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

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Intercomparison 0519: 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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REPORT

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Abstract

79 laboratories received samples for the intercomparison 0519, and 75 laboratories in 30 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 %, 73 % of the overall results were considered acceptable when the trace metals cadmium, lead and nickel was excluded from the evaluation. The best results were reported for the analytical variables sodium and sulphate, with 87 and 86 % acceptable results, respectively. Lowest percentage of acceptable results were observed for the heavy metals, especially for lead, cadmium and nickel. The main reason for this result was the very low concentrations of these metals in the samples used this time. Harmonization of the analytical methods used is necessary to improve the comparability for pH.

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CONVENTION ON LONG-RANGE
TRANSBOUNDARY AIR POLLUTION

INTERNATIONAL COOPERATIVE PROGRAMME ON
ASSESSMENT AND MONITORING OF ACIDIFICATION
OF RIVERS AND LAKES

Intercomparison 0519:

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

Prepared by the Programme Centre
Norwegian Institute for Water Research
Oslo, September 2005

Preface

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

The Programme objective is to establish an international network of surface water monitoring sites and promote international harmonization of monitoring practices. One of the tools in this work is inter-laboratory quality assurance tests. The bias between analyses carried out by the individual participants of the Programme has to be clearly identified and controlled.

We here report the results from the 19th intercomparison of chemical analysis.

Oslo, September 2005

Håvard Hovind

Contents

1. Summary

Intercomparison 0519 was organized as a part of the between-laboratory quality control programme, as stated in "Manual for Chemical and Biological Monitoring" (1), by the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes.

The intercomparison was performed in July - August 2005, and included the determination of major ions and metals in natural water samples. The participants were asked to determine pH, conductivity, alkalinity, nitrate + nitrite, chloride, 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. 131 laboratories were invited to participate in this intercomparison, and the samples were sent to the 79 laboratories who accepted to participate. 75 laboratories submitted results to the Programme Centre before the final statistical treatment of the data. 30 countries were represented in this laboratory group (see Appendix A, page 40).

The median value of the results received from the participants was selected as "true" value for each variable. 73 % of the result pairs were considered as acceptable when the trace metals cadmium, lead and nickel was excluded from the evaluation, the target limit being the median value ± 20 %, except for pH and conductivity where the special acceptance limits were selected, being ± 0,2 units and ± 10 %, respectively.

For pH, the accuracy limit was extended from 0,1 to ± 0,2 units, but still only 63 % of the result pairs were acceptable using this special limit. 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 reason for the great spread of pH results is mainly due to the fact that different routines are used for the determination of pH by the participants, leading to small systematic differences in the results. A harmonization of the analytical method used is necessary to improve the results for pH and alkalinity.

The best results were reported for the analytical variables sodium and sulphate where 87 and 86 % of the results, respectively, were acceptable. The worst results were observed for the heavy metals, especially for lead, cadmium and nickel. The main reason for this was the very low concentrations of these metals in the samples this time, and the fact that very few laboratories having equipment being sensitive enough for such low concentrations.

2. Introduction

As stated in "Manual for Chemical and Biological Monitoring" (1), between-laboratory quality control is necessary in a multilaboratory programme to assure clear identification and control of the bias between analyses carried out by individual participants of the Programme. Such biases may arise by use of different analytical methods, errors in the laboratory calibration solutions, or through inadequate within-laboratory control.

The between-laboratory control carried out by the Programme Centre is based on the "round robin" concept and the procedure of Youden (2, 3), which is briefly described in Appendix C. This nineteenth intercomparison test, called 0519, included the determination of the major components and some other ions in natural water samples: pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulphate, calcium, magnesium, sodium, potassium, iron, manganese, cadmium, lead, copper, nickel and zinc.

3. 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 2003 it was decided that two sample sets should be included in this intercomparison, one sample pair for the determination of the major ions, and one for the heavy metals.

The samples were mailed from the Programme Centre on June 24, 2005, and the following day. Most of the participating laboratories received the samples within one week, with some very few exceptions.

To ensure that the effect of possible alterations in the solutions is minimized, the participants were asked to analyze the samples as soon as possible, and return the analytical results within one month after the samples arrived at the laboratory. 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 August. Four laboratories who received samples did not return analytical results.

4. Results

131 laboratories were invited to participate in this intercomparison, and 79 laboratories accepted and therefore received samples. The 75 laboratories which submitted results to the Programme Centre, are representing 30 countries. Some laboratories submitted results a few weeks after the deadline, and a reminder letter was mailed to some few participants. A survey of the participants and their code numbers are listed in Appendix A, which also includes a table illustrating 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, are 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, as the "true value" for each analytical variable. The median value is considered to be an acceptable estimate of the true value for this purpose, as long as most of the participants are using essentially the same analytical method. For certain variables, like pH, this may represent a problem as the methods used may produce systematically different results (stirring, non-stirring, and equilibration), 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 defined in the sections below. A survey of the results of intercomparison 0519 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.

4.1 pH

The reported results for pH are graphically presented in Figure 1, where the radius of the circle is 0,2 pH units, and visualizes the degree of comparability between the pH results from the participating laboratories. The values reported by the laboratories are given in Table 5.1.

The participating laboratories determined pH in the test solutions using their own routine method. An electrometric method was used by all laboratories. 73 laboratories reported results for pH, 32 laboratories of this group indicated that they read the pH value i quiescent solution, and 39 during stirring the solution. The stirring are normally lowering the observed pH result. In this intercomparison the median values are not different in the stirred samples compared to the non-stirred samples (see Table 1). The differences between the mean values are not significantly different.

Two laboratories equilibrated the solutions by bubbling with air containing 350 ppm CO_2 before reading the pH value, reported only somewhat higher results than 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 of the methods are greater than here, it is questionable to establish a “true value” based on the median value for all the reported results for pH, and it should be discussed whether an individual “true value” for each method would be more appropriate.
The control analyses carried out at the Program Centre proved that the samples were stable when stored at 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 shows that the reported results are rather spread out along the 45 ° line, indicating that the results are influenced by systematic effects on the results. 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.

4.2 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 was mS/m at 25 °C, the reported results being at least one decade wrong. Some of these laboratories reported the unit they really used, and therefore 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. After correcting the wrong unit used, only a few laboratories reported results being systematically too high for both samples, or systematically too low. 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 had been extended to the target value of ± 20 %, defined in the Manual (1), seven more results located outside the 10 % acceptance circle, would be located within the circle and thus be defined as acceptable. An acceptance limit of ± 10 % seems to be a reasonable demand.

4.3 Alkalinity

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 5.3. 59 laboratories reported results for alkalinity, and nearly one half of the participants used the Gran plot titration method suggested in the Manual (1). The others used end point titration, either to pH = 4,5 and 4,2, or to one certain pH value only (4,5, 5,4 or 5,6). The results 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. Six laboratories used a method not being specified.

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. This is most likely due to the different methods used by the laboratories. By a closer examination of the results, a certain connection between the method used and the location in Figure 3 was observed. 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. With very few exceptions the results determined by the end point titration to pH 4,5 alone are located in the upper right part of Figure 3, the results in most cases beeing systematically too high. The end point titration to pH 5,4 gave results mainly located within the acceptance circle.

The overall result for alkalinity in this intercomparison is better than in the last intercomparisons, 63 % 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 this case, the relative error introduced by assuming a fixed end-point pH, is negligible. However, at lower alkalinities normally encountered in areas sensitive to acidification, the “total fixed end-point method” may overestimate the true alkalinity or the “equivalence” alkalinity.

4.4 Nitrate + nitrite

The results reported for this parameter are presented in Figure 4, and the reported values are given in Table 5.4. The circle in Figure 4 represents a general target accuracy of ± 20 %. Ion chromatography is used by more than half of the participants. The others are determining this analytical variable by photometric methods, most of these laboratories are using an automated version of the cadmium reduction method. There is no significant difference between the results determined by these two methods. The hydrazine method used by three laboratories gave acceptable results for two of them. One laboratory using photometric method 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 values close to the median values.

This time 82 % of the results are evaluated as acceptable, which is about the same as in the intercomparison one year ago. One probable reason for this may be that the concentrations of nitrate-nitrogen were rather high in these intercomparisons. 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.

4.5 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. 56 out of 68 laboratories determined chloride by ion chromatography. The greatest deviations are observed for a potentiometric method, and the results determined with the

argentometric method which were too low, while somewhat varying and systematically high results were reported for the mercurimetric method. Two laboratories using capillary electrophoresis reported values comparable to the median values.

86 % acceptable results in this intercomparison is the highest score for this analytical variable the last four intercomparisons.

4.6 Sulfate

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 56 of 67 laboratories for the determination of the sulfate content. Seven laboratories used a photometric method based on the dissociation of the barium-thorin complex, the results, on average, being comparable to the ion chromatographic method. None of the three result pairs were acceptable for the nephelometric method. One laboratory used ICP-AES for the determination of total sulphur, and then recalculated the result to mg/l sulphate.

81 % of the result pairs are acceptable.

4.7 Calcium

The calcium results are illustrated in Figure 7, and the reported values are given in Table 5.7. The target accuracy is ± 20 %, and is represented by the great circle in Figure 7. 66 laboratories reported results for calcium, and 21 of them used the traditional flame atomic absorption spectrometry for the determination. The ICP technique is used by 15 laboratories, and three of these used ICP-MS. An increasing number of laboratories, this time 27, used ion chromatography. Three laboratories used a titrimetric method with EDTA for the determination of calcium, produced results being being somewhat spread out. The systematic errors are dominating for this analytical variable.

79 % acceptable result pairs is comparable to the intercomparison last year.

4.8 Magnesium

The magnesium results are presented in Figure 8, and the reported values are given in Table 5.8. About one quarter of the participants are still using flame atomic absorption spectrometry for the determination of magnesium. ICP atomic emission spectrometry was used by 12 laboratories and ICP-MS by three, and 27 laboratories used ion chromatography. Systematic errors are dominating the results being outside the acceptance limit. This time, only 69 % 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. The most commonly used methods give comparable results.

4.9 Sodium

The sodium results are presented in Figure 9, where the great circle is representing the general target accuracy of ± 20 %. The reported values are given in Table 5.9. Only 17 laboratories used flame atomic absorption spectrometry for the determination this time, and ICP-AES was used by 10 laboratories. However, in many laboratories the ion chromatographic technique becomes increasingly more popular in routine determination of the alkaline metals, thus 26 participants used ion chromatography in this intercomparison. Seven laboratories used flame photometry. 89 % of the result pairs are located within the general target accuracy of ± 20 %, which is considered as a very good result.

4.10 Potassium

The potassium results are presented in Figure 10. The great circle is representing the target acceptance limit of ± 20 %. The reported values are given in Table 5.10. As for sodium, only 17 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. 73 % of the result pairs are considered acceptable this time.

4.11 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, only 57 % of the result pairs are located inside this circle. 37 laboratories submitted results for iron, of which 12 and 11 used ICP-AES and ICP-MS, respectively, while 9 and 5 used flame and graphite furnace atomic absorption, respectively.

Some laboratories using ICP-AES have rather high detection limits, and thus two participants reported their results as "less than" the value of the detection limit. The deviating results are mainly affected by systematic errors. There is observed a significant difference between the results determined by the different methods for iron, thus the flame atomic absorption gives systematically lower results than the graphite furnace. The ICP-MS results are somewhat lower than the ICP-AES results.

4.12 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. 65 % of the result pairs are located inside this circle, which is better than former intercomparisons, even when the concentrations used this time are rather low. 40 laboratories submitted results for manganese, of which 12 and 13 used ICP-AES and ICP-MS, respectively, while 4 and 14 used flame and graphite furnace atomic absorption, respectively. The flame atomic absorption spectrometry is not sensitive enough for these sample concentrations. ICP-AES and ICP-MS give comparable results.

4.13 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, only 18 % of the result pairs are located inside this circle. 38 laboratories submitted results for cadmium, of which 10 and 10 used ICP-AES and ICP-MS, respectively, while 14 used graphite furnace atomic absorption. The cadmium concentrations were very low in the samples used this time, and it is obvious that only a few laboratories have equipment and methods being sensitive enough for determination of cadmium at this level.

4.14 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. Only 8 % of the result pairs are located inside this circle. 39 laboratories submitted results for lead, of which 9 and 13 used ICP-AES and ICP-MS, respectively, while 13 used graphite furnace atomic absorption. Flame atomic absorption is not sensitive enough to determine these low lead concentrations. As for cadmium the lead concentrations were very low and only a few laboratories have equipment and methods being sensitive enough for determination of cadmium at this level.

4.15 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. 63 % of the result pairs are located inside this circle, which is much lower than earlier. The lower concentrations used for copper this time are most probably a reason for these results. 41 laboratories submitted results for copper, of which 11 used ICP-AES and 13 used ICP-MS, while 13 and 4 used graphite furnace and flame atomic absorption, respectively.

4.16 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 25 % of the result pairs are located inside this circle, and the reason for this situation is that he nickel concentrations were very low in the samples used this time. 36 laboratories submitted results for nickel, of which 9 and 12 used ICP-AES and ICP-MS, respectively, while 12 used graphite furnace atomic absorption. Both result pairs for FAAS were excluded.

4.17 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, only 54 % of the result pairs are located inside this circle, the zinc concentrations being relatively low. 41 laboratories submitted results for zinc, of which 14 and 11 used ICP-AES and ICP-MS, respectively, while 10 and 6 used flame and graphite furnace atomic absorption, respectively. Generally, the deviating results are affected by both systematic and random errors, some too high values indicate that contamination may be a problem for some laboratories when they are determining the zinc concentration.

Table 1. Statistical summary of intercomparison 0519

Analytical variable and method	Sample pair	True value 1	True value 2	Total no.	Labs. excl.	Median 1	Median 2	Mean/std.dev. Sample 1		Mean/std.av. Sample 2		Rel.std.dev. % 1	Rel.std.dev. % 2	Rel. error % 1	Rel. error % 2
pH	AB	6,70	7,20	73	3	6,70	7,20	6,64	0,21	7,17	0,24	3,2	3,3	-0,9	-0,4
No stirring				32	2	6,68	7,23	6,67	0,19	7,21	0,15	2,9	2,1	-0,5	0,1
Stirring				39	1	6,69	7,20	6,61	0,23	7,13	0,28	3,5	4,0	-1,4	-1,0
Equilibration				2	0			6,75		7,33				0,7	1,7
Conductivity	AB	2,96	6,40	72	6	2,96	6,40	2,95	0,18	6,38	0,27	6,1	4,2	-0,2	-0,3
Alkalinity	AB	0,094	0,312	59	10	0,094	0,312	0,095	0,019	0,307	0,038	19,6	12,4	0,9	-1,5
Gran plot titration				24	3	0,094	0,316	0,094	0,013	0,317	0,019	14,2	6,0	0,1	1,7
End point titration				10	3	0,096	0,310	0,097	0,019	0,287	0,061	19,3	21,4	3,3	-7,9
End point 5.6				1	0			0,088		0,311				-6,4	-0,3
End point 5.4				5	0	0,093	0,320	0,103	0,023	0,321	0,020	21,9	6,3	10,0	3,0
End point 4.5				12	3	0,098	0,307	0,102	0,021	0,292	0,059	20,4	20,2	8,4	-6,4
Colorimetry				1	0			0,050		0,300				-46,8	-3,8
Not documented				6	1	0,085	0,313	0,084	0,022	0,310	0,025	26,1	8,0	-10,4	-0,7
Nitrate + nitrite-nitrogen	AB	242	295	71	7	242	295	240	22	293	19	9,1	6,5	-0,8	-0,7
Autoanalyzer				17	1	245	297	247	24	294	22	9,5	7,4	2,2	-0,2
Photometry				8	3	243	289	235	37	297	27	15,8	9,0	-3,0	0,6
Ion chromatography				39	2	238	293	236	14	289	14	6,1	5,0	-2,5	-2,0
Hydrazine				3	1			243		317				0,2	7,5
Cap. electrophoresis				2	0			241		293				-0,6	-0,7
Photometry, undefined				1	0			261		291				7,8	-1,3
Electrometry				1	0			280		350				15,7	18,6
Chloride	AB	2,20	3,49	68	6	2,20	3,49	2,21	0,15	3,49	0,21	6,6	5,9	0,6	0,1
Ion chromatography				56	2	2,20	3,49	2,19	0,12	3,47	0,20	5,5	5,7	-0,6	-0,6
AA				1	0			2,20		3,44				0,0	-1,4
Argentometry				1	1			5,50		6,53				150,0	87,1
Manual, Hg				6	2	2,49	3,87	2,41	0,23	3,80	0,23	9,6	6,1	9,4	8,9
Cap. Electrophoresis				2	0			2,35		3,56				6,7	2,1
Potentiometry				1	1			5,47		4,12				148,6	18,1
Photometry				1	0			2,59		3,51				17,7	0,6
Sulfate	AB	2,92	6,01	67	8	2,92	6,01	2,87	0,21	6,01	0,39	7,5	6,5	-1,8	0,0
Ion chromatography				56	2	2,91	6,01	2,87	0,20	6,02	0,38	7,0	6,3	-1,8	0,2
Photometry				5	3			2,62		5,49				-10,4	-8,7
Nephelometry				3	3			4,64		8,18				59,0	36,1
ICP-AES				1	0			3,12		6,48				6,8	7,8
Cap. electrophoresis				2	0			2,99		6,03				2,4	0,4

Analytical variable and method	Sample pair	True value 1	True value 2	Total no.	Labs. excl.	Median 1	Median 2	Mean/std.dev. Sample 1		Mean/std.av. Sample 2		Rel.std.dev. % 1	Rel.std.dev. % 2	Rel. error % 1	Rel. error % 2
Calcium	AB	2,80	8,05	66	5	2,80	8,05	2,82	0,29	8,09	0,67	10,2	8,3	0,6	0,5
FAAS				21	4	2,74	7,92	2,74	0,23	7,86	0,47	8,5	5,9	-2,0	-2,4
ICP-AES				12	0	2,77	7,99	2,74	0,11	7,93	0,31	4,0	3,9	-2,3	-1,5
EDTA				3	0	2,80	7,60	2,68	0,28	7,60	0,53	10,3	7,0	-4,4	-5,6
Ion chromatography				26	1	2,91	8,23	2,93	0,37	8,37	0,82	12,5	9,7	4,6	4,0
ICP-MS				3	0	2,85	8,07	2,82	0,16	8,26	0,93	5,7	11,3	0,8	2,6
Cap. Electrophoresis				1	0			2,66		8,11				-5,0	0,7
Magnesium	AB	0,470	0,672	67	6	0,470	0,672	0,479	0,063	0,688	0,088	13,0	12,9	2,0	2,5
FAAS				21	4	0,464	0,670	0,489	0,057	0,701	0,080	11,7	11,4	4,0	4,5
ICP-AES				12	0	0,461	0,660	0,463	0,043	0,665	0,038	9,3	5,7	-1,4	-0,9
EDTA				3	0	0,560	0,850	0,550	0,056	0,820	0,147	10,1	18,0	17,0	22,2
Ion chromatography				27	1	0,475	0,680	0,471	0,073	0,672	0,096	15,4	14,3	0,3	0,2
ICP-MS				3	1			0,496		0,721				5,5	7,5
Cap. Electrophoresis				1	0			0,490		0,670				4,3	-0,1
Sodium	AB	1,69	2,68	63	2	1,69	2,68	1,68	0,11	2,67	0,17	6,8	6,2	-0,7	-0,5
FAAS				17	1	1,69	2,66	1,71	0,15	2,64	0,20	8,8	7,5	0,9	-1,5
ICP-AES				10	0	1,65	2,69	1,65	0,09	2,68	0,10	5,5	3,8	-2,2	-0,1
AES				7	0	1,65	2,63	1,61	0,15	2,62	0,18	9,0	6,9	-4,7	-2,2
Ion chromatography				26	1	1,69	2,68	1,69	0,08	2,68	0,17	5,0	6,2	-0,1	0,0
ICP-MS				2	0			1,76		2,81				3,8	4,9
Cap. Electrophoresis				1	0			1,60		2,69				-5,3	0,4
Potassium	AB	0,320	0,559	63	4	0,320	0,559	0,319	0,040	0,553	0,051	12,5	9,2	-0,4	-1,0
FAAS				17	1	0,335	0,560	0,341	0,041	0,566	0,055	12,1	9,8	6,5	1,3
ICP-AES				10	0	0,313	0,565	0,318	0,034	0,559	0,040	10,6	7,1	-0,5	0,0
AES				7	0	0,330	0,564	0,331	0,019	0,563	0,015	5,7	2,6	3,5	0,8
Ion chromatography				26	2	0,310	0,550	0,306	0,034	0,546	0,056	11,1	10,2	-4,5	-2,4
ICP-MS				2	1			0,316		0,520				-1,3	-7,0
Cap. Electrophoresis				1	0			0,200		0,440				-37,5	-21,3
Iron	CD	60,7	47,0	37	7	60,7	47,0	60,2	6,6	46,6	7,9	10,9	16,9	0,0	-0,9
FAAS				9	4	60,0	50,0	62,5	7,0	50,2	5,9	11,2	11,8	3,8	6,8
GFAAS				5	2	63,8	52,6	61,6	12,6	51,5	16,0	20,5	31,1	2,3	9,6
ICP-AES				12	0	61,6	47,0	61,4	3,7	46,3	5,2	6,0	11,2	2,0	-1,5
ICP-MS				11	1	57,0	41,6	56,8	6,9	43,3	8,3	12,2	19,1	-5,7	-7,8
Manganese	CD	3,07	2,40	40	6	3,07	2,40	3,08	0,29	2,40	0,38	9,3	15,6	0,8	0,1
FAAS				5	4			2,60		2,10				-14,8	-12,5
GFAAS				10	1	3,22	2,40	3,27	0,36	2,41	0,57	11,0	23,5	7,2	0,5
ICP-AES				12	1	3,00	2,30	2,98	0,20	2,32	0,36	6,8	15,4	-2,1	-3,3
ICP-MS				13	0	3,05	2,47	3,05	0,22	2,49	0,19	7,1	7,5	0,1	3,9

Analytical variable and method	Sample pair	True value 1	True value 2	Total no.	Labs. excl.	Median 1	Median 2	Mean/std.dev. Sample 1		Mean/std.av. Sample 2		Rel.std.dev. % 1	Rel.std.dev. % 2	Rel. error % 1	Rel. error % 2
Kadmium	CD	0,028	0,040	38	30	0,028	0,040	0,026	0,003	0,039	0,001	12,2	2,9	-2,6	-1,4
FAAS				4	4										
GFAAS				14	12			0,027		0,041				-1,9	1,3
ICP-AES				10	10										
ICP-MS				10	4	0,027	0,039	0,026	0,004	0,039	0,001	14,4	2,6	-3,0	-2,5
Bly	CD	0,075	0,040	39	36	0,075	0,040	0,076	0,004	0,042	0,005	5,3	11,3	0,9	4,2
FAAS				4	4										
GFAAS				13	13										
ICP-AES				9	9										
ICP-MS				13	10	0,075	0,040	0,076	0,004	0,042	0,005	5,3	11,3	0,9	4,2
Kopper	CD	12,90	3,01	41	15	12,90	3,01	12,84	0,51	3,05	0,27	4,0	8,8	-1,3	1,0
FAAS				4	3			13,00		2,90				0,0	-4,0
GFAAS				13	8	13,00	3,20	12,73	0,76	3,14	0,30	5,9	9,7	-2,1	4,0
ICP-AES				11	4	13,00	3,10	12,93	0,55	3,07	0,44	4,3	14,3	-0,5	1,6
ICP-MS				13	0	12,80	3,01	12,81	0,42	3,01	0,11	3,3	3,6	-1,4	-0,2
Nikkel	CD	0,47	0,45	36	23	0,45	0,46	0,45	0,07	0,47	0,10	15,3	20,5	-4,4	1,8
FAAS				3	3										
GFAAS				12	11			0,48		0,54				2,1	17,4
ICP-AES				9	6	0,40	0,40	0,37	0,05	0,36	0,07	14,0	19,2	-21,3	-21,7
ICP-MS				12	3	0,47	0,49	0,48	0,06	0,50	0,08	11,7	15,7	1,1	8,7
Zinc	CD	6,83	21,90	41	12	6,83	21,90	7,36	1,56	21,73	2,22	21,2	10,2	7,9	0,8
FAAS				10	6	10,00	22,28	10,01	0,03	23,64	4,75	0,2	20,1	46,8	9,7
GFAAS				6	4			7,00		20,95				2,6	-2,8
ICP-AES				14	2	6,35	20,70	6,75	1,19	20,74	1,39	17,7	6,7	-1,1	-3,8
ICP-MS				11	0	6,81	22,50	7,11	1,08	22,32	0,98	15,1	4,4	4,2	3,6

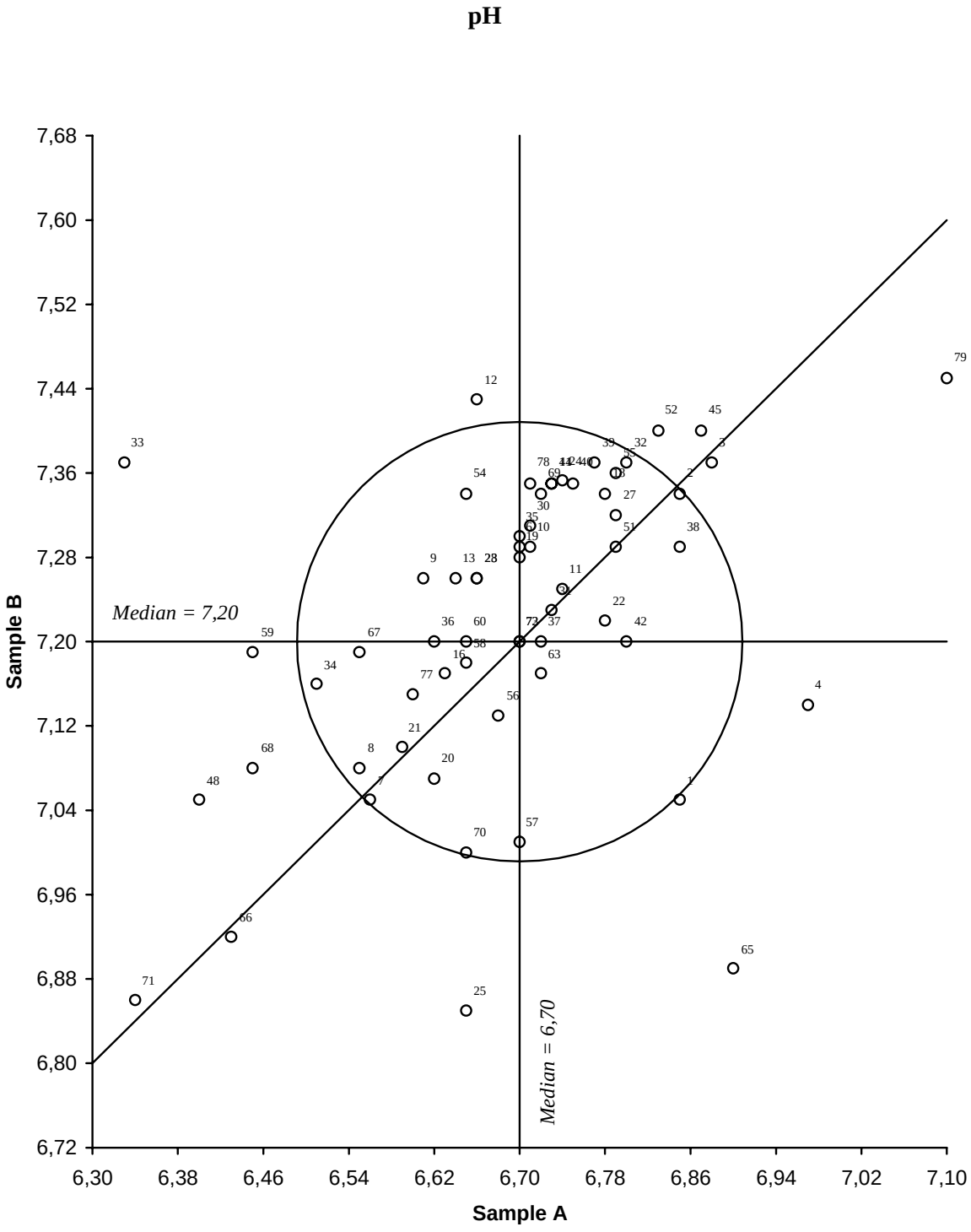

Figure 1. Youden diagramme for pH, sample pair AB
Acceptance limit, given by circle, is 0,2 pH units

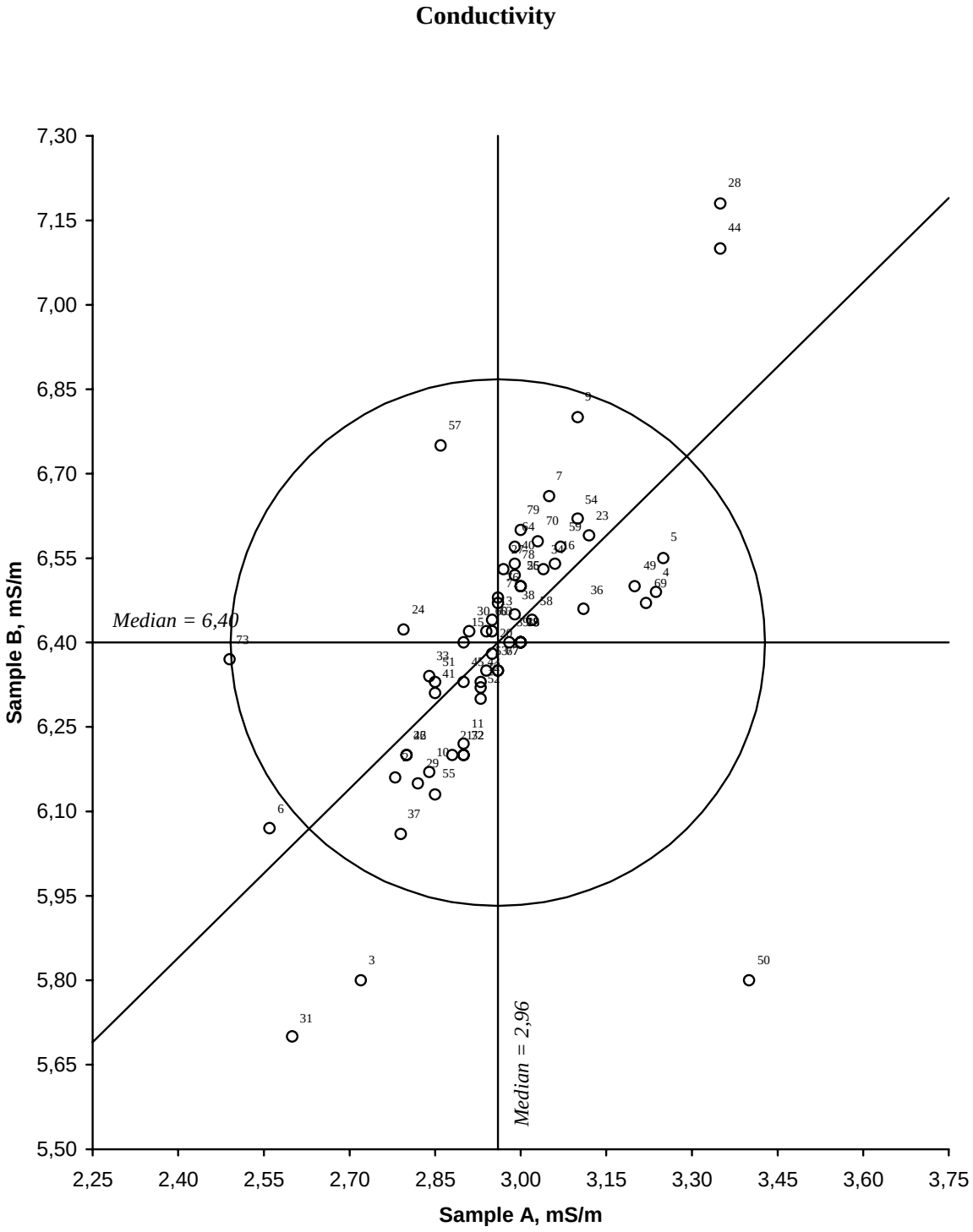

Figure 2. Youden diagramme for conductivity, sample pair AB
Acceptance limit, given by circle, is 10 %

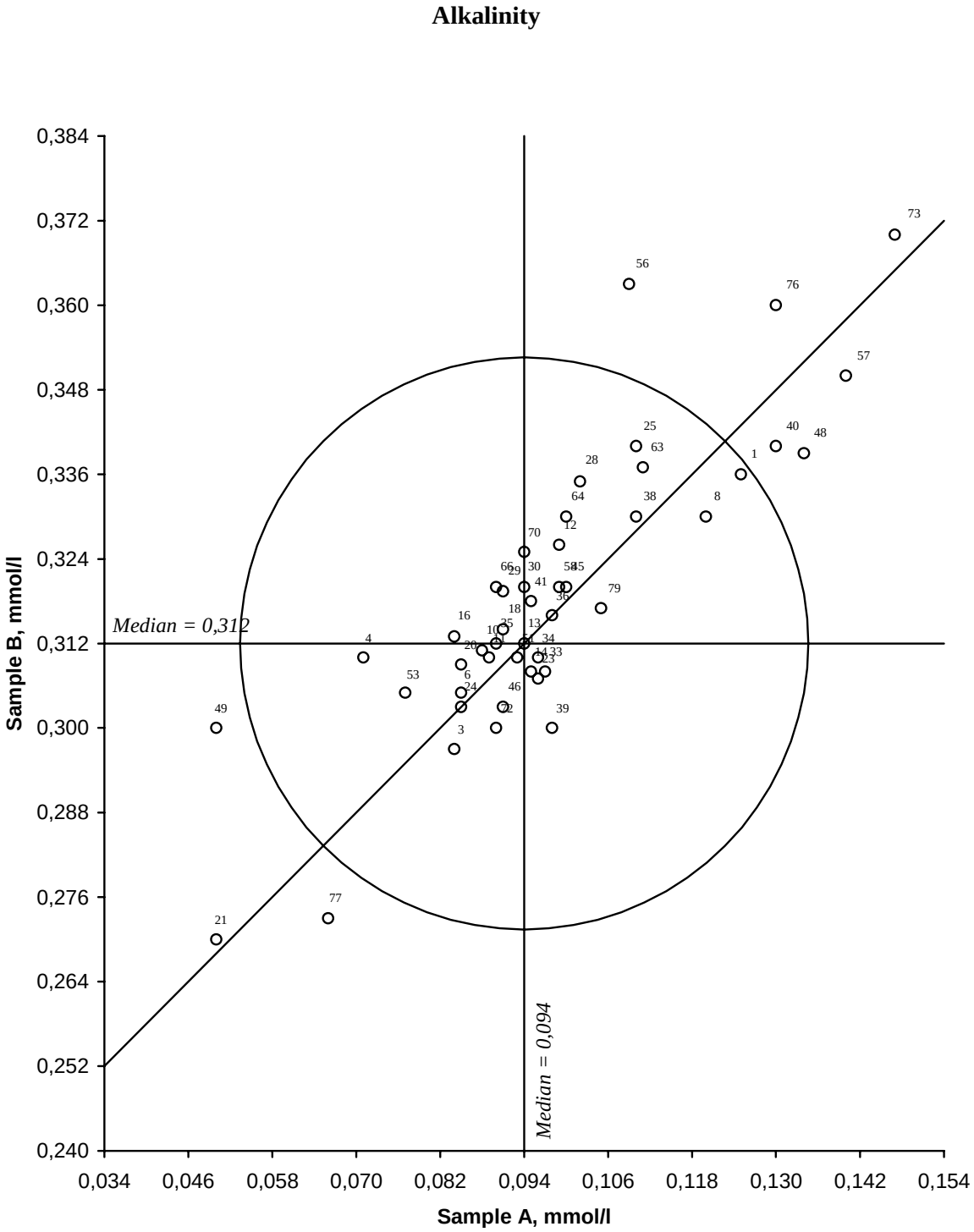

Figure 3. Youden diagramme for alkalinity, sample pair AB
Acceptance limit, given by circle, is 20 %

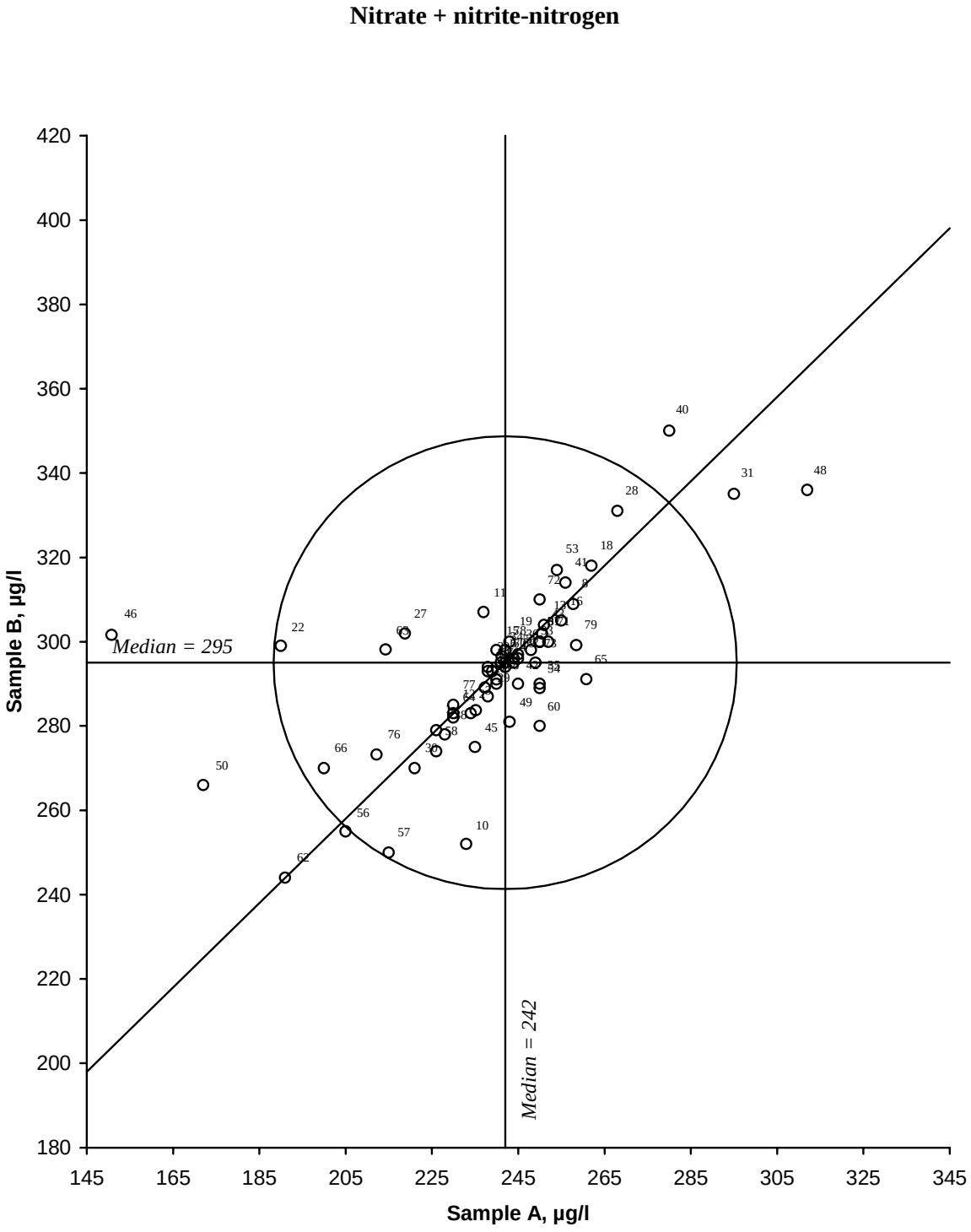

Figure 4. Youden diagramme for nitrate + nitrite-nitrogen, sample pair AB
Acceptance limit, given by circle, is 20 %

Chloride

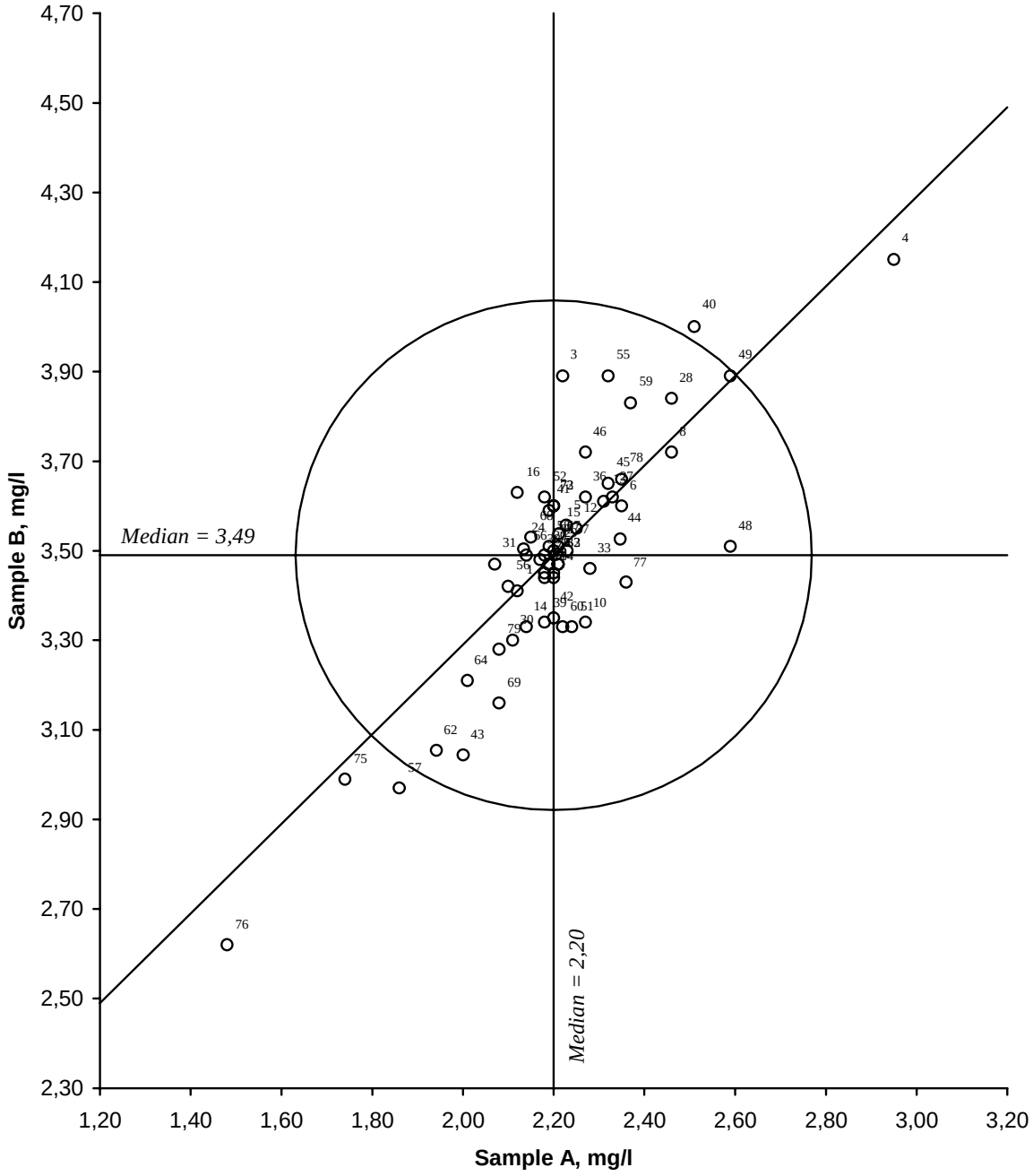

Figure 5. Youden diagramme for chloride, sample pair AB
Acceptance limit, given by circle, is 20 %

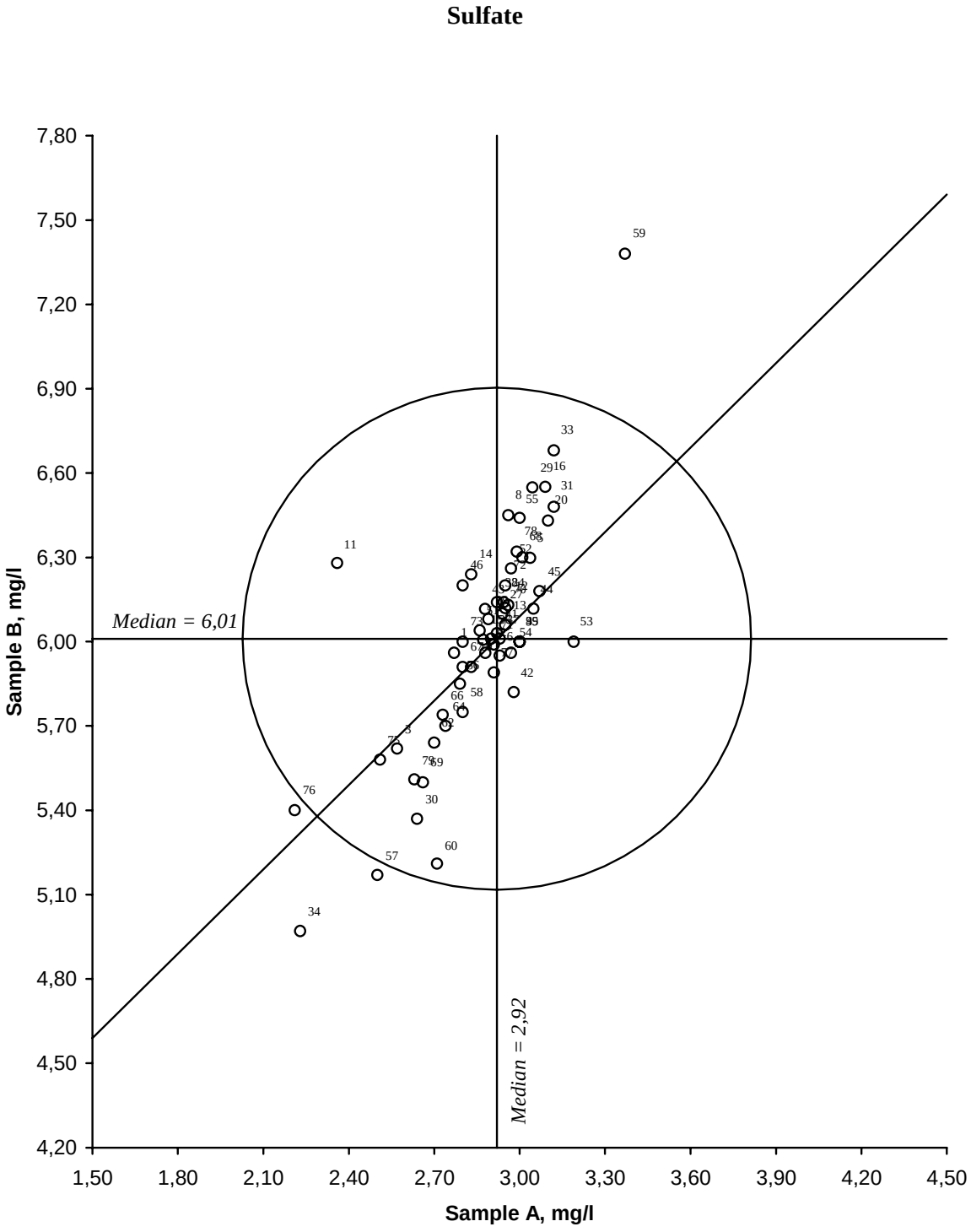

Figure 6. Youden diagramme for sulfate, sample pair AB
Acceptance limit, given by circle, is 20 %

Calcium

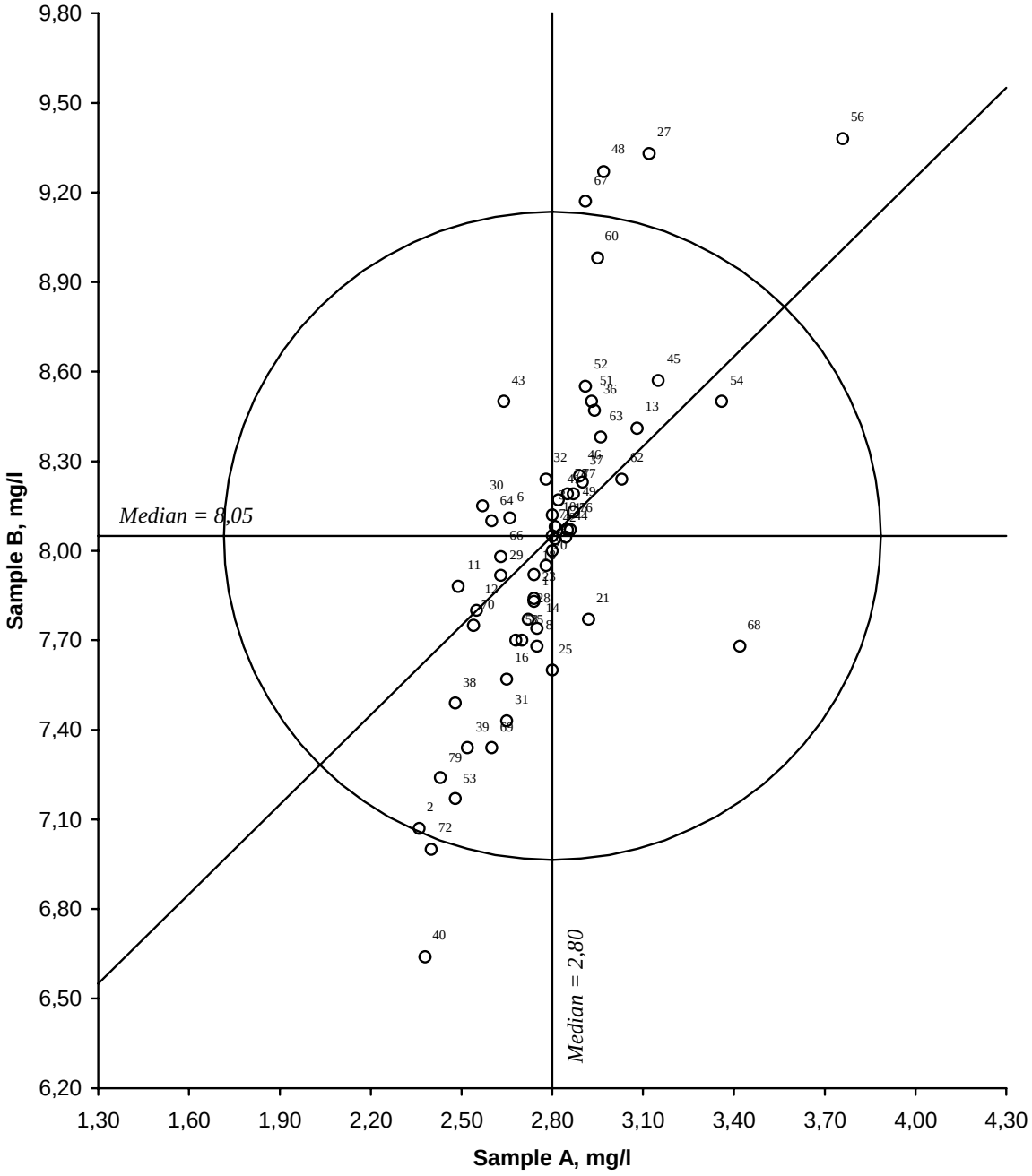

Figure 7. Youden diagramme for calcium, sample pair AB
Acceptance limit, given by circle, is 20 %

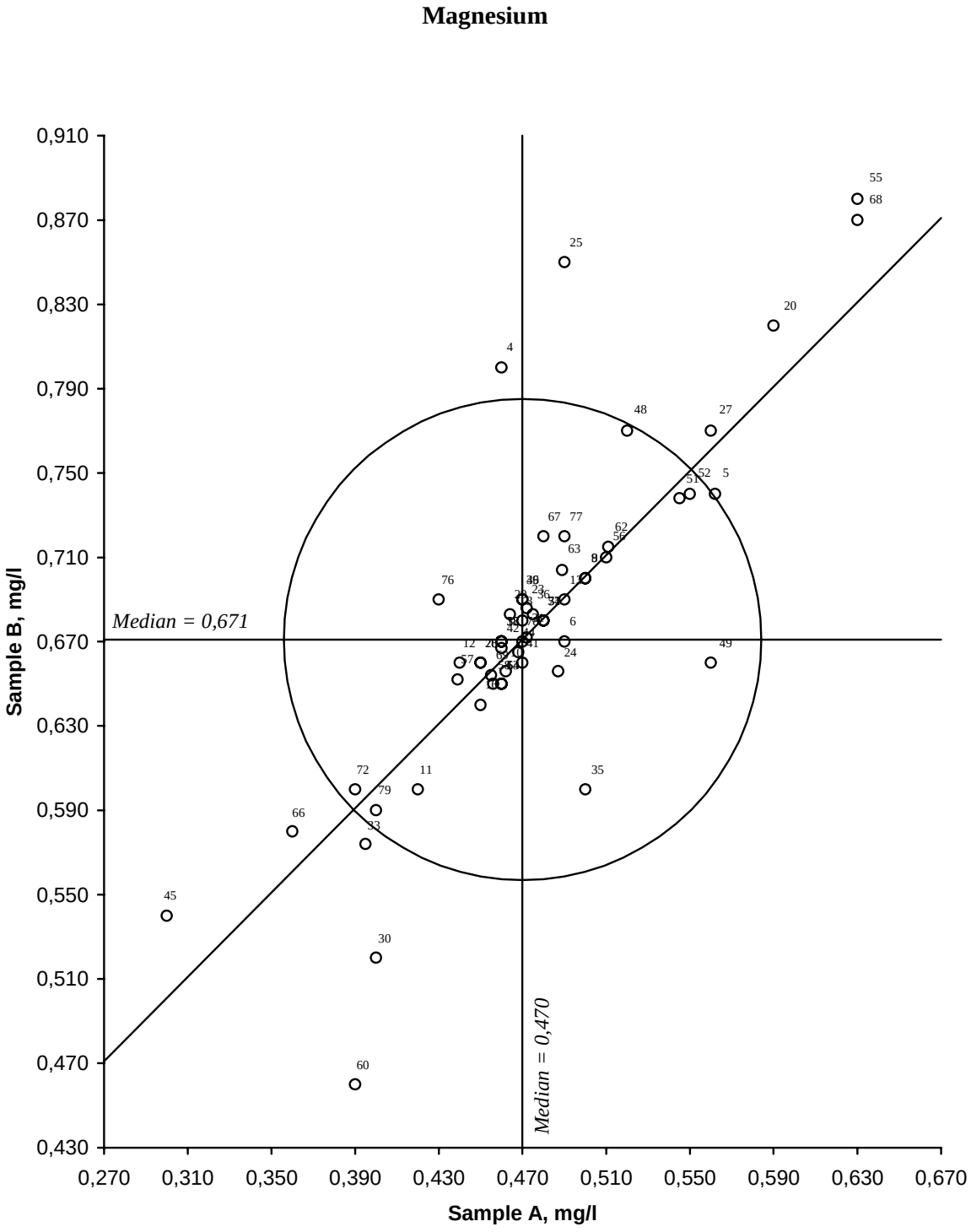

Figure 8. Youden diagramme for magnesium, sample pair AB
Acceptance limit, given by circle, is 20 %

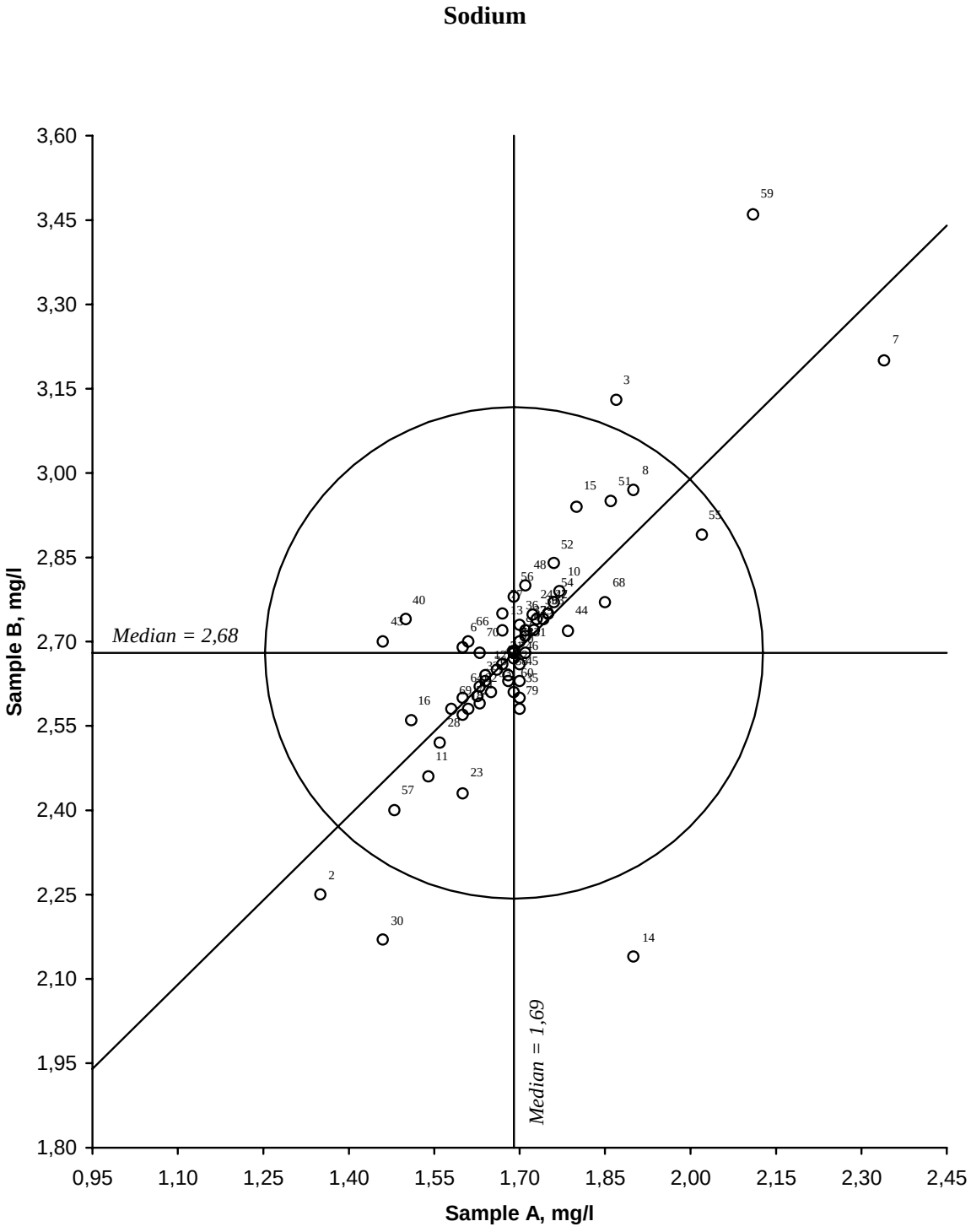

Figure 9. Youden diagramme for sodium, sample pair AB
Acceptance limit, given by circle, is 20 %

Potassium

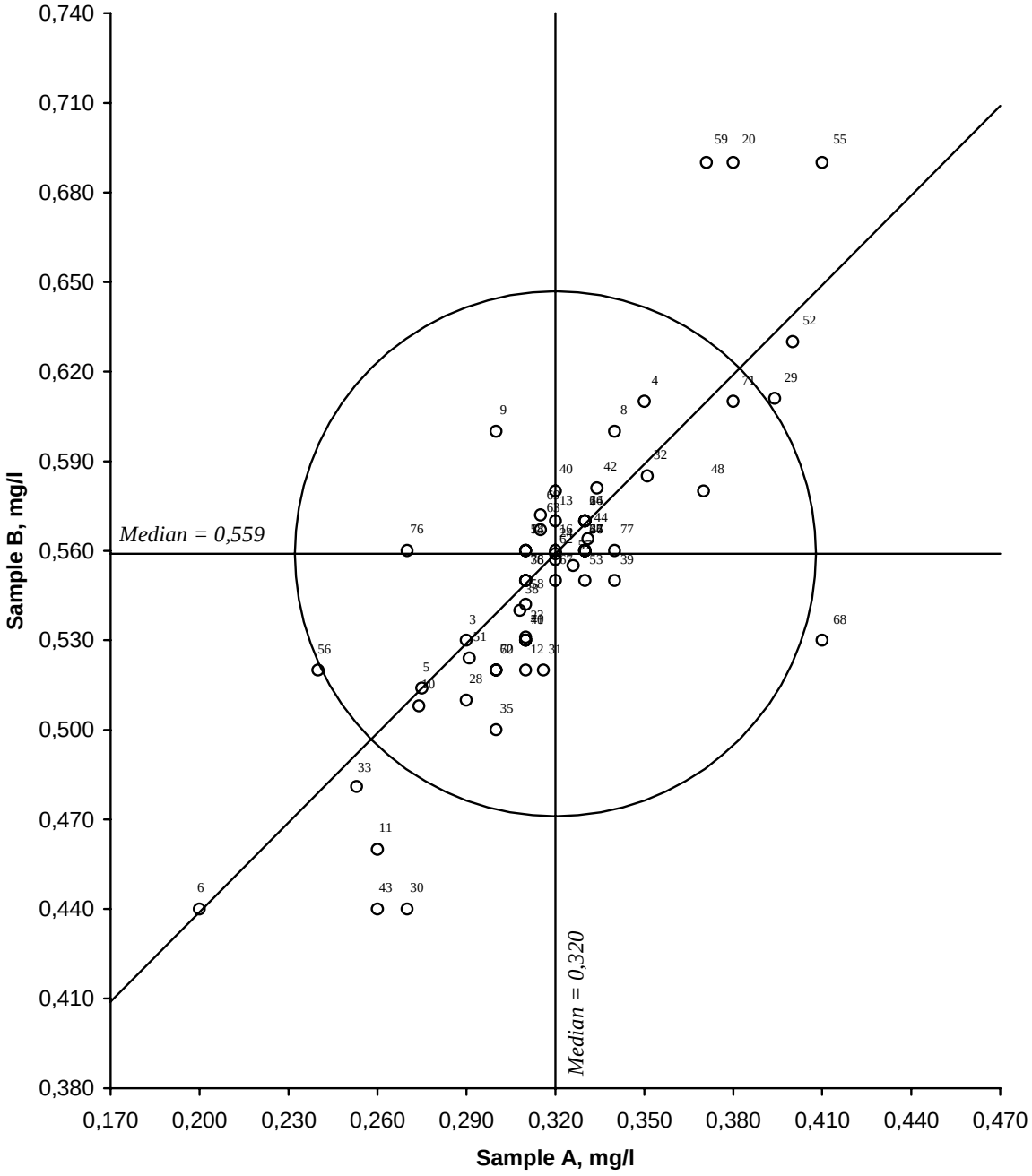

Figure 10. Youden diagramme for potassium, sample pair AB
Acceptance limit, given by circle, is 20 %

Iron

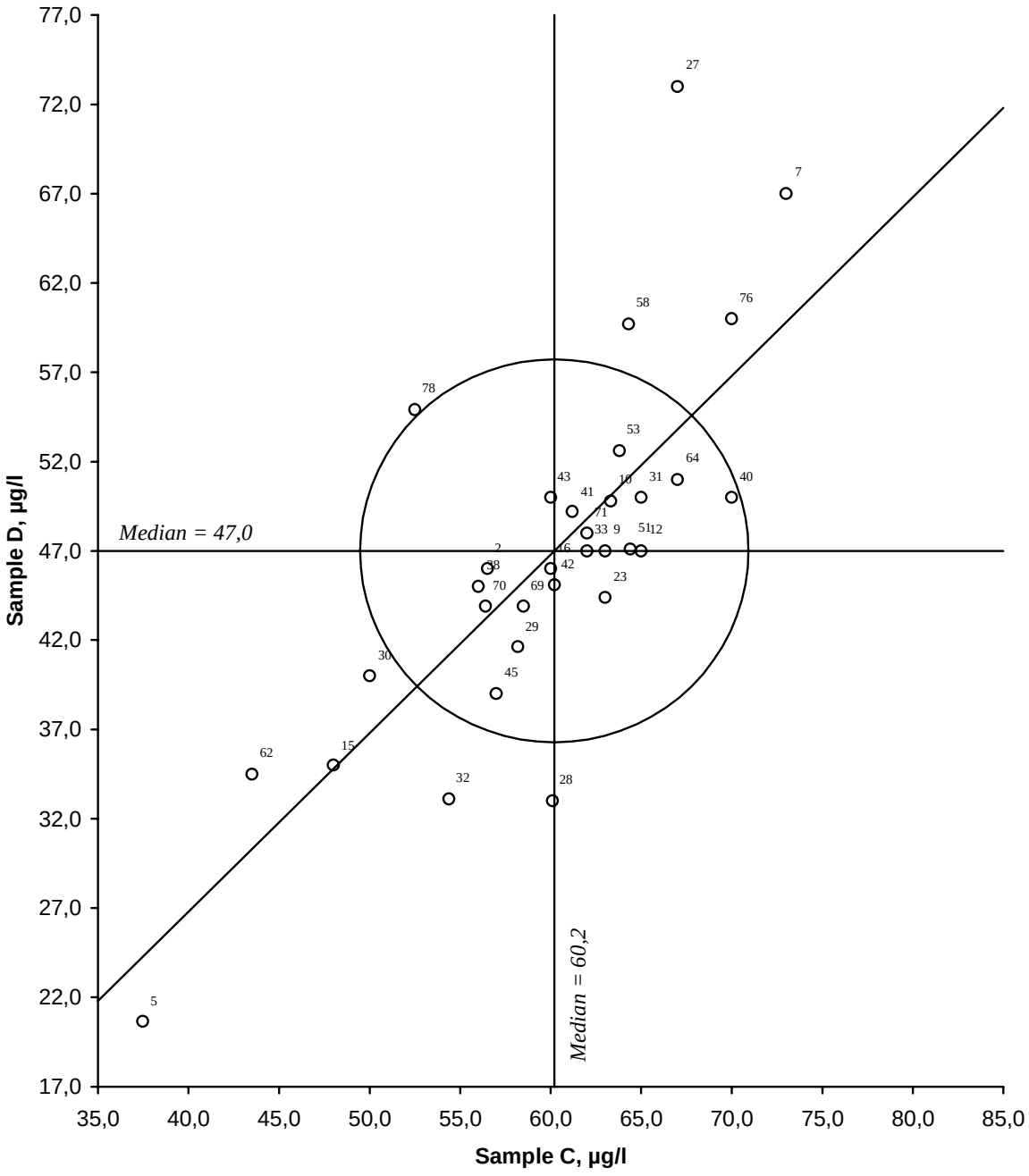

Figure 11. Youden diagramme for iron, sample pair CD
Acceptance limit, given by circle, is 20 %

Manganese

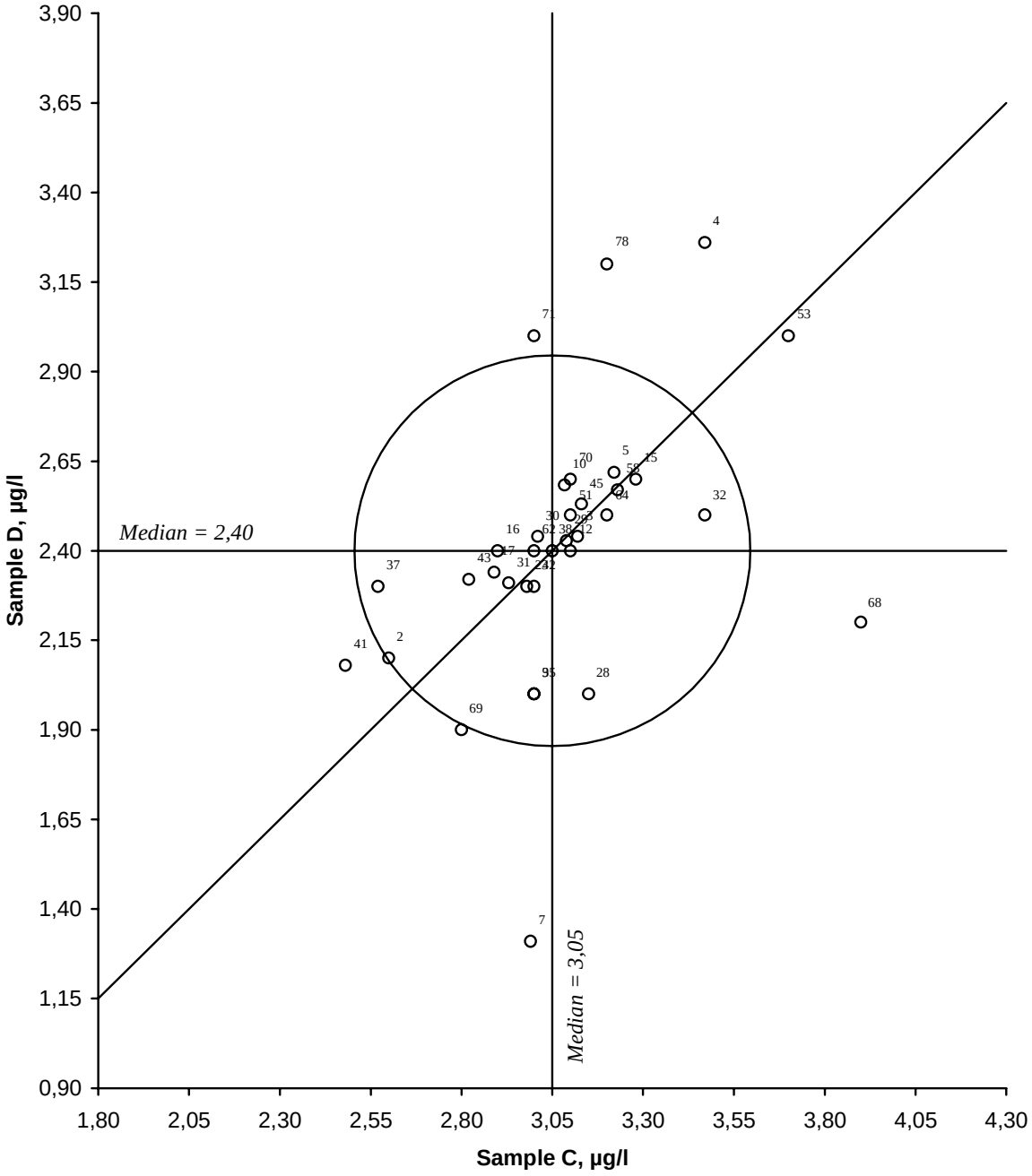

Figure 12. Youden diagramme for manganese, sample pair CD
Acceptance limit, given by circle, is 20 %

Cadmium

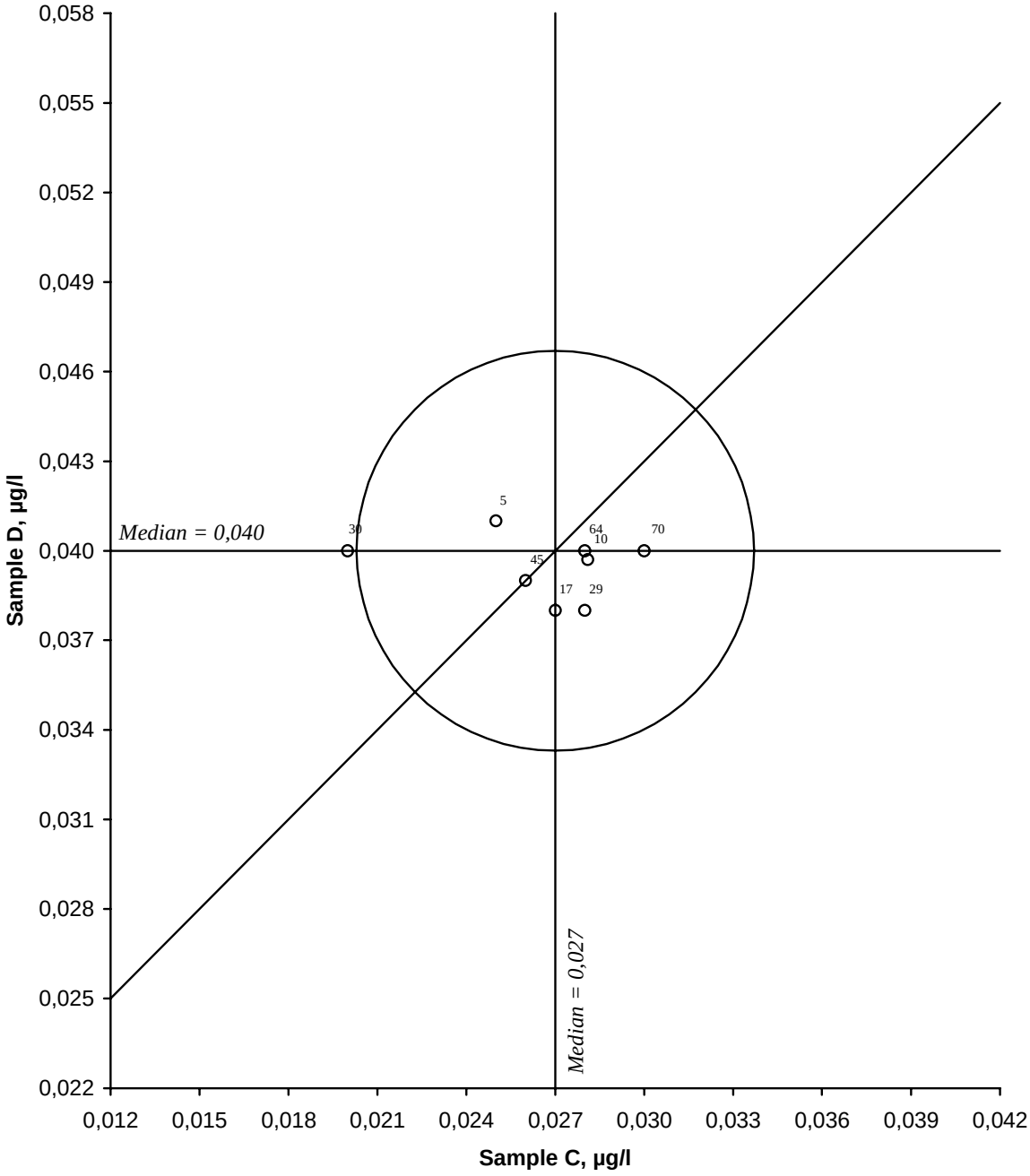

Figure 13. Youden diagramme for cadmium, sample pair CD
Acceptance limit, given by circle, is 20 %

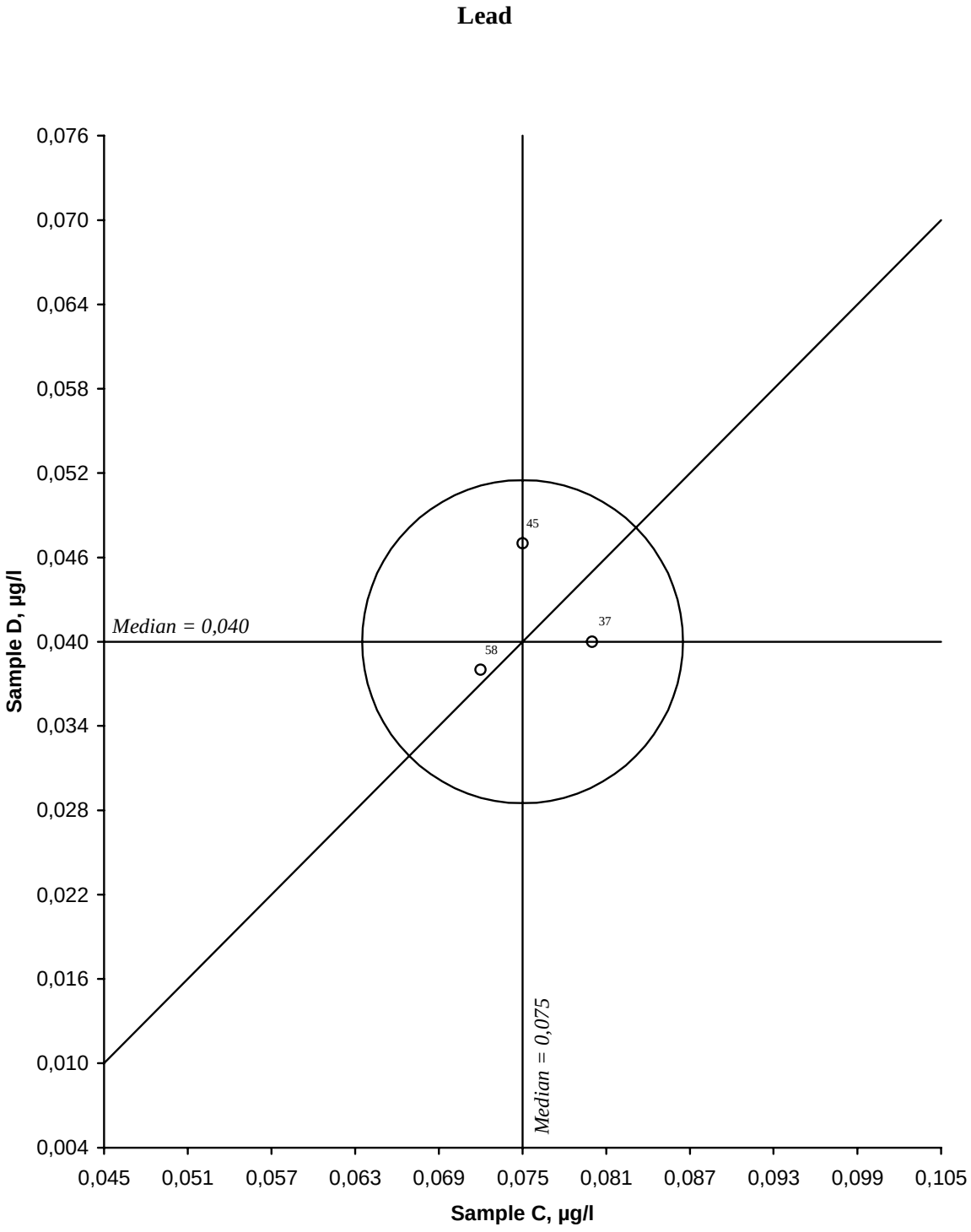

Figure 14. Youden diagramme for lead, sample pair CD
Acceptance limit, given by circle, is 20 %

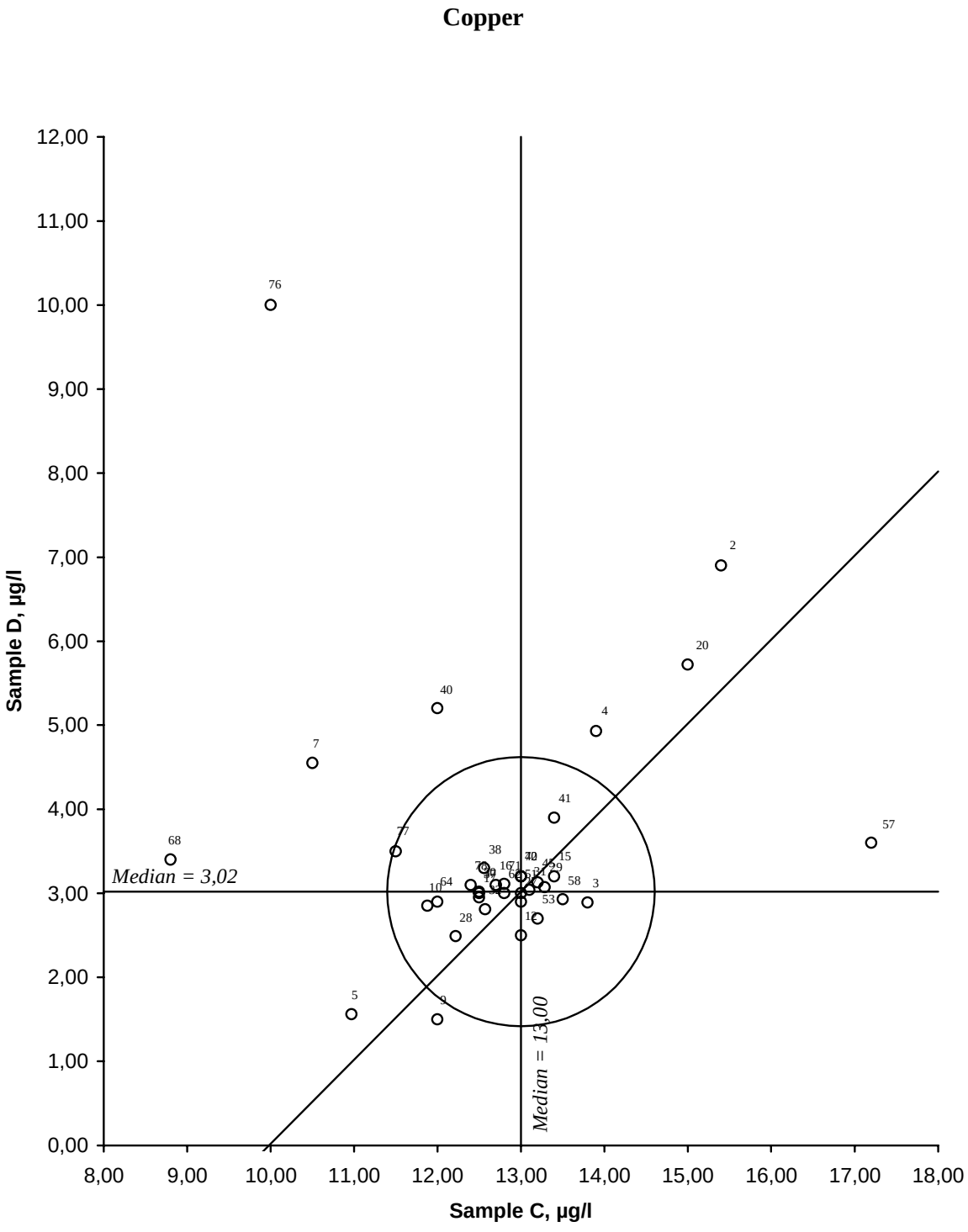

Figure 15. Youden diagramme for copper, sample pair CD
Acceptance limit, given by circle, is 20 %

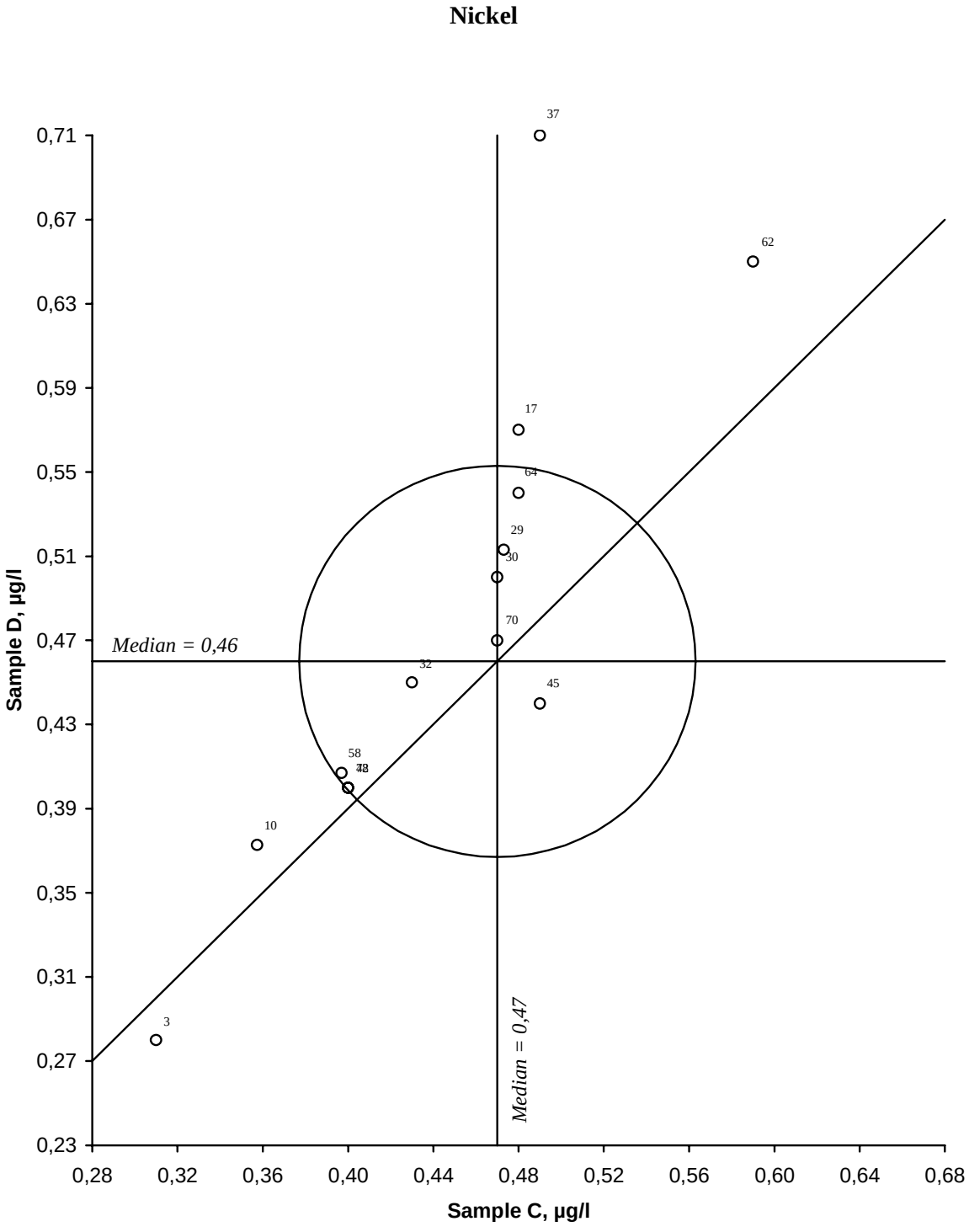

Figure 16. Youden diagramme for nickel, sample pair CD
Acceptance limit, given by circle, is 20 %

Zinc

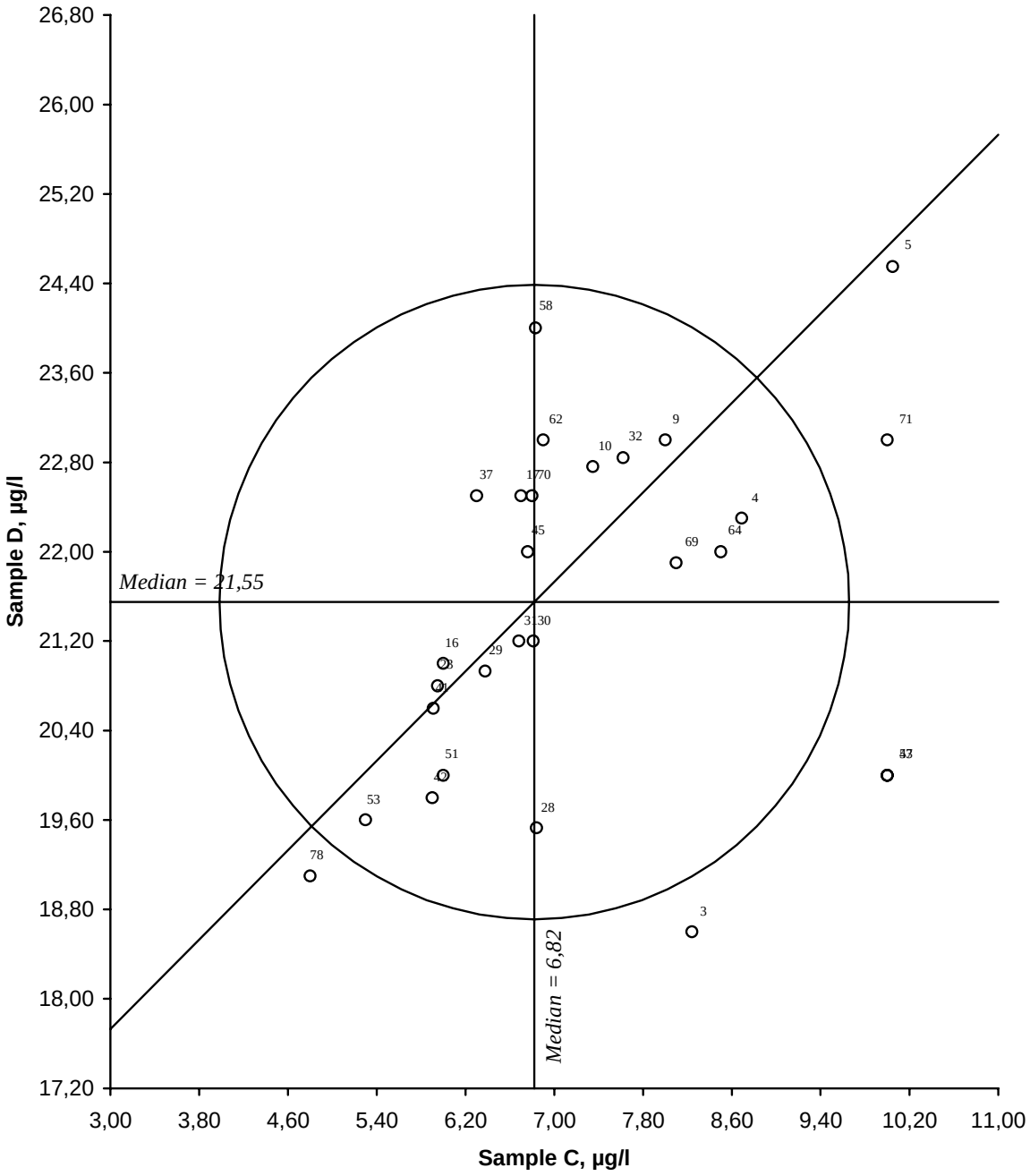

Figure 17. Youden diagramme for zinc, sample pair CD
Acceptance limit, given by circle, is 20 %

5. Discussion

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

In Table 2 an evaluation of the results of intercomparison 0519 is presented, based on the target accuracy (except for pH and conductivity), where the number and percentage of acceptable results are given. 73 % of the results submitted by the participants are acceptable when compared to the acceptance limits given above. Then the trace metals cadmium, lead and nickel, which were present in very low concentrations, had been excluded from the evaluation. By improvement of the routine analytical method, the laboratories should be able to obtain even more accurate and comparable results.

For pH, the general target accuracy is ± 0,1 pH units (1), and far less than 50 % of the result pairs are found within these accuracy limits. However, we have chosen to extend the acceptance limit to ± 0,2 pH units, because of the great spreading of the results for these two samples which are close to neutrality, and therefore are supposed not to be completely in CO_2-equilibrium. Even with this wider acceptance limit only 63 % of the result pairs are evaluated as acceptable.

Problems with poor comparability between the reported results for pH probably arise from the fact that the pH results are 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 for pH determination are used by the participating laboratories. This problem is well demonstrated for the equilibration method, which normally gives results quite higher than the other methods. 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 ± 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 to 90 %. It is still a problem that many laboratories report their results in the units they normally use at their laboratory. They very often do not write the unit used, nor do they use the unit asked for in this intercomparison, mS/m. Some correspondence with the laboratories was therefore 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 unit mS/m.

For alkalinity, as we have observed earlier, the reported results for solutions with low alkalinity values are more widely spread than in solutions with higher concentrations of bicarbonate. In this intercomparison, the results are a little better than in the last

intercomparison, probably because the concentrations of bicarbonate in the samples used this time is a little higher. Also for this parameter there is some confusion among the participants about the unit.

Table 2. Evaluation of the results of intercomparison 0519. N is the number of result pairs reported, and n is the number of acceptable results within the given target accuracy.

Analytical variable	Sample	True value		Accept.	N	n	% accept. res. for intercomp.			
and unit	pair	1	2	limit, %	Tot.	Accept.	0519	0418	0317	0216
pH	AB	6,70	7,20	0,2 *	73	46	63	57	57	66
Conductivity, mS/m	AB	2,96	6,40	10 ¤	72	58	81	80	82	75
Alkalinity, mmol/l	AB	0,094	0,312	20	59	37	63	52	58	53
Nitrate + nitrite-nitrogen, µg/l	AB	242	295	20	71	58	82	81	82	59
Chloride, mg/l	AB	2,20	3,49	20	69	59	86	84	81	66
Sulfate, mg/l	AB	2,92	6,01	20	68	55	81	86	83	76
Calcium, mg/l	AB	2,80	8,05	20	67	53	79	80	77	62
Magnesium, mg/l	AB	0,470	0,672	20	67	47	69	80	79	67
Sodium, mg/l	AB	1,69	2,68	20	64	57	89	87	92	88
Potassium, mg/l	AB	0,320	0,559	20	64	47	73	75	70	73
Iron, µg/l	CD	60,7	47	20	37	21	57	69	51	71
Manganese, µg/l	CD	3,07	2,40	20	40	26	65	59	36	76
Kadmium, µg/l	CD	0,028	0,040	20	(38)	(7)	(1)8	76	60	63
Bly, µg/l	CD	0,075	0,040	20	(39)	(3)	(8)	78	49	59
Kopper, µg/l	CD	12,9	3,01	20	41	26	63	95	83	73
Nikkel, µg/l	CD	0,47	0,45	20	(36)	(9)	(25)	80	68	68
Zinc, µg/l	CD	6,83	21,9	20	41	22	54	82	76	64
Total					**834**	**612**	**73**	**(77)**	**(71)**	**(68)**

* The acceptance limit is extended from the target value of ± 0,1 to ± 0,2 pH units
¤ The acceptance limit is reduced from the target value of ± 20 % to ± 10 %

For nitrate + nitrite 82 % of the result pairs are acceptable. This is comparable to the results last year, and the nitrate concentrations in this intercomparison are rather high. In some few earlier intercomparisons this analytical variable proved to be unstable, however, this time the control analyses at the Programme Centre demonstrated that the samples were stable with respect to the content of nitrate and nitrite, throughout the whole periode of the intercomparison.

For calcium and magnesium a smaller fraction of the result pairs are acceptable in this intercomparison compared to earlier years, and the fraction of acceptable results are 79 and 69 % for calcium and magnesium, respectively. For the other major ions, chloride, sulphate, sodium and potassium, the number of acceptable results are high as usual.

Some heavy metals were included in this intercomparison programme. The best results were obtained for manganese and copper where 65 and 63 % of the results, respectively, are

acceptable. This is not very good. For most of these elements the concentrations were very low this time, especially for the metals cadmium, lead and nickel which were present on the trace level. However, the concentrations of the other metals, except for iron, are also rather low. It is obvious that only very few laboratories have sensitive enough methods to determine heavy metals on the trace level, which is clearly demonstrated in the tables 5.13, 5.14 and 5.16 containing very many results reported as less than the detection limit. These tables also illustrate the big differences in detection limit at the participating laboratories. Therefore it is decided not to include these three metals in the evaluation of this intercomparison. This is illustrated in table 2 with parentheses around the values, and these values are not included in the total evaluation. It should be discussed what concentration levels for the heavy metals would be most useful for ICP Waters in the future.

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 laboratories.

6. Conclusion

75 laboratories submitted results for this intercomparison. The best results were reported for the analytical variables sodium and sulphate where 87 and 86 % of the results, respectively, were acceptable. The worst results were observed for the heavy metals where the concentrations are rather low.

Overall, 73 % of the evaluated results were located within the general target accuracy of ± 20 %, or the special accuracy limit for pH and conductivity. Cadmium, lead and nickel present in extremely low concentrations had then been excluded from the evaluation. Thus, more than two thirds of the reported results are acceptable. The low fraction of acceptable results for some variables, 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 total error of ± 0,2 pH units seems to be a reasonable assessment of the accuracy for pH measurements, when near neutral water samples - which are not in CO_2 equilibrium - are analyzed. There are obviously systematic differences between the methods used by the participating laboratories for the determination of pH, therefore it is necessary to use some wider acceptance limit for this variable.

7. Literature

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4. Hindar, A.: The Effect of Stirring on pH Readings in Solutions of Low and High Ionic Strength Measured with Electrodes of Different Condition. Vatten 1984, 40, pp 312 - 19 (in norwegian).

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

Appendix A.

The participating laboratories

Identiy	Name of participant	City	Country
1	Tallinn Technical University	Tallinn	Estonia
2	Geological Survey of Estonia	Tallinn	Estonia
3	Sezione Protezione Aria, Aqua & Suolo	Bellinzona	Switzerland
4	Republican Centre of Radiation Control	Minsk	Republic of Belarus
5	Vlaamse Milieumaatschappij	Antwerpen	Belgium
6	University of Barcelona	Vielha	Spain
7	Analist Service S.R.L.	Bucuresti	Romania
8	University of Alberta	Edmonton	Canada
9	Centre for Ecology & Hydrology	Wallingford	United Kingdom
10	Swedish University for Agricultural Sciences	Uppsala	Sweden
11	CNR-IRSA Water Research Institute	Brugherio	Italy
12	CNR Istituto Studio degli Ecosistemi	Pallanza	Italy
13	Institut fur Zologie, Universitat Innsbruck	Innsbruck	Austria
14	Adirondac Lakes Survey Corporation	Ray Brook	USA
15	Amt der Karntner Landesregierung	Klagenfurt	Austria
16	Umweltbundesamt	Langen	Germany
17	Umweltbundesamt - Messnetz	Langen	Germany
18	Aquatic Chemistry Project	Winnipeg	Canada
19	Freshwater Institute	Winnipeg	Canada
20	University of Helsinki	Helsinki	Finland
21	Environmental Protection Ministry	Vilnius	Lithuania
22	MOEE, Toronto Laboratory	Etobicoke	Canada
23	Institute for Ecology of Industrial Areas	Katowice	Poland
24	IVL AB	Gothenburg	Sweden
25	Virumaa Environmental Research	Johvi	Estonia
27	Air Quality and Noise Management Division	Bangkok	Thailand
28	ECOANALYT	Syktyvkar	Russia
29	LMTG/CNRS	Toulouse	France
30	Charles University, Hydrobiol. Station	Blatna	Czech Republic
31	The Environment Agency	Llanelli	United Kingdom
32	Freshwater Laboratory	Pitlocry	United Kingdom
33	Finnish Forest Research Institute	Rovaniemi	Finland
34	Lapland Water and Environment District	Rovaniemi	Finland
35	North Ostrobothnia Regional Env. Centre	Oulu	Finland
36	Kymen Environmental Laboratory	Kouvola	Finland
37	NILU, Avd. uorganisk analyse	Kjeller	Norway
38	Latvian Environmental Laboratory	Riga	Latvia
39	Shimane Prefectural Inst. Of Public Health	Shimane-ken	Japan
40	Laboratory for Monitoring of Atmosphere	Vladivostok	Russia
41	University of Maine	Orono	USA
42	Landesumweltamt NRW	Essen	Germany
43	Laboratorio do aguas de Santo Andre	Santo Andre	Portugal
44	Institute of Environmental Protection	Warsaw	Poland

Identiy	Name of participant	City	Country
45	Norsk institutt for vannforskning	Oslo	Norway
46	MOEE, Dorseth Research Facility	Dorset	Canada
48	Aquatische Oecologie en Milieubiologie	Nijmegen	Netherlands
49	Laboratory of Hydrochemistry at the	Tartu	Estonia
50	River Biology Laboratory of the EAU Institute	Tartu	Estonia
51	Tartun Environmental Research	Tartu	Estonia
52	Center for Chemical Analysis Keldnaholt	Reykjavik	Iceland
53	Kola Science Center	Apatity	Russia
54	Universita di Firenze	Firenze	Italy
55	Yantai Environmental Monitoring Centre	Yantai	P.R. of China
56	National Institute of Biology, LFTER	Ljubljana	Slovenia
57	Estonian Environment Research Laboratory	Tallinn	Estonia
58	Istituto Agrario di S. Michele	Saint Michele	Italy
59	EMB, DENR Compound	Quezon City	Philippines
60	Laboratorio Biologico Provinciale	Laives	Italy
62	Environmental Protection Agency	Dublin	Irland
63	Environmental Research and Training Center	Pathumthani	Thailand
64	ZAO "ROSSA"35-7 Rodnikovaya	Moscow	Russia
65	Universidad de Granada	Granada	Spain
66	SLU, Skoglig Marklæra	Uppsala	Sweden
67	Acid Deposition and Oxidant Research Center	Niigata-shi	Japan
68	Polish Academy of Sciences	Krakow	Poland
69	Finnish Forest Research Institute	Vantaa	Finland
70	Finnish Environment Institute	Helsinki	Finland
71	Bayerische Landesamt fur Wasserwirtschaft	Munchen	Germany
72	Institute of Hydrobiology, ASCR	Budejovice	Czech Republic
73	Staatliche Umweltbetriebgesellschaft im UBG	Chemnitz	Germany
75	T.G.Masaryk Water Research Institute	Praha	Czech Republic
76	Institute of Environmental Engineering	Zabrze	Poland
77	Chemical Laboratory of CGS	Praha	Czech Republic
78	ISSeP Colfontaine	Wasmes	Belgium
79	EAWAG Limnological Research Center	Kastanienbaum	Switzerland

Number of participating laboratories (N) from the different countries being represented in intercomparison 0519.

Country	N	Country	N	Country	N
Austria	2	Iceland	1	Portugal	1
Belarussia	1	Ireland	1	Romania	1
Belgium	2	Italy	5	Russia	4
Canada	5	Japan	2	Slovenia	1
China	1	Latvia	1	Spain	2
Czech Republic	4	Lithuania	1	Sweden	3
Estonia	7	Netherlands	1	Switzerland	2
Finland	7	Norway	2	Thailand	2
France	1	Philippines	1	United Kingdom	3
Germany	5	Poland	4	USA	2

Appendix B.

Preparation of samples

The sample solutions were prepared from tap water collected from two lakes located outside Oslo, Norway, named Harestuvannet and Maridalsvannet. 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. 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 2005, a few weeks before mailing the samples to the participants. The last sample was analyzed at the end of August 2005. 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.

Table 3. Summary of the control analyses.

Analytical variable	Sample A		Sample B	
	Mean	Std. dev.	Mean	Std. dev.
pH	6,66	0,27	7,14	0,36
Conductivity mS/m	2,91	0,01	6,30	0,02
Alkalinity mmol/l	0,096	0,005	0,316	0,003
Nitrate/nitrite µg/l	233	12,6	268	16,1
Chloride mg/l	2,25	0,06	3,54	0,10
Sulphate mg/l	2,93	0,12	5,97	0,20
Calcium mg/l	3,07	0,07	8,50	0,09
Magnesium mg/l	0,48	0,03	0,74	0,04
Sodium mg/l	1,70	0,03	2,62	0,05
Potassium mg/l	0,30	0,02	0,53	0,02
	Sample C		**Sample D**	
Iron, µg/l	60,7	3,2	44,3	5,0
Manganese, µg/l	3,32	0,16	2,69	0,14
Cadmium, µg/l	0,025	0,002	0,043	0,006
Lead, µg/l	0,085	0,009	0,052	0,007
Copper, µg/l	13,4	0,40	3,26	0,15
Nickel, µg/l	0,48	0,03	0,42	0,03
Zinc, µg/l	6,56	0,22	21,7	0,4

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-nitrogen, µg/l	
	A	B	A	B	A	B	A	B
1	6,85	7,05	3,0	6,4	0,125	0,336	226	279
2	6,85	7,34	2,78	6,16	0,21	0,41	234	283
3	6,88	7,37	2,72	5,80	0,084	0,297	235,2	283,7
4	6,97	7,14	3,237	6,490	0,071	0,310	355,8	469,9
5	6,34	6,62	3,25	6,55			244	296
6	6,70	7,29	2,56	6,07	0,085	0,305	241	295
7	6,56	7,05	3,05	6,66	0,06	0,10	471	577
8	6,55	7,08	2,25	4,85	0,12	0,33	257,8	308,9
9	6,61	7,26	3,1	6,8			250	300
10	6,71	7,29	2,84	6,17	0,088	0,311	233	252
11	6,74	7,25	2,90	6,22	0,089	0,310	237	307
12	6,66	7,43	2,93	6,32	0,099	0,326	230	283
13	6,64	7,26	2,95	6,44	0,094	0,312	251	304
14	6,73	7,35	292	635	0,095	0,308	238	293
15	6,1	6,7	2,9	6,4	0,23	0,45	240	298
16	6,63	7,17	3,06	6,54	0,084	0,313	255	305
17								
18	6,78	7,34	3,0	6,4	0,091	0,314	262	318
19	6,7	7,28	3,0	6,4			243	300
20	6,62	7,07	2,95	6,38	0,085	0,309	350	423
21	6,59	7,10	2,88	6,20	0,05	0,27	237,3	289,1
22	6,78	7,22	2,80	6,20			190	299
23	6,66	7,26	3,12	6,59	0,096	0,307		
24	6,740	7,353	2,795	6,423	0,085	0,303	242	294
25	6,65	6,85	3,0	6,5	0,11	0,34		
27	6,79	7,32	2,97	6,53	0,058	0,175	218,8	301,9
28	6,66	7,26	3,35	7,18	0,102	0,335	268	331
29	6,35	6,65	2,82	6,15	0,0910	0,3194	238	287
30	6,71	7,31	2,91	6,42	0,094	0,320	221	270
31	6,73	7,23	2,6	5,7	0,0707	0,1805	295	335
32	6,80	7,37	2,9	6,2	0,046	0,152	238	294
33	6,33	7,37	2,84	6,34	0,097	0,308	248	298
34	6,51	7,16	3,04	6,53	0,096	0,310	241,2	296,5
35	6,7	7,3	3,0	6,4	0,090	0,312	250	290
36	6,62	7,20	3,11	6,46	0,098	0,316	245	297
37	6,72	7,20	2,79	6,06			250	300
38	6,85	7,29	2,99	6,45	0,110	0,330	228	278
39	6,77	7,37	2,98	6,40	0,098	0,30	245	296
40	6,75	7,35	2,99	6,54	0,13	0,34	280	350
41	6,73	7,35	2,85	6,31	0,095	0,318	256	314
42	6,80	7,20	11,35	14,45			245	290
43	6,41	6,60	2,93	6,33	0,069	0,192	250,5	302,0
44	6,06	7,08	3,35	7,10			240	291
45	6,87	7,40	2,90	6,33	0,100	0,320	235	275
46	5,96	6,28	2,8	6,2	0,091	0,303	150,8	301,6
48	6,40	7,05			0,134	0,339	312	336
49	5,91	5,69	3,20	6,50	0,05	0,30	243	281

Lab.	pH		Conductivity, mS/m		Alkalinity, mmol/l		Nitrate-nitrogen, µg/l	
	A	B	A	B	A	B	A	B
50	6,14	5,83	3,4	5,8			172	266
51	6,79	7,29	2,85	6,33	0,093	0,31	250	300
52	6,83	7,40	2,93	6,30	0,087	0,222		
53	6,26	6,89	2,94	6,35	0,077	0,305	254	317
54	6,65	7,34	3,10	6,62			250	289
55	6,79	7,36	2,85	6,13			900	1330
56	6,68	7,13	3,0	6,5	0,109	0,363	205	255
57	6,70	7,01	2,86	6,75	0,14	0,35	215	250
58	6,65	7,18	3,02	6,44	0,099	0,320	226	274
59	6,45	7,19	3,07	6,57	0,060	0,078	185	168
60	6,65	7,20	2,94	6,42	0,890	0,294	250	280
62	7,5	7,45	0,00030	0,00065	0,090	0,190	191,0	244,0
63	6,72	7,17	2,95	6,42	0,111	0,337	214,3	298,1
64	6,92	7,71	2,99	6,57	0,10	0,33	230	282
65	6,90	6,89	31,1	64,7	0,37	1,84	260,8	291,1
66	6,43	6,92	228	451	0,09	0,32	200	270
67	6,55	7,19	2,96	6,35	0,104	0,136	239	293
68	6,45	7,08	2,40	5,47			240	290
69	6,72	7,34	3,22	6,47			244	295
70	6,65	7,00	3,03	6,58	0,094	0,325	242	295
71	6,34	6,86	2,96	6,47			252	300
72	6,7	7,2	2,9	6,2	0,09	0,30	250	310
73	6,7	7,2	2,49	6,37	0,147	0,370	249	295
75								
76	6,14	6,78	2,96	6,48	0,13	0,36	212,2	273,2
77	6,60	7,15	2,96	6,35	0,066	0,273	230	285
78	6,71	7,35	2,99	6,52			242	298
79	7,1	7,45	3,0	6,6	0,105	0,317	258,5	299,2

Lab.	Chloride, mg/l		Sulfate, mg/l		Calcium, mg/l		Magnesium, mg/l	
	A	B	A	B	A	B	A	B
1	2,12	3,41	2,77	5,96	2,74	7,83	0,80	0,80
2	5,50	6,53	<3,3	<3,3	2,36	7,07	0,60	0,95
3	2,22	3,89	2,57	5,62	2,80	8,12	0,47	0,68
4	2,95	4,15	4,41	8,52	0,79	4,16	0,46	0,80
5	2,228	3,557	3,037	6,298	3,749	10,295	0,562	0,740
6	2,35	3,60	2,93	5,95	2,66	8,11	0,49	0,67
7	5,47	4,12	1,52	3,60	2,91	3,72	0,79	0,99
8	2,46	3,72	2,96	6,45	2,75	7,68	0,50	0,70
9	2,2	3,5	3,0	6,0	2,8	8,0	0,50	0,70
10	2,27	3,34	2,83	5,91	2,81	8,08	0,462	0,656
11	2,18	3,44	2,36	6,28	2,49	7,88	0,42	0,60
12	2,25	3,55	2,96	6,13	2,55	7,80	0,44	0,66
13	2,31	3,61	2,95	6,06	3,08	8,41	0,49	0,69
14	2,14	3,33	2,83	6,24	2,75	7,74	0,46	0,65
15	2,212	3,538	2,873	6,007	2,85	8,07	<0,5	0,71
16	2,12	3,63	3,09	6,55	2,65	7,57	0,45	0,64
17								
18					2,74	7,92	0,46	0,67
19								
20	2,18	3,49	3,10	6,43	2,78	7,95	0,59	0,82
21	0,79	1,55	1,7	3,5	2,92	7,77	0,23	0,46
22								
23					2,74	7,84	0,472	0,686
24	2,134	3,504	2,944	6,140	3,463	10,159	0,487	0,656
25	5,00	5,00	7,00	6,00	2,8	7,6	0,49	0,85
27	2,33	3,62	2,94	6,10	3,12	9,33	0,560	0,770
28	2,46	3,84	4,61	7,09	2,72	7,77	0,45	0,66
29	2,206	3,492	3,045	6,549	2,630	7,917	0,464	0,683
30	2,11	3,30	2,64	5,37	2,57	8,15	0,40	0,52
31	2,07	3,47	3,12	6,48	2,65	7,43	0,472	0,672
32	2,21	3,47	2,88	5,96	2,78	8,24	0,46	0,67
33	2,28	3,46	3,12	6,68			0,395	0,574
34	2,20	3,44	2,23	4,97				
35	2,2	3,5	3,0	6,0	2,7	7,7	0,50	0,60
36	2,27	3,62	2,90	6,01	2,94	8,47	0,475	0,683
37	2,23	3,50	2,93	6,01	2,90	8,23	0,48	0,68
38	2,17	3,48	2,92	6,14	2,48	7,49	0,46	0,67
39	2,18	3,34	2,89	6,08	2,52	7,34	0,47	0,69
40	2,51	4,00	4,91	8,92	2,38	6,64	0,56	1,08
41	2,19	3,59	2,92	6,03	2,82	8,17	0,47	0,66
42	2,20	3,35	2,98	5,82	2,81	8,04	0,460	0,667
43	2,001	3,044	2,879	6,116	2,64	8,50	0,56	77,00
44	2,347	3,526	3,049	6,117	2,845	8,045	0,468	0,665
45	2,32	3,65	3,07	6,18	3,15	8,57	0,30	0,54
46	2,27	3,72	2,80	6,20	2,89	8,25	0,47	0,69
48	2,59	3,51			2,97	9,27	0,52	0,77
49	2,59	3,89	3,0	6,0	2,87	8,13	0,56	0,66
50								

Lab.	Chloride, mg/l		Sulfate, mg/l		Calcium, mg/l		Magnesium, mg/l	
	A	B	A	B	A	B	A	B
51	2,24	3,33	2,86	6,04	2,93	8,50	0,545	0,738
52	2,18	3,62	2,97	6,26	2,91	8,55	0,55	0,74
53	2,21	3,47	3,19	6,00	2,48	7,17	0,46	0,65
54	2,19	3,47	2,97	5,96	3,36	8,50	0,48	0,68
55	2,32	3,89	3,00	6,44	4,41	9,26	0,63	0,88
56	2,10	3,42	2,79	5,85	3,76	9,38	0,51	0,71
57	1,86	2,97	2,50	5,17	3,60	10,90	0,439	0,652
58	2,19	3,51	2,80	5,75	2,68	7,70	0,456	0,650
59	2,37	3,83	3,37	7,38	3,66	10,7	0,638	0,936
60	2,22	3,33	2,71	5,21	2,95	8,98	0,39	0,46
62	1,942	3,054	2,700	5,64	3,03	8,24	0,511	0,715
63	2,18	3,45	1,81	3,13	2,96	8,38	0,489	0,704
64	2,01	3,21	2,74	5,70	2,6	8,1	0,46	0,65
65		3,06		6,43		7,32		0,43
66	2,14	3,49	2,73	5,74	2,63	7,98	0,36	0,58
67	2,21	3,51	2,80	5,91	2,91	9,17	0,48	0,72
68	2,15	3,53	3,01	6,30	3,42	7,68	0,63	0,87
69	2,08	3,16	2,66	5,50	2,60	7,34	0,455	0,654
70	2,19	3,47	2,95	6,12	2,54	7,75	0,45	0,66
71	2,19	3,47	2,91	5,99	2,80	8,05	0,48	0,68
72	2,2	3,6	2,95	6,2	2,4	7,0	0,39	0,60
73	2,2	3,6	2,8	6,0				
75	1,74	2,99	2,51	5,58				
76	1,48	2,62	2,21	5,40	2,86	8,07	0,43	0,69
77	2,36	3,43	2,91	5,89	2,87	8,19	0,49	0,72
78	2,35	3,66	2,99	6,32	2,85	8,19	0,47	0,67
79	2,08	3,28	2,63	5,51	2,43	7,24	0,40	0,59

Lab.	Sodium, mg/l		Potassium, mg/l		Iron, µg/l		Manganese, µg/l	
	A	B	A	B	C	D	C	D
1								
2	1,35	2,25	0,33	0,57	56,5	46,0	2,6	2,1
3	1,87	3,13	0,29	0,53			3,12	2,44
4	1,63	2,59	0,35	0,61			3,47	3,26
5	1,689	2,683	0,275	0,514	37,5	20,7	3,220	2,618
6	1,60	2,69	0,20	0,44				
7	2,34	3,20	0,19	0,34	73,0	67,0	2,99	1,31
8	1,90	2,97	0,34	0,60				
9	1,7	2,7	0,30	0,60	63	47	3	2
10	1,77	2,79	0,274	0,508	63,32	49,79	3,084	2,583
11	1,54	2,46	0,26	0,46				
12	1,64	2,64	0,31	0,52	65	47	3,1	2,4
13	1,67	2,72	0,32	0,57				
14	1,90	2,14	0,33	0,57				
15	1,8	2,94	<0,6	0,79	48	35	3,28	2,60
16	1,51	2,56	0,32	0,56	60	46	2,9	2,4
17							2,89	2,34
18	1,60	2,57	0,31	0,56				
19								
20	1,69	2,67	0,38	0,69				
21								
22								
23	1,60	2,43	0,310	0,531	63,0	44,4	2,98	2,30
24	1,723	2,748	0,320	0,559				
25								
27	1,75	2,75	0,33	0,56	67	73	<20	<20
28	1,56	2,52	0,29	0,51	60,1	33,0	3,15	2
29	1,725	2,721	0,394	0,611	58,19	41,63	3,089	2,428
30	1,46	2,17	0,27	0,44	50	40	3,01	2,44
31	1,71	2,68	0,316	0,520	65	50	2,93	2,31
32	1,68	2,64	0,351	0,585	54,39	33,11	3,47	2,50
33	1,63	2,62	0,253	0,481	62	47	<5	<5
34								
35	1,7	2,6	0,30	0,50			3	2
36	1,70	2,73	0,31	0,55				
37	1,71	2,72	0,33	0,56		183,0	2,57	2,30
38	1,68	2,63	0,308	0,540	56,0	45,0	3,05	2,40
39	1,73	2,74	0,34	0,55				
40	1,50	2,74	0,32	0,58	70	50	5,0	8,1
41	1,66	2,65	0,31	0,53	61,2	49,2	2,48	2,08
42	1,75	2,75	0,334	0,581	60,2	45,1	3,00	2,30
43	1,46	2,70	0,26	0,44	60,0	50,0	2,82	2,32
44	1,785	2,719	0,331	0,564				
45	1,70	2,63	0,50	0,78	57,0	39,0	3,13	2,53
46	1,70	2,66	0,33	0,56				
48	1,71	2,80	0,37	0,58				
49								
50								

Lab.	Sodium, mg/l		Potassium, mg/l		Iron, µg/l		Manganese, µg/l	
	A	B	A	B	C	D	C	D
51	1,86	2,95	0,291	0,524	64,4	47,1	3,1	2,5
52	1,76	2,84	0,40	0,63				
53	1,65	2,61	0,33	0,55	63,8	52,6	3,7	3,0
54	1,76	2,77	0,310	0,560				
55	2,02	2,89	0,41	0,69				
56	1,69	2,78	0,24	0,52				
57	1,48	2,40	0,326	0,555	60,0	<50	<20	<20
58	1,69	2,68	0,310	0,542	64,3	59,7	3,23	2,57
59	2,11	3,46	0,371	0,690	118	74		
60	1,69	2,61	0,30	0,52				
62	1,626	2,603	0,320	0,557	43,5	34,5	3,00	2,40
63	1,742	2,740	0,315	0,567				
64	1,6	2,6	0,33	0,56	67	51	3,2	2,5
65		2,80		0,64				
66	1,61	2,70	0,33	0,57				
67	1,71	2,71	0,32	0,55				
68	1,85	2,77	0,41	0,53	27,5	7,2	3,9	2,2
69	1,58	2,58	0,315	0,572	58,5	43,9	2,8	1,9
70	1,63	2,68	0,31	0,53	56,4	43,9	3,10	2,60
71	1,67	2,66	0,38	0,61	62	48	3	3
72	1,61	2,58	0,30	0,52				
73								
75								
76	1,64	2,63	0,27	0,56	70	60	<10	<10
77	1,67	2,75	0,34	0,56	59	<50	<5	<5
78	1,69	2,68	0,31	0,55	52,5	54,9	3,2	3,2
79	1,70	2,58	0,25	0,36				

Lab.	Cadmium, µg/l		Lead, µg/l		Copper, µg/l		Nickel, µg/l		Zinc, µg/l	
	C	D	C	D	C	D	C	D	C	D
1										
2	<0,2	<0,2	<0,2	<0,2	15,4	6,9	<0,5	<5,0	12,0	29,5
3	0,05	0,06	0,43	0,75	13,8	2,89	0,31	0,28	8,24	18,6
4	<0,75	0,76	<7,5	<7,5	13,9	4,93	<2,75	<2,75	8,69	22,3
5	0,025	0,041	<DL	<DL	10,97	1,561	0,069	0,019	10,05	24,55
6										
7	<1	<1	2,03	1,70	10,5	4,55	1,88	<1	21,9	<1
8										
9	<1	<1	<10	<10	12,0	1,5	<1	<1	8	23,00
10	0,0281	0,0397	0,242	0,1978	11,88	2,851	0,3573	0,3727	7,345	22,76
11										
12	0,100	0,400	0,90	0,60	13	2,5	0,90	0,60	6,9	31
13										
14										
15	<0,1	<0,1	<0,5	<0,5	13,4	3,2	<1,0	<1,0	11,4	22,3
16	<4	<4	<15	<15	12,7	3,1	<5	<5	6	21
17	0,027	0,038	0,089	0,088	12,5	2,95	0,48	0,57	6,7	22,5
18										
19										
20					15,0	5,72				
21										
22										
23	<0,20	<0,20	<3,23	<3,23	18,3	7,85			5,95	20,8
24										
25										
27	<0,50	<0,50	<5,0	<5,0	13	2,9	<5,0	<5,0	<20	<20
28	<1,0	<1,0			12,22	2,49	<2,0	<2,0	6,84	19,53
29	0,028	0,038	0,608	0,079	13,283	3,072	0,473	0,513	6,378	20,93
30	0,02	0,04	0,04	<0,01	12,5	3,02	0,47	0,50	6,81	21,2
31	<0,1	<0,1	<2	<2	13,1	3,04	<3	<3	6,68	21,2
32	<0,194	<0,194	0,581	<0,162	12,57	2,81	0,43	0,45	7,62	22,84
33	<24	<24	<319	<319	<32	<32			<10	18
34										
35									<10	21
36										
37			0,08	0,04	12,5	3,0	0,49	0,71	6,3	22,5
38	0,05	0,06	0,82	0,63	12,56	3,30	0,71	0,97	11,37	19,75
39										
40	0,3	0,9	0,0	0,0	12,0	5,2	1,30	0,50	28,0	35,0
41	<0,5	<0,5	<2,0	<2,0	13,4	3,9	<2,0	<2,0	5,91	20,6
42	<0,10	<,01	<1,0	<1,0	13,0	3,2	0,40	0,40	5,9	19,8
43	<0,15	<0,15	<1,29	<1,29	3,77	10,39	<1,55	<1,55	10,0	20,0
44										
45	0,026	0,039	0,075	0,047	13,2	3,13	0,49	0,44	6,76	22,0
46										
48										
49										
50										
51	<0,1	<0,1	<1	<1	13,0	3,0	<1	<1	6	20

Lab.	Cadmium, µg/l		Lead, µg/l		Copper, µg/l		Nickel, µg/l		Zinc, µg/l	
	C	D	C	D	C	D	C	D	C	D
52										
53	<0,050	0,26	0,62	0,31	13,2	2,7	0,84	0,94	5,3	19,6
54										
55										
56										
57	0,2	<0,1	1,1	1,4	17,2	3,6	1,6	1,7	10	20
58			0,072	0,038	13,5	2,93	0,40	0,41	6,83	24,0
59	30	16	136	102	86	72			58	82
60										
62	<0,1	<0,1	<0,1	0,290	12,8	3,0	0,59	0,65	6,9	23,0
63										
64	0,028	0,040	0,20	<0,2	12	2,9	0,48	0,54	8,50	22
65										
66										
67										
68	0,07	0,11	1,65	2,05	8,8	3,4			2,5	10,5
69	<1	<1	<15	<15	13,2	<4	<10	<10	8,1	21,9
70	0,03	0,04	0,08	0,31	13,0	3,20	0,47	0,47	6,8	22,5
71	<0,1	<0,1	<1	<1	12,8	3,11	<1	<1	10	23
72										
73										
75										
76	<1	<1	<10	<10	10	10	<10	<10	10	30
77	<0,5	<0,5	0,4	<0,4	11,5	3,5	<0,5	<0,5	<10	19,40
78	<0,05	<0,05	<0,5	0,8	12,4	3,1	0,4	0,4	4,8	19,1
79										

Table 5.1. Statistics - pH

Sample A

Number of participants	73		Range		1,14
Number of omitted results	3		Variance		0,05
True value	6,70		Standard deviation		0,21
Mean value	6,64		Relative standard deviation		3,2%
Median value	6,70		Relative error		-0,9%

Analytical results in ascending order:

49	5,91	U	16	6,63		41	6,73	
46	5,96		13	6,64		11	6,74	
44	6,06		54	6,65		24	6,74	
15	6,10		25	6,65		40	6,75	
76	6,14		70	6,65		39	6,77	
50	6,14	U	58	6,65		18	6,78	
53	6,26		60	6,65		22	6,78	
33	6,33		23	6,66		55	6,79	
5	6,34		12	6,66		27	6,79	
71	6,34		28	6,66		51	6,79	
29	6,35		56	6,68		42	6,80	
48	6,40		19	6,70		32	6,80	
43	6,41		57	6,70		52	6,83	
66	6,43		73	6,70		2	6,85	
68	6,45		35	6,70		1	6,85	
59	6,45		72	6,70		38	6,85	
34	6,51		6	6,70		45	6,87	
67	6,55		78	6,71		3	6,88	
8	6,55		30	6,71		65	6,90	
7	6,56		10	6,71		64	6,92	
21	6,59		69	6,72		4	6,97	
77	6,60		63	6,72		79	7,10	
9	6,61		37	6,72		62	7,50	U
36	6,62		14	6,73				
20	6,62		31	6,73				

Sample B

Number of participants	73		Range		1,43
Number ofmitted results	3		Variance		0,06
True value	7,20		Standard deviation		0,24
Mean value	7,17		Relative standard deviation		3,3%
Median value	7,20		Relative error		-0,4%

Analytical results in ascending order:

49	5,69	U	77	7,15		35	7,30	
50	5,83	U	34	7,16		30	7,31	
46	6,28		63	7,17		27	7,32	
43	6,60		16	7,17		2	7,34	
5	6,62		58	7,18		54	7,34	
29	6,65		59	7,19		18	7,34	
15	6,70		67	7,19		69	7,34	
76	6,78		36	7,20		40	7,35	
25	6,85		42	7,20		14	7,35	
71	6,86		37	7,20		78	7,35	
53	6,89		73	7,20		41	7,35	
65	6,89		60	7,20		24	7,35	
66	6,92		72	7,20		55	7,36	
70	7,00		22	7,22		39	7,37	
57	7,01		31	7,23		32	7,37	
1	7,05		11	7,25		3	7,37	
48	7,05		9	7,26		33	7,37	
7	7,05		23	7,26		52	7,40	
20	7,07		28	7,26		45	7,40	
8	7,08		13	7,26		12	7,43	
68	7,08		19	7,28		62	7,45	U
44	7,08		6	7,29		79	7,45	
21	7,10		38	7,29		64	7,71	
56	7,13		10	7,29				
4	7,14		51	7,29				

U = Omitted result

Table 5.2. Statistics - Conductivity, mS/m

Sample A

Number of participants	72		Range	1,00	
Number of omitted results	6		Variance	0,03	
True value	2,96		Standard deviation	0,18	
Mean value	2,95		Relative standard deviation	6,1%	
Median value	2,96		Relative error	-0,2%	

Analytical results in ascending order:

62	0,00	U	32	2,90	1	3,00	
8	2,25	U	30	2,91	35	3,00	
68	2,40		43	2,93	56	3,00	
73	2,49		52	2,93	58	3,02	
6	2,56		12	2,93	70	3,03	
31	2,60		53	2,94	34	3,04	
3	2,72		60	2,94	7	3,05	
2	2,78		13	2,95	16	3,06	
37	2,79		63	2,95	59	3,07	
24	2,80		20	2,95	54	3,10	
22	2,80		77	2,96	9	3,10	
46	2,80		67	2,96	36	3,11	
29	2,82		76	2,96	23	3,12	
33	2,84		71	2,96	49	3,20	
10	2,84		27	2,97	69	3,22	
55	2,85		39	2,98	4	3,24	
41	2,85		38	2,99	5	3,25	
51	2,85		40	2,99	28	3,35	
57	2,86		78	2,99	44	3,35	
21	2,88		64	2,99	50	3,40	
72	2,90		79	3,00	42	11,35	U
45	2,90		19	3,00	65	31,10	U
11	2,90		18	3,00	66	228,00	U
15	2,90		25	3,00	14	292,00	U

Sample B

Number of participants	72		Range	1,71	
Number of omitted results	6		Variance	0,07	
True value	6,40		Standard deviation	0,27	
Mean value	6,38		Relative standard deviation	4,2%	
Median value	6,40		Relative error	-0,3%	

Analytical results in ascending order:

62	0,00	U	33	6,34	56	6,50	
8	4,85	U	53	6,35	49	6,50	
68	5,47		67	6,35	25	6,50	
31	5,70		77	6,35	78	6,52	
50	5,80		73	6,37	27	6,53	
3	5,80		20	6,38	34	6,53	
37	6,06		15	6,40	16	6,54	
6	6,07		39	6,40	40	6,54	
55	6,13		35	6,40	5	6,55	
29	6,15		1	6,40	64	6,57	
2	6,16		18	6,40	59	6,57	
10	6,17		19	6,40	70	6,58	
46	6,20		30	6,42	23	6,59	
22	6,20		60	6,42	79	6,60	
72	6,20		63	6,42	54	6,62	
21	6,20		24	6,42	7	6,66	
32	6,20		13	6,44	57	6,75	
11	6,22		58	6,44	9	6,80	
52	6,30		38	6,45	44	7,10	
41	6,31		36	6,46	28	7,18	
12	6,32		71	6,47	42	14,45	U
51	6,33		69	6,47	65	64,70	U
45	6,33		76	6,48	66	451,00	U
43	6,33		4	6,49	14	635,00	U

U = Omitted result

Table 5.3. Statistics - Alkalinity, mmol/l

Sample A

Number of participants	59	Range	0,090	
Number of omitted results	10	Variance	0,000	
True value	0,094	Standard deviation	0,019	
Mean value	0,095	Relative standard deviation	19,6%	
Median value	0,094	Relative error	0,9%	

Analytical results in ascending order:

32	0,046	U	35	0,090		45	0,100	
21	0,050		72	0,090		28	0,102	
49	0,050		66	0,090		67	0,104	U
27	0,058	U	18	0,091		79	0,105	
7	0,060	U	29	0,091		56	0,109	
59	0,060	U	46	0,091		25	0,110	
77	0,066		51	0,093		38	0,110	
43	0,069		13	0,094		63	0,111	
31	0,071		70	0,094		8	0,120	
4	0,071		30	0,094		1	0,125	
53	0,077		14	0,095		40	0,130	
16	0,084		41	0,095		76	0,130	
3	0,084		23	0,096		48	0,134	
6	0,085		34	0,096		57	0,140	
20	0,085		33	0,097		73	0,147	U
24	0,085		36	0,098		2	0,210	U
52	0,087		39	0,098		15	0,230	U
10	0,088		12	0,099		65	0,370	U
11	0,089		58	0,099		60	0,890	U
62	0,090		64	0,100				

Sample B

Number of participants	59	Range	0,183	
Number of omitted results	10	Variance	0,001	
True value	0,312	Standard deviation	0,038	
Mean value	0,307	Relative standard deviation	12,4%	
Median value	0,312	Relative error	-1,5%	

Analytical results in ascending order:

59	0,078	U	23	0,307		58	0,320	
7	0,100	U	33	0,308		70	0,325	
67	0,136	U	14	0,308		12	0,326	
32	0,152	U	20	0,309		64	0,330	
27	0,175	U	51	0,310		8	0,330	
31	0,181		4	0,310		38	0,330	
62	0,190		11	0,310		28	0,335	
43	0,192		34	0,310		1	0,336	
52	0,222		10	0,311		63	0,337	
21	0,270		35	0,312		48	0,339	
77	0,273		13	0,312		25	0,340	
60	0,294	U	16	0,313		40	0,340	
3	0,297		18	0,314		57	0,350	
49	0,300		36	0,316		76	0,360	
72	0,300		79	0,317		56	0,363	
39	0,300		41	0,318		73	0,370	U
46	0,303		29	0,319		2	0,410	U
24	0,303		45	0,320		15	0,450	U
6	0,305		30	0,320		65	1,840	U
53	0,305		66	0,320				

U = Omitted result

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

Sample A

Number of participants	71		Range	140	
Number of omitted results	7		Variance	483	
True value	242		Standard deviation	22	
Mean value	240		Relative standard deviation	9,1%	
Median value	242		Relative error	-0,8%	

Analytical results in ascending order:

52	0	U	21	237	60	250	
46	151	U	32	238	9	250	
50	172		29	238	35	250	
59	185	U	14	238	37	250	
22	190		67	239	51	250	
62	191		44	240	43	251	
66	200		15	240	13	251	
56	205		68	240	71	252	
76	212		6	241	53	254	
63	214		34	241	16	255	
57	215		24	242	41	256	
27	219		70	242	8	258	
30	221		78	242	79	259	
58	226		19	243	65	261	
1	226		49	243	18	262	
38	228		5	244	28	268	
77	230		69	244	40	280	
12	230		39	245	31	295	
64	230		42	245	48	312	
10	233		36	245	20	350	U
2	234		33	248	4	356	U
45	235		73	249	7	471	U
3	235		72	250	55	900	U
11	237		54	250			

Sample B

Number of participants	71		Range	106	
Number of omitted results	7		Variance	367	
True value	295		Standard deviation	19	
Mean value	293		Relative standard deviation	6,5%	
Median value	295		Relative error	-0,7%	

Analytical results in ascending order:

52	0	U	68	290	37	300	
59	168	U	35	290	19	300	
62	244		42	290	51	300	
57	250		44	291	71	300	
10	252		65	291	46	302	U
56	255		14	293	27	302	
50	266		67	293	43	302	
30	270		32	294	13	304	
66	270		24	294	16	305	
76	273		69	295	11	307	
58	274		73	295	8	309	
45	275		6	295	72	310	
38	278		70	295	41	314	
1	279		5	296	53	317	
60	280		39	296	18	318	
49	281		34	297	28	331	
64	282		36	297	31	335	
2	283		15	298	48	336	
12	283		33	298	40	350	
3	284		78	298	20	423	U
77	285		63	298	4	470	U
29	287		22	299	7	577	U
54	289		79	299	55	1330	U
21	289		9	300			

U = Omitted result

Table 5.5. Statistics - Chloride, mg/l

Sample A

Number of participants	68		Range		0,85		
Number of omitted results	6		Variance		0,02		
True value	2,20		Standard deviation		0,15		
Mean value	2,21		Relative standard deviation		6,6%		
Median value	2,20		Relative error		0,6%		
Analytical results in ascending order:							
65		U	11	2,18	12	2,25	
21	0,79	U	63	2,18	36	2,27	
76	1,48	U	70	2,19	10	2,27	
75	1,74		54	2,19	46	2,27	
57	1,86		41	2,19	33	2,28	
62	1,94		58	2,19	13	2,31	
43	2,00		71	2,19	45	2,32	
64	2,01		73	2,20	55	2,32	
31	2,07		72	2,20	27	2,33	
69	2,08		42	2,20	44	2,35	
79	2,08		34	2,20	6	2,35	
56	2,10		35	2,20	78	2,35	
30	2,11		9	2,20	77	2,36	
16	2,12		29	2,21	59	2,37	
1	2,12		67	2,21	8	2,46	
24	2,13		32	2,21	28	2,46	
66	2,14		53	2,21	40	2,51	
14	2,14		15	2,21	49	2,59	
68	2,15		60	2,22	48	2,59	
38	2,17		3	2,22	4	2,95	U
20	2,18		5	2,23	25	5,00	U
52	2,18		37	2,23	7	5,47	U
39	2,18		51	2,24	2	5,50	U

Sample B

Number of participants	68		Range		1,03		
Number of omitted results	6		Variance		0,04		
True value	3,49		Standard deviation		0,21		
Mean value	3,49		Relative standard deviation		5,9%		
Median value	3,49		Relative error		0,1%		
Analytical results in ascending order:							
21	1,55	U	9	3,45	41	3,59	
76	2,62	U	33	3,46	73	3,60	
57	2,97		71	3,47	6	3,60	
75	2,99		54	3,47	72	3,60	
43	3,04		70	3,47	13	3,61	
62	3,05		31	3,47	36	3,62	
65	3,06	U	53	3,47	52	3,62	
69	3,16		32	3,47	27	3,62	
64	3,21		38	3,48	16	3,63	
79	3,28		66	3,49	45	3,65	
30	3,30		20	3,49	78	3,66	
51	3,33		29	3,49	8	3,72	
14	3,33		37	3,50	46	3,72	
60	3,33		35	3,50	59	3,83	
10	3,34		24	3,50	28	3,84	
39	3,34		58	3,51	49	3,89	
42	3,35		67	3,51	3	3,89	
1	3,41		48	3,51	55	3,89	
56	3,42		44	3,53	40	4,00	
77	3,43		68	3,53	7	4,12	U
34	3,44		15	3,54	4	4,15	U
11	3,44		12	3,55	25	5,00	U
63	3,45		5	3,56	2	6,53	U

U = Omitted result

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

Number of participants	67		Range	1,16	
Number of omitted results	8		Variance	0,05	
True value	2,92		Standard deviation	0,21	
Mean value	2,87		Relative standard deviation	7,5%	
Median value	2,92		Relative error	-1,8%	
Analytical results in ascending order:					
2	<3,3	U	73	2,80	52	2,97	
65		U	10	2,83	42	2,98	
7	1,52	U	14	2,83	78	2,99	
21	1,70	U	51	2,86	9	3,00	
63	1,81	U	15	2,87	35	3,00	
76	2,21		43	2,88	49	3,00	
34	2,23		32	2,88	55	3,00	
11	2,36		39	2,89	68	3,01	
57	2,50		36	2,90	5	3,04	
75	2,51		77	2,91	29	3,05	
3	2,57		71	2,91	44	3,05	
79	2,63		38	2,92	45	3,07	
30	2,64		41	2,92	16	3,09	
69	2,66		37	2,93	20	3,10	
62	2,70		6	2,93	33	3,12	
60	2,71		27	2,94	31	3,12	
66	2,73		24	2,94	53	3,19	
64	2,74		70	2,95	59	3,37	
1	2,77		13	2,95	4	4,41	U
56	2,79		72	2,95	28	4,61	U
67	2,80		8	2,96	40	4,91	U
58	2,80		12	2,96	25	7,00	U
46	2,80		54	2,97			

Sample B

Number of participants	67		Range	2,41	
Number of omitted results	8		Variance	0,15	
True value	6,01		Standard deviation	0,39	
Mean value	6,01		Relative standard deviation	6,5%	
Median value	6,01		Relative error	0,0%	
Analytical results in ascending order:					
2	<3,3	U	1	5,96	24	6,14	
63	3,13	U	32	5,96	45	6,18	
21	3,50	U	54	5,96	46	6,20	
7	3,60	U	71	5,99	72	6,20	
34	4,97		35	6,00	14	6,24	
57	5,17		25	6,00	U	52	6,26	
60	5,21		49	6,00	11	6,28	
30	5,37		73	6,00	5	6,30	
76	5,40		53	6,00	68	6,30	
69	5,50		9	6,00	78	6,32	
79	5,51		15	6,01	20	6,43	
75	5,58		36	6,01	65	6,43	U
3	5,62		37	6,01	55	6,44	
62	5,64		41	6,03	8	6,45	
64	5,70		51	6,04	31	6,48	
66	5,74		13	6,06	29	6,55	
58	5,75		39	6,08	16	6,55	
42	5,82		27	6,10	33	6,68	
56	5,85		43	6,12	28	7,09	U
77	5,89		44	6,12	59	7,38	
10	5,91		70	6,12	4	8,52	U
67	5,91		12	6,13	40	8,92	U
6	5,95		38	6,14			

U = Omitted result

Table 5.7. Statistics - Calcium, mg/l

Sample A

Number of participants	66			Range		1,40		
Number of omitted results	5			Variance		0,08		
True value	2,80			Standard deviation		0,29		
Mean value	2,82			Relative standard deviation		10,2%		
Median value	2,80			Relative error		0,6%		
Analytical results in ascending order:								
65		U	28	2,72		67	2,91	
4	0,79	U	18	2,74		7	2,91	U
2	2,36		1	2,74		52	2,91	
40	2,38		23	2,74		21	2,92	
72	2,40		8	2,75		51	2,93	
79	2,43		14	2,75		36	2,94	
38	2,48		20	2,78		60	2,95	
53	2,48		32	2,78		63	2,96	
11	2,49		3	2,80		48	2,97	
39	2,52		25	2,80		62	3,03	
70	2,54		71	2,80		13	3,08	
12	2,55		9	2,80		27	3,12	
30	2,57		42	2,81		45	3,15	
69	2,60		10	2,81		54	3,36	
64	2,60		41	2,82		68	3,42	
29	2,63		44	2,85		24	3,46	
66	2,63		15	2,85		57	3,60	U
43	2,64		78	2,85		59	3,66	U
31	2,65		76	2,86		5	3,75	
16	2,65		77	2,87		56	3,76	
6	2,66		49	2,87		55	4,41	U
58	2,68		46	2,89				
35	2,70		37	2,90				

Sample B

Number of participants	66			Range		3,66		
Number of omitted results	5			Variance		0,45		
True value	8,05			Standard deviation		0,67		
Mean value	8,09			Relative standard deviation		8,3%		
Median value	8,05			Relative error		0,5%		
Analytical results in ascending order:								
7	3,72	U	1	7,83		62	8,24	
4	4,16	U	23	7,84		32	8,24	
40	6,64		11	7,88		46	8,25	
72	7,00		29	7,92		63	8,38	
2	7,07		18	7,92		13	8,41	
53	7,17		20	7,95		36	8,47	
79	7,24		66	7,98		54	8,50	
65	7,32	U	9	8,00		43	8,50	
69	7,34		42	8,04		51	8,50	
39	7,34		44	8,05		52	8,55	
31	7,43		71	8,05		45	8,57	
38	7,49		15	8,07		60	8,98	
16	7,57		76	8,07		67	9,17	
25	7,60		10	8,08		55	9,26	U
8	7,68		64	8,10		48	9,27	
68	7,68		6	8,11		27	9,33	
35	7,70		3	8,12		56	9,38	
58	7,70		49	8,13		24	10,16	
14	7,74		30	8,15		5	10,30	
70	7,75		41	8,17		59	10,70	U
21	7,77		77	8,19		57	10,90	U
28	7,77		78	8,19				
12	7,80		37	8,23				

U = Omitted result

Table 5.8. Statistics - Magnesium

Sample A

Number of participants		67		Range		0,338		
Number of omitted results		6		Variance		0,004		
True value		0,470		Standard deviation		0,062		
Mean value		0,479		Relative standard deviation		13,0%		
Median value		0,470		Relative error		2,0%		
Analytical results in ascending order:								
	15	<0,05	U	42	0,460	6	0,490	
	65		U	14	0,460	25	0,490	
	21	0,230	U	38	0,460	9	0,500	
	45	0,300		18	0,460	35	0,500	
	66	0,360		10	0,462	8	0,500	
	72	0,390		29	0,464	56	0,510	
	60	0,390		44	0,468	62	0,511	
	33	0,395		46	0,470	48	0,520	
	79	0,400		39	0,470	51	0,545	
	30	0,400		41	0,470	52	0,550	
	11	0,420		3	0,470	49	0,560	
	76	0,430		78	0,470	40	0,560	U
	57	0,439		23	0,472	27	0,560	
	12	0,440		31	0,472	43	0,560	U
	70	0,450		36	0,475	5	0,562	
	28	0,450		71	0,480	20	0,590	
	16	0,450		67	0,480	2	0,600	
	69	0,455		37	0,480	68	0,630	
	58	0,456		54	0,480	55	0,630	
	64	0,460		24	0,487	59	0,638	
	53	0,460		63	0,489	7	0,790	U
	32	0,460		13	0,490	1	0,800	U
	4	0,460		77	0,490			

Sample B

Number of participants		67		Range		0,490		
Number of omitted results		6		Variance		0,008		
True value		0,671		Standard deviation		0,088		
Mean value		0,688		Relative standard deviation		12,7%		
Median value		0,672		Relative error		2,5%		
Analytical results in ascending order:								
	65	0,430	U	70	0,660	63	0,704	
	60	0,460		41	0,660	56	0,710	
	21	0,460	U	44	0,665	15	0,710	U
	30	0,520		42	0,667	62	0,715	
	45	0,540		78	0,670	77	0,720	
	33	0,574		32	0,670	67	0,720	
	66	0,580		18	0,670	51	0,738	
	79	0,590		6	0,670	5	0,740	
	35	0,600		38	0,670	52	0,740	
	72	0,600		31	0,672	27	0,770	
	11	0,600		71	0,680	48	0,770	
	16	0,640		54	0,680	1	0,800	U
	64	0,650		3	0,680	4	0,800	
	53	0,650		37	0,680	20	0,820	
	14	0,650		29	0,683	25	0,850	
	58	0,650		36	0,683	68	0,870	
	57	0,652		23	0,686	55	0,880	
	69	0,654		13	0,690	59	0,936	
	24	0,656		39	0,690	2	0,950	
	10	0,656		46	0,690	7	0,990	U
	28	0,660		76	0,690	40	1,080	U
	49	0,660		8	0,700	43	77,000	U
	12	0,660		9	0,700			

U = Omitted result

Table 5.9. Statistics - Sodium, mg/l

Sample A

Number of participants	63			Range		0,67	
Number of omitted results	2			Variance		0,01	
True value	1,69			Standard deviation		0,11	
Mean value	1,68			Relative standard deviation		6,8%	
Median value	1,69			Relative error		-0,7%	
Analytical results in ascending order:							
65		U	53	1,65	37	1,71	
2	1,35		41	1,66	24	1,72	
30	1,46		13	1,67	29	1,73	
43	1,46		77	1,67	39	1,73	
57	1,48		71	1,67	63	1,74	
40	1,50		32	1,68	42	1,75	
16	1,51		38	1,68	27	1,75	
11	1,54		5	1,69	54	1,76	
28	1,56		20	1,69	52	1,76	
69	1,58		60	1,69	10	1,77	
64	1,60		78	1,69	44	1,79	
18	1,60		56	1,69	15	1,80	
6	1,60		58	1,69	68	1,85	
23	1,60		46	1,70	51	1,86	
66	1,61		9	1,70	3	1,87	
72	1,61		35	1,70	8	1,90	
62	1,63		79	1,70	14	1,90	
33	1,63		36	1,70	55	2,02	
4	1,63		45	1,70	59	2,11	U
70	1,63		31	1,71	7	2,34	U
76	1,64		67	1,71			
12	1,64		48	1,71			

Sample B

Number of participants	63			Range		0,99	
Number of omitted results	2			Variance		0,03	
True value	2,68			Standard deviation		0,17	
Mean value	2,67			Relative standard deviation		6,2%	
Median value	2,68			Relative error		-0,5%	
Analytical results in ascending order:							
14	2,14		32	2,64	39	2,74	
30	2,17		12	2,64	63	2,74	
2	2,25		41	2,65	24	2,75	
57	2,40		46	2,66	27	2,75	
23	2,43		71	2,66	42	2,75	
11	2,46		20	2,67	77	2,75	
28	2,52		58	2,68	54	2,77	
16	2,56		70	2,68	68	2,77	
18	2,57		31	2,68	56	2,78	
69	2,58		78	2,68	10	2,79	
72	2,58		5	2,68	48	2,80	
79	2,58		6	2,69	65	2,80	U
4	2,59		66	2,70	52	2,84	
35	2,60		43	2,70	55	2,89	
64	2,60		9	2,70	15	2,94	
62	2,60		67	2,71	51	2,95	
53	2,61		44	2,72	8	2,97	
60	2,61		13	2,72	3	3,13	
33	2,62		37	2,72	7	3,20	U
38	2,63		29	2,72	59	3,46	U
45	2,63		36	2,73			
76	2,63		40	2,74			

U = Omitted result

Table 5.10. Statistics - Potassium, mg/l

Sample A

Number of participants	63		Range	0,210	
Number of omitted results	4		Variance	0,002	
True value	0,320		Standard deviation	0,040	
Mean value	0,319		Relative standard deviation	12,5%	
Median value	0,320		Relative error	-0,4%	
Analytical results in ascending order:					

15	<06	U	36	0,310	37	0,330	
65		U	23	0,310	66	0,330	
7	0,190	U	70	0,310	2	0,330	
6	0,200		54	0,310	46	0,330	
56	0,240		12	0,310	44	0,331	
79	0,250	U	18	0,310	42	0,334	
33	0,253		41	0,310	8	0,340	
43	0,260		78	0,310	77	0,340	
11	0,260		69	0,315	39	0,340	
30	0,270		63	0,315	4	0,350	
76	0,270		31	0,316	32	0,351	
10	0,274		62	0,320	48	0,370	
5	0,275		40	0,320	59	0,371	
28	0,290		13	0,320	20	0,380	
3	0,290		24	0,320	71	0,380	
51	0,291		16	0,320	29	0,394	
72	0,300		67	0,320	52	0,400	
35	0,300		57	0,326	55	0,410	
9	0,300		53	0,330	68	0,410	
60	0,300		14	0,330	45	0,500	U
38	0,308		27	0,330			
58	0,310		64	0,330			

Sample B

Number of participants	63		Range	0,250	
Number of omitted results	4		Variance	0,003	
True value	0,559		Standard deviation	0,051	
Mean value	0,553		Relative standard deviation	9,2%	
Median value	0,559		Relative error	-1,0%	
Analytical results in ascending order:					

7	0,340	U	38	0,540	13	0,570	
79	0,360	U	58	0,542	66	0,570	
6	0,440		67	0,550	14	0,570	
43	0,440		78	0,550	69	0,572	
30	0,440		53	0,550	48	0,580	
11	0,460		39	0,550	40	0,580	
33	0,481		36	0,550	42	0,581	
35	0,500		57	0,555	32	0,585	
10	0,508		62	0,557	8	0,600	
28	0,510		24	0,559	9	0,600	
5	0,514		54	0,560	71	0,610	
31	0,520		46	0,560	4	0,610	
12	0,520		16	0,560	29	0,611	
56	0,520		76	0,560	52	0,630	
72	0,520		77	0,560	65	0,640	U
60	0,520		64	0,560	55	0,690	
51	0,524		18	0,560	20	0,690	
70	0,530		27	0,560	59	0,690	
68	0,530		37	0,560	45	0,780	U
3	0,530		44	0,564	15	0,790	U
41	0,530		63	0,567			
23	0,531		2	0,570			

U = Omitted result

Table 5.11. Statistics - Iron, µg/l

Sample C

Number of participants	37	Range	29,5
Number of omitted results	7	Variance	41,9
True value	60,2	Standard deviation	6,5
Mean value	60,3	Relative standard deviation	10,7%
Median value	60,7	Relative error	0,1%

Analytical results in ascending order:

37	0,0	U	69	58,5		53	63,8	
68	27,5	U	77	59,0	U	58	64,3	
5	37,5	U	57	60,0	U	51	64,4	
62	43,5		16	60,0		12	65,0	
15	48,0		43	60,0		31	65,0	
30	50,0		28	60,1		27	67,0	U
78	52,5		42	60,2		64	67,0	
32	54,4		41	61,2		40	70,0	
38	56,0		71	62,0		76	70,0	
70	56,4		33	62,0		7	73,0	
2	56,5		23	63,0		59	118,0	U
45	57,0		9	63,0				
29	58,2		10	63,3				

Sample D

Number of participants	37	Range	34,0
Number of omitted results	7	Variance	60,2
True value	47,0	Standard deviation	7,8
Mean value	46,7	Relative standard deviation	16,6%
Median value	47,0	Relative error	-0,7%

Analytical results in ascending order:

77	<50	U	23	44,4		43	50,0	
57	<50	U	38	45,0		40	50,0	
68	7,2	U	42	45,1		64	51,0	
5	20,7	U	2	46,0		53	52,6	
28	33,0		16	46,0		78	54,9	
32	33,1		12	47,0		58	59,7	
62	34,5		9	47,0		76	60,0	
15	35,0		33	47,0		7	67,0	
45	39,0		51	47,1		27	73,0	U
30	40,0		71	48,0		59	74,0	U
29	41,6		41	49,2		37	183,0	U
69	43,9		10	49,8				
70	43,9		31	50,0				

U = Omitted result

Table 5.12. Statistics - Manganese, µg/l

Sample C

Number of participants	40		Range	1,42
Number of omitted results	6		Variance	0,08
True value	3,05		Standard deviation	0,28
Mean value	3,08		Relative standard deviation	9,2%
Median value	3,07		Relative error	0,8%

Analytical results in ascending order:

57	<20	U	7	2,99	45	3,13	
27	<20	U	9	3,00	28	3,15	
76	<10	U	35	3,00	78	3,20	
77	<5	U	62	3,00	64	3,20	
33	<5	U	71	3,00	5	3,22	
41	2,48		42	3,00	58	3,23	
37	2,57		30	3,01	15	3,28	
2	2,60		38	3,05	4	3,47	
69	2,80		10	3,08	32	3,47	
43	2,82		29	3,09	53	3,70	
17	2,89		70	3,10	68	3,90	
16	2,90		51	3,10	40	5,00	U
31	2,93		12	3,10			
23	2,98		3	3,12			

Sample D

Number of participants	40		Range	1,95
Number of omitted results	6		Variance	0,14
True value	2,40		Standard deviation	0,37
Mean value	2,41		Relative standard deviation	15,4%
Median value	2,40		Relative error	0,3%

Analytical results in ascending order:

57	<20	U	23	2,30	64	2,50	
27	<20	U	42	2,30	45	2,53	
76	<10	U	31	2,31	58	2,57	
77	<5	U	43	2,32	10	2,58	
33	<5	U	17	2,34	70	2,60	
7	1,31		62	2,40	15	2,60	
69	1,90		12	2,40	5	2,62	
35	2,00		16	2,40	53	3,00	
9	2,00		38	2,40	71	3,00	
28	2,00		29	2,43	78	3,20	
41	2,08		3	2,44	4	3,26	
2	2,10		30	2,44	40	8,10	U
68	2,20		32	2,50			
37	2,30		51	2,50			

U = Omitted result

Table 5.13. Statistics - Cadmium, µg/l

Sample C

Number of participants	38	Range	0,010
Number of omitted results	30	Variance	0,000
True value	0,027	Standard deviation	0,003
Mean value	0,027	Relative standard deviation	11,4%
Median value	0,028	Relative error	-1,8%

Analytical results in ascending order:

33	<24	U	32	<0,194	U	17	0,027	
16	<4	U	43	<0,15	U	64	0,028	
9	<1	U	15	<0,1	U	29	0,028	
76	<1	U	42	<0,1	U	10	0,028	
69	<1	U	51	<0,1	U	70	0,030	
7	<1	U	71	<0,1	U	3	0,050	U
28	<1	U	62	<0,1	U	38	0,050	U
4	<0,75	U	31	<0,1	U	68	0,070	U
77	<0,5	U	78	<0,05	U	12	0,100	U
41	<0,5	U	53	<0,05	U	57	0,200	U
27	<0,5	U	30	0,020		40	0,300	U
2	<0,2	U	5	0,025		59	30,000	U
23	<0,2	U	45	0,026				

Sample D

Number of participants	38	Range	0,003
Number of omitted results	30	Variance	0,000
True value	0,040	Standard deviation	0,001
Mean value	0,039	Relative standard deviation	2,7%
Median value	0,040	Relative error	-1,3%

Analytical results in ascending order:

33	<24	U	43	<0,15	U	30	0,040	
16	<4	U	15	<0,1	U	64	0,040	
76	<1	U	42	<0,1	U	70	0,040	
69	<1	U	71	<0,1	U	5	0,041	
7	<1	U	57	<0,1	U	38	0,060	U
28	<1	U	62	<0,1	U	3	0,060	U
9	<1	U	31	<0,1	U	68	0,110	U
27	<0,5	U	51	<0,1	U	53	0,260	U
77	<0,5	U	78	<0,05	U	12	0,400	U
41	<0,5	U	29	0,038		4	0,760	U
2	<0,2	U	17	0,038		40	0,900	U
23	<0,2	U	45	0,039		59	16,000	U
32	<0,194	U	10	0,040				

U = Omitted result

Table 5.14. Statistics - Lead, µg/l

Sample C

Number of participants	39	Range	0,008
Number of omitted results	36	Variance	0,000
True value	0,075	Standard deviation	0,004
Mean value	0,076	Relative standard deviation	5,3%
Median value	0,075	Relative error	0,9%

Analytical results in ascending order:

33	<319	U	42	<1	U	64	0,200	U
69	<15	U	71	<1	U	10	0,242	U
16	<15	U	15	<0,5	U	77	0,400	U
76	<10	U	78	<0,5	U	3	0,430	U
9	<10	U	62	<0,1	U	32	0,581	U
4	<7,5	U	5	<0,1	U	29	0,608	U
27	<5	U	40	0,000	U	53	0,620	U
23	<3,23	U	30	0,040	U	38	0,820	U
2	<2	U	58	0,072		12	0,900	U
41	<2	U	45	0,075		57	1,100	U
31	<2	U	37	0,080		68	1,650	U
43	<1,29	U	70	0,080	U	7	2,030	U
51	<1	U	17	0,089	U	59	136,000	U

Sample D

Number of participants	39	Range	0,009
Number of omitted results	36	Variance	0,000
True value	0,040	Standard deviation	0,005
Mean value	0,042	Relative standard deviation	11,3%
Median value	0,040	Relative error	4,2%

Analytical results in ascending order:

33	<319	U	42	<1	U	17	0,088	U
69	<15	U	71	<1	U	10	0,198	U
16	<15	U	15	<0,5	U	62	0,290	U
76	<10	U	77	<0,4	U	70	0,310	U
9	<10	U	64	<0,2	U	53	0,310	U
4	<7,5	U	32	<0,162	U	12	0,600	U
27	<5	U	5	<0,1	U	38	0,630	U
23	<3,23	U	30	<0,01	U	3	0,750	U
41	<2	U	40	0,000	U	78	0,800	U
31	<2	U	58	0,038		57	1,400	U
2	<2	U	37	0,040		7	1,700	U
43	<1,29	U	45	0,047		68	2,050	U
51	<1	U	29	0,079	U	59	102,000	U

U = Omitted result

Table 5.15. Statistics - Copper, µg/l

Sample C

Number of participants	41	Range	2,30
Number of omitted results	15	Variance	0,28
True value	13,00	Standard deviation	0,53
Mean value	12,80	Relative standard deviation	4,2%
Median value	12,90	Relative error	-1,5%

Analytical results in ascending order:

33	<32	U	30	12,50		45	13,20	
43	3,77	U	17	12,50		69	13,20	U
68	8,80	U	38	12,56		29	13,28	
76	10,00	U	32	12,57		15	13,40	
7	10,50	U	16	12,70		41	13,40	
5	10,97	U	71	12,80		58	13,50	
77	11,50		62	12,80		3	13,80	
10	11,88		70	13,00		4	13,90	U
64	12,00		51	13,00		20	15,00	U
9	12,00	U	42	13,00		2	15,40	U
40	12,00	U	12	13,00		57	17,20	U
28	12,22		27	13,00		23	18,30	U
78	12,40		31	13,10		59	86,00	U
37	12,50		53	13,20				

Sample D

Number of participants	41	Range	1,41
Number of omitted results	15	Variance	0,08
True value	3,02	Standard deviation	0,28
Mean value	3,03	Relative standard deviation	9,3%
Median value	3,01	Relative error	0,3%

Analytical results in ascending order:

33	<32	U	51	3,00		68	3,40	U
69	<4	U	37	3,00		77	3,50	
9	1,50	U	62	3,00		57	3,60	U
5	1,56	U	30	3,02		41	3,90	
28	2,49		31	3,04		7	4,55	U
12	2,50		29	3,07		4	4,93	U
53	2,70		78	3,10		40	5,20	U
32	2,81		16	3,10		20	5,72	U
10	2,85		71	3,11		2	6,90	U
3	2,89		45	3,13		23	7,85	U
64	2,90		70	3,20		76	10,00	U
27	2,90		15	3,20		43	10,39	U
58	2,93		42	3,20		59	72,00	U
17	2,95		38	3,30				

U = Omitted result

Table 5.16. Statistics - Nickel, µg/l

Sample C

Number of participants	36	Range	0,28
Number of omitted results	23	Variance	0,00
True value	0,47	Standard deviation	0,07
Mean value	0,44	Relative standard deviation	16,0%
Median value	0,47	Relative error	-5,9%

Analytical results in ascending order:

76	<10	U	9	<1	U	29	0,47	
69	<10	U	15	<1	U	17	0,48	
27	<5	U	77	<0,5	U	64	0,48	
2	<5	U	5	0,07	U	45	0,49	
16	<5	U	3	0,31		37	0,49	U
31	<3	U	10	0,36		62	0,59	
4	<2,75	U	58	0,40		38	0,71	U
28	<2	U	42	0,40		53	0,84	U
41	<2	U	78	0,40		12	0,90	U
43	<1,55	U	32	0,43		40	1,30	U
51	<1	U	30	0,47		57	1,60	U
71	<1	U	70	0,47		7	1,88	U

Sample D

Number of participants	36	Range	0,37
Number of omitted results	23	Variance	0,01
True value	0,46	Standard deviation	0,10
Mean value	0,46	Relative standard deviation	20,7%
Median value	0,45	Relative error	0,2%

Analytical results in ascending order:

76	<120	U	9	<1	U	70	0,47	
69	<10	U	51	<1	U	30	0,50	
27	<5	U	7	<1	U	40	0,50	U
2	<5	U	77	<0,5	U	29	0,51	
16	<5	U	5	0,02	U	64	0,54	
31	<3	U	3	0,28		17	0,57	
4	<2,75	U	10	0,37		12	0,60	U
41	<2	U	42	0,40		62	0,65	
28	<2	U	78	0,40		37	0,71	U
43	<1,55	U	58	0,41		53	0,94	U
71	<1	U	45	0,44		38	0,97	U
15	<1	U	32	0,45		57	1,70	U

U = Omitted result

Table 5.17. Statistics - Zinc, µg/l

Sample C

Number of participants	41	Range	5,25
Number of omitted results	12	Variance	2,34
True value	6,82	Standard deviation	1,53
Mean value	7,36	Relative standard deviation	20,8%
Median value	6,83	Relative error	7,9%

Analytical results in ascending order:

27	<20	U	31	6,68		64	8,50	
77	<10	U	17	6,70		4	8,69	
35	<10	U	45	6,76		71	10,00	
33	<10	U	70	6,80		57	10,00	
68	2,50	U	30	6,81		43	10,00	
78	4,80		58	6,83		76	10,00	
53	5,30		28	6,84		5	10,05	
42	5,90		62	6,90		38	11,37	U
41	5,91		12	6,90	U	15	11,40	U
23	5,95		10	7,35		2	12,00	U
51	6,00		32	7,62		7	21,90	U
16	6,00		9	8,00		40	28,00	U
37	6,30		69	8,10		59	58,00	U
29	6,38		3	8,24				

Sample D

Number of participants	41	Range	11,40
Number of omitted results	12	Variance	4,77
True value	21,55	Standard deviation	2,18
Mean value	21,77	Relative standard deviation	10,0%
Median value	21,90	Relative error	1,0%

Analytical results in ascending order:

27	<20	U	41	20,60		17	22,50	
7	<1	U	23	20,80		10	22,76	
68	10,50	U	29	20,93		32	22,84	
33	18,00	U	35	21,00	U	62	23,00	
3	18,60		16	21,00		71	23,00	
78	19,10		30	21,20		9	23,00	
77	19,40	U	31	21,20		58	24,00	
28	19,53		69	21,90		5	24,55	
53	19,60		45	22,00		2	29,50	U
38	19,75	U	64	22,00		76	30,00	
42	19,80		4	22,30		12	31,00	U
51	20,00		15	22,30	U	40	35,00	U
57	20,00		70	22,50		59	82,00	U
43	20,00		37	22,50				

U = Omitted result

Appendix E. Reports and publications from ICP Waters

All reports from the ICP Waters programme from 1987 up to present are listed below. All reports are available from the Programme Centre. Publications from 2002 up to present can be found at http://www.iis.niva.no/ICP%2Dwaters

Manual for Chemical and Biological Monitoring. Programme Manual. Prepared by the Programme Centre, Norwegian Institute for Water Research. NIVA, Oslo 1987.

Norwegian Institute for Water Research, 1987. Intercalibration 8701. pH, Ks, SO_4, Ca. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1988. Data Report 1987 and available Data from Previous Years. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1988. Intercalibration 8802. pH, K_{25}, HCO_3, NO_3, SO, Cl, Ca, Mg, Na, K. Programme Centre, NIVA, Oslo.

Proceedings of the Workshop on Assessment and Monitoring of Acidification in Rivers and Lakes, Espoo, Finland, 3rd to 5th October 1988. Prepared by the Finnish Acidification Research Project, HAPRO, Ministry of Environment, October 1988.

Norwegian Institute for Water Research, 1989. Intercalibration 8903: Dissolved organic carbon and aluminium fractions. Programme Centre, NIVA, Oslo. NIVA-Report SNO 2238-89.

Note: Some reflections about the determination of pH and alkalinity. Prepared by the Programme Centre, Norwegian Institute for Water Research. Håvard Hovind, NIVA, Oslo October 1989.

Hovind, H. 1990. Intercalibration 9004: pH and alkalinity. Programme Centre, NIVA, Oslo. NIVA-Report SNO 2465-90.

Skjelkvåle, B.L. and Wright, R.F. 1990. Overview of areas sensitive to acidification: Europe. Programme Centre, NIVA, Oslo. Acid Rain Research Report 20/1990. NIVA-Report 2405-90. ISBN 82-577-1706-1.

Johannessen, M. 1990. Intercalibration in the framework of an international monitoring programme. Proceedings of the third annual Ecological Quality Assurance Workshop, Canada Centre for Inland Waters, Burlington Ontario. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1990. Data Report 1988. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1990. Data Report 1989. Programme Centre, NIVA, Oslo.

Proceedings for the 5th Meeting of the Programme Task Force Freiburg, Germany, October 17 -19, 1989. Prepared by the Umweltbundesamt, Berlin July 1990.

Hovind, H. 1991. Intercalibration 9105: pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K and TOC. Programme Centre, NIVA, Oslo. NIVA-Report 2591-91.

Norwegian Institute for Water Research, 1991. The Three Year Report. Summary and results 1987 – 1989: Results from the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1991. Summary of The Three Year Report 1987 – 1989. Programme Centre, NIVA, Oslo.

Scientific papers presented at the Sixth Task Force meeting in Sweden 23 - 24 October 1990. Swedish Environmental Protection Agency, Sweden, September 1991.

Seventh Task Force meeting of international Co-operative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes. Galway, Ireland. September 30 - October 3 1991. Proceedings.

Johannessen, M., Skjelkvåle, B.L. and Jeffries, D. 1992. International cooperative Programme on Assessment and Monitoring of Rivers and Lakes. In: Conference Abstracts, Intern. Conference on Acidic Deposition, Glasgow 16-21, sept. 1992, p. 449. Kluwer Academic Press.

Hovind, H. 1992. Intercalibration 9206: pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, Al and DOC. Programme Centre, NIVA, Oslo. NIVA-Report 2784-92.

Norwegian Institute for Water Research, 1992. Data Report 1990. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1992. Evaluation of the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes. Programme Centre, NIVA, Oslo.

Hovind, H. 1993. Intercalibration 9307: pH, k_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, reactive and non-labile aluminium, TOC and COD-Mn. Programme Centre, NIVA,Oslo. NIVA-Report 2948-93.

Raddum, G.G. 1993. Intercalibration of Invertebrate Fauna 9301. Programme Centre, NIVA, Oslo. NIVA-Report SNO 2952-93.

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Hovind, H. 1995. Intercomparison 9509. pH, k_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium-reactive and nonlabile, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3331-95. ISBN 82-577-2849-7.

Traaen, T.S. and Stoddard, J.L. 1995. An Assessment of Nitrogen Leaching from Watersheds included in ICP on Waters. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3201-95.

Norwegian Institute for Water Research, 1995. Data Report 1992-93. Draft 1994. Part 1, Introduction and Chemistry. Programme Centre, NIVA, Oslo.

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Norwegian Institute for Water Research, 1996. Programme Manual. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3547-96.

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Raddum, G.G. 1998. Intercalibration 9804: Invertebrate fauna. NIVA-Report SNO 3912-98, **ICP-Waters Report 47/1998**.

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