



Australian Government  
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**National  
Measurement  
Institute**

# **Proficiency Test Report AQA 18-06 Hexavalent Chromium in Soil**

August 2018



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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.

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## 1 SUMMARY

This report presents the results of the proficiency test AQA 18-06, Chromium (VI) in soil.

One sample was included in this study. Sample S1 was the NIST Standard Reference Material 2701 Hexavalent Chromium in Contaminated Soil.

Laboratories had the option of submitting more than one result and choosing whether or not to be scored for the reported results. Nine laboratories registered to participate, 11 results were submitted and 10 of those were scored.

The assigned value was the certified value of NIST Standard Reference Material 2701, Hexavalent Chromium in Contaminated Soil (High Level). It has been calculated by NIST as the unweighted mean of analytical measurements conducted by NIST and three other collaborating laboratories. The value was based on the extraction of hexavalent chromium from the material using USEPA Method 3060A, followed by determination using molecular speciated isotope dilution mass spectrometry, (USEPA Method 6800).

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

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

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

Of 11 results for which z-scores were calculated, 7 returned a satisfactory score of  $|z| \leq 2$ .

Of 11 results for which  $E_n$ -scores were calculated, 2 returned a satisfactory score of  $|E_n| \leq 1$ .

- ii. evaluate the laboratories' methods used in determination of Cr(VI) in soil;*

Some evidence was found in present and past PT studies that by adjusting the ratio of extraction liquid to dried sample size to at least 50 to 1, soil extraction efficiency may be improved and interference problems caused by the highly coloured extract may be overcome. As the samples encountered in a routine laboratory can vary in moisture content, laboratories should ideally determine samples' solid content first before calculating the sample amount to be used in analyses.

The regulatory limit for Cr (VI) in soil is 1 mg/kg. As the ratio of extracting solution to dried sample size has to be at least 50 to 1 to overcome matrix reducing properties (regardless of Cr (VI) level in sample), laboratories should use a determination method sensitive enough to accurately measure Cr (VI) at ppb level in the extracting solution or increase their reporting level.

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

All results, were reported with an expanded measurement uncertainty.

## **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."<sup>1</sup> 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 18-06 is the 23<sup>rd</sup> NMI proficiency study of inorganic analytes in soil and the second that involves measurement of Cr (VI).

### **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 Cr (VI) in soil; and
- develop the practical application of traceability and measurement uncertainty; and

### **2.3 Study Conduct**

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

NMI is accredited by National Association of Testing Authorities, Australia (NATA) to ISO/IEC 17043 as a provider of proficiency testing schemes.

Participants were asked to use the same extraction method (USEPA3060A) but the choice of the measurement technique was left to them.

## **3 STUDY INFORMATION**

### **3.1 Selection of Matrix and Analyte**

The test and the test level was selected from those for which an ecological investigation level is published in the National Environment Protection (Assessment of Site Contamination) Measure (NEPM) Schedule B(1) *Guidelines on the Investigation Levels for Soil and Groundwater*, promulgated by the National Environmental Protection Council (NEPC).<sup>5</sup>

### **3.2 Participation**

Nine laboratories participated and all submitted results.

The timetable of the study was:

Invitation issued: 07 May 2018  
Samples dispatched: 28 May 2018  
Results due: 15 June 2018  
Interim report issued: 18 June 2018

### **3.3 Test Material Specification**

One sample was provided for analysis:

**Sample S1** was 15 g of NIST SRM 2701.

### **3.4 Laboratory Code**

All participant laboratories were assigned a confidential code number. Participants had the option of submitting more than one result. Eleven laboratory code numbers were assigned to 9 participants.

### **3.5 Homogeneity and Stability Testing**

No homogeneity and stability testing were conducted for the study sample. Sample S1 was a standard reference material, its homogeneity and stability have been established during the certification process.

### **3.6 Sample Storage, Dispatch and Receipt**

The test sample was stored at ambient temperature prior to dispatch.

The sample was dispatched by courier on 28 May 2018.

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

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

### **3.7 Instructions to Participants**

Participants were instructed as follows:

- Quantitatively analyse the samples using the USEPA method 3060A or equivalent methods.
- The concentration of Cr (VI) in this sample is above 250 mg/kg level.
- Report the result for Cr (VI) as you would report to a client.
- Report the expanded measurement uncertainty associated with your analytical result (e.g.  $5.0 \pm 0.5$  mg/kg). Report the basis of your uncertainty estimates (i.e. control charts, proficiency testing).
- Please send us all the requested details regarding the test method.
- Return the completed results sheet by 15 June 2018.

### **3.8 Interim Report**

An interim report was emailed to participants on 18 June 2018.

## 4 PARTICIPANT LABORATORY INFORMATION

### 4.1 Test Method Summaries

Summaries of the test methods and participants' comments are transcribed in Table 3.

### 4.2 Basis of Participants' Measurement Uncertainty Estimates

Participants were requested to provide information about the basis of their uncertainty estimates (Table 1).

Table 1 Basis of Uncertainty Estimate

Lab. Code	Approach to Estimating MU	Information Sources for MU Estimation		Guide Document for Estimating MU
		Precision <sup>a</sup>	Method Bias <sup>a</sup>	
1	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate analysis	Recoveries of SS Instrument Calibration	Nordtest Report TR537
2	Top Down - precision and estimates of the method and laboratory bias			NATA Technical Note 33
3	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Duplicate Analysis Instrument Calibration	CRM Instrument Calibration	ISO/GUM
4	Top Down - precision and estimates of the method and laboratory bias	Control Sample-CRM Instrument Calibration	CRM Instrument Calibration	ISO/GUM
5	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples: CRM Duplicate Analysis Instrument Calibration	CRM Recoveries of SS Instrument Calibration	NMI Uncertainty Course
6	Top Down - precision and estimates of the method and laboratory bias	Duplicate Analysis	Laboratory bias from PT studies	Eurachem/CITAC Guide
7	Top Down - precision and estimates of the method and laboratory bias	Control Sample Duplicate analysis Instrument calibration	Recoveries of SS Instrument Calibration	NATA Technical Note 33
8	Top Down - precision and estimates of the method and laboratory bias	Control Samples Duplicate Analysis instrument Calibration	Recoveries of SS Instrument Calibration	NATA Technical Note 33
9	Bottom Up (ISO/GUM, fish bone/ cause and effect diagram)	Control Samples: SS Duplicate Analysis	CRM	Eurachem/CITAC Guide
10	Top Down - precision and estimates of the method and laboratory bias	Control Sample Duplicate analysis Instrument Calibration	Recoveries of SS Instrument Calibration	NATA Technical Note 33
11	3x standard deviation of 6 reads over 3 days gave an uncertainty of approximately $\pm 13\%$	Duplicate analysis	Recoveries of SS	

<sup>a</sup>RM = Reference Material, CRM = Certified Reference Material, SS = Spiked samples.

## 5 PRESENTATION OF RESULTS AND STATISTICAL ANALYSIS

### 5.1 Results Summary

Participant results are listed in Table 2 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 Figure 2.

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

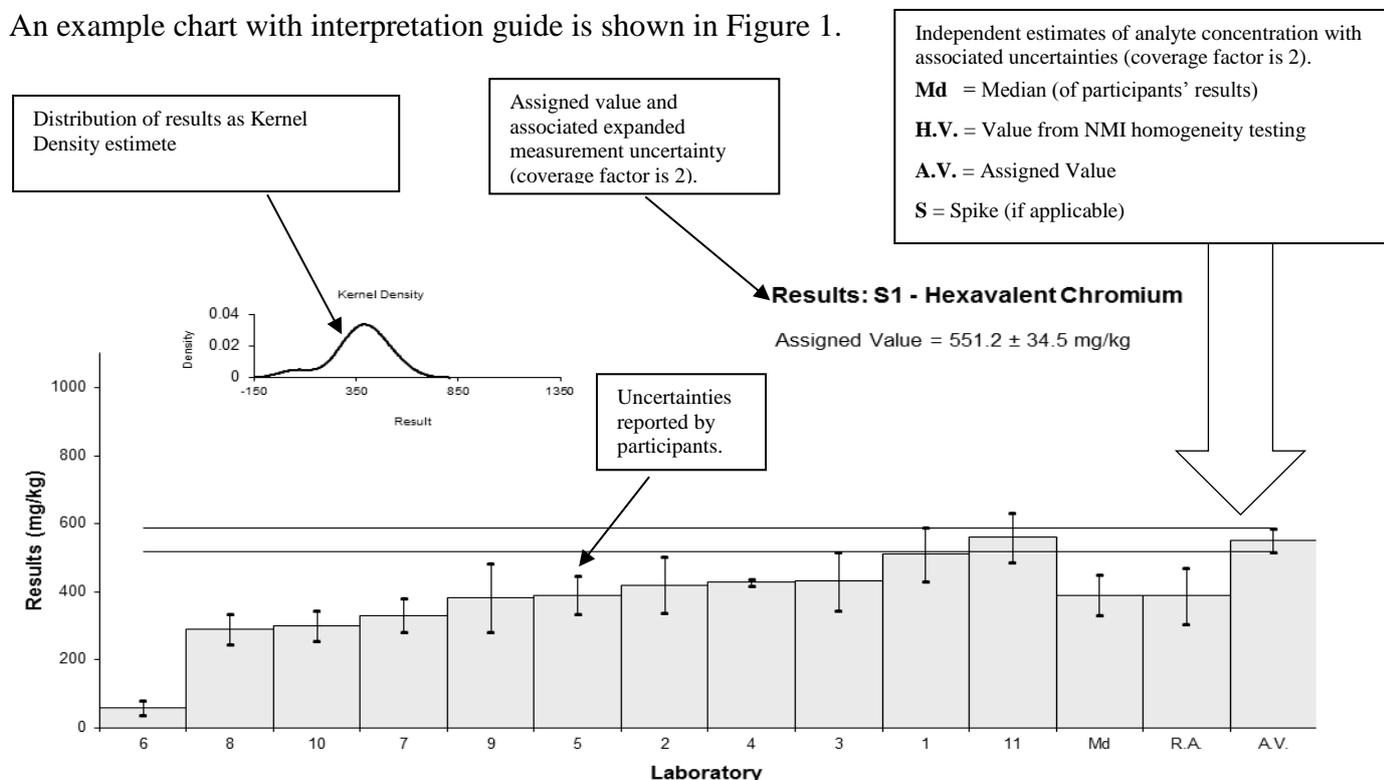


Figure 1 Guide to Presentation of Results

### 5.2 Assigned Value

The assigned value is defined as: ‘the value attributed to a particular property of a proficiency test item.’<sup>1</sup> In this study the property is the mass fraction of analyte. Assigned value was a certified value by molecular speciated isotope dilution mass spectrometry.

### 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)’.<sup>7</sup>

### 5.4 Robust Between-Laboratory Coefficient of Variation

The robust between-laboratory coefficient of variation (CV) is a measure of the variability of participants’ results and was calculated using the procedure described in ISO13528:2015(E).<sup>7</sup>

### 5.5 Target Standard Deviation

The target standard deviation ( $\sigma$ ) is used in the calculation of z-scores and provides scaling for laboratory deviation from the assigned value. It is important to note that the target standard deviation for this study is a fixed value established by the study coordinator and is not the standard deviation of participants’ results. The fixed value set for the target standard deviation is based on the existing regulation, the acceptance criteria indicated by the methods, the matrix, the concentration level of analyte and on experience from previous studies, and is

backed up by mathematical models such as the Thompson Horwitz equation.<sup>7</sup> By setting a fixed and realistic value for the performance standard deviation, the participants' performance (z-score) can be compared from study to study and against achievable performance. This provides a benchmark for progressive improvement.

## 5.6 z-Score

An example of z-score calculation using data from the present study is given in Appendix 2.

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

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

where:

- $z$  is z-score
- $\chi$  is participant result
- $X$  is the study assigned value
- $\sigma$  is the target standard deviation from Equation 1

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

- $|z| \leq 2$  is satisfactory;
- $2 < |z| < 3$  is questionable;
- $|z| \geq 3$  is unsatisfactory.

## 5.7 E<sub>n</sub>-Score

An example of E<sub>n</sub>-score calculation using data from the present study is given in Appendix 2.

The E<sub>n</sub>-score is complementary to the z-score in assessment of laboratory performance.

E<sub>n</sub>-score includes measurement uncertainty and is calculated according to Equation 2 below:

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

where:

- $E_n$  is E<sub>n</sub>-score
- $\chi$  is participant result
- $X$  is the study assigned value
- $U_\chi$  is the expanded uncertainty of the participant's result
- $U_X$  is the expanded uncertainty of the assigned value

An E<sub>n</sub>-score with absolute value ( $|E_n|$ ):

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

## 5.8 Traceability and Measurement Uncertainty

Laboratories accredited to ISO/IEC Standard 17025:2017<sup>8</sup> 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.<sup>9</sup>

## 6 TABLES AND FIGURES

Table 2

### Sample Details

Sample No.	S1
Matrix.	Soil
Analyte.	Hexavalent Chromium
Units	mg/kg

### Participant Results

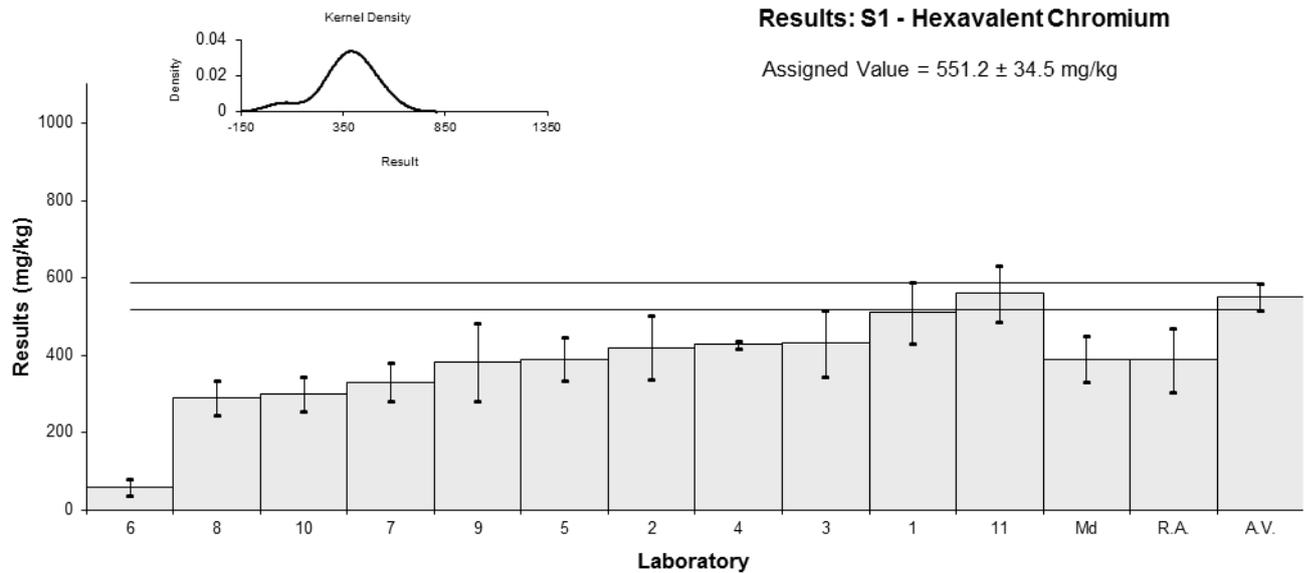
Lab Code	Result	Uncertainty	z-Score	E <sub>n</sub> -Score
1	510	80	-0.37	-0.47
2	420	84	-1.19	-1.44
3	430	86	-1.10	-1.31
4	428	10	-1.12	-3.43
5	390	55	-1.46	-2.48
6*	58	23		
7	330	49.7	-2.01	-3.66
8	290	43.7	-2.37	-4.69
9	382	100	-1.53	-1.60
10	300	45.2	-2.28	-4.42
11	560	73	0.08	0.11

\*Laboratory 6 chose not to be scored for the reported results

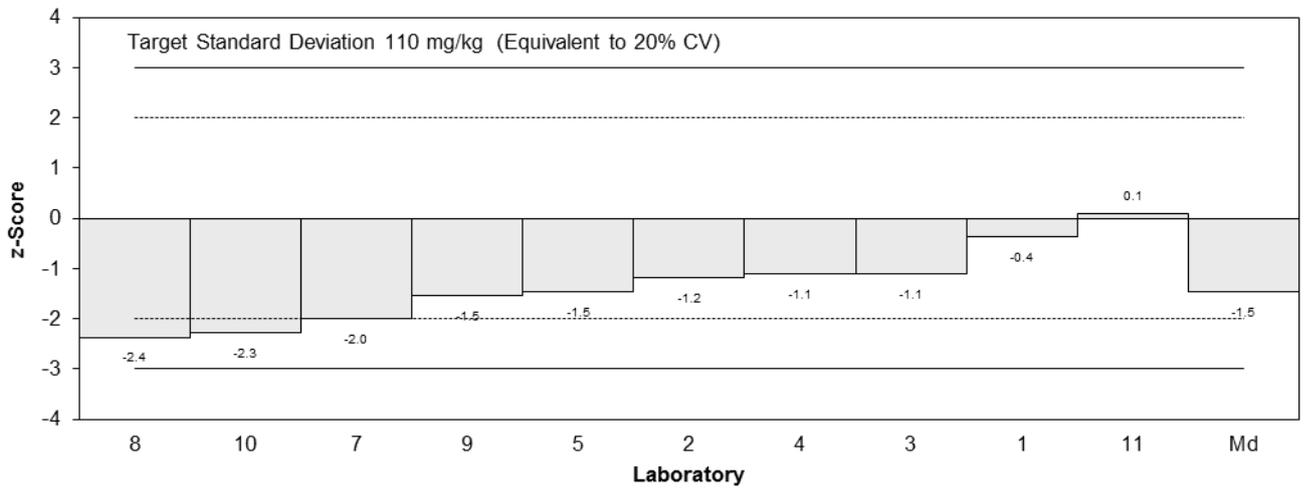
### Statistics

Assigned Value*	551.2	34.5
Spike	Not Spiked	
Certified Value	551.2	34.5
Robust Average	387	83
Median	390	60
Mean	373	
N	11	
Max.	560	
Min.	58	
Robust SD	110	
Robust CV	28%	

\*NIST Certified value by molecular speciated isotope dilution mass spectrometry



**z-Scores: S1 - Hexavalent Chromium**



**En-Scores: S1 - Hexavalent Chromium**

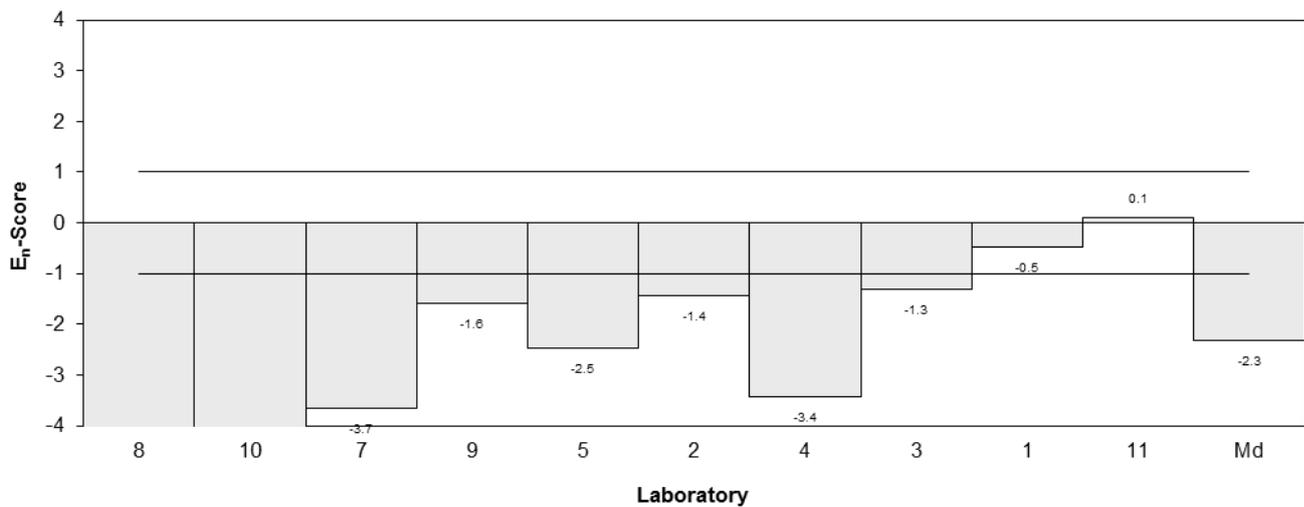


Figure 2

## 7 DISCUSSION OF RESULTS

### 7.1 Assigned Value

The single test sample (Sample S1), was the Standard Reference Material 2701, Hexavalent Chromium in Contaminated Soil (High Level) prepared by the National Institute of Standards and Technology (NIST).

Assigned Value was the certified value calculated by NIST from the robust average of analytical measurements conducted by NIST and three collaborating laboratories. The certified value was based on the extraction of hexavalent chromium from the material using the USEPA Method 3060A, and determination by speciated isotope dilution mass spectrometry, (Method 6800).<sup>10,11</sup>

### 7.2 Measurement Uncertainty Reported by Participants

Participants were asked to report an estimate of the expanded measurement uncertainty associated with their results. All numerical results were reported with an expanded measurement uncertainty as requested in ISO/IOC 17025:2005.<sup>9</sup> The participants used a wide variety of procedures to estimate the expanded measurement uncertainty. These are presented in Table 1.

Proficiency tests allow a check of the reasonableness of uncertainty estimates. Results and the expanded MU are presented in the bar chart in Figure 2. In this study in some cases, the reported expanded measurement uncertainty has been under-estimated (e.g. Lab 4). As a simple rule of thumb, when the uncertainty estimate is smaller than the assigned uncertainty value it should be viewed as suspect.

### 7.3 E<sub>n</sub>-score

E<sub>n</sub>-score should be interpreted only in conjunction with z-scores. The E<sub>n</sub>-score indicates how closely a result agrees with the assigned value taking into account the respective uncertainties. An unsatisfactory E<sub>n</sub> 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<sub>n</sub>-scores is graphically presented in Figure 3.

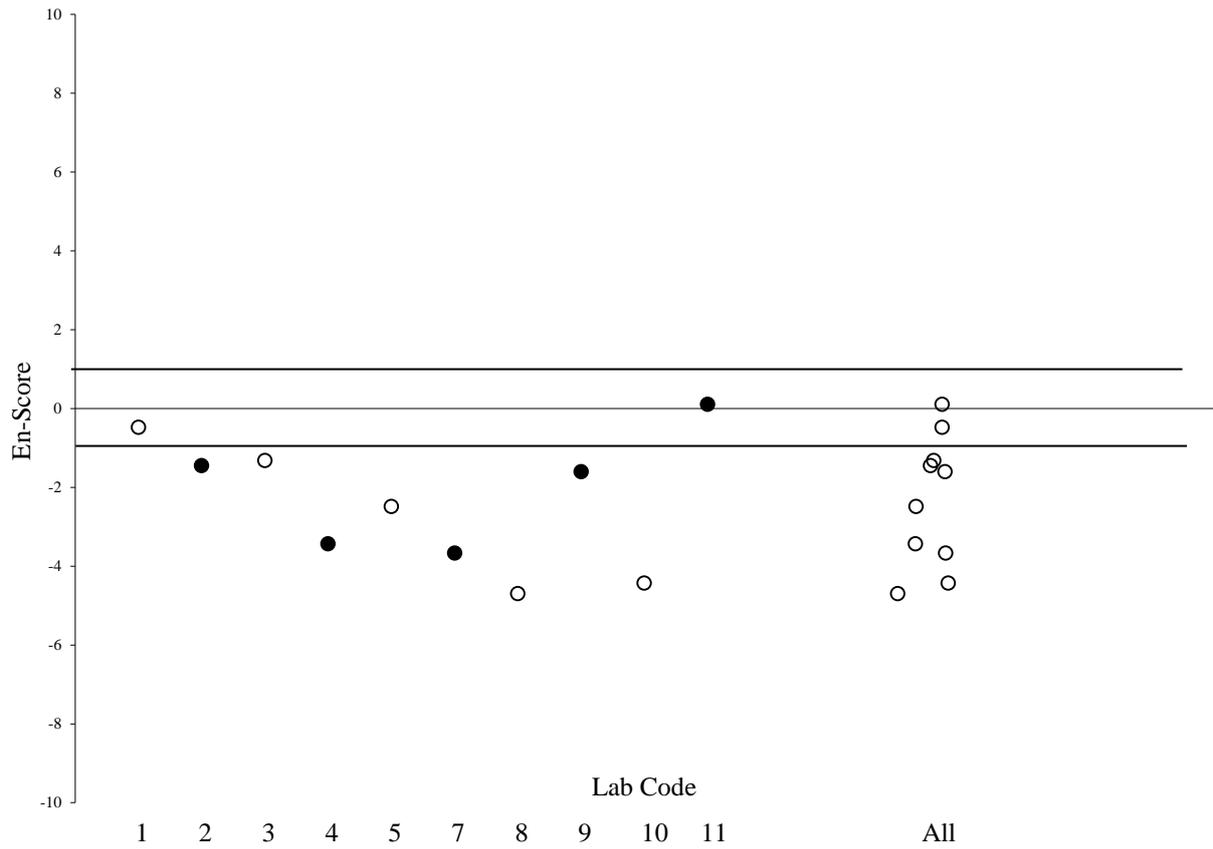
Of 11 results for which E<sub>n</sub>-scores were calculated, 2 returned a satisfactory score of  $|E_n| \leq 1$  indicating agreement of the participants' results with the assigned values within their respective expanded measurement uncertainties.

### 7.4 z-Score

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

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

The dispersal of participants' z-scores is presented in Figure 4. Of 11 results for which z-scores were calculated, 7 returned a satisfactory score of  $|z| \leq 2$  and 3 were questionable with a score of  $2 < |z| < 3$ .



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

Figure 3  $E_n$ -Score Dispersal by Laboratory

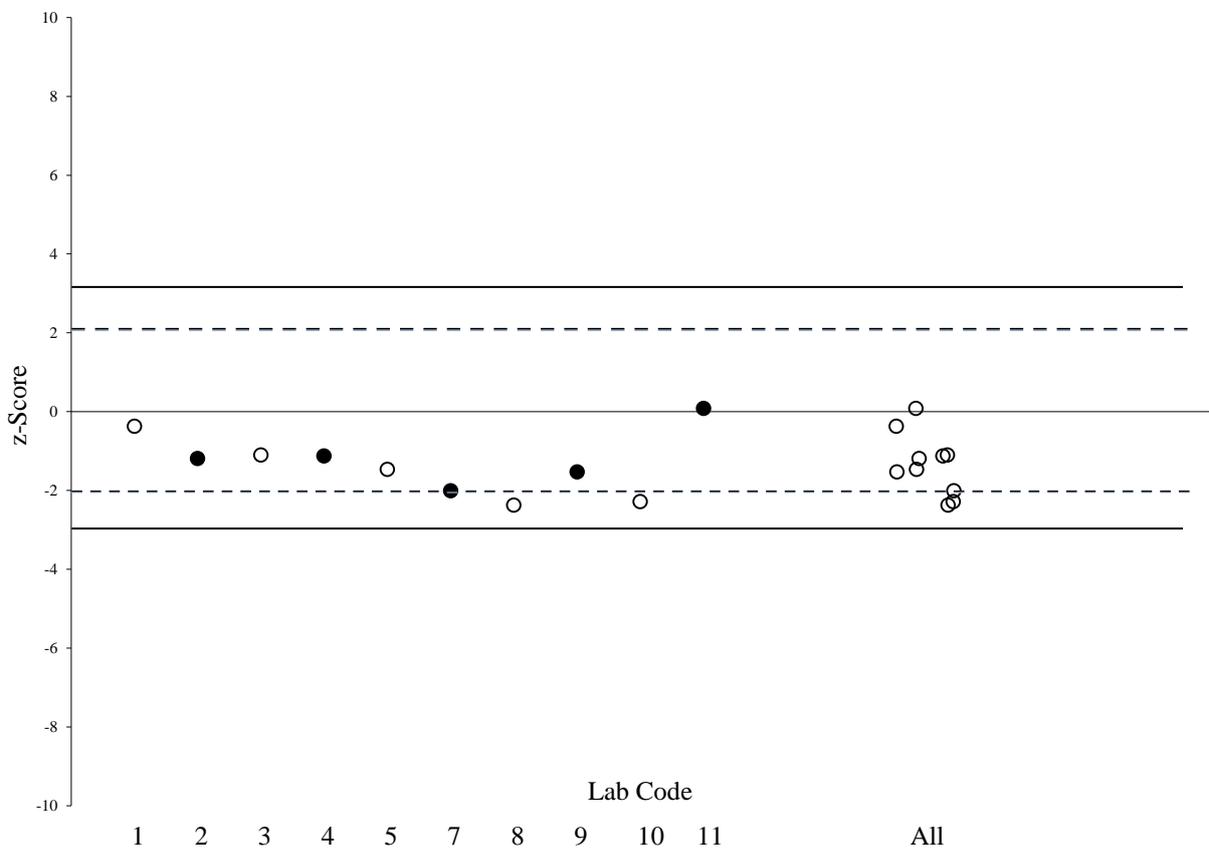


Figure 4 z-Score Dispersal by Laboratory

## 7.5 Participants' Results and Analytical Methods for Cr (VI) in Soil

Participants were instructed to use extraction method USEPA3060A (hot  $\text{Na}_2\text{CO}_3/\text{Na}(\text{OH})$  extraction) or equivalent.<sup>11</sup> The choice of the measurement technique for Cr (VI) in the alkaline extract was left to the participating laboratories.

A summary of the extraction methods and instrumental techniques used by participants together with their comments and findings are presented in Table 3. Plots of participants' results versus the extraction method and instrumental technique used are presented in Figure 5.

Laboratories 2 and 11 reported results for Cr (VI) in this study as well findings from a study conducted by them on Cr (VI) recovery with the sample size.

### Extraction Methods

Methods for extracting Cr (VI) from soil are based on alkaline extraction of total (water soluble and insoluble) Cr (VI), and on leaching procedures for easily soluble Cr (VI). When the potential environmental and health hazards of Cr (VI) are assessed, extraction methods for total Cr (VI) are used.<sup>12</sup> Extraction using hot  $\text{Na}_2\text{CO}_3/\text{NaOH}$  is the most effective for dissolving all forms of Cr (VI), with the exception of the partially-soluble hexavalent Cr compound  $\text{BaCrO}_4$ .<sup>12, 13</sup> This extraction method selectively extracts Cr (VI), but not Cr (III).

Ten participants used the alkaline extraction as per USEPA Method 3060A or a modified version. Laboratories 7, 8 and 10 used 25 mL of extracting solution and 200 mL of  $\text{MgCl}_2$ . All these 3 laboratories reported results that returned low and questionable z-scores, lower than (-2).

U.S. Geological Survey identified the use of  $\text{MgCl}_2$  as one of the possible causes of low Cr (VI) recoveries.<sup>14</sup> Cr (VI) can co-precipitate with the  $\text{Mg}(\text{CO}_3)/\text{Mg}(\text{OH})_2$  precipitate. This can be formed when  $\text{Mg}^{2+}$  is added to eliminate elements that may reduce Cr (VI). Recovery of Cr (VI) when  $\text{Mg}^{2+}$  was added was 75% and 85% when the  $\text{Mg}^{2+}$  was omitted. They also found that Mg co-precipitation agent resulted in a flocculent precipitate which was hard to wash and filter. Flocculation may also occur in the extract filtrate when the pH is further adjusted for Cr (VI) determination.<sup>21</sup>

Laboratory 6 used a leaching procedure recommended for easily soluble Cr (VI) and this might explain the low result reported by them.

Participants used various sample sizes from 0.1g to 3 g, 40 to 50 mL of alkaline extraction solution, and a digestion temperature of between 80 to 100°C (Table 3 and Figure 5).

The recoveries of Cr (VI) in the test sample generally increased with the decrease in sample size; a possible relationship was found between the high Cr (VI) results, closer to the reference value and a high ratio extracting solution (mL) to sample size (g) (Figure 6).

No significant relationship was found between the reported results and the shaking frequency, the digestion time or the digestion temperature used for extraction.

### Measurement Techniques

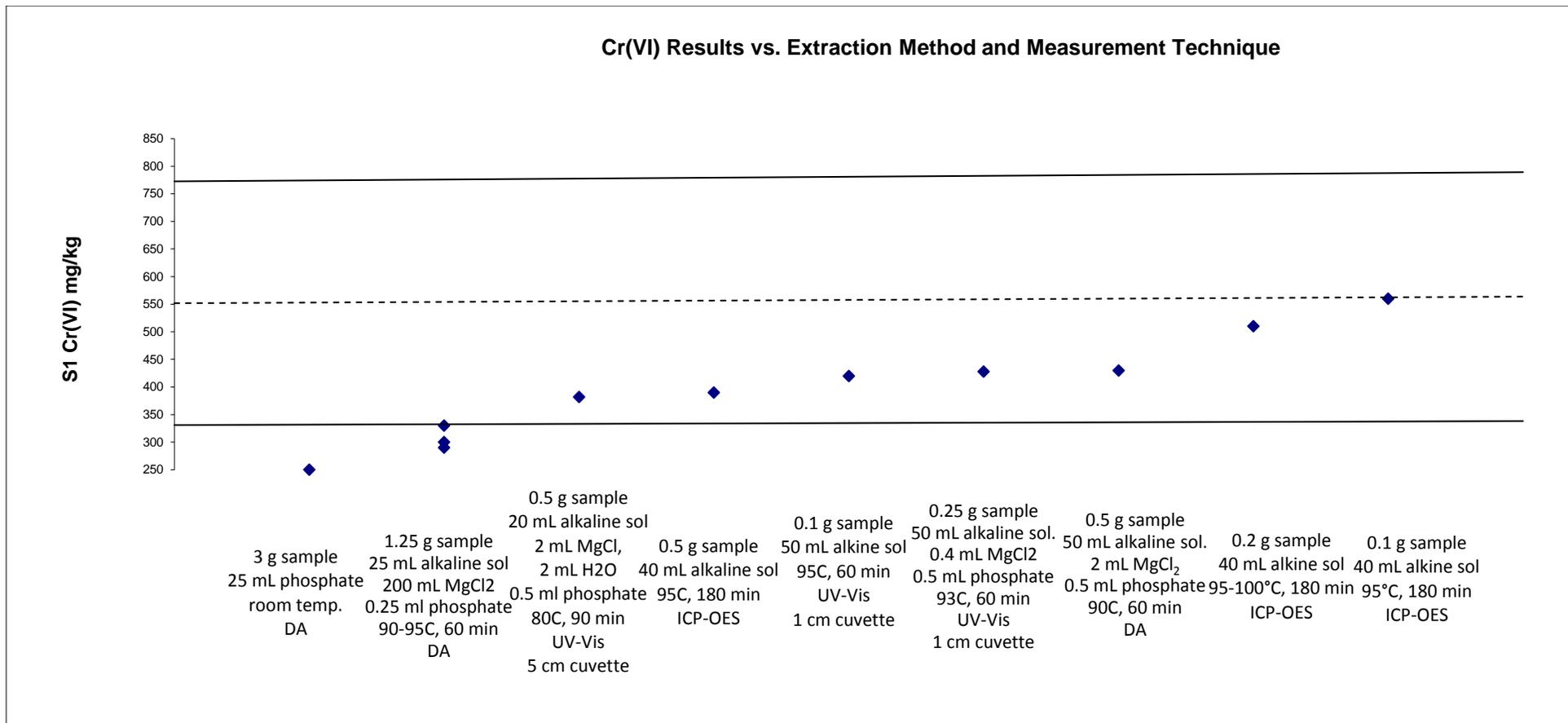
There are three commonly used EPA methods to quantify Cr (VI) (6800, 7199, 7196A). All three methods use the same extraction protocol: EPA3060A. Method 6800 uses ion-chromatography (IC) coupled to ICP-MS; Method 7199 uses IC with a post column addition of diphenylcarbazide followed by colorimetric determination; and Method 7196A uses the same colorimetric complex of Cr (VI) for quantification, but the assay is performed on the extract using UV-Vis or discrete-analyser (DA).<sup>14, 15, 17</sup>

Table 3 Summary of Test Methods and Participants' Comments

Lab. Code	Cr Result (mg/kg)	Sample Spike	Spike Recovery %	Result Corrected for Spike Recovery	Sample Mass (g)	Reagents Volume (mL)			Digestion Temp. (°C)	Digestion Time (min)	Shake Time	Measurement Method	Comments
						0.28 M Na <sub>2</sub> CO <sub>3</sub> / 0.5 M NaOH (mL)	Other	Phosphate buffer (mL)					
1	510	After digestion Cr standard	98	No	0.2	40			95-100	180	Every 30 min	ICP-OES	
2	420			No	0.100	50			95	60		UV-Vis 1 cm cell length	
3	430	Prior digestion 20 mg PbCrO <sub>4</sub>	90	No	0.5	50	MgCl <sub>2</sub> 2 mL	0.5	90	60	Every 15 min	Colorimetric DA	
4	428	No	NT	No	0.25	50	MgCl <sub>2</sub> 0.4 mL	0.5	93	60	Continuous stirring	UV-Vis 1 cm cell length	
5	390	No		No	0.5	40			95	180	Every 15 min	ICP-OES	Our standard methodology is to use 2 g of sample, however with a sample that has this high concentration we found the best recovery for the results using a 0.5 g digest weight. Weights we tried higher than (1g) extracted lower amounts of Cr (VI).
6	58	No		No	3	NT	NT	25	N/A	N/A	5 mins on orbital shaker for total extraction	Diphenylcarbazide colourimetry DA 540 nm	
7	330				1.25	25	MgCl <sub>2</sub> 200 mL	0.25	90 to 95	60	frequently	DA	The proficiency sample was not spiked, however a spiked sample was analysed within the Lab Batch

Table 3 Summary of Test Methods and Participants' Comments (continued)

Lab. Code	Cr Result (mg/kg)	Sample Spike	Spike Recovery %	Result Corrected for Spike Recovery	Sample Mass (g)	Reagents Volume (mL)			Digestion Temp. (°C)	Digestion Time (min)	Shake Time	Measurement Method	Comments
						0.28 M Na <sub>2</sub> CO <sub>3</sub> / 0.5 M NaOH (mL)	Other	Phosphate buffer (mL)					
8	290				1.25	25	MgCl <sub>2</sub> 200 mL	0.25	90 to 95	60	frequently	DA	The proficiency sample was not spiked, however a spiked sample was analysed within the Lab Batch
9	382	Prior digestion and After digestion 0.5 mL of 10mg/L Cr <sub>6</sub> (equivalent to 100ug/L)	After digestion 102% and Prior digestion 82%	No	0.5	20	MgCl <sub>2</sub> 2 mL and 27 mL H <sub>2</sub> O	0.5	80	90	twice	UV-Vis 5 cm cell length	
10	300				1.25	25	MgCl <sub>2</sub> 200 mL	0.25	90 to 95	60	frequently	DA	The proficiency sample was not spiked, however a spiked sample was analysed within the Lab Batch
11	560	Prior digestion KCr <sub>2</sub> O <sub>7</sub> 5mg/L	100	No	0.1	40			95	180	once	ICP-OES	It was found that the higher the reagent ratio the higher the Cr(VI) recovery. For example, weighing out 0.05 grams gave a result of 590 mg/kg. Weighing out 0.2 grams gave a result of 490 mg/kg and weighing out 0.5 grams gave a result of 390 mg/kg. We elected to report the results from weighing out 0.1 grams.



\*Result smaller than 250 mg/kg has been plotted as 250 mg/kg. Horizontal lines on charts correspond to z-scores of 2 and -2

Figure 5 S1-Cr (VI) Results vs. Extraction Method and Instrumental Technique

In this study, 8 participants used a colorimetric method for Cr (VI) determination in the soil extract, and 3 used ICP-OES (Figure 5).

No significant correlation between the instrumental technique and reported results was noted.

## **7.6 Comparison with Previous NMI Proficiency Study of Cr (VI) in Soil AQA 16-18**

AQA 16-18 was the first PT study for Cr (VI) in soil conducted by NMI, and possibly the first to be conducted in Australia. This study was also the first PT study for most participants in which they checked the methods used routinely for total Cr (VI) measurements in soil. No assigned value could be set in AQA 16-18 because the reported results were too variable.

Three major problems were identified by participants in AQA 16-18:

- reducing properties of the matrix;
- high colour background in the soil extract; and
- low level of Cr (VI) in the test sample.

### **Reducing properties of the matrix**

In soils or sediments without significant amounts of certain organics, metals and anions, Cr (VI) can usually be measured accurately. However many soils, sludges, sediments and solid wastes have the matrix components listed above. Iron, fulvic and humic acids, sulphides and various microorganisms can reduce Cr (VI) in the extracting solution to Cr (III), while Mn (IV) oxides present in soil can facilitate oxidation of Cr (III) to Cr (VI). High concentration of chloride and sulfate in the soil can also cause losses of Cr (VI) when measured by IC.<sup>14</sup>

Meaningful evidence was found in the present and the previous study of the importance of using a high ratio of extracting solution (mL) to dried sample size (g) of at least 50 to 1 in order to overcome matrix-reducing properties and improve Cr (VI) recovery.

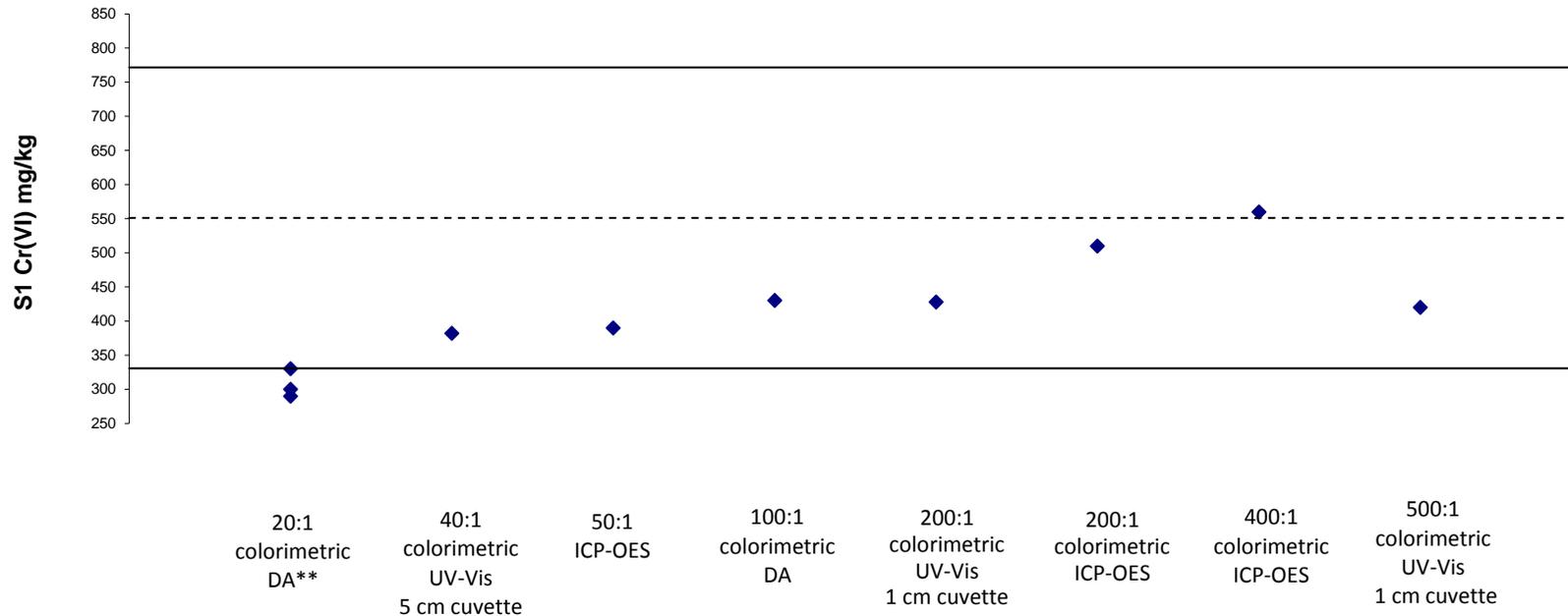
The sample in AQA 16-18 was dried biosoil with high organic content, and so was highly reducing. Laboratories participating in this study experienced problems with recovering the spiked Cr (VI), except for those laboratories who used a small sample size and so a larger ratio of extracting solution (mL) to sample size (g) of 50 to 1 and 100 to 1. In the present study, better recoveries of Cr (VI) in the dried soil sample were also achieved by those participants who used a smaller sample size; a relationship was noticed between the high Cr (VI) results, closer to the reference value and a large ratio of extracting solution (mL) to sample size (g) (Figure 6).

Three independent experiment on recoveries of Cr (VI) with various sample sizes were also conducted by the NMI and Laboratories 2 and 11. Measurements were made using the same amount of the extracting solution (Na<sub>2</sub>CO<sub>3</sub>/Na OH) and the same instrumental techniques, but different sample sizes. All three studies reached a similar conclusion: recoveries of Cr (VI) increased with decreases in sample size.

Laboratory 11 reported: “It was found that the higher the reagent ratio the higher the Cr (VI) recovery. For example, weighing out 0.05 g gave a result of 590 mg/kg. Weighing out 0.2 grams gave a result of 490 mg/kg and weighing out 0.5 grams gave a result of 390 mg/kg. We elected to report the results from weighing out 0.1 grams (560 mg/kg).”

The results from the experiments conducted by Laboratory 2 and the NMI are presented in Tables 4 and 5 respectively.

**Cr (VI) Results vs. Ratio Extracting Solution : Sample Size and Measurement Technique\***



\*Laboratory 6 not included. Horizontal lines on charts correspond to z-scores of 2 and -2. \*\* Ratio liquid to sample size 150:1.

Figure 6 S1Cr (VI) Results vs. Ratio Extracting Solution : Sample Size and Instrumental Technique

A similar extraction experiment was also conducted by Buckley and Stiles from New Jersey Department of Environmental Protection (NJDEP) in their study on the “Evaluation of Methods for Quantifying Cr (VI) and Cr (III) in Soils and Wastes.”<sup>15</sup> Their study also concluded that: ‘as the liquid to solid volumes are increased, the recoveries are also increased.’

Table 4 Cr (VI) Results from Different Sample Sizes by Laboratory 2

Sample Size (g)	Cr (VI) (mg/Kg)
0.051	393.0
0.051	372.1
0.101	417.2
0.101	426.0
0.100	420.3*
0.201	254.2
0.204	240.4
0.201	250.7
0.405	184.4
0.419	172.3
0.804	133.4
0.805	122.9
0.804	107.2

\*Result Reported

The NMI study also investigated the impact the digestion time and shaking frequency on Cr (VI) recoveries.

Table 5 Cr (VI) Results from Different Sample Sizes by NMI

Sample Size (g)	Time (min)	Sample Shaken During Extraction	Cr (VI) (mg/Kg)
0.2	180	Every 15 min	533
0.3	180	Not shaken	445
0.4	180	Every 15 min	465
1	180	Every 15 min	338
1	180	Not shaken	334
1	300	Every 15 min	314
1	300	Not shaken	310

No significant difference was found between Cr (VI) results coming from different digestion times and shaking frequencies.

The ratio of extracting solution to sample size has been found to be the main factor that affects Cr (VI) recovery. A high ratio extracting solution (mL) to dried sample size (g) of at least 50 to 1 has proven essential for overcoming matrix reducing properties and improving Cr (VI) extraction efficiency. While the test materials used in present and past studies were dried soil, the USEPA Method 3060A is designed for ‘field-moist samples’. The method recommends that laboratories use 2.5g of ‘field-moist’ moist sample and 50mL alkaline extracting solution. As the samples encountered in a routine laboratory can vary in moisture content, for a ratio extracting solution: dried sample size of at least 50 to 1, laboratories

should ideally determine samples' solid content first before calculating the amount of sample to be used in analyses.

### **High background colour**

In AQA 16-18, most of the participating laboratories that used a ratio of extracting solution to sample size of between 20:1 and 50:1 commented on the dark colour of the extract. These laboratories also reported using spectrophotometry for Cr (VI) determination.

Spectrophotometry has low specificity and is liable to interferences from coloured species.

Spectrophotometry was also the preferred technique for Cr (VI) measurements in the present study and there were no comments on the extract colour. Participants used a ratio of liquid to sample size between 1:40 to 1:500 (Figure 6). Laboratories 7, 8 and 10 used a ratio of extracting solution to sample size of 20 to 1, but these laboratories also used 200 mL MgCl<sub>2</sub>.

Using a larger ratio of extracting solution to sample size of at least 40 to 1 also helped to overcome the second problem signalled by participants: the high background colour.

### **Cr (VI) level in the test sample**

Colorimetric measurements are not only liable to interferences of coloured species but also are not sensitive enough for the determination of Cr (VI) concentration in soil extracts at low level. This was the third problem encountered by participating laboratories in the previous study: the low level of Cr (VI) in the test sample.

In the present study, Cr (VI) concentration was high and has not posed a problem for laboratories who used spectrophotometry.

Taking a small test portion of soil with Cr (VI) close to the regulatory limit may stretch DA and UV-Vis capabilities. Laboratories using spectrophotometry for Cr (VI) measurements should consider increasing their level of reporting or using a cell with a longer light path.

## **7.7 Conclusions**

Measurements of total Cr (VI) in soil are challenging. One such difficulty is overcoming matrix-reducing properties by using the right ratio of alkaline extraction solution to moist field sample. Interferences caused by coloured species in the extract and spectrophotometer's sensitivity also constitute a challenge to laboratories who measure Cr (VI) colorimetrically.

Some evidence was found in the present and past PT studies that by adjusting the ratio of extraction liquid to dried sample size to at least 50 to 1, soil extraction efficiency may improve and interference problems caused by the highly coloured extract can be overcome. As the samples encountered in a routine laboratory can vary in moisture content, laboratories should ideally determine samples' solid content first and then calculate the amount of the sample to be used in analyses.

The regulatory limit for Cr (VI) in soil is 1 mg/L.<sup>5</sup> As the ratio of extracting solution to dried sample size has to be at least 50 to 1 to overcome matrix-reducing properties (regardless of the Cr (VI) level in the sample), laboratories should use a determination method sensitive enough to accurately measure Cr (VI) at ppb level in the extracting solution or increase their reporting level. For most laboratories which use a colorimetric method for Cr (VI) measurements, a UV-Vis with a long absorption cell might be preferable.

## 8 REFERENCE MATERIALS AND CERTIFIED REFERENCE MATERIALS

Participants reported whether control samples (spiked samples, certified reference materials-CRMs or matrix specific reference materials-RMs) had been used (Table 6).

Table 6 Control Samples Used by Participants

Lab. Code	Description of Control Samples
4	CRM
5	CRM RTC Chromium (VI) - Clay Soil CRM060-30G
9	Environmental Resources Associates ERA876

Matrix matched control samples taken through all steps of the analytical process, are the 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'*<sup>17</sup>

## 9 REFERENCES

- [1] ISO/IEC 17043:2010, Conformity assessment – *General requirements for proficiency testing*, ISO, Geneva.
- [2] National Measurement Institute 2016, *NMI Chemical Proficiency Testing Study Protocol*, viewed 6 August 2018.  
<http://www.measurement.gov.au/Services/Documents/CPTStudyProtocol.pdf>
- [3] National Measurement Institute 2016, *NMI Chemical Proficiency Testing Statistical Manual*, viewed 6 August 2018.  
<http://www.measurement.gov.au/Services/Documents/CPTStatisticalManual.pdf>
- [4] Thompson, M, Ellison, S & Wood, R 2006, *The international harmonized protocol for proficiency testing of (chemical) analytical laboratories*, Pure Appl. Chem. 78, 145-196.
- [5] National Environmental Protection Council, *NEPM Schedule B (1) Guidelines on the Investigation Levels for Soil and Groundwater*, viewed 6 August 2018.  
<http://www.nepc.gov.au/nepms/assessment-site-contamination>
- [6] ISO13528:2015(E), *Statistical methods for use in proficiency testing by interlaboratory comparisons*.
- [7] Thompson, M, Ellison 2000, 'Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing', *Analyst*, vol 125, pp 385-386.
- [8] ISO/IEC 17025:2017, *General requirements for the competence of testing and calibration laboratories* ISO, Geneva, Switzerland.
- [9] Eurachem/CITAC Guide, *Quantifying uncertainty in analytical measurement* 2<sup>nd</sup> edition 2000, viewed January 2017, <http://www.eurachem.org/guides.pdf/QUAM2000-1.pdf>.
- [10] United States Environmental Protection Agency 1996, *Method 3060A Alkaline digestion for hexavalent chromium*, In test methods, SW846, update, Office of Solid Waste and Emergency Response, Washinton, DC.
- [11] United States Environmental Protection Agency 2014, *Method 6800 Elemental and Molecular Speciated Isotope Dilution Mass Spectrometry*, In test methods, SW846, update V, Office of Solid Waste and Emergency Response, Washinton, DC.
- [12] James, B R 1995, *Hexavalent Chromium Extraction from soil: A comparison of five methods*, *Environmental Science & Technology*, 29, 2377-2381.
- [13] Vitale, R J 1997, *Extraction of sparingly soluble chromate from soils: Evaluation of methods and E<sub>h</sub>-pH effects*. *Environmental Science & Technology*, 31, 390-394.
- [14] United States Geological Survey 2010, *Evaluation of Extraction Methods for Hexavalent Chromium Determination in Dusts, Ashes, and Soils*. United States Department of Interior.
- [15] Buckley, B & Stiles, R 2009, *Evaluation of Methods for Quantifying Cr(VI) and Cr(III) in Soils and Wastes SR06-051* , viewed January 2017,
- [16] Scancar, J 2016, *Development of Analytical Procedure for Determination of Exchangeable Cr(VI) in Soils by Anion-exchange Fast Protein Liquid Chromatography*

*with Electrothermal Atomic Absorption Spectrometry Detection*, Water Soil Pollution, 185, 121-129.

[17] JCGM 200:2008, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM)*, 3<sup>rd</sup> edition.

## **APPENDIX 1 - SAMPLE PREPARATION, ANALYSIS AND HOMOGENEITY TESTING**

### **Sample Preparation**

**Sample S1** was the standard reference material 2701 Hexavalent Chromium in Contaminated Soil (High Level) prepared by NIST. The material was gamma radiated at an average dosage of 50 kGy and further divided into portions of approximately 15 g each.

### **Sample Analysis and Homogeneity Testing**

No homogeneity testing was conducted by NMI for this material. The homogeneity of SRM 2701 was assessed by NIST as part of the certification process.

## APPENDIX 2 - Z-SCORE AND E<sub>n</sub> SCORE CALCULATION

For each participant's result a z-score and E<sub>n</sub>-score are calculated according to Equation 1 and Equation 2 respectively (see page 9).

A worked example is set out below in Table 7.

Table 7 z-Score and E<sub>n</sub>-score for Cr (VI) result reported by Laboratory 1 in S1

Cr (VI) Result mg/kg	Assigned Value mg/kg	Set Target Standard Deviation	z-Score	E <sub>n</sub> -Score
510±80	551.2±34.5	20% as CV or 0.20x551.2= =110.24 mg/kg	$z = \frac{(510 - 551.2)}{110.24}$  $z = -0.37$	$E_n = \frac{(510 - 551.2)}{\sqrt{80^2 + 34.5^2}}$  $E_n = -0.47$

### **APPENDIX 3 - ACRONYMS AND ABBREVIATIONS**

APHA	American Public Health Association
A.V.	Assigned Value
CRM	Certified Reference Material
CV	Coefficient of Variation
DA	Discreet Analyser
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometry
IC	Ion chromatograph
Max	Maximum value in a set of results
Md	Median
Min	Minimum value in a set of results
NIST	National Institute of Standards & Technology
NEPC	National Environmental Protection Council
NMI	National Measurement Institute (of Australia)
NR	Not Reported
NT	Not Tested
PT	Proficiency Test
RM	Reference Material
Robust CV	Robust Coefficient of Variation
Robust SD	Robust Standard Deviation
S	Spiked or formulated concentration of a PT sample
SS	Spiked sample
SI	The International System of Units
$s^2_{\text{sam}}$	Sampling variance
$s_a/\sigma$	Analytical standard deviation divided by the target standard deviation
SRM	Standard Reference Material (Trademark of NIST)
Target SD	Target standard deviation
$\sigma$	Target standard deviation
UC	Universal Cell

**END OF STUDY**