Convention on Long-Range Transboundary Air Pollution

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

ICP Waters Report 93/2008

Intercomparison 0822:

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

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Abstract

76 laboratories received samples for the intercomparison 0822, and 74 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 %, 69 % of the overall results were considered as acceptable. The best results were reported for the analytical variables sodium, chloride, and calcium, with 91, 85 and 85 % acceptable results, respectively. Low percentage of acceptable results was observed for some heavy metals, for instance copper with 20 % acceptable results. The main reason is the low concentrations of some metals in the samples used. Alkalinity was also a big problem this time, with only 35 % acceptable results. 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
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OF RIVERS AND LAKES

Intercomparison 0822

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

Prepared by the ICP Waters Programme Centre
Norwegian Institute for Water Research
Oslo, September 2008

Preface

The International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters) was established under the Executive Body of the Convention on Long-range Transboundary Air Pollution at its third session in Helsinki in July 1985. The Executive Body has also accepted Norway's offer to provide facilities for the Programme Centre, which has been established at the Norwegian Institute for Water Research, NIVA. A programme subcentre is established at the Laboratory of Freshwater Ecology and Inland Fisheries at University of Bergen. The ICP Water programme is lead by Berit Kvæven, Norwegian Pollution Control Authority (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 22nd intercomparison of chemical analysis.

Oslo, September 2008

Håvard Hovind

Contents

Summary

Intercomparison 0822 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 2008, 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, 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 78 laboratories who accepted to participate. 74 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 41).

The median value of the results received from the participants for each variable was selected as "true" value. On average 69 % 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 sodium, chloride, and calcium where 91, 85 and 85 % of the results, respectively, were acceptable. The worst results were observed for some heavy metals, especially copper (20 %). The main reason for less acceptable results for some metals is probably the low concentrations of these metals 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 conductivity, chloride, sulphate, calcium, sodium, iron and cadmium, 78 % acceptable results were obtained for magnesium, 60 – 69 % for pH, nitrate, potassium, lead and zinc.

The worst results were obtained for copper (20 %), alkalinity (35 %), manganese (40 %) and nickel (54 %).

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 twentysecond intercomparison test, called 0822, 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, 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 Nancy, France, in October 2007 it was decided that the same 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.

The samples were mailed from the Programme Centre on June 4th 2008, 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, two sets 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. Two laboratories who received samples did not return analytical results.

3. Results

120 laboratories were invited to participate in this ICP Waters intercomparison. 78 of the laboratories accepted and therefore samples were mailed to them, however, only 76 laboratories received the samples. The 74 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 40).

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 - 17, 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 survey of the results of intercomparison 0822 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 - 5.17 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. 71 laboratories reported results for pH, 28 of the laboratories of this group indicated that they read the pH value during stirring the solution, while about 40 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).

Three 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 0822 we have used the median value of all the reportede results, after the outliers have been excluded.

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. Several 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), 9 more results which is located outside the 10 % acceptance circle, would be located within the circle and thus be defined as acceptable (then 96 % 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. 51 laboratories reported results for alkalinity, and about 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 results close to the Gran plot method.

The results for alkalinity are spread out along the 45 ° line, most result pairs being quite close to this line, as illustrated in Figure 3, indicating that systematic effects are the dominating reason for the differences observed between many results. 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, with few exceptions, results located close to the centrum of the circle. Very many 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 rather bad compared to the last intercomparisons, only 35 % 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

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 used by one laboratory gave systematically too low results. Six laboratories obviously reported the results in a wrong unit, and the results were corrected to µg/l after clarification with the laboratory. Two laboratories using capillary electrophoresis reported systematically low er values.

In this intercomparison 64 % 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.

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. 85 % of the laboratories determined chloride by ion chromatography. The greatest deviations are observed for the argentometric method, the results being systematically low.

85 % 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 90 % 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. One laboratory used ICP-AES for the determination of total sulphur, and then recalculated the result to mg/l sulphate, the result being acceptable.

84 % of the result pairs are acceptable.

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. 66 laboratories reported results for calcium, and only 11 of them used the traditional flame atomic absorption spectrometry for the determination. The ICP technique is used by 20 laboratories, and two of these used ICP-MS. An increasing number of laboratories, this time 32, used ion chromatography. Three laboratories used a titrimetric method with EDTA for the determination of calcium, one of these were outside the acceptance limit.

85 % acceptable result pairs is good.

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. 11 laboratories are still using flame atomic absorption spectrometry for the determination of magnesium. ICP atomic emission spectrometry was used by 18 laboratories and ICP-MS by two, and 32 laboratories used ion chromatography. Systematic errors are dominating the results being outside the acceptance limit. This time, 78 % of the results are located inside the target accuracy of ± 20 %. The great deviations observed for the titrimetric

method indicate that the concentrations of the samples used in this intercomparison are rather low for this technique, only one of the result pairs produced by this method was acceptable.

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. Only 9 laboratories used flame atomic absorption spectrometry for the determination this time, and ICP-AES was used by 15 laboratories. However, in many laboratories the ion chromatographic technique becomes increasingly more popular in routine determination of the alkaline metals, thus 33 participants used ion chromatography in this intercomparison. Seven laboratories used flame photometry. 91 % of the result pairs are located within the general target accuracy of ± 20 %, which is considered as a very good result.

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 are given in Table 5.10. As for sodium, only 8 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 65 % of the result pairs are considered acceptable, and this is lower than in earlier intercomparisons.

3.11 Iron

The results for iron are illustrated in Figure 11, and the values reported by the participants are given in Table 5.11. The target accuracy is ± 20 %, and is represented by the great circle in Figure 11. This time, 83 % of the result pairs are located inside this circle, which is much better than the last intercomparison. One possible reason for this is the rather high concentrations used for iron in this intercomparison. 41 laboratories submitted results for iron, of which 17 and 15 used ICP-AES and ICP-MS, respectively, while 6 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. The Youden plot looks rather strange in this case, because the concentration in the two samples of the sample pair is very different.

3.12 Manganese

The manganese results 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 12. Only 40 % of the result pairs are located inside this circle, which is unacceptable, the great spread between the reported results is probably caused by the low

concentrations used this time. 43 laboratories submitted results for manganese, of which 17 and 16 used ICP-AES and ICP-MS, respectively, while 4 and 6 used flame and graphite furnace atomic absorption, respectively. Seven laboratories had problems with the sensitivity of the method for sample C with the lowest concentration, and reported "less than" their detection limit.

3.13 Cadmium

The results for cadmium 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. 80 % of the result pairs are located inside this circle. 44 laboratories submitted results for cadmium, of which 11 and 17 used ICP-AES and ICP-MS, respectively, while 13 used graphite furnace atomic absorption and two flame atomic absorption. One laboratory using polarography reported results being comparable to the others.

3.14 Lead

The results for lead 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. 67 % of the result pairs are located inside this circle, which is comparable to the last intercomparison. 45 laboratories submitted results for lead, of which 10 and 17 used ICP-AES and ICP-MS, respectively, while 15 used graphite furnace atomic absorption. Flame atomic absorption was used by 2 laboratories, even though the method is not very sensitive and is not suitable for determination of the lowest lead concentration. Polarography is also working well at one laboratory using this technique.

3.15 Copper

The copper results 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. The extremely low number of results being located inside this circle this time, 20 %, is probably caused by the very low concentrations used for copper. 44 laboratories submitted results for copper, of which 10 used ICP-AES and 18 used ICP-MS, while 12 and 3 used graphite furnace and flame atomic absorption, respectively. Three laboratories using flame atomic absorption, reported the results as < the detection limit. The polarographic method was not sensitive enough for these samples, here too the result was reported as <.

3.16 Nickel

The results for nickel 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. This time, only 54 % of the result pairs are located inside this circle, and the main reason for this situation is that the nickel concentrations are rather low in the samples used this time. 41 laboratories submitted results for nickel, of which 10 and 18 used ICP-AES

and ICP-MS, respectively, while 11 laboratories used graphite furnace atomic absorption, and two flame atomic absorption.

3.17 Zinc

The results for zinc 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, 62 % of the result pairs are located inside this circle, which is somewhat better than the last intercomparison. 42 laboratories submitted results for zinc, of which 16 used ICP-AES and 16 ICP-MS, respectively, while 6 and 3 used flame and graphite furnace atomic absorption, respectively. One laboratory used polarography. Generally, the deviating results are affected mainly by systematic errors. The low concentration of zinc in sample C is leading to many systematically high results, may be caused by a small contamination.

Table 1. Statistical summary of intercomparison 0822

Analytical variable and method	Sample pair	True value 1	True value 2	Total number	Labs exclud.	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	6,75	5,91	71	4	6,75	5,91	6,72	0,15	5,91	0,16	2,3	2,8		
No stirring				40	2	6,75	5,92	6,71	0,16	5,94	0,18	2,4	3,1		
Stirring				28	1	6,78	5,90	6,73	0,16	5,87	0,13	2,3	2,2		
Equilibrating				3	1			6,75		5,86					
Conductivity, mS/m	AB	2,69	2,52	68	4	2,69	2,52	2,68	0,13	2,53	0,11	4,9	4,3	-0,2	0,3
Alkalinity, mmol/l	AB	0,100	0,029	51	28	0,100	0,029	0,100	0,006	0,028	0,007	5,7	24,7	-0,2	-1,8
Gran plot titration				19	6	0,099	0,025	0,098	0,006	0,026	0,006	6,6	24,8	-2,2	-10,6
End point 4.5 & 4.2				10	5	0,103	0,032	0,103	0,003	0,032	0,005	2,8	15,4	3,2	11,0
End point 5.6				1	0			0,099		0,020				-1,0	-31,0
End point 5.4				1	0			0,098		0,026				-2,0	-10,3
End point				19	17			0,106		0,040				5,5	36,2
Colorimetry				1	0			0,101		0,032				1,0	10,3
Nitrate + nitrite-N, µg/l	AB	178	90	64	13	178	90	174	19	90	12	10,9	13,4	-2,1	0,0
Autoanalyzer				11	1	178	92	178	11	88	11	5,9	12,7	0,1	-2,2
Photometry				8	3	187	96	190	22	98	14	11,4	14,4	6,6	8,7
Ion chromatography				40	7	178	90	173	18	90	12	10,4	13,7	-2,7	-0,1
Flow injection anal.				1	0			169		86				-5,1	-4,2
Hydrazine				1	1			44		23				-75,3	-74,0
Cap. electrophoresis				2	0			135		84				-24,2	-7,2
Photometry				1	1			225		253				26,4	181,1
Chloride, mg/l	AB	2,00	2,69	65	3	2,00	2,69	1,96	0,15	2,68	0,23	7,8	8,7	-1,8	-0,4
Ion chromatography				55	1	2,00	2,69	1,97	0,13	2,67	0,19	6,7	7,1	-1,5	-0,7
AA				1	0			1,47		2,23				-26,5	-17,1
Argentometry				2	1			1,68		2,02				-16,0	-24,9
Manual, Hg				4	1	1,93	2,64	2,02	0,23	2,81	0,35	11,5	12,6	0,8	4,6
Cap. electrophoresis				2	0			2,07		2,99				3,5	11,2
Potentiometry				1	0			2,10		3,20				5,0	19,0

Analytical variable and method	Sample pair	True value 1	True value 2	Total number	Labs exclud.	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	1,85	61	7	1,82	1,85	1,83	0,10	1,86	0,12	5,4	6,2	0,4	0,7
Ion chromatography				55	6	1,82	1,85	1,83	0,09	1,86	0,10	4,9	5,3	0,6	0,6
Photometry				1	0			1,61		1,49				-11,5	-19,5
Nephelometry				2	1			2,02		2,14				11,0	15,7
ICP-AES				1	0			1,65		1,82				-9,3	-1,5
Cap. electrophoresis				2	0			1,86		1,98				2,3	7,1
Calcium, mg/l	AB	2,88	1,95	66	6	2,88	1,95	2,90	0,21	1,95	0,16	7,3	8,2	0,6	0,1
FAAS				11	1	2,86	1,96	2,89	0,19	2,00	0,19	6,5	9,7	0,2	2,3
ICP-AES				18	0	2,86	1,93	2,84	0,12	1,91	0,10	4,3	5,0	-1,3	-1,9
EDTA				3	1			3,26		2,22				13,2	13,8
Ion chromatography				31	3	2,91	1,97	2,90	0,24	1,94	0,16	8,3	8,3	0,7	-0,5
ICP-MS				2	1			2,88		1,84				0,0	-5,6
Cap. Electrophoresis				1	0			3,29		2,09				14,2	7,2
Magnesium, mg/l	AB	0,300	0,450	67	10	0,300	0,450	0,304	0,025	0,447	0,034	8,1	7,6	1,5	-0,7
FAAS				11	2	0,301	0,456	0,303	0,026	0,454	0,030	8,4	6,6	1,1	1,0
ICP-AES				18	0	0,300	0,440	0,304	0,014	0,449	0,025	4,7	5,5	1,3	-0,2
EDTA				3	2			0,250		0,350				-16,7	-22,2
Ion chromatography				32	5	0,310	0,460	0,307	0,028	0,447	0,036	9,3	8,1	2,2	-0,7
ICP-MS				2	1			0,292		0,407				-2,7	-9,6
Cap. Electrophoresis				1	0			0,330		0,470				10,0	4,4
Sodium, mg/l	AB	1,75	1,97	66	4	1,75	1,97	1,76	0,11	1,97	0,12	6,4	6,1	0,3	0,2
FAAS				9	2	1,80	2,02	1,73	0,16	1,98	0,16	9,3	8,0	-1,4	0,6
ICP-AES				15	2	1,72	1,94	1,73	0,08	1,96	0,10	4,7	4,9	-0,9	-0,4
AES				7	0	1,69	1,90	1,71	0,11	1,93	0,11	6,6	5,6	-2,5	-2,0
Ion chromatography				33	0	1,75	1,97	1,78	0,11	1,99	0,13	6,1	6,4	1,6	0,8
ICP-MS				1	0			1,72		1,90				-1,7	-3,6
Cap. Electrophoresis				1	0			1,93		2,05				10,3	4,1

Analytical variable and method	Sample pair	True value 1	True value 2	Total number	Labs exclud.	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	0,200	0,300	66	8	0,200	0,300	0,199	0,025	0,303	0,040	12,7	13,2	-0,3	1,1
FAAS				8	2	0,215	0,335	0,211	0,029	0,320	0,032	13,8	9,9	5,4	6,7
ICP-AES				15	0	0,204	0,309	0,204	0,017	0,308	0,049	8,1	15,9	1,8	2,7
AES				7	0	0,201	0,302	0,204	0,019	0,308	0,027	9,3	8,8	2,1	2,6
Ion chromatography				34	5	0,195	0,300	0,194	0,029	0,295	0,039	15,1	13,3	-2,9	-1,6
ICP-MS				1	1			<0,6		<0,6					
Cap. Electrophoresis				1	0			0,190		0,330				-5,0	10,0
Iron, µg/l	CD	1451	280	41	5	1451	280	1447	90	274	27	6,2	9,8	-0,3	-2,2
FAAS				6	2	1439	280	1457	58	275	18	4,0	6,7	0,4	-1,6
GFAAS				3	1			1427		262				-1,7	-6,4
ICP-AES				17	0	1476	284	1465	80	276	28	5,4	10,1	1,0	-1,4
ICP-MS				15	2	1434	269	1422	112	272	28	7,9	10,3	-2,0	-2,7
Manganese, µg/l	CD	1,70	6,04	43	15	1,70	6,04	1,76	0,30	6,28	0,67	17,2	10,7	3,6	3,9
FAAS				4	3			2,40		6,80				41,2	12,6
GFAAS				6	3	1,89	6,87	1,67	0,58	6,49	1,25	34,7	19,3	-2,0	7,4
ICP-AES				17	7	1,75	6,10	1,80	0,33	6,12	0,63	18,5	10,3	6,1	1,3
ICP-MS				16	2	1,64	6,00	1,71	0,15	6,31	0,61	8,9	9,7	0,3	4,5
Cadmium, µg/l	CD	2,00	3,00	44	4	2,00	3,00	1,99	0,20	2,93	0,26	10,1	8,7	-0,7	-2,3
FAAS				2	1			2,10		3,10				5,0	3,3
GFAAS				13	1	1,97	2,80	1,98	0,31	2,84	0,30	15,7	10,6	-1,2	-5,2
ICP-AES				11	1	2,00	3,00	1,96	0,18	2,94	0,32	9,0	10,9	-1,9	-2,0
ICP-MS				17	1	2,01	3,01	2,00	0,12	2,97	0,17	5,9	5,8	-0,2	-1,0
Polarography				1	0			2,03		3,06				1,6	1,9
Lead, µg/l	CD	4,99	6,08	45	6	4,99	6,08	4,93	0,56	5,98	0,80	11,4	13,4	-1,1	-1,7
FAAS				2	2			3,45		6,60				-30,9	8,6
GFAAS				15	1	4,94	5,85	4,85	0,70	5,71	0,98	14,5	17,1	-2,9	-6,1
ICP-AES				10	3	4,90	6,30	4,83	0,78	6,08	1,15	16,1	18,9	-3,2	0,0
ICP-MS				17	0	5,06	6,10	5,07	0,29	6,19	0,36	5,7	5,8	1,5	1,8
Polarography				1	0			4,65		5,47				-6,8	-10,1

Analytical variable and method	Sample pair	True value 1	True value 2	Total number	Labs exclud.	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
Copper, µg/l	CD	0,610	0,720	44	30	0,610	0,720	0,612	0,095	0,724	0,103	15,5	14,3	0,4	0,5
FAAS				3	3			1,200		2,300				96,7	219,4
GFAAS				12	7	0,620	0,760	0,590	0,098	0,754	0,039	16,6	5,2	-3,3	4,7
ICP-AES				10	9			0,440		0,560				-27,9	-22,2
ICP-MS				18	10	0,649	0,670	0,648	0,071	0,725	0,120	11,0	16,6	6,2	0,7
Polarography				1	1			<0,2		<0,2					
Nickel, µg/l	CD	3,14	2,30	41	10	3,14	2,30	3,18	0,43	2,34	0,29	13,6	12,5	1,2	1,6
FAAS				2	2			5,45		6,85				73,6	197,8
GFAAS				11	3	3,42	2,30	3,44	0,49	2,29	0,33	14,3	14,5	9,7	-0,6
ICP-AES				10	3	3,03	2,46	2,98	0,47	2,35	0,42	15,8	17,9	-5,0	2,0
ICP-MS				18	2	3,13	2,35	3,13	0,34	2,36	0,22	10,8	9,3	-0,3	2,5
Zinc, µg/l	CD	3,22	12,94	42	13	3,22	12,94	3,33	0,69	12,94	0,86	20,7	6,7	3,4	0,0
FAAS				6	6			3,50		12,47				8,7	-3,7
GFAAS				3	1			3,85		12,05				19,6	-6,9
ICP-AES				16	3	3,20	12,82	3,28	0,82	12,77	0,81	25,2	6,4	1,7	-1,3
ICP-MS				16	2	3,23	13,25	3,31	0,54	13,22	0,87	16,3	6,6	2,7	2,2
Polarography				1	1			4,86		13,09				51,0	1,2

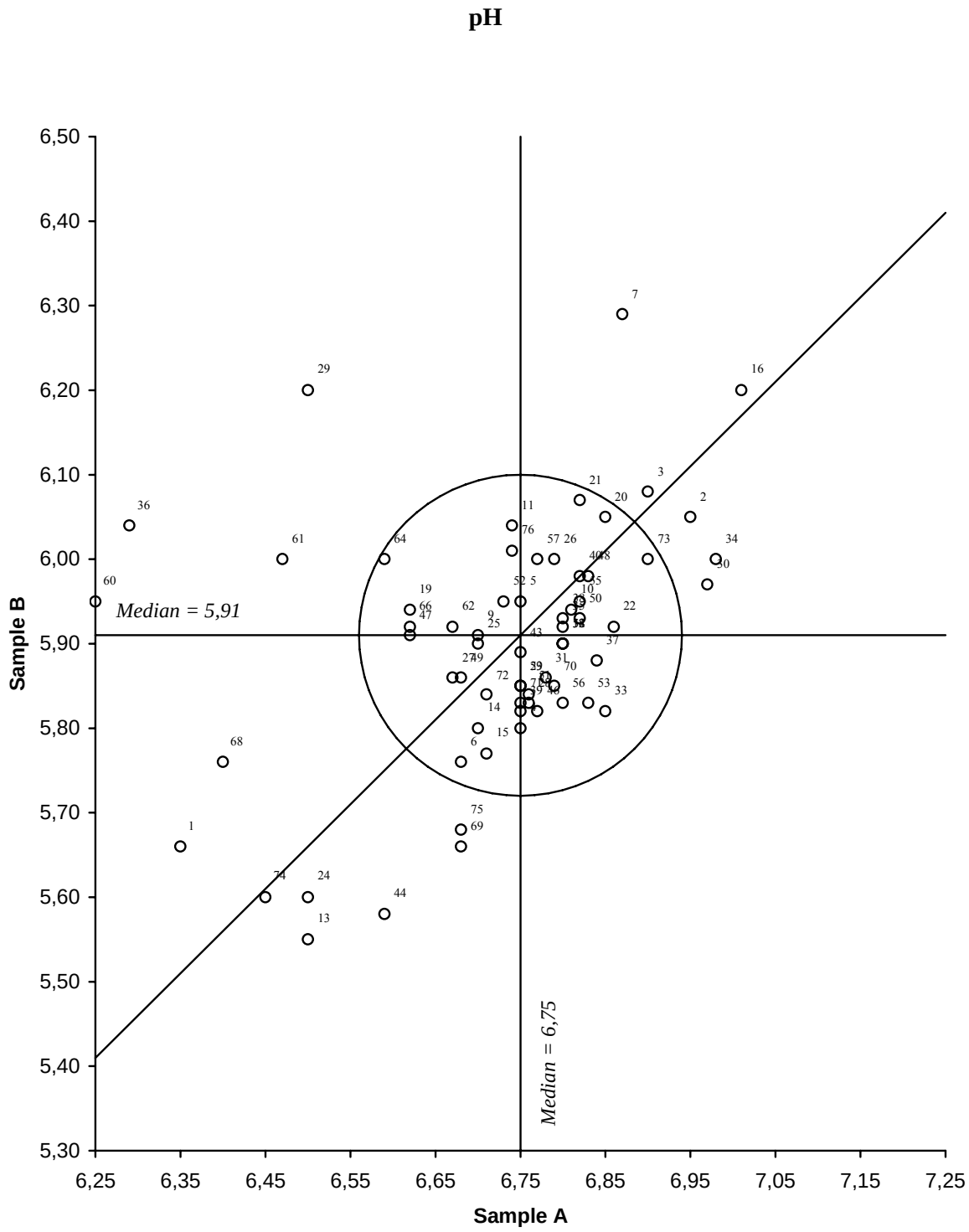

Figure 1. Youden diagramme for pH, sample pair AB
Acceptance limit, given by the circle, is 0,2 pH units

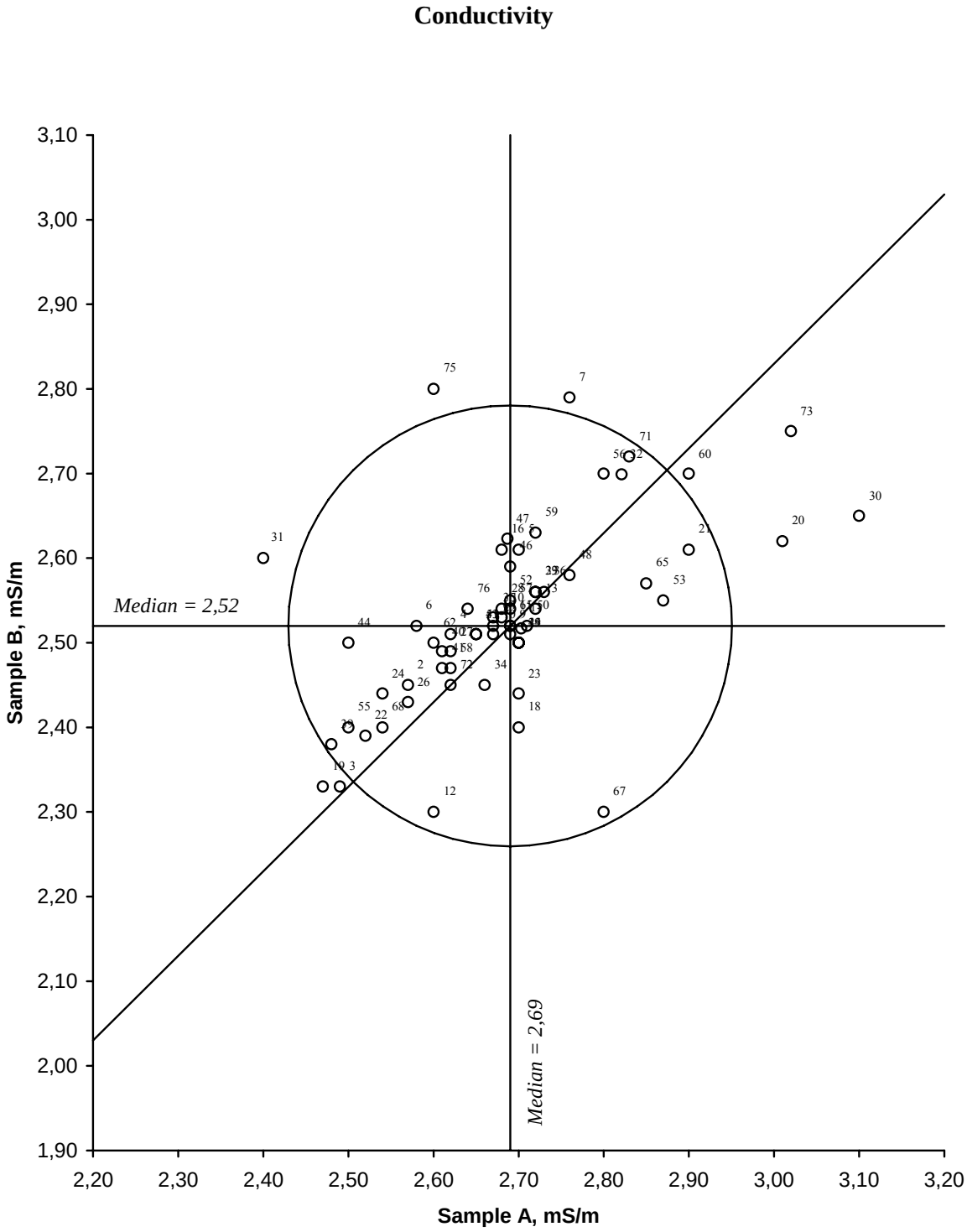

Figure 2. Youden diagramme for conductivity, sample pair AB
Acceptance limit, given by the circle, is 10 %

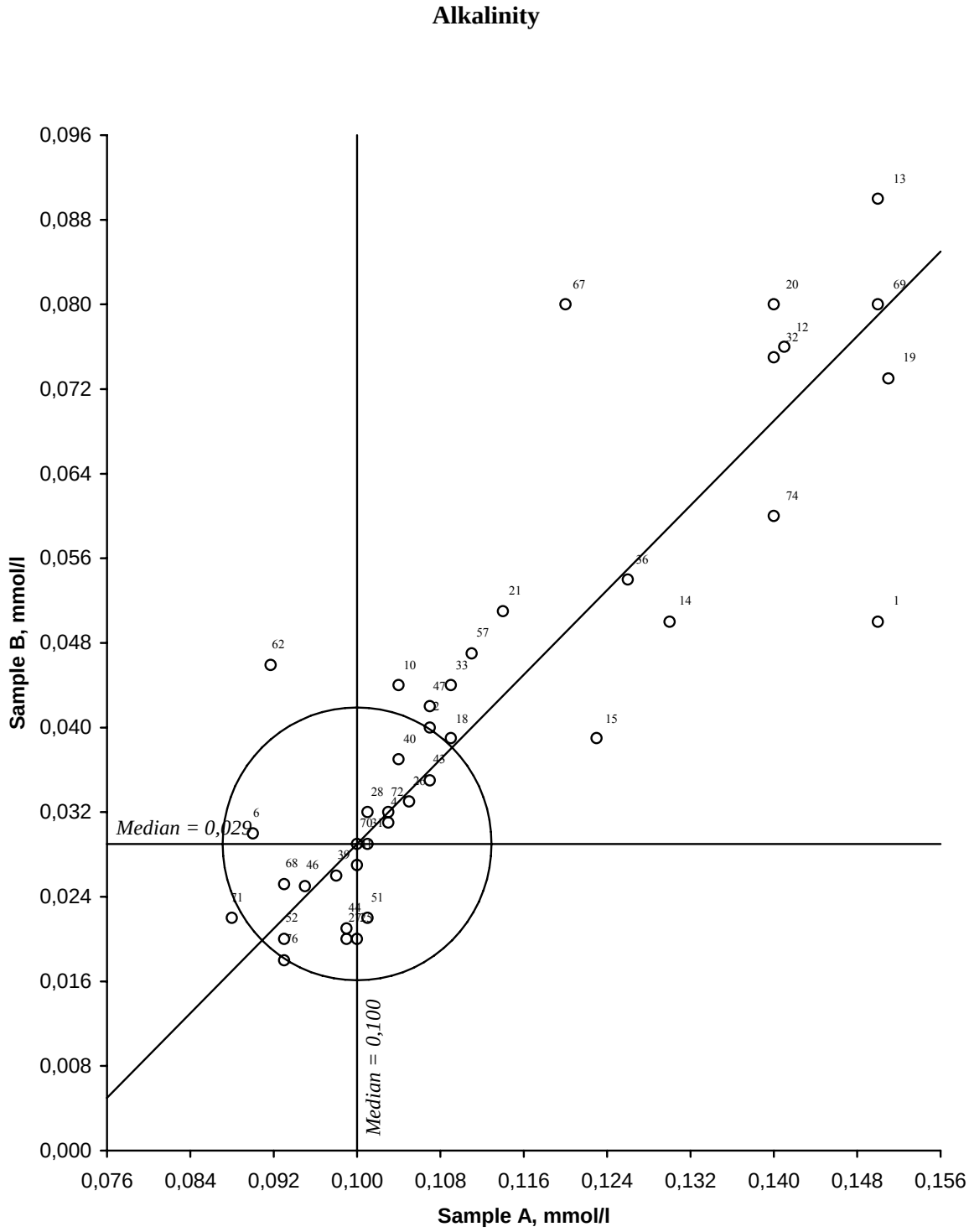

Figure 3. Youden diagramme for alkalinity, sample pair AB
Acceptance limit, given by the circle, is 20 %

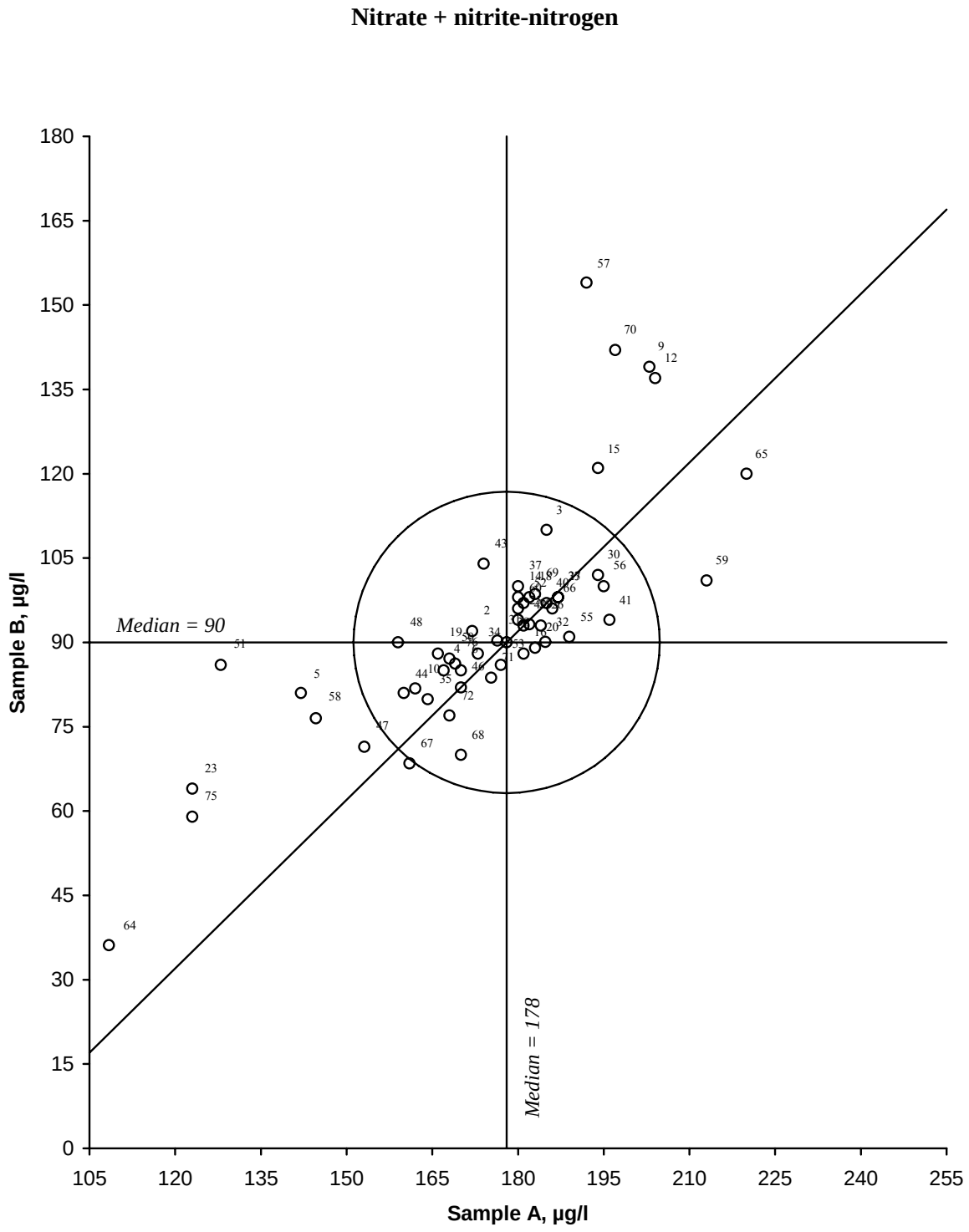

Figure 4. Youden diagramme for nitrate + nitrite-nitrogen, sample pair AB
Acceptance limit, given by the circle, is 20 %

Chloride

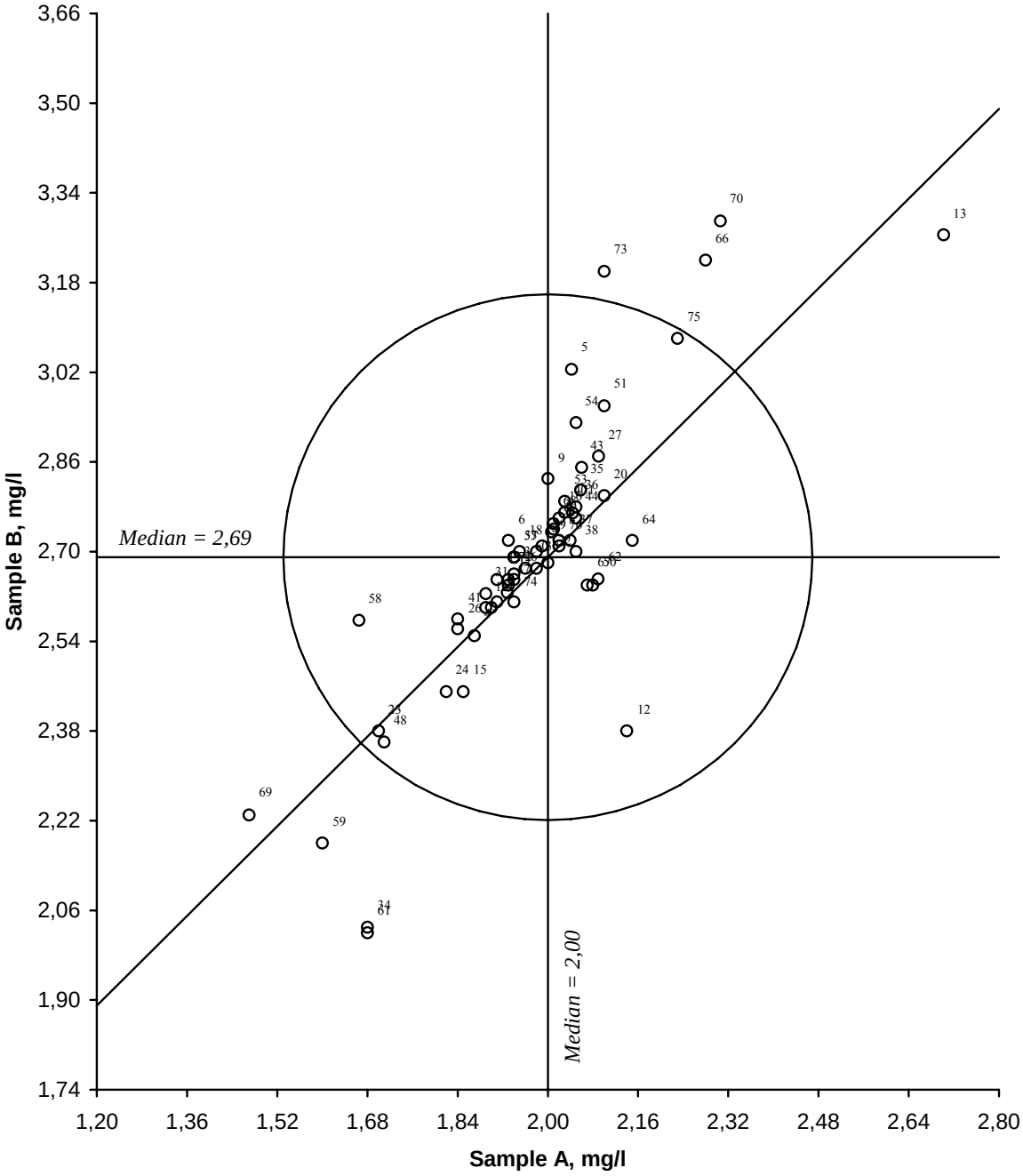

Figure 5. Youden diagramme for chloride, sample pair AB
Acceptance limit, given by the circle, is 20 %

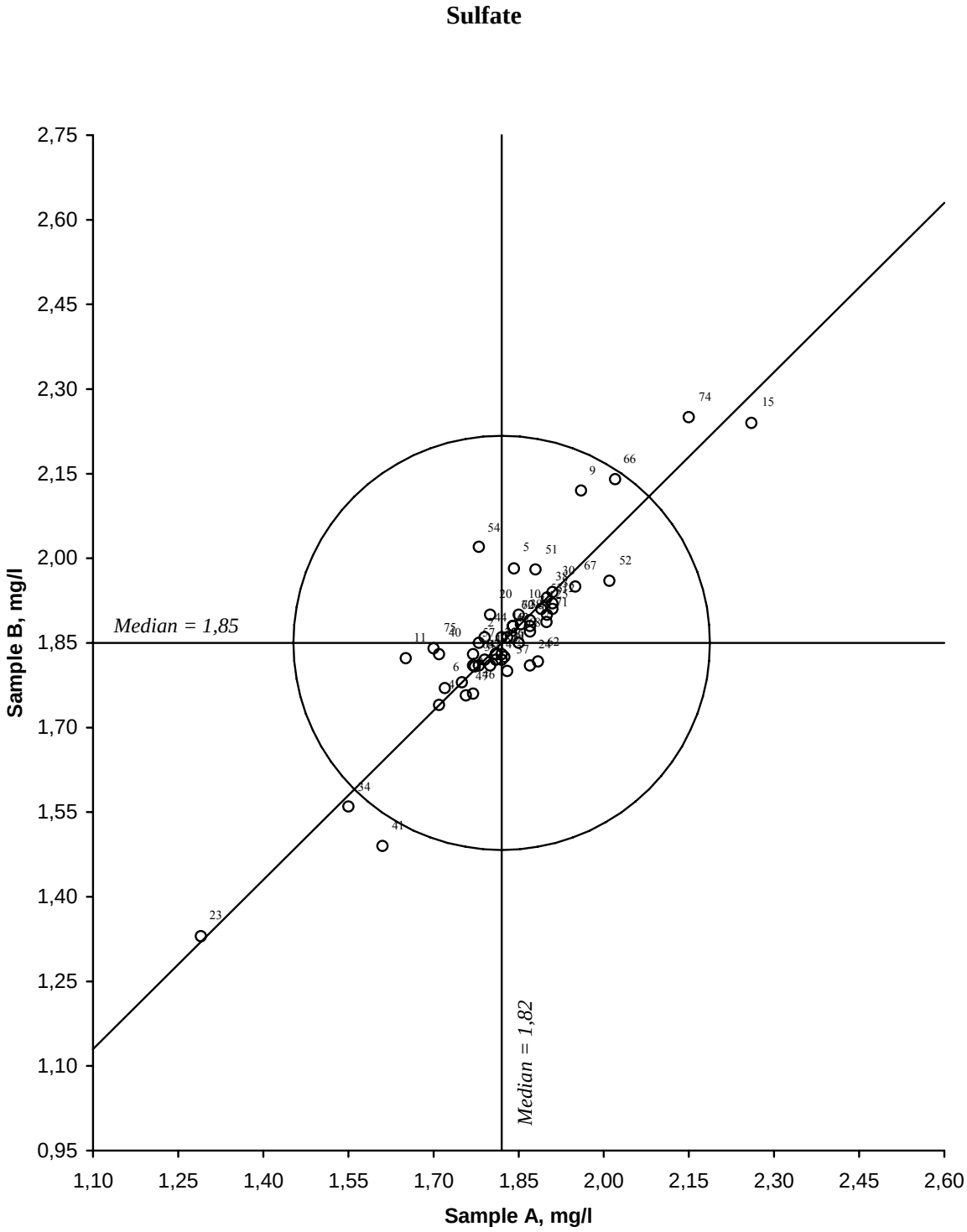

Figure 6. Youden diagramme for sulfate, sample pair AB
Acceptance limit, given by the circle, is 20 %

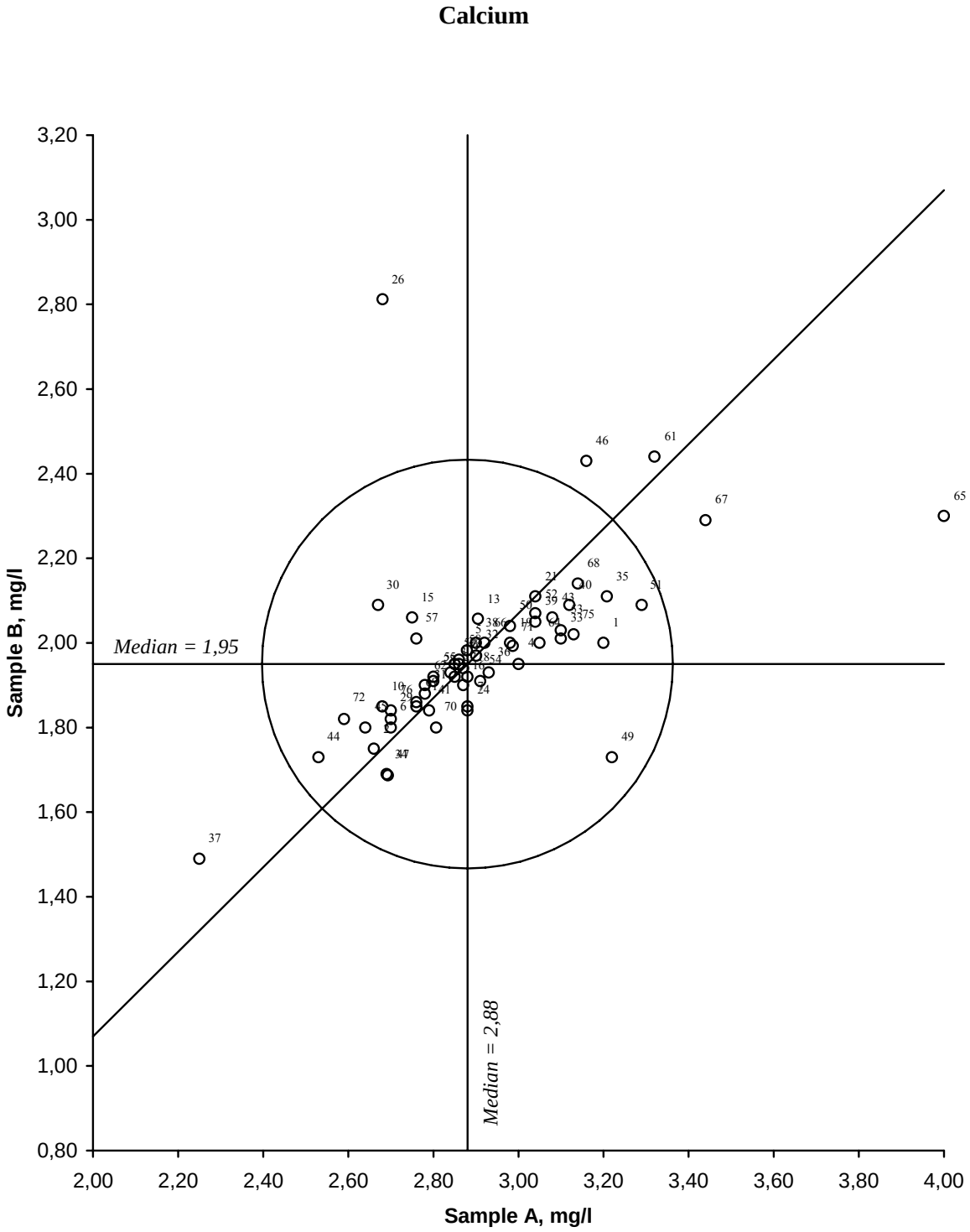

Figure 7. Youden diagramme for calcium, sample pair AB
Acceptance limit, given by the circle, is 20 %

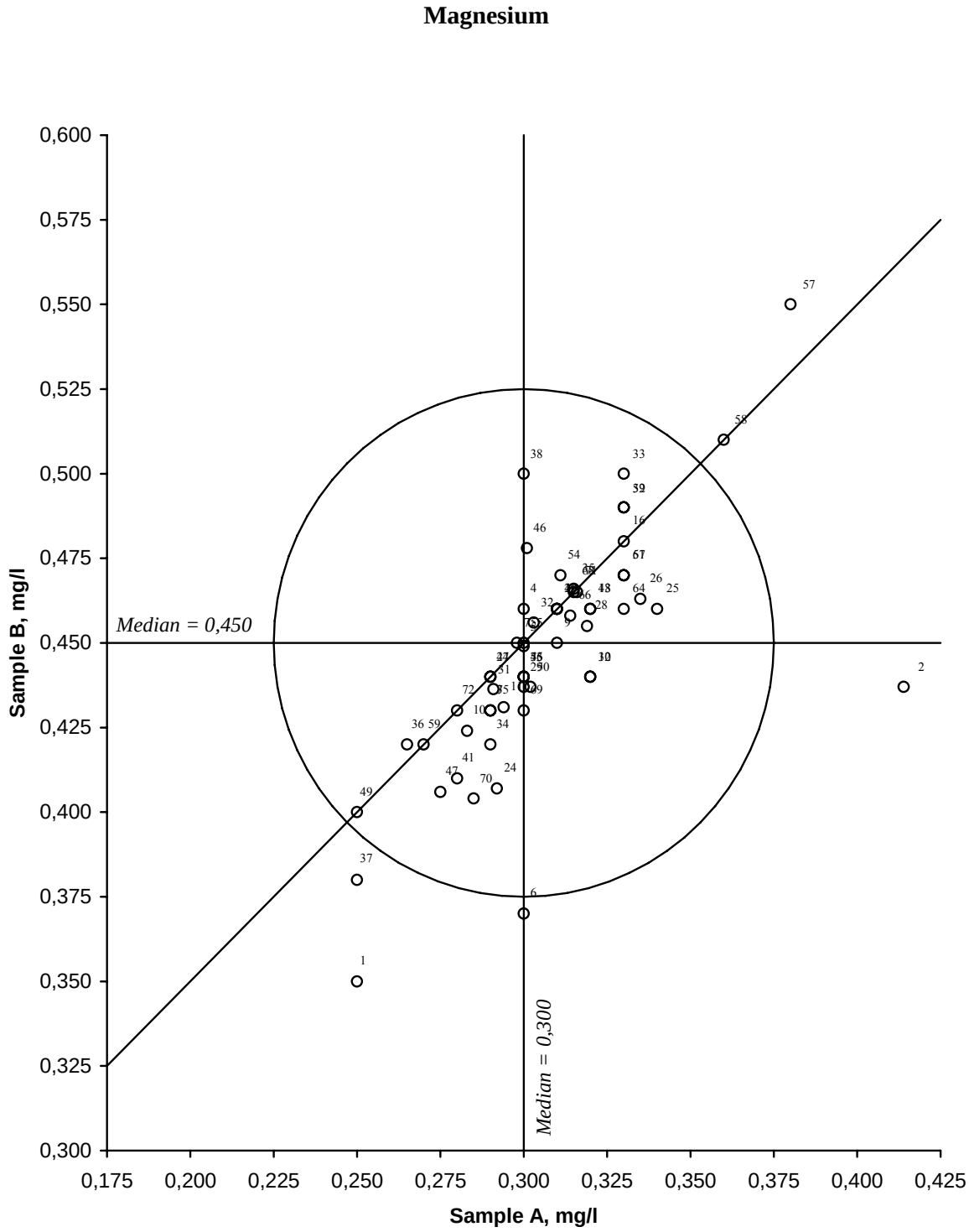

Figure 8. Youden diagramme for magnesium, sample pair AB
Acceptance limit, given by the circle, is 20 %

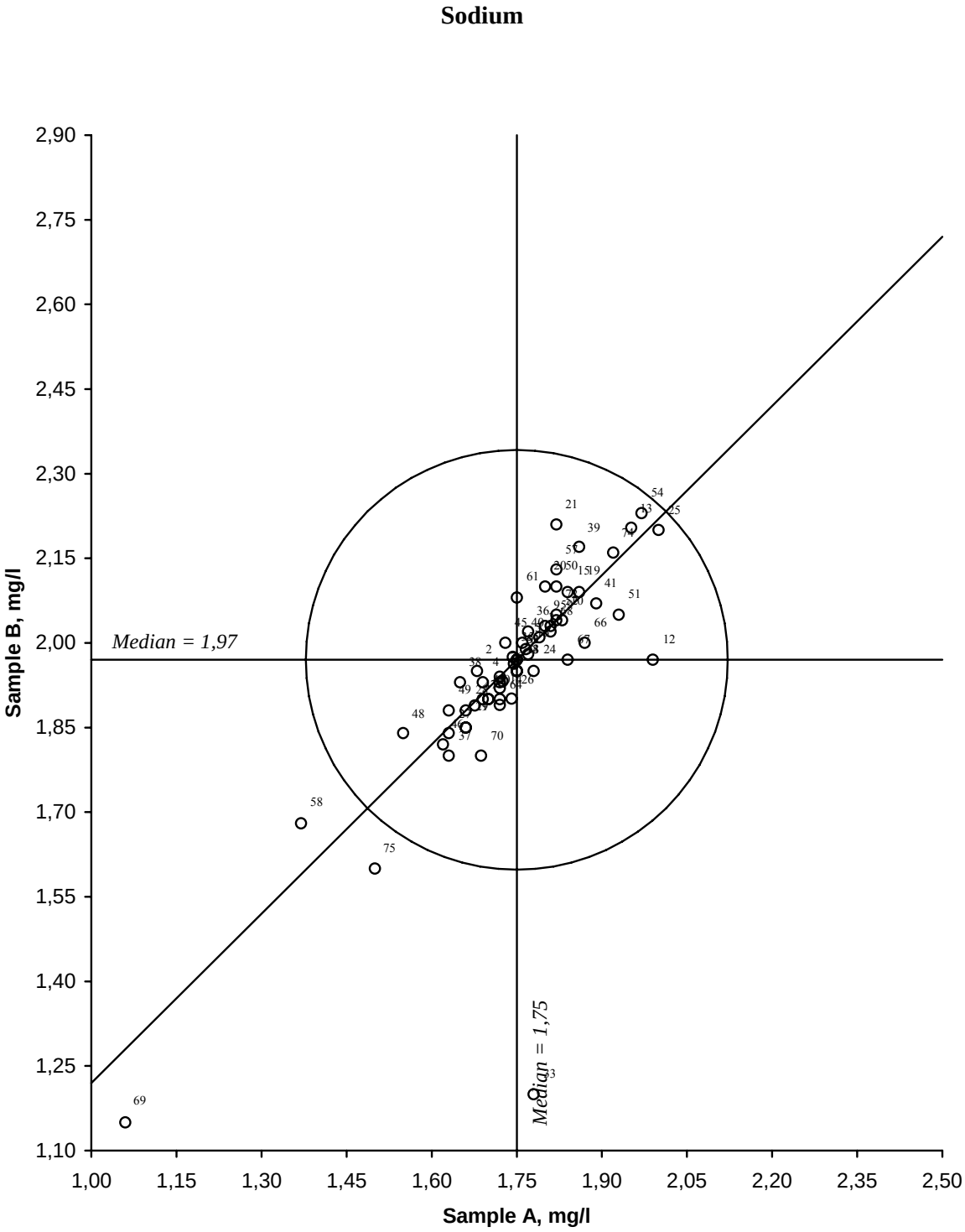

Figure 9. Youden diagram for sodium, sample pair AB
Acceptance limit, given by the circle, is 20 %

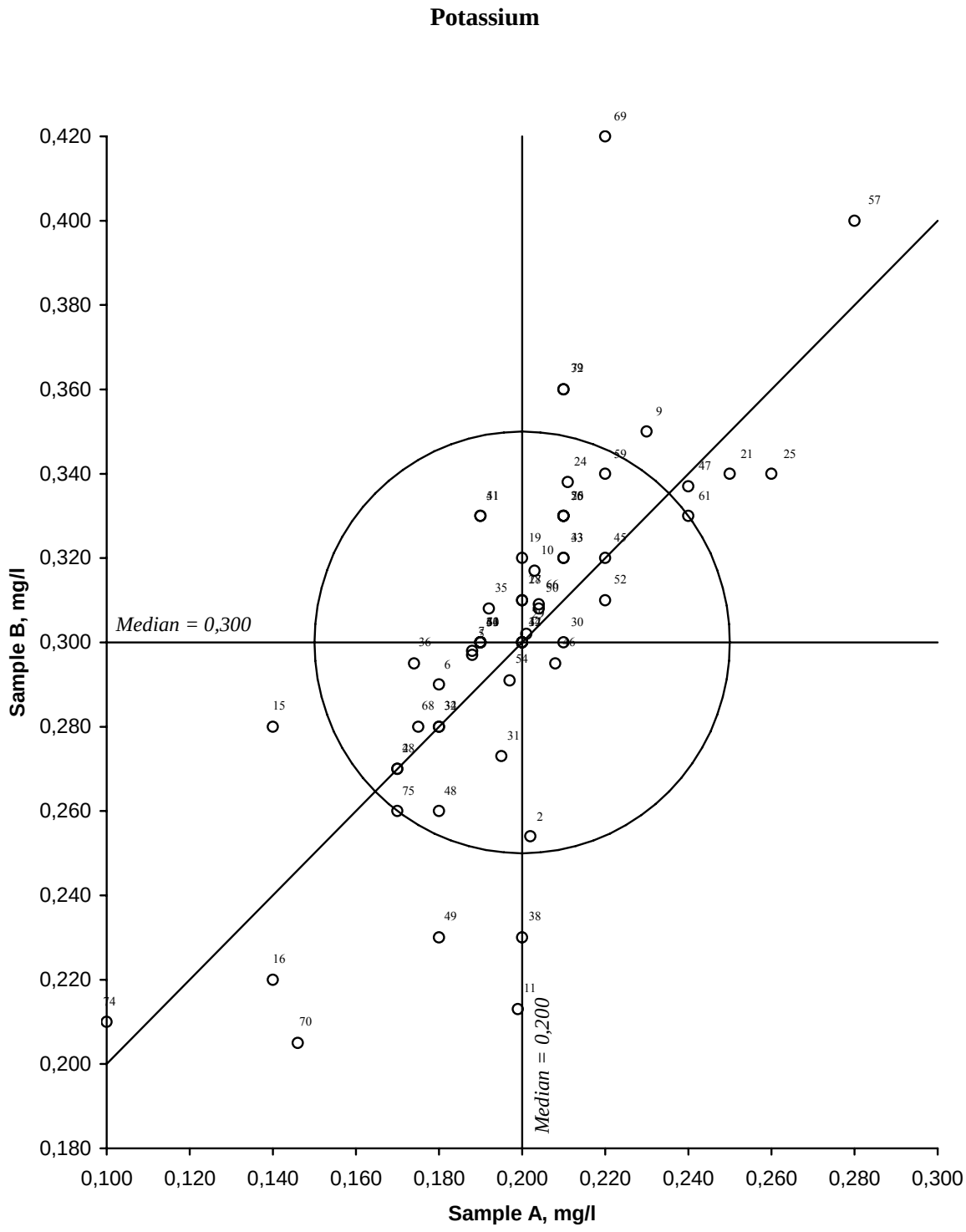

Figure 10. Youden diagramme for potassium, sample pair AB
Acceptance limit, given by the circle, is 20 %

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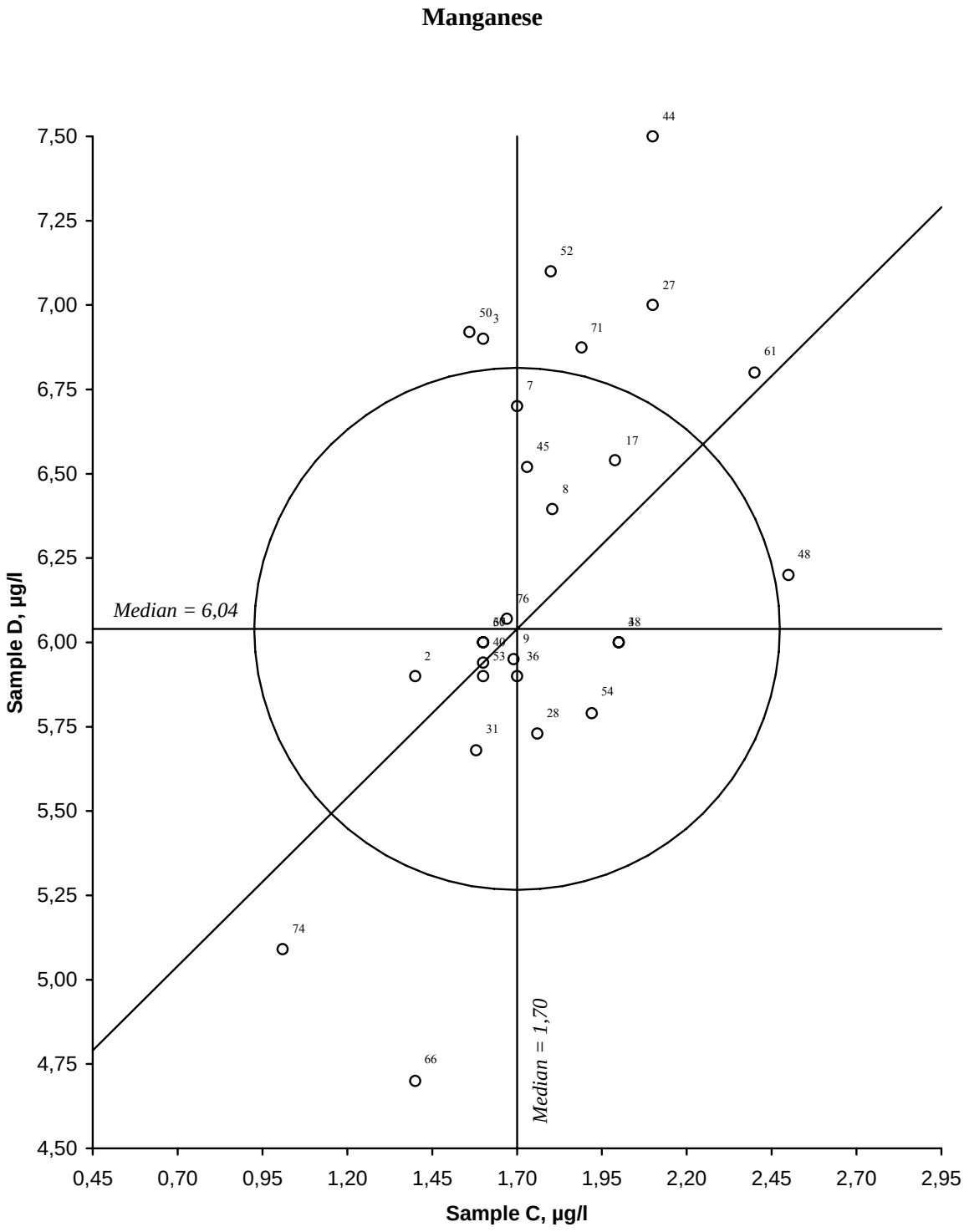

Figure 12. Youden diagramme for manganese, sample pair CD
Acceptance limit, given by the circle, is 20 %

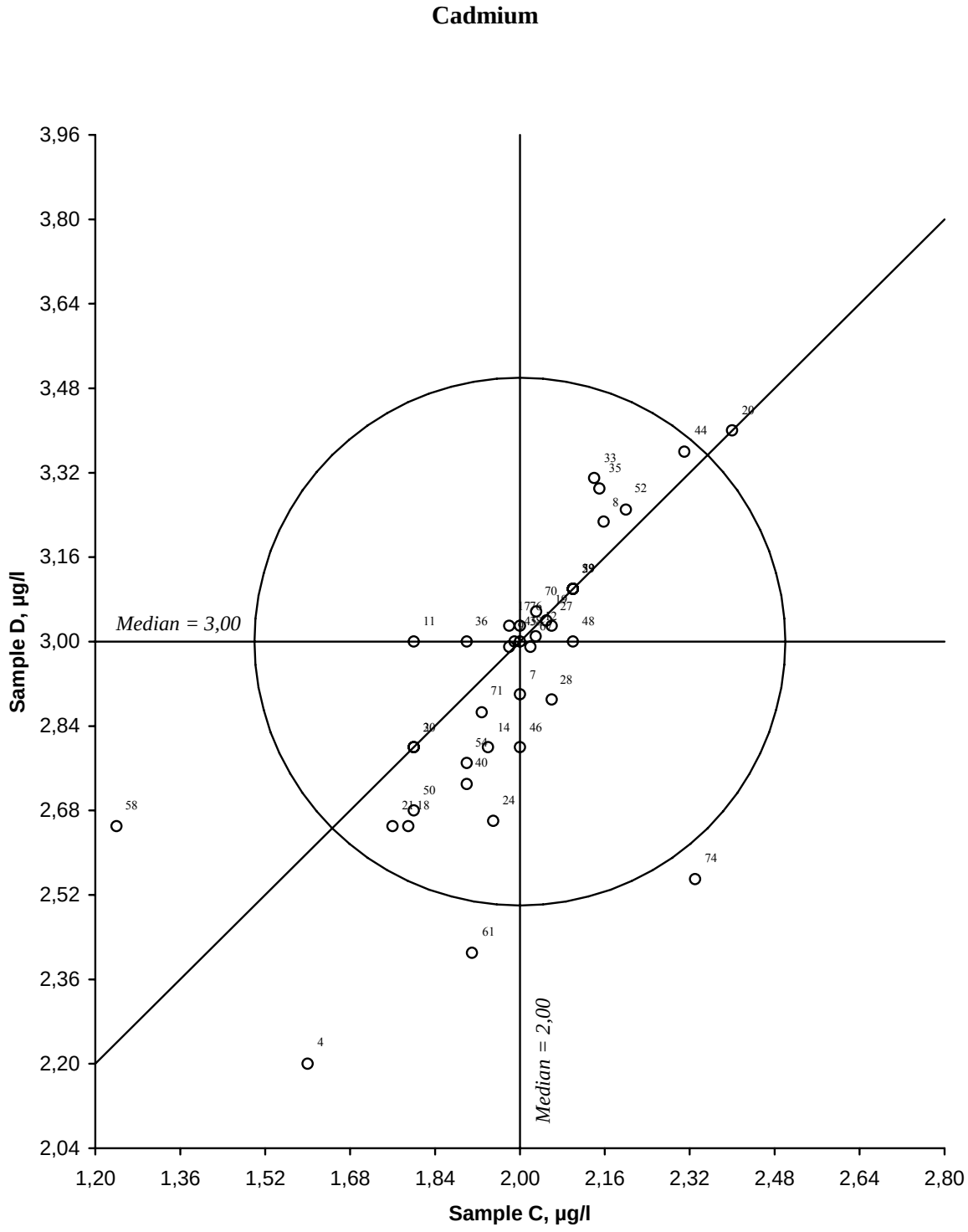

Figure 13. Youden diagramme for cadmium, sample pair CD
Acceptance limit, given by the circle, is 20 %

Lead

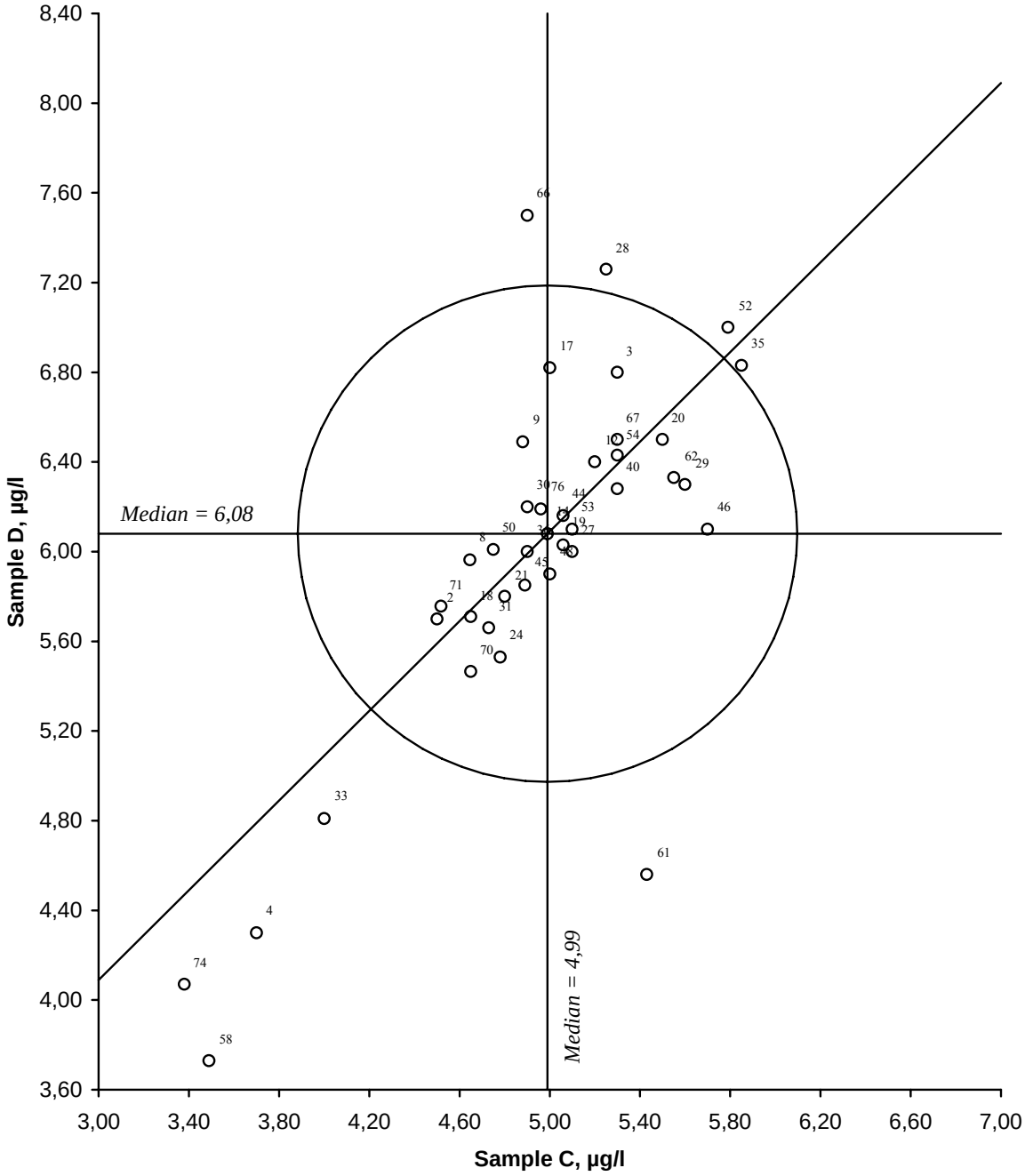

Figure 14. Youden diagramme for lead, sample pair CD
Acceptance limit, given by the circle, is 20 %

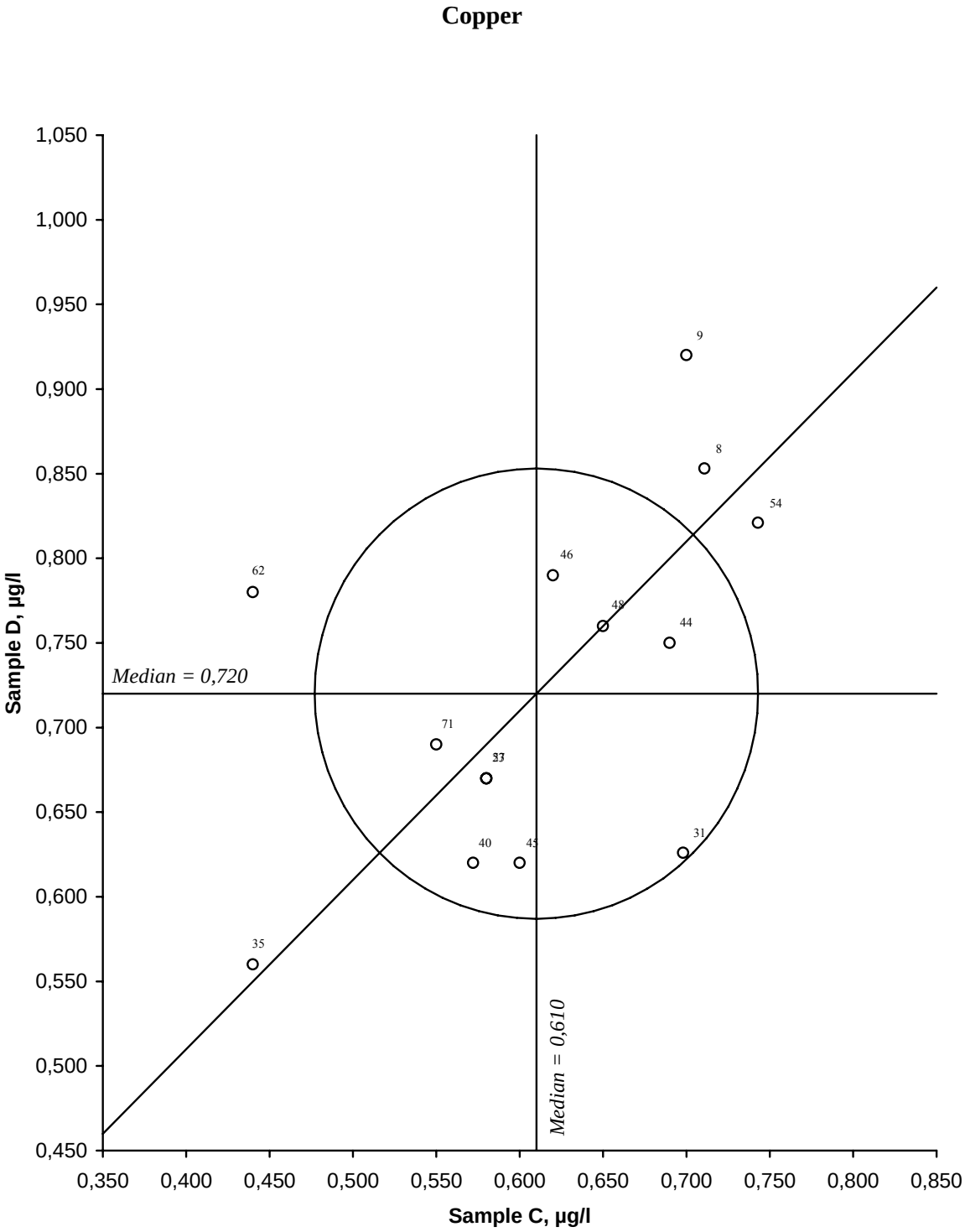

Figure 15. Youden diagramme for copper, sample pair CD
Acceptance limit, given by the circle, is 20 %

Nickel

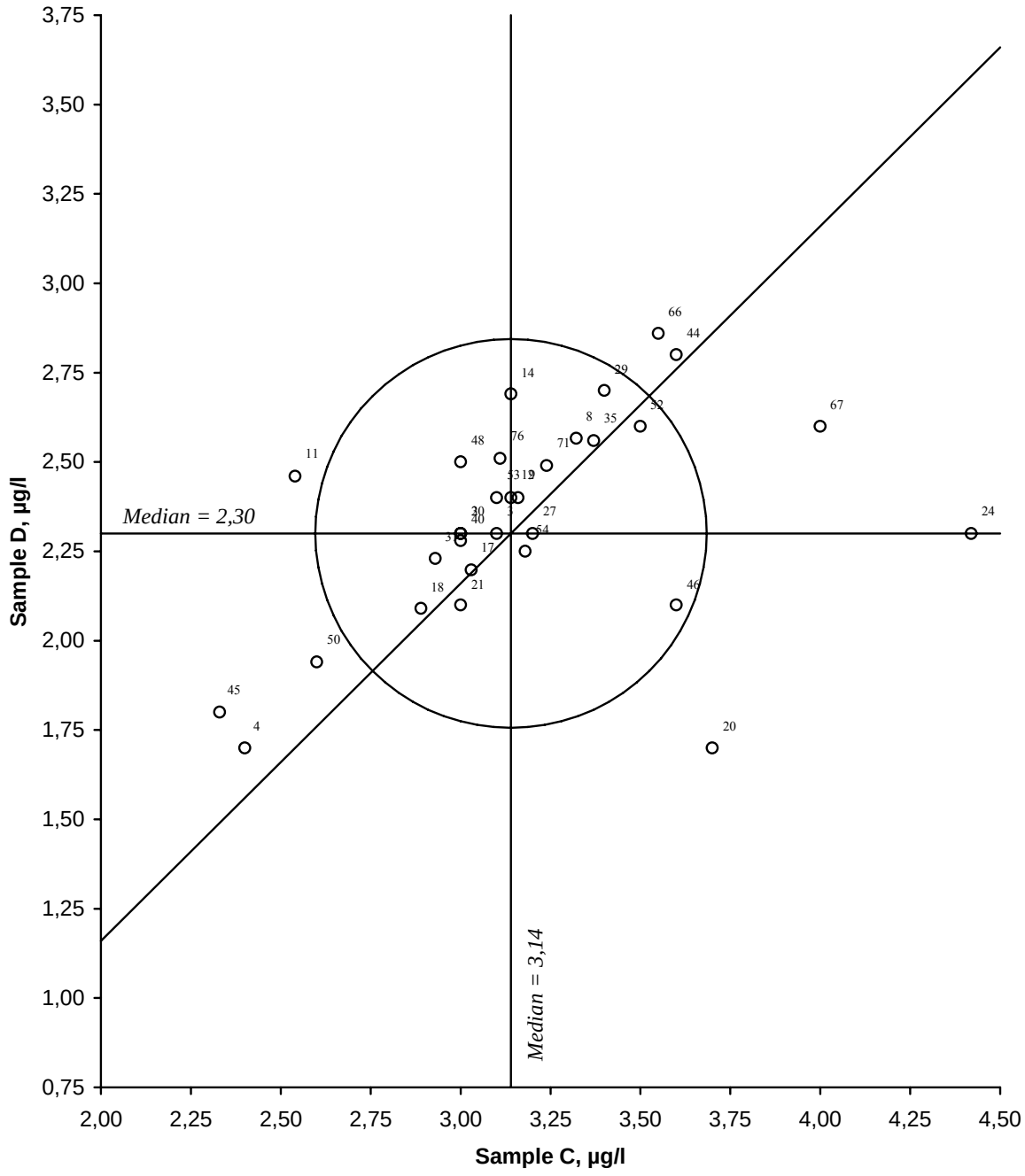

Figure 16. Youden diagramme for nickel, sample pair CD
Acceptance limit, given by the circle, is 20 %

Zinc

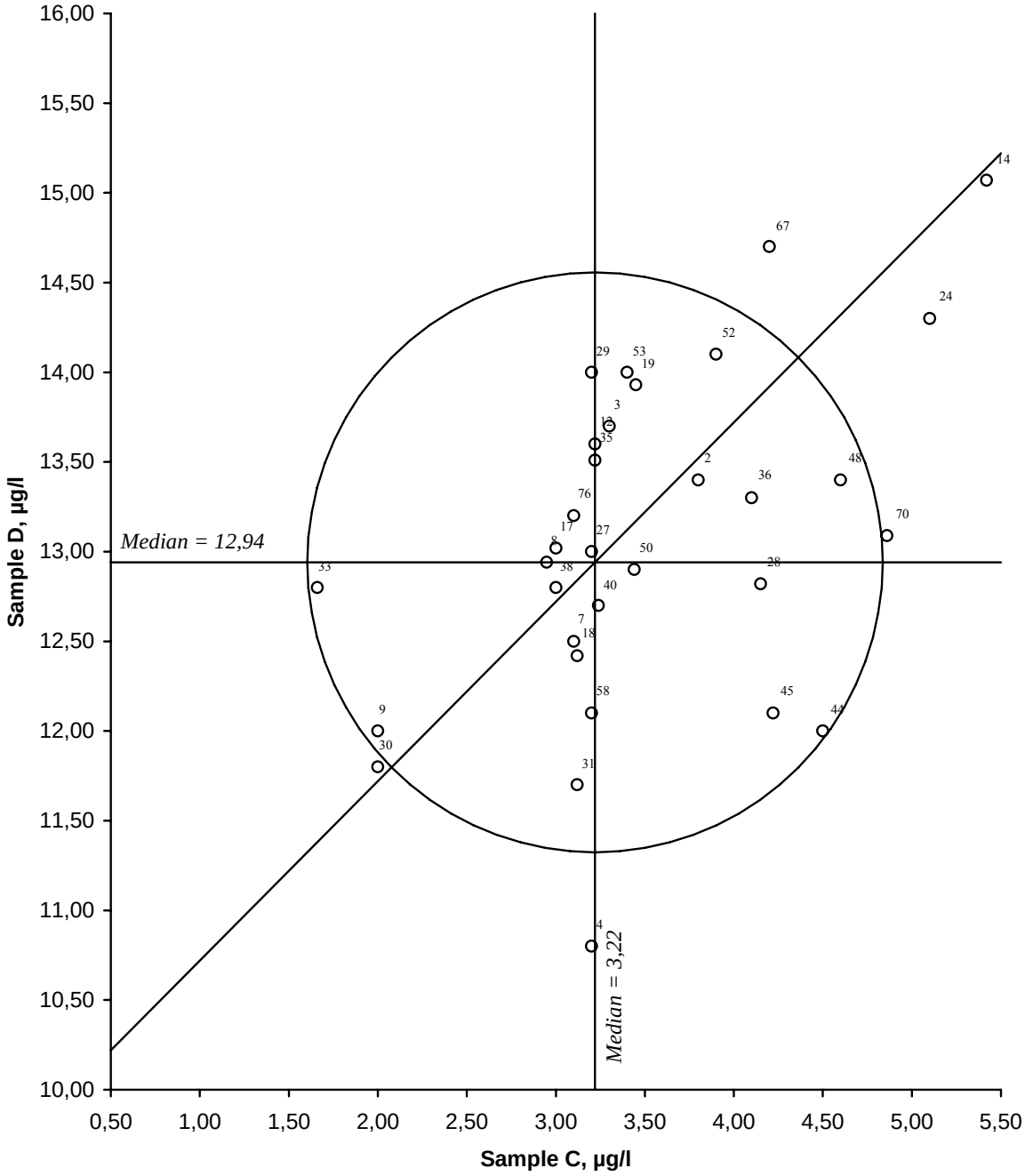

Figure 17. Youden diagramme for zinc, sample pair CD
Acceptance limit, given by the circle, is 20 %

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 0822 is presented, based on the target accuracy (except for pH and conductivity), where the number and percentage of acceptable results are given. 69 % 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, with the given number of digits, are printed. As can be observed, 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 far less than 50 % of the result pairs are found within these accuracy limits. However, we have chosen to extend the acceptance limit to ± 0,2 pH units. Even with this wider acceptance limit only 68 % 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 81 % (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.

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 extremely low, only 35 %, and the possible explanaltion for this result is the very low concentration in the sample B.

Table 2. Evaluation of the results of intercomparison 0721. N is the number of result pairs reported, and n is the number of acceptable results within the given target accuracy.

Parameter and unit	Sample pair	True value 1	True value 2	Accept. limit %	Number of pairs N	Number of pairs n	% acceptable results for intercomparison **0822**	0721	0620	0519
pH	AB	6,75	5,91	3	71	48	**68**	51	74	63
Conductivity, mS/m	AB	2,69	2,52	10	68	55	**81**	80	71	81
Alkalinity, mmol/l	AB	0,100	0,029	20	51	18	**35**	67	63	63
Nitrate-nitrogen, µg/l	AB	178	90	20	64	41	**64**	63	81	82
Chloride, mg/l	AB	2,00	2,69	20	65	55	**85**	79	82	86
Sulfate, mg/l	AB	1,82	1,85	20	61	51	**84**	81	89	81
Calcium, mg/l	AB	2,88	1,95	20	66	56	**85**	86	77	79
Magnesium, mg/l	AB	0,30	0,45	20	67	52	**78**	77	70	69
Sodium, mg/l	AB	1,75	1,97	20	66	60	**91**	92	88	89
Potassium, mg/l	AB	0,2	0,3	20	66	43	**65**	77	80	73
Iron, µg/l	CD	1451	280	20	41	34	**83**	63	77	57
Manganese, µg/l	CD	1,70	6,04	20	43	17	**40**	70	78	65
Cadmium, µg/l	CD	2,00	3,00	20	44	35	**80**	75	74	18
Lead, µg/l	CD	4,99	6,08	20	45	30	**67**	64	52	8
Copper, µg/l	CD	0,61	0,72	20	44	9	**20**	82	77	63
Nickel, µg/l	CD	3,14	2,3	20	41	22	**54**	62	63	25
Zinc, µg/l	CD	3,22	12,94	20	42	26	**62**	53	61	54
Total					945	652	**69**	(73)	(75)	(67)

For nitrate only 64 % 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.

For the major ions, chloride, sulphate, calcium, magnesium and sodium, the number of acceptable results are high as usual.

Some heavy metals are included in this intercomparison programme. The best results were obtained for iron and cadmium where 83 % and 80 % of the results, respectively, are acceptable. This is considered as acceptable, even if there should be possible to achieve better comparability. 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.

5. Conclusion

74 laboratories submitted results for this intercomparison. The best results were reported for the analytical variables sodium, chloride and calcium, where 91 %, 85 and 85 % of the results, respectively, were acceptable. The worst results were observed for some the heavy metals where the concentrations are rather low, especially copper with only 20 % acceptable results.

In this intecomparison 69 % 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 iron and alkalinity. This should be kept in mind when the samples for the next intercomparison is prepared.

6. Literature

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5. Galloway, J.N., Cosby, B.T., Likens, G.E.: Acid Precipitation: Measurement of pH and Alkalinity. Limnol. Oceanogr. 1979, 24, 1161.

Appendix A.

The participating laboratories

No.	Name of participant	City	Country
1	Centre for Limnology at Estonian University	Tartu County	Estonia
2	Tartu Environmental Reseach	Tartu	Estonia
3	Bayerische Landesamt für Wald und Forstwirtschaft	Freising	Germany
4	CNR IstitutoStudio Ecosistemi	Pallanza	Italy
5	Institute of Environmental Protection	Warsaw	Poland
6	Institute of Hydrobilogy	Budejovice	Czech Republic
7	Finnish Forest Research Institute	Vantaa	Finland
8	Yantai Environmental Monitoring Centre	Yantai	China
9	Bayerische Landesamt für Umwelt	München	Germany
10	Environmental Research and Training Center	Pathumthani	Thailand
11	Institute of Soil Science and Forest Nutrition	Göttingen	Germany
12	Laboratoire d'Ecologie Fonctionale	Castanet	France
13	Laboratory of Water Chemistry	Sosnowiec	Poland
14	Amt der Kärntner Landesregierung	Klagenfurt	Austria
15	Laboratorio Biologico	Laives	Italy
16	University of Florence, Soil solution	Firenze	Italy
17	University of Florence, Lab. Di Microanalisi	Firenze	Italy
18	Centre de Geochimie de la Surface	Strasbourg	France
19	Environmental Agency of the Republic of Slovenia	Ljubljana	Slovenia
20	Estonian Environmental Research Centre	Tallinn	Estonia
21	Czech Geological Survey	Prague	Czech Republic
22	Institute of Environmental Protection	Warsaw	Poland
23	Staatliche Umweltbetriebsgesellschaft	Chemnitz	Germany
24	T.G. Masaryk Water Research Institute	Prague	Czech Republic
25	IVL - Svenska Miljøinstitutet	Gothenburg	Sweden
26	Finnish Forest Research Institute	Rovaniemi	Finland
27	Swedish University of Agricultural Sciences	Uppsala	Sweden
28	Institute for Ecology of Industrial Areas	Katowice	Poland
29	Central Mining Institute	Katowice	Poland
30	Institute of Environmental Engineering	Zabrze	Poland
31	Freshwater Laboratory	Pitlochry	Scotland
32	Ewica Laboratories	Kouvola	Finland
33	Sawyer Environmental Chemistry Lab	Orono	USA
34	Environmental Research Department	Vilnius	Lithuania
35	ISSeP	Wasmes	Belgium
36	Department of Chemistry Malaysia	Selangor	Malaysia
37	Institute of Global Climate and Biology	Moscow	Russia
38	CEH Wallingford	Wallingford	United Kingdom
39	SLU, Skoglig Marklära	Uppsala	Sweden
40	Norwegian Institute for Water Research	Oslo	Norway
41	Northern Water Problems Institute	Petrozavodsk	Russia
42	Institute of Meteorology and Geophysics	Innsbruck	Austria
43	Institut für Ökologie	Innsbruck	Austria

No.	Name of participant	City	Country
44	Institute of North Ecological Problems	Apatity	Russia
45	Institute of North Ecological Problems, ICP lab	Apatity	Russia
46	Environmental Laboratory	Riga	Latvia
47	US EPA Western Ecology Division	Corvallis	USA
48	ZAO "Rossa"	Moscow	Russia
49	National Institute of Biology	Ljubljana	Slovenia
50	Landesamt für Natur, Umwelt und Verbrauchs.	Recklinghausen	Germany
51	CRAM, University of Barcelona	Vielha	Spain
52	Laboratory of Geology and Geography	Helsinki	Finland
53	Umweltbundesamt	Vienna	Austria
54	Laboratorio Integrado de CalidadAmbiental	Pamplona	Spain
55	Freshwater Institute	Winnipeg	Canada
56	Freshwater Institute, ELA Sattelite Lab+B11	Winnipeg	Canada
57	Acid Deposition and Oxidant Research Center	Niigata-shi	Japan
58	Institute of Botany Pasci	Krakow	Poland
59	Institute of Public Health	Kranj	Slovenia
60	Tallin University of Technology	Tallinn	Estonia
61	Geological Survey of Estonia	Tallinn	Estonia
62	Testing Laboratory for Environmental Monitoring	Banten	Indonesia
63	Experimental Station for Water Resource Env.	Bandung	Indonesia
64	Atmosphere Environmental Department	Chongqing	China
65	Laboratory of monitoring of pollution	Astrakhan	Russia
66	"Ecoanalyt" Ecoanalytical Laboratory	Syktyvkar	Russia
67	Environmental Protection Agency Irland	Dublin	Ireland
68	Dorset Environmental Science Centre	Dorset	Canada
69	Aquatische Ecologie en Milieubiologie	Nijmegen	Netherlands
70	Laboratorio SPAAS	Bellinzona	Switzerland
71	Vlaamse Milieumaatschappij	Antwerpen	Belgium
72	Water Research Institute	Brugherio	Italy
73	Virumaa Environmental Research	Johvi	Estonia
74	S.C. Analist Service S.R.L.	Bucharest	Romania
75	CCDR / Alentejo	St. Andre	Portugal
76	Finnish Environment Institute	Helsinki	Finland

Number of participating laboratories from the different countries being represented in intercomparison 0822

Country	Labs	Country	Labs	Country	Labs
Austria	4	Ireland	1	Romania	1
Belgium	2	Italy	5	Russia	7
Canada	3	Japan	1	Slovenia	3
China	2	Latvia	1	Spain	2
Czech Republic	3	Lithuania	1	Sweden	3
Estonia	6	Malaysia	1	Switzerland	1
Finland	5	Netherlands	1	Thailand	1
France	2	Norway	1	United Kingdom	2
Germany	5	Poland	7	USA	2
Indonesia	2	Portugal	1		
				Total	76

Appendix B.

Preparation of samples

The sample solutions were prepared from tap water collected from two locations outside Oslo, Norway, a lake named Mangensjøen and a river called Langlielva. The water was collected in 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 May/June 2008, a few weeks before mailing the samples to the participants. The last sample was analyzed medio August 2008. 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	6,84	0,06	7,44	0,08
Conductivity mS/m	2,87	0,01	6,66	0,02
Alkalinity mmol/l	0,099	0,005	0,338	0,014
Nitrate-nitrogen µg/l	157	3	255	0
Chloride mg/l	1,94	0,08	3,60	0,05
Sulphate mg/l	2,75	0,03	5,72	0,07
Calcium mg/l	3,06	0,06	9,02	0,12
Magnesium mg/l	0,43	0,02	0,73	0,03
Sodium mg/l	1,58	0,05	2,62	0,07
Potassium mg/l	0,27	0,01	0,56	0,00
	Sample C		**Sample D**	
Iron, µg/l	27,7	6,8	117	6
Manganese, µg/l	14,0	1,93	4,99	0,69
Cadmium, µg/l	1,41	0,04	5,97	0,17
Lead, µg/l	6,73	0,26	10,2	0,56
Copper, µg/l	19,8	1,1	20,1	1,4
Nickel, µg/l	6,57	0,35	3,51	0,32
Zinc, µg/l	6,11	1,12	11,20	0,40

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 - 17).

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 - 5.17. 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	
No	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**
1	6,35	5,66			0,15	0,05	100	60
2	6,95	6,05	2,57	2,45	0,107	0,040	172	92
3	6,90	6,08	2,49	2,33			185	110
4	6,75	5,80	2,62	2,51	0,103	0,031	167	85
5	6,75	5,95	2,70	2,61			142	81
6	6,68	5,76	2,58	2,52	0,09	0,03	170	85
7	6,87	6,29	2,76	2,79				
8								
9	6,70	5,91	2,69	2,51			203	139
10	6,81	5,94	2,68	2,53	0,104	0,044	162	81,8
11	6,74	6,04	2,703	2,517			<150	<150
12	9,6	5,9	2,6	2,3	0,141	0,076	204	137
13	6,50	5,55	2,72	2,54	0,15	0,09	293,2	0,0
14	6,7	5,8	2,7	2,5	0,13	0,05	180	98
15	6,71	5,77	2,69	2,52	0,123	0,039	194	121
16	7,01	6,20	2,68	2,61			181	88
17								
18	6,8	5,9	2,70	2,40	0,109	0,039	182	98
19	6,62	5,94	2,47	2,33	0,151	0,073	166	88
20	6,85	6,05	3,01	2,62	0,14	0,08	183	89
21	6,82	6,07	2,90	2,61	0,114	0,051		
22	6,86	5,92	2,52	2,39				
23	6,75	5,85	2,70	2,44	0,166	0,105	123	64
24	6,5	5,6	2,54	2,44	0,164	0,067	680	<500
25	6,7	5,9	2,7	2,5	0,10	0,02	180	94
26	6,79	6,00	2,57	2,43	0,105	0,033	184	93
27	6,67	5,86	2,62	2,49	0,099	0,020	187	98
28	6,76	5,83	2,68	2,54	0,101	0,032		
29	6,50	6,20	2,72	2,56			182	93,2
30	6,97	5,97	3,10	2,65			194	102
31	6,78	5,86	2,4	2,6	0,101	0,029	176,4	90,3
32	6,8	5,9	2,821	2,699	0,140	0,075	184,8	90,1
33	6,85	5,82	2,72	2,56	0,109	0,044	187	98
34	6,98	6,00	2,66	2,45			173	88
35	6,80	5,92	2,67	2,53			164,2	79,9

Lab.	pH		Conductivity, mS/m		Alkalinity, mmol/l		Nitrate-N, µg/l	
No	A	B	A	B	A	B	A	B
36	6,29	6,04	2,73	2,56	0,126	0,054	43,9	23,4
37	6,84	5,88	3,33	3,16			180	100
38	6,80	5,93					178	90
39	6,75	5,82	2,48	2,38	0,098	0,026		
40	6,82	5,98	2,61	2,49	0,104	0,037	185	97
41	6,78	6,85	2,61	2,47	0,100	0,027	196	94
42								
43	6,75	5,89	2,65	2,51	0,107	0,035	174	104
44	6,59	5,58	2,5	2,5	0,099	0,021	160	81
45								
46	6,77	5,82	2,69	2,59	0,095	0,025	170	82
47	6,62	5,91	2,687	2,623	0,107	0,042	153,1	71,4
48	6,83	5,98	2,76	2,58	0,11	<0,1	159	90
49	6,68	5,86	2,7	2,5	0,118	0,486	181	93
50	6,82	5,93	2,71	2,52			168	87,1
51	6,76	5,84	2,65	2,51	0,101	0,022	128	86
52	6,73	5,95	2,69	2,55	0,093	0,02	181	97
53	6,83	5,83	2,87	2,55	0,155	0,105	177	86
54	6,8	5,9	3,04	3,34			493	459
55	6,82	5,95	2,5	2,4			189	91
56	6,80	5,83	2,8	2,7			195	100
57	6,77	6,00	2,69	2,54	0,111	0,047	192	154
58	5,89	4,98	2,62	2,47			144,6	76,5
59	6,75	5,85	2,72	2,63	0,16	0,08	213	101
60	6,25	5,95	2,9	2,7			180	96
61	6,47	6,00	2,69	2,52	0,22	0,13	225	253
62	6,67	5,92	2,6	2,5	0,0917	0,0459		
63								
64	6,59	6,00	2,67	2,52	0,166	0,097	108,4	36,1
65	5,97	6,82	2,85	2,57	0,23	0,06	220	120
66	6,62	5,92	2,14	2,33	0,164	0,084	186	96
67	6,64	6,59	2,8	2,3	0,120	0,080	161	68,5
68	6,40	5,76	2,54	2,40	0,093	0,0252	170	70
69	6,68	5,66			0,15	0,08	183	98,6
70	6,79	5,85	2,67	2,51	0,100	0,029	197	142
71	6,75	5,83	2,83	2,72	0,088	0,022	175,3	83,7
72	6,71	5,84	2,62	2,45	0,103	0,032	168	77
73	6,90	6,00	3,02	2,75				
74	6,45	5,60	3,33	2,62	0,14	0,06	180	200
75	6,68	5,68	2,6	2,8	0,39	0,26	123	59
76	6,74	6,01	2,64	2,54	0,093	0,018	169	86,2

Lab.	Chloride, mg/l		Sulfate, mg/l		Calcium, mg/l		Magnesium, mg/l	
No	A	B	A	B	A	B	A	B
1	2,9	4,1			3,2	2,0	0,25	0,35
2	1,91	2,61	1,78	1,85	2,66	1,75	0,414	0,437
3	1,94	2,66	1,91	1,92	2,84	1,93	0,29	0,43
4	1,87	2,55	1,71	1,74	3,00	1,95	0,30	0,46
5	2,042	3,025	1,842	1,982	2,879	1,982	0,300	0,449
6	1,93	2,72	1,72	1,77	2,7	1,8	0,30	0,37
7					2,88	1,85	0,298	0,450
8								
9	2,00	2,83	1,96	2,12	2,87	1,94	0,31	0,45
10	2,02	2,76	1,85	1,90	2,68	1,85	0,283	0,424
11	1,93	2,64	1,651	1,823	2,76	1,85	0,294	0,431
12	2,14	2,38	1,91	1,91	2,86	1,95	0,32	0,44
13	2,702	3,265	3,924	2,873	2,905	2,057	0,231	0,287
14	1,98	2,70	1,80	1,81	2,82	<2	<0,5	<0,5
15	1,85	2,45	2,26	2,24	2,75	2,06	0,14	0,34
16	1,89	2,60	1,82	1,86	2,87	1,90	0,33	0,48
17								
18	1,95	2,70	1,82	1,82	2,88	1,92	0,32	0,46
19	1,91	2,65	1,75	1,78	2,98	2,00	0,31	0,46
20	2,1	2,8	1,8	1,9	5,0	3,4	0,40	0,63
21					3,04	2,11	0,31	0,46
22								
23	1,70	2,38	1,29	1,33				
24	1,82	2,45	1,87	1,81	2,88	1,84	0,292	0,407
25	1,9	2,6	1,9	1,9			0,34	0,46
26	1,840	2,562	0,637	0,674	2,681	2,812	0,335	0,463
27	2,09	2,87	1,87	1,87	2,85	1,92	0,29	0,44
28					2,80	1,91	0,319	0,455
29	1,99	2,71	1,81	1,83	2,70	1,82	0,30	0,437
30	1,98	2,67	1,91	1,94	2,67	2,09	0,32	0,44
31	1,89	2,625	1,825	1,825	2,78	1,88	0,2909	0,4363
32	2,00	2,68	1,78	1,81	2,901	1,970	0,303	0,456
33	1,94	2,69	1,81	1,83	3,10	2,01	0,33	0,50
34	1,68	2,03	1,55	1,56	2,69	1,69	0,29	0,42
35	2,058	2,810	1,773	1,808	3,208	2,110	0,315	0,466
36	2,05	2,78	1,82	1,83	2,93	1,93	0,265	0,420
37	2,04	2,72	1,83	1,80	2,25	1,49	0,25	0,38
38	2,05	2,70	1,90	1,93	2,90	2,00	0,30	0,50
39	2,007	2,735	1,854	1,883	3,04	2,05	0,33	0,49
40	2,03	2,77	1,71	1,83	3,12	2,09	0,31	0,46

Lab.	Chloride, mg/l		Sulfate, mg/l		Calcium, mg/l		Magnesium, mg/l	
No	A	B	A	B	A	B	A	B
41	1,84	2,58	1,61	1,49	2,79	1,84	0,28	0,41
42								
43	2,06	2,85	1,83	1,86	3,08	2,06	0,32	0,46
44	2,05	2,76	1,79	1,86	2,53	1,73	0,29	0,44
45					2,64	1,80	0,30	0,44
46	1,94	2,65	1,77	1,76	3,16	2,43	0,301	0,478
47	1,928	2,627	1,757	1,757	2,693	1,687	0,275	0,406
48	1,71	2,36	1,79	1,82	1,50	0,95	0,24	0,26
49	2,01	2,74	1,81	1,83	3,22	1,73	0,25	0,40
50	2,08	2,64	1,81	1,82	2,98	2,04	0,302	0,437
51	2,10	2,96	1,88	1,98	3,29	2,09	0,33	0,47
52	2,02	2,72	2,01	1,96	3,04	2,07	0,33	0,49
53	2,03	2,79	1,89	1,91	3,10	2,03	0,30	0,44
54	2,05	2,93	1,78	2,02	2,91	1,91	0,311	0,470
55					2,80	1,92	0,30	0,45
56								
57	1,94	2,69	1,77	1,83	2,76	2,01	0,38	0,55
58	1,665	2,577	0,785	0,870	2,860	1,960	0,36	0,51
59	1,60	2,18	1,87	1,88	2,85	1,95	0,27	0,42
60	1,96	2,67	1,84	1,88				
61	1,68	2,02			3,32	2,44	0	1,30
62	2,089	2,651	1,884	1,817	2,78	1,90	0,619	0,918
63								
64	2,15	2,72	1,77	1,81	3,05	2,00	0,33	0,46
65	3,3	2,5	5,2	13,0	4,0	2,3	1,6	1,7
66	2,28	3,22	2,02	2,14	2,92	2,00	0,314	0,458
67	2,07	2,64	1,95	1,95	3,44	2,29	0,33	0,47
68	2,01	2,75	1,85	1,85	3,14	2,14	0,315	0,465
69	1,47	2,23			2,76	1,86	0,30	0,43
70	2,306	3,290	2,195	2,950	2,807	1,800	0,285	0,404
71	2,044	2,769	1,899	1,887	2,987	1,993	0,316	0,465
72	1,93	2,65	1,84	1,88	2,59	1,82	0,28	0,43
73	2,1	3,2						
74	1,94	2,61	2,15	2,25	4,86	3,52	0,79	0,50
75	2,23	3,08	1,70	1,84	3,13	2,02	0,29	0,43
76	2,02	2,71	1,87	1,89	2,70	1,84	0,30	0,44

Lab.	Sodium, mg/l		Potassium, mg/l		Iron, µg/l		Manganese, µg/l	
No	A	B	A	B	C	D	C	D
1								
2	1,68	1,95	0,202	0,254	1470	238	1,4	5,9
3	1,79	2,01	0,19	0,30	1356	243	1,6	6,9
4	1,69	1,93	0,17	0,27	1490	291	2,0	6,0
5	1,766	1,989	0,188	0,297				
6	1,7	1,9	0,18	0,29				
7	1,72	1,92	0,188	0,298	1450	281	1,7	6,7
8					1434	314,1	1,804	6,395
9	1,80	2,03	0,23	0,35	1455	271	1,69	5,95
10	1,83	2,04	0,203	0,317				
11	1,66	1,85	0,199	0,213	1484	283	<10	<10
12	1,99	1,97	0,20	0,30	1341	272	1,61	7,70
13	1,952	2,204	0,00	0,517	1427	252	3,9	6,6
14	1,72	1,9	<0,6	<0,6	1439	259	<2	5,81
15	1,84	2,09	0,14	0,28				
16	1,77	1,98	0,14	0,22				
17							1,989	6,540
18	1,75	1,95	0,20	0,31	930	181	1,54	9,25
19	1,86	2,09	0,20	0,32				
20	1,8	2,1	0,21	0,33	1540	287	<20	<20
21	1,82	2,21	0,25	0,34	1410	270		
22								
23								
24	1,78	1,95	0,211	0,338	1400	295	<5	6,05
25	2,0	2,2	0,26	0,34				
26	1,74	1,90	<0,06	0,180				
27	1,63	1,84	0,20	0,31	1500	280	2,1	7,0
28	1,66	1,88	0,170	0,270	1249	252,4	1,76	5,73
29	1,66	1,85	0,201	0,302	1510	290	1,8	9,0
30	1,70	1,90	0,21	0,30	1574	327	1,6	6,0
31	1,725	1,932	0,195	0,273	1503	256	1,58	5,68
32	1,75	1,97	0,18	0,28				
33	1,78	1,20	0,21	0,32	1590	295	<10	<10
34	1,75	1,95	0,18	0,28				
35	1,743	1,975	0,192	0,308	1446,4	296,8	3,48	6,86
36	1,77	2,02	0,174	0,295	1168	225	1,7	5,9
37	1,63	1,80	0,20	0,30				
38	1,65	1,93	0,20	0,23	1476	280	2,0	6,0
39	1,86	2,17	0,21	0,36				
40	1,76	2,00	0,19	0,30	1360	260	1,60	5,94

Lab.	Sodium, mg/l		Potassium, mg/l		Iron, µg/l		Manganese, µg/l	
No	A	B	A	B	C	D	C	D
41	1,89	2,07	0,19	0,33				
42								
43	1,75	1,95	0,21	0,32				
44	1,69	1,90	0,20	0,30	1370	293	2,1	7,5
45	1,73	2,00	0,22	0,32	1520	284	1,73	6,52
46	1,62	1,82	0,208	0,295	1452	290	5,6	1,4
47	1,676	1,889	0,240	0,337				
48	1,55	1,84	0,18	0,26	1550	300	2,5	6,2
49	1,63	1,88	0,18	0,23				
50	1,82	2,10	0,204	0,308	1360	268	1,56	6,92
51	1,93	2,05	0,19	0,33				
52	1,82	2,04	0,22	0,31	1597	302	1,8	7,1
53	1,75	1,97	0,19	0,30	1450	270	1,6	5,9
54	1,97	2,23	0,197	0,291	1963	299	1,92	5,79
55	1,72	1,93	0,21	0,33	1820	<10	350	20
56								
57	1,82	2,13	0,28	0,40				
58	1,37	1,68	0,012	0,125	1484	231	0,8	3,2
59	1,81	2,03	0,22	0,34	1540	290	<5	5,9
60								
61	1,75	2,08	0,24	0,33	932	690	2,40	6,80
62	3,14	3,49	0,41	0,60				
63								
64	1,72	1,89	0,19	0,30				
65	3	4	<1	<1	987	432	1,10	2,70
66	1,87	2,00	0,204	0,309	1504	292	1,40	4,70
67	1,84	1,97	0,35	0,36	1367,3	265,2	1,6	6,0
68	1,81	2,02	0,175	0,280				
69	1,06	1,15	0,22	0,42				
70	1,687	1,800	0,146	0,205	1410	188	<2	2,62
71	1,745	1,963	0,190	0,300			1,89	6,874
72	1,82	2,05	0,21	0,36				
73								
74	1,92	2,16	0,10	0,21			1,01	5,09
75	1,50	1,60	0,17	0,26				
76	1,72	1,94	0,21	0,33	1401	269	1,67	6,07

Lab. No	Kadmium, µg/l C	Kadmium, µg/l D	Bly, µg/l C	Bly, µg/l D	Kopper, µg/l C	Kopper, µg/l D	Nikkel, µg/l C	Nikkel, µg/l D	Zinc, µg/l C	Zinc, µg/l D
1										
2	1,8	2,8	4,5	5,7	<1	<1	3,0	2,3	3,8	13,4
3	2,1	3,1	5,3	6,8	0,6	4,4	3,1	2,3	3,3	13,7
4	1,6	2,2	3,7	4,3	0,4	4,3	2,4	1,7	3,2	10,8
5										
6										
7	2,0	2,9	<15	<15	<4	5,9	<10	<10	3,1	12,5
8	2,158	3,227	4,646	5,963	0,7108	0,8530	3,322	2,566	2,948	12,940
9	1,98	2,99	4,88	6,49	0,70	0,92	3,16	2,40	2	12
10										
11	1,8	3,0	<1	<1	<10	<10	2,54	2,46	9,3	19,5
12	2,03	3,01	5,20	6,40	0,530	4,950	3,14	2,40	3,22	13,6
13	4,5	5,8	16,9	23,2	3,10	2,70	16,9	19,7	1,5	7,1
14	1,94	2,8	4,99	6,08	<1	<1	3,14	2,69	5,42	15,07
15										
16										
17	1,98	3,03	5,00	6,82	6,88	0,99	3,03	2,20	3,00	13,02
18	1,79	2,65	4,65	5,71	0,37	7,78	2,89	2,09	3,12	12,42
19	2,05	3,04	5,06	6,03	<1	<1	1,52	2,07	3,45	13,93
20	2,4	3,4	5,5	6,5	<1	5,5	3,7	1,7	<10	16,0
21	1,76	2,65	4,8	5,8			3,0	2,1	22,0	12,0
22										
23										
24	1,95	2,66	4,78	5,53	<2	<2	4,42	2,30	5,1	14,3
25										
26										
27	2,06	3,03	5,1	6,0	0,58	0,67	3,2	2,3	3,2	13,0
28	2,06	2,89	5,25	7,26	<2	5,38			4,15	12,82
29	2,1	3,1	5,6	6,3	<2	6,3	3,4	2,7	3,2	14,0
30	1,8	2,8	4,9	6,2	0,7	5,6	3,0	2,3	2,0	11,8
31	3,12	11,9	4,73	5,66	0,698	0,626	2,93	2,23	3,12	11,7
32										
33	2,14	3,31	4,00	4,81	<10	<10	<2	<2	1,66	12,8
34										
35	2,15	3,29	5,85	6,83	0,44	0,56	3,37	2,56	3,22	13,51
36	1,9	3,0	4,9	6,0	0,5	5,6	5,4	2,5	4,1	13,3
37										
38	2,0	3,0	<10	<10	<2	<2	<5	<5	3,0	12,8
39										
40	1,90	2,73	5,30	6,28	0,572	0,620	3,00	2,28	3,24	12,70

Lab.	Kadmium, µg/l		Bly, µg/l		Kopper, µg/l		Nikkel, µg/l		Zinc, µg/l	
No	C	D	C	D	C	D	C	D	C	D
41										
42										
43										
44	2,31	3,36	5,06	6,16	0,69	0,75	3,6	2,8	4,5	12,0
45	1,99	3,00	4,89	5,85	0,60	0,62	2,33	1,80	4,22	12,1
46	2,0	2,8	5,7	6,1	0,62	0,79	3,6	2,1	7,5	12,4
47										
48	2,1	3,0	5,0	5,9	0,65	0,76	3,0	2,5	4,6	13,4
49										
50	1,80	2,68	4,75	6,01	0,57	5,38	2,60	1,94	3,44	12,9
51										
52	2,20	3,25	5,79	7,0	0,600	5,300	3,5	2,6	3,9	14,1
53	2,1	3,1	5,1	6,1	0,58	0,67	3,1	2,4	3,4	14
54	1,90	2,77	5,30	6,43	0,743	0,821	3,18	2,25	1,36	7,65
55										
56										
57										
58	1,24	2,65	3,49	3,73	1,20	2,70			3,20	12,10
59	2,1	3,1	<10	<10	<5	<5	<6	<6	<10	11,40
60										
61	1,91	2,41	5,43	4,56	5,50	9,20	3,18	<3	10,0	15,9
62			5,55	6,33	0,44	0,78				
63										
64										
65	1,10	1,50	2,50	3,60	6,100	13,900	11,00	59,70	4,00	9,70
66	8,20	8,10	4,90	7,50	0,950	0,960	3,55	2,86	5,70	12,90
67	2,02	2,99	5,30	6,5	<1	6,0	4,0	2,6	4,2	14,7
68										
69										
70	2,031	3,057	4,650	5,465	<0,2	<0,2			4,861	13,089
71	1,928	2,866	4,518	5,757	0,55	0,69	3,239	2,490		
72										
73										
74	2,33	2,55	3,38	4,07	<1	<1	1,59	0,52		
75										
76	2,00	3,03	4,96	6,19	0,55	8,75	3,11	2,51	3,1	13,2

Table 5.1. Statistics - pH
Sample A

Number of participants	71		Range		0,76
Number of omitted results	4		Variance		0,02
True value	6,75		Standard deviation		0,15
Mean value	6,72		Relative standard deviation		2,3%
Median value	6,75		Relative error		-0,4%

Analytical results in ascending order:

58	5,89	U	9	6,70	38	6,80	
65	5,97	U	25	6,70	35	6,80	
60	6,25		72	6,71	32	6,80	
36	6,29		15	6,71	18	6,80	
1	6,35		52	6,73	10	6,81	
68	6,40		76	6,74	50	6,82	
74	6,45		11	6,74	21	6,82	
61	6,47		4	6,75	40	6,82	
13	6,50		71	6,75	55	6,82	
29	6,50		23	6,75	53	6,83	
24	6,50		43	6,75	48	6,83	
44	6,59		5	6,75	37	6,84	
64	6,59		39	6,75	20	6,85	
19	6,62		59	6,75	33	6,85	
66	6,62		51	6,76	22	6,86	
47	6,62		28	6,76	7	6,87	
67	-		57	6,77	73	6,90	
62	6,67		46	6,77	3	6,90	
27	6,67		31	6,78	2	6,95	
6	6,68		41	6,78 U	30	6,97	
75	6,68		70	6,79	34	6,98	
49	6,68		26	6,79	16	7,01	
69	6,68		56	6,80	12	9,60	U
14	6,70		54	6,80			

Sample B

Number of participants	71		Range		1,04
Number of omitted results	4		Variance		0,03
True value	5,91		Standard deviation		0,16
Mean value	5,91		Relative standard deviation		2,8%
Median value	5,91		Relative error		-0,1%

Analytical results in ascending order:

58	4,98	U	23	5,85	5	5,95	
13	5,55		31	5,86	30	5,97	
44	5,58		49	5,86	48	5,98	
24	5,60		27	5,86	40	5,98	
74	5,60		37	5,88	34	6,00	
69	5,66		43	5,89	61	6,00	
1	5,66		25	5,90	26	6,00	
75	5,68		32	5,90	73	6,00	
68	5,76		18	5,90	57	6,00	
6	5,76		54	5,90	64	6,00	
15	5,77		12	5,90 U	76	6,01	
14	5,80		47	5,91	11	6,04	
4	5,80		9	5,91	36	6,04	
46	5,82		62	5,92	20	6,05	
33	5,82		22	5,92	2	6,05	
39	5,82		66	5,92	21	6,07	
56	5,83		35	5,92	3	6,08	
28	5,83		38	5,93	29	6,20	
71	5,83		50	5,93	16	6,20	
53	5,83		10	5,94	7	6,29	
51	5,84		19	5,94	67	6,59	
72	5,84		60	5,95	65	6,82	U
59	5,85		55	5,95	41	6,85	U
70	5,85		52	5,95			

U = Omitted resultat

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

Number of participants	68	Range	0,70
Number of omitted results	4	Variance	0,02
True value	2,69	Standard deviation	0,13
Mean value	2,68	Relative standard deviation	4,9%
Median value	2,69	Relative error	-0,2%

Analytical results in ascending order:

66	2,14 U	43	2,65	50	2,71
31	2,40	51	2,65	59	2,72
19	2,47	34	2,66	13	2,72
39	2,48	64	2,67	29	2,72
3	2,49	35	2,67	33	2,72
44	2,50	70	2,67	36	2,73
55	2,50	28	2,68	48	2,76
22	2,52	10	2,68	7	2,76
24	2,54	16	2,68	56	2,80
68	2,54	47	2,69	67	2,80
26	2,57	57	2,69	32	2,82
2	2,57	52	2,69	71	2,83
6	2,58	46	2,69	65	2,85
62	2,60	61	2,69	53	2,87
75	2,60	9	2,69	21	2,90
12	2,60	15	2,69	60	2,90
40	2,61	49	2,70	20	3,01
41	2,61	23	2,70	73	3,02
72	2,62	14	2,70	54	3,04 U
58	2,62	18	2,70	30	3,10
4	2,62	25	2,70	37	3,33 U
27	2,62	5	2,70	74	3,33 U
76	2,64	11	2,70		

Sample B

Number of participants	68	Range	0,50
Number of omitted results	4	Variance	0,01
True value	2,52	Standard deviation	0,11
Mean value	2,53	Relative standard deviation	4,3%
Median value	2,52	Relative error	0,3%

Analytical results in ascending order:

67	2,30	62	2,50	29	2,56
12	2,30	44	2,50	65	2,57
19	2,33	9	2,51	48	2,58
3	2,33	4	2,51	46	2,59
66	2,33 U	51	2,51	31	2,60
39	2,38	43	2,51	5	2,61
22	2,39	70	2,51	16	2,61
68	2,40	11	2,52	21	2,61
55	2,40	15	2,52	74	2,62 U
18	2,40	50	2,52	20	2,62
26	2,43	6	2,52	47	2,62
24	2,44	64	2,52	59	2,63
23	2,44	61	2,52	30	2,65
72	2,45	10	2,53	32	2,70
2	2,45	35	2,53	56	2,70
34	2,45	76	2,54	60	2,70
41	2,47	28	2,54	71	2,72
58	2,47	13	2,54	73	2,75
27	2,49	57	2,54	7	2,79
40	2,49	53	2,55	75	2,80
14	2,50	52	2,55	37	3,16 U
25	2,50	36	2,56	54	3,34 U
49	2,50	33	2,56		

U = Omitted resultat

Table 5.3. Statistics - Alkalinity, mmol/l

Sample A

Number of participants	51	Range	0,021
Number of omitted results	28	Variance	0,000
True value	0,100	Standard deviation	0,006
Mean value	0,100	Relative standard deviation	5,7%
Median value	0,100	Relative error	-0,2%

Analytical results in ascending order:

71	0,088	72	0,103	20	0,140 U
6	0,090	10	0,104 U	32	0,140 U
62	0,092 U	40	0,104	74	0,140 U
68	0,093	26	0,105	12	0,141 U
76	0,093	43	0,107	13	0,150 U
52	0,093	47	0,107	69	0,150 U
46	0,095	2	0,107	1	0,150 U
39	0,098	18	0,109	19	0,151 U
44	0,099	33	0,109 U	53	0,155 U
27	0,099	48	0,110 U	59	0,160 U
41	0,100	57	0,111 U	24	0,164 U
70	0,100	21	0,114 U	66	0,164 U
25	0,100	49	0,118 U	64	0,166 U
31	0,101	67	0,120 U	23	0,166 U
51	0,101	15	0,123 U	61	0,220 U
28	0,101	36	0,126 U	65	0,230 U
4	0,103	14	0,130 U	75	0,390 U

Sample B

Number of participants	51	Range	0,024
Number of omitted results	28	Variance	0,000
True value	0,029	Standard deviation	0,007
Mean value	0,028	Relative standard deviation	24,7%
Median value	0,029	Relative error	-1,8%

Analytical results in ascending order:

48	< 0,1 U	72	0,032	74	0,060 U
76	0,018	26	0,033	24	0,067 U
27	0,020	43	0,035	19	0,073 U
25	0,020	40	0,037	32	0,075 U
52	0,020	15	0,039 U	12	0,076 U
44	0,021	18	0,039	67	0,080 U
71	0,022	2	0,040	20	0,080 U
51	0,022	47	0,042	59	0,080 U
46	0,025	33	0,044 U	69	0,080 U
68	0,025	10	0,044 U	66	0,084 U
39	0,026	62	0,046 U	13	0,090 U
41	0,027	57	0,047 U	64	0,097 U
31	0,029	1	0,050 U	23	0,105 U
70	0,029	14	0,050 U	53	0,105 U
6	0,030	21	0,051 U	61	0,130 U
4	0,031	36	0,054 U	75	0,260 U
28	0,032	65	0,060 U	49	0,486 U

U = Omitted resultat

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

Sample A

Number of participants	64	Range	97
Number of omitted results	13	Variance	357
True value	178	Standard deviation	19
Mean value	174	Relative standard deviation	10,9%
Median value	178	Relative error	-2,1%

Analytical results in ascending order:

11	< 150 U	46	170	3	185
36	44 U	2	172	40	185
1	100 U	34	173	66	186
64	108 U	43	174	27	187
23	123	71	175	33	187
75	123	31	176	55	189
51	128	53	177	57	192 U
5	142	38	178	15	194
58	145	14	180	30	194
47	153	74	180 U	56	195
48	159	25	180	41	196
44	160	37	180	70	197 U
67	161	60	180	9	203 U
10	162	16	181	12	204 U
35	164	52	181	59	213
19	166	49	181	65	220
4	167	29	182	61	225 U
72	168	18	182	13	293 U
50	168	20	183	54	493 U
76	169	69	183	24	680 U
6	170	26	184		
68	170	32	185		

Sample B

Number of participants	64	Range	62
Number of omitted results	13	Variance	145
True value	90	Standard deviation	12
Mean value	90	Relative standard deviation	13,4%
Median value	90	Relative error	0,0%

Analytical results in ascending order:

24	< 500 U	53	86	27	98
11	< 150 U	76	86	14	98
13	0 U	50	87	33	98
36	23 U	34	88	18	98
64	36 U	19	88	69	99
75	59	16	88	56	100
1	60 U	20	89	37	100
23	64	48	90	59	101
67	69	38	90	30	102
68	70	32	90	43	104
47	71	31	90	3	110
58	76	55	91	65	120
72	77	2	92	15	121
35	80	26	93	12	137 U
5	81	49	93	9	139 U
44	81	29	93	70	142 U
10	82	41	94	57	154 U
46	82	25	94	74	200 U
71	84	60	96	61	253 U
6	85	66	96	54	459 U
4	85	52	97		
51	86	40	97		

U = Omitted resultat

Table 5.5. Statistics - Chloride, mg/l

Sample A

Number of participants	65		Range		0,84
Number of omitted results	3		Variance		0,02
True value	2,00		Standard deviation		0,15
Mean value	1,96		Relative standard deviation		7,8%
Median value	2,00		Relative error		-1,8%

Analytical results in ascending order:

69	1,47	74	1,94	54	2,05
59	1,60	46	1,94	38	2,05
58	1,67	33	1,94	44	2,05
34	1,68	57	1,94	36	2,05
61	1,68	18	1,95	35	2,06
23	1,70	60	1,96	43	2,06
48	1,71	14	1,98	67	2,07
24	1,82	30	1,98	50	2,08
41	1,84	29	1,99	62	2,09
26	1,84	9	2,00	27	2,09
15	1,85	32	2,00	20	2,10
4	1,87	39	2,01	73	2,10
16	1,89	68	2,01	51	2,10
31	1,89	49	2,01	12	2,14
25	1,90	10	2,02	64	2,15
19	1,91	76	2,02	75	2,23
2	1,91	52	2,02	66	2,28
47	1,93	53	2,03	70	2,31
6	1,93	40	2,03	13	2,70 U
11	1,93	37	2,04	1	2,90 U
72	1,93	5	2,04	65	3,30 U
3	1,94	71	2,04		

Sample B

Number of participants	65		Range		1,27
Number of omitted results	3		Variance		0,05
True value	2,69		Standard deviation		0,23
Mean value	2,68		Relative standard deviation		8,7%
Median value	2,69		Relative error		-0,4%

Analytical results in ascending order:

61	2,02	11	2,64	68	2,75
34	2,03	46	2,65	10	2,76
59	2,18	72	2,65	44	2,76
69	2,23	19	2,65	71	2,77
48	2,36	62	2,65	40	2,77
12	2,38	3	2,66	36	2,78
23	2,38	60	2,67	53	2,79
15	2,45	30	2,67	20	2,80
24	2,45	32	2,68	35	2,81
65	2,50 U	33	2,69	9	2,83
4	2,55	57	2,69	43	2,85
26	2,56	18	2,70	27	2,87
58	2,58	14	2,70	54	2,93
41	2,58	38	2,70	51	2,96
16	2,60	76	2,71	5	3,03
25	2,60	29	2,71	75	3,08
2	2,61	6	2,72	73	3,20
74	2,61	37	2,72	66	3,22
31	2,63	52	2,72	13	3,27 U
47	2,63	64	2,72	70	3,29
67	2,64	39	2,74	1	4,10 U
50	2,64	49	2,74		

U = Omitted resultat

Table 5.6. Statistics - Sulfate, mg/l

Sample A

Number of participants	61	Range	0,60
Number of omitted results	7	Variance	0,01
True value	1,82	Standard deviation	0,10
Mean value	1,83	Relative standard deviation	5,4%
Median value	1,82	Relative error	0,4%

Analytical results in ascending order:

26	0,64 U	20	1,80	24	1,87
58	0,79 U	14	1,80	51	1,88
23	1,29 U	49	1,81	62	1,88
34	1,55	33	1,81	53	1,89
41	1,61	29	1,81	71	1,90
11	1,65	50	1,81	25	1,90
75	1,70	16	1,82	38	1,90
4	1,71	18	1,82	3	1,91
40	1,71	36	1,82	12	1,91
6	1,72	31	1,83	30	1,91
19	1,75	43	1,83	67	1,95
47	1,76	37	1,83	9	1,96
64	1,77	60	1,84	52	2,01
46	1,77	72	1,84	66	2,02
57	1,77	5	1,84	74	2,15
35	1,77	68	1,85	70	2,20 U
32	1,78	10	1,85	15	2,26 U
2	1,78	39	1,85	13	3,92 U
54	1,78	59	1,87	65	5,20 U
44	1,79	76	1,87		
48	1,79	27	1,87		

Sample B

Number of participants	61	Range	0,76
Number of omitted results	7	Variance	0,01
True value	1,85	Standard deviation	0,12
Mean value	1,86	Relative standard deviation	6,2%
Median value	1,85	Relative error	0,7%

Analytical results in ascending order:

26	0,67 U	31	1,83	25	1,90
58	0,87 U	49	1,83	10	1,90
23	1,33 U	57	1,83	53	1,91
41	1,49	40	1,83	12	1,91
34	1,56	29	1,83	3	1,92
4	1,74	33	1,83	38	1,93
47	1,76	36	1,83	30	1,94
46	1,76	75	1,84	67	1,95
6	1,77	2	1,85	52	1,96
19	1,78	68	1,85	51	1,98
37	1,80	43	1,86	5	1,98
35	1,81	44	1,86	54	2,02
32	1,81	16	1,86	9	2,12
24	1,81	27	1,87	66	2,14
64	1,81	72	1,88	15	2,24 U
14	1,81	60	1,88	74	2,25
62	1,82	59	1,88	13	2,87 U
48	1,82	39	1,88	70	2,95 U
18	1,82	71	1,89	65	13,00 U
50	1,82	76	1,89		
11	1,82	20	1,90		

U = Omitted resultat

Table 5.7. Statistics - Calcium, mg/l

Sample A

Number of participants	66	Range			1,19
Number of omitted results	6	Variance			0,04
True value	2,88	Standard deviation			0,21
Mean value	2,90	Relative standard deviation			7,3%
Median value	2,88	Relative error			0,6%

Analytical results in ascending order:

48	1,50 U	55	2,80	71	2,99
37	2,25	70	2,81	4	3,00
44	2,53	14	2,82 U	52	3,04
72	2,59	3	2,84	39	3,04
45	2,64	27	2,85	21	3,04
2	2,66	59	2,85	64	3,05
30	2,67	12	2,86	43	3,08
10	2,68	58	2,86	53	3,10
26	2,68 U	16	2,87	33	3,10
34	2,69	9	2,87	40	3,12
47	2,69	5	2,88	75	3,13
6	2,70	24	2,88	68	3,14
76	2,70	7	2,88	46	3,16
29	2,70	18	2,88	1	3,20
15	2,75	38	2,90	35	3,21
11	2,76	32	2,90	49	3,22
57	2,76	13	2,91	51	3,29
69	2,76	54	2,91	61	3,32
62	2,78	66	2,92	67	3,44
31	2,78	36	2,93	65	4,00 U
41	2,79	50	2,98	74	4,86 U
28	2,80	19	2,98	20	5,00 U

Sample B

Number of participants	66	Range			0,95
Number of omitted results	6	Variance			0,03
True value	1,95	Standard deviation			0,16
Mean value	1,95	Relative standard deviation			8,2%
Median value	1,95	Relative error			0,1%

Analytical results in ascending order:

14	< 2 U	62	1,90	33	2,01
48	0,95 U	28	1,91	75	2,02
37	1,49	54	1,91	53	2,03
47	1,69	55	1,92	50	2,04
34	1,69	27	1,92	39	2,05
44	1,73	18	1,92	13	2,06
49	1,73	36	1,93	43	2,06
2	1,75	3	1,93	15	2,06
45	1,80	9	1,94	52	2,07
70	1,80	12	1,95	51	2,09
6	1,80	4	1,95	40	2,09
29	1,82	59	1,95	30	2,09
72	1,82	58	1,96	21	2,11
24	1,84	32	1,97	35	2,11
41	1,84	5	1,98	68	2,14
76	1,84	71	1,99	67	2,29
11	1,85	38	2,00	65	2,30 U
10	1,85	66	2,00	46	2,43
7	1,85	19	2,00	61	2,44
69	1,86	1	2,00	26	2,81 U
31	1,88	64	2,00	20	3,40 U
16	1,90	57	2,01	74	3,52 U

U = Omitted resultat

Table 5.8. Statistics - Magnesium

Sample A

Number of participants	67		Range		0,130
Number of omitted results	10		Variance		0,001
True value	0,300		Standard deviation		0,025
Mean value	0,304		Relative standard deviation		8,1%
Median value	0,300		Relative error		1,5%

Analytical results in ascending order:

14	< 0,5 U	7	0,298	28	0,319
61	0,000 U	55	0,300	30	0,320
15	0,140 U	76	0,300	43	0,320
13	0,231 U	29	0,300	12	0,320
48	0,240 U	69	0,300	18	0,320
37	0,250	6	0,300	33	0,330
49	0,250	38	0,300	52	0,330
1	0,250	5	0,300	51	0,330
36	0,265	4	0,300	67	0,330
59	0,270	53	0,300	39	0,330
47	0,275	45	0,300	64	0,330
72	0,280	46	0,301	16	0,330
41	0,280	50	0,302	26	0,335
10	0,283	32	0,303	25	0,340
70	0,285	9	0,310	58	0,360
34	0,290	19	0,310	57	0,380
27	0,290	21	0,310	20	0,400 U
44	0,290	40	0,310	2	0,414 U
3	0,290	54	0,311	62	0,619 U
75	0,290	66	0,314	74	0,790 U
31	0,291	35	0,315	65	1,600 U
24	0,292	68	0,315		
11	0,294	71	0,316		

Sample B

Number of participants	67		Range		0,200
Number of omitted results	10		Variance		0,001
True value	0,450		Standard deviation		0,034
Mean value	0,447		Relative standard deviation		7,6%
Median value	0,450		Relative error		-0,7%

Analytical results in ascending order:

14	< 0,5 U	29	0,437	25	0,460
48	0,260 U	50	0,437	26	0,463
13	0,287 U	27	0,440	71	0,465
15	0,340 U	45	0,440	68	0,465
1	0,350	44	0,440	35	0,466
6	0,370	30	0,440	54	0,470
37	0,380	53	0,440	51	0,470
49	0,400	76	0,440	67	0,470
70	0,404	12	0,440	46	0,478
47	0,406	5	0,449	16	0,480
24	0,407	7	0,450	39	0,490
41	0,410	9	0,450	52	0,490
59	0,420	55	0,450	74	0,500 U
36	0,420	28	0,455	33	0,500
34	0,420	32	0,456	38	0,500
10	0,424	66	0,458	58	0,510
69	0,430	19	0,460	57	0,550
75	0,430	18	0,460	20	0,630 U
72	0,430	64	0,460	62	0,918 U
3	0,430	43	0,460	61	1,300 U
11	0,431	21	0,460	65	1,700 U
31	0,436	40	0,460		
2	0,437 U	4	0,460		

U = Omitted resultat

Table 5.9. Statistics - Sodium, mg/l

Sample A

Number of participants	66	Range			0,63
Number of omitted results	4	Variance			0,01
True value	1,75	Standard deviation			0,11
Mean value	1,76	Relative standard deviation			6,4%
Median value	1,75	Relative error			0,3%
Analytical results in ascending order:					
69	1,06 U	64	1,72	59	1,81
58	1,37	14	1,72	68	1,81
75	1,50	31	1,73	50	1,82
48	1,55	45	1,73	21	1,82
46	1,62	26	1,74	57	1,82
27	1,63	35	1,74	72	1,82
37	1,63	71	1,75	52	1,82
49	1,63	43	1,75	10	1,83
38	1,65	18	1,75	67	1,84
29	1,66	53	1,75	15	1,84
28	1,66	34	1,75	39	1,86
11	1,66	32	1,75	19	1,86
47	1,68	61	1,75	66	1,87
2	1,68	40	1,76	41	1,89
70	1,69	5	1,77	74	1,92
4	1,69	16	1,77	51	1,93
44	1,69	36	1,77	13	1,95
6	1,70	24	1,78	54	1,97
30	1,70	33	1,78 U	12	1,99
7	1,72	3	1,79	25	2,00
76	1,72	20	1,80	65	3,00 U
55	1,72	9	1,80	62	3,14 U

Sample B

Number of participants	66	Range			0,63
Number of omitted results	4	Variance			0,01
True value	1,97	Standard deviation			0,12
Mean value	1,97	Relative standard deviation			6,1%
Median value	1,97	Relative error			0,2%
Analytical results in ascending order:					
69	1,15 U	38	1,93	36	2,02
33	1,20 U	55	1,93	59	2,03
75	1,60	31	1,93	9	2,03
58	1,68	76	1,94	10	2,04
37	1,80	34	1,95	52	2,04
70	1,80	24	1,95	51	2,05
46	1,82	18	1,95	72	2,05
48	1,84	43	1,95	41	2,07
27	1,84	2	1,95	61	2,08
11	1,85	71	1,96	15	2,09
29	1,85	12	1,97	19	2,09
49	1,88	32	1,97	20	2,10
28	1,88	67	1,97	50	2,10
47	1,89	53	1,97	57	2,13
64	1,89	35	1,98	74	2,16
14	1,90	16	1,98	39	2,17
44	1,90	5	1,99	25	2,20
30	1,90	40	2,00	13	2,20
6	1,90	66	2,00	21	2,21
26	1,90	45	2,00	54	2,23
7	1,92	3	2,01	62	3,49 U
4	1,93	68	2,02	65	4,00 U

U = Omitted resultat

Table 5.10. Statistics - Potassium, mg/l

Sample A

Number of participants	66	Range	0,140
Number of omitted results	8	Variance	0,001
True value	0,200	Standard deviation	0,025
Mean value	0,199	Relative standard deviation	12,7%
Median value	0,200	Relative error	-0,3%

Analytical results in ascending order:

65	< 1 U	64	0,190	46	0,208
14	< 0,6 U	71	0,190	55	0,210
26	< 0,6 U	41	0,190	39	0,210
13	0,000 U	3	0,190	72	0,210
58	0,012 U	51	0,190	20	0,210
74	0,100 U	53	0,190	30	0,210
16	0,140	35	0,192	33	0,210
15	0,140	31	0,195	43	0,210
70	0,146	54	0,197	76	0,210
4	0,170	11	0,199	24	0,211
28	0,170	44	0,200	45	0,220
75	0,170	18	0,200	59	0,220
36	0,174	12	0,200	69	0,220
68	0,175	27	0,200	52	0,220
49	0,180	37	0,200	9	0,230
32	0,180	38	0,200	47	0,240
48	0,180	19	0,200	61	0,240
6	0,180	29	0,201	21	0,250
34	0,180	2	0,202	25	0,260
7	0,188	10	0,203	57	0,280
5	0,188	66	0,204	67	0,350 U
40	0,190	50	0,204	62	0,410 U

Sample B

Number of participants	66	Range	0,215
Number of omitted results	8	Variance	0,002
True value	0,300	Standard deviation	0,040
Mean value	0,303	Relative standard deviation	13,2%
Median value	0,300	Relative error	1,1%

Analytical results in ascending order:

65	< 1 U	46	0,295	45	0,320
14	< 0,6 U	36	0,295	33	0,320
58	0,125 U	5	0,297	19	0,320
26	0,180 U	7	0,298	55	0,330
70	0,205	40	0,300	41	0,330
74	0,210 U	64	0,300	61	0,330
11	0,213	12	0,300	76	0,330
16	0,220	30	0,300	51	0,330
38	0,230	44	0,300	20	0,330
49	0,230	3	0,300	47	0,337
2	0,254	71	0,300	24	0,338
48	0,260	53	0,300	59	0,340
75	0,260	37	0,300	25	0,340
4	0,270	29	0,302	21	0,340
28	0,270	50	0,308	9	0,350
31	0,273	35	0,308	67	0,360 U
68	0,280	66	0,309	72	0,360
32	0,280	27	0,310	39	0,360
15	0,280	52	0,310	57	0,400
34	0,280	18	0,310	69	0,420
6	0,290	10	0,317	13	0,517 U
54	0,291	43	0,320	62	0,600 U

U = Omitted resultat

Table 5.11. Statistics - Iron, µg/l

Sample C

Number of participants	41	Range	429
Number of omitted results	5	Variance	8093
True value	1451	Standard deviation	90
Mean value	1447	Relative standard deviation	6,2%
Median value	1451	Relative error	-0,3%

Analytical results in ascending order:

18	930 U	21	1410	27	1500
61	932 U	13	1427	31	1503
65	987 U	8	1434	66	1504
36	1168	14	1439	29	1510
28	1249	35	1446	45	1520
12	1341	7	1450	59	1540
3	1356	53	1450	20	1540
40	1360	46	1452	48	1550
50	1360	9	1455	30	1574
67	1367	2	1470	33	1590
44	1370	38	1476	52	1597
24	1400	58	1484	55	1820 U
76	1401	11	1484	54	1963 U
70	1410	4	1490		

Sample D

Number of participants	41	Range	139
Number of omitted results	5	Variance	722
True value	280	Standard deviation	27
Mean value	274	Relative standard deviation	9,8%
Median value	280	Relative error	-2,2%

Analytical results in ascending order:

55	< 10 U	76	269	4	291
18	181 U	21	270	66	292
70	188	53	270	44	293
36	225	9	271	24	295
58	231	12	272	33	295
2	238	27	280	35	297
3	243	38	280	54	299 U
13	252	7	281	48	300
28	252	11	283	52	302
31	256	45	284	8	314
14	259	20	287	30	327
40	260	59	290	65	432 U
67	265	46	290	61	690 U
50	268	29	290		

U = Omitted resultat

Table 5.12. Statistics - Manganese, µg/l

Sample C

Number of participants	43	Range	1,49
Number of omitted results	15	Variance	0,09
True value	1,70	Standard deviation	0,30
Mean value	1,76	Relative standard deviation	17,2%
Median value	1,70	Relative error	3,6%

Analytical results in ascending order:

20	< 20 U	40	1,60	71	1,89
11	< 10 U	67	1,60	54	1,92
33	< 10 U	3	1,60	17	1,99
24	< 5 U	30	1,60	38	2,00
59	< 5 U	53	1,60	4	2,00
14	< 2 U	12	1,61	44	2,10
70	< 2 U	76	1,67	27	2,10
58	0,80 U	9	1,69	61	2,40
74	1,01	36	1,70	48	2,50
65	1,10 U	7	1,70	35	3,48 U
66	1,40	45	1,73	13	3,90 U
2	1,40	28	1,76	46	5,60 U
18	1,54 U	52	1,80	55	350,00 U
50	1,56	29	1,80 U		
31	1,58	8	1,80		

Sample D

Number of participants	43	Range	3,00
Number of omitted results	15	Variance	0,45
True value	6,04	Standard deviation	0,67
Mean value	6,28	Relative standard deviation	10,7%
Median value	6,04	Relative error	3,9%

Analytical results in ascending order:

20	< 20 U	53	5,90	7	6,70
11	< 10 U	2	5,90	61	6,80
33	< 10 U	40	5,94	35	6,86 U
46	1,40 U	9	5,95	71	6,87
70	2,62 U	67	6,00	3	6,90
65	2,70 U	30	6,00	50	6,92
58	3,20 U	38	6,00	27	7,00
66	4,70	4	6,00	52	7,10
74	5,09	24	6,05 U	44	7,50
31	5,68	76	6,07	12	7,70
28	5,73	48	6,20	29	9,00 U
54	5,79	8	6,40	18	9,25 U
14	5,81 U	45	6,52	55	20,00 U
59	5,90 U	17	6,54		
36	5,90	13	6,60 U		

U = Omitted resultat

Table 5.13. Statistics - Cadmium, µg/l

Sample C

Number of participants	44	Range	1,16
Number of omitted results	4	Variance	0,04
True value	2,00	Standard deviation	0,20
Mean value	1,99	Relative standard deviation	10,1%
Median value	2,00	Relative error	-0,7%

Analytical results in ascending order:

65	1,10 U	24	1,95	29	2,10
58	1,24	9	1,98	59	2,10
4	1,60	17	1,98	3	2,10
21	1,76	45	1,99	53	2,10
18	1,79	46	2,00	33	2,14
50	1,80	38	2,00	35	2,15
30	1,80	7	2,00	8	2,16
11	1,80	76	2,00	52	2,20
2	1,80	67	2,02	44	2,31
40	1,90	12	2,03	74	2,33
54	1,90	70	2,03	20	2,40
36	1,90	19	2,05	31	3,12 U
61	1,91	27	2,06	13	4,50 U
71	1,93	28	2,06	66	8,20 U
14	1,94	48	2,10		

Sample D

Number of participants	44	Range	1,20
Number of omitted results	4	Variance	0,07
True value	3,00	Standard deviation	0,26
Mean value	2,93	Relative standard deviation	8,7%
Median value	3,00	Relative error	-2,3%

Analytical results in ascending order:

65	1,50 U	71	2,87	70	3,06
4	2,20	28	2,89	29	3,10
61	2,41	7	2,90	53	3,10
74	2,55	67	2,99	3	3,10
18	2,65	9	2,99	59	3,10
58	2,65	45	3,00	8	3,23
21	2,65	11	3,00	52	3,25
24	2,66	48	3,00	35	3,29
50	2,68	38	3,00	33	3,31
40	2,73	36	3,00	44	3,36
54	2,77	12	3,01	20	3,40
2	2,80	27	3,03	13	5,80 U
46	2,80	17	3,03	66	8,10 U
30	2,80	76	3,03	31	11,90 U
14	2,80	19	3,04		

U = Omitted resultat

Table 5.14. Statistics - Lead, µg/l

Sample C

Number of participants	45	Range	2,47
Number of omitted results	6	Variance	0,32
True value	4,99	Standard deviation	0,56
Mean value	4,93	Relative standard deviation	11,4%
Median value	4,99	Relative error	-1,1%

Analytical results in ascending order:

7	< 15 U	50	4,75	27	5,10
59	< 10 U	24	4,78	12	5,20
38	< 10 U	21	4,80	28	5,25
11	< 1 U	9	4,88	54	5,30
65	2,50 U	45	4,89	67	5,30
74	3,38	66	4,90	40	5,30
58	3,49	30	4,90	3	5,30
4	3,70	36	4,90	61	5,43
33	4,00	76	4,96	20	5,50
2	4,50	14	4,99	62	5,55
71	4,52	48	5,00	29	5,60
8	4,65	17	5,00	46	5,70
70	4,65	44	5,06	52	5,79
18	4,65	19	5,06	35	5,85
31	4,73	53	5,10	13	16,90 U

Sample D

Number of participants	45	Range	3,77
Number of omitted results	6	Variance	0,64
True value	6,08	Standard deviation	0,80
Mean value	5,98	Relative standard deviation	13,4%
Median value	6,08	Relative error	-1,7%

Analytical results in ascending order:

7	< 15 U	71	5,76	40	6,28
59	< 10 U	21	5,80	29	6,30
38	< 10 U	45	5,85	62	6,33
11	< 1 U	48	5,90	12	6,40
65	3,60 U	8	5,96	54	6,43
58	3,73	36	6,00	9	6,49
74	4,07	27	6,00	20	6,50
4	4,30	50	6,01	67	6,50
61	4,56	19	6,03	3	6,80
33	4,81	14	6,08	17	6,82
70	5,47	53	6,10	35	6,83
24	5,53	46	6,10	52	7,00
31	5,66	44	6,16	28	7,26
2	5,70	76	6,19	66	7,50
18	5,71	30	6,20	13	23,20 U

U = Omitted resultat

Table 5.15. Statistics - Copper, µg/l

Sample C

Number of participants	44	Range	0,303
Number of omitted results	30	Variance	0,009
True value	0,610	Standard deviation	0,095
Mean value	0,612	Relative standard deviation	15,5%
Median value	0,610	Relative error	0,4%

Analytical results in ascending order:

11	< 10 U	18	0,370 U	46	0,620
33	< 10 U	4	0,400 U	48	0,650
59	< 5 U	62	0,440	44	0,690
7	< 4 U	35	0,440	31	0,698
24	< 2 U	36	0,500 U	30	0,700 U
28	< 2 U	12	0,530 U	9	0,700
38	< 2 U	76	0,550 U	8	0,711
74	< 1 U	71	0,550	54	0,743
20	< 1 U	50	0,570 U	66	0,950 U
67	< 1 U	40	0,572	58	1,200 U
29	< 1 U	53	0,580	13	3,100 U
14	< 1 U	27	0,580	61	5,500 U
19	< 1 U	45	0,600	65	6,100 U
2	< 1 U	52	0,600 U	17	6,880 U
70	< 0,2 U	3	0,600 U		

Sample D

Number of participants	44	Range	0,360
Number of omitted results	30	Variance	0,011
True value	0,720	Standard deviation	0,103
Mean value	0,724	Relative standard deviation	14,3%
Median value	0,720	Relative error	0,5%

Analytical results in ascending order:

11	< 10 U	53	0,670	12	4,950 U
33	< 10 U	71	0,690	52	5,300 U
59	< 5 U	44	0,750	50	5,380 U
24	< 2 U	48	0,760	28	5,380 U
38	< 2 U	62	0,780	20	5,500 U
74	< 1 U	46	0,790	30	5,600 U
14	< 1 U	54	0,821	36	5,600 U
19	< 1 U	8	0,853	7	5,900 U
2	< 1 U	9	0,920	67	6,000 U
70	< 0,2 U	66	0,960 U	29	6,300 U
35	0,560	17	0,988 U	18	7,780 U
40	0,620	58	2,700 U	76	8,750 U
45	0,620	13	2,700 U	61	9,200 U
31	0,626	4	4,300 U	65	13,900 U
27	0,670	3	4,400 U		

U = Omitted resultat

Table 5.16. Statistics - Nickel, µg/l

Sample C

Number of participants	41	Range	2,09
Number of omitted results	10	Variance	0,19
True value	3,14	Standard deviation	0,43
Mean value	3,18	Relative standard deviation	13,6%
Median value	3,14	Relative error	1,2%

Analytical results in ascending order:

7	< 10 U	40	3,00	8	3,32
59	< 6 U	30	3,00	35	3,37
38	< 5 U	2	3,00	29	3,40
33	< 2 U	17	3,03	52	3,50
19	1,52 U	53	3,10	66	3,55
74	1,59 U	3	3,10	46	3,60
45	2,33	76	3,11	44	3,60
4	2,40	12	3,14	20	3,70
11	2,54	14	3,14	67	4,00
50	2,60	9	3,16	24	4,42
18	2,89	54	3,18	36	5,40 U
31	2,93	61	3,18 U	65	11,00 U
21	3,00	27	3,20	13	16,90 U
48	3,00	71	3,24		

Sample D

Number of participants	41	Range	1,16
Number of omitted results	10	Variance	0,09
True value	2,30	Standard deviation	0,29
Mean value	2,34	Relative standard deviation	12,5%
Median value	2,30	Relative error	1,6%

Analytical results in ascending order:

7	< 10 U	17	2,20	36	2,50 U
59	< 6 U	31	2,23	48	2,50
38	< 5 U	54	2,25	76	2,51
61	< 3 U	40	2,28	35	2,56
33	< 2 U	2	2,30	8	2,57
74	0,52 U	3	2,30	67	2,60
20	1,70	30	2,30	52	2,60
4	1,70	24	2,30	14	2,69
45	1,80	27	2,30	29	2,70
50	1,94	9	2,40	44	2,80
19	2,07 U	12	2,40	66	2,86
18	2,09	53	2,40	13	19,70 U
46	2,10	11	2,46	65	59,70 U
21	2,10	71	2,49		

U = Omitted resultat

Table 5.17. Statistics - Zinc, µg/l

Sample C

Number of participants	42	Range	2,94
Number of omitted results	13	Variance	0,48
True value	3,22	Standard deviation	0,69
Mean value	3,33	Relative standard deviation	20,7%
Median value	3,22	Relative error	3,4%

Analytical results in ascending order:

20	< 10 U	27	3,20	36	4,10
59	< 10 U	4	3,20	28	4,15
54	1,36 U	29	3,20	67	4,20
13	1,50 U	58	3,20	45	4,22
33	1,66	12	3,22	44	4,50
30	2,00	35	3,22	48	4,60
9	2,00	40	3,24	70	4,86 U
8	2,95	3	3,30	24	5,10 U
38	3,00	53	3,40	14	5,42 U
17	3,00	50	3,44	66	5,70 U
76	3,10	19	3,45	46	7,50 U
7	3,10	2	3,80	11	9,30 U
31	3,12	52	3,90	61	10,00 U
18	3,12	65	4,00 U	21	22,00 U

Sample D

Number of participants	42	Range	3,90
Number of omitted results	13	Variance	0,74
True value	12,94	Standard deviation	0,86
Mean value	12,94	Relative standard deviation	6,7%
Median value	12,94	Relative error	0,0%

Analytical results in ascending order:

13	7,10 U	7	12,50	2	13,40
54	7,65 U	40	12,70	35	13,51
65	9,70 U	38	12,80	12	13,60
4	10,80	33	12,80	3	13,70
59	11,40 U	28	12,82	19	13,93
31	11,70	66	12,90 U	29	14,00
30	11,80	50	12,90	53	14,00
44	12,00	8	12,94	52	14,10
21	12,00 U	27	13,00	24	14,30 U
9	12,00	17	13,02	67	14,70
58	12,10	70	13,09 U	14	15,07 U
45	12,10	76	13,20	61	15,90 U
46	12,40 U	36	13,30	20	16,00 U
18	12,42	48	13,40	11	19,50 U

U = Omitted resultat