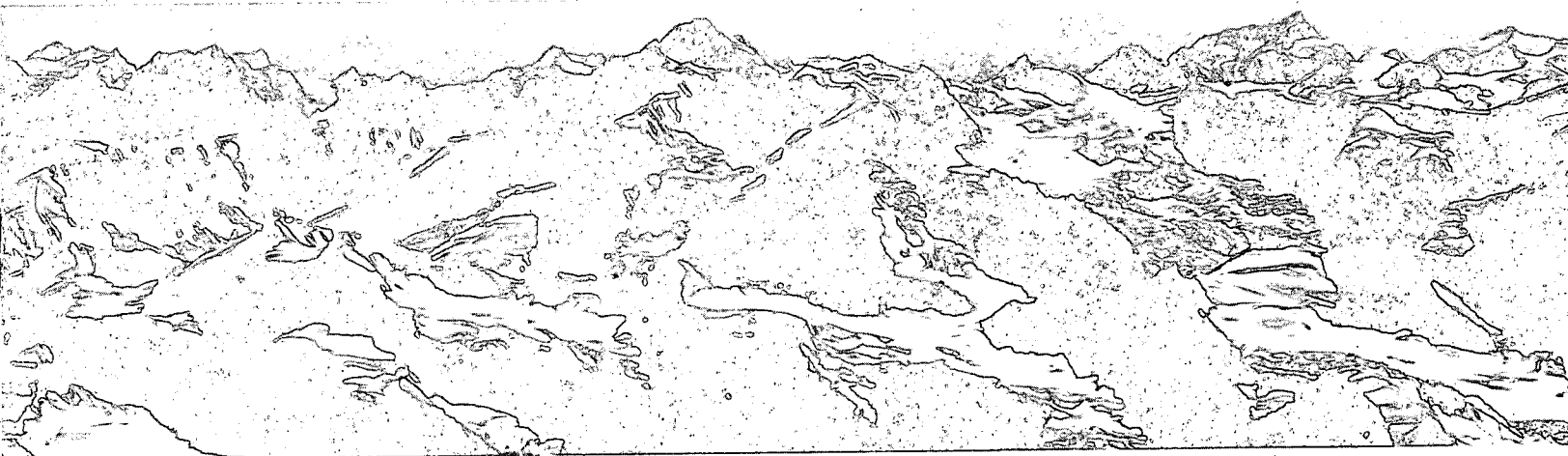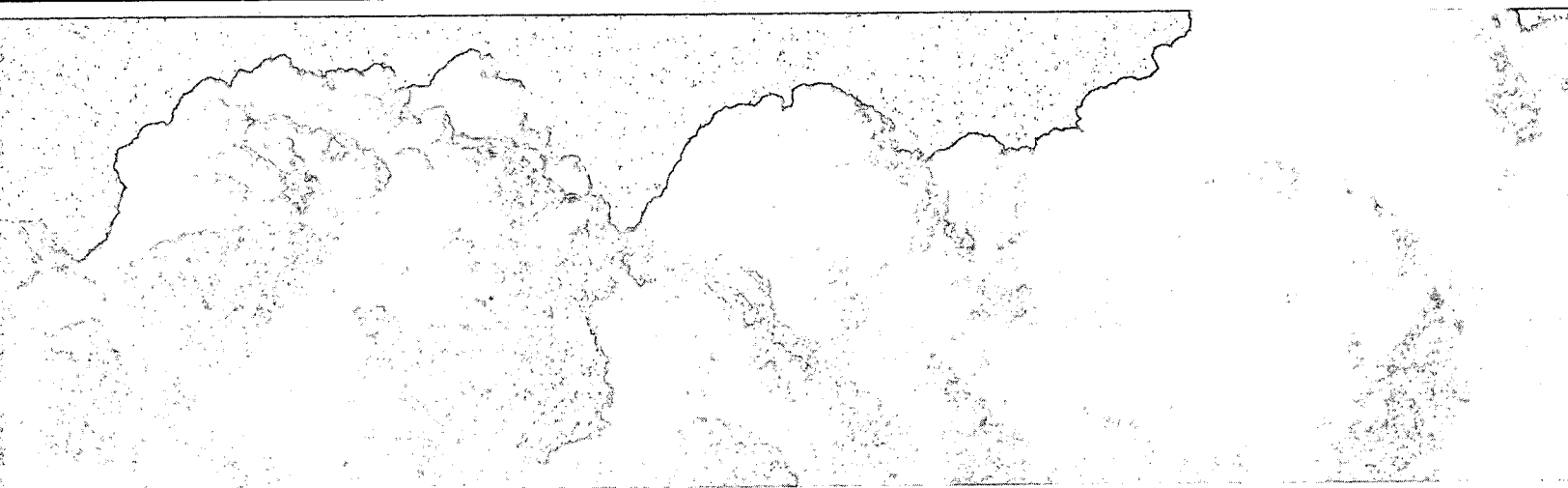# Interlaboratory Quality Control Study No. 4

Arsenic, Cadmium, Cobalt, Mercury and Nickel

D. J. McGirr and R. W. Wales

REPORT SERIES NO. 25

Interlaboratory Quality Control Study No. 4

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Summary

Synthetic samples containing arsenic, cadmium, cobalt, nickel and mercury were analyzed by nine laboratories participating in a study of trace metals. Most laboratories used atomic absorption methods for determining cadmium, cobalt and nickel; precision and accuracy were good for these three metals. Results were also acceptable for arsenic, which most laboratories determined by the silver diethyldithiocarbamate method. Both precision and accuracy were rather poor for mercury, which was analyzed by various procedures based on flameless atomic absorption; it is suggested that the laboratories should review their procedures.

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INTRODUCTION

This is the second of a series of three studies on trace metal analysis in which a total of fourteen trace metals will be determined. This study includes five commonly determined and environmentally important metals. The importance of mercury in particular needs no introduction either to the scientist or the general public, as mercury contamination of our inland waters has been in the news in Canada during the past few years.

In addition to the four laboratories of the Water Quality Branch (WQB) of Environment Canada, three provincial laboratories, one university and one industrial laboratory participated in this study. The participants are listed in Appendix A.

EXPERIMENTAL DESIGN

Stock solutions of each of the metals were prepared and aliquots of the stocks were mixed and diluted in a volumetric flask to prepare the concentrates which were shipped to the participating laboratories. The concentrates for samples 1 to 7 were preserved with 2 ml concentrated nitric acid per liter and were to be diluted by a factor of 100 and represerved by the recipient before analysis. Samples 8 to 12 which contained mercury only were preserved with 10 ml concentrated sulfuric acid per liter and were to be diluted by a factor of 10,000 and represerved before analysis. The concentrates were shipped in 125 ml polyethylene bottles.

The stocks used in samples 1 to 6 were made from cobaltous chloride, $CoCl_2 \cdot 6H_2O$; cadmium metal dissolved in HCl; nickel sulfate, $NiSO_4 \cdot 6H_2O$; and arsenic trioxide, As_2O_3. These are the compounds that are normally used to make standards for these metals in the WQB laboratories. Antimony in the form of antimony potassium tartrate, $K(SbO)C_4H_4O_6 \cdot 1/2 \ H_2O$, was added to samples 4 and 5 to see if it would interfere with the arsenic determination.

Mercury was added to samples 8 and 9 in the form of phenyl mercuric acetate, and to samples 10 and 12 in the form of mercuric chloride, $HgCl_2$. This was done to ascertain if the test methods in use were equally accurate with both organic and inorganic mercury.

The concentrations of the metals in the samples are given in Table I.

Table I. Actual Concentrations of Metals in Samples
(all concentrations in mg/1)

Sample Number	arsenic	cadmium	cobalt	nickel	mercury	antimony*
1	.000	.204	.028	.007	–	–
2	.005	.045	.008	.027	–	–
3	.071	.000	.080	.087	–	–
4	.033	.015	.028	.007	–	.100
5	.000	.045	.040	.000	–	.100
6	.005	.068	.016	.100	–	–
7	.015	.102	.000	.020	–	–
8	–	–	–	–	.00090	–
9	–	–	–	–	.00180	–
10	–	–	–	–	.00180	–
11	–	–	–	–	.00000	–
12	–	–	–	–	.00012	–

*analysis for antimony was not requested.

DATA EVALUATION

Results received from the laboratories were first reviewed for outliers. Rejection of outliers was done by the same method that was used in the previous two studies in this series (Dixon and Massey, 1969, p. 328). In this method the difference between the suspected outlier and the next farthest result is compared to the overall range of the results. Outliers are indicated by an R in the tables.

The remaining results were then analyzed for mean, standard deviation, relative standard deviation, mean error and relative error. The relative standard deviation, also called the coefficient of variation, is the standard deviation

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expressed as a per cent of the mean. The mean error is the difference between the mean and the true value (the amount added), and the relative error is the mean error expressed as a per cent of the true value.

The results from all the laboratories and the statistics derived from them are tabulated in Tables II to VI. In addition, the statistics for the laboratories that used the WQB methods were calculated separately and are listed in the bottom three rows of each table. Note that the laboratories using the WQB method are not necessarily the WQB laboratories, since some laboratories outside the Water Quality Branch use WQB methods, and occasionally a WQB laboratory will use a different method.

RESULTS

Arsenic

The results of the arsenic determinations are tabulated in Table II. Six laboratories determined arsenic, five by the silver diethyldithiocarbamate method used by the WQB (Traversy, 1971), and one by a colorimetric method using molybdenum blue.

No means or standard deviations were calculated and no outliers were rejected for the first four columns of Table II

because of the number of results reported as less than a detection limit, but the generally used detection limit of 0.005 ppm seems fairly conservative in view of the results reported.

The relative standard deviation increases moderately as the concentration increases in the other three samples, which is contrary to what is normally found. In this case the relative standard deviation of 28% in sample 3 can be considered an artificially high result caused by the presence of the two extreme values .040 and .100 mg/l. This set of figures demonstrates one of the characteristics of our method of rejecting outliers which depends on the range of the other values. The presence of an extreme value at either end of the range extends the range so that neither value can be rejected even though each of the values could have been rejected if the other had not been present.

Antimony was added to samples 4 and 5 to determine if it would cause any interference. No evidence of interference was observed at the level of 0.100 mg/l antimony in either sample 5, which was a blank, or sample 4, which contained 0.033 mg/l arsenic.

In general these results can be considered quite satisfactory, with reasonable precision and accuracy over the range tested, reasonable precision near the detection limit, and no indication of antimony interference.

Table II. Arsenic Results
(all concentrations in mg/1)

Laboratory Number	Sample Number							Method*
	1	5	2	6	7	4	3	
110	<.010	<.010	<.010	<.010	–	.02	.04	WQB
130	.002	.000	.005	.005	.017	.034	.064	WQB
160	<.005	<.005	<.005	<.005	.019	.037	.077	WQB
170	<.005	<.005	.005	.005	.015	.035	.065	Color
180	<.005	.006	.005	.012	.017	.030	.069	WQB
190	<.005	<.005	.005	.005	.023	.042	.100	WQB
true value	.000	.000	.005	.005	.015	.033	.071	
antimony interference		.100				.100		
mean					.018	.033	.069	
standard deviation					.0030	.0075	.0195	
relative std. dev.					17%	23%	28%	
mean error					+.0032	0	−.0018	
relative error					+21%	0	− 2.6%	
WQB results only:								
mean					.019	.033	.070	
relative std. dev.					15%	25%	31%	
relative error					+27%	−1.2%	−1.4%	

*WQB = WQB method (Traversy, 1971) – reduction to arsine by zinc/HCl, distillation, color development using silver diethyldithiocarbamate in pyridine.

Color = colorimetric method: addition of sulfuric and nitric acid to sample, concentration by evaporation to fumes of sulfuric and nitric acid, micro distillation, color development using molybdenum blue.

None of the laboratories had any comments regarding the arsenic determination.

Cadmium

Eight laboratories determined cadmium, seven by atomic absorption and one by a colorimetric method using dithizone. Of the seven that used atomic absorption, six followed essentially the method used by the WQB (extraction at pH 3.5 with APDC and MIBK for low level determination) while one used the Sample Boat Technique.

The precision and accuracy were very good, with most relative standard deviations and relative errors below 10% over the entire range tested, both for the WQB method alone and on an overall basis (Table III). There were more outliers than for the other metals, but in the case of samples 2, 4 and 5 this can be attributed to the fact that the bulk of the results were closely grouped.

There were several problems and comments for the higher levels of cadmium, particularly samples 7 and 1, which contained .102 and .204 mg/l respectively. One laboratory commented that the curve of peak height using solvent extraction vs. concentration was not linear above .025 mg/l, and another that it was not linear above .070 mg/l. Two other laboratories obtained very low results for samples 1 and 7; at least one of these laboratories used

extraction for all samples, and the possibility of a dilution or decimal error has been eliminated by subsequent checking.

Other participants, however, claim that the curve is linear and that extraction gives reliable results up to .100 mg/l. The question of whether or not the results obtained by extraction in this range are reliable is academic for most laboratories analyzing natural waters, since the cadmium concentration is normally far below this level.

Laboratory 170 obtained good results with the colorimetric method and reported that results obtained by atomic absorption agreed with the colorimetric values. They did not, however, report their atomic absorption results.

Cobalt

The Water Quality Branch method for cobalt is basically the same as the method for cadmium. Five laboratories determined cobalt in this manner, while a sixth laboratory used the Sample Boat Technique and a seventh used a colorimetric method with 2-nitroso-1-naphthol.

The results for cobalt were very good. There were no outliers despite the fact that the standard deviations were low, meaning that the results were tightly clustered about

Table III. Cadium Results
(all concentrations in mg/1)

Laboratory Number	Sample Number							Method*
	3	4	2	5	6	7	1	
110	<.001	.015	.042	.044	.068	.099	.19	WQB
120	.000	.021 (R)	.057 (R)	.057 (R)	.084	.114	.218	WQB
130	.000	.013	.040	.040	.060	.092	.185	WQB
140	.000	.014	.020 (R)	.028 (R)	.036	.013 (R)	.021 (R)	WQB
160	<.0001	.0150	.0450	.0450	.0700	.1000	.2000	Boat
170	<.005	.015	.045	.045	.065	.100	.200	Color
180	.001	.016	.043	.045	.063	.105	.205	WQB
190	<.001	.014	.045	.046	.052	.052 (R)	.041 (R)	WQB
true value	.000	.015	.045	.045	.068	.102	.204	
mean		.015	.043	.044	.062	.102	.200	
standard deviation		.0010	.0021	.0021	.0140	.0074	.0116	
relative std. dev.		6.7%	4.8%	4.8%	23%	7.2%	5.8%	
mean error		−.0004	−.0017	−.0008	−.0058	−.0003	−.0043	
relative error		−2.9%	−3.7%	−1.9%	−8.5%	−0.3%	−2.1%	
WQB results only								
mean		.014	.043	.044	.061	.103	.200	
relative std. dev.		7.9%	4.9%	6.0%	27%	9.1%	7.5%	
relative error		−4.0%	−5.6%	−2.8%	−11%	+0.5%	−2.2%	

*WQB = WQB method (Traversy, 1971) atomic absorption with extraction at low levels using APDC and MIBK.

Boat = atomic absorption using Sample Boat technique.

Color = colorimetric method: addition of sulfuric acid, concentration to fumes of sulfuric acid, color development using dithizone.

Table IV. Cobalt Results
(all concentrations in mg/l)

Laboratory Number	Sample Number							Method*
	7	2	6	1	4	5	3	
110	<.002	.010	.018	.028	.028	.038	.079	WQB
130	0.000	0.007	0.015	0.026	0.028	0.041	0.085	WQB
140	0.000	0.007	0.017	0.025	0.027	0.036	0.068	WQB
160	<0.001	0.010	0.015	0.030	0.030	0.040	0.085	DDC
170	<.005	.010	.015	.025	.025	.035	.065	Color
180	.005	.010	.020	.030	.029	.040	.079	WQB
190	<.002	.009	.020	.030	.030	.038	.076	WQB
true value	.000	.008	.016	.028	.028	.040	.080	
mean		.009	.017	.028	.028	.038	.077	
standard deviation		.0014	.0023	.0024	.0018	.0022	.0078	
relative std. dev.		16%	13%	8.5%	6.3%	5.8%	10%	
mean error		+.0010	+.0012	-.0003	+.0002	-.0017	-.0033	
relative error		+12%	+7%	-1.0%	+0.5%	-4.3%	-4.1%	
WQB results only:								
mean		.009	.018	.028	.028	.039	.077	
relative std. dev.		18%	12%	8.2%	4.0%	5.1%	8.0%	
relative error		+7.5%	+13%	-0.7%	+1.4%	-3.5%	-3.3%	

*WQB = WQB method (Traversy, 1971): atomic absorption with extraction at low levels using APDC and MIBK.

DDC = similar to WQB method but extraction with sodium diethyldithiocarbamate.

Color = colorimetric method: addition of sulfuric acid, concentration by evaporation to acid fumes, color development with 2-nitroso-1-napthol.

the mean. There was also no significant bias in the results as indicated by the low values for the relative error. The statistics calculated for the laboratories using the WQB method are not significantly different from those calculated for all laboratories.

None of the participants had any comments on the cobalt method.

Mercury

Six laboratories determined mercury. All used flameless atomic absorption, but only three followed the procedure of the Water Quality Branch (Traversy, 1971; Goulden and Afghan, 1970). This procedure involves an oxidation step at an elevated temperature followed by reduction to elemental mercury, all of which is carried out in an automated closed system which eliminates loss of mercury by volatilization during the high-temperature oxidation. The other three laboratories used manual methods which followed the same basic procedure but differed in details such as the type of oxidizing and reducing agents.

Most of the values for relative standard deviation and relative error in Table V are quite high, indicating fair to poor precision and accuracy throughout the range of the test. There were no outliers, but this was due to the wide scatter of all the results rather than lack of bad results.

Results tended to be about 10-20% low on samples 8, 9 and 10 which had the higher levels of mercury; this may correspond to a small loss of mercury during shipment and storage. It should be borne in mind, however, that the samples were shipped at a concentration 10,000 times the final test concentration. It has been our experience that instability of mercury solutions is a problem mainly at low concentrations. Of course, a loss of mercury could occur if participants diluted the samples some time before analyzing them, particularly if the dilutions were stored in glass.

In the case of sample 10, which contained .00180 mg/l Hg as $HgCl_2$, the WQB method alone gave an average value of .00098 mg/l for a relative error of -45%. The other three laboratories as a group had an average of .00167 mg/l on this sample for a relative error of only -7.2%. With sample 9, which also contained .00180 mg/l Hg but as phenyl mercuric acetate, the relative error was about the same for the WQB method as for the other methods (both about -20%). This could indicate that the WQB method recovers inorganic mercury less efficiently than organic mercury at high levels. It remains only an indication, however, because of the small number of laboratories involved.

One participant who did not determine mercury submitted a lengthy comment explaining his reasons for not doing so. He claimed that mercury results obtained by

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Table V. Mercury Results
(all concentrations in mg/l)

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Laboratory Number	Sample Number					Method*
	11	12	8	9	10	
100	†	–	.00030	.00055	.00150	manual
110	<.00005	.00006	.00077	.0016	.00070	WQB
160	–	.0001	.0009	.0016	.0015	ext.
170	<.00005	.00010	.00100	.00200	.00200	reflux
180	.00005	.00020	.00077	.0015	.0010	WQB
190	<.00005	.00025	.00115	.00125	.00125	WQB
true value	.00000	.00012	.00090	.00180	.00180	
source of mercury§	–	Hg Cl$_2$	PMA	PMA	Hg Cl$_2$	
mean		.00014	.00082	.00142	.00133	
standard deviation		.00008	.00029	.00049	.00045	
relative std. dev.		56%	36%	34%	34%	
mean error		+.000022	–.000085	–.00038	–.00048	
relative error		+18%	–9.4%	–21%	–26%	
WQB only:						
mean		.00017	.00090	.00145	.00098	
relative std. dev.		58%	24%	12%	28%	
relative error		+42%	–0.4%	–19%	–45%	

*manual = Similar to WQB method but not automated.

WQB = WQB method (Traversy, 1971): flameless atomic absorption after permanganate sulfuric acid oxidation and reduction in automated, closed system.

ext. = Method of Chau and Saitoh (1970): extraction with dithizone followed by flameless atomic absorption.

reflux = Refluxing with HCl and HNO$_3$ followed by reduction with stannous chloride and flameless atomic absorption.

† = not detected

§ PMA = phenylmercuric acetate

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Table VI. Nickel Results
(all concentrations in mg/l)

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Laboratory Number	Sample Number							Method*
	5	4	1	7	2	3	6	
110	<.002	.007	.008	.022	.028	.088	.099	WQB
130	0.000	0.010	0.008	0.023	0.030	0.100	0.108	WQB
140	0.002	0.010	0.007	0.029(R)	0.041(R)	0.080	0.104	WQB
160	<0.005	0.007	0.007	0.020	0.030	0.090	0.100	DDC
170	<.005	.005	.005	.020	.025	.080	.085(R)	Color
180	0.000	0.006	0.010	0.024	0.027	0.10	0.10	WQB
190	0.002	0.014	0.010	0.020	0.031	0.100	0.100	WQB
true value	.000	.007	.007	.020	.027	.087	.100	
mean		.0084	.0079	.022	.029	.091	.102	
standard deviation		.0031	.0018	.0018	.0023	.0091	.0035	
relative std. dev.		37%	23%	8.2%	7.9%	10%	3.4%	
mean error		+.0014	+.0009	+.0015	+.0015	+.0042	+.0018	
relative error		+20%	+12%	+7.5%	+5.6%	+4.8%	+1.8%	
WQB only:								
mean		.0094	.0086	.022	.029	.094	.102	
relative std. dev.		33%	16%	7.7%	6.3%	9.8%	3.7%	
relative error		+34%	+23%	+11%	+7.4%	+7.6%	+2.2%	

*WQB = WQB method (Traversy, 1971): atomic absorption with extraction at low levels using APDC and MIBK.

DDC = similar to WQB method but extraction with sodium diethyldithiocarbamate.

Color = colorimetric method: addition of sulfuric acid, evaporation to acid fumes, color development with aqueous dimethylglyoxime.

current procedures are of very limited validity, due to poor sample storage stability, significant and variable reagent contamination, and differences in the degree to which different mercury compounds are converted to elementary mercury.

This conclusion may be overly pessimistic but the results of this study show that mercury is definitely one of the poorer tests from the point of view of precision and accuracy. It should be remembered that these results were obtained on simple solutions of mercury compounds in distilled water, with no interfering substances, not even the other four metals which were included in the study. In natural waters the precision and accuracy may be even less.

In view of the many legal and ecological consequences of mercury pollution, it is important that fast and reliable methods for mercury analysis should be available. It is suggested that participants review their procedures carefully to ensure that methods are being followed properly. Possibly further development work to improve the precision of the WQB method in routine operation could be justified as it is the fastest of the methods available. Finally, further investigation by the WQB into means of preserving mercury samples is strongly recommended.

Nickel

Seven laboratories determined nickel. Five used the WQB method, one used a variation of the WQB method using sodium diethyldithiocarbamate, and one used a colorimetric method. (See Table VI).

The results were generally good by all methods. There was a small but consistent positive bias throughout the concentration range which was attributable mainly to the laboratories using the WQB method, as the results of the other two laboratories taken together do not show a significant bias.

One participant commented that he had switched from nickel sulfate to nickel nitrate for standard solutions because the nickel sulfate standard was unstable and gave low results. However, this participant obtained very good results running these samples, which were made from nickel sulfate, against his nickel nitrate standards.

CONCLUSION

The results obtained for arsenic, cadmium, cobalt and nickel were about as good as could be expected in an interlaboratory study of this type. Few serious problems were encountered by any of the participants.

As indicated above, the situation was less encouraging with mercury. Particularly in view of the current importance of mercury pollution, it is disturbing to notice that even at high levels, precision and accuracy are only fair.

It is planned that mercury will be included in another round robin late in 1972 or in 1973 to follow up on the results of this study. In the meantime it is suggested that participants who had problems with this set of samples should review their procedures carefully.

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Participating Laboratories

Environment Canada

Atlantic Region Water Quality Laboratory (Moncton)
Western Region Water Quality Laboratory (Calgary)
Ontario Region Water Quality Laboratory (Burlington)
Great Lakes and Ship Support Laboratory (Burlington)

Alberta Department of the Environment (Edmonton)
B.C. Water Resources Service (Vancouver)
Ministère des Richesses Naturelles (Québec)
Department of Chemical Engineering, University of Ottawa
  (Ottawa)
Cominco Limited (Trail, B.C.)