Australian Government
Department of Industry, Science and Resources

National Measurement Institute

Proficiency Test Final Report AQA 24-21 Metals in Paint

April 2025

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ACKNOWLEDGMENTS

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

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

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

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SUMMARY

This report presents the results of the proficiency test AQA 24-21 Metals in Paint. The study covers the measurement of acid extractable elements: Cd, Cr, Cu, Hg, Li, Mn, Ni, Pb and Zn.

The sample set consisted of one dried paint sample.

Twelve laboratories registered to participate, and eleven submitted results.

The assigned values were the robust average of participants' results. The associated uncertainties were evaluated 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 capabilities to measure acid extractable elements in paint;

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

Of 72 z-scores, 71 (99%) were acceptable with $|z| \leq 2.0$.

Of 72 E_n-scores, 63 (88%) were acceptable with $| E_n | < 1.0$.

Laboratories 3, **5**, **7**, **9**, **10** and **11** returned the highest number of acceptable z scores (8 out of 8 reported).

Laboratories 7, **10** and **11** returned the highest number of acceptable E_n-scores (8 out of 8 reported).

ii. evaluate the laboratories 'methods used in determination of acid extractable elements in paint;

Although participants used a wide variety of methods, all scored results were compatible except for one.

Mercury challenged most participants' analytical techniques, only 6 laboratories reported results for this test

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

Of 78 numerical results, 67 (86%) were reported with an expanded measurement uncertainty. The magnitude of the reported expanded uncertainties was within the range 2.9% to 27% of the reported value.

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

The test samples of this study were checked for homogeneity and are well characterised, both by in-house testing and from the results of the proficiency round. Surplus test samples are available for purchase from NMI.

1 INTRODUCTION

1.1 NMI Proficiency Testing Program

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

Proficiency testing (PT) "is evaluation of participant performance against pre-established criteria by means of inter-laboratory comparison."[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, paint and pharmaceuticals;
- pesticide residues in fruit and vegetables, soil and water;
- petroleum hydrocarbons in soil and water;
- PFAS in water, soil, biosolid, biota and food;
- chlorophyll a in water; and
- controlled drug assay, drugs in wipes and clandestine laboratory.

AQA 24-21 is the first NMI proficiency study of inorganic analytes in paint.

1.2 Study Aims

The aims of the study were to:

- compare the performance of participant laboratories and assess their capabilities to measure acid extractable elements in paint;
- evaluate the laboratories' methods used in determination of acid extractable elements in paint;
- develop the practical application of measurement uncertainty; and
- produce materials that can be used in method validation and as control samples.

1.3 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 17043:2023 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.

2 STUDY INFORMATION

2.1 Selection of Matrices and Inorganic Analytes

The 9 tests were selected from those suggested in the Expressions of Interest Letter for an NMI Special Study of inorganic analytes in paint.

2.2 Participation

Twelve laboratories participated and eleven submitted results.

The timetable of the study was:

Invitation issued:	11 November 2024
Samples dispatched:	2 December 2024
Results due:	20 January 2025
Interim report issued:	22 January 2025
Preliminary report issued:	23 January 2025

2.3 Test Material Specification

One sample was provided for analysis:

Sample S1 was 2 g of dried paint.

2.4 Laboratory Code

All participant laboratories were assigned a confidential code number.

2.5 Sample Preparation, Analysis and Homogeneity Testing

A full homogeneity test was conducted for all acid extractable elements in S1.

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

2.6 Stability of Analytes

No stability study was carried out in the present study. Participants results gave no reason to question sample stability.

2.7 Sample Storage, Dispatch and Receipt

The samples were dispatched by courier on 2 December 2024.

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

An Excel spreadsheet for the electronic reporting of results was e-mailed to participants.

2.8 Instructions to Participants

Participants were instructed as follows:

- Quantitatively analyse the samples using your normal test method.
- Report results for acid extractable elements on as received basis in units of mg/kg.
- Report results as you would report to a client. For each analyte, report the expanded measurement uncertainty.
- Please send us all the requested details regarding the test method.
- Return the completed results sheet by email by 20 January 2025.

SAMPLE S1 Dried Paint	
Test Acid Extractable	**Evaluated Values [mg/kg]**
Cd	5-200
Cr	5-200
Cu	5-200
Hg	0.5-20
Li	5-200
Mn	5-200
Ni	5-200
Pb	5-200
Zn	5-200

2.9 Interim and Preliminary Reports

An interim report was emailed participants on 22 January 2025. A preliminary report was issued on 23 January 2025. This report included: a summary of the results reported by laboratories, assigned values, performance coefficient of variations, z-scores and E_n-scores for each analyte tested by participants.

No data has been changed from the Preliminary Report in this Final Report.

3 PARTICIPANT LABORATORY INFORMATION

3.1 Test Method Summaries

Summaries of test methods are transcribed in Tables 1 and 2.

Table 1 Methodology for Acid Extractable Elements

Lab. Code	Method Reference	Staggered Digestion	Sample Mass (g)	Temp. (°C)	Time (min)	Vol. HNO_3 (mL)	Vol. HCl (mL)	Vol. HNO_3 (1:1) (mL)	Vol. HCl (1:1) (mL)	Vol. H_2O_2 (mL)	Other (mL)
1	in house	No	0.1	95	90	4					4 (H_2O)
2	In-House		0.250-0.300	105	60	2.5	0.5				2 (H_2O)
3	ISO 6713	Yes	0.1	95	40	10				2 drops	
4*	APHA 3125 B mod.	No	0.25	110	60	5	1.5				
5	In House	No	0.4	120	60	10					
6	ASTM E1645-01		0.299	170	20	4					
7	AS/NZS ISO 8124.3:2021		0.1	100	90	3					
8	in house		0.22	20	1440	10					40 (H_2O)
9	US EPA 200.7		0.2	110	60	5					
10*	ASTM E3203 – 19		0.18	100	480			2x10mL			
11*	In house:Referenced to ISO 6713.		0.1	95	30	10	2				
12*			0.5227	210	55	9					11 (H_2O)

*Additional information in Table 2.

3.2 Instruments Used for Measurements

The instruments and settings used by participants for acid extractable elements are presented in Appendix 4.

3.3 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
4	Final vol 40mL
10	The sample was digested with 50% HNO3 for 8 hours. We also compared the results with AquaRegia digestion method which was shown lower recovery for all metals.
11	- Metals in paint are determined following a specific acid digestion. The ICPAES technique ionises samples in a plasma, emitting a characteristic spectrum based on metals present. Intensities at selected wavelengths are compared against those of matrix matched standards. - After samples Remove from the Hot Block and allow to cool completely. Make up to the mark (50 mL) with UHP water. Mix sample well by capping and inverting the digest vessel several times.
12	1ppm of Au added for Hg evaluation.

3.4 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about the basis of their uncertainty estimates (Tables 3 and 4).

Table 3 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Evaluation[a]		Guide Document for Estimating MU
		Precision	Method Bias	
1	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control Samples - CRM	CRM	ISO/GUM
2	Standard deviation of replicate analyses multiplied by 2 or 3 Coverage factor not reported	Control Samples - Reference Material/ ex-PT sample Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	Eurachem/CITAC Guide
3*	Coverage factor not reported			Eurachem/CITAC Guide
4	Other: Internal Quality Guidelines Coverage factor not reported	Control Samples - SS Duplicate Analysis Instrument Calibration	Instrument Calibration Recoveries of SS	
5	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control Samples - CRM Duplicate Analysis	CRM	
6	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Instrument Calibration	Recoveries of SS	
7	Top Down - precision and estimates of the method and laboratory bias k = 2	Control Samples - CRM Duplicate Analysis	CRM Recoveries of SS	Nordtest Report TR537
8	Coverage factor not reported	Instrument Calibration	CRM Instrument Calibration	
9	Professional judgment Coverage factor not reported	Control Samples Duplicate Analysis Instrument Calibration	CRM	NATA Technical Guide
10	Standard deviation of replicate analyses multiplied by 2 or 3 k = 2	Control samples - Reference Material/ ex-PT sample Duplicate Analysis	Instrument Calibration Laboratory Bias from PT Studies Recoveries of SS	ISO/GUM
11	Top Down - precision and estimates of the method and laboratory bias Coverage factor not reported	Control Samples - Reference Material/ ex-PT sample Duplicate Analysis Instrument Calibration		Eurachem/CITAC Guide
12	Coverage factor not reported	Instrument Calibration	CRM Instrument Calibration	

*Additional information in Table 4. [a]RM = Reference Material, CRM = Certified Reference Material, SS =Spiked samples

Table 4 Additional Information for Basis of Uncertainty Estimate

Lab Code	Additional Information
3	The laboratory is not accredited for paints and does not currently routinely analyse this matrix. As such, MU has not yet been calculated for this matrix.

3.5 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.

Table 5 Participant Comments

Lab. Code	Participants' Comments	Study Coordinator's Response
1	As we provide analysis for lead paint content for remediation purposes, A higher level of Lead would be beneficial for us.	Thank you for your feedback. We were constrained by the availability of lead in oil standards at a high level.
10	The paint was not dry enough. It may affect the final results between the laboratories.	The sample homogeneity was assessed before dispatch (see Appendix 1).

4 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

4.1 Results Summary

Participant results are listed in Tables 6 to 14 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 10. An example chart with interpretation guide is shown in Figure 1.

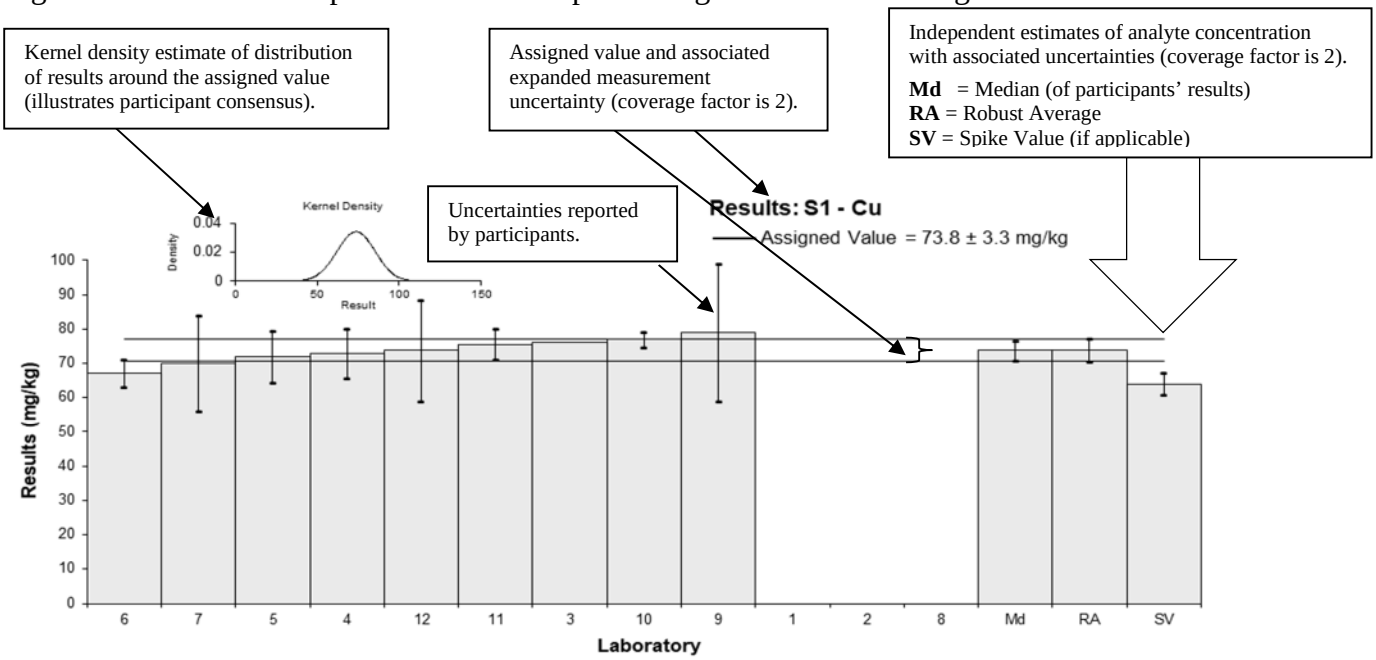


Figure 1 Guide to Presentation of Results

4.2 Assigned Value

An example of the assigned value calculation using data from the present study is given in Appendix 2. The assigned value is defined as: 'the value attributed to a particular property of a proficiency test item.'[1] In this study the property is the mass fraction of analyte. Assigned values were the robust average of participants' results, the expanded uncertainties were evaluated from the associated robust standard deviations.[4, 5]

4.3 Robust Average and Robust Between-Laboratory Coefficient of Variation

The robust averages and associated expanded measurement uncertainties were calculated using the procedure described in 'Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO13528.[5] 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.[5]

4.4 Target Standard Deviation for Proficiency Assessment

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

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

It is important to note that the PCV is a fixed value and is not the standard deviation of participants' results. The fixed value set for PCV is based on the existing regulation, the

acceptance criteria indicated by the methods, the matrix, the concentration level of analyte and on experience from previous studies. It is backed up by mathematical models such as the Thompson Horwitz equation.[6]

4.5 z-Score

An example of z-score calculation using data from the present study is given in Appendix 2. For each participant's result a z-score is calculated according to Equation 2 below:

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

Where:

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

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

- $|z| \leq 2.0$ is acceptable;
- $2.0 < |z| < 3.0$ is questionable;
- $|z| \geq 3.0$ is unacceptable.

4.6 E_n-Score

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

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

where:

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

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

- $|E_n| < 1.0$ is acceptable;
- $|E_n| \geq 1.0$ is unacceptable.

4.7 Traceability and Measurement Uncertainty

Laboratories accredited to AS ISO/IEC Standard 17025[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]

5 TABLES AND FIGURES

Table 6

Sample Details

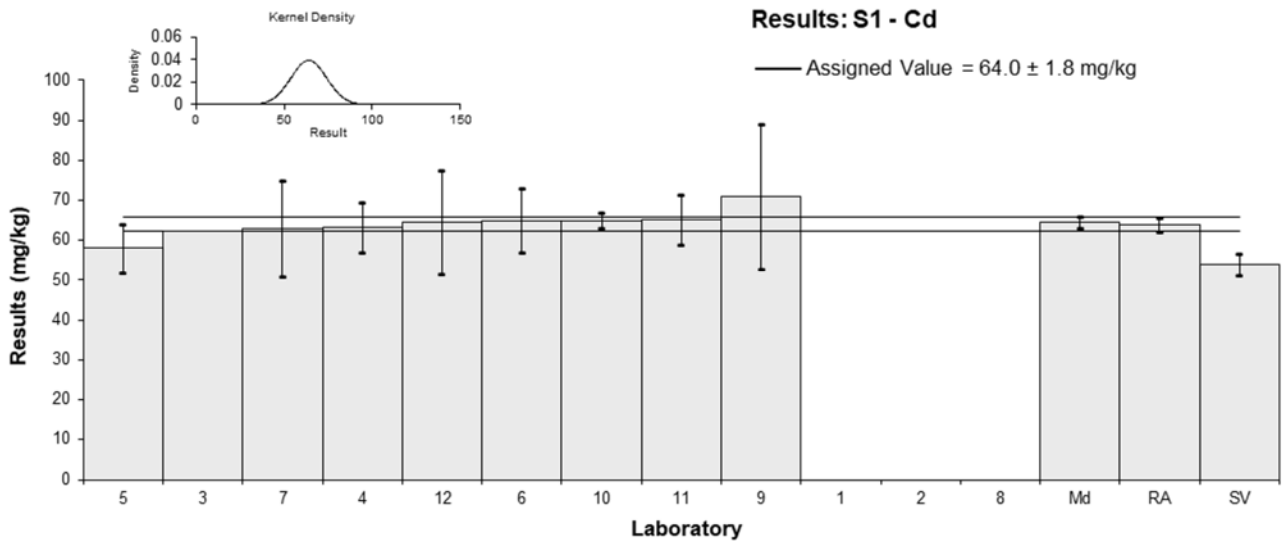
Sample No.	S1
Matrix	Paint
Analyte	Cd
Unit	mg/kg

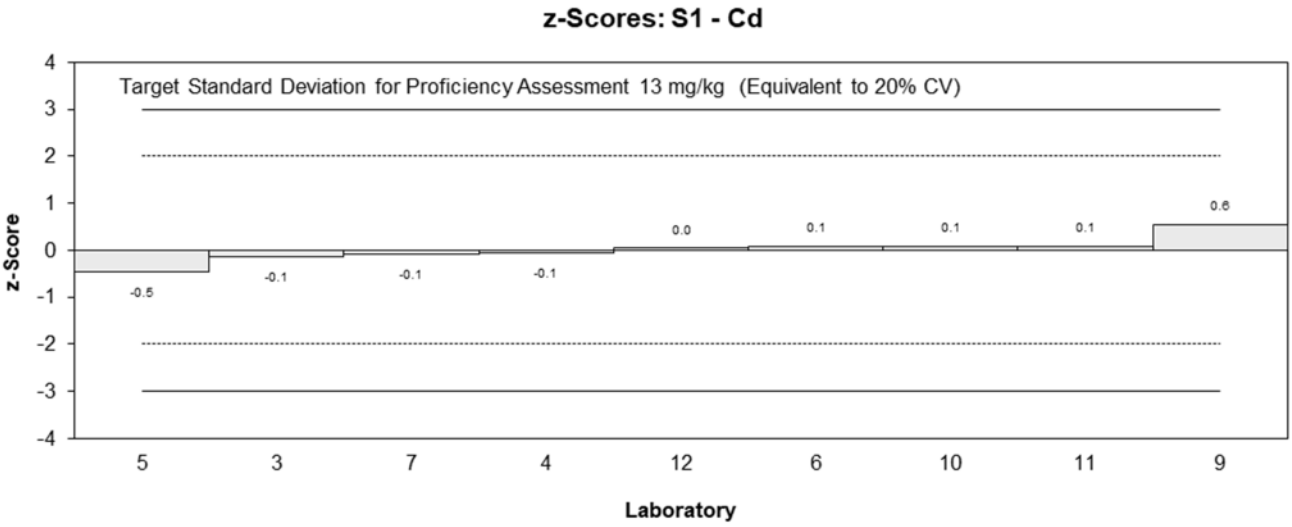
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	62.2	NR	-0.14	-1.00
4	63.36	6.3	-0.05	-0.10
5	58	6.0	-0.47	-0.96
6	65	8	0.08	0.12
7	63	12	-0.08	-0.08
8	NT	NT		
9	71	18	0.55	0.39
10	65	2.0	0.08	0.37
11	65.1	6.26	0.09	0.17
12	64.5	12.9	0.04	0.04

Statistics

Assigned Value	64.0	1.8
Spike Value	53.9	2.7
Homogeneity Value	58.2	5.8
Robust Average	64.0	1.8
Median	64.5	1.4
Mean	64.1	
N	9	
Max	71	
Min	58	
Robust SD	2.2	
Robust CV	3.4%	


Kernel Density
Density
Result
Results: S1 - Cd
Assigned Value = 64.0 ± 1.8 mg/kg
Results (mg/kg)
Laboratory
5 3 7 4 12 6 10 11 9 1 2 8 Md RA SV


z-Scores: S1 - Cd
Target Standard Deviation for Proficiency Assessment 13 mg/kg (Equivalent to 20% CV)
z-Score
Laboratory
5 3 7 4 12 6 10 11 9
-0.5 -0.1 -0.1 -0.1 0.0 0.1 0.1 0.1 0.6

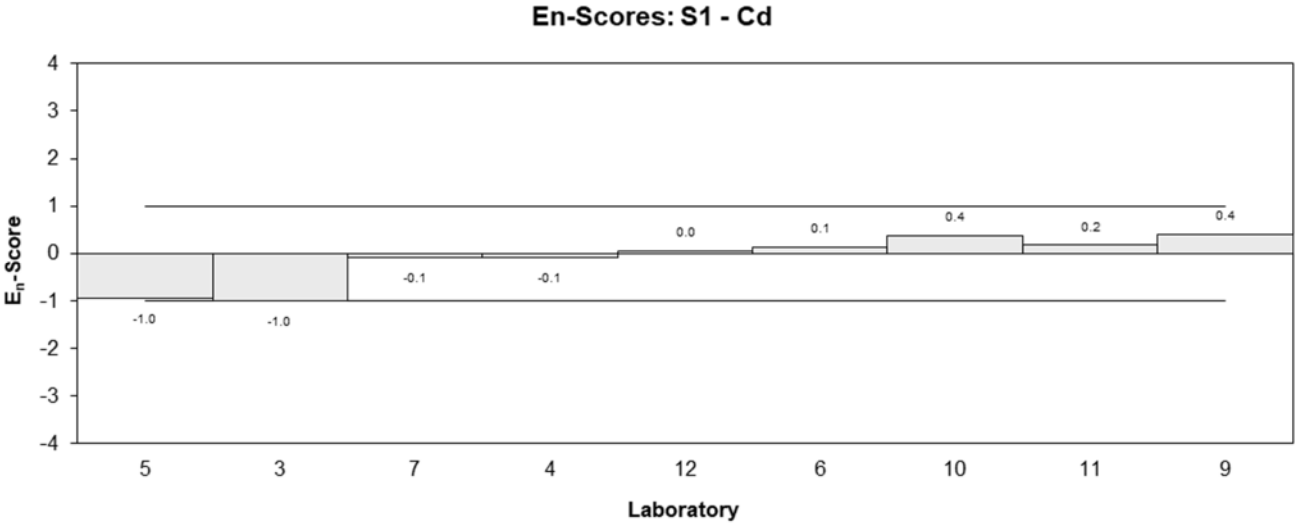

En-Scores: S1 - Cd
En-Score
Laboratory
5 3 7 4 12 6 10 11 9
-1.0 -1.0 -0.1 -0.1 0.0 0.1 0.4 0.2 0.4

Figure 2

Table 7

Sample Details

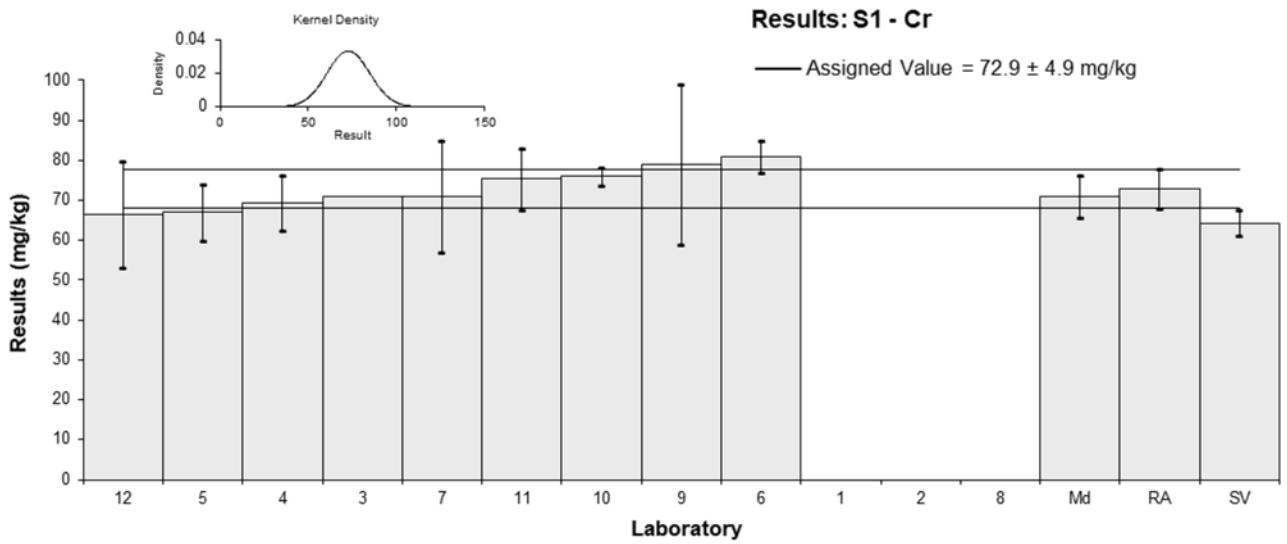
Sample No.	S1
Matrix	Paint
Analyte	Cr
Unit	mg/kg

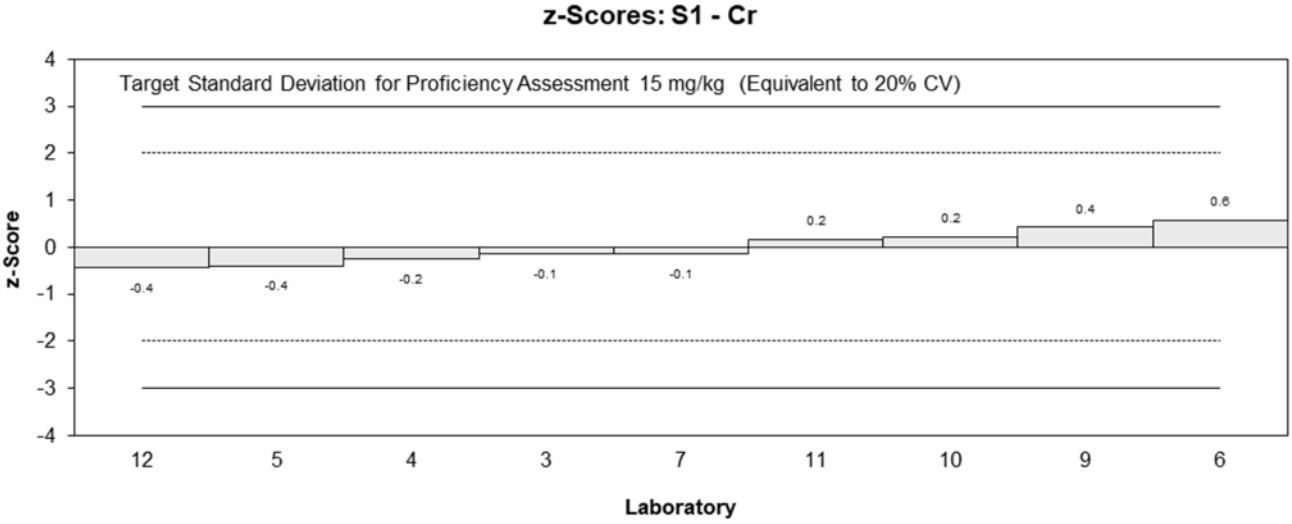
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	70.9	NR	-0.14	-0.41
4	69.38	6.9	-0.24	-0.42
5	67	7.0	-0.40	-0.69
6	81	4	0.56	1.28
7	71	14	-0.13	-0.13
8	NT	NT		
9	79	20	0.42	0.30
10	76	2.3	0.21	0.57
11	75.3	7.71	0.16	0.26
12	66.5	13.3	-0.44	-0.45

Statistics

Assigned Value	72.9	4.9
Spike Value	64.3	3.2
Homogeneity Value	68.7	6.9
Robust Average	72.9	4.9
Median	71.0	5.3
Mean	72.9	
N	9	
Max	81	
Min	66.5	
Robust SD	5.9	
Robust CV	8%	


Results: S1 - Cr
Assigned Value = 72.9 ± 4.9 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
12
5
4
3
7
11
10
9
6
1
2
8
Md
RA
SV


z-Scores: S1 - Cr
Target Standard Deviation for Proficiency Assessment 15 mg/kg (Equivalent to 20% CV)
z-Score
-0.4
-0.4
-0.2
-0.1
-0.1
0.2
0.2
0.4
0.6
Laboratory
12
5
4
3
7
11
10
9
6

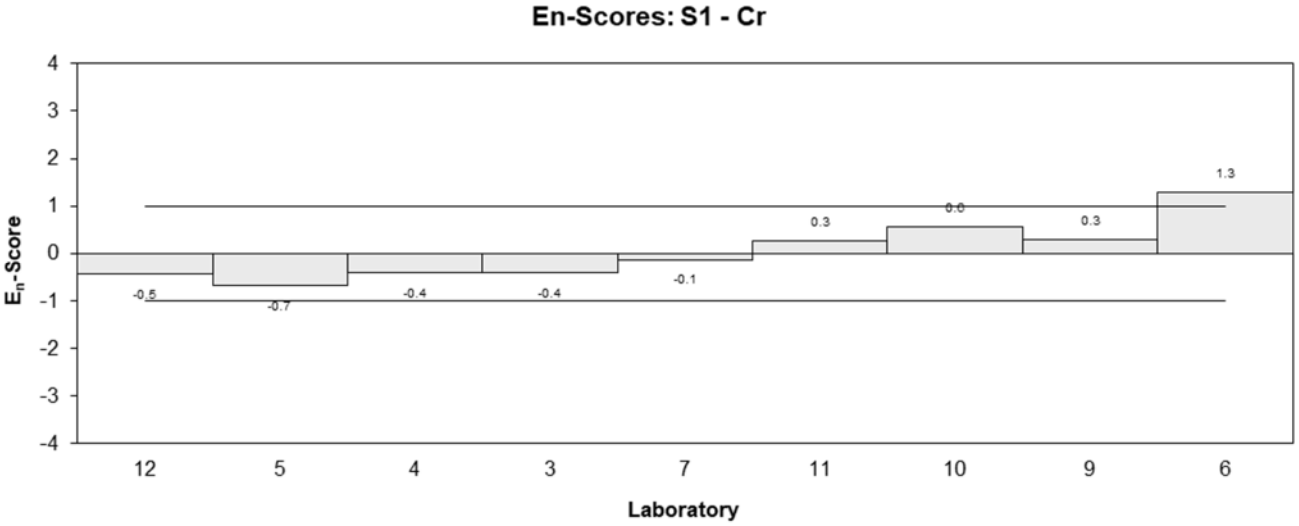

En-Scores: S1 - Cr
En-Score
-0.5
-0.7
-0.4
-0.4
-0.1
0.3
0.6
0.3
1.3
Laboratory
12
5
4
3
7
11
10
9
6

Figure 3

Table 8

Sample Details

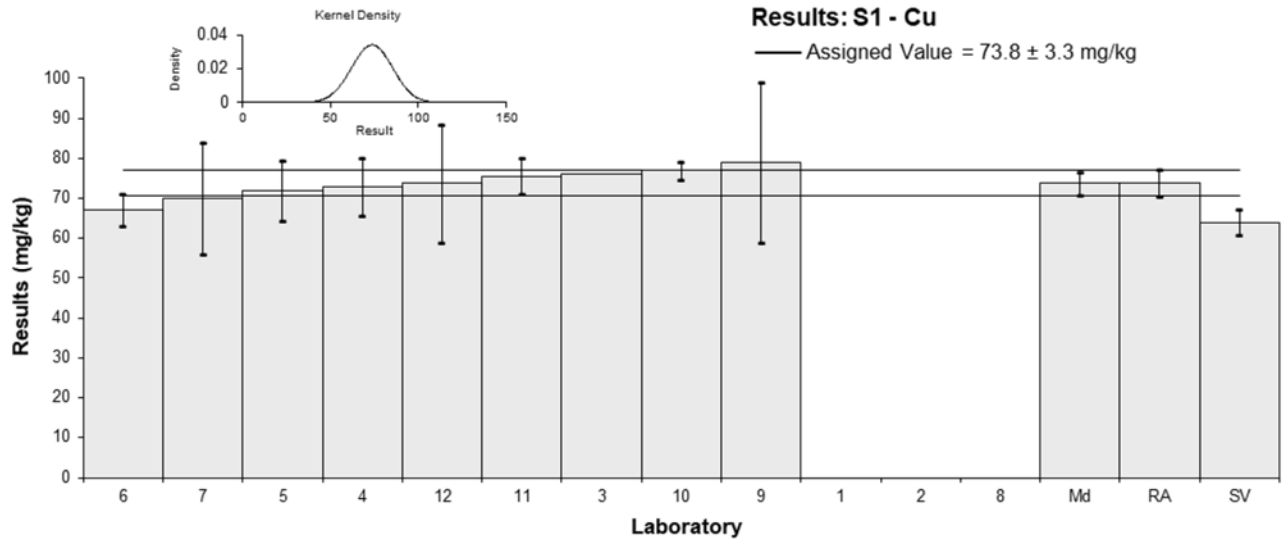
Sample No.	S1
Matrix	Paint
Analyte	Cu
Unit	mg/kg

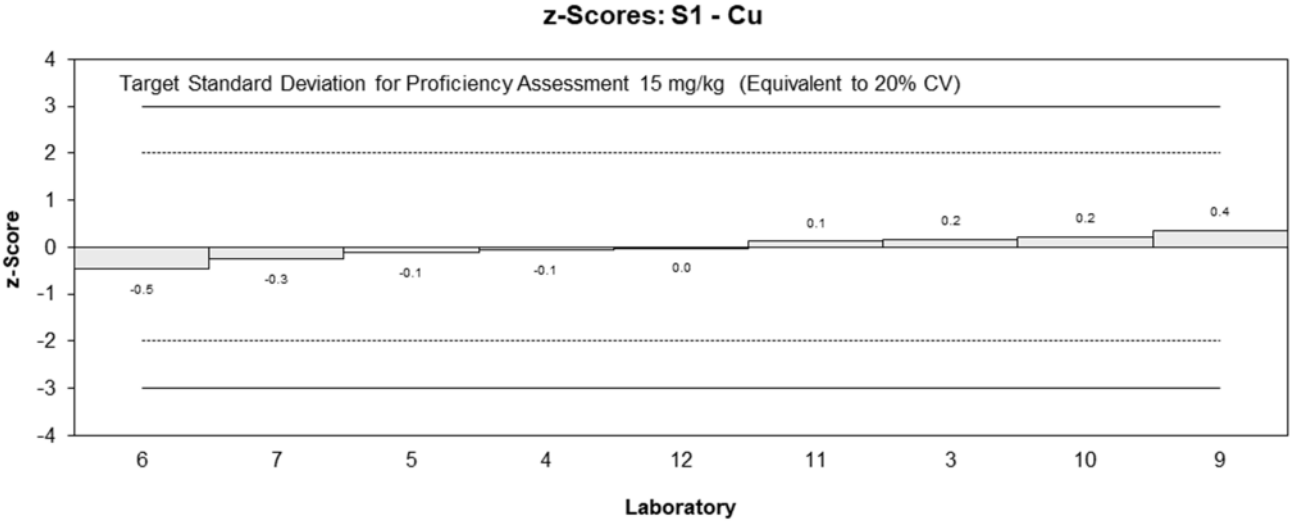
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	76.0	NR	0.15	0.67
4	72.94	7.3	-0.06	-0.11
5	72	7.5	-0.12	-0.22
6	67	4	-0.46	-1.31
7	70	14	-0.26	-0.26
8	NT	NT		
9	79	20	0.35	0.26
10	77	2.3	0.22	0.80
11	75.5	4.51	0.12	0.30
12	73.7	14.74	-0.01	-0.01

Statistics

Assigned Value	73.8	3.3
Spike Value	64.0	3.2
Homogeneity Value	73.7	7.4
Robust Average	73.8	3.3
Median	73.7	2.8
Mean	73.7	
N	9	
Max	79	
Min	67	
Robust SD	4.0	
Robust CV	5.4%	


Results: S1 - Cu
Assigned Value = 73.8 ± 3.3 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
6 7 5 4 12 11 3 10 9 1 2 8 Md RA SV


z-Scores: S1 - Cu
Target Standard Deviation for Proficiency Assessment 15 mg/kg (Equivalent to 20% CV)
z-Score
-0.5 -0.3 -0.1 -0.1 0.0 0.1 0.2 0.2 0.4
Laboratory
6 7 5 4 12 11 3 10 9

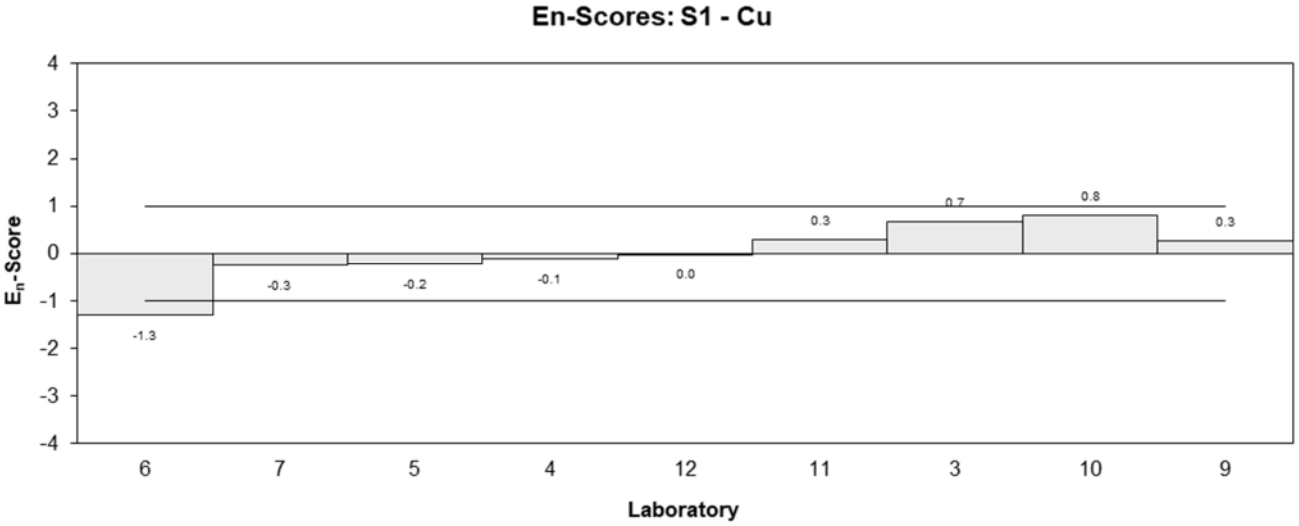

En-Scores: S1 - Cu
En-Score
-1.3 -0.3 -0.2 -0.1 0.0 0.3 0.7 0.8 0.3
Laboratory
6 7 5 4 12 11 3 10 9

Figure 4

Table 9

Sample Details

Sample No.	S1
Matrix	Paint
Analyte	Hg
Unit	mg/kg

Participant Results

Lab. Code	Result	Uncertainty
1	NT	NT
2	NT	NT
3	1.4	NR
4	1.65	0.2
5	1.7	0.2
6	NT	NT
7	<2.5	NR
8	NT	NT
9	0.89	0.10
10	NR	NR
11	1.6	0.0514
12	2.2	0.44

Statistics

Assigned Value	Not Set	
Spike Value	1.99	0.10
Homogeneity Value	1.96	0.20
Robust Average	1.57	0.49
Median	1.63	0.23
Mean	1.57	
N	6	
Max	2.2	
Min	0.89	
Robust SD	0.48	
Robust CV	31%	

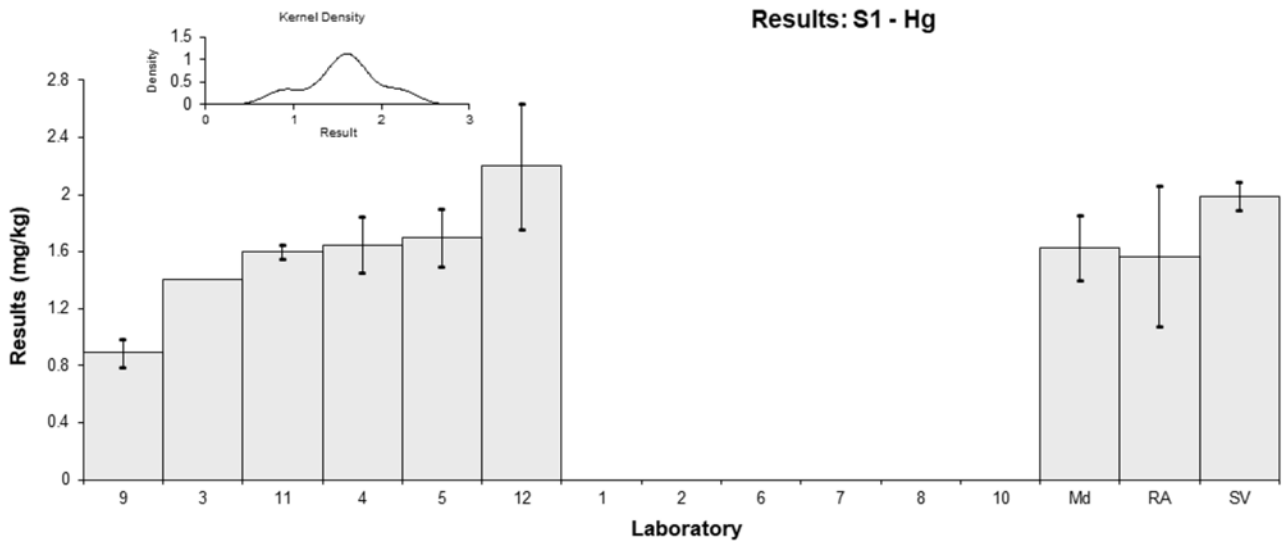

Results: S1 - Hg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
9
3
11
4
5
12
1
2
6
7
8
10
Md
RA
SV

Figure 5

Table 10

Sample Details

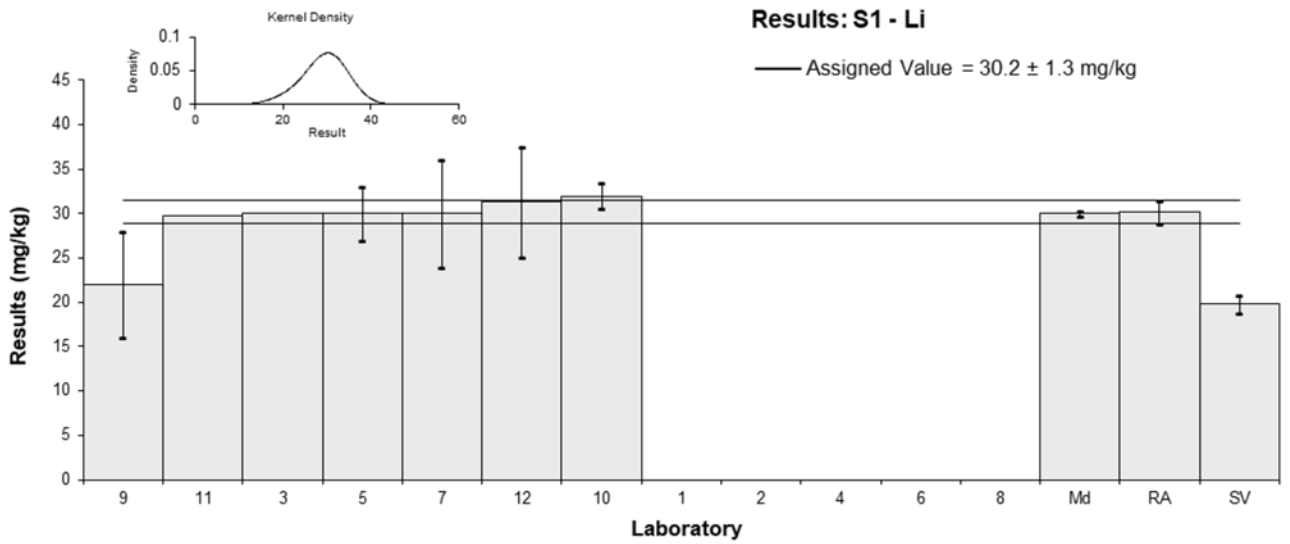
Sample No.	S1
Matrix	Paint
Analyte	Li
Unit	mg/kg

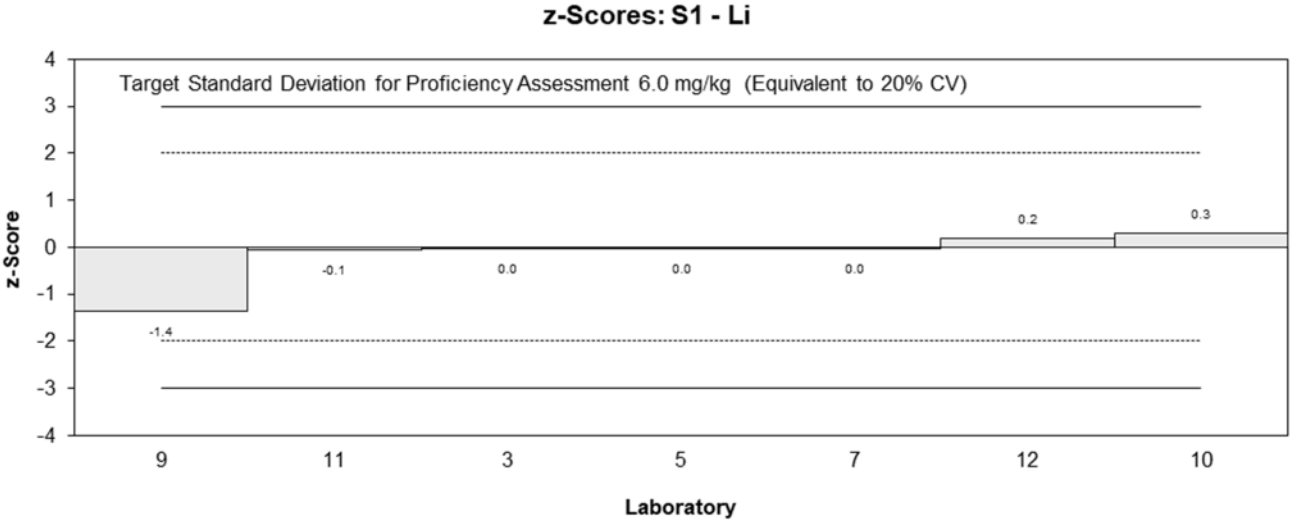
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	30.0	NR	-0.03	-0.15
4	NT	NT		
5	30	3.0	-0.03	-0.06
6	NT	NT		
7	30	6	-0.03	-0.03
8	NT	NT		
9	22	6	-1.36	-1.34
10	32	1.5	0.30	0.91
11	29.8	NR	-0.07	-0.31
12	31.3	6.24	0.18	0.17

Statistics

Assigned Value	30.2	1.3
Spike Value	19.8	1.0
Homogeneity Value	29.9	3.0
Robust Average	30.2	1.3
Median	30.0	0.3
Mean	29.3	
N	7	
Max	32	
Min	22	
Robust SD	1.4	
Robust CV	4.7%	


Kernel Density
Density
Result
Results: S1 - Li
Assigned Value = 30.2 ± 1.3 mg/kg
Results (mg/kg)
Laboratory
9
11
3
5
7
12
10
1
2
4
6
8
Md
RA
SV


z-Scores: S1 - Li
Target Standard Deviation for Proficiency Assessment 6.0 mg/kg (Equivalent to 20% CV)
z-Score
-1.4
-0.1
0.0
0.0
0.0
0.2
0.3
Laboratory
9
11
3
5
7
12
10

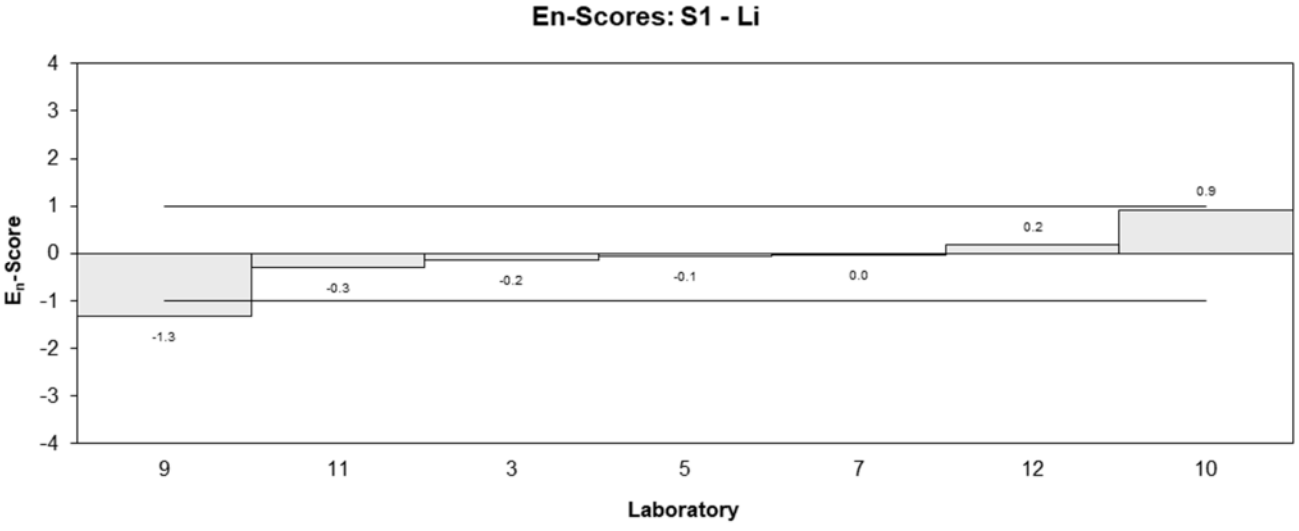

En-Scores: S1 - Li
En-Score
-1.3
-0.3
-0.2
-0.1
0.0
0.2
0.9
Laboratory
9
11
3
5
7
12
10

Figure 6

Table 11

Sample Details

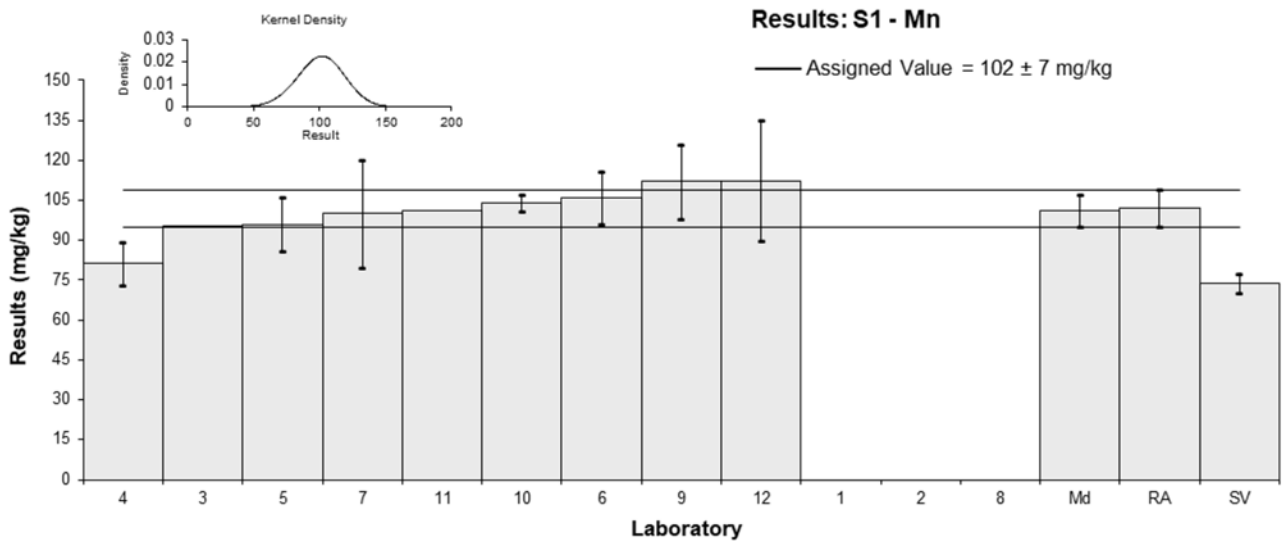
Sample No.	S1
Matrix	Paint
Analyte	Mn
Unit	mg/kg

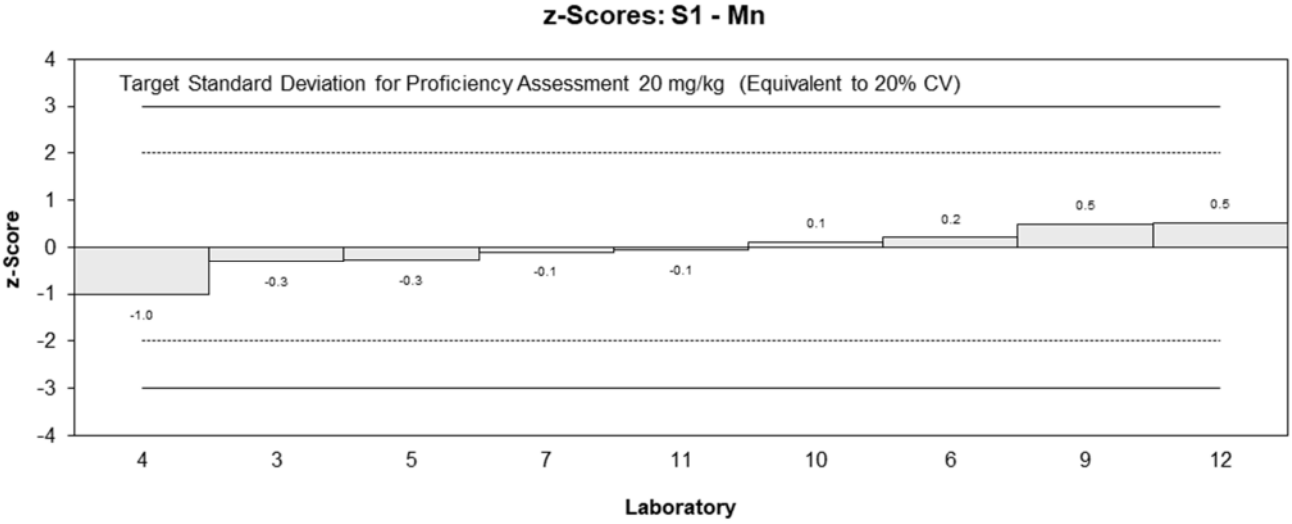
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	95.6	NR	-0.31	-0.91
4	81.25	8.1	-1.02	-1.94
5	96	10	-0.29	-0.49
6	106	10	0.20	0.33
7	100	20	-0.10	-0.09
8	NT	NT		
9	112	14	0.49	0.64
10	104	3.0	0.10	0.26
11	101	NR	-0.05	-0.14
12	112.4	22.48	0.51	0.44

Statistics

Assigned Value	102	7
Spike Value	73.9	3.7
Homogeneity Value	96.1	9.6
Robust Average	102	7
Median	101	6
Mean	101	
N	9	
Max	112.4	
Min	81.25	
Robust SD	8.9	
Robust CV	8.8%	


Results: S1 - Mn
Assigned Value = 102 ± 7 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
4 3 5 7 11 10 6 9 12 1 2 8 Md RA SV


z-Scores: S1 - Mn
Target Standard Deviation for Proficiency Assessment 20 mg/kg (Equivalent to 20% CV)
z-Score
-1.0 -0.3 -0.3 -0.1 -0.1 0.1 0.2 0.5 0.5
Laboratory
4 3 5 7 11 10 6 9 12

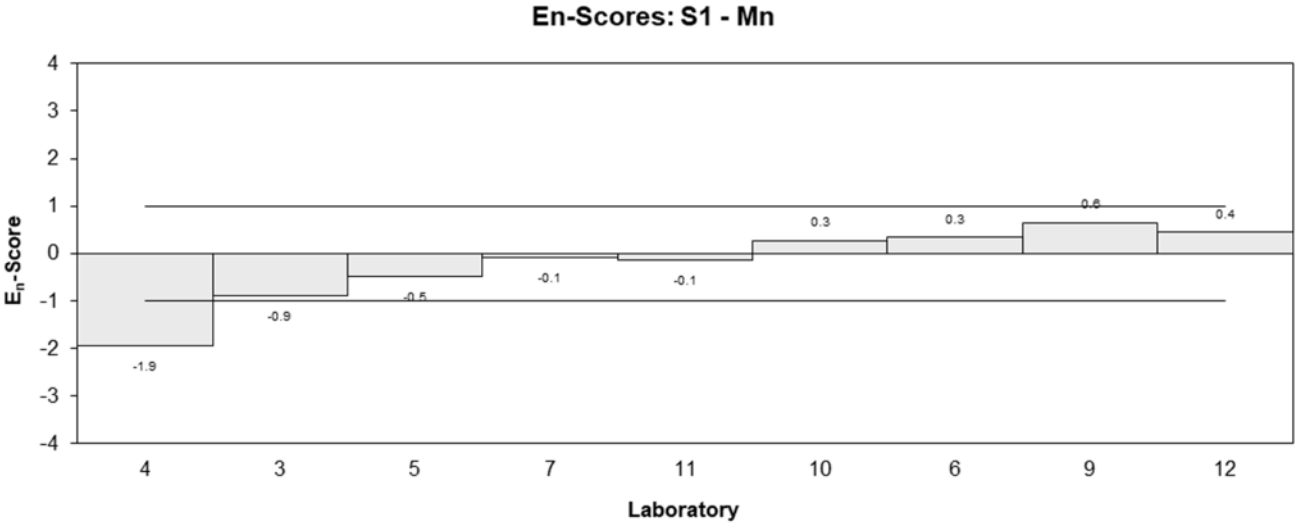

En-Scores: S1 - Mn
En-Score
-1.9 -0.9 -0.5 -0.1 -0.1 0.3 0.3 0.6 0.4
Laboratory
4 3 5 7 11 10 6 9 12

Figure 7

Table 12

Sample Details

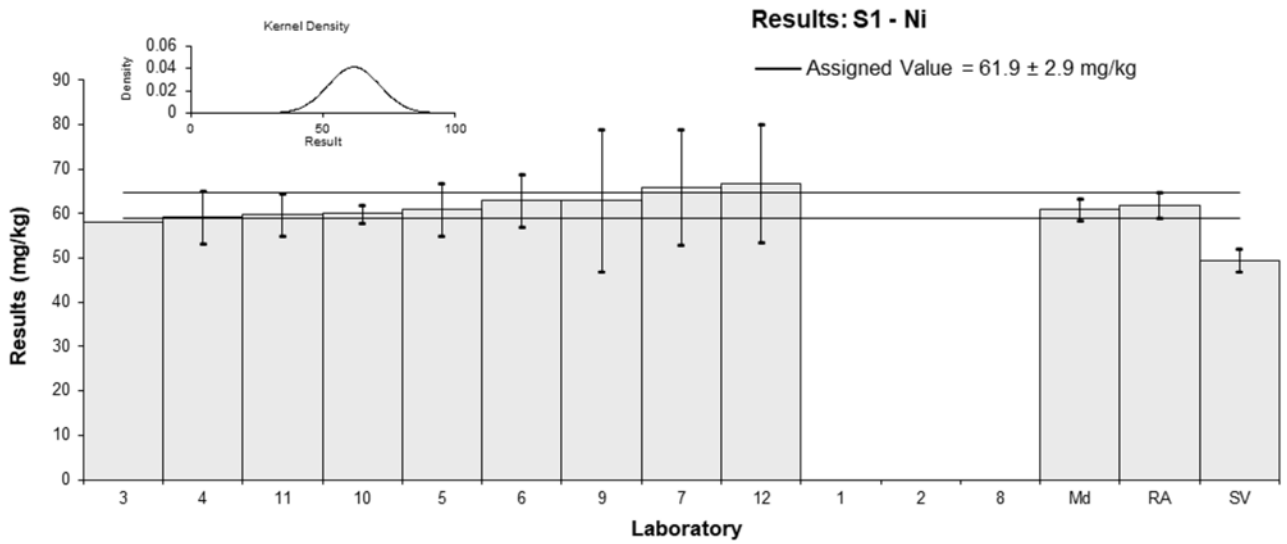
Sample No.	S1
Matrix	Paint
Analyte	Ni
Unit	mg/kg

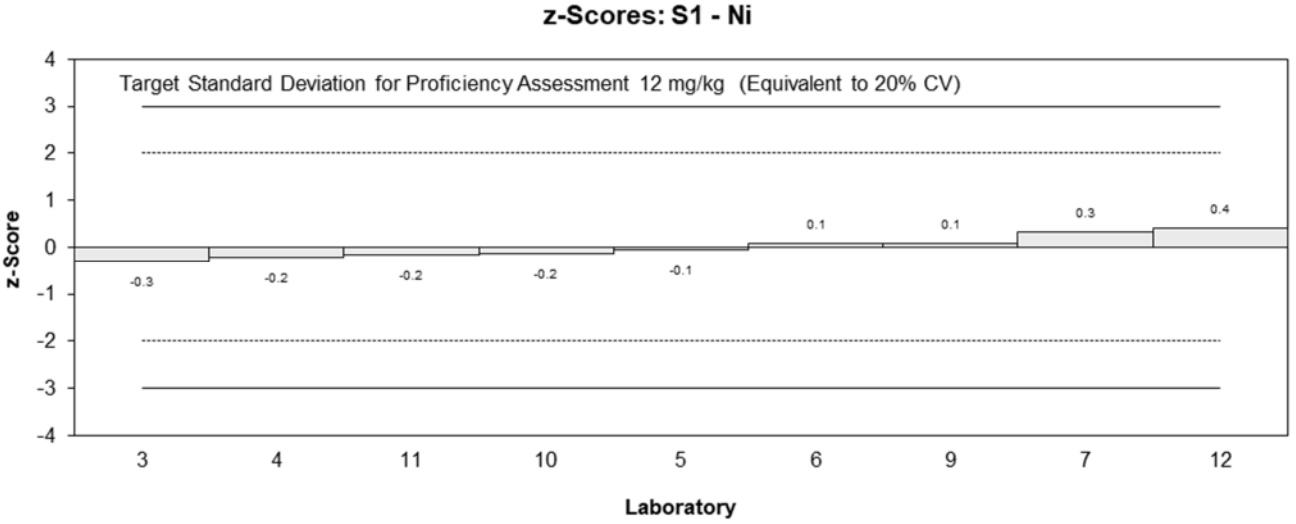
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	58.2	NR	-0.30	-1.28
4	59.17	5.9	-0.22	-0.42
5	61	6.0	-0.07	-0.14
6	63	6	0.09	0.17
7	66	13	0.33	0.31
8	NT	NT		
9	63	16	0.09	0.07
10	60	2.0	-0.15	-0.54
11	59.9	4.77	-0.16	-0.36
12	66.9	13.38	0.40	0.37

Statistics

Assigned Value	61.9	2.9
Spike Value	49.6	2.5
Homogeneity Value	59.6	6.0
Robust Average	61.9	2.9
Median	61.0	2.5
Mean	61.9	
N	9	
Max	66.9	
Min	58.2	
Robust SD	3.4	
Robust CV	5.6%	


Results: S1 - Ni
Kernel Density
Density
Result
Assigned Value = 61.9 ± 2.9 mg/kg
Results (mg/kg)
Laboratory
3
4
11
10
5
6
9
7
12
1
2
8
Md
RA
SV


z-Scores: S1 - Ni
Target Standard Deviation for Proficiency Assessment 12 mg/kg (Equivalent to 20% CV)
z-Score
-0.3
-0.2
-0.2
-0.2
-0.1
0.1
0.1
0.3
0.4
Laboratory

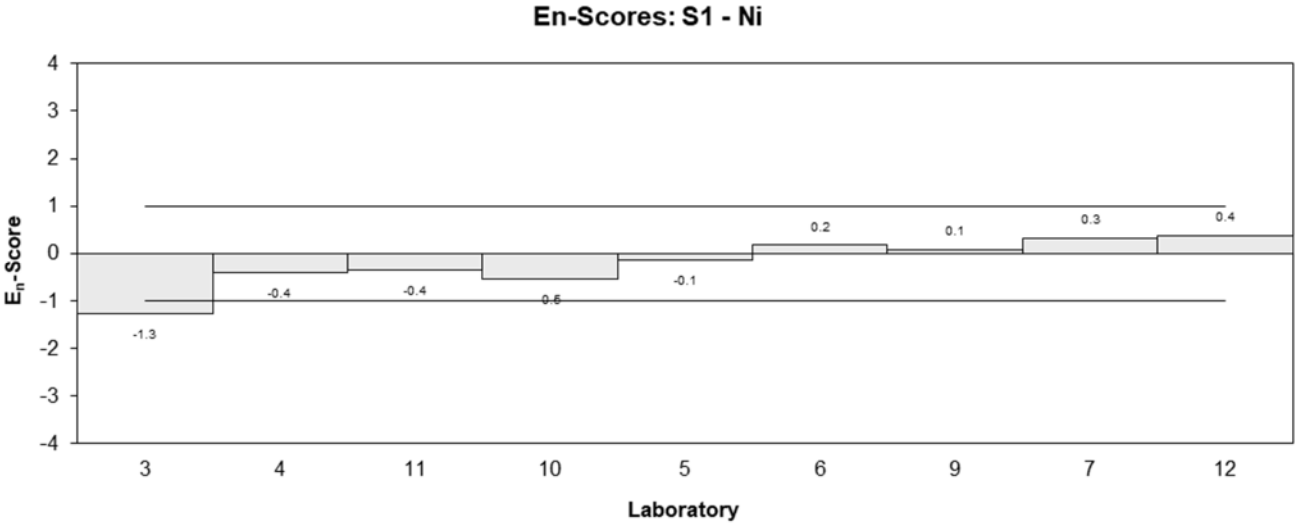

En-Scores: S1 - Ni
En-Score
-1.3
-0.4
-0.4
-0.6
-0.1
0.2
0.1
0.3
0.4
Laboratory

Figure 8

Table 13

Sample Details

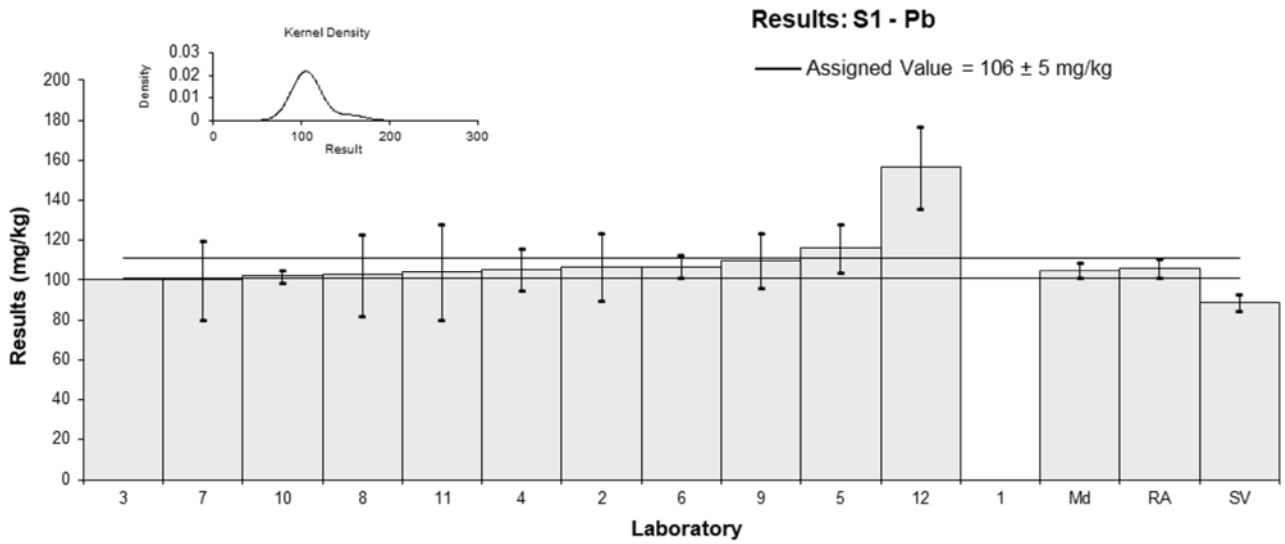
Sample No.	S1
Matrix	Paint
Analyte	Pb
Unit	mg/kg

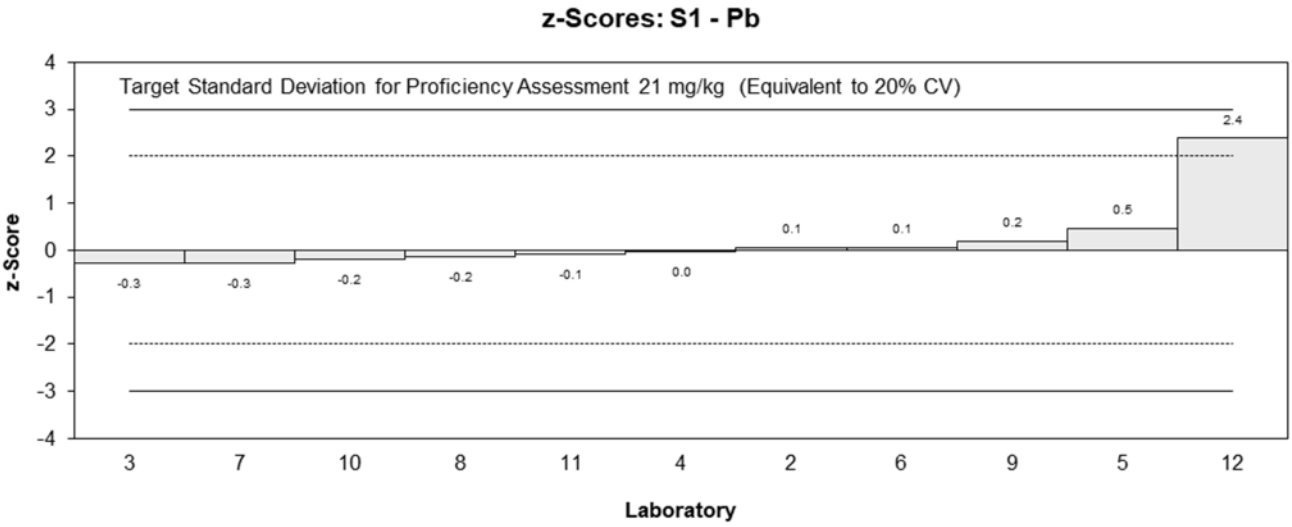
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	<100	NR		
2	107	17	0.05	0.06
3	100	NR	-0.28	-1.20
4	105.2	10.5	-0.04	-0.07
5	116	12	0.47	0.77
6	107	6	0.05	0.13
7	100	20	-0.28	-0.29
8	102.75	20.55	-0.15	-0.15
9	110	14	0.19	0.27
10	102	3.0	-0.19	-0.69
11	104	24.2	-0.09	-0.08
12	156.5	20.55	2.38	2.39

Statistics

Assigned Value	106	5
Spike Value	88.7	4.4
Homogeneity Value	108	11
Robust Average	106	5
Median	105	4
Mean	110	
N	11	
Max	156.5	
Min	100	
Robust SD	6.4	
Robust CV	6%	


Results: S1 - Pb
Assigned Value = 106 ± 5 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
3 7 10 8 11 4 2 6 9 5 12 1 Md RA SV


z-Scores: S1 - Pb
Target Standard Deviation for Proficiency Assessment 21 mg/kg (Equivalent to 20% CV)
z-Score
-0.3 -0.3 -0.2 -0.2 -0.1 0.0 0.1 0.1 0.2 0.5 2.4
Laboratory
3 7 10 8 11 4 2 6 9 5 12

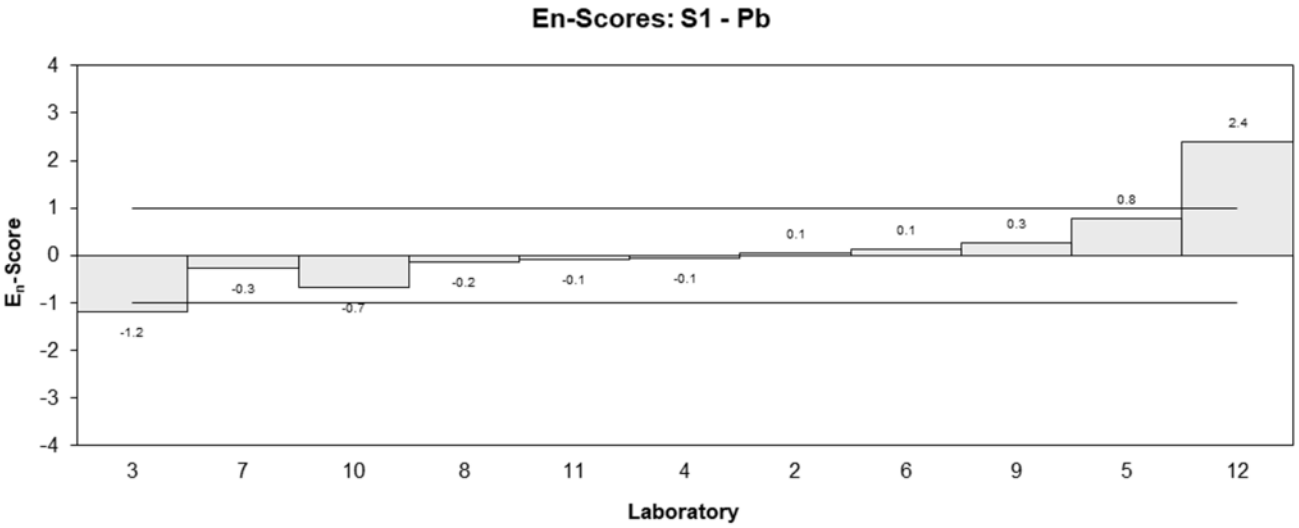

En-Scores: S1 - Pb
En-Score
-1.2 -0.3 -0.7 -0.2 -0.1 -0.1 0.1 0.1 0.3 0.8 2.4
Laboratory
3 7 10 8 11 4 2 6 9 5 12

Figure 9

Table 14

Sample Details

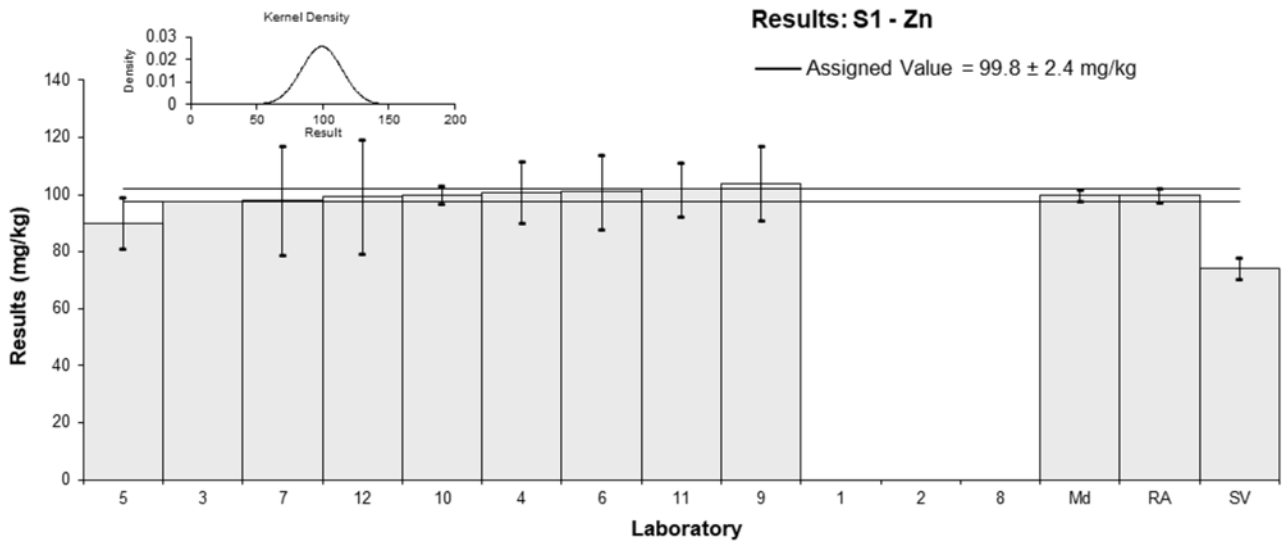
Sample No.	S1
Matrix	Paint
Analyte	Zn
Unit	mg/kg

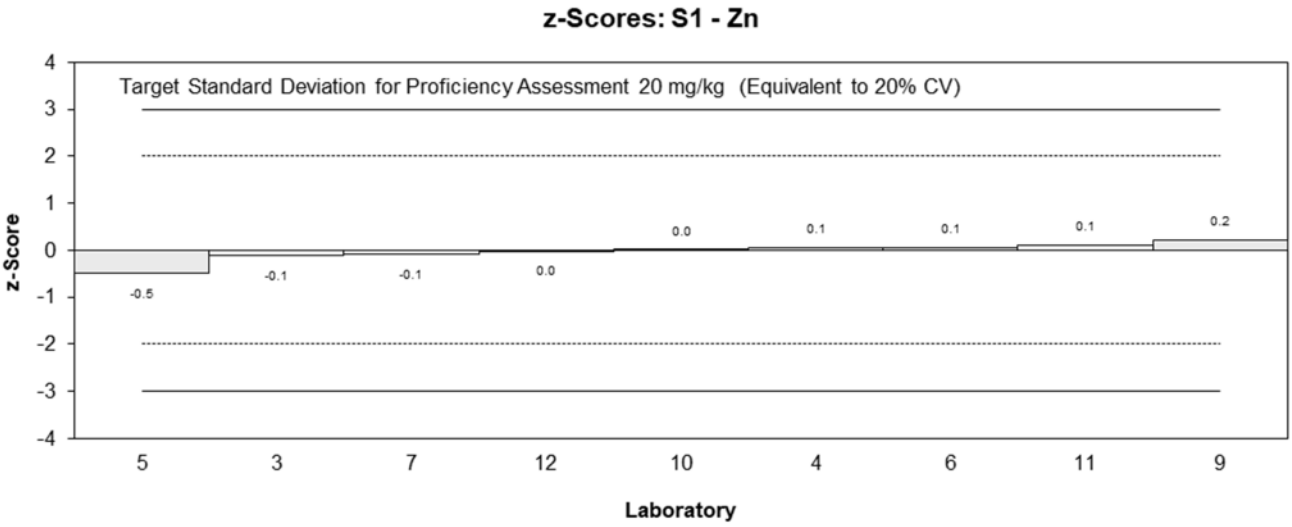
Participant Results

Lab. Code	Result	Uncertainty	z	E_n
1	NT	NT		
2	NT	NT		
3	97.6	NR	-0.11	-0.92
4	100.79	10.8	0.05	0.09
5	90	9.0	-0.49	-1.05
6	101	13	0.06	0.09
7	98	19	-0.09	-0.09
8	NT	NT		
9	104	13	0.21	0.32
10	100	3.0	0.01	0.05
11	102	9.39	0.11	0.23
12	99.4	19.88	-0.02	-0.02

Statistics

Assigned Value	99.8	2.4
Spike Value	74.2	3.7
Homogeneity Value	95.1	9.5
Robust Average	99.8	2.4
Median	100	2
Mean	99.2	
N	9	
Max	104	
Min	90	
Robust SD	2.9	
Robust CV	2.9%	


Results: S1 - Zn
Assigned Value = 99.8 ± 2.4 mg/kg
Kernel Density
Density
Result
Results (mg/kg)
Laboratory
5 3 7 12 10 4 6 11 9 1 2 8 Md RA SV


z-Scores: S1 - Zn
Target Standard Deviation for Proficiency Assessment 20 mg/kg (Equivalent to 20% CV)
z-Score
-0.5 -0.1 -0.1 0.0 0.0 0.1 0.1 0.1 0.2
Laboratory
5 3 7 12 10 4 6 11 9

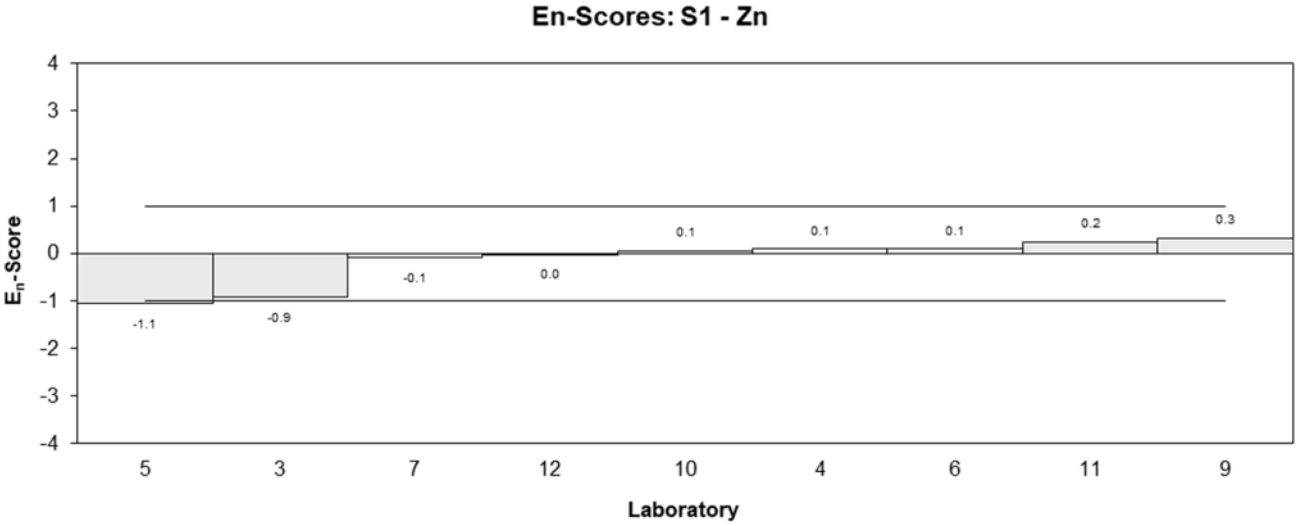

En-Scores: S1 - Zn
En-Score
-1.1 -0.9 -0.1 0.0 0.1 0.1 0.1 0.2 0.3
Laboratory
5 3 7 12 10 4 6 11 9

Figure 10

6 DISCUSSION OF RESULTS

6.1 Assigned Value and Traceability

Sample S1 was dry spiked paint.

Assigned Values were the robust average of participants' results. The robust averages used as assigned values and their associated expanded uncertainties were calculated using the procedure described in ISO13528 'Statistical methods for use in proficiency testing by interlaboratory comparisons'.[5] Appendix 2 sets out the calculation of the robust average of Pb in Sample S1 and its associated uncertainty.

No assigned value was set for Hg in S1 because the reported results were variable and too few. However, participants may still compare their reported results with the median of participants' results and/or the spike value. Descriptive statistics are presented in Section 5.

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.

6.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. Of 78 numerical results, 67 (86%) were reported with an expanded measurement uncertainty. The magnitude of these expanded uncertainties was within the range 2.88% to 27% of the reported value. The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 3.

Approaches to estimating measurement uncertainty can include standard deviation of replicate analysis, Horwitz formula, long term reproducibility, professional judgement, bottom-up approach, top down approach using precision and estimates of method and laboratory bias, and top down approach using only the reproducibility from inter-laboratory comparison studies.[8 – 13]

Participation in proficiency testing programs allows participants to check how reasonable their estimates of uncertainty are. Results and the expanded MU are presented in the bar charts for each analyte (Figures 2 to 10). As a simple rule of thumb, when the uncertainty estimate is smaller than uncertainty of the assigned value, or larger than the uncertainty of the assigned value plus twice the target standard deviation, then this should be reviewed as suspect. For example, 9 laboratories reported results for Cr in S1. The uncertainty of the assigned value evaluated from the robust standard deviation of the 9 laboratories' results is 4.9 mg/kg (6.7% of the assigned value). Therefore, Laboratory 6 might have under-estimated their expanded measurement uncertainty (4 mg/kg or 4.9% of their reported value) as an uncertainty evaluated from one measurement cannot be smaller than the uncertainty evaluated from 9 measurements. Alternatively, an estimate of uncertainty for Li in S1 larger than 13 mg/kg (the uncertainty of the assigned value, 1.3 mg/kg plus the allowable variation from the assigned value, the target standard deviation of 6.0 mg/kg, multiplied by 2, the coverage factor for a confidence interval of 95%), would also be viewed as suspect.

Laboratory 10 should review their calculation procedure for estimating measurement uncertainty as some of their uncertainties were unrealistically low.

An estimate of uncertainty expressed as a value cannot be attached to a result expressed as a range.[8] No laboratories attached estimates of the expanded measurement uncertainty to results reported as a range ("less than").

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 156.5 ± 20.55 mg/kg, it is better to report 157 ± 21 mg/kg.[8]

6.3 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 acceptable performance in a proficiency test. Target standard deviations equivalent to 20% PCV were used to calculate z-scores. Unlike the standard deviation based on between laboratories CV, setting the target standard deviation as a realistic, set value enables z-scores to be used as fixed reference value points for assessment of laboratory performance, independent of group performance.

The between laboratory coefficient of variation predicted by the Thompson equation[7] and the participants' coefficient of variation resulted in this study are presented for comparison in Table 15.

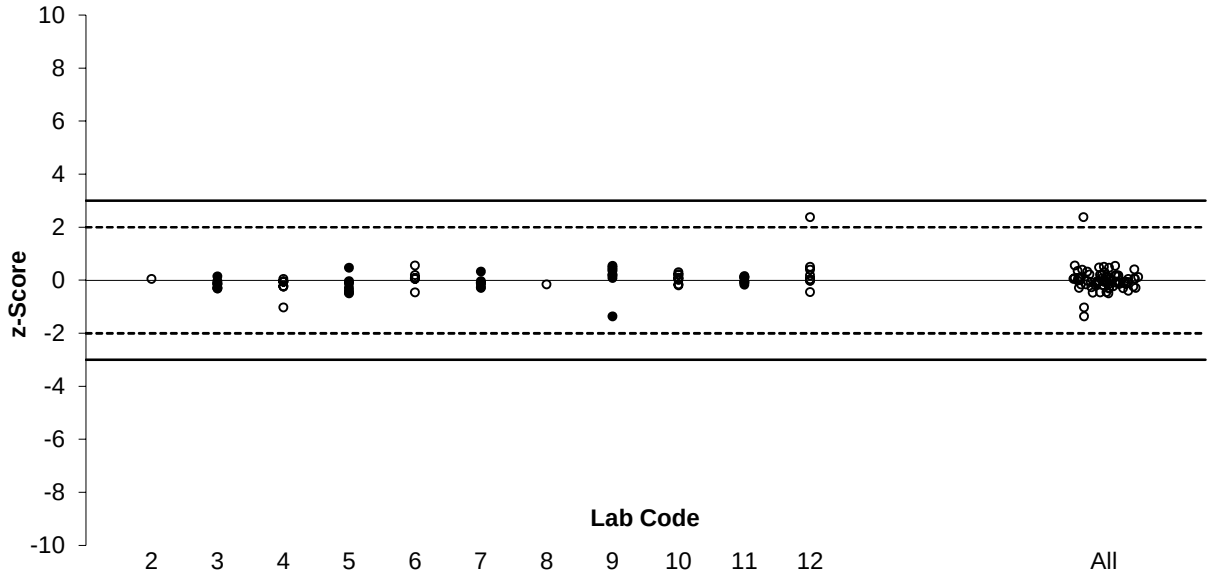


Figure 11 z-Score Dispersal by Laboratory

The dispersal of participants' z-scores is presented in Figure 11 (by laboratory code) and in Figure 13 (by test). Of 72 results for which z-scores were calculated, 71 (99%) returned an acceptable score of $|z| \leq 2.0$, and 1 (1%) was questionable with a score of $2.0 < |z| < 3.0$.

A summary of participants' reported results and performance is presented in Figure 14.

Laboratories 3, **5**, **7**, **9**, **10** and **11** all returned the highest number of acceptable z scores (8 out of 8 reported).

All results reported by L**aboratories 4** (7), **6** (7), **2** (1) and **8** (1) returned acceptable z scores.

6.4 E_n-score

E_n-score can be interpreted in conjunction with z-scores. The E_n-score indicates how closely a result agrees with the assigned value considering the respective uncertainties. An unacceptable E_n-score for an analyte can either be caused by an inappropriate measurement, an inappropriate evaluation of measurement uncertainty, or both.

The dispersal of participants' E_n-scores is graphically presented in Figure 12. 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 72 results for which E_n-scores were calculated, 63 (88%) returned an acceptable score of $|E_n| < 1.0$ indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.

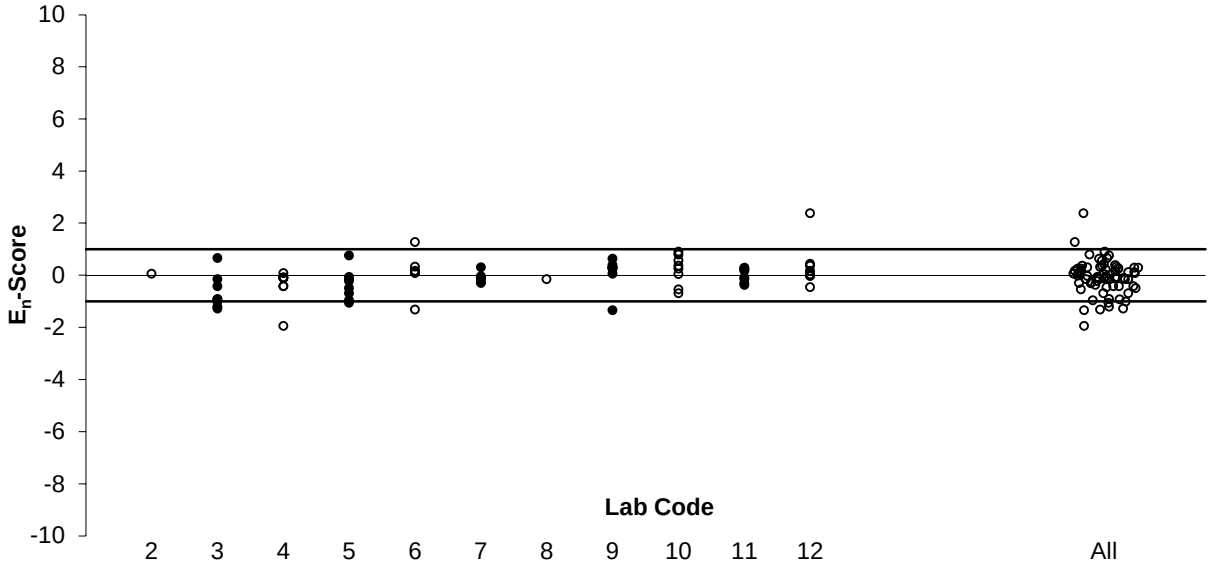


Figure 12 E_n-Score Dispersal by Laboratory

Laboratories 7, **10** and **11** returned the highest number of acceptable E_n-scores (8 out of 8 reported).

All results reported by **Laboratories 2** (1) and **8** (1) returned acceptable E_n-scores.

Table 15 Set Target SD, Thompson/Horwitz CV and Between-Laboratory CV of this Study

Sample	Test	Assigned value (mg/kg)	Target SD (as PCV)	Thompson/ Horwitz CV	Between-Laboratory CV*
S1	Cd	64.0	20%	8.6%	3.4%
S1	Cr	72.9	20%	8.4%	8.0%
S1	Cu	73.8	20%	8.4%	5.4%
S1	Hg	1.57**	Not Set	15%	31%
S1	Li	30.2	20%	9.6%	4.7%
S1	Mn	102	20%	8.0%	8.8%
S1	Ni	61.9	20%	8.6%	5.6%
S1	Pb	106	20%	7.9%	6.0%
S1	Zn	99.8	20%	8.0%	2.9%

*Robust between-laboratory CV with outliers removed**.** ** Robust Average (outliers excluded).

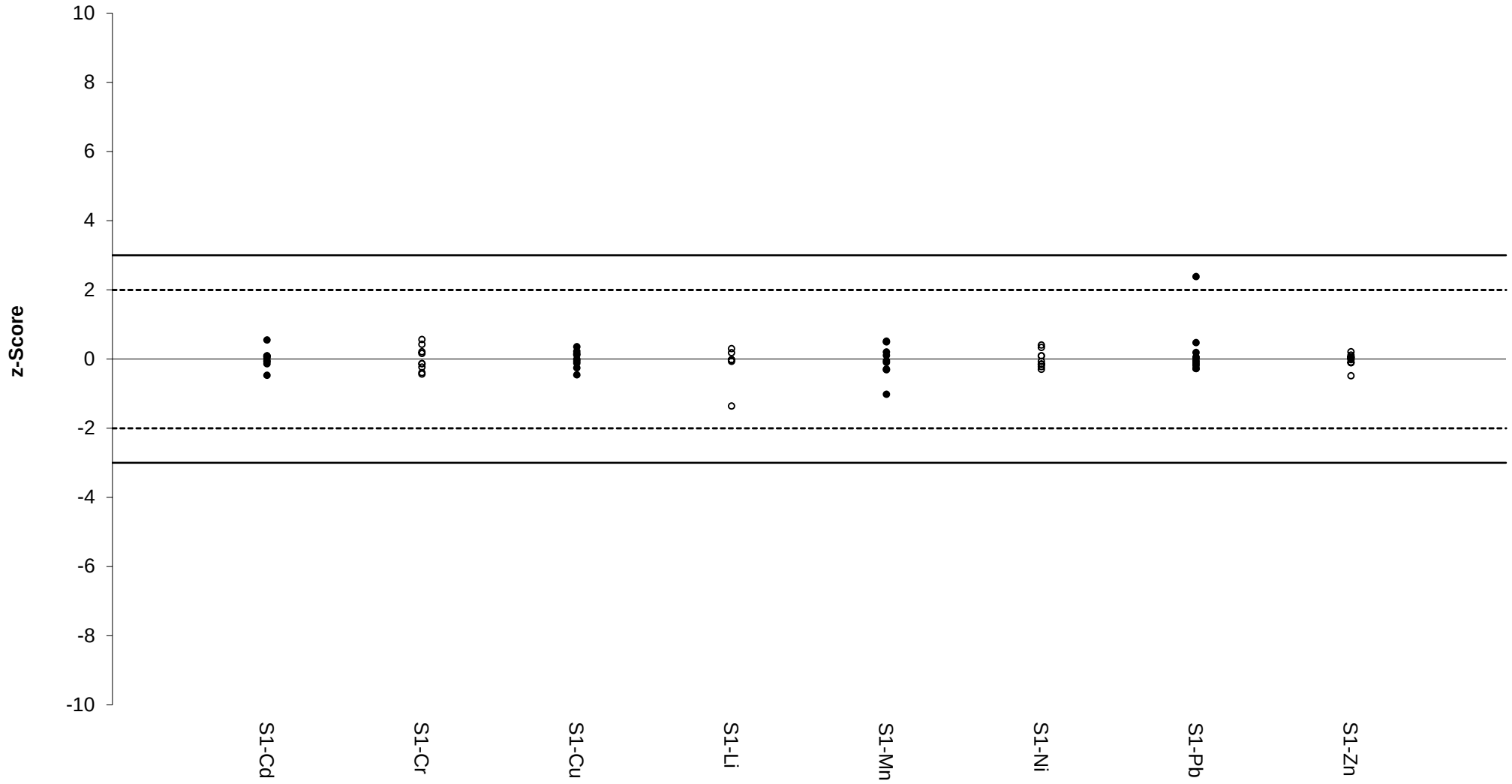


Figure 13 z-Score Dispersal by Test

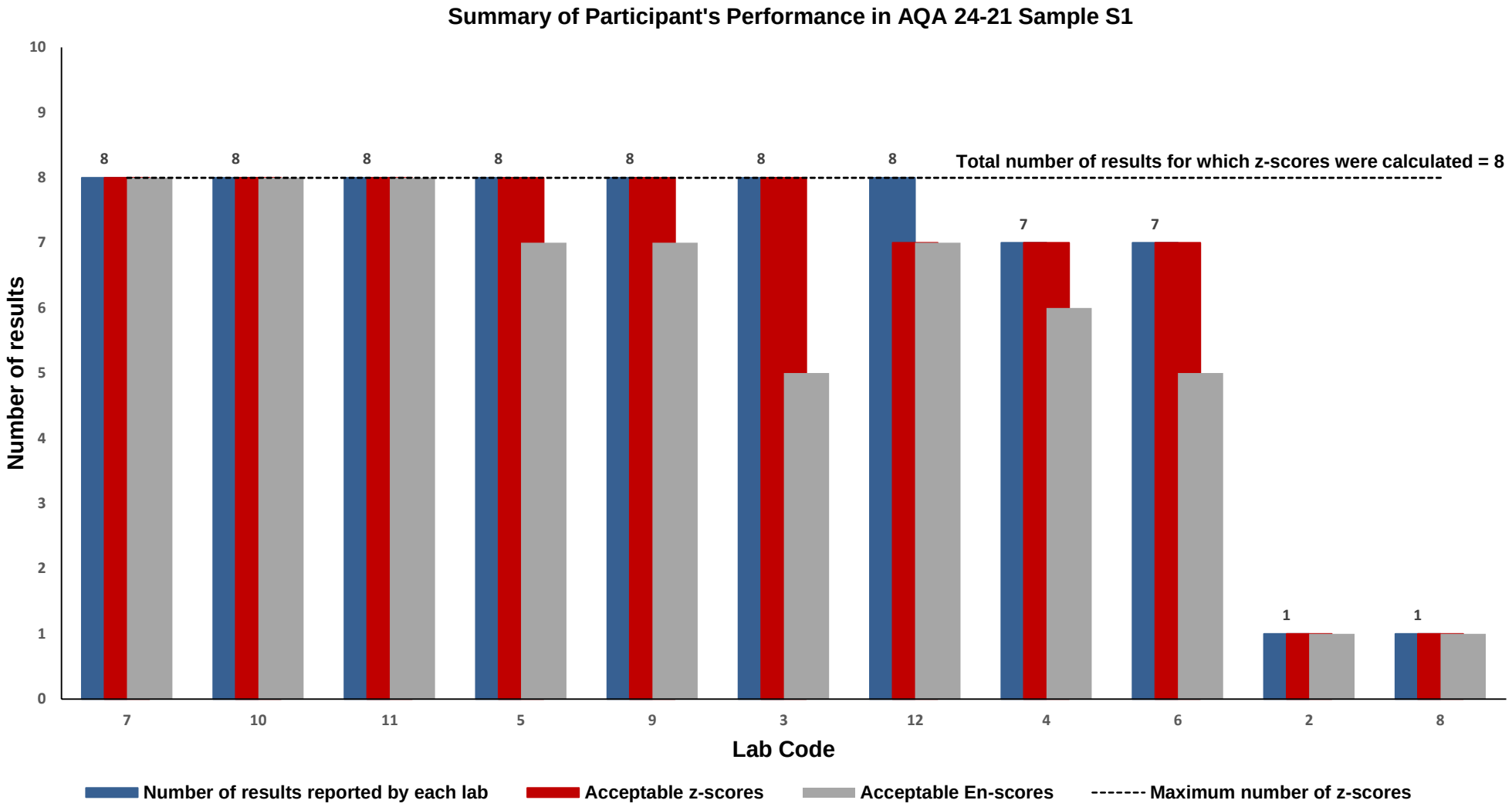
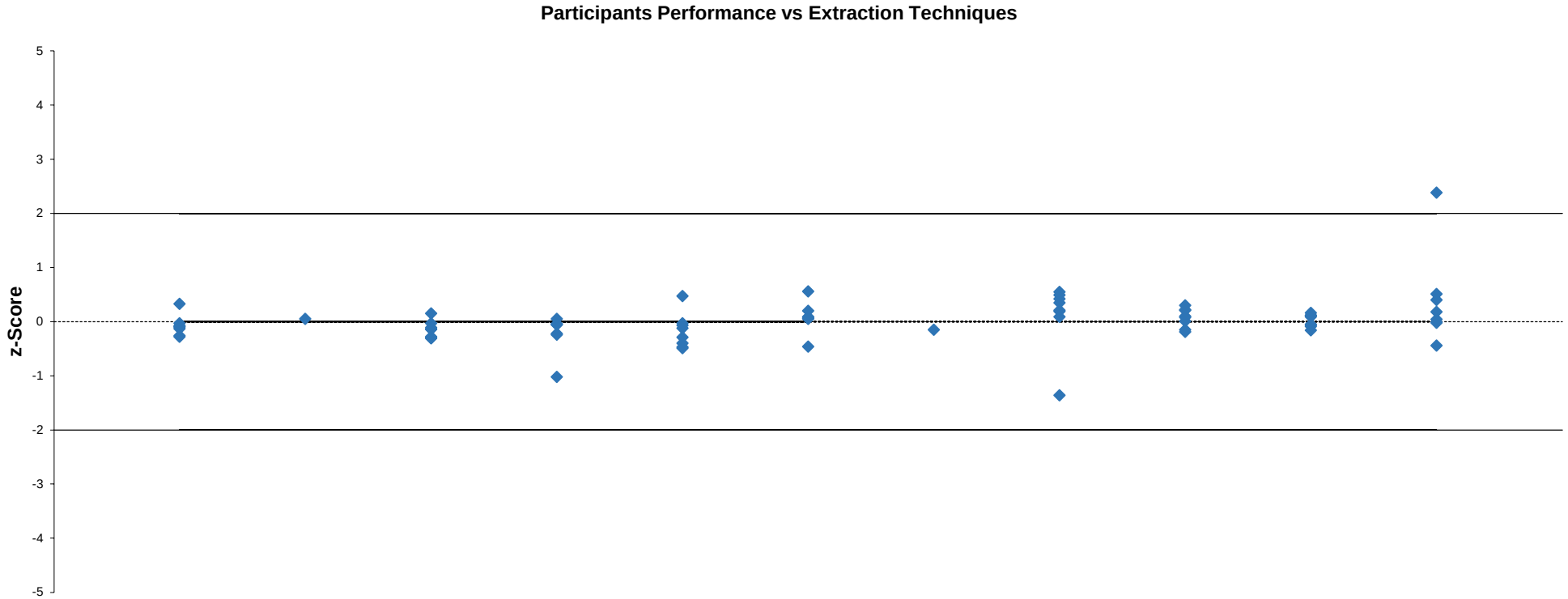


Figure 14 Summary of Participants' Performance

Table 16 Summary of Participants' Results and Performance in Sample S1

Lab Code	Cd mg/kg	Cr mg/kg	Cu mg/kg	Hg mg/kg	Li mg/kg	Mn mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
AV	64.0	72.9	73.8	Not Set	30.2	102	61.9	106	99.8
HV	58.2	68.7	73.7	1.96	29.9	96.1	59.6	108	95.1
SV	53.9	64.3	64.0	1.99	19.8	73.9	49.6	88.7	74.2
1	NT	NT	NT	NT	NT	NT	NT	<100	NT
2	NT	NT	NT	NT	NT	NT	NT	107	NT
3	62.2	70.9	76.0	1.4	30.0	95.6	58.2	100	97.6
4	63.36	69.38	72.94	1.65	NT	81.25	59.17	105.2	100.79
5	58	67	72	1.7	30	96	61	116	90
6	65	81	67	NT	NT	106	63	107	101
7	63	71	70	<2.5	30	100	66	100	98
8	NT	NT	NT	NT	NT	NT	NT	102.75	NT
9	71	79	79	0.89	22	112	63	110	104
10	65	76	77	NR	32	104	60	102	100
11	65.1	75.3	75.5	1.6	29.8	101	59.9	104	102
12	64.5	66.5	73.7	2.2	31.3	112.4	66.9	156.5	99.4

Shaded cells are results which returned a questionable or unacceptable z-score. AV = Assigned Value, HV = Homogeneity Value, SV = Spike Value. NT = Not Tested, NR = Not reported.



Sample size (g)	0.1g	0.250-0.300 g	0.100 g	0.25 g	0.4 mL	0.299 g	0.22 g	0.2 g	0.18 g	0.1 g	0.5227 g
Temp(C)/ Time min	95C/90min	105C/60min	95C/40min	110C/60min	120C/60min	170C/20min	20C/1440 min	110C/60min	100C/480min	95C/30min	210C/55min
HNO_3	4 mL-3 mL	2.5 mL	10 mL	5 mL	10 mL	4 mL	10 mL	5 mL		10 mL	9 mL
HCl	No	0.5 mL		1.5 mL						2 mL	
Other	0-4 mL H_20	2 mL H_2O	2 drops H_2O_2				40 mL H_2O		2x10 mL HNO_3 (1:1)		11 mL H_2O

Figure 15 Participants' Performance versus Extraction Techniques

6.5 Participants' Results and Analytical Methods for Acid Extractable Elements

A summary of participants' results, and performance is presented in Table 16 and in Figures 11 to 14.

Overall measurements of acid extractable elements in paint did not challenge participants' analytical techniques. With the exception of Hg, the between laboratories' CVs were lower than those predicted by Thompson and Horwitz (Table 15).

Mercury challenged participants' analytical techniques, only 6 laboratories reported results; the between laboratory CV for this analyte was high at 31%.

Extraction Methods

The request was for acid extractable elements in paint. Participants used various extraction methods, which are presented in Tables 1 and 2 and Figure 15. Although participants used a wide variety of methods all scores results reported by them were compatible but one.

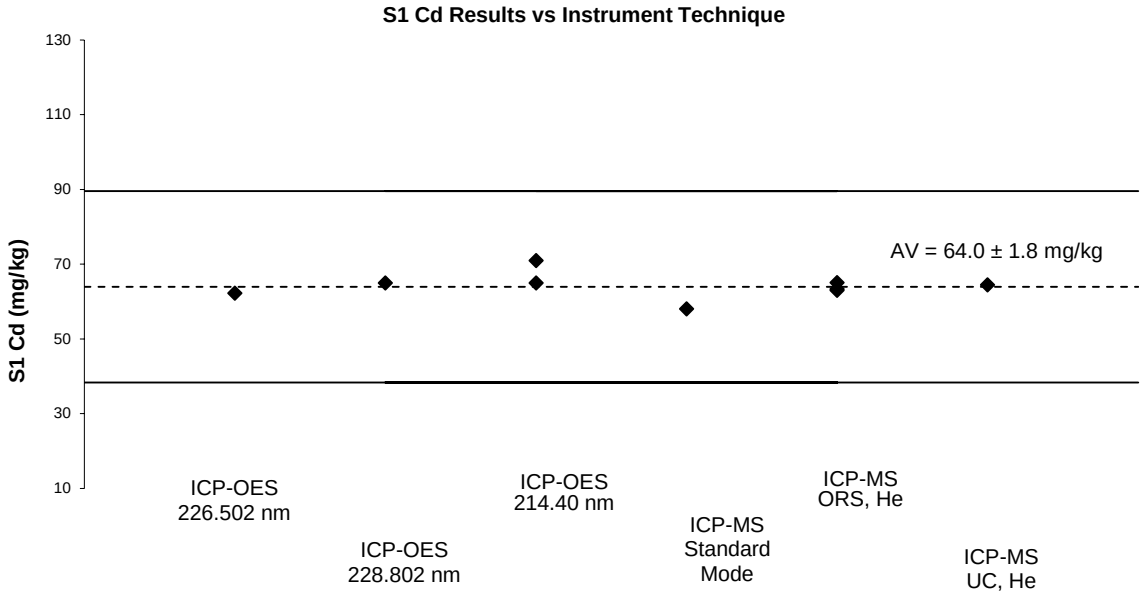
The most popular digestion methods involved: a sample size of between 0.2 g to 0.3 g, an extraction temperature of between 95ºC to 120ºC, an extraction time of 60 min, and a ratio HNO_3 to sample size of 25 to 1.

Laboratory 10 extracted their sample with diluted HNO3 for 8 hours. They also reported "*We also compared the results with AquaRegia digestion method which was shown lower recovery for all metals*."

Instrumental Techniques

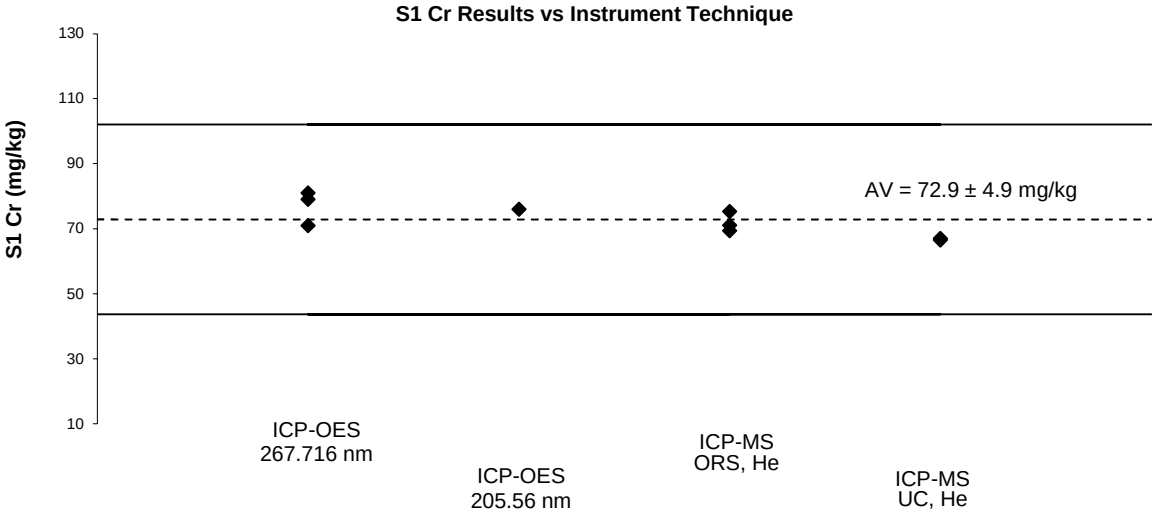
The instrumental conditions used by participants for measurement of acid extractable analytes in paint are presented in Appendix 4. Plots of participants performance versus instrumental techniques are presented in Figures 16 to 24.

Except for Hg, ICP-OES was the preferred instrumental technique. For Hg measurement in paint, laboratories used CVAAS or ICP-MS in standard mode or collision mode. All reported results were in good agreement with each other but one (Figure 19).



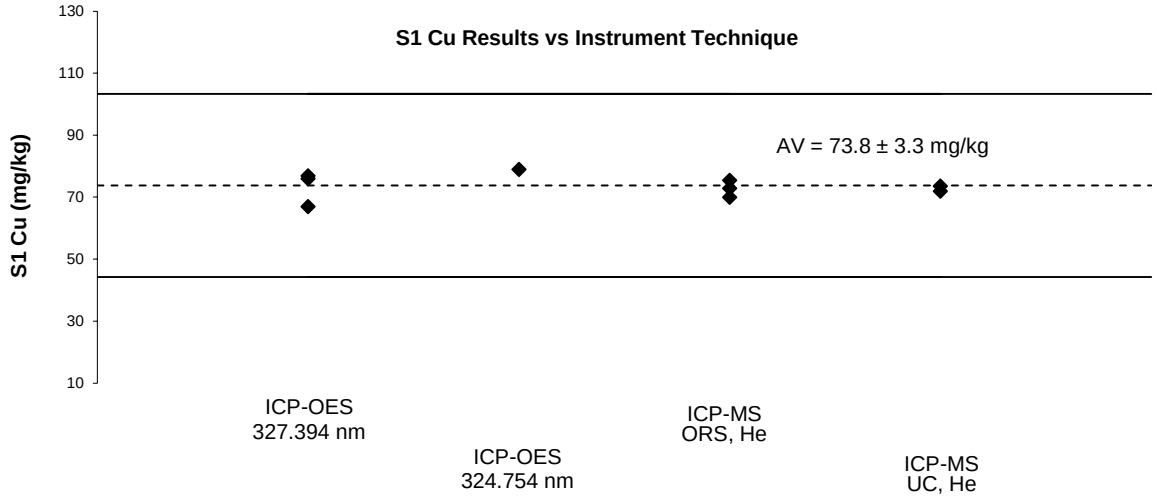
Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 16 S1-Cd Results vs. Instrumental Technique



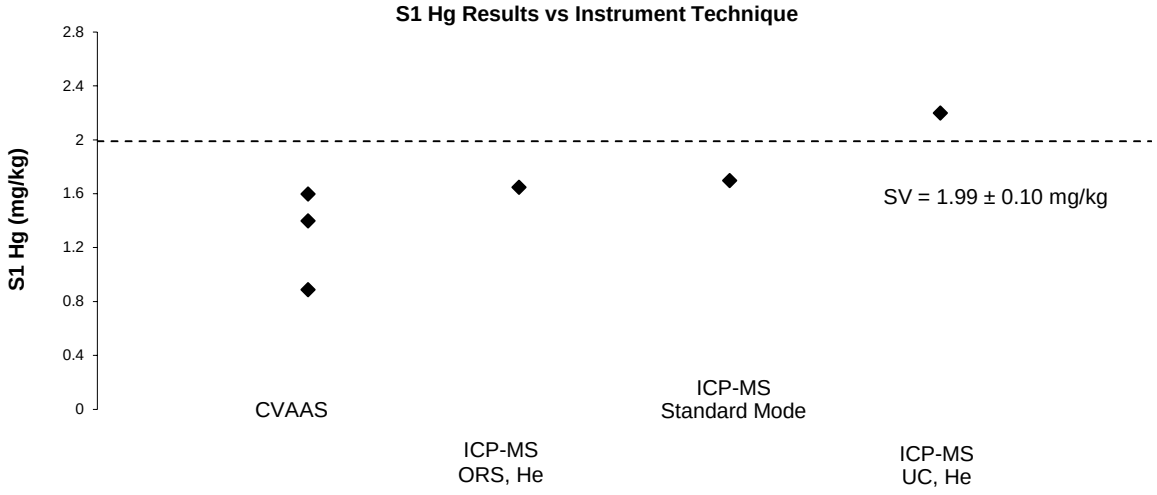
Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 17 S1-Cr Results vs. Instrumental Technique



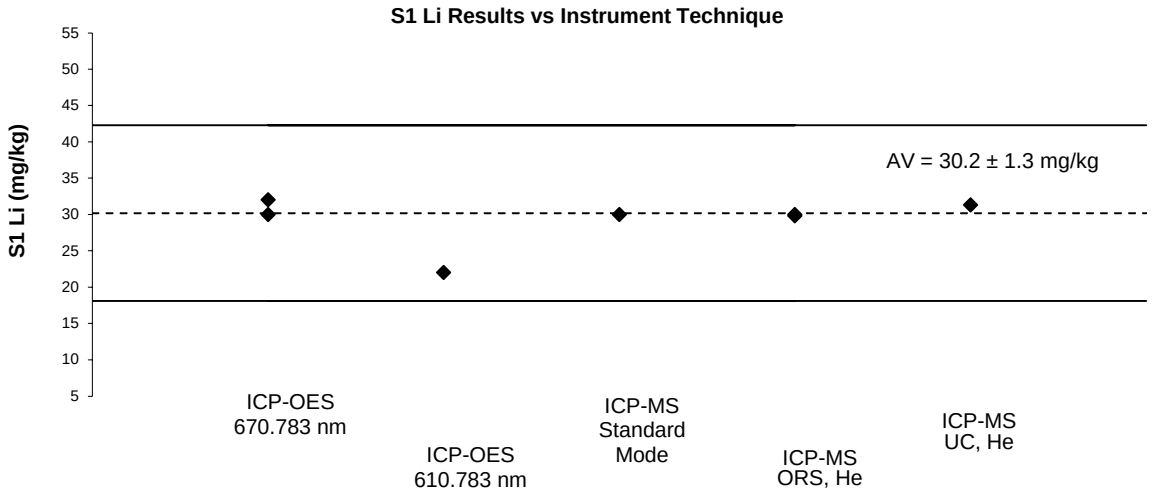
Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 18 S1-Cu Results vs. Instrumental Technique



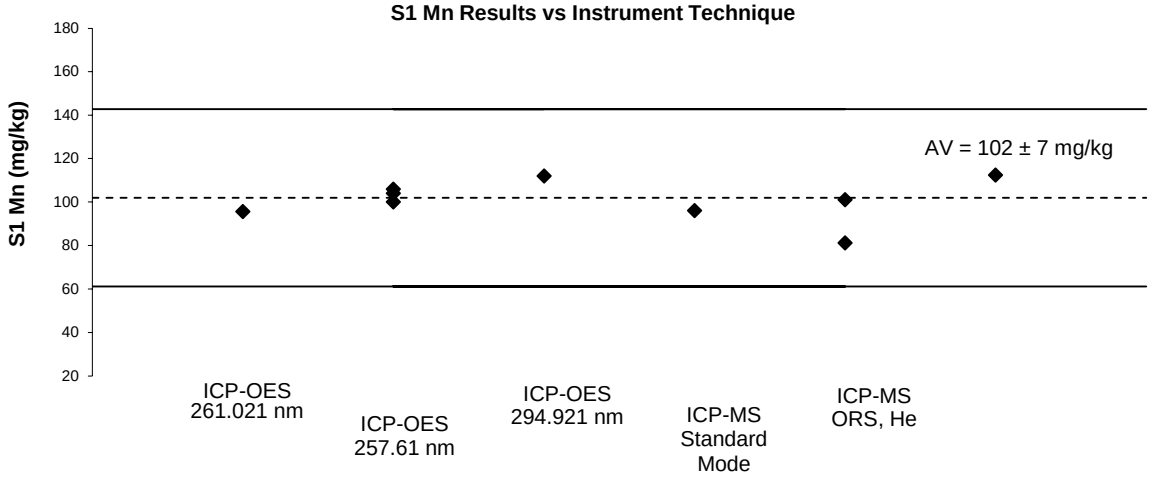
Horizontal line is the spike vale.

Figure 19 S1-Hg Results vs. Instrumental Technique



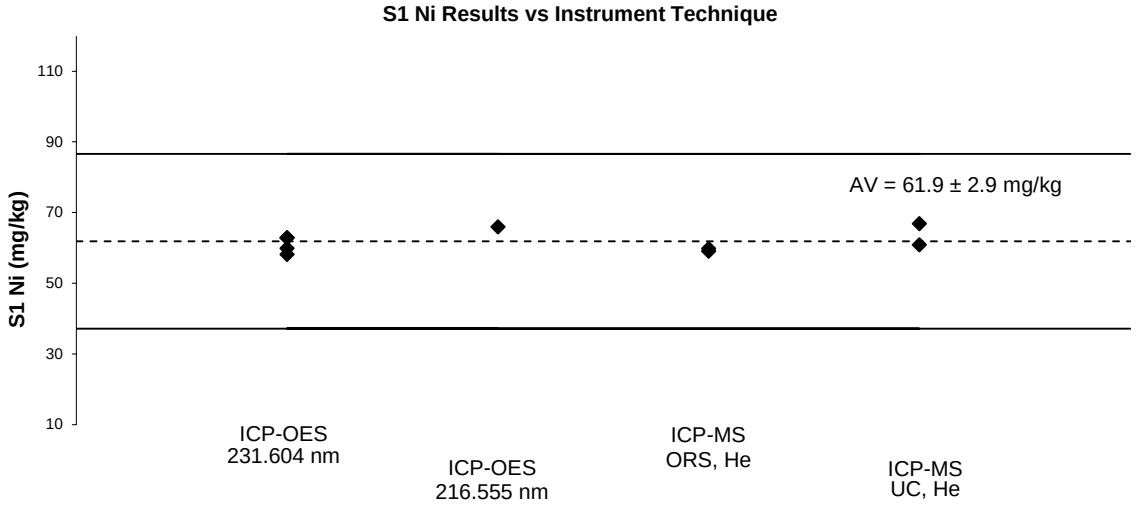
Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 20 S1-Li Results vs. Instrumental Technique



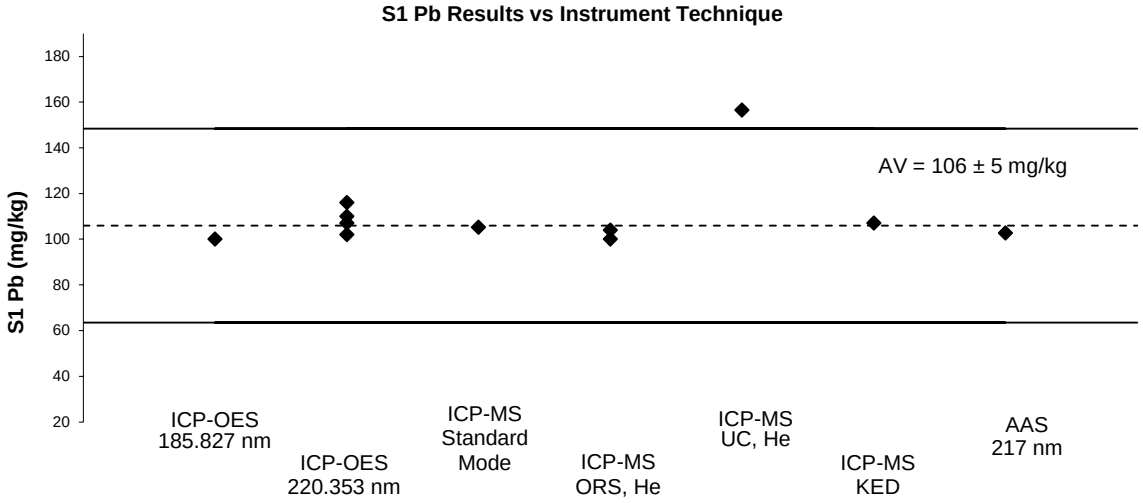
Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 21 S1-Mn Results vs. Instrumental Technique



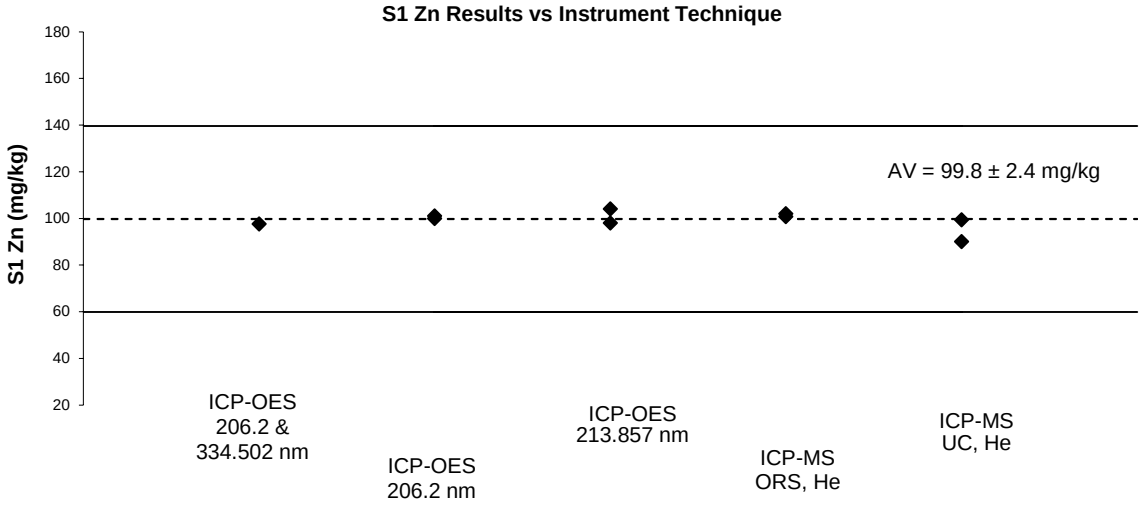
Horizontal lines on charts are the results corresponding to z-scores of 2 and -2.

Figure 22 S1-Ni Results vs. Instrumental Technique



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

Figure 23 S1-Pb Results vs. Instrumental Technique



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

Figure 24 S1-Zn Results vs. Instrumental Technique

6.6 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 17).

Table 17 Control Samples Used by Participants

Lab. Code	Description of Control Samples
1	CRM: Supelco Lead in Powdered Paint
2	RM
4	SS
5	CRM: Paint Chips CRM-PC-B
6	SS
7	CRM
8	CRM
9	CRM: Sigma Aldrich Certified Standard

Lab. Code	Description of Control Samples
10	RM
11	RM
12	CRM

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'*[14]

7 REFERENCES

Note: For all undated references, the latest edition of the referenced document (including any amendments) applies.

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[4] Thompson, M, Ellison, S.L.R & Wood, R 2006, 'The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories', Pure Appl. Chem, vol 78, pp 145-196.

[5] ISO13528, Statistical methods for use in proficiency testing by interlaboratory comparisons.

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[9] Bertil, M, Näykki, T, Hovind, H & Krysell, M 2012, *Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories*, Nordest Report TR 537 (ed 4)

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[11] ISO, Guide to the Expression of Uncertainty in Measurement (GUM), Geneva, Switzerland.

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[14] JCGM 200:2012, International vocabulary of metrology – Basic and General Concepts and Associated Terms (VIM), 3rd edition.

[15] Thompson, M. and Fearn, T., 2001, 'A new test for 'sufficient homogeneity'', *Analyst*, vol. 126, pp. 1414-1417.

[16] NMI Inorganics, Method NT2.49: Determination of Acid Extractable Elements in Soils, Sediments, Sludges and Solid Waste

APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING

Sample Preparation

Sample S1 was an oil-based paint which was mixed, spiked with 9 oil-based metal standards and allowed to mix further. The paint was then dried before being packaged into containers.

Sample Analysis and Homogeneity Testing

A full homogeneity test was conducted for all acid extractable elements in Sample S1. Homogeneity testing for this sample was based on that described by Thompson and Fearn,[15] which is also the procedure as described in the International Harmonised Protocol for Proficiency Testing.[4] A minimum of 6 bottles were selected at random. Duplicate test-portions were taken from each bottle and the concentration of all targeted analytes was measured. Measurements were made under repeatability conditions in random order.

Data for the full homogeneity testing of sample S1 can be found below in Tables 18 - 26.

Table 18 Sample S1 Cd Homogeneity Testing

Container Number	Result (mg/kg)	
	Replicate 1	Replicate 2
2	63.1	54.9
6	63.5	58.6
11	52.7	53.3
17	58.8	66.9
24	55.6	57.5
29	54.4	57.1
35	63.2	55.0
Mean	58.2	
CV	14%	

Thompson and Fearn Homogeneity Tests

Test	Value	Critical	Result
Cochran	0.29	0.73	**Pass**
s_{an}/σ	0.35	0.50	**Pass**
s^2_{sam}	2.8	50	**Pass**

Table 19 Sample S1 Cr Homogeneity Testing

Container Number	Result (mg/kg)	
	Replicate 1	Replicate 2
2	74.8	65.0
6	74.9	69.8
11	61.2	63.0
17	69.3	79.0
24	66.4	67.1
29	63.5	68.6
35	74.5	65.5
Mean	68.7	
CV	14%	

Thompson and Fearn Homogeneity Tests

Test	Value	Critical	Result
Cochran	0.29	0.73	**Pass**
s_{an}/σ	0.35	0.50	**Pass**
s^2_{sam}	5.3	69	**Pass**

Table 20 Sample S1 Cu Homogeneity Testing

Container Number	Result (mg/kg)	
	Replicate 1	Replicate 2
2	79.3	69.9
6	80.2	73.9
11	67.5	69.4
17	74.0	84.2
24	70.6	71.7
29	68.5	73.0
35	79.1	70.7
Mean	73.7	
CV	13%	

Thompson and Fearn Homogeneity Tests

Test	Value	Critical	Result
Cochran	0.32	0.73	**Pass**
s_{an}/σ	0.33	0.50	**Pass**
s^2_{sam}	2.7	74	**Pass**

Table 21 Sample S1 Hg Homogeneity Testing

Container Number	Result (mg/kg)	
	Replicate 1	Replicate 2
2	1.98	1.99
6	1.95	2.04
11	2.04	1.99
17	1.98	1.95
24	1.93	1.98
29	1.93	1.84
35	1.81	2.00
Mean	1.96	
CV	6.6%	

Thompson and Fearn Homogeneity Tests

Test	Value	Critical	Result
Cochran	0.64	0.73	**Pass**
s_{an}/σ	0.17	0.50	**Pass**
s^2_{sam}	0.00032	0.035	**Pass**

Table 22 Sample S1 Li Homogeneity Testing

Container Number	Result (mg/kg)	
	Replicate 1	Replicate 2
2	32.3	28.7
6	33.0	29.4
11	28.4	28.7
17	30.0	33.2
24	27.7	30.0
29	27.8	29.2
35	31.8	28.0
Mean	29.9	
CV	14%	

Thompson and Fearn Homogeneity Tests

Test	Value	Critical	Result
Cochran	0.25	0.73	**Pass**
s_{an}/σ	0.34	0.50	**Pass**
s^2_{sam}	0	13	**Pass**

Table 23 Sample S1 Mn Homogeneity Testing

Container Number	Result (mg/kg)	
	Replicate 1	Replicate 2
2	104	91.0
6	106	97.4
11	86.7	87.8
17	97.4	111
24	91.4	94.2
29	88.5	95.3
35	104	91.2
Mean	96.1	
CV	14%	

Thompson and Fearn Homogeneity Tests

Test	Value	Critical	Result
Cochran	0.28	0.73	**Pass**
s_{an}/σ	0.35	0.50	**Pass**
s^2_{sam}	11	140	**Pass**

Table 24 Sample S1 Ni Homogeneity Testing

Container Number	Result (mg/kg)	
	Replicate 1	Replicate 2
2	64.9	55.8
6	65.3	60.2
11	53.6	54.3
17	60.2	68.9
24	57.2	58.4
29	55.7	58.9
35	64.7	56.8
Mean	59.6	
CV	14%	

Thompson and Fearn Homogeneity Tests

Test	Value	Critical	Result
Cochran	0.32	0.73	**Pass**
s_{an}/σ	0.36	0.50	**Pass**
s^2_{sam}	3.6	53	**Pass**

Table 25 Sample S1 Pb Homogeneity Testing

Container Number	Result (mg/kg)	
	Replicate 1	Replicate 2
2	119	103
6	119	108
11	98.5	98.6
17	108	124
24	102	108
29	103	106
35	115	103
Mean	108	
CV	14%	

Thompson and Fearn Homogeneity Tests

Test	Value	Critical	Result
Cochran	0.31	0.73	**Pass**
s_{an}/σ	0.35	0.50	**Pass**
s^2_{sam}	7.7	170	**Pass**

Table 26 Sample S1 Zn Homogeneity Testing

Container Number	Result (mg/kg)	
	Replicate 1	Replicate 2
2	104	90.3
6	104	95.8
11	86.8	87.8
17	95.7	109
24	90.2	92.6
29	88.5	93.9
35	103	90.6
Mean	95.1	
CV	14%	

Thompson and Fearn Homogeneity Tests

Test	Value	Critical	Result
Cochran	0.30	0.73	**Pass**
s_{an}/σ	0.34	0.50	**Pass**
s^2_{sam}	6.9	130	**Pass**

Sample Analysis for Acid Extractable Elements

The analysis for homogeneity were conducted by CRV section of NMI as per method NT2.49. [16] A test portion of approximately 0.3 g of paint was weighed into a 50 mL graduated polypropylene centrifuge tube. The sample was digested using 3 mL of concentrated nitric acid and 3 mL of concentrated hydrochloric acid on a hot block at 95°C ± 5°C. 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, and matrix matched reference materials, 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 27.

Table 27 Instrumental Technique used for Acid Extractable Elements

Analyte	Instrument	Internal Standard	Reaction/ Collision Cell	Cell Mode/Gas	Final Dilution Factor	Ion (m/z)/ Wavelength (nm)
Cd	ICP-MS	Rh	NA	NA	20	111 m/z
Cr	ICP-MS	Rh	ORS	He	20	52 m/z
Cu	ICP-MS	Rh	ORS	He	20	63 m/z
Hg	ICP-MS				20	202 m/z
Li	ICP-MS	Rh	ORS	He	20	7 m/z
Mn	ICP-MS	Rh	ORS	He	20	55 m/z
Ni	ICP-MS	Rh	ORS	He	20	60 m/z
Pb	ICP-MS	Ir	ORS	He	20	206 m/z
Zn	ICP-MS	Rh	ORS	He	20	64 m/z

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

The assigned value was calculated as the robust average using the procedure described in 'ISO13528(E), Statistical methods for use in proficiency testing by inter-laboratory comparisons – Annex C'.[6] The uncertainty was evaluated 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 28.

Table 28 Uncertainty of Assigned Value for Pb in Sample S1

No. results (p)	11
Robust Average	106 mg/kg
$S_{rob\ av}$	6.4 mg/kg
$u_{rob\ av}$	2.4 mg/kg
k	2
$U_{rob\ av}$	4.8 mg/kg

The assigned value for **Pb** in Sample S1 is **106 ± 5 mg/kg**.

z-Score and E_n-score

For each participant's result a z-score and E_n-score are calculated according to Equation 1 and Equation 2 respectively (see page 9). A worked example is set out below in Table 29.

Table 29 z-Score and E_n-score for Pb Result Reported by Laboratory 11 in S1

Pb Result mg/kg	Assigned Value mg/kg	Set Target Standard Deviation	z-Score	E_n-Score
104 ± 24.2	106 ± 5	20% as CV or 0.20 x 106 = 21.2 mg/kg	$z = \frac{(104 - 106)}{21.2}$ z = -0.09	$En = \frac{(104 - 106)}{\sqrt{24.2^2 + 5^2}}$ E_n= -0.08

APPENDIX 3 - ACRONYMS AND ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
APHA	American Public Health Association
AV	Assigned Value
CITAC	Cooperation on International Traceability in Analytical Chemistry
CRM	Certified Reference Material
CV	Coefficient of Variation
CVAAS	Cold Vapour Atomic Absorption Spectroscopy
CV_{rob}	Robust Coefficient of Variation
FAAS	Flame Atomic Absorption Spectroscopy
GUM	Guide to the Expression of Uncertainty in Measurement
HV	Homogeneity Value
ICP-MS	Quadrupole - Inductively Coupled Plasma - Mass Spectrometry
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometry
ISO/IEC	International Organisation for Standardisation / International Electrotechnical Commission
k	Coverage Factor
Max	Maximum value in a set of results
Md	Median
Min	Minimum value in a set of results
MU	Measurement Uncertainty
M.V.	Median Value
N	Number of Participants
NATA	National Association of Testing Authorities
NMI	National Measurement Institute (of Australia)
NR	Not Reported
NT	Not Tested
ORS	Octopole Reaction System
PCV	Performance Coefficient of Variation
PT	Proficiency Test
RA	Robust Average
RM	Reference Material
CV_{rob}	Robust Coefficient of Variation
SD_{rob}	Robust Standard Deviation
SV	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

APPENDIX 4 - INSTRUMENT DETAILS

Table 30 Instrument Conditions Cd

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1						
2	NA	NA	NA	NA	NA	NA
3	ICP-OES	Eu & Cs	NA	NA	500	226.502nm
4	ICP-MS	Te-125	ORS	He	157	111
5	ICP-MS	Rh	NA	standard mode	625	111
6	ICP-OES 8300	NA	NA	NA	1.25	228.802
7	ICP-MS	Rh	ORS	He	10	111
8						
9	ICP-OES-AV	Yb			50	214.43 nm
10	ICP-OES-AV	Lu 291.556			300	214.39
11	ICP-MS	Rh	ORS	He	50	111
12	ICP-MS	Rh	UC	He	x10	

Table 31 Instrument Conditions Cr

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1						
2	NA	NA	NA	NA	NA	NA
3	ICP-OES	Eu & Cs	NA	NA	500	267.716nm
4	ICP-MS	Sc-45	ORS	He	157	52
5	ICP-MS	Sc	UC	He	625	52
6	ICP-OES 8300	Lu 261.542	NA	NA	1.25	267.716
7	ICP-MS	Rh	ORS	He	10	52
8						
9	ICP-OES-AV	Yb			50	267.716 nm
10	ICP-OES-AV	Lu 291.556			300	205.56
11	ICP-MS	Sc	ORS	He	50	52
12	ICP-MS	Rh	UC	He	x10	

Table 32 Instrument Conditions Cu

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1						
2	NA	NA	NA	NA	NA	NA
3	ICP-OES	Eu & Cs	NA	NA	500	327.395nm
4	ICP-MS	Rh-103	ORS	He	157	63
5	ICP-MS	Ge	UC	He	625	63
6	ICP-OES 8300	NA	NA	NA	1.25	327.393
7	ICP-MS	Rh	ORS	He	10	63
8						
9	ICP-OES-AV	Yb			50	324.754 nm
10	ICP-OES-AV	In 303.936			300	327.395
11	ICP-MS	Sc	ORS	He	50	50
12	ICP-MS	Rh	UC	He	x10	

Table 33 Instrument Conditions Hg

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1						
2	NA	NA	NA	NA	NA	NA
3	CETAC	NA	NA	NA	500	253.7nm
4	ICP-MS	Ir-193	ORS	He	1570	201
5	ICP-MS	Ir	NA	standard mode	625	201
6	NT	NA	NA	NA	NA	NA
7	ICP-MS	Rh	ORS	He	10	202
8						
9	CVAAS	SnCl2			50	
10						
11	CVAAS	N\A			50	253.7
12	ICP-MS	Rh	UC	He	x10	

Table 34 Instrument Conditions Li

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1						
2	NA	NA	NA	NA	NA	NA
3	ICP-OES	Eu & Cs	NA	NA	500	670.783nm
4	NA	NA	NA	NA	NA	NA
5	ICP-MS	Sc	NA	standard mode	625	7
6	NT	NA	NA	NA	NA	NA
7	ICP-MS	Rh	ORS	He	10	7
8						
9	ICP-OES-AV	Yb			50	610.783 nm
10	ICP-OES-AV	In 410.176			300	670.783
11	ICP-MS	Sc	ORS	He	50	7
12	ICP-MS	Rh	UC	He	x10	

Table 35 Instrument Conditions Mn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1						
2	NA	NA	NA	NA	NA	NA
3	ICP-OES	Eu & Cs	NA	NA	500	261.021nm
4	ICP-MS	Sc-45	ORS	He	157	55
5	ICP-MS	Sc	NA	standard mode	625	55
6	ICP-OES 8300	Lu 261.542	NA	NA	1.25	257.61
7	ICP-OES-AV	Y	NA	NA	10	257.61
8						
9	ICP-OES-AV	Yb			50	294.921 nm
10	ICP-OES-AV	Eu 271.700			300	257.61
11	ICP-MS	Sc	ORS	He	50	55
12	ICP-MS	Rh	UC	He	x10	

Table 36 Instrument Conditions Ni

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1						
2	NA	NA	NA	NA	NA	NA
3	ICP-OES	Eu & Cs	NA	NA	500	231.604nm
4	ICP-MS	Rh-103	ORS	He	157	60
5	ICP-MS	Ge	UC	He	625	60
6	ICP-OES 8300	Lu 261.542	NA	NA	1.25	231.604
7	ICP-OES-AV	Y	NA	NA	10	216.555
8						
9	ICP-OES-AV	Yb			50	231.604 nm
10	ICP-OES-AV	Lu 291.556			300	231.604
11	ICP-MS	Sc	ORS	He	50	65
12	ICP-MS	Rh	UC	He	x10	

Table 37 Instrument Conditions Pb

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1	FAAS					
2	ICP-MS	Tb	KED	He	20000	206+207+208
3	ICP-OES	Eu & Cs	NA	NA	500	185.827nm
4	ICP-MS	Ir-193	ORS	standard mode	1570	208
5	ICP-OES-AV	Lu	NA	NA	625	220.353
6	ICP-OES 8300	Lu 219.554	NA	NA	1.25	220.353
7	ICP-MS	Rh	ORS	He	10	208
8	AAS				1	217
9	ICP-OES-AV	Yb			50	220.353 nm
10	ICP-OES-AV	Lu 291.556			300	220.353
11	ICP-MS	Ir	ORS	He	50	209
12	ICP-MS	Rh	UC	He	x10	

Table 38 Instrument Conditions Zn

Laboratory Code	Instrument	Internal standard	Reaction Cell	Reaction Gas	S1 Final Dilution Factor	Wavelength (nm)/ Ion(m/z)/ Absorbance(nm)
1						
2	NA	NA	NA	NA	NA	NA
3	ICP-OES	Eu & Cs	NA	NA	500	206.2, 334.502nm
4	ICP-MS	Rh-103	ORS	He	1570	66
5	ICP-MS	Ge	UC	He	625	66
6	ICP-OES 8300	NA	NA	NA	1.25	206.2
7	ICP-OES-AV	Y	NA	NA	10	213.857
8						
9	ICP-OES-AV	Yb			50	213.857 nm
10	ICP-OES-AV	Lu 291.556			300	206.2
11	ICP-MS	Sc	ORS	He	50	66
12	ICP-MS	Rh	UC	He	x10	

END OF REPORT