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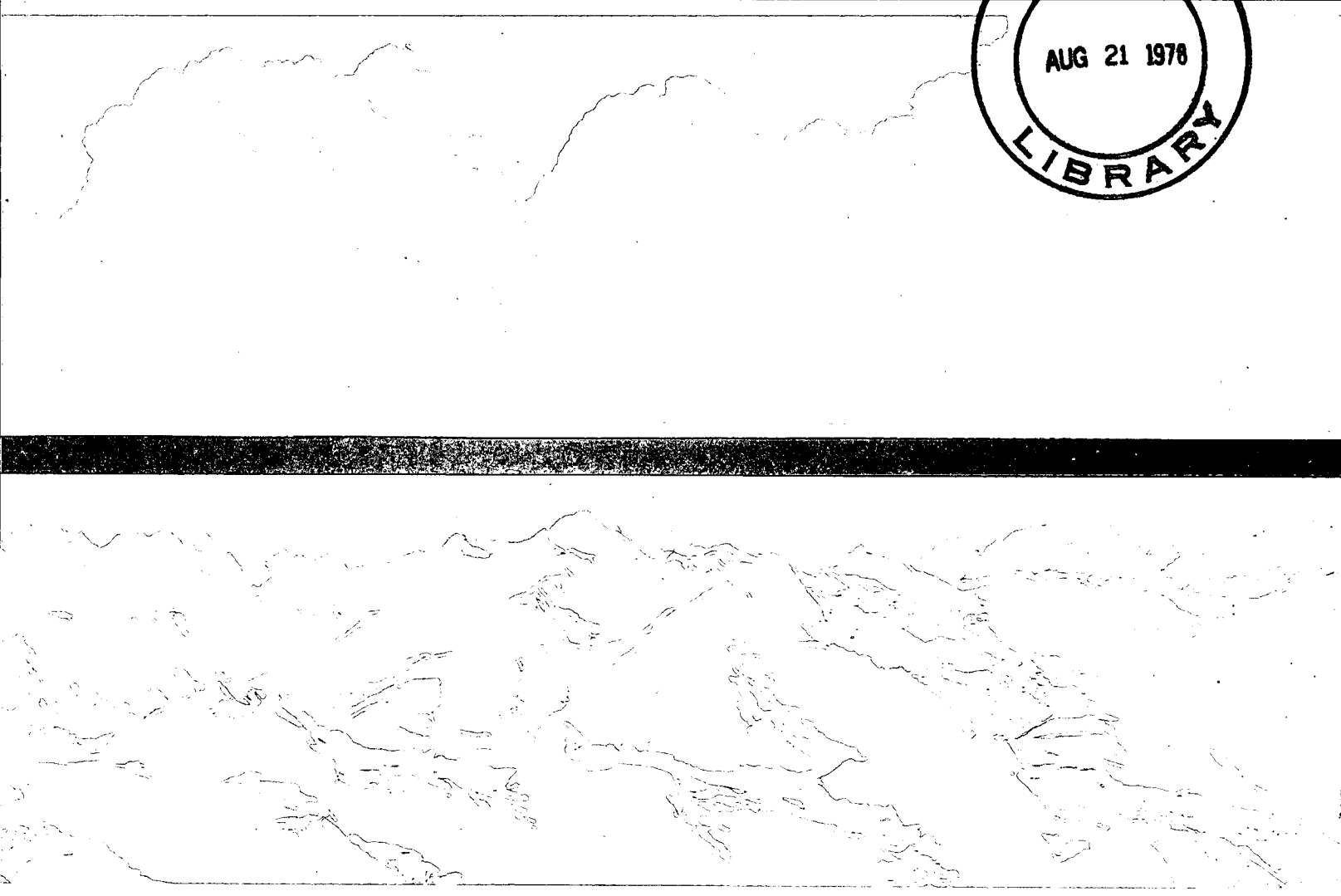
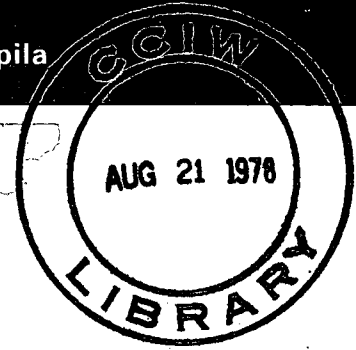
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# Interlaboratory Quality Control Study No. 14

Major Ions: Calcium, Magnesium, Sodium,  
Potassium, Hardness, Alkalinity, Chloride,  
Sulphate and Nitrate

J.M. Carron and K.I. Aspila



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*(Résumé en français)*

**INLAND WATERS DIRECTORATE, ONTARIO REGION,  
WATER QUALITY BRANCH,  
BURLINGTON, ONTARIO, 1978.**



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## **Abstract**

The results of interlaboratory quality control study No. 14 are described. This study was carried out during the spring and summer of 1975. It included three natural waters and two standard solutions. Data were submitted from 36 participating Canadian laboratories. The parameters were calcium, magnesium, sodium, potassium, hardness, alkalinity, chloride, sulphate and nitrate. Samples were at concentrations similar to natural inland waters. All samples were distributed without preservatives.

## **Résumé**

Le présent rapport traite des résultats de l'étude interlaboratoire n° 14 du contrôle de la qualité, effectuée au cours du printemps et de l'été de 1975 et se rapportant à trois échantillons d'eaux naturelles et deux solutions étalons. Trente-six laboratoires canadiens ont participé et fourni des données. Les paramètres étaient les suivants: calcium, magnésium, sodium, potassium, dureté, alcalinité, chlorure, sulfate et nitrate. Les échantillons renfermaient des concentrations comparables à celles des eaux naturelles intérieures. Aucun échantillon distribué ne comportait d'agent de préservation.

## List of Symbols

n	Number of results used in calculating the group mean ( $\bar{x}$ )
$\bar{x}$	Mean value [ $\bar{x} = (\Sigma x_i)/n$ ]
S.D.	Standard deviation, S.D. = $\sqrt{\frac{\Sigma(x_i - \bar{x})^2}{(n - 1)}}$
C.V.	Coefficient of variation or the relative standard deviation, C.V. = $(\sigma/\bar{x})100$
R	Identification of results which have been rejected in calculating $\bar{x}$ and S.D.

# Interlaboratory Quality Control Study No. 14

## Major Ions: Calcium, Magnesium, Sodium, Potassium, Hardness, Alkalinity, Chloride, Sulphate and Nitrate

J.M. Carron and K.I. Aspila

### INTRODUCTION

Interlaboratory quality control study No. 14 was conducted to obtain information on the quality of data obtained for a variety of major ions in natural unpreserved waters. The major ions included in this study are some of the more important parameters identifying the quality of natural waters and, for many laboratories and agencies, are those parameters analyzed in samples containing no stabilizers. Therefore the intent of this study was to present samples to participants in a manner similar to their normal operating procedures and to obtain data that permit statements on the compatibility of results. The study complements an earlier study (McGirr and Wales, 1974) in this series.

### EXPERIMENTAL DESIGN

The study consisted of five unpreserved water samples, of which two were synthetic and the remainder were natural. The sources of the samples used for this study are identified in Table 1.

The fortified distilled waters (referred to hereafter as the synthetic sample or the standard) were designed to contain the concentration of major ions shown in Table 2.

The reagents used to prepare the synthetic solutions were of high-purity analytical grade. Where known impurities were identified, correction factors were applied in preparing concentrated standards. The concentrated stock solutions were appropriately diluted in 50-litre containers to prepare the bulk samples, which in turn were portioned serially into 50 precleaned and sample-rinsed one-litre linear polyethylene bottles.

Participants were asked to provide a brief description of the method of analysis employed for the parameters they analyzed. Data were reported in milligrams per litre.

### EVALUATION OF DATA

The results submitted by participants were grouped according to the methods of analysis used. Where

sufficient data were available, the mean and standard deviation for a specific method are given. The compatibility of two methods was evaluated by calculating confidence intervals and applying the student t test. Some data that were clearly deviant were rejected by the method of Grubbs (1969).

For illustrative purposes, the raw data for similar paired samples (in most cases samples 1 and 5 and samples 2 and 4) are presented in Youden plots. Late data were not included. In the plots the sample means are represented by the crossed lines drawn on the 45° line. The length of these lines represents twice the average standard deviation for the paired samples. The standard deviations in all cases were very similar for the paired samples. Further discussion of the usefulness of the two-sample charts is provided by Youden and Steiner (1975).

Table 1. Samples Distributed to Participants

Sample number	Type	Sources
1	Natural	Calgary, Alberta
2	Distilled water, fortified	In-house
3	Natural	Ottawa River, Ontario
4	Distilled water, fortified	In-house
5	Natural	Lake Erie, Ontario

Table 2. Concentration of Parameters in Standard Solutions

Parameter	Design value (mg/l)	
	Sample 2	Sample 4
Calcium	39.75	34.78
Magnesium	10.40	8.33
Total hardness	142.1	121.1
Sodium	62.50	57.20
Potassium	5.52	9.68
Total alkalinity (as CaCO <sub>3</sub> )	173.9	89.2
Chloride	70.32	61.53
Sulphate	41.09	32.91
Nitrate (as N)	0.113	0.113



## RESULTS AND DISCUSSION

### Calcium

Thirty-eight results were received from 35 laboratories doing calcium analysis (Fig. 1). More than 60% of the laboratories employed atomic absorption methods, whereas the remainder used titration (Table 3). Precision was excellent, with overall variation of the sample means being less than 5% within the range from 16 mg/l to 44 mg/l Ca. The accuracy was also within the same percentage limits as the precision, with recoveries being better than 100%  $\pm$  5%. For the atomic absorption method, only a few participants identified the use of lanthanum salts to suppress interferences (if any). The excellent results may imply that this suppressant was also used by other laboratories which did not provide details of their atomic absorption method. Few details were given by those laboratories employing the titration method; EDTA was the predominant complexing agent used.

Comparison of the mean results of the two principal groups of methods employed for calcium analysis indicates there is no difference in values at the 95% confidence interval whenever titration or atomic absorption is used. Titration, however, did yield a slightly higher mean value, but only at the 76% confidence level ( $t = 1.35$ ). The mean relative standard deviation for the atomic absorption method was 3.7% and for the titration method, 3.4%.

### Magnesium

Magnesium was determined by 35 laboratories predominantly using atomic absorption methods

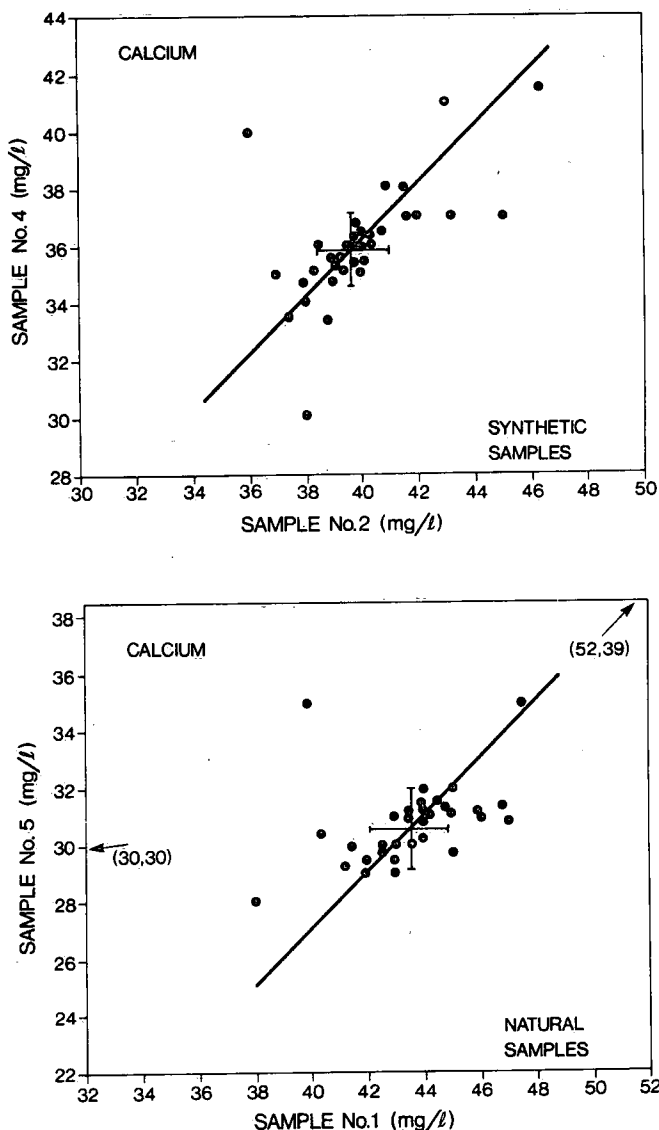


Figure 1. Calcium analysis results.

Table 3. Statistics on Calcium (mg/l)

Method	Statistical parameter	Sample number				
		1	2	3	4	5
Overall data	n	36	35	35	34	35
	$\bar{x}$	43.53	39.73	16.26	35.90	30.55
	S.D.	1.96	1.42	0.74	1.10	1.01
	C.V. (%)	4.5	3.6	4.5	3.1	3.3
	% Recovery		99.95		103.0	
Atomic absorption	n	23	24	22	23	22
	$\bar{x}$	43.88	39.69	16.10	35.74	30.55
	S.D.	1.85	1.41	0.71	1.10	0.91
Titration	n	8	8	8	8	8
	$\bar{x}$	43.65	39.64	16.56	36.24	30.83
	S.D.	1.26	1.58	0.63	1.20	0.86

(Table 4). Several laboratories calculated a magnesium value, presumably from the relationship:

$$\text{Total hardness (mg/l as CaCO}_3\text{)} = 2.497 \text{ mg/l Ca} + 4.116 \text{ mg/l Mg}$$

The overall mean variation for the five samples, which ranged from 3.79 mg/l to 11.25 mg/l Mg, was 6% (Fig. 2). The accuracy, based on the recovery (100%  $\pm$  1%) of magnesium from the synthetic samples, was better than the mean precision ( $\pm$  6%) in the concentration range from 8.34 mg/l to 10.38 mg/l Mg.

Comparing the mean atomic absorption values with the mean calculated values, the former are definitely higher at the 95% confidence level ( $t = 4.74$ ). The precision for the atomic absorption method is also somewhat better than for the calculated values.

When the total hardness and calcium values are considered, no explanation is readily available concerning the differences in the means for the magnesium values. Again, the difference in the two methods is shown by the bias depicted by an ellipse in the Youden plots.

In general, those laboratories that calculated a magnesium value did so from calcium and total hardness values that were previously determined by titration. This would imply that these other values, determined by titration methods, would similarly reveal lower mean values. This was found not to be the case at the 90% confidence level.

#### Total Hardness

Thirty-five laboratories submitted total hardness values (mg/l) for the five water samples (Table 5). Half of the values were obtained by calculation (from calcium and magnesium results) and the other half, by titration (Fig. 3).

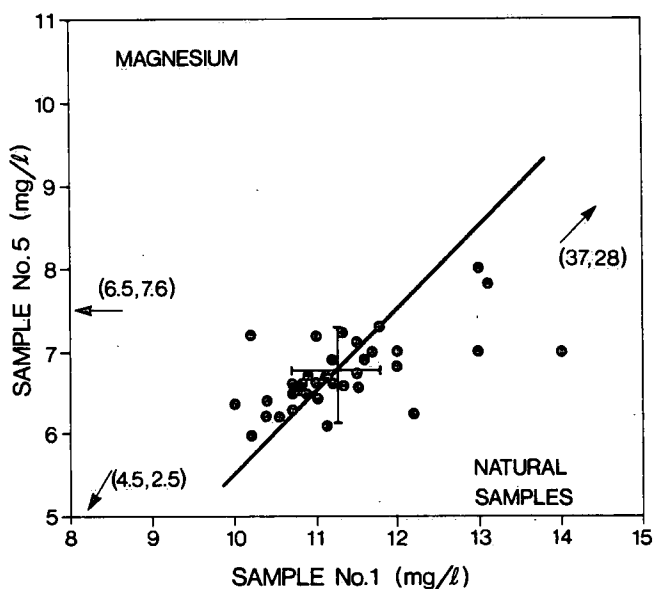
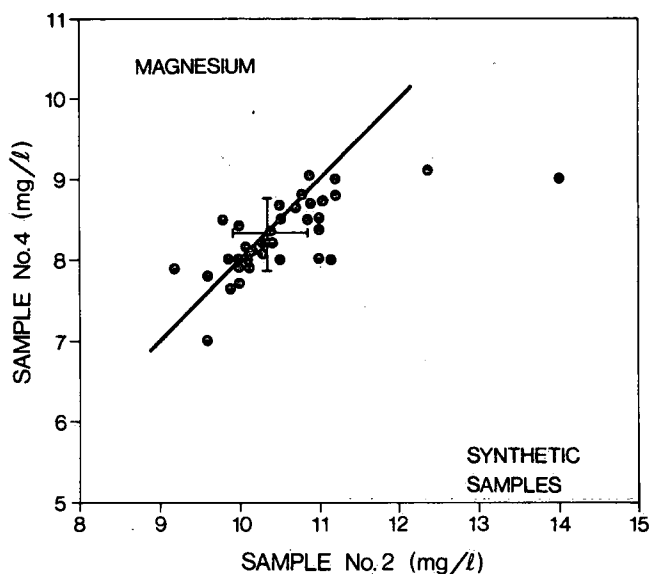


Figure 2. Magnesium analysis results.

Table 4. Statistics on Magnesium (mg/l)

Method	Statistical parameter	Sample number				
		1	2	3	4	5
Overall data	n	35	35	35	36	35
	$\bar{x}$	11.25	10.38	3.79	8.34	6.72
	S.D.	0.77	0.51	0.31	0.40	0.36
	C.V. (%)	6.8	4.9	8.2	4.8	5.4
	% Recovery		99.8		100	
Atomic absorption	n	24	25	25	26	25
	$\bar{x}$	11.30	10.45	3.87	8.36	6.75
	S.D.	0.66	0.50	0.20	0.40	0.34
Calculated value	n	7	6	6	7	6
	$\bar{x}$	11.19	10.10	3.43	8.13	6.53
	S.D.	1.26	0.57	0.49	0.70	0.47

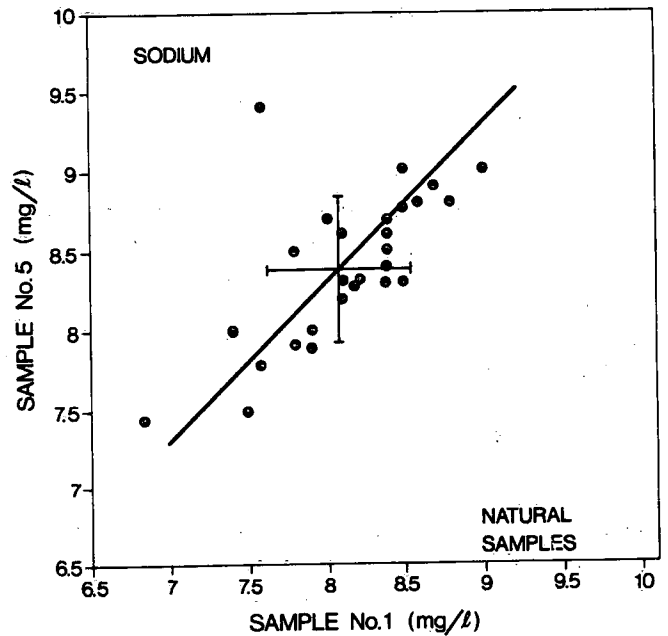
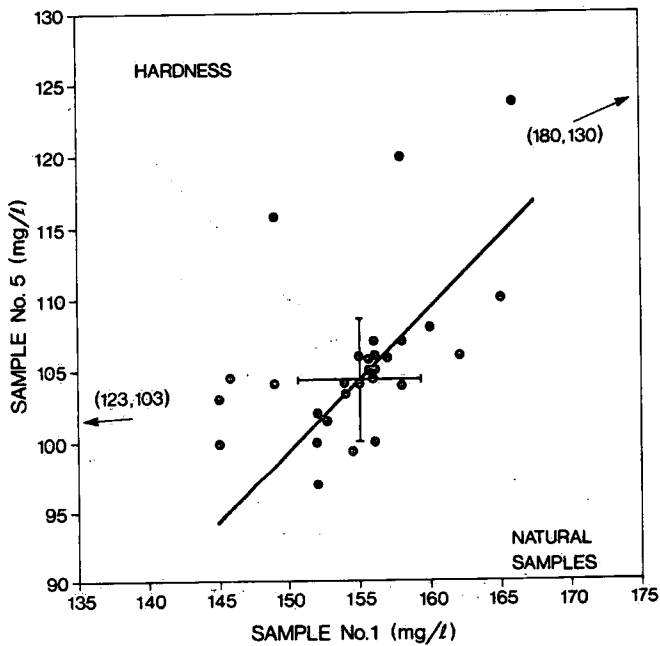
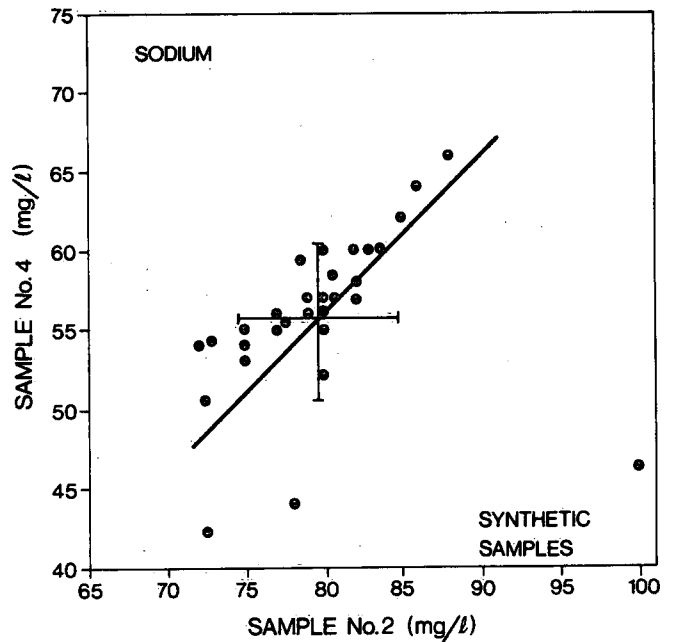
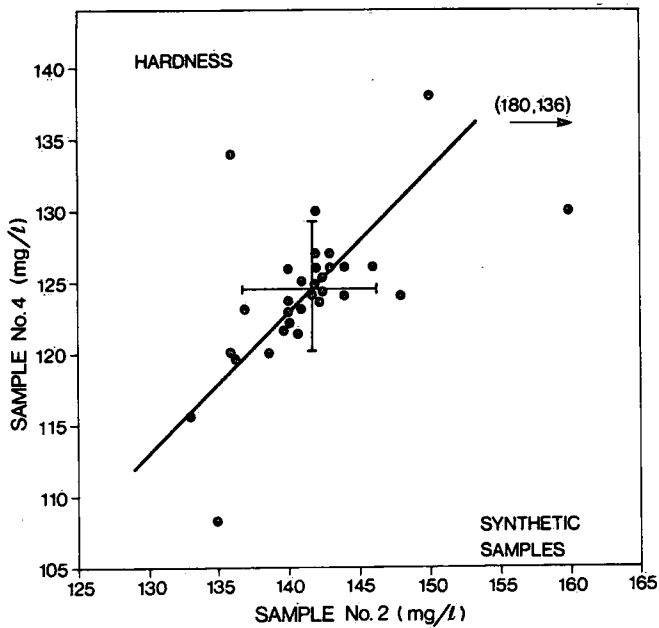


Figure 3. Total hardness analysis results.

Figure 4. Sodium analysis results.

The overall mean precision and accuracy were very comparable; the mean variation was 3.5% and the recovery was 100%  $\pm$  3% within the range from 56.2 mg/l to 155 mg/l  $\text{CaCO}_3$ .

At the 95% confidence interval there is no significant difference between the sample means obtained by either method. At the 88% confidence interval ( $t = 1.92$ ), the mean titration values are slightly higher than the mean calculated values even though the precision of both methods is very similar ( $\pm 3.4\%$ ,  $\pm 3.7\%$ ). This could

possibly be due to over-titration or the presence of other hardness-producing cations (Al, Fe, Mn, Zn and Sr).

As indicated in the section on "Magnesium," the hardness is related to the calcium and magnesium by the relationship:

$$\text{Mg (calculated)} + \text{Ca} = \text{Hardness (titration)}$$

$$\text{Mg (atomic absorption)} + \text{Ca} = \text{Hardness (calculated)}$$

**Table 5. Statistics on Total Hardness (mg/l)**

Method	Statistical parameter	Sample number				
		1	2	3	4	5
Overall data	n	37	37	34	36	36
	$\bar{x}$	155.0	141.7	56.2	124.8	104.3
	S.D.	4.86	4.67	2.63	4.01	3.56
	C.V. (%)	3.1	3.3	4.7	3.2	3.4
	% recovery		99.7		97.0	
Calculated from Ca and Mg results	n	16	17	16	17	17
	$\bar{x}$	153.9	141.7	55.37	123.9	104.1
	S.D.	4.56	5.57	1.55	5.96	4.17
Titration	n	19	18	16	18	17
	$\bar{x}$	155.6	141.3	56.71	124.7	104.3
	S.D.	4.74	3.58	3.09	3.92	2.84

**Table 6. Statistics on Sodium (mg/l)**

Method	Statistical parameter	Sample number				
		1	2	3	4	5
Overall data	n	33	34	33	34	31
	$\bar{x}$	8.08	79.67	4.72	55.91	8.39
	S.D.	0.48	5.31	0.56	4.98	0.44
	C.V. (%)	5.9	6.7	11.9	8.9	5.2
	% Recovery		128		97.7	
Atomic absorption	n	10	11	10	11	9
	$\bar{x}$	7.99	79.1	4.63	56.1	8.23
	S.D.	0.50	3.93	0.38	4.89	0.47
Emission on atomic absorption spectrophotometer	n	5	5	5	5	4
	$\bar{x}$	8.24	80.2	5.00	55.2	8.68
	S.D.	0.46	4.91	1.33	8.11	0.21
Emission on flame photometer	n	10	10	10	10	10
	$\bar{x}$	8.15	81.1	4.71	55.4	8.49
	S.D.	0.38	7.43	0.18	4.08	0.38

The mean values for the three variables are given in Tables 3, 4 and 5, and a correlation between them can be established.

#### Sodium

Sodium values were determined primarily by emission and secondarily by atomic absorption methods (Fig. 4). The overall sodium analysis showed an average sample variation of 5% to 12% at sodium levels from 5 mg/l to 80 mg/l; the recoveries of the two synthetic samples, 97.7% and 128%, were at levels of 55.9 mg/l and 79.7 mg/l, with the high value of 128% being rejected (Table 6).

There was no significant difference (at the 90% confidence interval) in the five means obtained when using either a simple flame photometer or the more elaborate atomic absorption spectrophotometer. Three of

the results displaying better precision, however, were obtained when the flame photometer was used. The means obtained using absorption data tended to be lower, but this is not significant, even at the 50% confidence interval.

#### Potassium

Potassium was measured in a manner similar to sodium (Fig. 5). Regardless of the technique employed, the precision remained about the same, with the variation being 10% or less in the range from 1 mg/l to 10 mg/l K (Table 7). Better accuracy seemed to be achieved when using emission on a flame photometer, but in actuality this is probably not so, since there is no significant difference (at even the 90% confidence interval) between the means of the sample results when emission on a flame photometer and emission on an atomic absorption spectrophotometer are compared ( $t = 1.831$ , 87%) or

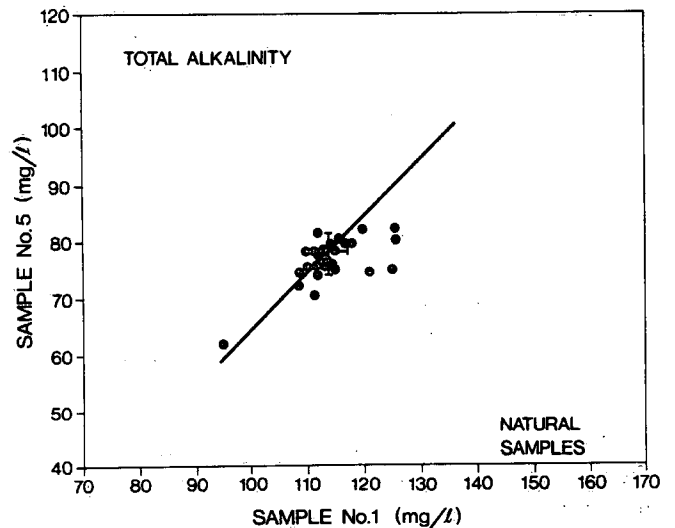
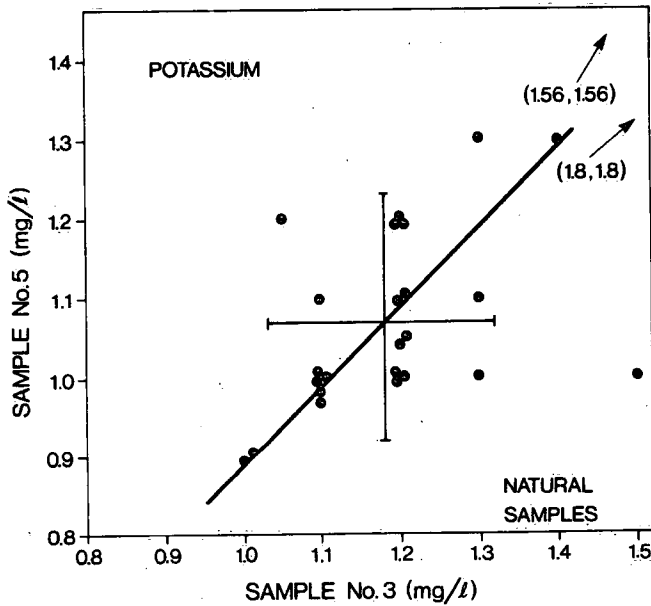
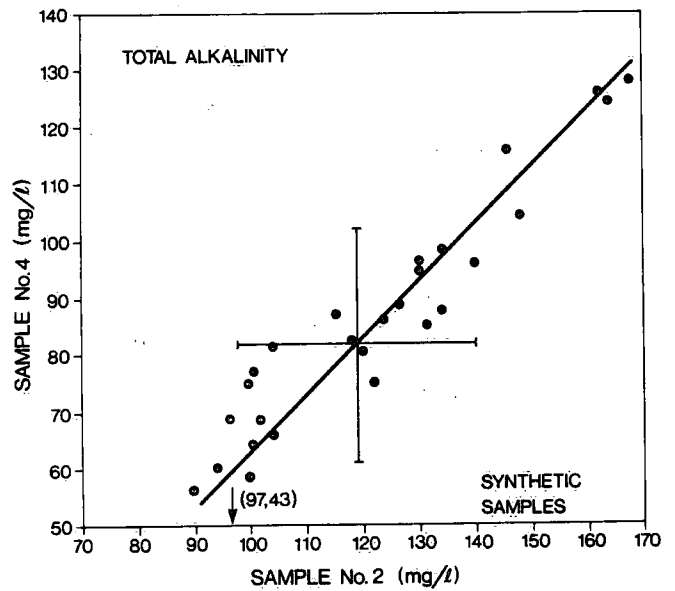
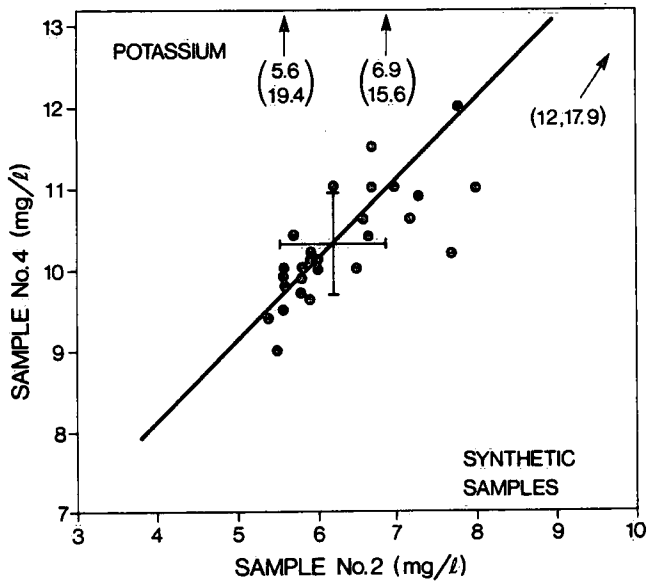


Figure 5. Potassium analysis results.

Figure 6. Total alkalinity analysis results.

between the means of the sample results when an atomic absorption spectrophotometer is used in either the absorption or the emission mode ( $t = 1.117, 67\%$ ).

Although the  $t$  test shows no significant difference between the method of analysis used for the five samples, Table 7 indicates that emission on the atomic absorption spectrophotometer provided the highest mean values and also the greatest variation on the lowest sample.

#### Total Alkalinity

Total alkalinity was determined almost entirely by the titration method (Fig. 6). Those laboratories that specified indicators used one of the following methods: methyl orange, mixed bromocresol green-methyl red (Standard Method No. 102, American Public Health Assoc., 1971), methyl purple, bromophenol blue or phenolphthalein. End points for titration were given as one of the following:

Table 7. Statistics on Potassium (mg/l)

Method	Statistical parameter	Sample number				
		1	2	3	4	5
Overall data	n	31	32	32	31	32
	$\bar{x}$	1.54	6.20	1.18	10.30	1.07
	S.D.	0.14	0.71	0.13	0.65	0.16
	C.V. (%)	9.1	11	11	6.3	15
	% Recovery		112		106	
Atomic absorption	n	8	8	8	8	8
	$\bar{x}$	1.48	6.03	1.20	10.5	1.06
	S.D.	0.15	0.57	0.15	0.90	0.11
Emission on atomic absorption spectrophotometer	n	5	6	6	5	6
	$\bar{x}$	1.54	6.89	1.21	10.5	1.07
	S.D.	0.09	0.67	0.19	0.36	0.30
Emission on flame photometer	n	10	10	10	10	10
	$\bar{x}$	1.51	6.02	1.12	9.99	1.04
	S.D.	0.10	0.68	0.08	0.51	0.12

Table 8. Statistics on Total Alkalinity (mg/l)

Method	Statistical parameter	Sample number				
		1	2	3	4	5
Overall data	n	33	33	31	33	33
	$\bar{x}$	114	119	40.4	81.7	77.3
	S.D.	4.45	22.6	2.85	21.4	2.65
	C.V. (%)	3.9	19	7.1	26	3.4
	% Recovery		68		92	
All methods by titration*	n	27	27	25	27	27
	$\bar{x}$	114	113	40.7	77.5	77.3
	S.D.	4.22	17.9	2.98	15.8	2.80
WQB titration	n	9	9	8	8	9
	$\bar{x}$	114	110	39.7	73.8	77.6
	S.D.	2.6	13.3	1.1	10.4	2.20
Automated methyl orange	n	3	3	3	3	3
	$\bar{x}$	117	165	38	126	77
	S.D.	8.3	3.1	2.1	2.0	2.6

\*The number of results includes all data obtained by a titration method [including the WQB method (Department of the Environment, 1974)]. Three participants did not identify their method of analysis.

pH 4.8, pH 4.5 or pH 4.2. Most laboratories used a standard solution of 0.02 N H<sub>2</sub>SO<sub>4</sub> acid for titrating the sample.

The natural samples were determined with less than 10% variation at the levels from 40.4 mg/l to 114 mg/l (Table 8).

With respect to sample 2 there were problems related to impure NaHCO<sub>3</sub>. In all probability the high (128%) sodium recovery reflects the low (68%) alkalinity recovery. Sample 4 was made using Na<sub>2</sub>CO<sub>3</sub> (sodium recovery

97.7%), but still gave a low recovery (92%). The ion balance was also very poor (10%) and implied low alkalinity values.

Three laboratories used the Technicon methyl orange method. A comparison of the mean results of the methyl orange method with the overall mean results shows no difference exists at the 90% confidence interval ( $t = 1.637, 83\%$ ). Even so, it must be noted that the mean value of the two synthetic samples is considerably higher for the methyl orange method. Also, when using these higher mean values in the ion balance, a noticeable

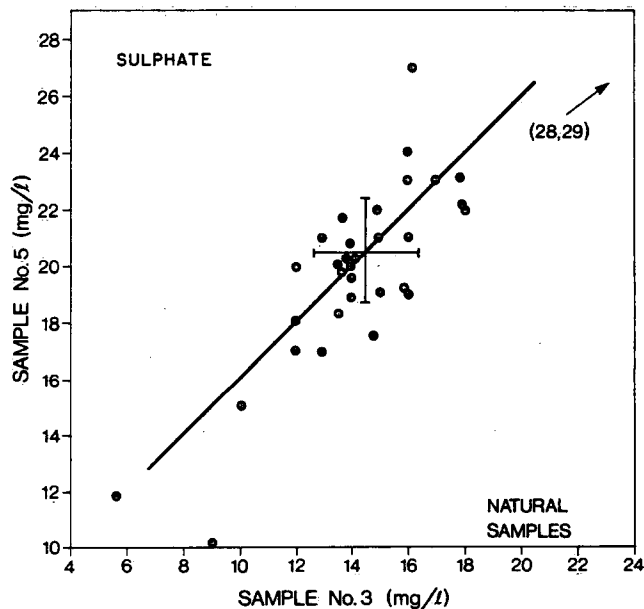
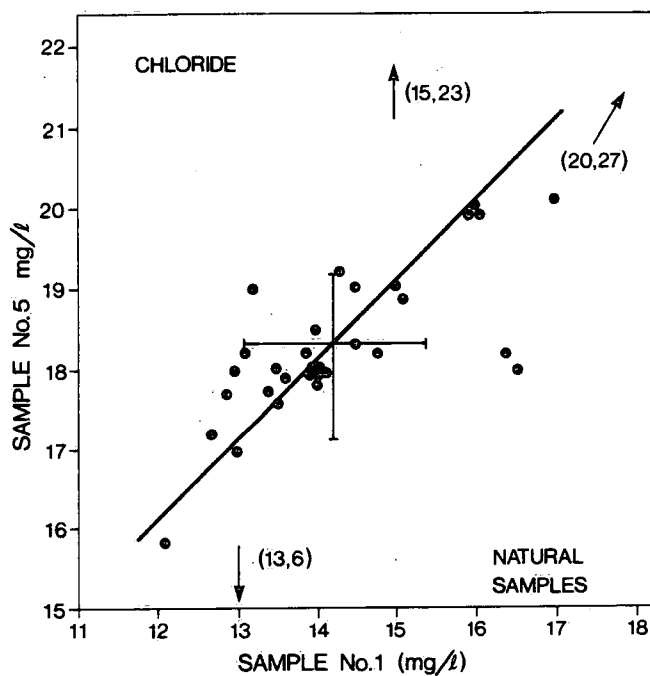
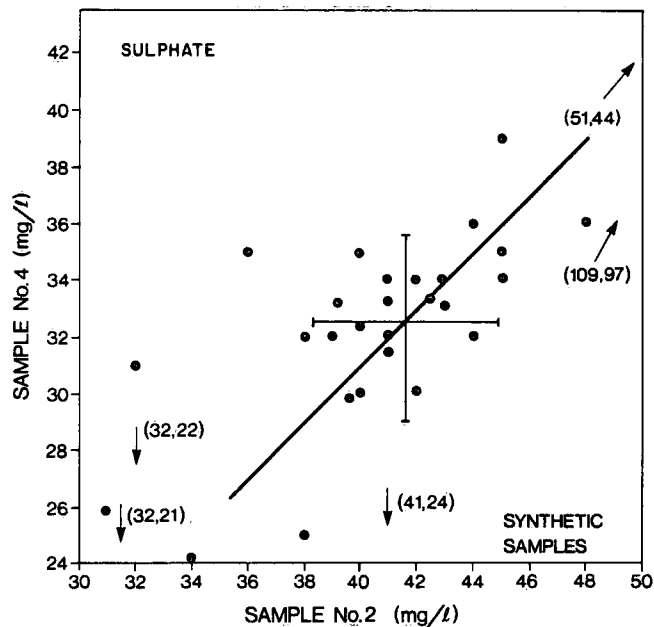
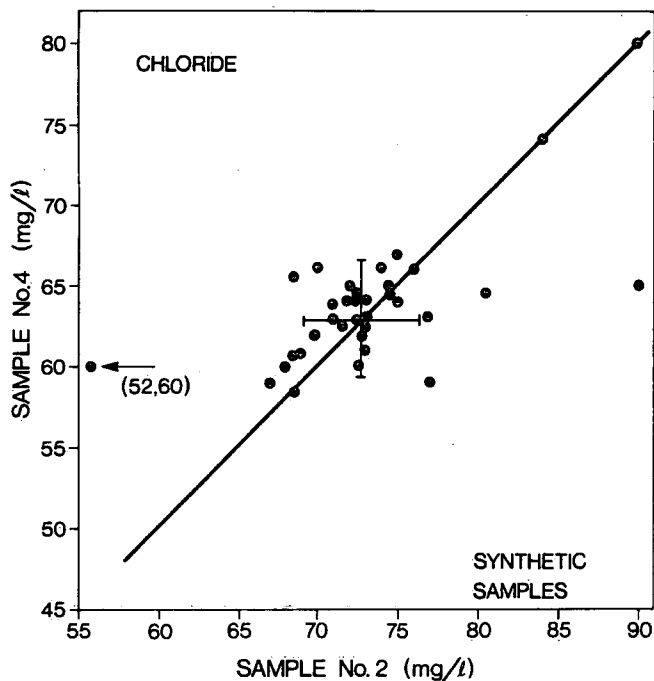


Figure 7. Chloride analysis results.

Figure 8. Sulphate analysis results.

improvement in the ion balance from 10% to 2% is realized (e.g., sample 2, 9.91% to 1.94%, and sample 4, 11.8% to 2.02%).

AAI, AAI<sub>2</sub> or CSM6 AutoAnalyzers. The use of either ferric ammonium sulphate or ferric nitrate in the colour reagent made no difference (Fig. 7).

#### Chloride

The overall mean precision improved from 12% to 5% variation as the mean sample concentration increased from 7.88 mg/l to 72.7 mg/l Cl (Table 9). The colorimetric methods were done mainly with Technicon

The titrimetric method was predominately the  $\text{AgNO}_3$  method (Standard Method No. 112A, American Public Health Assoc., 1971). Compatible results were also obtained by one laboratory using a Fisher Titrator with a chloride selective electrode (laboratory No. 36).

Table 9. Statistics on Chloride (mg/l)

Method	Statistical parameter	Sample number				
		1	2	3	4	5
Overall data	n	35	34	36	35	34
	$\bar{x}$	14.2	72.7	7.88	63.0	18.3
	S.D.	1.20	3.72	0.95	2.34	1.10
	C.V. (%)	8.5	5.1	12.1	3.7	6.0
	% Recovery		103		102	
Colorimetric	n	20	19	20	20	20
	$\bar{x}$	14.0	72.1	7.68	62.9	18.2
	S.D.	1.01	3.08	0.63	2.53	0.86
Titrimetric	n	12	12	13	12	11
	$\bar{x}$	14.6	73.7	8.25	63.5	18.7
	S.D.	1.33	4.58	1.33	1.94	1.06

Table 10. Statistics on Sulphate (mg/l)

Method	Statistical parameter	Sample number				
		1	2	3	4	5
Overall data	n	34	31	35	32	32
	$\bar{x}$	37.3	41.6	14.5	32.3	20.5
	S.D.	3.54	2.82	2.01	3.71	1.83
	C.V. (%)	9.5	6.8	14	11	8.9
	% Recovery		101		98	
Colorimetric	n	9	9	10	9	9
	$\bar{x}$	37.0	42.7	15.1	32.7	21.2
	S.D.	2.77	1.66	1.13	1.59	1.71
Turbidimetric	n	15	14	16	12	14
	$\bar{x}$	38.2	40.8	14.3	33.4	21.1
	S.D.	2.91	3.02	2.70	1.69	1.54
Titrimetric	n	5	5	5	5	5
	$\bar{x}$	37.4	39.3	13.9	29.5	18.4
	S.D.	5.54	5.30	1.59	4.42	1.17

The accuracy, as implied by the recoveries of 103% and 102% for the synthetic samples, was excellent. At the 99% confidence interval, the mean titrimetric values are higher than the mean colorimetric values ( $t = 3.73$ , 99.3%). This may be the result of slight over-titration or blank contamination, since the better low-level precision was obtained using the colorimetric method (sample 3).

#### Sulphate

Three different methods were predominantly used for the sulphate determination (Fig. 8). In order of decreasing preference they were turbidimetric, colorimetric and titrimetric (Table 10).

The mean recovery was  $100\% \pm 2\%$  at the range from 30 mg/l to 40 mg/l  $\text{SO}_4$ . The overall precision was 10% in the range from 14.5 mg/l to 41.6 mg/l.

At the 95% confidence interval there is no difference between the mean values obtained by either the colorimetric or the turbidimetric method ( $t = 0.368$ ).

There is a difference at the 95% confidence interval for the mean values obtained titrimetrically. They have greater variation and lower mean average values than either the colorimetric or turbidimetric method.

#### Nitrate

Nitrate was measured by 33 laboratories (Fig. 9). The overall variation was related almost directly to the sample concentration, which explains why the highest sample, with a mean of 0.476 mg/l  $\text{NO}_3$ , had only an overall variation of 12.8%, whereas the lowest sample, with a mean of 0.069 mg/l, had an overall variation of 24.6%



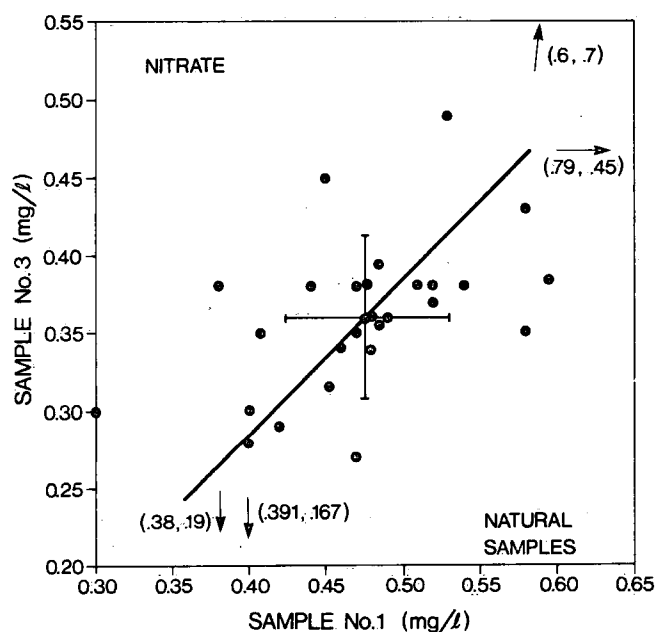
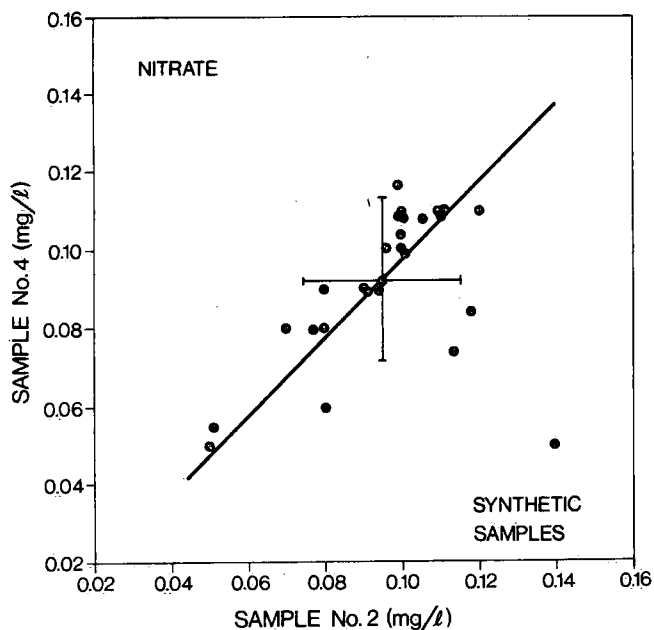


Figure 9. Nitrate analysis results.

(Table 11). The overall recovery on the synthetic samples, which were unpreserved, was just over 80%.

A number of different methods were used. Two methods, UV spectrophotometric (laboratory No. 7) and phenoldisulphonic acid (laboratory No. 32), provided a number of outliers.

Only three laboratories used the hydrazine sulphate reduction method. The trend in this limited amount of data shows a slightly higher overall mean variation of

23.6% as opposed to 19% for the other methods. The recoveries on the synthetic samples were considerably less. This may be the result of using a method beyond its optimum analytical range, since the laboratories (No. 4, No. 8 and No. 18) employing this method reported data only to the nearest 0.01 mg/l, at best.

Seven laboratories which used the Brucine method obtained values that compare favourably with the overall mean. Recovery on the synthetic was 80% and the overall mean variation was 18%. The optimum range of this method is from 0.1 mg/l to 2 mg/l  $\text{NO}_3$  (American Public Health Assoc., 1971), which partially explains why only three results could be used for calculating a mean for samples 2, 4 and 5.

By far the most popular method was the cadmium reduction method used on an automated Technicon system. Improved precision and accuracy were obtained on samples using this method.

At the 95% confidence interval there is no difference between the mean results obtained by using either one of the three methods above to analyze samples 1 to 5.

#### Synthetic Samples

The synthetic samples were prepared from reagents containing only those parameters presented for analysis in this study, with the exception of the addition of 0.15 ml of glacial acetic acid per litre of solution. This trace amount of acid was required to dissolve what appeared to be a suspended precipitate that had formed in the solution when the concentrates were mixed and diluted.

In most cases, the designed levels and the mean values obtained from results provided by the participants agreed within  $\pm 5\%$  (Table 12). In some cases, there were discrepancies, and as such, a laboratory value should be compared with the mean laboratory value rather than with the designed level. The discrepancies in sample 2 can in part be attributed to lack of preservation (e.g., nitrate) and to possible contamination in the sodium bicarbonate salt that was used.

The integrity of the calcium and chloride values for the two standard solutions is identified as excellent by the ratio of the Ca and Cl mean values, 1 Ca to 1.78 Cl. A similar ratio test, to confirm the stoichiometry, can be obtained from the experimental values for magnesium and sulphate. The recoveries for these four parameters were very good ( $100\% \pm 3\%$ ).

Table 11. Statistics on Nitrogen as NO<sub>3</sub>/NO<sub>2</sub> (mg/l)

Method	Statistical parameter	Sample number				
		1	2	3	4	5
Overall data	n	29	25	27	24	21
	$\bar{x}$	0.476	0.095	0.360	0.092	0.069
	S.D.	0.061	0.022	0.046	0.020	0.017
	C.V. (%)	12	23	13	22	25
	% Recovery		84		81	
Cadmium reduction	n	17	17	16	17	13
	$\bar{x}$	0.473	0.098	0.358	0.095	0.066
	S.D.	0.051	0.017	0.042	0.019	0.017
Hydrazine sulphate reduction	n	3	2	2	1	2
	$\bar{x}$	0.480	0.055	0.330	0.080	0.055
	S.D.	0.106	0.021	0.071		0.007
Brucine	n	6	3	6	3	3
	$\bar{x}$	0.473	0.089	0.367	0.093	0.074
	S.D.	0.083	0.018	0.066	0.015	0.013

Table 12. Recovery Data for the Standard Solutions

Parameter	Sample number 2		Sample number 4	
	Design value (mg/l)	Recovery (%)	Design value (mg/l)	Recovery (%)
Calcium	39.75	100.5	34.78	103
Magnesium	10.40	99.8	8.33	100
Total hardness	142.1	99.7	121.1	103
Sodium	62.50	128	57.20	97.7
Potassium	5.52	112	9.68	106
Total alkalinity (as CaCO <sub>3</sub> )	173.9	68.0	89.2	92.0
Chloride	70.32	103.4	61.53	102.3
Sulphate	41.09	101	32.91	98.0
Nitrate (as N)	0.113	84.1	0.113	81.4
Mean recovery		99.5 ± 16.5		98.2 ± 7.6

The quality of data for the solutions analyzed can be partially identified from an ion balance from sums of cations and sums of anions. The ion balance for the test solutions is given in Table 13. Although the balance for the synthetic solutions is in error by 10%, it can be improved if the higher alkalinity values obtained by the Technicon methyl orange method are the only values employed. The Youden plot for alkalinity for the pair of synthetic samples is elongated and suggests bias was present in many of the laboratories.

### SUMMARY

A summary of the data for nine parameters in the five test samples is given in Table 14. Outliers and very late data are not included in these calculations. The variability of data is larger for the synthetic sample than for the natural waters. The compatibility (interlaboratory preci-

sion) is similar to that obtained in an earlier study (McGirr and Wales, 1974) in this series.

Table 13. Ion Balance for Results of Test Samples

Sample	Parameters	Sums*	Percent error†
1	Cations	3.492	+0.04
	Anions	3.489	
2	Cations	6.463	+9.91
	Anions	5.301	
3	Cations	1.360	+0.10
	Anions	1.357	
4	Cations	5.175	+11.8
	Anions	4.089	
5	Cations	2.472	-0.41
	Anions	2.492	

\*The sums are expressed as milliequivalents CaCO<sub>3</sub>.  
 †The percent error is determined by the relationship:  

$$\frac{\text{anions} - \text{cations}}{\text{anions} + \text{cations}} \times 100\% = \text{Percent error}$$

Table 14. Round Robin Study No. 14—Major Ions

Analytical parameter	Statistical parameter	Sample number				
		1	2*	3	4*	5
Calcium	n	36	35	35	34	35
	$\bar{x}$	43.53	39.73	16.26	35.90	30.55
	S.D.	1.96	1.42	0.74	1.10	1.01
	C.V. (%)	4.5	3.6	4.5	3.1	3.3
	% Recovery		99.95		103.0	
Magnesium	n	35	35	35	36	35
	$\bar{x}$	11.25	10.38	3.79	8.34	6.72
	S.D.	0.77	0.51	0.31	0.40	0.36
	C.V. (%)	6.8	4.9	8.2	4.8	5.4
	% Recovery	99.8			100	
Hardness	n	37	37	34	36	36
	$\bar{x}$	155.0	141.7	56.2	124.8	104.3
	S.D.	4.86	4.67	2.63	4.01	3.56
	C.V. (%)	3.1	3.3	4.7	3.2	3.4
	% Recovery		99.7		121	
Sodium	n	33	34	33	34	31
	$\bar{x}$	8.08	79.67	4.72	55.91	8.39
	S.D.	0.48	5.31	0.56	4.98	0.44
	C.V. (%)	5.9	6.7	11.9	8.9	5.2
	% Recovery		128		97.7	
Potassium	n	31	32	32	31	32
	$\bar{x}$	1.54	6.20	1.18	10.30	1.07
	S.D.	0.14	0.71	0.13	0.65	0.16
	C.V. (%)	9.1	11	11	6.3	15
	% Recovery		112		106	
Alkalinity	n	33	33	31	33	33
	$\bar{x}$	114	119	40.4	81.7	77.3
	S.D.	4.45	22.6	2.85	21.4	2.65
	C.V. (%)	3.9	19	7.1	26	3.4
	% Recovery		68		92	
Chloride	n	35	34	36	35	34
	$\bar{x}$	14.2	72.7	7.88	63.0	18.3
	S.D.	1.20	3.72	0.95	2.34	1.10
	C.V. (%)	8.5	5.1	12.1	3.7	6.0
	% Recovery		103		102	
Sulphate	n	34	31	35	32	32
	$\bar{x}$	37.3	41.6	14.5	32.3	20.5
	S.D.	3.54	2.82	2.01	3.71	1.83
	C.V. (%)	9.5	6.8	14	11	8.9
	% Recovery		101		98	
Nitrate	n	29	25	27	24	21
	$\bar{x}$	0.476	0.095	0.360	0.092	0.069
	S.D.	0.061	0.022	0.046	0.020	0.017
	C.V. (%)	13	23	13	22	25
	% Recovery		84		81	

\*Samples 2 and 4 are synthetic.

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## FUTURE INTERLABORATORY STUDIES

- "Polychlorinated Biphenyls: Standards, Fish Extracts and Sediment Extracts."
- "Total Mercury in Natural Waters: Low-Level Range."
- "Total Mercury in Sediments."

**Appendix A**  
**Analytical Results for Interlaboratory**  
**Study No. 14**

## Analytical Results for Interlaboratory Study No. 14

Table A-1. Calcium (mg/l)

Laboratory number	Method	Sample number				
		1	2	3	4	5
1	AAS	44.5	40.4	16.5	36.3	31.5
2	AAS	30.0 R	38.5	15.0	36.0	30.0
3	AAS	42.5	39.0	16.0	35.5	30.0
4	Calculated	38.0	36.0 R	18.0	40.0 R	28.0
5	AAS	44.0	39.9	16.3	36.7	31.5
7	AAS	44.0	40.0	16.0	35.0	31.0
8	Titration	41.5	39.7	16.7	35.3	30.0
9	AAS	40.0	38.0	12.0 R	30.0 R	35.0 R
10	AAS	43.6	39.0	15.6	34.8	30.0
11	AAS	42.5	38.7	16.3	33.4	30.0
12	AAS	43.0	39.5	16.0	36.0	31.0
13	NI	44.0	39.2	16.5	35.5	30.8
15	AAS	52.0 R	45.0 R	20.0 R	37.0	39.0 R
16	Titration	44.7	40.8	15.9	36.5	31.4
18	Titration	44.1	38.4	17.1	35.1	31.0
20	AAS	46.8	43.1	16.7	37.0	31.7
21	AAS	42.0	39.0	15.0	35.5	29.5
22	AAS	48.0	43.0	18.0	41.0 R	35.0 R
24	Auto. cres.	40.2	39.8	15.6	36.0	30.4
26	NI	42.0	42.0	16.0	37.0	29.0
27	AAS	43.5	39.7	16.2	35.5	31.2
31	AAS	44.3	39.8	16.3	36.2	31.5
32a*	AAS	43.0	38.0	15.5	34.8	29.5
32b*	Titration	43.7	40.2	16.2	36.0	31.0
33	NI	44.5	46.4 R	16.5	41.5 R	32.2
34a*	AAS	41.3	37.4	15.6	33.5	29.2
34b*	Titration	44.8	41.6	17.6	38.0	31.6
36	Titration	45.0	41.0	17.0	38.0	32.0
37	AAS	43.0	38.0	15.5	34.0	29.0
41	AAS	46.0	40.0	16.0	36.0	31.0
43	AAS	43.0	40.0	17.0	36.5	31.0
44	AAS	44.0	40.4	16.8	36.4	32.0
45	AAS	43.3	40.0	16.2	35.4	30.4
46	AAS	45.0	40.0	15.0	37.5	29.2
47	AAS	44.9	39.4	16.6	36.1	31.1
49	Titration	43.0	37.0	16.0	35.0	30.0
50a*	Titration	42.4	38.4	16.0	36.0	29.6
50b*	AAS	47.0	41.7	26.3 R	37.0	30.8

\*a and b refer to duplicate determinations

AAS—Atomic absorption spectrophotometry

Calculated—Calculated from other data

NI—Insufficient information available

Auto. cres.—Automated cresolphthalein complexone used in analysis

Table A-2. Magnesium (mg/l)

Laboratory number	Method	Sample number				
		1	2	3	4	5
1	AAS	11.2	10.5	3.8	8.0	6.6
2	AAS	11.7	10.7	4.0	8.7	7.0
3	AAS	10.7	9.9	3.8	8.0	6.6
4	AAS	14.0 R	11.0	4.0	8.0	7.0
5	AAS	11.0	10.3	3.8	8.2	6.6
7	AAS	12.0	11.0	4.0	8.4	6.8
8	Calculated	10.2	10.1	4.2	8.0	7.2
9	AAS	12.0	10.0	4.0	8.0	7.0
10	AAS	10.9	10.2	3.9	8.2	6.7
11	AAS	6.52 R	10.9	2.46 R	9.04	7.58
12	AAS	10.0	9.2	3.5	7.9	6.4
13	NI	10.8	10.3	3.60	8.07	6.56
15	AAS	11.2	10.5	3.9	8.7	6.9
16	Calculated	10.8	9.8	3.9	8.5	6.5
18	Calculated	10.2	11.2	3.2	8.8	6.0
20	AAS	13.1	12.4 R	4.4	9.1	7.8 R
21	AAS	11.5	10.5	3.75	8.50	6.75
22	AAS	11.3	10.8	4.2	8.8	7.2
24	Colorimetric	10.8	10.1	3.8	8.1	6.5
26	NI	11.5	11.0	4.1	8.5	7.1
27	AAS	11.30	10.45	3.98	8.10	6.60
31	AAS	11.6	10.9	4.0	8.7	6.9
32	AAS	10.8	10.1	3.80	8.00	6.50
33	NI	11.1	10.3	4.02	8.42	6.90
34a	AAS	11.8	11.2	3.7	9.0	7.3
34b	Calculated	13.0	10.0	3.0	8.0	7.0
36	Calculated	10.4	9.6	3.2	7.0 R	6.2
37	AAS	11.5	10.9	3.9	8.5	6.6
41	AAS	11.0	11.0	4.0	8.5	7.2
43	AAS	10.5	10.0	3.9	7.7	6.2
44	AAS	10.4	10.0	3.6	8.4	6.4
45	AAS	11.5	11.0	3.9	8.7	6.8
46	AAS	12.2	9.6	3.6	7.8	6.2
47	Calculated	10.7	9.9	3.1	7.6	6.3
49	Calculated	13.0	14.0 R	5.0 R	9.0	8.0 R
50a	AAS	11.0	10.1	3.59	8.07	6.42
50b	AAS	11.1	10.4	3.68	8.35	6.61

AAS—Atomic absorption spectrophotometry

Calculated—Calculated from other data

Colorimetric—Colorimetric, calganite employed for analysis

NI—Insufficient information available

Table A-3. Total Hardness (mg/l as CaCO<sub>3</sub>)

Laboratory number	Method	Sample number				
		1	2	3	4	5
1	Calculated	157.0	144.0	56.9	124.0	106.0
2	Calculated	123.0 R	140.0	53.9	126.0	103.0
3*	Calculated	150.0	138.0	56.0	122.0	102.0
4	Titration	152.0	136.0	68.0 R	134.0	97.0
5	Calculated	155.0	142.0	56.3	125.0	106.0
7	Titration	156.0	136.0	52.0	120.0	100.0
8	Titration	145.8	140.7	59.1	121.2	104.8
9	Calculated	149.0	135.0	47.5 R	108.0 R	116.0
10	Calculated	154.0	139.0	55.0	121.0	103.0
11	Titration	158.0	141.0	67.0 R	125.0	120.0 R
12	Calculated	149.0	137.0	55.0	123.0	104.0
13	Calculated	155.0	140.0	56.0	122.0	104.0
15	Calculated	180.0 R	160.0 R	66.0 R	130.0	130.0 R
16	Titration	156.0	142.0	55.9	126.0	105.0
18	Technicon	152.0	142.0	56.0	124.0	102.0
20	Titration	145.0	133.0	51.5	115.5	100.0
21	Calculated	152.2	140.6	52.9	123.6	101.5
22	Technicon	165.0	150.0	62.0	138.0 R	110.0
23	Titration	156.0	142.0	66.0 R	130.0	106.0
24	Calculated	145.0	141.0	55.0	123.0	103.0
26*	Calculated	152.0	150.0	56.8	127.0	102.0
27	Titration	166.0	180.0 R	63.0	136.0 R	124.0 R
30	Titration	154.0	140.0	55.0	123.0	104.0
31a	Titration	156.0	142.0	56.0	125.0	105.0
31b	Calculated	158.0	144.0	57.0	176.0	107.0
32a	Calculated	152.0	136.0	54.3	120.0	100.0
32b	Titration	156.0	142.0	55.8	124.0	105.0
33*	Calculated	157.0	158.0	57.7	138.0	109.0
34	Titration	156.0	142.0	55.0	127.0	107.0
36	Titration	156.0	142.0	56.0	124.0	106.0
37	Calculated	154.8	138.6	54.8	120.0	99.6
41	Calculated	160.0	145.0	56.0	127.0	106.0
43	Titration	154.0	143.0	57.0	127.0	104.0
44	Titration	155.0	143.0	61.0	126.0	106.0
45	Titration	156.0	145.0	56.6	125.0	106.0
46*	Calculated	163.0	140.0	52.0	126.0	98.0
47	Titration	157.0	140.0	54.4	122.0	104.0
49	Titration	160.0	148.0	60.0	124.0	108.0
50	Titration	162.0	146.0	59.0	126.0	106.0

\*Data calculated by the authors

Calculated—Calculated from data for calcium and magnesium

Technicon—Automated Technicon method



Table A-4. Sodium (mg/l)

Laboratory number	Method	Sample number				
		1	2	3	4	5
1	E-flame	8.1	79.0	4.7	57.0	8.2
2	E-flame	7.6	100.0	4.7	46.0	9.4
3	E-flame	8.4	80.0	4.5	52.0	8.4
4	AAS	7.0	79.0	4.0	56.0	6.0 R
5	E-flame	8.1	77.5	4.7	55.5	8.3
7	AAS	8.5	80.0	4.9	57.0	8.3
9	AAS	<10.0	83.0	<10.0	60.0	<10.0
10	E-flame	8.1	76.0	4.6	56.0	8.4
11	E-AA	8.4	80.0	7.2	55.0	8.5
12	E-AA	7.7	86.0	3.9	64.0	6.4 R
13	NI	7.8	77.0	4.5	55.0	7.9
15	NI	7.9	75.0	4.8	53.0	7.9
16	E-flame	8.4	82.0	4.9	57.0	8.6
18	AAS	8.2	85.0	4.7	62.0	8.3
20	NI	6.83	78.5	4.41	59.4	7.47
21	AAS	8.8	82.0	5.4	60.0	8.8
22	NI	8.4	72.4	4.9	50.5	8.7
24	AAS	7.5	75.0	4.3	54.0	7.5
26	NI	8.0	80.3	5.0	58.5	8.7
27	E-AA	8.6	80.5	5.0	57.0	8.8
31	E-flame	8.4	80.0	4.8	56.0	8.3
32	AAS	8.20	78.0	4.80	44.0	8.30
33	NI	8.16	78.8	4.62	56.1	8.23
34	AAS	7.9	75.0	4.7	55.0	8.0
36	E-flame	7.4	72.0	4.4	54.0	8.0
37	E-AA	7.8	72.5	4.0	42.0	8.5
41	E-flame	8.5	84.0	5.0	60.0	8.5
43	NI	8.1	88.0	5.0	66.0	8.6
44	E-AA	8.7	82.0	4.9	58.0	8.9
45	AAS	7.85	77.0	4.50	54.8	8.05
46	AAS	8.00	83.3	4.40	60.0	9.00
47	E-flame	8.5	80.0	4.8	60.0	8.75
49	NI	9.0	77.0	4.0	56.0	9.0
50	AAS	7.95	72.9	4.57	54.1	7.79

E-flame—Emission on a flame photometer

AAS—Absorption on an atomic absorption spectrophotometer

E-AA—Emission on an atomic absorption spectrophotometer

NI—Insufficient information available

Table A-5. Potassium (mg/l)

Laboratory number	Method	Sample number				
		1	2	3	4	5
1	E-flame	1.5	5.6	1.1	9.9	1.0
2	E-flame	1.5	7.7	1.2	10.2	1.2
3	E-flame	1.5	5.5	1.2	9.0	1.0
4	AAS	1.2	5.4	1.5	9.4	1.2
5	E-flame	1.5	5.6	1.1	9.8	1.0
7	AAS	1.5	5.6	1.3	10.0	1.0
9	AAS	<2.0	7.8 R	<2.0	12.0	<2.0
10	E-flame	1.4	5.6	1.0	9.7	0.9
11	E-AA	1.6	6.9	1.2	15.6 R	1.1
12	E-AA	1.4	8.0	1.2	11.0	1.1
13	NI	1.56	5.92	1.12	10.1	1.03
15	NI	1.45	5.9	1.10	9.6	0.98
16	E-flame	1.5	5.7	1.0	10.4	0.9
18	AAS	1.6	6.7	1.2	11.5	1.2
20	NI	1.53	7.3	1.21	10.9	1.05
21	AAS	2.6 R	12.0 R	1.8 R	17.5 R	1.8 R
22	NI	1.5	5.6	1.1	9.5	1.1
24	AAS	1.4	7.0	1.0	11.0	0.9
26	NI	1.9	6.0	1.3	10.1	1.3
27	E-AA	2.18 R	6.62	1.56	10.40	1.56
31	E-flame	1.5	5.8	1.2	10.0	1.0
32	AAS	1.46	5.55	1.10	19.2 R	0.97
33	NI	1.44	5.07	1.17	10.5	1.03
34	AAS	1.5	5.8	1.1	9.7	1.0
36	E-flame	1.5	5.8	1.2	9.9	1.2
37	E-AA	1.6	6.6	1.1	10.6	1.0
41	E-flame	1.4	6.4	1.1	11.0	1.0
43	NI	1.7	6.2	1.3	11.0	1.1
44	E-AA	1.6	6.0	1.2	10.0	1.0
45	AAS	1.70	6.20	1.20	10.30	1.15
46	E-AA	1.50	7.19	1.00	10.6	0.63
47	E-flame	1.75	6.5	1.05	10.0	1.20
49	NI	1.9	6.7	1.3	11.0	1.4
50	AAS	1.50	5.95	1.20	10.2	1.04

E-flame—Emission on a flame photometer

AAS—Absorption on an atomic absorption spectrophotometer

E-AA—Emission by an atomic absorption spectrophotometer

NI—Insufficient information available

Table A-6. Alkalinity (mg/l as CaCO<sub>3</sub>)

Laboratory number	Method	Sample number				
		1	2	3	4	5
1	WQB	114.0	122.0	38.8	75.0	76.0
2	WQB	118.0	140.0	41.4	95.9	79.8
3	Technicon	110.0	164.0	39.0	124.0	75.0
4	Radiometer	95.0 R	97.0	47.0	69.0	62.0 R
5	Standard Methods	112.0	134.0	41.0	87.5	77.5
7	Standard Methods	110.0	130.0	42.0	94.0	78.0
8	Standard Methods	111.6	100.5	40.0	67.4	77.6
9	Radiometer	116.0	120.0	56.0 R	80.0	80.0
10	WQB	112.0	101.0	38.4	64.4	75.4
11	WQB	115.0	104.0	40.0	76.0	78.0
12	Other	113.0	118.0	36.0	81.0	77.0
13	NI	113.4	134.8	41.2	98.4	78.3
15	Other	113.0	123.0	40.6	86.2	76.2
16	WQB	114.0	102.0	40.6	69.8	75.6
18	Technicon	114.0	162.0	36.0	126.0	76.0
20	Other	112.0	94.0	39.5	60.0	77.0
21	Standard Methods	114.0	148.0	44.0	104.0	78.0
22	Technicon	126.0	168.0	40.0	128.0	80.0
23	Other	109.5	75.0	38.0	47.0	72.5
24	Modified Technicon	112.0	131.0	38.0	85.0	74.0
27	Other	125.0	100.0	50.0	75.0	75.0
30	Other	109.0	90.0	39.0	56.0	74.0
31	Other	111.0	-	40.0	-	78.0
32	WQB	117.0	104.0	40.7	66.0	79.4
34	Radiometer	116.0	127.0	41.0	89.0	80.0
36	NI	111.0	97.0	39.0	43.0	78.0
37	Standard Methods	111.0	101.0	38.5	64.5	70.0
41	WQB	112.0	104.0	39.0	65.0	78.0
43	Standard Methods	112.0	130.0	41.0	96.0	76.0
44	Other	114.0	118.0	38.0	82.5	78.5
45	NI	110.0	114.0	39.0	78.0	75.0
47	WQB	112.0	100.0	18.3 R	58.9	81.3
49	Radiometer	126.0	146.0	44.0	116.0	82.0
50	Standard Methods	120.0	116.0	55.0 R	87.0	82.0

WQB—Titration by Water Quality Branch method (Department of the Environment, 1974)

Technicon—Data from a Technicon AutoAnalyzer method

Radiometer—Data from a titration employing a radiometer

Standard Methods—Results from titration (American Public Health Assoc., 1971)

Other—Titration results by an unspecified method

NI—Insufficient information available

Modified Technicon—Technicon method No. 111-71W using bromophenol blue rather than methyl orange

Table A-7. Chloride (mg/l)

Laboratory number	Method	Sample number				
		1	2	3	4	5
1	Colorimetric	13.2	77.0	7.7	63.0	19.0
2	Colorimetric	15.0	76.0	9.4	66.0	19.0
3	Colorimetric	14.0	67.0	7.0	59.0	18.5
4	Colorimetric	13.0	70.0	8.0	66.0	18.0
5	Colorimetric	13.9	72.5	7.6	63.0	18.2
7	Colorimetric	14.0	73.0	8.0	61.0	18.0
8	Colorimetric	14.3	72.6	8.4	60.0	19.2
9	Colorimetric	13.0	68.0	7.0	60.0	17.0
10	Colorimetric	13.0	66.0	6.9	59.0	16.0
11	Colorimetric	13.6	73.0	7.9	62.6	17.9
12	Colorimetric	12.9	71.0	8.1	64.0	17.7
13	NI	13.5	71.7	7.37	62.5	17.6
15a	Titration	16.4	72.2	8.7	64.0	18.2
15b	Colorimetric	14.8	77.0	7.9	59.0	18.2
16	Colorimetric	14.5	74.5	7.9	65.0	19.0
18	Colorimetric	14.0	70.0	7.0	62.0	18.0
20	Titration	15.08	80.29	7.69	64.71	18.88
21	Titration	13.0	75.0	9.0	64.0	6.0 R
22	Colorimetric	16.0	90.0 R	8.0	80.0 R	20.0
23	Colorimetric	20.0 R	75.0	13.0 R	67.0	27.0 R
24	Colorimetric	14.0	71.0	8.0	63.0	18.0
26	NI	12.1	68.4	7.8	58.5	15.8
27	Titration	20.0 R	50.0 R	10.0	60.0	20.0
30	Colorimetric	14.0	72.0	7.3	64.0	18.0
31	Titration	13.5	73.0	7.0	64.0	18.0
32	Titration	14.5	74.6	6.70	64.7	18.3
33	NI	15.7	76.7	7.7	62.3	20.6
34	Colorimetric	12.7	72.0	6.65	65.0	17.2
36	Electrode	14.0	73.0	8.0	63.0	18.0
37	Titration	13.4	72.2	5.7	64.2	17.7
43	Titration	16.0	74.0	9.0	66.0	20.0
44	Titration	17.0	68.5	9.8	65.5	20.8
45	Colorimetric	13.4	72.8	7.5	64.6	18.2
47	Colorimetric	16.5	90.0 R	7.4	65.0	18.0
49	Titration	15.0	84.0	10.0	74.0 R	23.0 R
50a	Titration	14.0	69.0	7.7	60.8	17.8
50b	Titration	13.1	68.8	7.9	60.8	18.2

NI—Insufficient information available  
 Electrode—Specific ion electrode method

Table A-8. Sulphate (mg/l)

Laboratory number	Method	Sample number				
		1	2	3	4	5
1	Colorimetric	36.0	41.0	14.0	32.0	20.0
2	Colorimetric	39.0	45.0	16.0	35.0	24.0
3	Colorimetric	39.3	43.0	13.8	33.0	21.7
4	Turbidimetric	42.0	44.0	14.0	36.0	20.0
5	Titrimetric	39.9	42.3	13.6	33.4	21.6
7	Turbidimetric	35.0	40.0	12.0	35.0	20.0
8	Turbidimetric	40.3	40.0	18.0	32.4	22.2
9	Turbidimetric	40.0	41.0	14.0	34.0	20.0
10	Colorimetric	36.0	40.0	14.0	32.0	21.0
11	Titrimetric	38.0	40.0	12.0	30.0	17.0
12	Colorimetric	47.0 R	45.0	16.1	39.0	27.0 R
13	NI	34.1	39.7	14.1	29.9	18.9
15a	Titrimetric	36.0	38.0	16.0	24.0	19.0
15b	Colorimetric	31.0	32.0 R	16.0	31.0	19.0
16	Colorimetric	39.0	43.0	15.0	34.0	22.0
18	Turbidimetric	40.0	44.0	18.0	32.0	22.0
20	Turbidimetric	44.16	109.44 R	17.95	96.96 R	23.14
21	Turbidimetric	24.4 R	31.8 R	9.0	21.0 R	10.0 R
22	Turbidimetric	36.0	48.0	12.0	36.0	18.0
24	Colorimetric	39.0	42.0	17.0	34.0	23.0
26		28.9	31.7 R	5.6 R	22.1 R	11.9 R
27	Turbidimetric	50.0 R	51.0 R	28.0 R	44.0 R	29.0 R
30	Turbidimetric	40.0	36.0	16.0	35.0	23.0
31	Gravimetric	40.6	39.2	13.7	33.2	19.8
32	NI	35.3	41.1	14.7	23.7	17.5
33	NI	35.6	48.0	14.4	40.2	19.5
34	Colorimetric	38.5	43.1	14.0	33.3	20.8
36	Colorimetric	35.0	42.0	15.0	30.0	19.0
37	Turbidimetric	37.5	41.0	13.6	31.5	20.0
41	Turbidimetric	38.0	40.0	15.0	32.0	23.0
43	Turbidimetric	34.0	38.0	10.0	25.0	15.0 R
44	Turbidimetric	38.2	39.0	14.0	32.0	19.6
45	Turbidimetric	37.2	40.0	16.0	33.2	22.0
47	Titrimetric	29.0	31.0 R	13.0	26.0	17.0
49	Titrimetric	44.0	45.0	15.0	34.0	21.0
50a	Turbidimetric	35.0	42.0	13.0	—	21.0
50b	Turbidimetric	35.0	38.0	16.0	32.0	21.0

Colorimetric—Colorimetric (automated) method

NI—Insufficient information available

Table A-9. Nitrate (mg/l as N)

Laboratory number	Method	Sample number				
		1	2	3	4	5
1	Cadmium	0.48	0.11	0.36	0.11	0.08
2	Cadmium	0.47	0.08	0.35	0.08	0.14 R
3	Cadmium	0.408	0.099	0.350	0.100	0.068
4	Hydrazine	0.6	<0.1	0.7 R	<0.1	<0.1
5	Cadmium	0.49	0.10	0.36	0.11	0.08
7	UV spec.	0.54	0.23 R	0.38	0.27 R	0.11
8	Hydrazine	0.40	0.04	0.28	0.03 R	0.06
9	Cadmium	0.52	0.11	0.37	0.11	0.07
10	Cadmium	0.47	0.10	0.27	0.11	<0.005
11	Cadmium	0.46	0.12	0.34	0.11	0.070
12	Cadmium	0.452	0.113	316	0.068	0.068
13	NI	0.478	0.105	381	0.109	0.074
15	Cadmium	0.485	0.118	0.394	0.084	0.066
16	Cadmium	0.52	0.100	0.39	0.104	0.087
18	Hydrazine	0.44	0.07	0.38	0.08	0.05
22	Brucine	0.4	0.2 R	0.3	<0.1	<0.1
23	Cadmium	0.51	0.10	0.38	0.11	0.08
24	Cadmium	0.48	0.09	0.34	0.09	0.06
26	Cadmium	0.3 R	0.1	0.3	0.1	0.0 R
30	Brucine	0.58	0.077	0.43	0.080	0.083
31	Brucine	0.53	0.08	0.35	0.09	0.06
32	Phenoldisulphonic acid	0.91 R	0.14	0.86 R	0.05	0.13 R
33	NI	0.487	0.094	0.358	0.090	0.072
34	Cadmium	0.391	0.051	0.167 R	0.054	0.027
36	Cadmium	0.38	0.08	0.19 R	0.06	0.04
37	Brucine	0.38	0.28 R	0.38	0.28 R	0.28 R
43	Brucine	0.79 R	0.316 R	0.451	<0.23	<0.23
44	Brucine	0.53	0.11	0.49 R	0.11	0.08
45	Cadmium	0.596	0.098	0.384	0.117	0.198 R
47	Cadmium	0.47	0.09	0.38	0.09	0.06
49	Cadmium	0.45	<0.23	0.45	<0.23	<0.23
50	Brucine	0.42	<0.05	0.29	<0.05	<0.05

Cadmium—Cadmium reduction employed in analysis

Hydrazine—Hydrazine sulphate reduction used in analysis

UV spec.—UV spectrophotometric procedure (no details given)

NI—Insufficient information available

Brucine—Brucine method

Phenoldisulphonic acid—Phenoldisulphonic acid employed in analysis

**Appendix B**  
**List of Participants**

## List of Participants

### *Fisheries and Environment Canada, Environmental Management Service*

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)  
Western Region, Water Quality Branch Laboratory (Yellowknife)  
Pacific Region, Water Quality Branch Laboratory (Vancouver)

### *Fisheries and Environment Canada, Environmental Protection Service*

Atlantic Region, Surveillance and Analysis Division (Halifax)  
Environmental Health Centre, Tunney's Pasture (Ottawa)  
Northwest Region (Edmonton)  
Northwest Region (Winnipeg)  
Technology Development and Demonstration Division (Burlington)

### *Fisheries and Environment Canada, Fisheries and Marine Service*

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

### *Provincial Government Laboratories*

Alberta Department of the Environment, Pollution Control Laboratory (Edmonton)  
British Columbia Research Council, Division of Applied Biology (Vancouver)  
Government of British Columbia, Water Resources Service (Vancouver)  
Manitoba Department of Mines, Resources and

Environmental Management, Environmental Protection Branch (Winnipeg)

Ministère des Affaires sociales, Laboratoire de chimie et du contrôle sanitaire (Laval)  
Ministère des Richesses naturelles du Québec, Laboratoire de la qualité des eaux (Ste-Foy)  
New Brunswick Department of Fisheries and the Environment, Environment Branch (Fredericton)  
Nova Scotia Department of Public Health, Division of Clinical Chemistry (Halifax)  
Ontario Ministry of the Environment (Rexdale)  
Ontario Ministry of the Environment (Thunder Bay)  
Saskatchewan Department of Public Health, Provincial Laboratories (Regina)  
Service de la protection de l'environnement, Complexe scientifique (Ste-Foy)

### *Municipal Government Laboratories*

City of Winnipeg Waterworks and Waste Disposal (Winnipeg)  
Ville de Montréal, Usine de filtration (Verdun)

### *Industrial and Consulting Laboratories*

Analytical Centre, Aluminum Co. of Canada Ltd. (Arvida, Quebec)  
Beak Consultants Ltd. (Richmond, British Columbia)  
Chemex Labs. Ltd. (Calgary, Alberta)  
Chemex Labs. Ltd. (North Vancouver, British Columbia)  
Cominco Ltd. (Trail, British Columbia)  
Eco-Research Ltd. (Pointe-Claire, Quebec)  
Environmental Research Associates, Division of Korab Marine Ltd. (Lachine, Quebec)  
Shell Canada, Exploration and Production Laboratory (Calgary, Alberta)

### *University Laboratories*

Department of Biology, Life Sciences Centre, Dalhousie University (Halifax, Nova Scotia)



Environment Canada Library, Burlington



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