Environment Canada Environnement Canada

ACLAE CAEAL

METALS IN WATER PROFICIENCY TESTING STUDY

(APLAC T055)

PROFICIENCY TESTING REPORT

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INFORMATION AND QUALITY MANAGEMENT

Canada

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1.0 INTRODUCTION

This report summarizes the results of the proficiency testing study for metals in water (APLAC T055).

The study was organized by the Canadian Association for Environmental Analytical Laboratories (CAEAL) and Environment Canada under the auspices of the Asia-Pacific Laboratory Accreditation Cooperative (APLAC).

Accreditation bodies from APLAC and EA were invited to nominate up to four laboratories to participate in this study. In total, samples were prepared and shipped to 36 accreditation bodies covering 33 economies to be distributed to 119 separate laboratories. Results were reported from 114 of the 119 laboratories. Table 1 shows the breakdown by economy of the participants.

Table 1 Participation by economy in the T055 metals in water proficiency testing study.

Economy	Participating Labs
Australia	2
Belgium	3
Brunei Darussalam	3
Bulgaria	4
Canada	9
Cyprus	4
Czech Republic	4
Estonia	4
Finland	4
Germany	1
Greece	1
Hong Kong	4
Indonesia	4
Ireland	4
Israel	4
Italy	4
Japan	1
Malaysia	1
Mongolia	4
Netherlands	4
New Zealand	4

Economy	Participating Labs
Poland	4
Portugal	4
Singapore	4
Slovakia	1
Slovenia	3
South Africa	3
Sweden	1
Taiwan, Province Of China	4
Thailand	8
United Kingdom	2
United States	2
Viet Nam	4
Zambia	1

2.0 STUDY OBJECTIVES

This study aims at providing a means for participating laboratories to evaluate their performance in the analysis of metals in water against their international peers.

Test results from all participants were evaluated according to statistical techniques outlined in ISO 13528:2005 *Statistical Methods for use in Proficiency Testing by Interlaboratory Comparisons* and the *International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories* (IUPAC, 2006).

3.0 SAMPLES

Each laboratory received four separately prepared samples, each containing the following metals in an approximate concentration range of 0.25 – 1.6 mg/L,

Al, Ba, B, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Sr, Tl, Ti, V and Zn

As well, the hydride metals As, Se and Sb were included in an approximate concentration range of 1 – 100 μg/L.

Samples were prepared in large batches, in 0.2% nitric acid, and dispensed into single use, acid rinsed, 250 mL Nalgene™ bottles. Each bottle was labeled with the study date, sample ID, preservative and a sequential number. Each set of four samples was heat sealed in plastic film to prevent leaking during shipping (see Figure 1).

Figure 1 Sample container with label.

Homogeneity and stability of the test samples were determined in accordance with Appendix 1 and Appendix 2, respectively, of *The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories* (IUPAC 2006). Testing for homogeneity and stability was not conducted for arsenic, selenium or antimony. Although the same formulations have been used in the CAEAL proficiency testing program for many years, and have been demonstrated to be homogeneous and stable, the proficiency testing results for these three metals should be interpreted with caution.

4.0 TEST METHODS

Each participant laboratory was requested to determine the elemental concentration in each of the four samples in accordance with directions given in the *Instructions to Laboratory* (Appendix V). Laboratories were allowed to use their method of choice but were requested to indicate the instrumentation during reporting.

5.0 PERFORMANCE EVALUATION

5.1 *z*-Score

The performance of each participant result was estimated by means of the *z* score,

$$z = \frac{(x - X^*)}{s^*}$$

where: x = reported result
X^* = assigned value
S^* = assigned standard deviation

5.2 Outlier Removal

To minimize the impact of outlier data, but to ensure that the data was not unduly censored, results that deviated from the median by more than a factor of ten were excluded from the estimates of assigned value and assigned deviation. The rationale for this criterion is that results that deviate by this amount are likely the result of reporting in the wrong units, shifting a decimal place during reporting or not accounting for a dilution.

5.3 Assigned Value and Assigned Deviation

Assigned value and assigned deviation were estimated using the robust analysis described in ISO 13528:2005 and outlined below.

i) Results were sorted in increasing order ($X_i \ldots X_p$),

ii) Results were examined for any obvious outliers. Only non-detect results and results that deviated from the median by more than a factor

of ten were excluded from the estimate of robust mean and robust standard deviation.

iii) initial estimates of the robust average (X^*) and the robust standard deviation (S^*) were calculated as:

X^* = median of X_i

S^* = 1.483 x median of $|X_i - X^*|$

iv) Estimates of X^* and S^* were updated as follows:

$\delta = 1.5 \times S^*$

For each X_i calculate:

$X_i^* = X^* - \delta$ if $X_i < X^* - \delta$

$X_i^* = X^* + \delta$ if $X_i > X^* + \delta$

$X_i^* = X_i$ otherwise

v) New values of X^* and S^* were calculated from:

$$x^* = \sum x_i^* / p$$

$$s^* = 1.134\sqrt{\sum \left(x_i^* - x^*\right)^2 /(p-1)}$$

vi) Steps iv and v were repeated until the process converged. Convergence was assumed when there was no change from one iteration to the next in the third significant figure of the robust standard deviation and the robust average.

5.4 Composite PT Score

For each participant analyte, a composite score, based on the mean of the absolute z scores of the four samples, was determined. In estimating the

composite score, absolute *z* scores greater than 6.66 were capped at 6.66 to minimize the impact of outlier data on the composite score.

Interpretation of the scoring was as follows,

Individual sample:	
$\|z\| \leq 2.00$	Satisfactory
$2.00 < \|z\| \leq 3.00$	Questionable
$\|z\| > 3.00$	Unsatisfactory

Composite Score:	
$avg\|z\| \leq 2.00$	Satisfactory
$avg\|z\| > 2.00$	Unsatisfactory

5.5 Bias Evaluation

Analytical bias was based on the rescaled *z* score procedure.

$$RSZ = \frac{\sum z}{\sqrt{N}}$$

Flags for bias were assigned as follows,

RSZ ≥ -2 and ≤ 2	no flag assigned
RSZ > 2	H (High)
RSZ > 3	VH (Very High)
RSZ < -2	L (Low)
RSZ < -3	VL (Very Low)

Bias was only determined for labs that reported four measurable results for a metal.

6.0 TEST RESULTS SUMMARY

Test results are summarized in Table 2. The assigned value (X*) and the assigned standard deviation (s*) were estimated from the robust analysis described in ISO 13528. The number of results (N) is exclusive of non-detect values. The number of questionable results ($2<|z|\leq3$), the number

of unsatisfactory results (|z|>3) and the number of laboratories with composite scores > 2 are also detailed.

Table 2 Statistical summary of proficiency testing study.

Analyte	Summary Statistics	T055-1	T055-2	T055-3	T055-4	Comp. score > 2
Aluminum	X*	0.405	0.492	0.857	1.165	10
	S*	0.030	0.034	0.0557	0.0704	
	N	85	86	86	86	
	2<|z|≤3	2	2	3	4	
	|z|>3	9	11	6	7	
Antimony	X*	23.4	35.6	60.5	81.4	8
	S*	6.08	6.07	9.93	12.26	
	N	63	65	66	66	
	2<|z|≤3	4	5	6	5	
	|z|>3	3	5	2	4	
Arsenic	X*	18.66	28	104.4	78.3	12
	S*	3.07	3.58	9.72	7.88	
	N	80	83	84	83	
	2<|z|≤3	5	2	2	7	
	|z|>3	7	8	12	6	
Barium	X*	0.767	0.794	0.856	0.339	7
	S*	0.0504	0.0481	0.0512	0.0236	
	N	78	78	78	78	
	2<|z|≤3	2	4	3	6	
	|z|>3	3	5	4	4	
Boron	X*	1.283	0.474	0.318	0.915	9
	S*	0.062	0.0348	0.0292	0.0486	
	N	71	71	71	70	
	2<|z|≤3	5	3	2	4	
	|z|>3	7	5	4	5	
Chromium	X*	1.165	0.227	0.577	0.355	13
	S*	0.0708	0.0169	0.0309	0.0248	
	N	106	106	107	107	
	2<|z|≤3	7	8	6	7	
	|z|>3	7	8	7	7	
Cobalt	X*	0.346	0.452	0.813	1.114	7
	S*	0.024	0.0293	0.0498	0.0699	
	N	91	91	91	90	
	2<|z|≤3	2	3	6	7	

Analyte	Summary Statistics	T055-1	T055-2	T055-3	T055-4	Comp. score >2
	|z|>3	7	4	3	3	
Copper	X*	1.044	0.219	0.728	1.36	13
	S*	0.0502	0.0152	0.039	0.0664	
	N	110	109	111	110	
	2<|z|≤3	4	10	6	5	
	|z|>3	8	8	8	8	
Iron	X*	1.219	0.265	0.43	0.833	15
	S*	0.063	0.0237	0.028	0.0435	
	N	106	104	106	106	
	2<|z|≤3	11	8	11	6	
	|z|>3	7	5	4	6	
Lead	X*	0.637	0.246	0.324	0.338	16
	S*	0.0391	0.0164	0.0198	0.0223	
	N	107	105	107	106	
	2<|z|≤3	4	5	9	5	
	|z|>3	7	11	10	9	
Manganese	X*	0.567	0.45	0.423	0.329	11
	S*	0.0339	0.0269	0.0263	0.0223	
	N	108	108	108	107	
	2<|z|≤3	6	5	6	6	
	|z|>3	5	6	5	7	
Molybdenum	X*	0.923	0.409	0.626	0.799	7
	S*	0.0716	0.0313	0.0452	0.0602	
	N	72	72	72	72	
	2<|z|≤3	3	4	2	2	
	|z|>3	4	2	4	7	
Nickel	X*	0.402	0.34	0.273	0.5196	12
	S*	0.0298	0.022	0.0204	0.0361	
	N	109	109	109	108	
	2<|z|≤3	5	5	9	8	
	|z|>3	4	7	7	4	
Selenium	X*	34.2	66.5	1.911	60.2	11
	S*	6.61	8.18	0.646	8.53	
	N	71	70	48	71	
	2<|z|≤3	0	4	2	8	
	|z|>3	9	3	7	5	
Strontium	X*	0.36	1.04	1.12	0.581	6
	S*	0.0225	0.0649	0.0739	0.0364	

Analyte	Summary Statistics	T055-1	T055-2	T055-3	T055-4	Comp. score >2
	N	63	62	62	63	
	2<|z|≤3	3	2	4	3	
	|z|>3	4	3	3	3	
Thallium	X*	0.636	0.428	0.266	0.697	4
	S*	0.0467	0.0306	0.0207	0.0499	
	N	58	58	58	58	
	2<|z|≤3	2	2	1	2	
	|z|>3	3	3	4	1	
Titanium	X*	0.347	0.191	0.473	0.556	8
	S*	0.021	0.011	0.0253	0.0283	
	N	50	50	50	50	
	2<|z|≤3	5	2	4	3	
	|z|>3	3	4	3	4	
Vanadium	X*	0.997	0.774	0.277	0.661	8
	S*	0.0484	0.04	0.0148	0.0332	
	N	68	68	68	68	
	2<|z|≤3	1	4	6	5	
	|z|>3	5	3	1	3	
Zinc	X*	0.896	1.252	0.372	0.53	8
	S*	0.0626	0.0853	0.0297	0.0409	
	N	110	109	110	109	
	2<|z|≤3	3	1	6	5	
	|z|>3	8	8	6	6	

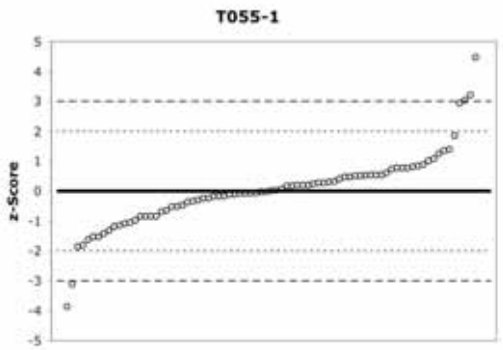
7.0 SUMMARY OF TEST RESULTS

The summary of PT data is contained in the *Proficiency Testing Summary Report*.

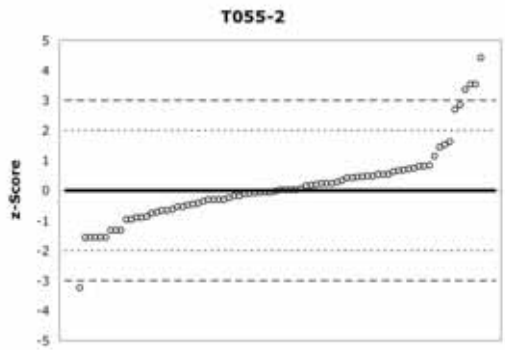
8.0 PERFORMANCE BY ELEMENT

The *z*-score plots for the APLAC T055 study are shown in Figure 2. As is common in PT studies, these plots show that the majority of reported results fall within a narrow distribution with a few results on either end of the distribution that could be considered outliers. These outliers could be due to poor analytical quality at the time of analysis, typographical or calculation error.

Aluminum



Not on chart: -12.4, 9.83, 11.37 and 499.



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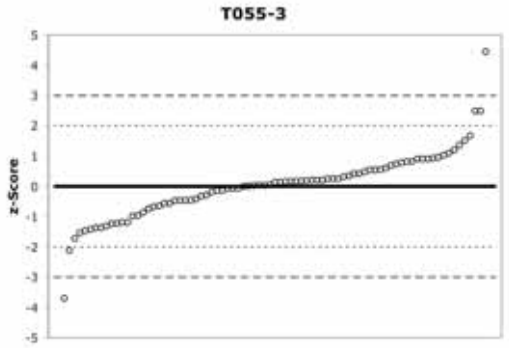

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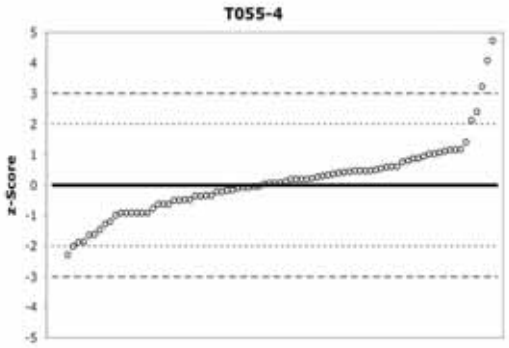
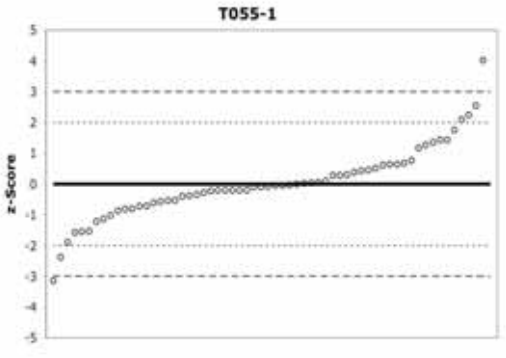
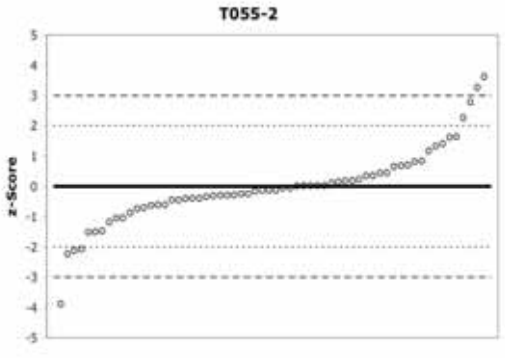


Not on chart: -15.01, -8.11, -7.74 and 732.

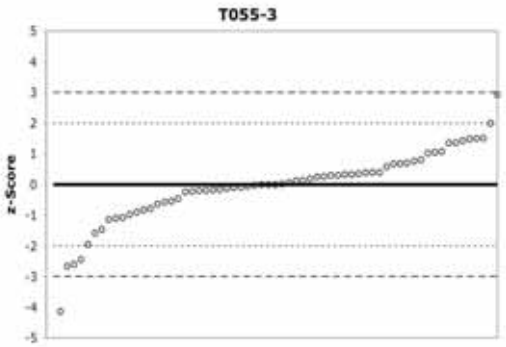
Antimony



Not on chart: 22.3



Not on chart: -5.50 and 44.4.



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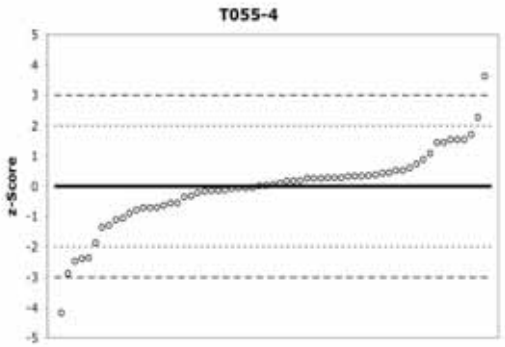
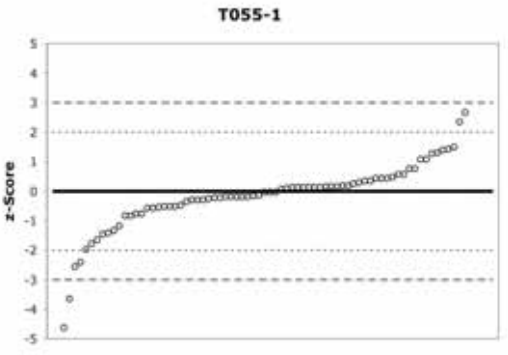


Not on chart: -6.27 and 8.21.

Arsenic



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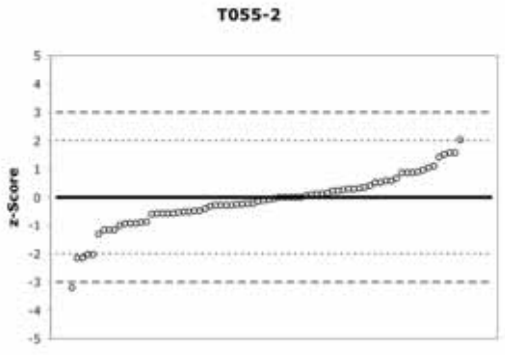

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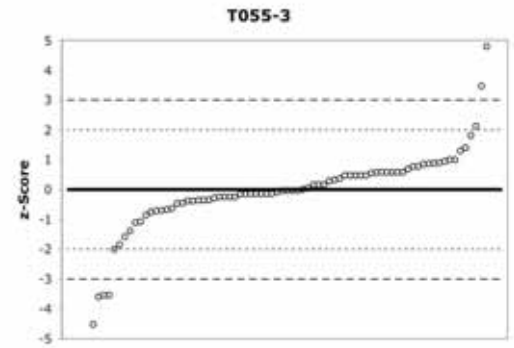
Arsenic (cont.)



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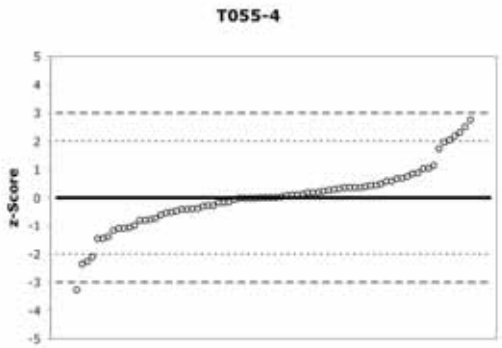

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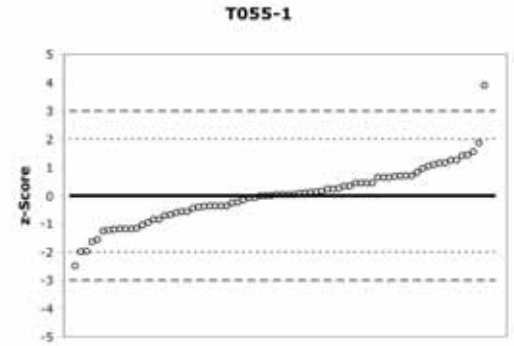
Barium



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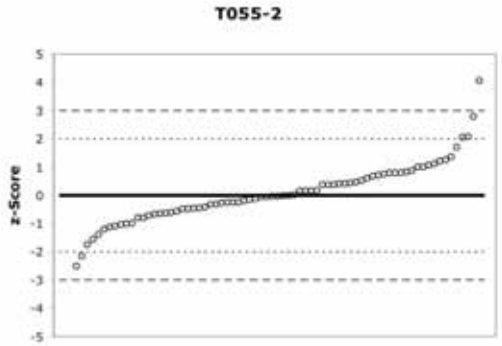

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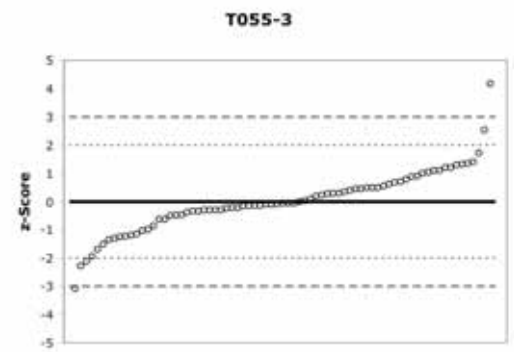

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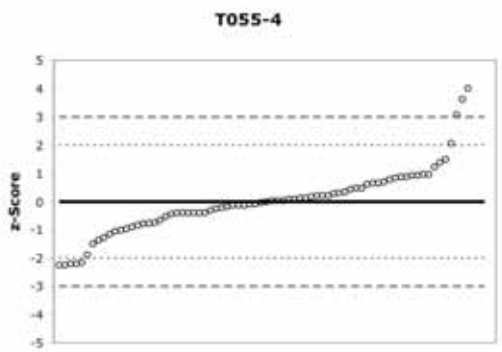

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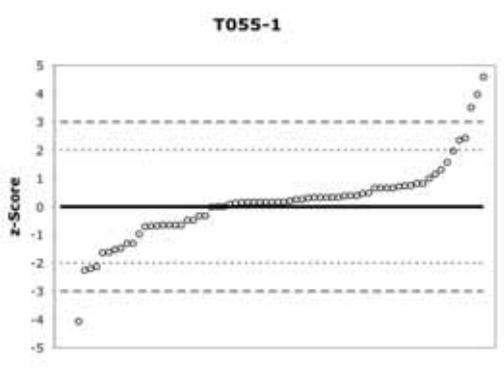
Boron



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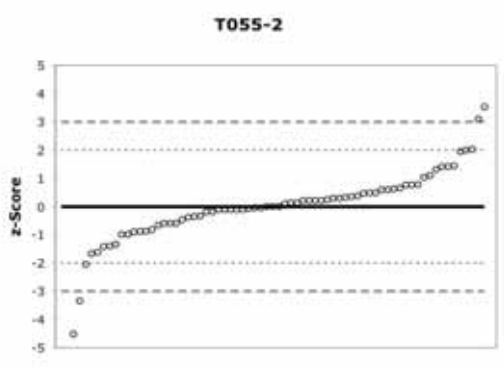

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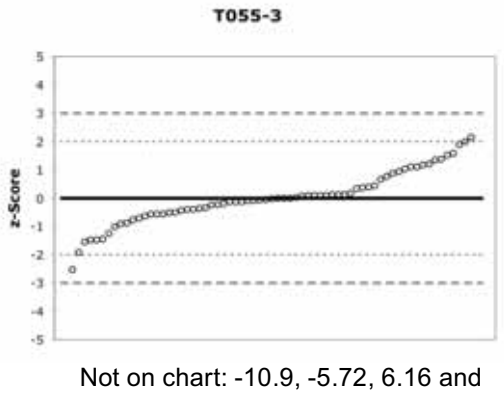

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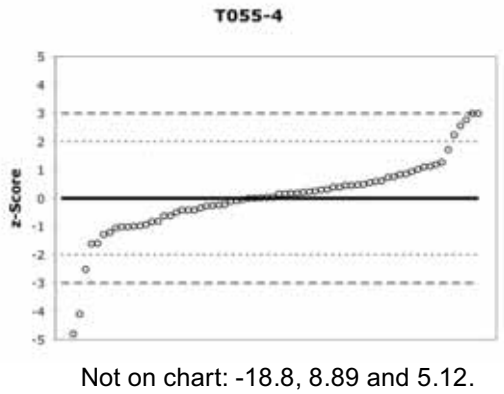

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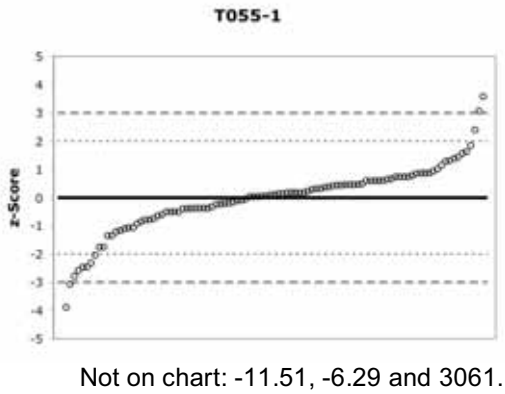
Chromium



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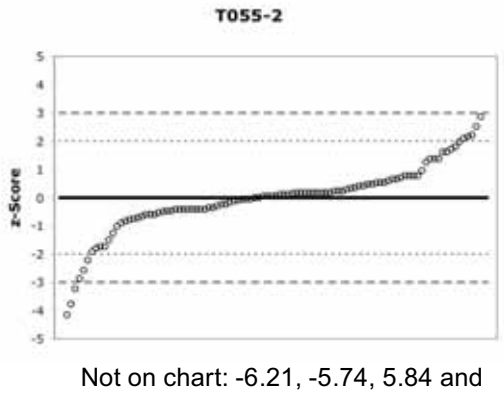

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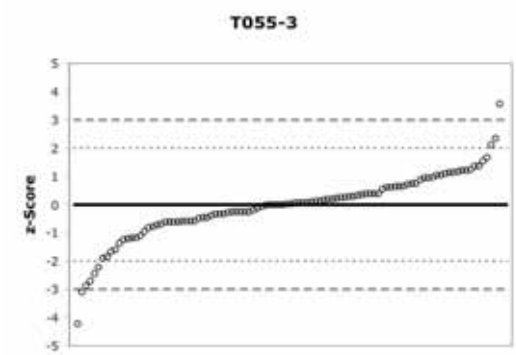
Chromium (cont.)



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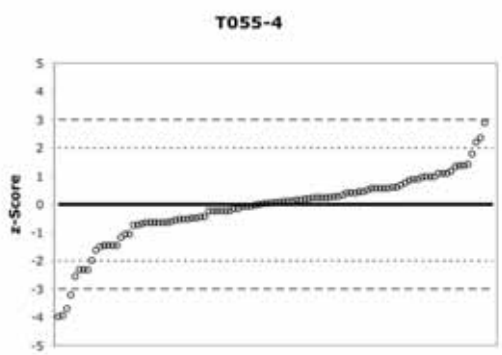

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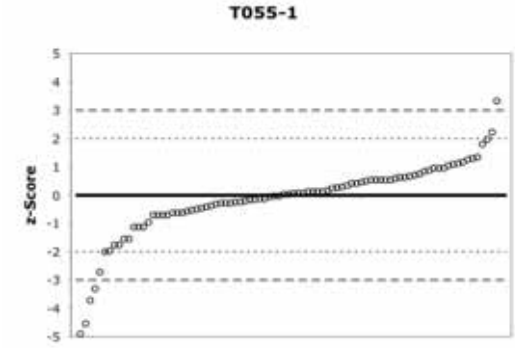

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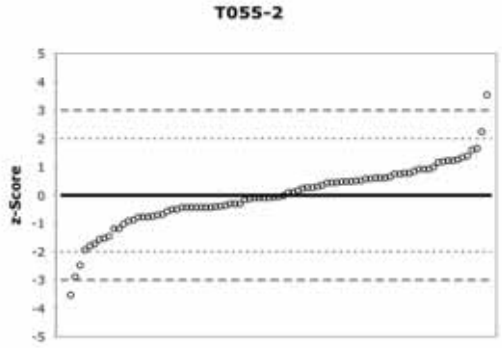

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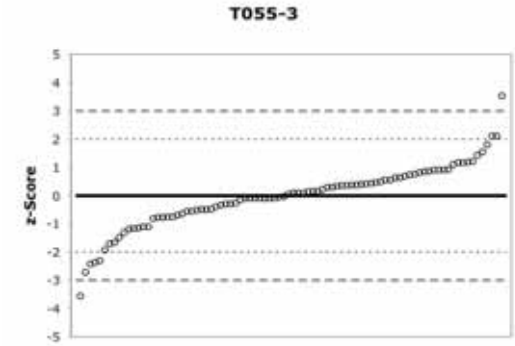
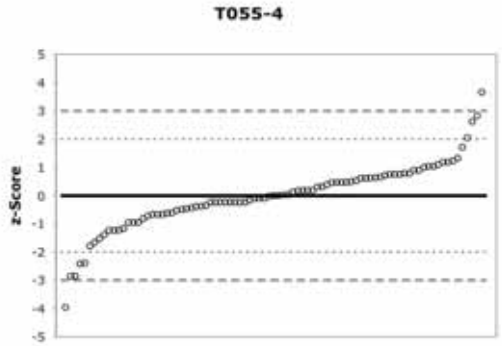
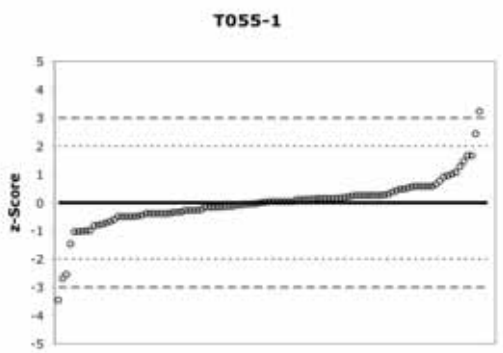


Not on chart: -11.2.

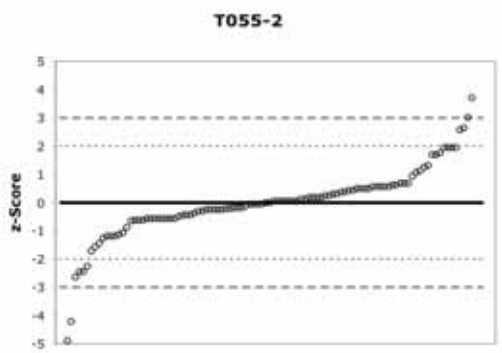


Not on chart: -7.75.

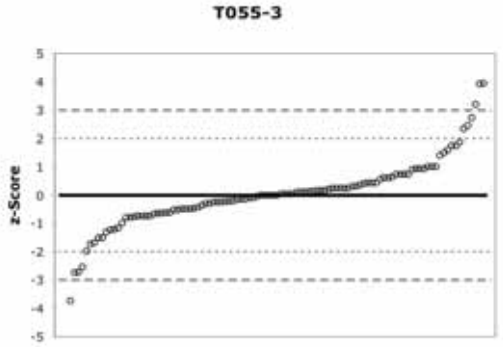
Copper



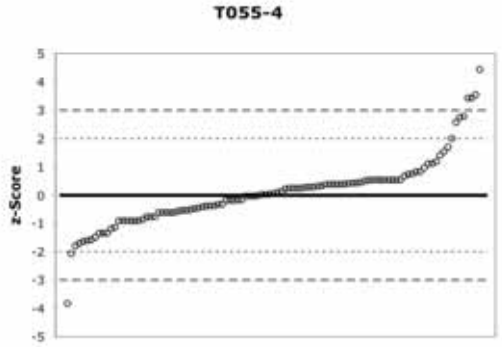
Not on chart: -6.32, 5.98 and 923.



Not on chart: -7.43, -6.51, -5.11, 15.86 and 643.

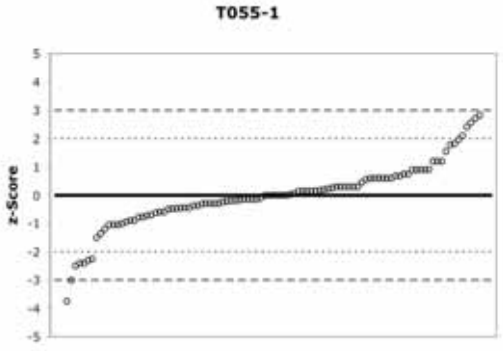


Not on chart: -6.95, -6.33, -5.73, and 797.

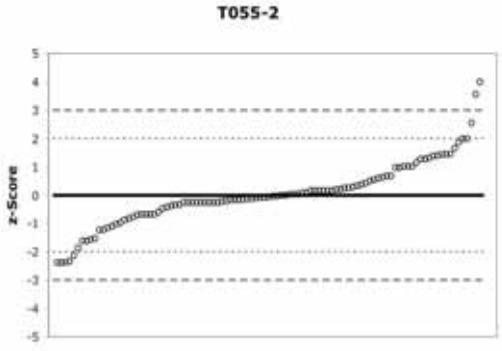


Not on chart: -5.84, -5.17, and 861.

Iron

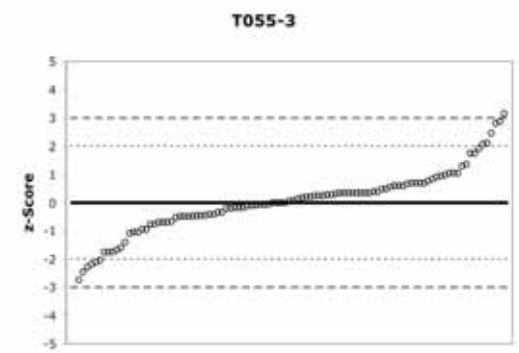


Not on chart: -17.1, -14.9, 5.79, 9.51 and 770.

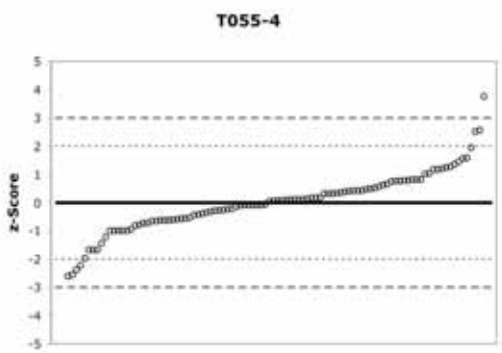


Not on chart: 491.

Iron (cont.)

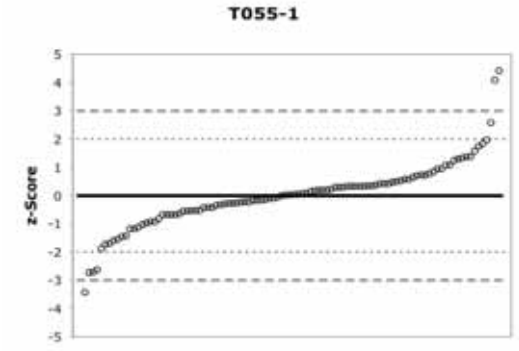


Not on chart: -10.61, -6.07 and 642.

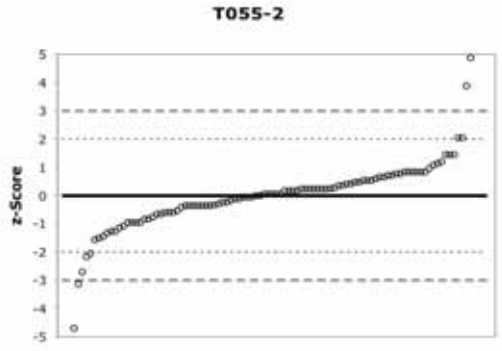


Not on chart:-16.7, -14.3, 6.14 and 802.

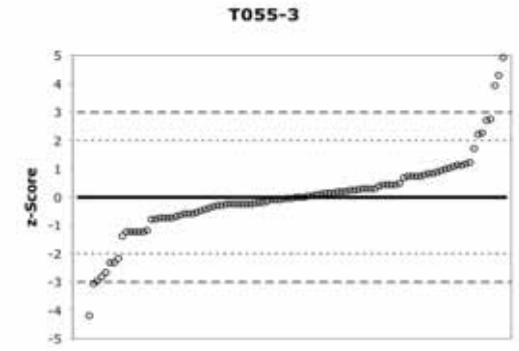
Lead



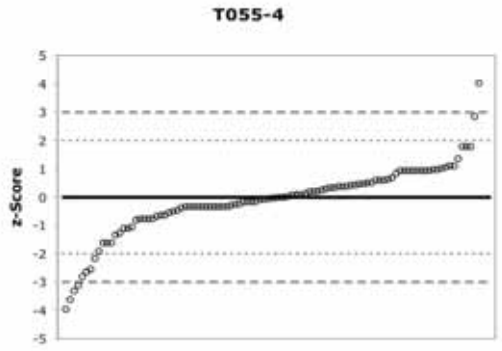
Not on chart: -11.0, -8.47, 8.26 and 6211.



Not on chart: -6.95, -6.74, -6.30, 7.56, 9.12 and 5256.

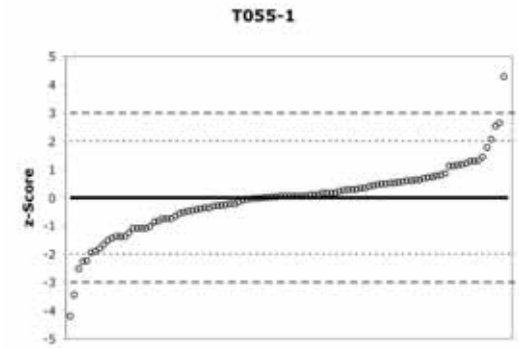


Not on chart: -11.31, -7.68, -5.17, 5.10, 12.36 and 5984.

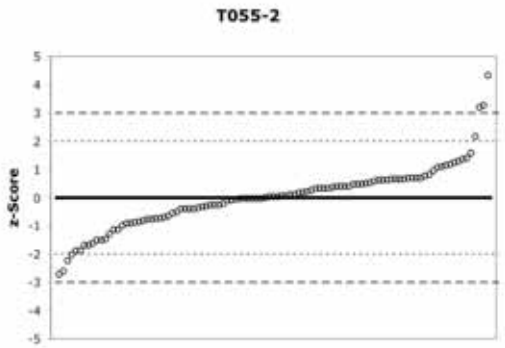


Not on chart: -7.22, 5.70, 9.31 and 5536.

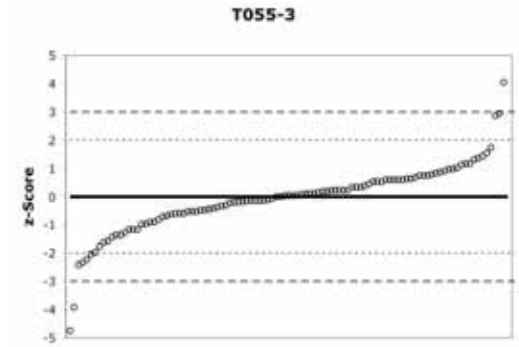
Manganese



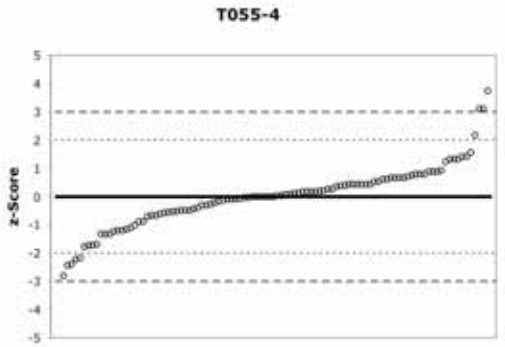
Not on chart: 47.88 and 3048.



Not on chart: -6.39, 22.3, and 3035.

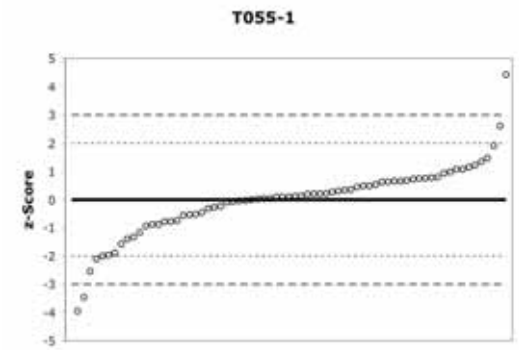


Not on chart: 34.9 and 2912.

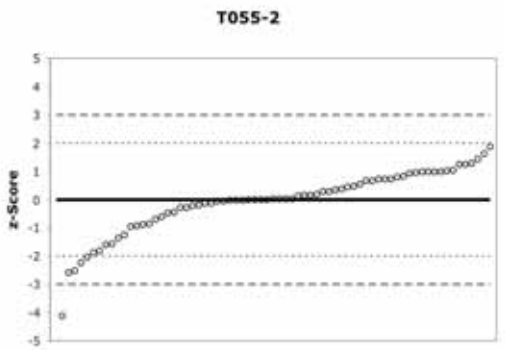


Not on chart: -7.49, -7.00, 82.6, and 2662.

Molybdenum

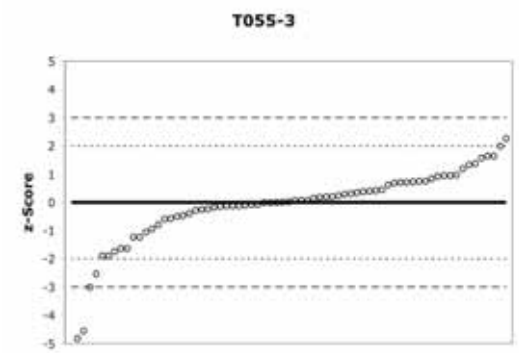


Not on chart: -5.77.

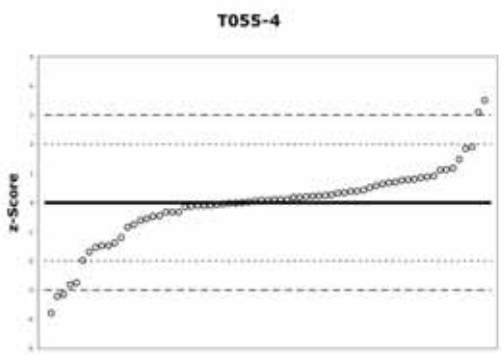


Not on chart: -7.00.

Molybdenum (cont.)

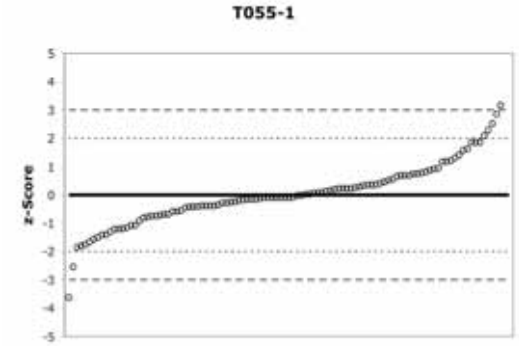


Not on chart: -5.66.

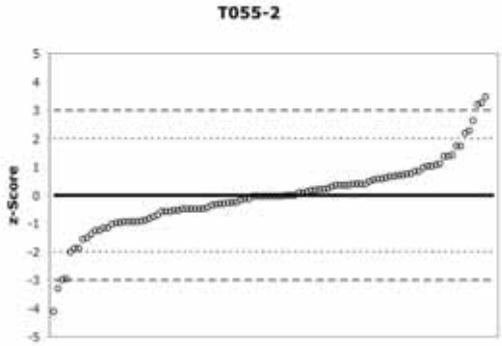


Not on chart: -8.41 and 17.3.

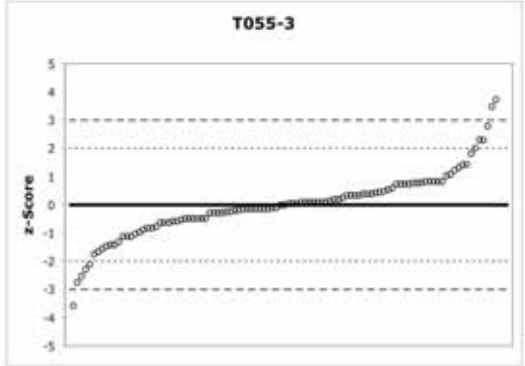
Nickel



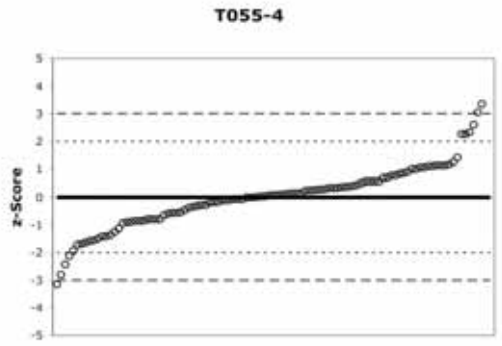
Not on chart: 11.98 and 6080.



Not on chart: 24.3 and 6953.

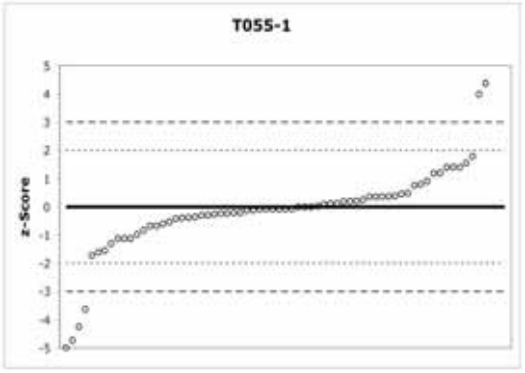


Not on chart: -5.87, 7.16, 13.19 and 5972

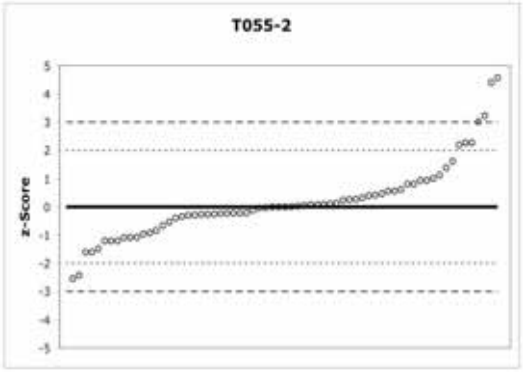


Not on chart: 6.44 and 6468.

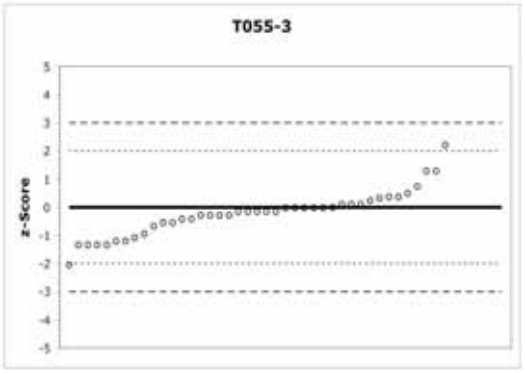
Selenium



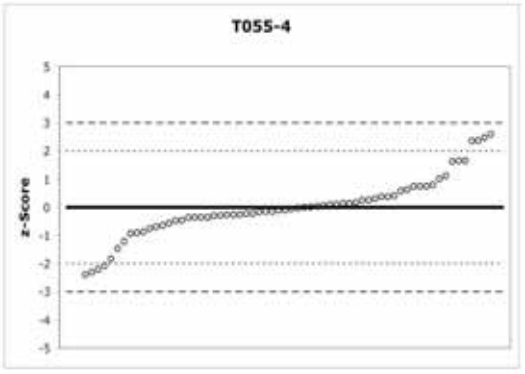
Not on chart: -5.17, 5.19, 7.78 and 8.44.



Not on chart: -7.15.

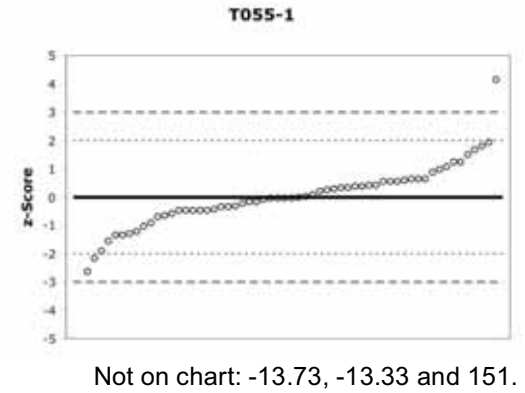


Not on chart: 8.50, 9.43, 26.4, 43.5, 58.0, 106 and 109.

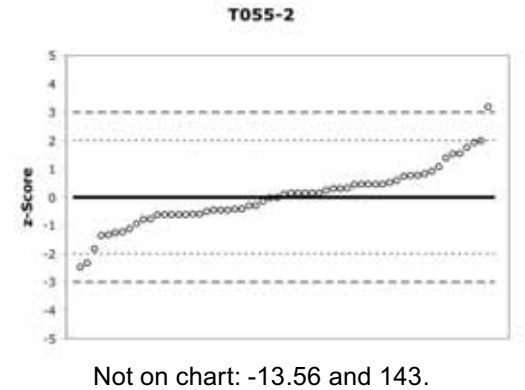


Not on chart: -6.68, -6.34, -5.83, 5.96 and 7.01.

Strontium

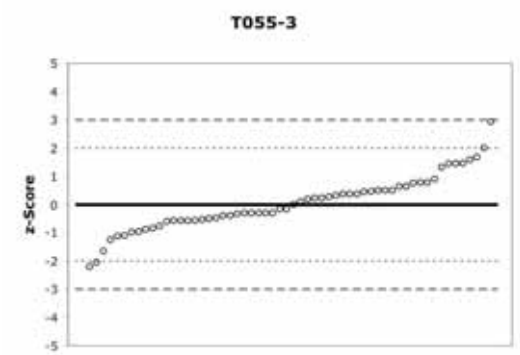


Not on chart: -13.73, -13.33 and 151.

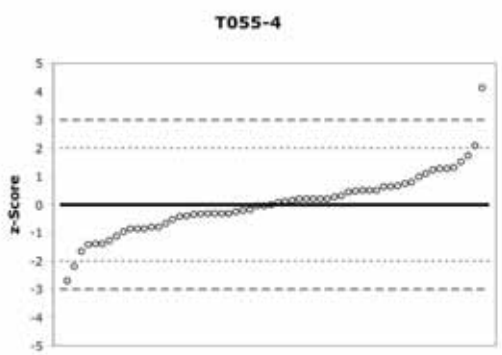


Not on chart: -13.56 and 143.

Strontium (cont.)

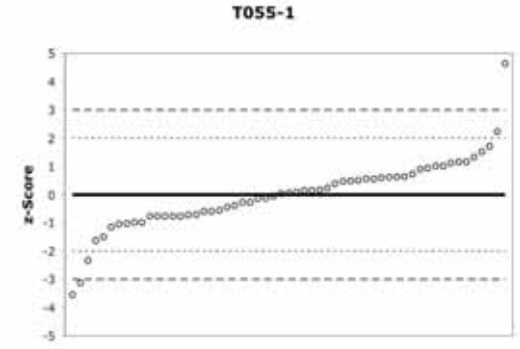


Not on chart: -13.56, -12.04 and 135.

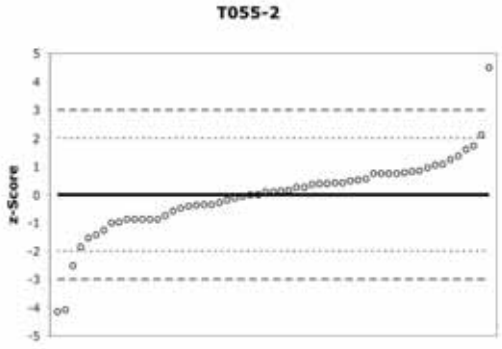


Not on chart: -13.49 and 147.

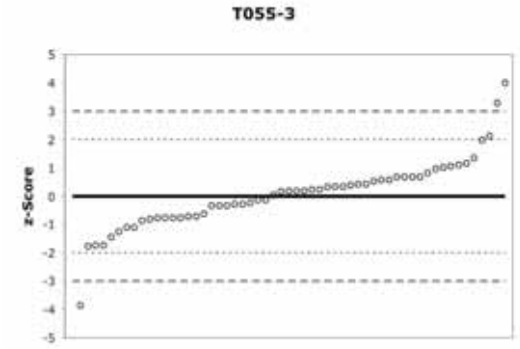
Thallium



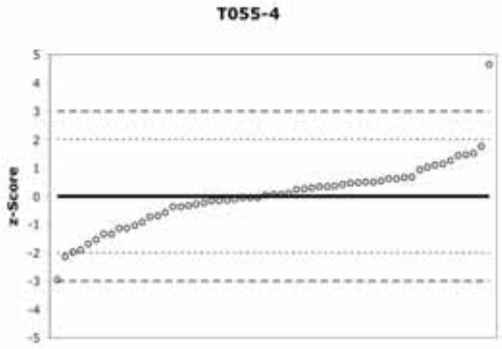
Not on chart:



Not on Chart:

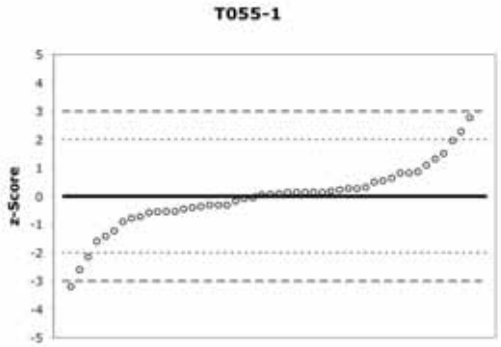


Not on chart: -5.12.

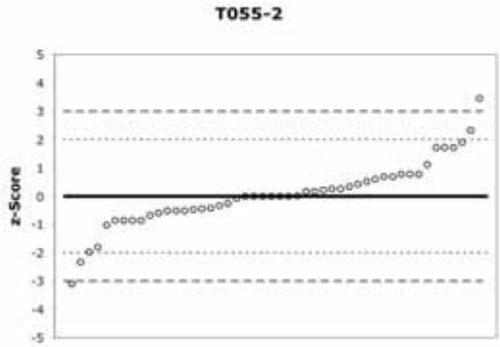


Not on chart:

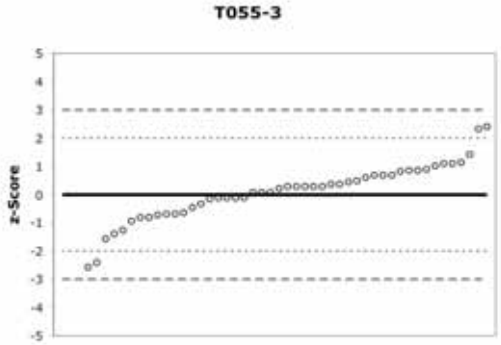
Titanium



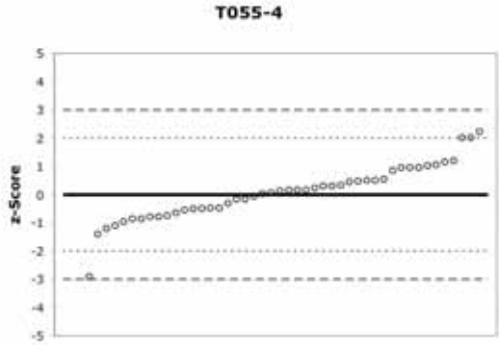
Not on chart: -5.57 and 37.5.



Not on chart: -5.55 and 23.9.

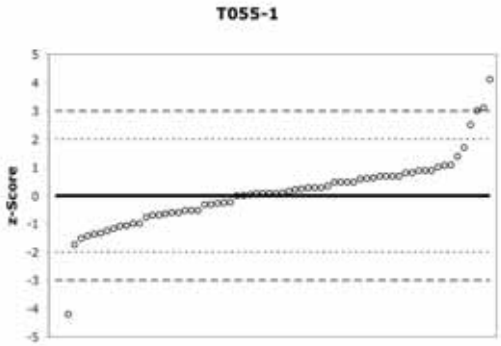


Not on chart: -16.01, -6.44 and -6.05.

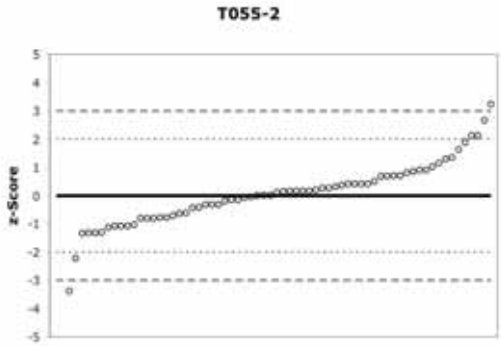


Not on chart: -7.24, -5.87, and 20.5.

Vanadium

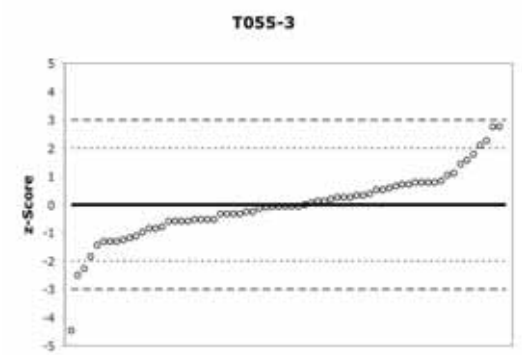


Not on chart: -9.73.

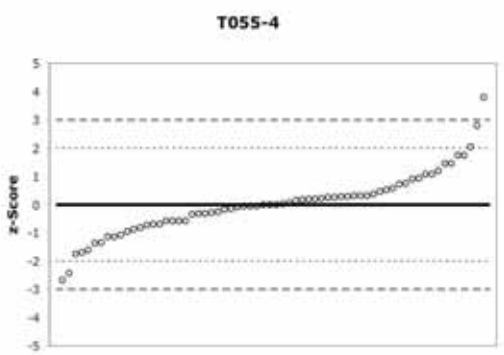


Not on chart: -9.43.

Vanadium (cont.)

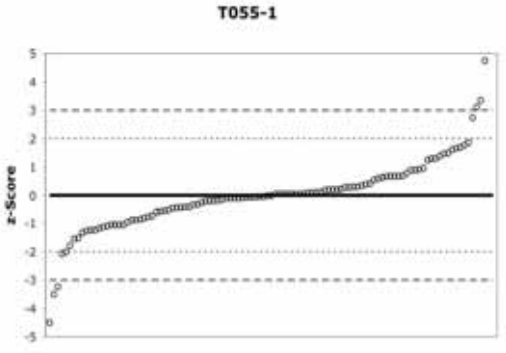


Not on chart: 30.26.

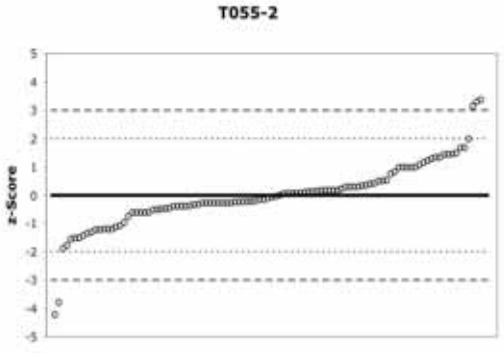


Not on chart: -9.46.

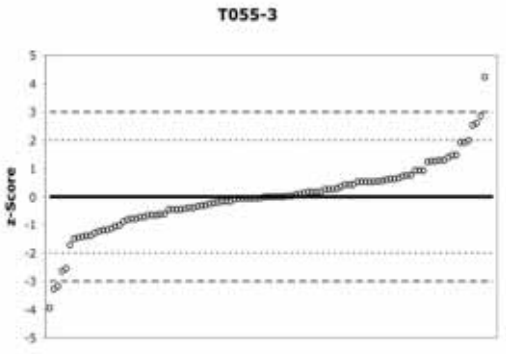
Zinc



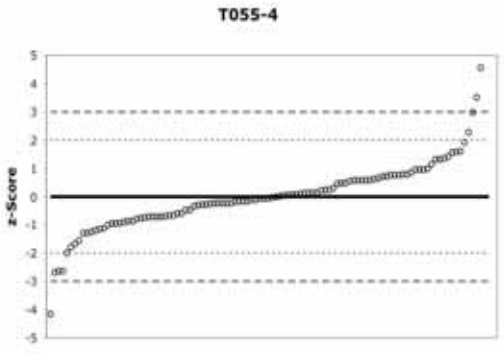
Not on chart: 5.34 and 690.



Not on chart: -13.42, 5.25 and 710.



Not on chart: 111 and 610.

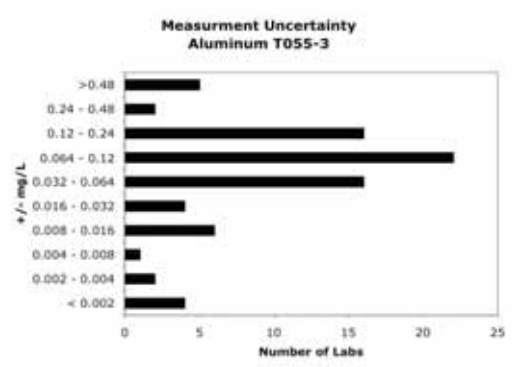


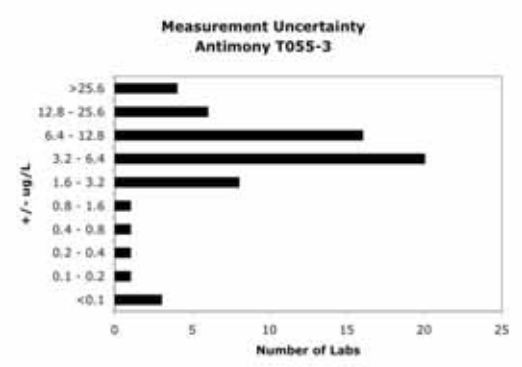
Not on chart: 111 and 630.

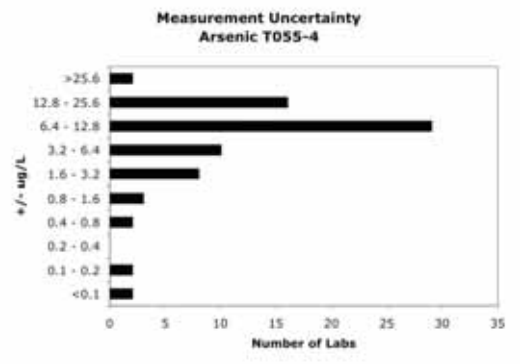
Figure 2 z-score charts for all analyte/sample combinations. Values not included are noted below each chart. Dashed and dotted lines indicate 3s and 2s limits, respectively.

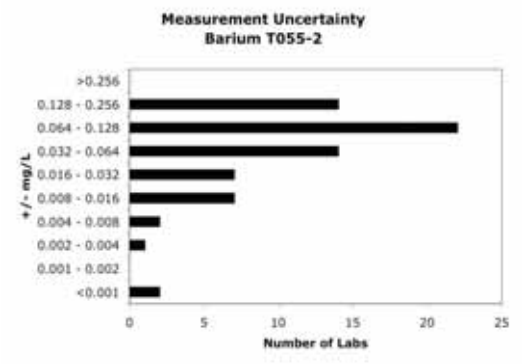
9.0 MEASUREMENT UNCERTAINTY

Participating laboratories were requested to report measurement uncertainty for each result in the units specified, using a coverage factor (k) of 2. Reported uncertainties varied considerably but, in general, the median uncertainty for any analyte/sample combination was approximately 10% of the assigned value. Figure 3 displays the frequency distributions for one of the samples for each analyte. Please note that the scale used is log 2.

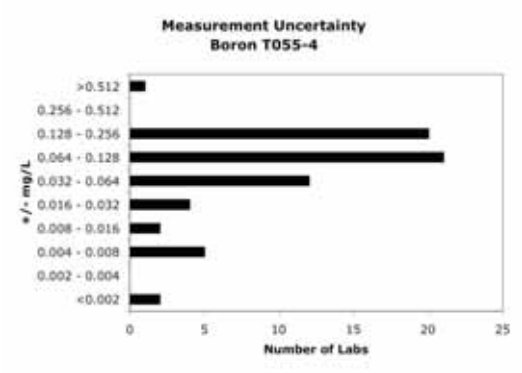


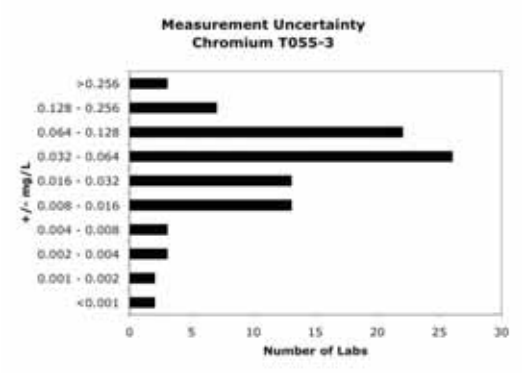


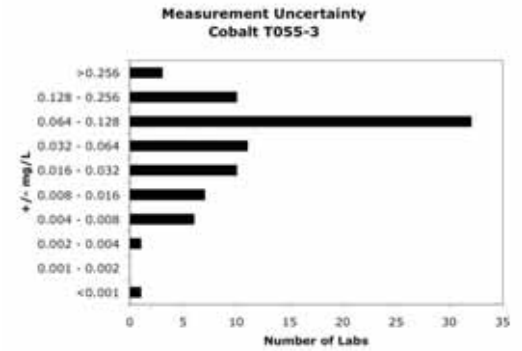


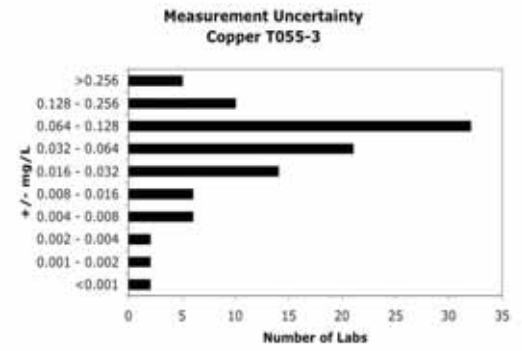


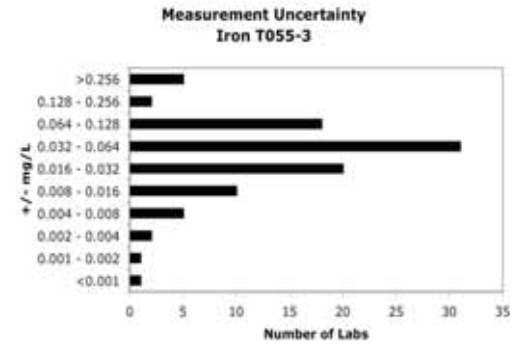
Measurement Uncertainty (cont.)

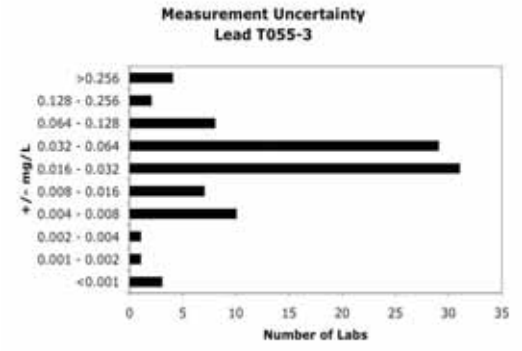












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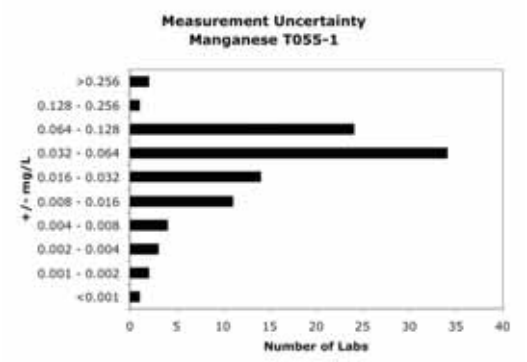
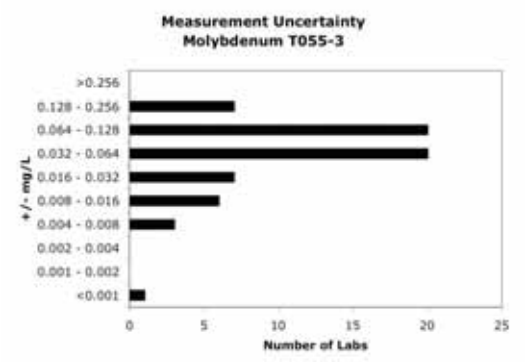
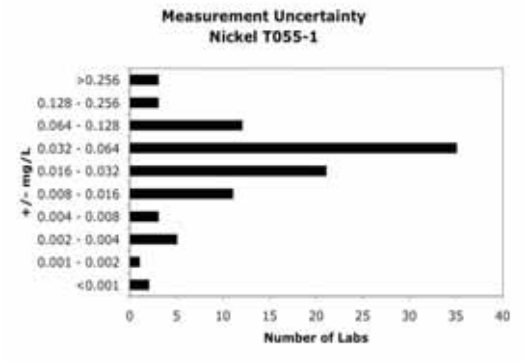
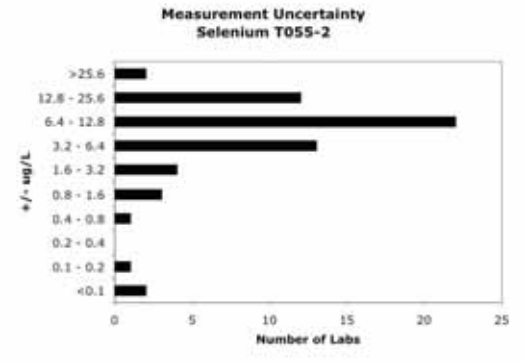
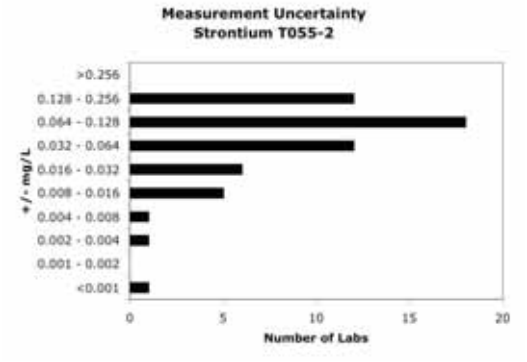
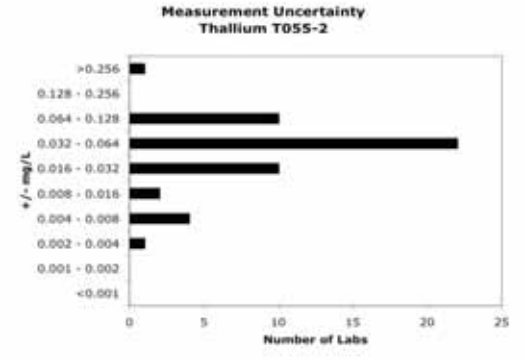












Measurement Uncertainty (cont.)

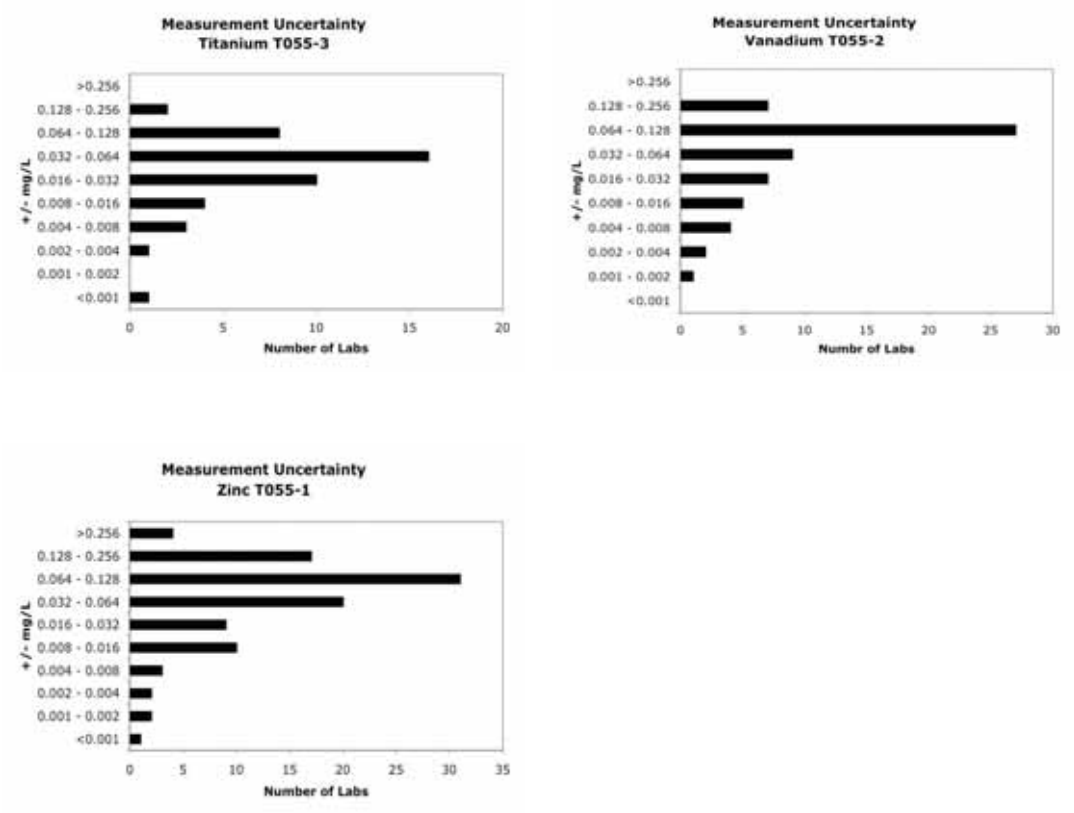


Figure 3 **Frequency distribution of reported measurement uncertainties for each analyte. Only one sample is displayed for each analyte as the relative uncertainties reported by most participants were consistent for all four samples.**

10.0 METHOD SUMMARY

For metals testing there has been a significant improvement in instrument precision and sensitivity over the last ten to fifteen years as ICP/OES and ICP/MS have become more reliable and affordable. It is important, therefore, to examine PT data within the context of the equipment that is used. Because there were few participants that reported using AA for any one analyte, it is difficult to compare on a analyte-by-analyte basis. Figure 4 shows the relative *z*-score distribution for all reported results, separated by instrument. Laboratories using ICP and ICP/MS demonstrated comparable performance whereas laboratories using AA had a wider spread of data.

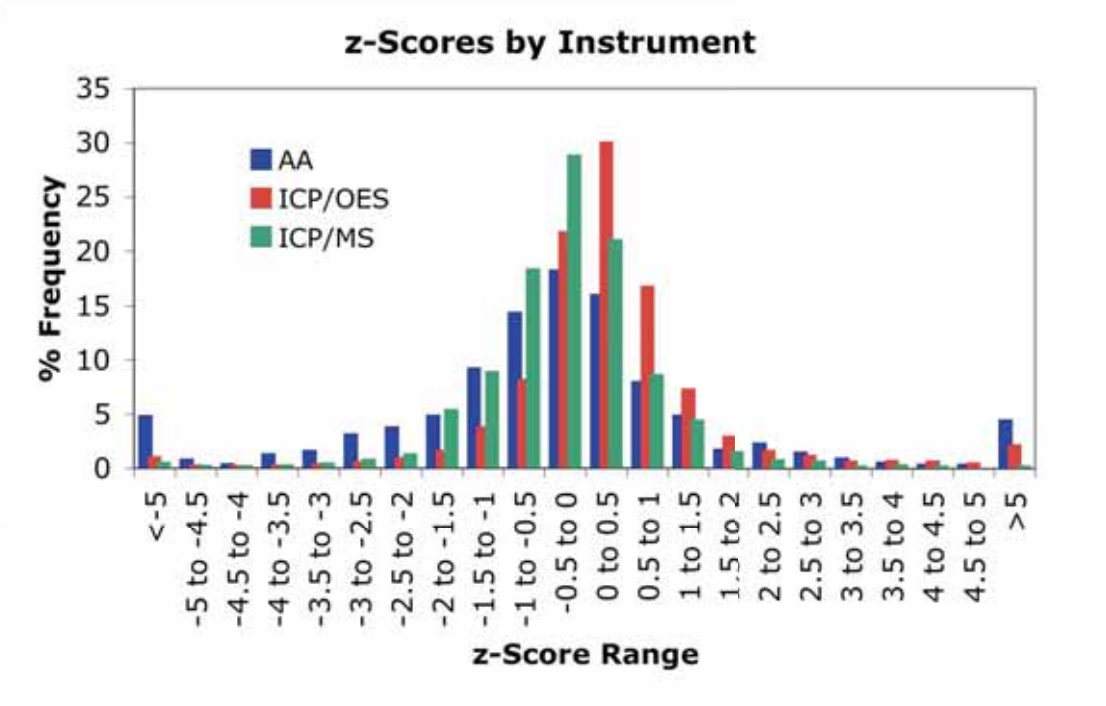


Figure 4 Distribution of *z*-scores for the three major pieces of equipment used, atomic absorption spectrophotometry (AA), inductively coupled plasma optical emission spectroscopy (ICP/OES), and inductively coupled plasma/mass spectrometry (ICP/MS).

11.0 IMPACT OF PT ON LAB PERFORMANCE

The optimal level of proficiency testing participation is a controversial issue, largely because of the lack of empirical evidence showing that the level of PT participation has an impact on laboratory performance. Due to the large number of participants in this study, it was felt that the data from APLAC T055 could be used to examine this issue.

At the conclusion of the study, the participating laboratories were asked to provide additional information on the number of similar PT studies they have participated in during the last year, the last two years and the last four years. A total of fifty-two laboratories responded to this request. The laboratory results were then divided into two groups,

- Laboratories that participated in less than four similar PT studies during the last two years (1521 results), and
- Laboratories that participated in at least four or more similar studies during the last two years (1163 results).

Figure five shows the distribution of the levels of PT participation reported by APLAC T055 participants. The largest frequency was around one study per year but a significant number of laboratories participate at a frequency higher than this.

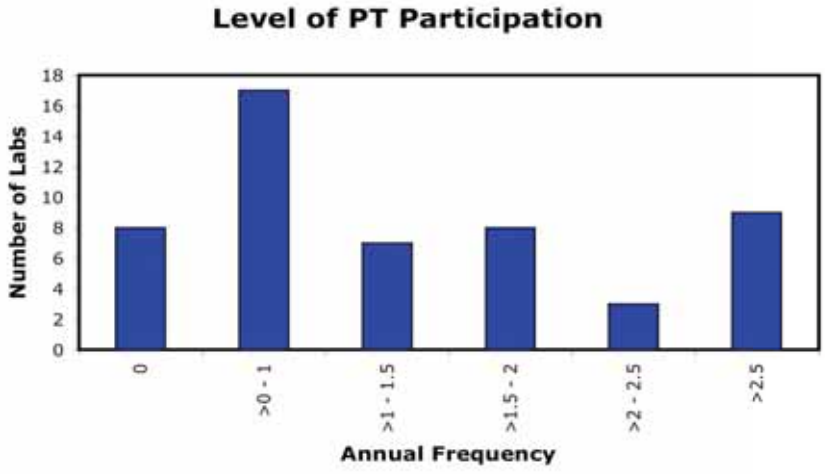


Figure 5 Distribution of average annual PT frequencies for APLAC T055 participants.

Robust means and robust standard deviations were estimated for each of the sample/analyte combinations for which there were at least eleven data points. In general, the robust mean for results from laboratories that participated in PT studies less than four times in the last two years were comparable to the robust means estimated from laboratories that participated in four or more studies in the same time frame (Figure 6). However, the plot of robust standard deviation shows that the spread in data (deviation) for laboratories with high levels of PT participation is consistently lower than the spread in data for laboratories with low levels of PT participation.

This clearly suggests that, as a group, laboratories that participate in a high level of PT perform better than laboratories that participate in a low level of PT.

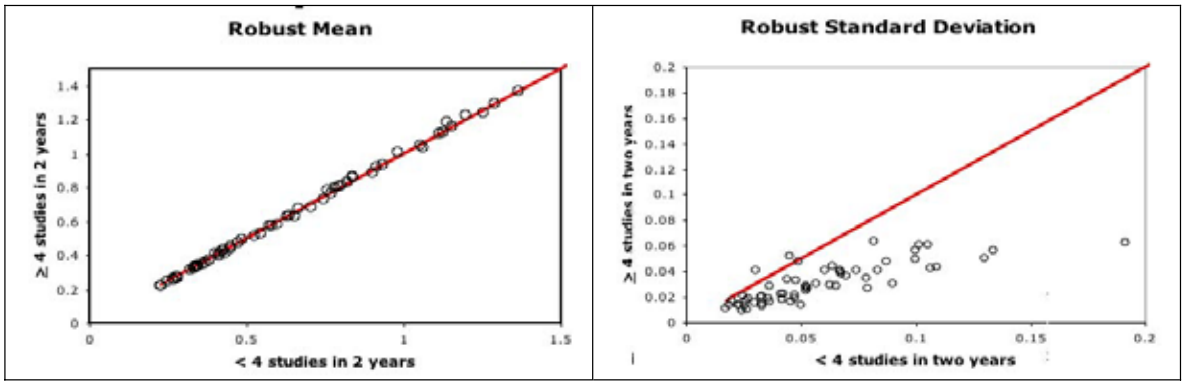


Figure 6 Plots of Robust means (left) and robust standard deviation (right) for laboratories with a high level of PT participation versus laboratories with low levels of participation. The line indicates the line of unity.

APPENDIX I: HOMOGENEITY AND STABILITY

A Homogeneity

Samples of similar composition and matrix have been produced for the CAEAL Proficiency Testing Program since 1991 (30 studies) and have consistently demonstrated sufficient homogeneity. However, the criteria that have been used in the CAEAL program to determine homogeneity are not consistent with the procedure recommended in the *Harmonized Protocol*. The procedure recommended in Appendix 1 of the *Harmonized Protocol* was adopted for this study

The samples were prepared in bulk form and then dispensed into sequentially numbered, single use bottles.

Ten samples were randomly selected from each batch using a sequential random procedure. Each sample was analysed in duplicate, in a random sequence, by a laboratory accredited to ISO/IEC 17025 for the method used. The initial analytical run experienced problems that were not identified until the data was being reviewed (low recovery and drifting). As such, the samples were re-analysed.

The Cochran Test Procedure for Duplicate Results was used to identify potential outlying pairs.

1. The sum , S_i , and difference D_i , for each duplicate pair were calculated as

$$S_i = (R_1 + R_2)$$
$$D_i = (R_1 - R_2)$$

Where R_1 and R_2 are the duplicate results.

2. The sum of squares S_{DD} of the differences was calculated as,

$$S_{DD} = \sum D_i^2$$

3. The Cochran's test statistic was estimated as,

$$C = \frac{D^2_{\max}}{S_{DD}}$$

Where $D^2_{\max}$ is the largest squared difference.

4. If the test statistic was greater than either the 95 % or the 99% critical test value, the analytical data was checked for possible transcription errors or other testing problems.

5. After investigation, only duplicate pairs that still were flagged as outliers at the 99% level were removed.

Of the 640 duplicate pairs that were examined, there were only two duplicate pairs that were flagged as outliers at the 99% level and removed from further evaluation.

The Test for Significant Inhomogeneity is as follows.

1. The sum of squared differences was used to calculate

$$s^2_{an} = \sum D_i^2 / 2m$$

Where *m* is the number of duplicate pairs.

2. The variance of the sums was calculated as,

$$V_S = \sum (S_i - \overline{S})^2 / (m-1)$$

Where $\overline{S} = (1/m)\sum S_i$

3. The sampling variance was calculated as,

$$s^2_{sam} = (V_S/2 - s_{an})/2$$

4. The allowable sampling variance was estimated as,

$$\sigma_{all}^2 = (0.3\sigma_p)^2$$

Where σ_p = the standard deviation for proficiency testing. For the purpose of homogeneity and stability testing, the standard deviation for proficiency testing was the standard deviation of participant results estimated by robust analysis.

5. The critical value for the test was estimated as,

$$c = F_1\sigma_{all}^2 + F_2 s_{an}^2$$

6. If $s_{sam}^2 > c$ then there is evidence at the 95% level that the test for homogeneity has failed.

Evaluation of the data indicate that production lots T055-1, T055-2, T055-3 and T055-4 were sufficiently homogeneous for all analytes.

B Stability

Due to the analytical problems encountered during the initial test for homogeneity (time = 0 for stability testing) it was not possible to perform the standard test for stability. However, it is well known that the biggest sources of instability for metals in water samples are precipitation of the metal and evaporation of the sample. Precipitation is prevented by acidification with nitric acid. Metals that are known to have stability problems, even with acidification (e.g., silver and tin), were not included in this study. Evaporation is not suspected to be a factor in this study due to the short duration of the study and the fact that an electric torque wrench is used to tighten the sample lids. As well, there were no participants that reported moisture on the inside of the plastic sleeve in which the sample bottles were sealed, as would be expected should there be any sample evaporation.

Further supporting the conclusion that instability was not a factor in this study is the fact that the same samples were used for a Canada-only PT study (approximately fifty participants) and the consensus deviation was generally consistent with historic studies (see Figure 7). If there were instability for any of the metals, the standard deviation would be higher than predicted from the historic data.

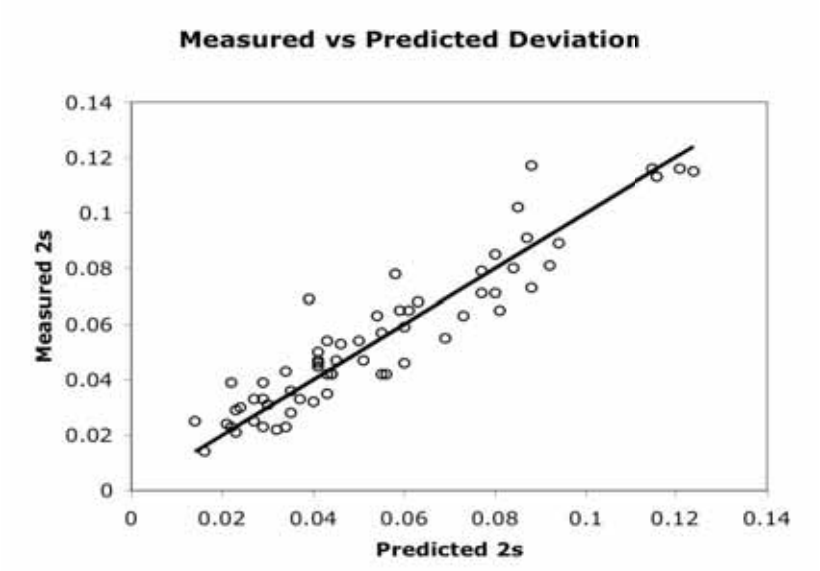


Figure 7 **Plot of measured deviation (2 x standard deviation) versus deviation predicted from historic studies. The displayed line indicates unity.**

APPENDIX II: INVITATION TO PARTICIPATE

APLAC T055 PROFICIENCY TESTING PROGRAM

INVITATION TO PARTICIPATE

The APLAC T00_ proficiency testing study is scheduled for October, 2006. This study is for metals in water in the approximate concentration range of 0.25 – 1.6 mg/L (As, Se and Sb in the range 1 – 100 ug/L). The metals included in the samples are:

Al, As, Ba, B, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Sb, Se, Sr, Tl, Ti, V and Zn

Please use the enclosed *Participating Laboratories Nomination Form* to indicate the laboratories from your economy that will participate in this study.

Please email or fax the completed form to:

Ken Middlebrook
CAEAL PT Manager
kmiddlebrook@caeal.ca
fax: (613)233-5501
phone: (613)233-5300

APLAC T055 PROFICIENCY TESTING PROGRAM

PARTICIPATING LABORATORIES NOMINATION FORM

1) Contact: Contact email: Lab Name: Shipping Address: Country: Phone: Fax: Accredited for tests Y/N:	**2)** Contact: Contact email: Lab Name: Shipping Address: Country: Phone: Fax: Accredited for tests Y/N:
3) Contact: Contact email: Lab Name: Shipping Address: Country: Phone: Fax: Accredited for tests Y/N:	**4)** Contact: Contact email: Lab Name: Shipping Address: Country: Phone: Fax: Accredited for tests Y/N:

From:
(National Accrediting Body)

Name:

Organization:

Postal Address:

Phone:

Fax:

Email:

APPENDIX III: INSTRUCTIONS TO ABs

1.0 SAMPLES

Each laboratory is supplied with four separate samples labeled T055-1, T055-2, T055-3 and T055-4. On receipt of samples, complete the enclosed *ACCREDITATION BODY RECEIPT OF SAMPLES FORM* and return it to CAEAL.

2.0 TESTS TO BE PERFORMED

Please refer to your copy of the *INSTRUCTIONS TO PARTICIPANTS* and *REQUISITION REPORTING FORMS* enclosed. These two documents are enclosed with every participant package.

3.0 SAMPLE DISTRIBUTION

The enclosed packages are addressed to each participating laboratory and contain the following,

- Four samples labeled T055-1, T055-2, T055-3 and T055-4
- Instruction sheets
- Customized Report Form, with laboratory code and data entry password
- Receipt of Samples form

Samples are to be shipped to participant laboratories within one week of receipt date. There is no need to open the individual packages.

Note: Please confirm that the laboratory address on each package is Correct.

4.0 DOCUMENTS TO BE SUBMITTED

Participant laboratories with internet access will be reporting all results via the Internet. For laboratories that do not have internet access, results will be reported to the accrediting body. We ask that the accrediting body forward the completed *REQUISITION REPORTING FORMS* to CAEAL.

Ken Middlebrook
CAEAL
Suite 310, 1565 Carling Avenue
Ottawa, Ontario, Canada K1Z 8R1
Phone: (613)233-5300*
Fax: (613)233-5501*
kmiddlebrook@caeal.ca

*** Ensure that the proper international calling codes for Canada are used.**

APPENDIX IV: RECEIPT OF SAMPLES FORM (AB)

In order to monitor the progress of this proficiency testing program, we ask each participating accreditation body, on receipt of the samples, to fill out this form and fax it to:

Ken Middlebrook
The Canadian Association For Environmental Analytical Laboratories
kmiddlebrook@caeal.ca
Fax (613)233-5501*
Phone (613)233-5300*

Thank you in advance for your cooperation.

The APLAC-T055 Samples were received on: _____ (DD-MON-YY)

Comments: _____

_____

_____

_____

Participating Accreditation Body: _____

Contact Person: _____

email: _____

fax: _____

*** Ensure that the proper international calling codes for Canada are used.**

APPENDIX V: INSTRUCTIONS TO LABORATORY

Samples

This proficiency testing program consists of four samples labeled T055-1, T055-2, T055-3 and T055-4. Each sample is free of particulates, preserved with 0.2% HNO3 and contains the following metals;

Al, As, Ba, B, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Sb, Se, Sr, Tl, Ti, V and Zn (0.25 – 1.6 mg/L): As, Se, Sb (1.0 – 100 ug/L)

Testing

Analysis may proceed as soon as samples are received in the laboratory.

Participants shall use routine test methods that would normally be used to test customer supplied samples. Samples do not require filtering or digestion.

Reporting

Enter all results and uncertainty values on the *REQUISITION REPORT FORMS*.

Report results to the T055 coordinator using the CAEAL web-data-entry system.

a. On the internet, go to the following web page,
   http://www.caeal.ca/aplac_t55.html
b. When prompted, enter the membership number (e.g., T012) and password, located in the top right hand portion of the enclosed *REQUISITION REPORT FORMS*.
c. Enter results (maximum three decimal places) in mg/L (ug/L for As, Se and Sb).
d. Enter date of analysis.
e. Enter measurement uncertainty in the units provided.
f. Press the **submit results** button and then **mark as complete**.
g. Within twenty-four hours, a confirmation report will be emailed to the contact listed in the registration. Changes may be made up until the reporting deadline.

Results must be reported no later than midnight of November 17, 2006.

Note: If results can not be reported through the internet, please forward the completed *REQUISITION REPORT FORMS* to your accreditation body.

Inquiries

Forward any questions to

Ken Middlebrook
CAEAL PT Manager
Phone: (613)233-5300*
Fax: (613)233-5501*
Email: kmiddlebrook@caeal.ca

* Ensure that the proper international calling codes are used.

APPENDIX VI: RECEIPT OF SAMPLES FORM (LAB)

In order to monitor the progress of this proficiency testing program, we ask each participating laboratory, on receipt of the samples, to fill out this form and fax it to:

Ken Middlebrook
The Canadian Association For Environmental Analytical Laboratories
kmiddlebrook@caeal.ca
Fax (613)233-5501*
Phone (613)233-5300*

Thank you in advance for your cooperation.

The APLAC-T055 Samples were received on: _____ (DD-MON-YY)

Comments: _____

_____

_____

_____

Participating Laboratory: _____

Accreditation Body: _____

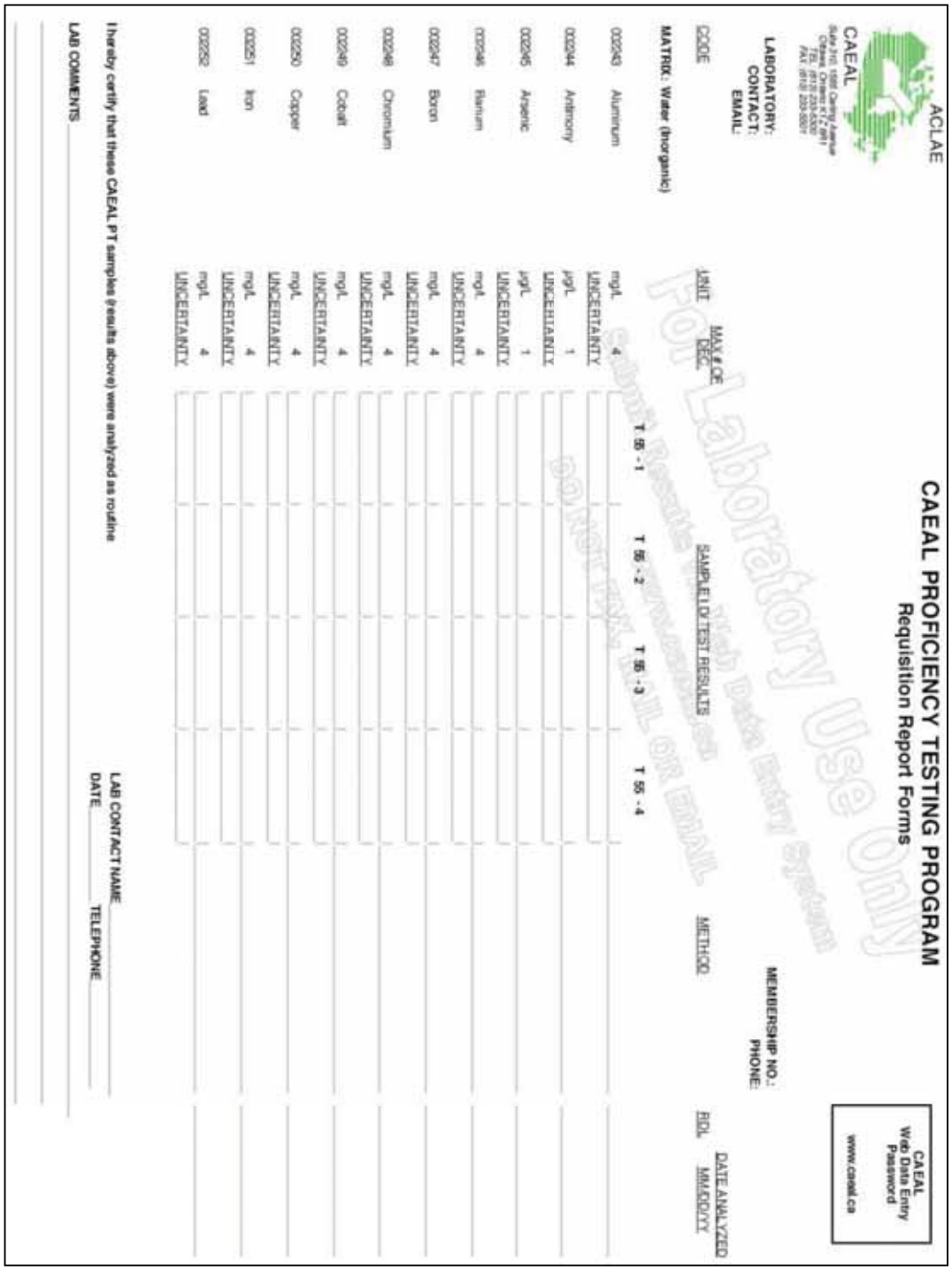
Contact Person: _____

email: _____

Fax: _____

*** Ensure that the proper international calling codes for Canada are used**.

APPENDIX VII: RESULTS REPORT FORM



ACLAE

CAEAL

CAEAL PROFICIENCY TESTING PROGRAM

Requisition Report Forms

CAEAL Web Data Entry Password www.caeal.ca

LABORATORY:
CONTACT:
EMAIL:

MEMBERSHIP NO.:
PHONE:

CODE | UNIT | MAX # OF DEC | SAMPLE ID/ TEST RESULTS | METHOD | RDL | DATE ANALYZED MM/DD/YY

MATRIX: Water (Inorganic)

			T 55 -1	T 55 -2	T 55 -3	T 55 -4			
002943	Aluminum	mg/L	4						
		UNCERTAINTY							
002944	Antimony	µg/L	1						
		UNCERTAINTY							
002945	Arsenic	µg/L	1						
		UNCERTAINTY							
002946	Barium	mg/L	4						
		UNCERTAINTY							
002947	Boron	mg/L	4						
		UNCERTAINTY							
002948	Chromium	mg/L	4						
		UNCERTAINTY							
002949	Cobalt	mg/L	4						
		UNCERTAINTY							
002950	Copper	mg/L	4						
		UNCERTAINTY							
002951	Iron	mg/L	4						
		UNCERTAINTY							
002952	Lead	mg/L	4						
		UNCERTAINTY							

I hereby certify that these CAEAL PT samples (results above) were analyzed as routine

LAB CONTACT NAME

DATE TELEPHONE

LAB COMMENTS