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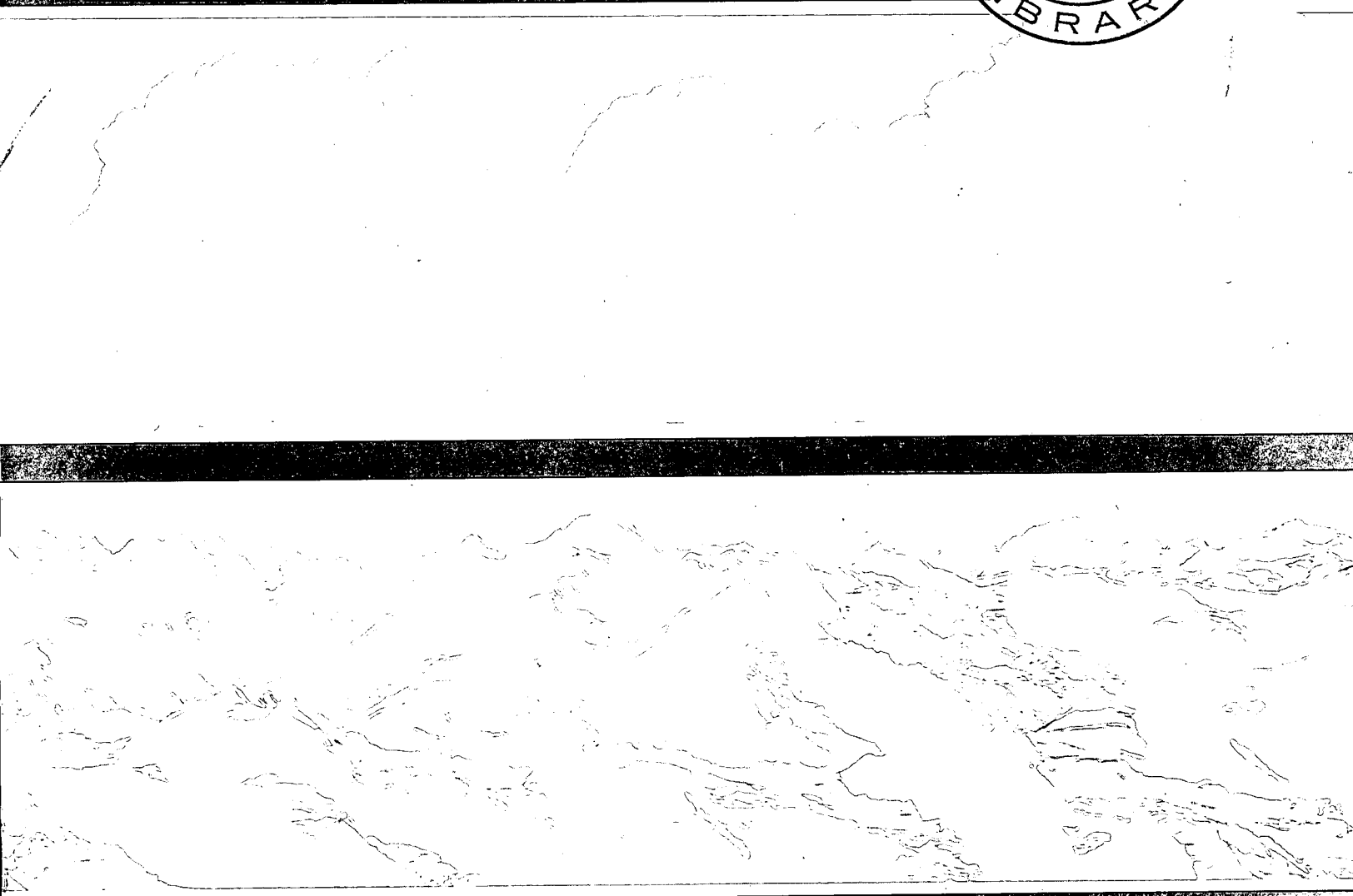
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Interlaboratory Quality Control Studies Nos. 12 and 13

Aluminum, Cadmium, Chromium,
Cobalt, Copper, Lead, Iron,
Manganese, Nickel and Zinc



J. M. Carron and K. I. Aspila



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REPORT SERIES NO. 44
(Résumé en français)

**INLAND WATERS DIRECTORATE, ONTARIO REGION,
WATER QUALITY BRANCH,
BURLINGTON, ONTARIO, 1976.**



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Abstract

A report on the results of interlaboratory quality control studies No. 12 and No. 13 is given. The studies involve the analysis of aluminum, cadmium, chromium, cobalt, copper, lead, iron, manganese, nickel and zinc in natural and synthetic water samples. All metals were at concentrations similar to those found in natural waters (1-50 μg metal/l).

Twelve water samples were analyzed for this combined report, including natural, fortified natural and synthetic samples. Combination of such samples provided percent recovery of trace metals from 1) synthetic standards, 2) samples fortified by participants and 3) samples fortified, but unknown, to participants.

Twenty-six laboratories provided data for this combined study. Five different methodologies were used, and results for each have been summarized and in some cases, discussed. Mean values, standard deviations and percent recoveries are provided for all samples and for each method.

Much of the data provided by participants were indicated as less than a designated value. Treatment of such data for computational purposes is discussed. Overall, the data provided by participants normally analyzing natural lake and river waters at low level metal concentrations (0.1-50 $\mu\text{g}/\text{l}$) were quite acceptable.

Résumé

Le présent rapport traite des résultats des études interlaboratoires n^{os} 12 et 13 du contrôle de la qualité, relativement à l'analyse, dans des échantillons naturels et synthétiques d'eau, des éléments suivants: aluminium, cadmium, chrome, cobalt, cuivre, plomb, fer, manganèse, nickel et zinc. Tous les métaux avaient des concentrations semblables à celles que l'on observe dans les eaux naturelles (de 1 à 50 $\mu\text{g}/\text{l}$).

Ce rapport conjoint a donné lieu à l'analyse de douze échantillons naturels, fortifiés et synthétiques. La combinaison de ces échantillons a permis de calculer le pourcentage de récupération des métaux à l'état de trace provenant (1) de solutions étalons synthétiques, (2) d'échantillons fortifiés par les participants et (3) d'échantillons fortifiés à l'insu des participants.

En tout, vingt-six laboratoires ont fourni des données dans le cadre de l'étude conjointe. Ils ont utilisé cinq méthodes, et pour chacune d'entre elles, on a résumé et parfois même discuté des résultats dans le présent rapport. Pour tous les échantillons et pour chaque méthode, on a calculé les valeurs moyennes, les écarts types et les pourcentages de récupération.

On a indiqué la majorité des données fournies par les participants comme étant inférieures à une valeur établie. Le rapport aborde aussi la question du traitement informatique des données. Dans l'ensemble, on a jugé très satisfaisantes les données présentées par les participants et touchant à l'analyse des eaux naturelles des lacs et des cours d'eau, à des concentrations normalement faibles en métaux (de 0.1 à 50 $\mu\text{g}/\text{l}$).

List of Symbols

METHODS OF ANALYSIS

- E = solvent extraction followed by flame atomic absorption spectrophotometry (*Analytical Methods Manual*, 1974). Some participants may have differed in their complexing agent or organic solvent
- F = non-flame atomic absorption analysis; this method may or may not have been preceded by preconcentration by solvent extraction
- C = analysis by flame atomic absorption spectrophotometry, after preconcentration by evaporation
- D = direct flame atomic absorption spectrophotometric analysis of water samples (no preconcentration step used)
- Col. = colorimetric analysis
- = method not specified

STATISTICAL ANALYSIS

- n = number of participants included for calculation of mean value
- \bar{x} = average (or mean) value ($\bar{x} = \sum x_i/n$), mg/l
- σ = standard deviation (S.D.), $\sigma = \sqrt{\frac{\sum(\bar{x} - x_i)^2}{(n-1)}}$, mg/l
- C.V. = coefficient of variation, C.V. = $(\sigma / \bar{x}) (100) \%$
- R = an outlier [using the method of Grubbs (1969)]
- < = a result that is less than a specified concentration
- ND = no data

Interlaboratory Quality Control Studies Nos. 12 and 13

Aluminum, Cadmium, Chromium, Cobalt, Copper, Lead, Iron, Manganese, Nickel and Zinc

INTRODUCTION

This is a summary report on the results obtained from trace metal data generated from interlaboratory quality control studies Nos. 12 and 13. Both of these round robins included natural waters and synthetic samples containing metal concentrations similar to those found in the environment. By carefully designing the program it was possible not only to monitor the variability of data generated by different methods but also to estimate within-lab precision and obtain the percent recovery from natural and synthetic samples. Twenty-six laboratories participated.

The metals chosen for study No. 12 were cadmium, chromium, lead, manganese and nickel. For study No. 13 the metals were copper, lead, iron and zinc. Two less commonly determined metals (cobalt and aluminum) were also added to study No. 13. All metals were chosen because they are both environmentally significant and commonly analyzed by most of the participants.

EXPERIMENTAL DESIGN

Sample Collection and Preparation

Samples for both studies included natural waters (spiked and unspiked) and synthetic metal standards. All natural samples were collected in 50-litre carboys and were filtered through glass wool. The bulk samples were then acidified to 0.2% (v/v) using an appropriate volume of concentrated nitric acid. For those natural samples that were fortified with additional metal, an appropriate quantity of suitable Fisher Certified atomic absorption standards was added to the bulk 50-litre carboys. A similar procedure was used for preparing the synthetic standards except that the water used was glass-distilled.

All subsamples were distributed in new, one-litre, linear, polyethylene, screw-cap bottles. These bottles were scrupulously cleaned by serial washing with Chromerge[®], hot tap water and then distilled water. All bottles were allowed to soak several weeks in 0.2% (v/v) nitric acid solution prior to a final rinse with an aliquot of sample. Before distribution, the test sample was added sequentially to each bottle to fill

the total number of bottles one-third full. The one-third filling was continued until all bottles were full (1 litre). The first and last bottles to be filled were set aside and checked for uniformity.

A storage check on the metal concentrations used in this study was made for various samples and synthetic standards. The results indicated no significant variation in the concentrations when these metals are preserved in 0.2% (v/v) nitric acid and monitored over a three-month interval.

Study No. 12

All references to samples in study No. 12 are suffixed by the letter *A* (e.g., 1A, 2A, etc.). Samples in study No. 13 are identified by the letter *B*.

The types of samples distributed for this study are tabulated below:

- 1A — synthetic sample; trace metal standard,
- 2A — Lake Ontario water,
- 3A — groundwater; obtained from a natural spring located near Burlington, Ontario,
- 4A — stream water; obtained from a creek near Burlington, Ontario, and
- 5A — Lake Ontario water; same sample as shown above (2A) but fortified with various metals.

Samples 1A and 5A were fortified to metal concentrations listed in the following table. The spike for sample 5A augments the natural background level.

Sample	Level of Fortification (mg/l)				
	Cd	Cr	Pb	Mn	Ni
1A	.0047	.0041*	.0000	.0490	.0000
5A	.0030	.0150†	.0070	.0090	.0006

* Chromous chloride (Cr⁺³)

† Potassium dichromate (Cr⁺⁶)

Samples 5A and 2A, as indicated in the previous list, are identical water samples except 5A was fortified with additional trace metals. The difference in results between

5A and 2A is a measure of the percent recovery. This fact was unknown to the participants, and in the following text, it is referred to as the unknown spike (or hidden recovery). A similar recovery was designed by measuring the difference in results obtained for sample 7A and sample 6A. Here the participants were instructed to provide a natural water of their own choice (sample 6A) and to fortify it with the concentrate that was provided. The recovery obtained from the difference between 7A and 6A is referred to as the known spike recovery. Unknown to the participants, the concentrate used for fortifying sample 6A was identical with that used for sample 5A so that the two recoveries could be correlated to estimate their in-house precision.

The groundwater sample (3A) was chosen because it had a relatively high total salt content and is a type of water frequently analyzed by participants.

Study No. 13

The samples distributed and designed for this study were similar to study No. 12. The types of samples provided are the following:

- 1B – lake water (Lake St. Clair, Ontario); filtered through 0.45 μ m cellulose acetate and then fortified with various metals,
- 2B – lake water (Georgian Bay, Ontario),
- 3B – rain water (fortified with various metals),
- 4B – synthetic standard,
- 5B – lake water (lac Rémigny, Quebec); fortified with various metals,
- 6B – synthetic standard, and
- 7B – river water (Magog, Quebec).

As noted in the previous section, all natural samples were filtered through glass wool to remove obvious debris. Sample 1B was an exception and required additional filtration to reduce turbidity that would otherwise have led to poor homogeneity.

The concentrations to which some of these samples were fortified over and above the background level are outlined in the following table:

Sample	Level of Fortification (mg/l)					
	Zn	Co	Cu	Fe	Pb	Al
1B	--	.0020	--	--	.0050	.020
3B	--	.0010	--	--	.0070	.060
4B	.0122	--	.0078	.0104	--	--
5B	--	.0030	--	--	.0060	--
6B	--	.0010	--	--	.0070	.060

Note: -- means none of this metal was added

This design was prepared mainly to determine the variability of data generated from laboratories analyzing

trace metals in natural samples. Except for the synthetic samples 4B and 6B, this level of fortification augments the natural background metal concentrations. Samples 2B and 7B were not fortified. The combination of samples 4B and 6B provides a means of determining blank or zero metal concentrations for distilled water. The pair of samples 5B and 6B was designed to determine if laboratories could discriminate the presence of lead in two samples that are expected to be .001 mg/l different in concentration. The synthetic standards were prepared to monitor the relative error or percent recovery from a sample of known concentration.

DATA EVALUATION

Results obtained from the laboratories were first reviewed for outliers, with data being rejected by the method of Grubbs (1969). Values for outliers are indicated by the letter *R*. All data received for the evaluation of studies No. 12 and No. 13 are given in Appendices A and B, respectively.

Because the samples provided for analysis were a combination of unpolluted fresh waters and synthetic standards at low metal concentrations, many of the participants were unable to detect the metals. Consequently, much of the data were given as a "less than" value which can lead to a difficult evaluation of overall data. Yet when the data are viewed in context with 1) the method of analysis (e.g., extraction versus direct analysis), 2) the results for synthetic standards and 3) the overall results from usually reliable participants (those obtaining good recoveries), the decision to ignore "less than" data can be partially substantiated in calculating mean values and estimating precision.

The following options were available for treatment of overall data:

- a) to use all data, including "less than" values, at face value,
- b) to call the "less than" value zero,
- c) to reject and ignore all "less than" values, or
- d) to include some "less than" values as zero values for those laboratories that have suitable methodology and have demonstrated adequate recoveries.

Option *a* led to a high bias and option *b*, to a low bias. Choice *d* was rather difficult to handle and may have been unfair to participants, since inadequate information was made available on the methodology. The decision to use option *c* was a reasonable compromise but is accepted as possibly giving a high bias because laboratories providing accurate low data would have their values rejected.

Statistical summaries are given in the text and in Appendix A. All of the raw data are presented in Appendices A and B.

Recovery of metal from spiked samples as well as synthetic standards was determined three different ways. The first and simplest way was from standards containing a known (i.e., true) concentration of metal, with recoveries being measured by comparing the true values with calculated values. Application of synthetic standards to trace metal recovery has accepted limitations in interpolating to natural samples because of the differing speciation of metals and natural complexing capacities of real samples. An alternative method was therefore designed and has already been described in the section on "Experimental Design." The known recovery (in study No. 12) used the difference between results for samples 7A and 6A. This difference relates to the concentrate provided and, if analyzed as instructed, was of unknown concentration to participants. A more realistic and accurate recovery was the hidden spike. This was accomplished by fortifying sample 2A and calling it sample 5A. In fact, this spiking was identical with the known spike (7A-6A) and provided a measure of the within-lab precision. This pair of recoveries (5A-2A versus 7A-6A), however, is subject to criticism as the samples chosen by participants (e.g., sample 6A) would have been more difficult to analyze unspiked.

The evaluation of study No. 13 was not quite as involved, since hidden or known spiked natural samples were not included to calculate percent recoveries. Outliers were rejected by the method of Grubbs. Data generated by those laboratories using insensitive methods were not considered for evaluating mean values and precision. The evaluation centred mainly on determining variability of reporting as well as determining the participants' ability to detect the various metals, especially if different samples contained only slight concentration differences.

RESULTS AND DISCUSSION

Both studies proved quite successful in design in spite of some limitations brought about by the participants reporting data as "less than" a certain value. The raw data provided by participants for studies No. 12 and No. 13 are given in Appendices A and B. Beneath each table in Appendix A some pertinent statistics are listed which provide a comparison of the methodologies employed. A list of symbols used in the Tables is given on page vii. Relevant comments regarding the results for each sample follow.

STUDY NO. 12

Cadmium

Most participants were unable to detect cadmium in the natural samples provided for analysis. Except for two outliers, the synthetic sample 1A was handled very well (102% recovery with 4% variation) by participants. For all

samples the overall average variation was 26% at a mean of .0053 mg/l (Appendix A, Table A-1).

Recovery data are listed in Table 1 and have been calculated from values provided by participants who were able to obtain positive numbers for all five pertinent samples.

Table 1. Cadmium Recovery Data (mg/l)

Laboratory number	Method	Synthetic sample 1A	Difference between paired samples	
			(5A-2A)*	(7A-6A)†
1202	E	.005	.003	.004
1203	E	.0046	.0025	.0028
1207	F	.0045	.002	.0025
1211	-	.005	.002	.0037
1218	E	.005	.003	.004
1219	-	.005	.002	.0025
<i>From table above</i>				
Designated value		.0047	.003	.003
n		6	6	6
\bar{x}		.0049	.0024	.00325
S.D.		.0002	.0005	.0007
C.V. (%)		4	21	22
% Recovery		102	80	108
<i>From Appendix ‡</i>				
Designated value		.0047	.003	.003
n		21	10	7
\bar{x}		.0053	.0020	.0032
S.D.		.0014	.0011	.0007
C.V. (%)		26	55	22
% Recovery		113	67	106

* unknown to the participants, sample 5A was fortified

† sample 6A was fortified by the participants using a concentrate that was provided

‡ data obtained from Appendix A, Table A-1, using all positive data for each sample and rejecting all "less than" data

It is interesting to note that the unknown spike (5A-2A) was not handled as well as the known spike (7A) which was supplied as a 100-fold concentrate. This difference in recovery may relate to variability of water samples used (e.g., sample 6A). Precision on recovery (7A-6A versus 5A-2A), however, was quite similar.

The synthetic sample 1A was analyzed with better precision than were the natural samples 2A to 5A (Appendix A, Table A-1). Although this undoubtedly relates to precision decreasing with reduced concentration, it does suggest that natural samples are more realistic in monitoring variation in interlaboratory results.

On relating methods used to obtain recovery data (Table 1) as well as noting variations in the precision of the different methods (Appendix A, Table A-1), one may suggest the extraction method is more accurate and precise.

Such a conclusion may be deceiving, since the concentration method had much of its data arbitrarily rejected (data expressed as "less than"). In essence, no one method is apparently superior.

It is encouraging to note that the non-flame technique is now being applied in trace metal analysis, especially since it has the potential of lowering detection limits. Unfortunately for this study insufficient data were available to evaluate its relative merits.

Chromium

The ability of the participants to analyze chromium at .015 mg/l concentrations was excellent. Recovery data for the unknown and known spikes are given in Table 2.

Table 2. Chromium Recovery Data (mg/l)

Laboratory number	Method	Synthetic sample 1A	Difference between paired samples	
			(5A-2A)	(7A-6A)
1202	E	.002	.018	.0146
1203	E	.0036	.0235	.0105
1207	F	.005	.020	.015
1208	-	<.005	.000	.014
1218	Col.	.005	.015	.025
1219	-	.004	.016	.012
<i>From table above</i>				
Designed value		.0041	.0150	.0150
n		6	6	6
\bar{x}		.0041	.0154	.0152
S.D.		.0012	.0081	.0051
C.V. (%)		29	52	34
% Recovery		100	102	101
<i>From Appendix A</i>				
Designed value		.0041	.0150	.0150
n		15	14	10
\bar{x}		.0051	.0159	.0150
S.D.		.0029	.0087	.0077
C.V. (%)		57	55	51
% Recovery		124	106	100

Both fortified samples 7A and 5A were analyzed equally well with almost 100% recovery. The precision was quite similar for all samples and for all methods. When the individual samples are compared within the limits of plus and minus one standard deviation (Appendix A, Table A-2), it is evident that all samples were equally well done.

The experimental design included two different oxidation states for chromium (Cr⁺³ for sample 1A and Cr⁺⁶ for sample 5A). The results for the extraction method are quite comparable indicating the participants used the necessary oxidation step needed prior to extraction and analysis of Cr⁺³.

Manganese

The synthetic sample 1A was analyzed fairly accurately (92% recovery) and precisely (20% variation) at the .049 mg/l level. Relating results for the synthetic sample to natural samples may be unjustified, since the concentration of manganese in sample 1A was slightly higher than in the natural samples. Recovery data on spiked samples (6A and 2A) are given in Table 3.

Table 3. Manganese Recovery Data (mg/l)

Laboratory number	Method	Synthetic sample 1A	Difference between paired samples	
			(5A-2A)	(7A-6A)
1202	D	.060	.020	.010
1203	E	.045	.0167	.0066
1205	E	.041	.017	.008
1207	F	.048	.015	.000
1209	E	.050	.014	.010
1210	E	.056	.014	.008
1213	E	.040	.016	.009
1215	C	.042	.014	.003
1219	-	.049	.015	.009
1220	C	.053	.015	.009
1223	E	.0508	.0163	.0123
1225	C	.048	.014	.006
<i>From table above</i>				
Designed value		.049	.0090	.0090
n		12	12	12
\bar{x}		.0486	.0156	.0076
S.D.		.006	.0018	.0033
C.V. (%)		12	12	43
% Recovery		99	173	85
<i>From Appendix A</i>				
Designed value		.049	.0090	.0090
n		20	13	14
\bar{x}		.0449	.0142	.0076
S.D.		.009	.0038	.0032
C.V. (%)		20	27	42
% Recovery		92	158	84

The unknown spike (sample 5A) could not be used for recovery of manganese because sample 5A was inadvertently contaminated by the use of a stainless steel propeller in sample preparation. In spite of the contamination of sample 5A, the recovery for the known spike (7A-6A) does indicate adequate accuracy at .009 mg/l levels. Twelve laboratories reported an average recovery of 84% with a coefficient of variation of 42%.

Regarding overall data (Appendix A), it is of interest to note that the average value for all methods did not exceed the true value. This might suggest a slight bias on the low side especially in view of a lower recovery indicated in Table 3.

Direct flame analysis of water samples tended to be less precise (Appendix A), the groundwater sample being notably poor. This may relate to the detection limit capability of the direct method. One participant, however, was successful (Table 3) in recovering the known spike (7A).

Nickel

The synthetic sample 1A was prepared as a blank, containing no nickel. Using results for this sample (Appendix A), an estimate of an overall blank reading could be .003 mg/l. Yet employing data from the more capable participants (e.g., those laboratories providing acceptable data for the paired samples, the standard, and the zero blank), it appears that less than .001 mg Ni/l was indeed present. The known spike added to sample 6A was definitely below the detection limit of all but a few participants. About five or six laboratories came close to recovering the .0006 mg/l spike.

Table 4. Nickel Recovery Data (mg/l)

Laboratory number	Method	Synthetic sample 1A	Difference between paired samples	
			(5A-2A)	(7A-6A)
1201	E	.004	.134	.0030
1202	E	.015 R	.094	.0020
1203	E	<.0005	.117	.0010
1208	C	<.005	.085	.0050
1209	E	.004	.098	.0000
1210	E	<.001	.118	.000
1218	E	.001	.126	.0030
1219	-	.001	.104	.0010
1220	E	.002	.120	.0010
1221	C	<.001	.121	.0010
1223	E	.0010	.114	.00053
1224	E	.001	.117	.0000
1225	C	<.005	.101	.005
1226	C	<.002	.117	.010
<i>From table above</i>				
Designed value		.0000	.0006	.0006
n		13	14	14
\bar{x}		.0022	.112	.0023
S.D.		.0017	.0135	.0028
C.V. (%)		77	12	122
% Recovery		ND	ND	390
<i>From Appendix A</i>				
Designed value		.0000	.0006	.0006
n		19	20	19
\bar{x}		.0027	.1111	.0017
S.D.		.0019	.0129	.0012
C.V. (%)		70	11.6	71
% Recovery		ND	ND	283

Recovery data for nickel are listed in Table 4. Recovery of nickel using samples 5A and 2A was impossible to calculate, since sample 5A was inadvertently contaminated (see section on "Manganese").

Precision on all samples (except 5A) was generally poor and relates to the very low levels of nickel in solution (below detection limit). Sample 5A, however, was fairly well analyzed (10% coefficient of variation), but unfortunately had a nickel concentration not representative of a natural sample.

Lead

Overall results for the synthetic sample 1A which contained no added lead indicated a blank level of approximately .003 mg/l. Percent recoveries for known and unknown spikes are summarized in Table 5.

Table 5. Lead Recovery Data (mg/l)

Laboratory number	Method	Synthetic sample 1A	Difference between paired samples	
			(5A-2A)	(7A-6A)
1201	E	.003	.005	.007
1202	E	<.002	.0075	.005
1203	E	.001	.006	.007
1207	F	.000	.002	.002
1208	C	<.005	.000	.008
1209	E	.002	.006	.005
1213	E	<.001	.005	.006
1215	C	<.002	.010	.003
1219	-	.007	.005	.005
1220	E	.003	.0085	.0085
1225	C	<.005	.007	.012
<i>From table above</i>				
Designed Value		.000	.007	.007
n		6	11	11
\bar{x}		.0027	.0056	.0062
S.D.		.0024	.0028	.0028
C.V. (%)		89	50	45
% Recovery		ND	80	89
<i>From Appendix A</i>				
Designed Value		.000	.007	.007
n		10	10	15
\bar{x}		.003	.0062	.006
S.D.		.0021	.0022	.0026
C.V. (%)		ND	36	43
% Recovery		ND	89	86

The percent recoveries obtained from paired data averaged 80% to 90%. For participants providing both recoveries (Table 5), the extraction method gave slightly more accurate results.

Lower mean values, however, were noted for laboratories using the extraction method for all natural samples. This may be caused either by a low extractability of naturally complexed lead or by the other methods being partially prone to anomalous absorbance values if background correction was not used in the atomic absorption analysis. The mean values, however, are only slightly different when the standard deviations are included. Insufficient details were provided by the participants to draw any firm conclusion.

STUDY NO. 13

Aluminum

Not many participants provided data for this metal. The synthetic sample 6B was handled quite well, with 90% recovery of the added spike (.060 mg/l). The coefficient of variation at this level was 34%.

The blank synthetic sample 4B with no added aluminum was reported to contain .01 mg/l on an overall basis. Most participants, however, gave "less than" values for this blank. Natural samples, with the exception of 1B, were reported in a similar way (<.02) suggesting that many participants would have difficulties with natural samples at these concentrations.

Sample 1B containing a high level of aluminum (.65 mg/l) was analyzed with the same level of precision as the synthetic sample 6B even though the concentration in the natural sample was over ten times greater (Table 6). This suggests that variability in data should be monitored with natural rather than synthetic samples. Synthetic samples (standards) are normally analyzed more precisely as opposed to natural samples containing metals at the same concentrations.

Cobalt

At first glance this metal may appear to have been poorly analyzed, but on close scrutiny of available data it appears that most participants were able to detect 0 mg/l, .001 mg/l, .002 mg/l and .003 mg/l levels of fortification (Table 7).

With respect to the blank synthetic sample (4B), ten laboratories reported less than .001 mg/l, one laboratory, .001 mg/l, and four laboratories, whole number data. The average cobalt value for sample 4B was less than .002 mg/l. This evidence suggests the blank value was distinctly less than .001 mg/l. Similarly, results for sample 2B and 7B would also appear to contain less than .001 mg/l.

The two spiked samples (3B and 6B), where 6B was a synthetic standard, indicated positive data by most participants. Although not definitive, the lack of less than values

Table 6. Comparison of Aluminum Results (mg/l)

Method	Parameter	Sample						
		1B	2B	3B	4B	5B	6B	7B
Overall	n	15	9	15	4	16	13	10
	\bar{x}	.654	.019	.084	.0125	.143	.054	.021
	S.D.	.161	.027	.016	.0087	.059	.019	.017
	C.V. (%)	25	147	19	70	41	34	79
	% Recovery				ND		90	
E	n	6	3	6	1	6	4	4
	\bar{x}	.620	.012	.083	ND	.105	.044	.026
	S.D.	.147	.007	.014	ND	.012	.020	.022
	C.V. (%)	24	62	17	ND	12	45	82
F	n	3	3	3	2	3	3	3
	\bar{x}	.677	.006	.078	.0100	.230	.049	.018
	S.D.	.341	.004	.024	.0141	.053	.018	.013
	C.V. (%)	51	70	31	141	23	37	73
C	n	3	2	3	1	3	3	2
	\bar{x}	.708	.053	.093	.0150	.160	.069	.027
	S.D.	.014	.053	.016	ND	.056	.001	.005
	C.V. (%)	20	100	17	ND	35	17	19
D	n	2	ND	2	ND	2	2	ND
	\bar{x}	.665		.090		.145	.050	
	S.D.	.021		.014		.050	.028	
	C.V. (%)	3		16		34	57	

Table 7. Comparison of Cobalt Results (mg/l)

Method	Parameter	Sample						
		1B	2B	3B	4B	5B	6B	7B
Overall	n	15	4	7	4	15	12	3
	\bar{x}	.0035	.0018	.0016	.0018	.003	.0018	.001
	S.D.	.0012	.0017	.001	.0012	.0013	.0009	.001
	C.V. (%)	34	95	63	67	44	50	100
	% Recovery				ND		180	
E	n	11	1	5	2	11	9	2
	\bar{x}	.0035	.000	.0015	.0010	.0028	.0016	.0014
	S.D.	.0013	ND	.0010	ND	.0012	.0009	.0010
	C.V. (%)	37	ND	67	ND	43	56	136
	% Recovery				ND		160	

Table 8. Comparison of Copper Results (mg/l)

Method	Parameter	Sample						
		1B	2B	3B	4B	5B	6B	7B
Overall	n	22	15	14	20	20	6	12
	\bar{x}	.0664	.0031	.0033	.0073	.0088	.0005	.0016
	S.D.	.0096	.0007	.0008	.0019	.0012	.0005	.0006
	C.V. (%)	14	23	24	26	14	100	38
	% Recovery				94		ND	
E	n	11	10	10	11	11	ND	8
	\bar{x}	.0694	.0031	.0032	.0075	.0084		.0014
	S.D.	.0117	.0003	.0003	.0014	.0008		.0004
	C.V. (%)	17	10	9	19	10		29
	% Recovery				96		ND	
F	n	3	3	3	3	3	ND	3
	\bar{x}	.0733	.0027	.003	.0073	.0087		.0017
	S.D.	.0192	.0006	.000	.0006	.0006		.0006
	C.V. (%)	26	22	0	8	7		35
	% Recovery				94		ND	
C	n	5	2	3	4	4	ND	ND
	\bar{x}	.0680	.0035	.0043	.0075	.0095		
	S.D.	.0037	.0021	.0015	.0017	.0021		
	C.V. (%)	5	60	35	23	22		
	% Recovery				96		ND	
D	n	2	ND	ND	ND	ND	ND	ND
	\bar{x}	.068						
	S.D.	.004						
	C.V. (%)	5						

in the raw data suggests that participants were able to see .001 mg/l Co.

Detection of the .002 mg/l and .003 mg/l spikes in natural samples 1B and 5B was more precise, with positive readings in most cases. The average values suggest that although the sample variation was high, the .002 mg/l and .003 mg/l levels of Co were all that were present.

Two thirds of the laboratories reporting on this metal used solvent extraction. Cobalt is not frequently encountered in natural water samples at levels equal to or higher than those examined in this study, which is probably why the majority used a similar method. The monitoring of environmental background levels of Co would require the same degree of sophistication as is required for Pb and Ni.

Copper

This metal was analyzed exceptionally well by all participants. For the unfortified blank (sample 6B), ten participants indicated less than .001 mg/l of copper, two had .000 mg/l and one had .0005 mg/l (Table 8).

The synthetic water sample (4B) with .0078 mg/l copper had an overall mean recovery of 94% with a coefficient of variation of 26%. The flameless method gave even better precision (8% variation) for this artificial sample.

Natural samples (1B, 2B, 3B, 5B and 7B) were analyzed equally well by all methods. Variations in average values for all the samples occur only with respect to the precision, not the accuracy. It is of interest to note that at a high concentration of copper (.066 mg/l), the overall precision was not significantly different from that at a much lower level (e.g., 14% variation at both .0664 mg/l and .0088 mg/l levels).

Iron

In keeping with evidence provided by laboratories routinely monitoring low-level iron concentrations, this study confirms that blank iron readings (possibly owing to contamination) are difficult to maintain at less than about .004 mg/l. This is evident from sample 6B, which was an iron blank. Eight participants (with positive data) averaged .0044 mg/l of iron. This value is biased high because of two

Table 9. Comparison of Iron Results (mg/l)

Method	Parameter	Sample						
		1B	2B	3B	4B	5B	6B	7B
Overall	n	25	19	20	19	24	8	21
	\bar{x}	1.1424	.0147	.0153	.0135	.1390	.0044	.0290
	S.D.	.1569	.0066	.0049	.0039	.0417	.0046	.0088
	C.V. (%)	14	45	32	29	30	105	30
	% Recovery				130		ND	
E	n	9	8	10	9	7	3	10
	\bar{x}	1.1378	.0140	.0145	.0117	.1350	.0050	.0280
	S.D.	.0717	.0055	.0041	.0029	.0266	.0053	.0093
	C.V. (%)	6.2	39	28	25	20	106	33
	% Recovery				113		ND	
F	n	3	3	3	3	3	2	3
	\bar{x}	.9967	.0103	.0147	.0137	.148	0.0010	.0303
	S.D.	.0551	.0042	.0029	.0032	.208	0.0014	.0087
	C.V. (%)	5.5	4.1	20	23	14	140	29
	% Recovery				132		ND	
C	n	5	3	4	3	4	2	4
	\bar{x}	1.2740	.0217	.0258	.0153	.1723	0.0090	.0348
	S.D.	.270	.0096	.0142	.0045	.0479	.0014	.0103
	C.V. (%)	21	44	55	29	28	16	30
	% Recovery				147		ND	
D	n	4	2	2	2	4	ND	2
	\bar{x}	1.0825	.0200	.0200	.0150	.1350		.025
	S.D.	.0395	0	0	.0071	.0191		.0071
	C.V. (%)	3.7	0	0	43	14		28
	% Recovery				144		ND	

values (.011 mg/l and .010 mg/l) which were included in calculating the mean for sample 6B.

The synthetic standard 4B was designed to be .0104 mg/l of iron, but analysis gave an overall average of .0135 mg/l. This may indicate a bias, but is not confirmed when the standard deviation is included with each mean value (Table 9).

Precision of analysis of the natural samples in the .01 mg Fe/l to .02 mg Fe/l range was fairly uniform but varied according to the method used. The flameless method seemed to give the best precision, although it was calculated with somewhat limited data.

The best overall precision was observed for the higher iron concentrations, where perhaps the blank error would be less critical.

Lead

The synthetic sample 4B containing no added lead was indicated by six laboratories as having .0029 mg/l \pm .0028 mg/l of lead. Ten participants, however, reported values of less than .001 mg/l, which might suggest either slight contamination or a flame blank reading was being measured.

The standard solution 6B containing .0070 mg/l of lead was analyzed well by all the laboratories, with an average of .0073 mg/l. The precision was \pm .0016 mg/l and the recovery was 104% (Table 10).

Two natural samples (2B and 7B) were reported to contain about .003 mg/l to .004 mg/l of lead. A large number of laboratories, however, reported less than .001 mg/l. In view of the reported data for the synthetic blank, one might say these two samples also had no detectable lead (e.g., <.002 mg/l).

Samples 5B and 6B, which were originally low in lead, were fortified to .006 mg Pb/l and .007 mg Pb/l, respectively. Comparison of these two samples should indicate a .001 mg Pb/l difference.

Scrutiny of the summary data for samples 5B and 6B indicates that most laboratories did differentiate the .001 mg/l concentration difference. Although not conclusive, it strongly suggests sample 5B contained less than .001 mg/l of lead prior to spiking.

Zinc

This metal is one which is usually difficult to analyze with a zero blank (Table 11). Sample 6B, a synthetic blank, proved to be no exception with thirteen laboratories reporting an average of .0033 mg/l. Two participants called the blank .000 mg/l and seven reported it as less than .001 mg/l.

Data for samples 2B, 5B and 7B (natural samples) were very similar to the blank (sample 6B), leading to the conclusion that the zinc level was not determined accurately and that the concentration of zinc relates to contamination from the same source.

Table 10. Comparison of Lead Results (mg/l)

Method	Parameter	Sample						
		1B	2B	3B	4B	5B	6B	7B
Overall	n	19	7	18	6	16	15	6
	\bar{x}	.0173	.0044	.0142	.0029	.0059	.0073	.0033
	S.D.	.0046	.0034	.0055	.0028	.0034	.0016	.0027
	C.V. (%)	27	77	39	97	59	22	82
	% Recovery				ND		104	
E	n	12	5	11	4	10	9	3
	\bar{x}	.0175	.0047	.0160	.0039	.0060	.0078	.0040
	S.D.	.0038	.0037	.0035	.0031	.0035	.0014	.0036
	C.V. (%)	22	79	22	80	58	18	90
	% Recovery				ND		110	
F	n	3	1	3	1	3	3	1
	\bar{x}	.0110	.001	.0120	.001	.0053	.0057	.001
	S.D.	.0017	ND	.0026	ND	.0025	.0006	ND
	C.V. (%)	16	ND	22	ND	47	11	
	% Recovery				ND		82	
C	n	3	1	3	1	3	2	1
	\bar{x}	.0217	.006	.0140	.001	.0063	.0085	.001
	S.D.	.0042	ND	.0087	ND	.0047	.0021	ND
	C.V. (%)	19	ND	62	ND	75	25	
	% Recovery				ND		120	

Table 11. Comparison of Zinc Results (mg/l)

Method	Parameter	Sample						
		1B	2B	3B	4B	5B	6B	7B
Overall	n	21	14	21	22	15	13	15
	\bar{x}	.0377	.0033	.078	.0136	.0038	.0033	.0035
	S.D.	.0072	.0036	.0111	.0038	.0036	.0034	.0030
	C.V. (%)	19	109	14	28	94	103	85
	% Recovery				112		ND	
E	n	10	8	11	12	11	7	9
	\bar{x}	.0362	.0010	.0800	.0117	.0028	.0023	.0018
	S.D.	.002	.0008	.0088	.0026	.0028	.0035	.0012
	C.V. (%)	6	80	11	22	100	152	67
	% Recovery				96		ND	
C	n	4	3	4	4	2	3	3
	\bar{x}	.0370	.0050	.0738	.0158	.0045	.0040	.0060
	S.D.	.0047	.0036	.008	.0022	.0007	.0010	.0036
	C.V. (%)	13	72	11	14	16	25	60
	% Recovery				130		ND	

Recovery of zinc from sample 4B, containing .0122 mg/l, was 112% with a coefficient of variation of 28%. The percent recovery being greater than 100% may be due to a background blank being included (e.g., sample 6B).

The natural samples 1B and 3B were reported to contain zinc above and below the standard (4B) sample. Both natural samples were analyzed well with precision being $\pm 10\%$ to 20%.

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FUTURE INTERLABORATORY STUDIES

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"Total Phosphorus in Natural Waters."

"Total Mercury in Natural Waters."

APPENDIX A

ANALYTICAL RESULTS FOR STUDY NO. 12

Table A-1. Analytical Results for Cadmium (mg/l) and Comparison of Methods

Laboratory number	Sample number						
	1A	2A	3A	4A	5A	6A	7A
1201 E	.005	.002	.001	.002	.005	<.001	.003
1202 E	.005	.001	<.001	<.001	.004	.001	.005
1203 E	.0046	.0005	.0001	.0001	.0030	.0005	.0033
1204 F	.005	.005	.005	.005	.005	<.005	.005
1205 F	.0048	<.0005	<.0005	<.0005	.0028	<.0005	.0028
1206 C	.14 R	.005	<.005	<.005	.005	<.005	.005
1207 F	.0045	.0003	.0000	.0003	.0023	.0000	.0025
1208 C	<.005	.006	<.005	.006 R	.005	<.005	.019
1209 E	.005	<.001	<.001	<.001	.004	<.001	.003
1210 E	.005	<.001	<.001	<.001	.002	<.001	.004
1211 E	.005	.001	.001	.0005	.003	.003	.0067
1212 D	.01	<.01	<.01	<.01	.01	<.01	<.01
1213 E	.005	<.001	<.001	<.001	.003	<.001	.003
1214 -	.026 R	<.001	<.001	.001	.018 R	<.001	.030
1215 C	.004	<.001	.002	<.001	.004	<.001	.004
1216 D	.008	<.002	<.002	<.002	.002	<.002	.045
1217 -	ND	ND	ND	ND	ND	ND	ND
1218 E	.005	.001	<.001	<.001	.004	.000	.004
1219 -	.005	.001	.002	.001	.003	.0005	.003
1220 E	.007	<.001	<.001	<.001	.003	<.001	.004
1221 C	.004	<.001	.001	<.001	.003	<.001	.005
1222 Col.	.005	<.005	<.005	<.005	<.005	<.005	.005
1223 E	ND	ND	ND	ND	ND	.00005	.00306
1224 E	.004	<.001	<.001	<.001	.003	<.001	.003
1225 C	.006	.003	.003	<.002	.005	<.002	.005
1226 C	.005	.002	.002	.002	.004	<.01	<.01
Method	Statistical parameter						
Overall	n	21	12	10	8	22	
	\bar{x}	.0053	.0023	.0017	.0016	.0039	
	σ	.0014	.0020	.0015	.0017	.0017	
	C.V. (%)	26	87	88	106	44	
Extraction	n	10	5	3	4	8	
	\bar{x}	.0051	.0011	.0007	.0009	.0034	
	σ	.0008	.0005	.0005	.0001	.0009	
	C.V. (%)	16	45	71	11	26	
Flameless	n	3	2	ND	ND	3	
	\bar{x}	.0048	.0027			.0034	
	σ	.0003	.0033			.0014	
	C.V. (%)	6	122			41	
Concentration	n	4	4	4	ND	6	
	\bar{x}	.0048	.0040	.0020		.0043	
	σ	.0010	.0018	.0008		.0008	
	C.V. (%)	21	45	40		19	

Table A-2. Analytical Results for Chromium (mg/l) and Comparison of Methods

Laboratory number	Sample number						
	1A	2A	3A	4A	5A	6A	7A
1201 E	<.006	<.006	<.006	<.006	.021	<.006	.017
1202 E	.002	.002	.0007	.0006	.020	.0007	.0153
1203 E	.0036	.0025	.0018	.0008	.0260	.0005	.0110
1204 F	.010	.010	.005	.005	.020	<.005	.015
1205 F	<.005	<.005	<.005	<.005	.023	<.005	.012
1206 C	<.005	<.005	<.005	<.005	.020	<.005	.015
1207 F	.005	.003	.000	.002	.023	.000	.015
1208 C	<.005	.005	.010	<.005	.005	.026	.040
1209 E	.003	<.001	<.001	<.001	.03	<.001	.018
1210 E	.005	.001	<.001	<.001	.014	<.001	.006
1211 E	ND	ND	ND	ND	ND	ND	ND
1212 D	<.01	<.01	.03 R	<.01	.04	<.01	<.01
1213 E	.005	.0020	.0015	.0005	.015	<.0005	.0015
1214 -	<.01	<.01	<.01	<.01	<.01	<.01	.02
1215 C	.004	.003	.006	.002	.020	<.001	.012
1216 D	.010	.008	.012	.021 R	.038	.012	.16
1217 -	<.0005	<.0005	<.0005	<.0005	<.0005	<.0005	.012
1218 E	.005	.005	.005	<.001	.020	.000	.025
1219 -	.004	.007	.013	.007	.023	.002	.014
1220 E	<.001	<.001	<.001	<.001	.010	<.001	.011
1221 C	.003	.002	<.001	.003	.017	<.001	.011
1222 Col.	.01	<.01	<.01	<.01	.02	<.01	.01
1223 E	.0008	0.000	0.000	0.000	.0014	.0002	.014
1224 E	<.01	.01	.01	.01	.04	.01	.02
1225 C	.005	<.005	<.005	<.005	.057 R	.011	.042
1226 C	ND	ND	ND	ND	ND	ND	ND
Method	Statistical parameter						
Overall	n	15	14	12	10	21	
	\bar{x}	.0051	.0043	.0054	.0031	.0213	
	σ	.0029	.0033	.0048	.0033	.0100	
	C.V. (%)	57	77	89	106	47	
Extraction	n	6	5	4	4	7	
	\bar{x}	.0037	.0015	.0010	.0005	.0166	
	σ	.0019	.0010	.0008	.0003	.0097	
	C.V. (%)	51	67	80	60	58	
Flameless	n	ND	2	2	2	3	
	\bar{x}		.0065	.0025	.0035	.0220	
	σ		.0049	.0035	.0021	.0017	
	C.V. (%)		75	140	60	8	
Concentration	n	3	4	3	3	5	
	\bar{x}	.0040	.005	.0087	.0050	.0204	
	σ	.0010	.0036	.0023	.0044	.0126	
	C.V. (%)	25	72	26	88	62	

Table A-3. Analytical Results for Manganese (mg/l) and Comparison of Methods

Laboratory number	Sample number						
	1A	2A	3A	4A	5A	6A	7A
1201 D	.050	<.010	<.010	.025	.025	<.010	.015
1202 D	.06	.01 R	.01	.03	.03	.11	.12
1203 E	.0450	.0043	.0006	.0220	.0210	.003	.0096
1204 F	.030	<.005	<.005	.010	.010	.010	.015
1205 F	.041	.005	<.001	.021	.023	.001	.009
1206 C	.045	.005	<.005	.020	.020	<.005	.010
1207 F	.048	.005	.000	.020	.020	.023	.023
1208 C	.42 R	.05 R	.02 R	.19 R	.17 R	2.50 R	2.50 R
1209 E	.05	.007	<.001	.020	.020	.07	.08
1210 E	.056	.006	<.001	.030	.020	.022	.030
1211 E	ND	ND	ND	ND	ND	ND	ND
1212 D	.04	<.01	.04 R	.03	.04	.04 R	.03 R
1213 E	.04	.004	<.001	.020	.020	.016	.025
1214 -	.04	<.02	<.02	.02	.02	<.02	<.02
1215 C	.042	.006	<.001	.020	.020	.007	.010
1216 D	.020	.008	.010	.045 R	.050 R	.040 R	.140 R
1217 -	ND	ND	ND	ND	ND	ND	ND
1218 E	ND	ND	ND	ND	ND	ND	ND
1219 -	.049	.005	.003	.024	.020	.015	.024
1220 E	ND	ND	ND	ND	ND	ND	ND
1221 C	.053	.005	.005	.021	.020	.013	.022
1222 Col.	.04	<.01	<.01	.015	.015	.15	.16
1223 E	.0508	.0033	.0004	.0208	.0196	.000	.0123
1224 E	.05	<.01	<.01	<.01	.02	.67	.67
1225 C	.048	.004	.003	.020	.018	.003	.009
1226 C	ND	ND	ND	ND	ND	ND	
Method	Statistical parameter						
Overall	n	20	13	8	18	19	
	\bar{x}	.0449	.0052	.004	.0216	.0211	
	σ	.009	.0013	.0041	.0050	.0060	
	C.V.	20	25	102	23	28	
Extraction	n	6	5	2	6	6	
	\bar{x}	.0471	.0047	.0005	.0223	.0204	
	σ	.0062	.0014	.0001	.0038	.0013	
	C.V. (%)	13	30	20	17	6	
Flameless	n	2	ND	1	2	2	
	\bar{x}	.0390		.0000	.0150	.0150	
	σ	.0127		ND	.0071	.0071	
	C.V. (%)	32		ND	47	47	
Concentration	n	5	4	3	4	5	
	\bar{x}	.0476	.0050	.0093	.0203	.0196	
	σ	.0043	.0008	.0093	.0005	.0009	
	C.V. (%)	9	16	100	2	5	
Direct	n	.5	ND	3	4	4	
	\bar{x}	.0420		.0200	.0263	.0288	
	σ	.0148		.0173	.0048	.0085	
	C.V. (%)	35		87	18	30	

Table A-4. Analytical Results for Nickel (mg/l) and Comparison of Methods

Laboratory number	Sample number						
	1A	2A	3A	4A	5A	6A	7A
1201 E	.004	.006	.004	.003	.14	.002	.005
1202 E	.015 R	.006	.006	.006	.10	.004	.006
1203 E	<.0005	.0030	.0005	.0010	.120	.0015	.0025
1204 F	.055 R	.055 R	.060 R	.040 R	.100 R	<.005 R	<.005 R
1205 F	<.005	<.005	<.005	<.005	.100	<.005	<.005
1206 C	<.005	<.005	<.005	<.005	.11	<.005	<.005
1207 F	<.005	.005	.000	.000	.103	<.005	<.005
1208 C	<.005	.012	.018 R	.012	.097	.018	.023
1209 E	.004	.002	<.001	.001	.10	.011	.011
1210 E	<.001	<.001	.001	<.001	.118	.002	.002
1211 E	<.005	<.005	<.005	<.005	.120	<.005	<.005
1212 D	<.06	<.06	<.06	<.06	.14	<.06	<.06
1213 E	<.001	.002	<.001	<.001	.13	<.001	<.001
1214 -	<.01	<.01	<.01	.01	.12	<.01	.01
1215 C	<.001	.005	.006	.005	.120	<.001	<.001
1216 D	<.01	<.01	<.01	<.01	.12	<.01	.06
1217 -	ND	ND	ND	ND	ND	ND	ND
1218 E	.001	.004	.002	.002	.130	.000	.003
1219 -	.001	.006	.012	.007	.11	.003	.004
1220 E	.002	.002	.001	.001	.122	.007	.008
1221 C	<.001	.002	.002	<.001	.123	.017	.018
1222 Col.	<.01	<.01	.03 R	.02 R	.09	.02	.02
1223 E	.0010	.0022	.0005	.0004	.116	.00097	.0015
1124 E	.001	.003	.001	.003	.120	.002	.002
1225 C	<.005	.005	.011	.006	.106	.006	.011
1226 C	<.002	.003	.005	.002	.12	.02	.03
Method	Statistical parameter						
Overall	n	19*	16	14	15	25	
	\bar{x}	.0027	.0043	.0037	.0040	.1150	
	σ	.0019	.0026	.0039	.0037	.0131	
	C.V. (%)	70	60	105	93	11	
Extraction	n	9	9	8	9	12	
	\bar{x}	.0017	.0034	.0020	.0030	.1197	
	σ	.0013	.0016	.0020	.0031	.0114	
	C.V. (%)	76	47	100	103	10	
Flameless	n	ND	ND	ND	ND	3	
	\bar{x}					.101	
	σ					.0017	
	C.V. (%)					2	
Concentration	n	ND	4	4	4	6	
	\bar{x}		.0055	.0060	.0065	.1127	
	σ		.0045	.0037	.0041	.0101	
	C.V. (%)		82	62	63	9	

*n equalling 19 includes all values less than .005

Table A-5. Analytical Results for Lead (mg/l) and Comparison of Methods

Laboratory Number	Sample number						
	1A	2A	3A	4A	5A	6A	7A
1201 E	.003	.005	.002	.003	.010	.003	.010
1202 E	<.002	<.002	<.002	.002	.0095	.015	.020
1203 E	.0010	.0020	.0010	.0010	.0080	.0010	.0080
1204 F	.005	.010	.010	.010	.010	<.005	<.005
1205 F	<.001	<.001	<.001	<.001	.006	<.001	.007
1206 C	<.01	.01	.01	.01	.01	<.01	.01
1207 F	.000	.001	.006	.002	.003	.002	.004
1208 C	<.005	.009	.025	.009	.009	.030	.038
1209 E	.002	.003	.003	.003	.009	.005	.010
1210 E	<.001	<.001	<.001	<.001	.006	<.001	.006
1211 E	<.005	<.005	<.005	<.005	.010	<.005	.010
1212 D	<.02	<.02	<.02	<.02	<.02	<.02	<.02
1213 E	<.001	.002	<.001	<.001	.007	.020	.026
1214 -	.002	.005	.005	.010	.060	<.001	.050
1215 C	<.002	.005	.012	.005	.015	.012	.015
1216 D	<.02	<.02	<.02	<.02	<.02	<.02	1.0
1217 -	<.004	<.004	<.004	<.004	.005	<.004	.007
1218 E	<.001	<.001	<.001	.001	.008	.000	.007
1219 -	.007	.013	.030	.019	.018	.008	.013
1220 E	.0030	.0015	.0013	.0015	.0100	.0045	.0130
1221 C	.002	.002	<.001	.001	.093	.005	.010
1222 Col.	<.05	.05 R	.17 R	.07 R	.05 R	.05	.05
1223 E	ND	ND	ND	ND	ND	.0005	.0076
1224 E	<.002	<.002	<.002	<.002	.006	.004	.006
1225 C	<.005	.005	.024	.012	.012	.007	.019
1226 C	.005	.006	.006	.009	.013	<.04	<.04
Method	Statistical parameter						
Overall	n	10	15	13	16	20	
	\bar{x}	.003	.0053	.0104	.0062	.0092	
	σ	.0021	.0037	.0098	.0053	.0053	
	C.V. (%)	70	70	94	85	58	
Extraction	n	4	5	5	7	12	
	\bar{x}	.0023	.0037	.0035	.0031	.0082	
	σ	.0010	.0036	.0037	.0032	.0018	
	C.V. (%)	43	97	105	102	22	
Flameless	n	3	3	ND	3	2	
	\bar{x}	.0023	.0053		.0073	.0080	
	σ	.0025	.0045		.0046	.0028	
	C.V. (%)	108	85		63	35	
Concentration	n	2	5	4	5	4	
	\bar{x}	.0035	.0054	.0168	.0074	.0123	
	σ	.0021	.0025	.0093	.0042	.0025	
	C.V. (%)	60	46	55	57	20	

APPENDIX B

ANALYTICAL RESULTS FOR STUDY NO. 13

Table B-1. Analytical Results for Aluminum (mg/l)

Laboratory number	Sample number						
	1B	2B	3B	4B	5B	6B	7B
1301 D	.68	<.06	.08	<.06	.11	.07	<.06
1302 E	.35	<.01	.10	.015	.10	.015	.015
1303 E	.650	.007	.075	<.002	.120	.060	.010
1304 -	ND	ND	ND	ND	ND	ND	ND
1305 F	.71	.01	.10	.02	.27	.07	.03
1306 F	0.32	.002	.053	.000	.17	.036	.004
1307 -	ND	ND	ND	ND	ND	ND	ND
1308 E	.65	.008	.07	<.001	.12	.05	.001
1309 E	.8	<.05	.10	<.05	.09	<.05	<.05
1310 -	.60	<.1	<.1	<.1	.1	<.1	<.1
1311 -	ND	ND	ND	ND	ND	ND	ND
1312 E	.62	<.01	.07	<.001	.10	.05	<.001
1313 E	.65	.02	.08	<.02	.10	.12 R	.06
1314 -	ND	ND	ND	ND	ND	ND	ND
1315 C	.70	<.06	.08	<.06	.10	.07	<.06
1316 C	.725	.015	.088	.015	.170	.068	.023
1317 -	ND	ND	ND	ND	ND	ND	ND
1318 Col.	ND	.01	.07	<.01	.09	.07	.02
1319 -	ND	ND	ND	ND	ND	ND	ND
1320 D	.65	<.02	.10	<.02	.18	.03	<.02
1321 C	.70	.09	.11	<.02	.21	.07	.03
1322 -	ND	ND	ND	ND	ND	ND	ND
1323 -	ND	ND	ND	ND	ND	ND	ND
1324 -	ND	ND	ND	ND	ND	ND	ND
1325 F	1.00	.005	.080	<.001	.250	.042	.020
1326 -	ND	ND	ND	ND	ND	ND	ND

Table B-2. Analytical Results for Cobalt (mg/l)

Laboratory number	Sample number						
	1B	2B	3B	4B	5B	6B	7B
1301 E	.004	<.002	<.002	.002	.004	.003	.002
1302 E	.004	<.002	.003	<.002	.004	.003	<.002
1303 E	.0025	<.001	.001	<.001	.0025	.001	<.001
1304 -	.003	.002	<.001	<.001	<.001	<.001	<.001
1305 E & F	<.005	<.005	<.005	<.005	<.005	<.005	<.005
1306 F	.005	.001	.001	.002	.003	.002	.001
1307 -	ND	ND	ND	ND	ND	ND	ND
1308 E	.003	<.001	.001	<.001	.002	.001	<.001
1309 E	.003	<.001	.002	<.001	.003	<.001	<.001
1310 -	<.03	<.03	<.03	<.03	<.03	<.03	<.03
1311 E	.003	<.001	<.001	<.001	.002	.001	<.001
1312 E	.003	<.001	<.001	<.001	.002	.001	<.001
1313 E	<.01	<.01	<.01	<.01	<.01	<.01	<.01
1314 -	ND	ND	ND	ND	ND	ND	ND
1315 C	.003	<.001	<.001	<.001	.003	.002	<.001
1316 C	.010 R	.004	.003	.003	.006	.003	.005 R
1317 D	<.02	<.02	<.02	<.02	<.02	<.02	<.02
1318 C	<.01	<.01	<.01	<.01	<.01	<.01	<.01
1319 E	.0037	.000	.0005	.0001	.0011	.0011	.00004
1320 E	.003	<.001	<.001	<.001	.002	.001	<.001
1321 E	.007	<.004	<.004	<.004	.005	<.004	<.004
1322 -	ND	ND	ND	ND	ND	ND	ND
1323 E	<.005	<.005	<.005	<.005	<.005	<.005	<.005
1324 E	.002	<.001	<.001	<.001	.003	.002	<.001
1325 F	.003	<.001	<.001	<.001	.003	<.001	<.001
1326 -	ND	ND	ND	ND	ND	ND	ND

Table B-3. Analytical Results for Copper (mg/l)

Laboratory number	Sample number						
	1B	2B	3B	4B	5B	6B	7B
1301 E	.070	.004	.003	.006	.008	<.001	<.001
1302 E	.075	.003	.003	.009	.010	<.002	<.002
1303 E	.060	.0030	.0035	.0080	.0080	.0005	.0015
1304 -	.042	<.001	<.001	.002	.010	<.001	<.001
1305 F	.07	.003	.003	.007	.009	<.001	.002
1306 F	.056	.002	.003	.008	.009	.000	.001
1307 D	.07	<.01	<.01	<.01	<.01	<.01	<.01
1308 E	.06	.003	.003	.007	.008	<.001	.001
1309 E	.064	.003	.003	.008	.008	<.001	.002
1310 -	.06	<.02	<.02	<.02	<.02	<.02	<.02
1311 E	.062	.003	.003	.007	.008	<.001	.001
1312 E	.062	.003	.003	.008	.009	<.001	.001
1313 E	.15 R	.05 R	.04 R	.05 R	.07 R	.04 R	.04 R
1314 E	.0720	.0030	.0030	.0065	.0090	.0000	.0015
1315 C	.070	.002	.003	.006	.010	<.001	<.001
1316 C	.068	.005	.004	.007	.009	.001	.003
1317 D	.065	<.015	<.015	<.015	<.015	<.015	<.015
1318 C	.068	<.005	.006	.010	.012	<.005	<.005
1319 -	ND	ND	ND	ND	ND	ND	ND
1320 E	.063	.003	.003	.008	.009	<.001	.001
1321 C	.062	<.002	<.002	.007	.007	<.002	<.002
1322 C	.072	.018 R	.017 R	.018 R	.023 R	.015 R	.019 R
1323 E	.11 R	<.005	<.005	.005	.008	<.005	<.005
1324 E	.075	.003	.010 R	.010	.007	.001	.002
1325 F	.094	.003	.007 R	.007	.008	<.001	.002
1326 E	.10 R	.01 R	.01 R	.01	.01	<.01	.01 R

Table B-4. Analytical Results for Iron (mg/l)

Laboratory number	Sample number						
	1B	2B	3B	4B	5B	6B	7B
1301 D	1.1	.04	<.04	<.04	.15	<.04	<.04
1302 D	1.05	.02	.02	.01	.11	<.01	.03
1303 E	1.1	.009	.013	.011	.075 R	<.001	.025
1304 -	1.4	.4 R	.1 R	.1 R	.6 R	.4 R	.1 R
1305 E & F	1.05	.007	.013	.015	.124	<.005	.023
1306 F	0.94	.009	.013	.010	.16	.000	.028
1307 D	1.05	<.05	<.05	<.05	.15	<.05	<.05
1308 E	1.1	.014	.016	.014	.10	.001	.02
1309 E	1.08	.022	.013	.008	.100	<.001	.022
1310 -	1.10	<.03	<.03	<.03	.14	<.03	<.03
1311 E	1.1	.008	.012	.010	.16	<.001	.021
1312 E	1.1	.008	.012	.010	.16	<.001	.025
1313 E	1.30	<.01	.01	.01	.20 R	<.01	.05
1314 Col.	1.03	.01	.01	<.01	.14	<.01	.02
1315 C	1.200	.020	.025	.015	.150	.010	.035
1316 C	1.20	.032	.022	.020	.15	.008	.048
1317 D	1.13	.02	.02	.02	.13	<.02	.02
1318 C	1.1	<.01	.045 R	<.01	.34 R	<.01	.023
1319 Col.	1.1	.008	.008	.013	.143	.000	.030
1320 E	1.10	.018	.022	.016	.125	.011	.034
1321 C	1.75	.013	.011	.011	.145	<.003	.033
1322 C	1.120	.112 R	.096 R	.112 R	.244 R	.068 R	.140 R
1323 E	1.2	.020	.020	.016	.15	<.005	.032
1324 E	ND	.017	.017	.021	.150	.003	.031
1325 F	1.00	.015	.018	.016	.160	.002	.040
1326 E	1.16	.01	.01	.01	.02 R	<.01	.02

Table B-5. Analytical Results for Lead (mg/l)

Laboratory number	Sample number						
	1B	2B	3B	4B	5B	6B	7B
1301 E	.019	.004	.015	<.004	.007	.008	<.004
1302 E	.027	.011	.023	.008	.015	.017 R	.008
1303 E	.017	<.001	.014	<.001	.005	.007	<.001
1304 -	.020	<.001	.001	<.001	<.001	.006	.002
1305 F	.013	<.001	.013	<.001	.005	.006	<.001
1306 F	.010	.001	.009	.001	.003	.006	.001
1307 D	.04 R	<.01	.04 R	<.01	<.01	<.01	<.01
1308 E	.014	<.001	.012	.001	.004	.006	<.001
1309 E	.019	.002	.014	.002	.002	.009	.003
1310 E	.02	<.02	<.02	<.02	<.02	<.02	<.02
1311 E	.014	<.001	.013	<.001	.005	.007	<.001
1312 E	.015	<.001	.014	<.001	.005	.006	<.001
1313 E	<.01	<.01	<.01	<.01	<.01	<.01	<.01
1314 E	.0140	.0045	.0185	.0045	.0035	.0080	.0010
1315 C	.023	.006	.020	<.001	.008	.010	<.001
1316 C	.025	.024 R	.018	.001	.010	.007	.005
1317 D	<.10	<.10	<.10	<.10	<.10	<.10	<.10
1318 C	<.025	<.025	<.025	<.025	<.025	<.025	<.025
1319 -	ND	ND	ND	ND	ND	ND	ND
1320 E	.015	.002	.014	<.001	.007	.009	<.001
1321 C	.017	<.001	.004	<.001	.001	<.001	<.001
1322 C	.054 R	.066 R	.050 R	.018 R	.030 R	.014 R	.054 R
1323 E	<.05	<.05	<.05	<.05	<.05	<.05	<.05
1324 E	.016	<.001	.019	<.001	.006	.010	<.001
1325 F	.010	<.001	.014	<.001	.008	.005	<.001
1326 E	.02	<.02	.02	<.02	<.02	<.02	<.02

Table B-6. Analytical Results for Zinc (mg/l)

Laboratory number	Sample number						
	1B	2B	3B	4B	5B	6B	7B
1301 E	.038	.002	.080	.014	.005	.002	.003
1302 E	.038	.002	.082	.015	.004	.002	.004
1303 E	.035	.001	.085	.011	.003	.001	.002
1304 -	.05	.01	.15 R	.02	.0	.01	.01
1305 -	.05	<.005	.08	.010	<.005	<.005	<.005
1306 F	.053	.002	.073	.016	.003	.001	.003
1307 D	.02	<.01	.05	.02	.02	<.01	<.01
1308 E	.04	.001	.08	.013	.001	<.001	.001
1309 E	.037	<.001	.075	.007	<.001	<.001	<.001
1310 -	.03	<.01	.07	.01	<.01	<.01	<.01
1311 E	.034	<.001	.08	.014	.002	<.001	.002
1312 E	.035	<.001	.08	.010	.001	<.001	<.001
1313 -	.04	<.01	.12 R	.02	<.01	<.01	.03 R
1314 E	.0340	.0000	.0980	.0070	.0000	.0000	.0000
1315 C	.040	.009	.080	.015	<.001	.005	.010
1316 C	.039	.004	.077	.015	.005	.004	.005
1317 D	.039	<.005	.082	.010	<.005	<.005	<.005
1318 C	.030	<.005	.076	.019	<.005	<.005	<.005
1319 E	ND	0.0	ND	.0128	.0003	.00	.0014
1320 E	.035	.001	.080	.012	.003	.001	.002
1321 C	.039	.002	.062	.014	.004	.003	.003
1322 C	.152 R	.126 R	.170 R	.062 R	.056 R	.048 R	.072 R
1323 E	.27 R	<.005	.080	.012	<.005	<.005	<.005
1324 E	.036	<.001	.060	.012	.002	<.001	.001
1325 F	.086 R	.002	.100	.036 R	.013	.004	.005
1326 E	.08 R	.01	.14 R	.04R	.01	.01	.02 R

APPENDIX C

LIST OF PARTICIPANTS

Environment Canada, Inland Waters Directorate

Atlantic Region, Water Quality Branch Laboratory
(Moncton)
Ontario Region, Water Quality Branch Laboratory;
Inorganic Laboratory (Burlington)
Ontario Region, Water Quality Branch Laboratory; Ships
Support Laboratory (Burlington)
Western Region, Water Quality Branch Laboratory
(Calgary)
Pacific Region, Water Quality Branch Laboratory
(Vancouver)

Environment Canada, Environmental Protection Service

Environmental Health Centre, Tunney's Pasture (Ottawa)
Analytical Services Section, Surveillance and Analysis
Division, Atlantic Region (Halifax)
Technology Development and Demonstration Division
(Burlington)
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Environment Canada, Fisheries and Marine Service

Fisheries Laboratory (Winnipeg)
Fisheries Service Laboratory (West Vancouver)

Provincial Government Laboratories

British Columbia Research Council, Vancouver
British Columbia Water Resources Service, Vancouver
Manitoba Department of Mines, Resources and Environ-
mental Management, Winnipeg
Gouvernement du Québec, Ministère des Affaires
sociales, Laval
Nova Scotia Department of Public Health
Ontario Ministry of the Environment, Rexdale
Ontario Ministry of the Environment, Thunder Bay

Municipal Government Laboratories

City of Montreal Filtration Plant, Verdun
City of Winnipeg Waterworks and Waste Disposal,
Winnipeg

Industrial and Consulting Laboratories

T.W. Beak Consultants Ltd., Richmond, British Columbia
Bondar-Clegg and Co. Ltd., Ottawa
Chemex Labs Ltd., Calgary, Alberta
Chemex Labs Ltd., North Vancouver, British Columbia
Cominco Limited, Trail, British Columbia
Exploration and Production Laboratory, Shell Canada,
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Environment Canada Library, Burlington



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