Convention on Long-Range Transboundary Air Pollution

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

ICP Waters Report 98/2009

# Intercomparison 0923:

pH, Cond, $HCO_3$, $NO_3$+$NO_2$, Cl, $SO_4$, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni and Zn.

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# REPORT

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Abstract

72 laboratories received samples for the intercomparison 0923, and 68 laboratories in 29 countries submitted results. Two sample sets were used, one for the determination of major ions, and one for heavy metals. Based on the general target accuracy of ± 20 %, 75 % of the overall results were considered as acceptable. The best results were reported for the analytical variables zinc, magnesium and sodium, with 90, 88 and 88 % acceptable results, respectively. Low percentage of acceptable results was observed for copper with only 37 % acceptable results, due to the low concentrations in the samples used. Harmonization of the analytical methods used, and the practical procedures followed, may probably be the most important way to improve the comparability for these parameters.

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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 0923

pH, Cond, $HCO_3$, $NO_3$-N,
Cl, $SO_4$, Ca, Mg, Na, K, TOC,
Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn

Prepared by the ICP Waters Programme Centre
Norwegian Institute for Water Research
Oslo, October 2009

# Preface

The International Cooperative Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP Waters) was established under the Executive Body of the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP) in July 1985. Since then ICP Waters has been an important contributor to document the effects of implementing the Protocols under the Convention. Numerous assessments, workshops, reports and publications covering the effects of long-range transported air pollution has been published over the years.

The ICP Waters Programme Centre is hosted by Norwegian Institute for Water Research (NIVA), while the Norwegian Pollution Control Authority (SFT) leads the programme. The Programme Centres work is supported financially by SFT.

The Programme objective is to establish an international network of surface water monitoring sites and promote international harmonization of monitoring practices. One of the aims is to detect long-term trends in effects of acidic deposition on surface water chemistry and aquatic biota, and to reveal the dose/response relationship between water chemistry and aquatic biota.

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 23rd intercomparison of chemical analysis.

Oslo, October 2009

*Håvard Hovind*

# Contents

# Summary

Intercomparison 0923 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 Cooperative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes (ICP Waters).

The intercomparison was performed in July - August 2009, and included the determination of major ions and metals in natural water samples. The participants were asked to determine pH, conductivity, alkalinity, nitrate, chloride, sulphate, calcium, magnesium, sodium, potassium, total organic carbon, aluminium, iron, manganese, cadmium, lead, copper, nickel and zinc.

Two sample sets were prepared for this intercomparison, one for the determination of the major ions, and one for the heavy metals. 120 laboratories were invited to participate in this intercomparison, and the samples were sent to the 72 laboratories who accepted to participate. 68 laboratories submitted results to the Programme Centre before the final statistical treatment of the data. 29 countries were represented in this laboratory group (see Appendix A, page 44).

The median value of the results received from the participants for each variable was selected as "true" value. On average 75 % of the result pairs were considered as acceptable, the target limit being the median value ± 20 %, except for pH and conductivity where the special acceptance limits were selected, being ± 0,2 pH units and ± 10 %, respectively.

For pH, the accuracy limit was as in earlier intercomparisons extended from the target acceptance limit of ± 0,1 units to ± 0,2 units, and this time 68 % of the result pairs were acceptable even using this special limit. This is somewhat better than in the intercomparison organized last year. A total error of ± 0,2 units for pH measurements is a more reasonable basis for the assessment of the accuracy between laboratories than the target limit of ± 0,1 units.

The best results were reported for the analytical variables zinc, magnesium, and sodium where 90, 88 and 88 % of the results, respectively, were acceptable. The worst results were observed for copper (37 %), and nitrate + nitrite (58 %). The main reason for less acceptable results is probably the low concentrations in the samples used, and also the fact that some laboratories are using equipment which is not sensitive enough for the low concentrations used in this intercomparison.

More than 80 % acceptable results were obtained for the seven parameters chloride, calcium, magnesium, sodium, total organic carbon, nickel and zinc, 70 - 79 % acceptable results were obtained for conductivity, sulphate, potassium, aluminium, iron, cadmium and lead, 60 – 69 % for pH, alkalinity and manganese.

# 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 C. This twentythird intercomparison test, called 0923, included the determination of the major components and some other ions in natural water samples: pH, conductivity, alkalinity, nitrate, chloride, sulphate, calcium, magnesium, sodium, potassium, total organic carbon, aluminium, iron, manganese, cadmium, lead, copper, nickel and zinc.

# 2. Accomplishment of the intercomparison

The preparation of the sample solutions is described in Appendix B. The results of the control analyses performed at the Programme Centre are also summarized in the same place. On the Task Force meeting in Budapest, Hungary, in October 2008, it was decided that two sample sets as earlier should be included in this intercomparison, one sample pair for the determination of the major ions, and one for the heavy metals. However, this time it was decided that total organic carbon and aluminium should be included.

The samples were mailed from the Programme Centre on July 6th 2009, and the following day. Most of the participating laboratories received the samples within one week, with some few exceptions. It is important that the delivery address for the samples is correctly given, one set of samples were not delivered to the laboratory, but were returned to the organizer of this intercomparison.

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. By different reasons a few laboratories asked for some delay for reporting the results to the Programme Centre, which they were permitted to do. However, the results had to be reported before the statistical calculations. Most results were received within the middle of August, the last results included in the report were received at the end of the month. Three laboratories who received samples did not return analytical results, and one box of samples were returned to the Programme Centre.

# 3. Results

120 laboratories were invited to participate in this ICP Waters intercomparison. 72 of the laboratories accepted and therefore samples were mailed to them, however, only 71 laboratories received the samples. The 68 laboratories which submitted results to the Programme Centre, are representing 29 countries. Some laboratories submitted results a couple of weeks after the deadline, after a reminder letter was mailed to them. The last results were received at the end of August. A survey of the participants and their code numbers are listed in Appendix A, which also includes a table summarizing how many laboratories are participating from each country (see page 44).

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, is presented in Appendix C. The purpose of this test is to evaluate the comparability of the analytical results produced by the laboratories participating in the International Cooperative Programme. The real "true value" is not known exactly for the natural water samples used in this intercomparison. Therefore, we selected the median value, determined from the analytical results submitted by the participating laboratories after outliers were excluded, 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, for instance pH, this may represent a problem as the different methods used may produce systematically different results (stirring, non-stirring, and equilibration of the test solution), and we cannot argue that one method is more correct than the others.

The results are illustrated in Figure 1 - 19, where each laboratory is represented by a small circle and an identification number. Some laboratories with strongly deviating results may be located outside the plot. The great circle in the figures are representing a selected accuracy limit, either the general target limit of ± 20 % of the mean true values for the sample pair, or a special accuracy limit as defined in the sections below. A summary of the results of intercomparison 0923 is presented in Table 1. The individual results of the participants are presented in Table 4 in Appendix D, sorted in order of increasing identification number. More extensive statistical informations are presented in the Tables 5.1 - 5.19 in Appendix D.

## 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. 64 laboratories reported results for pH, 25 of the laboratories of this group indicated that they read the pH value during stirring the solution, while about 35 read the pH value in a quiescent solution. The stirring are normally lowering the observed pH result. However, in this intercomparison the median values are not significantly different in the stirred samples compared to the non-stirred samples (see Table 1).

Four laboratories equilibrated the solutions by bubbling with air containing 350 ppm $CO_2$ before reading the pH value. The reported results are comparable to the other laboratories. The information obtained by pH measurement after equilibrating the solution, is different from pH-values read directly, or during stirring the sample. Especially in cases where the difference between the results produced by different methods are greater than here, it would be questionable to establish a "true value" based on the median value for all the reported results for pH. In such a case it should be discussed whether an individual "true value" for each method would be more appropriate. In the intercomparison 0923 we have used the median value of all the reportede results, after the outliers have been excluded. Then 61 % of the results were acceptable, that is within the median value ± 0,2 pH units.

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

Figure 1 is illustrating that the reported results are rather spread out along the 45 ° line, indicating that the results are influenced by systematic effects on the results. The systematically lowest pH results in Figure 1 are dominated by laboratories stirring the sample during reading the pH value. 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 is probably connected to the small differences in the analytical methods used by the participants. Random errors are also affecting the results, and to a greater degree for pH than many other variables, illustrated in Figure 1 by the spread of the small circles away from the 45° line for many laboratories.

## 3.2 **Conductivity**

The conductivity results are presented in Figure 2, where the great circle is representing an accuracy limit of ± 10 %, which is only half of the target accuracy limit given in the Manual (1). The reported results are given in Table 5.2. Some laboratories obviously reported the conductivity results in another unit than the requested one, which is mS/m at 25 °C, the reported results being at least one decade wrong. After questioning these laboratories about the unit used, some of them reported the unit they really used, and thus the results from these laboratories were recalculated to mS/m.

All participants used an electrometric method for the determination of conductivity. Most laboratories achieved very good agreement between the results for this variable. Figure 2 is showing that systematic errors are dominating the results, both in positive and negative directions. A proper temperature correction is necessary when determining this variable, as the conductivity is changing by about two percents pr. degree at room temperature. If the accuracy limit was extended to the target value of ± 20 %, defined in the Manual (1), 12 more results which is located outside the 10 % acceptance circle, would be located within the circle and thus be defined as acceptable (then 90 % of the results would have been acceptable). An acceptance limit of ± 10 % seems to be a more reasonable demand.

## 3.3 **Alkalinity**

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 5.3. 45 laboratories reported results for alkalinity, and more than one third of the participants used the Gran plot titration method which is the suggested reference method in the Manual (1). The others used end point titration, either to pH = 4,5 and 4,2, or to one certain pH value only (4,5, 5,4 or 5,6). The results reported for the method using titration to both pH = 4,5 and 4,2 were very close to the results produced with the Gran plot method. One laboratory used a colorimetric method and reported systematically higher results than the Gran plot method.

The results for alkalinity are spread out along the 45 ° line, as illustrated in Figure 3, indicating that systematic effects are the dominating reason for the differences observed between many results. At the same time some random errors are contributing to the spreading out of some results from the 45 ° line. Most of the deviating results in Figure 3 are systematically high. The laboratories using the Gran plot titration or titration to both pH 4,5 and 4,2, reported results located within the acceptance limits represented by the circle in figure 3. Some of the laboratories titrating to one end point only, have reported systematically higher results for both samples.

The overall result for alkalinity in this intercomparison is somewhat better compared to the last intercomparison, as 67 % of the results being acceptable. The alkalinity value varies significantly with the end-point pH used for the titration. In waters containing high concentrations of total inorganic carbon, the equivalence point is close to pH = 5,4. In such a case, the relative error introduced by assuming a fixed end-point pH, is negligible. However, at lower alkalinities normally encountered in areas sensitive to acidification, the “total fixed end-point method” may overestimate the true alkalinity or the “equivalence” alkalinity. It is possible that this may be the explanation of the many deviating results in this intercomparison.

## 3.4 **Nitrate + nitrite**

The results reported for this parameter are presented in Figure 4, and the reported values are given in Table 5.4. The circle in Figure 4 represents a general target accuracy of ± 20 %. Ion chromatography is used by about two third of the participants. The others are determining this analytical variable by photometric methods. Most of these laboratories are using an automated version of the cadmium reduction method. There is no significant difference between the results determined by these two methods. The hydrazine method was used by one laboratory with acceptable results. Five laboratories obviously reported the results in a wrong unit, and the results were corrected to µg/l after clarification with the laboratory. One laboratory using capillary electrophoresis reported systematically very low result for sample A.

In this intercomparison only 58 % of the results are evaluated as acceptable, which is comparable to the corresponding intercomparisons last year, however, this is not acceptable. The control analyses at the Programme Centre demonstrated that these samples were stable with respect to the content of nitrate and nitrite, throughout the whole periode of the intercomparison. However, some of the participants indicated that the samples were less stable with respect to the nitrate content. At the programme centre the samples were stored at

4 °C, and this is probably enough to stabilize the samples. During transport to the laboratories the samples may be affected by the environmental conditions. The spread of the results out from the 45 ° line may indicate that there are some contribution from random effects.

As nitrite is absent in the sample solutions used here, the results from the photometric and ion chromatographic methods should be directly comparable.

## 3.5 **Chloride**

The chloride results are presented in Figure 5, and the reported results from the participants are given in Table 5.5. The target accuracy of ± 20 % is represented by the great circle in figure 5. 83 % of the laboratories determined chloride by ion chromatography. The greatest deviations are observed for the argentometric method, the results being systematically too high. One laboratory used capillary electrophoresis, and reported acceptable results.

86 % of the result pairs in this intercomparison are acceptable.

## 3.6 **Sulphate**

The sulphate results are illustrated in Figure 6, and the reported values are given in Table 5.6. The circle is representing the target accuracy of ± 20 %. Ion chromatography is used by 88 % of the laboratories for determination of the sulphate content of the samples. Three laboratories used a photometric method based on the dissociation of the barium-thorin complex. Two laboratories used ICP-AES for the determination of total sulphur, and then recalculated the result to mg/l sulphate, the result being systematically too high. Capillary electrophoresis used by one laboratory gave systematically too low results.

77 % of the result pairs are acceptable this time, somewhat lower than earlier.

## 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 ± 20 %, and is represented by the great circle in Figure 7. 57 laboratories reported results for calcium, and only 12 of them used the traditional flame atomic absorption spectrometry for the determination. The ICP technique is used by 15 laboratories, and three of these used ICP-MS. An increasing part of the laboratories, this time 26, used ion chromatography. Three laboratories used a titrimetric method with EDTA for the determination of calcium. One laboratory using capillary electrophoresis reported acceptable results.

84 % acceptable result pairs is a good result.

## 3.8 **Magnesium**

The magnesium results are presented in Figure 8, and the reported values are given in Table 5.8. The analytical methods used by the participants are the same as for the determination of

calcium. 12 laboratories are still using flame atomic absorption spectrometry for the determination of magnesium. ICP atomic emission spectrometry was used by 15 laboratories and ICP-MS by three, and 26 laboratories used ion chromatography. Systematic errors are dominating the results being outside the acceptance limit. This time, 88 % of the results are located inside the target accuracy of ± 20 %. One laboratory using capillary electrophoresis reported acceptable results.

## 3.9 **Sodium**

The sodium results are presented in Figure 9, where the great circle is representing the general target accuracy of ± 20 %. The reported values are given in Table 5.9. 58 laboratories reported results for sodium, and only nine of these used flame atomic absorption spectrometry for the determination this time. ICP-AES was used by nine laboratories and ICP-MS by three. However, in many laboratories the ion chromatographic technique becomes increasingly more popular in routine determination of the alkaline metals, 27 participants used ion chromatography in this intercomparison. Nine laboratories used flame photometry. 88 % of the result pairs are located within the general target accuracy of ± 20 %, which is considered as a very good result. One laboratory using capillary electrophoresis reported acceptable results.

## 3.10 **Potassium**

The potassium results are presented in Figure 10. The great circle is representing the target acceptance limit of ± 20 %. The reported values from 57 laboratories are given in Table 5.10. As for sodium, only nine laboratories used flame atomic absorption spectrometry for the determination of this element, and emission spectrometry is used by the same laboratories as for the determination of sodium. The deviations observed in Figure 10 are both of systematic and random nature. This time 75 % of the result pairs are considered acceptable, and this is better than in the last intercomparison. One laboratory using capillary electrophoresis reported systematically too low results.

## 3.11 **Total organic carbon**

Total organic carbon was included in this intercomparison, after being out for some years, and the results are presented in Figure 11. The great circle is representing the target acceptance limit of ± 20 %. The reported values from 34 laboratories are given in Table 5.10. Combustion methods are used by most of the laboratories, only seven laboratories used UV/peroxodisulfate oxidation method for this determination. The deviations observed in Figure 10 are mainly of systematic nature. The combustion method gives a little higher average than the UV/peroxodisulfate technicque. This time 82 % of the result pairs are considered acceptable, which is rather good.

## 3.12 **Aluminium**

The results for aluminium are illustrated in Figure 12, and the values reported by the participants are given in Table 5.12. The target accuracy is ± 20 %, and is represented by the great circle in Figure 11. 77 % of the result pairs are located inside this circle. 31 laboratories submitted results for iron, of which 13 and 14 used ICP-AES and ICP-MS, respectively, while only 1 and 3 used flame and graphite furnace atomic absorption, respectively. The ICP emission methods are clearly taking over more and more on behalf of the atomic absorption methods.

The deviating results are mainly affected by systematic errors. There is not observed any statistically significant difference between the results determined by the different methods for iron.

## 3.13 **Iron**

The results for iron are illustrated in Figure 13, and the values reported by the participants are given in Table 5.13. The target accuracy is ± 20 %, and is represented by the great circle in Figure 13. This time, 73 % of the result pairs are located inside this circle, which is less than the last intercomparison. 40 laboratories submitted results for iron, of which 14 and 18 used ICP-AES and ICP-MS, respectively, while 5 and 3 used flame and graphite furnace atomic absorption, respectively. The ICP emission methods are clearly taking over more and more on behalf of the atomic absorption methods.

The deviating results are mainly affected by systematic errors. There is observed greater deviations for the atomic absorption methods. The Youden plot looks a little strange in this case, because the concentrations in the two samples of the sample pair are very different.

## 3.14 **Manganese**

The manganese results are illustrated in Figure 14, and the values reported by the participants are given in Table 5.14. The target accuracy is ± 20 %, and is represented by the great circle in Figure 14. This time 67 % of the result pairs are located inside this circle, the great spread between the reported results is probably caused by the low concentration used in sample D. 39 laboratories submitted results for manganese, of which 13 and 19 used ICP-AES and ICP-MS, respectively, while 4 and 3 used flame and graphite furnace atomic absorption, respectively. Eight laboratories had problems with the sensitivity of the method, especially for sample D with the lowest concentration, and reported “less than” their detection limit.

## 3.15 **Cadmium**

The results for cadmium are illustrated in Figure 15, and the values reported by the participants are given in Table 5.15. The target accuracy is ± 20 % and is represented by the great circle in Figure 15. 79 % of the result pairs are located inside this circle. 43 laboratories submitted results for cadmium, of which 7 and 25 used ICP-AES and ICP-MS, respectively, while nine used graphite furnace atomic absorption and two flame atomic absorption.

## 3.16 **Lead**

The results for lead are illustrated in Figure 16, and the values reported by the participants are given in Table 5.16. The target accuracy is ± 20 %, and is represented by the great circle in Figure 16. 74 % of the result pairs are located inside this circle, which is better than the last intercomparison. 42 laboratories submitted results for lead, of which 6 and 25 used ICP-AES and ICP-MS, respectively, while 9 used graphite furnace atomic absorption. Flame atomic absorption was used by one laboratory, even though the method is not very sensitive and is not suitable for determination of the lowest lead concentration.

## 3.17 **Copper**

The copper results are illustrated in Figure 17, and the values reported by the participants are given in Table 5.17. The target accuracy is ± 20 %, and is represented by the great circle in Figure 17. The extremely low number of results being located inside this circle this time, 37 %, is probably caused by the very low concentrations used for copper. 43 laboratories submitted results for copper, of which 8 used ICP-AES and 23 used ICP-MS, while 9 and 3 used graphite furnace and flame atomic absorption, respectively. Nine laboratories reported the results as less than the detection limit.

## 3.18 **Nickel**

The results for nickel are illustrated in Figure 18, and the values reported by the participants are given in Table 5.18. The target accuracy is ± 20 %, and is represented by the great circle in Figure 18. This time, 85 % of the result pairs are located inside this circle, which is very good, and the main reason for this situation is that the nickel concentrations are higher in the samples used this time than earlier. 41 laboratories submitted results for nickel, of which 8 and 23 used ICP-AES and ICP-MS, respectively, while 8 laboratories used graphite furnace atomic absorption, and two flame atomic absorption.

## 3.19 **Zinc**

The results for zinc are illustrated in Figure 19, and the values reported by the participants are given in Table 5.19. The target accuracy is ± 20 %, and is represented by the great circle in Figure 19. 90 % of the result pairs are located inside this circle, which is very good. 42 laboratories submitted results for zinc, of which 12 used ICP-AES and 22 ICP-MS, respectively, while 5 and 3 used flame and graphite furnace atomic absorption, respectively. Generally, the deviating results are affected mainly by systematic errors.

**Continue page 37**

**Table 1. Statistical summary for intercomparison 0923**

| Analytical variable and method | | Sample pair | True value 1 | True value 2 | Total number | Labs. excl. | Median 1 | Median 2 | Average/std.dev. Sample 1 | | Average/std.dev. Sample 2 | | Rel.std.dev. % 1 | Rel.std.dev. % 2 | Relative error % 1 | Relative error % 2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | | AB | 6,58 | 7,05 | 64 | 1 | 6,58 | 7,05 | 6,56 | 0,21 | 7,02 | 0,20 | 3,2 | 2,8 | -0,3 | -0,4 |
| | No stirring | | | | 35 | 1 | 6,57 | 7,04 | 6,55 | 0,23 | 7,00 | 0,22 | 3,5 | 3,1 | -0,4 | -0,7 |
| | Stirring | | | | 25 | 0 | 6,59 | 7,06 | 6,56 | 0,19 | 7,03 | 0,16 | 2,9 | 2,3 | -0,3 | -0,3 |
| | Equilibration | | | | 4 | 0 | 6,58 | 7,10 | 6,68 | 0,21 | 7,17 | 0,20 | 3,1 | 2,7 | 1,5 | 1,7 |
| Conductivity | mS/m | AB | 3,09 | 3,36 | 63 | 4 | 3,09 | 3,36 | 3,07 | 0,19 | 3,34 | 0,18 | 6,1 | 5,5 | -0,7 | -0,6 |
| | Electrometry | | | | 63 | 4 | 3,09 | 3,36 | 3,07 | 0,19 | 3,34 | 0,18 | 6,1 | 5,5 | -0,7 | -0,6 |
| Alkalinity | Mmol/l | AB | 0,099 | 0,200 | 45 | 11 | 0,099 | 0,200 | 0,099 | 0,013 | 0,201 | 0,014 | 13,3 | 7,2 | 0,3 | 0,6 |
| | Gran plot titration | | | | 19 | 3 | 0,099 | 0,202 | 0,099 | 0,010 | 0,203 | 0,011 | 10,3 | 5,7 | 0,2 | 1,5 |
| | End point titration | | | | 12 | 2 | 0,100 | 0,200 | 0,102 | 0,012 | 0,201 | 0,011 | 12,1 | 5,7 | 2,7 | 0,7 |
| | End point 5.6 | | | | 1 | 0 | | | 0,076 | | 0,192 | | | | -23,2 | -4,0 |
| | End point 5.4 | | | | 1 | 0 | | | 0,082 | | 0,187 | | | | -17,2 | -6,5 |
| | End point | | | | 11 | 6 | 0,098 | 0,190 | 0,095 | 0,007 | 0,191 | 0,019 | 7,2 | 9,7 | -4,2 | -4,4 |
| | Colorimetry | | | | 1 | 0 | | | 0,140 | | 0,240 | | | | 41,4 | 20,0 |
| Nitrate + nitrite-nitrogen, µgf/l | | AB | 187 | 154 | 59 | 11 | 187 | 154 | 185 | 22 | 153 | 25 | 11,8 | 16,5 | -1,0 | -0,6 |
| | Autoanalyzer | | | | 13 | 3 | 187 | 157 | 185 | 6 | 158 | 20 | 3,4 | 12,6 | -0,9 | 2,5 |
| | Photometry | | | | 6 | 1 | 181 | 115 | 178 | 18 | 131 | 28 | 10,2 | 21,4 | -4,9 | -15,1 |
| | Ion chromatography | | | | 37 | 5 | 188 | 155 | 187 | 25 | 155 | 26 | 13,3 | 16,6 | 0,1 | 0,7 |
| | Hydrazine | | | | 2 | 1 | | | 156 | | 154 | | | | -16,6 | 0,0 |
| | Cap. electrophoresis | | | | 1 | 1 | | | 42 | | 147 | | | | -77,5 | -4,5 |
| Chloride | mg/l | AB | 2,76 | 1,19 | 59 | 4 | 2,76 | 1,19 | 2,74 | 0,19 | 1,18 | 0,11 | 7,1 | 9,6 | -0,6 | -0,6 |
| | Ion chromatography | | | | 49 | 1 | 2,76 | 1,20 | 2,75 | 0,18 | 1,19 | 0,10 | 6,4 | 8,3 | -0,5 | 0,4 |
| | Autoanalyzer | | | | 1 | 1 | | | 1,86 | | 1,08 | | | | -32,6 | -9,2 |
| | Argentometry | | | | 2 | 2 | | | 5,50 | | 3,65 | | | | 99,3 | 206,7 |
| | Manual, Hg | | | | 5 | 0 | 2,95 | 1,18 | 2,74 | 0,36 | 1,13 | 0,15 | 13,3 | 13,4 | -0,7 | -5,4 |
| | Cap. electrophoresis | | | | 1 | 0 | | | 2,76 | | 1,23 | | | | 0,0 | 3,4 |
| | Potentiometry | | | | 1 | 0 | | | 2,60 | | 0,85 | | | | -5,8 | -28,6 |

| Analytical variable and method | | Sample pair | True value 1 | True value 2 | Total number | Labs. excl. | Median 1 | Median 2 | Average/std.dev. Sample 1 | | Average/std.dev. Sample 2 | | Rel.std.dev. % 1 | Rel.std.dev. % 2 | Relative error % 1 | Relative error % 2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sulfate | mg/l | AB | 1,82 | 2,12 | 56 | 5 | 1,82 | 2,12 | 1,84 | 0,16 | 2,16 | 0,20 | 8,6 | 9,1 | 1,3 | 1,7 |
| | Ion chromatography | | | | 49 | 2 | 1,81 | 2,11 | 1,82 | 0,12 | 2,13 | 0,18 | 6,7 | 8,6 | 0,2 | 0,7 |
| | Photometry | | | | 1 | 1 | | | 1,36 | | 1,18 | | | | -25,3 | -44,3 |
| | Nephelometry | | | | 3 | 1 | | | 1,89 | | 2,49 | | | | 3,8 | 17,5 |
| | ICP-AES | | | | 2 | 0 | | | 2,28 | | 2,35 | | | | 25,3 | 10,7 |
| | Cap. electrophoresis | | | | 1 | 1 | | | 1,20 | | 1,72 | | | | -34,1 | -18,9 |
| Calcium | mg/l | AB | 2,07 | 4,45 | 57 | 5 | 2,07 | 4,45 | 2,08 | 0,12 | 4,45 | 0,30 | 5,7 | 6,7 | 0,5 | 0,0 |
| | FAAS | | | | 12 | 1 | 2,05 | 4,40 | 2,08 | 0,10 | 4,39 | 0,17 | 4,9 | 3,8 | 0,4 | -1,3 |
| | ICP-AES | | | | 12 | 0 | 2,07 | 4,43 | 2,03 | 0,10 | 4,42 | 0,30 | 5,1 | 6,8 | -2,2 | -0,7 |
| | EDTA | | | | 3 | 0 | 2,06 | 4,43 | 2,04 | 0,04 | 4,30 | 0,26 | 1,9 | 6,0 | -1,3 | -3,4 |
| | Ion chromatography | | | | 26 | 4 | 2,09 | 4,48 | 2,10 | 0,13 | 4,47 | 0,34 | 6,1 | 7,5 | 1,5 | 0,3 |
| | ICP-MS | | | | 3 | 0 | 2,19 | 4,51 | 2,21 | 0,13 | 4,65 | 0,39 | 5,7 | 8,3 | 6,9 | 4,6 |
| | Cap. Electrophoresis | | | | 1 | 0 | | | 2,04 | | 4,93 | | | | -1,4 | 10,8 |
| Magnesium | mg/l | AB | 0,487 | 0,421 | 57 | 5 | 0,487 | 0,421 | 0,488 | 0,033 | 0,422 | 0,027 | 6,8 | 6,3 | 0,2 | 0,3 |
| | FAAS | | | | 12 | 0 | 0,475 | 0,424 | 0,490 | 0,032 | 0,426 | 0,035 | 6,6 | 8,3 | 0,7 | 1,3 |
| | ICP-AES | | | | 12 | 0 | 0,495 | 0,419 | 0,475 | 0,034 | 0,417 | 0,025 | 7,1 | 5,9 | -2,4 | -0,9 |
| | EDTA | | | | 3 | 1 | | | 0,482 | | 0,419 | | | | -1,1 | -0,6 |
| | Ion chromatography | | | | 26 | 3 | 0,489 | 0,423 | 0,495 | 0,034 | 0,424 | 0,025 | 7,0 | 5,9 | 1,7 | 0,6 |
| | ICP-MS | | | | 3 | 1 | | | 0,497 | | 0,431 | | | | 2,0 | 2,3 |
| | Cap. Electrophoresis | | | | 1 | 0 | | | 0,450 | | 0,400 | | | | -7,6 | -5,0 |
| Sodium | mg/l | AB | 3,25 | 1,26 | 58 | 4 | 3,25 | 1,26 | 3,27 | 0,18 | 1,26 | 0,08 | 5,6 | 6,6 | 0,5 | 0,1 |
| | FAAS | | | | 9 | 2 | 3,19 | 1,25 | 3,23 | 0,18 | 1,27 | 0,08 | 5,6 | 6,5 | -0,7 | 0,7 |
| | ICP-AES | | | | 9 | 0 | 3,32 | 1,27 | 3,36 | 0,22 | 1,26 | 0,07 | 6,4 | 5,4 | 3,3 | 0,4 |
| | AES | | | | 9 | 2 | 3,20 | 1,23 | 3,24 | 0,13 | 1,23 | 0,07 | 4,1 | 5,6 | -0,4 | -2,3 |
| | Ion chromatography | | | | 27 | 0 | 3,28 | 1,26 | 3,27 | 0,18 | 1,25 | 0,08 | 5,6 | 6,6 | 0,5 | -0,8 |
| | ICP-MS | | | | 3 | 0 | 3,23 | 1,35 | 3,20 | 0,24 | 1,34 | 0,09 | 7,5 | 6,4 | -1,4 | 6,3 |
| | Cap. Electrophoresis | | | | 1 | 0 | | | 3,20 | | 1,46 | | | | -1,5 | 15,9 |

| Analytical variable and method | | Sample pair | True value 1 | True value 2 | Total number | Labs. excl. | Median 1 | Median 2 | Average/std.dev. Sample 1 | | Average/std.dev. Sample 2 | | Rel.std.dev. % 1 | Rel.std.dev. % 2 | Relative error % 1 | Relative error % 2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Potassium | mg/l | AB | 0,299 | 0,231 | 57 | 7 | 0,299 | 0,231 | 0,295 | 0,028 | 0,230 | 0,022 | 9,5 | 9,8 | -1,3 | -0,5 |
| | FAAS | | | | 9 | 1 | 0,300 | 0,227 | 0,308 | 0,035 | 0,236 | 0,027 | 11,3 | 11,3 | 2,9 | 2,3 |
| | ICP-AES | | | | 9 | 1 | 0,305 | 0,240 | 0,306 | 0,016 | 0,241 | 0,010 | 5,3 | 4,3 | 2,3 | 4,3 |
| | AES | | | | 9 | 2 | 0,290 | 0,230 | 0,296 | 0,018 | 0,233 | 0,015 | 5,9 | 6,4 | -0,9 | 0,7 |
| | Ion chromatography | | | | 26 | 1 | 0,289 | 0,230 | 0,286 | 0,030 | 0,222 | 0,025 | 10,6 | 11,1 | -4,3 | -3,7 |
| | ICP-MS | | | | 3 | 1 | | | 0,305 | | 0,240 | | | | 1,8 | 3,9 |
| | Cap. Electrophoresis | | | | 1 | 1 | | | 0,140 | | -0,100 | | | | -53,2 | -143,3 |
| Total organic carbon, mg/l | | AB | 10,48 | 4,15 | 34 | 3 | 10,48 | 4,15 | 10,63 | 0,75 | 4,20 | 0,39 | 7,1 | 9,3 | 1,4 | 1,3 |
| | Combustion | | | | 27 | 3 | 10,60 | 4,25 | 10,73 | 0,79 | 4,28 | 0,40 | 7,4 | 9,4 | 2,4 | 3,2 |
| | UV/peroxodisulphate | | | | 7 | 0 | 10,27 | 3,99 | 10,29 | 0,48 | 3,93 | 0,17 | 4,7 | 4,3 | -1,8 | -5,3 |
| Aluminium | µg/l | CD | 122,5 | 72,8 | 31 | 5 | 122,5 | 72,8 | 121,4 | 7,4 | 71,9 | 7,4 | 6,1 | 10,3 | -0,9 | -1,2 |
| | FAAS | | | | 1 | 0 | | | 118,0 | | 69,0 | | | | -3,7 | -5,2 |
| | GFAAS | | | | 3 | 2 | | | 133,0 | | 79,0 | | | | 8,6 | 8,5 |
| | ICP-AES | | | | 13 | 3 | 120,0 | 70,9 | 117,7 | 8,1 | 68,8 | 10,6 | 6,9 | 15,5 | -3,9 | -5,5 |
| | ICP-MS | | | | 14 | 0 | 123,5 | 73,8 | 123,5 | 5,7 | 73,9 | 3,4 | 4,7 | 4,6 | 0,8 | 1,5 |
| Iron | µg/l | CD | 164,4 | 35,8 | 40 | 6 | 164,4 | 35,8 | 162,3 | 10,1 | 36,2 | 5,8 | 6,2 | 16,0 | -1,3 | 1,2 |
| | FAAS | | | | 5 | 3 | | | 180,0 | | 47,5 | | | | 9,5 | 32,7 |
| | GFAAS | | | | 3 | 1 | | | 146,5 | | 26,9 | | | | -10,9 | -25,0 |
| | ICP-AES | | | | 14 | 1 | 167,0 | 35,8 | 164,3 | 7,0 | 36,6 | 3,1 | 4,2 | 8,4 | -0,1 | 2,3 |
| | ICP-MS | | | | 18 | 1 | 161,0 | 35,6 | 160,5 | 9,8 | 35,7 | 5,7 | 6,1 | 16,0 | -2,4 | -0,3 |
| Manganese | µg/l | CD | 9,64 | 1,09 | 39 | 14 | 9,64 | 1,09 | 9,54 | 0,73 | 1,08 | 0,11 | 7,6 | 9,9 | -1,0 | -1,1 |
| | FAAS | | | | 4 | 3 | | | 10,10 | | 1,14 | | | | 4,8 | 4,6 |
| | GFAAS | | | | 3 | 2 | | | 7,14 | | 0,78 | | | | -25,9 | -28,4 |
| | ICP-AES | | | | 13 | 7 | 9,46 | 1,13 | 9,44 | 0,56 | 1,12 | 0,11 | 5,9 | 10,2 | -2,1 | 2,3 |
| | ICP-MS | | | | 19 | 2 | 9,75 | 1,09 | 9,69 | 0,53 | 1,08 | 0,08 | 5,5 | 7,5 | 0,5 | -1,1 |
| Cadmium | µg/ | CD | 3,56 | 6,13 | 43 | 4 | 3,56 | 6,13 | 3,52 | 0,32 | 6,12 | 0,55 | 9,2 | 8,9 | -1,1 | -0,2 |
| | FAAS | | | | 2 | 0 | | | 3,85 | | 6,80 | | | | 8,1 | 10,9 |
| | GFAAS | | | | 9 | 2 | 3,20 | 5,74 | 3,19 | 0,38 | 5,73 | 0,52 | 12,0 | 9,1 | -10,4 | -6,5 |
| | ICP-AES | | | | 7 | 1 | 3,53 | 6,05 | 3,52 | 0,34 | 5,89 | 0,62 | 9,6 | 10,5 | -1,2 | -4,0 |
| | ICP-MS | | | | 25 | 1 | 3,57 | 6,16 | 3,59 | 0,25 | 6,23 | 0,47 | 6,9 | 7,5 | 0,9 | 1,6 |

| Analytical variable and method | | Sample pair | True value 1 | True value 2 | Total number | Labs. excl. | Median 1 | Median 2 | Average/std.dev. Sample 1 | | Average/std.dev. Sample 2 | | Rel.std.dev. % 1 | Rel.std.dev. % 2 | Relative error % 1 | Relative error % 2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Lead | µg/l | CD | 4,00 | 6,14 | 42 | 5 | 4,00 | 6,14 | 3,97 | 0,44 | 6,06 | 0,56 | 11,2 | 9,2 | -0,7 | -1,3 |
| | FAAS | | | | 1 | 0 | | | 4,00 | | 5,90 | | | | 0,0 | -3,9 |
| | GFAAS | | | | 10 | 3 | 3,92 | 5,85 | 3,94 | 0,66 | 5,58 | 0,69 | 16,7 | 12,4 | -1,4 | -9,1 |
| | ICP-AES | | | | 6 | 2 | 3,85 | 6,41 | 4,02 | 0,61 | 6,43 | 0,57 | 15,1 | 8,9 | 0,4 | 4,7 |
| | ICP-MS | | | | 25 | 0 | 4,00 | 6,17 | 3,97 | 0,37 | 6,14 | 0,46 | 9,4 | 7,5 | -0,7 | 0,0 |
| Copper | µg/l | CD | 0,64 | 1,39 | 43 | 19 | 0,64 | 1,39 | 0,64 | 0,12 | 1,35 | 0,19 | 19,4 | 13,8 | -0,1 | -3,1 |
| | FAAS | | | | 3 | 2 | | | 0,58 | | 1,33 | | | | -9,4 | -4,3 |
| | GFAAS | | | | 9 | 5 | 0,55 | 1,25 | 0,54 | 0,11 | 1,27 | 0,22 | 21,0 | 17,2 | -16,4 | -9,0 |
| | ICP-AES | | | | 8 | 7 | | | 0,60 | | 1,10 | | | | -6,3 | -20,9 |
| | ICP-MS | | | | 23 | 5 | 0,71 | 1,40 | 0,67 | 0,12 | 1,38 | 0,18 | 18,2 | 13,0 | 4,4 | -0,7 |
| Nickel | µg/l | CD | 4,14 | 6,23 | 41 | 3 | 4,14 | 6,23 | 4,13 | 0,40 | 6,31 | 0,54 | 9,7 | 8,5 | -0,3 | 1,3 |
| | FAAS | | | | 2 | 1 | | | 4,30 | | 6,40 | | | | 3,9 | 2,7 |
| | GFAAS | | | | 8 | 2 | 4,00 | 6,11 | 4,20 | 0,53 | 6,46 | 0,90 | 12,5 | 14,0 | 1,5 | 3,7 |
| | ICP-AES | | | | 8 | 0 | 4,08 | 6,20 | 3,90 | 0,59 | 6,10 | 0,62 | 15,1 | 10,2 | -5,8 | -2,1 |
| | ICP-MS | | | | 23 | 0 | 4,15 | 6,25 | 4,18 | 0,26 | 6,34 | 0,40 | 6,3 | 6,3 | 0,9 | 1,8 |
| Zinc | µg/l | CD | 21,2 | 33,0 | 42 | 4 | 21,2 | 33,0 | 21,2 | 1,2 | 33,1 | 2,1 | 5,7 | 6,4 | 0,1 | 0,3 |
| | FAAS | | | | 5 | 0 | 19,8 | 31,0 | 20,6 | 2,3 | 32,4 | 3,6 | 11,2 | 11,1 | -2,7 | -1,7 |
| | GFAAS | | | | 3 | 2 | | | 20,0 | | 38,0 | | | | -5,7 | 15,2 |
| | ICP-AES | | | | 12 | 1 | 21,4 | 33,3 | 21,2 | 1,1 | 32,8 | 2,2 | 5,3 | 6,7 | 0,2 | -0,6 |
| | ICP-MS | | | | 22 | 1 | 21,4 | 33,0 | 21,4 | 0,9 | 33,2 | 1,4 | 4,1 | 4,2 | 1,1 | 0,5 |

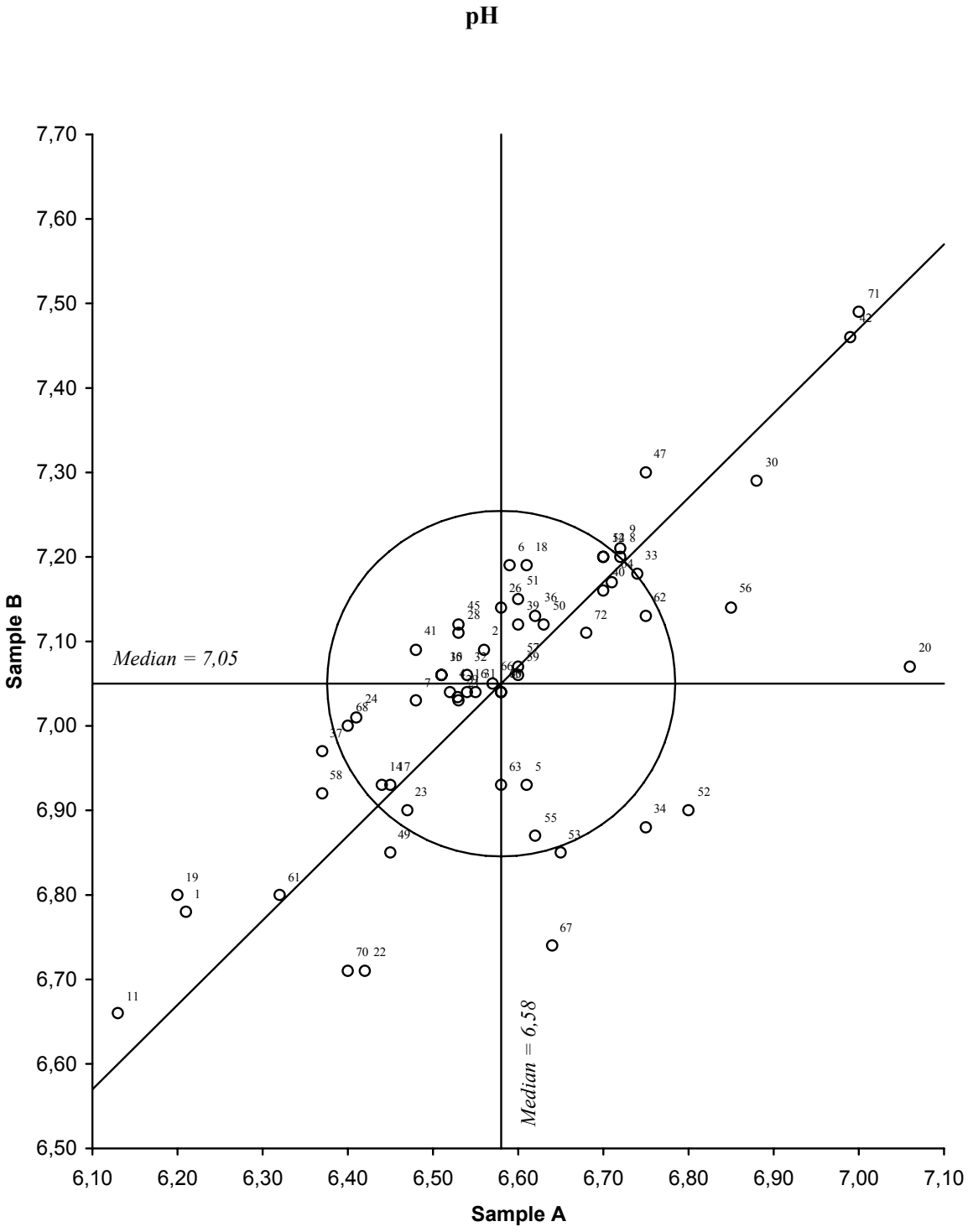


Figure 1. Youdendiagram for pH, sample pair AB
Acceptance limit, given by the circle, is 0,2 pH units

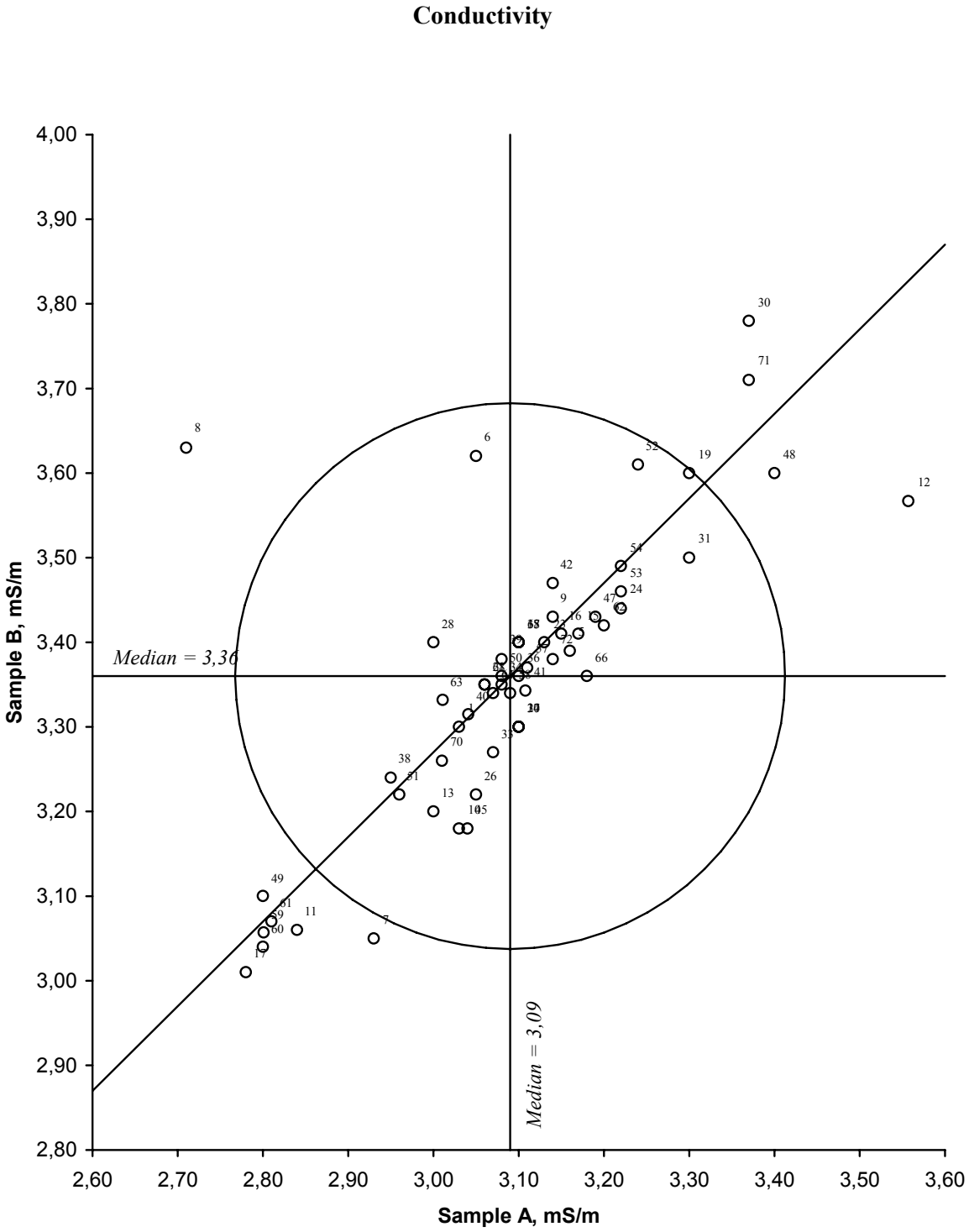


Figure 2. Youdendiagram for conductivity, sample pair AB
Acceptance limit, given by circle, is 10 %

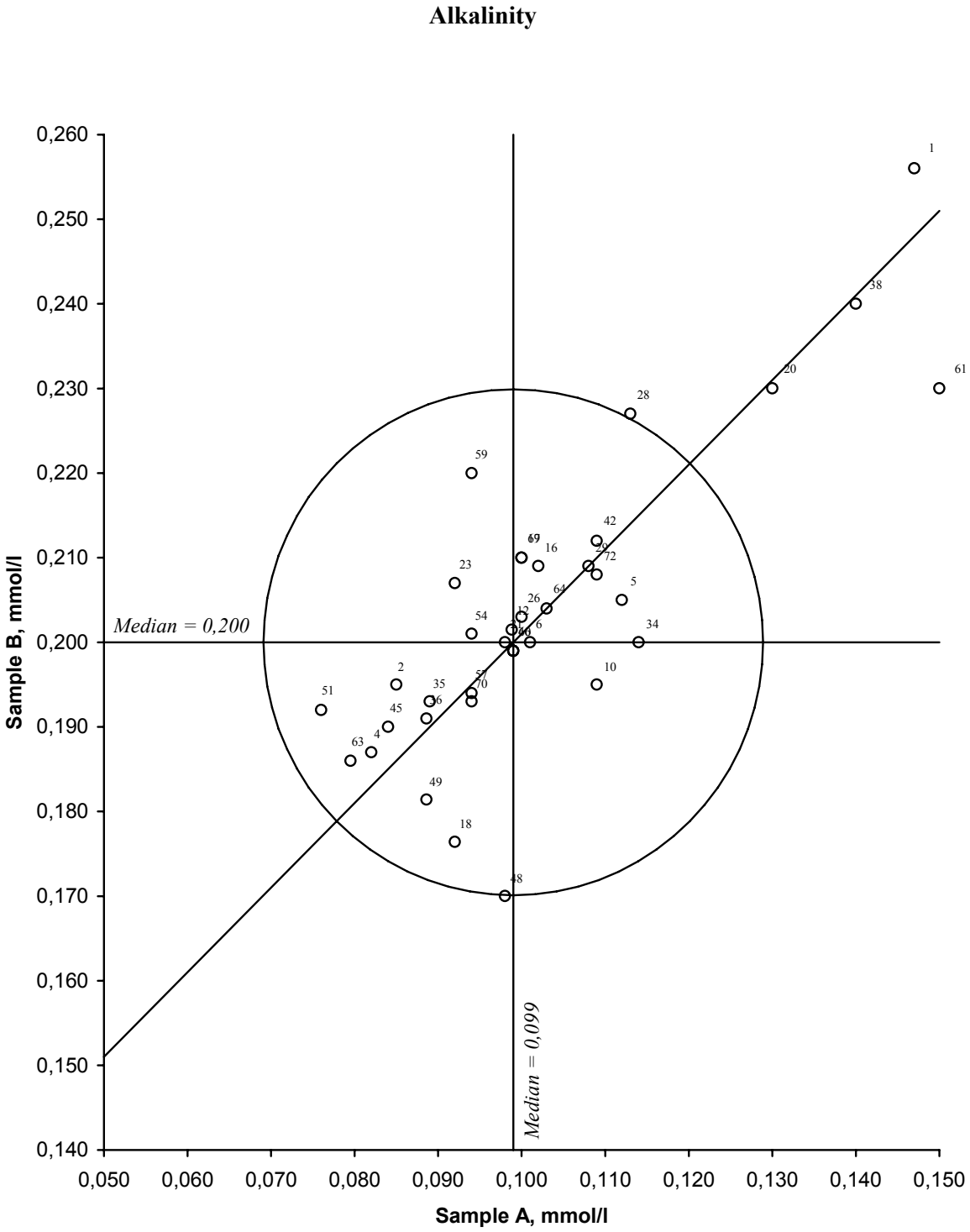


Figure 3. Youdendiagram for alkalinity, sample pair AB
Acceptance limit, given by circle, is 20 %

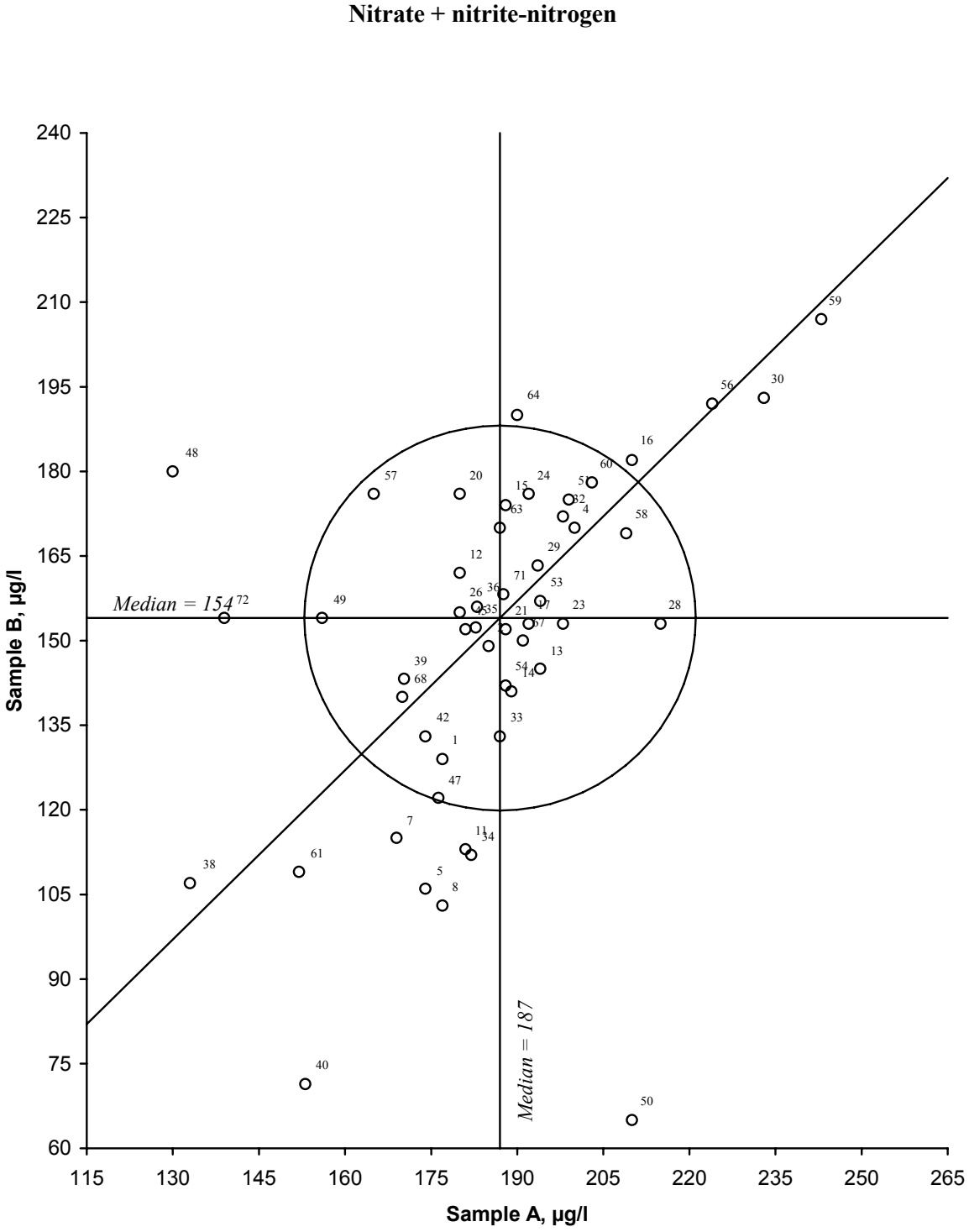


Figure 4. Youdendiagram for nitrate + nitrite-nitrogen, sample pair AB
Acceptance limit, given by the circle, is 20 %

**Chloride**

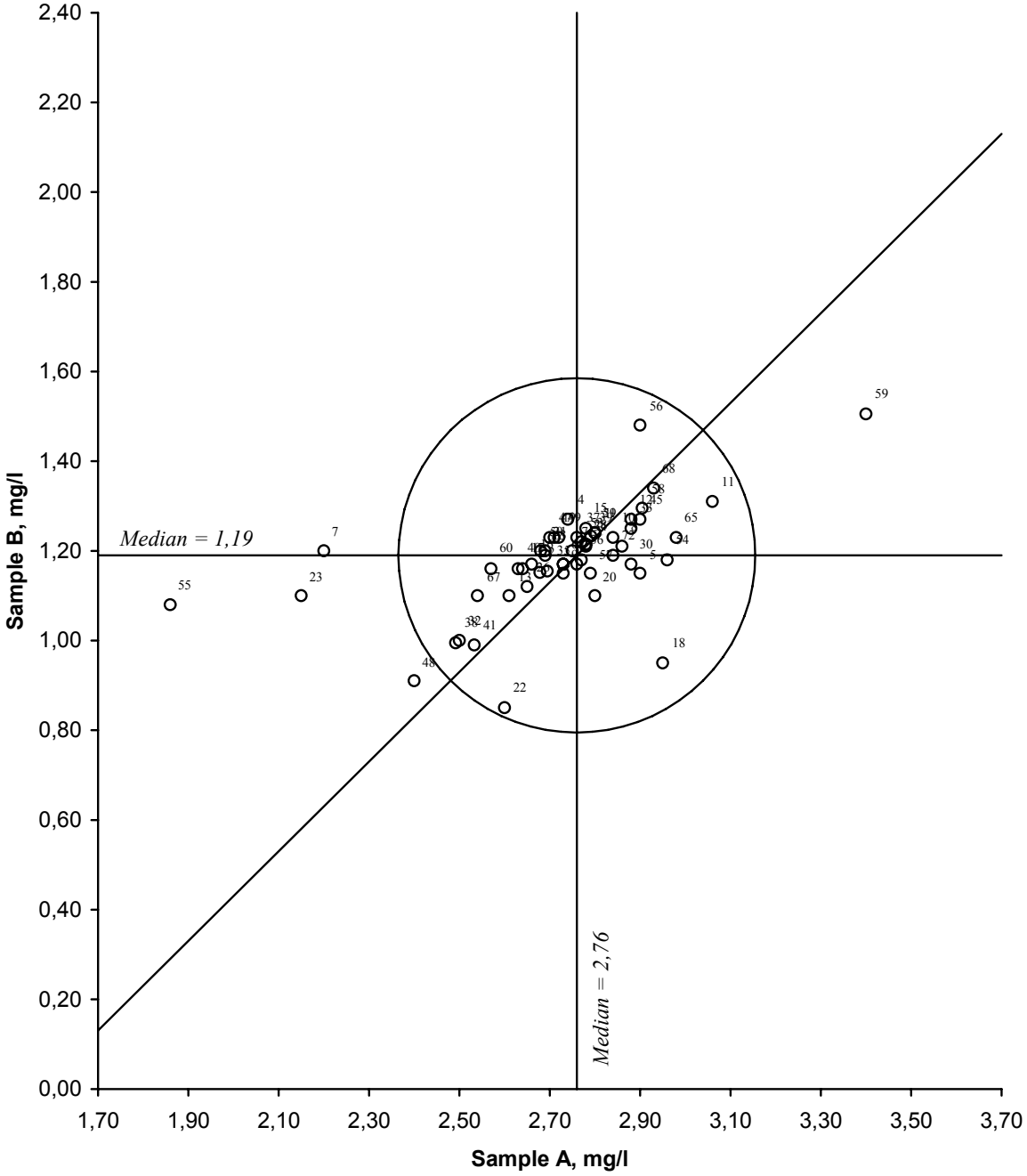


Figure 5. Youdendiagram for chloride, sample pair AB
Acceptance limit, given by the circle, is 20 %

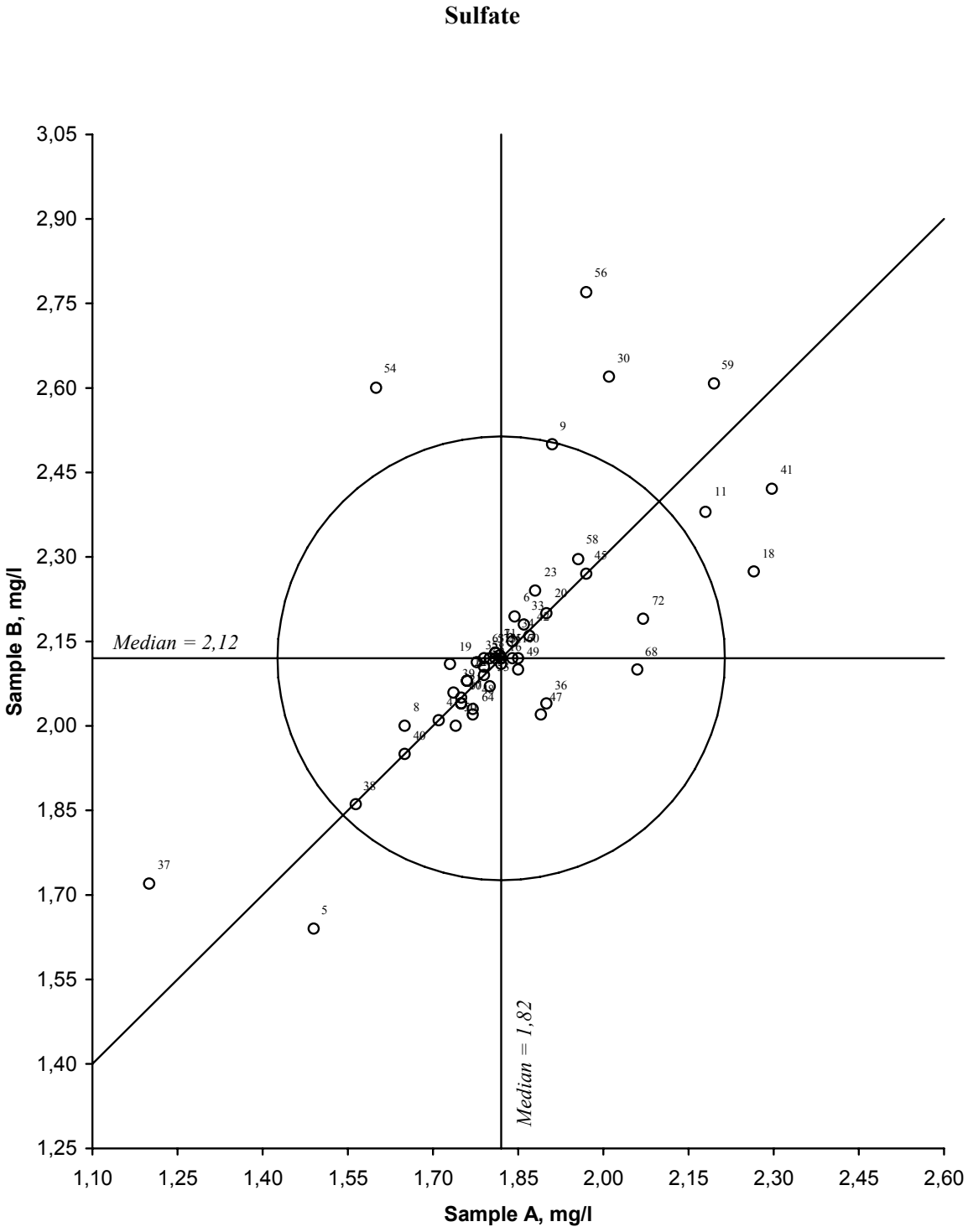


Figure 6. Youdendiagram for sulfate, sample pair AB
Acceptance limit, given by the circle, is 20 %

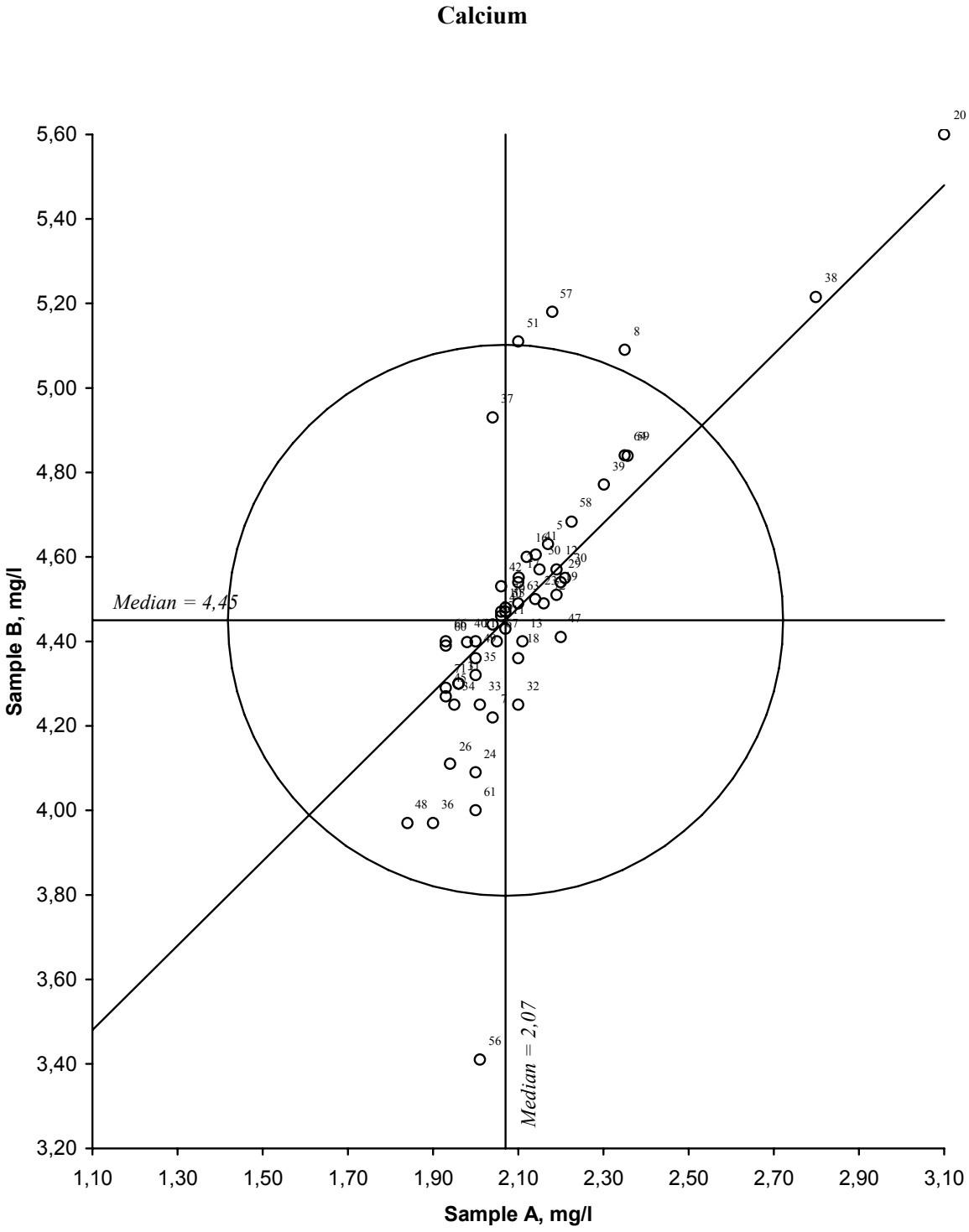


Figure 7. Youdendiagram for calcium, sample pair AB
Acceptance limit, given by the circle, is 20 %

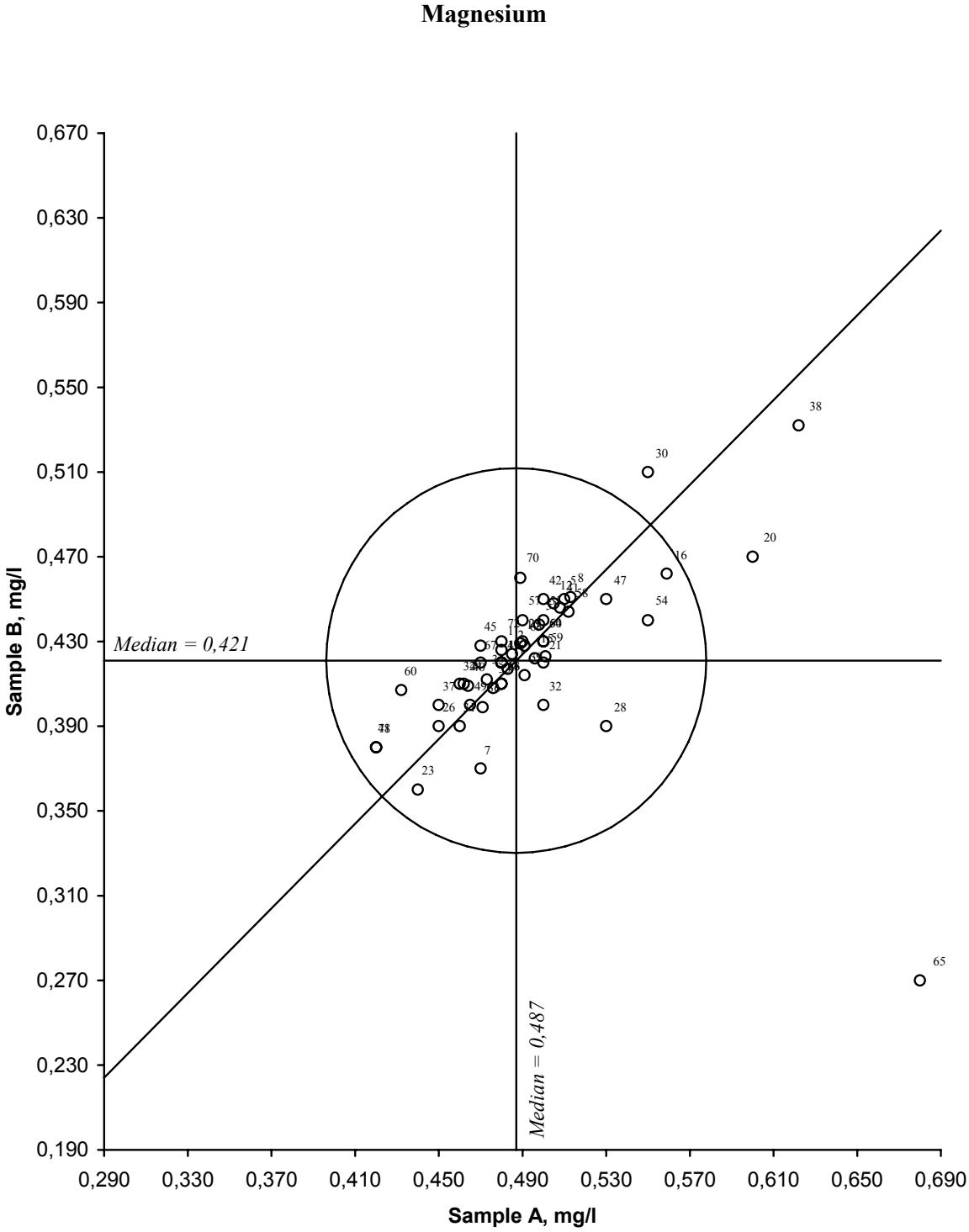


Figure 8. Youdendiagram for magnesium, sample pair AB
Acceptance limit, given by the circle, is 20 %

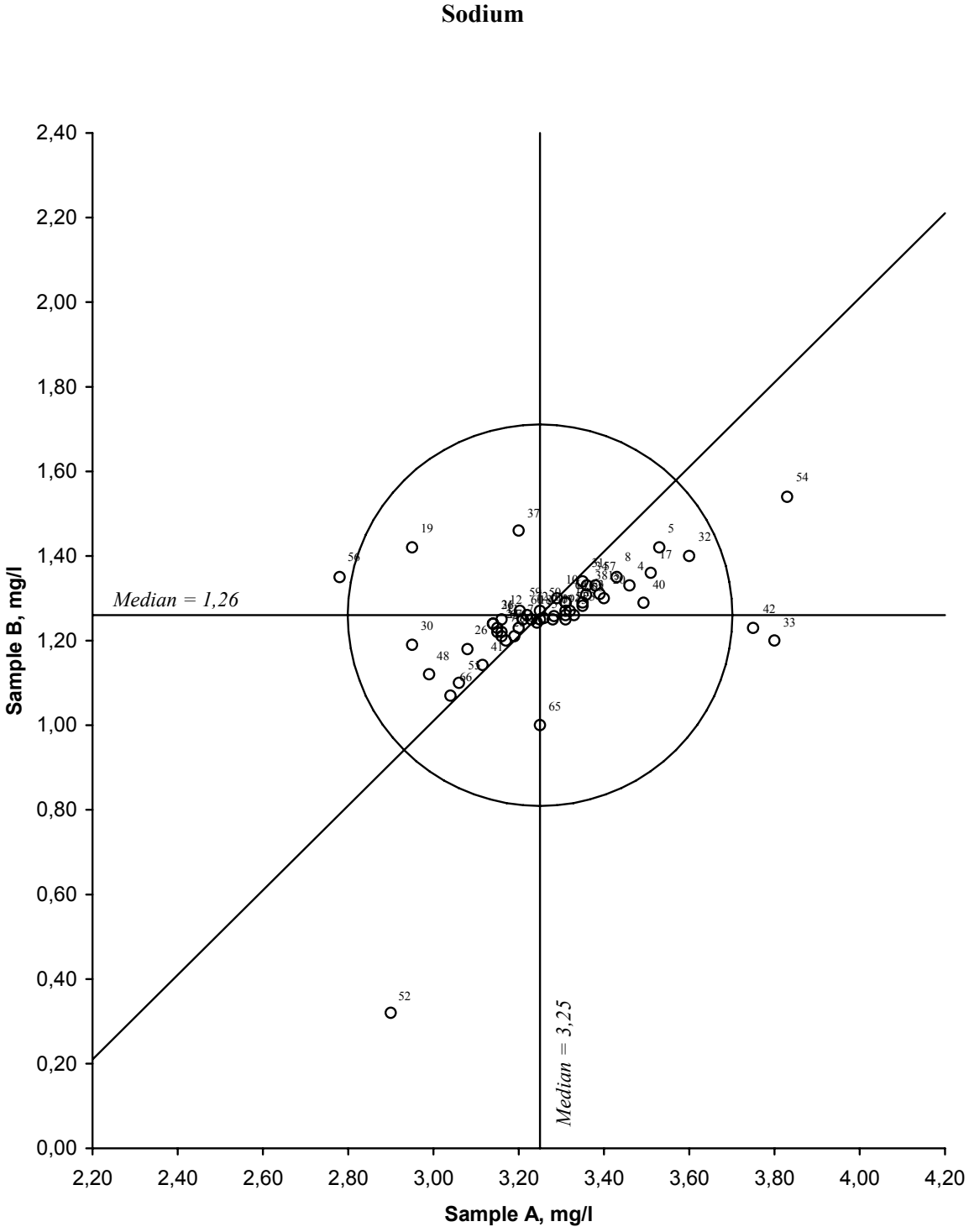


Figure 9. Youdendiagram for sodium, sample pair AB
Acceptance limit, given by the circle, is 20 %

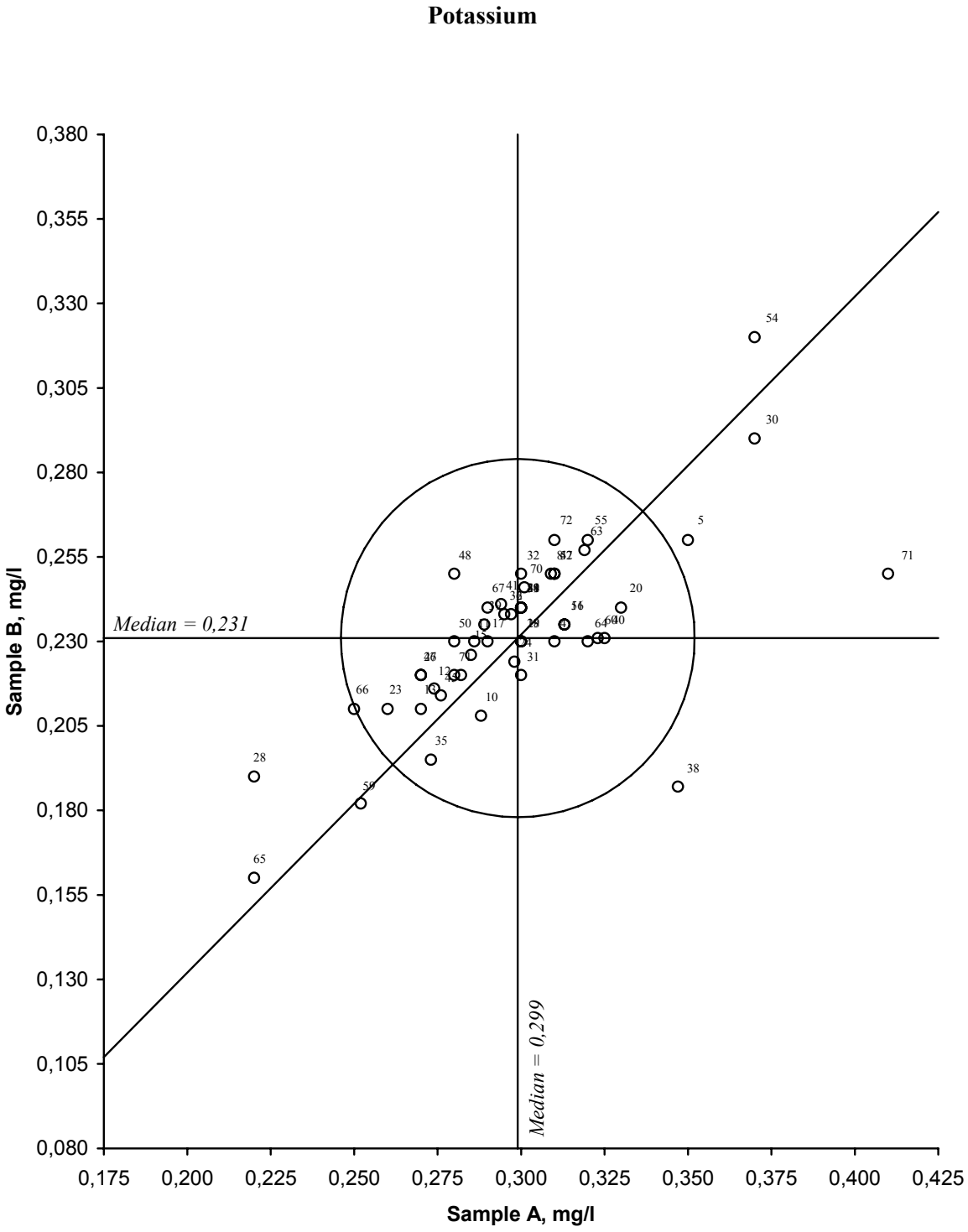


Figure 10. Youdendiagram for potassium, sample pair AB
Acceptance limit, given by the circle, is 20 %

**Total organic carbon**

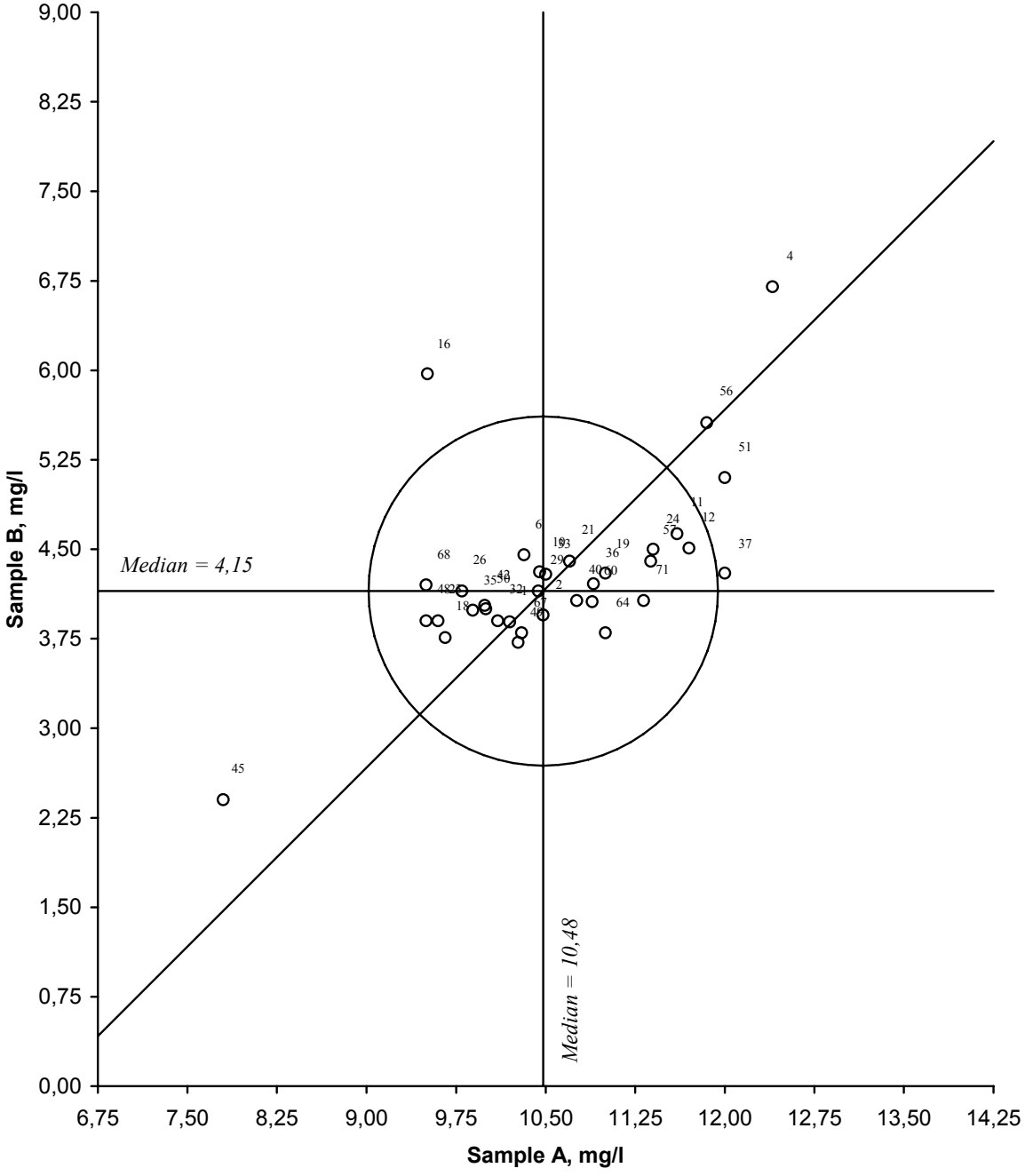


Figure 11. Youdendiagram for total organic carbon, sample pair AB
Acceptance limit, given by the circle, is 20 %

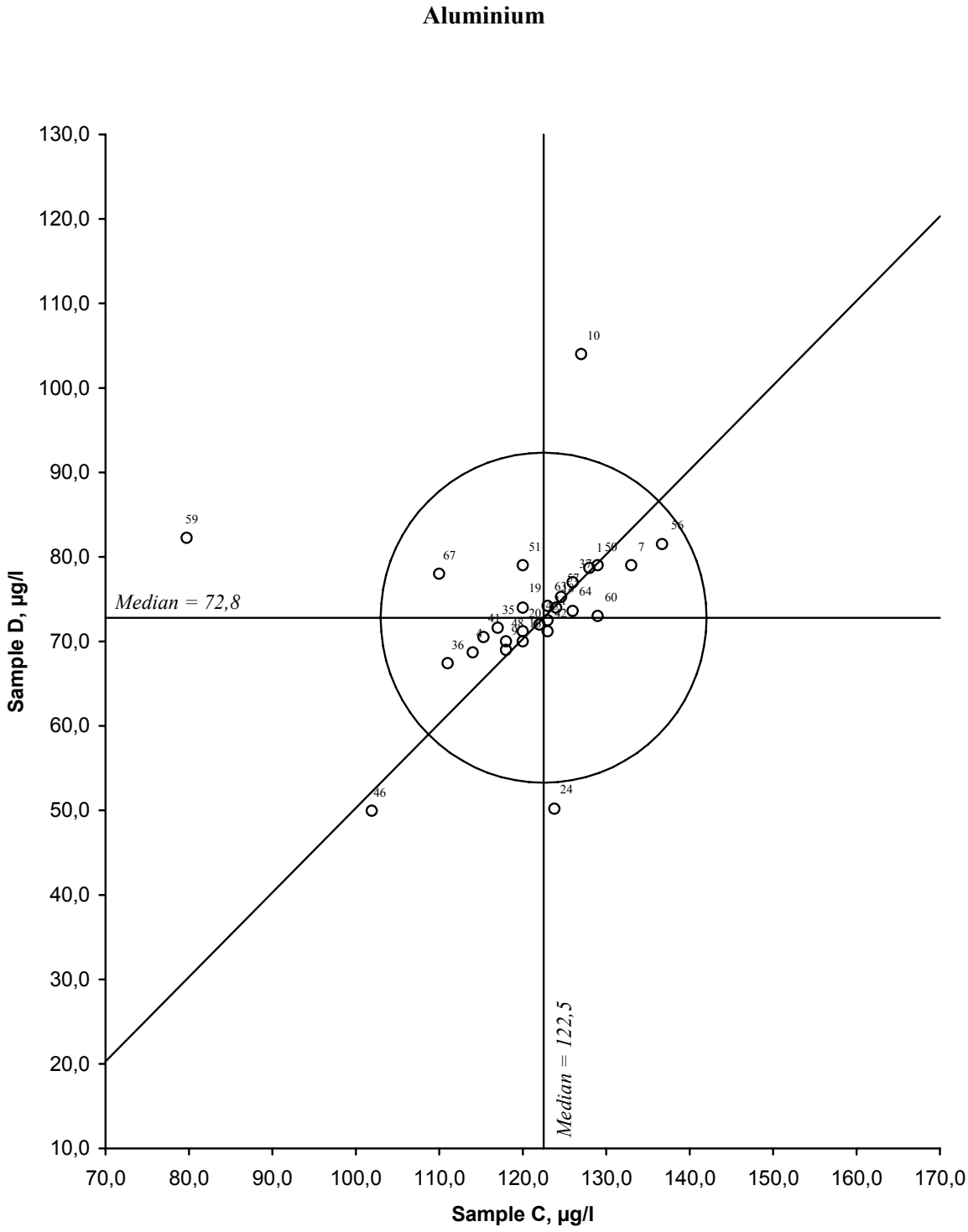


Figure 12. Youdendiagram for aluminium, sample pair CD
Acceptance limit, given by the circle, is 20 %

**Iron**

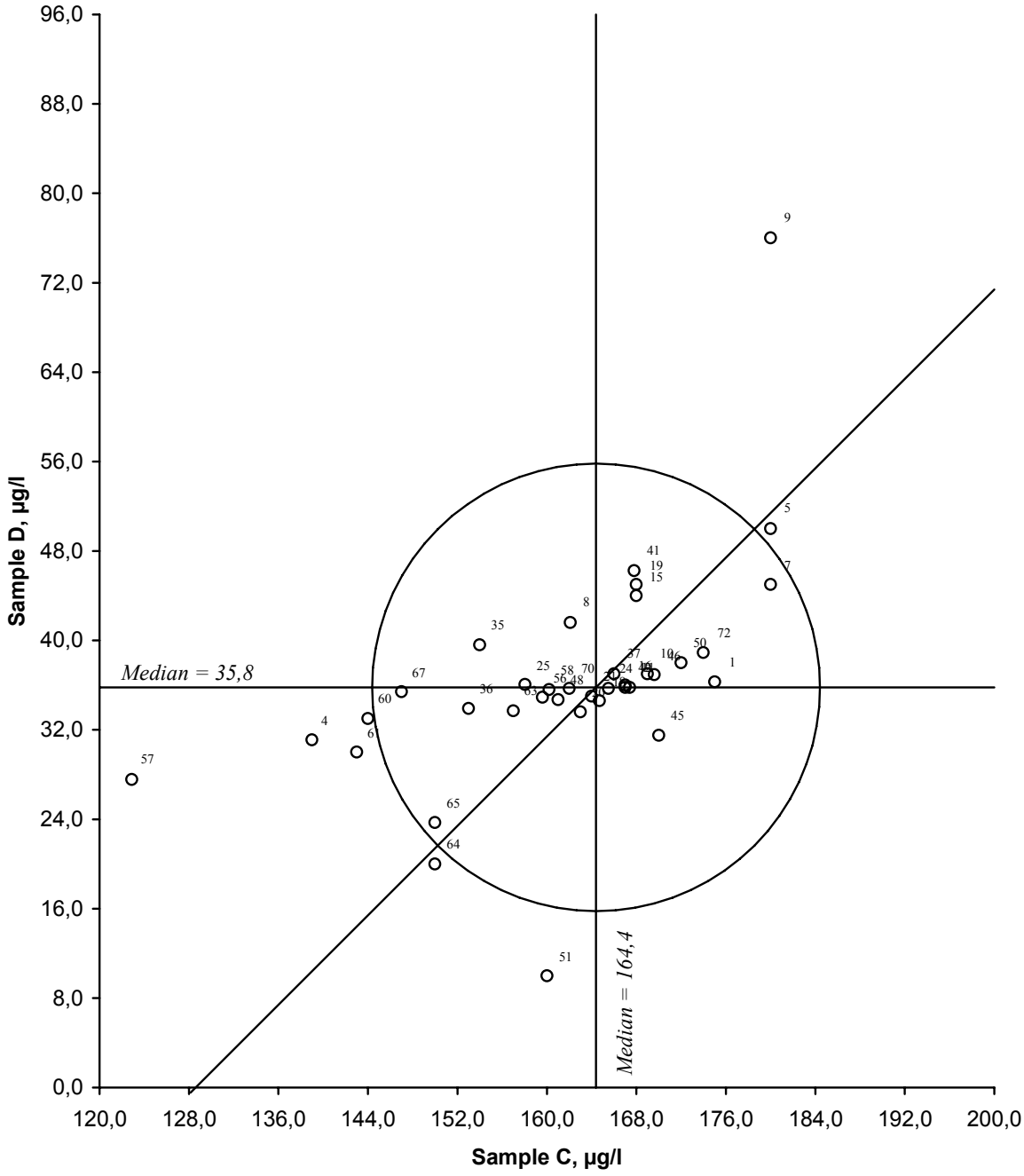


Figure 13. Youdendiagram for iron, sample pair CD
Acceptance limit, given by the circle, is 20 %

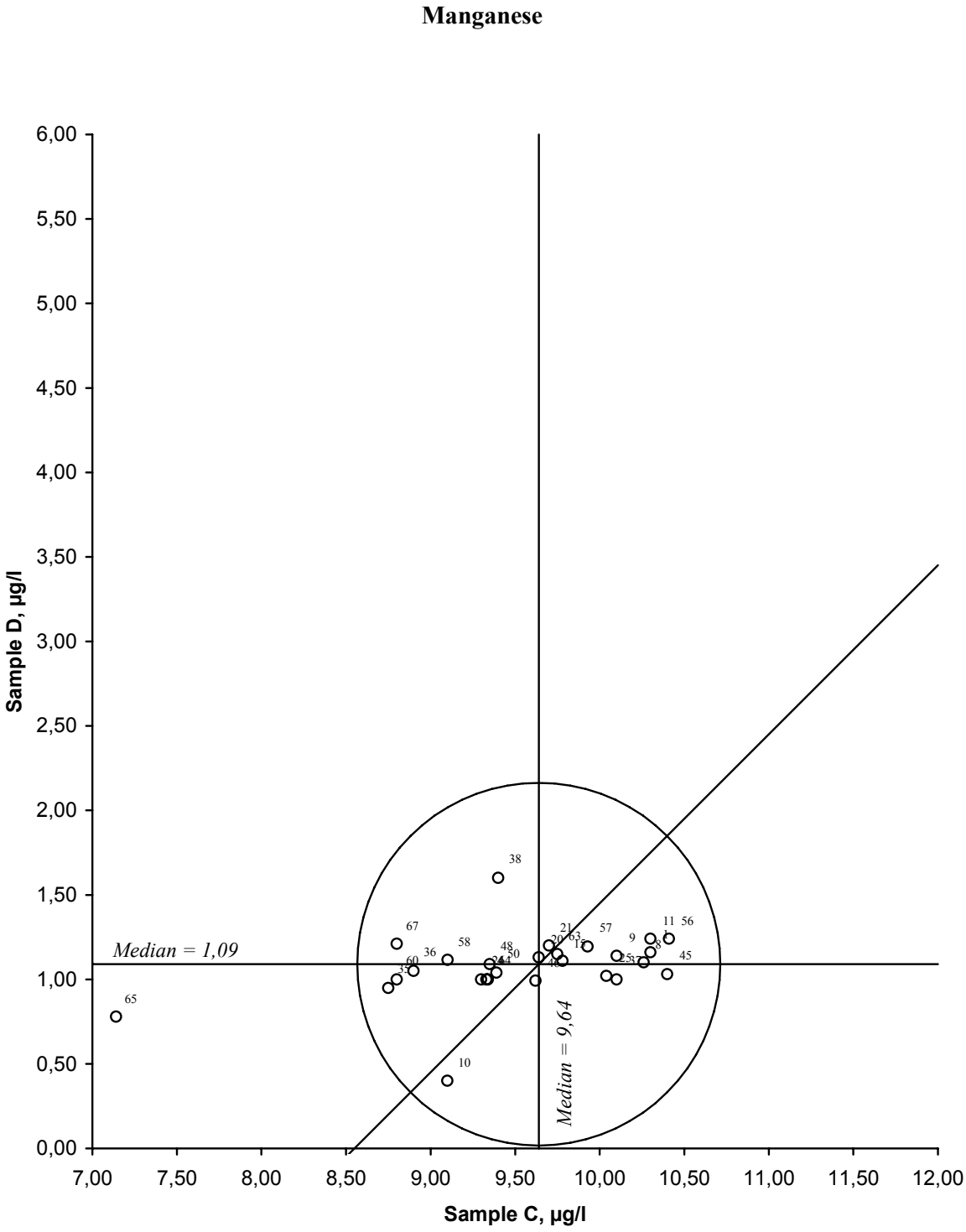


Figure 14. Youdendiagram for manganese, sample pair CD
Acceptance limit, given by the circle, is 20 %

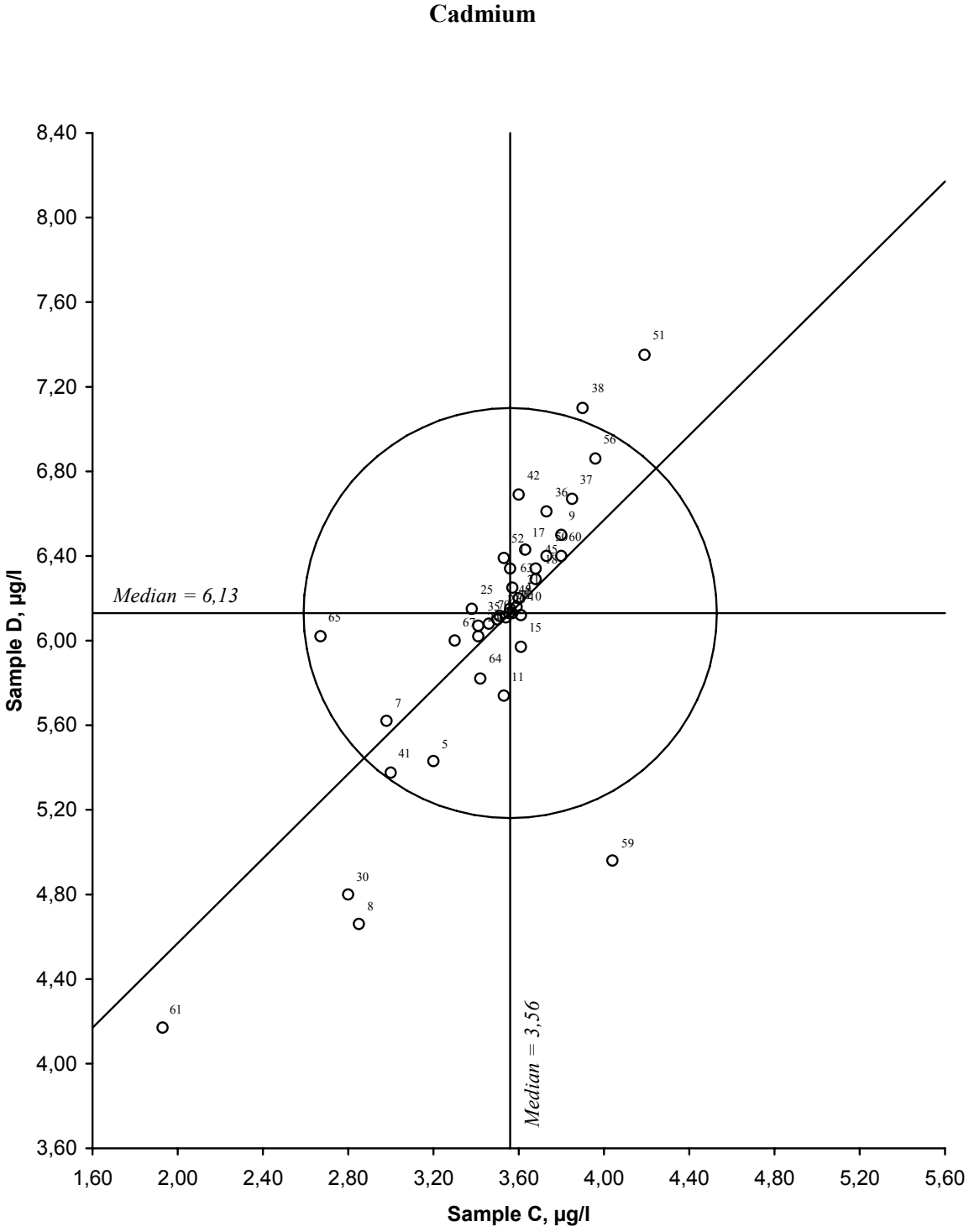


Figure 15. Youdendiagram for cadmium, sample pair CD
Acceptance limit, given by the circle, is 20 %

**Lead**

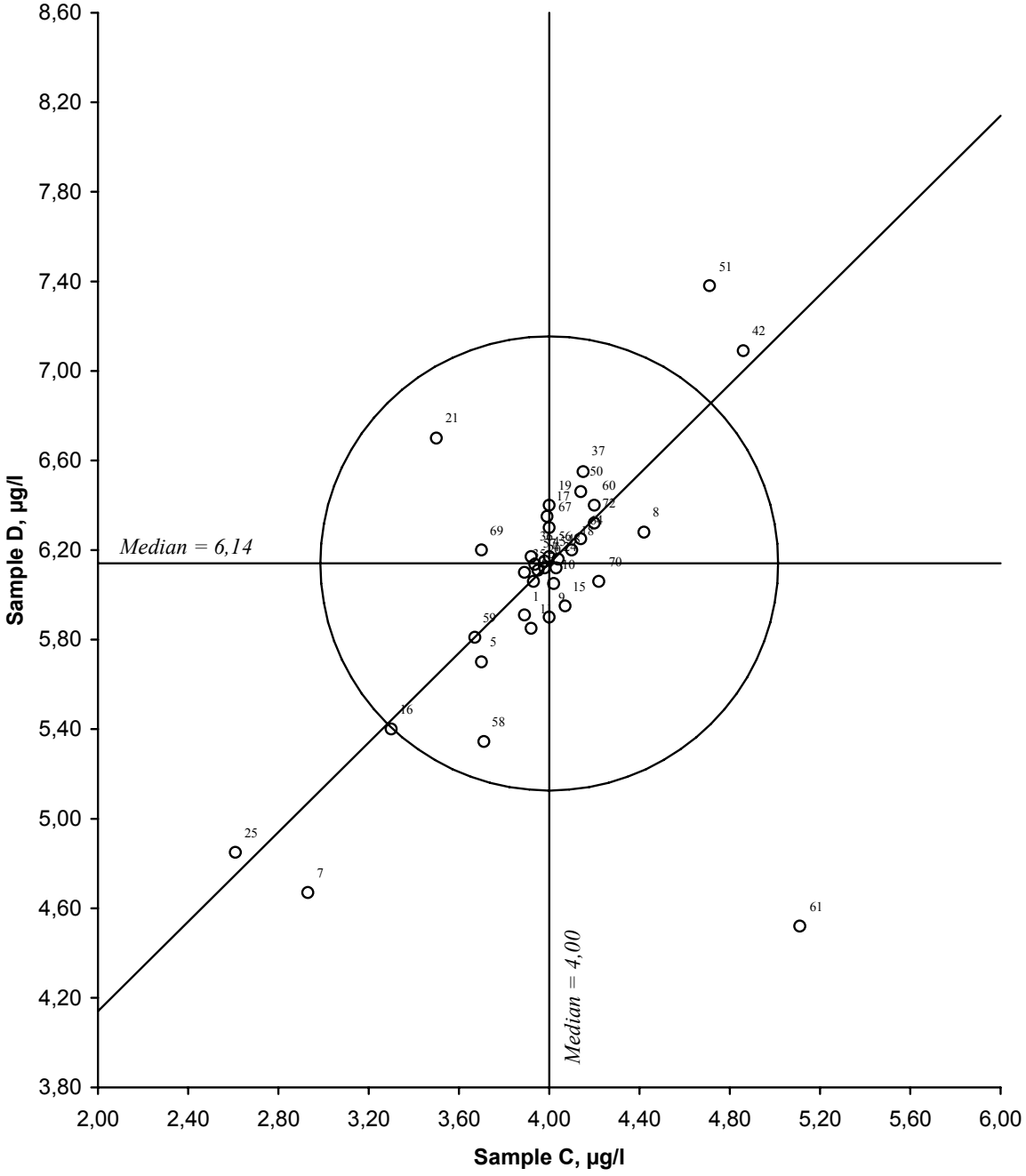


Figure 16. Youdendiagram for lead, sample pair CD
Acceptance limit, given by the circle, is 20 %

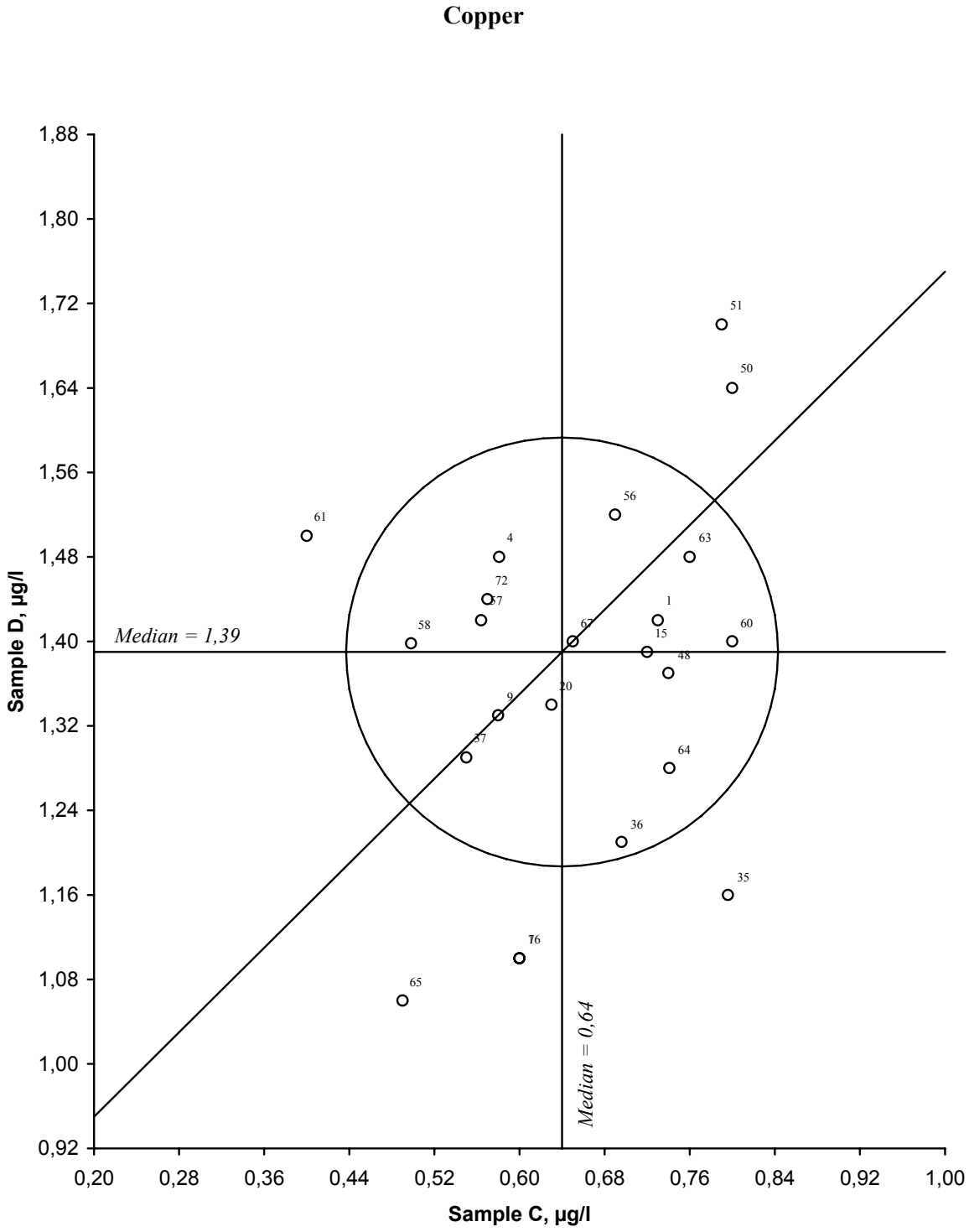


Figure 17. Youdendiagram for copper, sample pair CD
Acceptance limit, given by the circle, is 20 %

**Nickel**

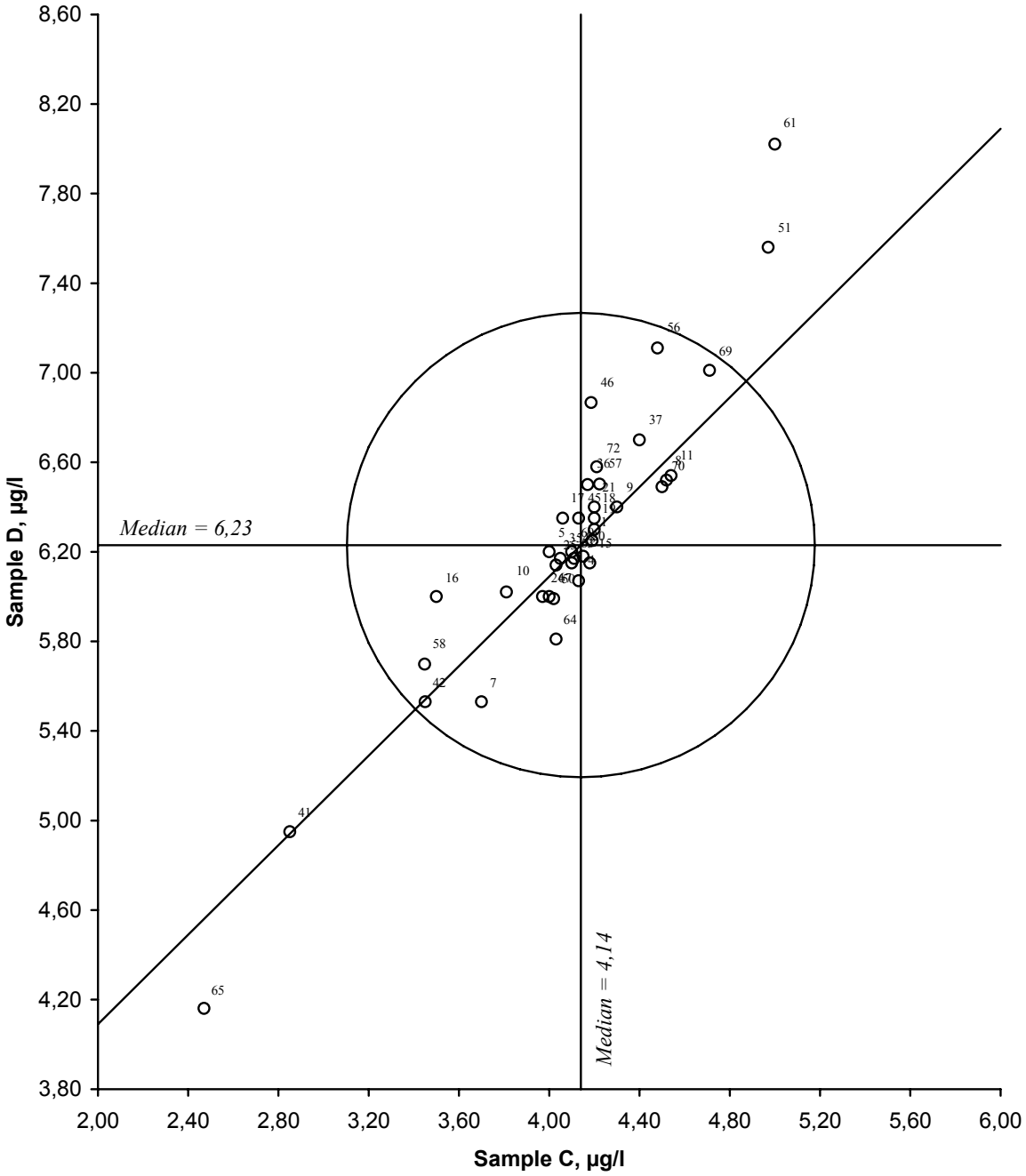


Figure 18. Youdendiagram for nickel, sample pair CD
Acceptance limit, given by the circle, is 20 %

**Zinc**

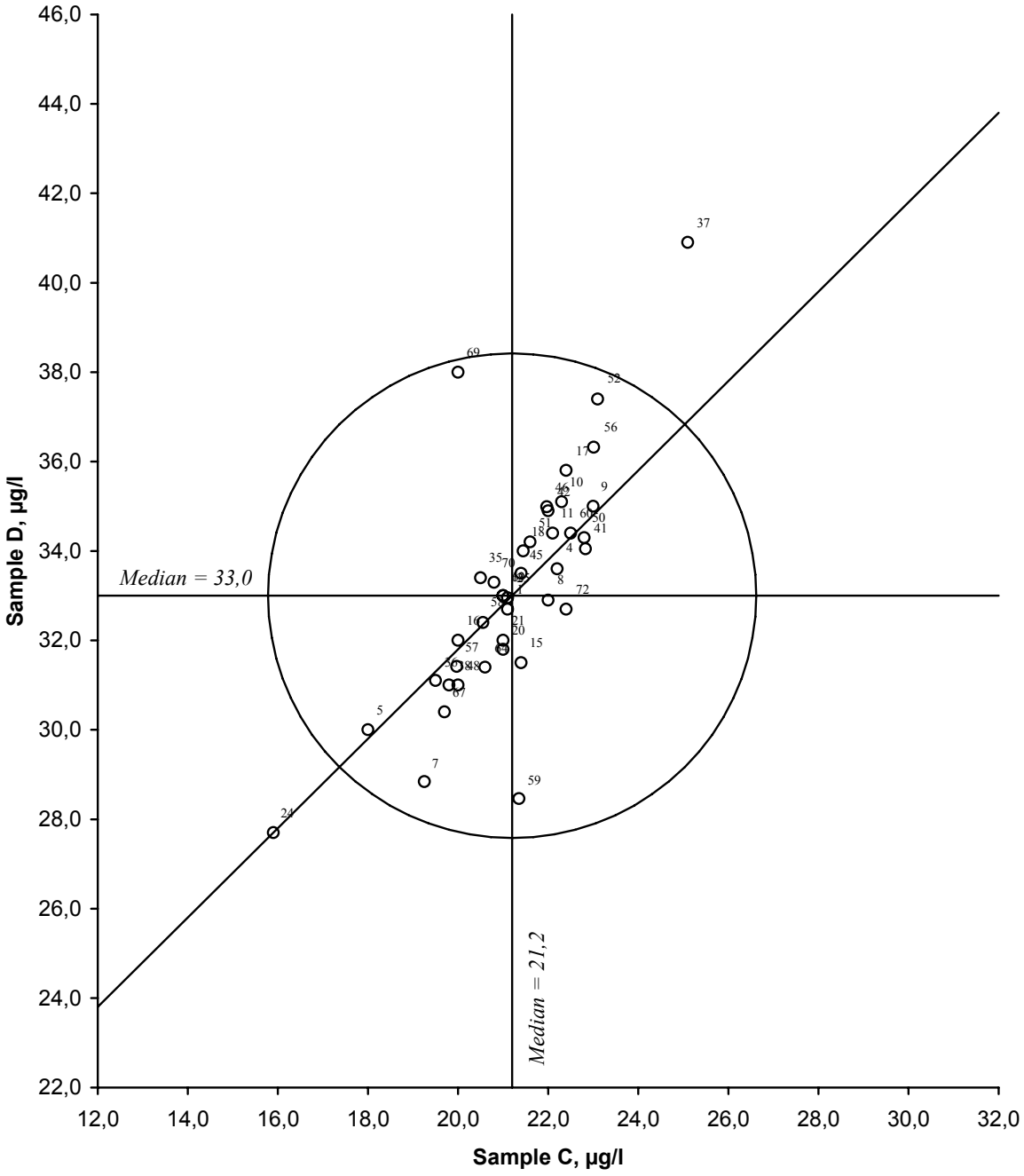


Figure 19. Youdendiagram for zinc, sample pair CD
Acceptance limit, given by the circle, is 20 %

# 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, i.e. fixed or relative acceptance limits.

In Table 2 an evaluation of the results of intercomparison 0923 is presented, based on the target accuracy (except for pH and conductivity), where the number and percentage of acceptable results are given. 75 % of the results submitted by the participants are acceptable when compared to the acceptance limits given above. By improvement of the routine analytical method, the laboratories should be able to obtain even more accurate and comparable results.

In table 4 the individual results of each laboratory are given. The results reported by the laboratory are printed, however, in some cases the result has been enhanced to one more digit than is statistically significant. There are some laboratories using far more digits than are statistically significant. This is absolutely unnecessary, and each laboratory should determine how many digits are significant for each of their analytical methods. Of course, one digit more than what is statistically significant can be accepted, this will reduce the round-off error in the statistical calculations of the reported results.

For pH, the general target accuracy is ± 0,1 pH units (1), and 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. Even with this wider acceptance limit only 61 % of the result pairs are evaluated as acceptable this time.

pH results may be strongly affected by the method used, when the measurement is performed in nearly neutral solutions. This problem has been demonstrated through several earlier intercomparisons, and will remain as a problem as long as different methods, and different working procedures and different instrumental equipment for pH determination are used by the participating laboratories. This time there were only minor differences between the pH results produced during stirring the solution and no stirring of the solution, and even when using equilibration of the samples before measurement.

Because of the high precision of the reported results for conductivity in earlier intercomparisons, we have reduced the acceptance limit for this analytical variable from the target value ± 20 % to ± 10 %. Still the number of acceptable results for conductivity is 71 % (Table 2). If we increase the acceptance limit to the target value, the number of acceptable results would increase. It is still a problem that many laboratories report their results in the units they normally use at their own laboratory, and they very often do not write the unit used. The unit asked for in this intercomparison is mS/m. For this reason some correspondence with the laboratories was necessary to clarify the right results. In some cases where the laboratory had given the necessary information together with the conductivity results, it was possible to recalculate the results to the unit mS/m.

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**Table 2. Evaluation of the results of intercomparison 0923. N is the number of result pairs reported, and n is the number of acceptable results within the given target accuracy.**

| Determinand and unit | Sample pair | True value 1 | True value 2 | limit % * | Number of pairs N | Number of pairs n | % accepatble results for intercalibration **0923** | 0822 | 0721 | 0620 |
|---|---|---|---|---|---|---|---|---|---|---|
| pH | AB | 6,58 | 7,05 | 0,2 | 64 | 39 | **61** | 68 | 51 | 74 |
| Conductivity, mS/m | AB | 3,09 | 3,36 | 10 | 63 | 45 | **71** | 81 | 80 | 71 |
| Alkalinity, mmol/l | AB | 0,099 | 0,2 | 20 | 45 | 30 | **67** | 35 | 67 | 63 |
| Nitrate + nitrite-nitrogen, µg/l | AB | 187 | 154 | 20 | 59 | 34 | **58** | 64 | 63 | 81 |
| Chloride, mg/l | AB | 2,76 | 1,19 | 20 | 59 | 51 | **86** | 85 | 79 | 82 |
| Sulfate, mg/l | AB | 1,82 | 2,12 | 20 | 56 | 43 | **77** | 84 | 81 | 89 |
| Calcium, mg/l | AB | 2,07 | 4,45 | 20 | 57 | 48 | **84** | 85 | 86 | 77 |
| Magnesium, mg/l | AB | 0,487 | 0,421 | 20 | 57 | 50 | **88** | 78 | 77 | 70 |
| Sodium, mg/l | AB | 3,25 | 1,26 | 20 | 58 | 51 | **88** | 91 | 92 | 88 |
| Potassium, mg/l | AB | 0,299 | 0,231 | 20 | 57 | 43 | **75** | 65 | 77 | 80 |
| Total organic carbon, mg/l | AB | 10,48 | 4,15 | 20 | 34 | 28 | **82** | - | - | - |
| Aluminium, µg/l | CD | 122,5 | 72,8 | 20 | 31 | 24 | **77** | - | - | - |
| Iron, µg/l | CD | 164,4 | 35,8 | 20 | 40 | 29 | **73** | 83 | 63 | 77 |
| Manganese, µg/l | CD | 9,64 | 1,09 | 20 | 39 | 26 | **67** | 40 | 70 | 78 |
| Cadmium, µg/l | CD | 3,56 | 6,13 | 20 | 43 | 34 | **79** | 80 | 75 | 74 |
| Lead, µg/l | CD | 4 | 6,14 | 20 | 42 | 31 | **74** | 67 | 64 | 52 |
| Copper, µg/l | CD | 0,64 | 1,39 | 20 | 43 | 16 | **37** | 20 | 82 | 77 |
| Nickel, µg/l | CD | 4,14 | 6,23 | 20 | 41 | 35 | **85** | 54 | 62 | 63 |
| Zinc, µg/l | CD | 21,2 | 33 | 20 | 42 | 38 | **90** | 62 | 53 | 61 |
| Total | | | | | 930 | 695 | **75** | (69) | (73) | (75) |

* Acceptance limit for pH is given in pH units

For alkalinity, as we have observed earlier, the reported results for solutions with low alkalinity values are much more widely spread than are solutions with higher concentrations of bicarbonate. In this intercomparison, the number of acceptable results were 67 %, and a possible explanaltion for this may be the higher concentrations of bicarbonate in the two samples.

For nitrate only 58 % of the result pairs are acceptable. This is too low, and it may perhaps be caused by some unstability for this parameter during transport of the samples. Control analyses at the Programme Centre demonstrated that the samples were stable with respect to the content of nitrate, throughout the whole periode of the intercomparison when the samples were stored at 4 °C. However, some participants pointed out that they observed a certain unstability for this parameter on storage of the samples.

For the major ions, chloride, sulphate, calcium, magnesium and sodium, the number of acceptable results are high as usual. Also the new parameter total organic carbon had 82 % acceptable results.

The best results for some heavy metals included in this intercomparison programme were obtained for zinc and nicel, where 90 % and 85 % of the results, respectively, are acceptable. This is considered as acceptable. For some of the elements the concentrations were low, and it is obvious that some laboratories do not have sensitive enough methods to determine heavy metals on the trace level.

It should be discussed what concentration levels for the heavy metals would be most useful for ICP Waters in the coming intercomparisons. It should also be discussed whether *absolute* acceptance limits should be used instead of the *relative* one (± 20 %), which is used in this intercomparison, in cases where the results are close to the detection limit. In such cases it is important that the steering committee decides what target detection limit should be obtained by the participating laboratories.

# 4. Conclusion

68 laboratories submitted results for this intercomparison. The best results were reported for the analytical variables zinc, magnesium and sodium, where 90 %, 88 and 88 % of the results, respectively, were acceptable. The worst results were observed for the heavy metal copper where the concentrations are rather low, with only 37 % acceptable results.

In this intecomparison 75 % of the evaluated results were located within the general target accuracy of ± 20 %, or the special accuracy limit for pH and conductivity. The low fraction of acceptable results for some variables, especially some of the heavy metals and alkalinity, may be explained by the rather low concentrations used for these analytical variables. When the concentrations are close to the detection limits for some of the methods used by the participants, it must be expected that the spread of the results will be greater than ± 20 %.

The laboratories which reported results outside this limit should improve their methods to obtain a better accuracy and comparability. Generally, the application of some analytical methods seems to be less suited for the water samples analyzed in this programme, as the detection limits of some methods applied by participants are too high. This is especially true for some manual methods, and some of the methods used for the determination of metals, especially when the concentration is very low. It is important that methods with sufficiently low detection limits are used by the participating laboratories.

A few laboratories do not report the results in the unit requested, in addition they very often do not specify which unit has really been used. It is very important that the unit used is clearly specified.

A total error of ± 0,2 pH units seems to be a reasonable assessment of the accuracy for pH measurements, when near neutral water samples - which are not in $CO_2$ equilibrium - are analyzed.

Considering the determination of metals in these samples, it is quite clear that the emission techniques (ICP-AES, ICP-MS etc.) are taking over for atomic absorption methods, which were the dominating methods some years ago. For the major ions the ion chromatography technique are clearly growing on behalf of the traditional methods, the photometric methods for the anions and the atomic absorption or emission methods for the cations.

The Youden technique for evaluating intercomparison results presupposes that the two samples in a sample set are comparable with respect to the concentration of each parameter. In this intercomparison there may be a little too big difference between the concentrations of the two samples for some parameters, especially manganese. This should be kept in mind when the samples for the next intercomparison is prepared.

# 5. Literature

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# Appendix A.

## The participating laboratories

| No. | Name of participant | City | Country |
|---|---|---|---|
| 1 | Umweltbundesamt | Vienna | Austria |
| 2 | Institut für Ökologie | Innsbruck | Austria |
| 3 | Institute of Meteorology and Geophysics | Innsbruck | Austria |
| 4 | SLU, Department of Soil Environment | Uppsala | Sweden |
| 5 | Institute of Environmental Protection | Warsaw | Poland |
| 6 | Finnish Forest Research Institute | Rovaniemi | Finland |
| 7 | Northern Water Problems Institute | Petrozavodsk | Russia |
| 8 | Laboratorio Integrado de Calidad Ambiental | Pamplona | Spain |
| 9 | Hydrochemistry and Chemistry of Atmosphere | Irkutsk | Russia |
| 10 | Tartu Environmental Reseach | Tartu | Estonia |
| 11 | "Ecoanalyt" Ecoanalytical Laboratory | Syktyvkar | Russia |
| 12 | KCL Kymen Laboratorio oy | Kuusankoski | Finland |
| 13 | Freshwater Institute | Winnipeg | Canada |
| 14 | Freshwater Institute, ELA Sattelite Lab | Winnipeg | Canada |
| 15 | Umweltbundesamt - Luftmessnetz | Langen | Germany |
| 16 | Centre de Geochimie de la Surface | Strasbourg | France |
| 17 | Environmental Agency of the Republic of Slovenia | Ljubljana | Slovenia |
| 18 | NLS Starcross Laboratory | Exeter | United Kingdom |
| 19 | Amt der Kärntner Landesregierung | Klagenfurt | Austria |
| 20 | Environmental Protection Agency Irland | Dublin | Ireland |
| 21 | CNR IstitutoStudio Ecosistemi | Pallanza | Italy |
| 22 | Virumaa Environmental Research | Johvi | Estonia |
| 23 | Laboratorio Biologico-APPA-BZ | Laives | Italy |
| 24 | Finnish Forest Research Institute | Vantaa | Finland |
| 25 | Yantai Environmental Monitoring Centre | Yantai | China |
| 26 | Institute of Hydrobilogy | Budejovice | Czech Republic |
| 27 | Water Research Institute | Brugherio | Italy |
| 28 | National Institute of Biology | Ljubljana | Slovenia |
| 29 | Adirondack Lakes Survey Corporation | Ray Brook | USA |
| 30 | Institute of Botany Pasci | Krakow | Poland |
| 31 | Institute of Public Health | Kranj | Slovenia |
| 32 | CEH Wallingford | Wallingford | United Kingdom |
| 33 | Environmental Research Department | Vilnius | Lithuania |
| 34 | Environmental Research and Training Center | Pathumthani | Thailand |
| 35 | Freshwater Laboratory | Pitlochry | Scotland |
| 36 | Landesamt für Natur, Umwelt und Verbrauchs. | Dusserldorf | Germany |
| 37 | CRAM, University of Barcelona | Vielha | Spain |
| 38 | Laboratory of Water Chemistry | Sosnowiec | Poland |
| 39 | ISSeP Colfontaine | Wasmes | Belgium |
| 40 | US EPA Western Ecology Division | Corvallis | USA |
| 41 | Buesgen Institute of Soil Science of Temperate - - - | Göttingen | Germany |
| 42 | Sawyer Environmental Chemistry Lab | Orono | USA |
| 43 | Institute of North Ecological Problems | Apatity | Russia |
| 44 | Institute of North Ecological Problems, ICP lab | Apatity | Russia |
| 45 | Environmental Laboratory | Riga | Latvia |

| No. | Name of participant | City | Country |
|---|---|---|---|
| 46 | University of Florence, Lab. Di Microanalisi | Firenze | Italy |
| 47 | University of Florence, Soil solution | Firenze | Italy |
| 48 | ECOLAB Universite de Toulouse | Castanet Tolosan | France |
| 49 | Dorset Environmental Science Centre | Dorset | Canada |
| 50 | Bayerische Landesamt für Umwelt | München | Germany |
| 51 | SLU, Skoglig Marklära | Uppsala | Sweden |
| 52 | Geological Survey of Estonia | Tallinn | Estonia |
| 53 | Tallin University of Technology | Tallinn | Estonia |
| 54 | Center for Environmental Monitoring | Vladivostok | Russia |
| 55 | Aquatische Ecologie en Milieubiologie | Nijmegen | Netherlands |
| 56 | Institute of Environmental Engineering | Zabrze | Poland |
| 57 | Acid Deposition and Oxidant Research Center | Niigata-shi | Japan |
| 58 | Vlaamse Milieumaatschappij | Antwerpen | Belgium |
| 59 | Laboratorio SPAAS | Bellinzona | Switzerland |
| 60 | Bayerische Landesamt für Wald und Forstwirtschaft | Freising | Germany |
| 61 | Laboratory of monitoring of pollution | Astrakhan | Russia |
| 62 | Institute of Environmental Protection | Warsaw | Poland |
| 63 | Finnish Environment Institute | Helsinki | Finland |
| 64 | Norwegian Institute for Water Research | Oslo | Norway |
| 65 | S.C. Analist Service S.R.L. | Bucharest | Romania |
| 66 | Charles University in Prague | Blatna | Czech Republic |
| 67 | ZAO "Rossa" | Moscow | Russia |
| 68 | Staatliche Umweltbetriebsgesellschaft | Chemnitz | Germany |
| 69 | Institute of Global Climate and Biology | Moscow | Russia |
| 70 | Institute for Ecology of Industrial Areas | Katowice | Poland |
| 71 | Forest nutrition and Water Resource | Freising | Germany |
| 72 | Laboratory of Geology and Geography | Helsinki | Finland |

## Number of participating laboratories from the different countries being represented in intercomparison 0923

| Country | Labs | Country | Labs | Country | Labs |
|---|---|---|---|---|---|
| Austria | 4 | Ireland | 1 | Russia | 9 |
| Belgium | 2 | Italy | 5 | Scotland | 1 |
| Canada | 3 | Japan | 1 | Slovenia | 3 |
| China | 1 | Latvia | 1 | Spain | 2 |
| Czech Republic | 2 | Lithuania | 1 | Sweden | 2 |
| Estonia | 4 | Netherlands | 1 | Switzerland | 1 |
| Finland | 5 | Norway | 1 | Thailand | 1 |
| France | 2 | Poland | 6 | United Kingdom | 2 |
| Germany | 7 | Romania | 1 | USA | 3 |
| | | | | Total | 27 |

# Appendix B.

## Preparation of samples

The sample solutions were prepared from water collected from two locations outside Oslo, Norway, two rivers called Kvisla and Langlielva. The water was collected in several 25 liter plastic containers and brought to the laboratory. The water was filtrated through 0,45 µm membrane filter, and the filtrate collected in polyethylene containers, and then stored at room temperature for several weeks at the laboratory to equilibrate. Small aliquots were removed from the filtrate to determine the background concentrations of the analytical variables of interest. The samples were prepared by spiking the filtrated water with stock solutions of stoichiometric compounds containing the major ions, or heavy metals. The samples C and D were prepared for the determination of metals, and preserved by addition of 5 ml concentrated nitric acid pr. liter sample. A few days before mailing the samples to the participants, the solutions were transferred to 1/2 liter high density polyethylene bottles with screw cap. These samples were stored at room temperature until mailing to the participating laboratories.

## 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 June 2009, a few weeks before mailing the samples to the participants. The last sample was analyzed medio August 2009. 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. Even nitrate proved to be stable in these solutions when stored at 4 °C.

**Table 3. Summary of the control analyses**

| Analytical variable | Sample A | | Sample B | |
|---|---|---|---|---|
| | Mean | Std. dev. | Mean | Std. dev. |
| pH | 6,79 | 0,20 | 7,21 | 0,08 |
| Conductivity mS/m | 3,06 | 0,03 | 3,29 | 0,04 |
| Alkalinity mmol/l | 0,100 | 0,002 | 0,201 | 0,002 |
| Nitrate-nitrogen µg/l | 198 | 5,0 | 190 | 4,1 |
| Chloride mg/l | 2,65 | 0,06 | 1,15 | 0,02 |
| Sulphate mg/l | 1,75 | 0,06 | 2,00 | 0,10 |
| Calcium mg/l | 2,23 | 0,08 | 4,80 | 0,13 |
| Magnesium mg/l | 0,48 | 0,02 | 0,41 | 0,02 |
| Sodium mg/l | 3,19 | 0,09 | 1,27 | 0,01 |
| Potassium mg/l | 0,28 | 0,04 | 0,22 | 0,01 |
| Total organic carbon, mg/l | 10,9 | 0,14 | 3,85 | 0,06 |
| | **Sample C** | | **Sample D** | |
| Aluminium, µg/l | 127 | 6,3 | 75,4 | 4,2 |
| Iron, µg/l | 153 | 5,0 | 27,5 | 5,0 |
| Manganese, µg/l | 8,60 | 1,33 | 0,96 | 0,12 |
| Cadmium, µg/l | 3,50 | 0,07 | 5,97 | 0,11 |
| Lead, µg/l | 4,26 | ,09 | 6,67 | 0,29 |
| Copper, µg/l | 0,79 | 0,03 | 1,33 | 0,09 |
| Nickel, µg/l | 4,11 | 0,11 | 5,89 | 0,23 |
| Zinc, µg/l | 21,2 | 0,50 | 32,2 | 0,71 |

# 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 - 19).

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 the participating laboratories. The results being omitted in the statistical calculations are not used in the determination of the median value and thus the true value. 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 source of error.

The statistical treatment of the analytical results was accomplished in this way: Pairs of results where one or both of the values are lying outside the true value ± 50 %, are omitted from the statistical calculations. The remaining results are used for the calculation of the mean value (x) and the standard deviation (s). Now the pairs of results where both of the values are lying outside $x \pm 3s$, are omitted. The remaining results are used for a final calculation, the results of which are presented in the tables 5.1 - 5.19. Results being omitted from the calculations, are marked with the letter "U".

# Appendix D

***Table 4. The results of the participating laboratories.***

| Lab. | pH | | Conductivity, mS/m | | Alkalinity, mmol/l | | Nitrate-N, µg/l | |
|---|---|---|---|---|---|---|---|---|
| | A | B | A | B | A | B | A | B |
| 1 | 6,21 | 6,78 | 3,03 | 3,30 | 0,147 | 0,256 | 177 | 129 |
| 2 | 6,56 | 7,09 | 0,31 | 0,34 | 0,085 | 0,195 | 185 | 149 |
| 3 | | | | | | | | |
| 4 | 6,52 | 7,04 | 2,5 | 2,8 | 0,082 | 0,187 | 200 | 170 |
| 5 | 6,61 | 6,93 | 3,16 | 3,39 | 0,112 | 0,205 | 174 | 106 |
| 6 | 6,59 | 7,19 | 3,05 | 3,62 | 0,101 | 0,200 | 87,0 | 180 |
| 7 | 6,48 | 7,03 | 2,93 | 3,05 | 5,58 | 12,00 | 169 | 115 |
| 8 | 6,72 | 7,20 | 2,71 | 3,63 | | | 177 | 103 |
| 9 | 6,72 | 7,21 | 3,14 | 3,43 | 0,64 | 0,181 | 0,73 | 0,53 |
| 10 | 6,51 | 7,06 | 3,03 | 3,18 | 0,109 | 0,195 | 107 | 166 |
| 11 | 6,13 | 6,66 | 2,84 | 3,06 | < 0,160 | 0,224 | 181 | 113 |
| 12 | 6,7 | 7,2 | 3,56 | 3,57 | 0,099 | 0,202 | 180 | 162 |
| 13 | 6,58 | 7,04 | 3,0 | 3,2 | | | 194 | 145 |
| 14 | 6,44 | 6,93 | 3,1 | 3,3 | | | 189 | 141 |
| 15 | | | 3,17 | 3,41 | | | 188 | 174 |
| 16 | 6,54 | 7,04 | 3,15 | 3,41 | 0,102 | 0,209 | 210 | 182 |
| 17 | 6,45 | 6,93 | 2,78 | 3,01 | 0,155 | 0,263 | 192 | 153 |
| 18 | 6,61 | 7,19 | 3,1 | 3,4 | 0,092 | 0,176 | 74 | 207 |
| 19 | 6,2 | 6,8 | 3,3 | 3,6 | 0,10 | 0,21 | 19 | 140 |
| 20 | 7,06 | 7,07 | 3,1 | 3,3 | 0,13 | 0,23 | 180 | 176 |
| 21 | 6,53 | 7,03 | 3,06 | 3,35 | 0,098 | 0,200 | 188 | 152 |
| 22 | 6,42 | 6,71 | 2,58 | 3,09 | | | | |
| 23 | 6,47 | 6,90 | 3,13 | 3,40 | 0,092 | 0,207 | 198 | 153 |
| 24 | 6,41 | 7,01 | 3,22 | 3,44 | | | 192 | 176 |
| 25 | | | | | | | | |
| 26 | 6,58 | 7,14 | 3,05 | 3,22 | 0,100 | 0,203 | 180 | 155 |
| 27 | | | | | | | | |
| 28 | 6,53 | 7,11 | 3,0 | 3,4 | 0,113 | 0,227 | 215 | 153 |
| 29 | 6,53 | 7,03 | 307,00 | 327,00 | 0,108 | 0,209 | 194 | 163 |
| 30 | 6,88 | 7,29 | 3,37 | 3,78 | | | 233 | 193 |
| 31 | 6,55 | 7,04 | 3,3 | 3,5 | | | | |
| 32 | 6,54 | 7,06 | | | | | 198 | 172 |
| 33 | 6,74 | 7,18 | 3,07 | 3,27 | | | 187 | 133 |
| 34 | 6,75 | 6,88 | 3,08 | 3,35 | 0,114 | 0,200 | 182 | 112 |
| 35 | 6,51 | 7,06 | 3,1 | 3,4 | 0,089 | 0,193 | 183 | 152 |

| Lab. | pH | | Conductivity, mS/m | | Alkalinity, mmol/l | | Nitrate-N, µg/l | |
|---|---|---|---|---|---|---|---|---|
| | A | B | A | B | A | B | A | B |
| 36 | 6,62 | 7,13 | 3,10 | 3,36 | 0,089 | 0,191 | 183 | 156 |
| 37 | 6,37 | 6,97 | 3,1 | 3,3 | 0,049 | 0,098 | 42 | 147 |
| 38 | 6,02 | 6,38 | 2,95 | 3,24 | 0,14 | 0,24 | 133 | 107 |
| 39 | 6,60 | 7,12 | 3,08 | 3,38 | | | 170 | 143 |
| 40 | 6,70 | 7,16 | 3,04 | 3,32 | 0,099 | 0,199 | 153 | 71 |
| 41 | 6,48 | 7,09 | 3,11 | 3,34 | | | 200 | <150 |
| 42 | 6,99 | 7,46 | 3,14 | 3,47 | 0,109 | 0,212 | 174 | 133 |
| 43 | | | | | | | | |
| 44 | | | | | | | | |
| 45 | 6,53 | 7,12 | 3,04 | 3,18 | 0,084 | 0,19 | 181 | 152 |
| 46 | | | | | | | | |
| 47 | 6,75 | 7,30 | 3,19 | 3,43 | | | 176 | 122 |
| 48 | 5,83 | 6,46 | 3,4 | 3,6 | 0,098 | 0,170 | 130 | 180 |
| 49 | 6,45 | 6,85 | 2,80 | 3,10 | 0,089 | 0,181 | 156 | 154 |
| 50 | 6,63 | 7,12 | 3,08 | 3,36 | | | 210 | 165 |
| 51 | 6,60 | 7,15 | 2,96 | 3,22 | 0,076 | 0,192 | 199 | 175 |
| 52 | 6,8 | 6,9 | 3,24 | 3,61 | | | | |
| 53 | 6,65 | 6,85 | 3,22 | 3,46 | | | 194 | 157 |
| 54 | 6,70 | 7,20 | 3,22 | 3,49 | 0,094 | 0,201 | 188 | 142 |
| 55 | 6,62 | 6,87 | | | 0,20 | 0,27 | 583 | 384 |
| 56 | 6,85 | 7,14 | 4,33 | 4,59 | | | 224 | 192 |
| 57 | 6,60 | 7,07 | 3,11 | 3,37 | 0,094 | 0,194 | 165 | 176 |
| 58 | 6,37 | 6,92 | 3,09 | 3,34 | | | 209 | 169 |
| 59 | 6,60 | 7,06 | 2,80 | 3,06 | 0,094 | 0,220 | 243 | 207 |
| 60 | 6,58 | 7,04 | 2,80 | 3,04 | | | 203 | 178 |
| 61 | 6,32 | 6,80 | 2,81 | 3,07 | 0,150 | 0,230 | 152 | 109 |
| 62 | 6,75 | 7,13 | 3,20 | 3,42 | | | | |
| 63 | 6,58 | 6,93 | 3,01 | 3,33 | 0,080 | 0,186 | 187 | 170 |
| 64 | 6,71 | 7,17 | 3,07 | 3,34 | 0,103 | 0,204 | 190 | 190 |
| 65 | 5,44 | 6,10 | 5,43 | 3,81 | 0,039 | 0,083 | 348 | 132 |
| 66 | 6,57 | 7,05 | 3,18 | 3,36 | 0,099 | 0,199 | | |
| 67 | 6,64 | 6,74 | 3,10 | 3,40 | 0,10 | 0,21 | 191 | 150 |
| 68 | 6,4 | 7,0 | 3,06 | 3,35 | 0,156 | 0,275 | 170 | 140 |
| 69 | | | | | | | | |
| 70 | 6,40 | 6,71 | 3,01 | 3,26 | 0,094 | 0,193 | | |
| 71 | 7,00 | 7,49 | 3,37 | 3,71 | 0,181 | 0,296 | 188 | 158 |
| 72 | 6,68 | 7,11 | 3,14 | 3,38 | 0,109 | 0,208 | 139 | 154 |

| Lab. | Chloride, mg/l | | Sulfate, mg/l | | Calcium, mg/l | | Magnesium, mg/l | |
|---|---|---|---|---|---|---|---|---|
| | A | B | A | B | A | B | A | B |
| 1 | 2,76 | 1,17 | 1,81 | 2,13 | 1,96 | 4,30 | 0,480 | 0,426 |
| 2 | 2,68 | 1,15 | 1,82 | 2,13 | 2,10 | 4,55 | 0,485 | 0,424 |
| 3 | | | | | | | | |
| 4 | 2,74 | 1,27 | 1,71 | 2,01 | 2,06 | 4,46 | 0,48 | 0,42 |
| 5 | 2,90 | 1,15 | 1,49 | 1,64 | 2,17 | 4,63 | 0,51 | 0,45 |
| 6 | 3,90 | 2,51 | 1,84 | 2,19 | | | | |
| 7 | 2,20 | 1,20 | 1,36 | 1,18 | 2,04 | 4,22 | 0,47 | 0,37 |
| 8 | 2,86 | 1,21 | 1,65 | 2,00 | 2,35 | 5,09 | 0,513 | 0,451 |
| 9 | 2,73 | 1,15 | 1,91 | 2,50 | | | | |
| 10 | 2,84 | 1,23 | 1,75 | 2,04 | 2,06 | 4,47 | 0,489 | 0,429 |
| 11 | 3,06 | 1,31 | 2,18 | 2,38 | 2,07 | 4,43 | 0,483 | 0,417 |
| 12 | 2,88 | 1,27 | 1,76 | 2,08 | 2,19 | 4,57 | 0,505 | 0,448 |
| 13 | 2,61 | 1,10 | 1,81 | 2,12 | 2,11 | 4,40 | 0,48 | 0,42 |
| 14 | | | | | | | | |
| 15 | 2,78 | 1,25 | 1,82 | 2,12 | 2,04 | 4,44 | 0,496 | 0,422 |
| 16 | 2,66 | 1,17 | 1,82 | 2,11 | 2,12 | 4,60 | 0,559 | 0,462 |
| 17 | 2,64 | 1,16 | 1,84 | 2,12 | 2,10 | 4,54 | 0,48 | 0,42 |
| 18 | 2,95 | 0,95 | 2,27 | 2,27 | 2,1 | 4,36 | 0,48 | 0,41 |
| 19 | 2,71 | 1,23 | 1,73 | 2,11 | 2,19 | 4,51 | <1 | <1 |
| 20 | 2,8 | 1,1 | 1,9 | 2,2 | 3,1 | 5,6 | 0,60 | 0,47 |
| 21 | 2,69 | 1,20 | 1,75 | 2,05 | 2,00 | 4,4 | 0,50 | 0,42 |
| 22 | 2,6 | 0,85 | | | | | | |
| 23 | 2,15 | 1,10 | 1,88 | 2,24 | 2,14 | 4,50 | 0,440 | 0,360 |
| 24 | | | | | 2,00 | 4,09 | 0,462 | 0,410 |
| 25 | | | | | | | | |
| 26 | 2,65 | 1,12 | 1,79 | 2,09 | 1,94 | 4,11 | 0,45 | 0,39 |
| 27 | | | | | | | | |
| 28 | 2,78 | 1,22 | 1,79 | 2,11 | 3,11 | 5,99 | 0,53 | 0,39 |
| 29 | 2,80 | 1,24 | 1,76 | 2,08 | 2,20 | 4,54 | 0,49 | 0,43 |
| 30 | 2,88 | 1,17 | 2,01 | 2,62 | 2,21 | 4,55 | 0,55 | 0,51 |
| 31 | | | | | 1,96 | 4,30 | 0,46 | 0,39 |
| 32 | 2,50 | 1,00 | 4,50 | 5,00 | 2,10 | 4,25 | 0,50 | 0,40 |
| 33 | 2,88 | 1,25 | 1,86 | 2,18 | 2,01 | 4,25 | 0,476 | 0,408 |
| 34 | 2,78 | 1,21 | 1,84 | 2,15 | 1,95 | 4,25 | 0,460 | 0,410 |
| 35 | 2,70 | 1,16 | 1,78 | 2,11 | 2,00 | 4,32 | 0,473 | 0,412 |

| Lab. | Chloride, mg/l | | Sulfate, mg/l | | Calcium, mg/l | | Magnesium, mg/l | |
|---|---|---|---|---|---|---|---|---|
| | A | B | A | B | A | B | A | B |
| 36 | 2,77 | 1,18 | 1,90 | 2,04 | 1,90 | 3,97 | 0,471 | 0,399 |
| 37 | 2,76 | 1,23 | 1,20 | 1,72 | 2,04 | 4,93 | 0,45 | 0,40 |
| 38 | 2,49 | 1,00 | 1,56 | 1,86 | 2,80 | 5,22 | 0,622 | 0,532 |
| 39 | 2,79 | 1,23 | 1,74 | 2,06 | 2,30 | 4,77 | 0,491 | 0,414 |
| 40 | 2,63 | 1,16 | 1,65 | 1,95 | 1,98 | 4,40 | 0,464 | 0,409 |
| 41 | 2,53 | 0,99 | 2,30 | 2,42 | 2,14 | 4,61 | 0,508 | 0,446 |
| 42 | 2,73 | 1,17 | 1,87 | 2,16 | 2,06 | 4,53 | 0,50 | 0,45 |
| 43 | | | | | | | | |
| 44 | | | | | | | | |
| 45 | 2,90 | 1,27 | 1,97 | 2,27 | 1,93 | 4,27 | 0,470 | 0,428 |
| 46 | | | | | | | | |
| 47 | 2,70 | 1,23 | 1,89 | 2,02 | 2,20 | 4,41 | 0,53 | 0,45 |
| 48 | 2,40 | 0,91 | 1,77 | 2,03 | 1,84 | 3,97 | 0,42 | 0,38 |
| 49 | 2,72 | 1,23 | 1,85 | 2,10 | 2,00 | 4,36 | 0,465 | 0,400 |
| 50 | 2,68 | 1,20 | 1,74 | 2,00 | 2,15 | 4,57 | 0,50 | 0,43 |
| 51 | 2,80 | 1,24 | 1,82 | 2,12 | 2,10 | 5,11 | 0,498 | 0,438 |
| 52 | 5,9 | 3,7 | | | | | | |
| 53 | 2,77 | 1,22 | 1,80 | 2,07 | | | | |
| 54 | 2,96 | 1,18 | 1,6 | 2,6 | 1,52 | 2,42 | 0,55 | 0,44 |
| 55 | 1,86 | 1,08 | | | 2,07 | 4,47 | 0,50 | 0,44 |
| 56 | 2,90 | 1,48 | 1,97 | 2,77 | 2,01 | 3,41 | 0,11 | 0,12 |
| 57 | 2,79 | 1,15 | 1,80 | 2,12 | 2,18 | 5,18 | 0,49 | 0,44 |
| 58 | 2,91 | 1,30 | 1,96 | 2,30 | 2,23 | 4,68 | 0,512 | 0,444 |
| 59 | 3,40 | 1,51 | 2,20 | 2,61 | 2,36 | 4,84 | 0,501 | 0,423 |
| 60 | 2,57 | 1,16 | 1,85 | 2,12 | 1,93 | 4,39 | 0,432 | 0,407 |
| 61 | 5,10 | 3,60 | 14,20 | 12,10 | 2,00 | 4,00 | 2,000 | 1,500 |
| 62 | | | | | | | | |
| 63 | 2,69 | 1,19 | 1,79 | 2,12 | 2,10 | 4,49 | 0,491 | 0,428 |
| 64 | 2,73 | 1,17 | 1,77 | 2,02 | 2,35 | 4,84 | 0,50 | 0,43 |
| 65 | 2,98 | 1,23 | 2,76 | 2,81 | 3,65 | 5,99 | 0,68 | 0,27 |
| 66 | | | | | 1,93 | 4,40 | 0,48 | 0,41 |
| 67 | 2,54 | 1,10 | 1,75 | 2,04 | 2,05 | 4,40 | 0,47 | 0,42 |
| 68 | 2,93 | 1,34 | 2,06 | 2,10 | | | | |
| 69 | | | | | | | | |
| 70 | | | | | 2,07 | 4,48 | 0,489 | 0,460 |
| 71 | 2,75 | 1,20 | 1,81 | 2,13 | 1,93 | 4,29 | 0,42 | 0,38 |
| 72 | 2,84 | 1,19 | 2,07 | 2,19 | 2,16 | 4,49 | 0,48 | 0,43 |

| Lab. | Sodium, mg/l | | Potassium, mg/l | | TOC, mg/l | | Aluminium, µg/l | |
|---|---|---|---|---|---|---|---|---|
| | A | B | A | B | A | B | C | D |
| 1 | 3,31 | 1,27 | 0,282 | 0,220 | 10,2 | 3,89 | 128 | 78,7 |
| 2 | 3,26 | 1,25 | 0,297 | 0,238 | 10,48 | 3,95 | | |
| 3 | | | | | | | | |
| 4 | 3,46 | 1,33 | 0,31 | 0,23 | 12,4 | 6,7 | 114 | 68,7 |
| 5 | 3,53 | 1,42 | 0,35 | 0,26 | | | | |
| 6 | | | | | 10,32 | 4,45 | | |
| 7 | 3,20 | 1,23 | 0,28 | 0,22 | | | 133 | 79 |
| 8 | 3,43 | 1,35 | 0,309 | 0,250 | | | | |
| 9 | | | | | | | 118 | 69 |
| 10 | 3,29 | 1,30 | 0,288 | 0,208 | 10,45 | 4,31 | 127 | 104 |
| 11 | 3,15 | 1,23 | 0,286 | 0,230 | 11,6 | 4,63 | 123,0 | 72,5 |
| 12 | 3,16 | 1,25 | 0,274 | 0,216 | 11,7 | 4,51 | | |
| 13 | 3,19 | 1,21 | 0,27 | 0,21 | | | | |
| 14 | | | | | | | | |
| 15 | 3,39 | 1,31 | 0,285 | 0,226 | | | | |
| 16 | 3,31 | 1,29 | 0,313 | 0,235 | 9,51 | 5,97 | 120 | 70 |
| 17 | 3,51 | 1,36 | 0,29 | 0,23 | | | | |
| 18 | 3,23 | 1,25 | 0,30 | 0,23 | 9,66 | 3,76 | 124 | 74 |
| 19 | 2,95 | 1,42 | -0,600 | -0,600 | 11,0 | 4,3 | 120 | 74 |
| 20 | 3,4 | 1,3 | 0,33 | 0,24 | | | 120 | 71,2 |
| 21 | 3,14 | 1,24 | 0,30 | 0,24 | 10,7 | 4,4 | 38 | 21 |
| 22 | | | | | | | | |
| 23 | 3,33 | 1,26 | 0,26 | 0,21 | 9,60 | 3,90 | | |
| 24 | 3,15 | 1,22 | 0,298 | 0,224 | 11,4 | 4,5 | 123,8 | 50,2 |
| 25 | | | | | | | | |
| 26 | 3,08 | 1,18 | 0,27 | 0,22 | 9,80 | 4,15 | | |
| 27 | | | | | | | | |
| 28 | 3,17 | 1,20 | 0,22 | 0,19 | | | | |
| 29 | 0,85 | 1,22 | 0,30 | 0,23 | 10,44 | 4,15 | | |
| 30 | 2,95 | 1,19 | 0,37 | 0,29 | | | 164 | 155 |
| 31 | 3,35 | 1,34 | 0,30 | 0,22 | | | | |
| 32 | 3,6 | 1,4 | 0,30 | 0,25 | 10,1 | 3,9 | | |
| 33 | 3,80 | 1,20 | | | 10,5 | 4,29 | | |
| 34 | 3,36 | 1,33 | 0,30 | 0,24 | | | | |
| 35 | 3,24 | 1,24 | 0,273 | 0,195 | 9,89 | 3,99 | 117 | 71,6 |

| Lab. | Sodium, mg/l | | Potassium, mg/l | | TOC, mg/l | | Aluminium, µg/l | |
|---|---|---|---|---|---|---|---|---|
| | A | B | A | B | A | B | C | D |
| 36 | 3,14 | 1,24 | 0,295 | 0,238 | 10,9 | 4,21 | 111 | 67,4 |
| 37 | 3,20 | 1,46 | 0,14 | <0,1 | 12,0 | 4,3 | 126 | 77 |
| 38 | 3,36 | 1,31 | 0,347 | 0,187 | | | | |
| 39 | 3,28 | 1,26 | 0,289 | 0,235 | | | | |
| 40 | 3,49 | 1,29 | 0,325 | 0,231 | 10,76 | 4,07 | | |
| 41 | 3,12 | 1,14 | 0,294 | 0,241 | | | 115,3 | 70,5 |
| 42 | 3,75 | 1,23 | 0,31 | 0,25 | 9,99 | 4,03 | 123 | 71,2 |
| 43 | | | | | | | | |
| 44 | | | | | | | | |
| 45 | 3,31 | 1,25 | 0,276 | 0,214 | 7,8 | 2,4 | 122 | 72 |
| 46 | | | | | | | 101,9 | 50,0 |
| 47 | 3,28 | 1,25 | 0,27 | 0,22 | | | | |
| 48 | 2,99 | 1,12 | 0,28 | 0,25 | 9,5 | 3,9 | 118 | 70 |
| 49 | 3,25 | 1,25 | 0,300 | 0,240 | 10,27 | 3,72 | | |
| 50 | 3,25 | 1,27 | 0,28 | 0,23 | 10,0 | 4,0 | 129 | 79 |
| 51 | 3,31 | 1,26 | 0,313 | 0,235 | 12,00 | 5,10 | 120 | 79 |
| 52 | 2,90 | 0,32 | 0,87 | 0,15 | | | 48,9 | 40,8 |
| 53 | | | | | | | | |
| 54 | 3,83 | 1,54 | 0,370 | 0,320 | | | | |
| 55 | 3,06 | 1,10 | 0,32 | 0,26 | | | | |
| 56 | 2,78 | 1,35 | <0,5 | <0,5 | 11,85 | 5,56 | 136,7 | 81,5 |
| 57 | 3,38 | 1,33 | 0,31 | 0,25 | 11,38 | 4,40 | 124,6 | 75,3 |
| 58 | 3,35 | 1,28 | 0,300 | 0,240 | | | | |
| 59 | 3,20 | 1,27 | 0,252 | 0,182 | | | 79,7 | 82,3 |
| 60 | 3,21 | 1,25 | 0,323 | 0,231 | 10,89 | 4,06 | 129 | 73 |
| 61 | 8,70 | 7,10 | -0,001 | -0,001 | | | | |
| 62 | | | | | | | | |
| 63 | 3,35 | 1,29 | 0,319 | 0,257 | | | 123 | 74,2 |
| 64 | 3,31 | 1,29 | 0,32 | 0,23 | 11,00 | 3,80 | 126,0 | 73,6 |
| 65 | 3,25 | 1,00 | 0,22 | 0,16 | | | | |
| 66 | 3,04 | 1,07 | 0,25 | 0,21 | | | | |
| 67 | 3,16 | 1,22 | 0,29 | 0,24 | 10,3 | 3,8 | 110 | 78 |
| 68 | | | | | 9,5 | 4,2 | | |
| 69 | | | | | | | | |
| 70 | 3,16 | 1,21 | 0,301 | 0,246 | | | | |
| 71 | 3,32 | 1,27 | 0,41 | 0,25 | 11,32 | 4,07 | | |
| 72 | 3,22 | 1,26 | 0,31 | 0,26 | | | | |

| Lab. | Iron, µg/l | | Manganese, µg/l | | Cadmium, µg/l | | Lead, µg/l | |
|---|---|---|---|---|---|---|---|---|
| | C | D | C | D | C | D | C | D |
| 1 | 175 | 36,3 | 10,3 | 1,16 | 3,56 | 6,34 | 3,89 | 5,91 |
| 2 | | | | | | | | |
| 3 | | | | | | | | |
| 4 | 139 | 31,1 | 9,33 | 1,00 | 3,59 | 6,16 | 3,98 | 6,12 |
| 5 | 180 | 50 | | | 3,20 | 5,43 | 3,7 | 5,7 |
| 6 | | | | | | | | |
| 7 | 180 | 45 | 0,91 | 9,51 | 2,98 | 5,62 | 2,93 | 4,67 |
| 8 | 162,1 | 41,6 | 10,26 | 1,10 | 2,85 | 4,66 | 4,42 | 6,28 |
| 9 | 180 | 76 | 10,1 | 1,14 | 3,8 | 6,5 | 4,0 | 5,9 |
| 10 | 169 | 37 | 9,1 | 0,4 | 3,61 | 6,12 | 4,02 | 6,05 |
| 11 | 167,4 | 35,8 | 10,3 | 1,24 | 3,53 | 5,74 | 3,92 | 5,85 |
| 12 | | | | | | | | |
| 13 | 220 | 80 | 10,0 | <10 | | | | |
| 14 | | | | | | | | |
| 15 | 168 | 44 | 9,78 | 1,11 | 3,61 | 5,97 | 4,07 | 5,95 |
| 16 | 167 | 36 | 7,50 | <1 | 1,2 | 2,2 | 3,3 | 5,4 |
| 17 | | | | | 3,63 | 6,43 | 3,99 | 6,35 |
| 18 | 164,7 | 34,6 | <10 | <10 | 3,68 | 6,29 | 4,1 | 6,2 |
| 19 | 168 | 45 | 10,00 | <2 | 3,50 | 6,10 | 4,0 | 6,4 |
| 20 | 163 | 33,6 | 9,64 | 1,13 | 3,54 | 6,11 | 3,95 | 6,11 |
| 21 | 164 | 35 | 9,7 | 1,2 | 3,6 | 6,2 | 3,5 | 6,7 |
| 22 | | | | | | | | |
| 23 | | | | | | | | |
| 24 | 165,5 | 35,7 | 9,3 | 1,0 | 3,41 | 6,02 | 4,03 | 6,12 |
| 25 | 158,1 | 36,1 | 10,04 | 1,02 | 3,38 | 6,15 | 2,61 | 4,85 |
| 26 | | | | | | | | |
| 27 | | | | | | | | |
| 28 | | | | | | | | |
| 29 | | | | | | | | |
| 30 | 15,0 | 3,4 | | | 2,8 | 4,8 | 8,0 | 9,5 |
| 31 | | | | | | | | |
| 32 | | | | | | | | |
| 33 | | | | | | | | |
| 34 | | | | | | | | |
| 35 | 154 | 39,6 | 8,75 | 0,95 | 3,41 | 6,07 | 3,89 | 6,10 |

| Lab. | Iron, µg/l | | Manganese, µg/l | | Cadmium, µg/l | | Lead, µg/l | |
|---|---|---|---|---|---|---|---|---|
| | C | D | C | D | C | D | C | D |
| 36 | 153 | 33,9 | 8,90 | 1,05 | 3,73 | 6,61 | 3,92 | 6,17 |
| 37 | 166 | 37 | 10,1 | 1,0 | 3,85 | 6,67 | 4,15 | 6,55 |
| 38 | 1653 | 35 | 9,4 | 1,6 | 3,9 | 7,1 | | |
| 39 | | | | | | | | |
| 40 | | | | | | | | |
| 41 | 167,8 | 46,3 | <10 | <10 | 3,00 | 5,38 | <1 | <1 |
| 42 | 167 | 35,8 | <10 | <10 | 3,60 | 6,69 | 4,86 | 7,09 |
| 43 | | | | | | | | |
| 44 | | | | | | | | |
| 45 | 170 | 31,5 | 10,4 | 1,03 | 3,68 | 6,34 | 3,98 | 6,15 |
| 46 | 169,6 | 36,9 | 9,62 | 0,99 | 0,37 | 0,19 | 3,49 | 3,18 |
| 47 | | | | | | | | |
| 48 | 161 | 34,7 | 9,35 | 1,09 | 3,56 | 6,15 | 4,04 | 6,16 |
| 49 | | | | | | | | |
| 50 | 172 | 38,0 | 9,39 | 1,04 | 3,73 | 6,40 | 4,14 | 6,46 |
| 51 | 160 | 10 | 44 | 1,30 | 4,19 | 7,35 | 4,71 | 7,38 |
| 52 | | | 9,47 | <2 | 3,53 | 6,39 | 2,35 | 3,57 |
| 53 | | | | | | | | |
| 54 | | | | | | | | |
| 55 | | | | | | | | |
| 56 | 159,6 | 34,9 | 10,41 | 1,24 | 3,96 | 6,86 | 4,00 | 6,17 |
| 57 | 122,9 | 27,6 | 9,93 | 1,20 | 3,51 | 6,12 | 3,94 | 6,14 |
| 58 | 160,2 | 35,6 | 9,10 | 1,12 | 3,56 | 6,13 | 3,71 | 5,34 |
| 59 | | | | | 4,04 | 4,96 | 3,67 | 5,81 |
| 60 | 144 | 33 | 8,8 | 1,0 | 3,8 | 6,4 | 4,20 | 6,40 |
| 61 | 143,0 | 30,0 | 33,30 | 14,50 | 1,93 | 4,17 | 5,11 | 4,52 |
| 62 | | | | | | | | |
| 63 | 157 | 33,7 | 9,75 | 1,15 | 3,57 | 6,25 | 3,93 | 6,06 |
| 64 | 150 | 20 | 9,34 | 1,0 | 3,42 | 5,82 | 4,14 | 6,25 |
| 65 | 150 | 23,7 | 7,14 | 0,78 | 2,67 | 6,02 | 1,04 | 3,66 |
| 66 | | | | | | | | |
| 67 | 147 | 35,4 | 8,8 | 1,21 | 3,30 | 6,0 | 4,0 | 6,3 |
| 68 | | | | | | | | |
| 69 | | | | | 1,86 | 3,44 | 3,70 | 6,20 |
| 70 | 162 | 35,7 | <73 | <73 | 3,46 | 6,08 | 4,22 | 6,06 |
| 71 | | | | | | | | |
| 72 | 174 | 38,9 | 12,5 | 1,49 | 3,57 | 6,13 | 4,20 | 6,32 |

| Lab. | Copper, µg/l | | Nickel, µg/l | | Zinc, µg/l | |
|---|---|---|---|---|---|---|
| | C | D | C | D | C | D |
| 1 | 0,73 | 1,42 | 4,19 | 6,25 | 21,1 | 32,7 |
| 2 | | | | | | |
| 3 | | | | | | |
| 4 | 0,58 | 1,48 | 4,13 | 6,07 | 22,2 | 33,6 |
| 5 | 2,0 | 1,6 | 4,0 | 6,2 | 18,0 | 30,0 |
| 6 | | | | | | |
| 7 | 0,60 | 1,10 | 3,70 | 5,53 | 19,3 | 28,8 |
| 8 | 1,13 | 1,67 | 4,52 | 6,52 | 22,0 | 32,9 |
| 9 | 0,58 | 1,33 | 4,3 | 6,4 | 23 | 35 |
| 10 | <1 | 1,37 | 3,81 | 6,02 | 22,3 | 35,1 |
| 11 | 1,02 | 2,00 | 4,54 | 6,54 | 22,1 | 34,4 |
| 12 | | | | | | |
| 13 | | | | | | |
| 14 | | | | | | |
| 15 | 0,72 | 1,39 | 4,18 | 6,15 | 21,4 | 31,5 |
| 16 | 0,6 | 1,1 | 3,5 | 6,0 | 20 | 32 |
| 17 | <1 | 1,38 | 4,06 | 6,35 | 22,4 | 35,8 |
| 18 | <1 | 1,05 | 4,2 | 6,35 | 21,5 | 34,0 |
| 19 | <1 | 1,10 | 4,2 | 6,3 | 21 | 33 |
| 20 | 0,63 | 1,34 | 4,15 | 6,18 | 21,0 | 31,8 |
| 21 | 0,2 | 0,6 | 4,2 | 6,4 | 21 | 32 |
| 22 | | | | | | |
| 23 | | | | | | |
| 24 | 1,09 | 1,53 | 3,97 | 6,00 | 15,9 | 27,7 |
| 25 | 0,37 | 0,90 | 4,03 | 6,14 | 21,1 | 33,0 |
| 26 | | | | | | |
| 27 | | | | | | |
| 28 | | | | | | |
| 29 | | | | | | |
| 30 | 63 | 7,0 | | | 7,0 | 16,0 |
| 31 | | | | | | |
| 32 | | | | | | |
| 33 | | | | | | |
| 34 | | | | | | |
| 35 | 0,80 | 1,16 | 4,05 | 6,17 | 20,5 | 33,4 |

| Lab. | Copper, µg/l | | Nickel, µg/l | | Zinc, µg/l | |
|---|---|---|---|---|---|---|
| | C | D | C | D | C | D |
| 36 | 0,70 | 1,21 | 4,17 | 6,50 | 19,5 | 31,1 |
| 37 | 0,55 | 1,29 | 4,4 | 6,7 | 25,1 | 40,9 |
| 38 | <1 | <1 | 4,8 | 9,5 | 19,8 | 31,0 |
| 39 | | | | | | |
| 40 | | | | | | |
| 41 | <10 | <10 | 2,85 | 4,95 | 22,8 | 34,1 |
| 42 | 5,70 | 6,46 | 3,45 | 5,53 | 22,0 | 34,9 |
| 43 | | | | | | |
| 44 | | | | | | |
| 45 | <1 | 1,49 | 4,13 | 6,35 | 21,4 | 33,5 |
| 46 | 1,21 | 3,18 | 4,19 | 6,87 | 22,0 | 35,0 |
| 47 | | | | | | |
| 48 | 0,74 | 1,37 | 4,11 | 6,17 | 20,0 | 31,0 |
| 49 | | | | | | |
| 50 | 0,80 | 1,64 | 4,02 | 5,99 | 22,8 | 34,3 |
| 51 | 0,79 | 1,7 | 4,97 | 7,56 | 21,6 | 34,2 |
| 52 | 6,23 | 7,37 | -5,00 | -5,00 | 23,1 | 37,4 |
| 53 | | | | | | |
| 54 | | | | | | |
| 55 | | | | | | |
| 56 | 0,69 | 1,52 | 4,48 | 7,11 | 23,0 | 36,3 |
| 57 | 0,56 | 1,42 | 4,22 | 6,50 | 20,0 | 31,4 |
| 58 | 0,50 | 1,40 | 3,45 | 5,70 | 20,6 | 32,4 |
| 59 | <0,2 | 0,94 | | | 21,4 | 28,5 |
| 60 | 0,8 | 1,4 | 4,1 | 6,2 | 22,5 | 34,4 |
| 61 | 0,40 | 1,50 | 5,00 | 8,02 | 10,5 | 16,0 |
| 62 | | | | | | |
| 63 | 0,76 | 1,48 | 4,10 | 6,15 | 21,0 | 33,0 |
| 64 | 0,74 | 1,28 | 4,03 | 5,81 | 20,6 | 31,4 |
| 65 | 0,49 | 1,06 | 2,47 | 4,16 | | |
| 66 | | | | | | |
| 67 | 0,65 | 1,4 | 4,0 | 6,0 | 19,7 | 30,4 |
| 68 | | | | | | |
| 69 | 1,32 | 1,55 | 4,71 | 7,01 | 20,0 | 38,0 |
| 70 | <2 | <2 | 4,50 | 6,49 | 20,8 | 33,3 |
| 71 | | | | | | |
| 72 | 0,57 | 1,44 | 4,21 | 6,58 | 22,4 | 32,7 |

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

| | | | | | |
|---|---|---|---|---|---|
| Number of participants | 64 | | Range | | 1,23 |
| Number of omitted results | 1 | | Variance | | 0,04 |
| True value | 6,58 | | Standard deviation | | 0,21 |
| Mean value | 6,56 | | Relative standard deviation | | 3,2% |
| Median value | 6,58 | | Relative error | | -0,3% |

Analytical results in ascending order:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 65 | 5,44 | U | 29 | 6,53 | 50 | 6,63 |
| 48 | 5,83 | | 45 | 6,53 | 67 | 6,64 |
| 38 | 6,02 | | 28 | 6,53 | 53 | 6,65 |
| 11 | 6,13 | | 21 | 6,53 | 72 | 6,68 |
| 19 | 6,20 | | 32 | 6,54 | 12 | 6,70 |
| 1 | 6,21 | | 16 | 6,54 | 54 | 6,70 |
| 61 | 6,32 | | 31 | 6,55 | 40 | 6,70 |
| 37 | 6,37 | | 2 | 6,56 | 64 | 6,71 |
| 58 | 6,37 | | 66 | 6,57 | 8 | 6,72 |
| 70 | 6,40 | | 63 | 6,58 | 9 | 6,72 |
| 68 | 6,40 | | 60 | 6,58 | 33 | 6,74 |
| 24 | 6,41 | | 13 | 6,58 | 47 | 6,75 |
| 22 | 6,42 | | 26 | 6,58 | 34 | 6,75 |
| 14 | 6,44 | | 6 | 6,59 | 62 | 6,75 |
| 17 | 6,45 | | 59 | 6,60 | 52 | 6,80 |
| 49 | 6,45 | | 57 | 6,60 | 56 | 6,85 |
| 23 | 6,47 | | 39 | 6,60 | 30 | 6,88 |
| 7 | 6,48 | | 51 | 6,60 | 42 | 6,99 |
| 41 | 6,48 | | 5 | 6,61 | 71 | 7,00 |
| 10 | 6,51 | | 18 | 6,61 | 20 | 7,06 |
| 35 | 6,51 | | 55 | 6,62 | | |
| 4 | 6,52 | | 36 | 6,62 | | |

**Sample B**

| | | | | | |
|---|---|---|---|---|---|
| Number of participants | 64 | | Range | | 1,11 |
| Number of omitted results | 1 | | Variance | | 0,04 |
| True value | 7,05 | | Standard deviation | | 0,20 |
| Mean value | 7,02 | | Relative standard deviation | | 2,8% |
| Median value | 7,05 | | Relative error | | -0,4% |

Analytical results in ascending order:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 65 | 6,10 | U | 68 | 7,00 | 50 | 7,12 |
| 38 | 6,38 | | 24 | 7,01 | 39 | 7,12 |
| 48 | 6,46 | | 7 | 7,03 | 36 | 7,13 |
| 11 | 6,66 | | 21 | 7,03 | 62 | 7,13 |
| 70 | 6,71 | | 29 | 7,03 | 56 | 7,14 |
| 22 | 6,71 | | 31 | 7,04 | 26 | 7,14 |
| 67 | 6,74 | | 16 | 7,04 | 51 | 7,15 |
| 1 | 6,78 | | 13 | 7,04 | 40 | 7,16 |
| 19 | 6,80 | | 4 | 7,04 | 64 | 7,17 |
| 61 | 6,80 | | 60 | 7,04 | 33 | 7,18 |
| 53 | 6,85 | | 66 | 7,05 | 6 | 7,19 |
| 49 | 6,85 | | 35 | 7,06 | 18 | 7,19 |
| 55 | 6,87 | | 59 | 7,06 | 8 | 7,20 |
| 34 | 6,88 | | 10 | 7,06 | 12 | 7,20 |
| 23 | 6,90 | | 32 | 7,06 | 54 | 7,20 |
| 52 | 6,90 | | 57 | 7,07 | 9 | 7,21 |
| 58 | 6,92 | | 20 | 7,07 | 30 | 7,29 |
| 17 | 6,93 | | 2 | 7,09 | 47 | 7,30 |
| 5 | 6,93 | | 41 | 7,09 | 42 | 7,46 |
| 63 | 6,93 | | 28 | 7,11 | 71 | 7,49 |
| 14 | 6,93 | | 72 | 7,11 | | |
| 37 | 6,97 | | 45 | 7,12 | | |

U = Omitted result

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

**Sample A**

| | | | | |
|---|---|---|---|---|
| Number of participants | 63 | Range | | 1,06 |
| Number of omitted results | 4 | Variance | | 0,03 |
| True value | 3,09 | Standard deviation | | 0,19 |
| Mean value | 3,07 | Relative standard deviation | | 6,1% |
| Median value | 3,09 | Relative error | | -0,7% |

Analytical results in ascending order:

| | | | | | | |
|---|---|---|---|---|---|---|
| 2 | 0,31 | U | 6 | 3,05 | 42 | 3,14 |
| 4 | 2,50 | | 26 | 3,05 | 9 | 3,14 |
| 22 | 2,58 | | 21 | 3,06 | 16 | 3,15 |
| 8 | 2,71 | | 68 | 3,06 | 5 | 3,16 |
| 17 | 2,78 | | 33 | 3,07 | 15 | 3,17 |
| 60 | 2,80 | | 64 | 3,07 | 66 | 3,18 |
| 49 | 2,80 | | 50 | 3,08 | 47 | 3,19 |
| 59 | 2,80 | | 39 | 3,08 | 62 | 3,20 |
| 61 | 2,81 | | 34 | 3,08 | 24 | 3,22 |
| 11 | 2,84 | | 58 | 3,09 | 53 | 3,22 |
| 7 | 2,93 | | 20 | 3,10 | 54 | 3,22 |
| 38 | 2,95 | | 35 | 3,10 | 52 | 3,24 |
| 51 | 2,96 | | 37 | 3,10 | 31 | 3,30 |
| 13 | 3,00 | | 14 | 3,10 | 19 | 3,30 |
| 28 | 3,00 | | 36 | 3,10 | 71 | 3,37 |
| 70 | 3,01 | | 18 | 3,10 | 30 | 3,37 |
| 63 | 3,01 | | 67 | 3,10 | 48 | 3,40 |
| 10 | 3,03 | | 41 | 3,11 | 12 | 3,56 |
| 1 | 3,03 | | 57 | 3,11 | 56 | 4,33 U |
| 45 | 3,04 | | 23 | 3,13 | 65 | 5,43 U |
| 40 | 3,04 | | 72 | 3,14 | 29 | 307,00 U |

**Sample B**

| | | | |
|---|---|---|---|
| Number of participants | 63 | Range | 0,98 |
| Number of omitted results | 4 | Variance | 0,03 |
| True value | 3,36 | Standard deviation | 0,18 |
| Mean value | 3,34 | Relative standard deviation | 5,5% |
| Median value | 3,36 | Relative error | -0,6% |

Analytical results in ascending order:

| | | | | | | |
|---|---|---|---|---|---|---|
| 2 | 0,34 | U | 37 | 3,30 | 16 | 3,41 |
| 4 | 2,80 | | 40 | 3,32 | 15 | 3,41 |
| 17 | 3,01 | | 63 | 3,33 | 62 | 3,42 |
| 60 | 3,04 | | 58 | 3,34 | 9 | 3,43 |
| 7 | 3,05 | | 64 | 3,34 | 47 | 3,43 |
| 59 | 3,06 | | 41 | 3,34 | 24 | 3,44 |
| 11 | 3,06 | | 21 | 3,35 | 53 | 3,46 |
| 61 | 3,07 | | 34 | 3,35 | 42 | 3,47 |
| 22 | 3,09 | | 68 | 3,35 | 54 | 3,49 |
| 49 | 3,10 | | 36 | 3,36 | 31 | 3,50 |
| 45 | 3,18 | | 66 | 3,36 | 12 | 3,57 |
| 10 | 3,18 | | 50 | 3,36 | 48 | 3,60 |
| 13 | 3,20 | | 57 | 3,37 | 19 | 3,60 |
| 26 | 3,22 | | 72 | 3,38 | 52 | 3,61 |
| 51 | 3,22 | | 39 | 3,38 | 6 | 3,62 |
| 38 | 3,24 | | 5 | 3,39 | 8 | 3,63 |
| 70 | 3,26 | | 28 | 3,40 | 71 | 3,71 |
| 33 | 3,27 | | 23 | 3,40 | 30 | 3,78 |
| 1 | 3,30 | | 18 | 3,40 | 65 | 3,81 U |
| 20 | 3,30 | | 67 | 3,40 | 56 | 4,59 U |
| 14 | 3,30 | | 35 | 3,40 | 29 | 327,00 U |

U = Omitted result

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

**Sample A**

| | | | |
|---|---|---|---|
| Number of participants | 45 | Range | 0,064 |
| Number of omitted results | 11 | Variance | 0,000 |
| True value | 0,099 | Standard deviation | 0,013 |
| Mean value | 0,099 | Relative standard deviation | 13,3% |
| Median value | 0,099 | Relative error | 0,3% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 11 | < 0,16 | U | 70 | 0,094 | | 72 | 0,109 | |
| 65 | 0,039 | U | 54 | 0,094 | | 42 | 0,109 | |
| 37 | 0,049 | U | 48 | 0,098 | | 5 | 0,112 | |
| 51 | 0,076 | | 21 | 0,098 | | 28 | 0,113 | |
| 63 | 0,080 | | 12 | 0,099 | | 34 | 0,114 | |
| 4 | 0,082 | | 40 | 0,099 | | 20 | 0,130 | |
| 45 | 0,084 | | 66 | 0,099 | | 38 | 0,140 | |
| 2 | 0,085 | | 19 | 0,100 | | 1 | 0,147 | U |
| 49 | 0,089 | | 67 | 0,100 | | 61 | 0,150 | U |
| 36 | 0,089 | | 26 | 0,100 | | 17 | 0,155 | U |
| 35 | 0,089 | | 6 | 0,101 | | 68 | 0,156 | U |
| 23 | 0,092 | | 16 | 0,102 | | 71 | 0,181 | U |
| 18 | 0,092 | | 64 | 0,103 | | 55 | 0,200 | U |
| 59 | 0,094 | | 29 | 0,108 | | 9 | 0,640 | U |
| 57 | 0,094 | | 10 | 0,109 | | 7 | 5,580 | U |

**Sample B**

| | | | |
|---|---|---|---|
| Number of participants | 45 | Range | 0,070 |
| Number of omitted results | 11 | Variance | 0,000 |
| True value | 0,200 | Standard deviation | 0,014 |
| Mean value | 0,201 | Relative standard deviation | 7,2% |
| Median value | 0,200 | Relative error | 0,6% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 65 | 0,083 | U | 2 | 0,195 | | 67 | 0,210 | |
| 37 | 0,098 | U | 40 | 0,199 | | 19 | 0,210 | |
| 48 | 0,170 | | 66 | 0,199 | | 42 | 0,212 | |
| 18 | 0,176 | | 21 | 0,200 | | 59 | 0,220 | |
| 9 | 0,181 | U | 6 | 0,200 | | 11 | 0,224 | U |
| 49 | 0,181 | | 34 | 0,200 | | 28 | 0,227 | |
| 63 | 0,186 | | 54 | 0,201 | | 20 | 0,230 | |
| 4 | 0,187 | | 12 | 0,202 | | 61 | 0,230 | U |
| 45 | 0,190 | | 26 | 0,203 | | 38 | 0,240 | |
| 36 | 0,191 | | 64 | 0,204 | | 1 | 0,256 | U |
| 51 | 0,192 | | 5 | 0,205 | | 17 | 0,263 | U |
| 35 | 0,193 | | 23 | 0,207 | | 55 | 0,270 | U |
| 70 | 0,193 | | 72 | 0,208 | | 68 | 0,275 | U |
| 57 | 0,194 | | 16 | 0,209 | | 71 | 0,296 | U |
| 10 | 0,195 | | 29 | 0,209 | | 7 | 12,000 | U |

U = Omitted result

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

**Sample A**

| | | | |
|---|---|---|---|
| Number of participants | 59 | Range | 113 |
| Number of omitted results | 11 | Variance | 474 |
| True value | 187 | Standard deviation | 22 |
| Mean value | 185 | Relative standard deviation | 11,8% |
| Median value | 187 | Relative error | -1,0% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 9 | 1 | U | 8 | 177 | | 24 | 192 | |
| 19 | 19 | U | 26 | 180 | | 29 | 194 | |
| 37 | 42 | U | 20 | 180 | | 53 | 194 | |
| 18 | 74 | U | 12 | 180 | | 13 | 194 | |
| 6 | 87 | U | 45 | 181 | | 23 | 198 | |
| 10 | 107 | U | 11 | 181 | | 32 | 198 | |
| 48 | 130 | | 34 | 182 | | 51 | 199 | |
| 38 | 133 | | 35 | 183 | | 4 | 200 | |
| 72 | 139 | | 36 | 183 | | 41 | 200 | U |
| 61 | 152 | | 2 | 185 | | 60 | 203 | |
| 40 | 153 | U | 33 | 187 | | 58 | 209 | |
| 49 | 156 | | 63 | 187 | | 16 | 210 | |
| 57 | 165 | | 71 | 188 | | 50 | 210 | U |
| 7 | 169 | | 54 | 188 | | 28 | 215 | |
| 68 | 170 | | 15 | 188 | | 56 | 224 | |
| 39 | 170 | | 21 | 188 | | 30 | 233 | |
| 42 | 174 | | 14 | 189 | | 59 | 243 | |
| 5 | 174 | | 64 | 190 | | 65 | 348 | U |
| 47 | 176 | | 67 | 191 | | 55 | 583 | U |
| 1 | 177 | | 17 | 192 | | | | |

**Sample B**

| | | | |
|---|---|---|---|
| Number of participants | 59 | Range | 104 |
| Number of omitted results | 11 | Variance | 638 |
| True value | 154 | Standard deviation | 25 |
| Mean value | 153 | Relative standard deviation | 16,5% |
| Median value | 154 | Relative error | -0,6% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 41 | < 150 | U | 39 | 143 | | 58 | 169 | |
| 9 | 1 | U | 13 | 145 | | 4 | 170 | |
| 50 | 65 | U | 37 | 147 | U | 63 | 170 | |
| 40 | 71 | U | 2 | 149 | | 32 | 172 | |
| 8 | 103 | | 67 | 150 | | 15 | 174 | |
| 5 | 106 | | 21 | 152 | | 51 | 175 | |
| 38 | 107 | | 45 | 152 | | 57 | 176 | |
| 61 | 109 | | 35 | 152 | | 20 | 176 | |
| 34 | 112 | | 17 | 153 | | 24 | 176 | |
| 11 | 113 | | 23 | 153 | | 60 | 178 | |
| 7 | 115 | | 28 | 153 | | 48 | 180 | |
| 47 | 122 | | 72 | 154 | | 6 | 180 | U |
| 1 | 129 | | 49 | 154 | | 16 | 182 | |
| 65 | 132 | U | 26 | 155 | | 64 | 190 | |
| 33 | 133 | | 36 | 156 | | 56 | 192 | |
| 42 | 133 | | 53 | 157 | | 30 | 193 | |
| 68 | 140 | | 71 | 158 | | 59 | 207 | |
| 19 | 140 | U | 12 | 162 | | 18 | 207 | U |
| 14 | 141 | | 29 | 163 | | 55 | 384 | U |
| 54 | 142 | | 10 | 166 | U | | | |

U = Omitted result

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

| | | | | | |
|---|---|---|---|---|---|
| Number of participants | 59 | | Range | | 1,25 |
| Number of omitted results | 4 | | Variance | | 0,04 |
| True value | 2,76 | | Standard deviation | | 0,19 |
| Mean value | 2,74 | | Relative standard deviation | | 7,1% |
| Median value | 2,76 | | Relative error | | -0,6% |

Analytical results in ascending order:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 55 | 1,86 | U | 47 | 2,70 | 72 | 2,84 | |
| 23 | 2,15 | | 19 | 2,71 | 10 | 2,84 | |
| 7 | 2,20 | | 49 | 2,72 | 8 | 2,86 | |
| 48 | 2,40 | | 9 | 2,73 | 30 | 2,88 | |
| 38 | 2,49 | | 42 | 2,73 | 12 | 2,88 | |
| 32 | 2,50 | | 64 | 2,73 | 33 | 2,88 | |
| 41 | 2,53 | | 4 | 2,74 | 5 | 2,90 | |
| 67 | 2,54 | | 71 | 2,75 | 45 | 2,90 | |
| 60 | 2,57 | | 37 | 2,76 | 56 | 2,90 | |
| 22 | 2,60 | | 1 | 2,76 | 58 | 2,91 | |
| 13 | 2,61 | | 36 | 2,77 | 68 | 2,93 | |
| 40 | 2,63 | | 53 | 2,77 | 18 | 2,95 | |
| 17 | 2,64 | | 34 | 2,78 | 54 | 2,96 | |
| 26 | 2,65 | | 15 | 2,78 | 65 | 2,98 | |
| 16 | 2,66 | | 28 | 2,78 | 11 | 3,06 | |
| 2 | 2,68 | | 57 | 2,79 | 59 | 3,40 | |
| 50 | 2,68 | | 39 | 2,79 | 6 | 3,90 | U |
| 63 | 2,69 | | 29 | 2,80 | 61 | 5,10 | U |
| 21 | 2,69 | | 51 | 2,80 | 52 | 5,90 | U |
| 35 | 2,70 | | 20 | 2,80 | | | |

**Sample B**

| | | | | | |
|---|---|---|---|---|---|
| Number of participants | 59 | | Range | | 0,66 |
| Number of omitted results | 4 | | Variance | | 0,01 |
| True value | 1,19 | | Standard deviation | | 0,11 |
| Mean value | 1,18 | | Relative standard deviation | | 9,6% |
| Median value | 1,19 | | Relative error | | -0,6% |

Analytical results in ascending order:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 22 | 0,85 | | 42 | 1,17 | 47 | 1,23 | |
| 48 | 0,91 | | 64 | 1,17 | 10 | 1,23 | |
| 18 | 0,95 | | 16 | 1,17 | 19 | 1,23 | |
| 41 | 0,99 | | 1 | 1,17 | 39 | 1,23 | |
| 38 | 1,00 | | 30 | 1,17 | 51 | 1,24 | |
| 32 | 1,00 | | 36 | 1,18 | 29 | 1,24 | |
| 55 | 1,08 | U | 54 | 1,18 | 15 | 1,25 | |
| 23 | 1,10 | | 72 | 1,19 | 33 | 1,25 | |
| 13 | 1,10 | | 63 | 1,19 | 12 | 1,27 | |
| 67 | 1,10 | | 21 | 1,20 | 4 | 1,27 | |
| 20 | 1,10 | | 71 | 1,20 | 45 | 1,27 | |
| 26 | 1,12 | | 7 | 1,20 | 58 | 1,30 | |
| 5 | 1,15 | | 50 | 1,20 | 11 | 1,31 | |
| 9 | 1,15 | | 34 | 1,21 | 68 | 1,34 | |
| 57 | 1,15 | | 8 | 1,21 | 56 | 1,48 | |
| 2 | 1,15 | | 28 | 1,22 | 59 | 1,51 | |
| 35 | 1,16 | | 53 | 1,22 | 6 | 2,51 | U |
| 17 | 1,16 | | 65 | 1,23 | 61 | 3,60 | U |
| 40 | 1,16 | | 37 | 1,23 | 52 | 3,70 | U |
| 60 | 1,16 | | 49 | 1,23 | | | |

U = Omitted result

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

| | | | |
|---|---|---|---|
| Number of participants | 56 | Range | 0,81 |
| Number of omitted results | 5 | Variance | 0,03 |
| True value | 1,82 | Standard deviation | 0,16 |
| Mean value | 1,84 | Relative standard deviation | 8,6% |
| Median value | 1,82 | Relative error | 1,3% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 37 | 1,20 | U | 28 | 1,79 | | 23 | 1,88 | |
| 7 | 1,36 | U | 26 | 1,79 | | 47 | 1,89 | |
| 5 | 1,49 | | 63 | 1,79 | | 20 | 1,90 | |
| 38 | 1,56 | | 53 | 1,80 | | 36 | 1,90 | |
| 54 | 1,60 | | 57 | 1,80 | | 9 | 1,91 | |
| 8 | 1,65 | | 71 | 1,81 | | 58 | 1,96 | |
| 40 | 1,65 | | 1 | 1,81 | | 56 | 1,97 | |
| 4 | 1,71 | | 13 | 1,81 | | 45 | 1,97 | |
| 19 | 1,73 | | 2 | 1,82 | | 30 | 2,01 | |
| 39 | 1,74 | | 15 | 1,82 | | 68 | 2,06 | |
| 50 | 1,74 | | 16 | 1,82 | | 72 | 2,07 | |
| 10 | 1,75 | | 51 | 1,82 | | 11 | 2,18 | |
| 67 | 1,75 | | 34 | 1,84 | | 59 | 2,20 | |
| 21 | 1,75 | | 17 | 1,84 | | 18 | 2,27 | |
| 29 | 1,76 | | 6 | 1,84 | | 41 | 2,30 | |
| 12 | 1,76 | | 60 | 1,85 | | 65 | 2,76 | U |
| 64 | 1,77 | | 49 | 1,85 | | 32 | 4,50 | U |
| 48 | 1,77 | | 33 | 1,86 | | 61 | 14,20 | U |
| 35 | 1,78 | | 42 | 1,87 | | | | |

**Sample B**

| | | | |
|---|---|---|---|
| Number of participants | 56 | Range | 1,13 |
| Number of omitted results | 5 | Variance | 0,04 |
| True value | 2,12 | Standard deviation | 0,20 |
| Mean value | 2,16 | Relative standard deviation | 9,1% |
| Median value | 2,12 | Relative error | 1,7% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 7 | 1,18 | U | 26 | 2,09 | | 33 | 2,18 | |
| 5 | 1,64 | | 49 | 2,10 | | 72 | 2,19 | |
| 37 | 1,72 | U | 68 | 2,10 | | 6 | 2,19 | |
| 38 | 1,86 | | 28 | 2,11 | | 20 | 2,20 | |
| 40 | 1,95 | | 16 | 2,11 | | 23 | 2,24 | |
| 50 | 2,00 | | 19 | 2,11 | | 45 | 2,27 | |
| 8 | 2,00 | | 35 | 2,11 | | 18 | 2,27 | |
| 4 | 2,01 | | 15 | 2,12 | | 58 | 2,30 | |
| 47 | 2,02 | | 60 | 2,12 | | 11 | 2,38 | |
| 64 | 2,02 | | 63 | 2,12 | | 41 | 2,42 | |
| 48 | 2,03 | | 51 | 2,12 | | 9 | 2,50 | |
| 10 | 2,04 | | 17 | 2,12 | | 54 | 2,60 | |
| 67 | 2,04 | | 13 | 2,12 | | 59 | 2,61 | |
| 36 | 2,04 | | 57 | 2,12 | | 30 | 2,62 | |
| 21 | 2,05 | | 2 | 2,13 | | 56 | 2,77 | |
| 39 | 2,06 | | 1 | 2,13 | | 65 | 2,81 | U |
| 53 | 2,07 | | 71 | 2,13 | | 32 | 5,00 | U |
| 29 | 2,08 | | 34 | 2,15 | | 61 | 12,10 | U |
| 12 | 2,08 | | 42 | 2,16 | | | | |

U = Omitted result

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

| | | | |
|---|---|---|---|
| Number of participants | 57 | Range | 0,52 |
| Number of omitted results | 5 | Variance | 0,01 |
| True value | 2,07 | Standard deviation | 0,12 |
| Mean value | 2,08 | Relative standard deviation | 5,7% |
| Median value | 2,07 | Relative error | 0,5% |

Analytical results in ascending order:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 54 | 1,52 | U | 7 | 2,04 | 41 | 2,14 | |
| 48 | 1,84 | | 15 | 2,04 | 50 | 2,15 | |
| 36 | 1,90 | | 37 | 2,04 | 72 | 2,16 | |
| 71 | 1,93 | | 67 | 2,05 | 5 | 2,17 | |
| 45 | 1,93 | | 42 | 2,06 | 57 | 2,18 | |
| 66 | 1,93 | | 10 | 2,06 | 12 | 2,19 | |
| 60 | 1,93 | | 4 | 2,06 | 19 | 2,19 | |
| 26 | 1,94 | | 55 | 2,07 | 29 | 2,20 | |
| 34 | 1,95 | | 70 | 2,07 | 47 | 2,20 | |
| 1 | 1,96 | | 11 | 2,07 | 30 | 2,21 | |
| 31 | 1,96 | | 63 | 2,10 | 58 | 2,23 | |
| 40 | 1,98 | | 18 | 2,10 | 39 | 2,30 | |
| 21 | 2,00 | | 17 | 2,10 | 64 | 2,35 | |
| 24 | 2,00 | | 51 | 2,10 | 8 | 2,35 | |
| 35 | 2,00 | | 32 | 2,10 | 59 | 2,36 | |
| 61 | 2,00 | | 2 | 2,10 | 38 | 2,80 | U |
| 49 | 2,00 | | 13 | 2,11 | 20 | 3,10 | U |
| 56 | 2,01 | | 16 | 2,12 | 28 | 3,11 | U |
| 33 | 2,01 | | 23 | 2,14 | 65 | 3,65 | U |

**Sample B**

| | | | |
|---|---|---|---|
| Number of participants | 57 | Range | 1,77 |
| Number of omitted results | 5 | Variance | 0,09 |
| True value | 4,45 | Standard deviation | 0,30 |
| Mean value | 4,45 | Relative standard deviation | 6,7% |
| Median value | 4,45 | Relative error | 0,0% |

Analytical results in ascending order:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 54 | 2,42 | U | 40 | 4,40 | 30 | 4,55 | |
| 56 | 3,41 | | 13 | 4,40 | 2 | 4,55 | |
| 48 | 3,97 | | 66 | 4,40 | 50 | 4,57 | |
| 36 | 3,97 | | 21 | 4,40 | 12 | 4,57 | |
| 61 | 4,00 | | 67 | 4,40 | 16 | 4,60 | |
| 24 | 4,09 | | 47 | 4,41 | 41 | 4,61 | |
| 26 | 4,11 | | 11 | 4,43 | 5 | 4,63 | |
| 7 | 4,22 | | 15 | 4,44 | 58 | 4,68 | |
| 33 | 4,25 | | 4 | 4,46 | 39 | 4,77 | |
| 32 | 4,25 | | 55 | 4,47 | 59 | 4,84 | |
| 34 | 4,25 | | 10 | 4,47 | 64 | 4,84 | |
| 45 | 4,27 | | 70 | 4,48 | 37 | 4,93 | |
| 71 | 4,29 | | 63 | 4,49 | 8 | 5,09 | |
| 31 | 4,30 | | 72 | 4,49 | 51 | 5,11 | |
| 1 | 4,30 | | 23 | 4,50 | 57 | 5,18 | |
| 35 | 4,32 | | 19 | 4,51 | 38 | 5,22 | U |
| 49 | 4,36 | | 42 | 4,53 | 20 | 5,60 | U |
| 18 | 4,36 | | 29 | 4,54 | 28 | 5,99 | U |
| 60 | 4,39 | | 17 | 4,54 | 65 | 5,99 | U |

U = Omitted result

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

| | | | |
|---|---|---|---|
| Number of participants | 57 | Range | 0,180 |
| Number of omitted results | 5 | Variance | 0,001 |
| True value | 0,487 | Standard deviation | 0,033 |
| Mean value | 0,488 | Relative standard deviation | 6,8% |
| Median value | 0,487 | Relative error | 0,2% |

Analytical results in ascending order:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 19 | < 1 | U | 18 | 0,480 | 55 | 0,500 | |
| 56 | 0,110 | U | 17 | 0,480 | 32 | 0,500 | |
| 71 | 0,420 | | 4 | 0,480 | 42 | 0,500 | |
| 48 | 0,420 | | 72 | 0,480 | 64 | 0,500 | |
| 60 | 0,432 | | 66 | 0,480 | 59 | 0,501 | |
| 23 | 0,440 | | 13 | 0,480 | 12 | 0,505 | |
| 26 | 0,450 | | 1 | 0,480 | 41 | 0,508 | |
| 37 | 0,450 | | 11 | 0,483 | 5 | 0,510 | |
| 31 | 0,460 | | 2 | 0,485 | 58 | 0,512 | |
| 34 | 0,460 | | 70 | 0,489 | 8 | 0,513 | |
| 24 | 0,462 | | 10 | 0,489 | 28 | 0,530 | |
| 40 | 0,464 | | 29 | 0,490 | 47 | 0,530 | |
| 49 | 0,465 | | 57 | 0,490 | 30 | 0,550 | |
| 67 | 0,470 | | 63 | 0,491 | 54 | 0,550 | |
| 45 | 0,470 | | 39 | 0,491 | 16 | 0,559 | |
| 7 | 0,470 | | 15 | 0,496 | 20 | 0,600 | |
| 36 | 0,471 | | 51 | 0,498 | 38 | 0,622 | U |
| 35 | 0,473 | | 50 | 0,500 | 65 | 0,680 | U |
| 33 | 0,476 | | 21 | 0,500 | 61 | 2,000 | U |

**Sample B**

| | | | |
|---|---|---|---|
| Number of participants | 57 | Range | 0,150 |
| Number of omitted results | 5 | Variance | 0,001 |
| True value | 0,421 | Standard deviation | 0,027 |
| Mean value | 0,422 | Relative standard deviation | 6,3% |
| Median value | 0,421 | Relative error | 0,3% |

Analytical results in ascending order:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 19 | < 1 | U | 66 | 0,410 | 64 | 0,430 | |
| 56 | 0,120 | U | 18 | 0,410 | 29 | 0,430 | |
| 65 | 0,270 | U | 35 | 0,412 | 51 | 0,438 | |
| 23 | 0,360 | | 39 | 0,414 | 54 | 0,440 | |
| 7 | 0,370 | | 11 | 0,417 | 55 | 0,440 | |
| 48 | 0,380 | | 21 | 0,420 | 57 | 0,440 | |
| 71 | 0,380 | | 17 | 0,420 | 58 | 0,444 | |
| 28 | 0,390 | | 67 | 0,420 | 41 | 0,446 | |
| 31 | 0,390 | | 13 | 0,420 | 12 | 0,448 | |
| 26 | 0,390 | | 4 | 0,420 | 47 | 0,450 | |
| 36 | 0,399 | | 15 | 0,422 | 5 | 0,450 | |
| 49 | 0,400 | | 59 | 0,423 | 42 | 0,450 | |
| 37 | 0,400 | | 2 | 0,424 | 8 | 0,451 | |
| 32 | 0,400 | | 1 | 0,426 | 70 | 0,460 | |
| 60 | 0,407 | | 45 | 0,428 | 16 | 0,462 | |
| 33 | 0,408 | | 63 | 0,428 | 20 | 0,470 | |
| 40 | 0,409 | | 10 | 0,429 | 30 | 0,510 | |
| 34 | 0,410 | | 50 | 0,430 | 38 | 0,532 | U |
| 24 | 0,410 | | 72 | 0,430 | 61 | 1,500 | U |

U = Omitted result

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

| | | | | | |
|---|---|---|---|---|---|
| Number of participants | 58 | | Range | | 1,02 |
| Number of omitted results | 4 | | Variance | | 0,03 |
| True value | 3,25 | | Standard deviation | | 0,18 |
| Mean value | 3,27 | | Relative standard deviation | | 5,6% |
| Median value | 3,25 | | Relative error | | 0,5% |

Analytical results in ascending order:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 29 | 0,85 | U | 7 | 3,20 | 58 | 3,35 | |
| 56 | 2,78 | | 59 | 3,20 | 31 | 3,35 | |
| 52 | 2,90 | U | 60 | 3,21 | 63 | 3,35 | |
| 30 | 2,95 | | 72 | 3,22 | 38 | 3,36 | |
| 19 | 2,95 | | 18 | 3,23 | 34 | 3,36 | |
| 48 | 2,99 | | 35 | 3,24 | 57 | 3,38 | |
| 66 | 3,04 | | 49 | 3,25 | 15 | 3,39 | |
| 55 | 3,06 | | 65 | 3,25 | 20 | 3,40 | |
| 26 | 3,08 | | 50 | 3,25 | 8 | 3,43 | |
| 41 | 3,12 | | 2 | 3,26 | 4 | 3,46 | |
| 21 | 3,14 | | 47 | 3,28 | 40 | 3,49 | |
| 36 | 3,14 | | 39 | 3,28 | 17 | 3,51 | |
| 24 | 3,15 | | 10 | 3,29 | 5 | 3,53 | |
| 11 | 3,15 | | 16 | 3,31 | 32 | 3,60 | |
| 67 | 3,16 | | 1 | 3,31 | 42 | 3,75 | |
| 12 | 3,16 | | 45 | 3,31 | 33 | 3,80 | |
| 70 | 3,16 | | 51 | 3,31 | 54 | 3,83 | U |
| 28 | 3,17 | | 64 | 3,31 | 61 | 8,70 | U |
| 13 | 3,19 | | 71 | 3,32 | | | |
| 37 | 3,20 | | 23 | 3,33 | | | |

**Sample B**

| | | | | | |
|---|---|---|---|---|---|
| Number of participants | 58 | | Range | | 0,46 |
| Number of omitted results | 4 | | Variance | | 0,01 |
| True value | 1,26 | | Standard deviation | | 0,08 |
| Mean value | 1,26 | | Relative standard deviation | | 6,6% |
| Median value | 1,26 | | Relative error | | 0,1% |

Analytical results in ascending order:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 52 | 0,32 | U | 35 | 1,24 | 16 | 1,29 | |
| 65 | 1,00 | | 12 | 1,25 | 10 | 1,30 | |
| 66 | 1,07 | | 18 | 1,25 | 20 | 1,30 | |
| 55 | 1,10 | | 49 | 1,25 | 38 | 1,31 | |
| 48 | 1,12 | | 45 | 1,25 | 15 | 1,31 | |
| 41 | 1,14 | | 60 | 1,25 | 57 | 1,33 | |
| 26 | 1,18 | | 47 | 1,25 | 4 | 1,33 | |
| 30 | 1,19 | | 2 | 1,25 | 34 | 1,33 | |
| 33 | 1,20 | | 39 | 1,26 | 31 | 1,34 | |
| 28 | 1,20 | | 23 | 1,26 | 8 | 1,35 | |
| 70 | 1,21 | | 51 | 1,26 | 56 | 1,35 | |
| 13 | 1,21 | | 72 | 1,26 | 17 | 1,36 | |
| 24 | 1,22 | | 59 | 1,27 | 32 | 1,40 | |
| 29 | 1,22 | U | 71 | 1,27 | 19 | 1,42 | |
| 67 | 1,22 | | 50 | 1,27 | 5 | 1,42 | |
| 42 | 1,23 | | 1 | 1,27 | 37 | 1,46 | |
| 11 | 1,23 | | 58 | 1,28 | 54 | 1,54 | U |
| 7 | 1,23 | | 40 | 1,29 | 61 | 7,10 | U |
| 36 | 1,24 | | 63 | 1,29 | | | |
| 21 | 1,24 | | 64 | 1,29 | | | |

U = Omitted result

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

| | | | |
|---|---|---|---|
| Number of participants | 57 | Range | 0,150 |
| Number of omitted results | 7 | Variance | 0,001 |
| True value | 0,299 | Standard deviation | 0,028 |
| Mean value | 0,295 | Relative standard deviation | 9,5% |
| Median value | 0,299 | Relative error | -1,3% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 19 | < 0,6 | U | 15 | 0,285 | | 8 | 0,309 | |
| 56 | < 0,5 | U | 11 | 0,286 | | 4 | 0,310 | |
| 61 | < 0,001 | U | 10 | 0,288 | | 57 | 0,310 | |
| 37 | 0,140 | U | 39 | 0,289 | | 42 | 0,310 | |
| 28 | 0,220 | | 67 | 0,290 | | 72 | 0,310 | |
| 65 | 0,220 | | 17 | 0,290 | | 51 | 0,313 | |
| 66 | 0,250 | | 41 | 0,294 | | 16 | 0,313 | |
| 59 | 0,252 | | 36 | 0,295 | | 63 | 0,319 | |
| 23 | 0,260 | | 2 | 0,297 | | 64 | 0,320 | |
| 47 | 0,270 | | 24 | 0,298 | | 55 | 0,320 | |
| 26 | 0,270 | | 34 | 0,300 | | 60 | 0,323 | |
| 13 | 0,270 | | 49 | 0,300 | | 40 | 0,325 | |
| 35 | 0,273 | | 18 | 0,300 | | 20 | 0,330 | |
| 12 | 0,274 | | 32 | 0,300 | | 38 | 0,347 | |
| 45 | 0,276 | | 29 | 0,300 | | 5 | 0,350 | |
| 7 | 0,280 | | 21 | 0,300 | | 54 | 0,370 | U |
| 50 | 0,280 | | 31 | 0,300 | | 30 | 0,370 | |
| 48 | 0,280 | | 58 | 0,300 | | 71 | 0,410 | U |
| 1 | 0,282 | | 70 | 0,301 | | 52 | 0,870 | U |

**Sample B**

| | | | |
|---|---|---|---|
| Number of participants | 57 | Range | 0,130 |
| Number of omitted results | 7 | Variance | 0,001 |
| True value | 0,231 | Standard deviation | 0,022 |
| Mean value | 0,230 | Relative standard deviation | 9,8% |
| Median value | 0,231 | Relative error | -0,5% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 19 | < 0,6 | U | 47 | 0,220 | | 20 | 0,240 | |
| 56 | < 0,5 | U | 1 | 0,220 | | 58 | 0,240 | |
| 37 | < 0,1 | U | 24 | 0,224 | | 67 | 0,240 | |
| 61 | < 0,001 | U | 15 | 0,226 | | 21 | 0,240 | |
| 52 | 0,150 | U | 64 | 0,230 | | 34 | 0,240 | |
| 65 | 0,160 | | 17 | 0,230 | | 41 | 0,241 | |
| 59 | 0,182 | | 11 | 0,230 | | 70 | 0,246 | |
| 38 | 0,187 | | 29 | 0,230 | | 71 | 0,250 | U |
| 28 | 0,190 | | 4 | 0,230 | | 57 | 0,250 | |
| 35 | 0,195 | | 18 | 0,230 | | 48 | 0,250 | |
| 10 | 0,208 | | 50 | 0,230 | | 8 | 0,250 | |
| 66 | 0,210 | | 60 | 0,231 | | 42 | 0,250 | |
| 23 | 0,210 | | 40 | 0,231 | | 32 | 0,250 | |
| 13 | 0,210 | | 39 | 0,235 | | 63 | 0,257 | |
| 45 | 0,214 | | 51 | 0,235 | | 72 | 0,260 | |
| 12 | 0,216 | | 16 | 0,235 | | 55 | 0,260 | |
| 7 | 0,220 | | 2 | 0,238 | | 5 | 0,260 | |
| 26 | 0,220 | | 36 | 0,238 | | 30 | 0,290 | |
| 31 | 0,220 | | 49 | 0,240 | | 54 | 0,320 | U |

U = Omitted result

**Table 5.11. Statistics - Total organic carbon, mg/l**

**Sample A**

| | | | | |
|---|---|---|---|---|
| Number of participants | 34 | Range | 2,50 | |
| Number of omitted results | 3 | Variance | 0,56 | |
| True value | 10,48 | Standard deviation | 0,75 | |
| Mean value | 10,63 | Relative standard deviation | 7,1% | |
| Median value | 10,48 | Relative error | 1,4% | |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 45 | 7,80 | U | 49 | 10,27 | 64 | 11,00 | | |
| 68 | 9,50 | | 67 | 10,30 | 71 | 11,32 | | |
| 48 | 9,50 | | 6 | 10,32 | 57 | 11,38 | | |
| 16 | 9,51 | U | 29 | 10,44 | 24 | 11,40 | | |
| 23 | 9,60 | | 10 | 10,45 | 11 | 11,60 | | |
| 18 | 9,66 | | 2 | 10,48 | 12 | 11,70 | | |
| 26 | 9,80 | | 33 | 10,50 | 56 | 11,85 | | |
| 35 | 9,89 | | 21 | 10,70 | 51 | 12,00 | | |
| 42 | 9,99 | | 40 | 10,76 | 37 | 12,00 | | |
| 50 | 10,00 | | 60 | 10,89 | 4 | 12,40 | U | |
| 32 | 10,10 | | 36 | 10,90 | | | | |
| 1 | 10,20 | | 19 | 11,00 | | | | |

**Sample B**

| | | | | |
|---|---|---|---|---|
| Number of participants | 34 | Range | 1,84 | |
| Number of omitted results | 3 | Variance | 0,15 | |
| True value | 4,15 | Standard deviation | 0,39 | |
| Mean value | 4,20 | Relative standard deviation | 9,3% | |
| Median value | 4,15 | Relative error | 1,3% | |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 45 | 2,40 | U | 42 | 4,03 | 57 | 4,40 | | |
| 49 | 3,72 | | 60 | 4,06 | 21 | 4,40 | | |
| 18 | 3,76 | | 71 | 4,07 | 6 | 4,45 | | |
| 67 | 3,80 | | 40 | 4,07 | 24 | 4,50 | | |
| 64 | 3,80 | | 26 | 4,15 | 12 | 4,51 | | |
| 1 | 3,89 | | 29 | 4,15 | 11 | 4,63 | | |
| 23 | 3,90 | | 68 | 4,20 | 51 | 5,10 | | |
| 48 | 3,90 | | 36 | 4,21 | 56 | 5,56 | | |
| 32 | 3,90 | | 33 | 4,29 | 16 | 5,97 | U | |
| 2 | 3,95 | | 37 | 4,30 | 4 | 6,70 | U | |
| 35 | 3,99 | | 19 | 4,30 | | | | |
| 50 | 4,00 | | 10 | 4,31 | | | | |

U = Omitted result

**Table 5.12. Statistics - Aluminium**

**Sample C**

| | | | |
|---|---|---|---|
| Number of participants | 31 | Range | 34,8 |
| Number of omitted results | 5 | Variance | 54,5 |
| True value | 122,5 | Standard deviation | 7,4 |
| Mean value | 121,4 | Relative standard deviation | 6,1% |
| Median value | 122,5 | Relative error | -0,9% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 21 | 38,0 | U | 16 | 120,0 | | 37 | 126,0 | |
| 52 | 48,9 | U | 51 | 120,0 | | 64 | 126,0 | |
| 59 | 79,7 | U | 20 | 120,0 | | 10 | 127,0 | U |
| 46 | 101,9 | | 19 | 120,0 | | 1 | 128,0 | |
| 67 | 110,0 | | 45 | 122,0 | | 50 | 129,0 | |
| 36 | 111,0 | | 42 | 123,0 | | 60 | 129,0 | |
| 4 | 114,0 | | 11 | 123,0 | | 7 | 133,0 | |
| 41 | 115,3 | | 63 | 123,0 | | 56 | 136,7 | |
| 35 | 117,0 | | 24 | 123,8 | | 30 | 164,0 | U |
| 48 | 118,0 | | 18 | 124,0 | | | | |
| 9 | 118,0 | | 57 | 124,6 | | | | |

**Sample D**

| | | | |
|---|---|---|---|
| Number of participants | 31 | Range | 31,5 |
| Number of omitted results | 5 | Variance | 55,4 |
| True value | 72,8 | Standard deviation | 7,4 |
| Mean value | 71,9 | Relative standard deviation | 10,3% |
| Median value | 72,8 | Relative error | -1,2% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 21 | 21,0 | U | 42 | 71,2 | | 67 | 78,0 | |
| 52 | 40,8 | U | 35 | 71,6 | | 1 | 78,7 | |
| 46 | 50,0 | | 45 | 72,0 | | 51 | 79,0 | |
| 24 | 50,2 | | 11 | 72,5 | | 7 | 79,0 | |
| 36 | 67,4 | | 60 | 73,0 | | 50 | 79,0 | |
| 4 | 68,7 | | 64 | 73,6 | | 56 | 81,5 | |
| 9 | 69,0 | | 19 | 74,0 | | 59 | 82,3 | U |
| 48 | 70,0 | | 18 | 74,0 | | 10 | 104,0 | U |
| 16 | 70,0 | | 63 | 74,2 | | 30 | 155,0 | U |
| 41 | 70,5 | | 57 | 75,3 | | | | |
| 20 | 71,2 | | 37 | 77,0 | | | | |

U = Omitted result

**Table 5.13. Statistics - Iron**

**Sample C**

| | | | |
|---|---|---|---|
| Number of participants | 40 | Range | 41,0 |
| Number of omitted results | 6 | Variance | 102,3 |
| True value | 164,4 | Standard deviation | 10,1 |
| Mean value | 162,3 | Relative standard deviation | 6,2% |
| Median value | 164,4 | Relative error | -1,3% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 30 | 15,0 | U | 58 | 160,2 | | 19 | 168,0 | |
| 57 | 122,9 | U | 48 | 161,0 | | 10 | 169,0 | |
| 4 | 139,0 | | 70 | 162,0 | | 46 | 169,6 | |
| 61 | 143,0 | | 8 | 162,1 | | 45 | 170,0 | |
| 60 | 144,0 | | 20 | 163,0 | | 50 | 172,0 | |
| 67 | 147,0 | | 21 | 164,0 | | 72 | 174,0 | |
| 64 | 150,0 | | 18 | 164,7 | | 1 | 175,0 | |
| 65 | 150,0 | | 24 | 165,5 | | 9 | 180,0 | U |
| 36 | 153,0 | | 37 | 166,0 | | 7 | 180,0 | |
| 35 | 154,0 | | 16 | 167,0 | | 5 | 180,0 | |
| 63 | 157,0 | | 42 | 167,0 | | 13 | 220,0 | U |
| 25 | 158,1 | | 11 | 167,4 | | 38 | 1653,0 | U |
| 56 | 159,6 | | 41 | 167,8 | | | | |
| 51 | 160,0 | U | 15 | 168,0 | | | | |

**Sample D**

| | | | |
|---|---|---|---|
| Number of participants | 40 | Range | 30,0 |
| Number of omitted results | 6 | Variance | 33,4 |
| True value | 35,8 | Standard deviation | 5,8 |
| Mean value | 36,2 | Relative standard deviation | 16,0% |
| Median value | 35,8 | Relative error | 1,2% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 30 | 3,4 | U | 56 | 34,9 | | 10 | 37,0 | |
| 51 | 10,0 | U | 38 | 35,0 | U | 50 | 38,0 | |
| 64 | 20,0 | | 21 | 35,0 | | 72 | 38,9 | |
| 65 | 23,7 | | 67 | 35,4 | | 35 | 39,6 | |
| 57 | 27,6 | U | 58 | 35,6 | | 8 | 41,6 | |
| 61 | 30,0 | | 24 | 35,7 | | 15 | 44,0 | |
| 4 | 31,1 | | 70 | 35,7 | | 19 | 45,0 | |
| 45 | 31,5 | | 42 | 35,8 | | 7 | 45,0 | |
| 60 | 33,0 | | 11 | 35,8 | | 41 | 46,3 | |
| 20 | 33,6 | | 16 | 36,0 | | 5 | 50,0 | |
| 63 | 33,7 | | 25 | 36,1 | | 9 | 76,0 | U |
| 36 | 33,9 | | 1 | 36,3 | | 13 | 80,0 | U |
| 18 | 34,6 | | 46 | 36,9 | | | | |
| 48 | 34,7 | | 37 | 37,0 | | | | |

U = Omitted result

**Table 5.14. Statistics - Manganese**

**Sample C**

| | | | |
|---|---|---|---|
| Number of participants | 39 | Range | 3,27 |
| Number of omitted results | 14 | Variance | 0,53 |
| True value | 9,64 | Standard deviation | 0,73 |
| Mean value | 9,54 | Relative standard deviation | 7,6% |
| Median value | 9,64 | Relative error | -1,0% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 70 | < 73 | U | 24 | 9,30 | | 19 | 10,00 | U |
| 18 | < 10 | U | 4 | 9,33 | | 13 | 10,00 | U |
| 42 | < 10 | U | 64 | 9,34 | | 25 | 10,04 | |
| 41 | < 10 | U | 48 | 9,35 | | 37 | 10,10 | |
| 7 | 0,91 | U | 50 | 9,39 | | 9 | 10,10 | |
| 65 | 7,14 | | 38 | 9,40 | U | 8 | 10,26 | |
| 16 | 7,50 | U | 52 | 9,47 | U | 11 | 10,30 | |
| 35 | 8,75 | | 46 | 9,62 | | 1 | 10,30 | |
| 60 | 8,80 | | 20 | 9,64 | | 45 | 10,40 | |
| 67 | 8,80 | | 21 | 9,70 | | 56 | 10,41 | |
| 36 | 8,90 | | 63 | 9,75 | | 72 | 12,50 | U |
| 10 | 9,10 | U | 15 | 9,78 | | 61 | 33,30 | U |
| 58 | 9,10 | | 57 | 9,93 | | 51 | 44,00 | U |

**Sample D**

| | | | |
|---|---|---|---|
| Number of participants | 39 | Range | 0,46 |
| Number of omitted results | 14 | Variance | 0,01 |
| True value | 1,09 | Standard deviation | 0,11 |
| Mean value | 1,08 | Relative standard deviation | 9,9% |
| Median value | 1,09 | Relative error | -1,1% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 70 | < 73 | U | 24 | 1,00 | | 9 | 1,14 | |
| 42 | < 10 | U | 37 | 1,00 | | 63 | 1,15 | |
| 13 | < 10 | U | 60 | 1,00 | | 1 | 1,16 | |
| 18 | < 10 | U | 4 | 1,00 | | 57 | 1,20 | |
| 41 | < 10 | U | 25 | 1,02 | | 21 | 1,20 | |
| 19 | < 2 | U | 45 | 1,03 | | 67 | 1,21 | |
| 52 | < 2 | U | 50 | 1,04 | | 56 | 1,24 | |
| 16 | < 1 | U | 36 | 1,05 | | 11 | 1,24 | |
| 10 | 0,40 | U | 48 | 1,09 | | 51 | 1,30 | U |
| 65 | 0,78 | | 8 | 1,10 | | 72 | 1,49 | U |
| 35 | 0,95 | | 15 | 1,11 | | 38 | 1,60 | U |
| 46 | 0,99 | | 58 | 1,12 | | 7 | 9,51 | U |
| 64 | 1,00 | | 20 | 1,13 | | 61 | 14,50 | U |

U = Omitted result

**Table 5.15. Statistics - Cadmium, µg/l**

**Sample C**

| | | | |
|---|---|---|---|
| Number of participants | 43 | Range | 1,52 |
| Number of omitted results | 4 | Variance | 0,10 |
| True value | 3,56 | Standard deviation | 0,32 |
| Mean value | 3,52 | Relative standard deviation | 9,2% |
| Median value | 3,56 | Relative error | -1,1% |

Analytical results in ascending order:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 46 | 0,37 | U | 70 | 3,46 | 10 | 3,61 |
| 16 | 1,20 | U | 19 | 3,50 | 17 | 3,63 |
| 69 | 1,86 | U | 57 | 3,51 | 45 | 3,68 |
| 61 | 1,93 | U | 52 | 3,53 | 18 | 3,68 |
| 65 | 2,67 | | 11 | 3,53 | 36 | 3,73 |
| 30 | 2,80 | | 20 | 3,54 | 50 | 3,73 |
| 8 | 2,85 | | 58 | 3,56 | 9 | 3,80 |
| 7 | 2,98 | | 48 | 3,56 | 60 | 3,80 |
| 41 | 3,00 | | 1 | 3,56 | 37 | 3,85 |
| 5 | 3,20 | | 63 | 3,57 | 38 | 3,90 |
| 67 | 3,30 | | 72 | 3,57 | 56 | 3,96 |
| 25 | 3,38 | | 4 | 3,59 | 59 | 4,04 |
| 35 | 3,41 | | 42 | 3,60 | 51 | 4,19 |
| 24 | 3,41 | | 21 | 3,60 | | |
| 64 | 3,42 | | 15 | 3,61 | | |

**Sample D**

| | | | |
|---|---|---|---|
| Number of participants | 43 | Range | 2,69 |
| Number of omitted results | 4 | Variance | 0,30 |
| True value | 6,13 | Standard deviation | 0,55 |
| Mean value | 6,12 | Relative standard deviation | 8,9% |
| Median value | 6,13 | Relative error | -0,2% |

Analytical results in ascending order:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 46 | 0,19 | U | 24 | 6,02 | 1 | 6,34 |
| 16 | 2,20 | U | 35 | 6,07 | 45 | 6,34 |
| 69 | 3,44 | U | 70 | 6,08 | 52 | 6,39 |
| 61 | 4,17 | U | 19 | 6,10 | 60 | 6,40 |
| 8 | 4,66 | | 20 | 6,11 | 50 | 6,40 |
| 30 | 4,80 | | 57 | 6,12 | 17 | 6,43 |
| 59 | 4,96 | | 10 | 6,12 | 9 | 6,50 |
| 41 | 5,38 | | 58 | 6,13 | 36 | 6,61 |
| 5 | 5,43 | | 72 | 6,13 | 37 | 6,67 |
| 7 | 5,62 | | 48 | 6,15 | 42 | 6,69 |
| 11 | 5,74 | | 25 | 6,15 | 56 | 6,86 |
| 64 | 5,82 | | 4 | 6,16 | 38 | 7,10 |
| 15 | 5,97 | | 21 | 6,20 | 51 | 7,35 |
| 67 | 6,00 | | 63 | 6,25 | | |
| 65 | 6,02 | | 18 | 6,29 | | |

U = Omitted result

**Table 5.16. Statistics - Lead, µg/l**

**Sample C**

| | | | |
|---|---|---|---|
| Number of participants | 42 | Range | 2,50 |
| Number of omitted results | 5 | Variance | 0,20 |
| True value | 4,00 | Standard deviation | 0,44 |
| Mean value | 3,97 | Relative standard deviation | 11,2% |
| Median value | 4,00 | Relative error | -0,7% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 41 | < 1 | U | 11 | 3,92 | | 48 | 4,04 | |
| 65 | 1,04 | U | 36 | 3,92 | | 15 | 4,07 | |
| 52 | 2,35 | U | 63 | 3,93 | | 18 | 4,10 | |
| 25 | 2,61 | | 57 | 3,94 | | 50 | 4,14 | |
| 7 | 2,93 | | 20 | 3,95 | | 64 | 4,14 | |
| 16 | 3,30 | | 45 | 3,98 | | 37 | 4,15 | |
| 46 | 3,49 | U | 4 | 3,98 | | 72 | 4,20 | |
| 21 | 3,50 | | 17 | 3,99 | | 60 | 4,20 | |
| 59 | 3,67 | | 67 | 4,00 | | 70 | 4,22 | |
| 5 | 3,70 | | 56 | 4,00 | | 8 | 4,42 | |
| 69 | 3,70 | | 9 | 4,00 | | 51 | 4,71 | |
| 58 | 3,71 | | 19 | 4,00 | | 42 | 4,86 | |
| 1 | 3,89 | | 10 | 4,02 | | 61 | 5,11 | |
| 35 | 3,89 | | 24 | 4,03 | | 30 | 8,00 | U |

**Sample D**

| | | | |
|---|---|---|---|
| Number of participants | 42 | Range | 2,86 |
| Number of omitted results | 5 | Variance | 0,31 |
| True value | 6,14 | Standard deviation | 0,56 |
| Mean value | 6,06 | Relative standard deviation | 9,2% |
| Median value | 6,14 | Relative error | -1,3% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 41 | < 1 | U | 15 | 5,95 | | 69 | 6,20 | |
| 46 | 3,18 | U | 10 | 6,05 | | 64 | 6,25 | |
| 52 | 3,57 | U | 63 | 6,06 | | 8 | 6,28 | |
| 65 | 3,66 | U | 70 | 6,06 | | 67 | 6,30 | |
| 61 | 4,52 | | 35 | 6,10 | | 72 | 6,32 | |
| 7 | 4,67 | | 20 | 6,11 | | 17 | 6,35 | |
| 25 | 4,85 | | 4 | 6,12 | | 19 | 6,40 | |
| 58 | 5,34 | | 24 | 6,12 | | 60 | 6,40 | |
| 16 | 5,40 | | 57 | 6,14 | | 50 | 6,46 | |
| 5 | 5,70 | | 45 | 6,15 | | 37 | 6,55 | |
| 59 | 5,81 | | 48 | 6,16 | | 21 | 6,70 | |
| 11 | 5,85 | | 36 | 6,17 | | 42 | 7,09 | |
| 9 | 5,90 | | 56 | 6,17 | | 51 | 7,38 | |
| 1 | 5,91 | | 18 | 6,20 | | 30 | 9,50 | U |

U = Omitted result

**Table 5.17. Statistics - Copper, µg/l**

**Sample C**

| | | | |
|---|---|---|---|
| Number of participants | 43 | Range | 0,43 |
| Number of omitted results | 19 | Variance | 0,02 |
| True value | 0,64 | Standard deviation | 0,12 |
| Mean value | 0,64 | Relative standard deviation | 19,4% |
| Median value | 0,64 | Relative error | -0,1% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 41 | < 10 | U | 57 | 0,56 | | 51 | 0,79 | |
| 70 | < 2 | U | 72 | 0,57 | | 35 | 0,80 | |
| 45 | < 1 | U | 9 | 0,58 | | 60 | 0,80 | |
| 19 | < 1 | U | 4 | 0,58 | | 50 | 0,80 | |
| 38 | < 1 | U | 7 | 0,60 | | 11 | 1,02 | U |
| 10 | < 1 | U | 16 | 0,60 | | 24 | 1,09 | U |
| 17 | < 1 | U | 20 | 0,63 | | 8 | 1,13 | U |
| 18 | < 1 | U | 67 | 0,65 | | 46 | 1,21 | U |
| 59 | < 0,2 | U | 56 | 0,69 | | 69 | 1,32 | U |
| 21 | 0,20 | U | 36 | 0,70 | | 5 | 2,00 | U |
| 25 | 0,37 | | 15 | 0,72 | | 42 | 5,70 | U |
| 61 | 0,40 | | 1 | 0,73 | | 52 | 6,23 | U |
| 65 | 0,49 | | 48 | 0,74 | | 30 | 63,00 | U |
| 58 | 0,50 | | 64 | 0,74 | | | | |
| 37 | 0,55 | | 63 | 0,76 | | | | |

**Sample D**

| | | | |
|---|---|---|---|
| Number of participants | 43 | Range | 0,80 |
| Number of omitted results | 19 | Variance | 0,03 |
| True value | 1,39 | Standard deviation | 0,19 |
| Mean value | 1,35 | Relative standard deviation | 13,8% |
| Median value | 1,39 | Relative error | -3,1% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 41 | < 10 | U | 9 | 1,33 | | 61 | 1,50 | |
| 70 | < 2 | U | 20 | 1,34 | | 56 | 1,52 | |
| 38 | < 1 | U | 48 | 1,37 | | 24 | 1,53 | U |
| 21 | 0,60 | U | 10 | 1,37 | U | 69 | 1,55 | U |
| 25 | 0,90 | | 17 | 1,38 | U | 5 | 1,60 | U |
| 59 | 0,94 | U | 15 | 1,39 | | 50 | 1,64 | |
| 18 | 1,05 | U | 58 | 1,40 | | 8 | 1,67 | U |
| 65 | 1,06 | | 60 | 1,40 | | 51 | 1,70 | |
| 19 | 1,10 | U | 67 | 1,40 | | 11 | 2,00 | U |
| 16 | 1,10 | | 57 | 1,42 | | 46 | 3,18 | U |
| 7 | 1,10 | | 1 | 1,42 | | 42 | 6,46 | U |
| 35 | 1,16 | | 72 | 1,44 | | 30 | 7,00 | U |
| 36 | 1,21 | | 63 | 1,48 | | 52 | 7,37 | U |
| 64 | 1,28 | | 4 | 1,48 | | | | |
| 37 | 1,29 | | 45 | 1,49 | U | | | |

U = Omitted result

**Table 5.18. Statistics - Nickel, µg/l**

**Sample C**

| | | | |
|---|---|---|---|
| Number of participants | 41 | Range | 2,15 |
| Number of omitted results | 3 | Variance | 0,16 |
| True value | 4,14 | Standard deviation | 0,40 |
| Mean value | 4,13 | Relative standard deviation | 9,7% |
| Median value | 4,14 | Relative error | -0,3% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 52 | < 5 | U | 35 | 4,05 | | 21 | 4,20 | |
| 65 | 2,47 | U | 17 | 4,06 | | 72 | 4,21 | |
| 41 | 2,85 | | 63 | 4,10 | | 57 | 4,22 | |
| 58 | 3,45 | | 60 | 4,10 | | 9 | 4,30 | |
| 42 | 3,45 | | 48 | 4,11 | | 37 | 4,40 | |
| 16 | 3,50 | | 45 | 4,13 | | 56 | 4,48 | |
| 7 | 3,70 | | 4 | 4,13 | | 70 | 4,50 | |
| 10 | 3,81 | | 20 | 4,15 | | 8 | 4,52 | |
| 24 | 3,97 | | 36 | 4,17 | | 11 | 4,54 | |
| 67 | 4,00 | | 15 | 4,18 | | 69 | 4,71 | |
| 5 | 4,00 | | 46 | 4,19 | | 38 | 4,80 | U |
| 50 | 4,02 | | 1 | 4,19 | | 51 | 4,97 | |
| 25 | 4,03 | | 19 | 4,20 | | 61 | 5,00 | |
| 64 | 4,03 | | 18 | 4,20 | | | | |

**Sample D**

| | | | |
|---|---|---|---|
| Number of participants | 41 | Range | 3,07 |
| Number of omitted results | 3 | Variance | 0,29 |
| True value | 6,23 | Standard deviation | 0,54 |
| Mean value | 6,31 | Relative standard deviation | 8,5% |
| Median value | 6,23 | Relative error | 1,3% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 52 | < 5 | U | 15 | 6,15 | | 70 | 6,49 | |
| 65 | 4,16 | U | 63 | 6,15 | | 36 | 6,50 | |
| 41 | 4,95 | | 48 | 6,17 | | 57 | 6,50 | |
| 7 | 5,53 | | 35 | 6,17 | | 8 | 6,52 | |
| 42 | 5,53 | | 20 | 6,18 | | 11 | 6,54 | |
| 58 | 5,70 | | 60 | 6,20 | | 72 | 6,58 | |
| 64 | 5,81 | | 5 | 6,20 | | 37 | 6,70 | |
| 50 | 5,99 | | 1 | 6,25 | | 46 | 6,87 | |
| 16 | 6,00 | | 19 | 6,30 | | 69 | 7,01 | |
| 67 | 6,00 | | 17 | 6,35 | | 56 | 7,11 | |
| 24 | 6,00 | | 45 | 6,35 | | 51 | 7,56 | |
| 10 | 6,02 | | 18 | 6,35 | | 61 | 8,02 | |
| 4 | 6,07 | | 21 | 6,40 | | 38 | 9,50 | U |
| 25 | 6,14 | | 9 | 6,40 | | | | |

U = Omitted result

**Table 5.19. Statistics - Zinc, µg/l**

**Sample C**

| | | | |
|---|---|---|---|
| Number of participants | 42 | Range | 5,1 |
| Number of omitted results | 4 | Variance | 1,5 |
| True value | 21,2 | Standard deviation | 1,2 |
| Mean value | 21,2 | Relative standard deviation | 5,7% |
| Median value | 21,2 | Relative error | 0,1% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 30 | 7,0 | U | 64 | 20,6 | | 42 | 22,0 | |
| 61 | 10,5 | U | 70 | 20,8 | | 8 | 22,0 | |
| 24 | 15,9 | U | 63 | 21,0 | | 11 | 22,1 | |
| 5 | 18,0 | | 20 | 21,0 | | 4 | 22,2 | |
| 7 | 19,3 | | 21 | 21,0 | | 10 | 22,3 | |
| 36 | 19,5 | | 19 | 21,0 | | 17 | 22,4 | |
| 67 | 19,7 | | 25 | 21,1 | | 72 | 22,4 | |
| 38 | 19,8 | | 1 | 21,1 | | 60 | 22,5 | |
| 57 | 20,0 | | 59 | 21,4 | | 50 | 22,8 | |
| 69 | 20,0 | | 45 | 21,4 | | 41 | 22,8 | |
| 16 | 20,0 | | 15 | 21,4 | | 9 | 23,0 | |
| 48 | 20,0 | | 18 | 21,5 | | 56 | 23,0 | |
| 35 | 20,5 | | 51 | 21,6 | | 52 | 23,1 | |
| 58 | 20,6 | | 46 | 22,0 | | 37 | 25,1 | U |

**Sample D**

| | | | |
|---|---|---|---|
| Number of participants | 42 | Range | 9,5 |
| Number of omitted results | 4 | Variance | 4,5 |
| True value | 33,0 | Standard deviation | 2,1 |
| Mean value | 33,1 | Relative standard deviation | 6,4% |
| Median value | 33,0 | Relative error | 0,3% |

Analytical results in ascending order:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 61 | 16,0 | U | 21 | 32,0 | | 41 | 34,1 | |
| 30 | 16,0 | U | 16 | 32,0 | | 51 | 34,2 | |
| 24 | 27,7 | U | 58 | 32,4 | | 50 | 34,3 | |
| 59 | 28,5 | | 1 | 32,7 | | 11 | 34,4 | |
| 7 | 28,8 | | 72 | 32,7 | | 60 | 34,4 | |
| 5 | 30,0 | | 8 | 32,9 | | 42 | 34,9 | |
| 67 | 30,4 | | 25 | 33,0 | | 46 | 35,0 | |
| 38 | 31,0 | | 19 | 33,0 | | 9 | 35,0 | |
| 48 | 31,0 | | 63 | 33,0 | | 10 | 35,1 | |
| 36 | 31,1 | | 70 | 33,3 | | 17 | 35,8 | |
| 64 | 31,4 | | 35 | 33,4 | | 56 | 36,3 | |
| 57 | 31,4 | | 45 | 33,5 | | 52 | 37,4 | |
| 15 | 31,5 | | 4 | 33,6 | | 69 | 38,0 | |
| 20 | 31,8 | | 18 | 34,0 | | 37 | 40,9 | U |

U = Omitted resultat