Australian Government
Department of Industry, Science, Energy and Resources

National Measurement Institute

Proficiency Test Report
AQA 20-05
Metals on Filters

July 2020

ACKNOWLEDGMENTS

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

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

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1 SUMMARY

This report presents the results of the proficiency test AQA 20-05 Metals on Filters. The study focused on the measurement of acid extractable elements: Ag, Al, As, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, P, Pb, Se, Sn, U, V and Zn.

The sample set consisted of one sample, comprised of three filters.

Eleven laboratories registered to participate and all submitted results.

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

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

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

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

Of 136 results, all returned a satisfactory score of $|z| \leq 2.0$.

Of 136 E_n-scores, 106 (78%) were satisfactory with $| E_n | \leq 1.0$.

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

The study sample was aimed at miming real life air filter samples which are routinely analysed by laboratories. As for routine air filter samples, the study sample required a good preparation/handling procedure to avoid material loss. The high number of satisfactory z-scores indicates that laboratories do not have difficulty with the measurement of inorganic analytes on air filters.

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

Of 166 numerical results, 148 (89%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 1.3% to 125% of the reported value.

2 INTRODUCTION

2.1 NMI Proficiency Testing Program

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

Proficiency testing (PT) "is evaluation of participant performance against pre-established criteria by means of interlaboratory comparison."[1] NMI PT studies target chemical testing in areas of high public significance such as trade, environment and food safety. NMI offers studies in:

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

AQA 20-05 is the first NMI proficiency study of inorganic analytes on filters.

2.2 Study Aims

The aims of the study were to:

- compare the performance of participant laboratories and assess their accuracy;
- evaluate the laboratories methods used in determination of inorganic analytes on filters;
- develop the practical application of traceability and measurement uncertainty.

2.3 Study Conduct

The conduct of NMI proficiency tests is described in the NMI Chemical Proficiency Testing Study Protocol.[2] The statistical methods used are described in the NMI Chemical Proficiency Statistical Manual.[3] These documents have been prepared with reference to ISO Standard 17043[1] and The International Harmonized Protocol for Proficiency Testing of (Chemical) Analytical Laboratories.[4]

NMI is accredited by National Association of Testing Authorities, Australia (NATA) to ISO/IEC 17043 as a provider of proficiency testing schemes. This proficiency test is not within the scope of NMI's accreditation.

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

3 STUDY INFORMATION

3.1 Selection of Matrices and Inorganic Analytes

The selection of the matrix and of the tests for this study was based on participants' expression of interest.

3.2 Participation

Eleven laboratories participated and all submitted results.

The timetable of the study was:

Invitation issued:	04 March 2020
Samples dispatched:	06 April 2020
Results due:	11 May 2020

3.3 Test Material Specification

One sample was provided for analysis:

- Sample S1 consisted of three loaded filters labelled AQA 20-05 S1A, AQA 20-05 S1B and AQA 20-05 S1C.

3.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

3.5 Sample Preparation, Analysis and Homogeneity Testing

A full homogeneity test was conducted for Sample S1. Sample S1 was demonstrated to be sufficiently homogeneous for the evaluation of participants' performance.

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

3.6 Stability of Analytes

A handling and transport stability study was carried out prior to the dispatch of the samples. The test samples were stable during transport. The results of the stability study can be found in Appendix 2.

3.7 Sample Storage, Dispatch and Receipt

The test samples were stored at ambient temperature prior to dispatch

The samples were dispatched by courier on 6 April 2020.

The following items were packaged with the samples:

- a covering letter which included a description of the test samples and instructions for participants; and
- a form to confirm the receipt and condition of 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:

- To handle the filters with care in order to avoid material loss, as no fixation or surface coating was applied. However, please note that a handling/transport stability study was conducted prior to sample dispatch.
- To remove the filter from the container by:
    - Gently tapping the lid of the PetriSlide to dislocate any particles stacked on the lid due to electrostatic charge.
    - Grasping the lid with the thumb and finger of one hand at the grip, whilst holding the bottom portion of the slide with the other hand.
    - Opening the lid with a slight upward twisting motion.
    - Picking up the filter membrane at the notched side using a tweezer.
    - Gently folding the filter and transferring it into a digestion tube.
- To analyse the filter as received.
- NOT to touch the surface of the filter containing the deposit.

- To use their normal method for acid extractable elements in fractions of airborne particulate matter loaded on filter media but to conduct analyses on the whole filter as received.
- To report results for each of the three filters in units of µg/filter. However, the average of the three results will be used for scoring.
- To report results using the electronic results sheet emailed to them with an associated expanded measurement uncertainty estimate. A brief summary of your test methods will also be requested.
- Return the completed results sheet via e-mail (proficiency@measurement.gov.au) by 11 May 2020.
- The approximate concentration range of the measurands in the test materials is: Ag >0.05 µg/filter, Al>50 µg/filter, As> 2.5 µg/filter, Be>0.003 µg/filter, Cd>0.1 µg/filter, Co>0.05 µg/filter, Cr>1µg/filter, Cu>1 µg/filter, Fe>50 µg/filter, Hg>0.1 µg/filter, Mn> 0.5 µg/filter, Ni>0.5 µg/filter, P>25 µg/filter, Pb>1 µg/filter, Se>0.05 µg/filter, Sn>0.1 µg/filter, U>0.005 µg/filter, V>1 µg/filter and Zn>0.5 µg/filter.

3.9 Interim Report

An interim report was emailed to participants on 12 May 2020.

4 PARTICIPANT LABORATORY INFORMATION

4.1 Test Method Summaries

Summaries of test methods are transcribed in Table 1.

Table 1 Methodology for Acid Extractable Elements

Lab. Code	Method Reference	Whole Filter Used	Digestion Temp. (ºC)	Digestion Time (min)	Vol. HNO_3 (mL)	Vol. HCl (mL)	Vol. HNO_3 (1:1) (mL)	Vol. HCl (1:1) (mL)	Vol. H_2O_2 (mL)	Other (mL)
1*		Yes	95 - 100	90	3	1				
2*	USEPA IO 3.1		95	120		1	4			5 (H_2O)
3	NIOSH 7303	Yes	90-98	30	3	3				
4	In House S6 – referencing APHA 3125	Yes	120	60	2.5	7.5				
5	NIOSH 7303	Yes	90-98		3	3				
6*	AS 4479.2-1997, AS 4479.4-1999	Yes	97	120	2	6				
7	200.8	Yes	95	30	2.5	2.5				10 (H_2O)
8	NIOSH 7303	Yes	90-98		1.5	1.5				
9	NIOSH Method 7303	Yes	90	60	2.5	0.5				2.0 (H_2O)
10*	In house acid digestion	Yes	104	60	5	1.5				
11	In-house Method	Yes	95	60	5					

*Additional information in Table 2

4.2 Instruments Used for Measurements

The instruments and settings used by participants for acid extractable elements are presented in Appendix 6.

4.3 Additional Information

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

Table 2 Additional information

Lab. Code	Additional Information
1	Methodology for Acid Extractable Elements Step 2: 10 mL H_2O at 95 – 100 ºC for 30 minutes.
2	S1: Our 1A had particulate deposited onto the storage cartridge that we were unable to successfully dislodge and believe it affected the results we determined so we have only reported the results for 1B and 1C.
6	S1: The results of Tin (Sn) were found to drop off from the solution. It has to analyse straight after sample extraction.
10	Filters digested with acid then diluted to 40 mL (0.04L). Samples analysed by MS and OES x1, x10 & x100. Reported results all taken from the x1 extract. Calculation to ug/filter = ppb * 0.04.

4.4 Basis of Participants' Measurement Uncertainty Estimates

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

Table 3 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
1	top down	Duplicate Analysis	Instrument Calibration Matrix Effects Recoveries of SS	
2	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM	CRM	NMI Uncertainty Course
3	Top Down - precision and estimates of the method and laboratory bias	Control Samples	Recoveries of SS	NATA Technical Note 33
4	Professional judgment	Control Samples Duplicate Analysis	Instrument Calibration Standard Purity	Nordtest Report TR537
5	Top Down - precision and estimates of the method and laboratory bias	Control Samples	Recoveries of SS	NATATechnical Note 33
6	Standard deviation of replicate analyses multiplied by 2 or 3	Duplicate Analysis	CRM Instrument Calibration Matrix Effects Laboratory Bias from PT Studies Recoveries of SS Standard Purity	NATA Technical Note 33
7	Professional judgment	Control Samples - RM Instrument Calibration	CRM Instrument Calibration	Professional Judgement
8	Top Down - precision and estimates of the method and laboratory bias	Control Samples	Recoveries of SS	NATA Technical Note 33
9	Not applicable			
10	Top Down - precision and estimates of the method and laboratory bias	Control Samples - CRM Duplicate Analysis Instrument Calibration	CRM Instrument Calibration Matrix Effects Laboratory Bias from PT Studies Recoveries of SS Standard Purity	ISO/GUM
11	Top Down - precision and estimates of the method and laboratory bias	Control Samples - SS Instrument Calibration	Instrument Calibration Recoveries of SS	NATA Technical Note 33

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

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

The study co-ordinator welcomes comments or suggestions from participants about this study or possible future studies. Such feedback may be useful in improving future studies. Participants' comments are reproduced in Table 4.

Table 4 Participants' Comments

Lab Code	Participants' Comments	Study Co-ordinator's Response
6	In the future study, if the samples can be pre-folded, It can prevent any particle lost during transferring into the digestion tubes.	Thank you for your suggestions. We run handling and transport stability studies on the filter sample in different forms: packed folded in PetriSlide, packed unfolded in PetriSlide and packed directly into 50 mL digestion tubes. All samples were stable during handling and transport. We decided to go with the second option because it most closely resembled the routine samples.

5 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

5.1 Results Summary

Participant results are listed in Tables 5 to 23 with resultant summary statistics: robust average, median, maximum, minimum, robust standard deviation (SD_{rob}) and robust coefficient of variation (CV_{rob}). Bar charts of results and performance scores are presented in Figures 2 to 20. An example chart with interpretation guide is shown in Figure 1.

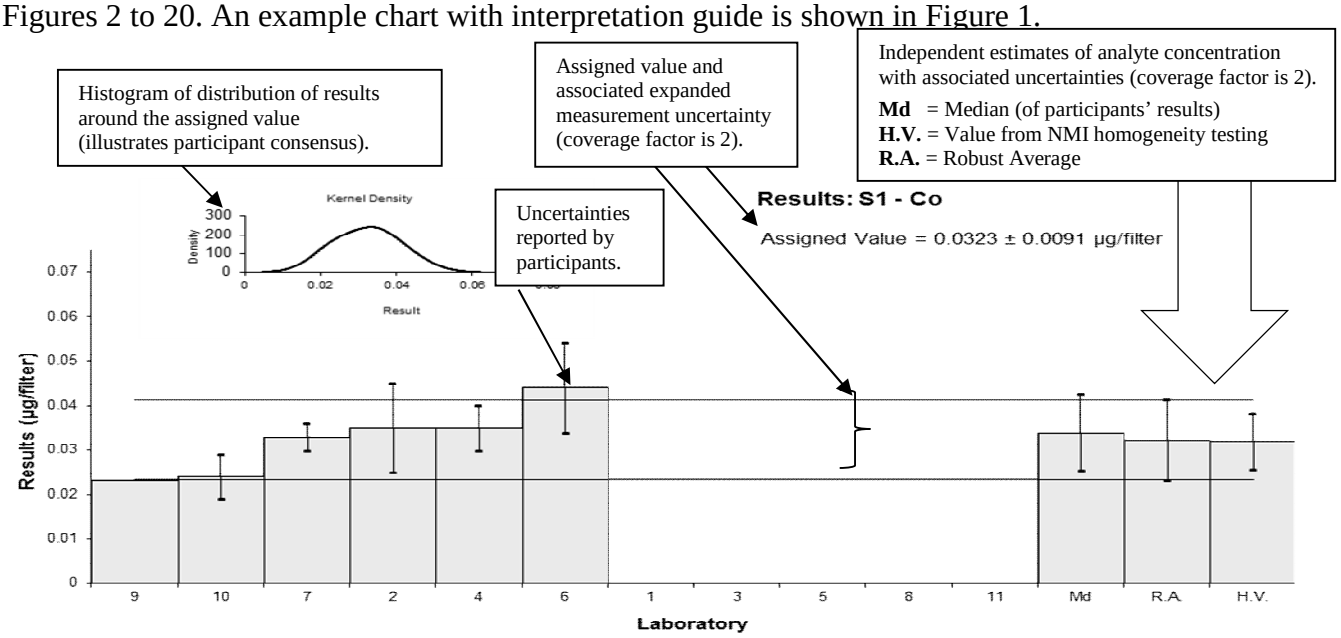


Figure 1 Guide to Presentation of Results

5.2 Assigned Value

An example of an assigned value calculation using data from the present study is given in Appendix 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 per filter. 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)'.[5]

5.4 Robust Between-Laboratory Coefficient of Variation

The robust between-laboratory coefficient of variation (robust CV) is a measure of the variability of participants' results and was calculated using the procedure described in ISO13528:2015(E).[5]

5.5 Target Standard Deviation

The target standard deviation (σ) is the product of the assigned value (*X)* and the performance coefficient of variation (PCV) as presented in Equation 1

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

This value is used for calculation of participant z-scores and provides scaling for laboratory deviation from the assigned value. It is important to note that the PCV is a fixed value and is not the standard deviation of participants' results. The fixed value set for PCV is based on the existing regulation, the acceptance criteria indicated by the methods, the matrix, the

concentration level of analyte and on experience from previous studies. It is backed up by mathematical models such as the Thompson Horwitz equation.[6] By setting a fixed and realistic value for the PCV, the participants' performance does not depend on other participants' performance and can be compared from study to study and against achievable performance.

5.6 z-Score

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

For each participant's result, a z-score is calculated according to Equation 2 below:

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

where:

z is z-score
χ is participants' result
X is the study assigned value
σ is the target standard deviation

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

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

5.7 E_n-Score

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

The E_n-score is complementary to the z-score in assessment of laboratory performance. E_n-score includes measurement uncertainty and is calculated according to Equation 3 below:

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

where:

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

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

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

5.8 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025:2018[7] 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.[8]

6 TABLES AND FIGURES

Table 5

Sample Details

Sample No.	S1
Matrix.	Filter
Analyte.	Ag
Units	µg/filter

Participant Results

Lab Code	Result	Uncertainty
1	0.086	0.017
2	0.0745	0.005
3	<0.5	NR
4	0.031	0.005
5	<0.5	NR
6	<0.1	NR
7	0.1	0.05
8	<0.05	NR
9	0.055	NR
10	0.05	0.01
11	NT	NT

Statistics

Assigned Value	Not Set	
Homogeneity Value	0.076	0.015
Robust Average	0.066	0.029
Median	0.065	0.028
Mean	0.066	
N	6	
Max.	0.1	
Min.	0.031	
Robust SD	0.029	
Robust CV	44%	

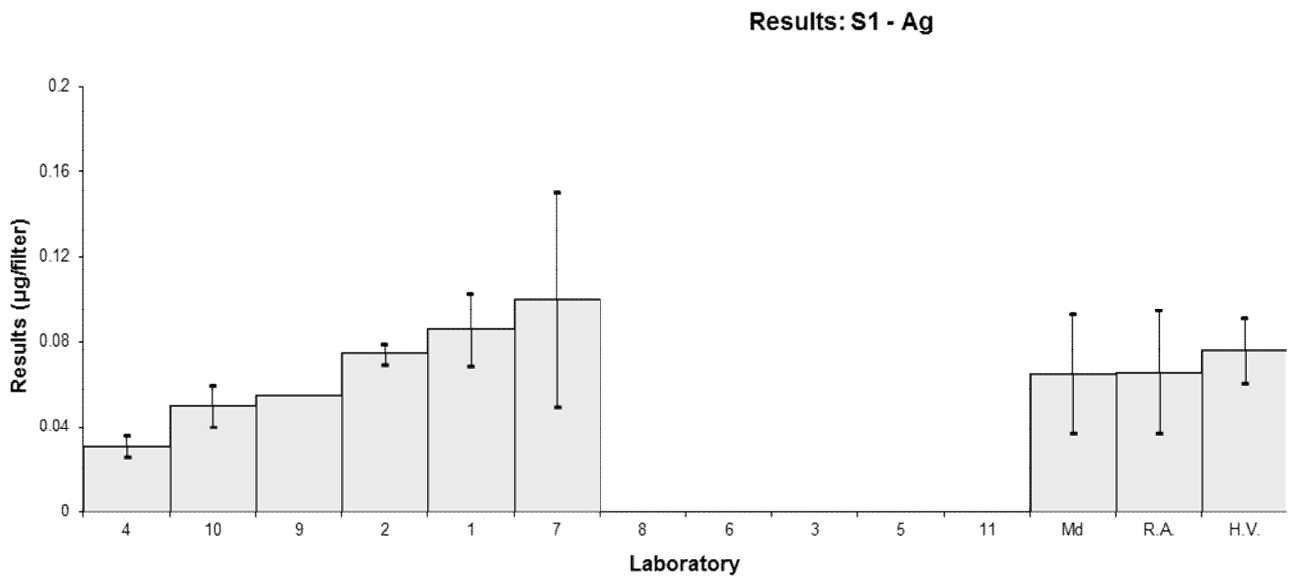

Results: S1 - Ag
Results (µg/filter)
0.2
0.16
0.12
0.08
0.04
0
4
10
9
2
1
7
8
6
3
5
11
Md
R.A.
H.V.
Laboratory

Figure 2

Table 6

Sample Details

Sample No.	S1
Matrix.	Filter
Analyte.	Al
Units	µg/filter

Participant Results

Lab Code	Result	Uncertainty
1	170	30
2	82	4.1
3	100	30
4	143	18
5	98	30
6	149	15
7	87	54
8	70	30
9	76	NR
10	84.6	8.46
11	NT	NT

Statistics

Assigned Value	Not Set	
Homogeneity Value	95	19
Robust Average	105	30
Median	93	14
Mean	106	
N	10	
Max.	170	
Min.	70	
Robust SD	38	
Robust CV	36%	

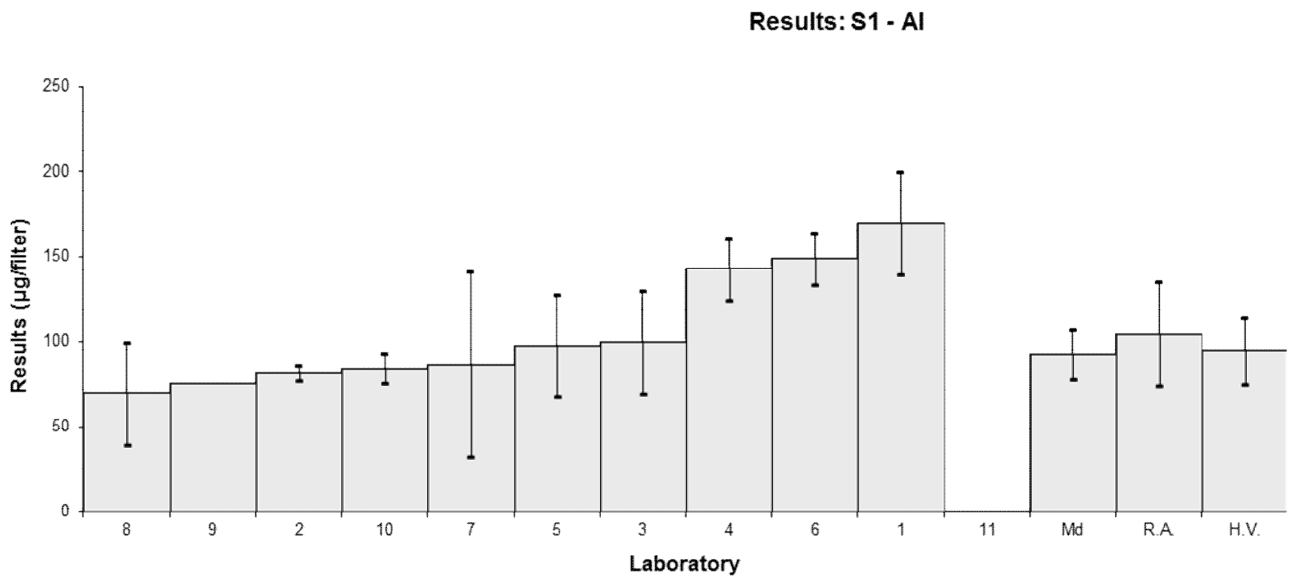

Results: S1 - Al
Results (µg/filter)
250
200
150
100
50
0
8
9
2
10
7
5
3
4
6
1
11
Md
R.A.
H.V.
Laboratory

Figure 3

Table 7

Sample Details

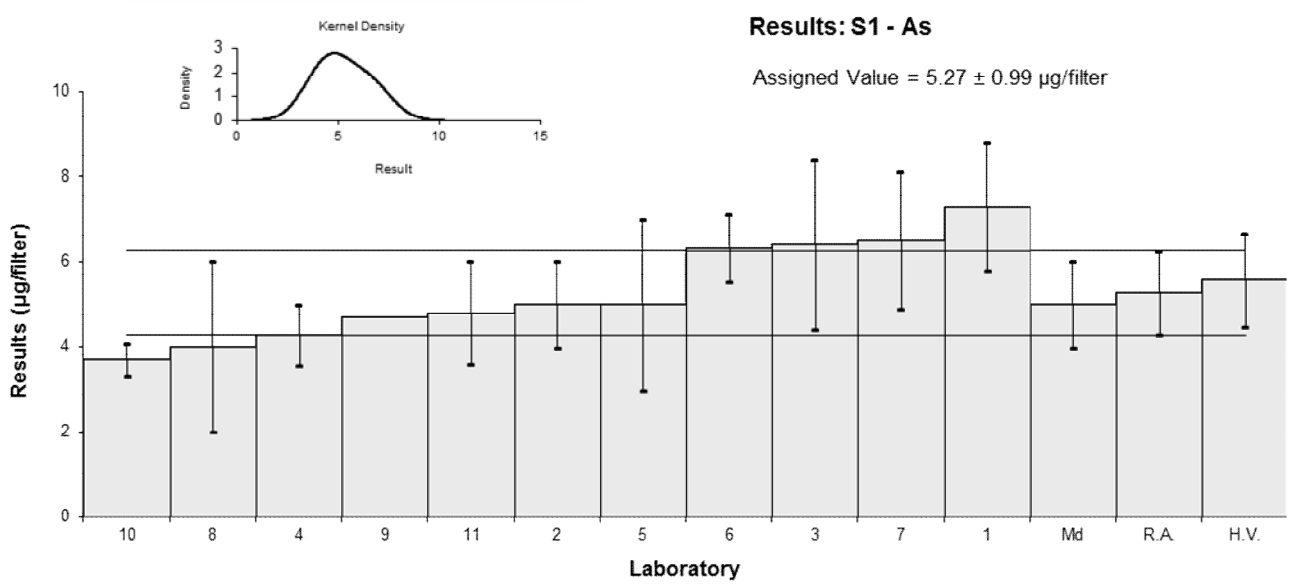
Sample No.	S1
Matrix.	Filter
Analyte.	As
Units	µg/filter

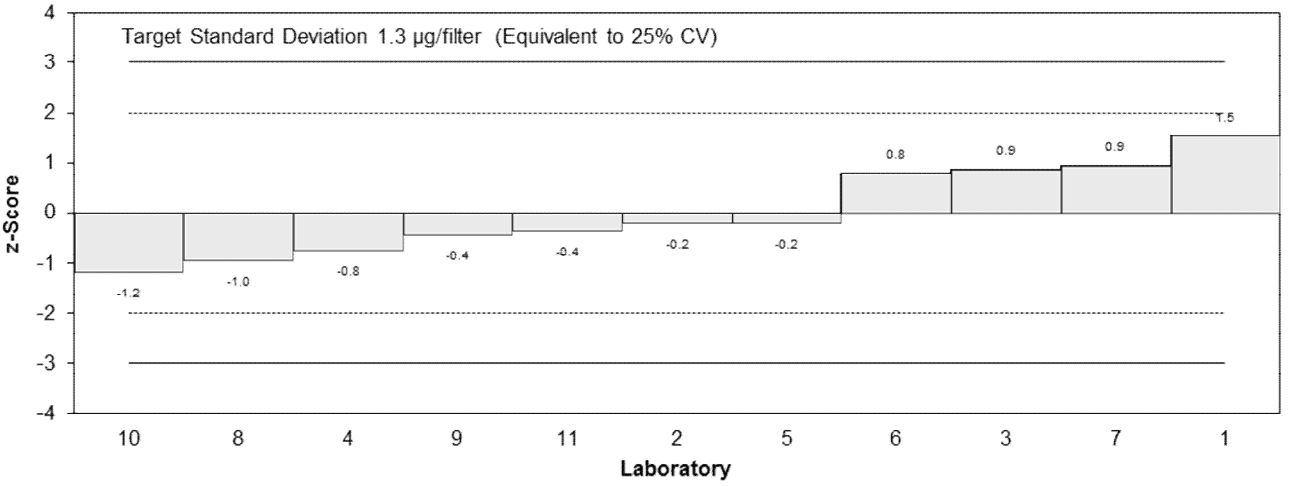
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	7.3	1.5	1.54	1.13
2	5	1	-0.20	-0.19
3	6.4	2	0.86	0.51
4	4.28	0.7	-0.75	-0.82
5	5	2	-0.20	-0.12
6	6.32	0.80	0.80	0.82
7	6.5	1.6	0.93	0.65
8	4	2	-0.96	-0.57
9	4.7	NR	-0.43	-0.58
10	3.71	0.371	-1.18	-1.48
11	4.8	1.2	-0.36	-0.30

Statistics

Assigned Value	5.27	0.99
Spike	Not Spiked	
Homogeneity Value	5.6	1.1
Robust Average	5.27	0.99
Median	5.0	1.0
Mean	5.27	
N	11	
Max.	7.3	
Min.	3.71	
Robust SD	1.3	
Robust CV	25%	


Kernel Density
Density
Result
Results: S1 - As
Assigned Value = 5.27 ± 0.99 µg/filter
Results (µg/filter)
Laboratory
10 8 4 9 11 2 5 6 3 7 1 Md R.A. H.V.


z-Scores: S1 - As
Target Standard Deviation 1.3 µg/filter (Equivalent to 25% CV)
z-Score
Laboratory
10 8 4 9 11 2 5 6 3 7 1
-1.2 -1.0 -0.8 -0.4 -0.4 -0.2 -0.2 0.8 0.9 0.9 1.5

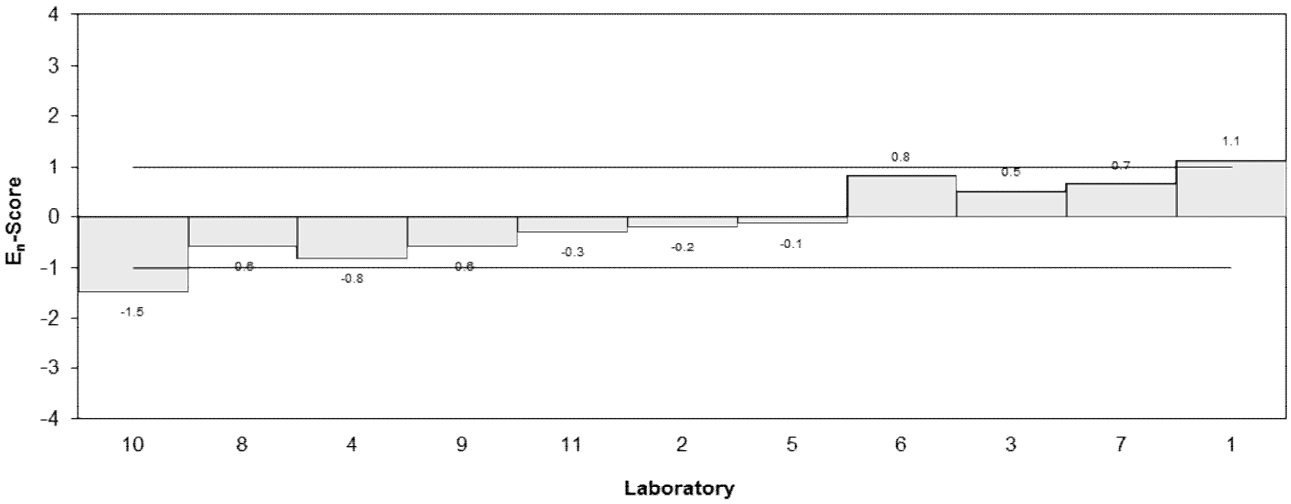

En-Scores: S1 - As
En-Score
Laboratory
10 8 4 9 11 2 5 6 3 7 1
-1.5 -0.6 -0.8 -0.6 -0.3 -0.2 -0.1 0.8 0.5 0.7 1.1

Figure 4

Table 8

Sample Details

Sample No.	S1
Matrix.	Filter
Analyte.	Be
Units	µg/filter

Participant Results

Lab Code	Result	Uncertainty
1	<0.05	NR
2	0.006	0.005
3	<0.01	NR
4	0.003	0.001
5	<0.01	NR
6	<0.01	NR
7	0.005	0.0003
8	<0.01	NR
9	0.005	NR
10	<0.02	0.005
11	NT	NT

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Homogeneity Value	0.0057	0.0011
Robust Average	0.0048	0.0018
Median	0.0050	0.0012
Mean	0.0048	
N	4	
Max.	0.006	
Min.	0.003	
Robust SD	0.0014	
Robust CV	29%	

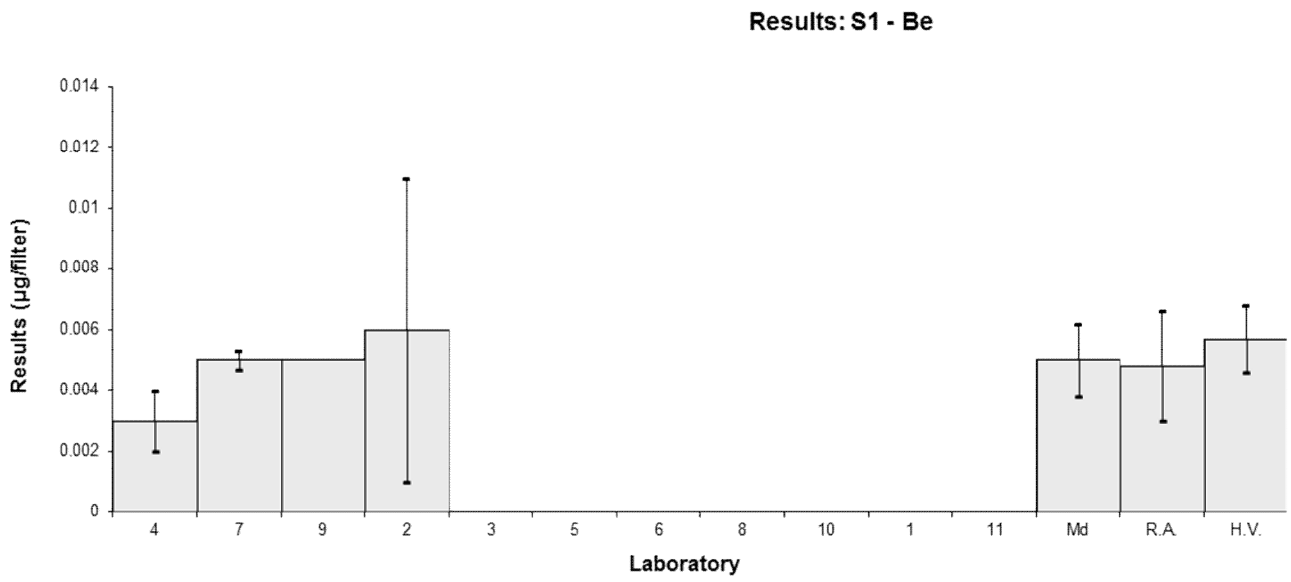

Results: S1 - Be
Results (µg/filter)
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
4
7
9
2
3
5
6
8
10
1
11
Md
R.A.
H.V.
Laboratory

Figure 5

Table 9

Sample Details

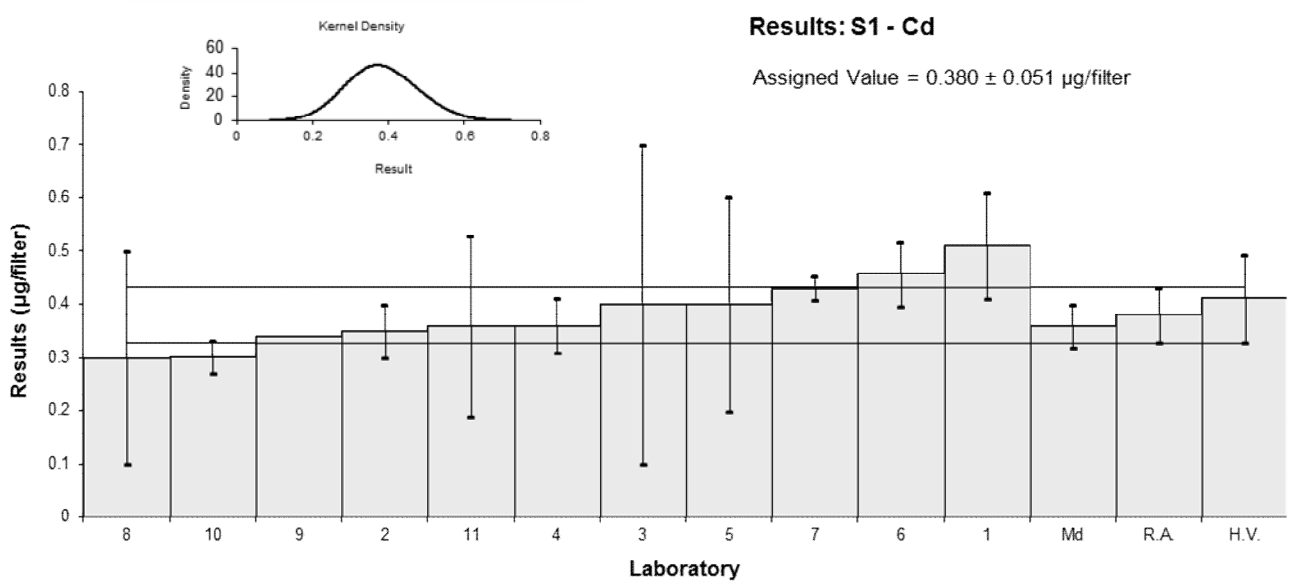
Sample No.	S1
Matrix.	Filter
Analyte.	Cd
Units	µg/filter

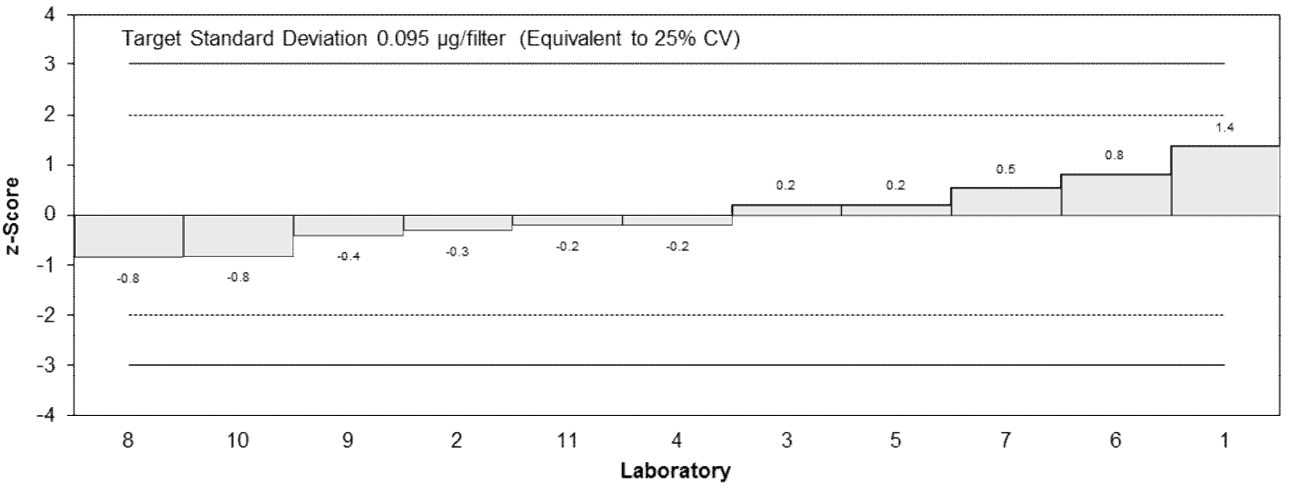
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.51	0.10	1.37	1.16
2	0.35	0.05	-0.32	-0.42
3	0.4	0.3	0.21	0.07
4	0.36	0.05	-0.21	-0.28
5	0.4	0.2	0.21	0.10
6	0.457	0.06	0.81	0.98
7	0.43	0.022	0.53	0.90
8	0.3	0.2	-0.84	-0.39
9	0.34	NR	-0.42	-0.78
10	0.301	0.030	-0.83	-1.34
11	0.36	0.17	-0.21	-0.11

Statistics

Assigned Value	0.380	0.051
Spike	Not Spiked	
Homogeneity Value	0.411	0.082
Robust Average	0.380	0.051
Median	0.360	0.040
Mean	0.383	
N	11	
Max.	0.51	
Min.	0.3	
Robust SD	0.067	
Robust CV	18%	


Kernel Density
Density
Result
Results: S1 - Cd
Assigned Value = 0.380 ± 0.051 µg/filter
Results (µg/filter)
Laboratory
8 10 9 2 11 4 3 5 7 6 1 Md R.A. H.V.


z-Scores: S1 - Cd
Target Standard Deviation 0.095 µg/filter (Equivalent to 25% CV)
z-Score
Laboratory
8 10 9 2 11 4 3 5 7 6 1
-0.8 -0.8 -0.4 -0.3 -0.2 -0.2 0.2 0.2 0.5 0.8 1.4

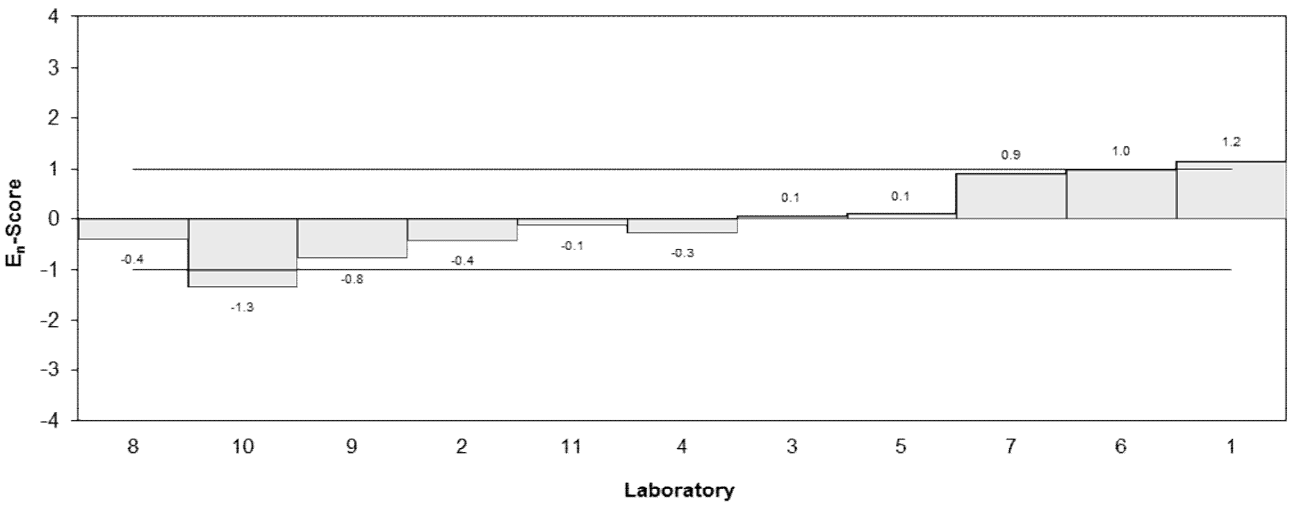

En-Scores: S1 - Cd
En-Score
Laboratory
8 10 9 2 11 4 3 5 7 6 1
-0.4 -1.3 -0.8 -0.4 -0.1 -0.3 0.1 0.1 0.9 1.0 1.2

Figure 6

Table 10

Sample Details

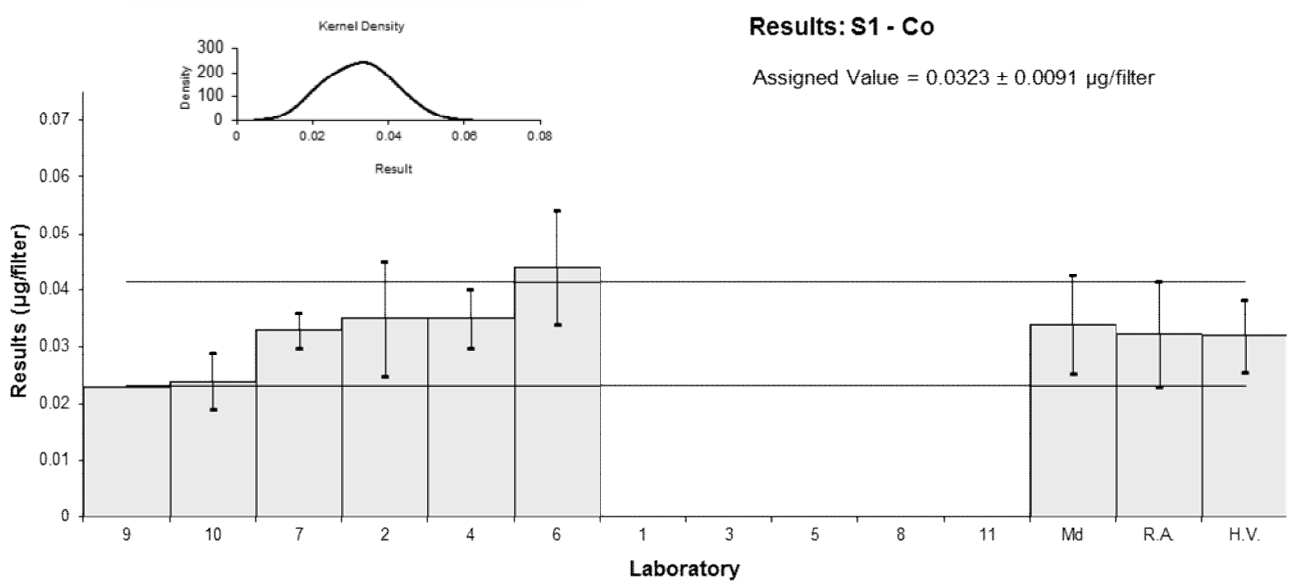
Sample No.	S1
Matrix.	Filter
Analyte.	Co
Units	µg/filter

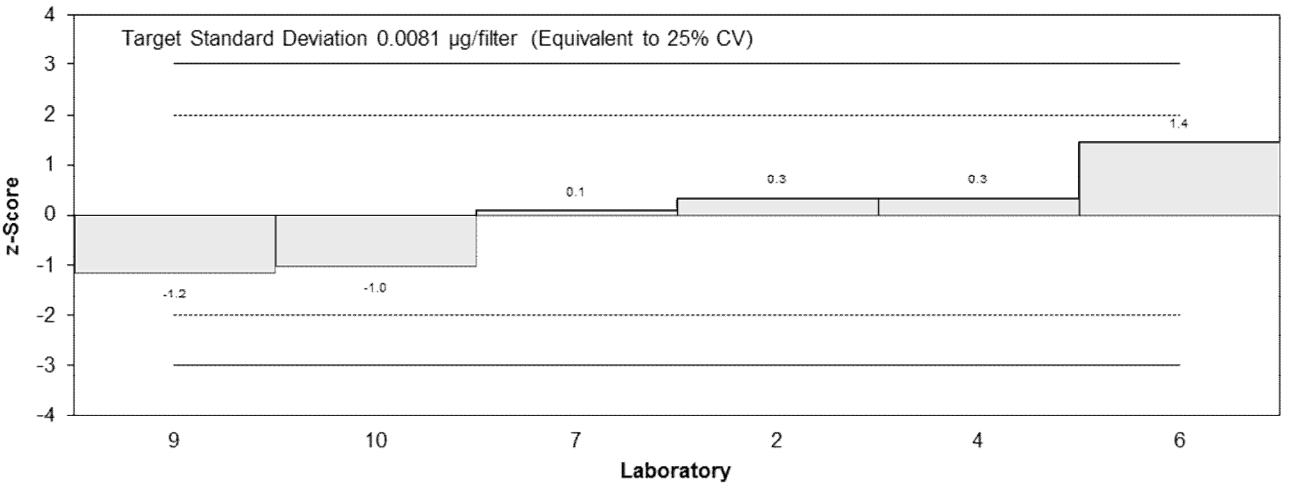
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	<0.05	NR		
2	0.035	0.01	0.33	0.20
3	<0.5	NR		
4	0.035	0.005	0.33	0.26
5	<0.5	NR		
6	0.044	0.01	1.45	0.87
7	0.033	0.003	0.09	0.07
8	<0.5	NR		
9	0.023	NR	-1.15	-1.02
10	0.024	0.005	-1.03	-0.80
11	NT	NT		

Statistics

Assigned Value	0.0323	0.0091
Spike	Not Spiked	
Homogeneity Value	0.0320	0.0064
Robust Average	0.0323	0.0091
Median	0.0340	0.0086
Mean	0.0323	
N	6	
Max.	0.044	
Min.	0.023	
Robust SD	0.0089	
Robust CV	28%	


Kernel Density
Density
300
200
100
0
0
0.02
0.04
0.06
0.08
Result
Results: S1 - Co
Assigned Value = 0.0323 ± 0.0091 µg/filter
Results (µg/filter)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
9
10
7
2
4
6
1
3
5
8
11
Md
R.A.
H.V.
Laboratory


z-Scores: S1 - Co
Target Standard Deviation 0.0081 µg/filter (Equivalent to 25% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.2
-1.0
0.1
0.3
0.3
1.4
9
10
7
2
4
6
Laboratory

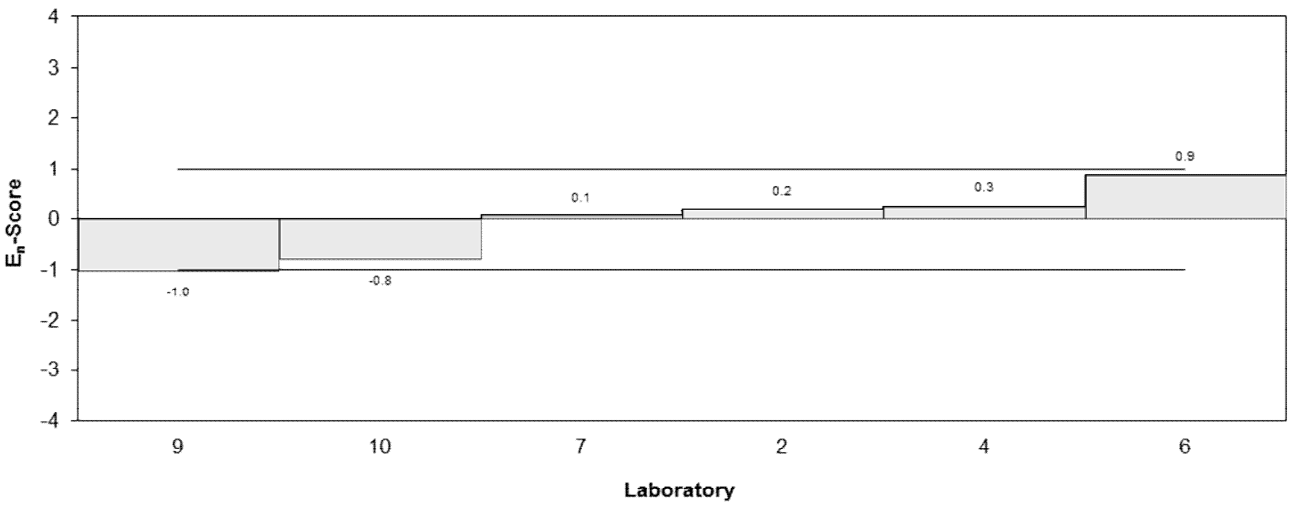

En-Scores: S1 - Co
En-Score
4
3
2
1
0
-1
-2
-3
-4
-1.0
-0.8
0.1
0.2
0.3
0.9
9
10
7
2
4
6
Laboratory

Figure 7

Table 11

Sample Details

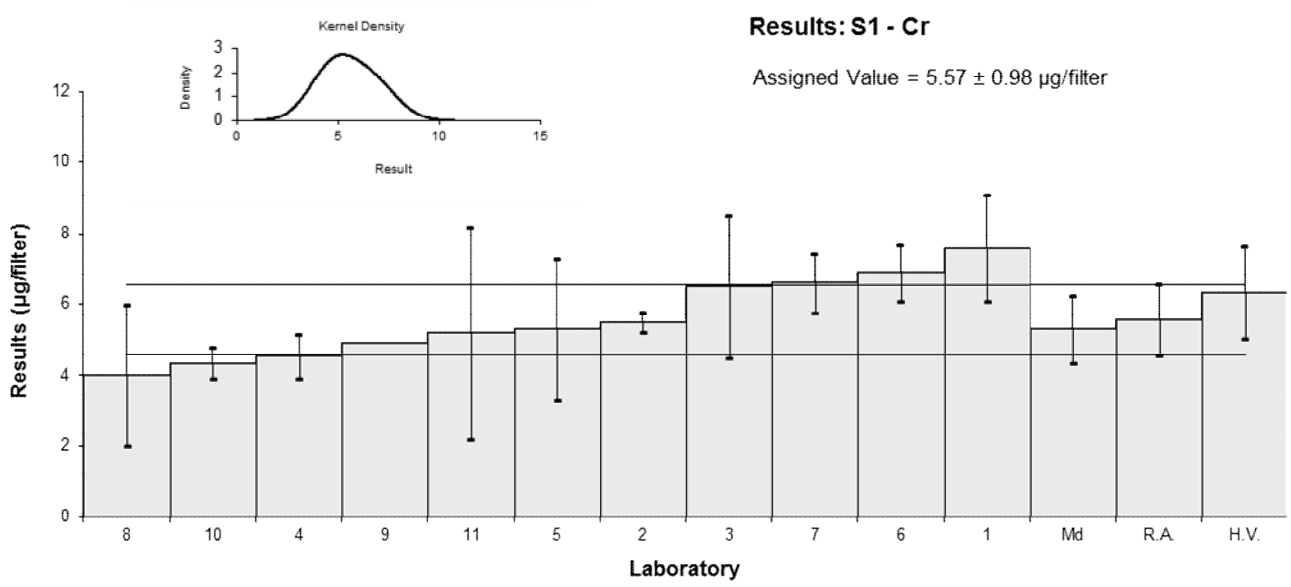
Sample No.	S1
Matrix.	Filter
Analyte.	Cr
Units	µg/filter

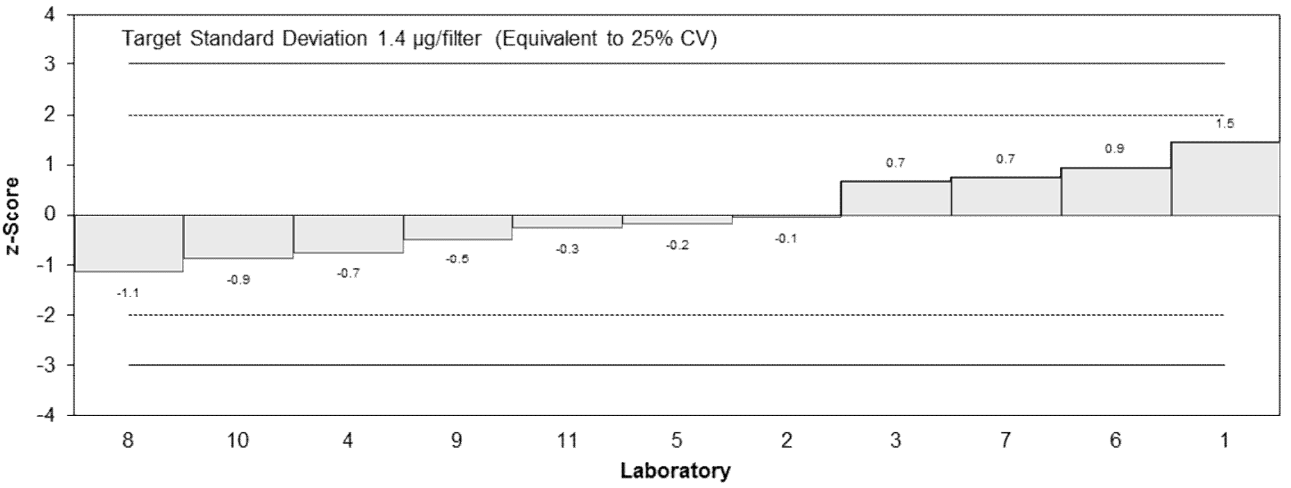
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	7.6	1.5	1.46	1.13
2	5.5	0.2775	-0.05	-0.07
3	6.5	2	0.67	0.42
4	4.54	0.6	-0.74	-0.90
5	5.3	2	-0.19	-0.12
6	6.89	0.80	0.95	1.04
7	6.6	0.83	0.74	0.80
8	4	2	-1.13	-0.70
9	4.9	NR	-0.48	-0.68
10	4.35	0.435	-0.88	-1.14
11	5.2	3.0	-0.27	-0.12

Statistics

Assigned Value	5.57	0.98
Spike	Not Spiked	
Homogeneity Value	6.3	1.3
Robust Average	5.57	0.98
Median	5.30	0.95
Mean	5.58	
N	11	
Max.	7.6	
Min.	4	
Robust SD	1.3	
Robust CV	23%	


Kernel Density
Density
Result
Results: S1 - Cr
Assigned Value = 5.57 ± 0.98 µg/filter
Results (µg/filter)
Laboratory
8
10
4
9
11
5
2
3
7
6
1
Md
R.A.
H.V.


z-Scores: S1 - Cr
Target Standard Deviation 1.4 µg/filter (Equivalent to 25% CV)
z-Score
Laboratory
-1.1
-0.9
-0.7
-0.5
-0.3
-0.2
-0.1
0.7
0.7
0.9
1.5

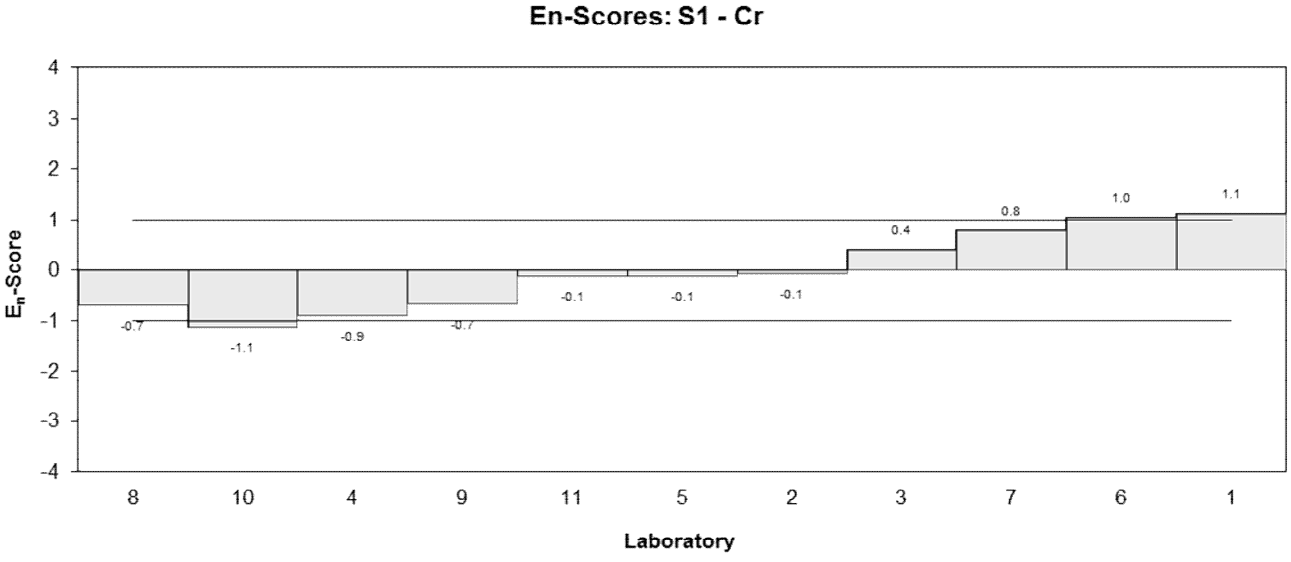

En-Scores: S1 - Cr
En-Score
Laboratory
-0.7
-1.1
-0.9
-0.7
-0.1
-0.1
-0.1
0.4
0.8
1.0
1.1

Figure 8

Table 12

Sample Details

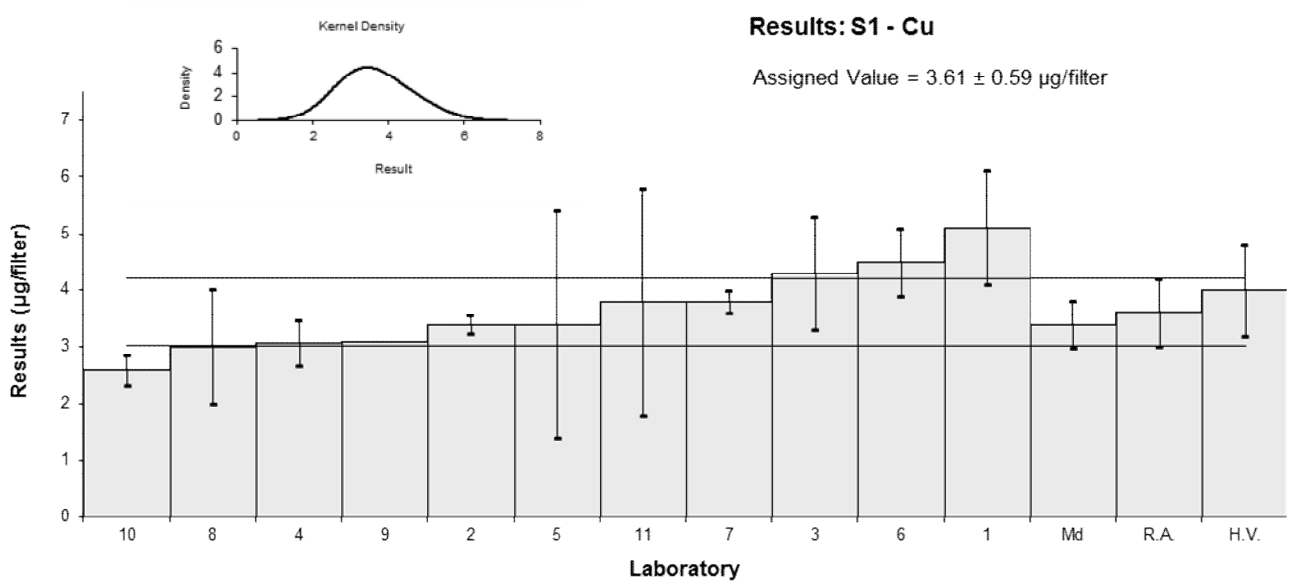
Sample No.	S1
Matrix.	Filter
Analyte.	Cu
Units	µg/filter

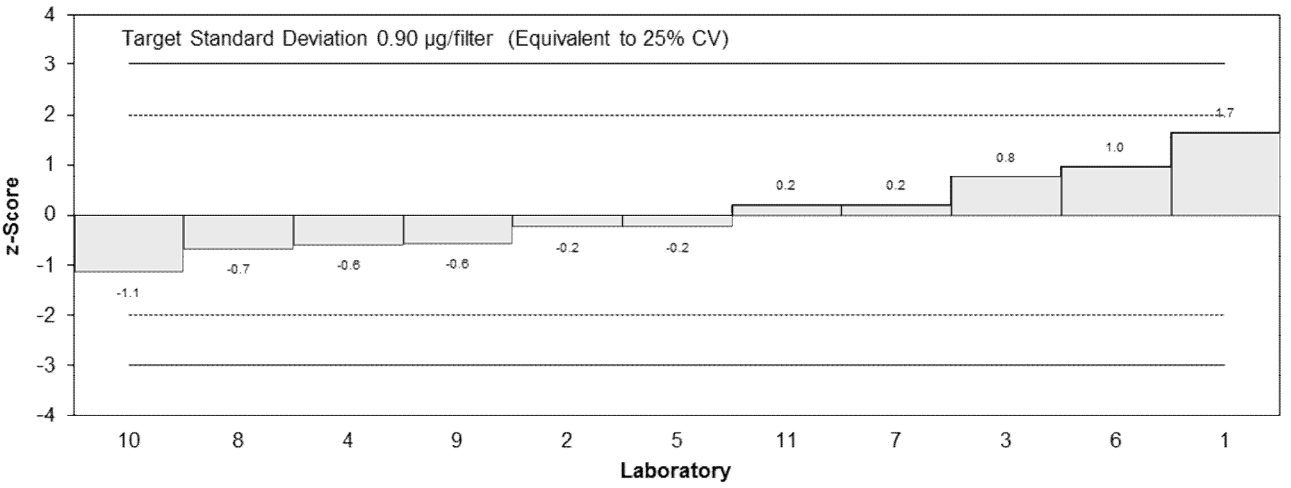
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	5.1	1.0	1.65	1.28
2	3.4	0.1675	-0.23	-0.34
3	4.3	1	0.76	0.59
4	3.07	0.4	-0.60	-0.76
5	3.4	2	-0.23	-0.10
6	4.49	0.60	0.98	1.05
7	3.8	0.19	0.21	0.31
8	3	1	-0.68	-0.53
9	3.1	NR	-0.57	-0.86
10	2.59	0.259	-1.13	-1.58
11	3.8	2.0	0.21	0.09

Statistics

Assigned Value	3.61	0.59
Spike	Not Spiked	
Homogeneity Value	3.99	0.80
Robust Average	3.61	0.59
Median	3.40	0.40
Mean	3.64	
N	11	
Max.	5.1	
Min.	2.59	
Robust SD	0.78	
Robust CV	22%	


Kernel Density
Density
Result
Results: S1 - Cu
Assigned Value = 3.61 ± 0.59 µg/filter
Results (µg/filter)
10 8 4 9 2 5 11 7 3 6 1 Md R.A. H.V.
Laboratory


z-Scores: S1 - Cu
Target Standard Deviation 0.90 µg/filter (Equivalent to 25% CV)
z-Score
-1.1 -0.7 -0.6 -0.6 -0.2 -0.2 0.2 0.2 0.8 1.0 1.7
10 8 4 9 2 5 11 7 3 6 1
Laboratory

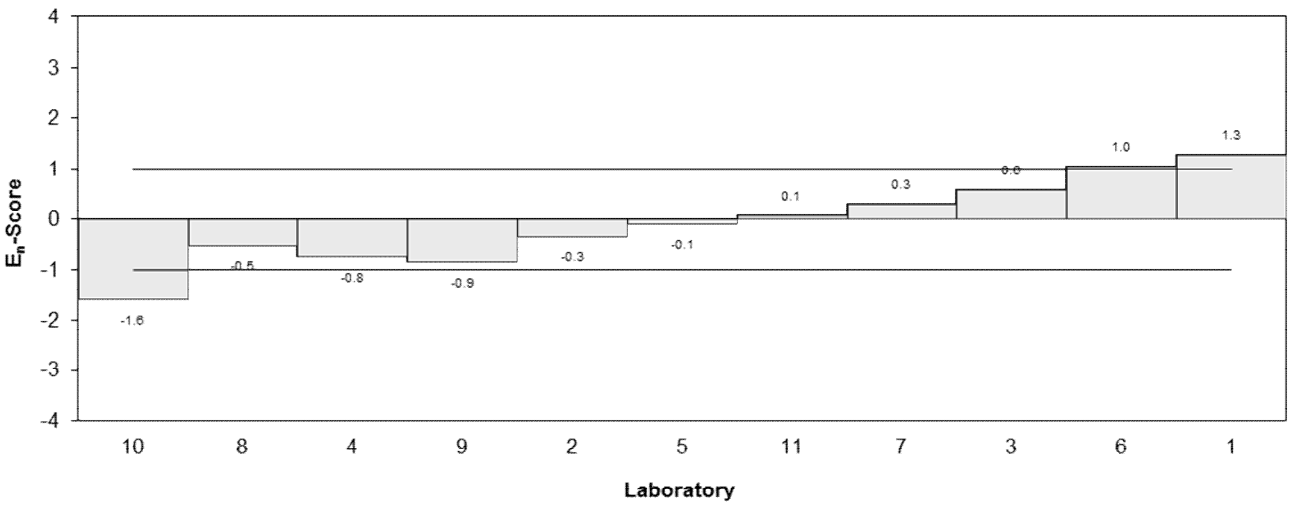

En-Scores: S1 - Cu
En-Score
-1.6 -0.5 -0.8 -0.9 -0.3 -0.1 0.1 0.3 0.6 1.0 1.3
10 8 4 9 2 5 11 7 3 6 1
Laboratory

Figure 9

Table 13

Sample Details

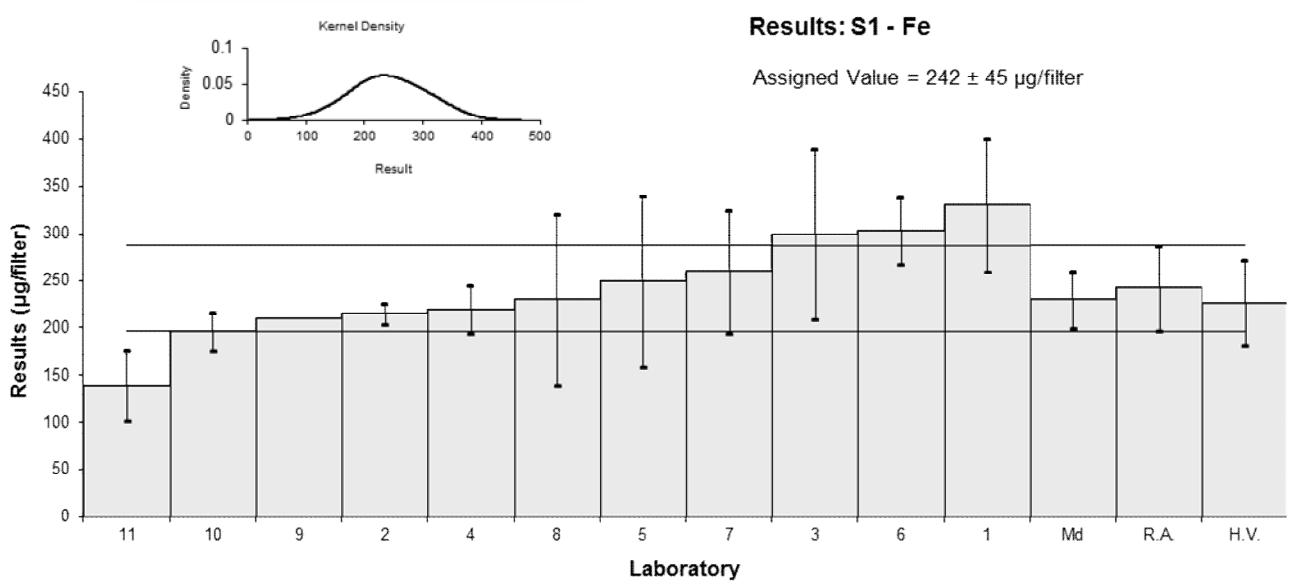
Sample No.	S1
Matrix.	Filter
Analyte.	Fe
Units	µg/filter

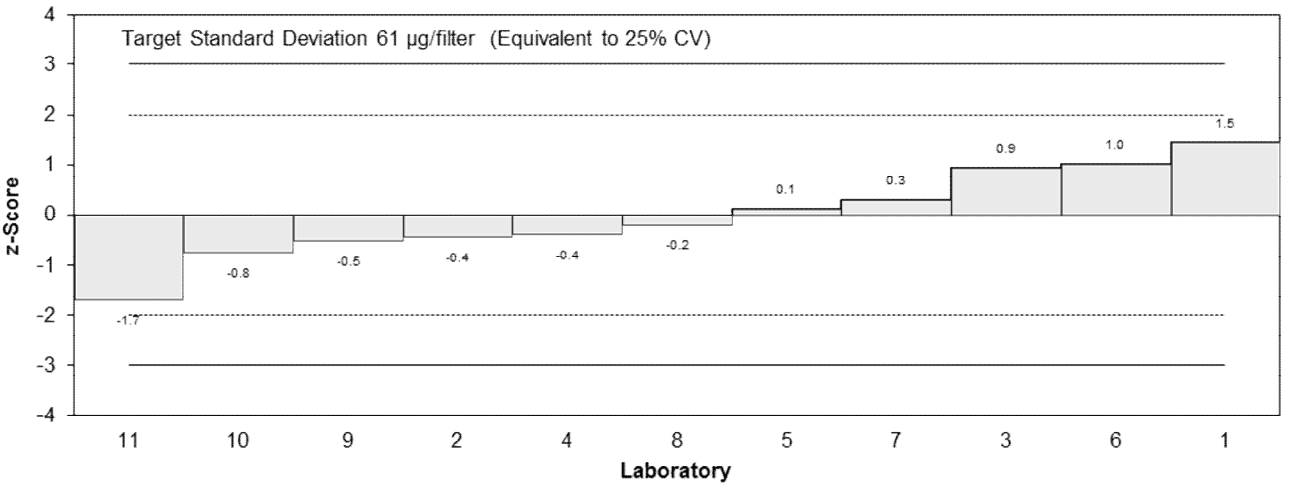
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	330	70	1.45	1.06
2	215	10.75	-0.45	-0.58
3	299	90	0.94	0.57
4	219	25	-0.38	-0.45
5	250	90	0.13	0.08
6	303	35	1.01	1.07
7	260	65	0.30	0.23
8	230	90	-0.20	-0.12
9	210	NR	-0.53	-0.71
10	196	19.6	-0.76	-0.94
11	140	37	-1.69	-1.75

Statistics

Assigned Value	242	45
Spike	Not Spiked	
Homogeneity Value	227	45
Robust Average	242	45
Median	230	30
Mean	241	
N	11	
Max.	330	
Min.	140	
Robust SD	60	
Robust CV	25%	


Kernel Density
Density
Result
Results: S1 - Fe
Assigned Value = 242 ± 45 µg/filter
Results (µg/filter)
Laboratory
11 10 9 2 4 8 5 7 3 6 1 Md R.A. H.V.


z-Scores: S1 - Fe
Target Standard Deviation 61 µg/filter (Equivalent to 25% CV)
z-Score
Laboratory
11 10 9 2 4 8 5 7 3 6 1
-1.7 -0.8 -0.5 -0.4 -0.4 -0.2 0.1 0.3 0.9 1.0 1.5

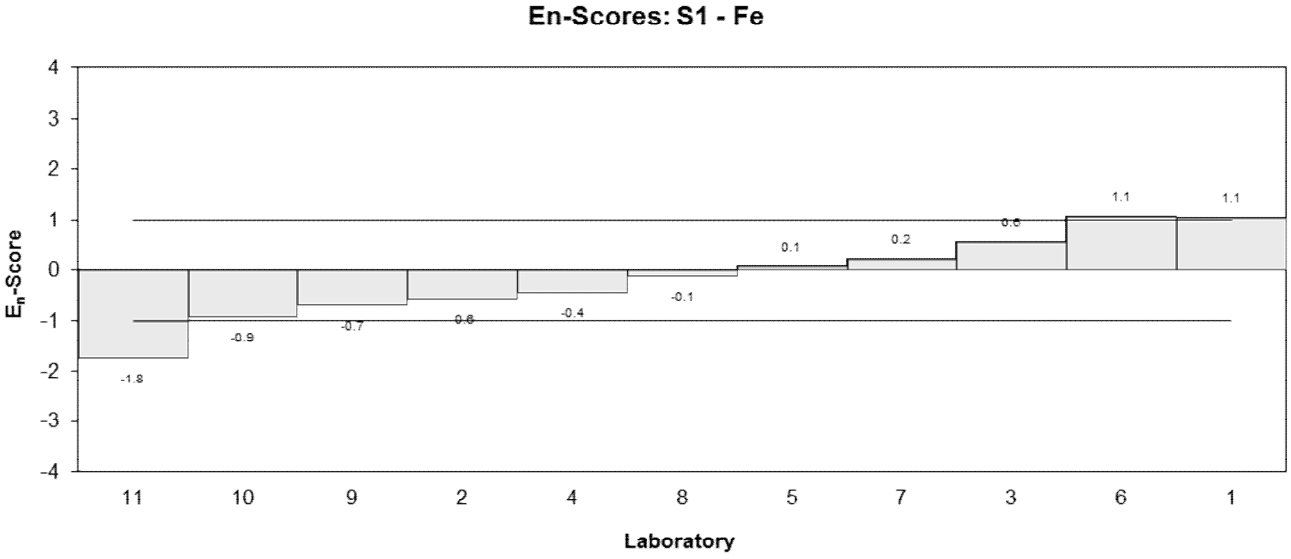

En-Scores: S1 - Fe
En-Score
Laboratory
11 10 9 2 4 8 5 7 3 6 1
-1.8 -0.9 -0.7 -0.6 -0.4 -0.1 0.1 0.2 0.5 1.1 1.1

Figure 10

Table 14

Sample Details

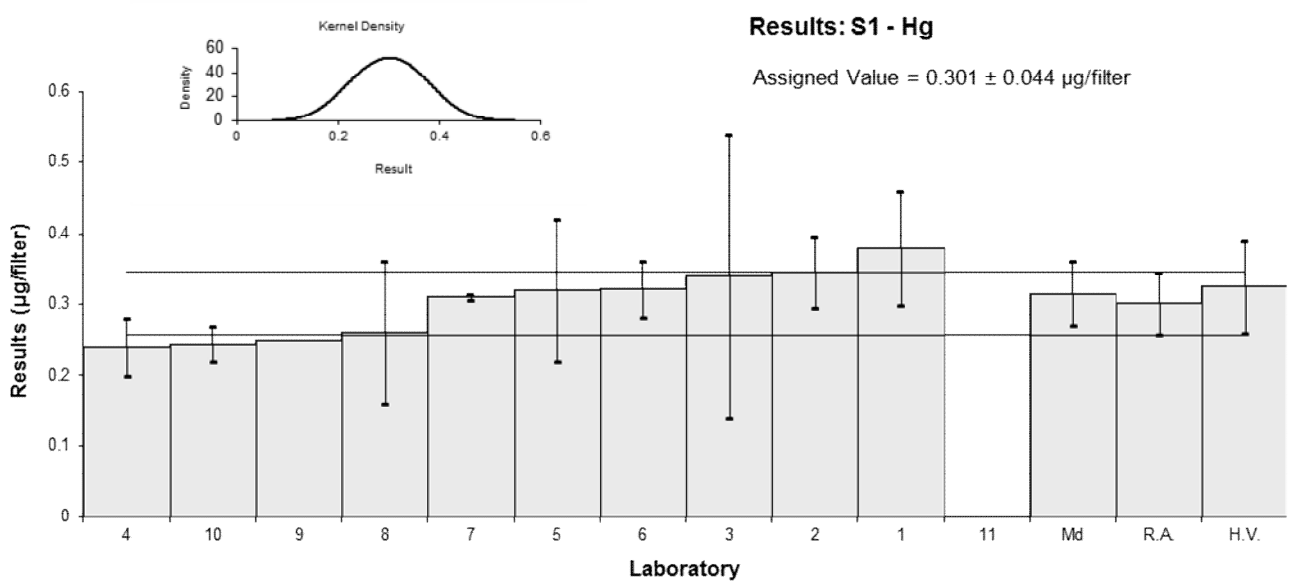
Sample No.	S1
Matrix.	Filter
Analyte.	Hg
Units	µg/filter

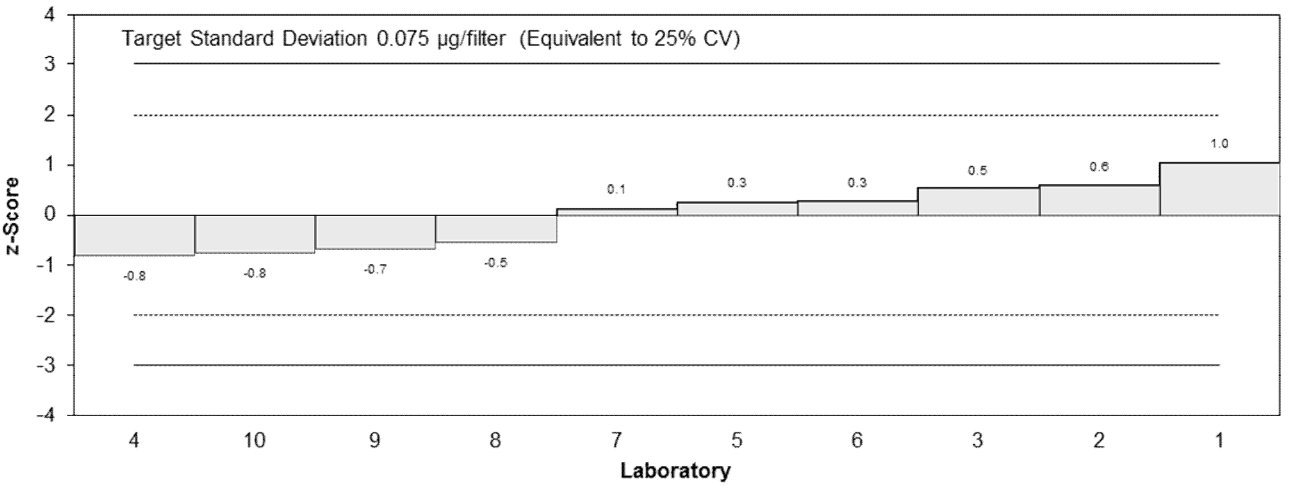
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	0.38	0.08	1.05	0.87
2	0.345	0.05	0.58	0.66
3	0.34	0.2	0.52	0.19
4	0.24	0.04	-0.81	-1.03
5	0.32	0.1	0.25	0.17
6	0.321	0.04	0.27	0.34
7	0.31	0.004	0.12	0.20
8	0.26	0.1	-0.54	-0.38
9	0.25	NR	-0.68	-1.16
10	0.244	0.024	-0.76	-1.14
11	NT	NT		

Statistics

Assigned Value	0.301	0.044
Spike	Not Spiked	
Homogeneity Value	0.325	0.065
Robust Average	0.301	0.044
Median	0.315	0.045
Mean	0.301	
N	10	
Max.	0.38	
Min.	0.24	
Robust SD	0.056	
Robust CV	19%	


Kernel Density
Density
Result
Results: S1 - Hg
Assigned Value = 0.301 ± 0.044 µg/filter
Results (µg/filter)
Laboratory
4 10 9 8 7 5 6 3 2 1 11 Md R.A. H.V.


z-Scores: S1 - Hg
Target Standard Deviation 0.075 µg/filter (Equivalent to 25% CV)
z-Score
Laboratory
4 10 9 8 7 5 6 3 2 1
-0.8 -0.8 -0.7 -0.5 0.1 0.3 0.3 0.5 0.6 1.0

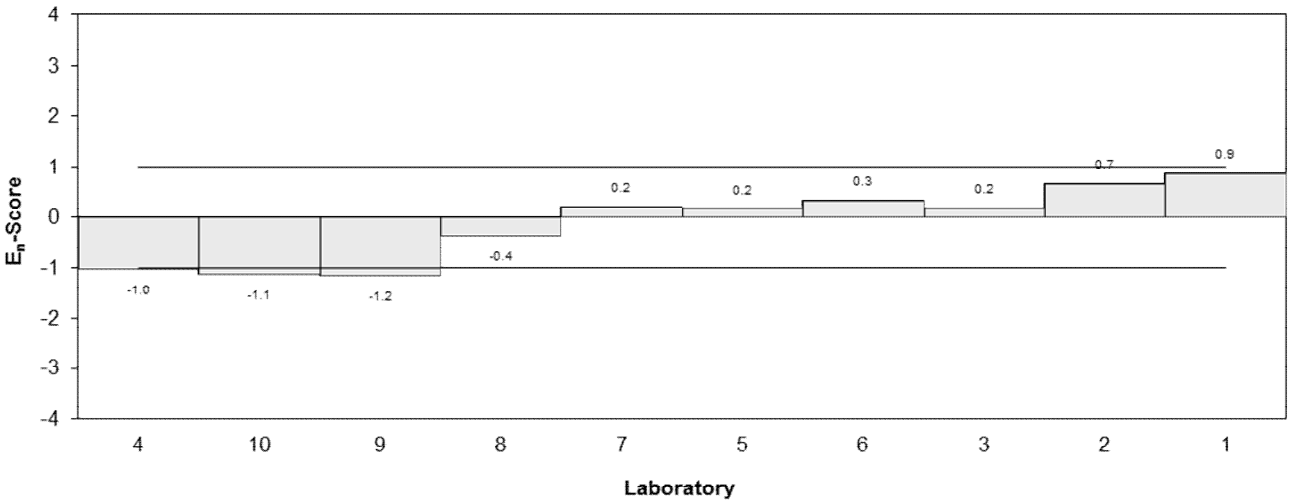

En-Scores: S1 - Hg
En-Score
Laboratory
4 10 9 8 7 5 6 3 2 1
-1.0 -1.1 -1.2 -0.4 0.2 0.2 0.3 0.2 0.7 0.9

Figure 11

Table 15

Sample Details

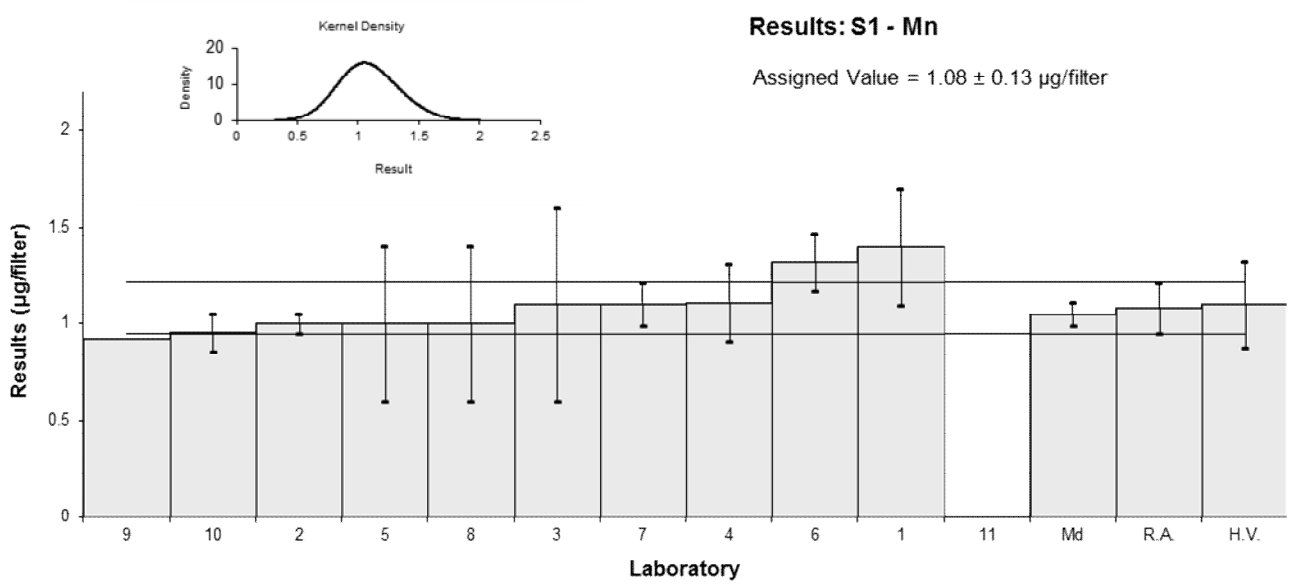
Sample No.	S1
Matrix.	Filter
Analyte.	Mn
Units	µg/filter

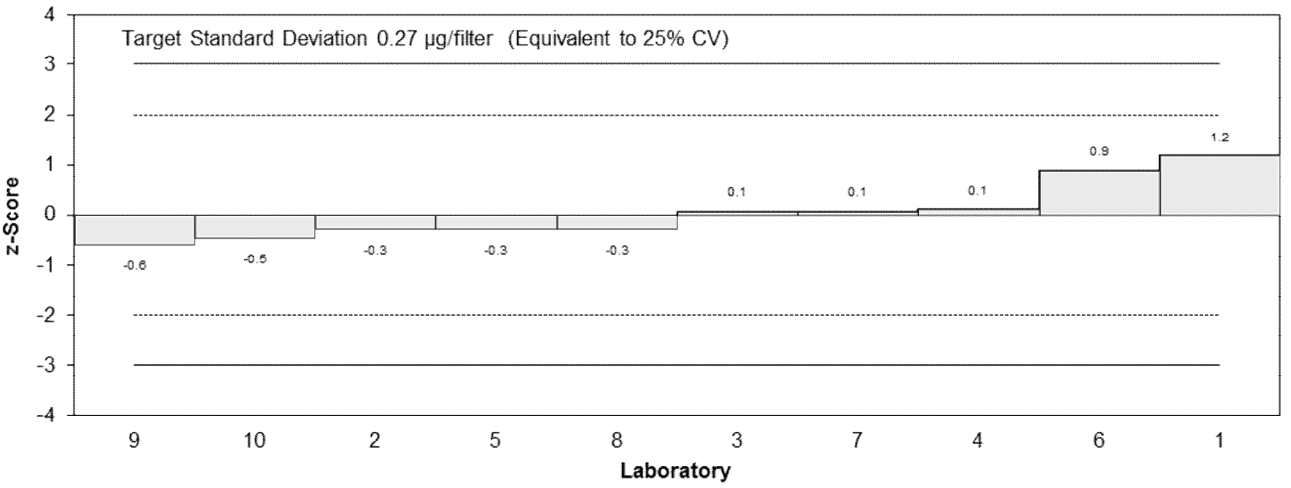
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.4	0.3	1.19	0.98
2	1	0.05	-0.30	-0.57
3	1.1	0.5	0.07	0.04
4	1.11	0.2	0.11	0.13
5	1.0	0.4	-0.30	-0.19
6	1.32	0.15	0.89	1.21
7	1.1	0.11	0.07	0.12
8	1	0.4	-0.30	-0.19
9	0.92	NR	-0.59	-1.23
10	0.956	0.096	-0.46	-0.77
11	<2.0	NR		

Statistics

Assigned Value	1.08	0.13
Spike	Not Spiked	
Homogeneity Value	1.10	0.22
Robust Average	1.08	0.13
Median	1.05	0.06
Mean	1.09	
N	10	
Max.	1.4	
Min.	0.92	
Robust SD	0.16	
Robust CV	15%	


Kernel Density
Density
Result
Results: S1 - Mn
Assigned Value = 1.08 ± 0.13 µg/filter
Results (µg/filter)
Laboratory
9
10
2
5
8
3
7
4
6
1
11
Md
R.A.
H.V.


z-Scores: S1 - Mn
Target Standard Deviation 0.27 µg/filter (Equivalent to 25% CV)
z-Score
Laboratory
-0.6
-0.5
-0.3
-0.3
-0.3
0.1
0.1
0.1
0.9
1.2

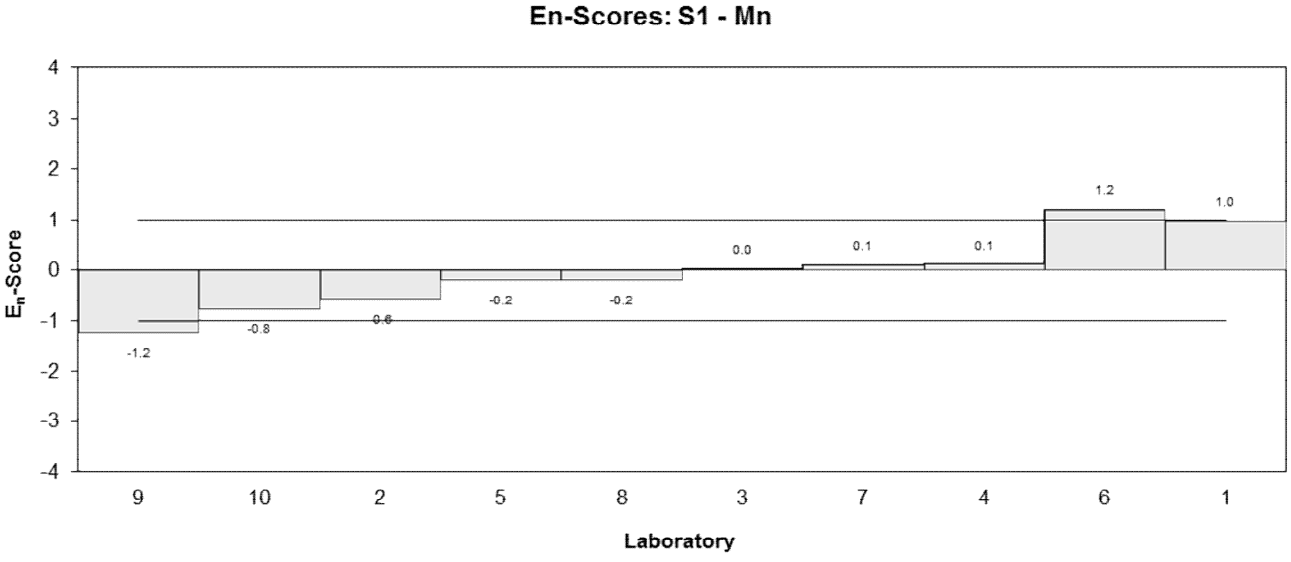

En-Scores: S1 - Mn
En-Score
Laboratory
-1.2
-0.8
-0.6
-0.2
-0.2
0.0
0.1
0.1
1.2
1.0

Figure 12

Table 16

Sample Details

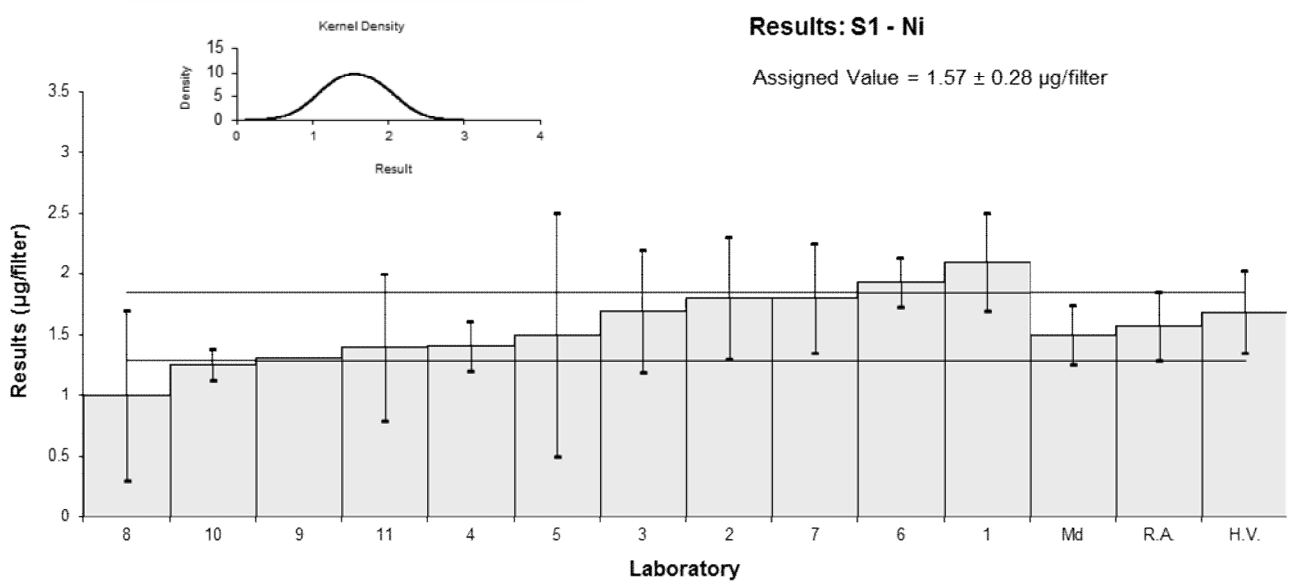
Sample No.	S1
Matrix.	Filter
Analyte.	Ni
Units	µg/filter

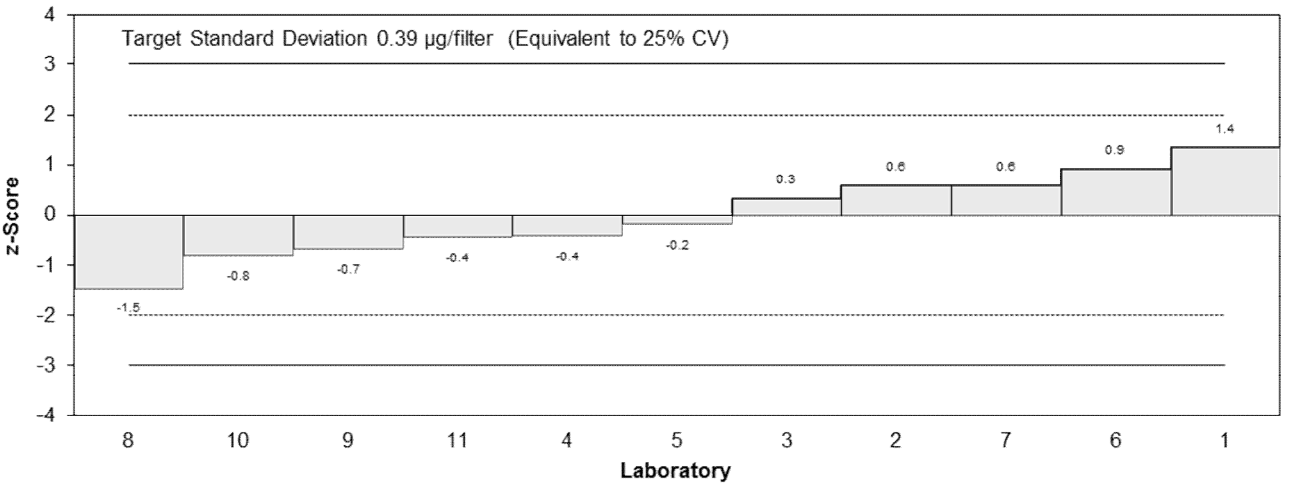
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	2.1	0.4	1.35	1.09
2	1.8	0.5	0.59	0.40
3	1.7	0.5	0.33	0.23
4	1.41	0.2	-0.41	-0.46
5	1.5	1	-0.18	-0.07
6	1.93	0.20	0.92	1.05
7	1.8	0.45	0.59	0.43
8	1	0.7	-1.45	-0.76
9	1.31	NR	-0.66	-0.93
10	1.26	0.126	-0.79	-1.01
11	1.4	0.60	-0.43	-0.26

Statistics

Assigned Value	1.57	0.28
Spike	Not Spiked	
Homogeneity Value	1.69	0.34
Robust Average	1.57	0.28
Median	1.50	0.24
Mean	1.56	
N	11	
Max.	2.1	
Min.	1	
Robust SD	0.37	
Robust CV	24%	


Kernel Density
Density
Result
Results: S1 - Ni
Assigned Value = 1.57 ± 0.28 µg/filter
Results (µg/filter)
Laboratory
8 10 9 11 4 5 3 2 7 6 1 Md R.A. H.V.


z-Scores: S1 - Ni
Target Standard Deviation 0.39 µg/filter (Equivalent to 25% CV)
z-Score
Laboratory
8 10 9 11 4 5 3 2 7 6 1
-1.5 -0.8 -0.7 -0.4 -0.4 -0.2 0.3 0.6 0.6 0.9 1.4

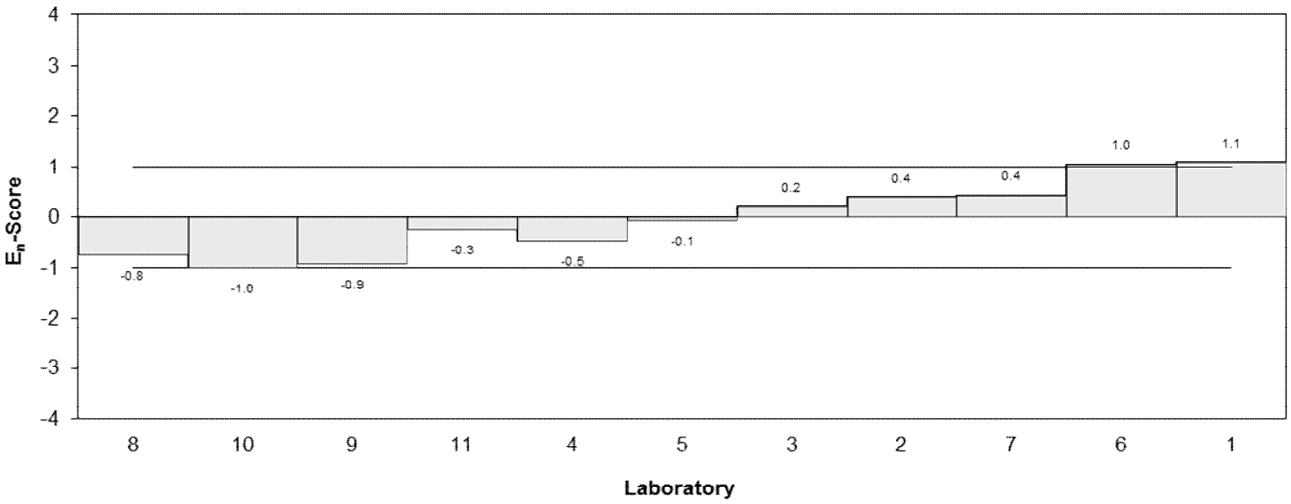

En-Scores: S1 - Ni
En-Score
Laboratory
8 10 9 11 4 5 3 2 7 6 1
-0.8 -1.0 -0.9 -0.3 -0.5 -0.1 0.2 0.4 0.4 1.0 1.1

Figure 13

Table 17

Sample Details

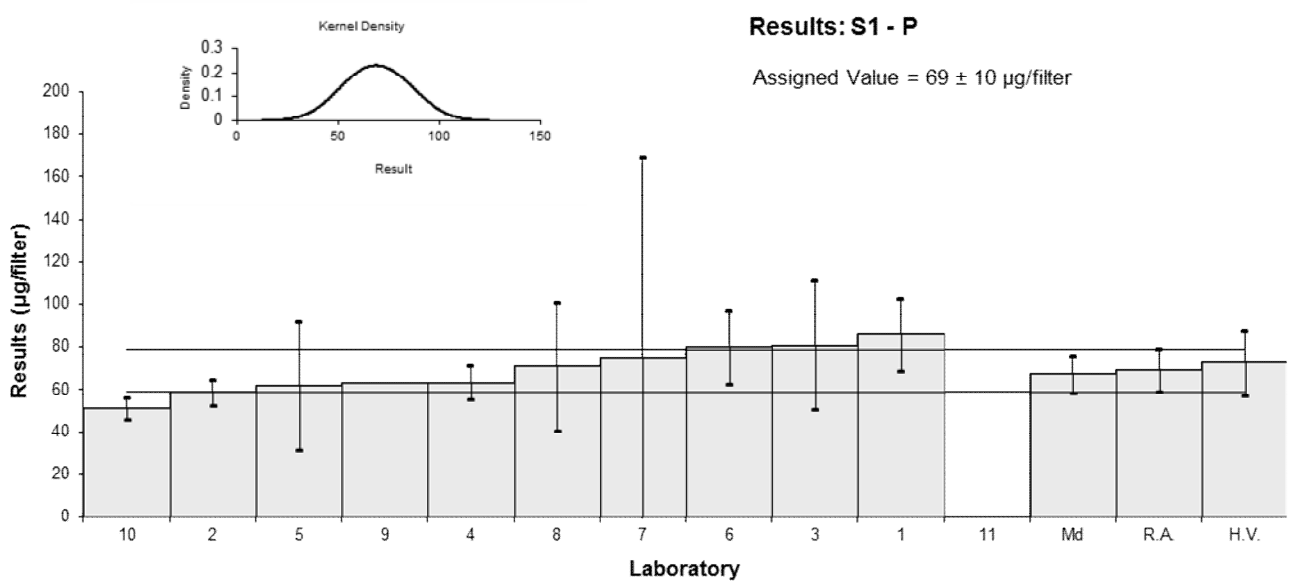
Sample No.	S1
Matrix.	Filter
Analyte.	P
Units	µg/filter

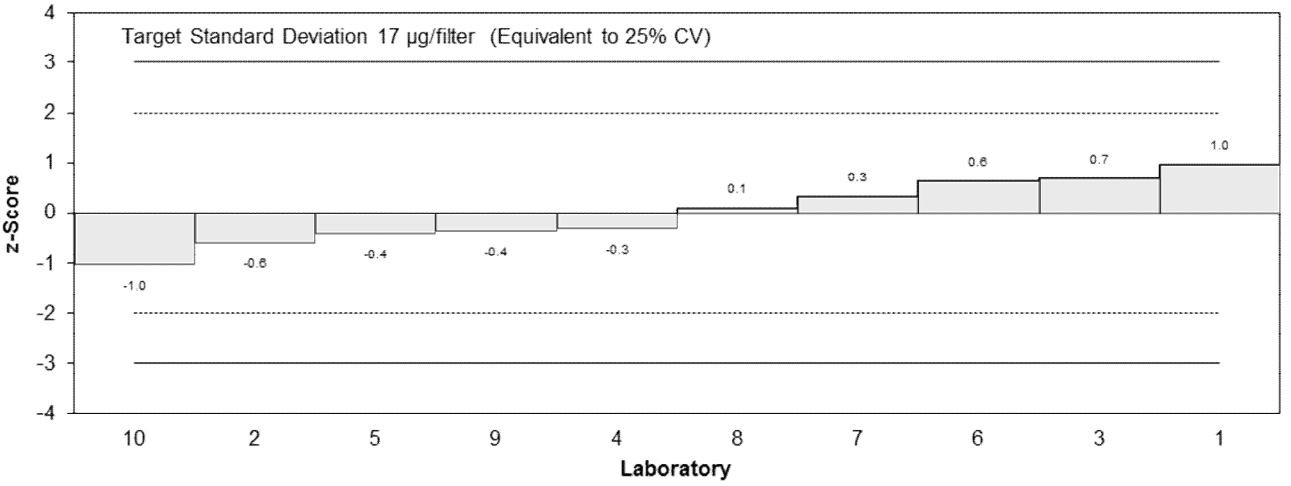
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	86	17	0.97	0.85
2	59	6	-0.59	-0.87
3	81	30	0.68	0.37
4	63.6	8.0	-0.32	-0.44
5	62	30	-0.42	-0.23
6	80.2	17	0.64	0.56
7	75	94	0.34	0.06
8	71	30	0.10	0.06
9	63	NR	-0.36	-0.62
10	51.5	5.15	-1.02	-1.57
11	NT	NT		

Statistics

Assigned Value	69	10
Spike	Not Spiked	
Homogeneity Value	73	15
Robust Average	69	10
Median	67	8
Mean	69	
N	10	
Max.	86	
Min.	51.5	
Robust SD	13	
Robust CV	19%	


Kernel Density
Density
Result
Results: S1 - P
Assigned Value = 69 ± 10 µg/filter
Results (µg/filter)
Laboratory
10 2 5 9 4 8 7 6 3 1 11 Md R.A. H.V.


z-Scores: S1 - P
Target Standard Deviation 17 µg/filter (Equivalent to 25% CV)
z-Score
Laboratory
10 2 5 9 4 8 7 6 3 1
-1.0 -0.6 -0.4 -0.4 -0.3 0.1 0.3 0.6 0.7 1.0

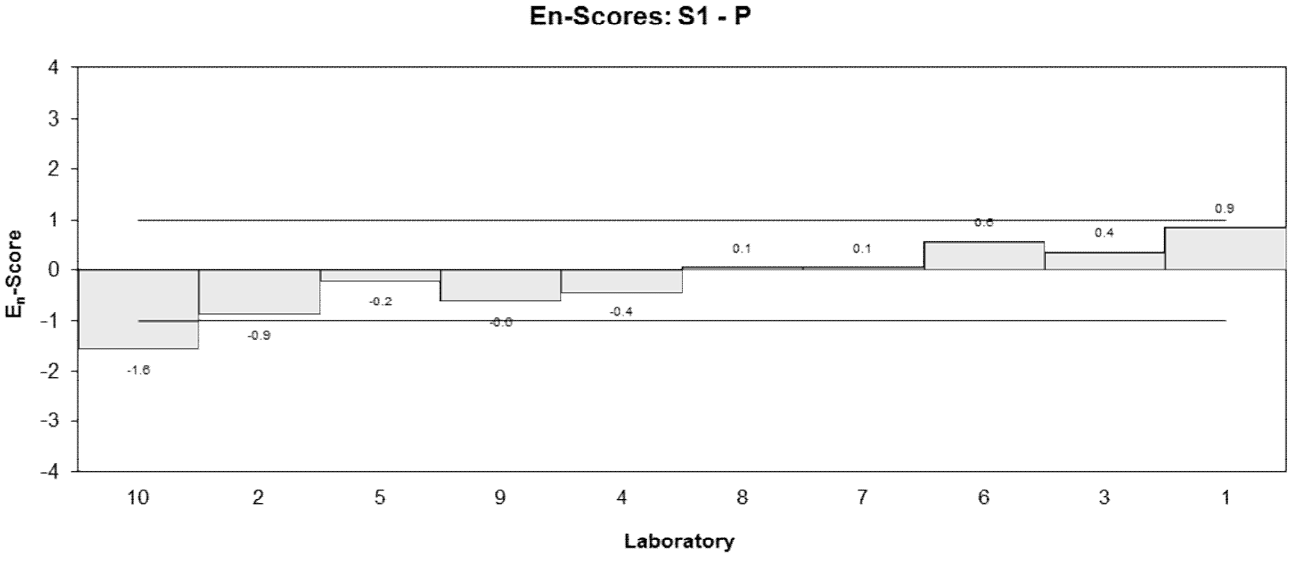

En-Scores: S1 - P
En-Score
Laboratory
10 2 5 9 4 8 7 6 3 1
-1.6 -0.9 -0.2 -0.0 -0.4 0.1 0.1 0.6 0.4 0.9

Figure 14

Table 18

Sample Details

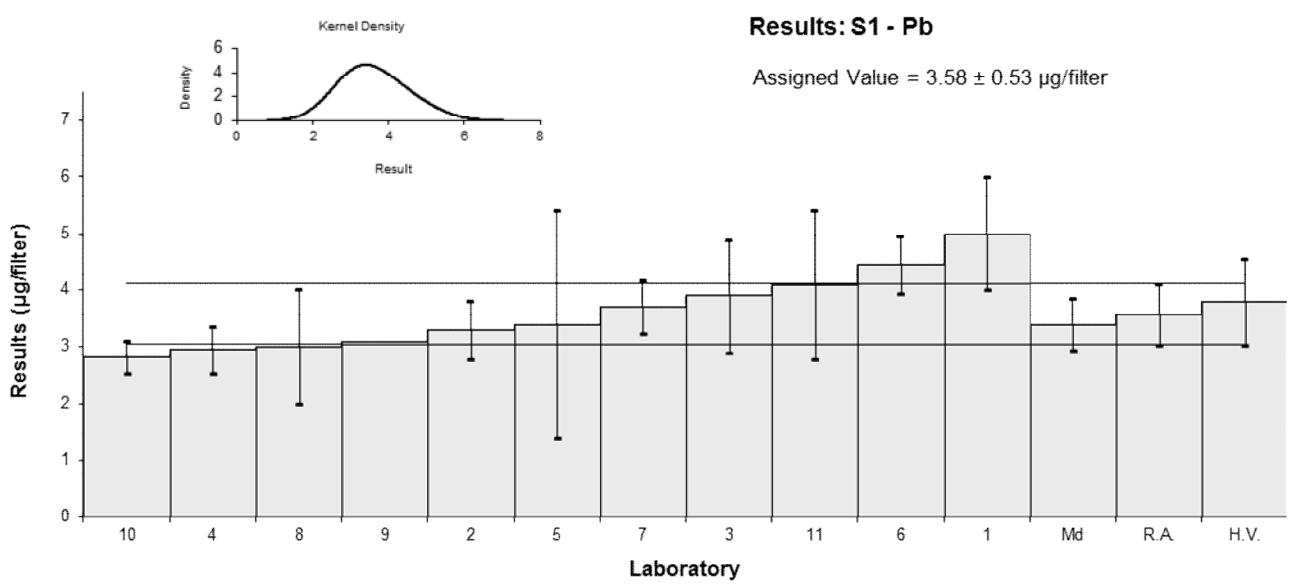
Sample No.	S1
Matrix.	Filter
Analyte.	Pb
Units	µg/filter

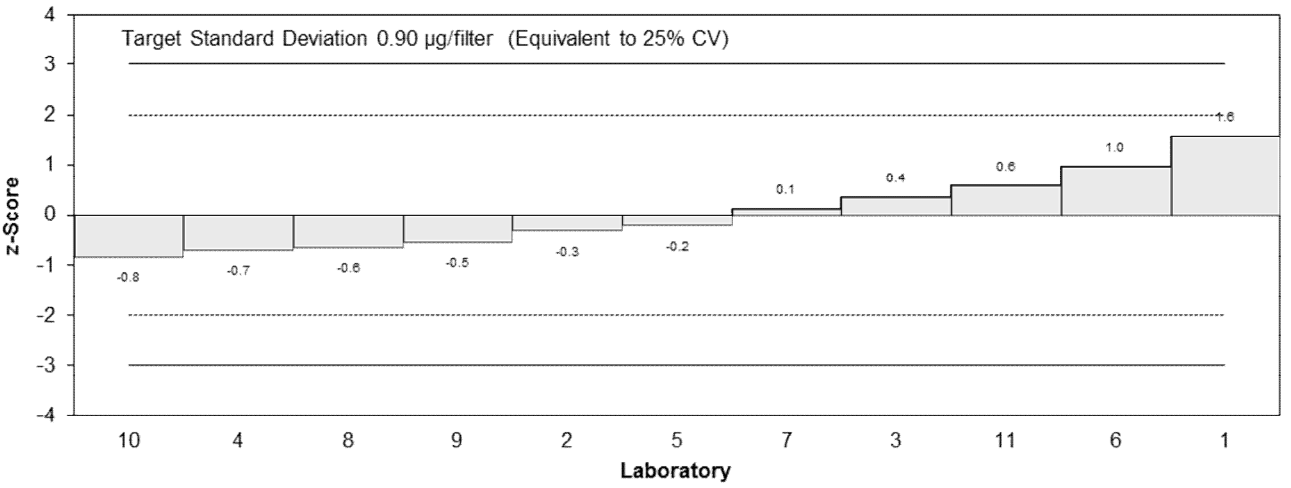
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	5.0	1.0	1.59	1.25
2	3.3	0.5	-0.31	-0.38
3	3.9	1	0.36	0.28
4	2.95	0.4	-0.70	-0.95
5	3.4	2	-0.20	-0.09
6	4.45	0.50	0.97	1.19
7	3.7	0.46	0.13	0.17
8	3	1	-0.65	-0.51
9	3.1	NR	-0.54	-0.91
10	2.83	0.283	-0.84	-1.25
11	4.1	1.3	0.58	0.37

Statistics

Assigned Value	3.58	0.53
Spike	Not Spiked	
Homogeneity Value	3.79	0.76
Robust Average	3.58	0.53
Median	3.40	0.45
Mean	3.61	
N	11	
Max.	5	
Min.	2.83	
Robust SD	0.71	
Robust CV	20%	


Kernel Density
Density
Result
Results: S1 - Pb
Assigned Value = 3.58 ± 0.53 µg/filter
Results (µg/filter)
10 4 8 9 2 5 7 3 11 6 1 Md R.A. H.V.
Laboratory


z-Scores: S1 - Pb
Target Standard Deviation 0.90 µg/filter (Equivalent to 25% CV)
z-Score
-0.8 -0.7 -0.6 -0.5 -0.3 -0.2 0.1 0.4 0.6 1.0 1.6
10 4 8 9 2 5 7 3 11 6 1
Laboratory

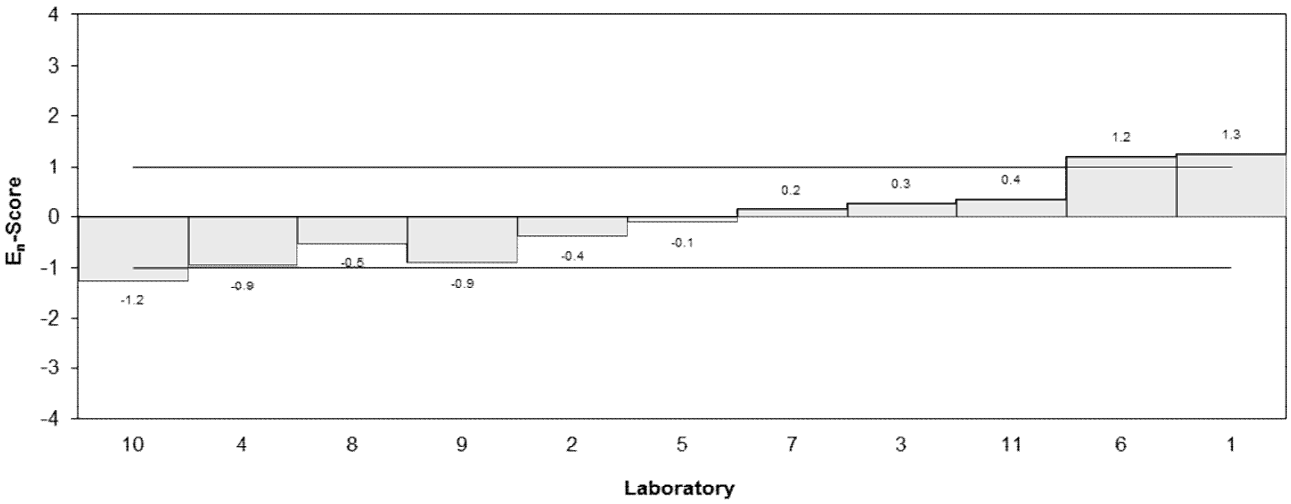

En-Scores: S1 - Pb
En-Score
-1.2 -0.9 -0.5 -0.9 -0.4 -0.1 0.2 0.3 0.4 1.2 1.3
10 4 8 9 2 5 7 3 11 6 1
Laboratory

Figure 15

Table 19

Sample Details

Sample No.	S1
Matrix.	Filter
Analyte.	Se
Units	µg/filter

Participant Results

Lab Code	Result	Uncertainty
1	<0.2	NR
2	<0.02	0.02
3	<0.5	NR
4	0.081	0.01
5	<0.5	NR
6	<0.05	NR
7	0.22	0.22
8	<0.5	NR
9	<0.05	NR
10	0.012	0.007
11	NT	NT

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Homogeneity Value	0.010	0.003
Median	0.08	0.25
Mean	0.10	
N	3	
Max.	0.22	
Min.	0.012	
Robust SD	0.12	
Robust CV	120%	

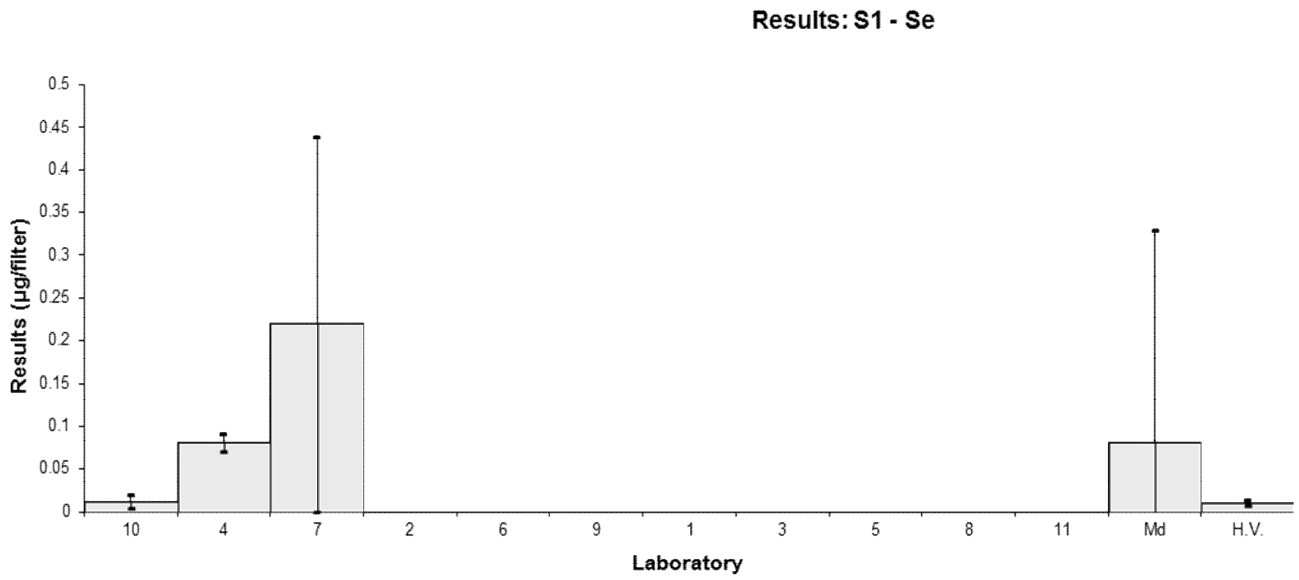

Results: S1 - Se
Results (µg/filter)
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
10
4
7
2
6
9
1
3
5
8
11
Md
H.V.
Laboratory

Figure 16

Table 20

Sample Details

Sample No.	S1
Matrix.	Filter
Analyte.	Sn
Units	µg/filter

Participant Results

Lab Code	Result	Uncertainty
1	0.19	0.037
2	0.2	0.1
3	<2	NR
4	0.34	0.05
5	<2	NR
6	0.214	0.04
7	0.40	0.20
8	<2	NR
9	0.15	NR
10	0.127	0.025
11	NT	NT

Statistics

Assigned Value	Not Set	
Spike	Not Spiked	
Homogeneity Value	0.190	0.038
Robust Average	0.23	0.11
Median	0.200	0.069
Mean	0.232	
N	7	
Max.	0.4	
Min.	0.127	
Robust SD	0.11	
Robust CV	48%	

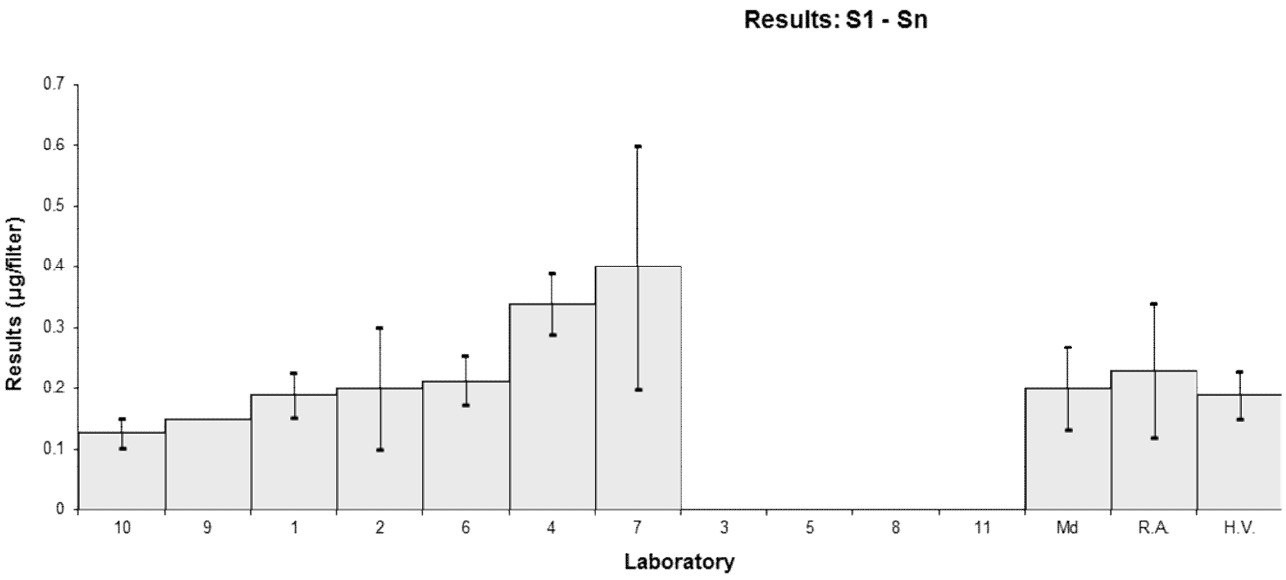

Results: S1 - Sn
Results (µg/filter)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
9
1
2
6
4
7
3
5
8
11
Md
R.A.
H.V.
Laboratory

Figure 17

Table 21

Sample Details

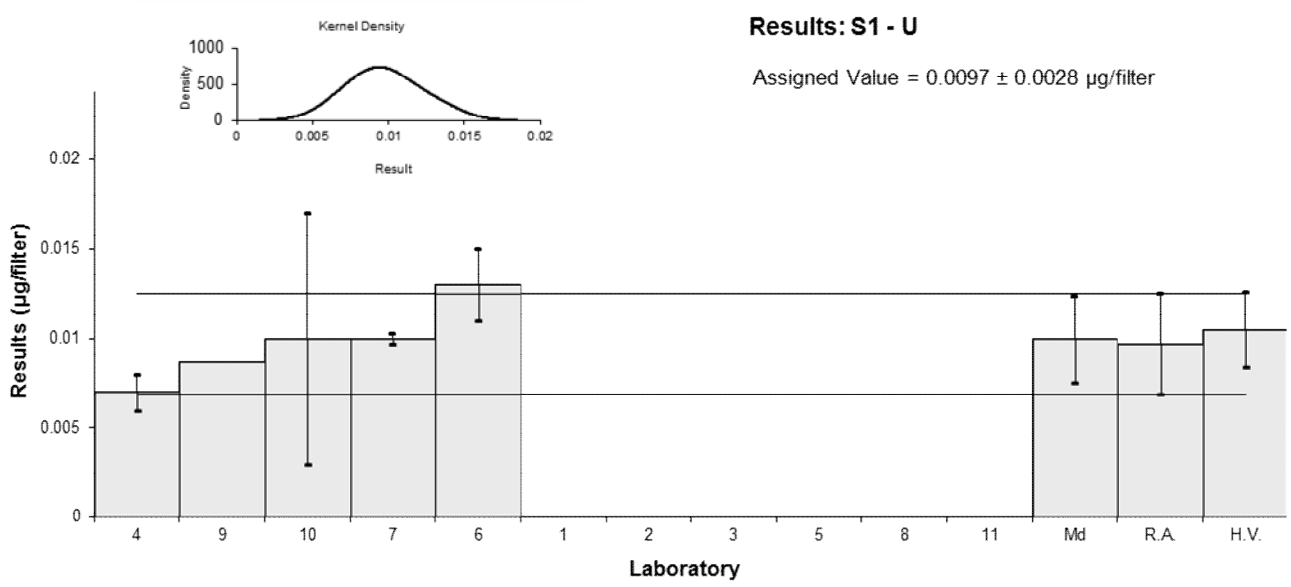
Sample No.	S1
Matrix.	Filter
Analyte.	U
Units	µg/filter

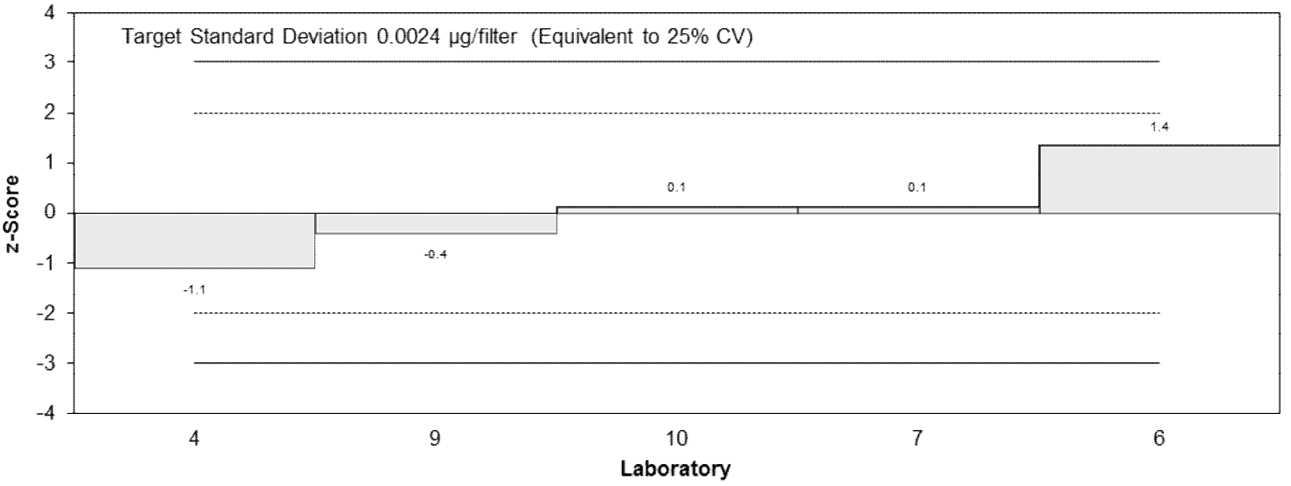
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	<0.05	NR		
2	<0.05	0.05		
3	<0.5	NR		
4	0.007	0.001	-1.11	-0.91
5	<0.5	NR		
6	0.013	0.002	1.36	0.96
7	0.01	0.0003	0.12	0.11
8	<0.5	NR		
9	0.0087	NR	-0.41	-0.36
10	0.010	0.007	0.12	0.04
11	NT	NT		

Statistics

Assigned Value	0.0097	0.0028
Spike	Not Spiked	
Homogeneity Value	0.0105	0.0021
Robust Average	0.0097	0.0028
Median	0.0100	0.0024
Mean	0.0097	
N	5	
Max.	0.013	
Min.	0.007	
Robust SD	0.0025	
Robust CV	26%	


Kernel Density
Density
1000
500
0
0
0.005
0.01
0.015
0.02
Result
Results: S1 - U
Assigned Value = 0.0097 ± 0.0028 µg/filter
Results (µg/filter)
0.02
0.015
0.01
0.005
0
4
9
10
7
6
1
2
3
5
8
11
Md
R.A.
H.V.
Laboratory


z-Scores: S1 - U
Target Standard Deviation 0.0024 µg/filter (Equivalent to 25% CV)
z-Score
4
3
2
1
0
-1
-2
-3
-4
-1.1
-0.4
0.1
0.1
1.4
4
9
10
7
6
Laboratory

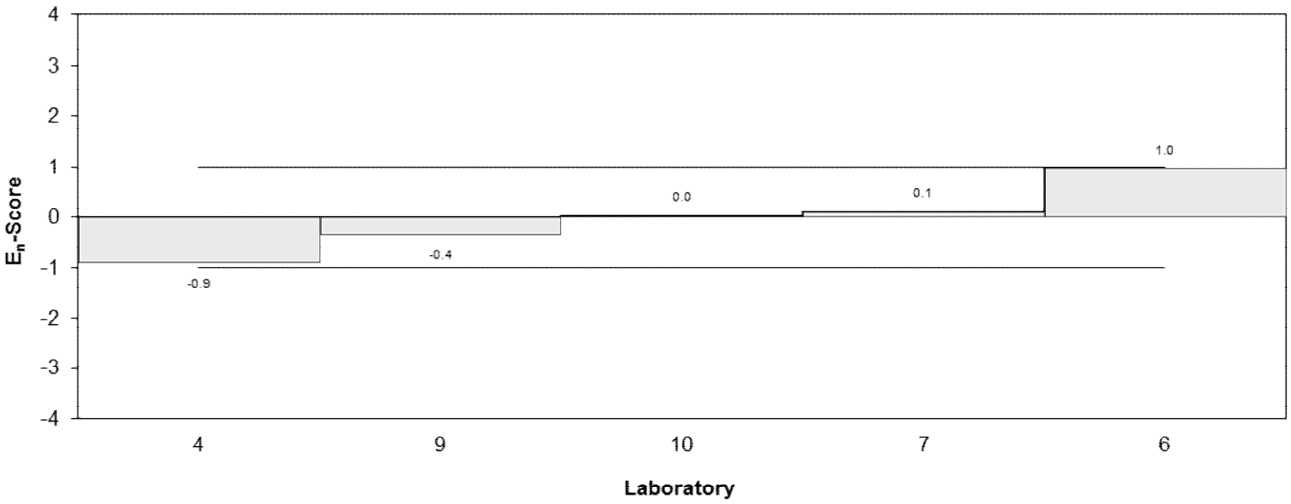

En-Scores: S1 - U
En-Score
4
3
2
1
0
-1
-2
-3
-4
-0.9
-0.4
0.0
0.1
1.0
4
9
10
7
6
Laboratory

Figure 18

Table 22

Sample Details

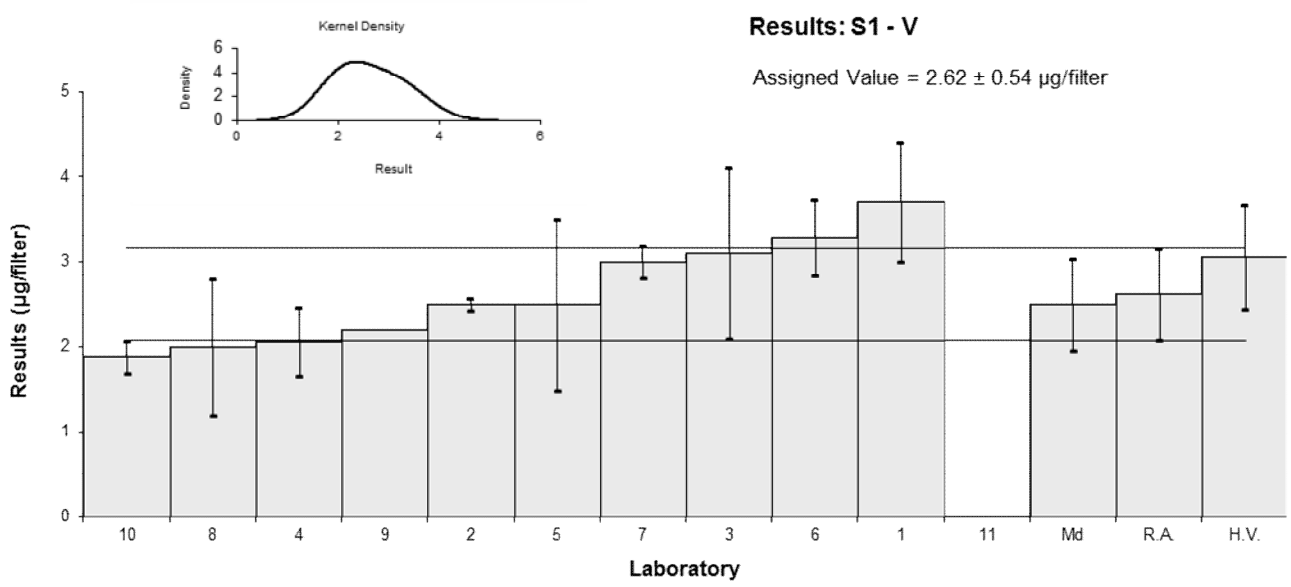
Sample No.	S1
Matrix.	Filter
Analyte.	V
Units	µg/filter

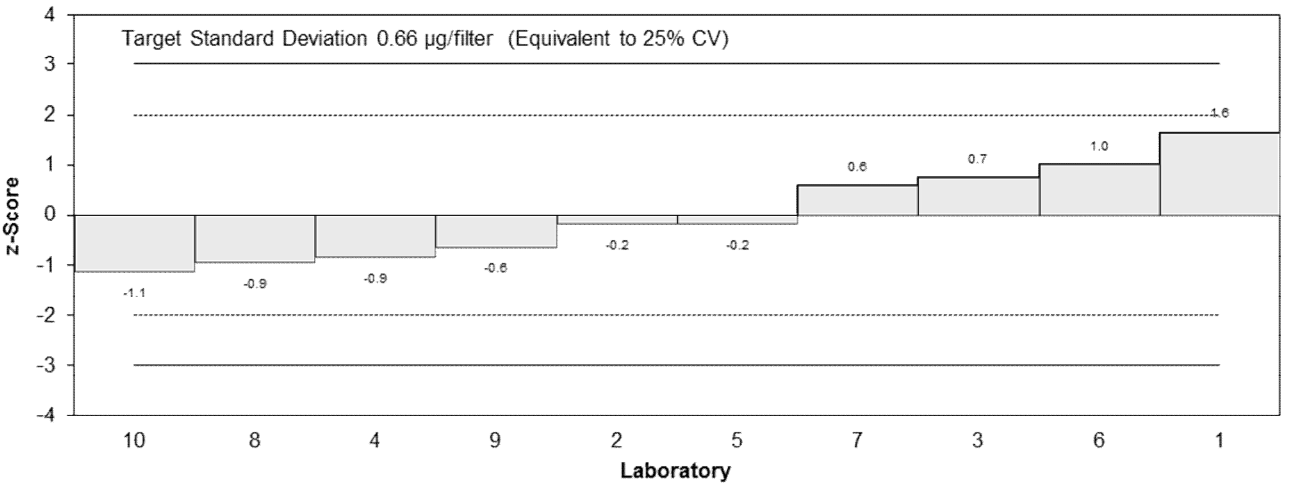
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	3.7	0.7	1.65	1.22
2	2.5	0.07	-0.18	-0.22
3	3.1	1	0.73	0.42
4	2.06	0.4	-0.85	-0.83
5	2.5	1	-0.18	-0.11
6	3.28	0.44	1.01	0.95
7	3.0	0.19	0.58	0.66
8	2	0.8	-0.95	-0.64
9	2.2	NR	-0.64	-0.78
10	1.88	0.188	-1.13	-1.29
11	NT	NT		

Statistics

Assigned Value	2.62	0.54
Spike	Not Spiked	
Homogeneity Value	3.06	0.61
Robust Average	2.62	0.54
Median	2.50	0.53
Mean	2.62	
N	10	
Max.	3.7	
Min.	1.88	
Robust SD	0.69	
Robust CV	26%	


Kernel Density
Density
Result
Results: S1 - V
Assigned Value = 2.62 ± 0.54 µg/filter
Results (µg/filter)
10 8 4 9 2 5 7 3 6 1 11 Md R.A. H.V.
Laboratory


z-Scores: S1 - V
Target Standard Deviation 0.66 µg/filter (Equivalent to 25% CV)
z-Score
-1.1 -0.9 -0.9 -0.6 -0.2 -0.2 0.6 0.7 1.0 1.6
10 8 4 9 2 5 7 3 6 1
Laboratory

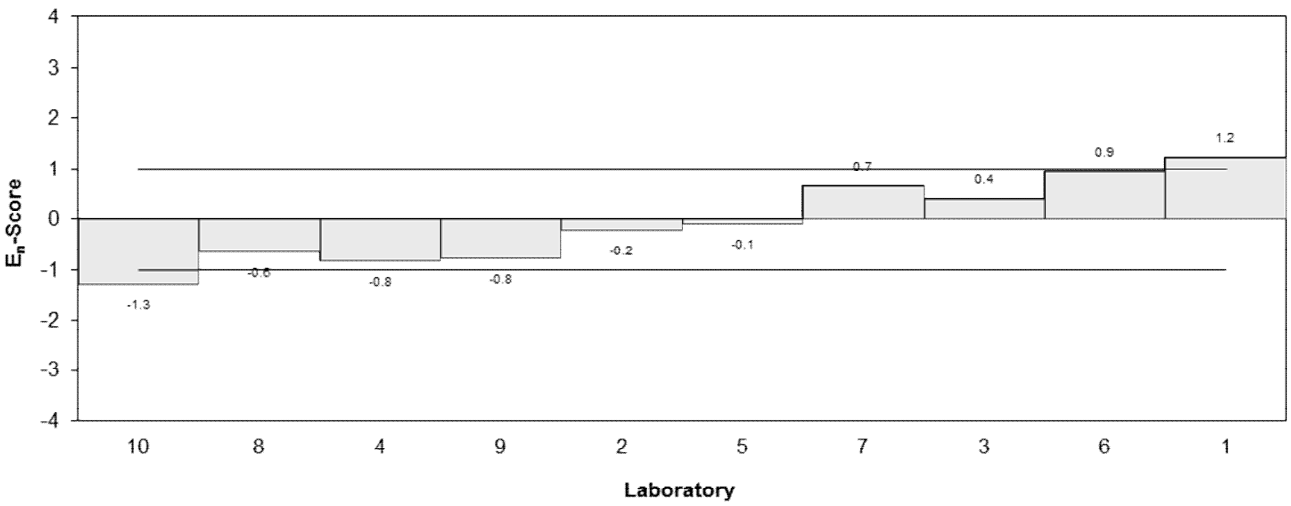

En-Scores: S1 - V
En-Score
-1.3 -0.6 -0.8 -0.8 -0.2 -0.1 0.7 0.4 0.9 1.2
10 8 4 9 2 5 7 3 6 1
Laboratory

Figure 19

Table 23

Sample Details

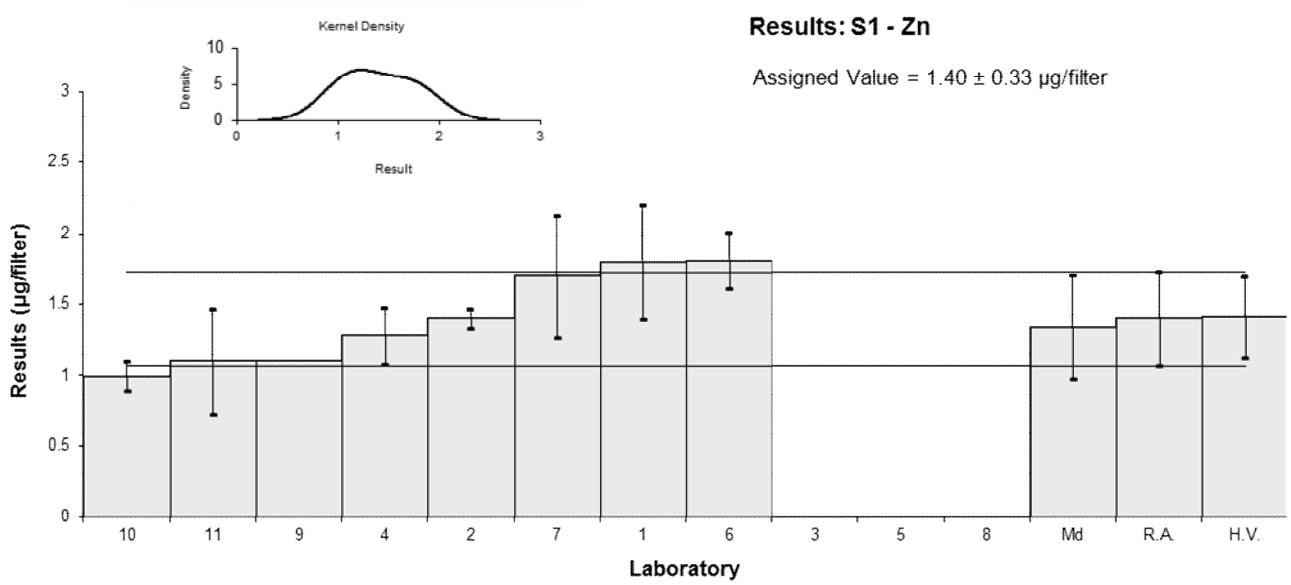
Sample No.	S1
Matrix.	Filter
Analyte.	Zn
Units	µg/filter

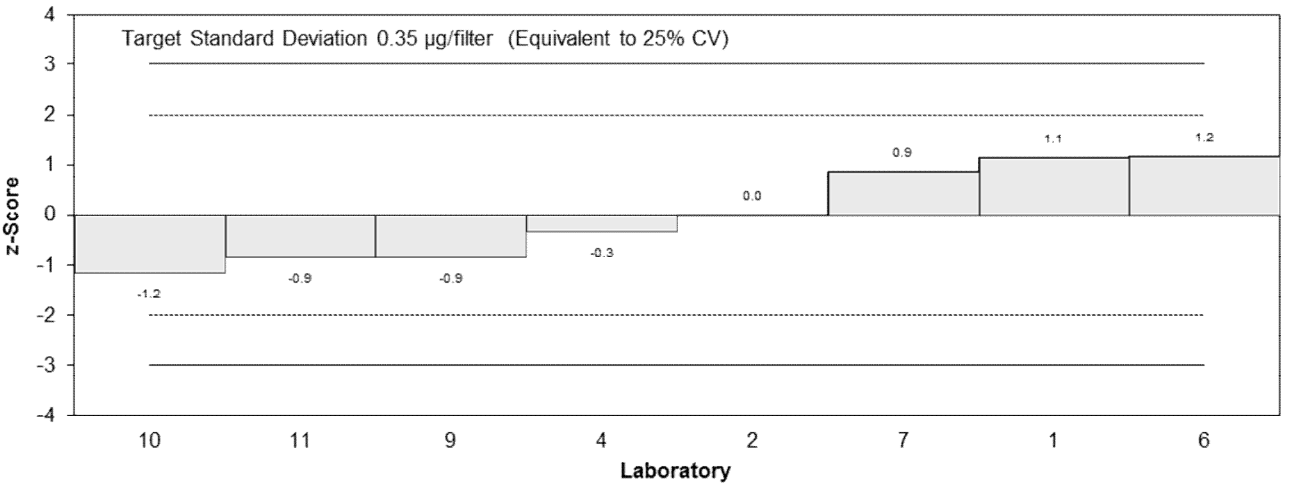
Participant Results

Lab Code	Result	Uncertainty	z-Score	E_n-Score
1	1.8	0.4	1.14	0.77
2	1.4	0.07	0.00	0.00
3	<5	NR		
4	1.28	0.2	-0.34	-0.31
5	<5	NR		
6	1.81	0.20	1.17	1.06
7	1.7	0.43	0.86	0.55
8	<5	NR		
9	1.10	NR	-0.86	-0.91
10	0.996	0.099	-1.15	-1.17
11	1.1	0.37	-0.86	-0.61

Statistics

Assigned Value	1.40	0.33
Spike	Not Spiked	
Homogeneity Value	1.41	0.28
Robust Average	1.40	0.33
Median	1.34	0.36
Mean	1.40	
N	8	
Max.	1.81	
Min.	0.996	
Robust SD	0.38	
Robust CV	27%	


Kernel Density
Density
Result
Results: S1 - Zn
Assigned Value = 1.40 ± 0.33 µg/filter
Results (µg/filter)
Laboratory
10 11 9 4 2 7 1 6 3 5 8 Md R.A. H.V.


z-Scores: S1 - Zn
Target Standard Deviation 0.35 µg/filter (Equivalent to 25% CV)
z-Score
-1.2 -0.9 -0.9 -0.3 0.0 0.9 1.1 1.2
Laboratory
10 11 9 4 2 7 1 6

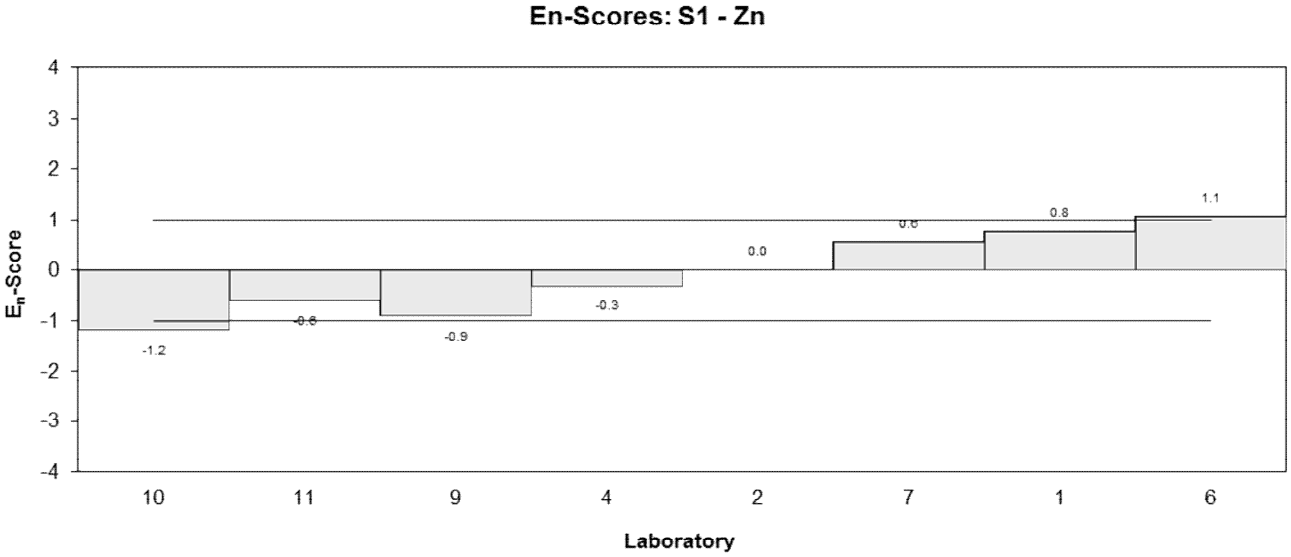

En-Scores: S1 - Zn
En-Score
-1.2 -0.6 -0.9 -0.3 0.0 0.6 0.8 1.1
Laboratory
10 11 9 4 2 7 1 6

Figure 20

7 DISCUSSION OF RESULTS

7.1 Assigned Value and Traceability

Assigned Values of the inorganic analytes in the study sample S1 were the robust averages of participants' results. The robust averages used as assigned values and their associated expanded uncertainties were calculated using the procedure described in 'Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO13528:2015(E)'.[5] Appendix 3 sets out the calculation for the robust average of Cr in Sample S1 and its associated uncertainty.

No assigned value was set for Ag, Be and Se in S1 because too few results were reported. However, participants may still compare their reported results for these elements with the median or robust average of participants' results and the homogeneity value. No assigned value was also set for Al and Sn in S1 because the results were too variable.

Traceability The assigned value is not traceable to any external reference; it is traceable to the consensus of participants' results deriving from a variety of measurement methods and (presumably) a variety of calibrators. So although expressed in SI units, the metrological traceability of the assigned values has not been established.

7.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. Of 166 numerical results, 148 (89%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 1.3% to 125% of the reported value. The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 3.

Approaches to estimating measurement uncertainty include: standard deviation of replicate analysis, Horwitz formula, professional judgement, bottom up approach, top down approach using precision and estimates of method and laboratory bias and top down approach using only the reproducibility from inter-laboratory comparisons studies.[8–14]

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 20). In this study, the reported expanded measurement uncertainty has been over-estimated in some cases (e.g. Lab 3 for Cd in S1) or under-estimated (e.g. Lab 10 for As in S1). As a simple rule of thumb, when the uncertainty estimate is either 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 reviewed as suspect.

Double counting the precision uncertainty components and overestimation of the laboratory or method bias are the most common error seen in the laboratories' estimated uncertainty budgets. According to General Accreditation Guidance, Estimating and reporting measurement uncertainty of chemical test results[11] and to NORDTEST TR 537,8 the most common sources used to estimate the precision component are from:

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

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

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

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

When a laboratory has successfully participated in at least 6 proficiency testing studies, the standard deviation from proficiency testing studies only, can also be used to estimate the uncertainty of their measurement results.[9, 11]

Laboratories 2 and 10 attached estimates of the expanded measurement uncertainty to results reported as less than their limit of detection. An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.[8]

Laboratory 7 reported an estimate of expanded uncertainty for their P measurement result larger than the result itself.

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 239.87 ± 44.96 µg/filter, it is better to report 240 ± 45 µg/filter or instead of 9910 ± 1486.50 µg/filter, it is better to report 9910 ± 1500 µg/filter.[8]

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 21. 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 136 results for which E_n-scores were calculated, 106 (78%) returned a satisfactory score of $|E_n| \leq 1.0$ indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.

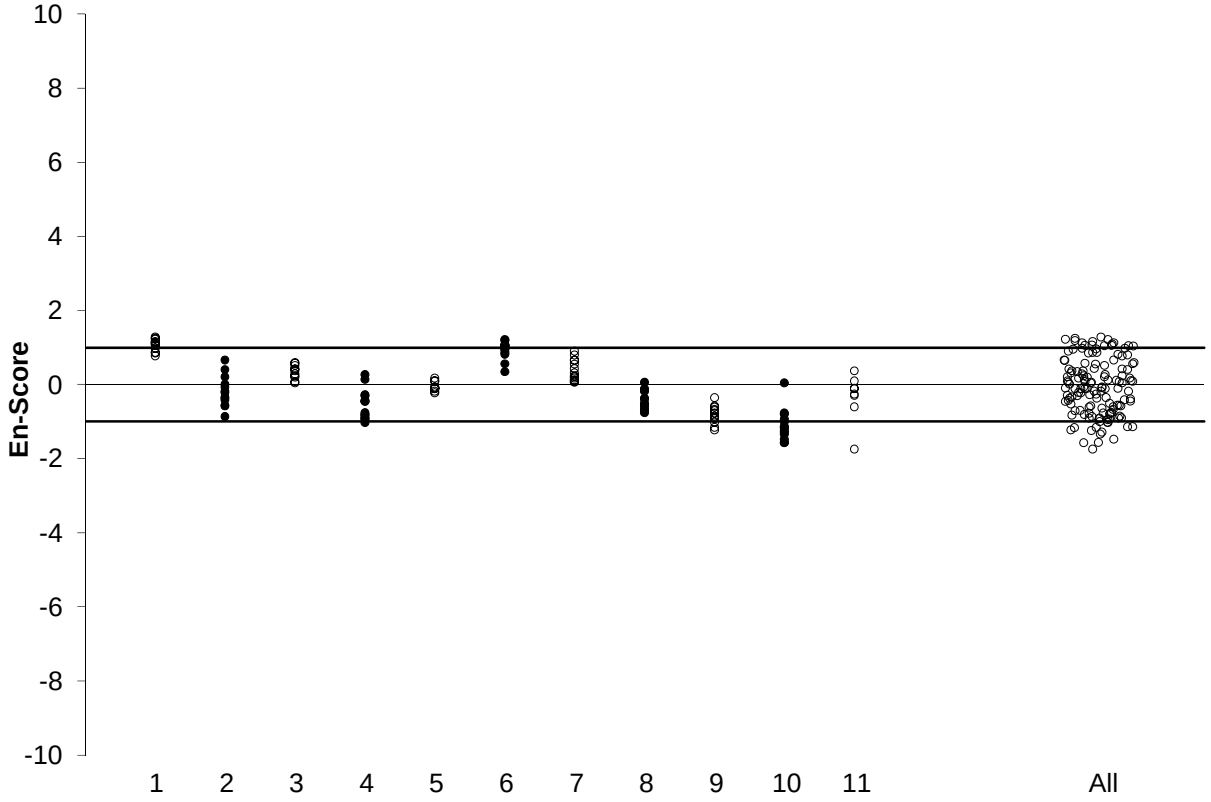
7.4 z-Score

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

The target standard deviation defines satisfactory performance in a proficiency test. This was the first study to be conducted by NMI for metals on filters and potentially the first study for many participants in which they could check their methods for measurement of inorganic analytes in air filters. A target standard deviation equivalent to 25% performance coefficient of variation (PCV) was used to calculate z-scores.

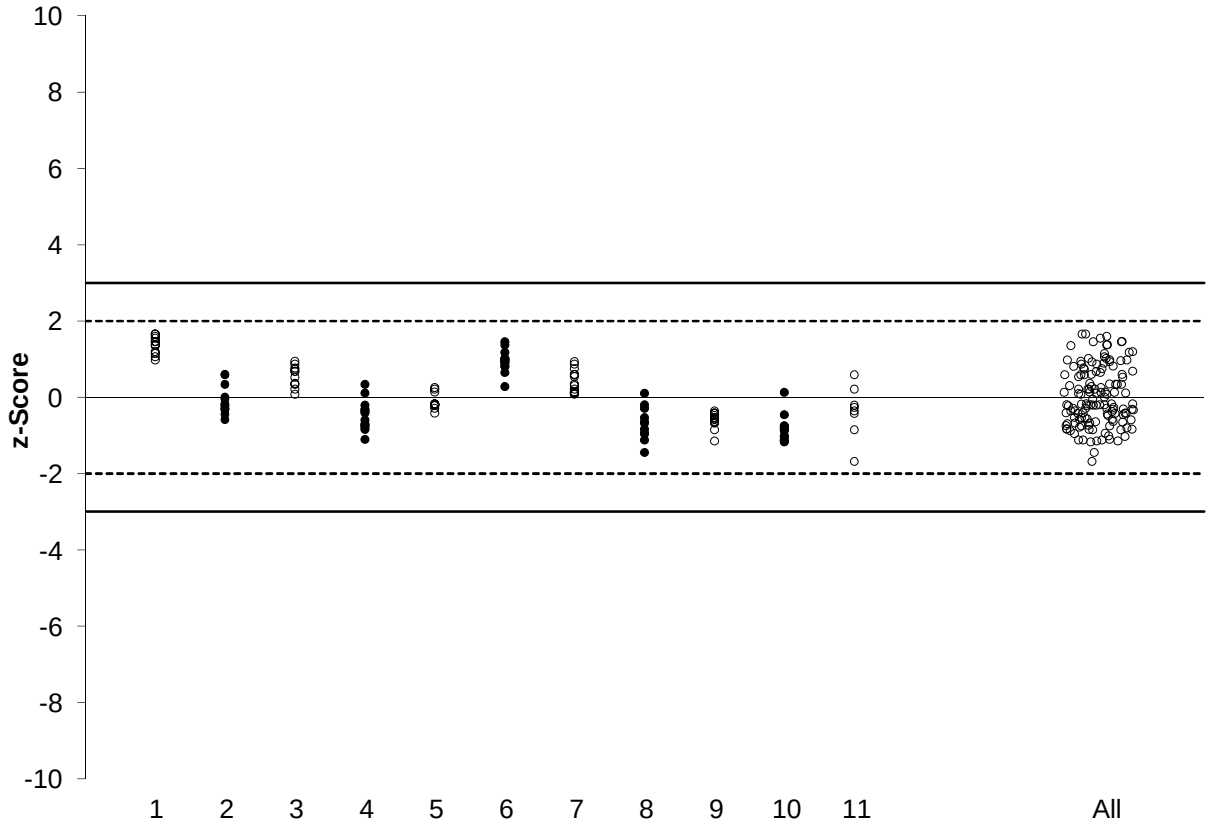
The between-laboratory coefficient of variation predicted by the Thompson equation[6] and the participants' coefficient of variation in this study are presented for comparison in Table 24. The set target deviation of 25% was found to be in good agreement with laboratories' coefficients of variation and with the coefficient of variation predicted by Thomson for most analytes of interest.

The dispersal of participants' z-scores is presented in Figure 22 (by laboratory code) and in Figure 23 (by test). Of 136 results for which z-scores were calculated, all returned a satisfactory score of $|z| \leq 2.0$.



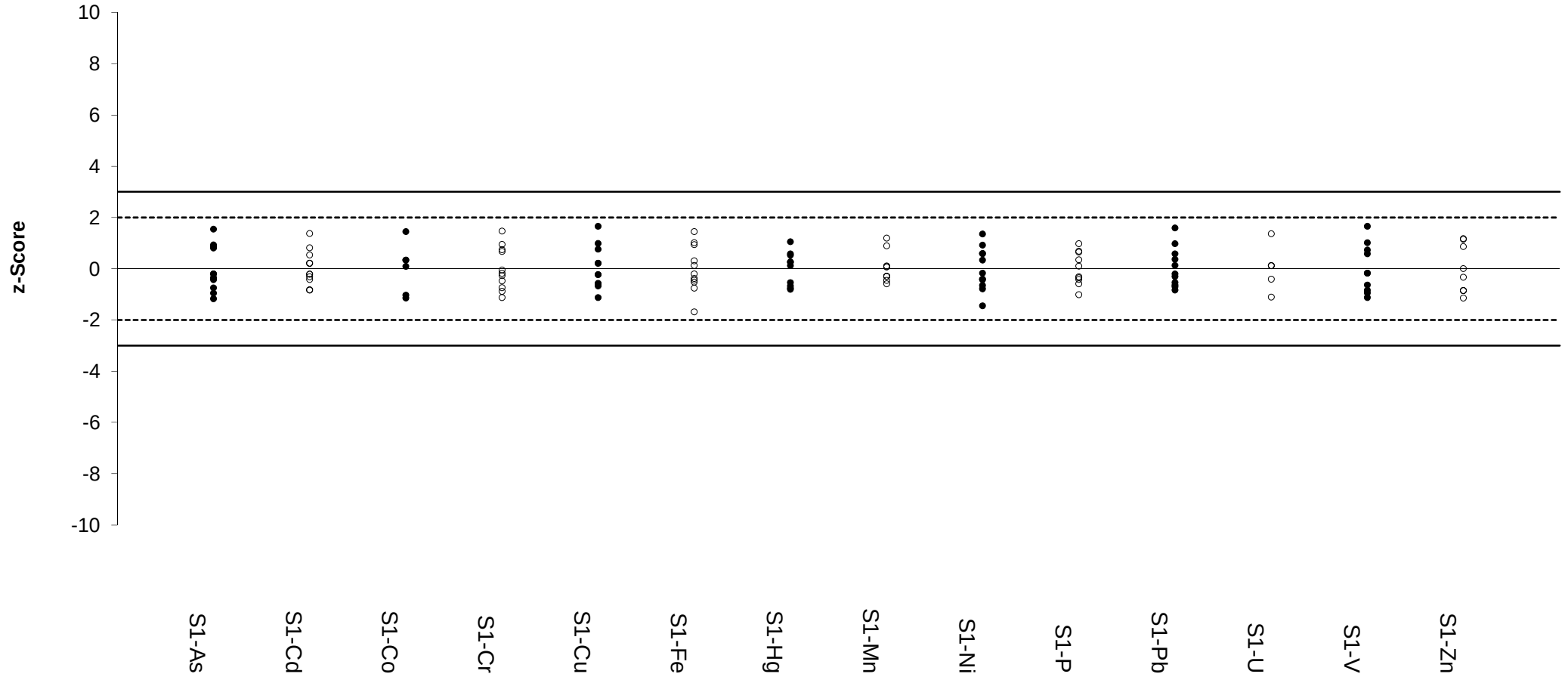
Scores of >10 or < -10 have been plotted as 10 or -10.

Figure 21 E_n-Score Dispersal by Laboratory



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

Figure 22 z-Score Dispersal by Laboratory



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

Figure 23 z-Score Dispersal by Test

Table 24 Between Laboratory CV of this Study, Thompson CV and Set Target SD

Sample	Test	Assigned value (µg/filter)	Between Laboratories CV	Thompson/ Horwitz CV	Target SD (as CV)
S1	Ag	0.066*	44%	22%	Not Set
S1	Al	105*	36%	20%	Not Set
S1	As	5.27	25%	22%	25%
S1	Be	0.0048*	29%	22%	Not Set
S1	Cd	0.380	18%	22%	25%
S1	Co	0.0323	28%	22%	25%
S1	Cr	5.57	23%	22%	25%
S1	Cu	3.61	22%	22%	25%
S1	Fe	242	25%	20%	25%
S1	Hg	0.301	19%	22%	25%
S1	Mn	1.08	15%	22%	25%
S1	Ni	1.57	24%	22%	25%
S1	P	69	19%	22%	25%
S1	Pb	3.58	20%	22%	25%
S1	Se	0.08*	120%	22%	Not Set
S1	Sn	0.185*	48%	22%	Not Set
S1	U	0.0097	26%	22%	25%
S1	V	2.62	26%	22%	25%
S1	Zn	1.40	27%	22%	25%

*Robust Average

7.5 Participants' Results and Analytical Methods for Acid Extractable Elements

The study's test sample consisted of three filter papers, each loaded with the same amount of air particulate matter. Participants were assessed on the average of the three measurements. Laboratories were advised as follows: "…report results for each of the three filters in units of µg/filter. However, the average of the three results will be used for scoring." A summary of participants' results and performance is presented in Table 25 and in Figures 22 and 23. Participants' results reported for each filter are presented in Appendix 5.

The study sample was aimed at mimick real life air filter samples which are routinely analysed by laboratories. As for routine air filter samples, the study sample required a good preparation/handling procedure as no fixation or surface coating was applied to avoid material loss. Of 136 reported results for which z-scores were calculated, all returned a satisfactory score indicating that laboratories do not have difficulty with the preparation of air filters.

The method descriptions provided by participants are presented in Table 1 while the instrumental conditions are presented in Appendix 6.

No laboratory used diluted HCl and H_2O_2.

With the exception of one, all laboratories used both HNO_3 and HCl. Laboratory 11 used HNO_3 only.

Laboratory 2 reported using HCl and diluted HNO_3.

Laboratory 1 digested the filter samples in two steps, with step 2 involving the addition of 10 mL water and further sample digestion at 95°C-100°C for 30 minutes.

Laboratories 7 and 3 extracted their sample at 95ºC -100ºC for 30 min only.

The most popular method was the NIOSH Method 7303 which involves a digestion temperature close to 95°C and a ratio of HNO_3 to HCl of 1 to 1.

Table 25 Summary of Participants' Results and Performance for Acid Extractable Elements in Sample S1

Lab Code	S1-Ag µg/filter	S1-Al µg/filter	S1-As µg/filter	S1-Be µg/filter	S1-Cd µg/filter	S1-Co µg/filter	S1-Cr µg/filter	S1-Cu µg/filter	S1-Fe µg/filter	S1-Hg µg/filter
H.V.	0.076	95	5.6	0.0057	0.411	0.0320	6.3	3.99	227	0.325
A.V.	Not Set	Not Set	5.27	Not Set	0.380	0.0323	5.57	3.61	242	0.301
1	0.086	170	7.3	<0.05	0.51	<0.05	7.6	5.1	330	0.38
2	0.0745	82	5	0.006	0.35	0.035	5.5	3.4	215	0.345
3	<0.5	100	6.4	<0.01	0.4	<0.5	6.5	4.3	299	0.34
4	0.031	143	4.28	0.003	0.36	0.035	4.54	3.07	219	0.24
5	<0.5	98	5	<0.01	0.4	<0.5	5.3	3.4	250	0.32
6	<0.1	149	6.32	<0.01	0.457	0.044	6.89	4.49	303	0.321
7	0.1	87	6.5	0.005	0.43	0.033	6.6	3.8	260	0.31
8	<0.05	70	4	<0.01	0.3	<0.5	4	3	230	0.26
9	0.055	76	4.7	0.005	0.34	0.023	4.9	3.1	210	0.25
10	0.05	84.6	3.71	<0.02	0.301	0.024	4.35	2.59	196	0.244
11	NT	NT	4.8	NT	0.36	NT	5.2	3.8	140	NT

A.V. = Assigned Value, H.V. = Homogeneity Value

Table 25 Summary of Participants' Results and Performance for Acid Extractable Elements in Sample S1 (continued)

Lab Code	S1-Mn µg/filter	S1-Ni µg/filter	S1-P µg/filter	S1-Pb µg/filter	S1-Se µg/filter	S1-Sn µg/filter	S1-U µg/filter	S1-V µg/filter	S1-Zn µg/filter
H.V.	1.10	1.69	73	3.79	0.010	0.190	0.0105	3.06	1.41
A.V.	1.08	1.57	69	3.58	Not Set	Not Set	0.0097	2.62	1.40
1	1.4	2.1	86	5.0	<0.2	0.19	<0.05	3.7	1.8
2	1	1.8	59	3.3	<0.02	0.2	<0.05	2.5	1.4
3	1.1	1.7	81	3.9	<0.5	<2	<0.5	3.1	<5
4	1.11	1.41	63.6	2.95	0.081	0.34	0.007	2.06	1.28
5	1.0	1.5	62	3.4	<0.5	<2	<0.5	2.5	<5
6	1.32	1.93	80.2	4.45	<0.05	0.214	0.013	3.28	1.81
7	1.1	1.8	75	3.7	0.22	0.40	0.01	3.0	1.7
8	1	1	71	3	<0.5	<2	<0.5	2	<5
9	0.92	1.31	63	3.1	<0.05	0.15	0.0087	2.2	1.10
10	0.956	1.26	51.5	2.83	0.012	0.127	0.010	1.88	0.996
11	<2.0	1.4	NT	4.1	NT	NT	NT	NT	1.1

A.V. = Assigned Value, H.V. = Homogeneity Value

The high number of satisfactory results reported for scored analytes demonstrates that participants' results are comparable and therefore indicates that they use methods which provide equivalent results for these tests. However, no agreement was found between the results reported for Al and Sn and no assigned value could be set for these elements.

Aluminium The between-laboratory coefficient of variation for Al in Sample S1 was high (36%), and larger than that predicted by Thomson (20%).[6] This element is known to be strongly dependent on the digestion regime.

High Al results were from by digestion regimes that involved a high digestion temperature (120°C) and/or longer digestion time (90 min to 120 min) (Figure 26).

Cobalt level in Sample S1 was low (0.0323 µg/filter) and this might have presented difficulty to some laboratories. The between laboratory coefficient of variation was high (28%). Plots of participants' results versus instrumental technique used are presented in Figure 24.

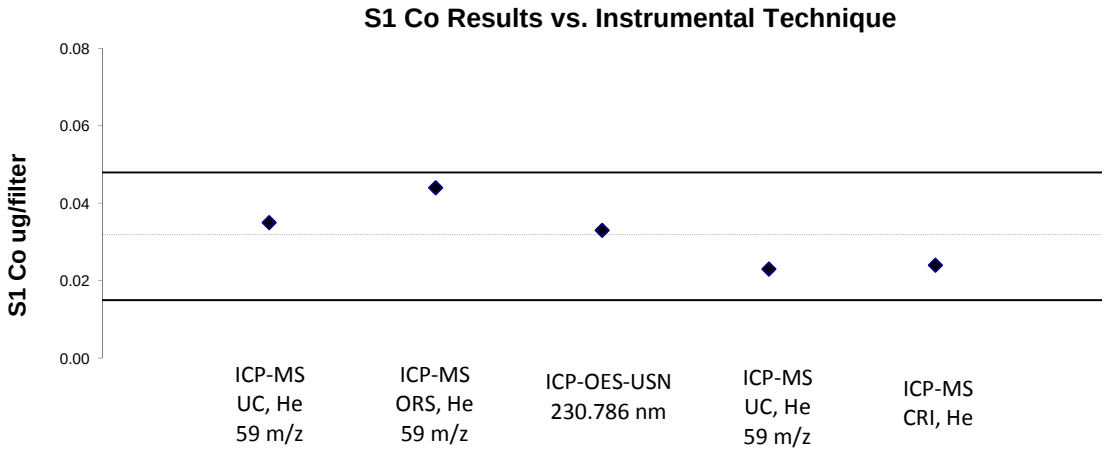
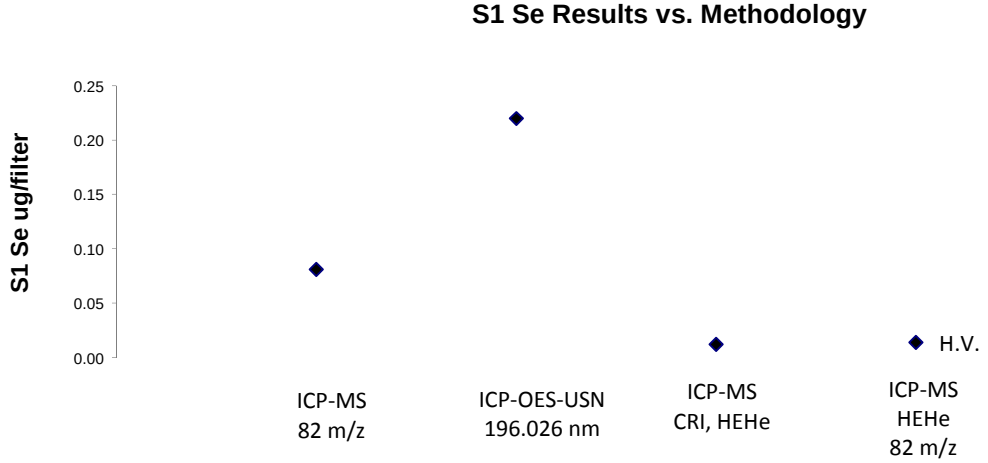


Figure 24 S1-Co Results vs. Instrumental Technique

Selenium level in Sample S1 was below the reporting level of most participating laboratories. Only three results were reported for this test: one from ICP-MS in standard mode, one from ICP-MS-CRI measurements with high energy He as collision gas and one from ICP-OES measurements with ultrasonic nebuliser. Se level in S1 might be too low for ICP-OES-USN measurements. Figure 25 presents plots of participants results versus technique used.



H.V. Homogeneity Value

Figure 25 S1-Se Results vs. Instrumental Technique

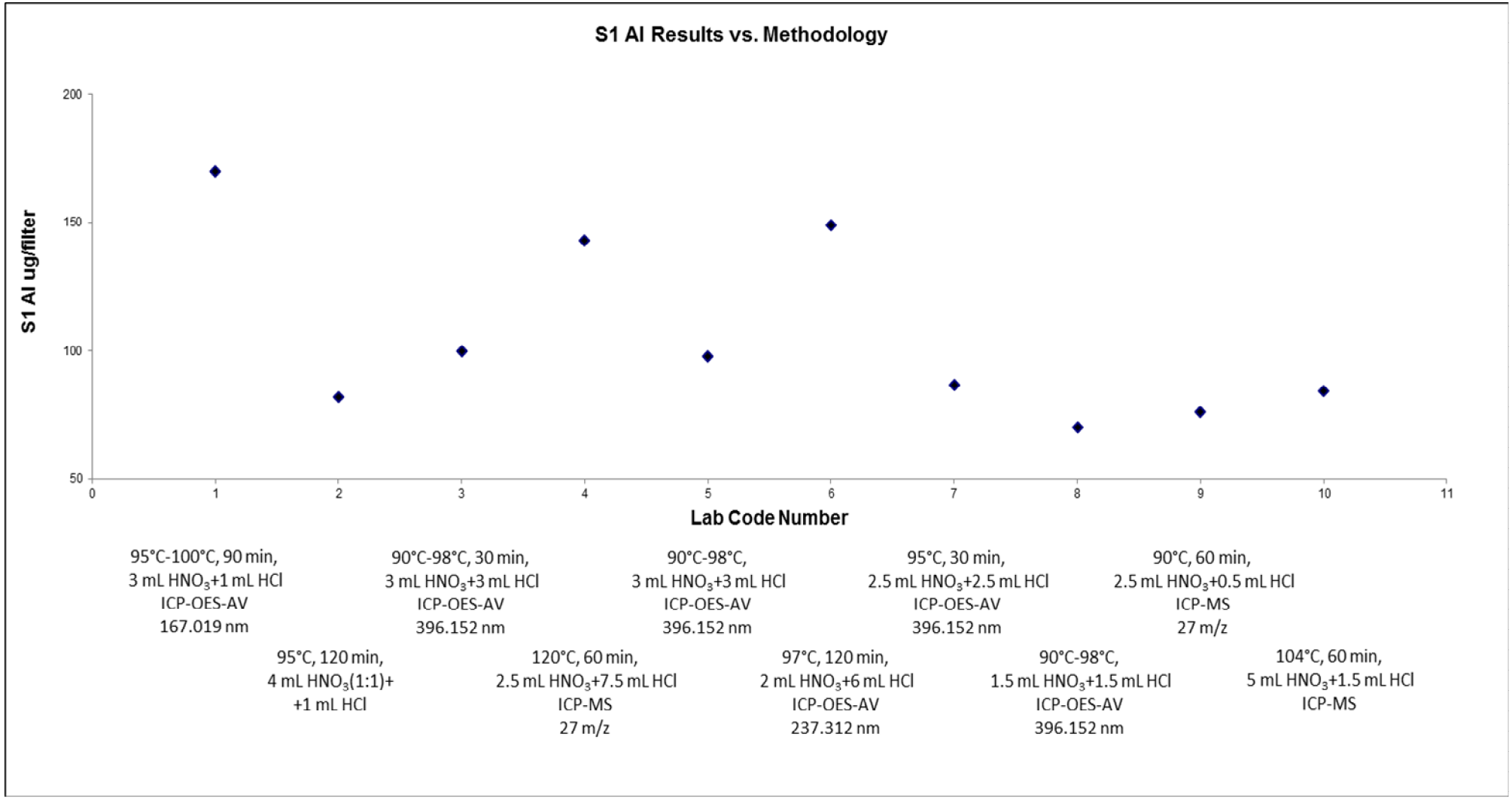


Figure 26: S1-Al Results vs. Methodology

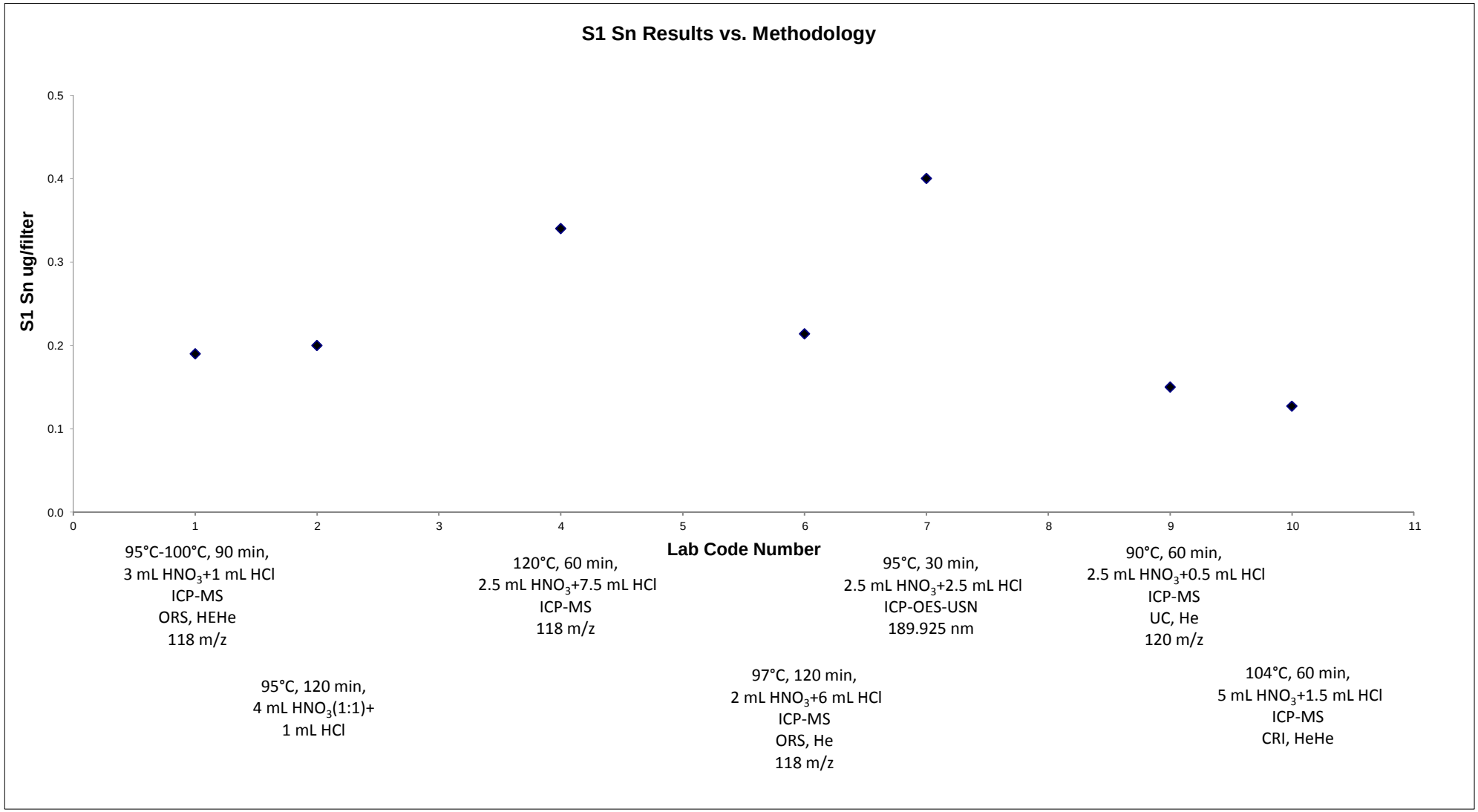


Figure 27: S1-Sn Results vs. Methodology

Tin results were variable (CV 48%) and no assigned value could be set for this test. Laboratory 6 reported:" The results of Tin (Sn) were found to drop off from the solution. It has to analyse straight after sample extraction."

Tin dissolves in hydrochloric acid with the formation of tin(II) (stannous) salts and in dilute nitric acid with the formation of tin(II) and ammonium ions. When nitric acid concentration in solution is high a white insoluble precipitate of hydrated tin(IV) oxide ($SnO_2.xH_2O$) is formed. It is recommended to keep the prepared sample in 5 mol/L HCl. $SnCl_4$ is highly volatile so the solution should not be further heated.[15,16, 17]

Plots of participants' results versus the extraction regime used are presented in Figure 27.

Cadmium, Mercury, Manganese and Phosphorus were the tests that presented the least analytical difficulty to participating laboratories with a between laboratory CV of less than 20%.

7.6 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 26).

Table 26 Control Samples Used by Participants

Lab. Code	Description of Control Samples
2	Certified Reference Material
7	Reference Material
10	Certified Reference Material
11	Spiked Sample

Matrix matched control samples taken through all steps of the analytical process, are most valuable quality control tools for assessing the methods' performance.

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]

8 REFERENCES

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APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

Sample Preparation

Sample S1 consisted of three filters labelled S1A, S1B and S1C, each loaded with the same amount of simulated air particulate matter. The preparation procedure was based on the paper published by Susan F. Heller-Zeisler.[19] Samples were spiked by dispensing an equal amount of a liquid suspension of a fortified, ground and sieved soil reference material onto a quartz filter mounted on a vacuum filtration unit. After filtering to dryness, the filters were allowed to air dry under a clean air flow cabinet. Each filter was mounted into a PetriSlide container.

Sample Analysis and Homogeneity Testing

Homogeneity testing was conducted for the elements of interest. Six samples (each consisting of three filters analysed separately) were analysed and the average of the results was reported as the homogeneity value.

Since the entire sample was used in each analysis, it was not possible to apply analysis of variance (ANOVA) to determine if samples were sufficiently homogeneous. When it is not possible to conduct replicate measurements, the standard deviation of the results (sd) will be compared with the target standard deviation of the PT (σ) calculated as described in section 5.5. The proficiency test samples may be considered sufficiently homogeneous if: $sd \leq 0.3\ \sigma$.[5]

Data from the homogeneity testing is presented in the tables below. The between sample sd as CV was between 3% to 7% less than 30% of the target standard deviation as CV set for this study (25%). [5]

The samples were found to be sufficiently homogeneous for the evaluation of participants' performance.

Table 27 Homogeneity Testing of As in Sample S1

Filter ID	Filter A Result (µg/filter)	Filter B Result (µg/filter)	Filter C Result (µg/filter)	Average Result (µg/filter)
Sample 1 (Filter 14A, 9B, 10C)	6.1	5.6	4.5	5.4
Sample 2 (Filter 25A, 18B, 13C)	5.1	7.3	5.2	5.9
Sample 3 (Filter 24A, 2B, 20C)	5.1	6.6	5.1	5.6
Sample 4 (Filter 19A, 25B, 11C)	5.4	6.0	4.5	5.3
Sample 5 (Filter 5A, 13B, 7C)	4.9	6.8	6.4	6.0
Sample 6 (Filter 3A, 22B, 14C)	4.4	5.3	6.1	5.3
			Overall Average	**5.6**
			CV	**5%**

	Value	Critical (<30% of Target CV)	Result
CV	5%	7.5%	**Pass**

Table 28 Homogeneity Testing of Cd in Sample S1

Filter ID	Filter A Result (µg/filter)	Filter B Result (µg/filter)	Filter C Result (µg/filter)	Average Result (µg/filter)
Sample 1 (Filter 14A, 9B, 10C)	0.458	0.400	0.320	0.393
Sample 2 (Filter 25A, 18B, 13C)	0.370	0.553	0.360	0.428
Sample 3 (Filter 24A, 2B, 20C)	0.380	0.477	0.391	0.416
Sample 4 (Filter 19A, 25B, 11C)	0.400	0.458	0.362	0.407
Sample 5 (Filter 5A, 13B, 7C)	0.362	0.490	0.477	0.443
Sample 6 (Filter 3A, 22B, 14C)	0.334	0.370	0.430	0.378
			Overall Average	**0.411**
			CV	**6%**

	Value	Critical (<30% of Target CV)	Result
CV	6%	7.5%	**Pass**

Table 29 Homogeneity Testing of Co in Sample S1

Filter ID	Filter A Result (µg/filter)	Filter B Result (µg/filter)	Filter C Result (µg/filter)	Average Result (µg/filter)
Sample 1 (Filter 14A, 9B, 10C)	0.0346	0.0310	0.0240	0.0299
Sample 2 (Filter 25A, 18B, 13C)	0.0290	0.0428	0.0280	0.0333
Sample 3 (Filter 24A, 2B, 20C)	0.0280	0.0382	0.0291	0.0318
Sample 4 (Filter 19A, 25B, 11C)	0.0300	0.0364	0.0291	0.0318
Sample 5 (Filter 5A, 13B, 7C)	0.0273	0.0420	0.0364	0.0352
Sample 6 (Filter 3A, 22B, 14C)	0.0264	0.0280	0.0350	0.0298
			Overall Average	**0.0320**
			CV	**6%**

	Value	Critical (<30% of Target CV)	Result
CV	6%	7.5%	**Pass**

Table 30 Homogeneity Testing of Cr in Sample S1

Filter ID	Filter A Result (µg/filter)	Filter B Result (µg/filter)	Filter C Result (µg/filter)	Average Result (µg/filter)
Sample 1 (Filter 14A, 9B, 10C)	7.2	6.3	4.7	6.1
Sample 2 (Filter 25A, 18B, 13C)	5.5	9.2	5.6	6.8
Sample 3 (Filter 24A, 2B, 20C)	5.6	7.5	5.9	6.3
Sample 4 (Filter 19A, 25B, 11C)	6.1	7.2	5.2	6.2
Sample 5 (Filter 5A, 13B, 7C)	5.3	7.7	7.5	6.9
Sample 6 (Filter 3A, 22B, 14C)	4.9	5.7	6.8	5.8
			Overall Average	**6.3**
			CV	**7%**

	Value	Critical (<30% of Target CV)	Result
CV	7%	7.5%	**Pass**

Table 31 Homogeneity Testing of Cu in Sample S1

Filter ID	Filter A Result (µg/filter)	Filter B Result (µg/filter)	Filter C Result (µg/filter)	Average Result (µg/filter)
Sample 1 (Filter 14A, 9B, 10C)	4.44	4.00	3.10	3.85
Sample 2 (Filter 25A, 18B, 13C)	3.60	5.25	3.60	4.15
Sample 3 (Filter 24A, 2B, 20C)	3.60	4.62	3.62	3.95
Sample 4 (Filter 19A, 25B, 11C)	3.81	4.44	3.35	3.87
Sample 5 (Filter 5A, 13B, 7C)	3.44	5.00	4.71	4.38
Sample 6 (Filter 3A, 22B, 14C)	3.17	3.70	4.40	3.76
			Overall Average	**3.99**
			CV	**6%**

	Value	Critical (<30% of Target CV)	Result
CV	6%	7.5%	**Pass**

Table 32 Homogeneity Testing of Fe in Sample S1

Filter ID	Filter A Result (µg/filter)	Filter B Result (µg/filter)	Filter C Result (µg/filter)	Average Result (µg/filter)
Sample 1 (Filter 14A, 9B, 10C)	224	260	200	228
Sample 2 (Filter 25A, 18B, 13C)	230	273	230	244
Sample 3 (Filter 24A, 2B, 20C)	230	238	189	219
Sample 4 (Filter 19A, 25B, 11C)	196	231	175	201
Sample 5 (Filter 5A, 13B, 7C)	168	330	238	245
Sample 6 (Filter 3A, 22B, 14C)	161	240	280	227
			Overall Average	**227**
			CV	**7%**

	Value	Critical (<30% of Target CV)	Result
CV	7%	7.5%	**Pass**

Table 33 Homogeneity Testing of Hg in Sample S1

Filter ID	Filter A Result (µg/filter)	Filter B Result (µg/filter)	Filter C Result (µg/filter)	Average Result (µg/filter)
Sample 1 (Filter 14A, 9B, 10C)	0.343	0.320	0.270	0.311
Sample 2 (Filter 25A, 18B, 13C)	0.310	0.412	0.310	0.344
Sample 3 (Filter 24A, 2B, 20C)	0.300	0.382	0.314	0.332
Sample 4 (Filter 19A, 25B, 11C)	0.333	0.333	0.275	0.314
Sample 5 (Filter 5A, 13B, 7C)	0.294	0.360	0.382	0.346
Sample 6 (Filter 3A, 22B, 14C)	0.265	0.300	0.350	0.305
			Overall Average	**0.325**
			CV	**5%**

	Value	Critical (<30% of Target CV)	Result
CV	5%	7.5%	**Pass**

Table 34 Homogeneity Testing of Mn in Sample S1

Filter ID	Filter A Result (µg/filter)	Filter B Result (µg/filter)	Filter C Result (µg/filter)	Average Result (µg/filter)
Sample 1 (Filter 14A, 9B, 10C)	1.28	1.10	0.82	1.07
Sample 2 (Filter 25A, 18B, 13C)	0.96	1.46	0.96	1.13
Sample 3 (Filter 24A, 2B, 20C)	0.97	1.28	1.09	1.11
Sample 4 (Filter 19A, 25B, 11C)	1.00	1.28	1.00	1.09
Sample 5 (Filter 5A, 13B, 7C)	0.91	1.30	1.28	1.16
Sample 6 (Filter 3A, 22B, 14C)	0.91	0.97	1.20	1.03
			Overall Average	**1.10**
			CV	**4%**

	Value	Critical (<30% of Target CV)	Result
CV	4%	7.5%	**Pass**

Table 35 Homogeneity Testing of Ni in Sample S1

Filter ID	Filter A Result (µg/filter)	Filter B Result (µg/filter)	Filter C Result (µg/filter)	Average Result (µg/filter)
Sample 1 (Filter 14A, 9B, 10C)	1.90	1.70	1.30	1.63
Sample 2 (Filter 25A, 18B, 13C)	1.50	2.24	1.50	1.75
Sample 3 (Filter 24A, 2B, 20C)	1.60	1.90	1.55	1.68
Sample 4 (Filter 19A, 25B, 11C)	1.55	1.90	1.47	1.64
Sample 5 (Filter 5A, 13B, 7C)	1.47	2.20	1.90	1.86
Sample 6 (Filter 3A, 22B, 14C)	1.38	1.60	1.80	1.59
			Overall Average	**1.69**
			CV	**6%**

	Value	Critical (<30% of Target CV)	Result
CV	6%	7.5%	**Pass**

Table 36 Homogeneity Testing of P in Sample S1

Filter ID	Filter A Result (µg/filter)	Filter B Result (µg/filter)	Filter C Result (µg/filter)	Average Result (µg/filter)
Sample 1 (Filter 14A, 9B, 10C)	76	75	64	72
Sample 2 (Filter 25A, 18B, 13C)	71	99	79	83
Sample 3 (Filter 24A, 2B, 20C)	72	74	62	70
Sample 4 (Filter 19A, 25B, 11C)	62	84	63	70
Sample 5 (Filter 5A, 13B, 7C)	51	94	76	74
Sample 6 (Filter 3A, 22B, 14C)	52	79	77	69
			Overall Average	**73**
			CV	**7%**

	Value	Critical (<30% of Target CV)	Result
CV	7%	7.5%	**Pass**

Table 37 Homogeneity Testing of Pb in Sample S1

Filter ID	Filter A Result (µg/filter)	Filter B Result (µg/filter)	Filter C Result (µg/filter)	Average Result (µg/filter)
Sample 1 (Filter 14A, 9B, 10C)	4.30	3.60	2.90	3.60
Sample 2 (Filter 25A, 18B, 13C)	3.30	5.10	3.40	3.93
Sample 3 (Filter 24A, 2B, 20C)	3.30	4.60	3.60	3.83
Sample 4 (Filter 19A, 25B, 11C)	3.80	4.30	3.30	3.80
Sample 5 (Filter 5A, 13B, 7C)	3.40	4.40	4.50	4.10
Sample 6 (Filter 3A, 22B, 14C)	3.10	3.40	4.00	3.50
			Overall Average	**3.79**
			CV	**6%**

	Value	Critical (<30% of Target CV)	Result
CV	6%	7.5%	**Pass**

Table 38 Homogeneity Testing of U in Sample S1

Filter ID	Filter A Result (µg/filter)	Filter B Result (µg/filter)	Filter C Result (µg/filter)	Average Result (µg/filter)
Sample 1 (Filter 14A, 9B, 10C)	0.0120	0.0100	0.0080	0.0100
Sample 2 (Filter 25A, 18B, 13C)	0.0090	0.0140	0.0090	0.0107
Sample 3 (Filter 24A, 2B, 20C)	0.0090	0.0130	0.0110	0.0110
Sample 4 (Filter 19A, 25B, 11C)	0.0110	0.0120	0.0080	0.0103
Sample 5 (Filter 5A, 13B, 7C)	0.0090	0.0120	0.0130	0.0113
Sample 6 (Filter 3A, 22B, 14C)	0.0080	0.0100	0.0110	0.0097
			Overall Average	**0.0105**
			CV	**6%**

	Value	Critical (<30% of Target CV)	Result
CV	6%	7.5%	**Pass**

Table 39 Homogeneity Testing of V in Sample S1

Filter ID	Filter A Result (µg/filter)	Filter B Result (µg/filter)	Filter C Result (µg/filter)	Average Result (µg/filter)
Sample 1 (Filter 14A, 9B, 10C)	3.57	2.90	2.20	2.89
Sample 2 (Filter 25A, 18B, 13C)	2.60	4.36	2.60	3.19
Sample 3 (Filter 24A, 2B, 20C)	2.60	3.86	2.97	3.14
Sample 4 (Filter 19A, 25B, 11C)	3.07	3.57	2.67	3.10
Sample 5 (Filter 5A, 13B, 7C)	2.67	3.50	3.76	3.31
Sample 6 (Filter 3A, 22B, 14C)	2.48	2.60	3.10	2.73
			Overall Average	**3.06**
			CV	**7%**

	Value	Critical (<30% of Target CV)	Result
CV	7%	7.5%	**Pass**

Table 40 Homogeneity Testing of Zn in Sample S1

Filter ID	Filter A Result (µg/filter)	Filter B Result (µg/filter)	Filter C Result (µg/filter)	Average Result (µg/filter)
Sample 1 (Filter 14A, 9B, 10C)	1.67	1.40	1.10	1.39
Sample 2 (Filter 25A, 18B, 13C)	1.20	1.86	1.20	1.42
Sample 3 (Filter 24A, 2B, 20C)	1.20	1.58	1.30	1.36
Sample 4 (Filter 19A, 25B, 11C)	1.40	1.58	1.21	1.40
Sample 5 (Filter 5A, 13B, 7C)	1.30	1.60	1.58	1.49
Sample 6 (Filter 3A, 22B, 14C)	1.30	1.30	1.60	1.40
			Overall Average	**1.41**
			CV	**3%**

	Value	Critical (<30% of Target CV)	Result
CV	3%	7.5%	**Pass**

Sample Analysis for Acid Extractable Elements in Air Filters

The entire filter was carefully placed into a 50 mL graduated polypropylene centrifuge tube. The sample was digested using 3 mL of concentrated nitric acid and 1 mL of concentrated hydrochloric acid on a hot block at 100°C ± 5°C for 2 hours. After digestion, each sample was diluted to 40 mL with Milli-Q water and then further diluted as necessary.

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. A summary of the instrument conditions used and the ion/wavelength monitored for each analyte is given in Table 41.

Table 41 Instrumental Technique used for Acid Extractable Elements

Analyte	Instrument	Internal Standard	Reaction/ Collision Cell (if applicable)	Cell Mode/Gas (if applicable)	S1Final Dilution Factor	Ion (m/z)/ Wavelength (nm)
Ag	ICP-MS	Rh	ORS	He	200	107 m/z
Al	ICP-MS	Rh	NA	NA	200	27 m/z
As	ICP-MS	Rh	ORS	He	200	75 m/z
Be	ICP-MS	Rh	NA	NA	200	9 m/z
Cd	ICP-MS	Rh	NA	NA	200	111 m/z
Co	ICP-MS	Rh	ORS	He	200	59 m/z
Cr	ICP-MS	Rh	ORS	He	200	52 m/z
Cu	ICP-MS	Rh	ORS	He	200	65 m/z
Fe	ICP-MS	Rh	NA	NA	200	56 m/z
Hg	ICP-MS	Rh	NA	NA	200	201 m/z
Mn	ICP-MS	Rh	ORS	He	200	55 m/z
Ni	ICP-MS	Rh	ORS	He	200	60 m/z

Table 42 Instrumental Technique used for Acid Extractable Elements

Analyte	Instrument	Internal Standard	Reaction/ Collision Cell (if applicable)	Cell Mode/Gas (if applicable)	S1Final Dilution Factor	Ion (m/z)/ Wavelength (nm)
P	ICP-OES	Rh	NA	NA	200	213.618 nm
Pb	ICP-MS	Ir	NA	NA	200	Average of 206, 207, 208 m/z
Se	ICP-MS	Rh	ORS	HEHe	200	78 m/z
Sn	ICP-MS	Rh	NA	NA	200	118 m/z
U	ICP-MS	Ir	NA	NA	200	238 m/z
V	ICP-MS	Rh	ORS	He	200	51 m/z
Zn	ICP-MS	Rh	ORS	He	200	66 m/z

APPENDIX 2 – HANDLING AND TRANSPORT STABILITY

A stability study was carried out to simulate conditions encountered by the study samples during handling and transport. Six filters ('trip' samples) were sent to NMI Victoria and returned to Sydney. The same packing procedure was used for the 'trip samples' as for the test samples sent to participants. The trip samples were analysed upon their return using the same procedure as that used for homogeneity testing.

A student t-test was used to assess whether there is a significant difference between the results from "trip" samples and from "control" samples (those selected for homogeneity analyses). At a significance level of α=0.05 (95% confidence interval), no significant change in concentration during handling and transport was observed for any of the tests in Sample S1 (Table 43).

Table 43 Handling and Transport Stability Study Results

Analyte	t-score	P	Is the change in analyte concentration for the trip samples significantly different from the analyte concentration in homogeneity samples at a 95% confidence interval? (P<0.05)
Ag	1.19	0.26	Pass
Al	0.18	0.86	Pass
As	0.82	0.43	Pass
Be	0.18	0.86	Pass
Cd	0.63	0.54	Pass
Co	0.077	0.94	Pass
Cr	0.40	0.69	Pass
Cu	0.51	0.62	Pass
Fe	0.76	0.46	Pass
Hg	1.0	0.33	Pass
Mn	-0.034	0.97	Pass
Ni	-0.31	0.38	Pass
P	0.09	0.93	Pass
Pb	0.60	0.56	Pass
Se	0.65	0.53	Pass
Sn	0.059	0.95	Pass
U	0.59	0.57	Pass
V	0.47	0.65	Pass
Zn	0.36	0.72	Pass

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 interlaboratory comparisons – Annex C'[5] the uncertainty was estimated as:

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

where:

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

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

A worked example is set out below in Table 44.

Table 44 Uncertainty of Assigned Value for Cr in Sample S1

No. results (p)	11
Robust Average	5.57 µg/filter
$S_{rob\ av}$	1.30 µg/filter
$u_{rob\ av}$	0.49 µg/filter
k	2
$U_{rob\ av}$	0.98 µg/filter

The assigned value for **Cr** in Sample S1 is **5.57 ± 0.98 µg/filter**

z-Score and E_n-score

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

A worked example is set out below in Table 45.

Table 45 z-Score and E_n-score for Cr Result Reported by Laboratory 6 in S1

Cr Result µg/filter	Assigned Value µg/filter	Set Target Standard Deviation	z-Score	E_n-Score
6.89 ± 0.80	5.57 ± 0.98	25% as CV or 0.25x5.57 = =1.39 µg/filter	$z = \frac{(6.89 - 5.57)}{1.39}$ z = 0.95	$En = \frac{(6.89 - 5.57)}{\sqrt{0.80^2 + 0.98^2}}$ E_n=1.04

APPENDIX 4 – ACRONYMS AND ABBREVIATIONS

APHA	American Public Health Association
A.V.	Assigned Value
CRI	Collision Reaction Interface
CRM	Certified Reference Material
CV	Coefficient of Variation
CVAAS	Cold Vapour Atomic Absorption Spectrometry
HEHe	High Energy He mode
H.V.	Homogeneity Value
ICP-MS	Quadrupole - Inductively Coupled Plasma - Mass Spectrometry
ICP-MS/MS	Quadrupole - Inductively Coupled Plasma - Tandem Mass Spectrometry
ICP-OES-AV	Inductively Coupled Plasma - Optical Emission Spectrometry- axial view
ICP-OES-RV	Inductively Coupled Plasma - Optical Emission Spectrometry- radial view
Max	Maximum value in a set of results
Md	Median
Min	Minimum value in a set of results
NMI	National Measurement Institute (of Australia)
NR	Not Reported
NT	Not Tested
ORS	Octopole Reaction System
PCV	Performance Coefficient of Variation
RA	Robust Average
RM	Reference Material
Robust CV	Robust Coefficient of Variation
Robust SD	Robust Standard Deviation
S.V.	Spiked value or formulated concentration of a PT sample
SS	Spiked Sample
SI	The International System of Units
s^2_{sam}	Sampling variance
s_a/σ	Analytical standard deviation divided by the target standard deviation
Target SD	Target standard deviation
σ	Target standard deviation
UC	Universal Cell
USN	Ultrasonic Nebuliser

APPENDIX 5 – PARTICIPANTS RESULTS

Table 46 Ag Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	0.087	0.017	0.087	0.017	0.085	0.017	0.086	0.017
2	NR	NR	0.074	0.005	0.075	0.005	0.0745	0.005
3	<0.5	NR	<0.5	NR	<0.5	NR	<0.5	NR
4	0.042	0.006	0.024	0.004	0.029	0.005	0.031	0.005
5	<0.5	NR	<0.5	NR	<0.5	NR	<0.5	NR
6	<0.1	NR	<0.1	NR	<0.1	NR	<0.1	NR
7	0.1	0.05	0.1	0.05	0.1	0.05	0.1	0.05
8	<0.5	NR	<0.5	NR	<0.5	NR	<0.05	NR
9	0.052	NR	0.055	NR	0.059	NR	0.055	NR
10	0.05	0.01	0.05	0.01	0.05	0.01	0.05	0.01
11	NT	NT	NT	NT	NT	NT	NT	NT

Table 47 Al Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	180	30	160	30	170	30	170	30
2	NR	NR	77	3.8	87	4	82	4.1
3	98	30	104	30	98	30	100	30
4	173	20	119	15	138	18	143	18
5	91	30	104	30	100	30	98	30
6	158	15	148	14	143	14	149	15
7	80	50	91	57	91	57	87	54
8	58	30	81	30	72	30	70	30
9	68	NR	76	NR	84	NR	76	NR
10	84.9	8.49	83.1	8.31	85.7	8.57	84.6	8.46
11	NT	NT	NT	NT	NT	NT	NT	NT

Table 48 As Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	7.4	1.5	7.4	1.5	7.1	1.5	7.3	1.5
2	NR	NR	4.9	1	5.1	1	5	1
3	6.0	2	6.8	2	6.5	3	6.4	2
4	5.08	0.8	3.69	0.6	4.08	0.7	4.28	0.7
5	5	2	5	2	5	2	5	2
6	6.78	0.80	6.20	0.80	6.00	0.80	6.32	0.80
7	5.6	1.4	7.0	1.8	7.3	1.8	6.5	1.6
8	3	2	5	2	4	2	4	2
9	4.3	NR	5.0	NR	4.7	NR	4.7	NR
10	3.71	0.371	3.58	0.358	3.85	0.385	3.71	0.371
11	5.9	1.5	4.6	1.2	3.9	0.98	4.8	1.2

Table 49 Be Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	<0.05	NR	<0.05	NR	<0.05	NR	<0.05	NR
2	NR	NR	0.006	0.005	0.006	0.005	0.006	0.005
3	<0.01	NR	<0.01	NR	<0.01	NR	<0.01	NR
4	0.003	0.001	0.003	0.001	0.004	0.001	0.003	0.001
5	<0.01	NR	<0.01	NR	<0.01	NR	<0.01	NR
6	<0.01	NR	<0.01	NR	<0.01	NR	<0.01	NR
7	0.003	0.00015	0.006	0.0003	0.006	0.0003	0.005	0.0003
8	<0.01	NR	<0.01	NR	<0.01	NR	<0.01	NR
9	<0.005	NR	<0.005	NR	0.005	NR	0.005	NR
10	<0.02	0.005	<0.02	0.005	<0.02	0.005	<0.02	0.005
11	NT	NT	NT	NT	NT	NT	NT	NT

Table 50 Cd Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	0.52	0.10	0.52	0.10	0.48	0.10	0.51	0.10
2	NR	NR	0.35	0.05	0.35	0.05	0.35	0.05
3	0.4	0.3	0.5	0.3	0.5	0.3	0.4	0.3
4	0.44	0.06	0.31	0.05	0.33	0.05	0.36	0.05
5	0.4	0.2	0.4	0.2	0.3	0.2	0.4	0.2
6	0.495	0.06	0.442	0.06	0.433	0.06	0.457	0.06
7	0.38	0.019	0.45	0.023	0.47	0.024	0.43	0.022
8	0.3	0.2	0.4	0.2	0.3	0.2	0.3	0.2
9	0.33	NR	0.35	NR	0.34	NR	0.34	NR
10	0.292	0.029	0.295	0.030	0.317	0.032	0.301	0.030
11	0.45	0.22	0.32	0.16	0.31	0.15	0.36	0.17

Table 51 Co Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	<0.05	NR	<0.05	NR	<0.05	NR	<0.05	NR
2	NR	NR	0.03	0.01	0.035	0.01	0.035	0.01
3	<0.5	NR	<0.5	NR	<0.5	NR	<0.5	NR
4	0.036	0.005	0.040	0.005	0.028	0.004	0.035	0.005
5	<0.5	NR	<0.5	NR	<0.5	NR	<0.5	NR
6	0.043	0.01	0.049	0.01	0.040	0.01	0.044	0.01
7	0.03	0.003	0.035	0.004	0.035	0.004	0.033	0.003
8	<0.5	NR	<0.5	NR	<0.5	NR	<0.5	NR
9	0.024	NR	0.021	NR	0.025	NR	0.023	NR
10	0.024	0.005	0.024	0.005	0.025	0.005	0.024	0.005
11	NT	NT	NT	NT	NT	NT	NT	NT

Table 52 Cr Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	7.7	1.5	7.7	1.5	7.4	1.5	7.6	1.5
2	NR	NR	5.5	0.27	5.6	0.3	5.5	0.2775
3	6.1	2	6.9	2	6.5	2	6.5	2
4	5.44	0.7	3.83	0.6	4.34	0.6	4.54	0.6
5	5.4	2	5.2	2	5.2	2	5.3	2
6	7.30	0.80	6.90	0.80	6.46	0.80	6.89	0.80
7	5.6	0.70	7.0	0.88	7.2	0.90	6.6	0.83
8	4	2	5.4	2	4	2	4	2
9	4.6	NR	5.1	NR	5.0	NR	4.9	NR
10	4.33	0.433	4.23	0.423	4.48	0.448	4.35	0.435
11	5.8	3.4	5.0	2.9	4.8	2.8	5.2	3.0

Table 53 Cu Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	5.1	1.0	5.2	1.0	5.0	1.0	5.1	1.0
2	NR	NR	3.2	0.16	3.5	0.2	3.4	0.1675
3	3.9	1	4.9	1	4.1	2	4.3	1
4	3.59	0.6	2.67	0.4	2.94	0.4	3.07	0.4
5	4	2	3	2	3	2	3.4	2
6	4.82	0.60	4.38	0.60	4.26	0.60	4.49	0.60
7	3.5	0.18	3.8	0.19	4.0	0.20	3.8	0.19
8	3	1	4	1	3	1	3	1
9	2.9	NR	3.2	NR	3.2	NR	3.1	NR
10	2.54	0.254	2.54	0.254	2.70	0.270	2.59	0.259
11	4.3	2.2	3.7	1.9	3.4	1.8	3.8	2.0

Table 54 Fe Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	340	70	330	70	320	70	330	70
2	NR	NR	209	10.43	215	11	215	10.75
3	295	90	307	90	295	90	299	90
4	259	30	182	20	216	25	219	25
5	240	90	260	90	250	90	250	90
6	324	35	295	35	289	35	303	35
7	220	55	270	68	280	70	260	65
8	190	90	260	90	240	90	230	90
9	196	NR	210	NR	220	NR	210	NR
10	195	19.5	190	19.0	204	20.4	196	19.6
11	160	42	130	34	130	34	140	37

Table 55 Hg Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	0.39	0.08	0.38	0.08	0.38	0.08	0.38	0.08
2	NR	NR	0.33	0.05	0.35	0.05	0.345	0.05
3	0.33	0.2	0.35	0.2	0.34	0.2	0.34	0.2
4	0.29	0.05	0.20	0.04	0.23	0.04	0.24	0.04
5	0.29	0.1	0.32	0.1	0.36	0.1	0.32	0.1
6	0.337	0.04	0.320	0.04	0.305	0.04	0.321	0.04
7	0.24	0.003	0.34	0.004	0.36	0.005	0.31	0.004
8	0.2	0.1	0.31	0.1	0.26	0.1	0.26	0.1
9	0.24	NR	0.26	NR	0.26	NR	0.25	NR
10	0.245	0.025	0.244	0.024	0.244	0.024	0.244	0.024
11	NT	NT	NT	NT	NT	NT	NT	NT

Table 56 Mn Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	1.5	0.3	1.4	0.3	1.4	0.3	1.4	0.3
2	NR	NR	1.01	0.05	1.00	0.05	1	0.05
3	1.1	0.3	1.2	0.4	1.1	0.3	1.1	0.5
4	1.28	0.3	0.93	0.2	1.11	0.2	1.11	0.2
5	1	0.4	1	0.4	1	0.4	1.0	0.4
6	1.41	0.15	1.30	0.15	1.25	0.15	1.32	0.15
7	1.0	0.1	1.1	0.11	1.2	0.12	1.1	0.11
8	1	0.4	1	0.4	1	0.4	1	0.4
9	0.84	NR	0.94	NR	0.97	NR	0.92	NR
10	0.936	0.094	0.931	0.093	1.00	0.100	0.956	0.096
11	<2.0	NR	<2.0	NR	<2.0	NR	<2.0	NR

Table 57 Ni Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	2.1	0.4	2.2	0.4	2.0	0.4	2.1	0.4
2	NR	NR	1.4	0.5	1.5	0.5	1.8	0.5
3	1.7	0.5	1.8	0.6	1.8	0.5	1.7	0.5
4	1.56	0.3	1.32	0.2	1.35	0.2	1.41	0.2
5	2	1	1	1	1	1	1.5	1
6	2.05	0.20	1.89	0.20	1.86	0.20	1.93	0.20
7	1.6	0.4	2	0.5	1.9	0.48	1.8	0.45
8	1	0.7	2	0.7	1	0.7	1	0.7
9	1.25	NR	1.35	NR	1.34	NR	1.31	NR
10	1.22	0.122	1.26	0.126	1.31	0.131	1.26	0.126
11	1.5	0.64	1.3	0.56	1.2	0.51	1.4	0.60

Table 58 P Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	82	17	94	17	83	17	86	17
2	NR	NR	59	3	58	3	59	6
3	73	30	86	30	83	30	81	30
4	64.7	8.0	51.2	6.0	74.9	8.0	63.6	8.0
5	55	30	65	30	66	30	62	30
6	89.5	17	78.9	17	72.3	17	80.2	17
7	62	78	80	100	82	100	75	94
8	62	30	79	30	71	30	71	30
9	54	NR	65	NR	69	NR	63	NR
10	46.5	4.65	51.0	5.10	57.0	5.70	51.5	5.15
11	NT	NT	NT	NT	NT	NT	NT	NT

Table 59 Pb Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	5.2	1.0	4.9	1.0	4.8	1.0	5.0	1.0
2	NR	NR	3.2	0.5	3.4	0.5	3.3	0.5
3	3.7	1	4.1	2	3.9	1	3.9	1
4	3.50	0.5	2.48	0.4	2.86	0.4	2.95	0.4
5	4	2	3	2	3	2	3.4	2
6	4.76	0.50	4.39	0.50	4.21	0.50	4.45	0.50
7	3.5	0.44	3.8	0.48	3.9	0.49	3.7	0.46
8	3	1	4	1	3	1	3	1
9	2.9	NR	3.2	NR	3.3	NR	3.1	NR
10	2.79	0.279	2.75	0.275	2.95	0.295	2.83	0.283
11	4.9	1.5	3.7	1.2	3.6	1.1	4.1	1.3

Table 60 Se Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	<0.2	NR	<0.2	NR	<0.2	NR	<0.2	NR
2	NR	NR	<0.02	0.02	<0.02	0.02	<0.02	0.02
3	<0.5	NR	<0.5	NR	<0.5	NR	<0.5	NR
4	0.084	0.01	0.078	0.01	0.083	0.01	0.081	0.01
5	<0.5	NR	<0.5	NR	0.5	NR	<0.5	NR
6	<0.05	NR	<0.05	NR	<0.05	NR	<0.05	NR
7	0.12	0.12	0.24	0.24	0.30	0.3	0.22	0.22
8	<0.5	NR	<0.5	NR	<0.5	NR	<0.5	NR
9	<0.05	NR	<0.05	NR	<0.05	NR	<0.05	NR
10	0.012	0.007	0.011	0.007	0.013	0.007	0.012	0.007
11	NT	NT	NT	NT	NT	NT	NT	NT

Table 61 Sn Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	0.19	0.04	0.20	0.04	0.17	0.04	0.19	0.037
2	NR	NR	0.21	0.1	0.2	0.1	0.2	0.1
3	<2	NR	<2	NR	<2	NR	<2	NR
4	0.42	0.06	0.31	0.05	0.30	0.05	0.34	0.05
5	<2	NR	<2	NR	<2	NR	<2	NR
6	0.233	0.04	0.203	0.04	0.206	0.04	0.214	0.04
7	0.40	0.02	0.37	0.19	0.43	0.22	0.40	0.20
8	<2	NR	<2	NR	<2	NR	<2	NR
9	0.15	NR	0.15	NR	0.16	NR	0.15	NR
10	0.127	0.025	0.121	0.024	0.134	0.027	0.127	0.025
11	NT	NT	NT	NT	NT	NT	NT	NT

Table 62 U Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	<0.05	NR	<0.05	NR	<0.05	NR	<0.05	NR
2	NR	NR	<0.05	0.05	<0.05	0.05	<0.05	0.05
3	<0.5	NR	<0.5	NR	<0.5	NR	<0.5	NR
4	0.009	0.002	0.006	0.001	0.007	0.001	0.007	0.001
5	<0.5	NR	<0.5	NR	<0.5	NR	<0.5	NR
6	0.014	0.002	0.013	0.002	0.012	0.002	0.013	0.002
7	0.009	0.0002	0.011	0.0002	0.011	0.0002	0.01	0.0003
8	<0.5	NR	<0.5	NR	<0.5	NR	<0.5	NR
9	0.0078	NR	0.0086	NR	0.0097	NR	0.0087	NR
10	0.009	0.007	0.009	0.007	0.012	0.007	0.010	0.007
11	NT	NT	NT	NT	NT	NT	NT	NT

Table 63 V Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	3.8	0.7	3.7	0.7	3.6	0.7	3.7	0.7
2	NR	NR	2.5	0.13	2.5	0.13	2.5	0.07
3	3.0	1	3.3	1	3.1	1	3.1	1
4	2.43	0.4	1.76	0.3	1.98	0.4	2.06	0.4
5	3	1	2	1	2	1	2.5	1
6	3.52	0.44	3.23	0.44	3.08	0.44	3.28	0.44
7	2.5	0.63	3.1	0.78	3.3	0.41	3.0	0.19
8	2	0.8	2	0.8	2	0.8	2	0.8
9	2.1	NR	2.3	NR	2.3	NR	2.2	NR
10	1.89	0.189	1.81	0.181	1.95	0.195	1.88	0.188
11	NT	NT	NT	NT	NT	NT	NT	NT

Table 64 Zn Results in S1

Lab Code	S1A (µg/filter)		S1B (µg/filter)		S1C (µg/filter)		Average (µg/filter)	
	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty	Results	Uncertainty
1	1.9	0.4	1.8	0.4	1.8	0.4	1.8	0.4
2	NR	NR	1.3	0.06	1.5	0.08	1.4	0.07
3	<5	NR	<5	NR	<5	NR	<5	NR
4	1.43	0.2	1.12	0.2	1.29	0.2	1.28	0.2
5	<5	NR	<5	NR	<5	NR	<5	NR
6	1.90	0.20	1.70	0.20	1.82	0.20	1.81	0.20
7	1.7	0.43	1.7	0.43	1.7	0.43	1.7	0.43
8	<5	NR	<5	NR	<5	NR	<5	NR
9	1.02	NR	1.15	NR	1.14	NR	1.10	NR
10	0.978	0.098	0.990	0.099	1.02	0.102	0.996	0.099
11	1.2	0.41	1.1	0.37	1.0	0.34	1.1	0.37

APPENDIX 6 - INSTRUMENT DETAILS

Table 65 Instrument Conditions Ag

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	200	Ag107
2						
3	ICP-MS	Rh			500	107
4	ICP-MS	Rh	NA	NA	1620	109
5	ICP-MS	Rh			500	107
6	ICP-MS	Rh 103	NA	He	100	107
7	GFAAS				50	
8	ICP-MS	In	ORS		250	107
9	ICP-MS	Rh	UC	He	50	109
10	ICP-MS	Rh	CRI		1	
11						

Table 66 Instrument Conditions Al

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV	Yttrium	NA		200	Al167.019
2						
3	ICP-OES-AV	Lu			50	396.152
4	ICP-MS	Sc	NA	NA	1620	27
5	ICP-OES-AV	Lu			50	396.152
6	ICP-OES-AV	Lu 219.556	ORS	NA	100	Al 237.312
7	ICP-OES-AV	Yb			50	396.152nm
8	ICP-OES-AV	Lu			25	396.152
9	ICP-MS	Sc	UC	He	50	27
10	ICP-MS	Sc	CRI		1	
11						

Table 67 Instrument Conditions As

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	200	As75
2						
3	ICP-MS	Rh	DRC	He	500	75
4	ICP-MS	Ge	UC	He	1620	75
5	ICP-MS	Ge	DRC	He	500	75
6	ICP-MS	Rh 103	ORS	He	100	75
7	ICP-OES-USN	Yb			50	188.98nm
8	ICP-MS	Ge	ORS	He	250	75
9	ICP-MS	Te	UC	He	50	75
10	ICP-MS	Rh	CRI	HeHe	1	
11	GFAAS				20	193.7

Table 68 Instrument Conditions Be

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	NA		200	Be9
2						
3	ICP-MS	Li			500	9
4	ICP-MS	Sc	NA	NA	1620	9
5	ICP-MS	Li6			500	9
6	ICP-MS	Sc 45	ORS	He	100	9
7	ICP-OES-USN	Yb			50	313.042nm
8	ICP-MS	Ge	ORS		250	9
9	ICP-MS	Sc	UC	He	50	9
10	ICP-MS	Sc	CRI		1	
11						

Table 69 Instrument Conditions Cd

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	200	Cd111
2						
3	ICP-MS	Rh	DRC	He	500	111
4	ICP-MS	Rh	NA	NA	1620	111
5	ICP-MS	In	DRC	He	500	111
6	ICP-MS	Rh 103	ORS	He	100	111
7	ICP-OES-USN	Yb			50	214.439nm
8	ICP-MS	In	ORS	He	250	111
9	ICP-MS	Rh	UC	He	50	111
10	ICP-MS	Rh	CRI	He	1	
11	GFAAS				20	228.8

Table 70 Instrument Conditions Co

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	200	Co59
2						
3	ICP-MS	Ge	DRC	He	500	59
4	ICP-MS	Ge	UC	He	1620	59
5	ICP-MS	Ge	DRC	He	500	59
6	ICP-MS	Rh 103	ORS	He	100	59
7	ICP-OES-USN	Yb			50	230.786nm
8	ICP-MS	Ge	ORS	He	250	59
9	ICP-MS	Ga	UC	He	50	59
10	ICP-MS	Rh	CRI	He	1	
11						

Table 71 Instrument Conditions Cr

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	200	Cr52
2						
3	ICP-MS	Ge	DRC	He	500	52
4	ICP-MS	Sc	UC	He	1620	52
5	ICP-MS	Ge	DRC	He	500	52
6	ICP-MS	Rh 103	ORS	He	100	52
7	ICP-OES-USN	Yb			50	267.716nm
8	ICP-MS	Ge	ORS	He	250	52
9	ICP-MS	Sc	UC	He	50	52
10	ICP-MS	Rh	CRI	He	1	
11	ICP-OES-AV				20	267.716

Table 72 Instrument Conditions Cu

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	200	Cu65
2						
3	ICP-MS	Ge	DRC	He	500	65
4	ICP-MS	Ge	UC	He	1620	63
5	ICP-MS	Ge	DRC	He	500	63
6	ICP-MS	Rh 103	ORS	He	100	63
7	ICP-OES-USN	Yb			50	327.395nm
8	ICP-MS	Ge	ORS	He	250	63
9	ICP-MS	Ga	UC	He	50	63
10	ICP-MS	Rh	CRI	He	1	
11	ICP-OES-AV				20	324.752

Table 73 Instrument Conditions Fe

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV	Yttrium	NA		200	Fe238.204
2						
3	ICP-OES-AV	Lu			50	238.204
4	ICP-MS	Sc	UC	He	1620	56
5	ICP-OES-AV	Lu			50	234.35
6	ICP-MS	Rh 103	ORS	He	100	56
7	ICP-OES-AV	Yb			50	238.204nm
8	ICP-OES-AV	Lu			25	234.35
9	ICP-MS	Sc	UC	He	50	56
10	ICP-MS	Sc	CRI	HeHe	1	
11	ICP-OES-RV				20	239.562

Table 74 Instrument Conditions Hg

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	200	Hg202
2						
3	CVAAS				250	253.7
4	ICP-MS	Ir	NA	NA	1620	201
5	CVAAS				500	253.7
6	ICP-MS	Ir 193	ORS	He	100	202
7	CVAAS	SnCl2			50	
8	CVAAS		ORS		250	
9	ICP-MS	Tb	UC	He	50	201
10	ICP-MS	Ir	CRI	He	1	
11						

Table 75 Instrument Conditions Mn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV	Yttrium	NA		200	Mn257.61
2						
3	ICP-MS	Ge	DRC	He	500	55
4	ICP-MS	Sc	UC	He	1620	55
5	ICP-MS	Ge	DRC	He	500	55
6	ICP-MS	Rh 103	ORS	He	100	55
7	ICP-OES-USN	Yb			50	260.568nm
8	ICP-MS	Ge	ORS	He	250	55
9	ICP-MS	Sc	UC	He	50	55
10	ICP-MS	Sc	CRI	He	1	
11	ICP-OES-RV				20	257.61

Table 76 Instrument Conditions Ni

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	200	Ni60
2						
3	ICP-MS	Ge	DRC	He	500	60
4	ICP-MS	Ge	UC	He	1620	60
5	ICP-MS	Ge	DRC	He	500	60
6	ICP-MS	Rh 103	ORS	He	100	60
7	ICP-OES-USN	Yb			50	231.604nm
8	ICP-MS	Ge	ORS	He	250	60
9	ICP-MS	Ga	UC	He	50	60
10	ICP-MS	Rh	CRI	He	1	
11	ICP-OES-AV				20	231.604

Table 77 Instrument Conditions P

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV	Yttrium	NA		200	P213.618
2						
3	ICP-OES-AV	Lu			50	213.618
4	ICP-MS	Sc	UC	He	1620	31
5	ICP-OES-AV	Lu			50	213.618
6	ICP-OES-AV	N/A	NA	NA	100	P185.878
7	ICP-OES-AV	Yb			50	177.434nm
8	ICP-OES-AV	Lu			25	213.618
9	ICP-MS	Sc	UC	He	50	31
10	ICP-OES-AV				1	
11						

Table 78 Instrument Conditions Pb

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	200	Pb207
2						
3	ICP-MS	Lu			500	208
4	ICP-MS	Ir	NA	NA	1620	206+207+208
5	ICP-MS	Lu			500	208
6	ICP-MS	Ir 193	ORS	He	100	208
7	ICP-OES-USN	Yb			50	220.353nm
8	ICP-MS	Lu	ORS		250	208
9	ICP-MS	Tb	UC	He	50	206, 207, 208
10	ICP-MS	Ir	CRI		1	
11	GFAAS				20	283.3

Table 79 Instrument Conditions Se

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	HEHe	200	Se78
2						
3	ICP-MS	Rh	DRC	H2	500	78
4	ICP-MS	Rh	NA	NA	1620	82
5	ICP-MS	Ge	DRC	He	500	78
6	ICP-MS	Rh 103	ORS	He	100	78
7	ICP-OES-USN	Yb			50	196.026nm
8	ICP-MS	Ge	ORS	H2	250	78
9	ICP-MS	Te	UC	He	50	82
10	ICP-MS	Rh	CRI	HeHe	1	
11						

Table 80 Instrument Conditions Sn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	200	Sn118
2						
3	ICP-MS	Rh	DRC	He	500	118
4	ICP-MS	Rh	NA	NA	1620	118
5	ICP-MS	In	DRC	He	500	118
6	ICP-MS	Rh 103	ORS	He	100	118
7	ICP-OES-USN	Yb			50	189.925nm
8	ICP-MS	In	ORS	He	250	118
9	ICP-MS	Rh	UC	He	50	120
10	ICP-MS	Rh	CRI	He	1	
11						

Table 81 Instrument Conditions U

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	200	U238
2						
3	ICP-MS	Lu			500	238
4	ICP-MS	Ir	NA	NA	1620	238
5	ICP-MS	Lu			500	238
6	ICP-MS	Ir 193	ORS	He	100	238
7	ICP-MS/MS	Ir	ORS		500	238m/z
8	ICP-MS	Lu	ORS		250	238
9	ICP-MS	Tb	UC	He	50	238
10	ICP-MS	Ir	CRI		1	
11						

Table 82 Instrument Conditions V

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-MS	Rh	ORS	He	200	V51
2						
3	ICP-MS	Ge	DRC	He	500	51
4	ICP-MS	Sc	UC	He	1620	51
5	ICP-MS	Ge	DRC	He	500	51
6	ICP-OES-AV	Rh 103	NA	NA	100	V292.401
7	ICP-OES-AV	Yb			50	292.401nm
8	ICP-MS	Ge	ORS	He	250	51
9	ICP-MS	Sc	UC	He	50	51
10	ICP-MS	Sc	CRI	He	1	
11						

Table 83 Instrument Conditions Zn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	ICP-OES-AV	Yttrium	NA		200	Zn213.857
2						
3	ICP-MS	Ge	DRC	He	500	66
4	ICP-MS	Ge	UC	He	1620	66
5	ICP-MS	Ge	DRC	He	500	66
6	ICP-MS	Rh 103	ORS	He	100	66
7	ICP-OES-AV	Yb			50	213.857nm
8	ICP-MS	Ge	ORS	He	250	66
9	ICP-MS	Te	UC	He	50	66
10	ICP-MS	Rh	CRI	He	1	
11	ICP-OES-RV				20	206.2

END OF REPORT