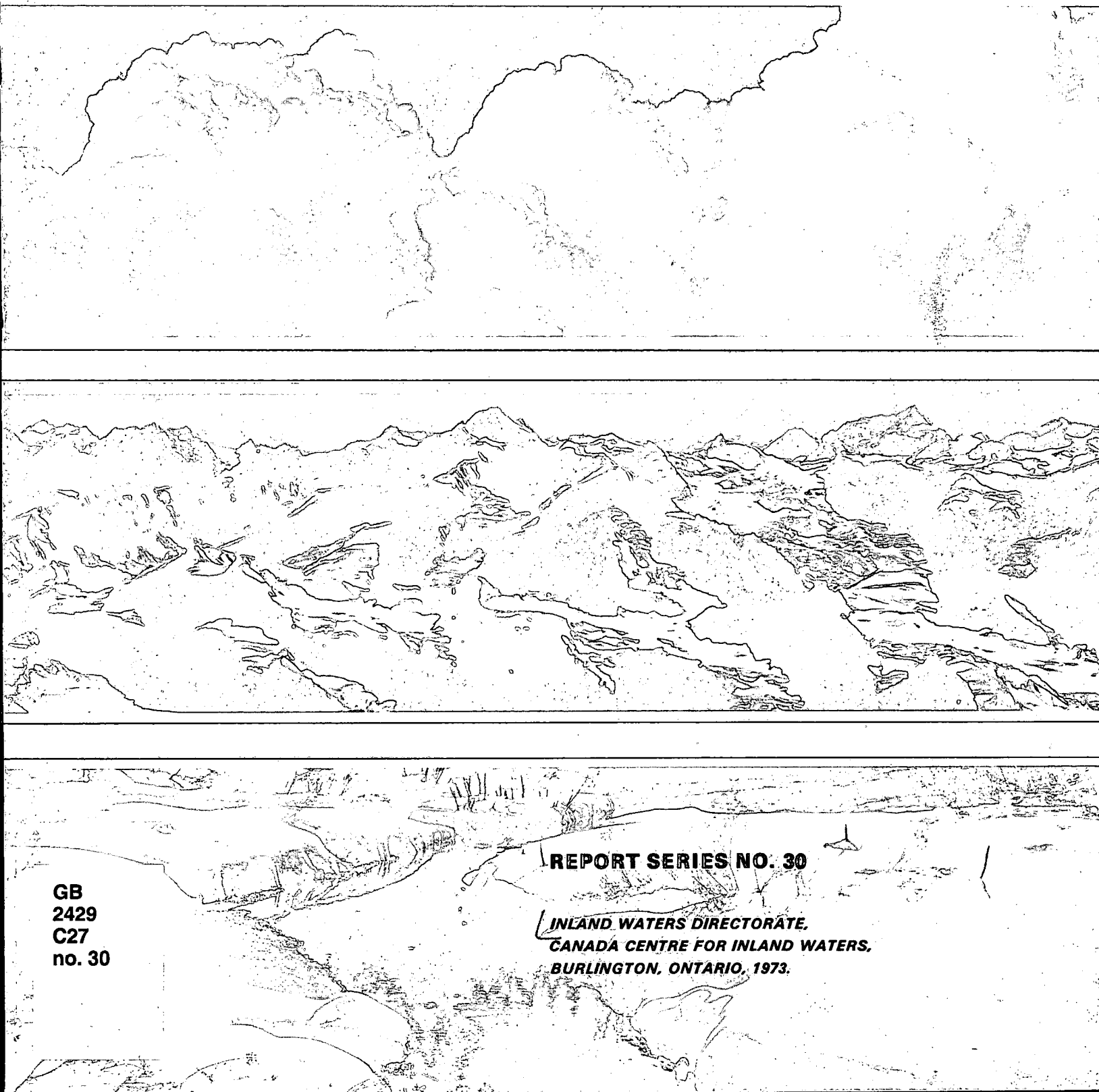




Interlaboratory Quality
Control Study No. 7
Major Cations and Anions

D. J. McGirr and R. W. Wales



REPORT SERIES NO. 30

INLAND WATERS DIRECTORATE,
CANADA CENTRE FOR INLAND WATERS,
BURLINGTON, ONTARIO, 1973.

GB
2429
C27
no. 30



Environment
Canada

Environnement
Canada

Interlaboratory Quality Control Study No. 7

Major Cations and Anions

D. J. McGirr and R. W. Wales

REPORT SERIES NO. 30

***INLAND WATERS DIRECTORATE,
CANADA CENTRE FOR INLAND WATERS,
BURLINGTON, ONTARIO, 1973.***

©
Information Canada
Ottawa, 1974

Cat. No.: En 36-508/30

CONTRACT # KL 327-4-8069
THORN PRESS LIMITED

Contents

	Page
SUMMARY	v
INTRODUCTION	1
EXPERIMENTAL DESIGN	1
EVALUATION OF DATA	1
DISCUSSION OF RESULTS	1
Calcium	1
Magnesium and total hardness	1
Sodium	2
Potassium	2
Total alkalinity	2
Chloride	2
Sulfate	2
Nitrate	2
STORAGE STABILITY	3
CONCLUSION	3
ACKNOWLEDGEMENTS	3
REFERENCES	3
OTHER REPORT SERIES PUBLICATIONS ON INTERLABORATORY STUDIES	4
APPENDIX A. LIST OF PARTICIPANTS	15

Tables

I. Calcium by titration, WQB method	7
II. Calcium by atomic absorption and other methods	7
III. Magnesium	7
IV. Total hardness	7
V. Sodium by flame emission photometry	8
VI. Sodium by atomic absorption	8
VII. Potassium by flame emission photometry	8
VIII. Potassium by atomic absorption	8
IX. Total alkalinity by WQB Potentiometric Method	9
X. Total alkalinity by other methods	9
XI. Chloride by thiocyanate method	9
XII. Chloride by silver nitrate and other methods	9

Tables (cont.)

	Page
XIII. Sulfate by WOB titrimetric method	10
XIV. Sulfate by turbidimetric methods	10
XV. Sulfate by gravimetric and colorimetric methods	10
XVI. Nitrate by WOB cadmium reduction method	10
XVII. Nitrate by other methods	11
XVIII. Three-month storage tests on sample 3	11
XIX. Comparison of results from local and distant laboratories	11

Summary

Two synthetic samples and one natural water sample were distributed to twenty-two participating laboratories for determination of calcium, magnesium, sodium, potassium, alkalinity, chloride, sulfate and nitrate. The results for calcium, magnesium and alkalinity were good even though the natural sample was unstable for these three parameters. The precision for calcium and total hardness was much better by titration than by atomic absorption. Precision and accuracy were good for sodium and potassium, and precision was about the same whether atomic absorption or flame emission photometry was used. Precision for nitrate at low levels was only fair by any of the variety of methods used, although the cadmium reduction method was satisfactory at higher levels. Sulfate was also determined by a variety of methods, but precision was satisfactory for most of them. Chloride was determined with acceptable precision.

The natural sample was supersaturated with carbonates and therefore was unstable with respect to calcium, magnesium and alkalinity. It was stable, however, with respect to the other parameters and the synthetic samples were stable with regard to all parameters tested over a three-month period of storage. Precision and accuracy were not seriously adversely affected by either sample instability or long-distance shipment.

Interlaboratory Quality Control Study No. 7

Major Cations and Anions

D. J. McGirr and R. W. Wales

INTRODUCTION

The major ions covered in this study define the general nature of most natural waters and are very commonly determined. The cation parameters were determined in the first study in this series (Quality Control Study No. 1), whereas the anions have never been included in these studies, with the exception of nitrate which was included in Quality Control Study No. 2.

EXPERIMENTAL DESIGN

The study consisted of two synthetic samples in distilled water and one natural sample. The synthetic samples contained the parameters to be tested at two levels — levels within the range in which these parameters are present in typical natural waters. The natural sample was taken from Hamilton Harbour and was filtered through a 1-micron glass fiber filter before being subdivided. All samples were shipped in used polyethylene bottles which had been cleaned by our usual procedure: chromic-sulfuric acid wash followed by several rinses with tap water and distilled water. Following the normal procedure of the Water Quality Branch (WQB), no preservatives were added.

Participants were asked to analyse the samples by their usual methods, and in the case of magnesium were asked to report either magnesium or total hardness.

EVALUATION OF DATA

The results received for each parameter were grouped according to the test method used. Each group of results was examined separately for outliers, and a separate set of statistics was calculated for each test method for which four or more sets of results were received. For many of the parameters, separate statistics could be calculated for two or more test methods. (A few laboratories used more than one method for some parameters, in which case their results were tabulated as if they had come from different laboratories.)

Outliers were rejected by the method of Grubbs [1], which was used in some previous studies in this series. After rejection of outliers (indicated by an R in the tables), the mean, standard deviation, relative standard deviation, mean error and relative error were calculated for each test for which four or more results were submitted. The *relative*

standard deviation is the standard deviation expressed as a percent of the mean. The *mean error* is the difference between the mean and the true value, and the *relative error* is the mean error expressed as a per cent of the true value.

DISCUSSION OF RESULTS

Calcium

Most of the participants determined calcium by titration or atomic absorption (eight laboratories used each method), both described in the WQB laboratory manual [2]. The atomic absorption method resulted in poorer precision and lower answers than the titration method (see Tables I and II). Although both methods are acceptable and are considered equivalent in many laboratory manuals, except with regard to interferences, the difference in precision is sufficient to justify a recommendation that titration should be employed unless there is a specific reason for using atomic absorption.

Three laboratories used flame emission spectroscopy to determine calcium. There were not enough results to calculate statistics, but the method does not appear to offer any advantage over the other two. One laboratory used atomic absorption with a potassium salt added to suppress ionization, a minor variation from the WQB method which used lanthanum chloride. The results were quite comparable to the other atomic absorption results.

Magnesium and Total Hardness

The results for magnesium and total hardness were analogous to those for calcium in that the titration procedure yielded greater precision than the atomic absorption procedure. (It is necessary to compare the relative standard deviations in Tables III and IV to observe this, as the standard deviations are not expressed on the same basis in both tables.) The relative standard deviation for total hardness in sample 1, calculated from the atomic absorption results for calcium and magnesium, would be about 14%, whereas the titration method gave a relative standard deviation of 2.3% (Table IV). Therefore, titration is distinctly preferable for total hardness. Of course if magnesium is specifically requested, it is generally still necessary to use atomic absorption or some other direct method, as the titration procedure is not specific to calcium and magnesium alone.

The titration method and the atomic absorption

method are both described in the WQB manual [2]. The one participant who used the automated EDTA method [3] obtained satisfactory results. Flame emission also gave reasonable results.

Sodium

The majority of participants determined sodium by flame emission photometry, and the results were satisfactory. All results obtained by flame emission were used to calculate the statistics in Table V, although some were obtained by the automated Technicon procedure [4] and others by various manual procedures. The statistics calculated separately for the automated method (participants 708, 711, 714, 717 and 721) are similar to the overall statistics except that the precision is somewhat better, as would be expected.

Those who used atomic absorption (Table VI) also obtained satisfactory results. There is not much to choose between the two methods as far as precision and accuracy are concerned.

Potassium

The results for potassium (Tables VII and VIII) were very similar to those for sodium. Nearly all participants used the same method for potassium that they used for sodium, and obtained a similar level of precision.

Total Alkalinity

The majority of the participants determined total alkalinity by the WQB potentiometric titration method [2] and obtained reasonable precision (Table IX) with a slight negative bias which may have been due to sample deterioration (see "Storage Stability" following). Two laboratories used the automated methyl orange method [5], which gave satisfactory results. The remainder used manual titration with a variety of indicators, some of which were rather erratic (Table X).

Laboratory 722 which had high results subsequently informed us that they had discovered an error of a factor of 2 in their calculations. Their results would be close to the true value if this correction were made.

Chloride

More than half of the participants determined chloride by the thiocyanate method, mostly in its automated version as used by the WQB [2]. This method gave good precision with a slight negative bias, for which there was no obvious explanation, relative to both the theoretical values and the average of the results obtained by the other methods. The two participants using the manual thiocyanate method obtained satisfactory results. Their results are not included in the statistics in Table XI.

The results obtained by the silver nitrate method [6] showed less precision (Table XII). This may be partly because of variations in details of the procedures used, and

also because laboratories not using the automated method probably do the test less frequently and therefore have less experience in its application.

The one participant who used the specific ion electrode obtained only fair results.

Sulfate

In contrast to all the other parameters in this study, there was no single method for sulfate that was used by anything close to a majority of the participants. This probably indicates that no one method has been found entirely satisfactory for a wide range of applications, and that individual laboratories have made various compromises among speed, precision and freedom from interferences.

At the time that this study was undertaken, the methylthymol blue method using AutoAnalyzer II equipment [7] was available but had not been widely adopted. The method was used by two participants, only one of whom (Laboratory 721) was using it routinely. The results were not too encouraging (bottom of Table XV), although the sample is too small to permit any conclusions. The methylthymol blue method is faster than most of the current methods; if it comes into widespread use, it would be interesting to undertake another study on sulfate.

Of the other methods, the WQB titrimetric method [2] gave the best precision and accuracy in these samples (Table XIII). The turbidimetric method, either manual [6] or automated, gave poorer but still acceptable results (Table XIV), while the one participant who performed a turbidimetric analysis using a field kit obtained quite high results.

The gravimetric method [6] yielded about the same precision as the turbidimetric method on these samples (Table XV). The laboratories that used this method did not indicate whether their precipitate was air-dried or ignited.

Nitrate

About half of the participants determined nitrate by the cadmium reduction method, mostly using the automated version as used by the WQB [2]. Laboratories 704 and 707 used methods which were modified for sewage and other high level samples. These methods follow the same chemistry as the WQB method but have a higher detection limit and lower precision, and therefore, the results have been omitted from the precision and accuracy calculations in Table XVI. Laboratory 716 used a slight variation from the WQB method, with sulfanilic acid in place of sulfanilamide in the diazotization step. The remaining laboratories used a variety of miscellaneous methods and their results are shown in Table XVII.

In this study the two synthetic samples had a low level of nitrate, close to the detection limit, while the natural sample had a high level due to the effect of a sewage treatment plant outfall in the area where the sample was taken. A previous study in this series (Study No. 2) had

included synthetic samples at intermediate nitrate levels. None of the methods used in this study appeared to give precise results at levels below 0.05 mg/l. The WQB method gave acceptable precision at levels of 0.05 mg/l and higher in both studies.

None of the methods in Table XVII appeared to offer any advantage over the WQB method for the type of samples analyzed in this study, although some of them could well be the method of choice in the presence of certain interferences. The specific ion electrode gave very poor results. In fact, one of the participants who used the specific ion electrode has advised they are abandoning this method and reverting to the WQB method. Most of the methods tended to give very high results on the low-level samples.

In Table XVI, the results for sample 3 from Laboratories 708 and 718 were rejected as outliers by the method of Tietjen and Moore [8].

STORAGE STABILITY

Aliquots of samples 1 and 3 were stored in the laboratory for three months in the same kind of bottle that was used for shipment, then re-analyzed. Sample 1 showed no significant change in the values of any of the parameters. The data for sample 3, the natural sample, are shown in Table XVIII. In this table the final values are the results of a single determination in our own laboratory, while the initial values are the averages of the results obtained by the participants who used the same method as was used to obtain the final results.

Sample 3 showed no significant change in the values for sodium, potassium and chloride, a minor decrease in the case of sulfate and nitrate (possibly due to biological activity) and a large decrease in the case of calcium, magnesium and alkalinity. This latter decrease, accompanied by an increase in pH from about 7.9 to 8.9 and by the formation of a precipitate, undoubtedly occurred because the original sample was supersaturated with respect to calcium and magnesium carbonates. Supersaturation is often encountered in the lower Great Lakes, although sample 3 was quite unintentionally more supersaturated and, therefore, more unstable than is commonly found.

It is noteworthy that the instability of the sample did not lead to a drastic decrease in the precision. The standard deviation for calcium and magnesium is a little higher in sample 3 than in sample 1 (after making allowance for the fact that the standard deviation will normally increase gradually as the level of the parameter increases). On the other hand, no such effect was noted for alkalinity. This is surprising because the samples were shipped in winter and may have been frozen en route; other work done in our laboratories [9] has shown that alkalinity is the parameter most sensitive to freezing among the parameters tested in this study.

A further analysis of the effect of storage and shipment can be made by comparing the results of the three "local" participants (the three participants located in the CCIW complex in Burlington) with the three most "distant" participants (the three laboratories located in Vancouver; their samples are shipped the longest distance and through the coldest climate). This is done in Table XIX (magnesium and total hardness were omitted due to insufficient results). The means of the local laboratories approximated the true values for sample 1, whereas the distant laboratories were slightly below the true value, and were generally slightly lower than the local laboratories for both samples. However, the difference is less than 5% in most cases, and the distant laboratories did not obtain more outliers or show noticeably less precision than the local laboratories. It is surprising that sample 1 showed a larger difference than sample 3 in this table, in spite of the fact that sample 1 had excellent storage stability and sample 3 did not.

CONCLUSION

The parameters covered in this study were analyzed with an acceptable degree of precision and accuracy, with some minor exceptions as noted. Also the precision and accuracy were not seriously affected by long distance shipment, nor were they greatly affected by the fact that one of the samples was unstable in storage. These results indicate that, in general, reasonable confidence can be placed in data for these parameters obtained by analysis of samples shipped to the laboratory, as is customarily done in the WQB network and surveillance programs. Moreover, with the great majority of WQB network samples, the sample instability, distance of shipment, and time of storage are much less than the conditions represented by Tables XVIII and XIX.

ACKNOWLEDGEMENTS

The assistance of Mr. D. P. Sturtevant regarding the storage stability studies and the cooperation of all the participants listed in Appendix A is gratefully acknowledged.

REFERENCES

- [1] Grubbs, F. E. Procedures for Detecting Outlying Observations in Samples. *Technometrics* 11: 1-21 (1969).
- [2] Traversy, W. J. Methods for Chemical Analysis of Waters and Wastewaters. Department of the Environment, Inland Waters Branch, Ottawa, (1971).
- [3] Technicon Corp. Industrial AutoAnalyzer Method 25-69W (1969).
- [4] Technicon Corp. AutoAnalyzer Method N-20b (1967).
- [5] Technicon Corp. Industrial AutoAnalyzer Method 111-71W (1971).

- [6] American Public Health Association. Standard Methods for the Examination of Water and Wastewater, 13th ed. (1971).
- [7] Technicon Corp. Industrial AutoAnalyzer Method 118-71W (1971).
- [8] Tietjen, G. L. and R. H. Moore. Some Grubbs-Type Statistics for the Detection of Several Outliers. *Technometrics* 14: 583-597 (1972).
- [9] Philbert, F. J. A Comparative Study of the Effect of Sample Preservation by Freezing Prior to Chemical Analysis of Great Lakes Waters. Presented to the 16th International Association for Great Lakes Research Conference in Huron, Ohio (1973).

OTHER REPORT SERIES PUBLICATIONS ON INTERLABORATORY STUDIES

Report Series No. 12. Traversy, W.J. and R.W. Wales. Interlaboratory Quality Control Study No. 1; Calcium, Total Hardness, Sodium and Potassium. Inland Waters Branch, Department of the Environment, Ottawa. 1970.

Report Series No. 19. Wales, R.W. and W.J. Traversy. Interlaboratory Quality Control Study No. 2; Total Phosphate, Organic Nitrogen, Nitrate Nitrogen and Organic Carbon. Inland Waters Branch, Department of the Environment, Ottawa. 1972.

Report Series No. 21. Wales, R.W. and D.J. McGirr. Interlaboratory Quality Control Study No. 3; Copper, Chromium, Lead, Manganese and Zinc. Inland Waters Branch, Department of the Environment, Ottawa. 1973.

Report Series No. 25. McGirr, D.J. and R.W. Wales. Interlaboratory Quality Control Study No. 4; Arsenic, Cadmium, Cobalt, Mercury and Nickel. Inland Waters Branch, Department of the Environment, Ottawa. 1973.

Report Series No. 26. Wales, R.W. and D.J. McGirr. Interlaboratory Quality Control Study No. 5; Chromium, Iron, Molybdenum and Vanadium. Inland Waters Branch, Department of the Environment, Ottawa. 1973.

Report Series No. 28. McGirr, D.J. Interlaboratory Quality Control Study No. 6; Specific Conductance, pH, Color and Residue. (In press).

Tables

Table I. Calcium by Titration, WQB Method

(All results in mg/l.)

Laboratory Number	Sample Number		
	1	2	3
702	36.	8.8	54.4
705	39.0	10.4	55.8
706	38.	10.	60.
711	40.3	10.8	64.6
714	42.5	10.0	60.1
716	37.1	9.0	54.1
717	39.6	9.9	59.6
718	37.7	8.87	58.1
True value (mg/l)	38.99	9.40	—
Mean (mg/l)	38.78	9.72	58.34
Standard deviation (mg/l)	2.04	0.75	3.52
Relative std.dev. (%)	5.3%	7.7%	6.0%
Mean error (mg/l)	-0.21	0.32	—
Relative error (%)	-0.6%	3.4%	—

Table III. Magnesium

(All results in mg/l)

All results obtained by WQB atomic absorption method [2]
unless indicated otherwise

Laboratory Number	Sample Number		
	1	2	3
702	8.6	1.9	13.4
703	7.55	1.65	10.6
704	8.6	2.0	14.0
706	4.8 R	1.2	6.0
707	7.8	1.6	10.7
708	7.2	1.5	—
712	8.4	1.7	12.2
715	7.8	1.7	12.
720	8.6	1.5	14.3
721	7.9	1.6	11.3
True value (mg/l)	8.00	1.60	—
Mean (mg/l)	8.05	1.64	11.61
Standard deviation (mg/l)	0.52	0.22	2.50
Relative std.dev. (%)	6.4%	14%	22%
Mean error (mg/l)	0.05	0.04	—
Relative error (%)	0.6%	2.2%	—
701*	8.2	1.7	11.7
709*	7.7	1.6	11.
718*	7.9	1.9	11.7
718†	8.86	2.55	13.8
722§	8.4	1.6	12.

*Flame emission

†Calculated

§Atomic absorption, potassium added to suppress ionization

R Indicates outlier

Table II. Calcium by Atomic Absorption and Other Methods

(all results in mg/l)

Laboratory Number	Sample Number		
	1	2	3
703	33.65	9.0	48.6
704	27.0	7.1	43.0
707	58.1 R	14.4	57.9
708	34.3	9.0	56.5
712	35.	8.7	54.
715	37.	9.6	58.
720	40.5	10.8	78.
721	37.	8.0	55.
True value (mg/l)	38.99	9.40	—
Mean (mg/l)	34.92	9.58	56.38
Standard deviation (mg/l)	4.17	2.23	10.14
Relative std.dev. (%)	12%	23%	18%
Mean error (mg/l)	-4.07	0.18	—
Relative error (%)	-10%	1.9%	—
Other methods:			
701*	35.0	9.6	50.4
709*	42.0	5.6	56.
718*	43.1	9.9	53.6
722†	38.	9.0	60.

*Flame emission spectroscopy

†Atomic absorption, potassium added to suppress ionization

R Indicates outlier

Table IV. Total Hardness

(all results in mg/l as CaCO₃)

All results obtained by WQB titration method
unless otherwise indicated

Laboratory Number	Sample Number		
	1	2	3
705	125.5	31.9	183.7
710	131.	32.	196.
711	150 R	31.3	198.
714	128.	29.3	191.
715	124.	31.	196.
716	127.5	37.5 R	194.0
717	133.	29.2	197.
718	130.5	32.6	202.
719	127.	30.	191.
True value (mg/l)	130.3	30.06	—
Mean (mg/l)	128.3	30.91	194.3
Standard deviation (mg/l)	3.0	1.28	5.2
Relative std. dev. (%)	2.3%	4.2%	2.7%
Mean error (mg/l)	-2.0	0.85	—
Relative error (%)	-1.5%	2.8%	—
Other methods:			
702*	126.	30.	192.

*Technicon EDTA method [3]

R Indicates outlier

Table V. Sodium by Flame Emission Photometry
(all results in mg/l)

Laboratory Number	Sample Number		
	1	2	3
702	52.	4.2	30.
703	51.5	4.55	29.75
704	55.	42. R	35.
706	43.5	4.0	28.3
708	49.0	4.4	29.5
709	23.6 R	5.2	24.5
710	52.0	4.2	30.0
711	43.0	4.2	29.8
712	52.	4.	29.
714	54.2	4.5	32.8
717	52.0	5.4	30.0
718	59.4	4.9	39.4
721	54.	4.4	30.
True value (mg/l)	52.99	4.30	-
Mean (mg/l)	51.47	4.50	30.62
Standard deviation (mg/l)	4.59	0.45	3.54
Relative std. dev. (%)	8.9%	10%	12%
Mean error (mg/l)	-1.52	0.20	-
Relative error (%)	-2.9%	4.6%	-

R Indicates outlier

Table VI. Sodium by Atomic Absorption
(all results in mg/l)

Laboratory Number	Sample Number		
	1	2	3
707	52.0	4.5	32.5
715	48.	4.0	28.
718	46.9	4.3	21.8
720	56.7	3.9	32.9
722	51.	4.0	28.
True value (mg/l)	52.99	4.30	-
Mean (mg/l)	50.92	4.14	28.64
Standard deviation (mg/l)	3.85	0.25	4.49
Relative std. dev. (%)	7.6%	6.1%	16%
Mean error (mg/l)	- 2.07	-0.16	-
Relative error (%)	- 3.9%	-3.7%	-

Table VII. Potassium by Flame Emission Photometry
(all results in mg/l)

Laboratory Number	Sample Number		
	1	2	3
701	18.1	3.9 R	5.8
702	19.	3.0	5.5
703	18.	3.0	5.0
704	19.0	3.1	5.9
706	22.5	3.1	6.2
708	17.5	2.9	5.3
709	17.6	2.8	4.9
710	21.2	3.1	5.4
711	18.0	2.9	5.1
714	18.0	3.0	4.8
717	18.6	2.7	5.0
718	20.6	2.80	5.50
721	18.7	2.9	5.2
True value (mg/l)	19.06	2.96	-
Mean (mg/l)	18.98	2.94	5.35
Standard deviation (mg/l)	1.53	0.13	0.42
Relative std. dev. (%)	8.0%	4.5%	7.8%
Mean error (mg/l)	- 0.08	-0.02	-
Relative error (%)	- 0.4%	-0.6%	-

Table VIII. Potassium by Atomic Absorption
(all results in mg/l)

Laboratory Number	Sample Number		
	1	2	3
707	19.9	3.2	5.0
715	18.	2.8	5.0
718	19.0	2.75	6.10
720	19.4	2.7	3.4
722	19.	2.8	5.4
True value (mg/l)	19.06	2.96	-
Mean (mg/l)	19.06	2.85	4.98
Standard deviation (mg/l)	0.70	0.20	0.99
Relative std.dev.(%)	3.7%	7.0%	20%
Mean error (mg/l)	0.00	-0.11	-
Relative error (%)	0.0%	-3.7%	-

Table IX. Total Alkalinity by QWB Potentiometric Method
(all results in mg/l as CaCO₃)

Laboratory Number	Sample Number		
	1	2	3
703	109	10.7	73.4
705	115	10.6	77.4
706	111	10.2	78.
708	103	9.0	-
709	120	12.	83.
710	115	11.	81.
711	116	9.3	79.4
713	110	10.3	78.
714	114	9.5	77.9
716	96.9	7.9	72.3
717	115	9.6	80.4
718	110	0 R	72.8
722	226 R	21.8 R	160 R
True value (mg/l)	115.4	11.41	-
Mean (mg/l)	111.2	10.01	77.60
Standard deviation (mg/l)	6.3	1.11	3.48
Relative std.dev. (%)	5.6%	11%	4.5%
Mean error (mg/l)	- 4.2	- 1.40	-
Relative error (%)	- 3.6%	-13%	-

R Indicates outlier

Table X. Total Alkalinity by Other Methods
(all results in mg/l as CaCO₃)

Laboratory Number	Sample Number		
	1	2	3
702*	108	8.	82.
721*	115	9.0	82.
701†	100	25.	75.
704†	112	15.	85.
715†	110	31.	82.
719†	110	10.	77.
720†	168	16.4	118.

*Technicon methyl orange method [5]

†Titration with indicator. Indicators used:

701 - bromcresol green and methyl red

704 - phenolphthalein and methyl orange

715 - phenolphthalein

719 - calmagite

720 - methyl orange

Table XI. Chloride by Thiocyanate Method
(all results in mg/l)

All results obtained by QWB automated method [2] unless indicated otherwise

Laboratory Number	Sample Number		
	1	2	3
702	64.	16.	59.
703	65.	17.0	55.0
704	60.	16.	51.
706	72.	16.	63.
708	62.0	16.5	60.0
710	70.	16.7	61.
711	67.7	16.0	60.1
714	67.0	16.5	60.0
717	66.1	16.3	60.4
719	87. R	22. R	79. R
721	68.	17.2	62.
True value (mg/l)	69.09	16.63	-
Mean (mg/l)	66.18	16.42	59.15
Standard deviation (mg/l)	3.60	0.44	3.56
Relative std. dev. (%)	5.4%	2.7%	6.0%
Mean error (mg/l)	-2.91	-0.21	-
Relative error (%)	-4.2%	-1.3%	-
Manual method:			
712	68.3	16.0	59.0
715	68.	17.	63.

R Indicates outlier

Table XII. Chloride by Silver Nitrate and other Methods
(all results in mg/l)

Laboratory Number	Sample Number		
	1	2	3
701	60.	20.	50.
705	64.3	17.5	58.4
709	74.	20.	65.
718	77.8	45.4 R	58.7
True value (mg/l)	69.09	16.63	-
Mean (mg/l)	69.03	19.17	58.03
Standard deviation (mg/l)	8.25	-	6.16
Relative std.dev. (%)	12%	-	11%
Mean error (mg/l)	- 0.07	2.54	-
Relative error (%)	- 0.1%	15%	-
Other methods:			
713*	64.	15.	57.
716*	69.7	19.9	64.2
720*	70.7	16.7	62.3
722†	65.	14.	75.

*Titration with mercuric nitrate

†Specific ion electrode

R Indicates outlier

Table XIII. Sulfate by WQB Titrimetric Method
(all results in mg/l)

Laboratory Number	Sample Number		
	1	2	3
703	52.3	10.0	66.8
708	53.	10.0	75.5
711	58.2	8.4	78.1
713	56.	8.6	7.7 R
714	54.7	10.0	75.5
717	55.5	12.2	69.0
True value (mg/l)	54.97	9.86	—
Mean (mg/l)	54.95	9.87	72.98
Standard deviation (mg/l)	2.14	1.36	4.82
Relative std.dev. (%)	3.9%	14%	6.6%
Mean error (mg/l)	-0.02	0.01	—
Relative error (%)	-0.04%	0.1%	—

R Indicates outlier

Table XIV. Sulfate by Turbidimetric Methods
(all results in mg/l)

All results obtained by manual method unless indicated otherwise

Laboratory Number	Sample Number		
	1	2	3
705	51.	8.	63.
706	57.	16.	73.
707	65.	11.	86.
715	54.	10.	78.
716	50.0	5.5	48.0
True value (mg/l)	54.97	9.86	—
Mean (mg/l)	55.40	10.10	69.60
Standard deviation (mg/l)	6.03	3.91	14.32
Relative std.dev. (%)	11%	39%	21%
Mean error (mg/l)	0.43	0.24	—
Relative error (%)	0.08%	2.4%	—
Other turbidimetric methods:			
701*	68.	13.	106.
702†	58	10.	76.

*Using Hach Kit

†Automated turbidimetric method

Table XV. Sulfate by Gravimetric and Colorimetric Methods
(all results in mg/l)

Laboratory Number	Sample Number		
	1	2	3
gravimetric*			
709	43.5	5.8	64.
710	60.	9.9	76.
718	49.4	4.94	70.8
722	55.	10.	75.
True value (mg/l)	54.97	9.86	—
Mean (mg/l)	51.98	7.66	71.45
Standard deviation (mg/l)	7.12	2.67	5.45
Relative std. dev. (%)	14%	35%	7.6%
Mean error (mg/l)	-2.99	-2.20	—
Relative error (%)	-5.5%	-22%	—
Colorimetric†			
721	45.	8.3	58.
714	61.	10.	79.

*BaSO₄ precipitation[6]

†Automated methylthymol blue method [7]

Table XVI. Nitrate by WQB Cadmium Reduction Method
(all results in mg/l N)

Laboratory Number	Sample Number		
	1	2	3
703	0.02	0.01	5.0
708	0.03	0.04	2.92 R
711	0.02	0.02	5.3
712	0.012	0.042	5.25
714	0.01	0.03	5.2
717	0.01	0.04	5.30
718	0.02	0.02	2.93 R
721	0.	0.	5.0
True value (mg/l)	0.010	0.030	—
Mean (mg/l)	0.015	0.025	5.18
Standard deviation (mg/l)	0.009	0.015	0.14
Relative std.dev. (%)	60%	61%	2.8%
Mean error (mg/l)	0.005	-0.005	—
Relative error (%)	50%	-16%	—
Other cadmium reduction methods:			
704*	<0.1	<0.1	6.2
707*	<0.1	<0.1	26.1
716†	0.023	0.033	4.94

*WQB method adjusted for high levels only

†Cadmium reduction with sulfanilic acid diazotization

R Indicates outlier

Table XVII. Nitrate by Other Methods

(all results in mg/l N)

Laboratory Number	Sample Number		
	1	2	3
702*	0.0	0.0	4.5
706*	0.25	0.25	1.50
719*	0.05	0.05	6.25
709†	0.025	0.020	1.19
720†	0.089	0.095	3.113
713§	0.033	0.065	3.2
715§	<0.05	0.10	5.2
701**	0.45	0.23	2.3
722**	4.6	2.0	25.
705††	<0.1	<0.1	5.
True value	0.010	0.030	

* Automated hydrazine reduction method

† Ultraviolet spectrophotometric method

§ Phenoldisulfonic acid method

** Specific ion electrode

†† Brucine method

Table XVIII. Three-Month Storage Tests on Sample 3

(all results in mg/l)

Parameter	Initial Value (average)	After 3 months (single determination)
Calcium as CaCO_3	58.3	41.3
Total hardness as CaCO_3	194.	128.
Sodium	30.6	30.2
Potassium	5.4	5.1
Alkalinity as CaCO_3	77.6	25.4
Phenolphthalein alkalinity	0.	20.6
Chloride	59.1	60.0
Sulfate	73.0	67.0
Nitrate	5.2	4.3

Table XIX. Comparison of Results from Local and Distant Laboratories

(all results in mg/l)

Parameter	Sample 1			Sample 3	
	True Value	Local	Distant	Local	Distant
Calcium	38.99	39.7	37.0	57.7	58.0
Sodium	52.99	53.4	50.5	31.8	29.8
Potassium	19.06	18.9	18.1	5.0	5.15
Alkalinity	115.4	115.	109.	80.0	79.2
Chloride	69.09	67.5	63.0	61.0	58.7
Sulfate	54.97	54.9	54.8	73.2	73.8
Nitrate	0.010	0.005	0.024	5.1	4.3

Appendix A

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, Northwest Region (Edmonton)

Environmental Protection Service, Technology Development and Demonstration Division (Burlington)

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

Service des Laboratoires, Ministère des Affaires Sociales, Québec

Environment Branch, New Brunswick Department of Fisheries and Environment, Fredericton

Environmental Chemistry Section, Nova Scotia Department of Public Health, Halifax

Nova Scotia Department of Agriculture and Marketing, Truro

Soil and Feed Testing Laboratories, P.E.I. Department of Agriculture, Charlottetown

Municipal Government Laboratories:

City of Winnipeg Waterworks and Waste Disposal

Industrial Laboratories:

Cominco Ltd., Trail, B.C.

Chemex Ltd., Calgary

Bondar-Clegg & Co. Ltd., Ottawa

Universities:

Department of Chemistry, University of Saskatchewan, Regina

Department of Biology, Dalhousie University, Halifax



3 9055 1017 2746 8

DATE DUE REMINDER

APR 1 '83

**Please do not remove
this date due slip.**