SIM.8.10P trace elements in drinking water

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https://doi.org/10.4224/40003215

National Research Council Canada
Conseil national de recherches Canada

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SIM.8.10P
Trace Elements in Drinking Water

Technical Report

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December 2003

Canada

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Introduction

Safe drinking water is fundamental to everyday life. The goal of SIM.8.10P is to determine state of the practice in SIM countries for the determination of trace elements in water. This exercise was co-ordinated by the Chemical Metrology Group of the Institute for National Measurement Standards (INMS) of the National Research Council of Canada (NRCC). This exercise is a follow-up to SIM.8.P2, conducted between October 1999 and September 2000 and co-ordinated by the National Institute of Standards and Technology (NIST), USA.

Participation in SIM.8.10P

A call for participation was sent out to each country within the SIM Region on March 8, 2003. In addition to NMIs within SIM or their official designees, several additional laboratories provided results. The majority of samples was distributed by courier from NRCC on May 8, 2003 or as soon as a response was received. The final set of samples was sent on August 25, 2003.

Two samples, labeled Sample A and Sample B, were sent to the participants along with instructions for sample storage and data submission. Laboratories were permitted to use their analytical method of choice to determine the primary elements for this study: Cr, Fe, Ni, Cu, Zn, As, Cd, Ba, and Pb. Results for other elements were accepted but not included in the evaluation. In particular, it was requested that determinations were to be performed on each bottle of Sample A and Sample B and replicate determinations for each bottle reported. A full uncertainty budget in accordance with the GUM [1] was also requested from the participants. The deadline for the submission of results was set as September 15, 2003. Table 1 lists the participants in SIM.8.10P.

Sample Preparation

Samples were prepared in-house at NRCC. Two 25 liter LDPE carboys were cleaned with 10 % (v/v) NRC sub-boiled nitric acid for 72 hours. Each carboy was emptied, rinsed with high purity water and refilled with 18 liters of bottled natural spring water (Labrador Laurentienne Inc., Quebec, Canada). This water is sold for use with water dispensers and packaged in 18 liter plastic containers. The samples were acidified by addition of 100 ml of NRC sub-boiled high purity nitric acid. Both Sample A and Sample B were fortified with Cr, Fe, Ni, Cu, Zn, As, Cd, Ba, and Pb by adding appropriate amounts of 1000 µg/ml stock solutions (ICP Grade, SCP Science, Montreal, Quebec) prepared from high purity materials and traceable to NIST. The

fortified concentrations for Sample A were chosen to approach the maximum acceptable limits of the USEPA and Canadian government guidelines for drinking water [2,3]. The concentrations for Sample B were approximately 10- fold greater than Sample A. The resulting solution was thoroughly mixed and sampled into precleaned 250 mL HDPE bottles.

A homogeneity test for all elements was performed on six randomly selected samples. In all cases, the coefficient of variation was less than 1.2% with the exception of As (3%). The latter measurement represented variation inherent to the analytical technique used (ETAAS) rather than reflecting between bottle differences. The material was deemed stable for at least one year at room temperature based on NRCC experience with similar samples.

Table 1. Participants in SIM.8.10P.

Institute	Country	Contact
Instituto de Tecnología Minera – SEGEMAR	Argentina	Ricardo Crubellati
INTI-CEQUIPE	Argentina	Celia Puglisi, Liliana Valiente
Laboratorio de Calidad Ambiental - LCA	Bolivia	Hugo Guerrero
Fundação Centro Tecnológico de Minas Gerais CETEC	Brazil	Olguita Geralda Ferreira Rocha
INMETRO	Brazil	Thiago de Oliveira Araujo
Instituto de Pesquisas Tecnológicas, IPT	Brazil	Vera Ponçano
SENAI/ CETIND	Brazil	Sérgio Motta
National Research Council of Canada (NRCC)	Canada	Ralph Sturgeon, Scott Willie
CENMA	Chile	Pablo Richter-Duk
INN	Chile	Nury Gras-Rebolledo
Fundación Chile	Chile	Gabriela Massiff
LACOMET	Costa Rica	Carlos Paniagua
Institute of Chemical Technology	Czech Republic	Miloslav Suchanek
Physikalisch-Technische Bundesanstalt, PTB	Germany	Detlef Schiel
University of the West Indies*	Jamaica	Robin Rattray
West Indies Alumina Company, WINDALCO*	Jamaica	Desmond Lawson
Envirolab	Peru	Luis Bueno Carbajal
Multipurpose Laboratory*	St. Kitts	Milton Whittaker
Caribbean Environmental Health Institute **	St. Lucia	Andrew Lewis
Laboratorio Tecnológico del Uruguay, LATU	Uruguay	Nury Prat
ICLAM SENCAMER	Venezuela	Haygas Kalustián

coordinated through:
* Bureau of Standards Jamaica
** St. Lucia Bureau of Standards

Results

Table 1 lists the participants in SIM.8.10P. The majority of results were received by the September 15th deadline. Only one laboratory (Trinidad and Tobago Bureau of Standards) was sent samples and did not return results. The final data set was received October 21, 2003. The submitted results were compiled in a database and a copy was returned by email on October 22, 2003 to the participants for verification that no transcription errors had occurred. A few minor changes were made.

Laboratories 2, 20 and 21 submitted two independent results based on alternative detection methodologies. In such cases, the independent results are listed separately and are delineated as the laboratory number accompanied by an alphabetical suffix.

Appendix A lists the submitted data: the mean, uncertainty and maximum of six values for each laboratory. Graphical representation of the results are presented on pages 8 to 25. The mean is shown as a square, and vertical error bars represent the reported expanded uncertainty. The assigned value is displayed as a solid horizontal line. Divergent data that would distort the graph are indicated with an arrow head near the graph's upper border.

Below each graph a table lists: the recommended values, uncertainties and instrumental techniques reported by the participants. For each element, the source of the assigned value and, for comparative purposes, a summary of submitted results, is also provided. In some cases, obvious outliers were subjectively rejected from the overall summary.

Only one laboratory reported results for additional elements outside the nine target analytes. These are listed in Appendix B.

Assigned Values

The assigned values for this exercise were determined from results submitted by laboratories having successful BIPM/CIPM experience. Thus, SIM.8.10P could provide international comparability for trace element analysis in drinking water by linking intercomparison results for SIM nations with BIPM/CIPM key comparison participants. However, this restriction limited data to only NRCC and PTB for calculation of the SIM.8.P10 assigned values. In some cases, NRCC and PTB were able to employ the method of isotope dilution sector field inductively coupled plasma mass spectrometry (ID-SF-ICP-MS). The use of isotope dilution as a calibration method is considered a primary method when properly employed. Unfortunately, for monoisotopic elements or elements suffering severe interferences, other techniques must be used.

The assigned values for Cr, Cu and Ni were calculated based on NRCC results using alternative methods of detection, such as inductively coupled atomic emission (ICP-AES) and electrothermal atomization atomic absorption (ETAAS). For As and Fe, the assigned value was based on only one NRCC method.

Gravimetric values were determined but not considered to be part of the calculation of the assigned value since an accurate analysis of the unspiked water was not performed. The assigned value generally agreed with the gravimetric calculation with the exceptions of Zn and Ba. For Ba there was a significant amount of the analyte naturally present in the unspiked sample, and for Zn a calculation error in the preparation of the spike most likely occurred.

Uncertainties

The majority of laboratories reported results with an uncertainty value calculated according to the principles outlined in the GUM [1]. Only a few participants included in their report details of the uncertainty budget calculation.

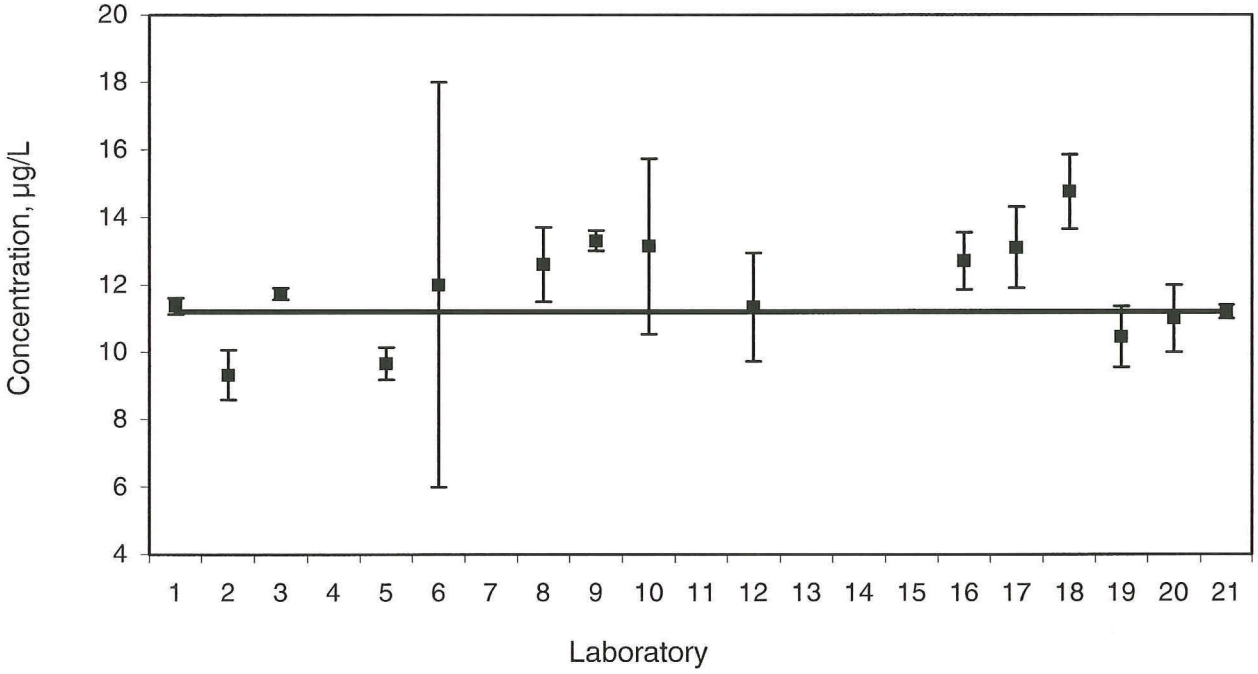
Several laboratories (12 and 15) did not report an expanded uncertainty. For these laboratories the uncertainty was derived by multiplying the standard deviation of replicate results by a factor of two.

Some laboratories did not state whether the uncertainty reported was an expanded uncertainty i.e., multiplied by the coverage factor, k.

Major sources contributing to overall uncertainty identified by several participants were calibration and dilution factors.

Chromium

Sample A



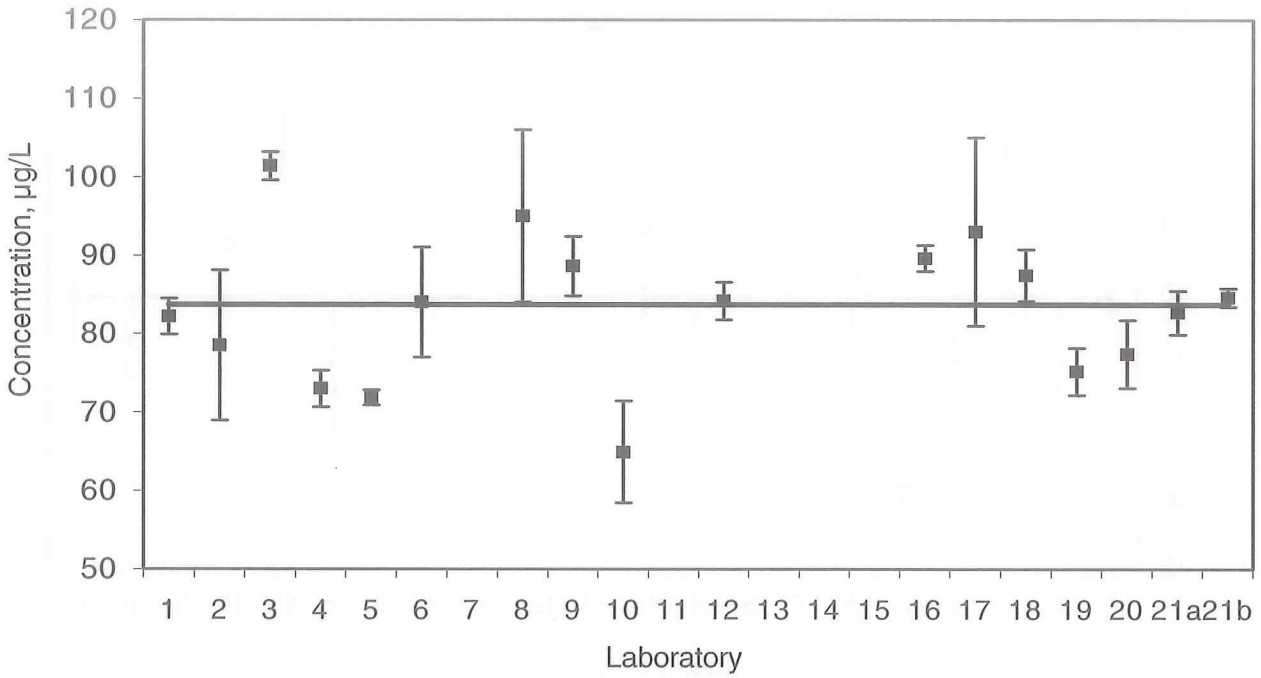
Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1	11.37	0.24	ETAAS
2	9.33	0.74	ETAAS
3	11.73	0.17	ETAAS
4	<2		ICP-AES
5	9.67	0.48	ETAAS
6	12	6	ICP-AES
7			
8	12.6	1.1	ETAAS
9	13.3	0.3	ETAAS
10	13.1	2.6	ETAAS
11			
12	11.3	1.5	ICP-AES
13			
14			
15			
16	12.7	0.848	ETAAS
17	13.1	1.2	ETAAS
18	14.8	1.1	ICP-AES
19	10.5	0.9	ICP-MS
20	11.0	1.0	ICP-AES
21	11.2	0.2	ETAAS

Assigned Value

A value of 11.2 µg/L was assigned to Cr in Sample A based on the ETAAS results from NRCC.

Overall Summary	
No. of results	15
Overall mean	11.8
Median	11.7
Sample S.D.	1.45
95% C.I.	0.95
gravimetric	11.0

Sample B



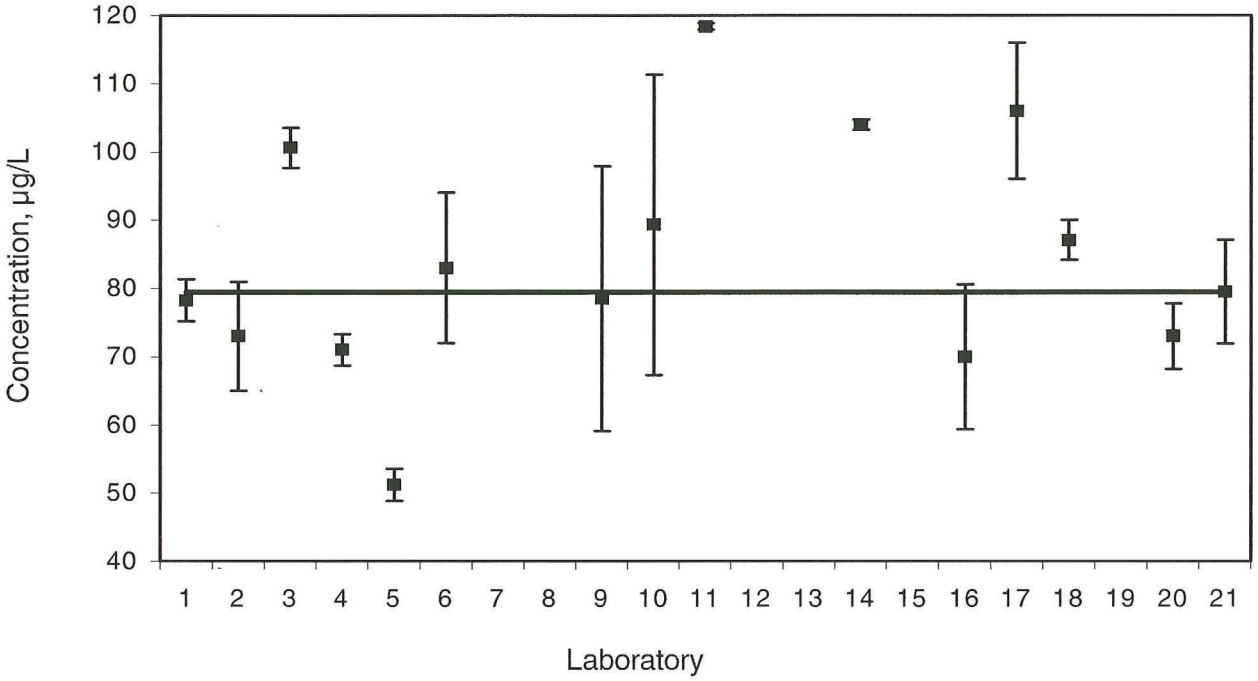
Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1	82.18	2.28	ETAAS
2	78.52	9.57	ICP-AES
3	101.4	1.78	ETAAS
4	73.0	2.3	ICP-AES
5	71.8	4.7	ETAAS
6	84	7	ICP-AES
7			
8	95	11	ETAAS
9	88.6	3.8	ETAAS
10	64.9	6.5	FAAS
11			
12	84.2	1.2	ICP-AES
13			
14			
15			
16	89.6	1.65	ETAAS
17	93	12	ETAAS
18	87.5	3.3	ICP-AES
19	75.2	3.0	ICP-MS
20	77.4	4.3	ICP-AES
21a	75.2	2.6	ETAAS
21b	84.6	1.2	ICP-AES

Assigned Value

A value of 83.7 µg/L was assigned to Cr in Sample B based on the ETAAS and ICP-AES results from NRCC.

Overall Summary	
No. of results	17
Overall mean	83.2
Median	84.0
Sample S.D.	9.1
95% C.I.	5.5
gravimetric	82.7

Sample A



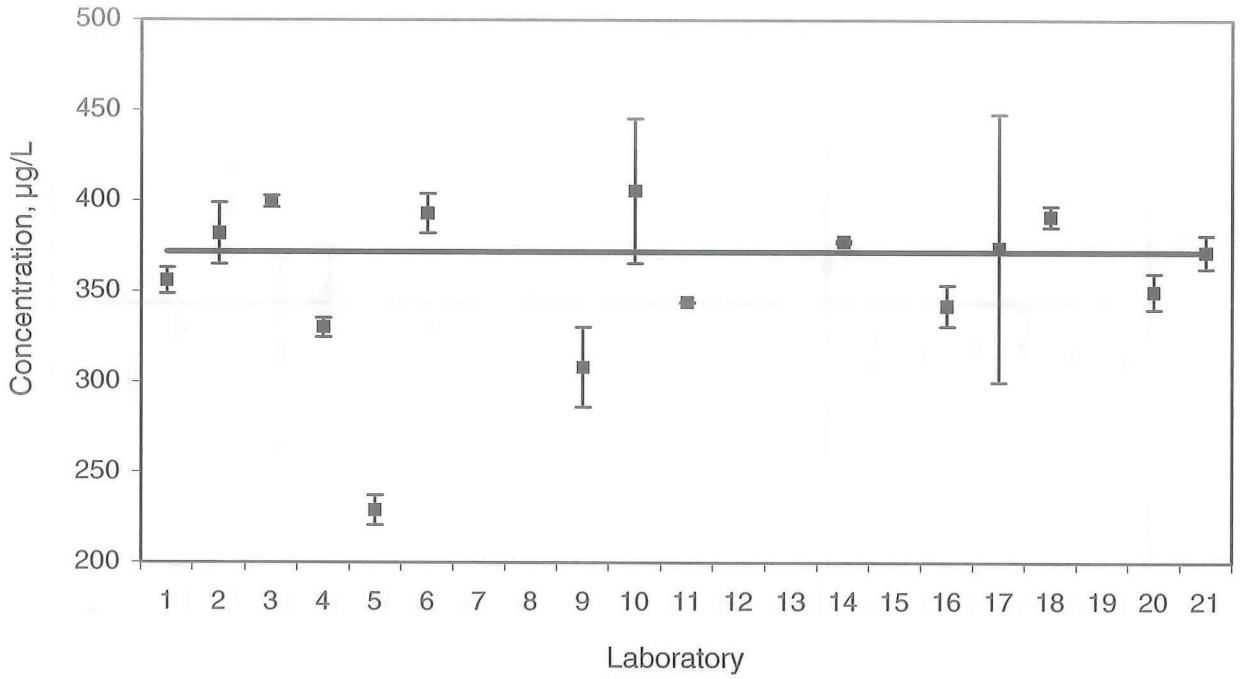
Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1	78.24	3.08	ETAAS
2	73	7.98	ICP-AES
3	100.6	2.91	ETAAS
4	71.0	2.3	ICP-AES
5	51.2	2.4	ETAAS
6	83	11	ICP-AES
7			
8			
9	78.5	19.4	ETAAS
10	89	22	FAAS
11	118.4	0.5	FAAS
12			
13			
14	103.99	0.734	ICP-AES
15			
16	70.0	10.6	FAAS
17	106	10	ETAAS
18	87.1	2.9	ICP-AES
19			
20	73.0	4.8	ICP-AES
21	79.5	7.6	ICP-AES

Assigned Value

A value of 79.5 µg/L was assigned to Fe in Sample A based on the ICP-AES results from NRCC.

Overall Summary	
No. of results	15
Overall mean	84.2
Median	79.5
Sample S.D.	17.2
95% C.I.	11.2
gravimetric	81.0

Sample B



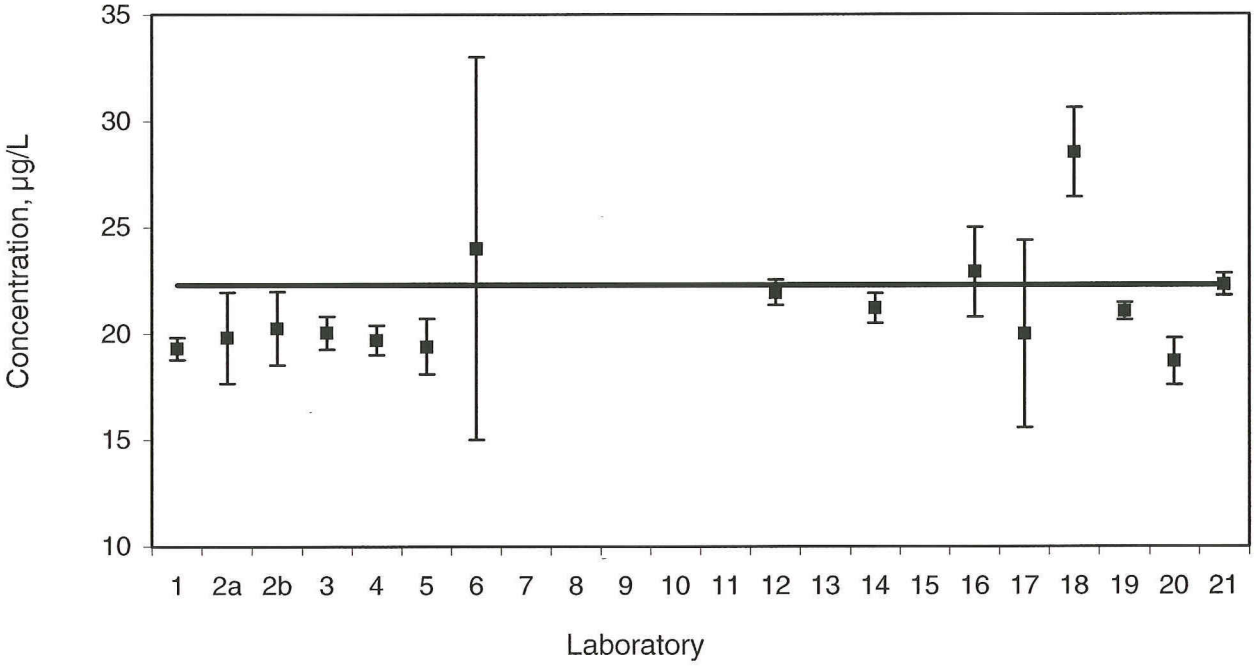
Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1	355.8	7.2	FAAS
2	381.85	16.92	ICP-AES
3	399.60	3.28	FAAS
4	330.0	5.4	ICP-AES
5	228.3	8.2	ETAAS
6	393	11	ICP-AES
7			
8			
9	308	22	FAAS
10	405	40	FAAS
11	343.9	0.4	FAAS
12			
13			
14	377.3	0.938	ICP-AES
15			
16	342	11.3	FAAS
17	374	74	FAAS
18	391.3	5.8	ICP-AES
19			
20	350	10	ICP-AES
21	371.6	9.2	ICP-AES

Assigned Value

A value of 372 µg/L was assigned to Fe in Sample B based on the ICP-AES results from NRCC.

Overall Summary	
No. of results	15
Overall mean	357
Median	371
Sample S.D.	45
95% C.I.	29
gravimetric	387

Sample A



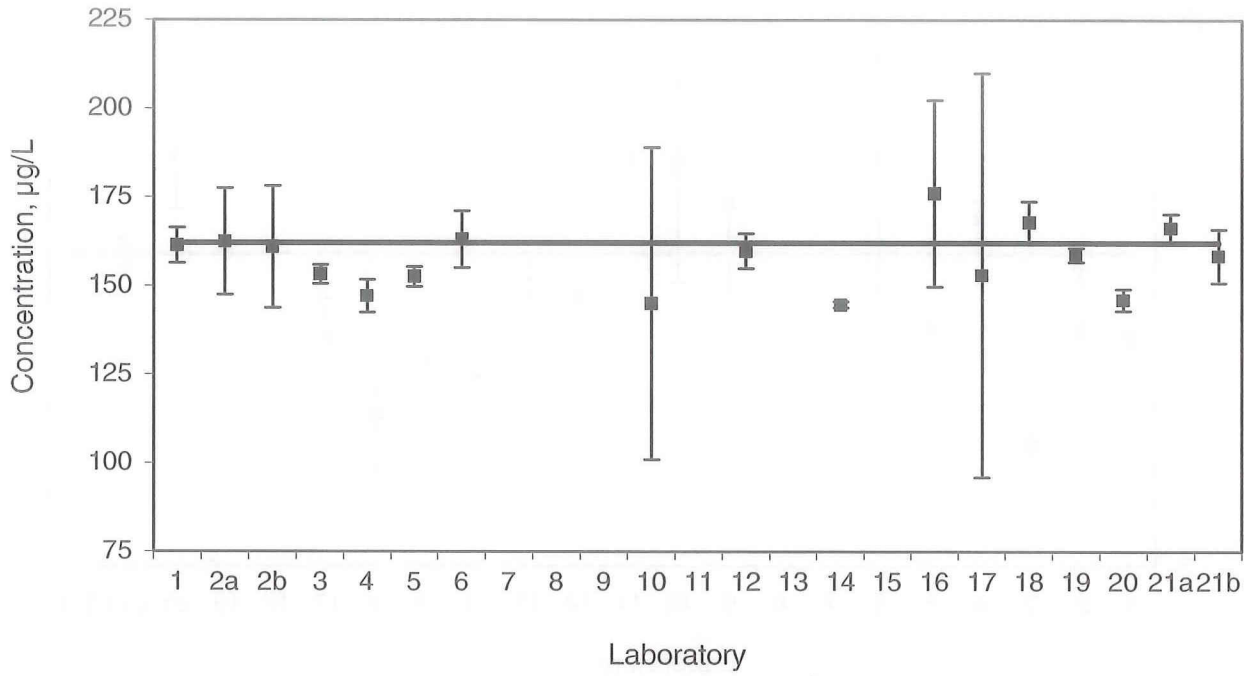
Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1	19.31	0.52	ETAAS
2a	19.81	2.14	ETAAS
2b	20.25	1.72	ICP-AES
3	20.05	0.78	ETAAS
4	19.7	0.7	ICP-AES
5	19.4	1.3	ETAAS
6	24	9	ICP-AES
7			
8			
9			
10			
11			
12	21.9	0.6	ICP-AES
13			
14	21.21	0.707	ICP-AES
15			
16	22.9	2.11	ETAAS
17	20.0	4.4	ETAAS
18	28.5	2.1	ICP-AES
19	21.1	0.4	ICP-MS
20	18.7	1.1	ICP-AES
21	22.31	0.53	ID-SF-ICP-MS

Assigned Value

A value of 22.3 µg/L was assigned to Ni in Sample A based on the ID-SF-ICP-MS results from NRCC.

Overall Summary	
No. of results	15
Overall mean	21.3
Median	20.3
Sample S.D.	2.5
95% C.I.	1.6
gravimetric	21.6

Sample B

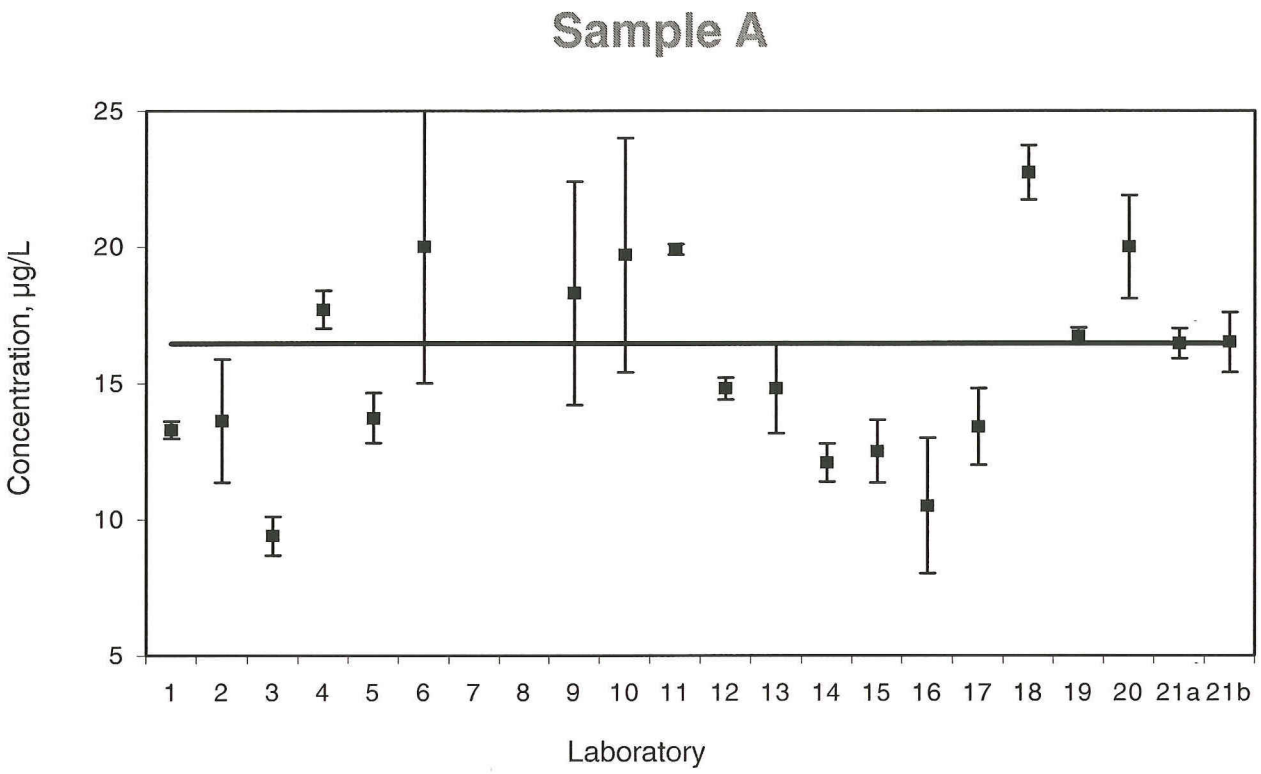


Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1	161.4	5.0	ETAAS
2a	162.43	14.99	ETAAS
2b	160.89	17.23	ICP-AES
3	153.2	2.62	ETAAS
4	147.0	4.7	ICP-AES
5	152.6	2.8	ETAAS
6	163	8	ICP-AES
7			
8			
9			
10	145	44	FAAS
11			
12	159.7	5.0	ICP-AES
13			
14	144.71	0.823	ICP-AES
15			
16	176	26.3	FAAS
17	153	57	FAAS
18	167.9	5.9	ICP-AES
19	159	2	ICP-MS
20	146	3	ICP-AES
21a	166.2	4.1	ID-SF-ICP-MS
21b	158.4	7.5	ICP-AES

Assigned Value

A value of 162 µg/L was assigned to Ni in Sample B based on the ID-SF-ICP-MS and ICP-AES results from NRCC.

Overall Summary	
No. of results	17
Overall mean	157
Median	159
Sample S.D.	8.8
95% C.I.	5.3
gravimetric	162



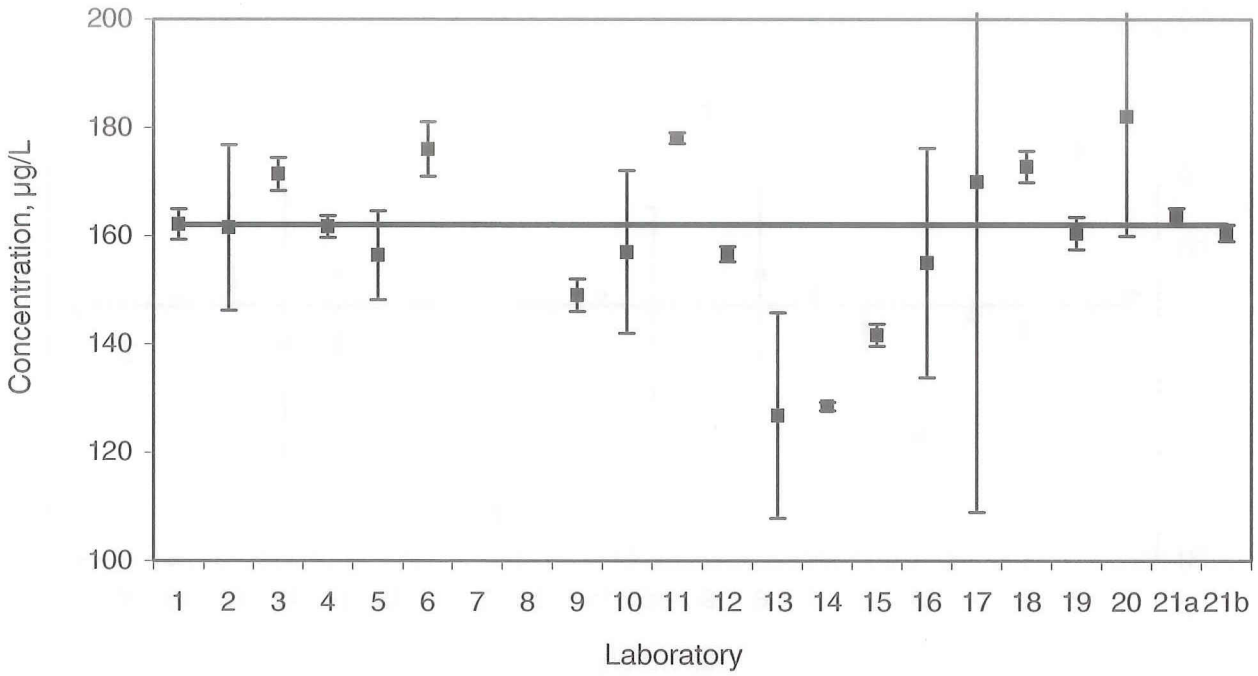
Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1	13.29	0.32	ETAAS
2	13.62	2.26	ICP-AES
3	9.40	0.71	ETAAS
4	17.7	0.7	ICP-AES
5	13.72	0.92	ETAAS
6	20	5	ICP-AES
7			
8			
9	18.3	4.1	ETAAS
10	19.7	4.3	ETAAS
11	19.9	0.2	FAAS
12	14.8	0.4	ICP-AES
13	14.8	1.64	AAS
14	12.09	0.707	ICP-AES
15	13	2	FAAS
16	10.5	2.49	ETAAS
17	13.4	1.4	ETAAS
18	22.7	1.0	ICP-AES
19	16.7	0.3	ICP-MS
20	20.0	1.9	ICP-AES
21a	16.45	0.56	ID-ICP-MS
21b	16.5	1.1	ICP-AES

Assigned Value

A value of 16.5 µg/L was assigned to Cu in Sample A based on the ID-SF-ICP-MS and ICP-AES results from NRCC.

Overall Summary	
No. of results	20
Overall mean	15.8
Median	15.6
Sample S.D.	3.6
95% C.I.	2.0
gravimetric	16.5

Sample B



Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1	162.1	2.8	FAAS
2	161.52	15.25	ICP-AES
3	171.38	3.061	ETAAS
4	161.7	2.0	ICP-AES
5	155.5	8.2	ETAAS
6	176	5	ICP-AES
7			
8			
9	149	3	FAAS
10	157	15	FAAS
11	178	1	FAAS
12	156.6	1.4	ICP-AES
13	126.8	19	AAS
14	128.55	0.800	ICP-AES
15	141	5	FAAS
16	155	21.2	FAAS
17	170	61	FAAS
18	172.8	2.9	ICP-AES
19	161	3	ICP-MS
20	182	22	ICP-AES
21a	163.5	1.6	ID-ICP-MS
21b	160.5	1.5	ICP-AES

Assigned Value

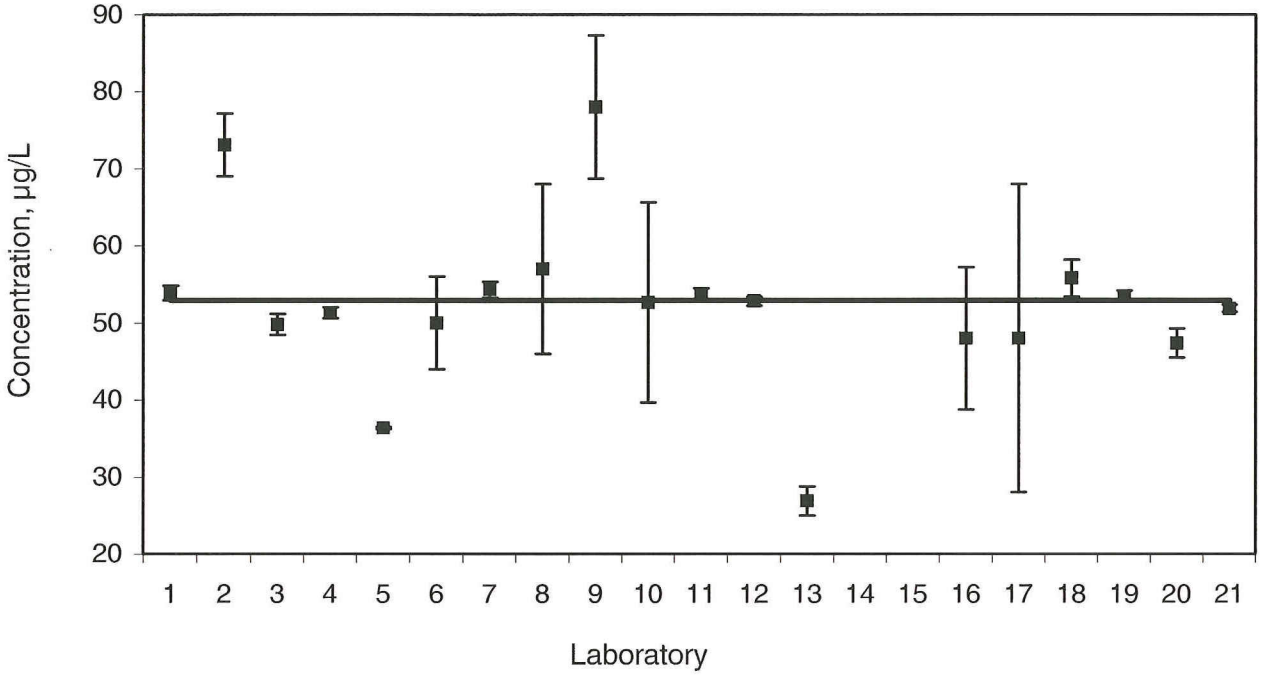
A value of 162 µg/L was assigned to Cu in Sample B based on the ID-SF-ICP-MS and ICP-AES results from NRCC.

Overall Summary	
No. of results	20
Mean*	163
Median*	161
Sample S.D.*	10
95% C.I.*	6
gravimetric	162

* Two results not included.

Zinc

Sample A



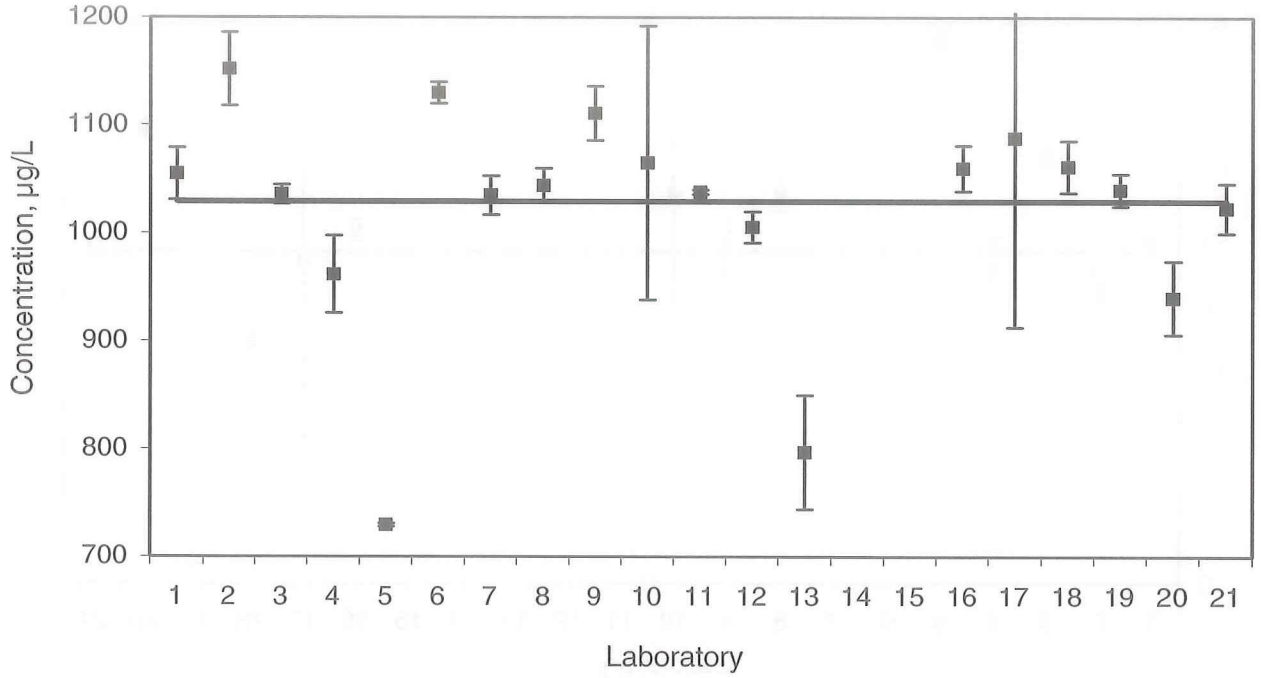
Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1	53.87	0.92	FAAS
2	73.06	4.08	ICP-AES
3	49.80	1.38	FAAS
4	51.3	0.7	ICP-AES
5	36.4	4.1	ETAAS
6	50	6	ICP-AES
7	54.3	1.0	ID-SF-ICP-MS
8	57	11	FAAS
9	78	9.3	FAAS
10	53	13	FAAS
11	53.7	0.8	FAAS
12	52.8	0.6	ICP-AES
13	26.9	1.9	AAS
14			
15			
16	48.0	9.24	FAAS
17	48	20	FAAS
18	55.8	2.4	ICP-AES
19	53.5	0.7	ICP-MS
20	47.4	1.9	ICP-AES
21	51.9	0.47	ID-SF-ICP-MS

Assigned Value

A value of 52.9 µg/L was assigned to Zn in Sample A based on the ID-SF-ICP-MS results from NRCC and ID-SF-ICP-MS results from PTB.

Overall Summary	
No. of results	19
Overall mean	52.3
Median	52.7
Sample S.D.	10.5
95% C.I.	6.1

Sample B



Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1	1055	24	FAAS
2	1151.86	34.02	ICP-AES
3	1036	9.21	FAAS
4	961.7	35.8	ICP-AES
5	714.6	57.5	ETAAS
6	1130	10	ICP-AES
7	1035	18	ID-SF-ICP-MS
8	1044	16	FAAS
9	1111	25	FAAS
10	1065	127	FAAS
11	1038	2	FAAS
12	1006	14.6	ICP-AES
13	797	53	AAS
14			
15			
16	1060	21.2	FAAS
17	1088	175	FAAS
18	1061.3	24	ICP-AES
19	1040	15	ICP-MS
20	940	34	ICP-AES
21	1023	23	ID-SF-ICP-MS

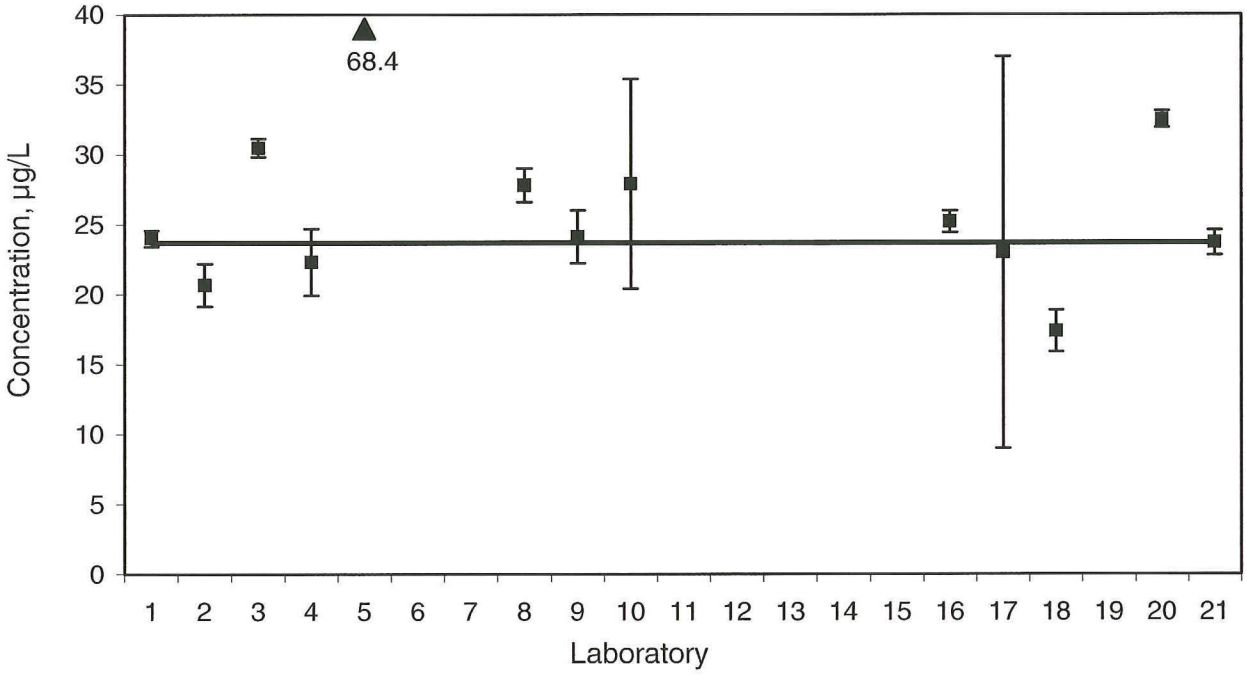
Assigned Value

A value of 1029 µg/L was assigned to Zn in Sample B based on the ID-SF-ICP-MS results from NRCC and ID-SF-ICP-MS results from PTB.

Overall Summary	
No. of results	17
Mean*	1050
Median*	1044
Sample S.D.*	52
95% C.I.*	30

* Two results not included.

Sample A



Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1	24.01	0.59	HGAAS
2	20.66	1.52	ETAAS
3	30.48	0.65	ETAAS
4	22.3	2.4	ICP-AES
5	68.4	3.9	ETAAS
6			
7			
8	27.8	1.2	ETAAS
9	24.1	1.9	HGAAS
10	27.9	7.5	ETAAS
11			
12			
13			
14			
15			
16	25.2	0.778	ETAAS
17	23	14	HGAAS
18	17.4	1.5	ICP-AES
19			
20	32.5	0.6	HGAAS
21	23.7	0.9	ETAAS

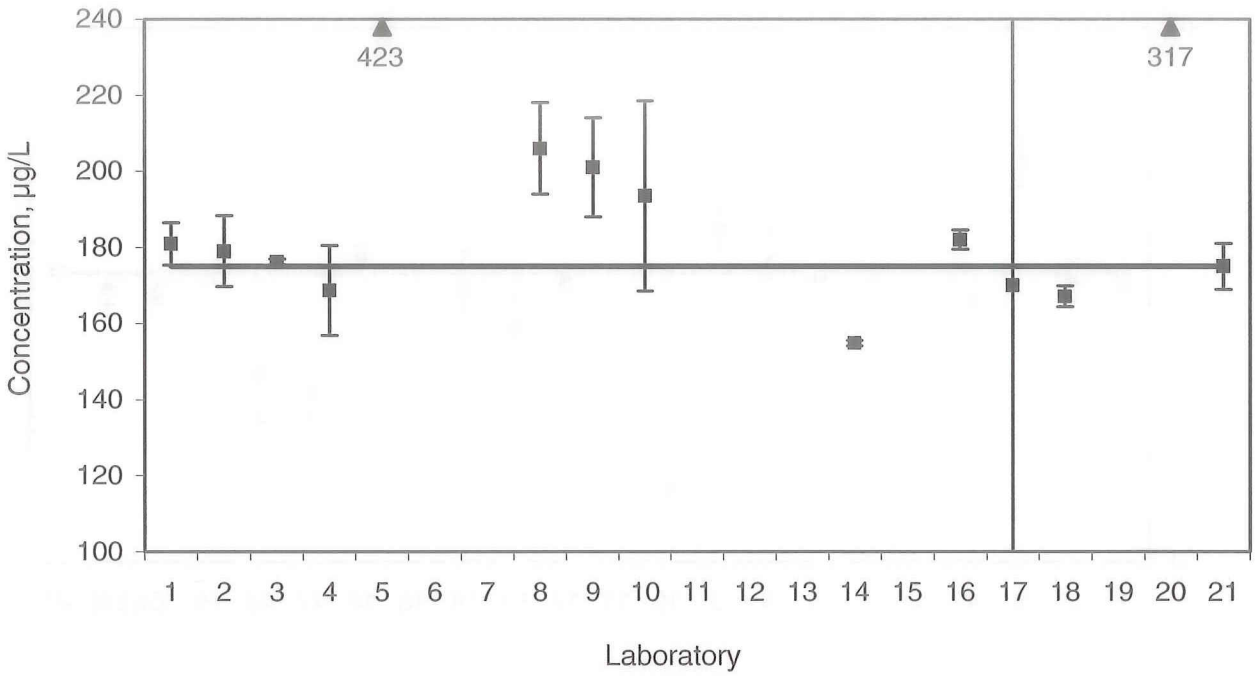
Assigned Value

A value of 23.7 µg/L was assigned to As in Sample A based on the ETAAS results from NRCC.

Overall Summary	
No. of results	13
Mean*	24.9
Median*	24.1
Sample S.D.*	4.2
95% C.I.*	3.1
gravimetric	23.0

* One result not included.

Sample B



Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1	180.9	5.6	HGAAS
2	179.02	9.24	ETAAS
3	176.2	0.71	ETAAS
4	168.7	11.8	ICP-AES
5	423.4	23	ETAAS
6			
7			
8	206	12	ETAAS
9	201	13	HGAAS
10	194	25	ETAAS
11			
12			
13			
14	154.88	0.722	ICP-AES
15			
16	182	2.53	ETAAS
17	170	70	HGAAS
18	167.1	2.8	ICP-AES
19			
20	317	14	HGAAS
21	175	6	ETAAS

Assigned Value

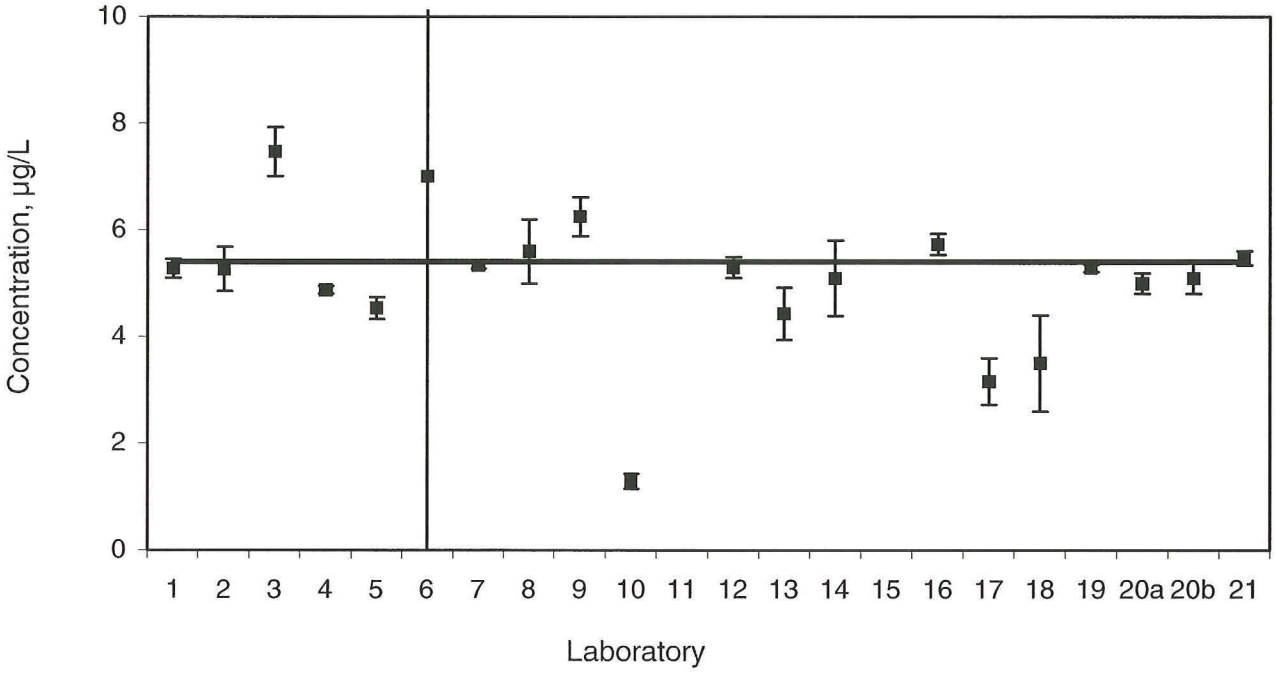
A value of 175 µg/L was assigned to As in Sample B based on the ETAAS results from NRCC.

Overall Summary	
No. of results	14
Mean*	179
Median*	178
Sample S.D.*	15
95% C.I.*	11
gravimetric	173

* Two results not included.

Cadmiun

Sample A



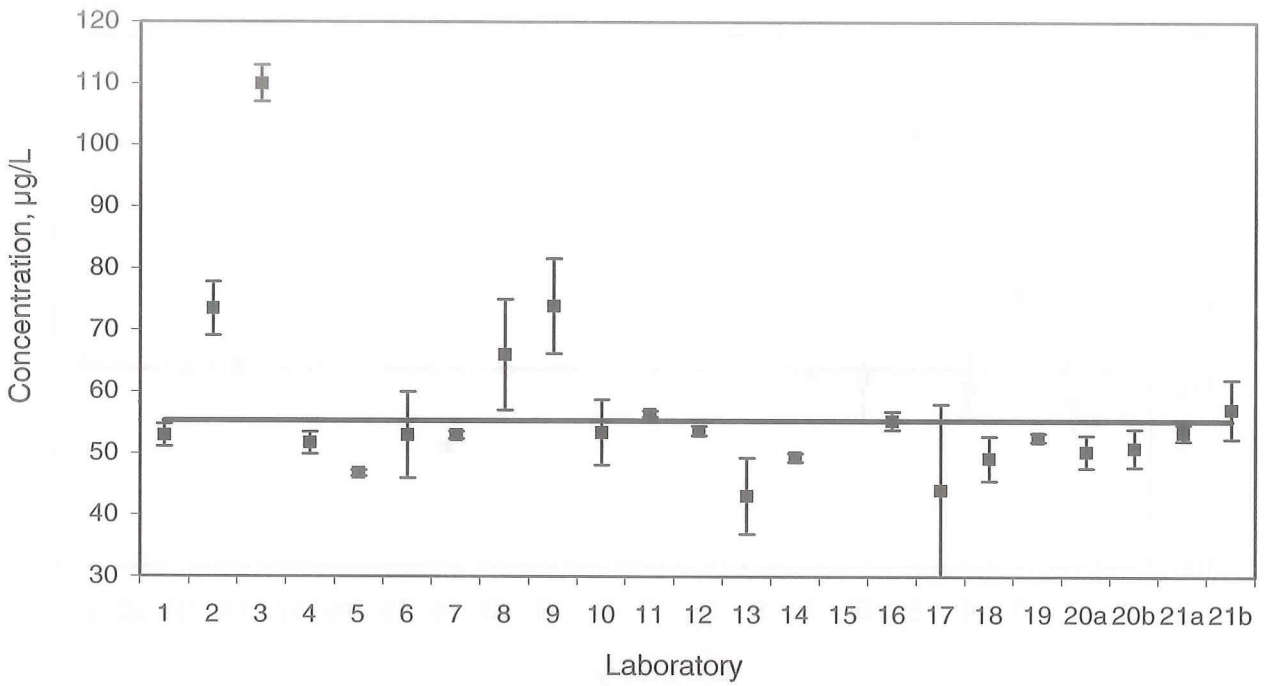
Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1	5.28	0.18	ETAAS
2	5.27	0.42	ETAAS
3	7.47	0.46	ETAAS
4	4.87	0.07	ICP-AES
5	4.53	0.20	ETAAS
6	7	7	ICP-AES
7	5.34	0.06	ID-SF-ICP-MS
8	5.6	0.6	ETAAS
9	6.25	0.36	ETAAS
10	1.30	0.14	ETAAS
11			
12	5.3	0.2	ICP-AES
13	4.43	0.49	AAS
14	5.10	0.707	ICP-AES
15			
16	5.73	0.196	ETAAS
17	3.16	0.43	ETAAS
18	3.5	0.9	ICP-AES
19	5.29	0.07	ICP-MS
20a	5.0	0.2	ICP-AES
20b	5.1	0.3	ASV
21	5.48	0.13	ID-SF-ICP-MS

Assigned Value

A value of 5.41 µg/L was assigned to Cd in Sample A based on the ID-SF-ICP-MS results from NRCC and ID-SF-ICP-MS results from PTB.

Overall Summary	
No. of results	20
Overall mean*	5.25
Median*	5.28
Sample S.D.*	1
95% C.I.*	0.56
gravimetric	5.40

Sample B



Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1	52.86	1.84	ETAAS
2	73.44	4.33	ETAAS
3	110.0	2.94	ETAAS
4	51.7	1.8	ICP-AES
5	46.86	0.50	ETAAS
6	53	7	ICP-AES
7	53.0	0.6	ID-SF-ICP-MS
8	66	9	ETAAS
9	73.9	7.7	FAAS
10	53.4	5.3	FAAS
11	56.4	0.5	FAAS
12	53.7	0.8	ICP-AES
13	43.1	6.2	AAS
14	49.36	0.709	ICP-AES
15			
16	55.3	1.52	ETAAS
17	44	14	ETAAS
18	49.2	3.6	ICP-AES
19	52.6	0.7	ICP-MS
20a	50.3	2.7	ICP-AES
20b	50.9	3.1	ASV
21a	53.4	1.3	ID-SF-ICP-MS
21b	57.2	4.8	ICP-AES

Assigned Value

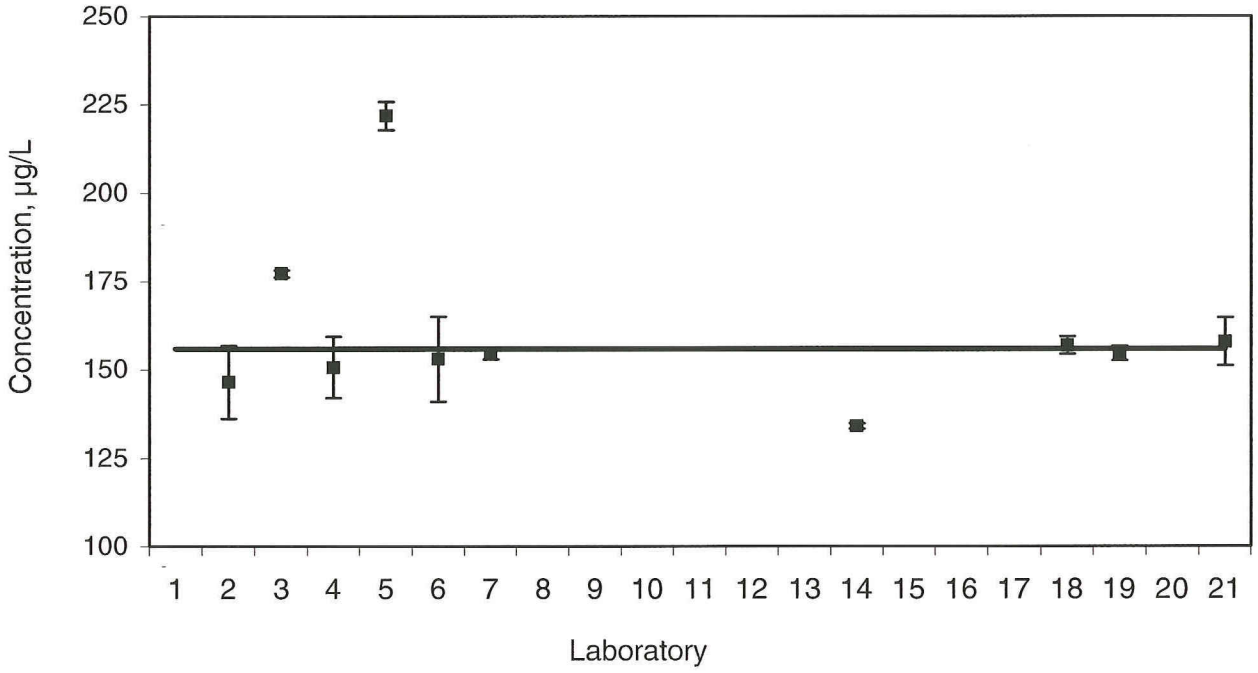
A value of 55.3 µg/L was assigned to Cd in Sample B based on the ID-SF-ICP-MS and ICP-AES results from NRCC and ID-SF-ICP-MS results from PTB.

Overall Summary	
No. of results	22
Overall mean	54.3
Median	53.0
Sample S.D.	8.0
95% C.I.	4.2
gravimetric	54.0

* One result not included.

Barium

Sample A



Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1			
2	146.53	10.34	ICP-AES
3	177.2	0.93	ETAAS
4	150.7	8.7	ICP-AES
5	221.6	19.1	ETAAS
6	153	12	ICP-AES
7	154.4	1.5	ID-SF-ICP-MS
8			
9			
10			
11			
12			
13			
14	134.04	0.708	ICP-AES
15			
16			
17			
18	156.9	2.5	ICP-AES
19	155	2	ICP-MS
20			
21	157.9	6.8	ICP-AES

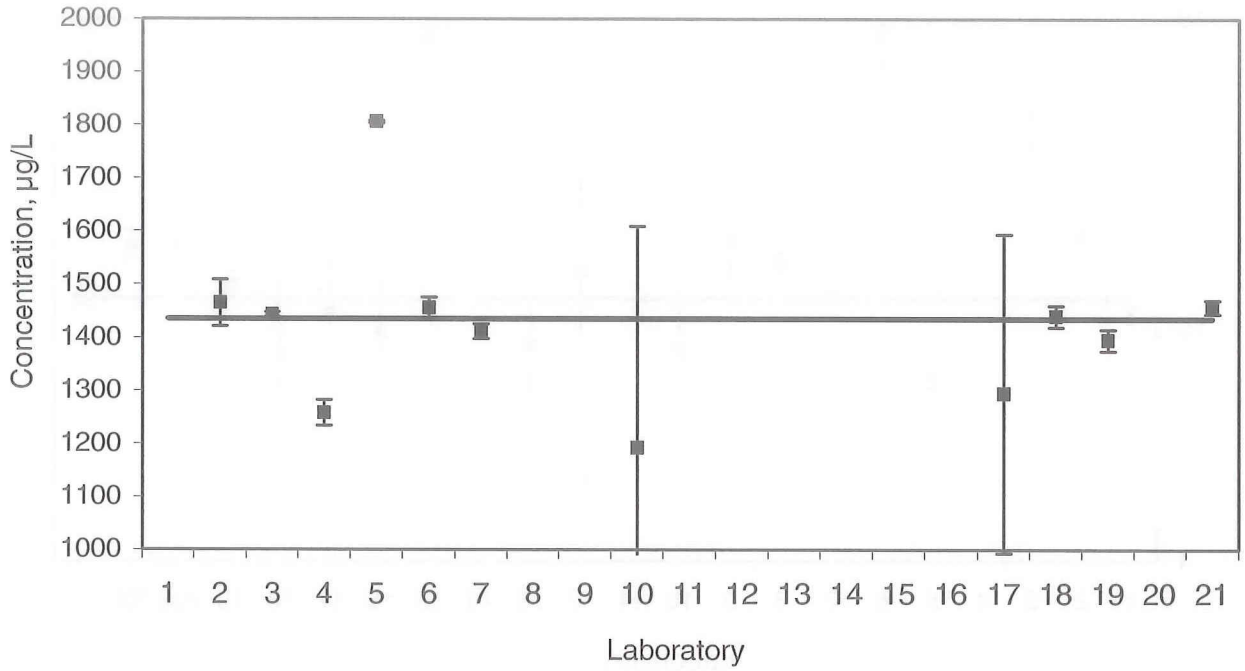
Assigned Value

A value of 156 µg/L was assigned to Ba in Sample A based on the ICP-AES results from NRCC and ID-SF-ICP-MS results from PTB.

Overall Summary	
No. of results	9
Mean*	154
Median*	154
Sample S.D.*	11
95% C.I.*	10

* One result not included.

Sample B



Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1			
2	1465.12	43.22	ICP-AES
3	1443	4.17	ETAAS
4	1258.0	23.5	ICP-AES
5	1811.4	101.2	ETAAS
6	1456	20	ICP-AES
7	1412	14	ID-SF-ICP-MS
8			
9			
10	1192	417	FAAS
11			
12			
13			
14			
15			
16			
17	1294	300	FAAS
18	1439.8	20	ICP-AES
19	1395	20	ICP-MS
20			
21	1458	13	ICP-AES

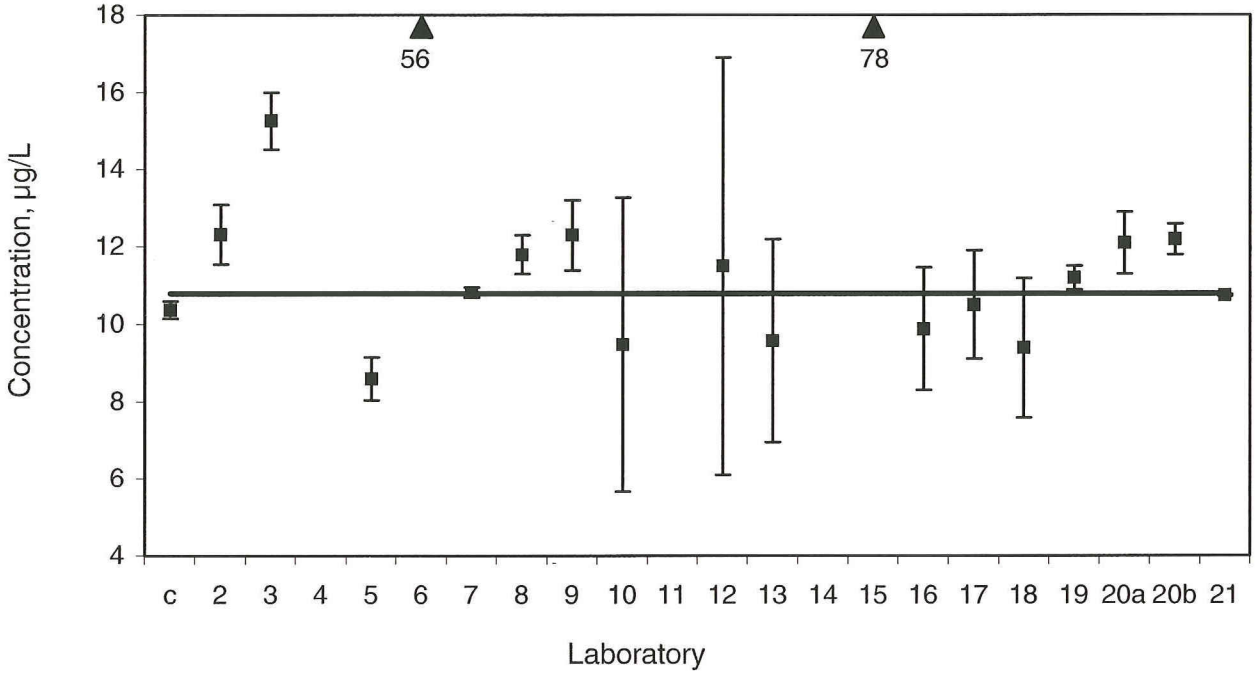
Assigned Value

A value of 1435 µg/L was assigned to Ba in Sample B based on the ICP-AES results from NRCC andID-SF-ICP-MS results from PTB.

Overall Summary	
No. of results	11
Overall mean	1420
Median	1440
Sample S.D.	158
95% C.I.	126

* Four results not included.

Sample A



Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1	10.37	0.22	ETAAS
2	12.32	0.77	ETAAS
3	15.26	0.74	ETAAS
4	<15		ICP-AES
5	8.59	0.55	ETAAS
6	56	10	ICP-AES
7	10.82	0.13	ID-SF-ICP-MS
8	11.8	0.5	ETAAS
9	12.3	0.9	ETAAS
10	9.5	3.8	ETAAS
11			
12	11.5	5.4	ICP-AES
13	9.57	2.63	AAS
14			
15	78	34	FAAS
16	9.88	1.58	ETAAS
17	10.5	1.4	ETAAS
18	9.4	1.8	ICP-AES
19	11.2	0.3	ICP-MS
20a	12.1	0.8	ICP-AES
20b	12.2	0.4	ASV
21	10.75	0.028	ID-ICP-MS

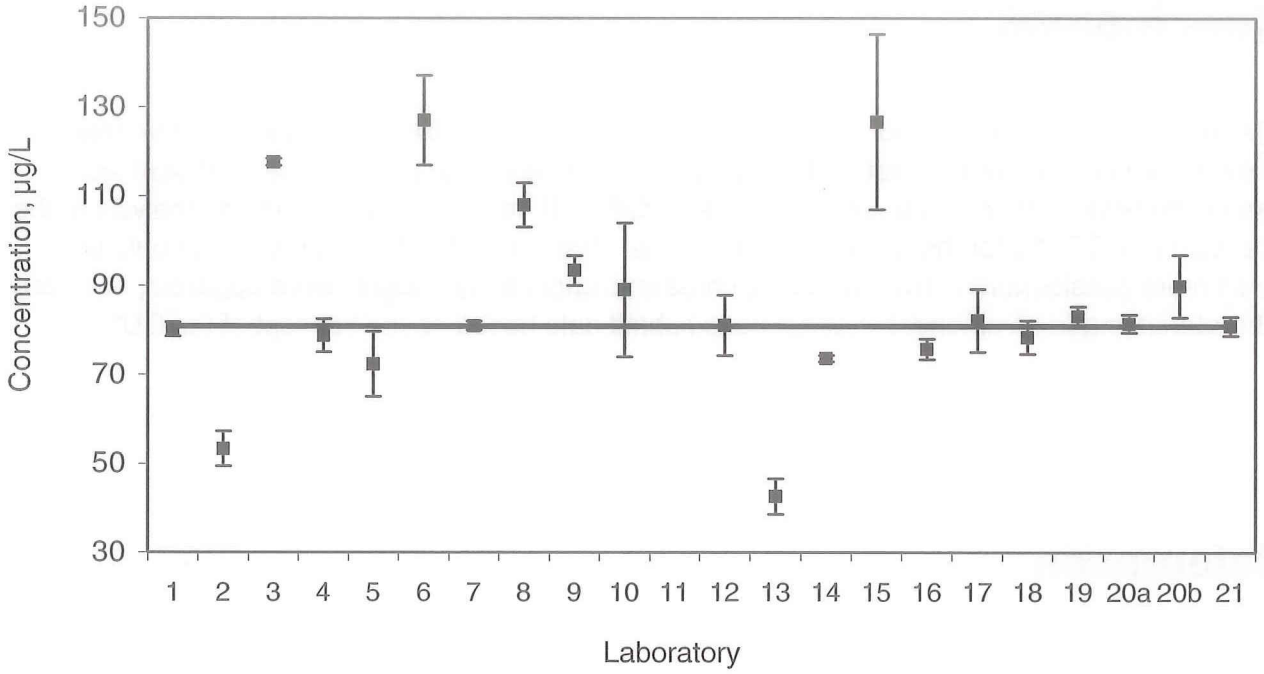
Assigned Value

A value of 10.8 µg/L was assigned to Pb in Sample A based on the ID-SF-ICP-MS results from NRCC and ID-SF-ICP-MS results from PTB.

Overall Summary	
No. of results	19
Mean*	11.1
Median*	10.8
Sample S.D.*	1.6
95% C.I.*	1.0
gravimetric	10.8

* Two results not included.

Sample B



Lab	Reported Value, µg/L	Uncertainty, µg/L	Technique
1	80.10	1.60	ETAAS
2	53.28	3.91	ETAAS
3	117.6	0.74	ETAAS
4	78.7	3.7	ICP-AES
5	72.3	7.3	ETAAS
6	127	10	ICP-AES
7	80.9	1.0	ID-SF-ICP-MS
8	108	5	ETAAS
9	93.3	3.3	ETAAS
10	89	15	FAAS
11			
12	81.0	6.8	ICP-AES
13	42.6	4	AAS
14	73.59	0.712	ICP-AES
15	127	40	FAAS
16	75.6	2.30	ETAAS
17	82.1	7.0	ETAAS
18	78.3	3.8	ICP-AES
19	83.1	2.1	ICP-MS
20a	81.4	2.0	ICP-AES
20b	89.8	7.0	ASV
21	80.8	2.1	ID-ICP-MS

Assigned Value

A value of 80.9 µg/L was assigned to Cr in Sample A based on the ID-SF-ICP-MS results from NRCC and ID-SF-ICP-MS results from PTB.

Overall Summary	
No. of results	21
Mean	85.5
Median	81.0
Sample S.D.	20.7
95% C.I.	10.9
gravimetric	80.9

Conclusions

It is clear from this study that for a few laboratories accuracy is difficult to achieve for the analysis of trace elements in drinking water. Most participants were able to use multiple analytical techniques; however, one might question the use of ICP-AES for some low level metal analysis or the application of ETAAS for the higher concentrations. The concept of "fit for purpose" should be given more consideration. In a few cases, unrealistic uncertainty budgets were apparent, but many laboratories made commendable attempts to submit data based on the concept of the GUM.

References

[1] Guide to the Expression of Uncertainty in Measurement, ISO, Geneva, 1995.

[2] Summary of Guidelines for Canadian Drinking Water Quality (04/02), Health Canada, April 2002.

[3] U.S. Environmental Protection Agency (EPA) National Primary Drinking Water Regulations. URL: http://www.epa.gov/safewater.consumer/2ndstandards.html

Acknowledgements

The authors would like to thank V. Boyko, C. Scriver and L. Yang of NRCC for supplying analytical results for the intercomparison.

CHROMIUM

Sample A
µg/L

Lab	value	U	Repeats					
1	11.37	0.24	11.31	11.28	11.51			
2	9.33	0.74	9.27	9.32	9.27	9.42	9.37	9.42
3	11.73	0.17						
4	<2							
5	9.67	0.48	9.76	9.58				
6	12	6	11.94	11.01	12.19			
7								
8	12.6	1.1	12.2	12.4	12.5	12.8	12.9	12.9
9	13.3	0.3	13.5	13.3	13.2			
10	13.1	2.6	14.1	12.4	12.9			
11								
12	11.3	1.5	10.9	12.2	10.9			
13								
14								
15								
16	12.7	0.848	12.79	12.50				
17	13.1	1.2	13.5	12.4	13.4			
18	14.8	1.1	14.9	14.6	15.3	13.9	15.7	14.1
19	10.5	0.9	10.8	11.2	9.4	11.0	10.6	9.7
20	11.0	1.0						
21	11.2	0.2	11.1	11.1	11.1	11.4	11.1	11.2

Sample B
µg/L

Lab	value	U	Repeats					
1	82.18	2.28	82.94	81.88	81.73			
2	78.52	9.57	78.05	78.33	78.46	80.32	77.46	-
3	101.4	1.78						
4	73.0	2.3	75	73	71			
5	71.9	0.94	74.49	69.25				
6	84	7	82.90	85.70	84.36			
7								
8	95	11	90	89	88	100	102	101
9	88.6	3.8	87.5	90.2	88.2			
10	64.9	6.5	64.8	64.8	65.2			
11								
12	84.2	2.4	82.9	85.2	84.5			
13								
14								
15								
16	89.6	1.65	87.85	91.29				
17	93	12	86	94	98			
18	87.5	3.3	87.7	88.1	88.7	87.0	86.6	86.6
19	75.2	3.0	71.9	79.4	74.3	71.9	79.4	74.3
20	77.4	4.3						
21a	82.7	2.8	82.30	81.30	83.20	82.90	82.30	84.10
21b	84.6	1.2	85.7	83.1	84.0	86.1	85.0	83.7

IRON

Sample A
µg/L

Lab	value	U	Repeats					
1	78.24	3.08	79.68	75.78	79.26			
2	73.60	7.98	74.72	74.19	75.49	73.22	72.52	71.47
3	100.6	2.91						
4	71.0	2.3	69	71	73			
5	51.2	2.4	51.7	50.7				
6	83	11	83.13	81.6	84.39			
7								
8								
9	78.5	19.4	77.7	78.5	79.5			
10	89	22	89	89	90			
11	118.4	0.5						
12								
13								
14	103.99	0.734	110.0	97.9	106.0	105.0	105.0	
15								
16	70.0	10.6	70.0	70.0				
17	106	10	112	96	109			
18	87.1	2.9	87.2	87.5	89.3	84.1	89.4	85.0
19	nd							
20	73.0	4.8						
21	79.5	7.6	80.4	78.4	79.7	79.7	79.3	79.5

Sample B
µg/L

Lab	value	U	Repeats					
1	355.8	7.2	355.4	352.6	359.5			
2	381.85	16.92	385.21	387.12	379.13	381.05	376.75	
3	399.60	3.28						
4	330.0	5.4	335	328	327			
5	229.0	8.2	227.3	229.2				
6	393	11	392.57	392.47	396.63			
7								
8								
9	308	22	315	311	298			
10	405	40	405	405	406			
11	343.9	0.4						
12								
13								
14	377.3	0.938	398.0	399.0	369.0	367.0	385.0	
15								
16	342	11.3	342	341				
17	374	74	369	379	374			
18	391.3	5.8	388.4	394.9	392.9	383.3	400.7	387.4
19								
20	350	10						
21	371.6	9.2	374.2	369.9	372.0	372.9	369.0	371.8

NICKEL

Sample A
µg/L

Lab	value	U	Repeats					
1	19.31	0.52	19.43	19.11	19.38			
2a	19.81	2.14	19.96	19.96	19.96	20.41	19.51	19.05
2b	20.25	1.72	20.57	19.99	16.77	23.94	19.99	19.62
3	20.05	0.78						
4	19.7	0.7	19	20	20			
5	19.4	1.3	19.5	19.3				
6	24	9	24.44	24.39	24.17			
7								
8								
9								
10								
11								
12	21.9	0.6	21.8	22.3	21.7			
13								
14	21.21	0.707	22.1	21.1	21.3	21.3	20.9	
15								
16	22.9	2.11	22.88	22.82				
17	20.0	4.4	19.6	20.3	20.0			
18	28.5	2.1	27.0	30.9	28.5	27.9	29.1	27.7
19	21.1	0.4	20.7	21.2	20.6	21.3	20.8	21.7
20	18.7	1.1						
21a	22.31	0.53	22.77	22.09	22.22	22.37	22.26	22.15
21b	22.5	6.7	24.0	23.9	20.3	23.4	21.1	22.5

Sample B
µg/L

Lab	value	U	Repeats					
1	161.4	5.0	161.5	167.2	155.4			
2a	162.43	14.99	163.59	160.60	162.60	167.58	158.61	161.60
2b	160.89	17.23	162.51	159.48	162.31	159.83	160.33	
3	153.2	2.62						
4	147.0	4.7	151	147	143			
5	152.6	2.8	152.1	153.1				
6	163	8	162.44	163.06	163.39			
7								
8								
9								
10	145	44	140	153	142			
11								
12	159.7	5.0	157.3	159.6	162.2			
13								
14	144.71	0.823	136.0	138.0	148.0	152.0	144.0	
15								
16	176	26.3	177	175				
17	153	57	153	156	153			
18	167.9	5.9	168.7	167.9	171.9	164.7	168.7	165.6
19	159	2	161	160	161	158	155	157
20	146	3						
21a	166.2	4.1	164.9	164.5	167.8	168.2	166.7	165.1
21b	158.4	7.5	158	156.5	161.7	158.6	154.5	161.2

COPPER

Sample A
µg/L

Lab	value	U	Repeats					
1	13.29	0.32	13.59	13.06	13.21			
2	13.62	2.26	13.75	13.76	13.53	14.20	12.84	13.48
3	9.40	0.71						
4	17.7	0.7	18	17	18			
5	13.72	0.92	13.27	14.17				
6	20	5	18.99	20.59	19.4			
7								
8								
9	18.3	4.1	17.4	16.5	20.9			
10	19.7	4.3	19.2	20.2				
11	19.9	0.2						
12	14.8	0.4	15.0	14.7	14.7			
13	14.8	1.64	15.06	14.41	14.86			
14	12.09	0.707	12.9	12.0	12.8	12.2	11.7	
15	13	2	14	12	12	14	12	11
16	10.5	2.49	10.8	10.3				
17	13.4	1.4	14.1	13.4	12.5			
18	22.7	1.0	23.2	23.1	23.5	22.2	22.2	22.1
19	16.7	0.3	16.8	16.7	17.0	16.6	16.3	16.9
20	20.0	1.9						
21a	16.45	0.56	16.33	16.20	16.37	16.44	16.66	16.67
21b	16.5	1.1	16.3	16.9	17.2	16.1	16.8	16.0

Sample B
µg/L

Lab	value	U	Repeats					
1	162.1	2.8	161.6	159.8	164.8			
2	161.52	15.25	161.43	163.36	158.49	161.00	163.33	-
3	171.38	3.061						
4	161.7	2.0	163	162	160			
5	156.4	8.2	161.7	151.2				
6	176	5	176.09	175.00	176.23			
7								
8								
9	149	3	150	149	149			
10	157	15	156	157	160	156	156	
11	178	1						
12	156.6	1.4	155.8	156.8	157.1			
13	126.8	19	118.85	122.60	138.85			
14	128.55	0.800	130.0	131.0	123.3	125.0	129.0	
15	141	5	144	140	141	144	142	137
16	155	21.2	155	155				
17	170	61	168	171	170			
18	172.8	2.9	173.3	174.1	174.2	170.7	172.7	171.7
19	161	3	161	160	161	161	160	160
20	182	22						
21a	163.5	1.6	165.5	163.6	163.8	164.3	163.4	160.6
21b	160.5	1.5	160.7	160.2	160.8	160.4	160.3	160.6

ZINC

Sample A
µg/L

Lab	value	U	Repeats					
1	53.87	0.92	53.47	54.02	54.13			
2	73.06	4.08	72.73	73.63	72.54	72.44	73.95	72.81
3	49.80	1.38						
4	51.3	0.7	52	51	51			
5	36.36	0.11	34.0	38.72				
6	50	6	50.81	49.99	49.30			
7	54.3	1.0						
8	57	11	55	57	56	56	58	57
9	78	9.3	80	76	77			
10	53	13	51	52	55			
11	53.7	0.8						
12	52.8	0.6	52.5	53.1	52.9			
13	26.9	1.9	26.6	26.4	27.7			
14								
15								
16	48.0	9.24	49.0	48.0				
17	48	20	49	49	47			
18	55.8	2.4	56.4	56.8	56.4	54.8	55.3	55.1
19	53.5	0.7	53.8	53.7	53.7	53.9	53.0	53.0
20	47.4	1.9						
21	51.9	0.47	51.7	51.2	52.3	52.4	52.3	51.8

Sample B
µg/L

Lab	value	U	Repeats					
1	1055	24	1052	1050	1062			
2	1151.86	34.02	1150.79	1159.22	1147.42	1155.33	1146.57	-
3	1036	9.21						
4	961.7	35.8	988	969	928			
5	729.39	1.57	687.34	771.43				
6	1130	10	1131.21	1133.72	1125.6			
7	1035	18						
8	1044	16	1036	1052	1044	1037	1050	1044
9	1111	25	1114	1113	1108			
10	1065	127	1060	1055	1080			
11	1038	2						
12	1006	14.6	997.7	1007	1012			
13	797	53	755	757	880			
14								
15								
16	1060	21.2	1050	1060				
17	1088	175	1101	1089	1075			
18	1061.3	24	1064.4	1069.4	1070.7	1050.3	1057.0	1056.0
19	1040	15	1020	1040	1050	1050	1040	1040
20	940	34						
21	1023	23	1013	1012	1024	1037	1026	1028

ARSENIC

Sample A
µg/L

Lab	value	U	Repeats					
1	24.01	0.59	24.44	24.21	23.39			
2	20.66	1.52	20.62	20.42	21.22	21.22	19.82	20.62
3	30.48	0.65						
4	22.3	2.4	24	23	20			
5	68.4	3.9	68.4	68.4				
6								
7								
8	27.8	1.2	27.6	28.0	27.8	27.9	27.7	27.8
9	24.1	1.9	24.6	24.4	23.0			
10	27.9	7.5	29.9	25.9				
11								
12								
13								
14								
15								
16	25.2	0.778	24.56	25.81				
17	23	14	24	22	23			
18	17.4	1.5	17.8	18.0	18.6	16.6	16.7	16.5
19								
20	32.5	0.6						
21	23.7	0.9	24.07	24.45	24.81	23.22	22.39	23.22

Sample B
µg/L

Lab	value	U	Repeats					
1	180.9	5.6	185.37	181.37	175.81			
2	179.02	9.24	181.64	178.42	180.84	175.19		
3	176.2	0.71						
4	168.7	11.8	176	173	157			
5	425.7	23.0	427.4	423.91				
6								
7								
8	206	12	204	208	206	206	204	205
9	201	13	203	194	206			
10	194	25	189	198				
11								
12								
13								
14	154.88	0.722	154.0	156.0	159.0	151.0	154.0	
15								
16	182	2.53	180	183.4				
17	170	70	178	163	170			
18	167.1	2.8	167.9	169.2	173.9	164.2	163.5	163.9
19								
20	317	14						
21	175	6	170	182	184	171	171	171

CADMIUM

Sample A
µg/L

Lab	value	U	Repeats					
1	5.28	0.18	5.20	5.37	5.28			
2	5.27	0.42	5.13	5.28	5.30	5.36	5.34	5.21
3	7.47	0.46						
4	4.87	0.07	4.8	4.9	4.9			
5	4.53	0.20	4.50	4.57				
6	7	7	7.09	7.14	7.15			
7	5.34	0.06						
8	5.6	0.6	5.6	5.7	5.6			
9	6.25	0.36	6.25	6.14	6.37			
10	1.30	0.14	1.27	1.32				
11								
12	5.3	0.2	5.4	5.3	5.2			
13	4.43	0.49	4.34	4.59	4.37			
14	5.10	0.707	5.2	5.2	5.1	5.2	5.4	
15								
16	5.73	0.196	5.762	5.706				
17	3.16	0.43	3.06	3.14	3.27			
18	3.5	0.9	3.6	3.5	3.4	3.6	3.6	3.3
19	5.29	0.07	5.22	5.25	5.24	5.37	5.35	5.31
20a	5.0	0.2						
20b	5.1	0.3						
21	5.48	0.13	5.38	5.46	5.46	5.49	5.58	5.51

Sample B
µg/L

Lab	value	U	Repeats					
1	52.86	1.84	51.93	53.28	53.27			
2	73.44	4.33	73.68	71.75	72.18	71.75	77.73	74.32
3	110.0	2.94						
4	51.7	1.8	53	52	50			
5	46.81	0.50	46.82	46.80				
6	53	7	52.93	52.53	53.13			
7	53.0	0.6						
8	66	9	68.4	71.0	70.0	60.9	64.2	62.5
9	73.9	7.7	73	74	74			
10	53.4	5.3	51.2	53.5	55.6			
11	56.4	0.5						
12	53.7	0.8	53.3	53.6	54.1			
13	43.1	6.2	42.53	43.84	42.86			
14	49.36	0.709	46.9	47.2	47.7	47.8	50.6	
15								
16	55.3	1.52	55.59	55.00				
17	44	14	40	45	47			
18	49.2	3.6	49.3	49.4	49.5	49.0	49.0	48.9
19	52.6	0.7	51.1	51.4	52.2	53.4	53.9	53.6
20a	50.3	2.7						
20b	50.9	3.1						
21a	53.4	1.3	53.3	53.2	54.1	52.9	54.2	52.7
21b	57.2	4.8	57.3	57.7	57.2	57.4	56.4	57.6

BARIUM

Sample A

µg/L

Lab	value	U	Repeats					
1								
2	146.53	10.34	145.83	149.53	145.11	146.74	145.46	146.55
3	177.2	0.93						
4	150.7	8.7	155	155	142			
5	221.8	3.99	208.0	235.64				
6	153	12	153.47	153.76	153.16			
7	154.4	1.5						
8								
9								
10								
11								
12								
13								
14	134.04	0.708	142.0	138.0	133.0	133.0	133.1	
15								
16								
17								
18	156.9	2.5	157.4	157.5	158.0	155.3	157.5	155.7
19	155	2	154	155	154	156	154	155
20								
21	157.9	6.8	158.8	157.4	157.9	158.8	156.7	158.0

Sample B

µg/L

Lab	value	U	Repeats					
1								
2	1465.12	43.22	1433.28	1503.32	1473.28	1470.59	1445.12	
3	1443	4.17						
4	1258.0	23.5	1277	1259	1238			
5	1806.2	2.81	1825.14	1781.25				
6	1456	20	1452.27	1463.6	1451.74			
7	1412	14						
8								
9								
10	1192	417	1148	1113	1315			
11								
12								
13								
14								
15								
16								
17	1294	300	1294	1229	1358			
18	1439.8	20	1442.6	1452.2	1450.0	1426.2	1434.3	1433.2
19	1395	20	1390	1400	1390	1400	1400	1390
20								
21	1458	13	1465	1452	1462	1458	1451	1459

LEAD

Sample A
µg/L

Lab	value	U	Repeats					
1	10.37	0.22	10.65	10.27	10.20			
2	12.32	0.77	11.39	12.98	12.98	13.78	10.60	12.19
3	15.26	0.74						
4	<15							
5	8.59	0.55	8.68	8.50				
6	56	10	57.49	56.68	55.34			
7	10.82	0.13						
8	11.8	0.5	11.8	11.7	11.8	11.4	12.2	11.9
9	12.3	0.9	12.7	12.2	11.8			
10	9.5	3.8	9.2	10.4	8.8			
11								
12	11.5	5.4	8.9	11.3	14.3			
13	9.57	2.63	8.65	9.52	10.54			
14								
15	78	17	100	60	90	70	90	60
16	9.88	1.58	9.553	10.20				
17	10.5	1.4	10.6	10.5	10.5			
18	9.4	1.8	9.0	12.1	10.5	8.9	8.1	7.7
19	11.2	0.3	11.1	11.2	11.7	11.0	11.0	11.2
20a	12.1	0.8						
20b	12.2	0.4						
21	10.75	0.028	10.72	10.74	10.76	10.76	10.79	10.72

Sample B
µg/L

Lab	value	U	Repeats					
1	80.10	1.60	79.98	81.45	78.85			
2	53.28	3.91	52.81	52.81	52.25	53.65	53.93	54.21
3	117.6	0.74						
4	78.7	3.7	80	81	75			
5	72.3	7.3	75.8	69.8				
6	127	10	125.92	124.66	129.59			
7	80.9	1.0						
8	108	5	107	113	110	110	104	107
9	93.3	3.3	94.21	92.80	92.93			
10	89	15	89	89	89			
11								
12	81.0	6.8	77.1	83.0	82.9			
13	42.6	4	41.04	43.82	42.96			
14	73.59	0.712	72.4	71.4	74.6	73.2	75.5	
15	127	20	100	160	120	130	130	120
16	75.6	2.30	76.15	75.08				
17	82.1	7.0	81.2	80.9	84.3			
18	78.3	3.8	79.0	78.0	77.5	78.1	78.4	78.9
19	83.1	2.1	81.4	86.0	82.9	82.3	82.3	83.5
20a	81.4	2.0						
20b	89.8	7.0						
21	80.8	2.1	81.08	80.59	81.00	80.73	80.73	80.42

Appendix B

Secondary Elements

Sample A

Ca	mg/L	43.14	43.43	43.07	43.16	43	43.18		ICP-AES
K	µg/L	1498.52	1489.97	1514.26	1517.79	1483.76	1407.65		ICP-AES
Mg	mg/L	9.8	9.66	9.66	9.75	9.61	9.73		ICP-AES
Na	mg/L	3.87	3.97	3.85	3.85	3.85	3.87		ICP-AES
Sr	µg/L	376.25	383.72	375.76	376.62	376	378.3		ICP-AES

Sample B

Ca	mg/L	42.71	43.83	43.22	42.85	42.11		ICP-AES
K	µg/L	1462.36	1497.51	1450.42	1502.42	1436.01		ICP-AES
Mg	mg/L	9.6	9.5	9.72	9.59	9.67		ICP-AES
Na	mg/L	3.73	3.96	3.85	3.84	3.79		ICP-AES
Sr	µg/L	366.6	382.33	373.71	369.62	362.67		ICP-AES

The results listed ont his page were submitted by Laboratory #2