

Convention on Long-range Transboundary Air Pollution

International Cooperative Programme on Assessment and
Monitoring of Acidification of Rivers and Lakes

ICP-WATERS REPORT



51/1999

Intercomparison 9913:

pH, K_{25} , HCO_3 , $NO_3 + NO_2$, Cl, SO_4 ,
Ca, Mg, Na, K, total aluminium,
aluminium - reactive and nonlabile,
TOC and COD-Mn

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| <p>Abstract</p> <p>57 laboratories in 24 countries participated in intercomparison 9913. Two sample sets were used, one for the determination of major ions and one for organic matter and aluminium fractions. Based on the general target accuracy of $\pm 20\%$, 78 % of the results were acceptable. More than 80 % of the result pairs were acceptable for conductivity, chloride, sulfate, magnesium, sodium, and dissolved organic carbon. For pH only 57 % of the result pairs were acceptable in relation to the extended target accuracy of ± 0.2 units. For three analytical variables it was decided not to evaluate the reported results, reactive and non-labile aluminium because of the great spread between the results from the few participants, and nitrate + nitrite because of the instability of sample A. Normalization of the methods is necessary to improve the comparability for pH and aluminium fractions. Manual methods are generally less sensitive compared to instrumental methods, and are not always suitable for acid rain monitoring.</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 9913

pH , K_{25} , HCO_3^- , $NO_3^-+NO_2^-$, Cl^- , SO_4^{--}
 Ca^{++} , Mg^{++} , Na^+ , K^+ ,
Al, Al-R, Al-I, DOC and Cod-Mn

Prepared by the Programme Centre
Norwegian Institute for Water Research
Oslo, September 1999

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 13th intercomparison of chemical analysis.

Oslo, September 1999

Håvard Hovind

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Summary

Intercomparison 9913 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 May-June 1999, and included the determination of major ions in natural water samples. The participants were asked to determine pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, total aluminium, reactive and non-labile aluminium, dissolved organic carbon and chemical oxygen demand (COD-Mn).

Two sample sets were prepared for this intercomparison, one for the determination of the major ions, and the other for aluminium fractions and unspecific organic matter. 57 laboratories determined all, or some of the analytical variables in the samples.

87 laboratories were invited to participate in this intercomparison, and the samples were sent to 65 laboratories who accepted to participate. 57 laboratories submitted results to the Programme Centre before the final statistical treatment of the data. 24 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. For two analytical variables - reactive and non-labile aluminium - this definition of the "true value" is not acceptable, because of the great spread between the results from the few laboratories determining this variable. It was therefore decided not to evaluate the reported results for these variables. The content of nitrate + nitrite proved to be unstable in sample A, therefore this variable was excluded from the evaluation too. Excluding these variables from the evaluation, 78 % of the result pairs were regarded as acceptable, the target limit being the median value ± 20 %, except for pH and conductivity where the acceptance limits were $\pm 0,02$ units and ± 10 %, respectively.

For pH the accuracy limit was extended to ± 0.2 units, and only 57 % of the result pairs were included by this special limit. A total error of ± 0.2 units for pH measurements seems to be a more reasonable assessment of the accuracy between laboratories, than the target limit of ± 0.1 units. The reason for the great spread of pH results is mainly due to the fact that different measurement routines are used by the participants, leading to systematically different results. To establish a "true value" based on the median value for **all** the reported results for pH, when the methods are different, is questionable, and on the next meeting it should be discussed whether a certain "true value" for **each method** would be more informative.

The best results were reported for conductivity, chloride, sulfate, magnesium, sodium, and dissolved organic carbon, as more than 80 % of the result pairs were acceptable. Rather poor comparability was observed for pH and aluminium species. To improve the comparability of the results for these variables, it is necessary to normalize the analytical method and the determination technique used.

1. Introduction

As stated in "Manual for Chemical and Biological Monitoring" (1), between-laboratory quality control is necessary in a multilaboratory programme to assure clear identification and control of the bias between analyses carried out by individual participants of the Programme. Such biases may arise 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 thirteenth intercomparison test, called 9913, included the determination of the major components and some other ions in natural water samples: pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, total aluminium, reactive and non-labile aluminium, dissolved organic carbon and chemical oxygen demand (COD-Mn).

2. Accomplishment of the intercalibration

The preparation of the sample solutions is described in Appendix 2. The results of the control analyses performed at the Programme Centre are also summarized in the same place. On the Task Force meeting in 1998 it was decided that two sample sets should be included in this intercomparison, one sample pair for the determination of the major ions, and one sample pair for aluminium fractions and unspecific organic compounds.

The samples were mailed from the Programme Centre on May 20, 1999. 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.

3. Results

87 laboratories were invited to participate in the intercomparison, and 65 laboratories accepted and received samples. The 57 laboratories who submitted results to the Programme Centre, are representing 24 countries. It was a problem that some of the laboratories submitted the results several weeks after the deadline, and a reminder letter had to be mailed to some of the participants. A survey of the participants and their code numbers are listed in Appendix 1.

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

The purpose of this test is to evaluate the comparability of the analytical results produced by different laboratories. The real "true value" is not known exactly for the natural samples used in this intercomparison. Therefore, we selected the median value, determined from the analytical results submitted by the participating laboratories, as the "true value" for each analytical variable. The median value is considered to be an acceptable estimate of the true value for this purpose, as long as most of the participants are using essentially the same analytical method. 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 - 15, 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 9913 is presented in Table 1. The individual results of the participants are presented in Table 4 in the Appendix, sorted in order of increasing identification number. More extensive statistical informations are presented in the Tables 5.1 - 5.15.

3.1 pH

The reported results for pH are graphically presented in Figure 1, where the radius of the 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. 54 laboratories reported results for pH, of this group 19 indicated that they read the pH value during stirring the solution. The stirring are normally lowering the observed pH result, however, as shown in Table 1, there is no significant difference between the results determined in a quiescent solution, and when determined during stirring the solution in this intercomparison.

Figure 1 shows that the reported results are spread out along the 45° line, indicating that the results are influenced by systematic effects. Two laboratories that equilibrated the solutions by bubbling with air containing 350 ppm CO_2 before reading the pH value, reported far higher results than the other laboratories. These results should not be evaluated by comparing them to the mean value of all the reported results, because this method is giving systematically different results. The information given by the pH measured after equilibrating the solution, is quite different from the two other methods where pH is read directly or after stirring.

The CO_2 concentration of samples in the circumneutral range may be above the atmospheric equilibrium. This may lead to systematic errors, the magnitude will vary between the

(The text continues on page 26)

Table 1. Statistical summary of intercomparison 9913

| Analytical variable and method | Sample pair | True value | | Total number | Number excluded | Median | | Mean | | St.dev. | | Rel.st.dev. % | | Rel. error % | |
|-----------------------------------|----------------|------------|-------|-----------------|--------------------|--------|-------|----------|----------|---------|-------|---------------|------|--------------|-------|
| | | 1 | 2 | | | 1 | 2 | Sample 1 | Sample 2 | 1 | 2 | 1 | 2 | | |
| pH | AB | 6,48 | 6,95 | 54 | 1 | 6,48 | 6,95 | 6,47 | 6,93 | 0,18 | 0,19 | 2,9 | 2,7 | -0,1 | -0,2 |
| | | 6,44 | 6,92 | 33 | 1 | 6,44 | 6,92 | 6,45 | 6,90 | 0,17 | 0,19 | 2,6 | 2,7 | -0,5 | -0,8 |
| | | 6,50 | 6,98 | 19 | 0 | 6,50 | 6,98 | 6,47 | 6,96 | 0,16 | 0,15 | 2,4 | 2,1 | -0,2 | 0,1 |
| | | | | 2 | 0 | | | 6,92 | 7,33 | | | | | 6,8 | 5,5 |
| Conductivity | AB | 3,00 | 4,80 | 53 | 4 | 3,00 | 4,80 | 2,99 | 4,76 | 0,13 | 0,21 | 4,3 | 4,4 | -0,2 | -0,8 |
| Alkalinity | AB | 0,085 | 0,170 | 48 | 12 | 0,085 | 0,170 | 0,088 | 0,171 | 0,014 | 0,016 | 16,4 | 9,4 | 3,0 | 0,8 |
| Gran plot titration | | | | 17 | 3 | 0,088 | 0,170 | 0,087 | 0,167 | 0,008 | 0,008 | 9,1 | 4,6 | 2,8 | -1,7 |
| End point titration | | | | 9 | 2 | 0,080 | 0,165 | 0,086 | 0,171 | 0,016 | 0,019 | 18,6 | 11,4 | 0,9 | 0,8 |
| End point 5.6 | | | | 1 | 0 | | | 0,072 | 0,161 | | | | | -15,3 | -5,3 |
| End point 5.4 | | | | 2 | 0 | | | 0,076 | 0,175 | | | | | -11,2 | 2,9 |
| End point 4.5 | | | | 13 | 4 | 0,100 | 0,180 | 0,098 | 0,185 | 0,018 | 0,017 | 18,9 | 9,4 | 15,0 | 8,8 |
| Not documented | | | | 6 | 3 | 0,074 | 0,158 | 0,075 | 0,152 | 0,007 | 0,013 | 9,4 | 8,4 | -11,3 | -10,8 |
| Nitrate + nitrite-nitrogen | AB | 120 | 182 | 52 | 17 | 118 | 182 | 119 | 179 | 35 | 18 | 29,4 | 10,3 | -0,7 | -1,7 |
| Autoanalyzer | | | | 17 | 4 | 128 | 185 | 126 | 182 | 29 | 13 | 22,8 | 7,1 | 5,1 | -0,2 |
| Photometry | | | | 9 | 5 | 132 | 183 | 128 | 185 | 56 | 14 | 43,7 | 7,6 | 6,9 | 1,4 |
| Ion chromatography | | | | 24 | 7 | 110 | 180 | 113 | 178 | 35 | 21 | 31,2 | 11,9 | -5,5 | -2,3 |
| Hydrazine | | | | 1 | 1 | | | 203 | 213 | | | | | 69,2 | 17,0 |
| Cap. electrophoresis | | | | 1 | 0 | | | 90 | 138 | | | | | -25,0 | -24,2 |
| Chloride | AB | 2,03 | 3,58 | 54 | 2 | 2,03 | 3,58 | 2,05 | 3,55 | 0,19 | 0,22 | 9,1 | 6,3 | 0,8 | -0,7 |
| Ion chromatography | | | | 41 | 1 | 2,01 | 3,56 | 2,02 | 3,52 | 0,15 | 0,19 | 7,3 | 5,4 | -0,5 | -1,7 |
| Autoanalyzer | | | | 3 | 0 | 2,18 | 3,69 | 2,17 | 3,73 | 0,18 | 0,12 | 8,3 | 3,2 | 6,7 | 4,3 |
| Argentometry | | | | 3 | 0 | 2,20 | 3,95 | 2,29 | 3,92 | 0,19 | 0,20 | 8,1 | 5,2 | 12,6 | 9,4 |
| Manual, Hg | | | | 5 | 1 | 2,19 | 3,77 | 2,16 | 3,63 | 0,29 | 0,36 | 13,2 | 10,0 | 6,4 | 1,3 |
| Cap. electrophoresis | | | | 1 | 0 | | | 1,56 | 3,27 | | | | | -23,1 | -8,6 |
| Potentiometry | | | | 1 | 0 | | | 2,04 | 3,43 | | | | | 0,5 | -4,2 |

| Analytical variable and method | Sample pair | True value | | Total number | Number excluded | Median | | Mean | | St.dev. | | Mean | | St.dev. | | Rel.st.dev. % | | Rel. error % | |
|-----------------------------------|----------------|------------|------|-----------------|--------------------|--------|------|----------|----------|----------|----------|------|------|---------|-------|---------------|---|--------------|--|
| | | 1 | 2 | | | 1 | 2 | Sample 1 | Sample 2 | Sample 1 | Sample 2 | 1 | 2 | 1 | 2 | 1 | 2 | | |
| Sulfate | AB | 4,00 | 5,33 | 52 | 3 | 4,00 | 5,33 | 3,95 | 0,30 | 5,24 | 0,40 | 7,6 | 7,7 | -1,3 | -1,7 | | | | |
| Ion chromatography | | | | 41 | 1 | 4,01 | 5,34 | 3,96 | 0,21 | 5,26 | 0,26 | 5,2 | 5,0 | -1,0 | -1,3 | | | | |
| Photometry | | | | 4 | 2 | | | 3,73 | | 4,93 | | | | -6,9 | -7,6 | | | | |
| Nephelometry | | | | 5 | 0 | 4,20 | 5,60 | 3,97 | 0,75 | 5,22 | 1,07 | 18,8 | 20,5 | -0,7 | -2,1 | | | | |
| ICP | | | | 1 | 0 | | | 4,20 | | 5,23 | | | | 5,0 | -1,9 | | | | |
| Cap. electrophoresis | | | | 1 | 0 | | | 3,56 | | 5,02 | | | | -11,0 | -5,8 | | | | |
| Calcium | AB | 2,75 | 3,55 | 55 | 4 | 2,75 | 3,55 | 2,77 | 0,26 | 3,60 | 0,37 | 9,5 | 10,2 | 0,6 | 1,4 | | | | |
| FAAS | | | | 25 | 3 | 2,68 | 3,49 | 2,67 | 0,26 | 3,45 | 0,31 | 9,7 | 9,0 | -3,0 | -2,8 | | | | |
| ICP | | | | 12 | 0 | 2,83 | 3,75 | 2,87 | 0,14 | 3,74 | 0,21 | 4,9 | 5,6 | 4,2 | 5,4 | | | | |
| EDTA | | | | 4 | 1 | 2,81 | 4,01 | 2,85 | 0,18 | 3,66 | 0,75 | 6,3 | 20,5 | 3,8 | 3,2 | | | | |
| Ion chromatography | | | | 13 | 0 | 2,77 | 3,57 | 2,80 | 0,33 | 3,70 | 0,43 | 11,8 | 11,5 | 1,8 | 4,4 | | | | |
| ICP-MS | | | | 1 | 0 | | | 3,00 | | 3,60 | | | | 9,1 | 1,4 | | | | |
| Magnesium | AB | 0,47 | 0,86 | 55 | 5 | 0,47 | 0,86 | 0,47 | 0,05 | 0,87 | 0,08 | 10,7 | 9,1 | 0,9 | 1,5 | | | | |
| FAAS | | | | 25 | 1 | 0,46 | 0,85 | 0,46 | 0,05 | 0,85 | 0,05 | 10,1 | 5,9 | -2,3 | -0,8 | | | | |
| ICP | | | | 12 | 0 | 0,48 | 0,90 | 0,49 | 0,05 | 0,91 | 0,06 | 10,5 | 7,0 | 5,2 | 6,1 | | | | |
| EDTA | | | | 4 | 3 | | | 0,61 | | 0,61 | | | | 29,8 | -29,1 | | | | |
| Ion chromatography | | | | 13 | 0 | 0,48 | 0,87 | 0,47 | 0,04 | 0,89 | 0,09 | 8,2 | 10,3 | 0,7 | 3,8 | | | | |
| ICP-MS | | | | 1 | 1 | | | 1,00 | | 1,00 | | | | 112,8 | 16,3 | | | | |
| Sodium | AB | 1,73 | 2,84 | 53 | 2 | 1,73 | 2,84 | 1,74 | 0,12 | 2,85 | 0,20 | 7,1 | 7,1 | 0,5 | 0,3 | | | | |
| FAAS | | | | 18 | 2 | 1,72 | 2,86 | 1,71 | 0,05 | 2,84 | 0,12 | 3,2 | 4,2 | -1,1 | -0,1 | | | | |
| ICP | | | | 10 | 0 | 1,70 | 2,78 | 1,70 | 0,14 | 2,78 | 0,26 | 8,5 | 9,4 | -2,0 | -2,3 | | | | |
| AES | | | | 10 | 0 | 1,78 | 2,98 | 1,80 | 0,16 | 2,94 | 0,27 | 9,1 | 9,1 | 4,1 | 3,3 | | | | |
| Ion chromatography | | | | 14 | 0 | 1,75 | 2,83 | 1,76 | 0,13 | 2,86 | 0,19 | 7,4 | 6,5 | 1,4 | 0,5 | | | | |
| ICP-MS | | | | 1 | 0 | | | 1,80 | | 2,80 | | | | 4,0 | -1,4 | | | | |
| Potassium | AB | 0,36 | 0,37 | 53 | 6 | 0,36 | 0,37 | 0,36 | 0,03 | 0,37 | 0,03 | 8,9 | 9,4 | -0,2 | -0,6 | | | | |
| FAAS | | | | 19 | 0 | 0,37 | 0,37 | 0,37 | 0,02 | 0,36 | 0,02 | 5,2 | 5,9 | 1,4 | -1,6 | | | | |
| ICP | | | | 9 | 2 | 0,36 | 0,37 | 0,35 | 0,05 | 0,35 | 0,05 | 13,7 | 14,7 | -1,9 | -4,5 | | | | |
| AES | | | | 10 | 2 | 0,35 | 0,36 | 0,34 | 0,02 | 0,35 | 0,03 | 6,1 | 7,4 | -4,7 | -4,7 | | | | |
| Ion chromatography | | | | 14 | 2 | 0,36 | 0,38 | 0,36 | 0,04 | 0,39 | 0,04 | 11,3 | 9,8 | 0,3 | 5,2 | | | | |
| ICP-MS | | | | 1 | 0 | | | 0,40 | | 0,40 | | | | 11,1 | 8,1 | | | | |

| Analytical variable and method | Sample pair | True value | | Total number | Number excluded | Median | | Mean | | St.dev. | | Rel.st.dev. % | | Rel. error % | |
|--|----------------|------------|------|-----------------|--------------------|--------|------|----------|----------|---------|------|---------------|------|--------------|------|
| | | 1 | 2 | | | 1 | 2 | Sample 1 | Sample 2 | 1 | 2 | 1 | 2 | | |
| Aluminium GFAAS ICP ICP-MS Photometry | CD | 87 | 148 | 22 | 1 | 87 | 148 | 86 | 145 | 17 | 22 | 19,8 | 15,1 | -0,8 | -1,9 |
| | | | | 7 | 0 | 89 | 146 | 88 | 143 | 20 | 27 | 23,1 | 18,6 | 1,0 | -3,3 |
| | | | | 6 | 0 | 85 | 140 | 88 | 144 | 21 | 28 | 23,4 | 19,3 | 1,5 | -3,0 |
| | | | | 3 | 0 | 83 | 149 | 85 | 149 | 4 | 1 | 5,0 | 0,7 | -2,1 | 0,7 |
| | | | | 6 | 1 | 89 | 156 | 82 | 148 | 16 | 18 | 19,6 | 12,5 | -5,3 | -0,3 |
| Aluminium, reactive | CD | 31 | 44 | 12 | 8 | 31 | 44 | 30 | 45 | 5 | 10 | 16,0 | 23,3 | -4,4 | 1,5 |
| Aluminium, nonlabile | CD | 49 | 95 | 10 | 4 | 49 | 95 | 51 | 96 | 7 | 9 | 14,2 | 9,0 | 4,1 | 1,2 |
| Dissolved organic carbon Combustion UV/S2O8 Phenolphthalein | CD | 3,79 | 3,69 | 23 | 1 | 3,79 | 3,69 | 3,79 | 3,76 | 0,39 | 0,42 | 10,4 | 11,2 | -0,1 | 1,8 |
| | | | | 14 | 0 | 3,71 | 3,61 | 3,77 | 3,75 | 0,43 | 0,43 | 11,3 | 11,4 | -0,5 | 1,6 |
| | | | | 4 | 0 | 3,62 | 3,62 | 3,64 | 3,58 | 0,18 | 0,20 | 4,9 | 5,6 | -3,9 | -3,0 |
| | | | | 5 | 1 | 3,99 | 3,94 | 4,00 | 3,97 | 0,43 | 0,55 | 10,7 | 13,7 | 5,4 | 7,6 |
| Chemical oxygen demand | CD | 4,39 | 4,30 | 13 | 0 | 4,39 | 4,30 | 4,31 | 4,12 | 0,73 | 0,63 | 17,0 | 15,3 | -1,8 | -4,2 |

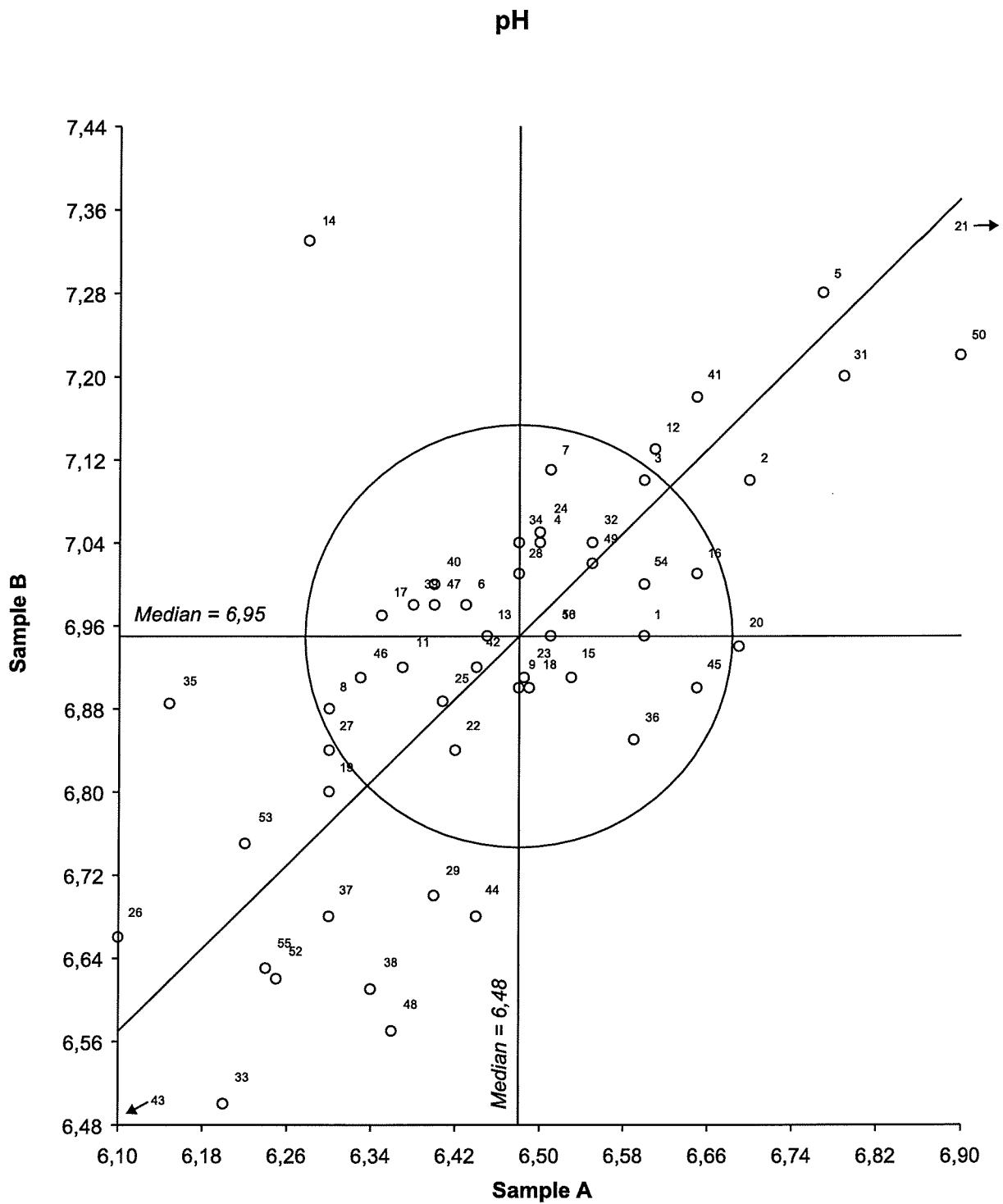


Figure 1. Youden diagramme for pH, Sample pair AB
Acceptance limit is 0,2 pH units

Conductivity

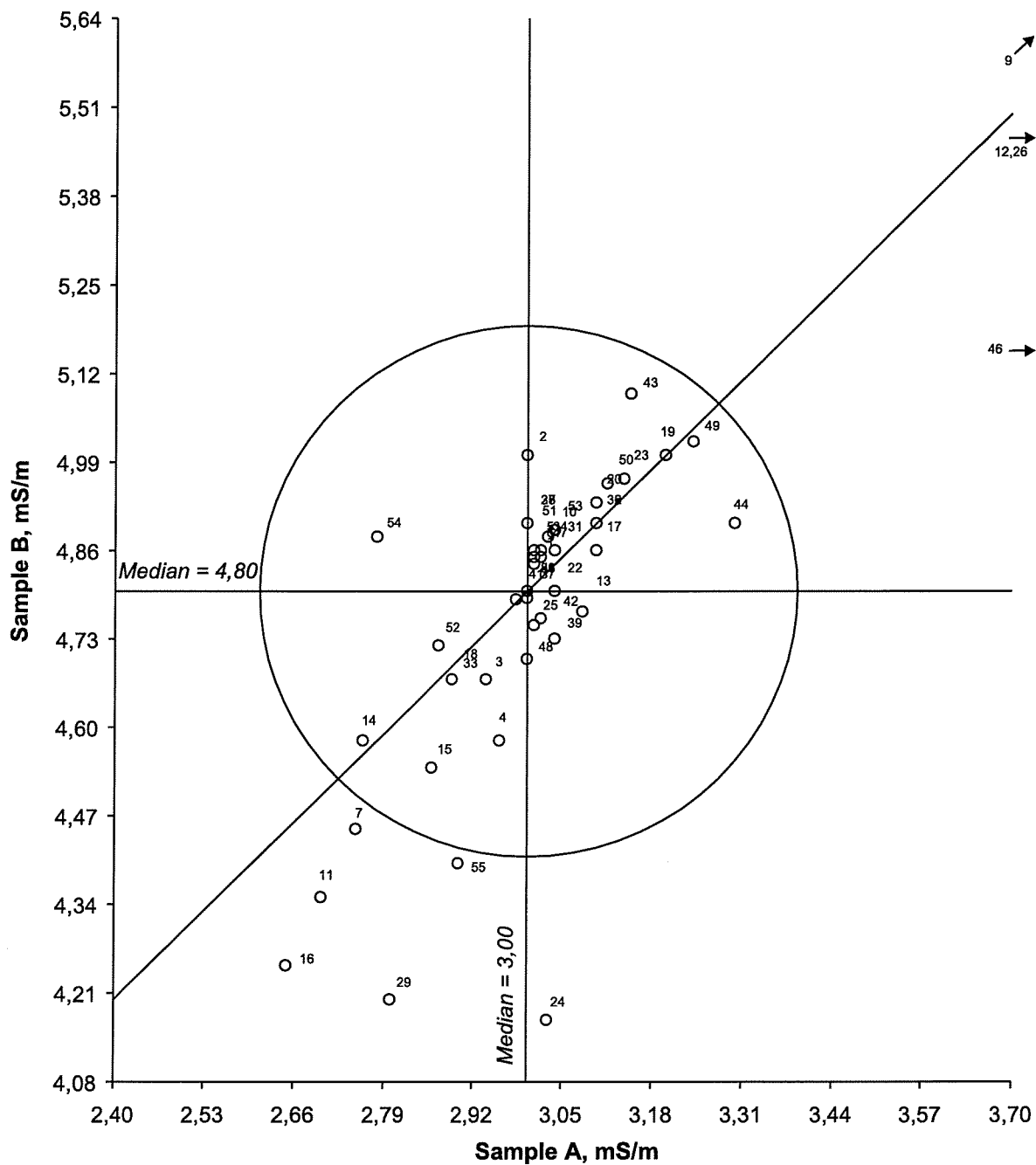


Figure 2. Youden diagram for conductivity, Sample pair AB
Acceptance limit is 10 %

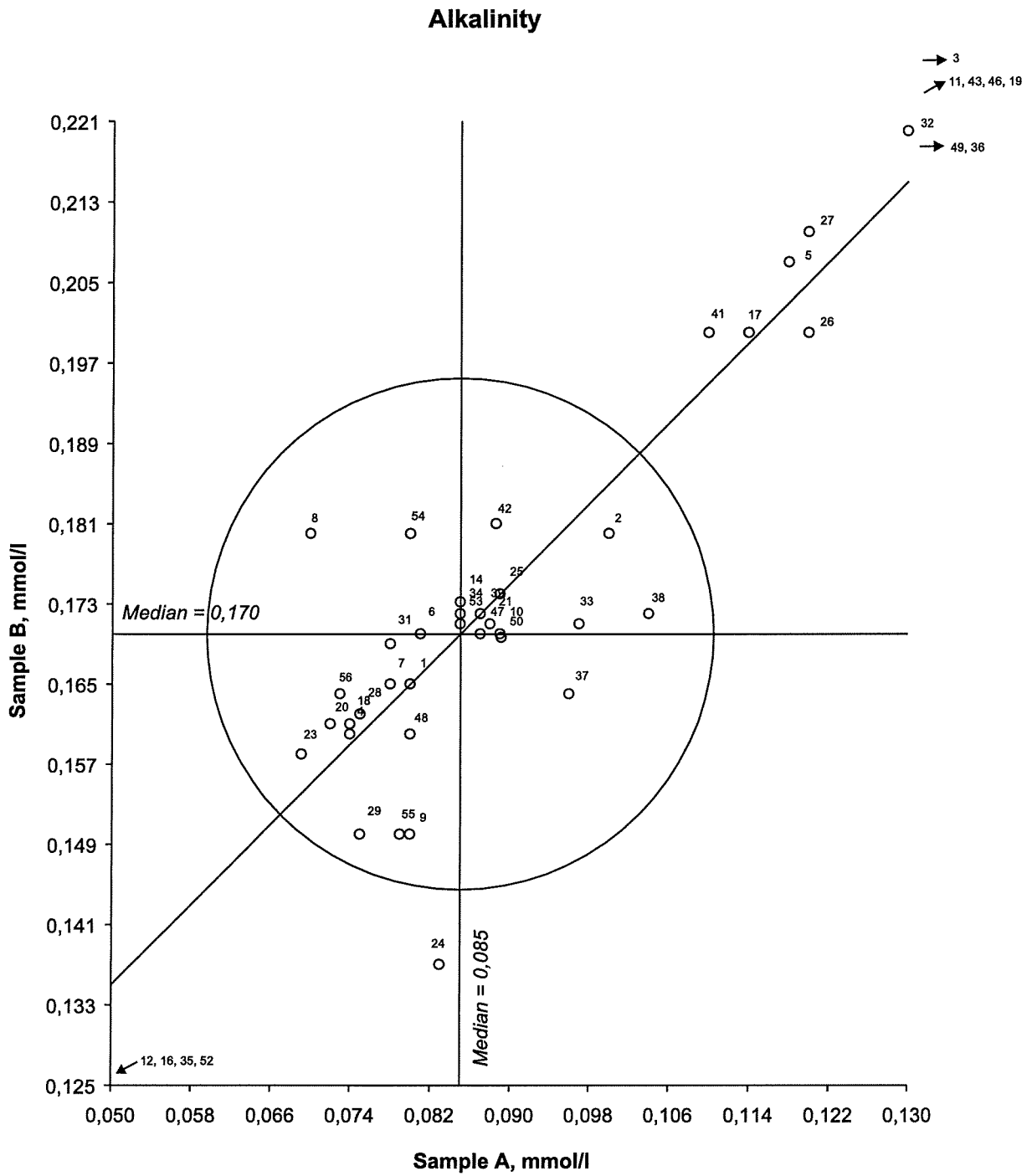


Figure 3. Youden diagram for alkalinity, Sample pair AB
Acceptance limit is 20 %

Nitrate + nitrite-nitrogen

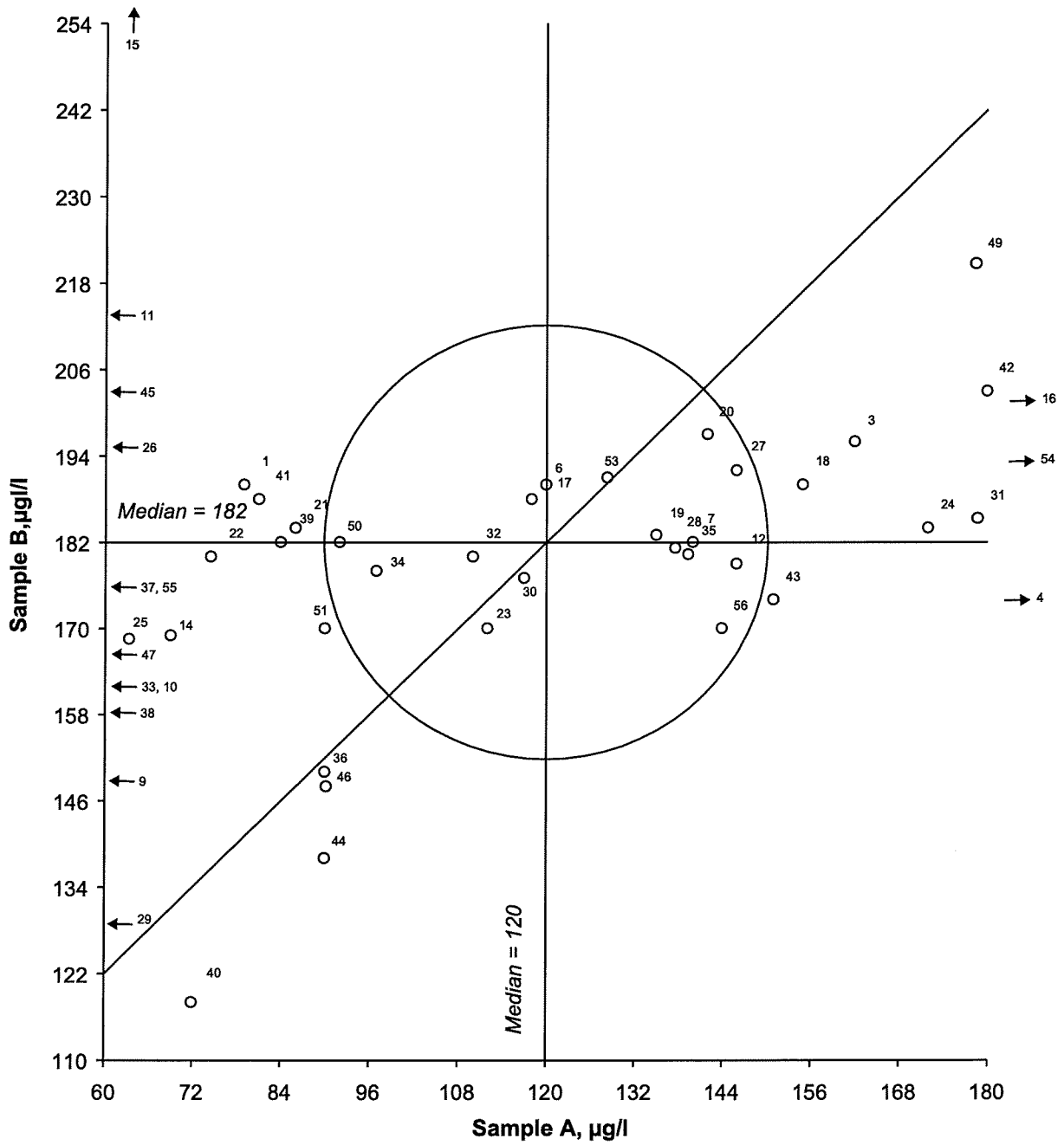


Figure 4. Youden diagramme for nitrate + nitrite-nitrogen, Sample pair AB
Acceptance limit is 20 %

Chloride

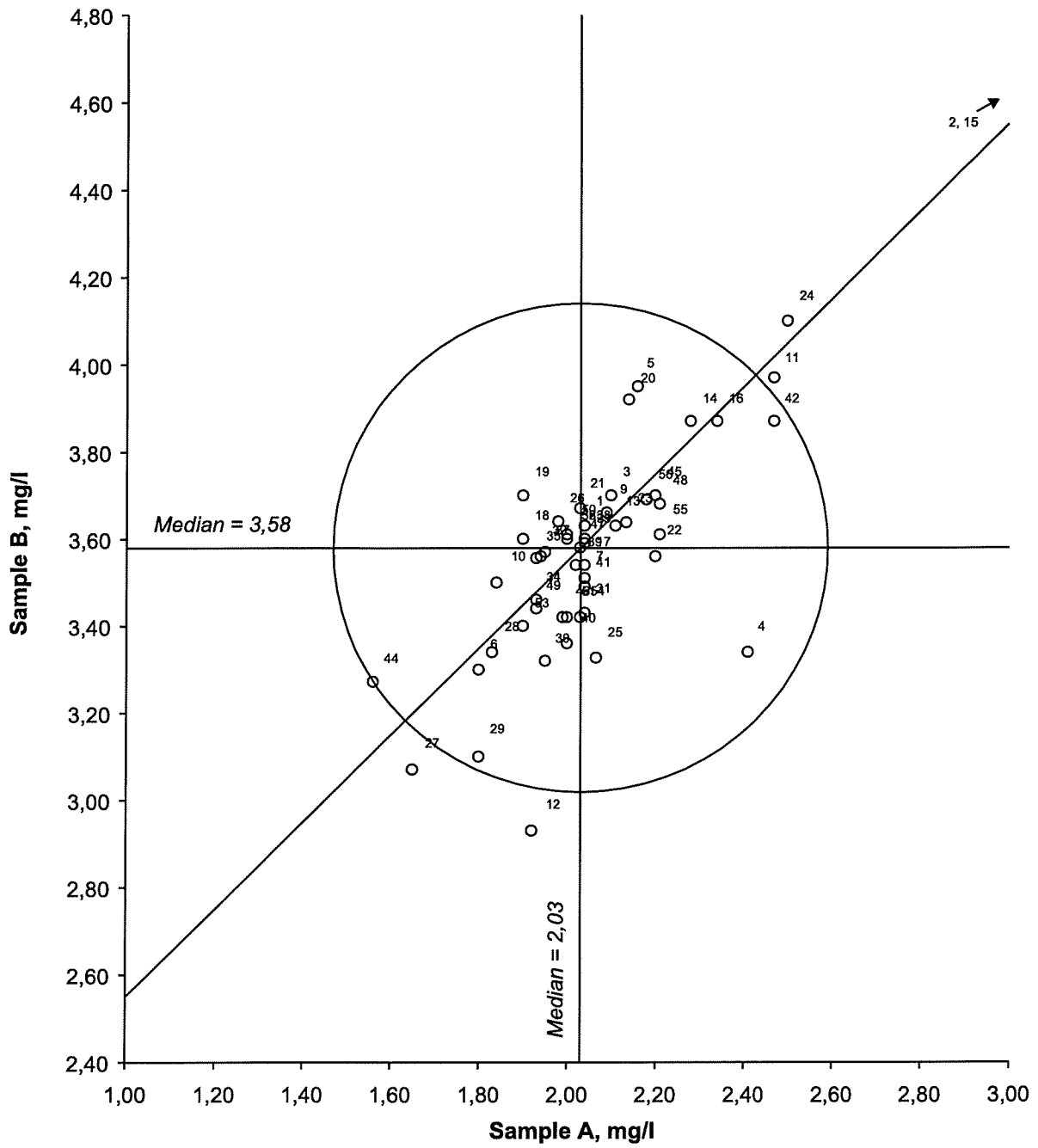


Figure 5. Youden diagramme for chloride, Sample pair AB
Acceptance limit is 20 %

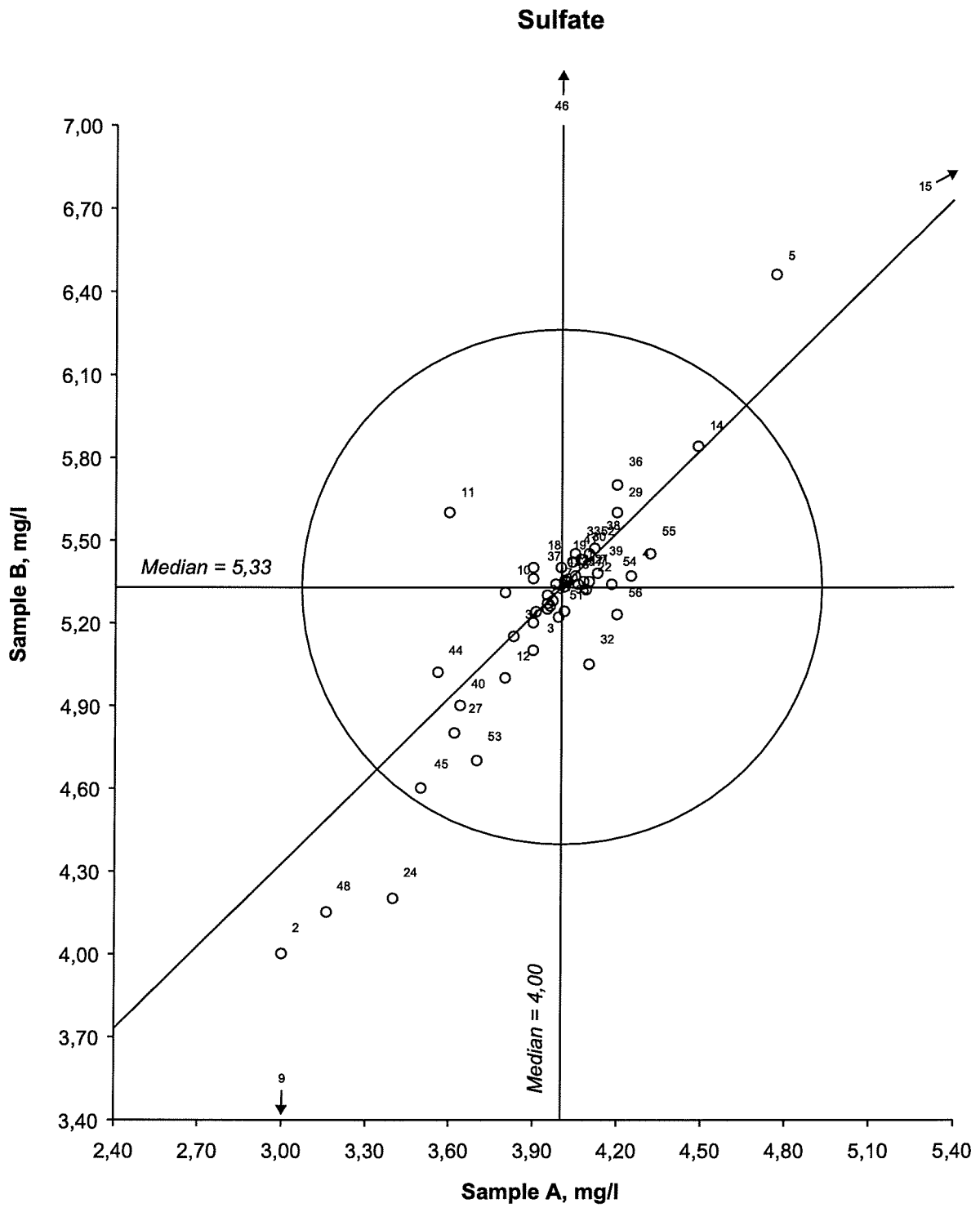


Figure 6. Youden diagramme for sulfate, Sample pair AB
Acceptance limit is 20 %

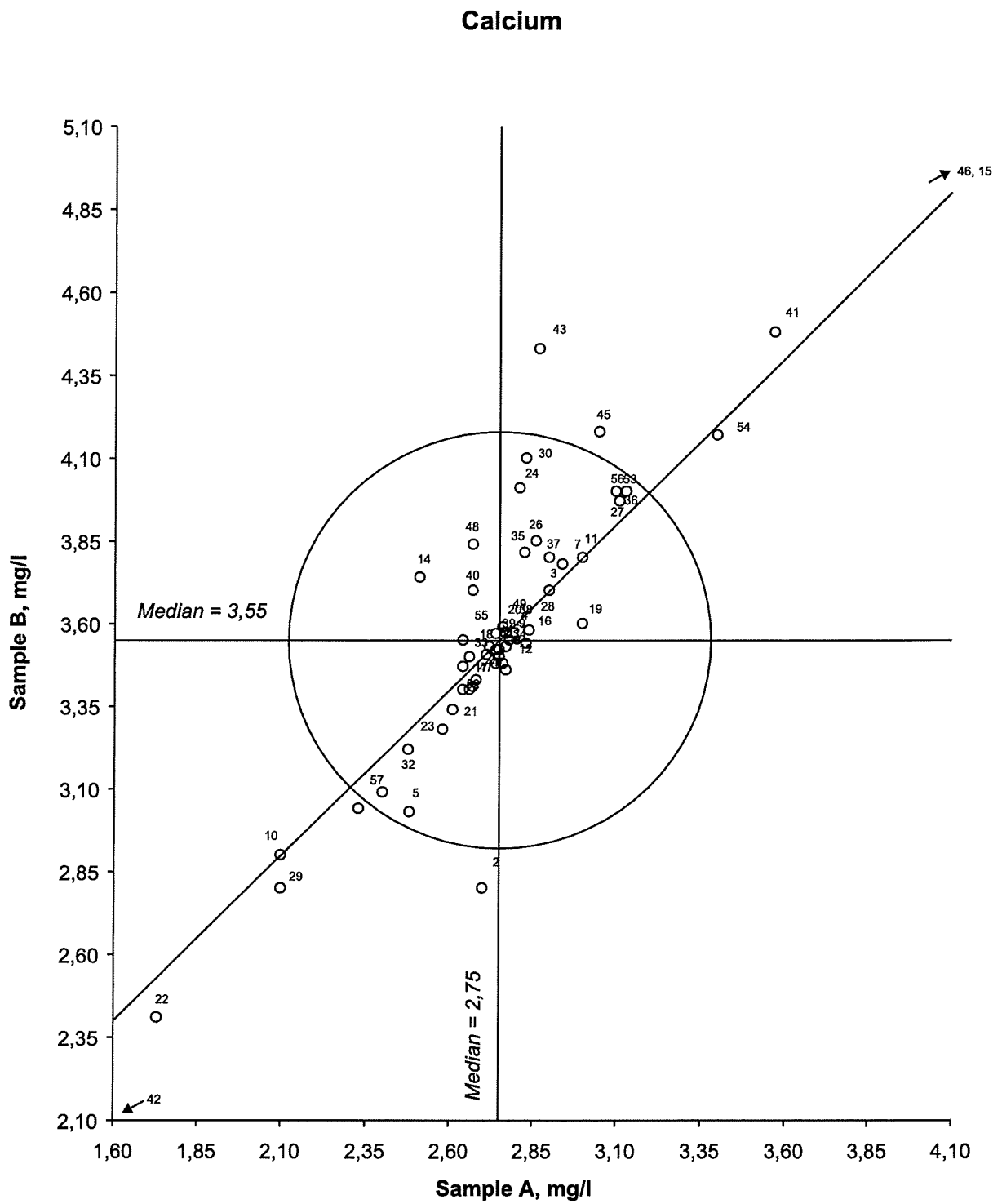


Figure 7. Youden diagramme for calcium, Sample pair AB
Acceptance limit is 20 %

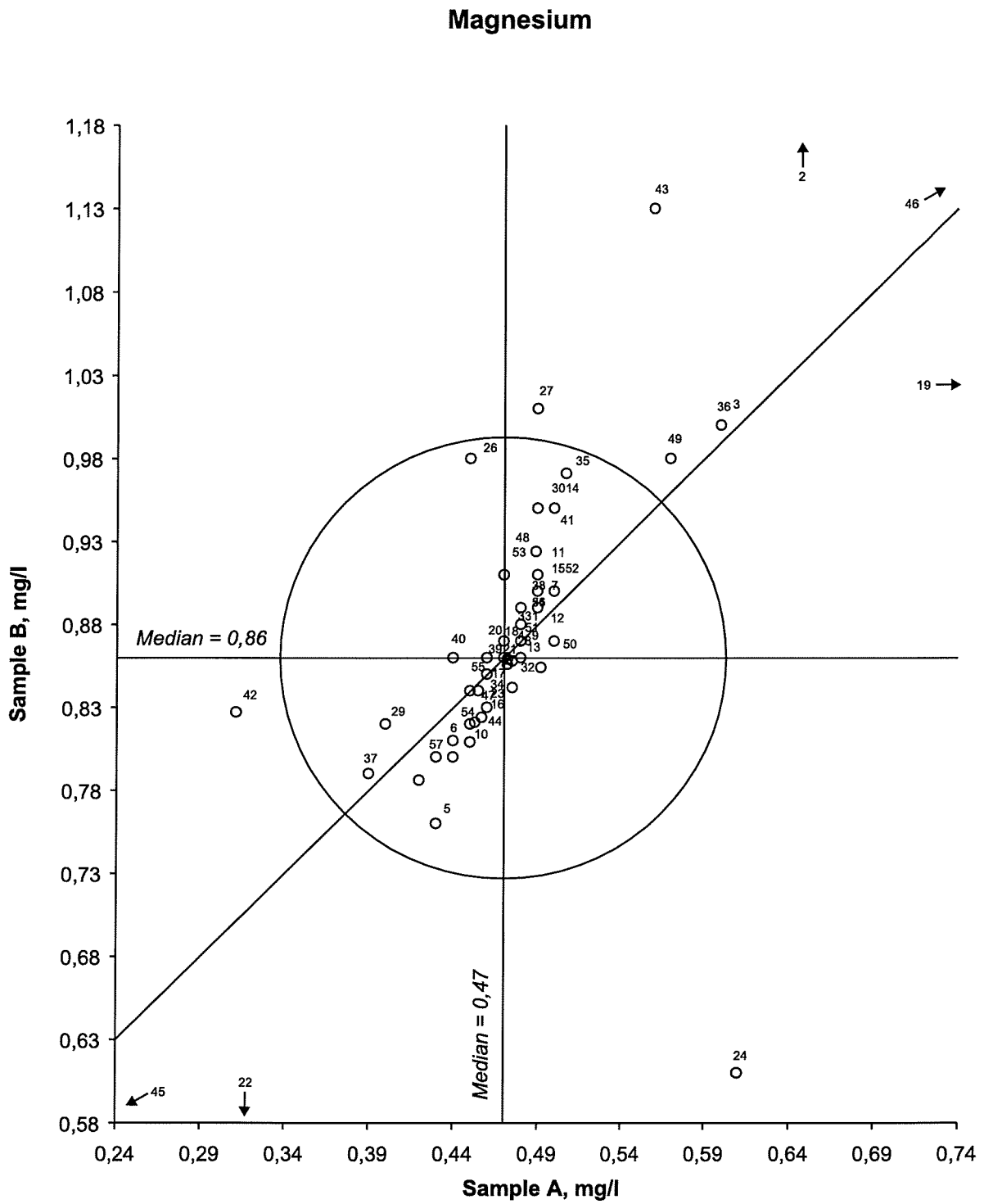


Figure 8. Youden diagramme for magnesium, Sample pair AB
Acceptance limit is 20 %

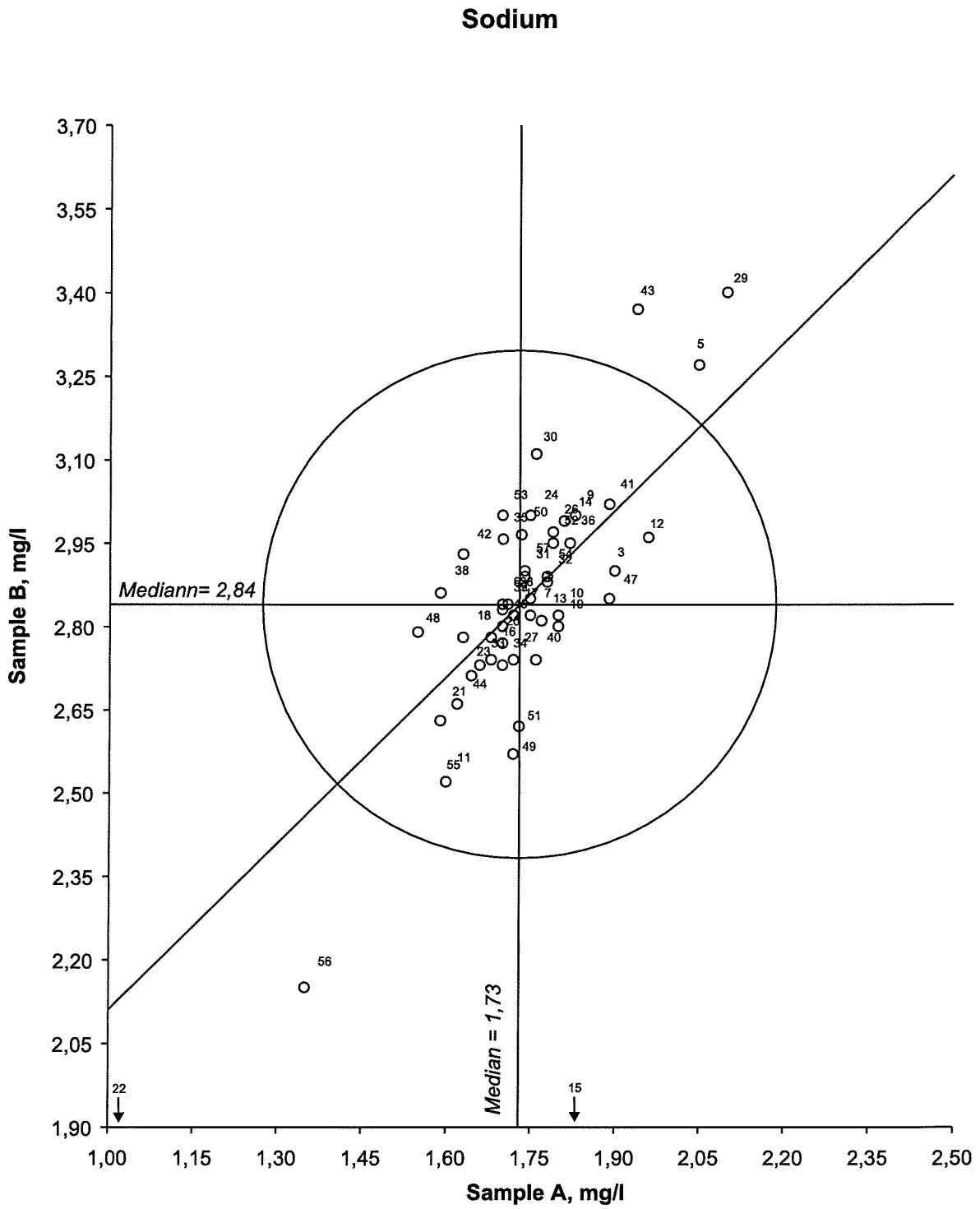
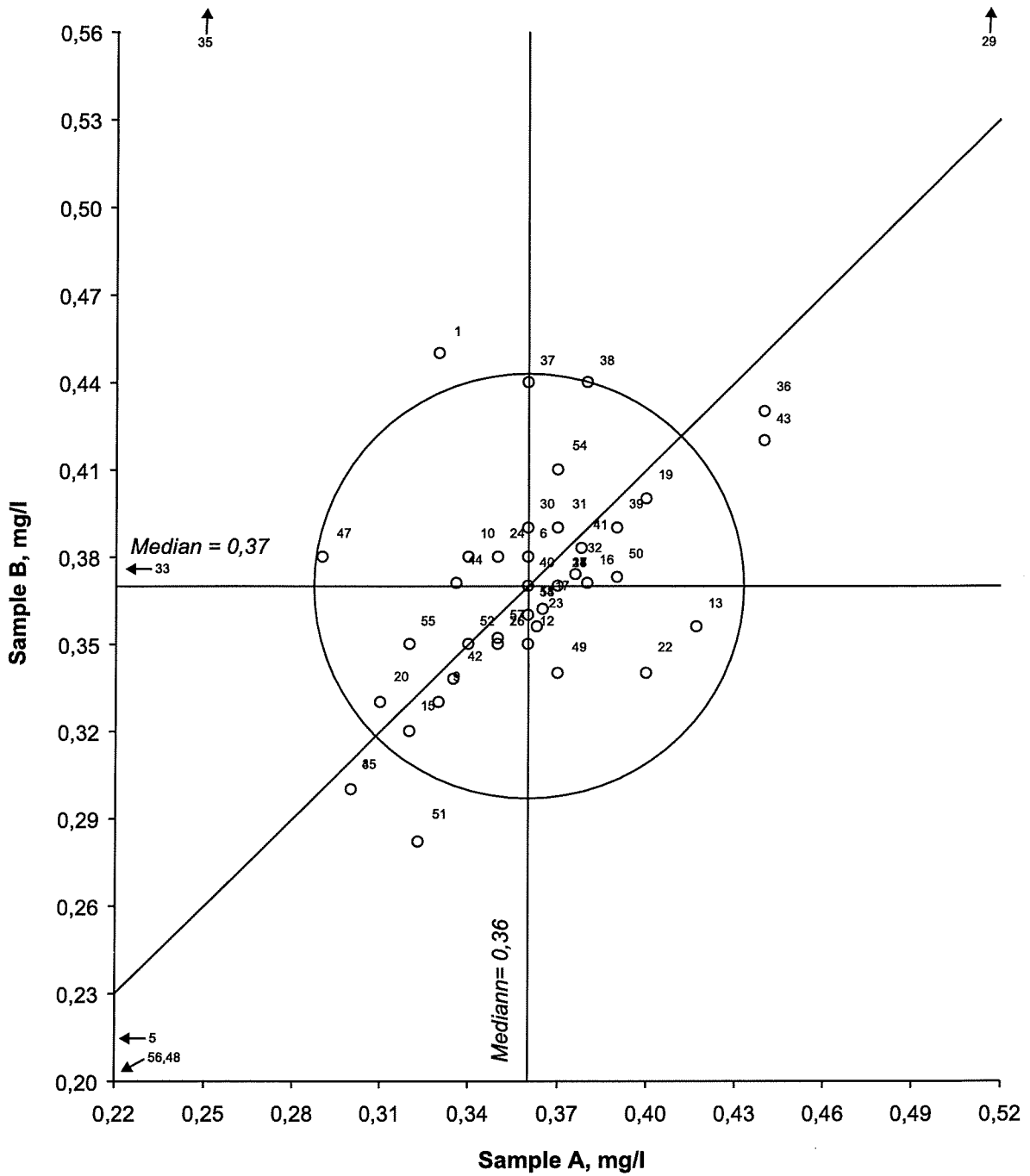


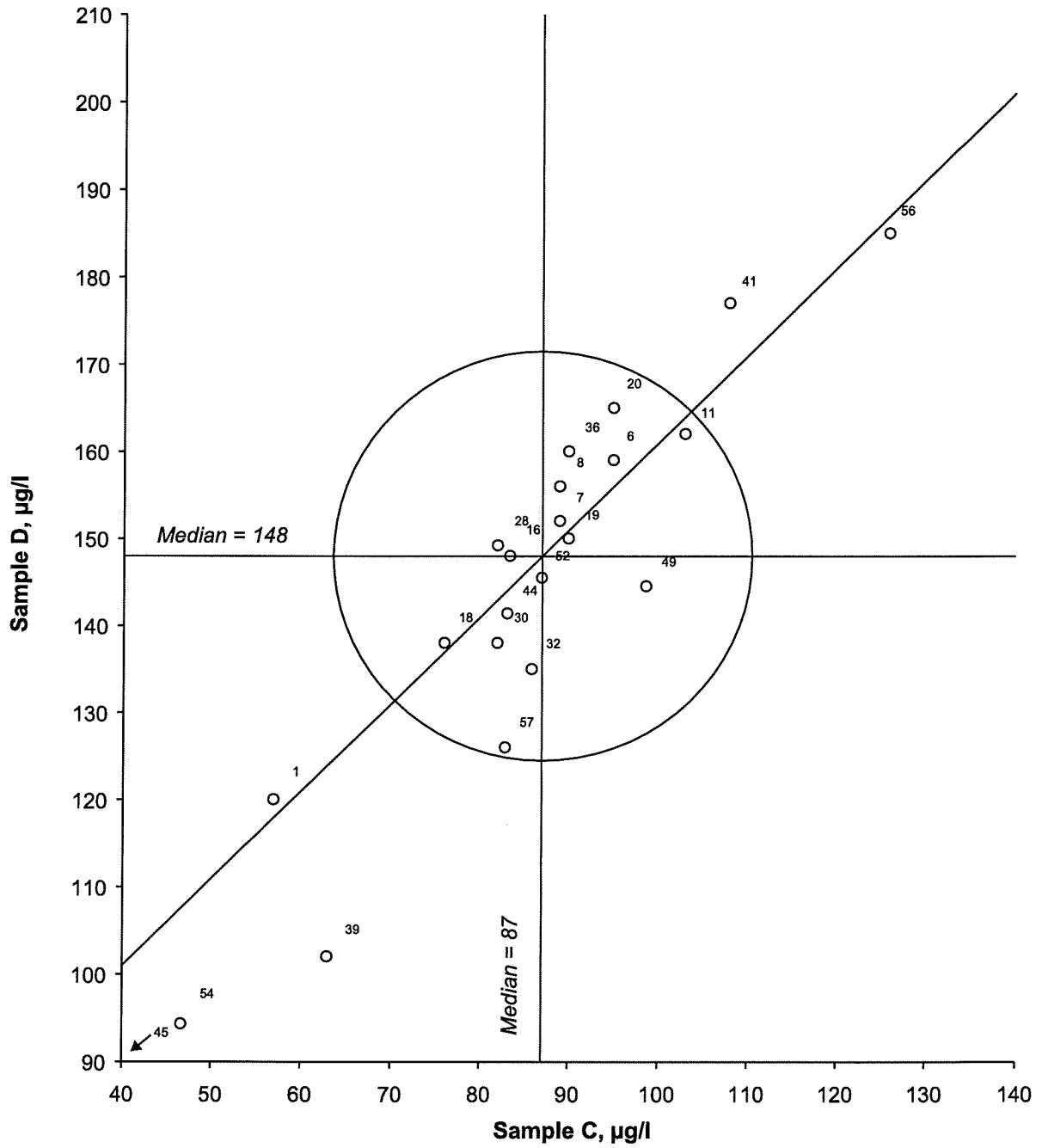
Figure 9. Youden diagramme for sodium, Sample pair AB
Acceptance limit is 20 %

Potassium



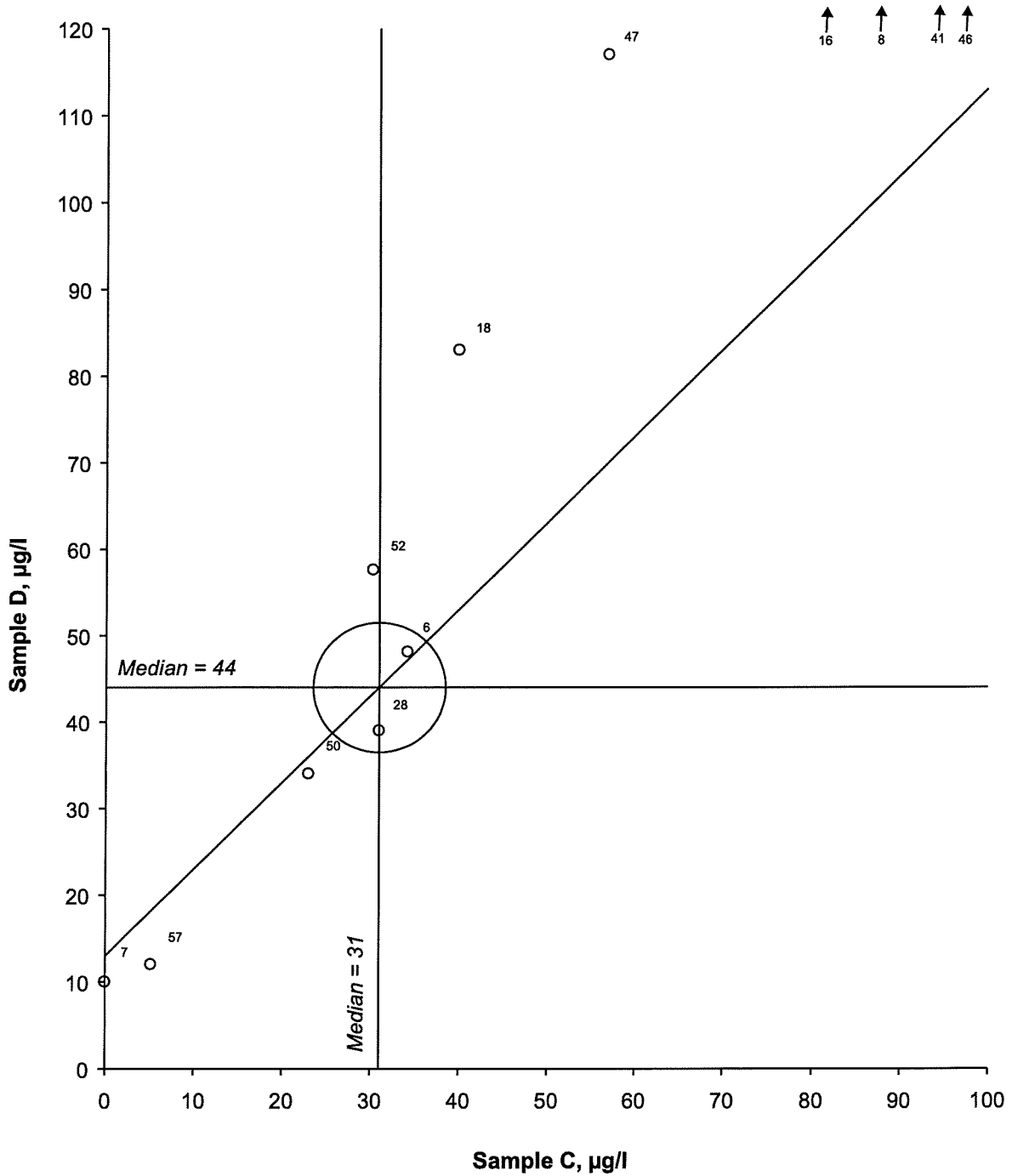
**Figure 10. Youden diagramme for potassium, Sample pair AB
Acceptance limit is 20 %**

Aluminium



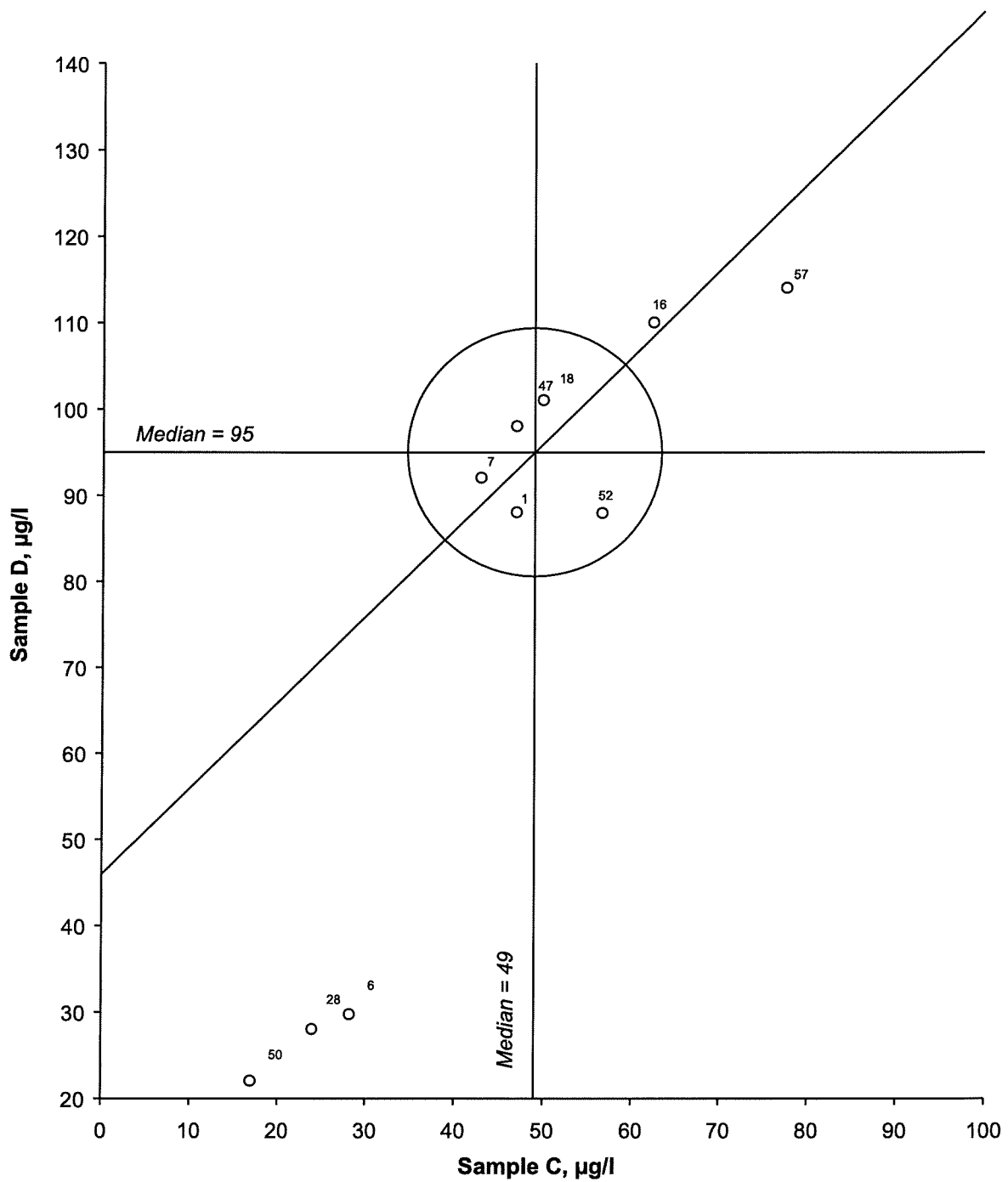
**Figure 11. Youden diagram for aluminium, Sample pair CD
Acceptance limit is 20 %**

Aluminium, reactive



**Figure 12. Youdendiagram for aluminium, reactive, Sample pair CD
Acceptance limit is 20 %**

Aluminium, nonlabile



**Figure 13. Youden diagram for aluminium, nonlabile, Sample pair CD
Acceptance limit is 20 %**

Dissolved organic carbon

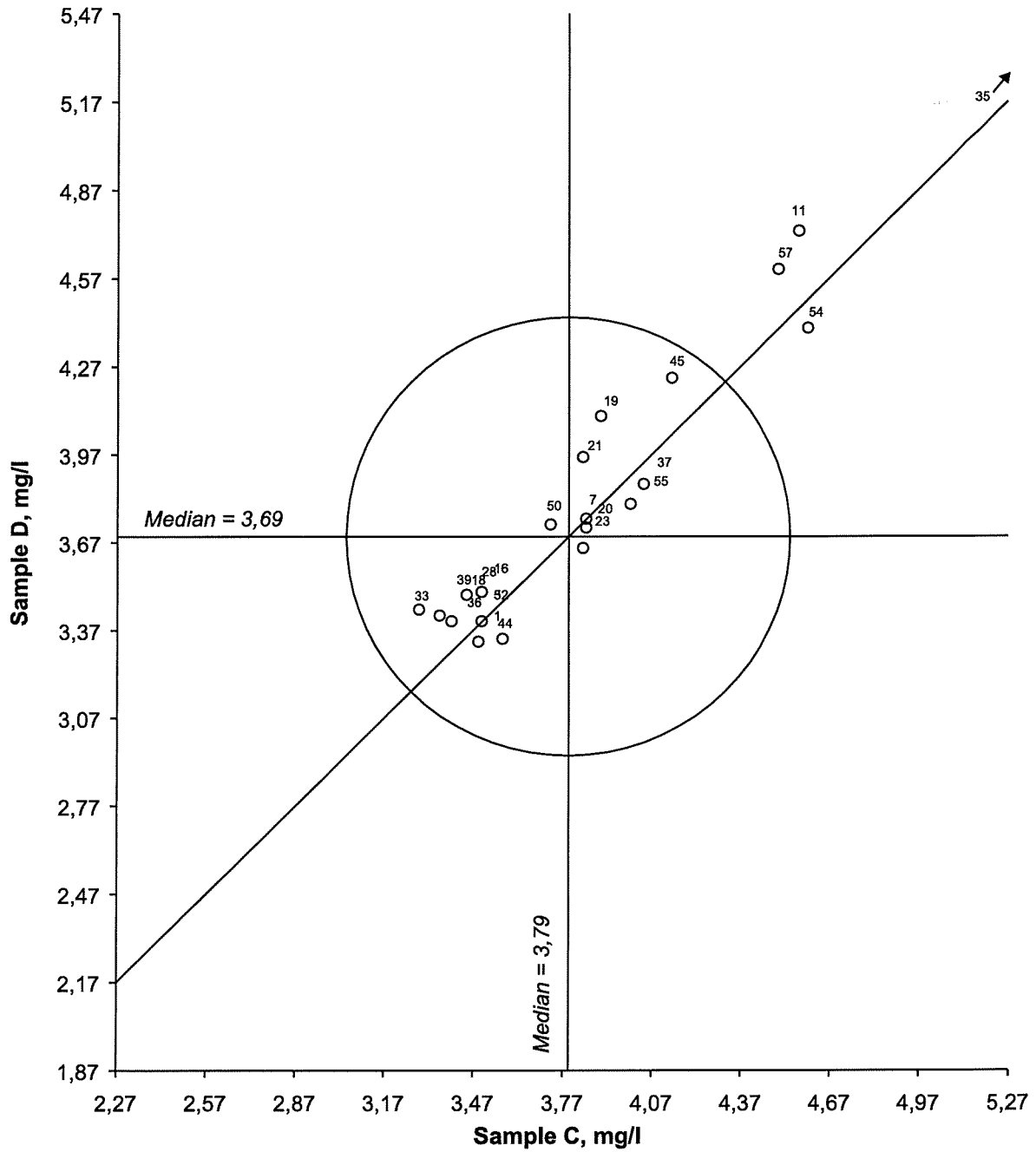
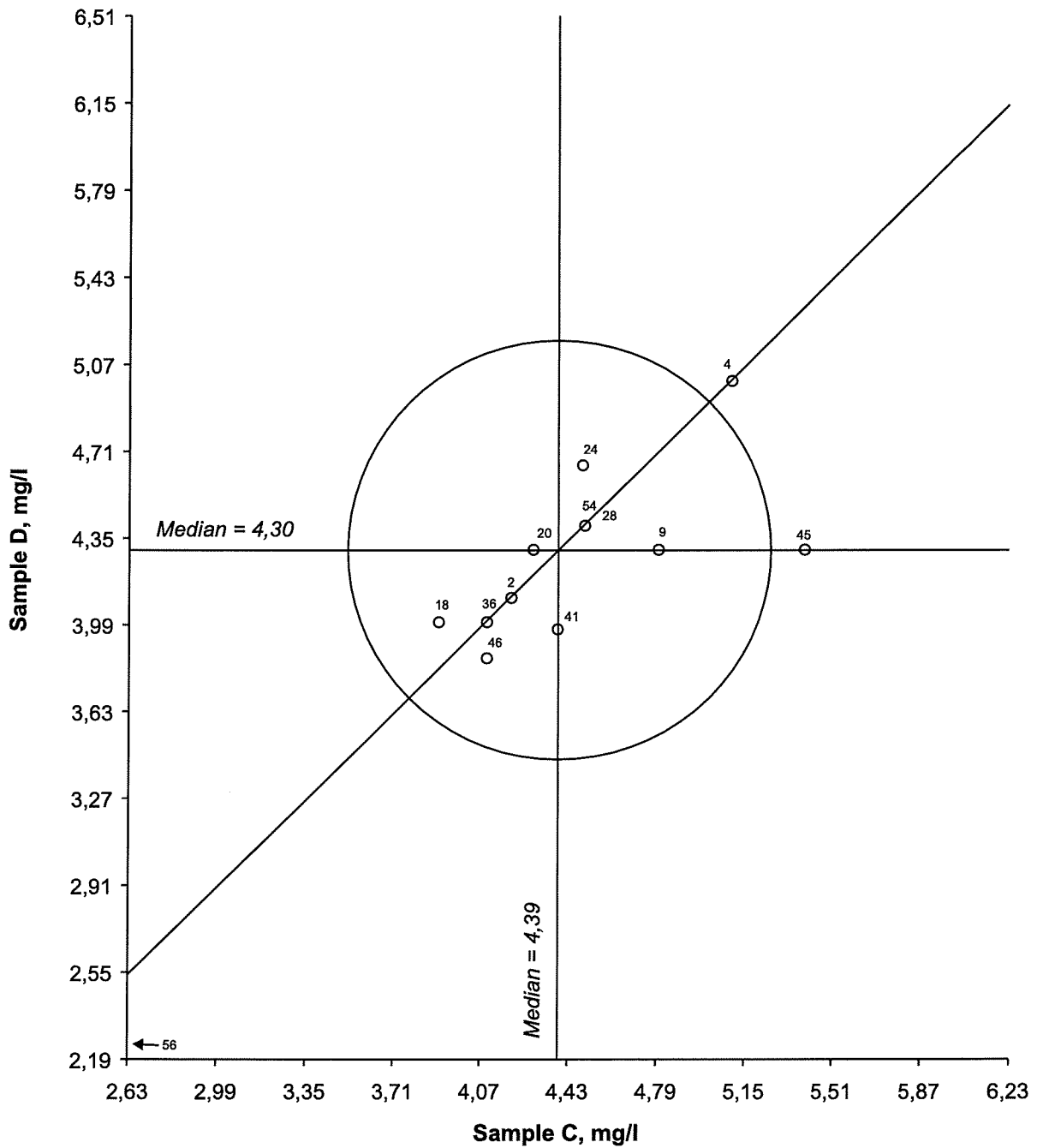


Figure 14. Youndendiagram for dissolved organic carbon, Sample pair CD
Acceptance limit is 20 %

Chemical oxygen demand



**Figure 15. Youdendiagram for chemical oxygen demand, Sample pair CD
Acceptance limit is 20 %**

laboratories due to the different levels of partial pressure of CO₂ 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 CO₂.

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

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

3.2 Conductivity

The conductivity results are presented in Figure 2, where the great circle is representing an accuracy limit of $\pm 10\%$. The reported results are given in Table 5.2. Six laboratories reported the conductivity results in the unit $\mu\text{S}/\text{cm}$, which is the unit they use routinely, instead of the requested mS/m at 25 °C. These results were recalculated to mS/cm by the Programme Center. For one laboratory the result had to be multiplied by the factor 100 to obtain values comparable to the other laboratories.

All participants used an electrometric method for the determination of conductivity. Most laboratories achieved very good agreement between the results for this variable. Four laboratories reported results being systematically too high for both samples, and six laboratories reported results being systematically too low. If the accuracy limit is extended to $\pm 20\%$, the lower results would be located within the circle. A proper temperature correction is necessary when determining this variable, as the conductivity is changing by about two percents pr degree at room temperature.

3.3 Alkalinity

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 5.3. 48 laboratories reported results for alkalinity, and about one third of the participants used the Gran plot titration method suggested in the Manual (1). The others used end point titration, either to $\text{pH} = 4.5$ and 4.2 , or to one certain pH value only (4.2 , 4.5 , 5.4 , or 5.6).

The results for alkalinity are spread out along the 45° line in Figure 3, indicating systematic differences between the results. This is obviously 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 $\text{pH} 4.2$ or 4.5 alone, are located in the upper right part of Figure 3, being systematically too high. The end point titration to $\text{pH} 5.6$ or 5.4 gave results mainly located within the acceptance circle.

Two laboratories reported values being about half of the median value, they have probably calculated the result as mmol/l CO_3^{2-} instead of HCO_3^- . Division of the results from four laboratories by a factor of 1000, gave values comparable to the other laboratories. For one laboratory the results had to be divided by a factor of 100. These laboratories have reported the results in another unit than the requested mmol/l, with no indication of what unit they use.

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" overestimates the true alkalinity or the "equivalence" alkalinity.

3.4 Nitrate + nitrite

The results reported for this parameter are presented in Figure 4, and the reported results are given in Table 5.4. The circle in Figure 4 is representing a general target accuracy of $\pm 20\%$. Ion chromatography is used by an increasing number of laboratories, and is now used by more than one third of the participants. The others are determining this analytical variable by photometric methods, most of these laboratories are using an automated version of the cadmium reduction method. There is a small difference between the results determined by the different methods, the photometric methods are producing higher results than ion chromatography. 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 several times 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 sample A was decreasing during the weeks after the samples were mailed to the participants, this variable is excluded from the evaluation of this intercomparison.

3.5 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 circle. 41 out of 54 laboratories determined chloride by ion chromatography. The greatest deviations are observed for the manual photometric methods, and the argentometric method which have too high detection limit, the latter method is not sensitive enough for most of the acid rain samples. The results produced by ion chromatography are lower than for the other methods. One laboratory determined chloride with capillary electrophoresis, the result being somewhat lower than results determined with ion chromatography.

3.6 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 41 of 52 laboratories for the determination of this analytical variable. Four laboratories used a photometric method based on the dissociation of the barium-thorin complex, and five laboratories used a nephelometric method. The results produced by these methods are higher than with ion chromatography, and the relative standard deviation is much greater too. One laboratory used capillary electrophoresis with acceptable results.

3.7 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. 25 of the participants used flame atomic absorption spectrometry for the determination of calcium. ICP techniques and ion chromatography are used by 12 and 13 laboratories, respectively. The atomic absorption results are slightly lower than the median value, and the ICP results slightly higher than the median value. The complexometric titration method, used by four laboratories, is not sensitive enough for most of this kind of samples. The result pairs being not acceptable are dominated by systematic errors.

3.8 Magnesium

The magnesium results are presented in Figure 8, and the reported values are given in Table 5.8. Most of the participants are still using flame atomic absorption spectrometry for the determination of magnesium. ICP emission spectrometry and ion chromatography was used by 12 and 13 laboratories, respectively. Systematic deviations are dominating the results outside the target accuracy of $\pm 20\%$, and the greatest deviations are observed for manual titrations, indicating that the concentrations of the samples used in this intercomparison are rather low for this technique. The most used methods give comparable results.

3.9 Sodium

The sodium results are presented in Figure 9, where the great circle is representing the general target accuracy of $\pm 20\%$. The reported values are given in Table 5.9. Most laboratories used flame atomic absorption spectrometry for this determination. However, in many laboratories the emission spectrometric techniques are slowly taking over the routine determinations, thus 10 participants used ICP, and 10 used flame photometry. The relative standard deviation was smaller for the results produced with flame atomic absorption. 89% of the result pairs are located within the general target accuracy of $\pm 20\%$.

3.10 Potassium

The potassium results are presented in Figure 10. The great circle is representing a general acceptance limit of $\pm 20\%$. The reported values are given in Table 5.10. As for sodium, many laboratories used flame atomic absorption spectrometry for the determination of this element, however, 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.

3.11 Total aluminium

The results for total aluminium are illustrated in Figure 11, and the reported values are given in Table 5.11. The great circle is representing the general accuracy target of $\pm 20\%$. Nine laboratories used emission techniques, and six of the participants used photometry for the determination of aluminium. Graphite furnace atomic absorption was used by seven laboratories. 73 % of the result pairs are located within the target accuracy.

3.12 Reactive aluminium

The results for reactive aluminium are illustrated in Figure 12, and the reported values are given in Table 5.12. Twelve laboratories reported results for reactive aluminium, however, the results are very different. The results are strongly affected by systematic effects caused by the analytical method used. The statistical treatment according to Youden is not applicable for this situation, therefore none of the results are located within the acceptance circle. The median value used as a picture of the "true" value, therefore, has to be considered as indicative only.

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

3.13 Non-labile aluminium

The results for non-labile aluminium are illustrated in Figure 13, and the reported values are given in Table 5.13. 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.

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

3.14 Dissolved organic carbon

The results for this variable are presented in Figure 14, and the reported values are given in Table 5.14. 23 laboratories determined this analytical variable in the sample pair CD. 14 laboratories used a combustion technique, and a wet oxidation technique with UV and peroxodisulfate was used by four laboratories only. There is no evidence for any significant differences between the reported results determined with these two methods for the samples used in this intercomparison. Five laboratories used the photometric method based on the use of phenolphthalein, and on average their results are slightly higher than the others.

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

3.15 Chemical oxygen demand, COD-Mn

The results for this parameter are presented in Figure 15, and the reported values are given in Table 5.15. Only 13 of the laboratories determined this parameter, which was included in the intercomparison because there are laboratories which do not have equipment for the determination of dissolved organic carbon. Ten of the result pairs are located within the circle representing the target accuracy of $\pm 20\%$.

4. Discussion

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

In Table 2 an evaluation of the results of intercomparison 9913 is presented, based on the target accuracy (except for pH and conductivity), where the number and percentage of

acceptable results are given. 78 % of the results are acceptable when compared to the acceptance limits given above. For the reported results in this intercomparison, on average, one laboratory out of four is located outside the acceptance limit. By some improvement of the routine analytical method, these laboratories should be able to obtain results more comparable to the other participants.

For pH the general target accuracy is ± 0.1 pH units, and far less than 50 % of the result pairs are found within these accuracy limits. However, we have chosen to extend the acceptance limit to ± 0.2 pH units, because of the great spread of the results for these two samples which are nearly neutral, and therefore are supposed not to be completely in CO₂-equilibrium. Even with this limit only 57 % of the result pairs are evaluated as acceptable.

Table 2. Evaluation of the results of intercomparison 9913. 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.

| Variable | Sample pair | N | Limit | n | % |
|----------------------------|-------------|------|--------|------|------|
| pH | AB | 54 | 0.2 * | 31 | 57 |
| Conductivity | AB | 53 | 10 % □ | 43 | 81 |
| Alkalinity | AB | 48 | 20 % | 30 | 63 |
| Nitrate + nitrite-nitrogen | AB | (52) | 20 % | (16) | (31) |
| Chloride | AB | 54 | 20 % | 48 | 89 |
| Sulfate | AB | 52 | 20 % | 45 | 87 |
| Calcium | AB | 55 | 20 % | 43 | 78 |
| Magnesium | AB | 55 | 20 % | 44 | 80 |
| Sodium | AB | 53 | 20 % | 48 | 91 |
| Potassium | AB | 53 | 20 % | 41 | 77 |
| Aluminium, total | AB | 22 | 20 % | 16 | 73 |
| Aluminium, reactive | CD | (12) | 20 % | (2) | - |
| Aluminium, non-labile | CD | (10) | 20 % | (5) | - |
| Dissolved organic carbon | CD | 23 | 20 % | 19 | 83 |
| Chemical oxygen demand | CD | 13 | 20 % | 10 | 77 |
| Sum | | 535 | | 418 | 78 |

* 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 %

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

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 slightly better than in some earlier intercomparisons, probably because of the somewhat higher bicarbonate concentrations in the samples this time.

Because of the high precision of the reported results for conductivity, we have decided to reduce the acceptance limit for this analytical variable. If we increase the acceptance limit to the target value, the six lower result pairs being outside the circle in Figure 2, would be inside the circle.

For nitrate + nitrite a very strange picture is observed, as only 31 % of the result pairs are acceptable. This is caused by the fact that the results for sample A is very widely spread out, especially many laboratories have reported very low results for nitrate in this sample. The samples A and B have been prepared from the same water, the only difference is that sample B have been spiked to increase the concentrations of the analytical variables. In sample A no additions were made. The control analyses performed at the laboratory of the Programme Centre disclosed that the content of nitrate and nitrite in sample A was not stable, therefore this variable is excluded from the evaluation of this intercomparison. So far we have not found any explanation for the instability of this solution.

We have decided to exclude two more variables, reactive and non-labile aluminium, from the evaluation of the intercomparison, because of the very great differences between the few reported values. To evaluate the determination of aluminium fractions, it seems to be necessary that the laboratories normalize their analytical methods to improve the comparability for these variables. There are some confusions about what aluminium fractions should be determined. The intention in this intercomparison was to compare the results for the

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

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

variables printed in bold in the scheme presented in Figure 16. There have obviously been reported some results for other fractions than we asked for. This may be due to the fact that the Programme centre has chosen the definitions of aluminium species given by Driscoll (7), well aware of the fact that 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.

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

5. Conclusion

57 laboratories submitted results for this intercomparison. The best results were reported for the variables conductivity, chloride, sulfate, magnesium, sodium, and dissolved organic carbon. More than 80 % of the results were evaluated as acceptable for these analytical variables.

Rather poor comparability was observed for the results of aluminium species and nitrate + nitrite. The differences between the methods used for the determination of aluminium species, are probably the reason for the poor comparability for these variables. For nitrate + nitrite the poor results are due to the wide spread of the results reported for sample A, however, so far no explanation has been found to why this solution has proved to be instable.

Overall, 78 % of the evaluated results were located within the general target accuracy of ± 20 %. The laboratories which reported results outside this limit should improve their methods to obtain a better comparability. Generally, the application of manual analytical methods seem to be less suited for the water samples which are analyzed in this programme, as the detection limit of several manual methods may be too high. If these laboratories are going to analyze the low concentration samples in the future, it is important that they lower the detection limit of their methods.

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

A total error of ± 0.2 pH units seems to be a reasonable assessment of the accuracy for pH measurements when weakly acid or neutral water samples - which is not in CO_2 equilibrium - are analyzed. On the next meeting, it should be discussed whether we are continuing to use only one "true value" for all the pH results, or to have different "true value" for each method, because there are obviously systematic differences between the methods used by the participating laboratories.

6. Literature

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Appendix A. The participating laboratories

| Identity | Name | Town | Country |
|----------|--|------------------|----------------|
| 1 | Institute of Hydrobiology | Budejovice | Czech Republic |
| 2 | Virumaa Environmental Research | Joehvi | Estonia |
| 3 | Staatliche Umweltbetriebgesellschaft im UBG | Chemnitz | Germany |
| 4 | Institute for Ecology of Industrial Areas | Katowice | Poland |
| 5 | Food and Environment Agency | Torshavn | Faeroe Islands |
| 6 | ITM Stockholm University | Stockholm | Sweden |
| 7 | DAFS Freshwater Laboratory | Pitlochry | Scotland |
| 8 | Länsstyrelsen i Kalmar Län | Kalmar | Sweden |
| 9 | Northern Water Problems Institute | Petrozavodsk | Russia |
| 10 | Laboratorio Biologico Provinciale | Laives | Italy |
| 11 | T.G.Masaryk Water Research Institute | Prague | Czech Republic |
| 12 | Environmental Research Unit | Dublin | Ireland |
| 13 | NILU, Dept. Inorganic Analysis | Kjeller | Norway |
| 14 | University of Helsinki | Helsinki | Finland |
| 15 | University of Bern | Bern | Switzerland |
| 16 | National Rivers Authority | Llanelli | United Kingdom |
| 17 | MOEE, Dorseth Research Centre | Dorset | Canada |
| 18 | Norwegian Institute for Water Research | Oslo | Norway |
| 19 | Kärntner Institut für Seewasser Forschung | Klagenfurt | Austria |
| 20 | Swedish University for Agricultural Sciences | Uppsala | Sweden |
| 21 | Aquatic Chemistry Project | Winnipeg | Canada |
| 22 | Polish Academy of Sciences | Krakow | Poland |
| 23 | Great Lakes Forest Centre | Sault Ste. Marie | Canada |
| 24 | Environmental Protection Ministry | Vilnius | Lithuania |
| 25 | Adirondac Lakes Survey Corporation | New York | USA |
| 26 | Werkgroep Milieubiologie | Nijmegen | Netherlands |
| 27 | Federal Environmental agency | Salzburg | Austria |
| 28 | National Board of Waters and the | Helsinki | Finland |
| 29 | Institute of Biology | Syktvykar | Russia |
| 30 | Swiss Federal Institute for Forest, Snow and | Birmensdorf | Switzerland |
| 31 | Lapland Water and Environment District | Rovaniemi | Finland |
| 32 | MOEE, Toronto Laboratory | Etobicoke | Canada |
| 33 | CNR Istituto Italiano di Idrobiologia | Pallanza | Italy |
| 34 | Czech Geologic Survey Prague | Prague | Czech Republic |
| 35 | Forest Ecosystem Research Group | Dublin | Ireland |
| 36 | Bayerische Landesamt für Wasserwirtschaft | Munchen | Germany |
| 37 | Institut für Zoologie, Universität Innsbruck | Innsbruck | Austria |
| 38 | University of Innsbruck | Innsbruck | Austria |
| 39 | Centre National de la Recherche Scientifique | Toulouse | France |
| 40 | Karelian Research Centre | Petrozavodsk | Russia |
| 41 | South Estonian Environm. Protection Agency | Tartu | Estonia |
| 42 | Water Pollution Observation Laboratory | Riga | Latvia |
| 43 | Bayerisches Landesamt für Wasserwirtschaft | Wielenbach | Germany |
| 44 | Institute of Environmental Protection | Warszaw | Poland |
| 45 | Institute for Ecological Toxicology | Baikalsk | Russia |

| | | | |
|----|---|-------------|----------------|
| 46 | Huumaa Environmental Laboratory | Kärdla | Estonia |
| 47 | Charles University | Prague | Czech Republic |
| 48 | Center for Marine Analytical Ref. and Stds. | Trivandrum | India |
| 49 | D.R. Ambiente Alentejo | Santo Andre | Portugal |
| 50 | METI, US Environmental Protection Agency | Corvallis | USA |
| 51 | Landesumweltamt Nordrhein Westfalen | Essen | Germany |
| 52 | University of Maine | Orono | USA |
| 53 | Kymen Water and Environment District | Kouvola | Finland |
| 54 | Estonian Environment Research Laboratory | Tallinn | Estonia |
| 55 | University of Barcelona | Barcelona | Spain |
| 56 | Center for Chemical Analysis Keldnaholt | Reykjavik | Iceland |
| 57 | Swedish Environmental Research Institute | Stockholm | Sweden |

Appendix B. Preparation of samples

The sample solutions were prepared from natural water collected from the lake Maridalsvannet, located outside Oslo, Norway. Raw water was collected in polyethylene containers and brought to the laboratory for storage. These containers were stored at room temperature for several weeks at the laboratory. During this stabilization period suspended matter settled. The solutions were filtrated through 0.45 μm membrane filter, and small aliquots were removed from the filtrate to determine the concentrations of the analytical variables of interest.

Sample B was prepared by spiking the filtrated water with stock solutions of stoichiometric compounds containing the major ions. No additions were made to prepare sample A.

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

Table 3. Summary of the control analyses.

| Parameter | Sample A | | Sample B | | Sample C | | Sample D | |
|------------------------------------|----------|-----------|----------|-----------|----------|-----------|----------|-----------|
| | Mean | Std. dev. | Mean | Std. dev. | Mean | Std. dev. | Mean | Std. dev. |
| pH | 6,45 | 0,07 | 6,78 | 0,10 | | | | |
| Conductivity mS/m | 2,89 | 0,02 | 4,58 | 0,17 | | | | |
| Alkalinity mmol/l | 0,083 | 0,005 | 0,162 | 0,009 | | | | |
| Nitrate/nitrite $\mu\text{g/l}$ | 125 | 74 | 184 | 13 | | | | |
| Chloride mg/l | 2,05 | 0,09 | 3,60 | 0,00 | | | | |
| Sulfate mg/l | 4,02 | 0,08 | 5,39 | 0,02 | | | | |
| Calcium mg/l | 2,74 | 0,06 | 3,58 | 0,09 | | | | |
| Magnesium mg/l | 0,45 | 0,01 | 0,85 | 0,02 | | | | |
| Sodium mg/l | 1,64 | 0,04 | 2,79 | 0,08 | | | | |
| Potassium mg/l | 0,35 | 0,02 | 0,35 | 0,02 | | | | |
| Aluminium total, $\mu\text{g/l}$ | | | | | 74 | 4,0 | 142 | 4,8 |
| Reactive aluminium $\mu\text{g/l}$ | | | | | 47 | 6,0 | 97 | 9,0 |
| Non-labile alumin. $\mu\text{g/l}$ | | | | | 40 | 5,3 | 81 | 10,9 |
| Diss.org. C mg/l | | | | | 3,52 | 0,08 | 3,46 | 0,09 |
| COD.Mn, mg/l | | | | | 3,90 | 0,00 | 3,90 | 0,10 |

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 beginning of May 1999, a couple of weeks before mailing the samples to the participants. The last sample was analyzed in the middle of July 1999. 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.

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 - 15).

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

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

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

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

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

| Lab. no. | pH | pH | Cond. | Cond. | Alkaline. | Alkaline. | NO ₃ +NO ₂ | NO ₃ +NO ₂ |
|-------------|------|------|-----------|-----------|-------------|-------------|----------------------------------|----------------------------------|
| | A | B | mS/m A | mS/m B | mmol/l A | mmol/l B | µg/l A | µg/l B |
| 1 | 6,60 | 6,95 | 3,01 | 4,84 | 0,080 | 0,165 | 79 | 190 |
| 2 | 6,70 | 7,10 | 3,00 | 5,00 | 0,100 | 0,180 | | |
| 3 | 6,60 | 7,10 | 2,94 | 4,67 | 0,140 | 0,230 | 162 | 196 |
| 4 | 6,50 | 7,04 | 2,96 | 4,58 | 0,074 | 0,160 | 268 | 170 |
| 5 | 6,77 | 7,28 | 3,01 | 4,86 | 0,118 | 0,207 | 169 | 259 |
| 6 | 6,43 | 6,98 | 3,01 | 4,85 | 0,081 | 0,170 | 120 | 190 |
| 7 | 6,51 | 7,11 | 2,75 | 4,45 | 0,078 | 0,165 | 140 | 182 |
| 8 | 6,30 | 6,88 | 3,00 | 4,80 | 0,070 | 0,180 | | |
| 9 | 6,48 | 6,90 | 3,77 | 5,81 | 0,080 | 0,150 | 15 | 150 |
| 10 | 6,51 | 6,95 | 3,03 | 4,88 | 0,089 | 0,170 | 40 | 160 |
| 11 | 6,37 | 6,92 | 2,70 | 4,35 | 0,150 | 0,250 | 18 | 215 |
| 12 | 6,61 | 7,13 | 4,10 | 5,50 | 0,005 | 0,009 | 146 | 179 |
| 13 | 6,45 | 6,95 | 3,08 | 4,77 | | | | |
| 14 | 6,28 | 7,33 | 2,76 | 4,58 | 0,085 | 0,173 | 69 | 169 |
| 15 | 6,53 | 6,91 | 2,86 | 4,54 | | | 0 | 1400 |
| 16 | 6,65 | 7,01 | 2,65 | 4,25 | 0,038 | 0,084 | 203 | 213 |
| 17 | 6,35 | 6,97 | 3,10 | 4,86 | 0,114 | 0,200 | 118 | 188 |
| 18 | 6,49 | 6,90 | 2,89 | 4,67 | 0,074 | 0,161 | 155 | 190 |
| 19 | 6,30 | 6,80 | 3,20 | 5,00 | 0,350 | 0,490 | 135 | 183 |
| 20 | 6,69 | 6,94 | 3,10 | 4,93 | 0,072 | 0,161 | 142 | 197 |
| 21 | 7,07 | 7,38 | 3,00 | 4,80 | 0,088 | 0,171 | 86 | 184 |
| 22 | 6,42 | 6,84 | 3,04 | 4,80 | | | 75 | 180 |
| 23 | 6,49 | 6,91 | 3,14 | 4,97 | 0,069 | 0,158 | 112 | 170 |
| 24 | 6,50 | 7,05 | 3,03 | 4,17 | 0,083 | 0,137 | 172 | 184 |
| 25 | 6,41 | 6,89 | 3,01 | 4,75 | 0,089 | 0,174 | 63 | 169 |
| 26 | 6,10 | 6,66 | 4,00 | 5,50 | 0,120 | 0,200 | 48 | 195 |
| 27 | 6,30 | 6,84 | 3,00 | 4,90 | 0,120 | 0,210 | 146 | 192 |
| 28 | 6,48 | 7,01 | 3,00 | 4,90 | 0,075 | 0,162 | 138 | 181 |
| 29 | 6,40 | 6,70 | 2,80 | 4,20 | 0,075 | 0,150 | 2 | 130 |
| 30 | | | | | | | 117 | 177 |
| 31 | 6,79 | 7,20 | 3,04 | 4,86 | 0,078 | 0,169 | 179 | 185 |
| 32 | 6,55 | 7,04 | 3,10 | 4,90 | 0,130 | 0,220 | 110 | 180 |
| 33 | 6,20 | 6,50 | 2,89 | 4,67 | 0,097 | 0,171 | 0 | 160 |
| 34 | 6,48 | 7,04 | 3,02 | 4,86 | 0,085 | 0,172 | 97 | 178 |
| 35 | 6,15 | 6,89 | 3,00 | 4,90 | 0,015 | 0,050 | 139 | 180 |
| 36 | 6,59 | 6,85 | 3,10 | 4,90 | 0,150 | 0,220 | 90 | 150 |
| 37 | 6,30 | 6,68 | 3,00 | 4,79 | 0,096 | 0,164 | 0 | 173 |
| 38 | 6,34 | 6,61 | 3,00 | 4,80 | 0,104 | 0,172 | 14 | 158 |
| 39 | 6,38 | 6,98 | 3,04 | 4,73 | 0,087 | 0,172 | 84 | 182 |
| 40 | 6,40 | 7,00 | | | | | 72 | 118 |
| 41 | 6,65 | 7,18 | 2,98 | 4,79 | 0,110 | 0,200 | 81 | 188 |
| 42 | 6,44 | 6,92 | 3,02 | 4,76 | 0,089 | 0,181 | 180 | 203 |
| 43 | 5,70 | 5,80 | 3,15 | 5,09 | 0,200 | 0,300 | 151 | 174 |
| 44 | 6,44 | 6,68 | 3,30 | 4,90 | | | 90 | 138 |
| 45 | 6,65 | 6,90 | | | | | 34 | 202 |

| Lab. no. | pH | | Cond. mS/m | | Alkalin. mmol/l | | NO ₃ +NO ₂ µg/l | |
|-------------|------|------|---------------|------|--------------------|-------|--|-----|
| | A | B | A | B | A | B | A | B |
| 46 | 6,33 | 6,91 | 4,12 | 5,15 | 0,260 | 0,340 | 90 | 148 |
| 47 | 6,40 | 6,98 | 3,02 | 4,85 | 0,087 | 0,170 | 22 | 168 |
| 48 | 6,36 | 6,57 | 3,00 | 4,70 | 0,080 | 0,160 | 84 | 863 |
| 49 | 6,55 | 7,02 | 3,24 | 5,02 | 0,136 | 0,220 | 179 | 221 |
| 50 | 6,90 | 7,22 | 3,12 | 4,96 | 0,089 | 0,170 | 92 | 182 |
| 51 | | | 3,00 | 4,90 | | | 90 | 170 |
| 52 | 6,25 | 6,62 | 2,87 | 4,72 | 0,045 | 0,088 | | |
| 53 | 6,22 | 6,75 | 3,04 | 4,89 | 0,085 | 0,171 | 128 | 191 |
| 54 | 6,60 | 7,00 | 2,78 | 4,88 | 0,080 | 0,180 | 191 | 196 |
| 55 | 6,24 | 6,63 | 2,90 | 4,40 | 0,079 | 0,150 | 12 | 174 |
| 56 | 6,51 | 6,95 | 3,00 | 4,80 | 0,073 | 0,164 | 144 | 170 |
| 57 | | | | | | | | |

| Lab. no. | Cl mg/l A | Cl mg/l B | SO4 mg/l A | SO4 mg/l B | Ca mg/l A | Ca mg/l B | Mg mg/l A | Mg mg/l B |
|-------------|-----------------|-----------------|------------------|------------------|-----------------|-----------------|-----------------|-----------------|
| 1 | 2,04 | 3,63 | 4,05 | 5,37 | 2,74 | 3,52 | 0,48 | 0,87 |
| 2 | 5,50 | 7,50 | 3,00 | 4,00 | 2,70 | 2,80 | 0,65 | 1,30 |
| 3 | 2,10 | 3,70 | 3,90 | 5,10 | 2,90 | 3,70 | 0,60 | 1,00 |
| 4 | 2,41 | 3,34 | 4,25 | 5,37 | 2,78 | 3,55 | 0,47 | 0,86 |
| 5 | 2,16 | 3,95 | 4,77 | 6,46 | 2,48 | 3,03 | 0,43 | 0,76 |
| 6 | 1,80 | 3,30 | 3,90 | 5,20 | 2,76 | 3,48 | 0,43 | 0,80 |
| 7 | 2,04 | 3,51 | 4,10 | 5,35 | 2,94 | 3,78 | 0,49 | 0,89 |
| 8 | | | | | | | | |
| 9 | 2,09 | 3,66 | 3,00 | 3,30 | 2,77 | 3,53 | 0,48 | 0,86 |
| 10 | 1,84 | 3,50 | 3,80 | 5,31 | 2,10 | 2,90 | 0,44 | 0,80 |
| 11 | 2,47 | 3,97 | 3,60 | 5,60 | 3,00 | 3,80 | 0,49 | 0,91 |
| 12 | 1,92 | 2,93 | 3,80 | 5,00 | 2,77 | 3,46 | 0,50 | 0,87 |
| 13 | 2,11 | 3,63 | 4,01 | 5,33 | 2,74 | 3,48 | 0,48 | 0,86 |
| 14 | 2,28 | 3,87 | 4,49 | 5,84 | 2,51 | 3,74 | 0,50 | 0,95 |
| 15 | 5,13 | 9,72 | 7,08 | 8,39 | 5,16 | 5,47 | 0,49 | 0,90 |
| 16 | 2,34 | 3,87 | | | 2,83 | 3,54 | 0,45 | 0,82 |
| 17 | 2,04 | 3,54 | 3,95 | 5,30 | 2,64 | 3,40 | 0,46 | 0,84 |
| 18 | 1,90 | 3,60 | 3,90 | 5,40 | 2,66 | 3,50 | 0,46 | 0,86 |
| 19 | 1,90 | 3,70 | 4,00 | 5,40 | 3,00 | 3,60 | 1,00 | 1,00 |
| 20 | 2,14 | 3,92 | 3,96 | 5,26 | 2,74 | 3,57 | 0,46 | 0,86 |
| 21 | 2,03 | 3,67 | 4,08 | 5,35 | 2,58 | 3,28 | 0,46 | 0,85 |
| 22 | 2,20 | 3,56 | 4,09 | 5,32 | 1,73 | 2,41 | 0,32 | 0,56 |
| 23 | 2,13 | 3,64 | 4,01 | 5,35 | 2,48 | 3,22 | 0,46 | 0,82 |
| 24 | 2,50 | 4,10 | 3,40 | 4,20 | 2,81 | 4,01 | 0,61 | 0,61 |
| 25 | 2,07 | 3,33 | 4,02 | 5,35 | | | | |
| 26 | 1,98 | 3,64 | | | 2,86 | 3,85 | 0,45 | 0,98 |
| 27 | 1,65 | 3,07 | 3,62 | 4,80 | 3,13 | 4,00 | 0,49 | 1,01 |
| 28 | 1,83 | 3,34 | 3,91 | 5,24 | 2,84 | 3,58 | 0,47 | 0,86 |
| 29 | 1,80 | 3,10 | 4,20 | 5,60 | 2,10 | 2,80 | 0,40 | 0,82 |
| 30 | 1,95 | 3,32 | 4,07 | 5,43 | 2,83 | 4,10 | 0,49 | 0,95 |
| 31 | 2,04 | 3,43 | 3,95 | 5,25 | 2,68 | 3,43 | 0,48 | 0,88 |
| 32 | 1,94 | 3,56 | 4,10 | 5,05 | 2,40 | 3,09 | 0,48 | 0,84 |
| 33 | 2,04 | 3,59 | 4,05 | 5,45 | 2,64 | 3,47 | 0,47 | 0,87 |
| 34 | 1,93 | 3,46 | 3,83 | 5,15 | 2,75 | 3,50 | 0,46 | 0,83 |
| 35 | 1,93 | 3,56 | 4,01 | 5,24 | 2,83 | 3,82 | 0,51 | 0,97 |
| 36 | 2,00 | 3,60 | 4,20 | 5,70 | 3,10 | 4,00 | 0,60 | 1,00 |
| 37 | 1,95 | 3,57 | 3,90 | 5,36 | 2,90 | 3,80 | 0,39 | 0,79 |
| 38 | 2,04 | 3,60 | 4,12 | 5,47 | 2,77 | 3,57 | 0,48 | 0,89 |
| 39 | 2,02 | 3,54 | 4,13 | 5,38 | 2,72 | 3,53 | 0,46 | 0,85 |
| 40 | 2,00 | 3,36 | 3,64 | 4,90 | 2,67 | 3,70 | 0,44 | 0,86 |
| 41 | 2,04 | 3,49 | 4,04 | 5,42 | 3,57 | 4,48 | 0,49 | 0,92 |
| 42 | 2,47 | 3,87 | | | 0,18 | 0,64 | 0,31 | 0,83 |
| 43 | 1,99 | 3,42 | 3,98 | 5,34 | 2,87 | 4,43 | 0,56 | 1,13 |
| 44 | 1,56 | 3,27 | 3,56 | 5,02 | 2,67 | 3,41 | 0,45 | 0,81 |
| 45 | 2,20 | 3,70 | 3,50 | 4,60 | 3,05 | 4,18 | 0,23 | 0,23 |

| Lab. no. | Cl mg/l A | Cl mg/l B | SO4 mg/l A | SO4 mg/l B | Ca mg/l A | Ca mg/l B | Mg mg/l A | Mg mg/l B |
|---------------------|--------------------------|--------------------------|---------------------------|---------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| 46 | | | 4,00 | 49,10 | 4,19 | 5,28 | 1,10 | 1,38 |
| 47 | 2,03 | 3,58 | 4,06 | 5,34 | 2,66 | 3,40 | 0,45 | 0,82 |
| 48 | 2,21 | 3,68 | 3,16 | 4,15 | 2,67 | 3,84 | 0,47 | 0,91 |
| 49 | 1,93 | 3,44 | 3,95 | 5,27 | 2,76 | 3,59 | 0,57 | 0,98 |
| 50 | 2,00 | 3,61 | 3,97 | 5,28 | 2,71 | 3,51 | 0,49 | 0,85 |
| 51 | 2,00 | 3,42 | 3,99 | 5,22 | 2,75 | 3,52 | 0,47 | 0,86 |
| 52 | 2,00 | 3,60 | 4,10 | 5,45 | 2,61 | 3,34 | 0,50 | 0,90 |
| 53 | 1,90 | 3,40 | 3,70 | 4,70 | 3,10 | 4,00 | 0,47 | 0,91 |
| 54 | 2,03 | 3,42 | 4,18 | 5,34 | 3,40 | 4,17 | 0,44 | 0,81 |
| 55 | 2,21 | 3,61 | 4,32 | 5,45 | 2,64 | 3,55 | 0,45 | 0,84 |
| 56 | 2,18 | 3,69 | 4,20 | 5,23 | 3,11 | 3,97 | 0,48 | 0,88 |
| 57 | | | | | 2,33 | 3,04 | 0,42 | 0,79 |

| Lab. no. | Na mg/l A | Na mg/l B | K mg/l A | K mg/l B | Al µg/l C | Al µg/l D | Al-R µg/l C | Al-R µg/l D |
|-------------|-----------------|-----------------|----------------|----------------|-----------------|-----------------|-------------------|-------------------|
| 1 | 1,75 | 2,85 | 0,33 | 0,45 | 57 | 120 | | |
| 2 | | | | | | | | |
| 3 | 1,90 | 2,90 | 0,30 | 0,30 | | | | |
| 4 | 1,70 | 2,77 | 0,36 | 0,37 | | | | |
| 5 | 2,05 | 3,27 | 0,16 | 0,22 | | | | |
| 6 | 1,70 | 2,84 | 0,36 | 0,38 | 95 | 159 | 34 | 48 |
| 7 | 1,75 | 2,82 | 0,35 | 0,35 | 89 | 152 | 0 | 10 |
| 8 | | | | | 89 | 156 | 87 | 147 |
| 9 | 1,83 | 3,00 | 0,33 | 0,33 | | | | |
| 10 | 1,80 | 2,82 | 0,34 | 0,38 | | | | |
| 11 | 1,60 | 2,52 | 0,36 | 0,36 | 103 | 162 | | |
| 12 | 1,96 | 2,96 | 0,36 | 0,35 | | | | |
| 13 | 1,77 | 2,81 | 0,42 | 0,36 | | | | |
| 14 | 1,81 | 2,99 | 0,36 | 0,36 | | | | |
| 15 | 1,71 | 1,83 | 0,32 | 0,32 | | | | |
| 16 | 1,68 | 2,74 | 0,38 | 0,37 | 83 | 148 | 81 | 133 |
| 17 | 1,72 | 2,82 | 0,37 | 0,36 | | | | |
| 18 | 1,63 | 2,78 | 0,37 | 0,37 | 76 | 138 | 40 | 83 |
| 19 | 1,80 | 2,80 | 0,40 | 0,40 | 90 | 150 | | |
| 20 | 1,68 | 2,78 | 0,31 | 0,33 | 95 | 165 | | |
| 21 | 1,59 | 2,63 | 0,37 | 0,37 | | | | |
| 22 | 1,01 | 1,74 | 0,40 | 0,34 | | | | |
| 23 | 1,65 | 2,71 | 0,36 | 0,36 | | | | |
| 24 | 1,75 | 3,00 | 0,35 | 0,38 | | | | |
| 25 | | | | | | | | |
| 26 | 1,79 | 2,97 | 0,35 | 0,35 | | | | |
| 27 | 1,72 | 2,74 | 0,37 | 0,37 | | | | |
| 28 | 1,71 | 2,84 | 0,37 | 0,37 | 82 | 149 | 31 | 39 |
| 29 | 2,10 | 3,40 | 0,52 | 0,59 | | | | |
| 30 | 1,76 | 3,11 | 0,36 | 0,39 | 82 | 138 | | |
| 31 | 1,74 | 2,89 | 0,37 | 0,39 | | | | |
| 32 | 1,78 | 2,88 | 0,38 | 0,37 | 86 | 135 | | |
| 33 | 1,66 | 2,73 | 0,11 | 0,38 | | | | |
| 34 | 1,70 | 2,73 | 0,37 | 0,37 | | | | |
| 35 | 1,70 | 2,96 | 0,29 | 0,60 | | | | |
| 36 | 1,82 | 2,95 | 0,44 | 0,43 | 90 | 160 | | |
| 37 | 1,70 | 2,83 | 0,36 | 0,44 | | | | |
| 38 | 1,59 | 2,86 | 0,38 | 0,44 | | | | |
| 39 | 1,70 | 2,83 | 0,39 | 0,39 | 63 | 102 | | |
| 40 | 1,76 | 2,74 | 0,36 | 0,37 | | | | |
| 41 | 1,89 | 3,02 | 0,38 | 0,38 | 108 | 177 | 93 | 164 |
| 42 | 1,63 | 2,93 | 0,34 | 0,34 | | | | |
| 43 | 1,94 | 3,37 | 0,44 | 0,42 | | | | |
| 44 | 1,62 | 2,66 | 0,34 | 0,37 | 83 | 141 | | |
| 45 | 1,70 | 2,80 | 0,30 | 0,30 | 41 | 42 | | |

| Lab. no. | Na mg/l A | Na mg/l B | K mg/l A | K mg/l B | Al µg/l C | Al µg/l D | Al-R µg/l C | Al-R µg/l D |
|-------------|-----------------|-----------------|----------------|----------------|-----------------|-----------------|-------------------|-------------------|
| 46 | | | | | | | 96 | 132 |
| 47 | 1,89 | 2,85 | 0,29 | 0,38 | | | 57 | 117 |
| 48 | 1,55 | 2,79 | 0,20 | 0,17 | | | | |
| 49 | 1,72 | 2,57 | 0,37 | 0,34 | 99 | 145 | | |
| 50 | 1,73 | 2,97 | 0,39 | 0,37 | | | 23 | 34 |
| 51 | 1,73 | 2,62 | 0,32 | 0,28 | | | | |
| 52 | 1,79 | 2,95 | 0,34 | 0,35 | 87 | 146 | 30 | 58 |
| 53 | 1,70 | 3,00 | 0,36 | 0,36 | | | | |
| 54 | 1,78 | 2,89 | 0,37 | 0,41 | 47 | 94 | | |
| 55 | 1,60 | 2,52 | 0,32 | 0,35 | | | | |
| 56 | 1,35 | 2,15 | 0,10 | 0,10 | 126 | 185 | | |
| 57 | 1,74 | 2,90 | 0,35 | 0,35 | 83 | 126 | 5 | 12 |

| Lab. no. | Al-I µg/l C | Al-I µg/l D | DOC mg/l C | DOC mg/l D | COD-Mn mg/l C | COD-Mn mg/l D |
|----------|-------------------|-------------------|------------------|------------------|---------------------|---------------------|
| 1 | 47 | 88 | 3,49 | 3,33 | | |
| 2 | | | | | 4,20 | 4,10 |
| 3 | | | | | | |
| 4 | | | | | 5,10 | 5,00 |
| 5 | | | | | | |
| 6 | 28 | 30 | | | | |
| 7 | 43 | 92 | 3,85 | 3,75 | | |
| 8 | | | | | | |
| 9 | | | | | 4,80 | 4,30 |
| 10 | | | | | | |
| 11 | | | 4,57 | 4,73 | | |
| 12 | | | | | | |
| 13 | | | | | | |
| 14 | | | | | | |
| 15 | | | | | | |
| 16 | 63 | 110 | 3,50 | 3,50 | | |
| 17 | | | | | | |
| 18 | 50 | 101 | 3,40 | 3,40 | 3,90 | 4,00 |
| 19 | | | 3,90 | 4,10 | | |
| 20 | | | 3,85 | 3,72 | 4,29 | 4,30 |
| 21 | | | 3,84 | 3,96 | | |
| 22 | | | | | | |
| 23 | | | 3,84 | 3,65 | | |
| 24 | | | | | 4,49 | 4,65 |
| 25 | | | | | | |
| 26 | | | | | | |
| 27 | | | | | | |
| 28 | 24 | 28 | 3,45 | 3,49 | 4,50 | 4,40 |
| 29 | | | | | | |
| 30 | | | | | | |
| 31 | | | | | | |
| 32 | | | 3,50 | 3,40 | | |
| 33 | | | 3,29 | 3,44 | | |
| 34 | | | | | | |
| 35 | | | 27,27 | 27,10 | | |
| 36 | | | 3,40 | 3,40 | 4,10 | 4,00 |
| 37 | | | 4,04 | 3,87 | | |
| 38 | | | | | | |
| 39 | | | 3,36 | 3,42 | | |
| 40 | | | | | | |
| 41 | | | | | 4,39 | 3,97 |
| 42 | | | | | | |
| 43 | | | | | | |
| 44 | | | 3,57 | 3,34 | | |
| 45 | | | 4,14 | 4,23 | 5,40 | 4,30 |

| Lab. no. | Al-I µg/l C | Al-I µg/l D | DOC mg/l C | DOC mg/l D | COD-Mn mg/l C | COD-Mn mg/l D |
|---------------------|----------------------------|----------------------------|---------------------------|---------------------------|------------------------------|------------------------------|
| 46 | | | | | 4,10 | 3,85 |
| 47 | 47 | 98 | | | | |
| 48 | | | | | | |
| 49 | | | | | | |
| 50 | 17 | 22 | 3,73 | 3,73 | | |
| 51 | | | | | | |
| 52 | 57 | 88 | 3,50 | 3,40 | | |
| 53 | | | | | | |
| 54 | | | 4,60 | 4,40 | 4,50 | 4,40 |
| 55 | | | 4,00 | 3,80 | | |
| 56 | | | | | 2,30 | 2,30 |
| 57 | 78 | 114 | 4,50 | 4,60 | | |

Table 5.1. Statistics - pH**Sample A**

| | | | |
|---------------------------|------|-----------------------------|-------|
| Number of participants | 54 | Range | 0,97 |
| Number of omitted results | 1 | Variance | 0,03 |
| True value | 6,48 | Standard deviation | 0,18 |
| Mean value | 6,47 | Relative standard deviation | 2,9% |
| Median value | 6,48 | Relative error | -0,1% |

Analytical results in ascending order:

| | | | | | |
|----|--------|----|------|----|------|
| 43 | 5,70 U | 29 | 6,40 | 7 | 6,51 |
| 26 | 6,10 | 47 | 6,40 | 15 | 6,53 |
| 35 | 6,15 | 40 | 6,40 | 49 | 6,55 |
| 33 | 6,20 | 25 | 6,41 | 32 | 6,55 |
| 53 | 6,22 | 22 | 6,42 | 36 | 6,59 |
| 55 | 6,24 | 6 | 6,43 | 1 | 6,60 |
| 52 | 6,25 | 42 | 6,44 | 3 | 6,60 |
| 14 | 6,28 | 44 | 6,44 | 54 | 6,60 |
| 37 | 6,30 | 13 | 6,45 | 12 | 6,61 |
| 19 | 6,30 | 9 | 6,48 | 41 | 6,65 |
| 27 | 6,30 | 28 | 6,48 | 45 | 6,65 |
| 8 | 6,30 | 34 | 6,48 | 16 | 6,65 |
| 46 | 6,33 | 23 | 6,49 | 20 | 6,69 |
| 38 | 6,34 | 18 | 6,49 | 2 | 6,70 |
| 17 | 6,35 | 24 | 6,50 | 5 | 6,77 |
| 48 | 6,36 | 4 | 6,50 | 31 | 6,79 |
| 11 | 6,37 | 56 | 6,51 | 50 | 6,90 |
| 39 | 6,38 | 10 | 6,51 | 21 | 7,07 |

Sample B

| | | | |
|---------------------------|------|-----------------------------|-------|
| Number of participants | 54 | Range | 0,88 |
| Number of omitted results | 1 | Variance | 0,04 |
| True value | 6,95 | Standard deviation | 0,19 |
| Mean value | 6,93 | Relative standard deviation | 2,7% |
| Median value | 6,95 | Relative error | -0,2% |

Analytical results in ascending order:

| | | | | | |
|----|--------|----|------|----|------|
| 43 | 5,80 U | 18 | 6,90 | 40 | 7,00 |
| 33 | 6,50 | 45 | 6,90 | 28 | 7,01 |
| 48 | 6,57 | 9 | 6,90 | 16 | 7,01 |
| 38 | 6,61 | 23 | 6,91 | 49 | 7,02 |
| 52 | 6,62 | 15 | 6,91 | 34 | 7,04 |
| 55 | 6,63 | 46 | 6,91 | 4 | 7,04 |
| 26 | 6,66 | 42 | 6,92 | 32 | 7,04 |
| 37 | 6,68 | 11 | 6,92 | 24 | 7,05 |
| 44 | 6,68 | 20 | 6,94 | 2 | 7,10 |
| 29 | 6,70 | 1 | 6,95 | 3 | 7,10 |
| 53 | 6,75 | 13 | 6,95 | 7 | 7,11 |
| 19 | 6,80 | 56 | 6,95 | 12 | 7,13 |
| 22 | 6,84 | 10 | 6,95 | 41 | 7,18 |
| 27 | 6,84 | 17 | 6,97 | 31 | 7,20 |
| 36 | 6,85 | 39 | 6,98 | 50 | 7,22 |
| 8 | 6,88 | 6 | 6,98 | 5 | 7,28 |
| 35 | 6,89 | 47 | 6,98 | 14 | 7,33 |
| 25 | 6,89 | 54 | 7,00 | 21 | 7,38 |

U = Omitted result

Table 5.2. Statistics - Conductivity, mS/m**Sample A**

| | | | |
|---------------------------|------|-----------------------------|-------|
| Number of participants | 53 | Range | 0,65 |
| Number of omitted results | 4 | Variance | 0,02 |
| True value | 3,00 | Standard deviation | 0,13 |
| Mean value | 2,99 | Relative standard deviation | 4,3% |
| Median value | 3,00 | Relative error | -0,2% |

Analytical results in ascending order:

| | | | | | |
|----|------|----|------|----|--------|
| 16 | 2,65 | 56 | 3,00 | 22 | 3,04 |
| 11 | 2,70 | 27 | 3,00 | 39 | 3,04 |
| 7 | 2,75 | 8 | 3,00 | 13 | 3,08 |
| 14 | 2,76 | 28 | 3,00 | 32 | 3,10 |
| 54 | 2,78 | 37 | 3,00 | 17 | 3,10 |
| 29 | 2,80 | 48 | 3,00 | 36 | 3,10 |
| 15 | 2,86 | 21 | 3,00 | 20 | 3,10 |
| 52 | 2,87 | 1 | 3,01 | 50 | 3,12 |
| 18 | 2,89 | 5 | 3,01 | 23 | 3,14 |
| 33 | 2,89 | 6 | 3,01 | 43 | 3,15 |
| 55 | 2,90 | 25 | 3,01 | 19 | 3,20 |
| 3 | 2,94 | 34 | 3,02 | 49 | 3,24 |
| 4 | 2,96 | 42 | 3,02 | 44 | 3,30 |
| 41 | 2,98 | 47 | 3,02 | 9 | 3,77 U |
| 2 | 3,00 | 10 | 3,03 | 26 | 4,00 U |
| 51 | 3,00 | 24 | 3,03 | 12 | 4,10 U |
| 38 | 3,00 | 31 | 3,04 | 46 | 4,12 U |
| 35 | 3,00 | 53 | 3,04 | | |

Sample B

| | | | |
|---------------------------|------|-----------------------------|-------|
| Number of participants | 53 | Range | 0,92 |
| Number of omitted results | 4 | Variance | 0,04 |
| True value | 4,80 | Standard deviation | 0,21 |
| Mean value | 4,76 | Relative standard deviation | 4,4% |
| Median value | 4,80 | Relative error | -0,8% |

Analytical results in ascending order:

| | | | | | |
|----|------|----|------|----|--------|
| 24 | 4,17 | 41 | 4,79 | 36 | 4,90 |
| 29 | 4,20 | 37 | 4,79 | 44 | 4,90 |
| 16 | 4,25 | 38 | 4,80 | 35 | 4,90 |
| 11 | 4,35 | 8 | 4,80 | 32 | 4,90 |
| 55 | 4,40 | 22 | 4,80 | 27 | 4,90 |
| 7 | 4,45 | 56 | 4,80 | 28 | 4,90 |
| 15 | 4,54 | 21 | 4,80 | 20 | 4,93 |
| 14 | 4,58 | 1 | 4,84 | 50 | 4,96 |
| 4 | 4,58 | 6 | 4,85 | 23 | 4,97 |
| 18 | 4,67 | 47 | 4,85 | 19 | 5,00 |
| 3 | 4,67 | 31 | 4,86 | 2 | 5,00 |
| 33 | 4,67 | 34 | 4,86 | 49 | 5,02 |
| 48 | 4,70 | 17 | 4,86 | 43 | 5,09 |
| 52 | 4,72 | 5 | 4,86 | 46 | 5,15 U |
| 39 | 4,73 | 54 | 4,88 | 26 | 5,50 U |
| 25 | 4,75 | 10 | 4,88 | 12 | 5,50 U |
| 42 | 4,76 | 53 | 4,89 | 9 | 5,81 U |
| 13 | 4,77 | 51 | 4,90 | | |

U = Omitted result

Table 5.3. Statistics - Alkalinity, mmol/l**Sample A**

| | | | |
|---------------------------|-------|-----------------------------|-------|
| Number of participants | 48 | Range | 0,051 |
| Number of omitted results | 12 | Variance | 0,000 |
| True value | 0,085 | Standard deviation | 0,014 |
| Mean value | 0,088 | Relative standard deviation | 16,4% |
| Median value | 0,085 | Relative error | 3,0% |

Analytical results in ascending order:

| | | | | | |
|----|---------|----|-------|----|---------|
| 12 | 0,005 U | 48 | 0,080 | 33 | 0,097 |
| 35 | 0,015 U | 1 | 0,080 | 2 | 0,100 |
| 16 | 0,038 U | 54 | 0,080 | 38 | 0,104 |
| 52 | 0,045 U | 6 | 0,081 | 41 | 0,110 |
| 23 | 0,069 | 24 | 0,083 | 17 | 0,114 |
| 8 | 0,070 | 14 | 0,085 | 5 | 0,118 |
| 20 | 0,072 | 34 | 0,085 | 27 | 0,120 |
| 56 | 0,073 | 53 | 0,085 | 26 | 0,120 |
| 18 | 0,074 | 39 | 0,087 | 32 | 0,130 U |
| 4 | 0,074 | 47 | 0,087 | 49 | 0,136 U |
| 28 | 0,075 | 21 | 0,088 | 3 | 0,140 U |
| 29 | 0,075 | 42 | 0,089 | 36 | 0,150 U |
| 31 | 0,078 | 25 | 0,089 | 11 | 0,150 U |
| 7 | 0,078 | 10 | 0,089 | 43 | 0,200 U |
| 55 | 0,079 | 50 | 0,089 | 46 | 0,260 U |
| 9 | 0,080 | 37 | 0,096 | 19 | 0,350 U |

Sample B

| | | | |
|---------------------------|-------|-----------------------------|-------|
| Number of participants | 48 | Range | 0,073 |
| Number of omitted results | 12 | Variance | 0,000 |
| True value | 0,170 | Standard deviation | 0,016 |
| Mean value | 0,171 | Relative standard deviation | 9,4% |
| Median value | 0,170 | Relative error | 0,8% |

Analytical results in ascending order:

| | | | | | |
|----|---------|----|-------|----|---------|
| 12 | 0,009 U | 7 | 0,165 | 54 | 0,180 |
| 35 | 0,050 U | 1 | 0,165 | 2 | 0,180 |
| 16 | 0,084 U | 31 | 0,169 | 42 | 0,181 |
| 52 | 0,088 U | 50 | 0,170 | 17 | 0,200 |
| 24 | 0,137 | 47 | 0,170 | 26 | 0,200 |
| 55 | 0,150 | 10 | 0,170 | 41 | 0,200 |
| 29 | 0,150 | 6 | 0,170 | 5 | 0,207 |
| 9 | 0,150 | 33 | 0,171 | 27 | 0,210 |
| 23 | 0,158 | 53 | 0,171 | 32 | 0,220 U |
| 48 | 0,160 | 21 | 0,171 | 36 | 0,220 U |
| 4 | 0,160 | 34 | 0,172 | 49 | 0,220 U |
| 20 | 0,161 | 39 | 0,172 | 3 | 0,230 U |
| 18 | 0,161 | 38 | 0,172 | 11 | 0,250 U |
| 28 | 0,162 | 14 | 0,173 | 43 | 0,300 U |
| 56 | 0,164 | 25 | 0,174 | 46 | 0,340 U |
| 37 | 0,164 | 8 | 0,180 | 19 | 0,490 U |

U = Omitted result

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

| | | | |
|---------------------------|-----|-----------------------------|-------|
| Number of participants | 52 | Range | 117 |
| Number of omitted results | 17 | Variance | 1230 |
| True value | 120 | Standard deviation | 35 |
| Mean value | 119 | Relative standard deviation | 29,4% |
| Median value | 118 | Relative error | -0,7% |

Analytical results in ascending order:

| | | | | | |
|----|------|----|------|----|-------|
| 37 | 0 U | 48 | 84 U | 7 | 140 |
| 33 | 0 U | 39 | 84 | 20 | 142 |
| 15 | 0 U | 21 | 86 | 56 | 144 |
| 29 | 2 U | 36 | 90 | 27 | 146 |
| 55 | 12 U | 44 | 90 | 12 | 146 |
| 38 | 14 U | 51 | 90 | 43 | 151 |
| 9 | 15 U | 46 | 90 | 18 | 155 |
| 11 | 18 U | 50 | 92 | 3 | 162 |
| 47 | 22 U | 34 | 97 | 5 | 169 U |
| 45 | 34 U | 32 | 110 | 24 | 172 |
| 10 | 40 U | 23 | 112 | 49 | 179 |
| 26 | 48 U | 30 | 117 | 31 | 179 |
| 25 | 63 | 17 | 118 | 42 | 180 |
| 14 | 69 | 6 | 120 | 54 | 191 U |
| 40 | 72 | 53 | 128 | 16 | 203 U |
| 22 | 75 | 19 | 135 | 4 | 268 U |
| 1 | 79 | 28 | 138 | | |
| 41 | 81 | 35 | 139 | | |

Sample B

| | | | |
|---------------------------|-----|-----------------------------|-------|
| Number of participants | 52 | Range | 103 |
| Number of omitted results | 17 | Variance | 341 |
| True value | 182 | Standard deviation | 18 |
| Mean value | 179 | Relative standard deviation | 10,3% |
| Median value | 182 | Relative error | -1,7% |

Analytical results in ascending order:

| | | | | | |
|----|-------|----|-----|----|--------|
| 40 | 118 | 43 | 174 | 1 | 190 |
| 29 | 130 U | 30 | 177 | 18 | 190 |
| 44 | 138 | 34 | 178 | 53 | 191 |
| 46 | 148 | 12 | 179 | 27 | 192 |
| 36 | 150 | 22 | 180 | 26 | 195 U |
| 9 | 150 U | 32 | 180 | 54 | 196 U |
| 38 | 158 U | 35 | 180 | 3 | 196 |
| 33 | 160 U | 28 | 181 | 20 | 197 |
| 10 | 160 U | 50 | 182 | 45 | 202 U |
| 47 | 168 U | 39 | 182 | 42 | 203 |
| 25 | 169 | 7 | 182 | 16 | 213 U |
| 14 | 169 | 19 | 183 | 11 | 215 U |
| 4 | 170 U | 24 | 184 | 49 | 221 |
| 56 | 170 | 21 | 184 | 5 | 259 U |
| 51 | 170 | 31 | 185 | 48 | 863 U |
| 23 | 170 | 41 | 188 | 15 | 1400 U |
| 37 | 173 U | 17 | 188 | | |
| 55 | 174 U | 6 | 190 | | |

U = Omitted result

Table 5.5. Statistics - Chloride, mg/l**Sample A**

| | | | |
|---------------------------|------|-----------------------------|------|
| Number of participants | 54 | Range | 0,94 |
| Number of omitted results | 2 | Variance | 0,03 |
| True value | 2,03 | Standard deviation | 0,19 |
| Mean value | 2,05 | Relative standard deviation | 9,1% |
| Median value | 2,03 | Relative error | 0,8% |

Analytical results in ascending order:

| | | | | | |
|----|------|----|------|----|--------|
| 44 | 1,56 | 40 | 2,00 | 3 | 2,10 |
| 27 | 1,65 | 52 | 2,00 | 13 | 2,11 |
| 6 | 1,80 | 50 | 2,00 | 23 | 2,13 |
| 29 | 1,80 | 36 | 2,00 | 20 | 2,14 |
| 28 | 1,83 | 51 | 2,00 | 5 | 2,16 |
| 10 | 1,84 | 39 | 2,02 | 56 | 2,18 |
| 19 | 1,90 | 54 | 2,03 | 45 | 2,20 |
| 53 | 1,90 | 21 | 2,03 | 22 | 2,20 |
| 18 | 1,90 | 47 | 2,03 | 48 | 2,21 |
| 12 | 1,92 | 33 | 2,04 | 55 | 2,21 |
| 49 | 1,93 | 17 | 2,04 | 14 | 2,28 |
| 35 | 1,93 | 31 | 2,04 | 16 | 2,34 |
| 34 | 1,93 | 41 | 2,04 | 4 | 2,41 |
| 32 | 1,94 | 38 | 2,04 | 11 | 2,47 |
| 37 | 1,95 | 1 | 2,04 | 42 | 2,47 |
| 30 | 1,95 | 7 | 2,04 | 24 | 2,50 |
| 26 | 1,98 | 25 | 2,07 | 15 | 5,13 U |
| 43 | 1,99 | 9 | 2,09 | 2 | 5,50 U |

Sample B

| | | | |
|---------------------------|------|-----------------------------|-------|
| Number of participants | 54 | Range | 1,17 |
| Number of omitted results | 2 | Variance | 0,05 |
| True value | 3,58 | Standard deviation | 0,22 |
| Mean value | 3,55 | Relative standard deviation | 6,3% |
| Median value | 3,58 | Relative error | -0,7% |

Analytical results in ascending order:

| | | | | | |
|----|------|----|------|----|--------|
| 12 | 2,93 | 10 | 3,50 | 23 | 3,64 |
| 27 | 3,07 | 7 | 3,51 | 26 | 3,64 |
| 29 | 3,10 | 17 | 3,54 | 9 | 3,66 |
| 44 | 3,27 | 39 | 3,54 | 21 | 3,67 |
| 6 | 3,30 | 35 | 3,56 | 48 | 3,68 |
| 30 | 3,32 | 22 | 3,56 | 56 | 3,69 |
| 25 | 3,33 | 32 | 3,56 | 19 | 3,70 |
| 4 | 3,34 | 37 | 3,57 | 45 | 3,70 |
| 28 | 3,34 | 47 | 3,58 | 3 | 3,70 |
| 40 | 3,36 | 33 | 3,59 | 14 | 3,87 |
| 53 | 3,40 | 36 | 3,60 | 16 | 3,87 |
| 51 | 3,42 | 38 | 3,60 | 42 | 3,87 |
| 54 | 3,42 | 52 | 3,60 | 20 | 3,92 |
| 43 | 3,42 | 18 | 3,60 | 5 | 3,95 |
| 31 | 3,43 | 55 | 3,61 | 11 | 3,97 |
| 49 | 3,44 | 50 | 3,61 | 24 | 4,10 |
| 34 | 3,46 | 1 | 3,63 | 2 | 7,50 U |
| 41 | 3,49 | 13 | 3,63 | 15 | 9,72 U |

U = Omitted result

Table 5.6. Statistics - Sulfate, mg/l**Sample A**

| | | | |
|---------------------------|------|-----------------------------|-------|
| Number of participants | 52 | Range | 1,77 |
| Number of omitted results | 3 | Variance | 0,09 |
| True value | 4,00 | Standard deviation | 0,30 |
| Mean value | 3,95 | Relative standard deviation | 7,6% |
| Median value | 4,00 | Relative error | -1,3% |

Analytical results in ascending order:

| | | | | | |
|----|--------|----|--------|----|--------|
| 2 | 3,00 | 31 | 3,95 | 21 | 4,08 |
| 9 | 3,00 U | 17 | 3,95 | 22 | 4,09 |
| 48 | 3,16 | 49 | 3,95 | 52 | 4,10 |
| 24 | 3,40 | 20 | 3,96 | 32 | 4,10 |
| 45 | 3,50 | 50 | 3,97 | 7 | 4,10 |
| 44 | 3,56 | 43 | 3,98 | 38 | 4,12 |
| 11 | 3,60 | 51 | 3,99 | 39 | 4,13 |
| 27 | 3,62 | 46 | 4,00 U | 54 | 4,18 |
| 40 | 3,64 | 19 | 4,00 | 56 | 4,20 |
| 53 | 3,70 | 13 | 4,01 | 29 | 4,20 |
| 10 | 3,80 | 35 | 4,01 | 36 | 4,20 |
| 12 | 3,80 | 23 | 4,01 | 4 | 4,25 |
| 34 | 3,83 | 25 | 4,02 | 55 | 4,32 |
| 18 | 3,90 | 41 | 4,04 | 14 | 4,49 |
| 3 | 3,90 | 33 | 4,05 | 5 | 4,77 |
| 6 | 3,90 | 1 | 4,05 | 15 | 7,08 U |
| 37 | 3,90 | 47 | 4,06 | | |
| 28 | 3,91 | 30 | 4,07 | | |

Sample B

| | | | |
|---------------------------|------|-----------------------------|-------|
| Number of participants | 52 | Range | 2,46 |
| Number of omitted results | 3 | Variance | 0,16 |
| True value | 5,33 | Standard deviation | 0,40 |
| Mean value | 5,24 | Relative standard deviation | 7,7% |
| Median value | 5,33 | Relative error | -1,7% |

Analytical results in ascending order:

| | | | | | |
|----|--------|----|------|----|---------|
| 9 | 3,30 U | 31 | 5,25 | 39 | 5,38 |
| 2 | 4,00 | 20 | 5,26 | 18 | 5,40 |
| 48 | 4,15 | 49 | 5,27 | 19 | 5,40 |
| 24 | 4,20 | 50 | 5,28 | 41 | 5,42 |
| 45 | 4,60 | 17 | 5,30 | 30 | 5,43 |
| 53 | 4,70 | 10 | 5,31 | 33 | 5,45 |
| 27 | 4,80 | 22 | 5,32 | 52 | 5,45 |
| 40 | 4,90 | 13 | 5,33 | 55 | 5,45 |
| 12 | 5,00 | 54 | 5,34 | 38 | 5,47 |
| 44 | 5,02 | 47 | 5,34 | 11 | 5,60 |
| 32 | 5,05 | 43 | 5,34 | 29 | 5,60 |
| 3 | 5,10 | 25 | 5,35 | 36 | 5,70 |
| 34 | 5,15 | 7 | 5,35 | 14 | 5,84 |
| 6 | 5,20 | 21 | 5,35 | 5 | 6,46 |
| 51 | 5,22 | 23 | 5,35 | 15 | 8,39 U |
| 56 | 5,23 | 37 | 5,36 | 46 | 49,10 U |
| 28 | 5,24 | 4 | 5,37 | | |
| 35 | 5,24 | 1 | 5,37 | | |

U = Omitted result

Table 5.7. Statistics - Calcium, mg/l**Sample A**

| | | | | |
|---------------------------|------|-----------------------------|--|------|
| Number of participants | | | | |
| Number of omitted results | 55 | Range | | 1,47 |
| True value | 4 | Variance | | 0,07 |
| Mean value | 2,75 | Standard deviation | | 0,26 |
| Median value | 2,77 | Relative standard deviation | | 9,5% |
| | 2,75 | Relative error | | 0,6% |

Analytical results in ascending order:

| | | | | | |
|----|--------|----|------|----|--------|
| 42 | 0,18 U | 31 | 2,68 | 28 | 2,84 |
| 22 | 1,73 U | 2 | 2,70 | 26 | 2,86 |
| 10 | 2,10 | 50 | 2,71 | 43 | 2,87 |
| 29 | 2,10 | 39 | 2,72 | 3 | 2,90 |
| 57 | 2,33 | 13 | 2,74 | 37 | 2,90 |
| 32 | 2,40 | 20 | 2,74 | 7 | 2,94 |
| 23 | 2,48 | 1 | 2,74 | 11 | 3,00 |
| 5 | 2,48 | 34 | 2,75 | 19 | 3,00 |
| 14 | 2,51 | 51 | 2,75 | 45 | 3,05 |
| 21 | 2,58 | 49 | 2,76 | 36 | 3,10 |
| 52 | 2,61 | 6 | 2,76 | 53 | 3,10 |
| 17 | 2,64 | 9 | 2,77 | 56 | 3,11 |
| 55 | 2,64 | 38 | 2,77 | 27 | 3,13 |
| 33 | 2,64 | 12 | 2,77 | 54 | 3,40 |
| 47 | 2,66 | 4 | 2,78 | 41 | 3,57 |
| 18 | 2,66 | 24 | 2,81 | 46 | 4,19 U |
| 48 | 2,67 | 35 | 2,83 | 15 | 5,16 U |
| 40 | 2,67 | 30 | 2,83 | | |
| 44 | 2,67 | 16 | 2,83 | | |

Sample B

| | | | | |
|---------------------------|------|-----------------------------|--|-------|
| Number of participants | | | | |
| Number of omitted results | 55 | Range | | 1,68 |
| True value | 4 | Variance | | 0,13 |
| Mean value | 3,55 | Standard deviation | | 0,37 |
| Median value | 3,60 | Relative standard deviation | | 10,2% |
| | 3,55 | Relative error | | 1,4% |

Analytical results in ascending order:

| | | | | | |
|----|--------|----|------|----|--------|
| 42 | 0,64 U | 34 | 3,50 | 11 | 3,80 |
| 22 | 2,41 U | 18 | 3,50 | 37 | 3,80 |
| 2 | 2,80 | 50 | 3,51 | 35 | 3,82 |
| 29 | 2,80 | 51 | 3,52 | 48 | 3,84 |
| 10 | 2,90 | 1 | 3,52 | 26 | 3,85 |
| 5 | 3,03 | 9 | 3,53 | 56 | 3,97 |
| 57 | 3,04 | 39 | 3,53 | 27 | 4,00 |
| 32 | 3,09 | 16 | 3,54 | 53 | 4,00 |
| 23 | 3,22 | 4 | 3,55 | 36 | 4,00 |
| 21 | 3,28 | 55 | 3,55 | 24 | 4,01 |
| 52 | 3,34 | 20 | 3,57 | 30 | 4,10 |
| 47 | 3,40 | 38 | 3,57 | 54 | 4,17 |
| 17 | 3,40 | 28 | 3,58 | 45 | 4,18 |
| 44 | 3,41 | 49 | 3,59 | 43 | 4,43 |
| 31 | 3,43 | 19 | 3,60 | 41 | 4,48 |
| 12 | 3,46 | 40 | 3,70 | 46 | 5,28 U |
| 33 | 3,47 | 3 | 3,70 | 15 | 5,47 U |
| 6 | 3,48 | 14 | 3,74 | | |
| 13 | 3,48 | 7 | 3,78 | | |

U = Omitted result

Table 5.8. Statistics - Magnesium, mg/l**Sample A**

| | | | |
|---------------------------|------|-----------------------------|-------|
| Number of participants | | | |
| Number of omitted results | 55 | Range | 0,30 |
| True value | 5 | Variance | 0,00 |
| Mean value | 0,47 | Standard deviation | 0,05 |
| Median value | 0,47 | Relative standard deviation | 10,7% |
| | 0,47 | Relative error | 0,9% |

Analytical results in ascending order:

| | | | | | |
|----|--------|----|------|----|--------|
| 45 | 0,23 U | 20 | 0,46 | 7 | 0,49 |
| 42 | 0,31 | 21 | 0,46 | 15 | 0,49 |
| 22 | 0,32 U | 34 | 0,46 | 27 | 0,49 |
| 37 | 0,39 | 39 | 0,46 | 30 | 0,49 |
| 29 | 0,40 | 33 | 0,47 | 50 | 0,49 |
| 57 | 0,42 | 4 | 0,47 | 12 | 0,50 |
| 6 | 0,43 | 48 | 0,47 | 52 | 0,50 |
| 5 | 0,43 | 53 | 0,47 | 14 | 0,50 |
| 40 | 0,44 | 51 | 0,47 | 35 | 0,51 |
| 54 | 0,44 | 28 | 0,47 | 43 | 0,56 |
| 10 | 0,44 | 13 | 0,48 | 49 | 0,57 |
| 26 | 0,45 | 32 | 0,48 | 36 | 0,60 |
| 47 | 0,45 | 38 | 0,48 | 3 | 0,60 |
| 44 | 0,45 | 1 | 0,48 | 24 | 0,61 |
| 55 | 0,45 | 31 | 0,48 | 2 | 0,65 U |
| 16 | 0,45 | 56 | 0,48 | 19 | 1,00 U |
| 17 | 0,46 | 9 | 0,48 | 46 | 1,10 U |
| 23 | 0,46 | 41 | 0,49 | | |
| 18 | 0,46 | 11 | 0,49 | | |

Sample B

| | | | |
|---------------------------|------|-----------------------------|------|
| Number of participants | | | |
| Number of omitted results | 55 | Range | 0,52 |
| True value | 5 | Variance | 0,01 |
| Mean value | 0,86 | Standard deviation | 0,08 |
| Median value | 0,87 | Relative standard deviation | 9,1% |
| | 0,86 | Relative error | 1,5% |

Analytical results in ascending order:

| | | | | | |
|----|--------|----|------|----|--------|
| 45 | 0,23 U | 39 | 0,85 | 15 | 0,90 |
| 22 | 0,56 U | 21 | 0,85 | 48 | 0,91 |
| 24 | 0,61 | 50 | 0,85 | 11 | 0,91 |
| 5 | 0,76 | 28 | 0,86 | 53 | 0,91 |
| 57 | 0,79 | 13 | 0,86 | 41 | 0,92 |
| 37 | 0,79 | 51 | 0,86 | 30 | 0,95 |
| 6 | 0,80 | 9 | 0,86 | 14 | 0,95 |
| 10 | 0,80 | 4 | 0,86 | 35 | 0,97 |
| 44 | 0,81 | 20 | 0,86 | 49 | 0,98 |
| 54 | 0,81 | 18 | 0,86 | 26 | 0,98 |
| 47 | 0,82 | 40 | 0,86 | 3 | 1,00 |
| 29 | 0,82 | 33 | 0,87 | 19 | 1,00 U |
| 16 | 0,82 | 12 | 0,87 | 36 | 1,00 |
| 23 | 0,82 | 1 | 0,87 | 27 | 1,01 |
| 42 | 0,83 | 31 | 0,88 | 43 | 1,13 |
| 34 | 0,83 | 56 | 0,88 | 2 | 1,30 U |
| 55 | 0,84 | 7 | 0,89 | 46 | 1,38 U |
| 17 | 0,84 | 38 | 0,89 | | |
| 32 | 0,84 | 52 | 0,90 | | |

U = Omitted result

Table 5.9. Statistics - Sodium, mg/l**Sample A**

| | | | | |
|---------------------------|------|-----------------------------|--|------|
| Number of participants | | | | |
| Number of omitted results | 53 | Range | | 0,75 |
| True value | 2 | Variance | | 0,02 |
| Mean value | 1,73 | Standard deviation | | 0,12 |
| Median value | 1,74 | Relative standard deviation | | 7,1% |
| | 1,73 | Relative error | | 0,5% |

Analytical results in ascending order:

| | | | | | |
|----|--------|----|--------|----|------|
| 22 | 1,01 U | 37 | 1,70 | 13 | 1,77 |
| 56 | 1,35 | 6 | 1,70 | 54 | 1,78 |
| 48 | 1,55 | 39 | 1,70 | 32 | 1,78 |
| 38 | 1,59 | 35 | 1,70 | 26 | 1,79 |
| 21 | 1,59 | 15 | 1,71 U | 52 | 1,79 |
| 55 | 1,60 | 28 | 1,71 | 19 | 1,80 |
| 11 | 1,60 | 17 | 1,72 | 10 | 1,80 |
| 44 | 1,62 | 27 | 1,72 | 14 | 1,81 |
| 18 | 1,63 | 49 | 1,72 | 36 | 1,82 |
| 42 | 1,63 | 51 | 1,73 | 9 | 1,83 |
| 23 | 1,65 | 50 | 1,73 | 47 | 1,89 |
| 33 | 1,66 | 57 | 1,74 | 41 | 1,89 |
| 20 | 1,68 | 31 | 1,74 | 3 | 1,90 |
| 16 | 1,68 | 1 | 1,75 | 43 | 1,94 |
| 45 | 1,70 | 7 | 1,75 | 12 | 1,96 |
| 34 | 1,70 | 24 | 1,75 | 5 | 2,05 |
| 53 | 1,70 | 30 | 1,76 | 29 | 2,10 |
| 4 | 1,70 | 40 | 1,76 | | |

Sample B

| | | | | |
|---------------------------|------|-----------------------------|--|------|
| Number of participants | | | | |
| Number of omitted results | 53 | Range | | 1,25 |
| True value | 2 | Variance | | 0,04 |
| Mean value | 2,84 | Standard deviation | | 0,20 |
| Median value | 2,85 | Relative standard deviation | | 7,1% |
| | 2,84 | Relative error | | 0,3% |

Analytical results in ascending order:

| | | | | | |
|----|--------|----|------|----|------|
| 22 | 1,74 U | 48 | 2,79 | 3 | 2,90 |
| 15 | 1,83 U | 45 | 2,80 | 42 | 2,93 |
| 56 | 2,15 | 19 | 2,80 | 36 | 2,95 |
| 11 | 2,52 | 13 | 2,81 | 52 | 2,95 |
| 55 | 2,52 | 10 | 2,82 | 35 | 2,96 |
| 49 | 2,57 | 7 | 2,82 | 12 | 2,96 |
| 51 | 2,62 | 17 | 2,82 | 50 | 2,97 |
| 21 | 2,63 | 37 | 2,83 | 26 | 2,97 |
| 44 | 2,66 | 39 | 2,83 | 14 | 2,99 |
| 23 | 2,71 | 6 | 2,84 | 24 | 3,00 |
| 34 | 2,73 | 28 | 2,84 | 53 | 3,00 |
| 33 | 2,73 | 47 | 2,85 | 9 | 3,00 |
| 16 | 2,74 | 1 | 2,85 | 41 | 3,02 |
| 27 | 2,74 | 38 | 2,86 | 30 | 3,11 |
| 40 | 2,74 | 32 | 2,88 | 5 | 3,27 |
| 4 | 2,77 | 54 | 2,89 | 43 | 3,37 |
| 18 | 2,78 | 31 | 2,89 | 29 | 3,40 |
| 20 | 2,78 | 57 | 2,90 | | |

U = Omitted result

Table 5.10. Statistics - Potassium, mg/l**Sample A**

| | | | | | |
|--|--------|----|-----------------------------|----|--------|
| Number of participants | | | | | |
| Number of omitted results | 53 | | Range | | 0,15 |
| True value | 6 | | Variance | | 0,00 |
| Mean value | 0,36 | | Standard deviation | | 0,03 |
| Median value | 0,36 | | Relative standard deviation | | 8,9% |
| | 0,36 | | Relative error | | -0,2% |
| Analytical results in ascending order: | | | | | |
| 56 | 0,10 U | 7 | 0,35 | 18 | 0,37 |
| 33 | 0,11 U | 57 | 0,35 | 31 | 0,37 |
| 5 | 0,16 U | 26 | 0,35 | 49 | 0,37 |
| 48 | 0,20 U | 24 | 0,35 | 28 | 0,37 |
| 47 | 0,29 | 14 | 0,36 | 27 | 0,37 |
| 35 | 0,29 U | 12 | 0,36 | 32 | 0,38 |
| 3 | 0,30 | 11 | 0,36 | 41 | 0,38 |
| 45 | 0,30 | 40 | 0,36 | 38 | 0,38 |
| 20 | 0,31 | 30 | 0,36 | 16 | 0,38 |
| 15 | 0,32 | 4 | 0,36 | 39 | 0,39 |
| 55 | 0,32 | 6 | 0,36 | 50 | 0,39 |
| 51 | 0,32 | 37 | 0,36 | 19 | 0,40 |
| 1 | 0,33 | 53 | 0,36 | 22 | 0,40 |
| 9 | 0,33 | 23 | 0,36 | 13 | 0,42 |
| 42 | 0,34 | 17 | 0,37 | 43 | 0,44 |
| 44 | 0,34 | 34 | 0,37 | 36 | 0,44 |
| 10 | 0,34 | 54 | 0,37 | 29 | 0,52 U |
| 52 | 0,34 | 21 | 0,37 | | |

Sample B

| | | | | | |
|--|--------|----|-----------------------------|----|--------|
| Number of participants | | | | | |
| Number of omitted results | 53 | | Range | | 0,17 |
| True value | 6 | | Variance | | 0,00 |
| Mean value | 0,37 | | Standard deviation | | 0,03 |
| Median value | 0,37 | | Relative standard deviation | | 9,4% |
| | 0,37 | | Relative error | | -0,6% |
| Analytical results in ascending order: | | | | | |
| 56 | 0,10 U | 13 | 0,36 | 24 | 0,38 |
| 48 | 0,17 U | 23 | 0,36 | 10 | 0,38 |
| 5 | 0,22 U | 53 | 0,36 | 47 | 0,38 |
| 51 | 0,28 | 11 | 0,36 | 33 | 0,38 U |
| 3 | 0,30 | 14 | 0,36 | 41 | 0,38 |
| 45 | 0,30 | 17 | 0,36 | 39 | 0,39 |
| 15 | 0,32 | 40 | 0,37 | 30 | 0,39 |
| 20 | 0,33 | 34 | 0,37 | 31 | 0,39 |
| 9 | 0,33 | 4 | 0,37 | 19 | 0,40 |
| 42 | 0,34 | 28 | 0,37 | 54 | 0,41 |
| 22 | 0,34 | 21 | 0,37 | 43 | 0,42 |
| 49 | 0,34 | 18 | 0,37 | 36 | 0,43 |
| 55 | 0,35 | 27 | 0,37 | 37 | 0,44 |
| 7 | 0,35 | 44 | 0,37 | 38 | 0,44 |
| 52 | 0,35 | 16 | 0,37 | 1 | 0,45 |
| 12 | 0,35 | 50 | 0,37 | 29 | 0,59 U |
| 26 | 0,35 | 32 | 0,37 | 35 | 0,60 U |
| 57 | 0,35 | 6 | 0,38 | | |

U = Omitted result

Table 5.11. Statistics - Aluminium, µg/l**Sample C**

| | | | |
|---------------------------|----|-----------------------------|-------|
| Number of participants | | | |
| Number of omitted results | 22 | Range | 79 |
| True value | 1 | Variance | 291 |
| Mean value | 87 | Standard deviation | 17 |
| Median value | 86 | Relative standard deviation | 19,8% |
| | 87 | Relative error | -0,8% |

Analytical results in ascending order:

| | | | | | |
|----|------|----|----|----|-----|
| 45 | 41 U | 44 | 83 | 6 | 95 |
| 54 | 47 | 16 | 83 | 20 | 95 |
| 1 | 57 | 32 | 86 | 49 | 99 |
| 39 | 63 | 52 | 87 | 11 | 103 |
| 18 | 76 | 7 | 89 | 41 | 108 |
| 30 | 82 | 8 | 89 | 56 | 126 |
| 28 | 82 | 36 | 90 | | |
| 57 | 83 | 19 | 90 | | |

Sample D

| | | | |
|---------------------------|-----|-----------------------------|-------|
| Number of participants | | | |
| Number of omitted results | 22 | Range | 91 |
| True value | 1 | Variance | 479 |
| Mean value | 148 | Standard deviation | 22 |
| Median value | 145 | Relative standard deviation | 15,1% |
| | 148 | Relative error | -1,9% |

Analytical results in ascending order:

| | | | | | |
|----|------|----|-----|----|-----|
| 45 | 42 U | 44 | 141 | 6 | 159 |
| 54 | 94 | 49 | 145 | 36 | 160 |
| 39 | 102 | 52 | 146 | 11 | 162 |
| 1 | 120 | 16 | 148 | 20 | 165 |
| 57 | 126 | 28 | 149 | 41 | 177 |
| 32 | 135 | 19 | 150 | 56 | 185 |
| 30 | 138 | 7 | 152 | | |
| 18 | 138 | 8 | 156 | | |

U = Omitted result

Table 5.12. Statistics - Aluminium, reactive, µg/l**Sample C**

| | | | | |
|---------------------------|----|-----------------------------|--|-------|
| Number of participants | | | | |
| Number of omitted results | 12 | Range | | 11 |
| True value | 8 | Variance | | 22 |
| Mean value | 31 | Standard deviation | | 5 |
| Median value | 30 | Relative standard deviation | | 16,0% |
| | 31 | Relative error | | -4,4% |

Analytical results in ascending order:

| | | | | | |
|----|-----|----|------|----|------|
| 7 | 0 U | 28 | 31 | 16 | 81 U |
| 57 | 5 U | 6 | 34 | 8 | 87 U |
| 50 | 23 | 18 | 40 U | 41 | 93 U |
| 52 | 30 | 47 | 57 U | 46 | 96 U |

Sample D

| | | | | |
|---------------------------|----|-----------------------------|--|-------|
| Number of participants | | | | |
| Number of omitted results | 12 | Range | | 24 |
| True value | 8 | Variance | | 108 |
| Mean value | 44 | Standard deviation | | 10 |
| Median value | 45 | Relative standard deviation | | 23,3% |
| | 44 | Relative error | | 1,5% |

Analytical results in ascending order:

| | | | | | |
|----|------|----|-------|----|-------|
| 7 | 10 U | 6 | 48 | 46 | 132 U |
| 57 | 12 U | 52 | 58 | 16 | 133 U |
| 50 | 34 | 18 | 83 U | 8 | 147 U |
| 28 | 39 | 47 | 117 U | 41 | 164 U |

U = Omitted result

Table 5.13. Statistics - Aluminium, nonlabile, µg/l**Sample C**

| | | | | |
|---------------------------|----|-----------------------------|--|-------|
| Number of participants | | | | |
| Number of omitted results | 10 | Range | | 20 |
| True value | 4 | Variance | | 52 |
| Mean value | 49 | Standard deviation | | 7 |
| Median value | 51 | Relative standard deviation | | 14,2% |
| | 49 | Relative error | | 4,1% |

Analytical results in ascending order:

| | | | | | |
|----|------|----|----|----|------|
| 50 | 17 U | 1 | 47 | 16 | 63 |
| 28 | 24 U | 47 | 47 | 57 | 78 U |
| 6 | 28 U | 18 | 50 | | |
| 7 | 43 | 52 | 57 | | |

Sample D

| | | | | |
|---------------------------|----|-----------------------------|--|------|
| Number of participants | | | | |
| Number of omitted results | 10 | Range | | 22 |
| True value | 4 | Variance | | 74 |
| Mean value | 95 | Standard deviation | | 9 |
| Median value | 96 | Relative standard deviation | | 9,0% |
| | 95 | Relative error | | 1,2% |

Analytical results in ascending order:

| | | | | | |
|----|------|----|-----|----|-------|
| 50 | 22 U | 1 | 88 | 16 | 110 |
| 28 | 28 U | 7 | 92 | 57 | 114 U |
| 6 | 30 U | 47 | 98 | | |
| 52 | 88 | 18 | 101 | | |

U = Omitted result

Table 5.14. Statistics - Dissolved organic carbon, mg/l**Sample C**

| | | | |
|---------------------------|------|-----------------------------|-------|
| Number of participants | | | |
| Number of omitted results | 23 | Range | 1,31 |
| True value | 1 | Variance | 0,16 |
| Mean value | 3,79 | Standard deviation | 0,39 |
| Median value | 3,79 | Relative standard deviation | 10,4% |
| | 3,79 | Relative error | -0,1% |

Analytical results in ascending order:

| | | | | | |
|----|------|----|------|----|---------|
| 33 | 3,29 | 32 | 3,50 | 55 | 4,00 |
| 39 | 3,36 | 44 | 3,57 | 37 | 4,04 |
| 18 | 3,40 | 50 | 3,73 | 45 | 4,14 |
| 36 | 3,40 | 21 | 3,84 | 57 | 4,50 |
| 28 | 3,45 | 23 | 3,84 | 11 | 4,57 |
| 1 | 3,49 | 20 | 3,85 | 54 | 4,60 |
| 52 | 3,50 | 7 | 3,85 | 35 | 27,27 U |
| 16 | 3,50 | 19 | 3,90 | | |

Sample D

| | | | |
|---------------------------|------|-----------------------------|-------|
| Number of participants | | | |
| Number of omitted results | 23 | Range | 1,40 |
| True value | 1 | Variance | 0,18 |
| Mean value | 3,69 | Standard deviation | 0,42 |
| Median value | 3,76 | Relative standard deviation | 11,2% |
| | 3,69 | Relative error | 1,8% |

Analytical results in ascending order:

| | | | | | |
|----|------|----|------|----|---------|
| 1 | 3,33 | 28 | 3,49 | 21 | 3,96 |
| 44 | 3,34 | 16 | 3,50 | 19 | 4,10 |
| 18 | 3,40 | 23 | 3,65 | 45 | 4,23 |
| 52 | 3,40 | 20 | 3,72 | 54 | 4,40 |
| 32 | 3,40 | 50 | 3,73 | 57 | 4,60 |
| 36 | 3,40 | 7 | 3,75 | 11 | 4,73 |
| 39 | 3,42 | 55 | 3,80 | 35 | 27,10 U |
| 33 | 3,44 | 37 | 3,87 | | |

U = Omitted result

Table 5.15. Statistics - Chemical oxygen demand, mg/l**Sample C**

| | | | |
|---------------------------|------|-----------------------------|-------|
| Number of participants | | | |
| Number of omitted results | 13 | Range | 3,10 |
| True value | 0 | Variance | 0,54 |
| Mean value | 4,39 | Standard deviation | 0,73 |
| Median value | 4,31 | Relative standard deviation | 17,0% |
| | 4,39 | Relative error | -1,8% |

Analytical results in ascending order:

| | | | | | |
|----|------|----|------|----|------|
| 56 | 2,30 | 20 | 4,29 | 9 | 4,80 |
| 18 | 3,90 | 41 | 4,39 | 4 | 5,10 |
| 46 | 4,10 | 24 | 4,49 | 45 | 5,40 |
| 36 | 4,10 | 28 | 4,50 | | |
| 2 | 4,20 | 54 | 4,50 | | |

Sample D

| | | | |
|---------------------------|------|-----------------------------|-------|
| Number of participants | | | |
| Number of omitted results | 13 | Range | 2,70 |
| True value | 0 | Variance | 0,40 |
| Mean value | 4,30 | Standard deviation | 0,63 |
| Median value | 4,12 | Relative standard deviation | 15,3% |
| | 4,30 | Relative error | -4,2% |

Analytical results in ascending order:

| | | | | | |
|----|------|----|------|----|------|
| 56 | 2,30 | 2 | 4,10 | 54 | 4,40 |
| 46 | 3,85 | 9 | 4,30 | 24 | 4,65 |
| 41 | 3,97 | 20 | 4,30 | 4 | 5,00 |
| 18 | 4,00 | 45 | 4,30 | | |
| 36 | 4,00 | 28 | 4,40 | | |

U = Omitted result

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

1. Manual for Chemical and Biological Monitoring. Programme Manual. Prepared by the Programme Centre, Norwegian Institute for Water Research. NIVA, Oslo 1987.
2. Norwegian Institute for Water Research, 1987. Intercalibration 8701: pH, K_s, SO₄, Ca. Programme Centre, NIVA, Oslo.
3. Norwegian Institute for Water Research, 1988. Data Report 1987 and available Data from Previous Years. Programme Centre, NIVA, Oslo.
4. Norwegian Institute for Water Research, 1988. Intercalibration 8802: pH, K₂₅, HCO₃, NO₃, SO, Cl, Ca, Mg, Na, K. NIVA, Oslo.
5. Proceedings of the Workshop on Assessment and Monitoring of Acidification in Rivers and Lakes, Espoo, Finland, 3rd to 5th October 1988. Prepared by the Finnish Acidification Research Project, HAPRO, Ministry of Environment, October 1988.
6. Norwegian Institute for Water Research, 1989. Intercalibration 8903: Dissolved organic carbon and aluminium fractions. Programme Centre, NIVA, Oslo. NIVA Rep. 2238-89. ISBN 82-577-1534-4.
7. Note: Some reflections about the determination of pH and alkalinity. Prepared by the Programme Centre, Norwegian Institute for Water Research. Håvard Hovind, NIVA, Oslo October 1989.
8. Hovind, H. 1990. Intercalibration 9004: pH and alkalinity. Programme Centre, NIVA, Oslo. NIVA Rep. 2465-90. ISBN 82-577-1776-2.
- Skjelkvåle, B.L., and Wright, R.F. 1990. Overview of areas sensitive to acidification: Europe. Programme Centre, NIVA, Oslo. Acid Rain Research Report 20/1990. NIVA-report 2405-90. ISBN 82-577-1706-1.
9. Johannessen, M. 1990. Intercalibration in the framework of an international monitoring programme. Proceedings of the third annual Ecological Quality Assurance Workshop, Canada Centre for Inland Waters, Burlington Ontario. Programme Centre, NIVA, Oslo.
10. Norwegian Institute for Water Research, 1990. Data Report 1988. Programme Centre, NIVA, Oslo.
11. Norwegian Institute for Water Research, 1990. Data Report 1989. Programme Centre, NIVA, Oslo.
12. Proceedings for the fifth Meeting of the Programme Task Force Freiburg, Germany, October 17 -19, 1989. Prepared by the Umweltbundesamt, Berlin July 1990.
13. Hovind, H. 1991. Intercalibration 9105: pH, K₂₅, HCO₃, NO₃ + NO₂, Cl, SO₄, Ca, Mg, Na, K and TOC. Programme Centre, NIVA, Oslo. NIVA Rep. 2591-91. ISBN 82-577-1931-5.
14. Norwegian Institute for Water Research, 1991. The Three Year Report. Summary and results 1987 – 1989: Results from the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes. Programme Centre, NIVA, Oslo.
15. Norwegian Institute for Water Research, 1991. Summary of The Three Year Report 1987 – 1989. Programme Centre, NIVA, Oslo.

16. Scientific papers presented at the Sixth Task Force meeting in Sweden 23 - 24 October 1990. Swedish Environmental Protection Agency, Sweden, September 1991.
17. Seventh Task Force meeting of international Co-operative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes. Galway, Ireland. September 30 - October 3 1991. Proceedings.
18. Johannessen, M., Skjelkvåle, B.L. and Jeffries, D. 1992. International cooperative Programme on Assessment and Monitoring of Rivers and Lakes. In: Conference Abstracts, Intern. Conference on Acidic Deposition, Glasgow 16-21, sept. 1992, p. 449. Kluwer Academic Press.
19. Hovind, H. 1992. Intercalibration 9206: pH, K_{25} , HCO_3 , $NO_3 + NO_2$, Cl, SO_4 , Ca, Mg, Na, K, Al and DOC. Programme Centre, NIVA, Oslo. NIVA Rep. 2784-92. ISBN 82-577-2164-6.
20. Norwegian Institute for Water Research, 1992. Data Report 1990. Programme Centre, NIVA, Oslo.
21. Norwegian Institute for Water Research, 1992. Evaluation of the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes. Programme Centre, NIVA, Oslo.
22. Hovind, H. 1993. Intercalibration 9307: pH, K_{25} , HCO_3 , $NO_3 + NO_2$, Cl, SO_4 , Ca, Mg, Na, K, total aluminium, reactive and non-labile aluminium, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA Rep. 2948-93. ISBN 82-577-2370-3.
23. Raddum, G.G. 1993. Intercalibration 9301: Invertebrate Fauna. Programme Centre, NIVA, Oslo. ISBN 82-577-2376-2.
24. Proceedings of the 9th Task Force Meeting in Oisterwijk, the Netherlands, November 1-3, 1993. Programme Centre, NIVA, Oslo.
25. Skjelkvåle, B.L., Newell, A.D. and Johannessen, M. 1993. International Cooperative Programme on Assessment and Monitoring of Rivers and lakes: Status and Results. In: BIOGEMON - Symposium on Ecosystem Behaviour: Evaluation of Integrated Monitoring in small catchments. Prague, September 18-20, 1993. Czech Geological Survey, Prague 1993. s. 274-275.
26. Hovind, H. 1994. Intercomparison 9408: pH, K_{25} , HCO_3 , $NO_3 + NO_2$, Cl, SO_4 , Ca, Mg, Na, K, total aluminium, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA Rep. 3142-94. ISBN 82-577-2616-8.
27. Skjelkvåle, B.L., Newell, A.D., Raddum, G.G, Johannessen, M., Hovind, H., Tjomsland, T. and Wathne, B.M. 1994. The six year report: Acidification of surface water in Europe and North America. Dose/response relationships and long-term trend. Programme Centre NIVA Oslo. Norwegian Institute for Water Research. NIVA Report 3041-94: 135 pp. ISBN 82-577-2499-8.
28. Norwegian Institute for Water Research, 1994. Data Report 1991. Programme Centre, NIVA, Oslo. ISBN 82-577-2662-5.
29. Stoddard, J.L, and Traaen, T.S. 1994. The stages of Nitrogen Saturation: Classification of catchments included in "ICP on Waters". In: M. Hornung, M.A. Stutton and R.B. Wilson (eds.) Mapping and Modelling of Critical Loads for Nitrogen: a Workshop Report. Proceedings of a workshop held in Grange-over-Sands (UK), 24-26 October 1994. pp.69-76.
30. Hovind, H. 1995. Intercomparison 9509: pH, k_{25} , HCO_3 , $NO_3 + NO_2$, Cl, SO_4 , Ca, Mg, Na, K, total aluminium - reactive and nonlabile, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA Rep. 3331-95. ISBN 82-577-2849-7.
31. Traaen, T.S., and Stoddard, J.L. 1995. An assessment of nitrogen leaching from watersheds included in ICP on Waters. Norwegian Institute for Water Research, NIVA Report 86001-3201, 39 pp.

32. Norwegian Institute for Water Research, 1995. Data Report 1992-93. Draft 1994. Programme Centre, NIVA, Oslo. ISBN 82-577-2852-7.
33. Norwegian Institute for Water Research, 1995. Data Report 1992-93. Draft 1994. Part 2, Biology and Site-data. Programme Centre, NIVA, Oslo. ISBN 82-577-2852-7.
34. Raddum, G.G. 1995. Aquatic Fauna: Dose/response and long-term trends. Programme Centre, NIVA, Oslo.
35. Raddum, G.G. 1995. Intercalibration 9502: Invertebrate Fauna. Programme Centre, NIVA, Oslo.
36. Raddum, G.G., and Skjelkvåle, B.L. 1995. Critical limits to invertebrates in different regions in Europe. *Water Air and Soil Poll.* 85: 475-480.
37. Hovind, H. 1996. Intercomparison 9610: pH, K₂₅, HCO₃, NO₃ + NO₂, Cl, SO₄, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA Rep. 3550-96. ISBN 82-577-3099-8.
38. Newell, A.D, and Skjelkvåle, B.L. 1996. Acidification trends in surface waters in the International Program on Acidification of Rivers and Lakes. *Water Air Soil Poll.* 93:27-57.
39. Norwegian Institute for Water Research, 1996. Programme Manual. Programme Centre, NIVA, Oslo. NIVA Rep. 3547-96. ISBN 82-577-3094-7.
40. Raddum, G.G. 1996. Intercalibration 9603: Invertebrate Fauna. Programme Centre, NIVA, Oslo. ISBN 82-577-3095-5.
41. Lükewille, A., Jeffries, D., Johannessen, M., Raddum, G.G., Stoddard, J.L, and Traaen, T.S. 1997. The Nine Year report. Acidification of Surface Waters in Europe and North America. Long-term Development (1980s and 1990s). Programme Centre, NIVA, Oslo ISBN 82-577-3195-1. 168 pp.
42. Hovind, H. 1997. Intercomparison 9711. pH, K₂₅, HCO₃, NO₃ + NO₂, Cl, SO₄, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3716-97. ISBN 82-577-3284-2.
43. Johannessen, M., and Skjelkvåle, B.L. 1997. International Co-operative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes - ICP-Waters; Programme objectives, organization and main results. In: Proceedings to "International Conference on management of Transboundary Waters in Europe" 22-25 September 1997 in Poland. Programme Centre, NIVA, Oslo. ICP-Waters Report 43/1997. ISBN 82-577-3297-4.
44. Henriksen, A., and Posch, M. 1998. Critical load and their exceedances for ICP-Waters sites. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3821-98, ICP-Waters Report 44/1998. ISBN 82-577-3399-7
45. Stoddard, J.L., Traaen, T.S., Skjelkvåle B.L., and Johannessen, M. 1998 Assessment of Nitrogen Leaching at UN/ECE ICP-Waters sites. In press *Environmental Pollution*.
46. Summary of The Nine Year Report. NIVA-Report SNO 3879-98, ICP-Waters Report 44/1998. ICP-Waters report 46/1998. ISBN 82-577-3463-2
47. Raddum, G.G. 1998. Intercalibration 9804: Invertebrate fauna. NIVA-Report SNO 3912-98, ICP-Waters Report 47/1998. ISBN 82-577-3500-0
48. Skjelkvåle, B.L. and Henriksen, A. 1998 Assessment of The ICP-Waters database for the future. ICP-Waters Report 48/1998 in prep.

49. Hovind, H. 1998. Intercomparison 9812. pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, total aluminium, reactive and non-labile aluminium, dissolved organic carbon, and chemical oxygen demand. NIVA-Report SNO 3939-98, ICP-Waters Report 47/1998. ISBN 82-577-3530-2
50. Rosseland, B.O., Raddum, G.G. and Bowman, J. 1999. Workshop on biological assessment and monitoring; evaluation and models. NIVA-Report SNO 4091-99, ICP Waters Report 50/1999. ISBN 82-577-3698-8.
51. Hovind, H. 1999. Intercomparison 9913. pH, K_{25} , HCO_3 , $NO_3 + NO_2$, Cl, SO_4 , Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC and COD-Mn. NIVA-Report SNO 4093-99, ICP-Waters Report 51/1999. ISBN 82-577-3700-3.

All reports and publications are available at:
Norwegian Institute for Water Research,
P.O.Box. 173, Kjelsås, N-0411 Oslo, Norway