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Intercomparison 9812:

pH, K_{25} , HCO_3 , $\text{NO}_3 + \text{NO}_2$, Cl, SO_4 ,
Ca, Mg, Na, K, total aluminium,
aluminium - total and nonlabile, TOC
and COD-Mn

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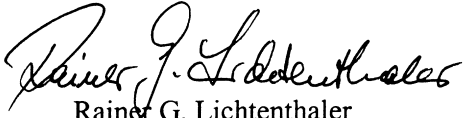
Abstract
43 laboratories in 20 countries participated in intercomparison 9812. One sample set for the determination of major ions, organic matter and aluminium fractions, were used. Based on the general target accuracy of $\pm 20\%$, 74 % of the results were acceptable. More than 80 % of the result pairs were acceptable for conductivity, nitrate + nitrite, sulfate, sodium, and dissolved organic carbon. For pH only 55 % of the result pairs were acceptable in relation to the extended target accuracy of ± 0.2 units. For two analytical variables, reactive and non-labile aluminium, it was decided **not** to evaluate the reported results, because of the great spread between the results from the few participants. Normalization of the methods is necessary to improve the comparability for these variables. Manual methods are generally less sensitive compared to instrumental methods, and are not always suitable for acid rain monitoring.

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CONVENTION ON LONG-RANGE
TRANSBOUNDARY AIR POLLUTION

INTERNATIONAL COOPERATIVE PROGRAMME ON
ASSESSMENT AND MONITORING OF ACIDIFICATION
OF RIVERS AND LAKES

Intercomparison 9812

*p*H, K₂₅, HCO₃⁻, NO₃⁻+NO₂⁻, Cl⁻, SO₄⁻⁻
Ca⁺⁺, Mg⁺⁺, Na⁺, K⁺,
Al, Al-R, Al-I, DOC and Cod-Mn

Prepared by the Programme Centre
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Preface

The International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP-Waters) was established under the Executive Body of the Convention on Long-Range Transboundary Air Pollution at its third session in Helsinki in July 1985. The Executive Body has also accepted Norway's offer to provide facilities for the Programme Centre, which has been established at the Norwegian Institute for Water Research, NIVA. A programme subcentre is established at the Laboratory of Freshwater Ecology and Inland Fisheries at University of Bergen. The ICP-Waters programme has been lead by Berit Kvæven, Norwegian Pollution Control Authority.

The Programme objective is to establish an international network of surface water monitoring sites and promote international harmonization of monitoring practices. One of the tools in this work is inter-laboratory quality assurance tests. The bias between analyses carried out by the individual participants of the Programme has to be clearly identified and controlled.

We here report the results from the 12th intercomparison of chemical analysis.

Oslo, October 1998

Håvard Hovind

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Summary

Intercomparison 9812 was organized as a part of the between-laboratory quality control programme, as stated in "Manual for Chemical and Biological Monitoring" (1), by the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes.

The intercomparison was performed in June 1998, and included the determination of major ions in natural water samples. The participants were asked to determine pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, total aluminium, reactive and non-labile aluminium, dissolved organic carbon and chemical oxygen demand (COD-Mn).

Two sample sets was prepared for this intercomparison, one for the determination of the major ions, and the other for aluminium fractions and unspecific organic matter. 43 laboratories determined all, or some of the analytical variables in the samples.

70 laboratories were invited to participate in this intercomparison, and the samples were sent to nearly 50 laboratories who wished to participate. 43 laboratories submitted results to the Programme Centre before the final statistical treatment of the data. 20 countries were represented in this laboratory group.

As "true" value for each variable was selected the median value of the results received from the participants. For two analytical variables - reactive and non-labile aluminium - this definition of the "true value" is not acceptable, because of the great spread between the results from the few participants of this variable. It was therefore decided not to evaluate the reported results for these variables. Excluding these two variables from the evaluation, 74 % of the result pairs were regarded as acceptable, the target limit being the median value ± 20 %.

For pH the accuracy limit was extended to ± 0.2 units, and only 55 % of the result pairs were included by this special limit. A total error of ± 0.2 units for pH measurements seems to be a more reasonable assessment of the accuracy between laboratories, than the target limit of ± 0.1 units. The reason for the great spread of pH results is mainly due to the fact that different measurement routines are used by the participants, leading to systematically different results. To establish a "true value" based on the mean value for **all** the reported results for pH, when the methods are different, is questionable, and should be discussed on the next meeting.

The best results were reported for conductivity, nitrate + nitrite, sulfate, sodium dissolved organic carbon. Rather poor comparability was observed for pH and aluminium species. To improve the comparability of the results for pH and aluminium species, it is necessary to normalize the analytical method and determination technique used.

1. Introduction

As stated in "Manual for Chemical and Biological Monitoring" (1), between-laboratory quality control is necessary in a multilaboratory programme to assure clear identification and control of the bias between analyses carried out by individual participants of the Programme. Such biases may arise through the use of different analytical methods, errors in the laboratory calibration solutions, or through inadequate within-laboratory control.

The between-laboratory control carried out by the Programme Centre is based on the "round robin" concept and the procedure of Youden (2, 3), which is briefly described in Appendix 3. This twelfth intercomparison test, called 9812, included the determination of the major components and some other ions in natural water samples: pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, total aluminium, reactive and non-labile aluminium, dissolved organic carbon and chemical oxygen demand (COD-Mn).

2. Accomplishment of the intercalibration

The preparation of the sample solutions is described in Appendix 2. The results of the control analyses performed at the Programme Centre are also summarized in the same place. On the Task Force meeting in 1997 it was decided that two sample sets should be included in this intercomparison, one sample pair for the determination of the major ions, and one sample pair for aluminium fractions and unspecific organic compounds.

The samples were mailed from the Programme Centre on May 26, 1998. Most of the participating laboratories received the samples within one week, with some few exceptions. To ensure that the effect of possible alterations in the solutions is minimized, the participants were asked to analyze the samples as soon as possible, and return the analytical results within one month after the samples arrived at the laboratory. Most results were received within the end of June.

3. Results

70 laboratories were invited to participate in the intercomparison, and nearly 50 laboratories accepted and received samples. The 43 laboratories who submitted results to the Programme Centre, are representing 20 countries. It was a problem that some of the laboratories submitted the results several weeks after the deadline, and a reminder letter had to be mailed to some of the participants. A survey of the participants and their code numbers are listed in Appendix 1.

The analytical results received from the laboratories were treated by the method of Youden (2, 3). A short description of this method, and the statistical treatment of the analytical data, are presented in Appendix 3.

The purpose of this test is to evaluate the comparability of the analytical results produced by different laboratories. The real "true value" is not known exactly for the natural samples used in this intercomparison. Therefore, we selected the median value, determined from the analytical results submitted by the participating laboratories, as the "true value" for each analytical variable. The median value is considered to be an acceptable estimate of the true value for this purpose, as long as most of the participants are using essentially the same analytical method.

The results are illustrated in Figure 1 - 15, where each laboratory is represented by a small circle and an identification number. The great circle in the figures are representing a selected accuracy limit, either the general target limit of $\pm 20\%$ of the mean true values of the sample pair, or a special accuracy limit defined in the sections below. A survey of the results of intercomparison 9812 is presented in Table 1. The individual results of the participants are presented in Table 4 in the Appendix, sorted in order of increasing identification number. More extensive statistical informations are presented in the Tables 5.1 - 5.15.

3.1 pH

The reported results for pH are graphically presented in Figure 1, where the radius of the great circle is 0.2 pH units, and visualizes the degree of comparability between the pH results from the participating laboratories. The reported pH values are given in Table 5.1.

Figure 1 shows that the reported results are spread out along the 45° line, most of the results determined during stirring the solution are lowered compared to the nonstirred readings, and most of the results determined without stirring the solution are located in the upper right part of the diagramme. One laboratory that equilibrated the solutions by bubbling with air containing 350 ppm CO_2 before reading the pH value, reported far higher results than the other laboratories.

The participating laboratories determined pH in the test solutions by their own routine method. An electrometric method was used by all laboratories. 42 laboratories reported results for pH, of this group 19 indicated that they read the pH value during stirring the solution. As shown in Table 1, there is no significant difference between the results determined in a quiescent solution, and when determined during stirring the solution.

The stirring are normally lowering the reported pH results. As the CO_2 concentration of samples in the circumneutral range may be far above the atmospheric equilibrium, the relatively high pCO_2 levels will lead to large systematic errors, the magnitude of which will vary between the laboratories due to different pCO_2 levels in the samples caused by different storage and handling conditions. This effect may also increase the random error as the samples may contain different amount of excess CO_2 .

(The text continues on page 27)

The control analyses carried out at the Program Centre proved that the samples were stable when stored at our laboratory. However, the equilibrium of the samples may be influenced by variations in pressure and temperature when they are mailed to the participants.

Some systematic deviations observed in Figure 1 may also be due to errors in the instrument, or more likely in the electrodes, as different electrodes may give rise to different results (4, 5). The main reason for the differences in the reported results, however, is obviously connected to the different measurement methods used by the participants.

3.2 Conductivity

The conductivity results are presented in Figure 2, where the great circle is representing an accuracy limit of $\pm 20\%$. The reported results are given in Table 5.2. Some laboratories reported the conductivity results in the unit $\mu\text{S}/\text{cm}$, which is the unit they use routinely, instead of the requested mS/m at $25\text{ }^\circ\text{C}$. These results were recalculated to mS/cm by the Programme Center. All participants used an electrometric method for the determination of conductivity.

Most laboratories achieved very good agreement between the results for this variable. One laboratory reported results being systematically too high for both the samples, and three laboratories reported results being systematically too low. A proper temperature correction is necessary when determining this analytical variable, as the conductivity is changing by about two percents per degree at room temperature.

3.3 Alkalinity

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 5.3. About one third of the participating laboratories used the Gran plot titration method suggested in the Manual (1). The others used end point titration, either to pH 4.5 and 4.2, or to one given pH value only (4.2, 4.5, 5.4, or 5.6).

There is a systematic spread of the results for alkalinity at this intercomparison, and this is mainly due to the different methods used by the laboratories. By a closer examination of the results, a clear connection between the method used and the location in Figure 3 was observed. The laboratories using the Gran plot titration reported results located close to the centrum of the circle. The results determined by the end point titration to pH 4.2 or 4.5 alone, are mainly located in the upper right part of Figure 3. The end point titration to pH 5.6 or 5.4 gave results mainly located within the acceptance circle.

A few laboratories have reported values being about half of the median value, they have probably calculated the result as $\text{mmol}/\text{l CO}_3^{2-}$ instead of HCO_3^- . The strongly deviating results have been produced mainly by not documented methods.

The alkalinity value may vary significantly with the end-point pH used for the titration. In waters containing high concentrations of total inorganic carbon, the equivalence point is close to pH = 5.4. In this case, the relative error introduced by assuming a fixed end-point pH, is negligible. However, at lower alkalinities normally encountered in areas sensitive to acidification, the “total fixed end-point method” overestimates the true alkalinity or the “equivalence” alkalinity.

3.4 Nitrate + nitrite

The results reported for this parameter are presented in Figure 4, and the reported results are given in Table 5.4. The circle in Figure 4 is representing a general target accuracy of $\pm 20\%$. Ion chromatography is used by an increasing number of laboratories, and is now used by more than one third of the participants. The others are determining this analytical variable by photometric methods, most of these laboratories are using an automated version of the cadmium reduction method. There is no statistically significant difference between the results determined by the different methods. However, some few strongly deviating results are determined by manual methods. Laboratory no. 31 may have reported the results as mg/l NO₃ instead of mg/l NO₃-N.

3.5 Chloride

The chloride results are presented in Figure 5, and the reported results from the participants are given in Table 5. 29 out of 40 laboratories determined chloride by ion chromatography. The greatest deviations are observed for the manual photometric methods, and the argentometric method which have too high detection limit, the latter method is not sensitive enough for most of this kind of samples.

3.6 Sulfate

The sulfate results are illustrated in Figure 6, and the reported values are given in Table 5.6. Ion chromatography is used by 29 of 38 laboratories for the determination of this analytical variable. Three laboratories used a photometric method based on the dissociation of the barium-thorin complex, and five laboratories used a nephelometric method. One laboratory used capillary chromatography with acceptable results.

An accuracy limit of $\pm 20\%$ is represented by the circle in Figure 6. The strongly deviating results are mainly determined by manual photometric or turbidimetric methods.

3.7 Calcium

The calcium results are illustrated in Figure 7, and the reported values are given in Table 5.7. 21 of the participants used flame atomic absorption spectrometry for the determination of

calcium. ICP techniques and ion chromatography are used by nine and six laboratories, respectively. The complexometric titration method, used by two laboratories, is not sensitive enough for most of this kind of samples. The result pairs being not acceptable are dominated by too low results for sample A. The difference between the calcium concentrations in the two samples A and B is too large for the use of the Youden method, which is based on sample pairs with slightly different concentrations.

3.8 Magnesium

The magnesium results are presented in Figure 8, and the reported values are given in Table 5.8. Most of the participants are still using flame atomic absorption spectrometry for the determination of magnesium. ICP emission spectrometry and ion chromatography was used by nine and six laboratories, respectively. Systematic deviations are dominating the results outside the target accuracy of $\pm 20\%$, and the greatest deviations are observed for manual titrations, indicating that the concentrations of the samples used in this intercomparison are rather low for this technique.

3.9 Sodium

The sodium results are presented in Figure 9, where the great circle is representing the general target accuracy of $\pm 20\%$. The reported values are given in Table 5.9. Most laboratories used flame atomic absorption spectrometry for this determination. However, in many laboratories the emission spectrometric techniques are slowly taking over the routine determinations, thus six participants used ICP, and eight used flame photometry.

92 % of the result pairs are located within the general target accuracy of $\pm 20\%$. Two laboratories reported results which are systematically low, and one where the deviations are of random nature.

3.10 Potassium

The potassium results are presented in Figure 10. The great circle is representing a general acceptance limit of $\pm 20\%$. The reported values are given in Table 5.10. As for sodium, most laboratories used flame atomic absorption spectrometry for the determination of this element, however, emission spectrometry is used by 14 of the laboratories. The deviations are mainly of systematic nature. However, for some laboratories the deviations are quite random. Three laboratories reported results as less than the detection limit.

3.11 Total aluminium

The results for total aluminium are illustrated in Figure 11, and the reported values are given in Table 5.11. The great circle is representing the general accuracy target of $\pm 20\%$. Five

laboratories are using emission techniques, and two of the participants used photometry for the determination of aluminium. About half of the result pairs are located within the target accuracy. One of the deviating results are highly affected by random errors.

3.12 Reactive aluminium

The results for reactive aluminium are illustrated in Figure 12, and the reported values are given in Table 5.12. Only six laboratories reported results for reactive aluminium. The statistical treatment according to Youden is not applicable for this situation, where the results are rather different, and only two out of six results are located within the acceptance circle. The median value used as a picture of the “true” value, therefore, has to be considered as indicative only.

The reported values for this aluminium fraction are strongly dependent on the chemical conditions in the reaction mixture. Most methods are based on the direct determination of aluminium in a non-acidified sample, preferably accomplished as soon as possible after sampling. By these methods acid is added as a part of the determination step. However, there are some methods based on acid pretreatment of the sample, then the results are dependent on how long time the acidified samples have been stored before the aluminium content is determined. Such acidification is no digestion, but will lead to dissolution of complexes and even dissolution of some particulate matter containing aluminium. The results are expected to increase towards an upper limit when the pretreatment time is prolonged.

3.13 Non-labile aluminium

The results for non-labile aluminium are illustrated in Figure 13, and the reported values are given in Table 5.13. Four of the six result pairs were located outside the acceptance limits based on statistical treatment of the data, because of the great spread in the reported analytical values. Most laboratories have indicated that they determined non-labile aluminium according to the automated method of Røgeberg and Henriksen (6), which is based on the method of Driscoll (7). By this method non-labile aluminium is the fraction that passes through a cation exchange column, and consists of monomeric alumino-organic complexes (see Figure 16, page 30). Some of the informations given by the participants indicate that different resin forms have been used for this intercomparison, and it is well known that different resins have different exchange properties, and therefore will affect the results.

It is not possible to evaluate the analytical results properly when the result pairs are very spread out. Therefore, the “true” values and the 20 % circle in Figure 13 are indicative only. The main problem is the systematic deviations observed between the participating laboratories, indicating that the laboratories have applied different methods or slightly different modifications of a method, affecting the analytical results.

3.14 Dissolved organic carbon

The results for this variable are presented in Figure 14, and the reported values are given in Table 5.14. Only 17 laboratories determined this analytical variable in the sample pair CD. A wet oxidation technique with UV and peroxodisulfate is used by six laboratories, and eleven laboratories used a combustion technique. There is no clear evidence for any differences in the reported results determined with these two methods for the samples used in this intercomparison. However, it is rather strange that the median value of the reported results determined by the UV/peroxodisulfate method is somewhat higher than the corresponding combustion results.

The great circle in Figure 14 and 15 is representing a general target accuracy of $\pm 20\%$. Only three laboratories reported results located outside this limit.

3.15 Chemical oxygen demand, COD-Mn

The results for this parameter are presented in Figure 15, and the reported values are given in Table 5.15. Only twelve of the laboratories determined this parameter, which was included in the intercomparison because there are laboratories which do not have equipment for the determination of dissolved organic carbon. Eight of the result pairs were acceptable.

4. Discussion

The general rule for target accuracies, outlined in the Manual for Chemical and Biological Monitoring (1), shall normally be used as acceptance limits for the results of the intercomparison test. These limits are corresponding to either the detection limit of the method, or 20 % of the true value, whichever being the greater.

In table 2 an evaluation of the results of intercomparison 9812 is presented, based on the target accuracy (except for pH), where the number and percentage of acceptable results are given. 74 % of the results are acceptable when compared to the acceptance limits given above. For the reported results in this intercomparison, on average, one laboratory out of four is located outside the acceptance limit. By some improvement of the routine analytical method, these laboratories should obtain results more comparable to the other participants.

For pH the general target accuracy is ± 0.1 pH units, and far less than 50 % of the result pairs are found within these accuracy limits. However, we have chosen to extend the acceptance limit to ± 0.2 pH units, because of the great spread of the results for these two samples which are nearly neutral, and therefore are supposed not to be completely in CO_2 -equilibrium. Even then only 55 % of the result pairs are evaluated as acceptable.

Table 2. Evaluation of the results of intercalibration 9711. N is the number of result pairs reported, and n is the number of acceptable results within the given target accuracy. Numbers in brackets are not evaluated.

Variable	Sample pair	N	Limit	n	%
pH	AB	42	0.2*	23	55
Conductivity	AB	41	20 %	37	90
Alkalinity	AB	35	20 %	21	60
Nitrate + nitrite-nitrogen	AB	41	20 %	35	85
Chloride	AB	40	20 %	29	73
Sulfate	AB	38	20 %	31	82
Calcium	AB	40	20 %	28	70
Magnesium	AB	40	20 %	30	75
Sodium	AB	39	20 %	36	92
Potassium	AB	39	20 %	28	72
Aluminium, total	AB	17	20 %	9	53
Aluminium, reactive	CD	(6)	20 %	(2)	-
Aluminium, non-labile	CD	(6)	20 %	(2)	-
Dissolved organic carbon	CD	17	20 %	14	82
Chemical oxygen demand	CD	12	20 %	8	67
Sum		453		333	74

* The acceptance limit is extended from the target value 0.1 to 0.2 pH units

For pH the problem of comparability between the reported results is dominated by the fact that the pH values in nearly neutral solutions are much more spread out than in more acid solutions. The difference between pH values measured in stirred solutions are systematically lower than in quiescent solutions. This problem has been demonstrated through several intercomparisons, and will remain as a problem as long as different methods for pH determination are used at the participating laboratories. Therefore it should be discussed whether a more “correct” approach should be used, with different “true values”, one for each method?

For alkalinity, as we also have observed earlier, the reported results for solutions with low alkalinity values are spread out much more than in solutions with higher concentrations of bicarbonate. In this intercomparison the results are better than in the last intercomparisons, probably because of the somewhat higher bicarbonate concentrations in these samples.

For two variables, reactive and non-labile aluminium, we have decided to exclude these from the evaluation, because of the very great spread of the few reported values.

To evaluate the determination of aluminium fractions, it seems to be necessary that the laboratories normalize their analytical methods to improve the comparability for these variables. There are some confusions about what aluminium fractions should be determined. The intention in this intercomparison was to compare the results for the variables printed in bold in the scheme presented in Figure 16. There have obviously been reported some results

for other fractions than we asked for. This may be due to the fact that the Programme centre has chosen the definitions of aluminium species given by Driscoll (7), well aware of the possibility that other laboratories may use a slightly different definition system.

Figure 16. Schematic representation of aluminium fractions according to Driscoll (7).

Aluminium measurement	Total aluminium acid digested			
	Reactive aluminium Total monomeric aluminium, no acid digestion			
	Monomeric aluminium, cation exchange treated			
Aluminium fraction	Non-labile monomeric aluminium	Labile monomeric aluminium	Acid soluble aluminium	
Fraction composition	Monomeric aluminorganic complexes	Free aluminium, aluminumsulfate, fluoride and hydroxide complexes	Colloidal polymeric aluminium, strong aluminorganic complexes	

The non-exchangeable aluminium initially present in the samples of this intercomparison, is assumed to be associated with organic matter. The fact that the laboratories used different modifications and even different methods for the determination of aluminium species, may explain some of the great spread of the results for the aluminium fractions.

For the major constituents the results are fairly well in this intercomparison, as 70 - 90 % of the results are acceptable. Some of the laboratories that reported results outside the acceptance limits used methods being different from the major group of participants. Many of the manual methods are not sensitive enough for samples typically analyzed for acid rain monitoring.

5. Conclusion

43 laboratories submitted results for this intercomparison. Good results were reported for conductivity, nitrate + nitrite, sulfate, sodium, and dissolved organic carbon, more than 80 % being evaluated as acceptable for these analytical variables.

Rather poor comparability was observed for the results of aluminium species. The differences between the methods used for the determination of aluminium species, are probably the reason for the poor comparability for these variables. This time the chemical oxygen demand had a rather low score with 67 % acceptable results.

Overall, 74 % of the reported results were located within the general target accuracy of ± 20 %. The laboratories which reported results outside this limit should improve their methods to obtain a better comparability. Generally, the application of manual analytical methods seem to be less suited for the water samples which are analyzed in this programme, as the detection limit of many manual methods may be too high. If these laboratories are going to analyze the low concentration samples in the future, it is important that they lower the detection limit of their methods.

To improve the comparability of the analytical results for aluminium fractions, it seems to be necessary to normalize the analytical methods and determination techniques used for these determinations, for instance to meet the definitions given in Figure 16.

A total error of ± 0.2 pH units seems to be a reasonable assessment of the accuracy for pH measurements when weakly acid or neutral water samples - which is not in CO₂ equilibrium - are analyzed. On the next meeting it should be discussed whether we are continuing to use only one "true value" for all the pH results, or to have different "true value" for each method as there obviously are systematic differences between the methods.

6. Literature

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Appendix A. The participating laboratories

Appendix B. Preparation of samples

The sample solutions were prepared from natural water collected at two locations, a creek from a pond in a marsh area (Svartkulp), and from a creek (Sørkedalselva), both locations outside Oslo, Norway. Raw water was collected in polyethylene containers and brought to the laboratory for storage. Sample A was prepared from the water from the pond called Svartkulp. Sample B was prepared from water sampled in the creek Sørkedalselva. These solutions were stored at room temperature for several weeks at the laboratory. During this stabilization period suspended matter settled. The solutions were filtrated through 0.45 µm membrane filter, and small aliquots were removed from the filtrate to determine the concentrations of the parameters of interest.

A few days before mailing to the participants, the solutions were transferred to 1/2 liter (and some few 1 liter) polyethylene bottles with screw cap. These samples were stored at room temperature until mailing to the participating laboratories.

Table 3. Summary of the control analyses.

Parameter	Sample A		Sample B		Sample C		Sample D	
	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.
pH	7,26	0.12	6.86	0.07				
Conductivity mS/m	4,56	0.05	2,48	0.04				
Alkalinity mmol/l	0,284	0.006	0,096	0.004				
Nitrate/nitrite µg/l	275	12	215	8				
Chloride mg/l	2,0	0.10	2,2	0.12				
Sulfate mg/l	4,9	0.06	2,9	0.05				
Calcium mg/l	7,23	0.21	1,11	0.07				
Magnesium mg/l	0,56	0.03	0,25	0.02				
Sodium mg/l	1,65	0.06	3,26	0.05				
Potassium mg/l	0,36	0.02	0,16	0.02				
Aluminium total, µg/l					81	4	73	4
Reactive aluminium µg/l					55	3	63	4
Non-labile alumin. µg/l					41	4	52	5
Diss.org. C mg/l					1,9	0.13	4,7	0.14
COD.Mn, mg/l					1,9	0.19	4,9	0.14

Sample control analyses

During the intercalibration period, four sets of samples were randomly selected from the batch for control analyses. The determinations were carried out by the laboratory at the Programme Centre, the first sample set being analyzed some days before mailing of the samples to the participants. The last sample was analyzed at the end of June 1997. A summary of the control results is presented in Table 3. The control results confirmed that the stability of the sample solutions were acceptable during the intercalibration period for all analytical variables except nitrate + nitrite, which was decreasing during the control periode.

Appendix C. Treatment of analytical data

The intercalibration was carried out by the method of Youden. This procedure requires two samples to be analyzed, and every laboratory shall report only one result for each sample and analytical variable. In a coordinate system the result of sample B is plotted against the result of sample A (see Figures 1 - 15).

The graphical presentation creates a possibility to distinguish between random and systematic errors affecting the results. The two straight lines drawn in the diagram are representing the true values of the samples; or - as in this case, when the true value is not known - the median value of the results from all the participating laboratories. The diagram is thus divided into four quadrants. In a hypothetical case, when the analysis is affected by random errors only, the results will spread randomly over the four quadrants.

However, the results are usually located in the lower left and the upper right quadrant, constituting a characteristic elliptical pattern along the 45 ° line. This is reflecting the fact that many laboratories - due to systematic deviations - have attained too low or too high values for both samples.

The acceptance limit of the results may be represented by a circle with its centrum at the intersection of the two straight lines in the diagram (true or median values). The distance between the centrum of the circle, and the mark representing the laboratory, is a measure of the total error of the results. The distance along the 45 ° line is giving the magnitude of the systematic error, while the distance perpendicular to the 45 ° line is indicating the magnitude of the random error. The location of the laboratory in the diagram is an important information about the size and type of analytical error, making it easier to disclose the cause of error.

The statistical treatment of the analytical results was accomplished in this way: Pairs of results where one or both of the values are lying outside the true value $\pm 50\%$, are omitted from the statistical calculations. The remaining results are used for the calculation of the mean value (\bar{x}) and the standard deviation (s). Now the pairs of results where both of the values are lying outside $\bar{x} \pm 3s$, are omitted. The remaining results are used for a final calculation, the results of which are presented in the tables 5.1 - 5.15. Results being omitted from the calculations, are marked with the letter "U".

Appendix D. Table 4. The results of the participating laboratories.

Appendix E. Reports and publications from the ICP-Waters Programme

1. Manual for Chemical and Biological Monitoring. Programme Manual. Prepared by the Programme Centre, Norwegian Institute for Water Research. NIVA, Oslo 1987.
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3. Norwegian Institute for Water Research, 1988. Data Report 1987 and available Data from Previous Years. Programme Centre, NIVA, Oslo.
4. Norwegian Institute for Water Research, 1988. Intercalibration 8802: pH, K₂₅, HCO₃, NO₃, SO, Cl, Ca, Mg, Na, K. NIVA, Oslo.
5. Proceedings of the Workshop on Assessment and Monitoring of Acidification in Rivers and Lakes, Espoo, Finland, 3rd to 5th October 1988. Prepared by the Finnish Acidification Research Project, HAPRO, Ministry of Environment, October 1988.
6. Norwegian Institute for Water Research, 1989. Intercalibration 8903: Dissolved organic carbon and aluminium fractions. Programme Centre, NIVA, Oslo. NIVA Rep. 2238-89. ISBN 82-577-1534-4.
7. Note: Some reflections about the determination of pH and alkalinity. Prepared by the Programme Centre, Norwegian Institute for Water Research. Håvard Hovind, NIVA, Oslo October 1989.
8. Hovind, H. 1990. Intercalibration 9004: pH and alkalinity. Programme Centre, NIVA, Oslo. NIVA Rep. 2465-90. ISBN 82-577-1776-2.
- Skjelkvåle, B.L., and Wright, R.F. 1990. Overview of areas sensitive to acidification: Europe. Programme Centre, NIVA, Oslo. Acid Rain Research Report 20/1990. NIVA-report 2405-90. ISBN 82-577-1706-1.
9. Johannessen, M. 1990. Intercalibration in the framework of an international monitoring programme. Proceedings of the third annual Ecological Quality Assurance Workshop, Canada Centre for Inland Waters, Burlington Ontario. Programme Centre, NIVA, Oslo.
10. Norwegian Institute for Water Research, 1990. Data Report 1988. Programme Centre, NIVA, Oslo.
11. Norwegian Institute for Water Research, 1990. Data Report 1989. Programme Centre, NIVA, Oslo.
12. Proceedings for the fifth Meeting of the Programme Task Force Freiburg, Germany, October 17-19, 1989. Prepared by the Umweltbundesamt, Berlin July 1990.
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14. Norwegian Institute for Water Research, 1991. The Three Year Report. Summary and results 1987 – 1989: Results from the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes. Programme Centre, NIVA, Oslo.
15. Norwegian Institute for Water Research, 1991. Summary of The Three Year Report 1987 – 1989. Programme Centre, NIVA, Oslo.

16. Scientific papers presented at the Sixth Task Force meeting in Sweden 23 - 24 October 1990. Swedish Environmental Protection Agency, Sweden, September 1991.
17. Seventh Task Force meeting of international Co-operative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes. Galway, Ireland. September 30 - October 3 1991. Proceedings.
18. Johannessen, M., Skjelkvåle, B.L. and Jeffries, D. 1992. International cooperative Programme on Assessment and Monitoring of Rivers and Lakes. In: Conference Abstracts, Intern. Conference on Acidic Deposition, Glasgow 16-21, sept. 1992, p. 449. Kluwer Academic Press.
19. Hovind, H. 1992. Intercalibration 9206: pH, K₂₅, HCO₃, NO₃ + NO₂, Cl, SO₄, Ca, Mg, Na, K, Al and DOC. Programme Centre, NIVA, Oslo. NIVA Rep. 2784-92. ISBN 82-577-2164-6.
20. Norwegian Institute for Water Research, 1992. Data Report 1990. Programme Centre, NIVA, Oslo.
21. Norwegian Institute for Water Research, 1992. Evaluation of the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes. Programme Centre, NIVA, Oslo.
22. Hovind, H. 1993. Intercalibration 9307: pH, K₂₅, HCO₃, NO₃ + NO₂, Cl, SO₄, Ca, Mg, Na, K, total aluminium, reactive and non-labile aluminium, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA Rep. 2948-93. ISBN 82-577-2370-3.
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25. Skjelkvåle, B.L., Newell, A.D, and Johannessen, M. 1993. International Cooperative Programme on Assessment and Monitoring of Rivers and lakes: Status and Results. In: BIOGEOMON - Symposium on Ecosystem Behaviour: Evaluation of Integrated Monitoring in small catchments. Prague, September 18-20, 1993. Czech Geological Survey, Prague 1993. s. 274-275.
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27. Skjelkvåle, B.L., Newell, A.D., Raddum, G.G, Johannessen, M., Hovind, H., Tjomsland, T. and Wathne, B.M. 1994. The six year report: Acidification of surface water in Europe and North America. Dose/response relationships and long-term trend. Programme Centre NIVA Oslo. Norwegian Institute for Water Research. NIVA Report 3041-94: 135 pp. ISBN 82-577-2499-8.
28. Norwegian Institute for Water Research, 1994. Data Report 1991. Programme Centre, NIVA, Oslo. ISBN 82-577-2662-5.
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31. Traaen, T.S., and Stoddard, J.L. 1995. An assessment of nitrogen leaching from watersheds included in ICP on Waters. Norwegian Institute for Water Research, NIVA Report 86001-3201, 39 pp.

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34. Raddum, G.G. 1995. Aquatic Fauna: Dose/response and long-term trends. Programme Centre, NIVA, Oslo.
35. Raddum, G.G. 1995. Intercalibration 9502: Invertebrate Fauna. Programme Centre, NIVA, Oslo.
36. Raddum, G.G., and Skjelkvåle, B.L. 1995. Critical limits to invertebrates in different regions in Europe. *Water Air and Soil Poll.* 85: 475-480.
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44. Henriksen, A., and Posch, M. 1998. Critical load and their exceedances for ICP-Waters sites. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3821-98, ICP-Waters Report 44/1998. ISBN 82-577-3399-7
45. Stoddard, J.L., Traaen, T.S., Skjelkvåle B.L., and Johannessen, M. 1998 Assessment of Nitrogen Leaching at UN/ECE ICP-Waters sites. In press *Environmental Pollution*.
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All reports and publications are available at:
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