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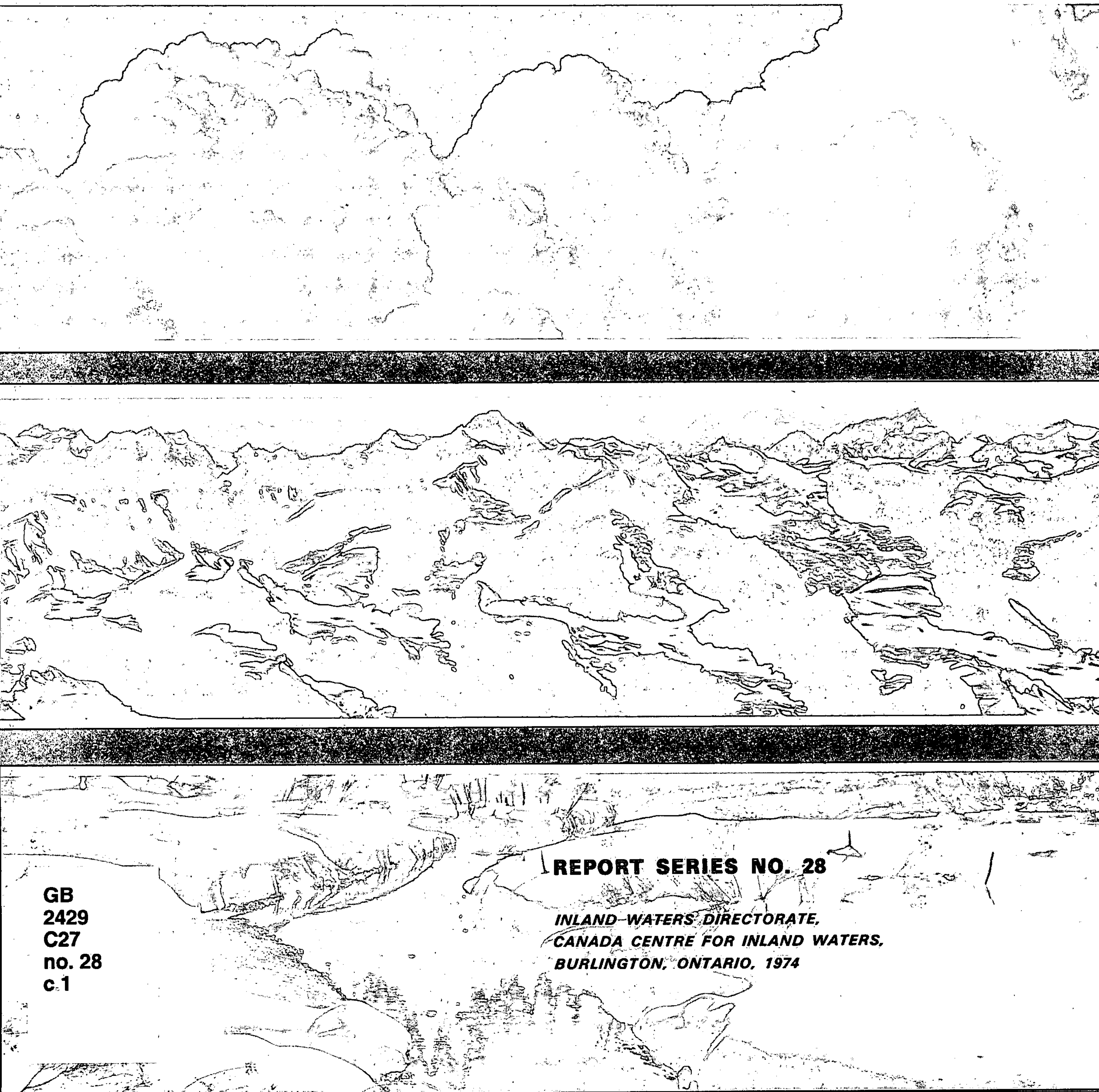
Interlaboratory Quality Control Study No. 6

Specific Conductance, pH, Colour and Residue

D. J. McGirr



REPORT SERIES NO. 28

INLAND WATERS DIRECTORATE,
CANADA CENTRE FOR INLAND WATERS,
BURLINGTON, ONTARIO, 1974

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Summary

Three synthetic samples and two filtered natural samples were sent to eighteen participating laboratories for the determination of specific conductance, pH, colour and filterable residue. The pH of the natural samples was determined with a standard deviation of 0.3 – 0.5 pH units, which is distinctly higher than the value of about 0.1 pH units which is found for buffered synthetic samples. The precision of the colour measurements was fair, as would be expected for the visual method used. Generally good precision was obtained for specific conductance using the conductivity meter. Results for residue were surprisingly poor on the synthetic samples but satisfactory on the natural samples. It appeared from the nature of the results and from the participants' comments that weighing difficulties were an important problem in residue determination.

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INTRODUCTION

The methods evaluated in this study include some of the most common tests performed by water analysis laboratories. These tests are important in the evaluation of waters that are to be used for drinking water or for industrial or recreational purposes.

This is the first study in the Quality Control Program in which natural samples as well as synthetic samples were included. This was done to observe if there was a significant difference in precision between natural and synthetic samples, so as to guard against the possibility of obtaining a low estimate of the standard deviation of a method based on synthetic samples, which may not contain the variety of interferences found in natural samples. Samples of both the natural and the synthetic samples were set aside for storage tests at the time the samples were prepared.

The parameters to be determined were specific conductance, pH, colour, filterable residue and fixed filterable residue, as defined by Traversy [1]. Participants were asked to use their usual procedures, except in the case of residue which is defined by the procedure used. The participating laboratories are listed in Appendix A.

EXPERIMENTAL DESIGN

Samples 1,2 and 5 were synthetic samples while samples 3 and 4 were natural samples.

Sample 1 contained 0.0745 gr KCl per liter of deionized water having conductance less than 1 micromho/cm. This solution has an accepted conductance of 147 micromhos/cm, since KCl solutions are used for conductance standards [2], and also has a known residue content. Dissolved carbon dioxide was not completely removed from the sample before shipment, and the pH when the sample was shipped was approximately 6.3. Since the sample was completely unbuffered, some pH drift may have occurred during shipment. The colour of the sample was, of course, 0.

Sample 2 contained 90 ml of commercial 500-unit platinum-cobalt colour standard solution (Fisher Scientific Co. catalog No. So-P-120) per liter of distilled water. The colour of the sample was 45 units. This strongly acidic solution has a pH well outside the normal operating range and would probably not behave like a natural water sample during solids determination. It was felt best to ask the participants to determine only colour on this sample as the other results would be of doubtful value.

Sample 5 contained 1.00 gr $KHCO_3$ per liter of CO_2-free, deionized water having a specific conductance of less than 1 micromho/cm. This sample has a known specific conductance of 1100 micromhos/cm [3]. The calculated pH of this sample lies between 8.3 and 8.4 (the uncertainty being due to conflicting literature values for pK_1, pK_2 etc.) and a "theoretical value" of 8.35 was originally reported to participants. However, the pH tends to drift slightly higher and the "initial value" of 8.4 given in Table I more nearly represents the pH when shipped. (Nearly all participants obtained a value of 8.4 or higher for this sample). Its colour is 0.

Samples 3 and 4 were natural samples taken in the vicinity of the laboratory at Burlington, Ontario. Sample 3 was taken from the west end of Lake Ontario near the Burlington Canal. Sample 4 was taken from near the mouth of Grindstone Creek, a small creek flowing through Waterdown and Burlington. Both these samples were filtered through a 2 micron glass fiber filter.

All samples were shipped in used polyethylene bottles which had been cleaned by our usual procedure (chromic acid wash followed by several rinses with tap and distilled water). The bottles were rinsed twice with distilled water and once with the sample before filling.

DATA EVALUATION

The method of evaluation of data was similar to that used in previous studies in this series. The results were tested for the presence of outliers using the T-test method outlined by Grubbs [4], in which the difference between the suspected outlier and the mean is expressed as a multiple of the standard deviation, and the multiple is compared to a table of critical values. A 1% significance level was used. Exceptions to this procedure are discussed later.

Once the outliers were rejected, the remaining results were used to calculate the mean, standard deviation, relative standard deviation, mean error and relative error. Relative standard deviation (also known as the coefficient of variation) is the standard deviation expressed as a per cent of the mean. Mean error, also referred to as bias, is the difference between the mean and the true value; relative error is the mean error expressed as a per cent of the true value. In the case of some of the parameters in this study the significance of the "true value" must be understood in order to avoid misinterpreting the tables. These cases are discussed in the appropriate sections below.

All the results reported in Tables I to V were obtained by the Water Quality Branch (WQB) methods [1] except where indicated otherwise. All the statistics generated apply to the WQB methods; since there were very few results obtained by other methods, no statistics for other methods were generated.

The "R" or "S" in the right hand column of Tables I to V indicates whether the participant stated that he determined the parameter routinely or seldom.

DISCUSSION OF RESULTS

pH

It is well known that most natural water samples are subject to pH drift, which is greatest immediately after they are taken. The main difficulty in designing synthetic samples for pH determination in a study such as this, is to design samples that have reasonable storage stability and at the same time are reasonably similar to the type of sample normally analyzed by water analysis laboratories. The $KHCO_3$ solution, sample 5, represents a compromise between these two goals. This solution contains the carbonate-bicarbonate buffer system that is found in most natural waters. At the same time it is more stable than most natural waters, although a slight upward drift due to loss of CO_2 into the air space above the sample does occur. The fact that the average of the reported pH values was 8.54 compared to the initial pH of 8.4 probably represents a slight upward drift in pH rather than a bias in the pH readings. For this reason the value 8.4 is referred to as an "initial value" rather than a "true value" in Table I.

Storage tests indicate that the pH drift is reduced if the bottles are filled to the top with no air space left. Unfortunately it has been the experience of the Water Quality Branch that a small air space is necessary to act as a shock absorber during transit, and that if bottles are filled completely the incidence of breakage is much higher.

Table I. pH

Analytical Results in pH units

Laboratory No.	Sample No. 1	3	4	5	Routine or Seldom
601	6.8	7.7	7.9	8.64	r
602	7.2	6.5	6.5†	8.3	r
603	5.9	7.8	7.8	8.5	
604	5.64	7.65	7.50	8.50	r
605	9.45†	7.80	7.55	8.42	r
606	4.4	7.7	7.5	8.5	r
607	6.21	7.85	7.82	8.68	r
608	5.0	7.7	7.5	8.5	r
609	7.2	6.8	7.9	8.4	r
610	5.25	7.71	7.76	8.45	r
612	6.0	7.9	7.5	8.5	r
613	5.4	7.8	8.2	8.7	r
614	6.8	8.2	8.3	8.8	r
615	5.9	7.6	7.5	8.4	r
616	6.04	7.88	8.24	8.60	r
617	5.4	7.7	7.5	8.5	s
618	7.00	6.40	7.50	8.65	r
619	4.7	7.8	8.0	8.6	r
Average	5.93	7.58	7.76	8.54	
Std. Deviation	0.86	0.49	0.29	0.13	
Initial Value	6.3			8.4	
Other Methods:					
602*	6.5	7.7	7.7	8.4	

*Obtained using Hach Chemical Co. wide-range indicator soln (pH 4-10)

†Indicates outliers

Samples 3 and 4, the natural samples, were stored in the laboratory for two to three weeks and filtered before being filled off for shipment. It was felt that any rapid drift in pH in these samples would have occurred during these operations, so that the samples would have reached a point of near stability by the time they were shipped. In practice it was found that the samples drifted by less than 0.5 pH units in a 6-month period after the shipment date, so that there should have been negligible drift between shipment and analysis if analysis was not delayed. Of course, the samples when shipped no longer represented the natural waters from which they were taken, but this is not important in determining the precision and comparing test results.

The standard deviation on these "stabilized" natural samples was 0.3 to 0.5 pH units. The variability of fresh natural samples may be a little greater owing to faster pH drift, which is one of several factors contributing to the uncertainty of pH readings. This is probably the best precision that can be expected on routine samples of natural waters that are shipped to the laboratory. Field testing by skilled personnel would improve the accuracy (by avoiding drift) but not necessarily the precision.

The standard deviation of 0.13 units for sample 5 (the $KHCO_3$ solution) demonstrates the extent to which data obtained from simple buffer solutions may underestimate the standard deviation to be expected with natural samples. The results for sample 1 demonstrate the opposite extreme, a completely unbuffered sample. This sample was intended, of course, primarily as a conductivity standard, and the pH may have drifted slightly during shipment. Nevertheless, participants who obtained a result far from the mean on this sample should investigate their technique, as poorly buffered natural samples are occasionally encountered. One common source of error in a poorly buffered sample is inadequate cleaning of the buffer solution or the previous sample from the electrode, causing the meter to give a reading between that of the sample and that of the buffer or previous sample.

Colour

Colour by the visual comparison method was determined with reasonable accuracy on the three samples with a known value. These were sample 2, a standard with a colour of 45 units, and samples 1 and 5 which were synthetic samples in distilled water having a colour of 0.

Table II. Colour

Analytical Results in Color Units

Laboratory No.	Sample No. 1	2	3	4	5	Routine or Seldom
601	<5	40	5	40	<5	s
602	0	55	11	48	0	s
604	0	45	5	40	5	s
605	0	40	<5	35	0	r
606	5	60	10	55	1	r
608	<5	30	<5	20	<5	r
610	1	45	2	40	1	s
612	<5	40	<5	30	<5	r
613	0	35	0	30	0	r
614	<5	35	<5	25	<5	r
616	0	38	2	35	0	r
618	<5	40	<5	30	<5	r
619	5-10	40	5-10	30-40	<5	r
True Value	0	45	–	–	0	
Average	<5	42	Appr. 5	36	<5	
Standard Deviation	–	8.1	–	9.3	–	
Mean Error	–	−3	–	–	–	

The precision was only fair for the two samples for which precision could be calculated (samples 2 and 4 in Table III). The lack of precision is probably inherent in the visual test method used rather than being due to any failing of the participating laboratories.

There was no significant change in colour in these samples during storage.

Specific Conductance

Good precision and accuracy were found for this test, with the exception of laboratory No. 604, which demonstrated a severe positive bias in all results, which was later found to be due to a calculation error. The relative error on the known samples was negligible, and the relative standard deviation was in the range 6-10% throughout the range tested. The standard deviation for the natural samples was about the same as for the synthetic samples (see Table III).

Table III. Specific Conductance

Analytical Results in umhos/cm

Laboratory No.	Sample No. 1	3	4	5	Routine or Seldom
601	160	300	660	1200	r
602	165	474R	781	1273	r
603	147	359	650	1110	r
604	524.3R	1267R	2264R	3861R	s
605	184	351	633	1098	r
606	145	350	620	1140	r
607	151	364	663	1140	s
608	130	326	615	1010	r
610	148	350	630	1075	r
612	147	345	622	1068	r
613	147	353	616	1067	r
614	156	365	650	1130	r
615	125	300	550	950	s
616	160	368	659	1133	r
617	136	340	520	990	s
618	162	379	650	1150	r
619	145	350	640	1110	r
True Value	147	–	–	1100	
Average	150.5	347	635	1103	
Std. Deviation	14.5	23	55	79	
Relative Std. Deviation	9.5%	6.6%	8.7%	7.2%	
Mean Error	3.5	–	–	3	
Relative Error	2.4%	–	–	0.3%	

There was no appreciable change in specific conductance during storage.

Residue and Fixed Residue

Most of the participants used the Water Quality Branch methods [1] for residue. Participants who normally use a different method (i.e. different drying conditions) were requested to submit results for both their own method and the WQB method. Two laboratories submitted double sets of results in accordance with this request. The results obtained with the WQB method by these two laboratories are included in the main part of Tables IV and V and were used in the calculations. The results obtained by the two laboratories with their own methods are inserted at the bottom of Tables IV and V, and were not used in the calculations.

Table IV. Residue

Analytical Results in mg/l

Laboratory No.	Sample No. 1	3	4	5	Routine or Seldom
601	84	239	447	816	–
602	73.33	207.06	429.46	716.39	s
603	105	224	461	802	r
604	78.5	227	395.5	755.9	–
607	83	228	429	799	s
608	76	225	417	910	r
610	105	251	349	751	r
612	145R	193	430	901	r
613	4.5R	214	419	766	–
614	77	223	442	–	r
615	74	210	415	830	r
616	80	229	453	865	r
617	74.0	198.0	397.0	525.3	s
618	85	245	385	695	r
619	109	188	438	828	r
True Value	75	–	–	(690)*	
Average	84.9	220	420	783	
Std. Dev.	12.8	18.4	29.3	97	
Relative Std. Dev.	15%	8.4%	7.0%	12%	
Mean Error	9.9	–	–	–	
Relative Error	13%	–	–	–	
Other Methods:					
603†	82	229	453	799	
614§	76	224	444	–	

*Assuming conversion of bicarbonate to carbonate (not quantitative in practice).

†Dried one hour at 103-105°C.

§Dried one hour at 105°C.

In the discussion below, "residue" refers to the residue obtained by drying overnight at 105°C, and "fixed residue" refers to the residue obtained by igniting at 550°C for 2$^1/_2$ hours. In both cases filterable (dissolved) residue was determined. Since the samples were either synthetic or filtered natural samples, nonfilterable (suspended) residue was negligible.

In the case of sample 5, the $KHCO_3$ sample, "theoretical" values were calculated based on the assumption that the bicarbonate would be decomposed to carbonate during residue determination and to oxide during fixed residue determination. These theoretical values are given in Tables IV and V for reference; however, it is well known that the conversions are far from quantitative in practice, so participants should compare their results to the average, not to the "theoretical" value.

For sample 1, Laboratory 612 submitted results well above the mean and Laboratory 613 submitted results well below the mean. The case of a suspected outlier on both sides of the mean can be treated by the W/S statistic described on page 7-9 of Grubbs' paper [4]. This involves calculating the ratio of the range to the standard deviation of the entire sample and comparing the ratio to a table of critical values. Using this test the results from Laboratories 612 and 613 for residue are calculated to be outliers. The use of this technique for sample 1 is not strictly correct because the distribution of the results is not normal; however, the two results were so far from the mean that they were judged to be outliers regardless of the sample

Table V. Fixed Residue

Analytical Results in mg/l

Laboratory No.	Sample No. 1	3	4	5	Routine or Seldom
601	66	148	321	689	–
602	35.33	115.33	239.46	621.33	s
603	93	155	261	711	s
604	78.5	211	381	755.9	s
607	57	160	308	717	r
608	73.6	168	305	826	r
610	74	175	245	653	r
612	142R	161	297	805	r
613	4.0R	148	293	694	r
614	71	142	277	–	–
615	73	180	350	730	s
617	48.0	141.3	294.0	390.0	s
618	35	60	80R	460	s
True Value	75	–	–	(471)*	
Average	64.0	151	298	671	
Std. Dev.	18.3	35.6	40.9	129	
Relative Std. Dev.	29%	24%	14%	19%	
Mean Error	-11.0	–	–	–	
Relative Error	15%	–	–	–	
Other Methods:					
603†	68	148	275	730	
614§	74	158	316	–	

*Assuming conversion of carbonates to oxides (not quantitative in practice).

†Ignited 20 min. at 600°C.

§Ignited one hour at 550°C.

distribution. The corresponding results for fixed residue were also rejected as they obviously suffered from the same experimental difficulties.

It was rather surprising that the outliers were obtained for sample 1, which is a simple solution of KCl in water, and that even with the outliers rejected the precision for this sample was the worst of the four. In fact, the precision was best for the two natural samples and worst for the two synthetic samples, which is the reverse of the usual situation.

The results from the two laboratories that determined residue by drying one hour instead of overnight did not differ appreciably from the others. Similarly, the results obtained by using different ignition conditions for fixed residue did not differ appreciably from the others. In fact, of fourteen results for residue and fixed residue obtained by "other methods", only one was more than one standard deviation from the mean of the results obtained by the Water Quality Branch method. This suggests that minor deviations in drying conditions are not the main source of variability in the test method. (Drying conditions might have been expected to be critical because of partial decomposition of bicarbonates, slow release of adsorbed or occluded water, etc.)

It is probable that weighing errors are at least as important as drying conditions. In commenting on the residue determination, two laboratories mentioned difficulties in obtaining constant weights. Contamination (by dust, etc.) during the evaporation step or in the oven could also be a factor, especially in laboratories where many other tests are being performed at the same time, as is commonly the case.

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APPENDIX A

LIST OF PARTICIPANTS

Environment Canada:

Pacific Region Water Quality Branch (Vancouver)
Western Region Water Quality Branch (Calgary)
Water Quality Laboratory & Network (Ontario Region):
  - Analytical Services Section (Burlington)
  - Great Lakes and Ship Support Laboratory (Burlington)

Atlantic Region Water Quality Branch (Moncton)
Fisheries Service Laboratory (Vancouver)
Environmental Protection Service, Atlantic Region (Halifax)

Provincial Government Laboratories:

Water Resources Service, B.C. Department of Lands, Forests and Water Resources, Vancouver
Pollution Control Laboratory, Alberta Department of the Environment, Edmonton
Environmental Protection Branch, Manitoba Department of Mines, Resources and Environmental Management, Winnipeg
Service de la Qualité des Eaux, Ministère des Richesses Naturelles, Québec
Service des Laboratoires, Ministère des Affaires Sociales, Québec
Soil and Feed Testing Laboratories, P.E.I. Department of Agriculture, Charlottetown

Industrial Laboratories:

Placer Development Ltd., Vancouver
Cominco Ltd., Trail, B.C.
Chemex Ltd., Calgary

Universities:

Department of Chemistry, University of Saskatchewan, Regina
Department of Biology, Dalhousie University, Halifax