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Intercomparison 0014:

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Norwegian Institute for Water Research

REPORT

Main Office
P.O. Box 173, Kjelsås
N-0411 Oslo
Norway
Phone (47) 22 18 51 00
Telefax (47) 22 18 52 00
Internet: www.niva.no

Regional Office, Sørlandet
Televeien 3
N-4879 Grimstad
Norway
Phone (47) 37 29 50 55
Telefax (47) 37 04 45 13

Regional Office, Østlandet
Sandvikaveien 41
N-2312 Ottestad
Norway
Phone (47) 62 57 64 00
Telefax (47) 62 57 66 53

Regional Office, Vestlandet
Nordnesboder 5
N-5008 Bergen
Norway
Phone (47) 55 30 22 50
Telefax (47) 55 30 22 51

Akvaplan-NIVA A/S
N-9005 Tromsø
Norway
Phone (47) 77 68 52 80
Telefax (47) 77 68 05 09

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Abstract

71 laboratories received samples for the intercomparison 0014, and 65 laboratories in 26 countries submitted results. Three sample sets were used, one for the determination of major ions, one for organic matter and aluminium fractions, and one for heavy metals. Based on the general target accuracy of ± 20 %, 63 % of the results were considered acceptable. About 90 % of the result pairs were acceptable for sodium and dissolved organic carbon. For pH only 57 % of the result pairs were acceptable in relation to the extended target accuracy of ± 0.2 units. For nitrate + nitrite it was decided not to evaluate the reported results, because of the instability of this analytical variable in the samples A and B. Determination of heavy metals was included in the intercomparison for the first time, with fairly good results for iron and manganese. For lead, nickel and zinc where less than 50 % of the results were acceptable, may be due to the low concentrations used for these metals. Normalization of the analytical methods used is necessary to improve the comparability for pH. For the heavy metals it should be discussed whether an absolute acceptance limit should be used instead of the general target of ± 20 % when the concentrations are close to the detection limit of the recommended method.

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Håvard Hovind
Project manager
Håvard Hovind

Rainer J. Lichtenthaler
Research manager
Rainer Lichtenthaler

Georg Becher
Head of research department
Georg Becher

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CONVENTION ON LONG-RANGE
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INTERNATIONAL COOPERATIVE PROGRAMME ON
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OF RIVERS AND LAKES

Intercomparison 0014

pH, Cond, HCO_3^-, $NO_3^-+NO_2^-$, Cl^-, SO_4^{--} Ca^{++}, Mg^{++}, Na^+, K^+, Al, Al-R, Al-I, DOC, COD-Mn, Fe, Mn, Cd, Pb, Cu, Ni, and Zn

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 14th intercomparison of chemical analysis.

Oslo, September 2000

Håvard Hovind

Contents

1. Summary

Intercomparison 0014 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 - July 2000, and included the determination of major ions and metals 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, chemical oxygen demand (COD-Mn), iron, manganese, cadmium, lead, copper, nickel and zinc.

Three sample sets were prepared for this intercomparison, one for the determination of the major ions, one for aluminium fractions and unspecific organic matter, and the third for the heavy metals. 99 laboratories were invited to participate in this intercomparison, and the samples were sent to 71 laboratories who accepted to participate. 65 laboratories submitted results to the Programme Centre before the final statistical treatment of the data. 26 countries were represented in this laboratory group.

The median value of the results received from the participants was selected as "true" value for each variable. The content of nitrate + nitrite proved to be unstable in sample A and B, the concentration being reduced during storage, therefore this variable was excluded from the evaluation. For the remaining variables, 63 % of the result pairs were regarded as acceptable, the target limit being the median value ± 20 %, except for pH and conductivity where the acceptance limits were ± 0,2 units and ± 10 %, respectively.

For pH, the accuracy limit was extended from 0,1 to ± 0.2 units, but still only 57 % of the result pairs were included using 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 spreading of pH results is mainly due to the fact that different routines are used for measurement by the participants, leading to systematically different results. It is terefore questionable to establish a “true value” based on the median value for all the reported results for pH, and it should be discussed whether an individual “true value” for each method would be more appropriate.

The best results were obtained for sodium and dissolved organic carbon, with about 90 % of the result pairs being acceptable. Rather poor comparability was observed for alkalinity, non-labile aluminium, lead, nickel and zinc, the number of acceptable results were between 40 and 47 %. To improve the comparability of the results for these variables, it is necessary to normalize the analytical methods used.

For the first time in this intercomparison programme, the heavy metals iron, manganese, cadmium, lead, copper, nickel, and zinc were included. The best results were obtained for iron and manganese, where 74 and 75 % of the results were acceptable. For these elements the concentrations were at least somewhat higher than the detection limit of the most sensitive methods used. For the metals lead, nickel and zinc, only 42 - 47 % of the results were acceptable. However, the concentrations of these elements are close to the detection limit for the methods used.

2. 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 by 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 forteenth intercomparison test, called 0014, 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, chemical oxygen demand (COD-Mn), iron, manganese, cadmium, lead, copper, nickel and zinc.

3. Accomplishment of the intercomparison

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 1999 it was decided that three sample sets should be included in this intercomparison, one sample pair for the determination of the major ions, one sample pair for aluminium fractions and unspecific organic compounds, and one for the heavy metals.

The samples were mailed from the Programme Centre on June 5 and the following days, 2000. Most of the participating laboratories received the samples within one week, with very 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.

4. Results

99 laboratories were invited to participate in the intercomparison, and 71 laboratories accepted and received samples. The 65 laboratories who submitted results to the Programme Centre, are representing 26 countries. It was a problem that some laboratories submitted the results several weeks after the deadline, and a reminder letter had to be mailed to some few 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 the laboratories participting in the International Cooperative Programme. 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. For certain variables, like pH, this may represent a problem as the methods used are producing systematically different results.

The results are illustrated in Figure 1 - 23, where each laboratory is represented by a small circle and an identification number. Some laboratories with strongly deviating results may be located outside the plot. The great circle in the Figures are representing a selected accuracy limit, either the general target limit of ± 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 0014 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 - 5.23.

4.1 pH

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

The participating laboratories determined pH in the test solutions using their own routine method. An electrometric method was used by all laboratories. 63 laboratories reported results for pH, of this group 35 indicated that they read the pH value during stirring the solution. The stirring are normally lowering the observed pH result. However, in this intercomparison the median values are slightly higher in the stirred samples compared to the quiescent samples (see Table 1), the difference is small and is not statistically significant.

Figure 1 shows that the reported results are spread out along the 45 ° line, indicating that the influence by systematic effects on the results are dominating. 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 pH-values are about half a unit higher than obtained with the two other methods. These results should not be evaluated by comparing them to the mean value of all the reported results, because this method is systematically different from the two other methods. The information obtained by pH measurement after equilibrating the solution, is different from pH-values read directly, or during stirring the sample.

(The text continues on page 36)

The CO_2 concentration of samples in the circumneutral range may be above the atmospheric equilibrium. This may lead to systematic errors, the magnitude will vary between the laboratories due to the different levels of partial pressure of CO_2 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 control analyses carried out at the Program Centre proved that the samples were fairly 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 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 probably connected to the small differences in the analytical methods used by the participants.

4.2 Conductivity

The conductivity results are presented in Figure 2, where the great circle is representing an accuracy limit of ± 10 %. The reported results are given in Table 5.2. Seven laboratories have obviously reported the conductivity results in another unit than the requested one, mS/m at 25°C, the reported results being one or two decades too high. The results from the laboratories which informed the Programme Center about this mistake, were recalculated to mS/m.

All participants used an electrometric method for the determination of conductivity. Most laboratories achieved very good agreement between the results for this variable. Ten laboratories reported results being systematically far too high for both samples, and three laboratories reported results being systematically far too low. If the accuracy limit is extended to the target value of ± 20 %, defined in the Manual (1), the results located just outside the 10 % acceptance circle, would be located within the circle and thus be defined as acceptable. A proper temperature correction is necessary when determining this variable, as the conductivity is changing by about two percents pr degree at room temperature.

4.3 Alkalinity

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 5.3. 54 laboratories reported results for alkalinity, and more than one third of the participants 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 certain pH value only (4.5, 5.4, or 5.6).

The results for alkalinity are spread out along the 45 ° line, as illustrated in Figure 3, indicating systematic effects are the dominating the reason for the differences between the results. This is probably 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 normally located close to the centrum of the circle. With one exception all the results determined by the end point titration to pH 4.2 or 4.5 alone, are located in the upper right part of Figure 3, beeing systematically too high. The end point titration to pH 5.6 or 5.4 gave results mainly located within the acceptance circle.

The overall result for alkalinity In this intercomparison is not good, as nearly one third of the results are excluded from the statistical calculations, and less than half of the results are acceptable. The alkalinity value varies 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" may overestimate the true alkalinity or the "equivalence" alkalinity.

4.4 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 represents a general target accuracy of ± 20 %. Ion chromatography is used by an increasing number of laboratories, and is now used by nearly half 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 significant difference between the results determined by the different methods, the concentrations in the samples being too low. Most of the very low results reported have been determined by ion chromatography.

The results reported for sample A and B are quite different, the results for sample A are much more spread out than for sample B. Thus, the relative standard deviation for sample A is considerably greater than for sample B. This is strange, because the two samples are prepared from the same water, the only difference is that sample B is spiked to increase the concentration for some of the analytical variables. As the control analyses at the laboratory of the Programme Centre disclosed that the content of nitrate and nitrite in the samples A and B was decreasing during the weeks after the samples were mailed to the participants, this variable is excluded from the evaluation of this intercomparison.

The enormous spread of the results reported is clearly demonstrated in Figure 4. The systematical differences between the result pairs may probably be due to the instability of nitrate in the samples used here. Thus, the determined value may be expected to be dependent on the date of analysis. In addition to this unexpected instability of nitrate, the low nitrate concentration in these samples may represent a problem for some of the laboratories, and may to a certain extent explain the random errors affecting the results. Several laboratories have reported results as below their detection limit or zero.

4.5 Chloride

The chloride results are presented in Figure 5, and the reported results from the participants are given in Table 5. The target accuracy of ± 20 % is represented by the great circle in figure 5. 41 out of 56 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 many of the acid rain samples. Two laboratories determined chloride with capillary electrophoresis, one result pair being acceptable.

4.6 Sulfate

The sulfate results are illustrated in Figure 6, and the reported values are given in Table 5.6. The circle is representing the target accuracy of ± 20 %. Ion chromatography is used by 47 of 56 laboratories for the determination of the sulfate content. Seven laboratories used a photometric method based on the dissociation of the barium-thorin complex, three of these result pairs deviated too much from the true value. One laboratory used a nephelometric method, and one capillary electrophoresis, both result pairs being acceptable. The results produced by these methods are higher than with ion chromatography, and the relative standard deviation is much greater too.

4.7 Calcium

The calcium results are illustrated in Figure 7, and the reported values are given in Table 5.7. The target accuracy is ± 20 %, and is represented by the circle in Figure 7. 60 laboratories reported results for calcium, and 27 of them used flame atomic absorption spectrometry for the determination. ICP and ICP-MS techniques are used by 12 and 2 laboratories, respectively, and 16 laboratories used ion chromatography. The complexometric titration method, used by two laboratories, is not sensitive enough for this kind of samples.

The result pairs being not acceptable are dominated by systematic errors, as several laboratories have reported systematically too high or too low results for both samples. This may partly be due to the lower calcium concentrations used this time.

4.8 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 ICP-MS was used by 12 and 2 laboratories, respectively, and 16 laboratories used ion chromatography. Systematic deviations are dominating the results, and as much as 42 % of the results are located outside the target accuracy of ± 20 %. The great deviations observed for manual titrations indicate that the concentrations of the samples used in this intercomparison are rather low for this technique. The most used methods give comparable results.

4.9 Sodium

The sodium results are presented in Figure 9, where the great circle is representing the general target accuracy of ± 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 ion chromatographic techniques are slowly taking over the routine determinations of the alkaline metals, thus 15 participants used this technique. ICP was used by 8 laboratories, and 13 used flame photometry. The relative standard deviation was smalles for the results produced with flame atomic absorption. 93 % of the result pairs are located within the general target accuracy of ± 20.

4.10 Potassium

The potassium results are presented in Figure 10. The great circle is representing the target acceptance limit of ± 20 %. The reported values are given in Table 5.10. As for sodium, many laboratories used flame atomic absorption spectrometry for the determination of this element, and emission spectrometry is used by the same number of laboratories. The greatest deviations observed in the Figure 10 are mainly of systematic nature. Only one laboratory reported results as less than the detection limit.

4.11 Aluminium

The results for aluminium are illustrated in Figure 11 for sample pair CD, and Figure 12 for sample pair EF, and the reported values are given in Table 5.11 and 5.12, respectively. The great circle is representing the general target accuracy of ± 20 %. Ten laboratories used ICP and 5 ICP-MS techniques, the results for both methods being higher than for the other methods, ICP-MS giving the highest results. Seven of the participants used photometry for the determination of aluminium, the results being considerably lower than for the other methods. Graphite furnace atomic absorption was used by six laboratories. Some results are affected by random errors, however, 73 % of the result pairs in both sample sets are located within the target accuracy.

4.12 Reactive aluminium

The results for reactive aluminium are illustrated in Figure 13, and the reported values are given in Table 5.13. Twelve laboratories reported results for reactive aluminium, and 10 of these used the pyrocathechol violet method. The results are dominated by systematic effects, probably caused by the small differences in the analytical method used.

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.

4.13 Non-labile aluminium

The results for non-labile aluminium are illustrated in Figure 14, and the reported values are given in Table 5.14. The situation is very much alike what we observe for reactive aluminium. 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 32).

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. Thus, 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 strongly. It is not possible to evaluate the analytical results properly when the result pairs are very spread out, and only few laboratories determine this analytical variable. Therefore, the “true” values and the 20 % circle in Figure 14 have to be considered as indicative only.

4.14 Dissolved organic carbon

The results for this variable are presented in Figure 15, and the reported values are given in Table 5.15. 28 laboratories determined this analytical variable in the sample pair CD. 16 laboratories used a combustion technique, and a wet oxidation technique with UV and peroxodisulfate was used by eleven laboratories. For the samples used in this intercomparison there is no evidence for any significant differences between the reported results determined with these two methods.

The great circle in Figure 15 is representing the general target accuracy of ± 20 %, and only three laboratories reported results located outside this limit.

4.15 Chemical oxygen demand, COD-Mn

Several participating laboratories are not equipped with carbon analyzer, therefore this analytical variable is included in the intercomparison. The results for this parameter are presented in Figure 16, and the reported values are given in Table 5.16. Only 15 of the laboratories determined this parameter. Eleven of the result pairs are located within the circle representing the target accuracy of ± 20 %.

4.16 Iron

The results for iron are illustrated in Figure 17, and the values reported by the participants are given in Table 5.17. The target accuracy is ± 20 %, and is represented by the great circle in Figure 17, 74 % of the result pairs are located inside this circle. 34 laboratories submitted results for iron, of which 12 and 8 used ICP and ICP-MS, respectively, while 6 and 5 used flame and graphite furnace atomic absorption, respectively. Only three laboratories used photometric methods. There is no significant difference between the results determined by the different methods for iron. The deviating results are mainly affected by systematic errors.

4.17 Manganese

The manganese results are illustrated in Figure 18, and the values reported by the participants are given in Table 5.18. The target accuracy is ± 20 %, and is represented by the great circle in Figure 18, 75 % of the result pairs are located inside this circle. 35 laboratories submitted results for manganese, of which 10 used ICP and ICP-MS, respectively, while 4 and 10 used flame and graphite furnace atomic absorption, respectively. Only one laboratory used a photometric method. There is no significant difference between the results determined by the different methods for manganese, except that the relative standard deviation between the laboratories is greater for graphite furnace than the other methods. The deviating results are mainly affected by systematic errors.

4.18 Cadmium

The results for cadmium are illustrated in Figure 19, and the values reported by the participants are given in Table 5.19. The target accuracy is ± 20 %, and is represented by the great circle in Figure 19, 65 % of the result pairs are located inside this circle. 30 laboratories submitted results for cadmium, of which 6 and 10 used ICP and ICP-MS, respectively, while 14 used graphite furnace atomic absorption. There is no significant difference between the results determined by the different methods for cadmium. The deviating results are affected by both systematic and random errors. Because of the low concentration, the random errors are more dominating for the cadmium results.

4.19 Lead

The results for lead are illustrated in Figure 20, and the values reported by the participants are given in Table 5.20. The target accuracy is ± 20 %, and is represented by the great circle in Figure 20, only 47 % of the result pairs are located inside this circle. Only 30 laboratories submitted results for lead, of which 6 and 9 used ICP and ICP-MS, respectively, while 15 used graphite furnace atomic absorption. There is no significant difference between the results determined by the different methods for lead. The deviating results are affected by both systematic and random errors. Because of the low concentration, the random errors are more pronounced for the lead results. The concentration is close to the detection limit of the method used at some of the laboratories, and three laboratories reported their results as below their detection limit.

4.20 Copper

The copper results are illustrated in Figure 21, and the values reported by the participants are given in Table 5.21. The target accuracy is ± 20 %, and is represented by the great circle in Figure 21, 67 % of the result pairs are located inside this circle. 35 laboratories submitted results for copper, of which 7 and 10 used ICP and ICP-MS, respectively, while 15 and 3 used graphite furnace and flame atomic absorption, respectively. There is no significant difference between the results determined by the different methods for copper, except that the results from the flame method is clearly lower than for the other methods. The deviating results are affected mainly by systematic errors.

4.21 Nickel

The results for nickel are illustrated in Figure 22, and the values reported by the participants are given in Table 5.22. The target accuracy is ± 20 %, and is represented by the great circle in Figure 22, only 42 % of the result pairs are located inside this circle. 30 laboratories submitted results for nickel, of which 6 and 10 used ICP and ICP-MS, respectively, while 14 used graphite furnace atomic absorption. There is no significant difference between the results determined by the different methods for nickel, however, many laboratories using ICP reported results as less than a value representing their detection limit. The deviating results are affected mainly by systematic errors.

4.22 Zinc

The results for zinc are illustrated in Figure 23, and the values reported by the participants are given in Table 5.23. The target accuracy is ± 20 %, and is represented by the great circle in Figure 23, only 47 % of the result pairs are located inside this circle. 35 laboratories submitted results for zinc, of which 10 used ICP and ICP-MS, respectively, while 8 and 7 used flame and graphite furnace atomic absorption, respectively. The results determined by ICP-MS are slightly higher than for the other methods. The deviating results are affected by both systematic and random errors, a lot of too high valyes indicate that contamination may be a problem for the zinc determination.

5. 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 0014 is presented, based on the target accuracy (except for pH and conductivity), where the number and percentage of acceptable results are given. 63 % of the results submitted by the participants are acceptable when compared to the acceptance limits given above, i.e. on average, one out of three result pairs is located outside the acceptance limit. By improvement of the routine analytical method, the laboratories should be able to obtain more comparable results.

For pH, the general target accuracy is ± 0.1 pH units (1), 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 spreading of the results for these two samples which are close to neutral, and therefore are supposed not to be completely in CO_2-equilibrium. Even with this acceptance limit only 57 % of the result pairs are evaluated as acceptable.

Problems with poor comparability between the reported results for pH arise probably from the fact that the pH results are much more affected by the method used, when measuring in nearly neutral solutions. This problem has been demonstrated through several earlier intercomparisons, and will remain as a problem as long as different methods for pH determination are used by the participating laboratories. Therefore, it should be discussed whether a different approach should be used for the comparison of the results, for instance different “true values” for pH, one for each method? This is especially important for the equilibration method, which is definitely different from the others.

Table 2. Evaluation of the results of intercomparison 0014. 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 icluded in the evaluation.

* The acceptance limit is extended from the target value 0.1 to 0.2 pH units
¤ The acceptance limit is reduced from the target value 20 to 10 %

Because of the high precision of the reported results for conductivity in earlier intercomparisons, we reduced the acceptance limit for this analytical variable to ± 10 %. However, the number of acceptable results for conductivity, 63 %, is much lower than in the three last intercomparisons (Table 2). If we increase the acceptance limit to the target value, ten more result pairs would be inside the circle, and the number of acceptable results would increase to 80 %. And if the results reported in wrong units were recalculated to mS/m, the number of acceptable results would increase to 90 %.

For alkalinity, as we have observed earlier, the reported results for solutions with low alkalinity values are more widely spread than in solutions with higher concentrations of bicarbonate. In this intercomparison, the results are worse than in the last three intercomparisons, probably because of the low bicarbonate concentrations in the samples this time.

For nitrate + nitrite only 51 % of the result pairs are acceptable. This is caused by the fact that the results for both samples are widely spread out, especially many laboratories have reported very low results for nitrate for both samples. The control analyses performed at the laboratory of the Programme Centre disclosed that the content of nitrate and nitrite in the samples was decreasing over time. Therfore this variable is excluded from the evaluation of this intercomparison. So far, we have not found any reasonable explanation for the instability of these samples. In fact, this problem has been observed in some earlier intercomparisons too.

To evaluate the determination of aluminium fractions, it seems 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 24. There have obviously been reported some results for other fractions than we asked for. The Programme Centre has chosen the definitions of aluminium species given by Driscoll (7), however, other laboratories may use a slightly different definition system. 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 between the results for the aluminium fractions.

Figure 24. Schematic representation of aluminium fractions according to Driscoll (7).

<table>
<tr><td></td><td colspan="3">Total aluminium
acid digested</td></tr>
<tr><td>Aluminium measurement</td><td colspan="2">Reactive aluminium
Total monomeric aluminium, no acid digestion</td><td></td></tr>
<tr><td></td><td>Monomeric aluminium, cation exchange treated</td><td></td><td></td></tr>
<tr><td>Aluminium fraction</td><td>Non-labile monomeric aluminium</td><td>Labile monomeric aluminium</td><td>Acid soluble aluminium</td></tr>
<tr><td>Fraction composition</td><td>Monomeric alumino-organic complexes</td><td>Free aluminium, monomeric aluminiumsulfate, Fluoride and hydroxide complexes</td><td>Colloidal polymeric aluminium, strong alumino-organic complexes</td></tr>
</table>

For sodium and potassium the fraction of acceptable results, and the concentrations, are comparable to earlier intercomparisons. For the other major constituents, somewhat fewer results are acceptable compared to earlier intercomparisons. One possible explanation for this observation may be that the concentrations are fairly lower than usual, Some of the laboratories that reported results outside the acceptance limits used methods being different from the major group of participants, some of the methods used may not be sensitive enough for samples typically analyzed for acid rain monitoring.

The heavy metals iron, manganese, cadmium, lead, copper, nickel, and zinc were included in this intercomparison Programme for the first time. The best results were obtained for iron and manganese, where 74 and 75 % of the results are acceptable. For these elements the concentrations were at least somewhat higher than the detection limit of the most sensitive methods used. For the metals lead, nickel and zinc, only 42 - 47 % of the results were acceptable. However, the concentrations of these elements are close to the detection limit for the methods used, and even below this limit for some of the laboratories. Therefore, it should be discussed whether absolute acceptance limits should be used instead of the relative one (20 %) used in this intercomparison, when the results are close to the detection limit. If so, it is important that it is decided what target detection limit should be obtained by the laboratories.

6. Conclusion

65 laboratories submitted results for this intercomparison. The best results were reported for the analytical variables sodium and dissolved organic carbon. About 90 % of the results were evaluated as acceptable for these variables. For nitrate + nitrite the poor results are due to the instability of the samples A and B with respect to this variable. In the next intercomparison remedial actions will be taken to stabilize nitrate + nitrite.

Overall, 63 % of the evaluated results were located within the general target accuracy of ± 20 %, or the special accuracy limit for pH and conductivity. The worsening of the performance is in part explained by the introduction of seven heavy metals, where the number of acceptable results for three elements are rather low. However, the generally lower concentrations of many other variables may also contribute to a reduced number of acceptable results.

The laboratories which reported results outside this limit should improve their methods to obtain a better comparability. Generally, the application of some analytical methods seems to be less suited for the water samples analyzed in this programme, as the detection limit of some methods employed are too high. It is important that methods with sufficiently detection limit are used by the participating laboratories

To improve the comparability of the analytical results for aluminium fractions, it may be necessary to normalize the analytical methods and the determination techniques used for these determinations, for instance to meet the operational definitions given in Figure 24.

A total error of ± 0.2 pH units seems to be a reasonable assessment of the accuracy for pH measurements when near neutral water samples - which are not in CO_2 equilibrium - are analyzed. There are obviously systematic differences between the methods used by the participating laboratories. On the next meeting, it should therefore 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.

7. Literature

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Appendix A.

The participating laboratories

Identity	Laboratory	City	Country
1	Instuitute of Biology	Syktyvkar	Russia
2	Forest Ecosystem Research Group	Dublin	Ireland
3	University of Barcelona	Vielha	Spain
4	Norwegian Institute for Water research	Oslo	Norway
5	National Water Quality laboratory	Burlington	Canada
6	University of Alberta	Edmonton	Canada
7	D.R. Ambiente Alentejo	Santo Andre	Portugal
8	Swedish University for Agricultural Sciences	Uppsala	Sweden
9	T.G.Masaryk Water Research Institute	Prague	Czech Republic
10	Aquatic Chemistry Project	Winnipeg	Canada
11	Swedish Environmental Research Institute	Stockholm	Sweden
12	Environmental Research Unit	Dublin	Ireland
13	Universita degli Studi di Siena	Siena	Italy
14	Finnish Forest Research Institute	Vantaa	Finland
15	Adirondac Lakes Survey Corporation	Raybrook	USA
16	Polish Academy of Sciences	Krakow	Poland
17	Environmental Protection Ministry	Vilnius	Lithuania
18	Toulouse University	Toulouse	France
19	Center for Marine Analytical Ref. and Stds.	Trivandrum	India
20	Institute of Environmental Protection	Warsawa	Poland
21	Lapland Water and Environment District	Rovaniemi	Finland
22	Food and Environment Agency	Torshavn	Faroe Island
23	DAFS Freshwater Laboratory	Pitlochry	Scotland
24	Kymen Water and Environment District	Kouvola	Finland
25	Virumaa Environmental Research	Johvi	Estonia
26	CNR-IRSA Water Research Institute	Milano	Italy
27	Huumaa Environmental Laboratory	Kardla	Estonia
28	Institute for Ecology of Industrial Areas	Katowice	Poland
29	Institute for Ecological Toxicology	Baikalsk	Russia
30	Swiss Federal Institute for Forest, Snow and	Birmensdorf	Switzerland
31	Karelian Research Centre	Petrozavodsk	Russia
32	Czech Geologic Survey Prague	Prague	Czech Republic
33	Staatliche Umweltbetriebgesellschaft im UBG	Chemnitz	Germany
34	Laboratorio Biologico Provinciale	Laives	Italy
35	Bayerische Landesamt fur Wasserwirtschaft	Munchen	Germany
36	Northern Water Problems Institute	Petrozavodsk	Russia
37	National Institute of Biology, LFTER	Ljubljana	Slovenia

38	Estonian Environment Research Laboratory	Tallinn	Estonia
39	Gewasser- und Bodenschutzlabor	Bern	Switzerland
40	Laboratorio Studi Ambientali	Paradiso	Switzerland
41	Landesumweltamt NRW	Dusseldorf	Germany
42	Institute of Global Climate and Ecology	Moscow	Russia
43	Werkgroep Milieubiologie	Nijmegen	Netherland
44	CNR Istituto Italiano di Idrobiologia	Pallanza	Italy
45	Kola Science Center	Apatity	Russia
46	ITMm Stockholm University	Stockholm	Sweden
47	MOEE, Toronto Laboratory	Etobicoke	Canada
48	Water Pollution Observation Laboratory	Minsk	Belarussia
49	Water Pollution Observation Laboratory	Riga	Latvia
50	Geological Survey of Estonia	Tallinn	Estonia
51	Center for Chemical Analysis Keldnaholt	Reykjavik	Iceland
52	North Ostrobothnia Regional Env. Centre	Oulu	Finland
53	New York USGS	Albany	USA
54	Umweltbundesamt, Abt. II	Langen	Germany
55	Istituto Agrario di S. Michele	S. Michele	Italy
56	Institute of Hydrobiology	Budejovice	Czech Republic
57	South Estonian Environm. Protection Agency	Tartu	Estonia
58	National Board of Waters and the Environment	Helsinki	Finland
59	Finnish Forest Research Institute	Rovaniemi	Finland
60	Charles University	Prague	Czech Republic
61	METI, US Environmental Protection Agency	Corvallis	USA
62	Centre de Reserches Ecologiques	Metz	France
63	Norwegian Institute for Air Research	Kjeller	Norway
64	University of Maine	Orono	USA
65	Umweltbundesamt, Analytik 1	Vienna	Austria
66	Great Lakes Forest Centre	Sault Ste Marie	Canada
67	MOEE, Dorseth Research Centre	Dorseth	Canada
68	Karntner Institut fur Seewasser Forschung	Klagenfurt	Austria
69	University of Innsbruck	Innsbruck	Austria
70	Institut fur Zologie, Universitat Innsbruck	Innsbruck	Austria
71	University of Helsinki	Helsinki	Finland

Appendix B.

Preparation of samples

The sample solutions were prepared from natural water collected from a creek, Langtjernelva, located in Gulsvik, Norway. Raw water was collected in polyethylene containers and brought to the laboratory for storage. These containers 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 aliquouts were removed from the filtrate to determine the concentrations of the analytical variables of interest.

The samples were prepared by spiking the filtrated water with stock solutions of stoichiometric compounds containing the major ions, or heavy metals. The samples E and F were prepared for the determination of metals, and preserved by addition of 5 ml concentrated nitric acid pr. liter sample. A few days before mailing the samples to the participants, the solutions were transferred to 1/2 liter high density 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	
	Mean	Std. dev.	Mean	Std. dev.
pH	6,62	0,06	6,42	0,04
Conductivity mS/m	2,01	0,015	1,58	0,012
Alkalinity mmol/l	0,092	0,002	0,054	0,008
Nitrate/nitrite µg/l	-	-	-	-
Chloride mg/l	0,87	0,06	0,53	0,12
Sulfate mg/l	1,23	0,12	1,50	0,17
Calcium mg/l	0,95	0,02	0,76	0,04
Magnesium mg/l	0,133	0,012	0,197	0,015
Sodium mg/l	3,03	0,06	2,09	0,03
Potassium mg/l	0,46	0,017	0,61	0,010
	Sample C		Sample D	
Aluminium, µg/l	269	5,1	222	7,1
Reactive aluminium µg/l	185	5,5	155	8,2
Non-labile aluminium, µg/l	153	6,1	130	8,7
Dissolved organic carbon, mg/l	8,9	0,75	10,8	0,80
COD.Mn, mg/l	12,4	0,6	14,8	0,9
	Sample E		Sample F	
Aluminium, µg/l	332	10,8	252	6,8
Iron, µg/l	252	7,6	274	14,3
Manganese, µg/l	16,3	0,6	17,3	0,6
Cadmium, µg/l	0,99	0,04	1,87	0,06
Lead, µg/l	3,0	0,18	3,5	0,17
Copper, µg/l	13,8	0,4	8,7	0,6
Nickel, µg/l	3,1	0,30	2,2	0,35
Zinc, µg/l	11,5	0,5	16,6	1,5

Sample control analyses

During the intercomparison 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 in the middle of May 2000, a couple of weeks before mailing the samples to the participants. The last sample was analyzed at the end of July 2000. 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 for nitrate + nitrite in sample A and B.

Appendix C.

Treatment of analytical data

The intercomparison 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 - 23).

The graphical presentation creates a possibility to distinguish between random and systematic errors affecting the results. The two stright 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 mangitude 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 ± 50 %, are omitted from the statistical calculations. The remaining results are used for the calculation of the mean value (x) and the standard deviation (s). Now the pairs of results where both of the values are lying outside x ± 3s, are omitted. The remaining results are used for a final calculation, the results of which are presented in the tables 5.1 - 5.23. Results being omitted from the calculations, are marked with the letter "U".

Appendix D.

Table 4. The results of the participating laboratories.

Lab. no.	**pH A**	**pH B**	**Cond mS/m, A**	**Cond mS/m, B**	**Alk mmol/l, A**	**Alk mmol/l, B**	**NO3+NO2 µg/l**	**NO3+NO2 µg/l**
1	6,5	6,3	1,83	1,68	0,096	0,052	20	70
2	6,49	6,30	2,00	1,70	0,038	0,027		
3	6,36	6,27	2,11	1,67	0,090	0,046		70
4	6,55	6,46	2,01	1,65	0,090	0,056	25	69
5	6,43	6,22	2,14	1,73	0,082	0,042	23	71
6	6,3	6,12	2,06	1,69	0,117	0,08	29,63	78,5
7	6,79	6,53	2,2	1,8	0,066	0,055		102,5
8	6,47	6,23	2,14	1,75	0,082	0,042	20	63
9	6,27	6,07	1,86	1,61	0,168	0,120	0	0
10	6,98	6,65	2,20	1,70	0,097	0,060	27	71
11								
12	6,54	6,29	2,94	2,46	0,085	0,040	24	69
13	6,66	6,31	2,10	1,70	0,098	0,061	25	69
14	6,62	6,36	2,13	1,75			23	68
15	6,65	6,31	2,05	1,68	0,101	0,065	25	66
16	6,46	6,23	19,34	15,60			79	149
17	6,70	6,50	2,10	1,69	0,043	0,043	28	73
20	6,24	6,15	1,90	1,57			31	83
21	6,46	6,19	2,13	1,72	0,092	0,057	23	65
22	6,55	6,30	1,46	1,42	0,140	0,100	27	68
23	6,50	6,25	2,00	1,60	0,093	0,055	27	78
24	6,54	6,30	2,12	1,78	0,100	0,060	29	78
25	6,05	5,90	2,00	1,00	0,061	0,051	130	170
26	6,30	6,02	1,85	1,57	0,070	0,030	25	26
27	6,54	6,30	2,26	1,79	0,140	0,920	26	70
28	6,56	6,35	2,10	1,75	0,084	0,051		
29	6,63	6,38					0	0
30	6,82	6,56	2,24	1,83			0	0
31	6,69	6,45						
32	6,47	6,30	2,07	1,71	0,105	0,062	38	72
33	6,70	6,50	2,16	1,75	0,155	0,116	< 60	< 60
34	6,53	6,30	2,13	1,74	0,090	0,055	60	100
35	6,53	6,19	2,04	1,67	0,210	0,190	34	76
36	6,55	6,43	2,00	1,70	0,096	0,052	21	78
37	5,92	5,63	2,10	1,70	0,075	0,021	42	93
38	6,40	6,20	27,90	21,20	0,080	0,050	37	78
39	6,31	6,06	21,30	17,20	0,182	0,132	< 200	< 200
40	6,66	6,28	21,10	17,10	0,092	0,051	28	62
41	6,52	6,32	2,89	1,94			50	70
43	6,25	5,92	3,29	2,79	0,140	0,090	38	88
44	7,02	6,31	2,08	1,71	0,101	0,060	35	75
47	6,57	6,33	2,02	1,70	0,130	0,090	24	72
49	6,34	6,12	2,05	1,68	0,114	0,085	22	56
50	7,21	6,20	1,92	1,60	0,150	0,150	137	183
51	6,14	5,97	2,12	1,74	0,095	0,057	45	77
52	6,40	6,20	2,10	1,70	0,100	0,060	22	70
54	6,15	5,75	2,12	1,79	0,130	0,080	39	73
55	5,60	5,30	21,80	18,00	0,065	0,038	20	60
56	6,45	6,25	2,08	1,71	0,100	0,065	25	70
57	6,64	6,37	2,03	1,69	0,135	0,096	28	75
58	6,64	6,32	2,08	1,72	0,092	0,055	25	71
59	5,88	5,82	1,35	1,06			< 50	58
60	6,44	6,23	2,11	1,73	0,098	0,058		
61	6,66	6,43	2,05	1,65	0,107	0,067	9	64
62	6,20	6,00	2,06	1,70	0,082	0,050	28	74
63	6,77	6,43	2,20	1,91			25	73
64	6,43	6,16	1,99	1,61	0,049	0,030		
65	6,62	5,98	1,93	1,57	0,150	0,110	29	76
66	6,40	6,23	212,00	178,00	0,083	0,046	12	46
67	6,45	6,17	2,07	1,69	0,090	0,055	26	73
68	6,50	6,30	2,20	1,90	0,400	0,350		
69	6,38	6,12	2,05	1,72	0,109	0,065		
70	6,54	6,26	207,00	169,00	0,099	0,058	27	70
71	6,62	6,48	2,10	1,72	0,110	0,060	27	78

Lab. no.	**Cl mg/l, A**	**Cl mg/l, B**	**SO4 mg/l, A**	**SO4 mg/l, B**	**Ca mg/l, A**	**Ca mg/l, B**	**Mg mg/l, A**	**Mg mg/l, B**
1	0,91	0,54	1,20	1,91	0,51	0,37	0,153	0,2
2	0,9	0,4	1,23	1,55	0,75	0,62	0,11	0,18
3	0,9	0,5	1,39	1,82	0,62	0,52	0,11	0,17
4	0,9	0,6	1,30	1,60	0,93	0,76	0,13	0,20
5	1,35	0,86	4,00	3,70	0,89	0,71	0,14	0,21
6	0,87	0,47	1,42	1,76	0,91	0,72	0,15	0,22
7	0,84	0,46	1,33	1,69	0,92	0,78	0,16	0,23
8	0,9	0,5	1,34	1,58	0,83	0,67	0,14	0,21
9	0,7	0,5	0,83	1,10	0,84	0,67	0,13	0,21
10	0,9	0,5	1,43	1,66	0,91	0,75	0,14	0,21
11					0,85	0,70	0,13	0,20
12	0,8	0,5	1,37	1,55	1,19	1,01	0,21	0,30
13	0,9	0,7	1,45	1,73	1,59	1,30	0,15	0,24
14	1,0	0,5	1,40	1,72	0,83	0,70	0,13	0,20
15	0,9	0,5	1,27	1,56	0,79	0,63	0,13	0,20
16	0,9	0,4	1,09	1,36	0,91	0,75	0,13	0,20
17	2,1	1,8	1,59	1,46	0,76	0,59	0,26	0,29
20	0,9	0,4	1,26	1,55	0,86	0,70	0,14	0,21
21	0,9	0,4	1,47	1,68				
22	< 1	< 1			0,45	0,32	0,14	0,21
23	0,9	0,5	1,30	1,58	1,30	1,04	0,19	0,29
24	0,9	0,4	1,84	2,03	0,91	0,73	0,12	0,19
25	2,3	2,1	2,50	2,50	1,00	1,00		
26	0,9	0,5	1,51	1,72	1,31	1,12	0,17	0,26
27			1,28	1,49	1,09	1,06	0,17	0,25
28								
29			1,00	1,20	0,80	0,80	0,00	0,24
30	0,9	0,5	1,40	1,67	0,88	0,72	0,14	0,23
31					0,75	0,95	0,15	0,20
32	0,8	0,5	1,38	1,65	0,87	0,70	0,12	0,18
33	1,1	0,4	1,38	1,35	0,98	0,80	0,17	0,25
34	0,9	0,4	1,41	1,62	0,74	0,55	0,11	0,18
35	0,8	0,5	1,21	1,52	0,90	0,70	0,10	0,20
36	1,0	0,5	0,85	1,25	0,86	0,67	0,13	0,20
37	1,2	0,6	1,38	1,69	0,92	0,74	0,09	0,16
38	1,0	0,5	1,56	1,68	0,84	0,62	0,13	0,21
39	1,1	0,6	< 5	< 5	< 5	< 5	< 0,5	< 0,5
40	1,0	0,5	1,41	1,70	0,46	0,50	0,07	0,14
41	1,2	< 1	1,80	2,00	2,28	1,88	0,37	0,40
43	1,5	1,2			1,20	0,90	0,15	0,22
44	0,9	0,5	1,35	1,65	0,53	0,49	0,09	0,15
47	0,9	0,5	1,15	1,45	0,71	0,63	0,12	0,20
49	1,4	0,9	1,24	0,33	0,07	0,04	0,12	0,15
50	3,5	3,0	< 2	< 2	1,20	1,00	0,36	0,49
51	1,7	1,1	1,35	1,63	0,90	0,76	0,14	0,23
52	0,9	0,5	1,20	1,50	0,90	0,70	0,10	0,20
54	0,9	0,5	1,33	1,61	0,88	0,69	0,14	0,23
55	1,0	0,5	1,08	1,25	0,85	0,70	0,13	0,21
56	0,9	0,5	1,44	1,74	0,85	0,75	0,15	0,23
57	1,0	0,6	1,25	1,53	1,06	1,02	0,15	0,23
58	0,9	0,5	1,27	1,55	0,97	0,78	0,14	0,21
59	0,9	0,4	1,37	1,64	0,89	0,71	0,13	0,19
60								
61	0,9	0,5	1,37	1,68	0,34	0,26	0,13	0,20
62	1,0	0,5	1,32	1,59	1,50	1,00	0,15	0,20
63	0,9	0,5	1,30	1,66	0,98	0,82	0,14	0,22
64	0,9	0,5	1,30	1,59	0,95	0,75	0,14	0,20
65	1,0	0,6	1,29	1,59	0,87	0,71	0,14	0,22
66	0,9	0,5	1,33	1,59	0,64	0,52	0,11	0,18
67	1,0	0,5	1,35	1,65	0,86	0,68	0,11	0,17
68					< 3	< 3	< 1	< 1
69								
70	0,87	0,47	1,28	1,53	1,07	0,84	0,14	0,22
71	0,9	0,5	1,40	1,71	0,96	0,78	0,14	0,22

Lab. no.	Na mg/l, A	Na mg/l, B	K mg/l, A	K mg/l, B	Al µg/l, C	Al µg/l, D	Al µg/l, E	Al µg/l, F
1	3,2	2,5	0,82	0,81				
2	2,79	1,94	0,34	0,35	239	203		
3	3,25	2,17	0,39	0,55				
4	3,10	2,10	0,47	0,62	248	207	420	300
5	3,11	2,09	0,46	0,59				
6	3,15	2,22	0,48	0,62				
7	3,04	1,97	0,4	0,55	260	374	309	280
8	2,91	1,95	0,39	0,47	285	240	330	242
9	3,03	2,11	0,53	0,67	318	270	370	295
10	2,96	2,00	0,48	0,60				
11	3,12	2,11	0,45	0,59	289	255	358	280
12	3,32	2,22	0,38	0,52			288	213
13	3,25	2,27	0,42	0,50				
14	3,16	2,12	0,44	0,56	275	226	336	249
15	3,08	2,08	0,41	0,54	283	84		
16	3,12	3,20	0,35	0,48			325	210
17	3,00	2,10	0,46	0,57				
20	3,10	2,09	0,45	0,59	287	240	342	262
21								
22	2,62	1,64	0,50	0,71				
23	3,17	2,16	0,43	0,59			269	212
24	2,90	2,00	0,48	0,63				
25								
26	3,22	2,15	0,40	0,55				
27								
28					251	209		
29	2,60	1,70	0,10	0,20	0	0		
30	3,10	2,28	0,47	0,65	336	278	386	290
31	3,05	2,06	0,39	0,53				
32	3,02	2,01	0,47	0,59	320	290		
33	3,10	2,10	0,41	0,56	344	262		
34	3,26	2,27	0,44	0,59				
35	3,19	2,14	0,45	0,59	313	257	370	270
36	3,00	2,00	0,58	0,48	310	260	340	280
37	3,28	2,33	0,62	0,82				
38	3,08	2,01	0,45	0,59	257	216	501	384
39	3,30	2,40	< 0,5	< 0,5				
40	2,95	2,00	0,43	0,53	246	175	229	168
41	3,69	2,61	0,52	0,65			359	264
43	3,70	2,20	0,40	0,60				
44	3,25	2,25	0,44	0,55				
47	3,09	2,30	0,46	0,61				
49	2,72	1,88	0,43	0,61				
50	3,13	1,94	0,58	0,50				
51	2,98	2,08	0,43	0,59	300	242		
52	3,10	2,10	0,50	0,60				
54	2,99	2,11	0,65	0,74	360	257		
55	3,00	2,00	0,50	0,60	387	240		
56	3,30	2,40	0,36	0,47	210	167		
57	3,12	2,26	0,45	0,57	240	200		
58	3,10	2,08	0,47	0,61	293	240	354	262
59	3,12	2,10	0,44	0,59				
60					181	152		
61	3,07	1,89	0,23	0,31				
62	2,95	2,06	0,47	0,59				
63	3,20	2,20	0,44	0,61			332	239
64	3,08	2,16	0,50	0,62	290	237	355	267
65	3,18	2,15	0,45	0,60				
66	3,08	2,05	0,41	0,54	297	256	300	231
67	3,00	2,12	0,45	0,59				
68	3,20	2,10	0,50	0,60	310	270	370	290
69								
70	3,09	2,11	0,39	0,53				
71	3,10	2,08	0,44	0,60				

Lab. no.	Al-R µg/l, C	Al-R µg/l, D	Al-I µg/l, C	Al-I µg/l D	DOC mg/l, C	DOC mg/l, D	COD-Mn mg/l, C	COD-Mn mg/l, D
1								
2			171	104	10,1	9,8		
3					9,7	10,9		
4	180	146	146	120	9,0	10,8	12,6	15,4
5								
6								
7							12,6	13,8
8					9,6	11,3	13,2	16,8
9					10,8	12,8	12,8	14,9
10					9,8	10,1		
11					9,0	11,1		
12								
13								
14					10,4	11,8		
15	194	153	131	119	10,0	11,4		
16								
17							13,7	15,5
20					10,0	11,2		
21							12,2	14,9
22								
23	205	162	104	104	10,2	11,5		
24								
25							11,0	11,6
26								
27	0,68	0,94					12	14,1
28								
29							15,8	14,8
30	< 135	< 135	< 135	< 135	8,9	10,8		
31					4,3	9,2		
32								
33								
34								
35					9,1	11,1		
36	170	120			12,1	13,0	11,6	11,2
37								
38					9,8	11,2	12,5	13,5
39					9,2	10,7		
40					10,1	10,9		
41								
43								
44								
47					8,7	10,4		
49								
50								
51							23,0	26,0
52							11,9	14,3
54								
55								
56			155	127	8,5	9,7		
57	165	125			9,8	11,6	12,5	14,3
58	161	129	109	94	9,0	10,8	13,4	15,9
59	172	144	125	104	9,1	12,2		
60	145	121						
61	167	136	113	94	9,5	11,2		
62								
63								
64	100	70	190	167	10,0	11,2		
65								
66					8,9	10,6		
67								
68					8,7	10,3		
69								
70					9,2	10,6		
71								

Lab. no.	Fe µg/l, E	Fe µg/l, F	Mn µg/l, E	Mn µg/l, F	Pb µg/l, E	Pb µg/l, F	Cd µg/l, E	Cd µg/l, F
1			18,6	18,5	2,9	3,3	1,05	1,81
2								
3								
4	260	290	17	18	3,2	3,7	1	1,9
5	274	293	16,9	19,8	2,88	3,63	1,08	1,94
6								
7	230	253	22,7	23,0	1,30	1,50		
8	243	268	15,1	16,2	2,68	3,20	0,83	1,62
9	259	279	17,0	17,5	3,79	4,21	0,89	1,68
10	295	314	21,1	21,7	3,45	3,94	0,84	1,70
11	277	285	20,5	21,8				
12	229	252	15,3	16,1	1,30	4,20	0,80	1,67
13								
14	246	268	15,5	18,2	< 10	< 10	1,10	1,70
15								
16	195	220	15	16	22	75	0,8	2,2
17	327	365	17,5	17,9	2,52	2,62	1,68	2,30
20	250	279	16,7	17,4	< 5	5,00	0,90	1,60
21								
22								
23	200	200	11	13				
24								
25	300	320						
26								
27	150	120	16,7	16,9				
28	240	261	14,7	15,4	5,66	6,65	0,97	1,79
29								
30	263	297	18,4	20,0	3,70	4,20	1,10	2,10
31			8,0	10,0	2,20	2,90	0,80	2,10
32	270	280	16,0	19,0	1,50	2,00	0,70	1,15
33	217	236	16,1	16,8	2,79	3,27	0,93	1,84
34								
35	266	266	17,0	17,0	3,40	3,50	1,26	2,07
36	264	277	15,0	14,0				
37								
38	234	257	16,4	17,6	3,04	3,86	1,01	1,88
39								
40					2,2	2,8	1	2,1
41	237	259	15,5	16,2	3,61	3,49	0,80	1,49
43								
44								
47								
49	150	250						
50	190	198	15,9	18,0	2,60	3,30	0,66	1,27
51	263	293	16,1	17,1				
52			17,0	18,0	3,00	3,00	0,90	1,90
54	255	283	17,5	18,3	3,60	4,10	0,90	2,00
55	269	283	18,3	21,3	2,80	3,20	0,99	1,83
56								
57	260	280	17,0	17,0	3,00	3,70	1,20	2,30
58	249	272	17,0	17,9	2,97	3,54	0,92	1,85
59								
60								
61	319	361						
62								
63			16,0	17,4	3,07	3,60	0,91	1,73
64	279	292	15,2	15,2	2,90	3,47	1,16	1,85
65								
66	220	252	13,2	15,3	< 20	< 20	< 2	< 2
67								
68	270	290	18,0	18,0			1,00	1,80
69								
70								
71								

Lab. no.	Cu µg/l, E	Cu µg/l, F	Ni µg/l, E	Ni µg/l, F	Zn µg/l, E	Zn µg/l, F
1	28	20	2,7	1,9	18	20
2						
3						
4	14	9,1	3,4	2,6	12	18
5	13,8	10,3	3,0	2,8	12,0	21,1
6						
7	14,7	11,7	< 1,5	< 1,5	9,0	12,0
8	12,8	8,3	2,9	2,0	9,9	14,0
9	12,7	9,7	3,0	2,0	12,7	16,8
10	14,5	8,5	3,1	2,2	17,1	41,1
11						
12	14,0	9,2	2,6	2,0	9,4	14,5
13						
14	14,1	8,0	< 4,5	< 4,5	10,2	14,2
15						
16	25	18	7	2	20	24
17	15,0	9,8	5,4	5,0	9,6	10,0
20	17,3	11,6	2,0	< 2	10,9	15,1
21						
22						
23	13	9			10	13
24						
25						
26						
27						
28	14,8	9,4	12,3	7,2	10,3	14,4
29						
30	15,9	10,1	3,4	2,5	13,3	18,9
31	20,5	15,8			12,0	16,0
32	13,5	9,5	3,0	2,0	12,0	19,0
33	13,6	8,5	2,8	2,1	11,0	17,6
34						
35	14,3	8,9	3,8	2,1	14,0	16,0
36	14,0	7,0			10,0	11,0
37						
38	13,6	8,3	2,5	1,7	10,0	15,0
39						
40	14,3	8,8	3,2	2,2	10,2	16,3
41	12,4	7,6	< 4	< 4	10,0	14,3
43						
44						
47						
49	12,0	6,9			9,8	17,2
50	8,7	5,6	< 3	< 3	29,5	36,5
51	< 14	< 14			8,8	15,2
52	15,0	9,0	3,0	2,0	11,0	15,0
54	15,1	9,6	3,5	2,8	9,8	13,9
55	21,5	8,4	3,2	2,3	19,3	13,8
56						
57	14,0	9,4	3,1	2,3	12,0	16,0
58	14,0	8,9	3,0	2,2	11,0	16,5
59						
60						
61	10,0	6,0				
62						
63	11,0	6,6	2,3	1,7	8,8	12,1
64			3,2	0,0	10,6	15,8
65						
66	12,1	7,9	< 2	< 2	7,8	12,1
67						
68	15,0	9,0	3,0	2,0	20,0	32,0
69						
70						
71						

Table 5.1. Statistics - pH

Sample A

Number of participants	63	Range	1,33
Number of omitted results	1	Variance	0,05
True value	6,51	Standard deviation	0,23
Mean value	6,50	Relative standard deviation	3,6%
Median value	6,51	Relative error	-0,2%

Analytical results in ascending order:

55	5,60 U	60	6,44	28	6,56
59	5,88	67	6,45	47	6,57
37	5,92	56	6,45	14	6,62
25	6,05	21	6,46	65	6,62
51	6,14	16	6,46	71	6,62
54	6,15	32	6,47	29	6,63
62	6,20	8	6,47	58	6,64
20	6,24	2	6,49	57	6,64
43	6,25	23	6,50	15	6,65
9	6,27	1	6,50	61	6,66
26	6,30	68	6,50	40	6,66
6	6,30	41	6,52	13	6,66
39	6,31	35	6,53	31	6,69
49	6,34	34	6,53	33	6,70
3	6,36	27	6,54	17	6,70
69	6,38	12	6,54	63	6,77
38	6,40	24	6,54	7	6,79
66	6,40	70	6,54	30	6,82
52	6,40	4	6,55	10	6,98
64	6,43	22	6,55	44	7,02
5	6,43	4	6,55	50	7,21

Sample B

Number of participants	63	Range	1,02
Number of omitted results	1	Variance	0,04
True value	6,28	Standard deviation	0,19
Mean value	6,24	Relative standard deviation	3,1%
Median value	6,28	Relative error	-0,6%

Analytical results in ascending order:

55	5,30 U	50	6,20	15	6,31
37	5,63	38	6,20	44	6,31
54	5,75	5	6,22	13	6,31
59	5,82	66	6,23	58	6,32
25	5,90	8	6,23	41	6,32
43	5,92	60	6,23	47	6,33
51	5,97	16	6,23	28	6,35
65	5,98	56	6,25	14	6,36
62	6,00	23	6,25	57	6,37
26	6,02	70	6,26	29	6,38
39	6,06	3	6,27	61	6,43
9	6,07	40	6,28	36	6,43
49	6,12	12	6,29	63	6,43
69	6,12	2	6,30	31	6,45
6	6,12	27	6,30	4	6,46
20	6,15	22	6,30	71	6,48
64	6,16	68	6,30	33	6,50
67	6,17	1	6,30	17	6,50
21	6,19	24	6,30	7	6,53
35	6,19	32	6,30	30	6,56
52	6,20	34	6,30	10	6,65

U = Omitted result

Table 5.2. Statistics - Conductivity, mS/m

Sample A

Number of participants	61	Range	0,80
Number of omitted results	12	Variance	0,02
True value	2,08	Standard deviation	0,13
Mean value	2,06	Relative standard deviation	6,3%
Median value	2,08	Relative error	-1,1%

Analytical results in ascending order:

59	1,35 U	62	2,06	5	2,14
22	1,46	6	2,06	8	2,14
1	1,83	32	2,07	33	2,16
26	1,85	67	2,07	10	2,20
9	1,86	58	2,08	7	2,20
20	1,90	44	2,08	68	2,20
50	1,92	56	2,08	63	2,20
65	1,93	71	2,10	30	2,24
64	1,99	13	2,10	27	2,26
36	2,00	17	2,10	41	2,89
25	2,00 U	28	2,10	12	2,94
23	2,00	52	2,10	43	3,29
2	2,00	37	2,10	16	19,34
4	2,01	3	2,11	40	21,10
47	2,02	60	2,11	39	21,30
57	2,03	24	2,12	55	21,80
35	2,04	51	2,12	38	27,90
61	2,05	54	2,12	70	207,00
49	2,05	21	2,13	66	212,00
15	2,05	14	2,13		
69	2,05	34	2,13		

Sample B

Number of participants	61	Range	0,49
Number of omitted results	12	Variance	0,01
True value	1,70	Standard deviation	0,08
Mean value	1,70	Relative standard deviation	4,8%
Median value	1,70	Relative error	0,0%

Analytical results in ascending order:

25	1,00 U	13	1,70	8	1,75
59	1,06 U	2	1,70	14	1,75
22	1,42	52	1,70	24	1,78
26	1,57	37	1,70	27	1,79
20	1,57	47	1,70	54	1,79
65	1,57	36	1,70	7	1,80
50	1,60	62	1,70	30	1,83
23	1,60	10	1,70	68	1,90
64	1,61	32	1,71	63	1,91
9	1,61	44	1,71	41	1,94
61	1,65	56	1,71	12	2,46
4	1,65	58	1,72	43	2,79
35	1,67	21	1,72	16	15,60
3	1,67	71	1,72	40	17,10
1	1,68	69	1,72	39	17,20
49	1,68	5	1,73	55	18,00
15	1,68	60	1,73	38	21,20
57	1,69	34	1,74	70	169,00
17	1,69	51	1,74	66	178,00
67	1,69	28	1,75		
6	1,69	33	1,75		

U = Omitted result

Table 5.3. Statistics - Alkalinity, mmol/l

Sample A

Number of participants	54	Range	0,081
Number of omitted results	16	Variance	0,000
True value	0,094	Standard deviation	0,016
Mean value	0,092	Relative standard deviation	17,0%
Median value	0,094	Relative error	-2,5%

Analytical results in ascending order:

2	0,038	U	58	0,092	61	0,107
17	0,043	U	21	0,092	69	0,109
64	0,049		40	0,092	71	0,110
25	0,061		23	0,093	49	0,114
55	0,065		4	0,095	6	0,117
7	0,066		51	0,095	47	0,130
26	0,070		1	0,096	54	0,130
37	0,075	U	36	0,096	57	0,135
38	0,080		10	0,097	27	0,140
8	0,082		13	0,098	22	0,140
62	0,082		60	0,098	43	0,140
5	0,082		70	0,099	65	0,150
66	0,083		56	0,100	50	0,150
28	0,084		52	0,100	33	0,155
12	0,085		24	0,100	9	0,168
34	0,090		44	0,101	39	0,182
3	0,090		15	0,101	35	0,210
67	0,090		32	0,105	68	0,400

Sample B

Number of participants	54	Range	0,050
Number of omitted results	16	Variance	0,000
True value	0,055	Standard deviation	0,011
Mean value	0,055	Relative standard deviation	19,8%
Median value	0,055	Relative error	-0,4%

Analytical results in ascending order:

37	0,021	U	34	0,055	15	0,065
2	0,027	U	58	0,055	56	0,065
26	0,030		7	0,055	61	0,067
64	0,030		23	0,055	54	0,080
55	0,038		67	0,055	6	0,080
12	0,040		51	0,057	49	0,085
8	0,042		21	0,057	47	0,090
5	0,042		60	0,058	43	0,090
17	0,043	U	70	0,058	27	0,092
66	0,046		52	0,060	57	0,096
3	0,046		71	0,060	22	0,100
62	0,050		10	0,060	65	0,110
38	0,050		44	0,060	33	0,116
40	0,051		24	0,060	9	0,120
28	0,051		4	0,061	39	0,132
25	0,051		13	0,061	50	0,150
1	0,052		32	0,062	35	0,190
36	0,052		69	0,065	68	0,350

U = Omitted result

Table 5.4. Statistics - Nitrate + nitrite-nitrogen, µg/l

Sample A

Number of participants	55	Range	19
Number of omitted results	17	Variance	26
True value	26	Standard deviation	5
Mean value	27	Relative standard deviation	18,8%
Median value	26	Relative error	4,2%

Analytical results in ascending order:

7	U	12	24	62	28
2	U	47	24	65	29
39	< 200 U	26	25 U	24	29
33	< 60 U	15	25	6	30
59	< 50 U	56	25	20	31
3	0 U	13	25	35	34
9	0 U	58	25	44	35
29	0 U	4	25	38	37
61	9 U	63	25	43	38
66	12 U	67	26	32	38
1	20	27	26	54	39
55	20	22	27	37	42
8	20	23	27	51	45
36	21	71	27	41	50
52	22	70	27	34	60
49	22	10	27	30	69
21	23	40	28	16	79
5	23	17	28	25	130
14	23	57	28	50	137

Sample B

Number of participants	55	Range	32
Number of omitted results	17	Variance	38
True value	72	Standard deviation	6
Mean value	72	Relative standard deviation	8,6%
Median value	72	Relative error	-0,2%

Analytical results in ascending order:

39	< 200 U	52	70	35	76
33	< 60 U	41	70 U	65	76
9	0 U	3	70 U	51	77
29	0 U	70	70	23	78
26	26 U	56	70	36	78
66	46 U	1	70	71	78
49	56	27	70	24	78
59	58 U	10	71	38	78
55	60	5	71	6	79
40	62	58	71	20	83
8	63	47	72	30	88
61	64 U	32	72	43	88
21	65	63	73	2	88
15	66	67	73	37	93
22	68	54	73	34	100
14	68	17	73	7	103
12	69	62	74	16	149
13	69	44	75	25	170
4	69	57	75	50	183

U = Omitted result

Table 5.5. Statistics - Chloride, mg/l

Sample A

Number of participants	56	Range	0,5
Number of omitted results	10	Variance	0,0
True value	0,9	Standard deviation	0,1
Mean value	0,9	Relative standard deviation	8,7%
Median value	0,9	Relative error	1,7%

Analytical results in ascending order:

22	< 1 U	63	0,9	38	1,0
9	0,7	13	0,9 U	14	1,0
32	0,8	54	0,9	36	1,0
12	0,8	61	0,9	65	1,0
35	0,8	23	0,9	57	1,0
7	0,8	52	0,9	62	1,0
20	0,9	4	0,9	55	1,0
64	0,9	2	0,9	33	1,1
59	0,9	24	0,9	39	1,1
34	0,9	71	0,9	41	1,2
47	0,9	1	0,9	37	1,2
70	0,9	44	0,9	5	1,4
6	0,9	30	0,9	49	1,4
16	0,9	66	0,9	43	1,5
21	0,9	3	0,9	51	1,7
58	0,9	10	0,9	17	2,1
56	0,9	15	0,9	25	2,3
8	0,9	67	1,0	50	3,5
26	0,9	40	1,0		

Sample B

Number of participants	56	Range	0,2
Number of omitted results	10	Variance	0,0
True value	0,5	Standard deviation	0,0
Mean value	0,5	Relative standard deviation	9,7%
Median value	0,5	Relative error	-2,3%

Analytical results in ascending order:

41	< 1 U	54	0,5	61	0,5
22	< 1 U	26	0,5	36	0,5
33	0,4	8	0,5	10	0,5
20	0,4	44	0,5	1	0,5
2	0,4	66	0,5	9	0,5
24	0,4	47	0,5	65	0,6
21	0,4	38	0,5	57	0,6
34	0,4	30	0,5	39	0,6
59	0,4	71	0,5	37	0,6
16	0,4	23	0,5	4	0,6
64	0,5	52	0,5	13	0,7
12	0,5	40	0,5	5	0,9
32	0,5	3	0,5	49	0,9
56	0,5	55	0,5	51	1,1
7	0,5	67	0,5	43	1,2
35	0,5	14	0,5	17	1,8
6	0,5	15	0,5	25	2,1
70	0,5	63	0,5	50	3,0
58	0,5	62	0,5		

U = Omitted result

Table 5.6. Statistics - Sulfate, mg/l

Sample A

Number of participants	56	Range	1,0
Number of omitted results	6	Variance	0,0
True value	1,3	Standard deviation	0,2
Mean value	1,3	Relative standard deviation	13,5%
Median value	1,3	Relative error	2,3%

Analytical results in ascending order:

22	U	70	1,3	3	1,4
39	< 5 U	65	1,3	30	1,4
50	< 2 U	4	1,3	71	1,4
9	0,8	64	1,3	14	1,4
36	0,9	23	1,3	40	1,4
29	1,0	63	1,3	34	1,4
55	1,1	62	1,3	6	1,4
16	1,1	66	1,3	10	1,4
47	1,2	7	1,3	56	1,4
1	1,2	54	1,3	13	1,5
52	1,2	67	1,4	21	1,5
35	1,2	51	1,4	26	1,5
2	1,2	44	1,4	38	1,6
49	1,2 U	59	1,4	17	1,6
57	1,3	61	1,4	41	1,8
20	1,3	12	1,4	24	1,8
15	1,3	33	1,4	25	2,5
58	1,3	37	1,4	8	2,7
27	1,3	32	1,4	5	4,0

Sample B

Number of participants	56	Range	0,9
Number of omitted results	6	Variance	0,0
True value	1,6	Standard deviation	0,2
Mean value	1,6	Relative standard deviation	11,0%
Median value	1,6	Relative error	0,0%

Analytical results in ascending order:

39	< 5 U	58	1,6	61	1,7
50	< 2 U	15	1,6	21	1,7
49	0,3 U	23	1,6	37	1,7
9	1,1	66	1,6	7	1,7
29	1,2	65	1,6	40	1,7
36	1,3	64	1,6	71	1,7
55	1,3	62	1,6	14	1,7
33	1,4	4	1,6	26	1,7
16	1,4	54	1,6	13	1,7
47	1,5	34	1,6	56	1,7
17	1,5	51	1,6	6	1,8
27	1,5	59	1,6	3	1,8
52	1,5	32	1,7	1	1,9
35	1,5	67	1,7	41	2,0
70	1,5	44	1,7	24	2,0
57	1,5	63	1,7	22	2,2
12	1,6	10	1,7	25	2,5
20	1,6	30	1,7	8	3,2
2	1,6	38	1,7	5	3,7

U = Omitted result

Table 5.7. Statistics - Calcium, mg/l

Sample A

Number of participants	60	Range	0,84
Number of omitted results	9	Variance	0,03
True value	0,88	Standard deviation	0,16
Mean value	0,88	Relative standard deviation	18,6%
Median value	0,88	Relative error	-0,1%

Analytical results in ascending order:

39	< 5 U	9	0,84	7	0,92
68	< 3 U	11	0,85	37	0,92
49	0,07 U	56	0,85	4	0,93
61	0,34 U	55	0,85	64	0,95
22	0,45 U	20	0,86	71	0,96
40	0,46	36	0,86	58	0,97
1	0,51	67	0,86	63	0,98
44	0,53	32	0,87	33	0,98
3	0,62	65	0,87	25	1,00
66	0,64	30	0,88	57	1,06
47	0,71	54	0,88	70	1,07
34	0,74	59	0,89	27	1,09
2	0,75	5	0,89	12	1,19
31	0,75	52	0,90	43	1,20
17	0,76	51	0,90	50	1,20
15	0,79	35	0,90	23	1,30
29	0,80	24	0,91	26	1,31
14	0,83	10	0,91	62	1,50
8	0,83	16	0,91	13	1,59
38	0,84	6	0,91	41	2,28

Sample B

Number of participants	60	Range	0,69
Number of omitted results	9	Variance	0,02
True value	0,71	Standard deviation	0,15
Mean value	0,73	Relative standard deviation	20,0%
Median value	0,71	Relative error	3,4%

Analytical results in ascending order:

39	< 5 U	54	0,69	4	0,76
68	< 3 U	14	0,70	58	0,78
49	0,04 U	55	0,70	7	0,78
61	0,26 U	35	0,70	71	0,78
22	0,32 U	32	0,70	29	0,80
1	0,37	52	0,70	33	0,80
44	0,49	11	0,70	63	0,82
40	0,50	20	0,70	70	0,84
3	0,52	59	0,71	43	0,90
66	0,52	5	0,71	31	0,95
34	0,55	65	0,71	50	1,00
17	0,59	6	0,72	62	1,00
38	0,62	30	0,72	25	1,00
2	0,62	24	0,73	12	1,01
47	0,63	37	0,74	57	1,02
15	0,63	64	0,75	23	1,04
9	0,67	56	0,75	27	1,06
8	0,67	10	0,75	26	1,12
36	0,67	16	0,75	13	1,30
67	0,68	51	0,76	41	1,88

U = Omitted result

Table 5.8. Statistics - Magnesium, mg/l

Sample A

Number of participants	59	Range	0,12
Number of omitted results	7	Variance	0,00
True value	0,14	Standard deviation	0,02
Mean value	0,13	Relative standard deviation	16,3%
Median value	0,14	Relative error	-4,7%

Analytical results in ascending order:

68	< 1 U	38	0,13	22	0,14
39	< 0,5 U	55	0,13	58	0,14
29	0,00 U	59	0,13	6	0,15
40	0,07	15	0,13	31	0,15
44	0,09	36	0,13	43	0,15
37	0,09	16	0,13	62	0,15
52	0,10	4	0,13	56	0,15
35	0,10	11	0,13	13	0,15
3	0,11	20	0,14	1	0,15
34	0,11	30	0,14	57	0,15
67	0,11	64	0,14	7	0,16
66	0,11	54	0,14	27	0,17
2	0,11	71	0,14	26	0,17
47	0,12	10	0,14	33	0,17
32	0,12	51	0,14	23	0,19
24	0,12	63	0,14	12	0,21
49	0,12	65	0,14	17	0,26
9	0,13	5	0,14	50	0,36
61	0,13	70	0,14	41	0,37
14	0,13	8	0,14		

Sample B

Number of participants	59	Range	0,15
Number of omitted results	7	Variance	0,00
True value	0,20	Standard deviation	0,03
Mean value	0,21	Relative standard deviation	13,4%
Median value	0,20	Relative error	2,9%

Analytical results in ascending order:

68	< 1 U	64	0,20	71	0,22
39	< 0,5 U	36	0,20	70	0,22
40	0,14	62	0,20	6	0,22
44	0,15	4	0,20	30	0,23
49	0,15	16	0,20	7	0,23
37	0,16	1	0,20	54	0,23
67	0,17	35	0,20	56	0,23
3	0,17	31	0,20	51	0,23
2	0,18	9	0,21	57	0,23
66	0,18	38	0,21	29	0,24
34	0,18	55	0,21	13	0,24
32	0,18	10	0,21	33	0,25
24	0,19	8	0,21	27	0,25
59	0,19	22	0,21	26	0,26
47	0,20	5	0,21	23	0,29
61	0,20	20	0,21	17	0,29
11	0,20	58	0,21	12	0,30
14	0,20	43	0,22	41	0,40
52	0,20	65	0,22	50	0,49
15	0,20	63	0,22		

U = Omitted result

Table 5.9. Statistics - Sodium, mg/l

Sample A

Number of participants	58	Range	1,09
Number of omitted results	1	Variance	0,03
True value	3,10	Standard deviation	0,17
Mean value	3,09	Relative standard deviation	5,5%
Median value	3,10	Relative error	-0,5%

Analytical results in ascending order:

		61	3,07	6	3,15
29	2,60	66	3,08	14	3,16
22	2,62	15	3,08	23	3,17
49	2,72	64	3,08	65	3,18
2	2,79	38	3,08	35	3,19
24	2,90	47	3,09	68	3,20
8	2,91	70	3,09	1	3,20
40	2,95	30	3,10	63	3,20
62	2,95	20	3,10	26	3,22
10	2,96	4	3,10	44	3,25
51	2,98	33	3,10	13	3,25
54	2,99	58	3,10	3	3,25
67	3,00	71	3,10	34	3,26
17	3,00	52	3,10	37	3,28
36	3,00	5	3,11	39	3,30
55	3,00	59	3,12	56	3,30
32	3,02	57	3,12	12	3,32
9	3,03	11	3,12	41	3,69
7	3,04	16	3,12	43	3,70
31	3,05	50	3,13		

Sample B

Number of participants	58	Range	0,97
Number of omitted results	1	Variance	0,03
True value	2,10	Standard deviation	0,17
Mean value	2,11	Relative standard deviation	7,8%
Median value	2,10	Relative error	0,6%

Analytical results in ascending order:

		58	2,08	23	2,16
22	1,64	15	2,08	64	2,16
29	1,70	51	2,08	3	2,17
49	1,88	20	2,09	63	2,20
61	1,89	5	2,09	16	2,20
50	1,94	59	2,10	43	2,20
2	1,94	33	2,10	12	2,22
8	1,95	4	2,10	6	2,22
7	1,97	52	2,10	44	2,25
10	2,00	68	2,10	57	2,26
55	2,00	17	2,10	13	2,27
24	2,00	11	2,11	34	2,27
36	2,00	54	2,11	30	2,28
40	2,00	9	2,11	47	2,30
32	2,01	70	2,11	37	2,33
38	2,01	14	2,12	56	2,40
66	2,05	67	2,12	39	2,40
31	2,06	35	2,14	1	2,50
62	2,06	65	2,15	41	2,61
71	2,08	26	2,15		

U = Omitted result

Table 5.10. Statistics - Potassium, mg/l

Sample A

Number of participants	58	Range	0,31
Number of omitted results	5	Variance	0,00
True value	0,45	Standard deviation	0,06
Mean value	0,45	Relative standard deviation	12,6%
Median value	0,45	Relative error	0,1%

Analytical results in ascending order:

39	< 0,5 U	23	0,43	62	0,47
29	0,10 U	51	0,43	4	0,47
61	0,23 U	14	0,44	32	0,47
2	0,34	71	0,44	10	0,48
16	0,35	63	0,44	6	0,48
56	0,36	44	0,44	24	0,48
12	0,38	34	0,44	52	0,50
3	0,39	59	0,44	55	0,50
31	0,39	35	0,45	22	0,50
70	0,39	11	0,45	64	0,50
8	0,39	65	0,45	68	0,50
7	0,40	67	0,45	41	0,52
43	0,40	38	0,45	9	0,53
26	0,40	57	0,45	36	0,58
33	0,41	20	0,45	50	0,58
15	0,41	47	0,46	37	0,62
66	0,41	5	0,46	54	0,65
13	0,42	17	0,46	1	0,82
40	0,43	30	0,47		
49	0,43	58	0,47		

Sample B

Number of participants	58	Range	0,39
Number of omitted results	5	Variance	0,00
True value	0,59	Standard deviation	0,06
Mean value	0,58	Relative standard deviation	10,8%
Median value	0,59	Relative error	-2,4%

Analytical results in ascending order:

39	< 0,5 U	33	0,56	52	0,60
29	0,20 U	14	0,56	71	0,60
61	0,31 U	57	0,57	10	0,60
2	0,35	17	0,57	47	0,61
8	0,47	67	0,59	63	0,61
56	0,47	59	0,59	49	0,61
36	0,48	35	0,59	58	0,61
16	0,48	11	0,59	4	0,62
50	0,50	20	0,59	64	0,62
13	0,50	5	0,59	6	0,62
12	0,52	38	0,59	24	0,63
31	0,53	23	0,59	41	0,65
70	0,53	32	0,59	30	0,65
40	0,53	62	0,59	9	0,67
15	0,54	34	0,59	22	0,71
66	0,54	51	0,59	54	0,74
44	0,55	65	0,60	1	0,81
26	0,55	55	0,60	37	0,82
7	0,55	43	0,60		
3	0,55	68	0,60		

U = Omitted result

Table 5.11. Statistics - Aluminium, µg/l

Sample C

Number of participants	28	Range	206
Number of omitted results	3	Variance	2179
True value	290	Standard deviation	47
Mean value	287	Relative standard deviation	16,2%
Median value	290	Relative error	-0,9%

Analytical results in ascending order:

29	0 U	14	275	36	310
60	181	15	283 U	35	313
56	210	8	285	9	318
2	239	20	287	32	320
57	240	11	289	30	336
40	246	64	290	33	344
4	248	58	293	54	360
28	251	66	297	55	387
38	257	51	300		
7	260 U	68	310		

Sample D

Number of participants	28	Range	138
Number of omitted results	3	Variance	1251
True value	240	Standard deviation	35
Mean value	234	Relative standard deviation	15,1%
Median value	240	Relative error	-2,6%

Analytical results in ascending order:

29	0 U	14	226	54	257
15	84 U	64	237	36	260
60	152	58	240	33	262
56	167	55	240	68	270
40	175	20	240	9	270
57	200	8	240	30	278
2	203	51	242	32	290
4	204	11	255	7	374
28	209	66	256		
38	216	35	257		

U = Omitted result

Table 5.12. Statistics - Aluminium, µg/l

Sample E

Number of participants	21	Range	272
Number of omitted results	1	Variance	3042
True value	342	Standard deviation	55
Mean value	345	Relative standard deviation	16,0%
Median value	342	Relative error	0,8%

Analytical results in ascending order:

65	U	63	332	68	370
40	229	14	336	35	370
23	269	36	340	9	370
12	288	20	342	30	386
66	300	58	354	4	420
7	309	64	355	38	501
16	325	11	358		
8	330	41	359		

Sample F

Number of participants	21	Range	216
Number of omitted results	1	Variance	1928
True value	264	Standard deviation	44
Mean value	261	Relative standard deviation	16,8%
Median value	264	Relative error	-1,0%

Analytical results in ascending order:

40	168	20	262	11	280
16	210	58	262	68	290
23	212	41	264	30	290
12	213	64	267	9	295
66	231	35	270	4	300
63	239	65	271 U	38	384
8	242	7	280		
14	249	36	280		

U = Omitted result

Table 5.13. Statistics - Aluminium, reactive, µg/l

Sample C

Number of participants	12	Range	105
Number of omitted results	2	Variance	820
True value	169	Standard deviation	29
Mean value	166	Relative standard deviation	17,3%
Median value	169	Relative error	-1,8%

Analytical results in ascending order:

30	< 135 U	58	161	59	172
27	1 U	57	165	4	180
64	100	61	167	15	194
60	145	36	170	23	205

Sample D

Number of participants	12	Range	92
Number of omitted results	2	Variance	649
True value	133	Standard deviation	25
Mean value	131	Relative standard deviation	19,5%
Median value	133	Relative error	-1,8%

Analytical results in ascending order:

30	< 135 U	60	121	59	144
27	1 U	57	125	4	146
64	70	58	129	15	153
36	120	61	136	23	162

Table 5.14. Statistics - Aluminium, nonlabile, µg/l

Sample C

Number of participants	10	Range	67
Number of omitted results	2	Variance	567
True value	128	Standard deviation	24
Mean value	132	Relative standard deviation	18,1%
Median value	128	Relative error	2,9%

Analytical results in ascending order:

30	< 135 U	59	125	2	171
23	104	15	131	64	190
58	109	4	146		
61	113	56	155		

Sample D

Number of participants	10	Range	33
Number of omitted results	2	Variance	152
True value	104	Standard deviation	12
Mean value	108	Relative standard deviation	11,4%
Median value	104	Relative error	4,1%

Analytical results in ascending order:

30	< 135 U	59	104	56	127
58	94	2	104	64	167
61	94	15	119		
23	104	4	120		

U = Omitted result

Table 5.15. Statistics - Dissolved organic carbon, mg/l

Sample C

Number of participants	28	Range	2,3
Number of omitted results	2	Variance	0,4
True value	9,6	Standard deviation	0,6
Mean value	9,5	Relative standard deviation	6,3%
Median value	9,6	Relative error	-1,0%

Analytical results in ascending order:

31	4,3 U	59	9,1	20	10,0
56	8,5	70	9,2	15	10,0
68	8,7	39	9,2	2	10,1
47	8,7	61	9,5	40	10,1
66	8,9	8	9,6	23	10,2
30	8,9	3	9,7	14	10,4
4	9,0	57	9,8	9	10,8
58	9,0	38	9,8	36	12,1
11	9,0	10	9,8		
35	9,1	64	10,0		

Sample D

Number of participants	28	Range	3,1
Number of omitted results	2	Variance	0,5
True value	11,0	Standard deviation	0,7
Mean value	11,0	Relative standard deviation	6,2%
Median value	11,0	Relative error	0,0%

Analytical results in ascending order:

31	9,2 U	30	10,8	8	11,3
56	9,7	58	10,8	15	11,4
2	9,8	40	10,9	23	11,5
10	10,1	3	10,9	57	11,6
68	10,3	11	11,1	14	11,8
47	10,4	35	11,1	59	12,2
70	10,6	61	11,2	9	12,8
66	10,6	20	11,2	36	13,0
39	10,7	64	11,2		
4	10,8	38	11,2		

U = Omitted result

Table 5.16. Statistics - Chemical oxygen demand, mg/l

Sample C

Analytical method: All
Unit: mg/l

Number of participants	15	Range	4,8
Number of omitted results	1	Variance	1,3
True value	12,6	Standard deviation	1,1
Mean value	12,7	Relative standard deviation	9,0%
Median value	12,6	Relative error	0,8%

Analytical results in ascending order:

25	11,0	57	12,5	8	13,2
36	11,6	38	12,5	58	13,4
52	11,9	4	12,6	17	13,7
27	12,0	7	12,6	29	15,8
21	12,2	9	12,8	51	23,0

Sample D

Number of participants	15	Range	5,6
Number of omitted results	1	Variance	2,3
True value	14,6	Standard deviation	1,5
Mean value	14,4	Relative standard deviation	10,6%
Median value	14,6	Relative error	-1,7%

Analytical results in ascending order:

36	11,2	52	14,3	4	15,4
25	11,6	57	14,3	17	15,5
38	13,5	29	14,8	58	15,9
7	13,8	21	14,9	8	16,8
27	14,1	9	14,9	51	26,0

U = Omitted result

Table 5.17. Statistics - Iron, µg/l

Sample E

Number of participants	34	Range	177
Number of omitted results	1	Variance	1316
True value	259	Standard deviation	36
Mean value	251	Relative standard deviation	14,4%
Median value	259	Relative error	-2,9%

Analytical results in ascending order:

27	150 U	8	243	55	269
49	150	14	246	32	270
50	190	58	249	68	270
16	195	20	250	5	274
23	200	54	255	11	277
33	217	9	259	64	279
66	220	57	260	10	295
12	229	4	260	25	300
7	230	51	263	61	319
38	234	30	263	17	327
41	237	36	264		
28	240	35	266		

Sample F

Number of participants	34	Range	167
Number of omitted results	1	Variance	1265
True value	279	Standard deviation	36
Mean value	275	Relative standard deviation	12,9%
Median value	279	Relative error	-1,5%

Analytical results in ascending order:

27	120 U	35	266	4	290
50	198	8	268	68	290
23	200	14	268	64	292
16	220	58	272	51	293
33	236	36	277	5	293
49	250	9	279	30	297
66	252	20	279	10	314
12	252	57	280	25	320
7	253	32	280	61	361
38	257	55	283	17	365
41	259	54	283		
28	261	11	285		

U = Omitted result

Table 5.18. Statistics - Manganese, µg/l

Sample E

Number of participants	35	Range	11,7
Number of omitted results	1	Variance	4,5
True value	16,7	Standard deviation	2,1
Mean value	16,7	Relative standard deviation	12,7%
Median value	16,7	Relative error	-0,2%

Analytical results in ascending order:

65	U	50	15,9	35	17,0
31	8,0 U	63	16,0	4	17,0
23	11,0	32	16,0	9	17,0
66	13,2	51	16,1	54	17,5
28	14,7	33	16,1	17	17,5
16	15,0	38	16,4	68	18,0
36	15,0	20	16,7	55	18,3
8	15,1	27	16,7	30	18,4
64	15,2	5	16,9	1	18,6
12	15,3	58	17,0	11	20,5
41	15,5	57	17,0	10	21,1
14	15,5	52	17,0	7	22,7

Sample F

Number of participants	35	Range	10,0
Number of omitted results	1	Variance	4,6
True value	17,6	Standard deviation	2,2
Mean value	17,7	Relative standard deviation	12,2%
Median value	17,6	Relative error	0,5%

Analytical results in ascending order:

31	10,0 U	57	17,0	4	18,0
23	13,0	35	17,0	14	18,2
36	14,0	51	17,1	54	18,3
64	15,2	20	17,4	1	18,5
66	15,3	63	17,4	65	18,5
28	15,4	9	17,5	32	19,0
16	16,0	38	17,6	5	19,8
12	16,1	17	17,9	30	20,0
41	16,2	58	17,9	55	21,3
8	16,2	50	18,0	10	21,7
33	16,8	52	18,0	11	21,8
27	16,9	68	18,0	7	23,0

U = Omitted result

Table 5.19. Statistics - Kadmium, µg/l

Sample E

Number of participants	30	Range	0,60
Number of omitted results	2	Variance	0,02
True value	0,93	Standard deviation	0,14
Mean value	0,95	Relative standard deviation	15,3%
Median value	0,93	Relative error	1,8%

Analytical results in ascending order:

65	U	20	0,90	38	1,01
66	< 2 U	52	0,90	1	1,05
50	0,66	54	0,90	5	1,08
32	0,70	63	0,91	14	1,10
12	0,80	58	0,92	30	1,10
41	0,80	33	0,93	64	1,16
31	0,80	28	0,97	57	1,20
16	0,80	55	0,99	35	1,26
8	0,83	68	1,00	17	1,68
10	0,84	40	1,00		
9	0,89	4	1,00		

Sample F

Number of participants	30	Range	1,15
Number of omitted results	2	Variance	0,07
True value	1,84	Standard deviation	0,26
Mean value	1,82	Relative standard deviation	14,1%
Median value	1,84	Relative error	-1,3%

Analytical results in ascending order:

66	< 2 U	28	1,79	54	2,00
32	1,15	68	1,80	65	2,03
50	1,27	1	1,81	35	2,07
41	1,49	55	1,83	31	2,10
20	1,60	33	1,84	30	2,10
8	1,62	64	1,85	40	2,10
12	1,67	58	1,85	16	2,20
9	1,68	38	1,88	57	2,30
10	1,70	52	1,90	17	2,30
14	1,70	4	1,90		
63	1,73	5	1,94		

U = Omitted result

Table 5.20. Statistics - Lead, µg/l

Sample E

Number of participants	30	Range	2,29
Number of omitted results	7	Variance	0,29
True value	2,97	Standard deviation	0,54
Mean value	2,95	Relative standard deviation	18,2%
Median value	2,97	Relative error	-0,7%

Analytical results in ascending order:

65		U	8	2,68	4	3,20
66	< 20	U	33	2,79	35	3,40
14	< 10	U	55	2,80	10	3,45
20	< 5	U	5	2,88	54	3,60
7	1,30	U	64	2,90	41	3,61
12	1,30	U	1	2,90	30	3,70
32	1,50		58	2,97	9	3,79
31	2,20		57	3,00	28	5,66
40	2,20		52	3,00	16	22,00
17	2,52		38	3,04		
50	2,60		63	3,07		

Sample F

Number of participants	30	Range	2,21
Number of omitted results	7	Variance	0,28
True value	3,49	Standard deviation	0,52
Mean value	3,41	Relative standard deviation	15,4%
Median value	3,49	Relative error	-2,2%

Analytical results in ascending order:

66	< 20	U	1	3,30	65	3,88
14	< 10	U	50	3,30	10	3,94
7	1,50	U	64	3,47	54	4,10
32	2,00		41	3,49	12	4,20
17	2,62		35	3,50	30	4,20
40	2,80		58	3,54	9	4,21
31	2,90		63	3,60	20	5,00
52	3,00		5	3,63	28	6,65
55	3,20		57	3,70	16	75,00
8	3,20		4	3,70		
33	3,27		38	3,86		

U = Omitted result

Table 5.21. Statistics - Copper, µg/l

Sample E

Number of participants	35	Range	8,6
Number of omitted results	5	Variance	2,9
True value	14,0	Standard deviation	1,7
Mean value	13,6	Relative standard deviation	12,5%
Median value	14,0	Relative error	-2,6%

Analytical results in ascending order:

65	U	33	13,6	7	14,7
51	< 14 U	38	13,6	28	14,8
50	8,7	5	13,8	68	15,0
61	10,0	58	14,0	52	15,0
63	11,0	36	14,0	17	15,0
49	12,0	4	14,0	54	15,1
66	12,1	57	14,0	30	15,9
41	12,4	12	14,0	20	17,3
9	12,7	14	14,1	31	20,5
8	12,8	40	14,3	55	21,5
23	13,0	35	14,3	16	25,0
32	13,5	10	14,5	1	28,0

Sample F

Number of participants	35	Range	6,1
Number of omitted results	5	Variance	2,0
True value	9,0	Standard deviation	1,4
Mean value	8,7	Relative standard deviation	16,1%
Median value	9,0	Relative error	-2,9%

Analytical results in ascending order:

51	< 14 U	33	8,5	32	9,5
50	5,6	10	8,5	54	9,6
61	6,0	40	8,8	9	9,7
63	6,6	35	8,9	17	9,8
49	6,9	58	8,9	30	10,1
36	7,0	68	9,0	5	10,3
41	7,6	23	9,0	65	10,5
66	7,9	52	9,0	20	11,6
14	8,0	4	9,1	7	11,7
8	8,3	12	9,2	31	15,8
38	8,3	57	9,4	16	18,0
55	8,4 U	28	9,4	1	20,0

U = Omitted result

Table 5.22. Statistics - Nickel, µg/l

Sample E

Number of participants	30	Range	1,5
Number of omitted results	10	Variance	0,1
True value	3,0	Standard deviation	0,4
Mean value	3,0	Relative standard deviation	11,7%
Median value	3,0	Relative error	0,8%

Analytical results in ascending order:

65	U	33	2,8	40	3,2
14	< 4,5 U	8	2,9	55	3,2
41	< 4 U	52	3,0	4	3,4
50	< 3 U	9	3,0	30	3,4
66	< 2 U	5	3,0	54	3,5
7	< 1,5 U	32	3,0	35	3,8
20	2,0 U	68	3,0	17	5,4
63	2,3	58	3,0	16	7,0
38	2,5	10	3,1	28	12,3
12	2,6	57	3,1		
1	2,7	64	3,2 U		

Sample F

Number of participants	30	Range	1,1
Number of omitted results	10	Variance	0,1
True value	2,1	Standard deviation	0,3
Mean value	2,2	Relative standard deviation	14,2%
Median value	2,1	Relative error	3,0%

Analytical results in ascending order:

64	U	32	2,0	57	2,3
14	< 4,5 U	52	2,0	55	2,3
41	< 4 U	16	2,0 U	65	2,5
50	< 3 U	12	2,0	30	2,5
66	< 2 U	68	2,0	4	2,6
20	< 2 U	8	2,0	5	2,8
7	< 1,5 U	33	2,1	54	2,8
38	1,7	35	2,1	17	5,0
63	1,7	58	2,2	28	7,2
1	1,9	40	2,2		
9	2,0	10	2,2		

U = Omitted result

Table 5.23. Statistics - Zinc, µg/l

Sample E

Number of participants	35	Range	6,2
Number of omitted results	6	Variance	2,0
True value	10,2	Standard deviation	1,4
Mean value	10,6	Relative standard deviation	13,4%
Median value	10,2	Relative error	4,1%

Analytical results in ascending order:

65	U	41	10,0	57	12,0
66	7,8	23	10,0	4	12,0
51	8,8	14	10,2	31	12,0
63	8,8	40	10,2	9	12,7
7	9,0	28	10,3	30	13,3
12	9,4	64	10,6	35	14,0
17	9,6	20	10,9	10	17,1
49	9,8	58	11,0	1	18,0
54	9,8	33	11,0	55	19,3
8	9,9	52	11,0	68	20,0
38	10,0	32	12,0	16	20,0
36	10,0	5	12,0	50	29,5

Sample F

Number of participants	35	Range	11,1
Number of omitted results	6	Variance	6,2
True value	15,1	Standard deviation	2,5
Mean value	15,2	Relative standard deviation	16,4%
Median value	15,1	Relative error	0,7%

Analytical results in ascending order:

17	10,0	12	14,5	49	17,2
36	11,0	38	15,0	33	17,6
7	12,0	52	15,0	4	18,0
63	12,1	20	15,1	30	18,9
66	12,1	51	15,2	32	19,0
23	13,0	64	15,8	65	19,3
55	13,8 U	57	16,0	1	20,0
54	13,9	35	16,0	5	21,1
8	14,0	31	16,0	16	24,0
14	14,2	40	16,3	68	32,0
41	14,3	58	16,5	50	36,5
28	14,4	9	16,8	10	41,1

U = Omitted result