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## **Intercomparison 0014:**

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Ca, Mg, Na, K, total-aluminium,  
aluminium - reactive and nonlabile,  
DOC, COD-Mn, Fe, Mn, Cd, Pb, Cu,  
Ni and Zn

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| <p><b>Abstract</b></p> <p>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 <math>\pm 20\%</math>, 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 <math>\pm 0.2</math> 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 <math>\pm 20\%</math> when the concentrations are close to the detection limit of the recommended method.</p> |
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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 0014**

pH, Cond,  $\text{HCO}_3^-$ ,  $\text{NO}_3^- + \text{NO}_2^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{--}$   
 $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , 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*

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# 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  $\pm 20$  %, except for pH and conductivity where the acceptance limits were  $\pm 0,2$  units and  $\pm 10$  %, respectively.

For pH, the accuracy limit was extended from 0,1 to  $\pm 0.2$  units, but still only 57 % of the result pairs were included using this special limit. A total error of  $\pm 0.2$  units for pH measurements seems to be a more reasonable assessment of the accuracy between laboratories, than the target limit of  $\pm 0.1$  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 therefore 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 fourteenth 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 participating 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  $\pm 20\%$  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 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>.

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  $\pm 10\%$ . 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  $\pm 20\%$ , 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 per 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, being 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  $\pm 20\%$ . 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 systematic 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  $\pm 20\%$  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  $\pm 20\%$ . 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  $\pm 20\%$ , 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  $\pm 20\%$ . 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  $\pm 20\%$ . The reported values are given in Table 5.9. Most laboratories used flame atomic absorption spectrometry for this determination. However, in many laboratories the 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 smallest for the results produced with flame atomic absorption. 93% of the result pairs are located within the general target accuracy of  $\pm 20\%$ .

#### **4.10 Potassium**

The potassium results are presented in Figure 10. The great circle is representing the target acceptance limit of  $\pm 20\%$ . 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  $\pm 20\%$ . 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 pyrocatechol 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  $\pm 20\%$ , 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  $\pm 20\%$ .

#### **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  $\pm 20\%$ , 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  $\pm 20\%$ , 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  $\pm 20\%$ , 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  $\pm 20\%$ , 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  $\pm 20\%$ , 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  $\pm 20\%$ , 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  $\pm 20\%$ , 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 values 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  $\pm 0.1$  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  $\pm 0.2$  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<sub>2</sub>-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 included 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  $\pm 10\%$ . 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

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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. Therefore 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).**

|                       |   |  |   |
|-----------------------|---|--|---|
|                       | <b>Total aluminium</b><br>acid digested                                   |  |   |
| Aluminium measurement | <b>Reactive aluminium</b><br>Total monomeric aluminium, no acid digestion |  |   |
|                       | Monomeric aluminium,<br>cation exchange treated                           |  |   |
| Aluminium fraction    | <b>Non-labile monomeric aluminium</b>                                     | Labile monomeric aluminium   | Acid soluble aluminium  |
| Fraction composition  | Monomeric aluminorganic complexes   | Free aluminium, monomeric aluminiumsulfate, Fluoride and hydroxide complexes | Colloidal polymeric aluminium, strong aluminorganic complexes |

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  $\pm 20$  %, 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  $\pm 0.2$  pH units seems to be a reasonable assessment of the accuracy for pH measurements when near neutral water samples - which are not in CO<sub>2</sub> 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

1. Convention on Long-range Transboundary Air Pollution. International Cooperative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes. Manual for Chemical and Biological Monitoring. March 1987, revised september 1996.
2. Youden, W.J.: Graphical Diagnosis of Interlaboratory Test Results. Industrial Quality Control. 1959, pp 15 - 24.
3. Youden, W.J., Steiner, E.H.: Statistical Manual of the Association of Official Analytical Chemists. Statistical Techniques for Collaborative Tests. Arlington, 1975.
4. Hindar, A.: The Effect of Stirring on pH Readings in Solutions of Low and High Ionic Strength Measured with Electrodes of Different Condition. Vatten 1984, 40, pp 312 - 19 (in norwegian).
5. Galloway, J.N., Cosby, B.T., Likens, G.E.: Acid Precipitation: Measurement of pH and Alkalinity. Limnol. Oceanogr. 1979, 24, 1161.
6. Røgeberg, E.J.S., Henriksen, A.: An Automated Method for Fractionation and Determination of Aluminium Species in Fresh-Waters. Vatten 1985, 41, pp 48 - 53.
7. Driscoll, C.T.: A Procedure for the Fractionation of Aqueous Aluminium in Dilute Acidic Waters. Intern. J. Environ. Anal. Chem. 1984, 16, pp 267 - 83.

## Appendix A.

### The participating laboratories

| Identity | Laboratory                                   | City         | Country        |
|----------|--|--------------|----------------|
| 1        | Institute 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, LFTR          | Ljubljana    | Slovenia       |



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|    |  |                 |                |
|----|--|-----------------|----------------|
| 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 Zoologie, Universitat Innsbruck | Innsbruck       | Austria        |
| 71 | University of Helsinki                       | Helsinki        | Finland        |

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## 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  $\mu\text{m}$  membrane filter, and small aliquots 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 $\mu\text{g/l}$       | -        | -         | -        | -         |
| 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, $\mu\text{g/l}$            | 269      | 5,1       | 222      | 7,1       |
| Reactive aluminium $\mu\text{g/l}$    | 185      | 5,5       | 155      | 8,2       |
| Non-labile aluminium, $\mu\text{g/l}$ | 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, $\mu\text{g/l}$            | 332      | 10,8      | 252      | 6,8       |
| Iron, $\mu\text{g/l}$                 | 252      | 7,6       | 274      | 14,3      |
| Manganese, $\mu\text{g/l}$            | 16,3     | 0,6       | 17,3     | 0,6       |
| Cadmium, $\mu\text{g/l}$              | 0,99     | 0,04      | 1,87     | 0,06      |
| Lead, $\mu\text{g/l}$                 | 3,0      | 0,18      | 3,5      | 0,17      |
| Copper, $\mu\text{g/l}$               | 13,8     | 0,4       | 8,7      | 0,6       |
| Nickel, $\mu\text{g/l}$               | 3,1      | 0,30      | 2,2      | 0,35      |
| Zinc, $\mu\text{g/l}$                 | 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 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 - 5.23. 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<br>A | pH<br>B | Cond<br>mS/m, A | Cond<br>mS/m, B | Alk<br>mmol/l, A | Alk<br>mmol/l, B | NO <sub>3</sub> +NO <sub>2</sub><br>µg/l | NO <sub>3</sub> +NO <sub>2</sub><br>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<br>mg/l, A | Cl<br>mg/l, B | SO4<br>mg/l, A | SO4<br>mg/l, B | Ca<br>mg/l, A | Ca<br>mg/l, B | Mg<br>mg/l, A | Mg<br>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<br>mg/l, A | Na<br>mg/l, B | K<br>mg/l, A | K<br>mg/l, B | Al<br>µg/l, C | Al<br>µg/l, D | Al<br>µg/l, E | Al<br>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<br>µg/l, C | Al-R<br>µg/l, D | Al-I<br>µg/l, C | Al-I<br>µg/l, D | DOC<br>mg/l, C | DOC<br>mg/l, D | COD-Mn<br>mg/l, C | COD-Mn<br>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<br>µg/l, E | Fe<br>µg/l, F | Mn<br>µg/l, E | Mn<br>µg/l, F | Pb<br>µg/l, E | Pb<br>µg/l, F | Cd<br>µg/l, E | Cd<br>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<br>µg/l, E | Cu<br>µg/l, F | Ni<br>µg/l, E | Ni<br>µg/l, F | Zn<br>µg/l, E | Zn<br>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 |      | 14   | 3,16 |
|  | 22 | 2,62 |      | 23   | 3,17 |
|  | 49 | 2,72 |      | 65   | 3,18 |
|  | 2  | 2,79 |      | 35   | 3,19 |
|  | 24 | 2,90 |      | 68   | 3,20 |
|  | 8  | 2,91 |      | 1    | 3,20 |
|  | 40 | 2,95 |      | 63   | 3,20 |
|  | 62 | 2,95 |      | 26   | 3,22 |
|  | 10 | 2,96 |      | 44   | 3,25 |
|  | 51 | 2,98 |      | 13   | 3,25 |
|  | 54 | 2,99 |      | 3    | 3,25 |
|  | 67 | 3,00 |      | 34   | 3,26 |
|  | 17 | 3,00 |      | 37   | 3,28 |
|  | 36 | 3,00 |      | 39   | 3,30 |
|  | 55 | 3,00 |      | 56   | 3,30 |
|  | 32 | 3,02 |      | 12   | 3,32 |
|  | 9  | 3,03 |      | 41   | 3,69 |
|  | 7  | 3,04 |      | 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 |      | 64   | 2,16 |
|  | 29 | 1,70 |      | 3    | 2,17 |
|  | 49 | 1,88 |      | 63   | 2,20 |
|  | 61 | 1,89 |      | 16   | 2,20 |
|  | 50 | 1,94 |      | 43   | 2,20 |
|  | 2  | 1,94 |      | 12   | 2,22 |
|  | 8  | 1,95 |      | 6    | 2,22 |
|  | 7  | 1,97 |      | 44   | 2,25 |
|  | 10 | 2,00 |      | 57   | 2,26 |
|  | 55 | 2,00 |      | 13   | 2,27 |
|  | 24 | 2,00 |      | 34   | 2,27 |
|  | 36 | 2,00 |      | 30   | 2,28 |
|  | 40 | 2,00 |      | 47   | 2,30 |
|  | 32 | 2,01 |      | 37   | 2,33 |
|  | 38 | 2,01 |      | 56   | 2,40 |
|  | 66 | 2,05 |      | 39   | 2,40 |
|  | 31 | 2,06 |      | 1    | 2,50 |
|  | 62 | 2,06 |      | 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