Total Kjeldahl Nitrogen	TKN=TN-NOx, Persulfate Digestion, colorimetric sulfanilamine NEDD Cd reduction	FIA
Total Phosphorus	ICP Method	ICP-OES
Total Nitrogen	Persulfate Digestion, colorimetric sulfanilamine NEDD Cd reduction	FIA
Total Organic Carbon	High-Temperature Oxidation	NIR- detector

APPENDIX 2 - STABILITY STUDY

Samples S1 No stability study was carried out for total elements in S1. Stability studies conducted for previous proficiency studies of metals in water found no significant changes in any of the analytes' concentration. ^{6,7}

Samples S2 and S3 Participants were advised to store the Samples S2 and S3B frozen if analyses cannot be commenced on the day of receipt. Samples' condition on receipt and the date when the samples were received and analysed by the participants are presented in Table 64. No significant trends between participants' results and samples' condition on receipt were noticed.

Table 64 Samples S2 and S3 Condition on Receipt and the Date When the Samples were Received and Analysed

Lab	Received	S	2	S3	S A	S3B		
Code	Date	Condition on Receipt	Date of Analysis	Condition on Receipt	Date of Analysis	Condition on Receipt	Date of Analysis	
1	17.04.2018	frozen				Frozen		
2	17.04.2018	NA	NA	cold	03.05.2018	Partially frozen	03.05.2018	
3	17.04.2018	frozen	30.04.2018	cold	30.04.2018	frozen	30.04.2018	
4	17.04.2018	frozen		cold		frozen		
5	18.04.2018	cold	18.04.2018	cold	18.04.2018	frozen	18.04.2018	
6	17.04.2018	11°C	24.04.2018	11°C	24.04.2018	11℃	24.04.2018	
8	17.04.2018	frozen	18.04.2018	cold	27.04.2018	frozen	27.04.2018	
9	17.04.2018	NA	NA	12.5 ℃	20.04.2018	Frozen	20.04.2018	
10	17.04.2018	frozen	20.04.2018	cold	24.04.2018	frozen	24.04.2018	
11	17.04.2018	cold	19.04.2018	cold	19.04.2018	cold	19.04.2018	
12	17.04.2018	frozen	26.04.2018	cold	17.04.2018	frozen	17.04.2018	
13	17.04.2018	frozen	19.04.2018	cold	19.04.2018	frozen	19.04.2018	
14	17.04.2018	cold	02.05.2018	cold	02.05.2018	cold	02.05.2018	
15	16.04.2018	frozen	10.05.2018	cold	03.05.2018	frozen	03.05.2018	
17	17.04.2018	frozen	15.05.2018	cold	15.05.2018	Frozen	15.05.2018	
18	17.04.2018	frozen	18.04.2018	cold	19.04.2018	frozen	19.04.2018	
19*	27.04.2018	cold	03.05.2018	cold	03.05.2018	cold	03.05.2018	
20	17.04.2018	frozen		cold		frozen		
21	19.04.2018	frozen	23.04.2018	cold	23.04.2018	frozen	23.04.2018	
22	18.04.2018	frozen		cold	11.05.2018	frozen	11.05.2018	

^{*}The samples have been dispatched on 24.04.2018, NA = Not Applicable

Stability Study

Stability studies conducted for nutrients and physical tests in water in the previous studies found no significant changes in any of the analytes' concentration. ^{6,7} A stability study was however conducted in the present study for the less stabile analytes: NH₃-N, NO₃-N and DOC in S2 and for turbidity, TN, TOC and silicon in S3.

Two main factors were considered to affect these tests stability in water: storage condition and time.

To test for storage stability two sets of samples were kept at -20°C (reference samples), two samples were stored at 4°C and two samples were left out on laboratory table for one week. Theses samples were analysed in duplicate, in random order at the same time, one week after samples' distribution.

For short term stability testing 6 more sets of samples were kept 4°C and analyse over the study period, before the samples' dispatch, three weeks after the samples' dispatch and at the end of the study after results' submission. Each sample was analysed in duplicate together with a set of quality control samples consisting of blanks, blank matrix spikes, control samples, duplicates and sample matrix spikes.

Linear regression was used to check for significant trends possibly indicating degradation of the material. The observed slopes were also tested for significance using a t-test, with $t_{\alpha\,df}$ being the critical t-value (two-tailed) for a significance level α =0.05 (95% confidence interval).

No significant change in concentration was observed for any of the tests less stable tests in Samples S2 and S3 (Table 65).

Table 65 Stability Study Results

Test	Slope	Standard error of the slope	t-score	Р	Is the slope significantly different from 0 at a 95% confidence interval? (P<0.05)
Ammonia-N	-0.0004	0.00032	1.89	0.085	No
Nitrate-N	-0.0003	0.00028	1.08	0.302	No
DOC	-0.0375	0.052	0.74	0.48	No
Si (as SiO ₂)	0.1265	0.345	0.367	0.72	No
TN	-0.0175	0.0167	1.05	0.32	No
TOC	0.1	0.241	0.415	0.66	No
Turbidity	0.0083	0.019	0.436	0.67	No

APPENDIX 3 - 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(E), Statistical methods for use in proficiency testing by inter-laboratory comparisons – Annex C⁸ The uncertainty was estimated as:

$$u_{\text{rob av}} = 1.25 * S_{rob av} / \sqrt{p}$$
 Equation 3

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.

The robust average of all As results is given in Table 66.

Table 66 Robust average for all As results in Sample S1

Lab. Code	As (mg/L)
1	0.004
2	0.004
3	0.004
4	0.00419
5	0.006
6	0.00506
8	0.00438
9	0.00439
10	NT
11	0.004
12	0.004
13	0.0042
14	4.32
15	NT
16	0.005
17	NT
18	0.006
19	0.0047
20	NT
21	0.004
22	0.005
Robust average	0.00458

The result from laboratory 14 was removed as this is outside the range \pm 50% of the robust average. The robust average and associated uncertainty of the remaining results were then used as the assigned value for this analyte (Table 67).

Table 67 Uncertainty estimate for As in Sample S1 after removing outlier

No. results (p)	16
Robust Average	0.00448 mg/L
$S_{rob\ av}$	0.00058 mg/L
Urob av	0.00018 mg/L
k	2
Urob av	0.00037 mg/L

The assigned value for As in Sample S1 is 0.00448 ± 0.00037 mg/L.

z-Score and E_n-score

For each participant's result a z-score and E_n -score are calculated according to Equation 1 and Equation 2 respectively (see page 13).

A worked example is set out below in Table 68.

Table 68 z-Score and E_n-score for As result reported by Laboratory 1 in S1

As Result mg/L	Assigned Value mg/L	Set Target Standard Deviation	z-Score	E _n -Score
0.004±0.001	0.00448±0.00037	10% as CV or 0.10x0.00448= =0.000448 mg/L	$z = \frac{(0.004 - 0.00448)}{0.000448}$ $z = -1.07$	$En = \frac{(0.004 - 0.00448)}{\sqrt{0.001^2 + 0.00037^2}}$ $E_n = -0.45$

APPENDIX 4 - 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 be used to estimate the uncertainty of their measurement results. ^{14, 12} An example is given below.

Between 2007 and 2014, NMI carried out fifteen proficiency tests of metals in water. These studies involved analyses of dissolved or acid-extractable metals at low and high levels in potable, fresh (river), saline water, ground water and waste water. Laboratory X participated and submitted satisfactory results in ten of these PTs.

Table 69 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
AOA 09 10	Fresh	20 ± 3	18.9 ± 0.6	7.8	26
AQA 08-10	Fresh	200 ± 20	191 ± 5	5.5	26
AQA 09-05	Saline	5.0 ± 1.2	5.5 ± 0.6	13.3	14
AQA 09-03	Saline	43 ± 5	44.7 ± 3.3	10.8	18
AOA 00 19	Fresh	5.3 ± 0.5	5.04 ± 0.27	7.4	14
AQA 09-18	Fresh	49 ± 4	48.9 ± 1.2	3.3	16
AQA 10-06	Potable	49 ± 4	50 ± 1	5.9	20
AQA 10-00	Potable	48 ± 4	50 ± 1	3	20
AOA 11 17	Waste water	97 ± 9	99 ± 1	1.5	15
AQA 11-17	Waste water	97 ± 9	98 ± 1	1.5	15
AOA 12.00	Fresh	43 ± 6	45 ± 2	6.6	19
AQA 12-09	Fresh	51 ± 7	53 ± 2	7.5	19
AQA 12-20	Sea water	40 ± 4.4	38.4 ± 2.1	11	22
AOA 12 00	Fresh	4.3 ± 0.5	4.09 ± 0.17	8.5	15
AQA 13-09	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
Avera	ge			6.8**	

^{*} Expanded uncertainty at approximately 95% confidence. ** The mean value of Robust CV was used. The pooled standard deviation could also be used. In this case the pooled standard deviation is 7.5%. Using a coverage factor of 2 gives an estimate of 15%.

Taking the average of the robust CV over these PT samples gives an estimate of the relative standard uncertainty of 6.8%. Using a coverage factor of 2 gives a relative expanded uncertainty of 14%, at a level of confidence of approximately 95%. Table 70 sets out the expanded uncertainty for results of the measurement of Ni in fresh, saline, waste or potable water over the range $5-200~\mu g/L$.

Table 70 Uncertainty of Ni results estimated using PT data.

Results	Uncertainty
μg/L	μg/L
5.0	0.7
20.0	2.8
50	7
200	28

The MU estimates made using PT data is close to Laboratory X's own uncertainty estimates reported with their PT results. The estimate of 14% passes the test of being reasonable, and the analysis of the six different matrices over three years can safely be assumed to include all the relevant uncertainty components (different operators, reagents, calibrants etc.), and so complies with ISO 17025. 10

APPENDIX 5 - ACRONYMS AND ABBREVIATIONS

AAS Atomic Absorption Spectrometry
AFS Atomic fluorescence spectroscopy
CRI Collision Reaction Interface
CV Coefficient of Variation
DA Discreet Analyser
DRC Dynamic Reaction Cell

IDMS Isotope dilution mass spectrometry

FIA Flow Injection Analyser
FSE Fluoride Selective Electrode
HEHe High energy He mode

ICP-MS Inductively Coupled Plasma - Mass Spectrometry

ICP-OES-AV Inductively Coupled Plasma - Optical Emission Spectrometry- axial view

ICP-OES-AV-eq Inductively Coupled Plasma - Optical Emission Spectrometry- axial view with correction

equation

ICP-OES-RV Inductively Coupled Plasma - Optical Emission Spectrometry- radial view

IC Ion chromatograph
ISE Ion selective electrode

Max Maximum value in a set of results

Md Median

Min Minimum value in a set of results

NEDD N-(1-naphthyl)-ethylenediamine dihhydrochloride (NED dihydrochloride)

NMI National Measurement Institute (of Australia)

NR Not Reported

NIR Near-infrared

NT Not Tested

ORS Octopole Reaction System

PT Proficiency Test
RM Reference Material

Robust CV Robust Coefficient of Variation

Robust SD Robust Standard Deviation

S Spiked or formulated concentration of a PT sample

seaFAST-ICP-MS Automated inductively coupled plasma spectrometry preconcentration system for undiluted

seawater

SFA Segment Flow Analyser

SI The International System of Units

s²_{sam} Sampling variance

 s_a/σ Analytical standard deviation divided by the target standard deviation

SPANDS 2-(4-Sulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonic acid trisodium salt, or

4,5-Dihydroxy-3-(4-sulfophenylazo)-2,7-naphthalene disulfonic acid trisodium salt, or 4,5-Dihydroxy-3-(4-sulfophenylazo)-2,7-naphthalenedisulfonic Acid Trisodium Salt.

SRM Standard Reference Material (Trademark of NIST)

UC Universal Cell

UV-Vis Ultraviolet and Visible Spectroscopy

VGA Vapour Generator Accessory

APPENDIX 6 - INSTRUMENT DETAILS FOR DISSOLVED ELEMENTS

Table 71 Instrument Conditions Al

Lab Code	Instrument	Internal standard	Reaction /Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	UC	Не	1	NA	27
2	ICP-OES-AV	Yb	NA		1	NA	396.152
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	27
4	ICP-MS/MS					NA	
5	ICP-MS		NA		10	NA	
6	ICP-MS	Sc	ORS	Не	1	NA	27
8	ICP-MS	Sc	ORS	Не	1	NA	27
9	ICP-MS	Sc	NA	NA	1	NA	27
10					NA	NA	
11	ICP-MS	Ge	UC	Не	Neat	NA	27
12	ICP-OES-AV-buffer	Y			1	NA	308.215
13	ICP-MS	Sc 45	ORS	NA	1	NA	27 m/z
14	ICP-MS		CRI	Не		NA	27
15						NA	
16						NA	
17					NA	NA	
18	ICP-OES-AV					NA	
19	ICP-MS	Sc	CRI	Не		NA	26.9815
20					NA	NA	
21	ICP-MS		ORS	Не	10	NA	
22	ICP-MS	Sc 44.9559			1	NA	26.9815

Table 72 Instrument Conditions As

Lab Code	Standard		Instrument standard		Reaction/Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ge	UC	Не	1	NA	75		
2	ICP-MS	Y	ORS	Не	1	NA	75		
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	75		
4	ICP-MS/MS					NA			
5	ICP-MS		CRI		10	NA			
6	ICP-MS	Y	ORS	Не	1	NA	75		
8	ICP-MS	Rh	ORS	Не	1	NA	75		
9	ICP-MS	Te	UC	Не	1	NA	75		
10					NA	NA			
11	ICP-MS	Ge	UC	Не	Neat	NA	75		
12	ICP-MS	Ge	DRC	Не	1	NA	75		
13	ICP-MS	Rh 103	ORS	O2	1	NA	91 m/z		
14	ICP-MS		CRI	Не		NA	75		
15						NA			
16						NA			
17					NA	NA			
18	ICP-MS					NA			
19	ICP-MS	Y	CRI	Не		NA	74.9216		
20					NA	NA			
21	ICP-MS		ORS	Не	1	NA			
22	ICP-MS	Te 124.904			1	NA	74.9216		

Table 73 Instrument Conditions B

Lab. Code	Instrument	Internal standard	Reaction/ Collision Cell	Cell Gas	S1 Final Dilution factor	S2 Final Dilution factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	NA	NA	NA	1	10
2	ICP-OES-AV	Yb	NA		NA	1	249.772
3	ICP-MS	Rh, Sc, Ir	ORS	NA	NA		11
4	ICP-MS/MS				NA		
5	ICP-MS		NA		NA	10	
6	ICP-MS	Sc	ORS	NA	NA	1	11
8	ICP-MS	Sc	ORS	Не	NA	1	11
9	ICP-MS	Sc	NA	NA	NA	1	10
10	ICP-MS	Y	ORS	Не	NA	1	11
11	ICP-MS	Ge	UC	NA	NA	Neat	11
12	ICP-OES-AV-buffer	Y			NA	1	208.959
13	ICP-OES-AV	Eu 271.700	NA	NA	NA	1	B 249.678
14	ICP-MS		CRI	Не	NA		11
15					NA		
16					NA	NA	
17					NA		
18					NA		
19					NA		
20	ICP-OES-RV				NA	0.7	249.772
21	ICP-MS		ORS	Не	NA	1	
22	ICP-MS	Sc 44.9559			NA	1	11.0093

Table 74 Instrument Conditions Ba

Lab Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Rh	NA	NA	1	NA	138
2	ICP-MS	In	ORS	NA	1	NA	135
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	137
4	ICP-MS/MS					NA	
5	ICP-MS		NA		10	NA	
6	ICP-MS	Lu	ORS	Не	1	NA	137
8	ICP-MS	Rh	ORS	Не	1	NA	135
9	ICP-MS	Lu	NA	NA	1	NA	137
10					NA	NA	
11	ICP-MS	Ir	UC	NA	Neat	NA	137
12	ICP-MS	In			1	NA	137
13	ICP-MS	Ir 193	ORS	O2	1	NA	153 m/z
14	ICP-MS		CRI	Не		NA	137
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19	ICP-MS	In	CRI	Не		NA	137.905
20					NA	NA	
21	ICP-MS		ORS	Не	1	NA	
22	ICP-MS	Rh 102.905			1	NA	136.905

Table 75 Instrument Conditions Be

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	NA	NA	1	NA	9
2	ICP-MS	Li	ORS	NA	1	NA	9
4	ICP-MS	Rh, Sc, Ir	ORS	NA		NA	9
5	ICP- MS/MS					NA	
6	ICP-MS		NA		10	NA	
8	ICP-MS	Sc	ORS	NA	1	NA	9
9	ICP-MS	Sc	ORS	NA	1	NA	9
10	ICP-MS	Sc	NA	NA	1	NA	9
11					NA	NA	
12	ICP-MS	Ge	UC	NA	Neat	NA	9
13	ICP-MS	Sc			1	NA	9
14	ICP-MS	Sc 45	ORS	NA	1	NA	9 m/z
15	ICP-MS		CRI	Не		NA	9
16						NA	
17						NA	
18					NA	NA	
19	ICP-MS					NA	
20	ICP-MS	Sc	CRI	Не		NA	9.0122
21					NA	NA	
22	ICP-MS		ORS	Не	1	NA	

Table 76 Instrument Conditions Bi

Lab Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ir	NA	NA	1	NA	209
2	ICP-MS	Ir	ORS	NA	1	NA	209
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	209
4	ICP- MS/MS					NA	
5	ICP-MS		NA		10	NA	
6	ICP-MS	Lu	ORS	Не	1	NA	209
8	ICP-MS	Lu	ORS	Не	10	NA	209
9	ICP-MS	Lu	NA	NA	1	NA	209
10					NA	NA	
11	ICP-MS	Ir	UC	NA	Neat	NA	209
12						NA	
13	ICP-MS	Ir 193	ORS	O2	1	NA	209 m/z
14	ICP-MS		CRI	Не		NA	209
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19						NA	
20					NA	NA	
21	ICP-MS		ORS	Не	1	NA	
22	ICP-MS	Ir 192.963			1	NA	208.98

Table 77 Instrument Conditions Ca

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	Sc	UC	Не	NA	1	44
2	ICP-OES-AV	Yb	NA		NA	1	373.69
3	ICP-OES-RV	Y, Cs			NA		315.887
4	ICP-OES-AV				NA		
5	ICP-MS		CRI		NA	10	
6	ICP-OES-RV	Lu	NA	NA	NA	1	317.941
8	ICP-MS	Sc	ORS	H2	NA	1	40
9	ICP-MS	Sc	NA	NA	NA	1	43
10	ICP-MS	Sc	ORS	Не	NA	1	44
11	ICP-OES-AV	Lu	NA	NA	NA	Neat	317.933
12	ICP-OES-AV-buffer	Y			NA	1	317.933
13	ICP-OES-AV	Eu 290.667	NA	NA	NA	1	Ca 370.602
14	ICP-OES-RV				NA		315.8
15					NA		
16					NA	NA	
17					NA		
18	ICP-OES-AV				NA		
19					NA		
20	ICP-OES-RV				NA	0.7	422.673
21	ICP-OES-AV		ORS	NA	NA	1	
22	ICP-OES-RV				NA	1	317.933

Table 78 Instrument Conditions Cd

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Rh	NA	NA	1	NA	111
2	ICP-MS	In	ORS	NA	1	NA	111
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	111
4	ICP-MS/MS					NA	
5	ICP-MS		NA		10	NA	
6	ICP-MS	Y	ORS	Не	1	NA	111
8	ICP-MS	Rh	ORS	Не	1	NA	111
9	ICP-MS	Rh	NA	NA	1	NA	111
10					NA	NA	
11	ICP-MS	Ge	UC	NA	Neat	NA	111
12	ICP-MS	In			1	NA	111
13	ICP-MS	Rh 103	ORS	O2	1	NA	111 m/z
14	ICP-MS		CRI	Не		NA	114
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19	ICP-MS	In	CRI	Не		NA	110.904
20					NA	NA	
21	ICP-MS		ORS	Не	1	NA	
22	ICP-MS	Rh 102.905			1	NA	110.904

Table 79 Instrument Conditions Co

Lab Code	Instrument	Internal standard	Reaction/Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ge	UC	Не	1	NA	59
2	ICP-MS	Sc	ORS	NA	1	NA	59
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	59
4	ICP-MS/MS					NA	
5	ICP-MS		CRI		10	NA	
6	ICP-MS	Y	ORS	Не	1	NA	59
8	ICP-MS	Sc	ORS	Не	1	NA	59
9	ICP-MS	Ga	UC	Не	1	NA	59
10					NA	NA	
11	ICP-MS	Ge	UC	Не	Neat	NA	59
12	ICP-MS	Ga	DRC	Не	1	NA	59
13	ICP-MS	Rh 103	ORS	O2	1	NA	59 m/z
14	ICP-MS		CRI	Не		NA	59
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19	ICP-MS	Sc	CRI	Не		NA	58.9332
20					NA	NA	
21	ICP-MS		ORS	Не	1	NA	
22	ICP-MS	Rh 102.905			1	NA	58.9332

Table 80 Instrument Conditions Cr

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	UC	He	1	NA	52
2	ICP-MS	Sc	ORS	NA	1	NA	52
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	52
4	ICP-MS/MS					NA	
5	ICP-MS		CRI		10	NA	
6	ICP-MS	Sc	ORS	Не	1	NA	52
8	ICP-MS	Sc	ORS	Не	1	NA	52
9	ICP-MS	Sc	UC	He	1	NA	52
10					NA	NA	
11	ICP-MS	Ge	UC	Не	Neat	NA	52
12	ICP-MS	Ge	DRC	NH3	1	NA	52
13	ICP-MS	Sc 45	ORS	O2	1	NA	52 m/z
14	ICP-MS		CRI	He		NA	52
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19	ICP-MS	Sc	CRI	Не		NA	51.9405
20					NA	NA	
21	ICP-MS		ORS	Не	1	NA	
22	ICP-MS	Rh 102.905			1	NA	51.9405

Table 81 Instrument Conditions Cu

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ge	UC	Не	1	NA	63
2	ICP-MS	Y	ORS	NA	1	NA	65
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	63
4	ICP-MS/MS					NA	
5	ICP-MS		CRI		10	NA	
6	ICP-MS	Y	ORS	Не	1	NA	63
8	ICP-MS	Sc	ORS	Не	1	NA	63
9	ICP-MS	Ga	UC	Не	1	NA	63
10					NA	NA	
11	ICP-OES-AV	Lu	NA	NA	Neat	NA	327.395
12	ICP-OES-AV- buffer	Y			1	NA	324.754
13	ICP-MS	Rh 103	ORS	O2	1	NA	63 m/z
14	ICP-MS		CRI	Не		NA	63
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19	ICP-MS	Sc	CRI	Не		NA	62.9298
20					NA	NA	
21	ICP-MS		ORS	Не	10	NA	
22	ICP-MS	Rh 102.905			1	NA	62.9298

Table 82 Instrument Conditions Fe

Lab Code	Instrument	Internal standard	Reaction/Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	UC	He	1	NA	56
2	ICP-MS	Sc	ORS	NA	1	NA	56
3	ICP-MS	Rh, Sc, Ir	ORS	НЕНе		NA	56
4	ICP-MS/MS					NA	
5	ICP-MS		CRI		10	NA	
6	ICP-MS	Y	ORS	Не	1	NA	56
8	ICP-MS	Sc	ORS	Не	1	NA	56
9	ICP-MS	Sc	UC	Не	1	NA	56
10					NA	NA	
11	ICP-MS	Ge	UC	Не	Neat	NA	56
12	ICP-OES- AV-buffer	Y			1	NA	259.941
13	ICP-MS	Rh 103	ORS	O2	10	NA	56 m/z
14	ICP-MS		CRI	Не		NA	56
15						NA	
16						NA	
17					NA	NA	
18	ICP-OES-AV					NA	
19	ICP-MS	Sc	CRI	Не		NA	56.9354
20					NA	NA	
21	ICP-MS		ORS	Не	10	NA	
22	ICP-OES-AV				1	NA	238.204

Table 83 Instrument Conditions Hg

Lab Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ir	NA	NA	1	NA	201
2	CVAAS	SnC12	NA		1	NA	3470
3	AAS					NA	253.7
4	AAS					NA	
5	ICP-MS		NA		10	NA	
6	ICP-MS	Lu	ORS	Не	1	NA	202
8	ICP-MS	Lu	ORS	Не	1	NA	202
9	Atomic Fluorescence	NA	NA	NA	5	NA	254 nm
10					NA	NA	
11	Cetac Hg Analyser	NA	NA	NA	Neat	NA	253.7
12	AAS				2	NA	253.7
13	ICP-MS	Ir 193	ORS	O2	1	NA	193 m/z
14	ICP-MS		CRI	Не		NA	202
15						NA	
16						NA	
17					NA	NA	
18	VGA-AAS					NA	
19						NA	
20					NA	NA	
21	ICP-MS		ORS	Не	1	NA	
22	ICP-MS	Ir 192.963			1	NA	201.971

Table 84 Instrument Conditions K

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	Sc	UC	Не	NA	1	39
2	ICP-OES-AV	Yb	NA		NA	1	769.897
3	ICP-OES-RV	Y, Cs			NA		766.491
4	ICP-OES-AV				NA		
5	ICP-MS		CRI		NA	10	
6	ICP-OES-RV	Lu	NA	NA	NA	1	766.502
8	ICP-MS	Sc	ORS	Не	NA	1	39
9	ICP-MS	Sc	UC	Не	NA	1	39
10	ICP-MS	Sc	ORS	Не	NA	1	39
11	ICP-OES-AV	Lu	NA	NA	NA	Neat	769.897
12	ICP-OES-AV-buffer	Y			NA	1	769.896
13	ICP-OES-AV	Cs 697.327	NA	NA	NA	1	K 766.491
14	ICP-OES-RV				NA		766.4
15					NA		
16					NA	NA	
17					NA		
18	ICP-OES-AV				NA		
19					NA		
20	ICP-OES-RV				NA	0.7	766.491
21	ICP-OES-AV		ORS	NA	NA	1	
22	ICP-OES-RV				NA	1	766.49

Table 85 Instrument Conditions Li

Lab Code	Instrument	Internal standard	Reaction/Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	NA	NA	1	NA	7
2	ORS	NA	1	NA	9		VGA-ICP-MS
3	ICP-MS	Rh, Sc, Ir	ORS	NA		NA	7
4						NA	
5					10	NA	
6	ICP-MS	Sc	ORS	NA	1	NA	7
8	ICP-MS	Sc	ORS	NA	1	NA	7
9	ICP-MS	Sc	NA	NA	1	NA	7
10					NA	NA	
11	ICP-MS	Ge	UC	NA	Neat	NA	7
12	ICP-MS	Sc			1	NA	7
13	ICP-MS	Sc 45	ORS	NA	1	NA	7 m/z
14	ICP-MS		CRI	Не		NA	7
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19						NA	
20					NA	NA	
21	ICP-MS		ORS	NA	1	NA	
22	ICP-MS	Sc 44.9559			1	NA	7.016

Table 86 Instrument Conditions Mg

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	Sc	UC	Не	NA	1	25
2	ICP-OES-AV	Yb	NA		NA	1	383.829
3	ICP-OES-RV	Y, Cs			NA		383.829
4	ICP-OES-AV				NA		
5	ICP-MS		CRI		NA	10	
6	ICP-OES-RV	Lu	NA	NA	NA	1	285.217
8	ICP-MS	Sc	ORS	Не	NA	1	24
9	ICP-MS	Sc	NA	NA	NA	1	25
10	ICP-MS	Sc	ORS	Не	NA	1	24
11	ICP-OES-AV	Lu	NA	NA	NA	Neat	383.829
12	ICP-OES-AV- buffer	Y			NA	1	285.213
13	ICP-OES-AV	Eu 390.711	NA	NA	NA	1	Mg 383.829
14	ICP-OES-RV				NA		279.8
15					NA		
16					NA	NA	
17					NA		
18	ICP-OES-AV				NA		
19					NA		
20	ICP-OES-RV				NA	0.7	285.213
21	ICP-OES-AV		ORS	NA	NA	1	
22	ICP-OES-RV				NA	1	285.213

Table 87 Instrument Conditions Mn

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	UC	Не	1	NA	55
2	ICP-MS	Sc	ORS	NA	1	NA	55
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	55
4	ICP-MS/MS					NA	
5	ICP-MS		CRI		10	NA	
6	ICP-MS	Y	ORS	Не	1	NA	55
8	ICP-MS	Sc	ORS	Не	1	NA	55
9	ICP-MS	Sc	UC	Не	1	NA	55
10					NA	NA	
11	ICP-MS	Ge	UC	Не	Neat	NA	55
12	ICP-OES-AV-buffer	Y			1	NA	257.611
13	ICP-MS	Rh 103	ORS	O2	1	NA	55 m/z
14	ICP-MS		CRI	Не		NA	55
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19	ICP-MS	Sc	CRI	Не		NA	54.9381
20					NA	NA	
21	ICP-MS		ORS	Не	10	NA	
22	ICP-MS	Rh 102.905			1	NA	54.9381

Table 88 Instrument Conditions Mo

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Rh	NA	NA	1	NA	95
2	ICP-MS	Y	ORS	NA	1	NA	97
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	95
4	ICP-MS/MS					NA	
5	ICP-MS		NA		10	NA	
6	ICP-MS	Y	ORS	Не	1	NA	95
8	ICP-MS	Rh	ORS	Не	1	NA	95
9	ICP-MS	Rh	UC	Не	1	NA	98
10					NA	NA	
11	ICP-MS	Ge	UC	Не	Neat	NA	95
12	ICP-MS	In			1	NA	95
13	ICP-MS	Rh 103	ORS	O2	1	NA	95 m/z
14	ICP-MS		CRI	Не		NA	95
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19						NA	
20					NA	NA	
21	ICP-MS		ORS	Не	1	NA	
22	ICP-MS	Rh 102.905			1	NA	94.9058

Table 89 Instrument Conditions Na

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	Sc	UC	Не	NA	1	23
2	ICP-OES-AV	Yb	NA		NA	1	589.592
3	ICP-OES-RV	Y, Cs			NA		589.592
4	ICP-OES-AV				NA		
5	ICP-MS		CRI		NA	10	
6	ICP-OES-RV	Lu	NA	NA	NA	1	330.227
8	ICP-MS	Sc	ORS	Не	NA	1	23
9	ICP-MS	Sc	UC	Не	NA	1	23
10	ICP-MS	Lu	ORS	Не	NA	1	23
11	ICP-OES-AV	Lu	NA	NA	NA	Neat	589.592
12	ICP-OES-AV-buffer	Y			NA	1	589.592
13	ICP-OES-AV	NA	NA	NA	NA	1	Na 568.821
14	ICP-OES-RV				NA		589.5
15					NA		
16					NA	NA	
17					NA		
18	ICP-OES-AV				NA		
19					NA		
20	ICP-OES-RV				NA	0.7	589.592
21	ICP-OES-AV		ORS	NA	NA	1	
22	ICP-OES-RV				NA	1	589.592

Table 90 Instrument Conditions Ni

Lab		Internal	Reaction/	Reaction	S1 Dilution	S2 Dilution	Wavelength (nm)/
Code	Instrument	standard	Collision Cell	Gas	Factor	Factor	Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ge	UC	Не	1	NA	60
2	ICP-MS	Sc	ORS	Не	1	NA	60
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	60
4	ICP-MS/MS					NA	
5	ICP-MS		CRI		10	NA	
6	ICP-MS	Y	ORS	Не	1	NA	60
8	ICP-MS	Sc	ORS	Не	1	NA	60
9	ICP-MS	Ga	UC	Не	1	NA	60
10					NA	NA	
11	ICP-MS	Ge	UC	Не	Neat	NA	60
12	ICP-MS	Ga	DRC	Не	1	NA	60
13	ICP-MS	Rh 103	ORS	O2	1	NA	60 m/z
14	ICP-MS		CRI	Не		NA	60
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19	ICP-MS	Sc	CRI	Не		NA	59.9332
20					NA	NA	
21	ICP-MS		ORS	Не	1	NA	
22	ICP-MS	Rh 102.905			1	NA	59.9332

Table 91 Instrument Conditions P

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	UC	Не	NA	1	31
2	ICP-OES-AV	Yb	NA		NA	1	177.434
3	ICP-OES-RV	Y, Cs			NA		185.827
4	ICP-MS/MS				NA		
5	if other please type	IC			NA	10	
6	ICP-OES-RV	Lu	NA	NA	NA	1	178.221
8	ICP-MS	Sc	ORS	Не	NA	1	31
9	ICP-MS	Sc	NA	NA	NA	1	31
10					NA	NA	
11	ICP-OES-AV	Lu	NA	NA	NA	Neat	178.222
12	ICP-OES-AV- buffer				NA	1	177.495
13	ICP-OES-AV	NA	NA	NA	NA	1	P 185.878
14					NA		
15					NA		
16					NA	NA	
17					NA		
18	FIA				NA		
19					NA		
20	ICP-OES-RV				NA	0.7	214.914
21	ICP-OES-AV		ORS	NA	NA	1	
22	ICP-OES-AV				NA	1	213.617

Table 92 Instrument Conditions Pb

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Final Dilution Factor	S2 Final Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ir	NA	NA	1	NA	206+207+208
2	ICP-MS	Ir	ORS	NA	1	NA	206
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	208
4	ICP-MS/MS					NA	
5	ICP-MS		NA		10	NA	
6	ICP-MS	Lu	ORS	Не	1	NA	208
8	ICP-MS	Lu	ORS	Не	1	NA	208
9	ICP-MS	Lu	NA	NA	1	NA	206, 207, 208
10					NA	NA	
11	ICP-MS	Ir	UC	NA	Neat	NA	208
12	ICP-MS	Ir			1	NA	208
13	ICP-MS	Ir 193	ORS	O2	1	NA	208 m/z
14	ICP-MS		CRI	Не		NA	SUM ISOTOPES
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19						NA	
20					NA	NA	
21	ICP-MS		ORS	Не	1	NA	
22	ICP-MS	Ir 192.963			1	NA	207.977

Table 93 Instrument Conditions Sb

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Rh	NA	NA	1	NA	121
2	ICP-MS	In	ORS	Не	1	NA	123
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	121
4	ICP- MS/MS					NA	
5	ICP-MS		NA		10	NA	
6	ICP-MS	Но	ORS	Не	1	NA	121
8	ICP-MS	Rh	ORS	Не	1	NA	123
9	ICP-MS	Rh	NA	NA	1	NA	121
10					NA	NA	
11	ICP-MS	Ge	UC	NA	Neat	NA	121
12	ICP-MS	In			1	NA	121
13	ICP-MS	Ir 193	ORS	O2	1	NA	121 m/z
14	ICP-MS		CRI	Не		NA	121
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19	ICP-MS	In	CRI	Не		NA	120.904
20					NA	NA	
21	ICP-MS		ORS	Не	1	NA	
22	ICP-MS	Rh 102.905			1	NA	120.904

Table 94 Instrument Conditions Se

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Rh	DRC	NH3	1	NA	82
2	ICP-MS	Y	ORS	Не	1	NA	78
3	ICP-MS	Rh, Sc, Ir	ORS	НЕНе		NA	78
4	ICP-MS/MS					NA	
5	ICP-MS		CRI		10	NA	
6	ICP-MS	Lu	ORS	HEHe	1	NA	78
8	ICP-MS	Rh	ORS	H2	1	NA	78
9	ICP-MS	Те	NA	NA	1	NA	82
10					NA	NA	
11	ICP-MS	Ge	UC	CH4	Neat	NA	80
12	ICP-MS	Ge	DRC	NH3	1	NA	82
13	ICP-MS	Rh 103	ORS	O2	1	NA	94 m/z
14	ICP-MS		CRI	HEHe		NA	78
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19						NA	
20					NA	NA	
21	ICP-MS		ORS	НЕНе	1	NA	
22	ICP-MS	Te 124.904			1	NA	77.9173

Table 95 Instrument Conditions Sn

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1						NA	
2	ICP-MS	In	ORS	Не	1	NA	118
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	118
4	ICP-MS/MS					NA	
5					10	NA	
6	ICP-MS	Lu	ORS	Не	1	NA	118
8	ICP-MS	Rh	ORS	Не	1	NA	118
9	ICP-MS	Rh	NA	NA	1	NA	120
10					NA	NA	
11	ICP-MS	Ge	UC	NA	Neat	NA	118
12	ICP-MS	In			1	NA	118
13	ICP-MS	Ir 193	ORS	O2	1	NA	134 m/z
14	ICP-MS		CRI	Не		NA	118
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19						NA	
20					NA	NA	
21	ICP-MS		ORS	Не	1	NA	
22	ICP-MS	Rh 102.905			1	NA	117.902

Table 96 Instrument Conditions Sr

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Rh	NA	NA	1	NA	88
2	ICP-MS	Y	ORS	NA	1	NA	88
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	88
4	ICP-MS/MS					NA	
5					10	NA	
6	ICP-MS	Y	ORS	Не	1	NA	88
8	ICP-MS	Rh	ORS	Не	1	NA	88
9	ICP-MS	Rh	NA	NA	1	NA	88
10					NA	NA	
11	ICP-MS	Ge	UC	NA	Neat	NA	88
12	ICP-MS	In			1	NA	88
13	ICP-MS	Rh 103	ORS	O2	1	NA	88 m/z
14	ICP-MS		CRI	Не		NA	88
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19						NA	
20					NA	NA	
21	ICP-MS		ORS	Не	1	NA	
22	ICP-MS	Rh 102.905			1	NA	87.9056

Table 97 Instrument Conditions Tl

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ir	NA	NA	1	NA	205
2	ICP-MS	Ir	ORS	NA	1	NA	205
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	205
4	ICP-MS/MS					NA	
5	ICP-MS		NA		10	NA	
6	ICP-MS	Lu	ORS	Не	1	NA	205
8	ICP-MS	Lu	ORS	Не	1	NA	205
9	ICP-MS	Lu	NA	NA	1	NA	205
10					NA	NA	
11	ICP-MS	Ir	UC	NA	Neat	NA	205
12	ICP-MS	Ir			1	NA	203
13	ICP-MS	Ir 193	ORS	O2	1	NA	205 m/z
14	ICP-MS		CRI	Не		NA	205
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19						NA	
20					NA	NA	
21	ICP-MS		ORS	Не	1	NA	
22	ICP-MS	Ir 192.963			1	NA	204.975

Table 98 Instrument Conditions U

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Ir	NA	NA	1	NA	238
2	ICP-MS	Ir	ORS	NA	1	NA	238
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	238
4	ICP-MS/MS					NA	
5	ICP-MS		NA		10	NA	
6	ICP-MS	Lu	ORS	Не	1	NA	238
8	ICP-MS	Lu	ORS	Не	1	NA	238
9	ICP-MS	Lu	NA	NA	1	NA	238
10					NA	NA	
11	ICP-MS	Ir	UC	NA	Neat	NA	238
12						NA	
13	ICP-MS	Ir 193	ORS	Не	1	NA	238 m/z
14	ICP-MS		CRI	Не		NA	238
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19						NA	
20					NA	NA	
21	ICP-MS		ORS	Не	1	NA	
22	ICP-MS	Ir 192.963			1	NA	238.05

Table 99 Instrument Conditions V

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion (m/z)/Absorbance (nm)
1	ICP-MS	Sc	UC	Не	1	NA	51
2	ICP-MS	Sc	ORS	Не	1	NA	51
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	51
4	ICP-MS/MS					NA	
5	ICP-MS		CRI		10	NA	
6	ICP-MS	Sc	ORS	Не	1	NA	51
8	ICP-MS	Sc	ORS	Не	1	NA	51
9	ICP-MS	Sc	UC	Не	1	NA	51
10					NA	NA	
11	ICP-MS	Ge	UC	Не	Neat	NA	51
12	ICP-MS	Ga	DRC	Не	1	NA	51
13	ICP-MS	Sc 45	ORS	O2	1	NA	67 m/z
14	ICP-MS		CRI	Не		NA	51
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19	ICP-MS	Sc	CRI	Не		NA	50.944
20					NA	NA	
21	ICP-MS		ORS	Не	1	NA	
22	ICP-MS	Rh 102.905			1	NA	50.944

Table 100 Instrument Conditions Zn

Lab Code	Instrument	Internal standard	Reaction/ Collision Cell	Reaction Gas	S1 Dilution Factor	S2 Dilution Factor	Wavelength (nm)/ Ion(m/z)/Absorbance(nm)
1	ICP-MS	Ge	UC	Не	1	NA	66
2	ICP-MS	Y	ORS	NA	1	NA	66
3	ICP-MS	Rh, Sc, Ir	ORS	Не		NA	66
4	ICP-MS/MS					NA	
5	ICP-MS		CRI		10	NA	
6	ICP-MS	Y	ORS	Не	1	NA	66
8	ICP-MS	Sc	ORS	Не	1	NA	66
9	ICP-MS	Te	UC	Не	1	NA	66
10					NA	NA	
11	ICP-OES-AV	Lu	NA	NA	Neat	NA	213.857
12	ICP-OES-AV-buffer	Y			1	NA	231.856
13	ICP-MS	Rh 103	ORS	O2	10	NA	66 m/z
14	ICP-MS		CRI	Не		NA	66
15						NA	
16						NA	
17					NA	NA	
18	ICP-MS					NA	
19	ICP-MS	Y	CRI	Не		NA	65.926
20					NA	NA	
21	ICP-MS		ORS	Не	10	NA	
22	ICP-OES-RV				1	NA	206.2

APPENDIX 7 - METHODOLOGY FOR TESTS OTHER THAN TOTAL ELEMENTS IN S2 AND S3

Table 101 Measurement Methods and Instrumental Techniques for Dissolved Organic Carbon in S2

Lab. Code	Measurement Method	Instrument	Method Reference
1	High-Temperature Oxidation	NIR-detector	n/a
2	NA	NA	NA
3	if other method please type	if other technique please type	In house
4	High-Temperature Oxidation	NIR-detector	
5			
6	High-Temperature Oxidation	NIR-detector	
8			
9	NA	NA	NA
10	High-Temperature Oxidation	FI-detector	1.603
11	High-Temperature Oxidation	NIR-detector	APHA5310B
12			
13	High-Temperature Oxidation	NIR-detector	АРНА
14			
15	High-Temperature Oxidation	NIR-detector	APHA
16	NA	NA	NA
17			
18			
19			
20			
21	High-Temperature Oxidation	NIR-detector	
22			

Table $\,\,102$ Measurement Methods and Instrumental Techniques for Fluoride in S2

Lab. Code	Measurement Method	Instrument	Method Reference
1	SPADNS Colorimetric Method	UV-Vis Spectrophotometer	W1
2	NA	NA	NA
3	Ion Selective Electrode Method	Ion Selective Electrode	In house
4	Ion Selective Electrode Method	IC	
5	Ion Chromatographic Method	IC	APHA 4110B
6	Ion Selective Electrode Method	Ion Selective Electrode	
8			
9	NA	NA	NA
10	Ion Selective Electrode Method	Ion Selective Electrode	1.602
11	Ion Selective Electrode Method	Ion Selective Electrode	APHAF-C
12	Ion Chromatographic Method	IC	
13	Ion Chromatographic Method	IC	APHA 4110B.AWWA.WPCF
14	Ion Selective Electrode Method	Ion Selective Electrode	4500-F C
15	Ion Selective Electrode Method	Ion Selective Electrode	АРНА
16	NA	NA	NA
17			
18			
19	Ion Chromatographic Method	IC	APHA 4110B
20	Ion Chromatographic Method	IC	
21	Ion Chromatographic Method	IC	
22	Ion Chromatographic Method	IC	

Table 103 Measurement Methods and Instrumental Techniques for Orthophosphate-P (FRP) in S2 $\,$

Lab. Code	Measurement Method	Instrument	Method Reference
1	Ascorbic Acid Colorimetric Method	FIA	W8
2	NA	NA	NA
3	Ascorbic Acid Colorimetric Method	DA	In house
4	Ascorbic Acid Colorimetric Method	DA	
5			
6	Ascorbic Acid Colorimetric Method	DA	
8	Ascorbic Acid Colorimetric Method	DA	APHA
9	NA	NA	NA
10	Ascorbic Acid Colorimetric Method	FIA	FIA.011A
11	Ascorbic Acid Colorimetric Method	DA	APHA4500-P F
12			
13	Ascorbic Acid Colorimetric Method	FIA	In-house, based on Standard Methods 2005 - 4500-P G
14	Ascorbic Acid Colorimetric Method	FIA	4500-P G
15	Ascorbic Acid Colorimetric Method	DA	APHA
16	NA	NA	NA
17	Ascorbic Acid Colorimetric Method	FIA	APHA
18			
19			
20	Ascorbic Acid Colorimetric Method	FIA	
21	Vanadomolybdophosphoric Colorimetric Method	FIA	
22			

Table $\,$ 104 Measurement Methods and Instrumental Techniques for Nitrate-N in S2 $\,$

Lab. Code	Measurement Method	Instrument	Method Reference
1	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	W7
2	NA	NA	NA
3	Calculation	DA	In house
4	Ion Chromatographic Method	IC	
5	Ion Chromatographic Method	IC	APHA 4110B
6	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	
8			
9	NA	NA	NA
10	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	FIA.010C
11	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	APHA4500-NO3-F
12			
13	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	In-house, based on Standard Methods 2005 - 4500-NO3 I
14	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	4500-NO3 I
15	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	АРНА
16	NA	NA	NA
17	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	АРНА
18			
19	Ion Chromatographic Method	IC	APHA 4110B
20	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	
21	Colorimetric-Sulfanilamide-NEDD Cd reduction	FIA	
22	Ion Chromatographic Method	IC	

Table 105 Measurement Methods and Instrumental Techniques for Sulfate in S2

Lab. Code	Measurement Method	Instrument	Method Reference
1	ICP	ICP-MS	W32
2	NA	NA	NA
3	Turbidimetric Method	DA	In house
4	Ion Chromatographic Method	IC	
5	Ion Chromatographic Method	IC	APHA 4110B
6	Turbidimetric Method	DA	
8	Ion Chromatographic Method	IC	USEPA
9	NA	NA	NA
10	ICP Method	ICP-MS	5.308
11	Turbidimetric Method	DA	APHA4500-SO42
12	Ion Chromatographic Method	IC	
13	Ion Chromatographic Method	IC	APHA 4110B.AWWA.WPCF
14	ICP Method	ICP-OES	3120 B
15	Turbidimetric Method	DA	APHA
16	NA	NA	NA
17			
18			
19	Ion Chromatographic Method	IC	APHA 4110B
20	Ion Chromatographic Method	IC	
21	Turbidimetric Method	UV-Vis Spectrophotometer	
22	Ion Chromatographic Method	IC	

Table 106 Measurement Methods and Instrumental Techniques for Total Dissolved Nitrogen in S2

Lab. Code	Measurement Method	Instrument	Method Reference
1	Persulfate digestion	FIA	W4
2	NA	NA	NA
3	Calculation (TKN+NOx)	DA	In house
4	Calculation (TKN+NOx)		
5			
6	Persulfate digestion	SFA	
8			
9	NA	NA	NA
10	Persulfate digestion	FIA	FIA.013
11	Calculation (TKN+NOx)	Not Applicable	
12			
13	Persulfate digestion	FIA	In-house method based on Standard Methods, APHA
14			
15	Persulfate digestion	FIA	АРНА
16	NA	NA	NA
17	Persulfate digestion		АРНА
18			
19			
20			
21			
22			

Table 107 Measurement Methods and Instrumental Techniques for Total Dissolved Phosphorus in S2

Lab. Code	Measurem	ent Method	Instrument	Method Reference
1	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	W4
2	NA	NA	NA	NA
3	if other please type	Ascorbic Acid Colorimetric Method	DA	In house
4	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	
5				
6	No Digestion	ICP Method	ICP-OES	USEPA6020
8	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	DA	АРНА
9	NA	NA	NA	NA
10	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	FIA.011B
11	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	
12				
13	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	In-house method based on Standard Methods, APHA
14	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	4500-P B3 P
15				
16	NA	NA	NA	NA
17	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	АРНА
18				
19				
20				
21				
22		ICP Method	ICP-OES	

Table 108 Measurement Methods and Instrumental Techniques for Alkalinity to pH4.5 as (Ca CO_3) in S3

Lab. Code	Measurement Method	Instrument	Method Reference
1	Titration	N/A	W22
2	Titration	Auto Titration	APHA2320
3	Titration	Auto Titration	In house
4	Titration	Auto Titration	
5	Titration		APHA 2320
6	Titration	Auto Titration	
8	Titration	Ion Selective Electrode	АРНА
9	NT	NT	NT
10	Titration	Auto Titration	1.012
11	Titration	Auto Titration	APHA2320
12	Titration	Ion Selective Electrode	
13	Titration		APHA 2320B
14	Titration	Auto Titration	2320 B
15	Titration	Auto Titration	АРНА
16	NA	NA	NA
17			
18			
19	Titration	Manual Analysis	APHA 2320 B
20			
21	Titration	Ion Selective Electrode	
22	Titration	Manual Analysis	

Table 109 Measurement Methods and Instrumental Techniques for Colour (Apparent) in S3

Lab. Code	Measurement Method	Instrument	Method Reference
1	Spectrophotometric Method	UV-Vis Spectrophotometer	W1
2	Visual Comparison Method	Manual Analysis	APHA2120B
3	Visual Comparison Method	Manual Analysis	In house
4			
5			
6	Visual Comparison Method	Manual Analysis	
8			
9	NT	NT	NT
10	Spectrophotometric Method	UV-Vis Spectrophotometer	5.102
11	Spectrophotometric Method	DA	APHA2120C
12	Spectrophotometric Method		
13	Spectrophotometric Method		APHA 2120B
14	Spectrophotometric Method	UV-Vis Spectrophotometer	2120 C
15	Spectrophotometric Method	DA	
16	NA	NA	NA
17			
18			
19	Visual Comparison Method	BDH Lovibond Nesslerizer	APHA 2120 B
20			
21	Visual Comparison Method	Not Applicable	
22	Spectrophotometric Method	UV-Vis Spectrophotometer	

Table 110 Measurement Methods and Instrumental Techniques Used for Silica (as SiO_2) in S3

Lab. Code	Measurement Method	Instrument	Method Reference
1	ICP-Method	ICP-MS	W32
2	ICP-Method	ICP-OES	APHA3120B
3	ICP-Method	ICP-OES	In house
4	Molybdosilicate Method	DA	
5			
6	ICP-Method	ICP-OES	
8			
9	NT	NT	NT
10	Calculation	ICP-MS	5.308
11	ICP-Method	ICP-OES	APHA3120B
12			
13	ICP-Method	ICP-OES	APHA 3120B
14	Molybdosilicate Method	FIA	4500-SIO2 F
15			
16	NA	NA	NA
17	Molybdosilicate Method	FIA	АРНА
18			
19	Molybdosilicate Method	UV-Vis Spectrophotometer	APHA 4500-Si C
20			
21	Heteropoly Blue Method	FIA	
22	ICP-Method	ICP-OES	

Table 111 Measurement Methods and Instrumental Techniques Used for Total Hardness (as $CaCO_3$) in S3

Lab. Code	Measurement Method	Instrument	Method Reference
1	Titration	N/A	W21
2	Calculation	Not Applicable	APHA3120B
3	Calculation	ICP-OES	
4	Calculation		
5	Titration		APHA 2340
6	Calculation	ICP-OES	
8	Calculation	ICP-MS	USEPA6020
9	NT	NT	NT
10	Calculation	ICP-MS	5.308
11	Calculation	Not Applicable	
12			
13	Calculation	ICP-OES	APHA 2340B
14	Calculation	ICP-OES	2340 B
15	Calculation		
16	NA	NA	NA
17			
18			
19			
20			
21	Calculation	ICP-OES	
22	Calculation	ICP-OES	

Table 112 Measurement Methods and Instrumental Techniques Used for Total Kjeldahl Nitrogen in S3

Lab. Code			Instrument	Method Reference
1	K2S2O8 digestion (TKN=TN-NOx)	Colorimetric-Sulfanilamide- NEDD Cd reduction	FIA	W4
2	Kjeldahl digest	Colorimetric - salicylate method	DA	USEPA351.2
3		Colorimetric - salicylate method	DA	In house
4	Semi-Micro-Kjeldahl Method	Colorimetric - salicylate method	DA	
5				
6	Calculation (TN-NOx)	TKN = TN-NOx (Dumas)	SFA & FIA	
8				
9	Semi-Micro-Kjeldahl Method	Colorimetric - salicylate method	DA	APHA 4500-Norg D. (modified) 4500 NH3 F (modified) 22nd ed. 2012.
10	Calculation (TN-NOx)	TKN = TN-NOx (Dumas)	FIA	NA
11	if other please type, H2SO4+K2SO4-Digestion	Colorimetric - salicylate method	DA	APHA4500 Norg
12				
13	In-house, based on Standard Methods 2005 – 4500-Norg D	Colorimetric - salicylate method	SFA	In-house, based on APHA
14				
15				
16	NA	NA	NA	NA
17				
18				
19				
20				
21	K2S2O8 digestion (TKN=TN-NOx)	Colorimetric-Sulfanilamide- NEDD Cd reduction	FIA	
22	K2S2O8 digestion (TKN=TN-NOx)	Colorimetric-Sulfanilamide- NEDD Cd reduction	FIA	

Table 113 Measurement Methods and Instrumental Techniques Used for Total Phosphorus in S3

Lab. Code	Measureme	Measurement Method		Method Reference
1	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	W4
2	No Digestion	ICP Method	ICP-OES	APHA3120B
3		Ascorbic Acid Colorimetric Method	DA	In house
4	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	
5	K2S2O8-Digestion	Ion Chromatographic Method	IC	APHA 4500-P J
6	No Digestion	ICP Method	ICP-OES	USEPA6020
8	No Digestion	ICP Method	ICP-MS	USEPA6020
9	NT	NT	NT	NT
10	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	FIA.011B
11	H2SO4+K2SO4-Digestion	Ascorbic Acid Colorimetric Method	DA	APHA4500P F
12				
13	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	In-house
14				
15				
16	NA	NA	NA	NA
17	K2S2O8-Digestion	Ascorbic Acid Colorimetric Method	FIA	АРНА
18				
19				
20	Nitric/hydrochloric + peroxide.	ICP Method	ICP-OES	
21	K2S2O8-Digestion	Vanadomolybdophosphoric Colorimetric Method	FIA	
22		ICP Method	ICP-OES	

Table 114 Measurement Methods and Instrumental Techniques Used for Total Nitrogen in S3

Lab. Code	Measurement Method	Instrument	Method Reference
1	Persulfate digestion	FIA	W4
2	Calculation (TKN+NOx)	Not Applicable	APHA4500N
3	Calculation (TKN+NOx)	DA	In house
4	Calculation (TKN+NOx)		
5	Persulfate digestion	IC	APHA 4500-P J
6	Persulfate digestion	SFA	
8			
9	Persulfate digestion	FIA	APHA 4500-N C & 4500-NO3-I 22nd ed. 2012 (modified).
10	Persulfate digestion	FIA	FIA.013
11	Calculation (TKN+NOx)	Not Applicable	
12			
13	Persulfate digestion	FIA	In-house
14			
15	Persulfate digestion	FIA	АРНА
16	NA	NA	NA
17	Persulfate digestion	FIA	АРНА
18			
19	Persulfate digestion	DA	APHA 4500-N C
20			
21	Persulfate digestion	FIA	
22	Persulfate digestion	UV-Vis Spectrophotometer	

Table 115 Measurement Methods and Instrumental Techniques Used for Total Organic Carbon in S3

Lab. Code	Measurement Method	Instrument	Method Reference
1	High-Temperature Oxidation	NIR-detector	n/a
2	High-Temperature Oxidation	NIR-detector	APHA5310B
3	if other method please type	if other technique please type	NT
4	High-Temperature Oxidation	NIR-detector	
5			
6	High-Temperature Oxidation	NIR-detector	
8			
9	Persulfate-Ultraviolet Oxidation	NIR-detector	APHA 5310 C (modified) 22nd edition 2012
10	High-Temperature Oxidation	NIR-detector	1.603
11	High-Temperature Oxidation	NIR-detector	APHA5310B
12			
13	High-Temperature Oxidation	NIR-detector	АРНА
14	Persulfate-Ultraviolet Oxidation	NIR-detector	5310-C
15	High-Temperature Oxidation	NIR-detector	АРНА
16	NA	NA	NA
17			
18			
19	Persulfate-Ultraviolet Oxidation	TOC	APHA 5310 C
20			
21	High-Temperature Oxidation	NIR-detector	
22		UV-Vis Spectrophotometer	

END OF STUDY