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

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Intercomparison 0721: pH, Cond, HCO_3, NO_3-N, 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

75 laboratories received samples for the intercomparison 0721, and 72 laboratories in 28 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 as acceptable. The best results were reported for the analytical variables sodium and calcium, with 92 and 86 % acceptable results, respectively. Low percentage of acceptable results was observed for some heavy metals, especially zinc with 53 % acceptable results. The main reason is the low concentrations of the metals in the samples used. This time the worst case was pH with only 51 % of the results being acceptable. Harmonization of the analytical methods used and the practical procedures followed is probably most important 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 0721:

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

Prepared by the ICP Waters Programme Centre
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Preface

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

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

One of the tools in this work is inter-laboratory quality assurance tests. The bias between analyses carried out by the individual participants of the Programme has to be clearly identified and controlled.

We here report the results from the 21th intercomparison of chemical analysis.

Oslo, September 2007

Håvard Hovind

Contents

1. Summary

Intercomparison 0721 was organized as a part of the between-laboratory quality control programme, as stated in "Manual for Chemical and Biological Monitoring" (1), by the International Cooperative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes (ICP Waters).

The intercomparison was performed in July - August 2007, and included the determination of major ions and metals in natural water samples. The participants were asked to determine pH, conductivity, alkalinity, nitrate, chloride, sulphate, calcium, magnesium, sodium, potassium, iron, manganese, cadmium, lead, copper, nickel and zinc.

Two sample sets were prepared for this intercomparison, one for the determination of the major ions, and one for the heavy metals. 127 laboratories were invited to participate in this intercomparison, and the samples were sent to the 75 laboratories who accepted to participate. 72 laboratories submitted results to the Programme Centre before the final statistical treatment of the data. 28 countries were represented in this laboratory group (see Appendix A, page 40).

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

For pH, the accuracy limit was as in earlier intercomparisons extended from the target acceptance limit of ± 0,1 units to ± 0,2 units, and this time only 51 % of the result pairs were acceptable even using this special limit. This is the worst result for pH within several years of the ICP Waters intercomparison. 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 different routines for the determination of pH by the participants, leading to small systematic differences in the results. A further harmonization of the analytical method used, and the practical procedures applied, is necessary to improve the results for pH and alkalinity.

The best results were reported for the analytical variables sodium and calcium where 92 and 86 % of the results, respectively, were acceptable. The worst results were observed for pH (51 %) and some heavy metals, especially zinc (53 %). The main reason for less acceptable results for some metals is probably the low concentrations of these metals in the samples used, and also the fact that some laboratories are using equipment which is not sensitive enough for the low concentrations used in this intercomparison.

More than 80 % acceptable results were obtained for the five parameters conductivity, sulphate, calcium, sodium and copper, 70 – 79 % acceptable results were obtained for chloride, magnesium, potassium, manganese, and cadmium, 60 – 69 % for alkalinity, nitrate, iron, lead and nickel.

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 twentyfirst intercomparison test, called 0721, included the determination of the major components and some other ions in natural water samples: pH, conductivity, alkalinity, nitrate, chloride, sulphate, calcium, magnesium, sodium, potassium, iron, manganese, cadmium, lead, copper, nickel and zinc.

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 Bergen in October 2006 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 25th 2007, and the following day. Most of the participating laboratories received the samples within one week, with some few exceptions. It is important that the delivery address for the samples is correctly given, two sets of samples were not delivered to the laboratory, but returned to the organizer of this intercomparison.

To ensure that the effect of possible alterations in the solutions is minimized, the participants were asked to analyze the samples as soon as possible, and return the analytical results within one month after the samples arrived at the laboratory. By different reasons a few laboratories asked for some delay for reporting the results to the Programme Centre, which they were permitted to do. However, the results had to be reported before the statistical calculations. Most results were received within the middle of August, the last results included in the report were received in the beginning of September. Three laboratories who received samples did not return analytical results.

4. Results

127 laboratories were invited to participate in this ICP Waters intercomparison. 75 of the laboratories accepted and therefore samples were mailed to them. The 72 laboratories which submitted results to the Programme Centre, are representing 28 countries. Some laboratories submitted results a couple of weeks after the deadline, and a reminder letter was mailed to some few participants. The last results were received in the beginning of September. 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, is presented in Appendix C. The purpose of this test is to evaluate the comparability of the analytical results produced by the laboratories participating in the International Cooperative Programme. The real "true value" is not known exactly for the natural water samples used in this intercomparison. Therefore, we selected the median value, determined from the analytical results submitted by the participating laboratories, as the "true value" for each analytical variable. The median value is considered to be an acceptable estimate of the true value for this purpose, as long as most of the participants are using essentially the same analytical method. For certain variables, for instance pH, this may represent a problem as the methods used may produce systematically different results (stirring, non-stirring, and equilibration of the test solution), and we cannot argue that one method is more correct than the others.

The results are illustrated in Figure 1 - 17, where each laboratory is represented by a small circle and an identification number. Some laboratories with strongly deviating results may be located outside the plot. The great circle in the figures are representing a selected accuracy limit, either the general target limit of ± 20 % of the mean true values for the sample pair, or a special accuracy limit as defined in the sections below. A survey of the results of intercomparison 0721 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. 69 laboratories reported results for pH, nearly 50 % of the laboratories of this group indicated that they read the pH value during stirring the solution, while about 50 % read the pH value in a quiescent solution. The stirring are normally lowering the observed pH result. However, in this intercomparison the median values are not significantly different in the stirred samples compared to the non-stirred samples (see Table 1).

One laboratory equilibrated the solutions by bubbling with air containing 350 ppm CO_2 before reading the pH value. The reported result was only somewhat lower 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 produced by different methods are greater than here, it would be questionable to establish a "true value" based on the median value for all the reported results for pH. In such a case it should be discussed whether an individual "true value" for each method would be more appropriate.

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

Figure 1 is illustrating that the reported results are rather spread out along the 45 ° line, indicating that the results are influenced by systematic effects on the results. The systematically lowest pH results in Figure 1 are dominated by laboratories stirring the sample during reading the pH value. Some systematic deviations observed in Figure 1 may also be due to errors in the instrument, or more likely the electrodes, as different electrodes may give rise to different results (4, 5). The main reason for the differences in the reported results is probably connected to the small differences in the analytical methods used by the participants. Random errors are also affecting the results, and to a greater degree for pH than many other variables, illustrated in Figure 1 by the spread of the small circles away from the 45° line for many laboratories.

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 is mS/m at 25 °C, the reported results being at least one decade wrong. After questioning these laboratories about the unit used, some of them reported the unit they really used, and thus the results from these laboratories were recalculated to mS/m.

All participants used an electrometric method for the determination of conductivity. Most laboratories achieved very good agreement between the results for this variable. Figure 2 shows that systematic errors are dominating the results, both in positive and negative directions. A proper temperature correction is necessary when determining this variable, as the conductivity is changing by about two percents pr. degree at room temperature. If the accuracy limit had been extended to the target value of ± 20 %, defined in the Manual (1), 10 more results which is 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 more reasonable demand.

4.3 Alkalinity

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 5.3. 48 laboratories reported results for alkalinity, and nearly one half of the participants used the Gran plot titration method which is the suggested reference method in the Manual (1). The others used end point titration, either to pH = 4,5 and 4,2, or to one certain pH value only (4,5, 5,4 or 5,6). The results reported for the method using titration to both pH = 4,5 and 4,2 were very close to the results produced with the Gran plot method. One laboratory used a 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. Most of the deviating results in Figure 3 are systematically high, however, three result pairs are systematically very low. Both single end point titration and titration to pH 4,5 and 4,2 are represented by these high results. 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.

The overall result for alkalinity in this intercomparison is better about the same as in the last intercomparisons, 67 % of the results being acceptable. The alkalinity value varies significantly with the end-point pH used for the titration. In waters containing high concentrations of total inorganic carbon, the equivalence point is close to pH = 5,4. In 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

The results reported for this parameter are presented in Figure 4, and the reported values are given in Table 5.4. The circle in Figure 4 represents a general target accuracy of ± 20 %. Ion chromatography is used by about two third of the participants. The others are determining this analytical variable by photometric methods. Most of these laboratories are using an automated version of the cadmium reduction method. There is no significant difference between the results determined by these two methods. The hydrazine method used by one laboratory gave acceptable results. Six laboratories obviously reported the results in a wrong unit, and the results from some of the laboratories were corrected to µg/l after clarification with the laboratory. Two laboratories did not respond to the question about the unit used. One laboratory using capillary electrophoresis reported values close to the median values.

In this intercomparison 63 % of the results are evaluated as acceptable, which is much worse than in the corresponding intercomparisons the last few years. The concentration of nitrate-nitrogen is comparable 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. However, some of the participants indicated that the samples were less stable with respect to the nitrate content. This may be verified by the fact that most of the deviating results are systematically low. At the programme centre the samples were stored at 4 °C, and this is probably enough to stabilize

the samples. During transport to the laboratories the samples may be affected by the environmental conditions.

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

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. 82 % of the laboratories determined chloride by ion chromatography. The greatest deviations are observed for a potentiometric method and the argentometric method, while somewhat varying and systematically high results were reported for the mercurimetric method.

79 % of the result pairs in this intercomparison are acceptable.

4.6 Sulphate

The sulphate results are illustrated in Figure 6, and the reported values are given in Table 5.6. The circle is representing the target accuracy of ± 20 %. Ion chromatography is used by 84 % of the laboratories for determination of the sulphate content of the samples. Three laboratories used a photometric method based on the dissociation of the barium-thorin complex. Only two of the four 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, the result being acceptable. One laboratory used a gravimetric method, the result for sample B was far too low.

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. 65 laboratories reported results for calcium, and only 13 of them used the traditional flame atomic absorption spectrometry for the determination. The ICP technique is used by 17 laboratories, and three of these used ICP-MS. An increasing number of laboratories, this time 29, used ion chromatography. Six laboratories used a titrimetric method with EDTA for the determination of calcium, five of these were outside the acceptance limit. This method is probably not sensitive enough for the concentrations used in these test.

86 % acceptable result pairs is good.

4.8 Magnesium

The magnesium results are presented in Figure 8, and the reported values are given in Table 5.8. The analytical methods used by the participants are the same as for the determination of calcium. 13 laboratories are still using flame atomic absorption spectrometry for the determination of magnesium. ICP atomic emission spectrometry was used by 14 laboratories and ICP-MS by three, and 29 laboratories used ion chromatography. Systematic errors are dominating the results being outside the acceptance limit. This time, 77 % of the results are located inside the target accuracy of ± 20 %. The great deviations observed for the titrimetric method indicate that the concentrations of the samples used in this intercomparison are rather low for this technique, only one of the result pairs produced by this method was acceptable. 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 13 laboratories used flame atomic absorption spectrometry for the determination this time, and ICP-AES was used by 11 laboratories. However, in many laboratories the ion chromatographic technique becomes increasingly more popular in routine determination of the alkaline metals, thus 29 participants used ion chromatography in this intercomparison. Six laboratories used flame photometry. 92 % 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 13 laboratories used flame atomic absorption spectrometry for the determination of this element, and emission spectrometry is used by the same laboratories as for the determination of sodium. The deviations observed in Figure 10 are both of systematic and random nature. This time 77 % of the result pairs are considered acceptable, and this is comparable to the earlier intercomparisons.

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, 63 % of the result pairs are located inside this circle, which is worse than the last intercomparison, one possible reason for this is the lower concentrations used for iron in this intercomparison. 38 laboratories submitted results for iron, of which 16 and 11 used ICP-AES and ICP-MS, respectively, while 8 and 2 used flame and graphite furnace atomic absorption, respectively. The ICP emission methods are clearly taking over more and more on behalf of the atomic absorption methods.

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

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. 70 % of the result pairs are located inside this circle, which is less than the last intercomparison, probably because the concentrations used this time are somewhat lower than earlier. 44 laboratories submitted results for manganese, of which 15 and 15 used ICP-AES and ICP-MS, respectively, while 7 and 7 used flame and graphite furnace atomic absorption, respectively. One laboratory had problems with the sensitivity of the method for sample D with the lowest concentration, and reported "less than" their detection limit. 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, 75 % of the result pairs are located inside this circle. 44 laboratories submitted results for cadmium, of which 10 and 17 used ICP-AES and ICP-MS, respectively, while 12 used graphite furnace atomic absorption. One laboratory using polarography reported results being comparable to the others. Flame atomic absorption gave systematically lower results than the other methods.

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. 64 % of the result pairs are located inside this circle, which is somewhat better than the last intercomparison. 42 laboratories submitted results for lead, of which 10 and 16 used ICP-AES and ICP-MS, respectively, while 8 used graphite furnace atomic absorption. Flame atomic absorption was used by four laboratories, even though the method is not very sensitive and are not suitable for determination of these low lead concentrations. Polarography is working well.

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. 82 % of the result pairs are located inside this circle, which is acceptable. The higher concentrations used for copper this time are most probably a reason for these results. 44 laboratories submitted results for copper, of which 12 used ICP-AES and 17 used ICP-MS, while 9 and 6 used graphite furnace and flame atomic absorption, respectively. Two laboratories using flame atomic absorption, reported the results as < the detection limit. Polarography is comparable to the other methods.

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 62 % of the result pairs are located inside this circle, and the main reason for this situation is that the nickel concentrations are rather low in the samples used this time. 42 laboratories submitted results for nickel, of which 12 and 15 used ICP-AES and ICP-MS, respectively, while 11 used graphite furnace atomic absorption. ICP-MS are leading to results being systematically a little higher than the other methods.

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 53 % of the result pairs are located inside this circle, which is rather bad. One of the reasons is probably that som laboratories are using methods which are not sensitive enough. 43 laboratories submitted results for zinc, of which 14 and 16 used ICP-AES and ICP-MS, respectively, while 8 and 4 used flame and graphite furnace atomic absorption, respectively. Generally, the deviating results are affected mainly by systematic errors.

Table 1. Statistical summary of intercomparison 0721

Analytical variable and method	Sample pair	True value 1	True value 2	Total number	Labs excl.	Median 1	Median 2	Average/Std.dev. Sample 1		Average/Std.dev. Sample 2		Rel.std.dev. % 1	Rel.std.dev. % 2	Relative error % 1	Relative error % 2
pH	AB	6,69	7,25	69	1	6,69	7,25	6,65	0,26	7,18	0,29	3,9	4,0	-0,6	-0,9
No stirring				35	1	6,71	7,25	6,69	0,26	7,23	0,25	3,8	3,5	0,1	-0,3
Stirring				33	0	6,68	7,25	6,61	0,26	7,14	0,32	3,9	4,5	-1,2	-1,5
Equilibration				1	0			6,53		7,08				-2,4	-2,3
Conductivity	AB	2,84	6,60	66	3	2,84	6,60	2,84	0,17	6,55	0,27	6,0	4,1	0,1	-0,7
Alkalinity	AB	0,106	0,356	48	9	0,106	0,356	0,114	0,020	0,360	0,024	17,3	6,8	7,1	1,1
Gran plot titration				22	3	0,105	0,358	0,109	0,017	0,359	0,020	15,9	5,6	3,0	0,8
End point titration				8	0	0,113	0,350	0,118	0,021	0,356	0,030	17,9	8,5	11,6	0,0
End point 5.6				1	0			0,105		0,349				-0,9	-2,0
End point 5.4				2	0			0,102		0,343				-4,2	-3,7
End point				14	6	0,118	0,367	0,125	0,024	0,372	0,031	18,9	8,2	18,0	4,6
Not documented				1	0			0,100		0,360				-5,7	1,1
Nitrate-nitrogen	AB	160	255	64	15	160	255	154	21	252	27	13,4	10,9	-3,6	-1,3
Autoanalyzer				14	4	161	255	158	6	255	10	4,0	3,8	-1,5	-0,1
Photometry				7	2	164	253	146	33	260	20	22,3	7,8	-8,5	2,0
Ion chromatography				40	8	158	255	154	22	249	33	14,5	13,1	-3,8	-2,2
Hydrazine				1	0			168		261				5,2	2,4
Cap. electrophoresis				1	0			155		249				-3,1	-2,4
Photometry				1	1			409		425				155,6	66,7
Chloride	AB	1,86	3,41	66	6	1,86	3,41	1,88	0,21	3,41	0,25	11,1	7,5	1,3	0,1
Ion chromatography				54	3	1,86	3,41	1,86	0,17	3,41	0,26	9,0	7,7	-0,3	-0,1
AA				1	0			1,87		3,37				0,5	-1,2
Argentometry				3	3			2,86		4,98				53,9	46,1
Manual, Hg				4	0	1,78	3,39	1,91	0,34	3,42	0,29	17,6	8,4	2,4	0,3
Cap. electrophoresis				1	0			1,80		3,32				-3,1	-2,6
Potentiometry				2	0			2,45		3,60				31,7	5,6
Photometry				1	0			2,28		3,42				22,6	0,3

Analytical variable and method	Sample pair	True value 1	True value 2	Total number	Labs excl.	Median 1	Median 2	Average/Std.dev. Sample 1		Average/Std.dev. Sample 2		Rel.std.dev. % 1	Rel.std.dev. % 2	Relative error % 1	Relative error % 2
Sulphate	AB	2,72	5,75	64	9	2,72	5,75	2,71	0,17	5,74	0,34	6,4	5,9	-0,5	-0,2
Ion chromatography				54	6	2,73	5,76	2,72	0,14	5,73	0,34	5,3	5,9	0,0	-0,4
Photometry				3	0	2,56	5,87	2,53	0,07	5,92	0,52	2,8	8,7	-7,0	3,0
Nephelometry				4	2			2,72		5,83				0,0	1,3
ICP-AES				1	0			2,60		5,49				-4,4	-4,5
Cap. electrophoresis				1	0			2,72		5,66				-0,2	-1,6
Gravimetry				1	1			2,47		1,23				-9,2	-78,6
Calcium	AB	2,81	8,53	65	7	2,81	8,53	2,84	0,23	8,57	0,46	8,0	5,4	1,1	0,4
FAAS				13	1	2,79	8,43	2,85	0,28	8,44	0,28	9,7	3,3	1,6	-1,1
ICP-AES				14	0	2,86	8,50	2,83	0,15	8,51	0,39	5,3	4,6	0,9	-0,2
EDTA				6	2	3,10	8,49	3,00	0,27	8,49	0,34	9,0	4,0	6,7	-0,5
Ion chromatography				29	4	2,83	8,80	2,84	0,23	8,75	0,50	8,3	5,7	1,1	2,6
ICP-MS				3	0	2,59	8,14	2,62	0,06	7,90	0,50	2,2	6,4	-6,6	-7,4
Magnesium	AB	0,40	0,69	65	11	0,40	0,69	0,40	0,03	0,69	0,05	8,1	6,7	0,3	-0,2
FAAS				13	1	0,40	0,70	0,41	0,03	0,69	0,05	8,0	7,6	2,5	0,1
ICP-AES				14	1	0,41	0,69	0,41	0,02	0,70	0,03	5,1	3,9	1,3	1,2
EDTA				6	5			0,30		0,57				-25,0	-17,4
Ion chromatography				29	4	0,41	0,70	0,40	0,03	0,69	0,05	8,3	6,9	0,3	0,2
ICP-MS				3	0	0,39	0,66	0,38	0,01	0,66	0,02	2,9	3,5	-4,7	-4,8
Sodium	AB	1,59	2,67	62	4	1,59	2,67	1,59	0,09	2,66	0,14	5,5	5,4	0,1	-0,2
FAAS				13	2	1,59	2,67	1,58	0,09	2,68	0,13	6,0	4,8	-0,5	0,4
ICP-AES				11	0	1,60	2,64	1,63	0,12	2,65	0,16	7,5	6,2	2,5	-0,6
AES				6	1	1,60	2,69	1,58	0,13	2,70	0,24	8,0	9,0	-0,7	1,3
Ion chromatography				29	1	1,60	2,68	1,59	0,06	2,67	0,12	3,8	4,6	-0,1	-0,1
ICP-MS				3	0	1,54	2,47	1,52	0,03	2,52	0,10	1,9	3,8	-4,2	-5,6
Potassium	AB	0,280	0,556	61	5	0,280	0,556	0,283	0,037	0,549	0,048	13,2	8,8	1,0	-1,3
FAAS				13	1	0,282	0,565	0,285	0,034	0,559	0,050	11,9	8,9	1,6	0,6
ICP-AES				10	2	0,294	0,583	0,295	0,035	0,576	0,050	11,8	8,7	5,3	3,6
AES				6	1	0,287	0,556	0,302	0,046	0,527	0,045	15,2	8,6	7,7	-5,2
Ion chromatography				29	1	0,274	0,550	0,275	0,038	0,542	0,048	13,7	8,8	-1,7	-2,6
ICP-MS				3	0	0,292	0,541	0,283	0,050	0,535	0,023	17,5	4,2	1,2	-3,8

Analytical variable and method	Sample pair	True value 1	True value 2	Total number	Labs excl.	Median 1	Median 2	Average/Std.dev. Sample 1		Average/Std.dev. Sample 2		Rel.std.dev. % 1	Rel.std.dev. % 2	Relative error % 1	Relative error % 2
Iron	CD	31	130	38	9	31	130	33	6	130	11	19,8	8,6	5,1	-0,1
FAAS				8	3	31	134	34	8	130	10	25,3	7,5	8,1	0,4
GFAAS				2	0			37		121				18,4	-7,3
ICP-AES				16	3	32	130	33	6	130	11	17,2	8,8	6,4	0,2
ICP-MS				11	3	32	132	32	4	132	9	13,1	6,7	3,4	1,7
Photometry				1	0			19		122				-38,7	-6,2
Manganese	CD	15,4	5,7	44	8	15,4	5,7	15,4	1,2	5,5	0,6	7,6	11,3	0,0	-2,8
FAAS				7	5			15,5		5,5				0,6	-3,5
GFAAS				7	1	14,8	5,2	15,1	1,8	5,4	0,7	11,7	13,8	-2,1	-4,6
ICP-AES				15	1	15,3	5,7	15,4	1,0	5,4	0,7	6,7	12,9	0,1	-4,5
ICP-MS				15	1	15,5	5,7	15,5	1,1	5,7	0,5	7,4	9,0	0,7	-0,3
Cadmium	CD	1,48	6,30	44	1	1,48	6,30	1,42	0,22	6,08	0,94	15,9	15,4	-4,2	-3,4
FAAS				4	0	1,20	4,71	1,19	0,32	4,87	1,41	26,5	28,9	-19,4	-22,7
GFAAS				12	0	1,41	6,00	1,38	0,28	5,89	0,87	20,1	14,8	-6,7	-6,5
ICP-AES				10	1	1,42	6,30	1,42	0,09	6,22	0,27	6,5	4,3	-4,1	-1,3
ICP-MS				17	0	1,52	6,57	1,49	0,19	6,39	0,91	12,9	14,3	0,7	1,5
Polarography				1	0			1,48		6,79				0,0	7,8
Lead	CD	6,2	9,3	42	6	6,2	9,3	6,0	1,0	9,0	1,6	16,7	17,8	-3,6	-3,5
FAAS				4	0	5,1	7,2	5,2	1,8	7,4	2,1	33,8	29,0	-15,7	-20,8
GFAAS				11	2	5,9	9,0	5,6	0,8	8,2	1,5	13,9	18,1	-9,6	-12,4
ICP-AES				10	4	5,7	8,8	5,5	1,2	9,2	2,4	21,5	26,2	-11,9	-1,4
ICP-MS				16	0	6,5	9,8	6,5	0,5	9,8	0,5	7,0	4,8	5,6	4,9
Polarography				1	0			6,4		9,2				3,2	-0,8
Copper	CD	19,6	20,5	44	2	19,6	20,5	19,6	1,9	20,3	2,0	9,9	10,1	0,1	-0,7
FAAS				6	2	18,5	19,2	17,8	2,8	18,5	3,4	16,0	18,3	-9,2	-9,8
GFAAS				8	0	19,0	19,7	18,9	1,7	19,4	1,9	8,9	9,6	-3,7	-5,5
ICP-AES				12	0	19,8	20,9	20,6	2,5	21,1	2,2	12,1	10,5	5,2	2,9
ICP-MS				17	0	19,9	20,7	19,8	0,8	20,8	1,2	4,2	5,6	0,8	1,7
Polarography				1	0			18,4		18,2				-6,2	-11,1

Analytical variable and method	Sample pair	True value 1	True value 2	Total number	Labs excl.	Median 1	Median 2	Average/Std.dev. Sample 1		Average/Std.dev. Sample 2		Rel.std.dev. % 1	Rel.std.dev. % 2	Relative error % 1	Relative error % 2
Nickel	CD	6,55	3,69	42	7	6,55	3,69	6,42	0,69	3,60	0,52	10,7	14,4	-1,9	-2,5
FAAS				4	2			5,33		3,16				-18,7	-14,5
GFAAS				11	1	6,17	3,59	6,26	0,77	3,60	0,67	12,4	18,6	-4,5	-2,5
ICP-AES				12	4	6,52	3,36	6,43	0,74	3,46	0,54	11,6	15,6	-1,8	-6,2
ICP-MS				15	0	6,84	3,80	6,68	0,45	3,73	0,34	6,8	9,2	2,0	1,2
Zinc	CD	6,0	12,5	43	9	6,0	12,5	5,9	1,2	12,4	2,1	19,8	17,0	-1,4	-0,7
FAAS				8	5	6,0	13,0	6,0	1,0	11,9	1,8	17,2	15,5	0,6	-4,5
GFAAS				4	1	4,8	10,7	4,8	0,9	10,0	2,2	18,2	22,4	-20,7	-20,0
ICP-AES				14	2	6,1	12,3	6,2	1,5	12,6	2,5	24,4	19,6	4,0	0,4
ICP-MS				16	1	6,0	12,6	5,9	0,9	12,9	1,7	15,1	13,2	-2,0	3,5
Polarography				1	0			5,7		11,7				-4,8	-6,7

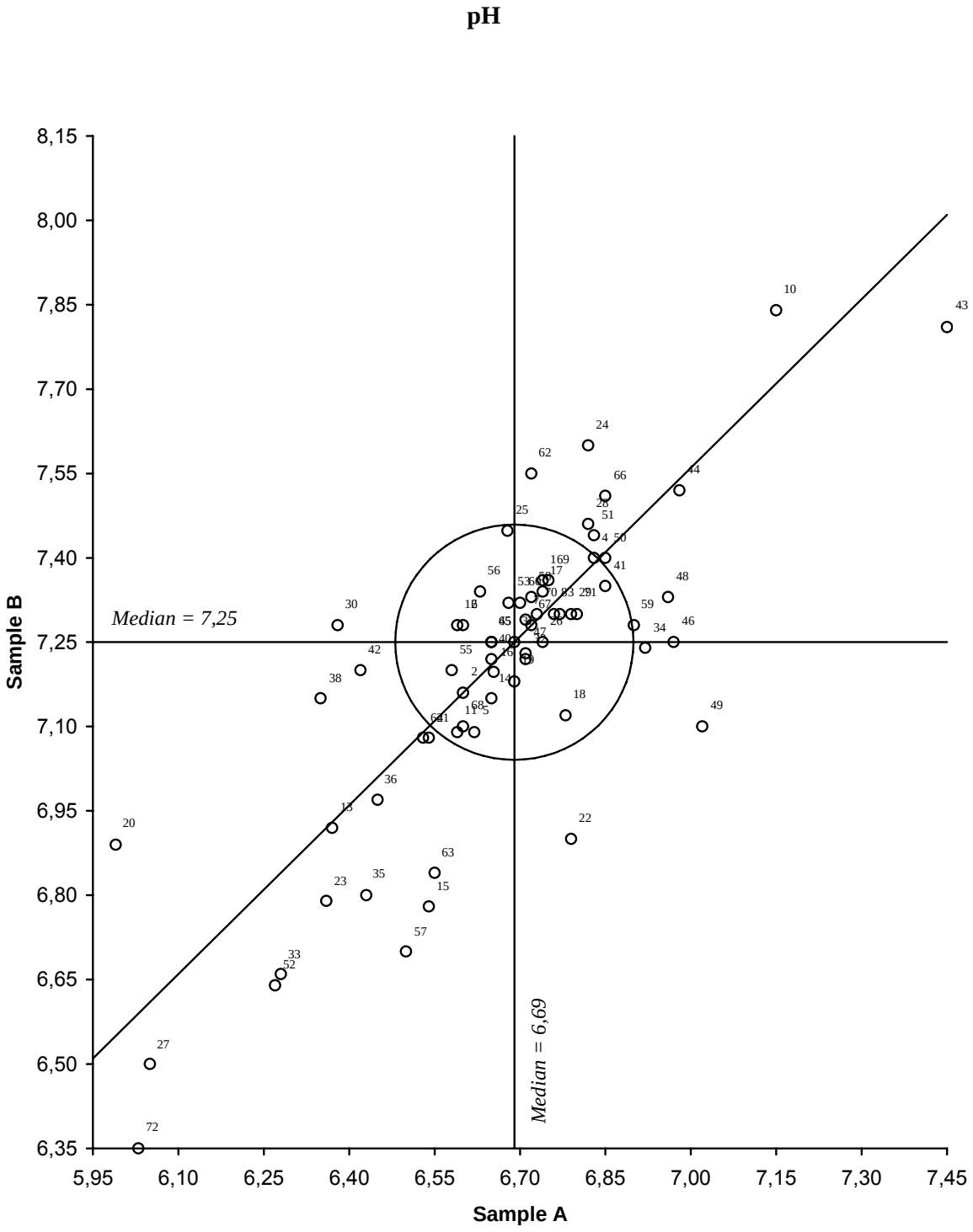

Figure 1. Youden diagramme for pH, sample pair AB
Acceptance limit, given by the circle, is 0,2 pH units

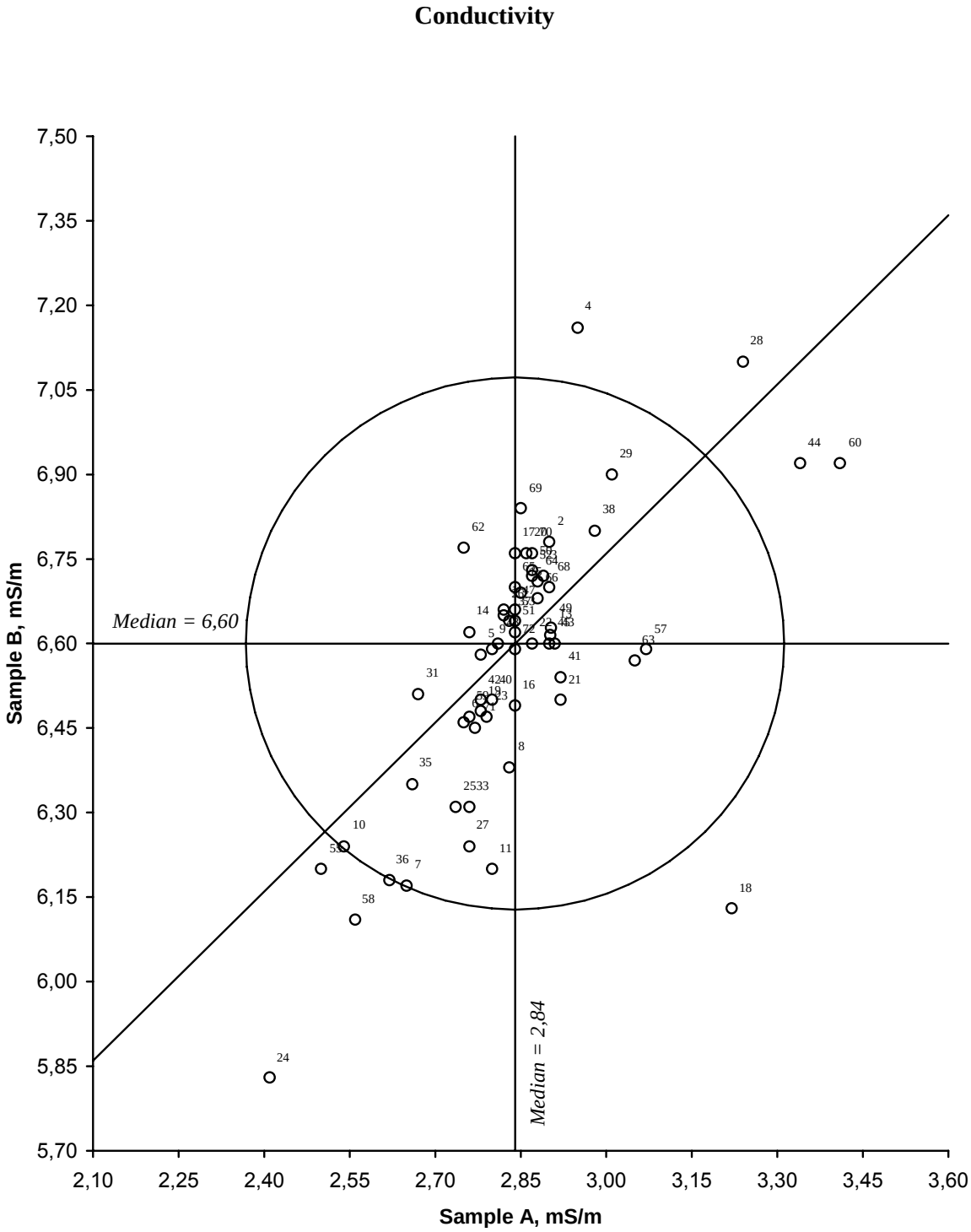

Figure 2. Youden diagramme for conductivity, sample pair AB
Acceptance limit, given by the circle, is 10 %

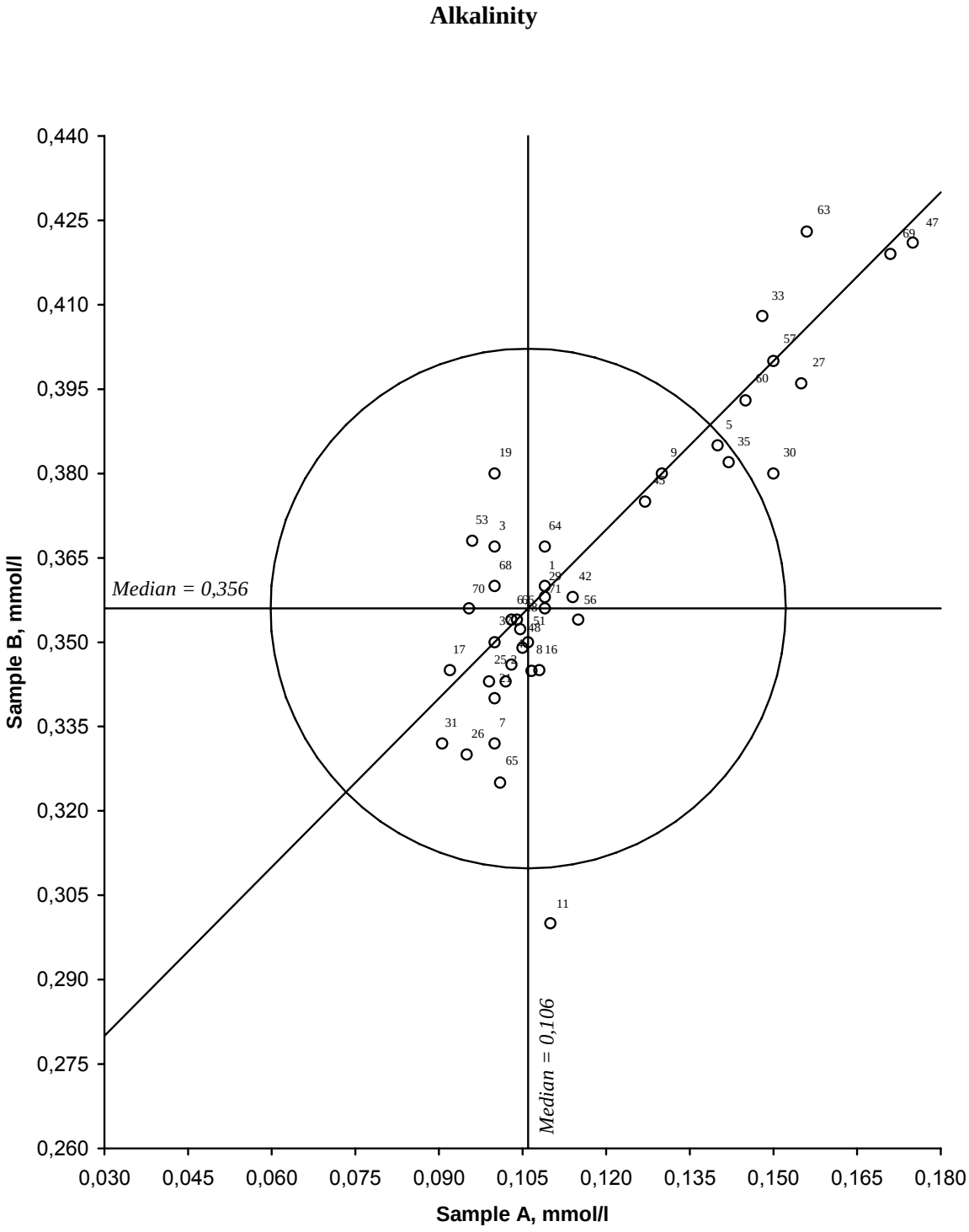

Figure 3. Youden diagramme for alkalinity, sample pair AB
Acceptance limit, given by the circle, is 20 %

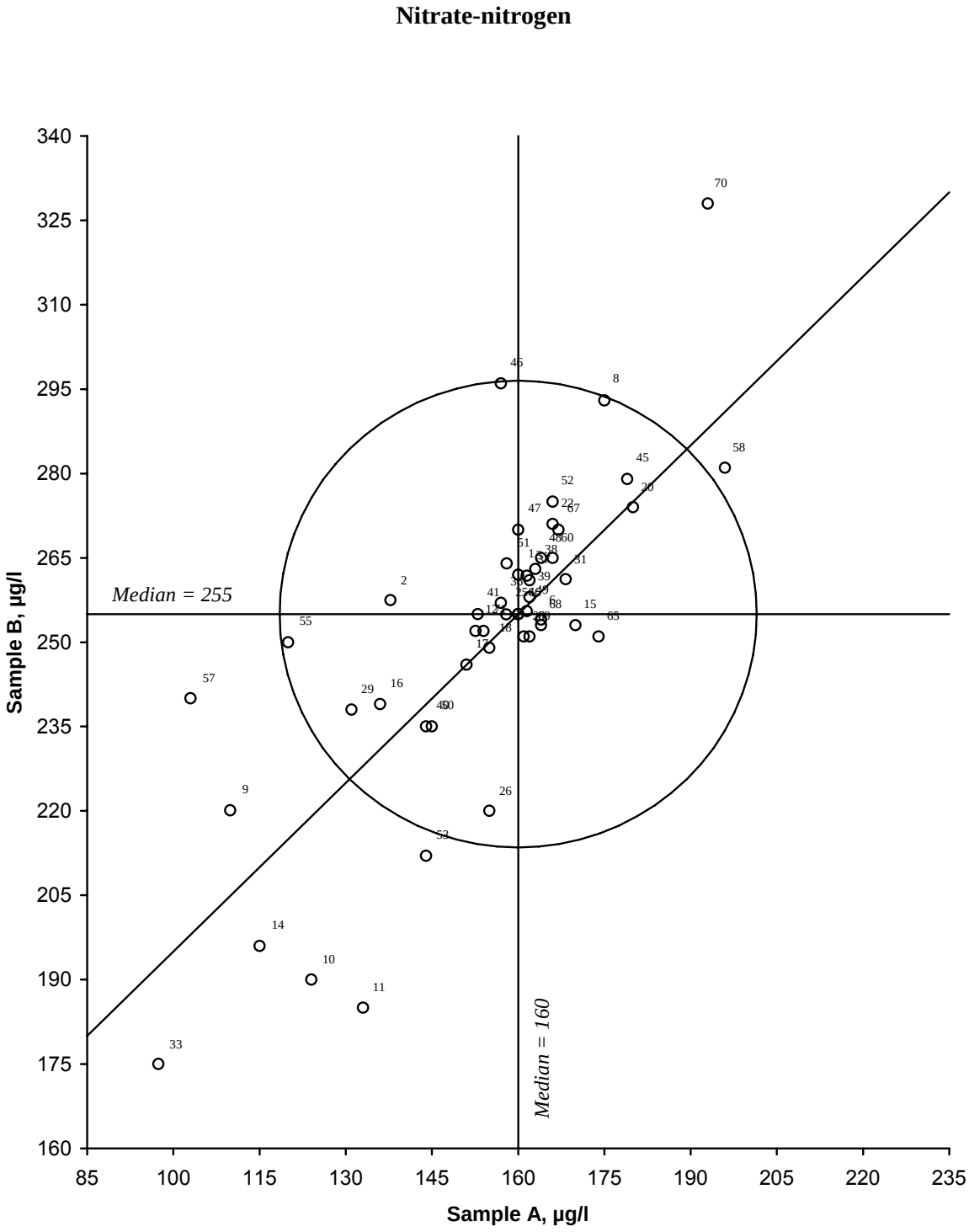

Figure 4. Youden diagramme for nitrate+nitrite-nitrogen, sample pair AB
Acceptance limit, given by the circle, is 20 %

Chloride

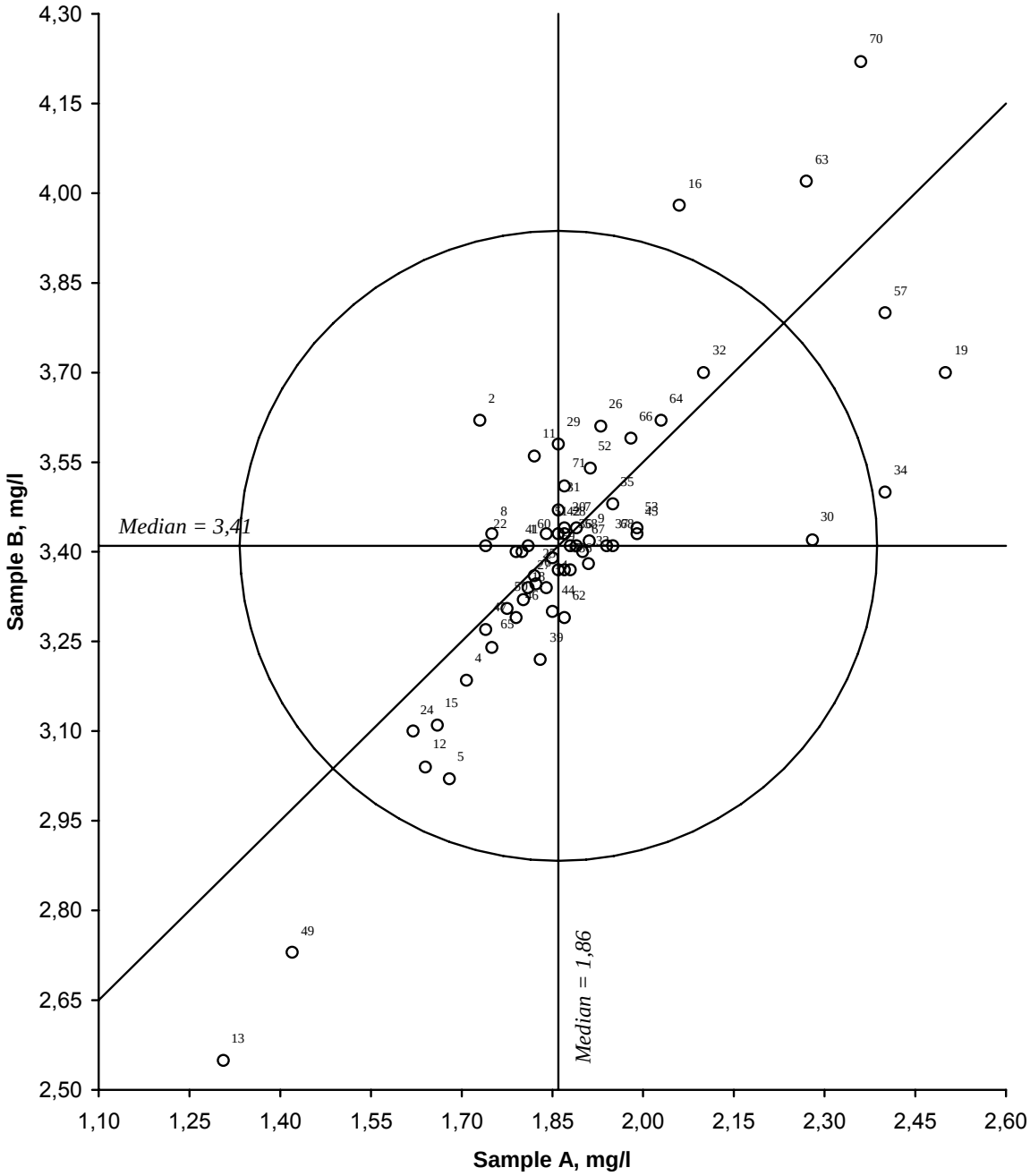

Figure 5. Youden diagramme for chloride, sample pair AB
Acceptance limit, given by the circle, is 20 %

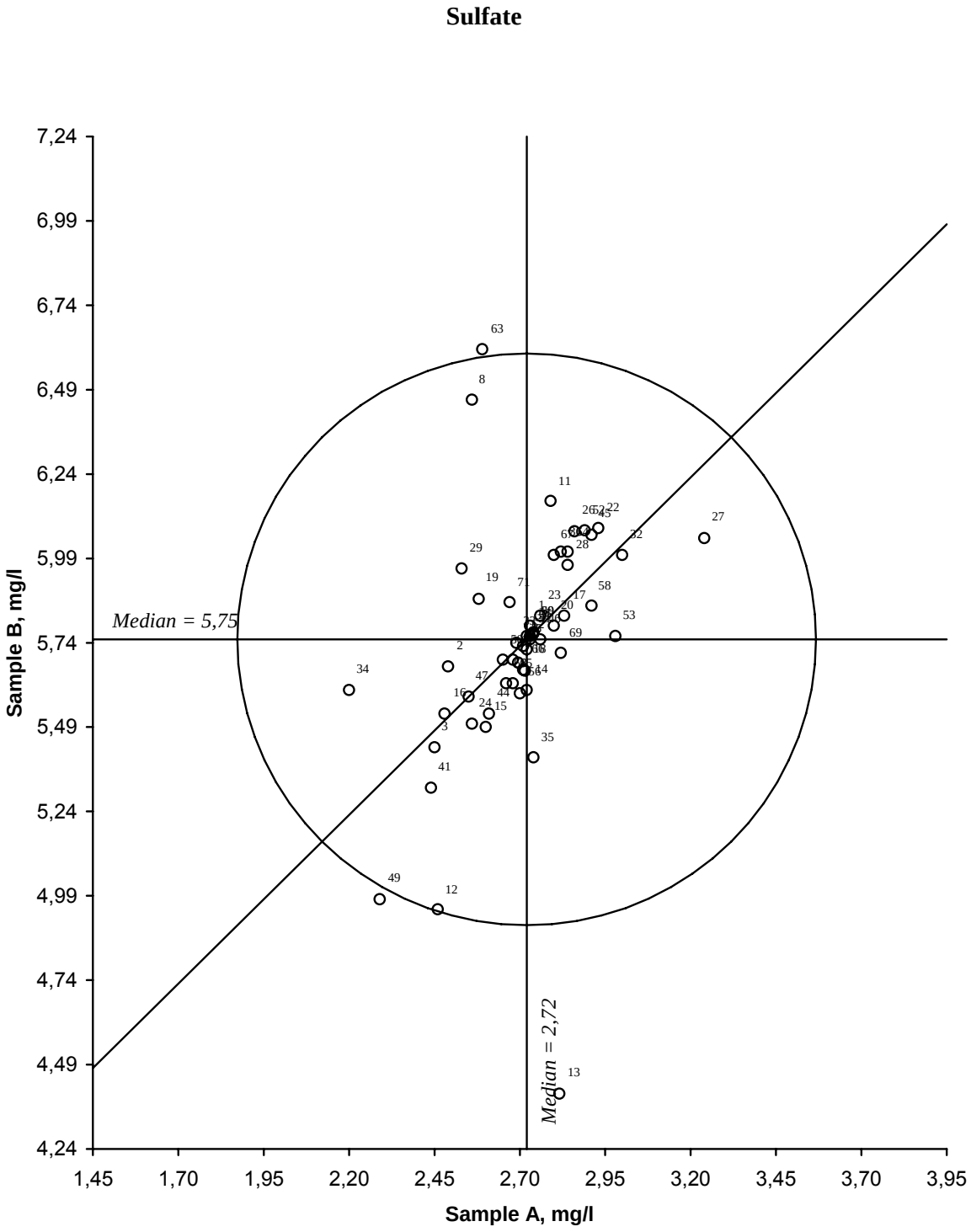

Figure 6. Youden diagramme for sulfate, sample pair AB
Acceptance limit, given by the circle, is 20 %

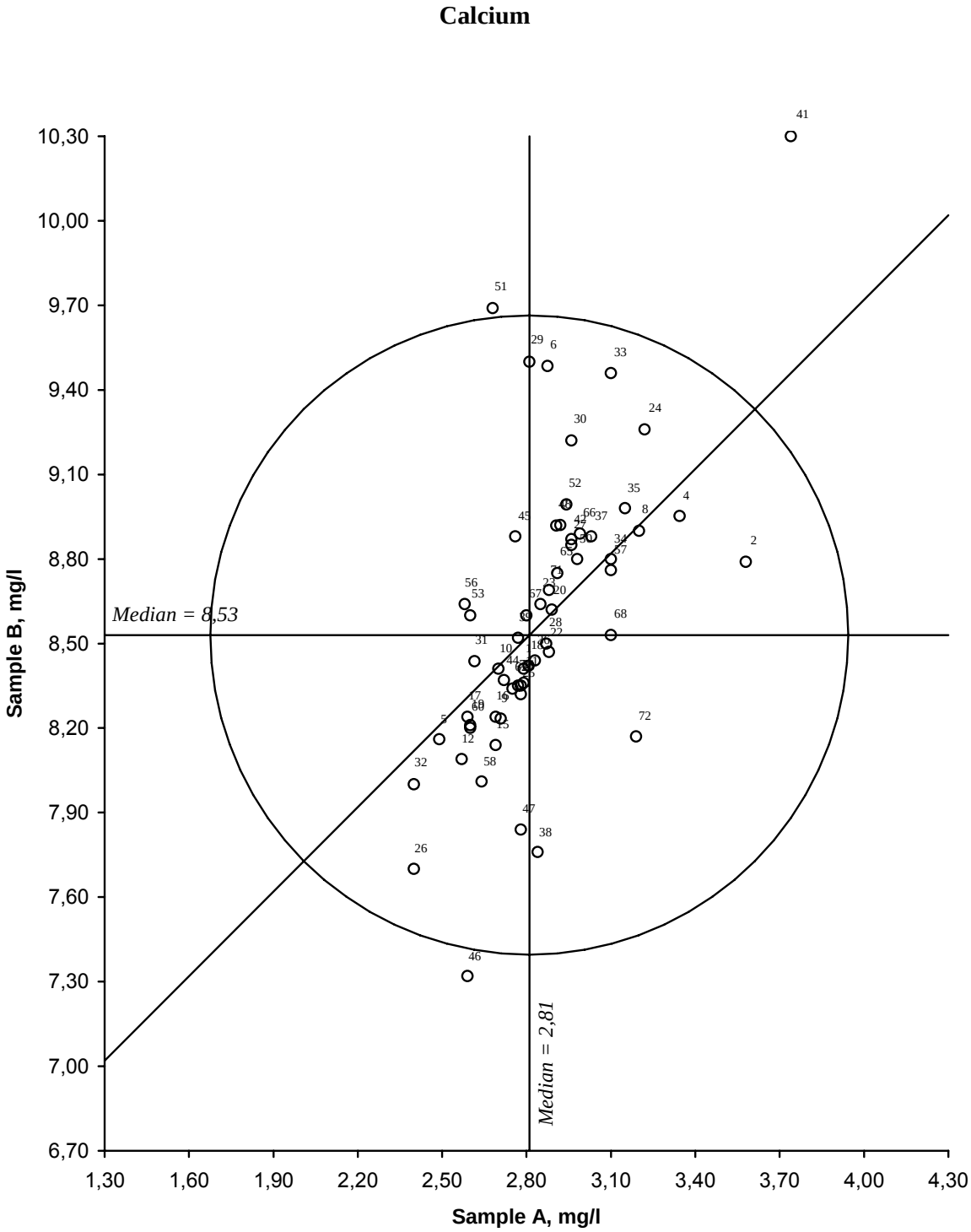

Figure 7. Youden diagramme for calcium, sample pair AB
Acceptance limit, given by the circle, is 20 %

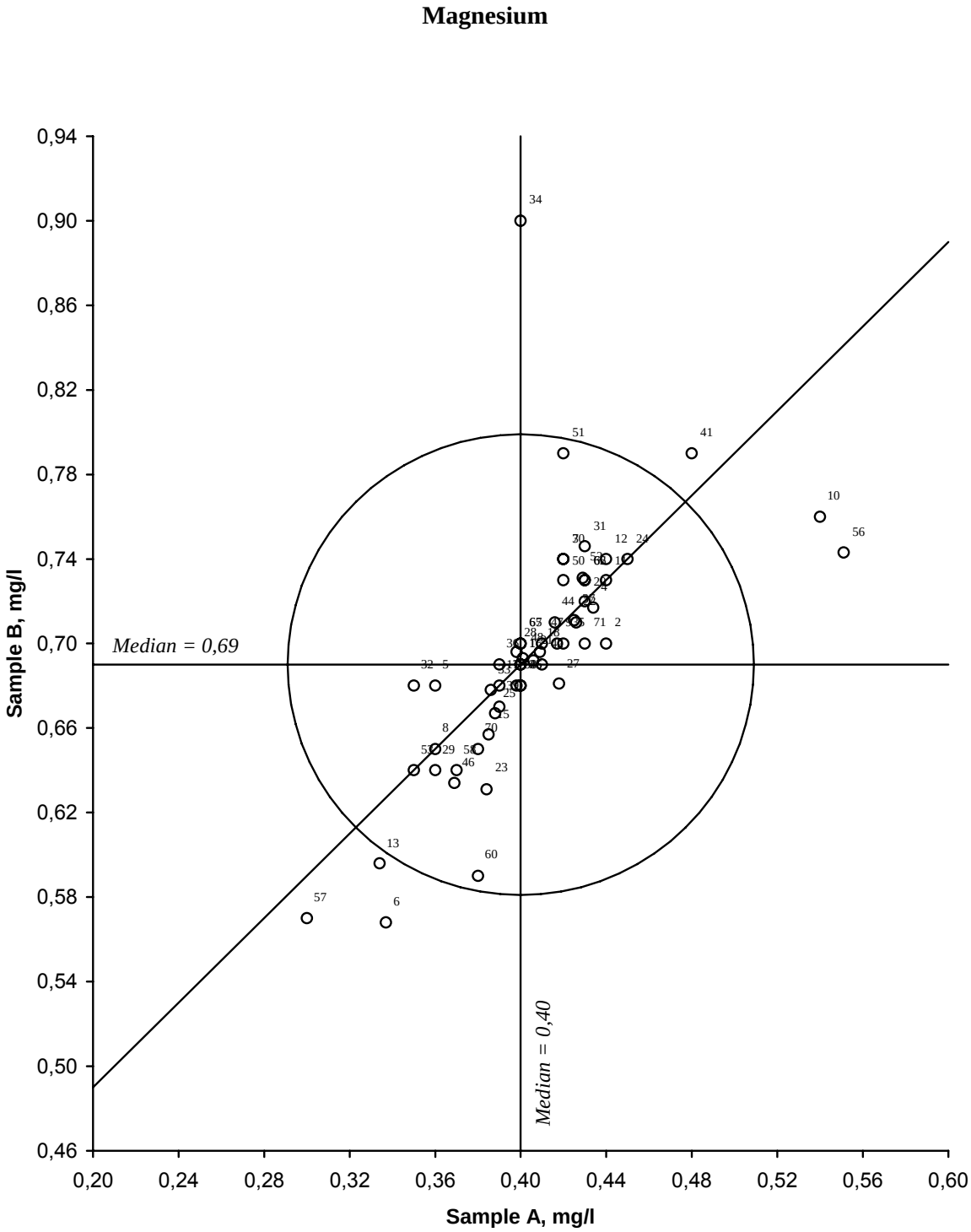

Figure 8. Youden diagramme for magnesium, sample pair AB
Acceptance limit, given by the circle, is 20 %

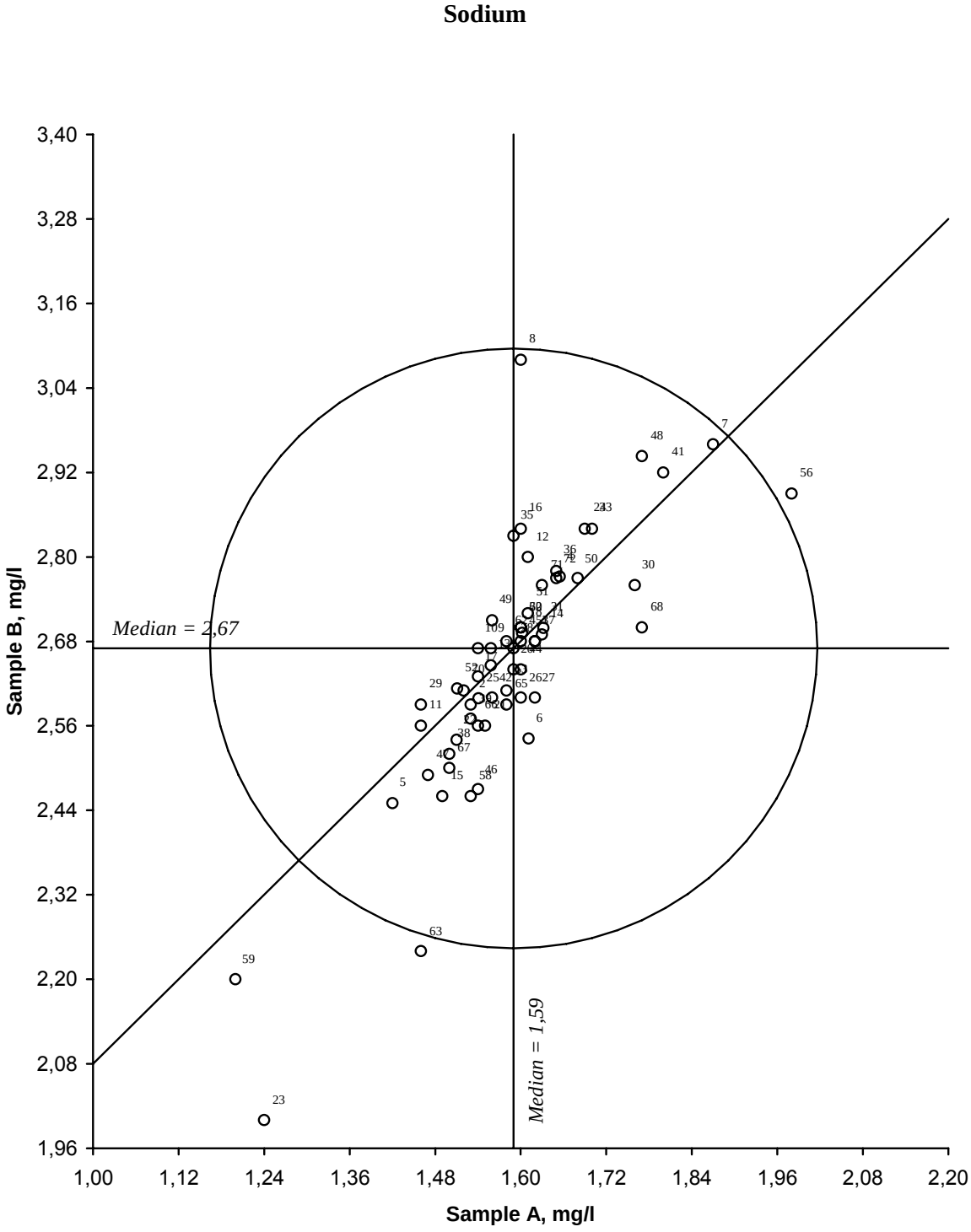

Figure 9. Youden diagramme for sodium, sample pair AB
Acceptance limit, given by the circle, is 20 %

Potassium

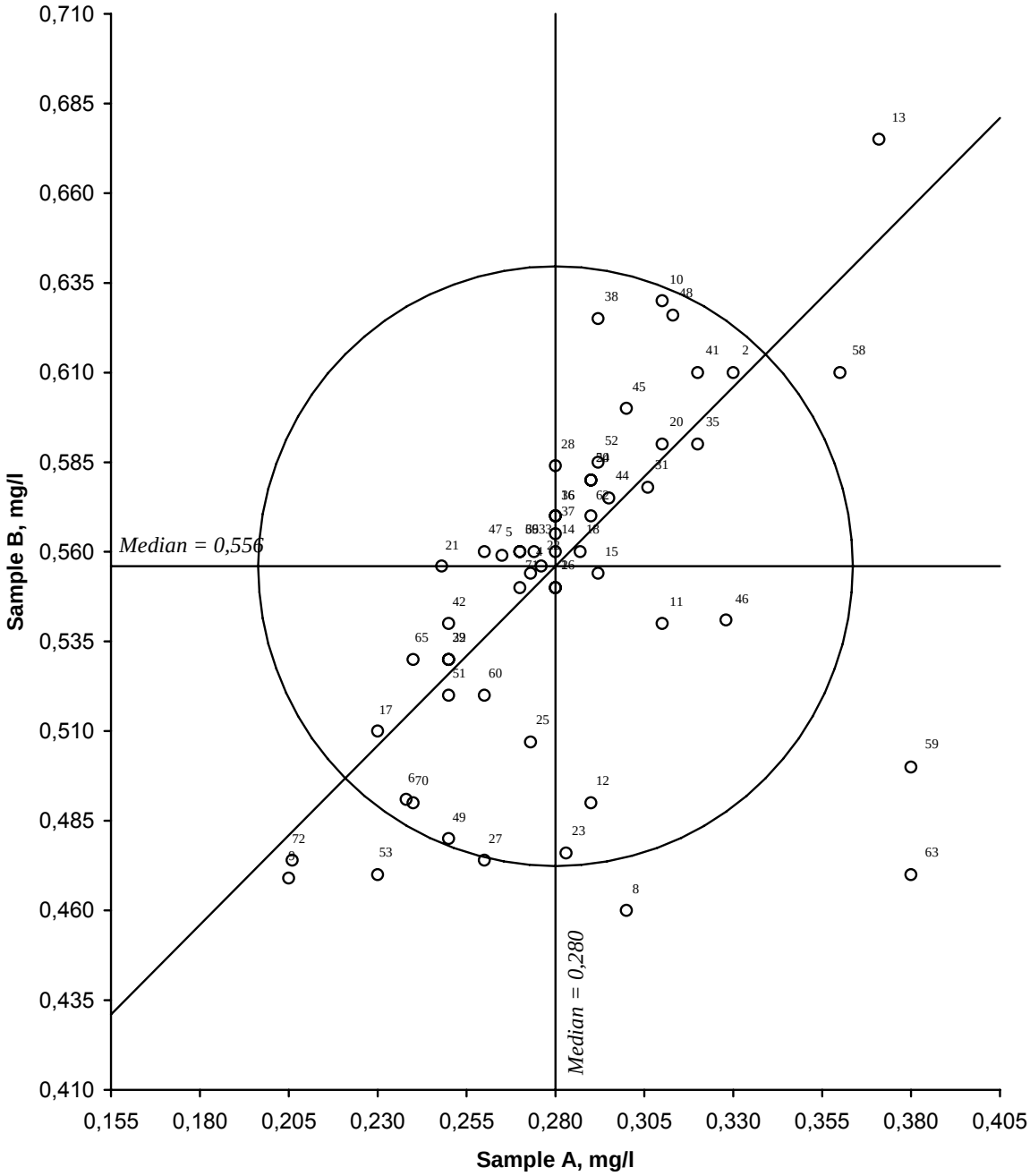

Figure 10. Youden diagramme for potassium, sample pair AB
Acceptance limit, given by the circle, is 20 %

Iron

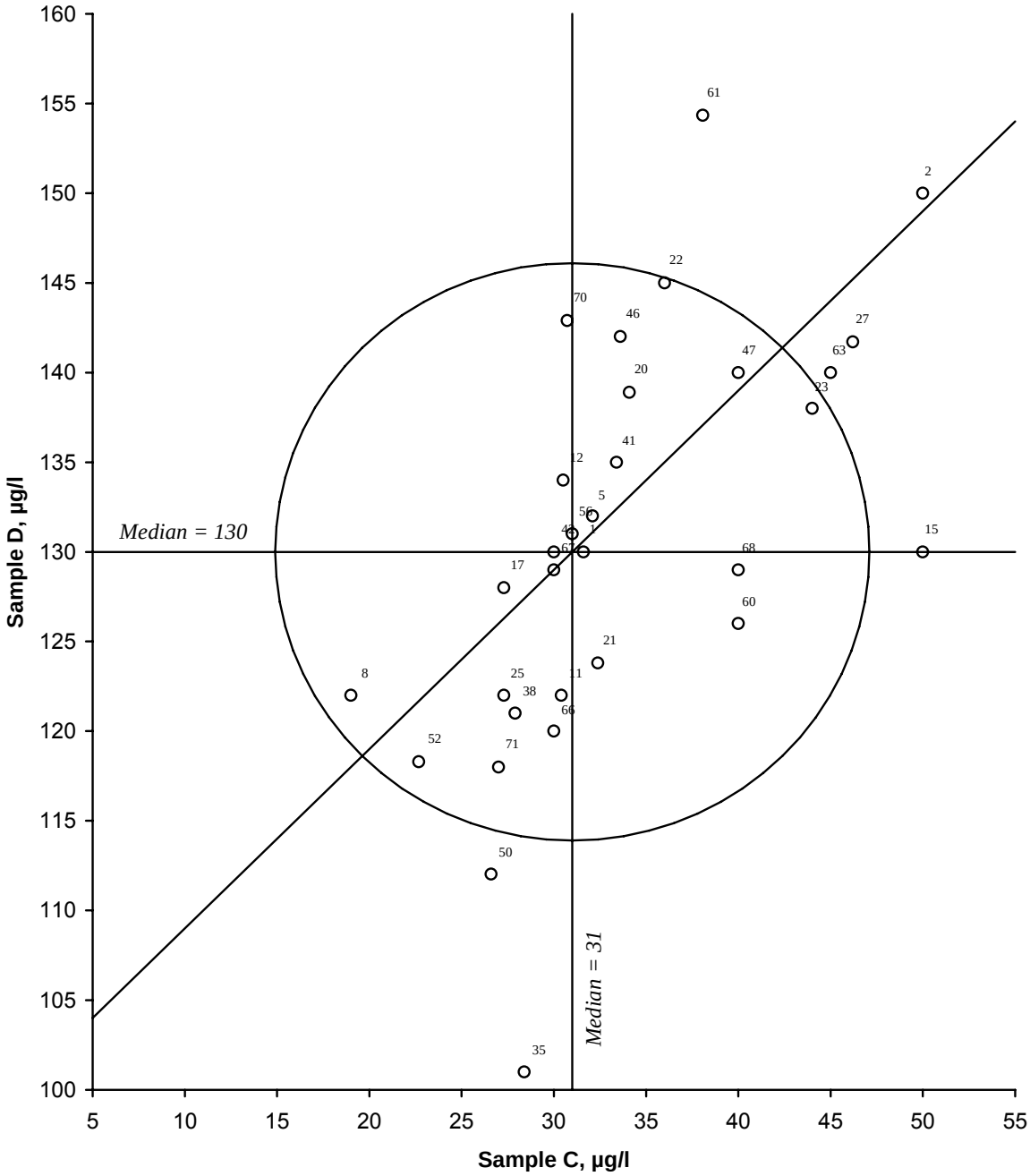

Figure 11. Youden diagramme for iron, sample pair CD
Acceptance limit, given by the circle, is 20 %

Manganese

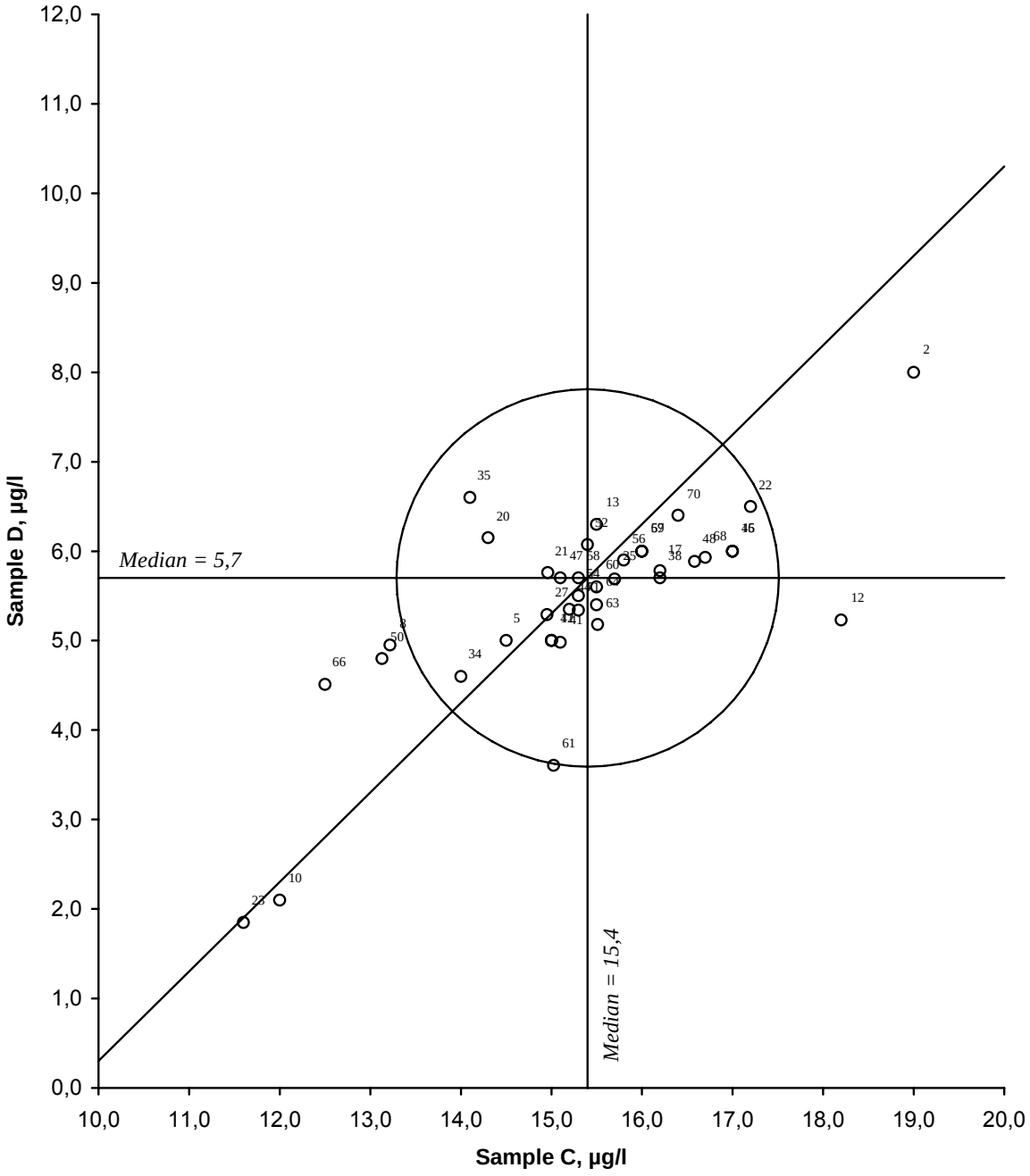

Figure 12. Youden diagramme for manganese, sample pair CD
Acceptance limit, given by the circle, is 20 %

Cadmium

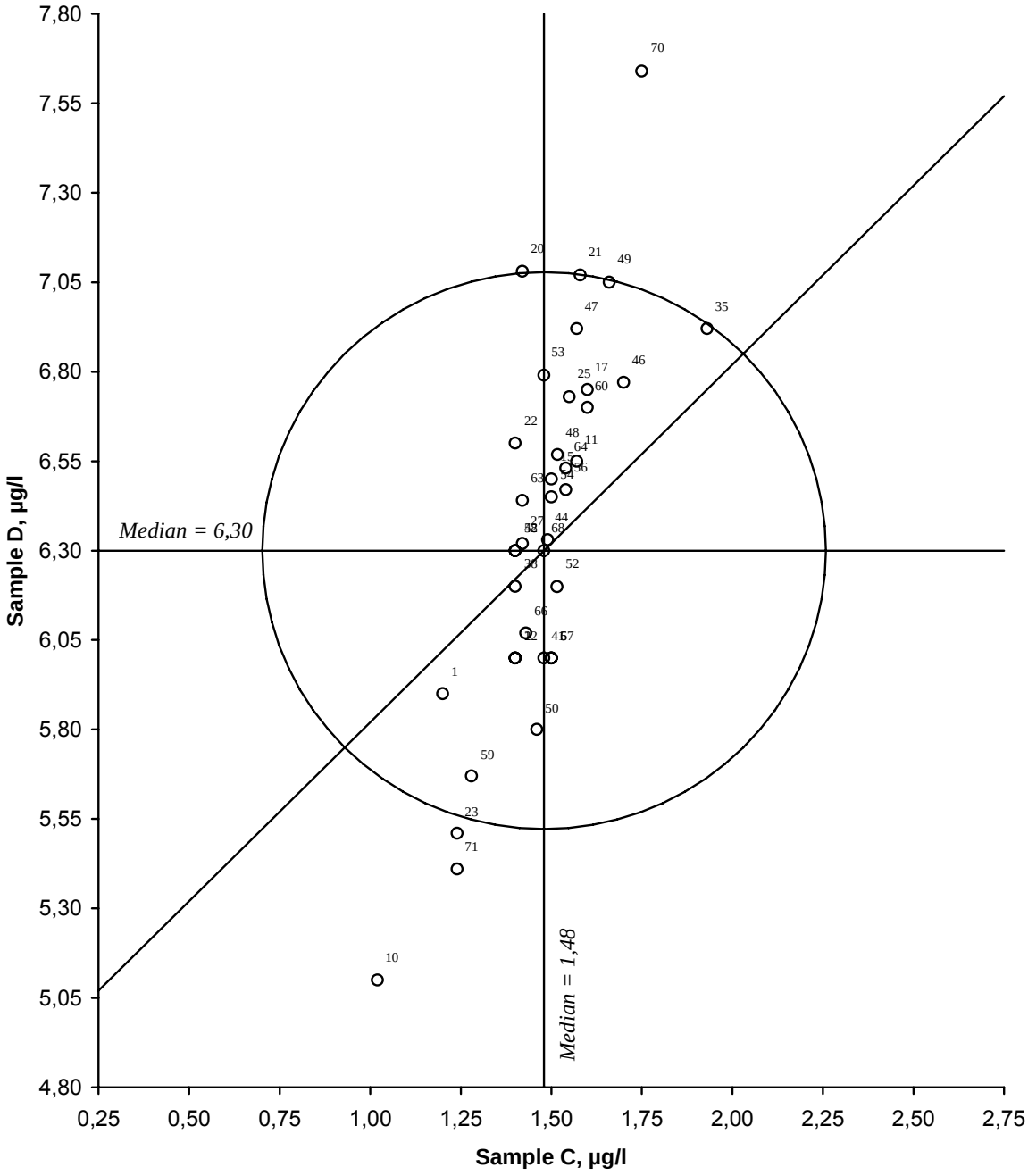

Figure 13. Youden diagramme for cadmium, sample pair CD
Acceptance limit, given by the circle, is 20 %

Lead

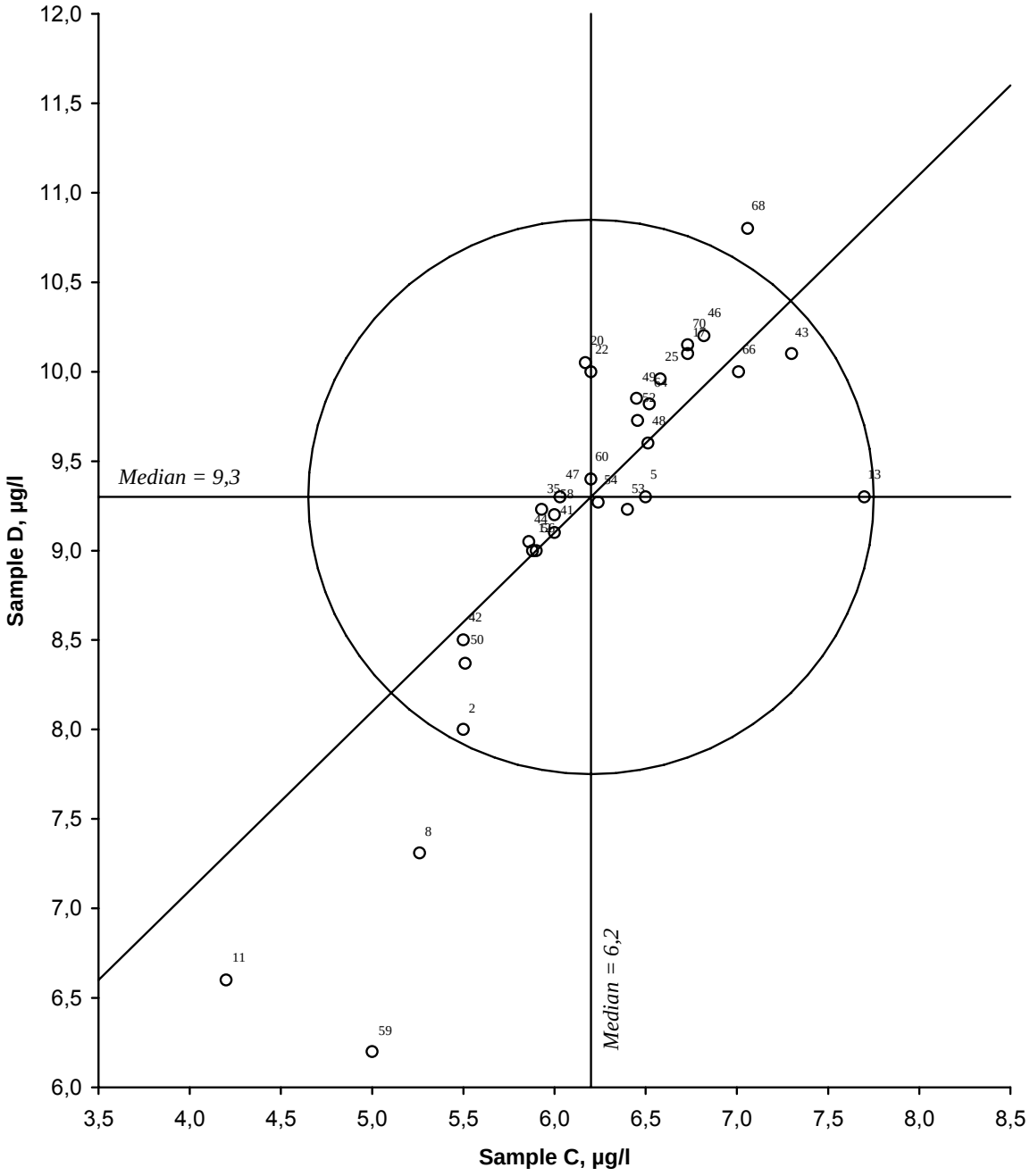

Figure 14. Youden diagramme for lead, sample pair CD
Acceptance limit, given by the circle, is 20 %

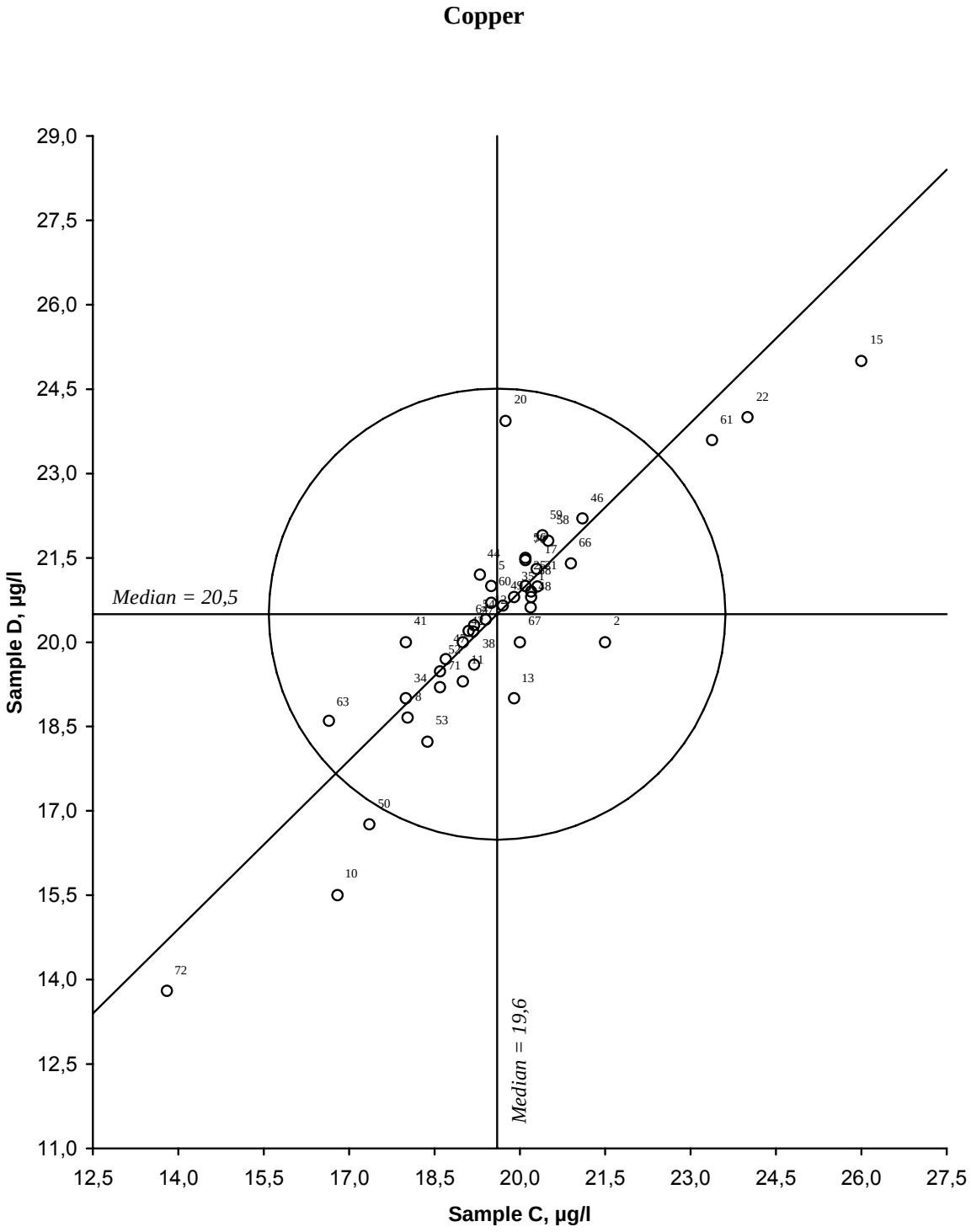

Figure 15. Youden diagramme for copper, sample pair CD
Acceptance limit, given by the circle, is 20 %

Nickel

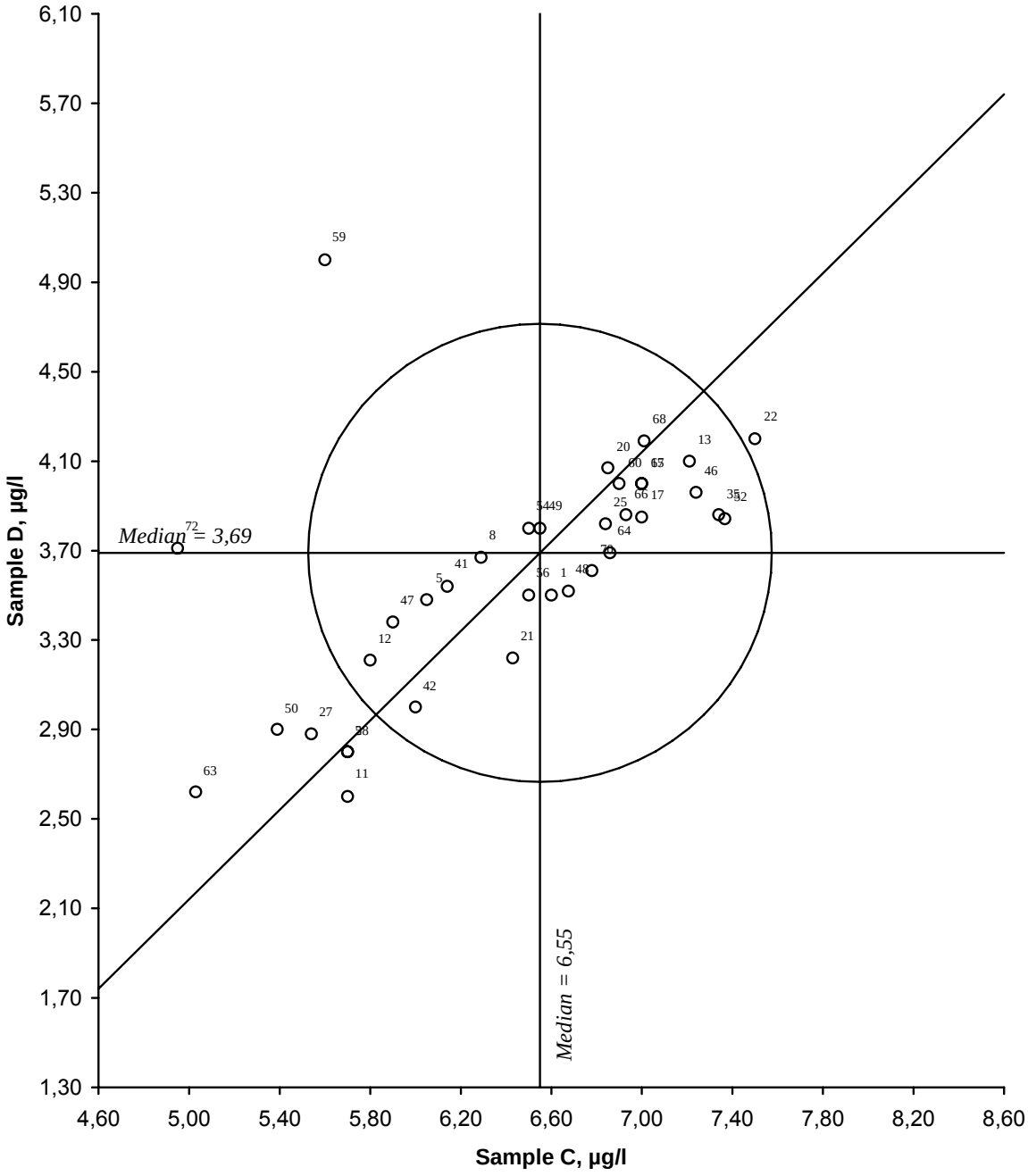

Figure 16. Youden diagramme for nickel, sample pair CD
Acceptance limit, given by the circle, is 20 %

Zinc

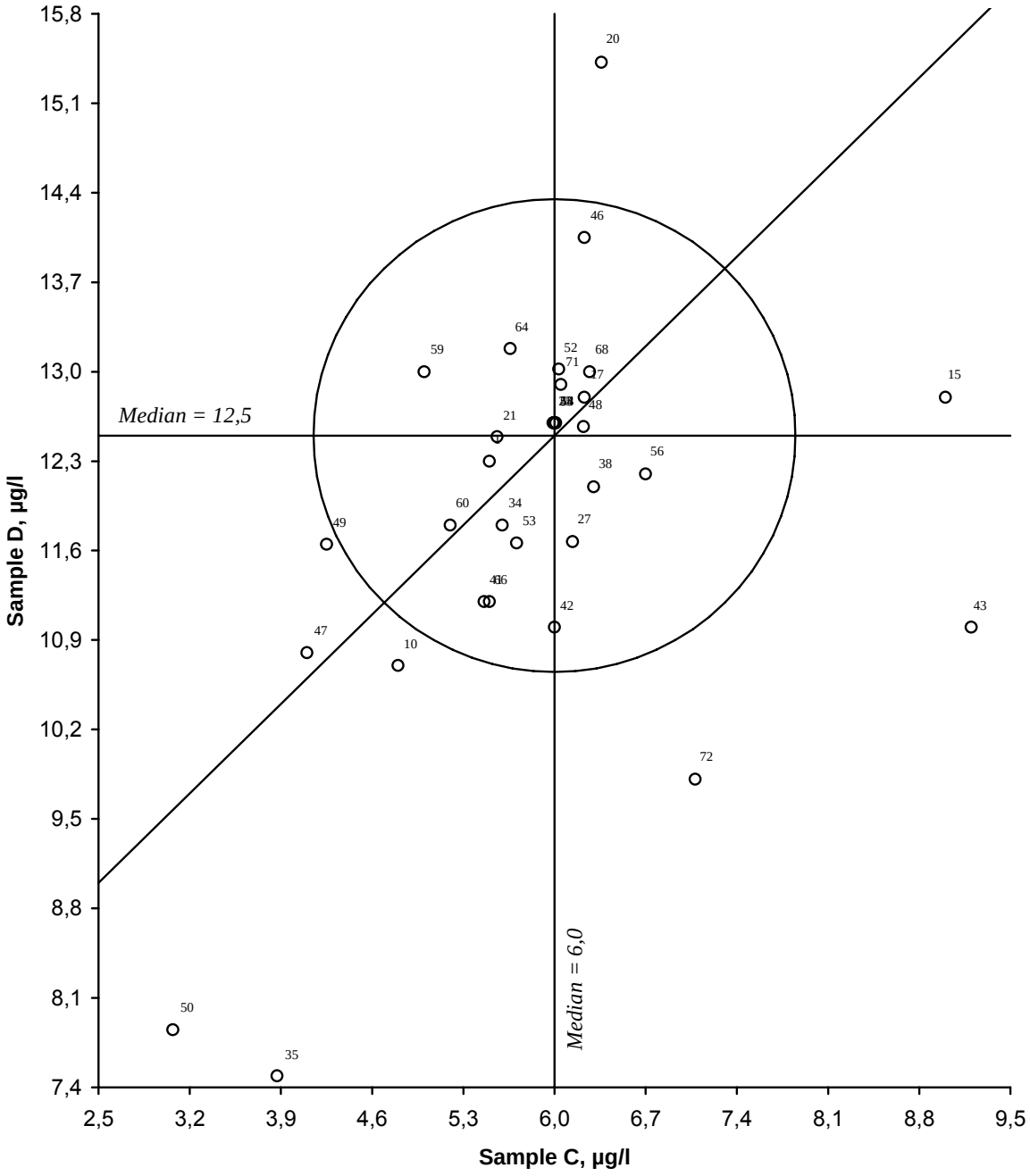

Figure 17. Youden diagramme for zinc, sample pair CD
Acceptance limit, given by the circle, is 20 %

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 0721 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. By improvement of the routine analytical method, the laboratories should be able to obtain even more accurate and comparable results.

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

For pH, the general target accuracy is ± 0,1 pH units (1), and far less than 50 % of the result pairs are found within these accuracy limits. However, we have chosen to extend the acceptance limit to ± 0,2 pH units, 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 51 % of the result pairs are evaluated as acceptable this time.

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, and different working procedures and different instrumental equipment for pH determination are used by the participating laboratories. This time there were only minor differences between the pH results produced during stirring the solution and no stirring of the solution, and even when using equilibration of the samples before measurement.

Because of the high precision of the reported results for conductivity in earlier intercomparisons, we have reduced the acceptance limit for this analytical variable from the target value ± 20 % to ± 10 %. Still the number of acceptable results for conductivity is 80 % (Table 2). If we increase the acceptance limit to the target value, the number of acceptable results would increase. It is still a problem that many laboratories report their results in the units they normally use at their laboratory, and they very often do not write the unit used. The unit asked for in this intercomparison is mS/m. For this reason some correspondence with the laboratories was 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 results to 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 are solutions with higher concentrations of bicarbonate. In this intercomparison, the results are comparable with the last intercomparison, probably because the concentrations of bicarbonate in the samples used this time is not too low. Also for this parameter there is some confusion among the participants about the unit to be used, mmol/l.

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

Parameter and unit	Sample pair	True value		Accept. limit	Number of pairs		% acceptable results for intercomparison			
		1	2	%	N	n	0721	0620	0519	0418
pH	AB	6,69	7,25	0,2*	69	35	51	74	63	57
Conductivity, mS/m	AB	2,84	6,6	10¤	66	53	80	71	81	80
Alkalinity, mmol/l	AB	0,106	0,356	20	48	32	67	63	63	52
Nitrate-nitrogen,µg/l	AB	160	255	20	64	40	63	81	82	81
Chloride, mg/l	AB	1,86	3,41	20	66	52	79	82	86	84
Sulfate, mg/l	AB	2,72	5,75	20	64	52	81	89	81	86
Calcium, mg/l	AB	2,81	8,53	20	65	56	86	77	79	80
Magnesium, mg/l	AB	0,4	0,69	20	65	50	77	70	69	80
Sodium, mg/l	AB	1,59	2,67	20	62	57	92	88	89	87
Potassium, mg/l	AB	0,28	0,556	20	61	47	77	80	73	75
Iron, µg/l	CD	31	130	20	38	24	63	77	57	69
Manganese, µg/l	CD	15,4	5,7	20	44	31	70	78	65	59
Cadmium, µg/l	CD	1,48	6,3	20	44	33	75	74	18	76
Lead, µg/l	CD	6,2	9,3	20	42	27	64	52	8	78
Copper, µg/l	CD	19,6	20,5	20	44	36	82	77	63	95
Nickel, µg/l	CD	6,55	3,69	20	42	26	62	63	25	80
Zinc, µg/l	CD	6	12,5	20	43	23	53	61	54	82
Total					927	674	73	(75)	(67)	(77)

* 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 only 63 % of the result pairs are acceptable. This is worse than last year, and it seems to be affected by some unstability for this parameter during transport of the samples. Control analyses at the Programme Centre demonstrated that the samples were stable with respect to the content of nitrate, throughout the whole periode of the intercomparison when stored at 4 °C.

For calcium and magnesium a greater fraction of the result pairs are acceptable this time compared to earlier years, and the fraction of acceptable results are 86 % and 77 % 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 copper and cadmium where 82 % and 75 % of the results, respectively, are acceptable. This is considered as acceptable, even if there should be possible to achieve better comparability. For some of the elements the concentrations were low, and it is obvious that some laboratories have sensitive enough methods to determine heavy metals on the trace level.

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

6. Conclusion

72 laboratories submitted results for this intercomparison. The best results were reported for the analytical variables sodium and calcium where 92 % and 86 % of the results, respectively, were acceptable. The worst results were observed for the heavy metals where the concentrations are rather low.

In this intecomparison 73 % of the evaluated results were located within the general target accuracy of ± 20 %, or the special accuracy limit for pH and conductivity. The low fraction of acceptable results for some variables, especially some of the heavy metals, may be explained by the rather low concentrations used for these analytical variables. When the concentrations are close to the detection limits for some of the methods used by the participants, it must be expected that the spread of the results will be greater than ± 20 %.

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

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

The results reported for pH were much more spread out in this intercomparison than the last three years, only 51 % of the result pairs being acceptable. A rather low fraction of acceptable pH results have also been observed some times in earlier intercomparisons, however, a reasonable explanation for this has never been found. Samples with pH around the neutrality point are more exposed to effect caused by storage and transport conditions, and might thus be more unstable. This may be a part of the explanation for the spread of the pH results. Also, 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. A total error of ± 0,2 pH units seems to be a reasonable assessment of the accuracy for pH measurements, when near neutral water samples - which are not in CO_2 equilibrium - are analyzed.

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

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

7. Literature

1. Convention on Long-range Transboundary Air Pollution. International Cooperative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes. Manual for Chemical and Biological Monitoring. March 1987, revised september 1996.

2. Youden, W.J.: Graphical Diagnosis of Interlaboratory Test Results. Industrial Quality Control. 1959, pp 15 - 24.

3. Youden, W.J., Steiner, E.H.: Statistical Manual of the Association of Official Analytical Chemists. Statistical Techniques for Collaborative Tests. Arlington, 1975.

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

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

Appendix A.

The participating laboratories

No.	Name of participant	City	Country
1	Sawyer Environmental Chemistry Lab	Orono	USA
2	Czech Geological Survey	Prague	Czech Republic
3	Lapland Regional Environment Centre	Rovaniemi	Finland
4	Finnish Forest Research Institute	Rovaniemi	Finland
5	T.G. Masaryk Water Research Institute	Prague	Czech Republic
6	IVL - Svenska Miljøinstitutet	Gothenburg	Sweden
7	SLU, Skoglig Marklära	Uppsala	Sweden
8	Northern Water Problems Institute	Petrozavodsk	Russia
9	Laboratory of Water Chemistry	Sosnowiec	Poland
10	Institute of Botany Pasci	Krakow	Poland
11	Institute of Public Health	Kranj	Slovenia
12	Environmental Research Department	Vilnius	Lithuania
13	Institute of Environmental Engineering	Zabrze	Poland
14	Environmental Research and Training Center	Pathumthani	Thailand
15	Institute of Soil Science and Forest Nutrition	Göttingen	Germany
16	Adirondack Lakes Survey Corporation	Ray Brook	USA
17	Finnish Environment Institute	Helsinki	Finland
18	Institute of Environmental Protection	Warsaw	Poland
19	Virumaa Environmental Research	Johvi	Estonia
20	Bayerische Landesamt für Umwelt	München	Germany
21	Institute for Ecology of Industrial Areas	Katowice	Poland
22	Central Mining Institute	Katowice	Poland
23	Testing Laboratory for Environmental Monitoring	Banten	Indonesia
24	Pollution Control Department	Bangkok	Thailand
25	Freshwater Laboratory	Pitlochry	Scotland
26	Institute of Hydrobilogy	Budejovice	Czech Republic
27	"Ecoanalyt" Ecoanalytical Laboratory	Syktyvkar	Russia
28	Ewica Laboratories	Kouvola	Finland
29	Laboratorio Biologico	Laives	Italy
30	Aquatische Ecologie en Milieubiologie	Nijmegen	Netherlands
31	Ministry of Environment Ontario	Dorset	Canada
32	Shimane Prefecture Institute of Public Health	Shimane-ken	Japan
33	Department of Chemistry Malaysia	Selangor	Malaysia
34	Testing Laboratory of Water Quality	Petrozavodsk	Russia
35	Atmosphere Environmental Department	Chongqing	China
36	Institute of Meteorology and Geophysics	Innsbruck	Austria
37	Institut für Ökologie	Innsbruck	Austria
38	Finnish Forest Research Institute	Vantaa	Finland
39	Freshwater Institute	Winnipeg	Canada
40	Freshwater Institute, ELA Sattelite Lab+B11	Winnipeg	Canada
41	Norwegian Institute for Air Research	Kjeller	Norway
42	CNR IstitutoStudio Ecosistemi	Pallanza	Italy
43	Laboratory of monitoring of pollution	Astrakhan	Russia
44	Landesamt für Natur, Umwelt und Verbrauchschütz	Recklinghausen	Germany
45	National Institute of Biology	Ljubljana	Slovenia
46	Laboratorio Integrado de CalidadAmbiental	Pamplona	Spain
47	Environmental Laboratory	Riga	Latvia

No.	Name of participant	City	Country
48	Swedish University of Agricultural Sciences	Uppsala	Sweden
49	Environmental Protection Agency Irland	Dublin	Ireland
50	ISSeP	Wasmes	Belgium
51	Acid Deposition and Oxidant Research Center	Niigata-shi	Japan
52	Vlaamse Milieumaatschappij	Antwerpen	Belgium
53	Laboratorio SPAAS	Bellinzona	Switzerland
54	Umweltbundesamt - Messnetz	Langen	Germany
55	River Biology, Estonian University	Tartu	Estonia
56	Tartu Environmental Reseach	Tartu	Estonia
57	Centre for Limnology at Estonian University	Tartu County	Estonia
58	Bayerische Landesamt für Wald und Forstwirtschaft	Freising	Germany
59	Geological Survey of Estonia	Tallinn	Estonia
60	ZAO "Rossa"	Moscow	Russia
61	University of Florence, Lab. Di Microanalisi	Firenze	Italy
62	University of Florence, Soil solution	Firenze	Italy
63	S.C. Analist Service S.R.L.	Bucharest	Romania
64	Hydrobiological Station Velky Palenec	Blatna	Czech Republic
65	Water Research Institute	Brugherio	Italy
66	Norwegian Institute for Water Research	Oslo	Norway
67	CEH Wallingford	Wallingford	United Kingdom
68	Amt der Kärntner Landesregierung	Klagenfurt	Austria
69	Staatliche Umweltbetriebsgesellschaft	Chemnitz	Germany
70	Laboratory of Geology and Geography	Helsinki	Finland
71	Centre de Geochimie de la Surface	Strasbourg	France
72	Experimental Station for Water Resource Environm.	Bandung	Indonesia

Number of participating laboratories from the different countries being represented in intercomparison 0721

Country	Labs	Country	Labs	Country	Labs
Austria	3	Ireland	1	Russia	5
Belgium	2	Italy	6	Slovenia	2
Canada	3	Japan	2	Spain	1
China	1	Latvia	1	Sweden	3
Czech Republic	4	Lithuania	1	Switzerland	1
Estonia	5	Malaysia	1	Thailand	2
Finland	6	Netherlands	1	United Kingdom	2
France	1	Norway	2	USA	2
Germany	5	Poland	6		
Indonesia	2	Romania	1	Total	72

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 to equilibrate. Small aliquots were removed from the filtrate to determine the background concentrations of the analytical variables of interest. The samples were prepared by spiking the filtrated water with stock solutions of stoichiometric compounds containing the major ions, or heavy metals. The samples C and D were prepared for the determination of metals, and preserved by addition of 5 ml concentrated nitric acid pr. liter sample. A few days before mailing the samples to the participants, the solutions were transferred to 1/2 liter high density polyethylene bottles with screw cap. These samples were stored at room temperature until mailing to the participating laboratories.

Sample control analyses

During the intercomparison period, four sets of samples were randomly selected from the batch for control analyses. The determinations were carried out by the laboratory at the Programme Centre, the first sample set being analyzed in May/June 2007, a few weeks before mailing the samples to the participants. The last sample was analyzed at the end of August 2007. A summary of the control results is presented in Table 3. The control results confirmed that the stability of the sample solutions were acceptable during the intercalibration period for all analytical variables. Even nitrate proved to be stable in these solutions when stored at 4 °C.

Table 3. Summary of the control analyses

Analytical variable	**Sample A**		**Sample B**	
	Mean	Std. dev.	Mean	Std. dev.
pH	6,84	0,06	7,44	0,08
Conductivity mS/m	2,87	0,01	6,66	0,02
Alkalinity mmol/l	0,099	0,005	0,338	0,014
Nitrate-nitrogen µg/l	157	3	255	0
Chloride mg/l	1,94	0,08	3,60	0,05
Sulphate mg/l	2,75	0,03	5,72	0,07
Calcium mg/l	3,06	0,06	9,02	0,12
Magnesium mg/l	0,43	0,02	0,73	0,03
Sodium mg/l	1,58	0,05	2,62	0,07
Potassium mg/l	0,27	0,01	0,56	0,00
	Sample C		**Sample D**	
Iron, µg/l	27,7	6,8	117	6
Manganese, µg/l	14,0	1,93	4,99	0,69
Cadmium, µg/l	1,41	0,04	5,97	0,17
Lead, µg/l	6,73	0,26	10,2	0,56
Copper, µg/l	19,8	1,1	20,1	1,4
Nickel, µg/l	6,57	0,35	3,51	0,32
Zinc, µg/l	6,11	1,12	11,20	0,40

Appendix C.

Treatment of analytical data

The intercomparison was carried out by the method of Youden. This procedure requires two samples to be analyzed, and every laboratory shall report only one result for each sample and analytical variable. In a coordinate system the result of sample B is plotted against the result of sample A (see Figures 1 - 17).

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

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

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

The statistical treatment of the analytical results was accomplished in this way: Pairs of results where one or both of the values are lying outside the true value ± 50 %, are omitted from the statistical calculations. The remaining results are used for the calculation of the mean value (x) and the standard deviation (s). Now the pairs of results where both of the values are lying outside $x \pm 3s$, are omitted. The remaining results are used for a final calculation, the results of which are presented in the tables 5.1 - 5.17. Results being omitted from the calculations, are marked with the letter "U".

Appendix D.

Table 4. The results of the participating laboratories.

Lab.	pH		Conductivity, mS/m		Alkalinity, mmol/l		Nitrate-N, µg/l	
no.	A	B	A	B	A	B	A	B
1	6,74	7,36	2,82	6,66	0,109	0,360	160	262
2	6,60	7,16	2,90	6,78	0,102	0,343	137,8	257,5
3	6,77	7,30	2,89	6,72	0,100	0,367	161,5	261,8
4	6,83	7,40	2,95	7,16	0,103	0,346	160	255
5	6,62	7,09	2,78	6,58	0,14	0,385	< 0,5	0,93
6	6,60	7,28	2,75	6,46	0,103	0,354	164	254
7	6,71	7,29	2,65	6,17	0,1	0,332		
8	6,76	7,30	2,83	6,38	0,1066	0,3449	175	293
9	5,81	7,19	2,80	6,59	0,13	0,38	109,9	220,1
10	7,15	7,84	2,54	6,24			124	190
11	6,59	7,09	2,8	6,2	0,11	0,30	133	185
12	6,59	7,28	3,85	9,54			152,6	252,0
13	6,37	6,92	2,902	6,615	0,183	0,487	536	1131
14	6,65	7,15	2,76	6,62	0,049	0,136	115	196
15	6,54	6,78	2,85	6,69			170	253
16	6,654	7,197	2,84	6,49	0,108	0,345	136	239
17	6,74	7,34	2,84	6,76	0,092	0,345	151	246
18	6,78	7,12	3,22	6,12			155	249
19	6,69	7,18	2,78	6,48	0,100	0,38		
20	5,99	6,89	2,86	6,76			180	274
21	6,54	7,08	2,92	6,50	0,100	0,340		
22	6,79	6,90	2,87	6,60			166	271
23	6,36	6,79	2,79	6,47	0,274	0,776	27,5	98
24	6,82	7,60	2,41	5,83	0,07	0,20	0,12	0,22
25	6,678	7,448	2,736	6,31	0,099	0,343	157,92	254,94
26	6,74	7,25	2,82	6,65	0,095	0,330	155	220
27	6,05	6,50	2,76	6,24	0,155	0,396	174	142
28	6,82	7,46	3,24	7,10	0,1046	0,3523	161	251
29	6,79	7,30	3,01	6,90	0,109	0,358	131	238
30	6,38	7,28			0,15	0,38	368	515
31	5,93	6,43	2,67	6,51	0,0906	0,332	168,3	261,2
32	6,71	7,22	2,71	5,61	0,113	0,175	66	127
33	6,28	6,66	2,76	6,31	0,148	0,408	97,4	175
34	6,92	7,24						
35	6,43	6,80	2,66	6,35	0,142	0,382	-	88,1
36	6,45	6,97	2,62	6,18			157	257
37	6,69	7,25	2,83	6,64	0,100	0,350	162	261
38	6,35	7,15	2,98	6,80			163	263
39							162	258
40	6,65	7,22	2,8	6,5			144	235

Lab.	pH		Conductivity, mS/m		Alkalinity, mmol/l		Nitrate-N, µg/l	
no.	A	B	A	B	A	B	A	B
41	6,85	7,35	2,92	6,54			153	255
42	6,42	7,20	2,78	6,50	0,114	0,358	32	260
43	7,45	7,81	2,91	6,60	2,08	2,28	37	58
44	6,98	7,52	3,34	6,92			721	1081
45	6,65	7,25	2,9	6,6	0,127	0,375	179	279
46	6,97	7,25	2,28	4,11			157	296
47	6,71	7,23	2,84	6,66	0,175	0,421	160	270
48	6,96	7,33	2,81	6,60	0,105	0,349	164	265
49	7,02	7,1	2,903	6,628	0,065	0,19	161,5	255,5
50	6,85	7,40	2,87	6,73			145	235
51	6,83	7,44	2,84	6,62	0,106	0,350	158	264
52	6,27	6,64	2,87	6,72			166	275
53	6,68	7,32	2,84	6,64	0,096	0,368	144	212
54								
55	6,58	7,2	2,5	6,2			120	250
56	6,63	7,34	4,66	6,50	0,115	0,354	80	270
57	6,50	6,70	3,07	6,59	0,15	0,40	103	240
58	6,72	7,33	2,56	6,11			196	281
59	6,90	7,28	2,76	6,47				
60	6,70	7,32	3,41	6,92	0,145	0,393	166	265
61								
62	6,72	7,55	2,75	6,77			57,00	156,00
63	6,55	6,84	3,05	6,57	0,156	0,423		
64	6,53	7,08	2,88	6,71	0,109	0,367	29	134
65	6,65	7,25	2,84	6,70	0,101	0,325	174	251
66	6,85	7,51	2,88	6,68	0,104	0,354	160	255
67	6,72	7,28					167	270
68	6,6	7,1	2,9	6,7	0,1	0,36	164	253
69	6,75	7,36	2,85	6,84	0,171	0,419	162	251
70	6,73	7,30	2,87	6,76	0,0954	0,356	193	328
71	6,8	7,3	2,77	6,45	0,109	0,356	154	252
72	6,03	6,35	2,84	6,59			409	425

Lab.	Chloride, mg/l		Sulphate, mg/l		Calcium, mg/l		Magnesium, mg/l	
no.	A	B	A	B	A	B	A	B
1	1,8	3,4	2,73	5,79	2,79	8,41	0,40	0,69
2	1,73	3,62	2,49	5,67	3,58	8,79	0,44	0,70
3	1,87	3,37	2,45	5,43				
4	1,708	3,185	0,980	2,125	3,344	8,952	0,434	0,717
5	1,68	3,02	2,72	5,72	2,49	8,16	0,36	0,68
6	1,823	3,346	0,929	1,994	2,875	9,485	0,337	0,568
7	1,89	3,44	0,94	1,94	2,92	8,92	0,42	0,74
8	1,75	3,43	2,56	6,46	3,20	8,90	0,36	0,65
9	1,911	3,418	2,695	5,681	2,708	8,233	0,417	0,700
10	1,41	2,38	1,44	3,84	2,70	8,41	0,54	0,76
11	1,82	3,56	2,79	6,16	2,79	8,36	0,44	0,73
12	1,64	3,04	2,46	4,95	2,57	8,09	0,44	0,74
13	1,306	2,549	2,816	4,404	5,358	15,111	0,334	0,596
14	1,84	3,34	2,72	5,60	2,86	0,71	0,41	8,76
15	1,66	3,11	2,60	5,49	2,69	8,14	0,39	0,66
16	2,06	3,98	2,48	5,53	2,69	8,24	0,40	0,69
17	1,86	3,37	2,83	5,82	2,59	8,24	0,39	0,68
18	1,802	3,320	2,715	5,657	2,808	8,421	0,409	0,696
19	2,5	3,7	2,58	5,87	2,60	8,21	0,49	1,56
20	1,87	3,44	2,80	5,79	2,89	8,62	0,43	0,72
21					2,78	8,35	0,406	0,692
22	1,74	3,41	2,93	6,08	2,88	8,47	0,426	0,71
23	-0,10	2,98	2,76	5,82	2,85	8,64	0,384	0,631
24	1,62	3,10	2,56	5,50	3,22	9,26	0,45	0,74
25	1,82	3,36	2,738	5,764	2,78	8,32	0,388	0,667
26	1,93	3,61	2,86	6,07	2,4	7,7	0,40	0,68
27	1,81	3,34	3,24	6,05	2,96	8,85	0,418	0,681
28	1,87	3,43	2,84	5,97	2,87	8,50	0,398	0,696
29	1,86	3,58	2,53	5,96	2,81	9,50	0,36	0,64
30	2,28	3,42			2,96	9,22	0,42	0,74
31	1,86	3,47	2,73	5,75	2,615	8,437	0,430	0,746
32	2,1	3,7	3,0	6,0	2,4	8,0	0,35	0,68
33	1,91	3,38	2,69	5,74	3,10	9,46	0,386	0,678
34	2,4	3,5	2,2	5,6	3,1	8,8	0,40	0,90
35	1,95	3,48	2,74	5,40	3,15	8,98	0,42	0,70
36	1,88	3,41	2,82	6,01	2,83	8,44	0,39	0,69
37	1,94	3,41	2,72	5,76	3,03	8,88	0,425	0,711
38					2,84	7,76	0,398	0,680
39	1,83	3,22	2,74	5,77	2,77	8,52	0,39	0,67
40								

Lab.	Chloride, mg/l		Sulfate, mg/l		Calcium, mg/l		Magnesium, mg/l	
no.	A	B	A	B	A	B	A	B
41	1,79	3,40	2,44	5,31	3,74	10,3	0,48	0,79
42	1,86	3,43	2,68	5,69	2,96	8,87	0,41	0,69
43	3,1	6,2	9,27	18,54	2,86	6,10	< 0,1	1,79
44	1,85	3,30	2,61	5,53	2,72	8,37	0,416	0,710
45	1,99	3,43	2,91	6,06	2,76	8,88	0,40	0,68
46	1,79	3,29	2,76	5,75	2,59	7,32	0,369	0,634
47	1,74	3,27	2,55	5,58	2,78	7,84	0,41	0,70
48	0,053	0,095	0,056	0,118	2,906	8,918	0,401	0,693
49	1,42	2,73	2,29	4,98	5,3	10,88	0,63	0,89
50	1,775	3,305	2,65	5,69	2,98	8,80	0,42	0,73
51	1,84	3,43	2,73	5,76	2,68	9,69	0,42	0,79
52	1,913	3,540	2,890	6,073	2,942	8,993	0,429	0,731
53	1,99	3,44	2,98	5,76	2,60	8,60	0,35	0,64
54								
55								
56	1,88	3,37	2,70	5,59	2,58	8,64	0,551	0,743
57	2,4	3,8			3,10	8,76	0,30	0,57
58	1,89	3,41	2,91	5,85	2,64	8,01	0,37	0,64
59	2,45	5,71	2,47	1,23	1,95	5,85	0,59	1,18
60	1,81	3,41	2,74	5,77	2,6	8,2	0,38	0,59
61								
62	1,87	3,29	2,71	5,73	2,75	8,34	0,43	0,73
63	2,27	4,02	2,59	6,61	6,00	10,75	0,30	0,36
64	2,03	3,62	2,84	6,01				
65	1,75	3,24	2,68	5,62	2,91	8,75	0,40	0,70
66	1,98	3,59	2,71	5,66	2,99	8,89	0,43	0,73
67	1,9	3,4	2,8	6,0	2,8	8,6	0,4	0,7
68	1,95	3,41	2,66	5,62	3,1	8,53	< 0,5	0,71
69	1,85	3,39	2,82	5,71				
70	2,36	4,22	3,98	8,00	2,77	8,35	0,38	0,65
71	1,87	3,51	2,67	5,86	2,88	8,69	0,43	0,70
72	3,04	3,04	4,70	4,40	3,19	8,17	1,78	1,70

Lab.	Sodium, mg/l		Potassium, mg/l		Iron, µg/l		Manganese, µg/l	
no.	A	B	A	B	C	D	C	D
1	1,62	2,68	0,28	0,55	31,6	130	13,7	< 10
2	1,53	2,59	0,33	0,61	50	150	19	8
3								
4	1,655	2,772	0,273	0,554				
5	1,42	2,45	0,265	0,559	32,1	132	14,5	5
6	1,611	2,542	0,238	0,491				
7	1,87	2,96						
8	1,60	3,08	0,30	0,46	19	122	13,22	4,95
9	1,558	2,670	0,205	0,469				
10	1,54	2,67	0,31	0,63			12,0	2,1
11	1,46	2,56	0,31	0,54	30,4	122	15,0	5,0
12	1,61	2,80	0,29	0,49	30,5	134	18,2	5,23
13	1,558	2,646	0,371	0,675	77,0	165,5	15,5	6,30
14	1,63	2,69	0,28	0,56				
15	1,49	2,46	0,292	0,554	50	130	17	6
16	1,60	2,84	0,28	0,57				
17	1,54	2,63	0,23	0,51	27,3	128	16,2	5,8
18	1,602	2,692	0,287	0,560			15,5	5,4
19								
20	1,59	2,64	0,31	0,59	34,1	138,9	14,3	6,15
21	1,55	2,56	0,248	0,556	32,38	123,8	14,96	5,76
22	1,51	2,54	0,276	0,556	36	145	17,2	6,5
23	1,24	2,00	0,283	0,476	44	138	11,6	1,85
24	1,69	2,84	0,29	0,58				
25	1,541	2,599	0,273	0,507	27,3	122	15,7	5,69
26	1,6	2,6	0,28	0,55				
27	1,62	2,60	0,260	0,474	46,2	141,7	14,95	5,29
28	1,59	2,67	0,280	0,584				
29	1,46	2,59	0,25	0,53				
30	1,76	2,76	0,51	0,70				
31	1,632	2,699	0,306	0,578				
32	1,6	2,7	0,25	0,53				
33	1,70	2,84	0,274	0,560				
34							14	4,6
35	1,59	2,83	0,32	0,59	28,4	101	14,1	6,60
36	1,65	2,78	0,28	0,57				
37	1,62	2,68	0,280	0,565				
38	1,50	2,52	0,292	0,625	27,9	121	16,2	5,7
39	1,53	2,57	0,27	0,56	140,00	220,00	20,00	20,00
40								

Lab.	Sodium, mg/l		Potassium, mg/l		Iron, µg/l		Manganese, µg/l	
no.	A	B	A	B	C	D	C	D
41	1,80	2,92	0,32	0,61	33,4	135	15,1	4,98
42	1,56	2,60	0,25	0,54	30	130	15,0	5,0
43	7,48	5,18	< 1	< 1	68	239	28,9	13,0
44	1,60	2,64	0,295	0,575	51,8	12,6	15,2	5,35
45	1,6	2,68	0,30	0,60				
46	1,54	2,47	0,328	0,541	33,6	142	17,0	6,0
47	1,47	2,49	0,26	0,56	40	140	15,1	5,7
48	1,770	2,943	0,313	0,626	65,04	134,5	16,58	5,885
49	1,56	2,71	0,25	0,48	< 50	115,4	20,15	7,15
50	1,68	2,77	0,29	0,58	26,6	112,02	13,13	4,80
51	1,61	2,72	0,25	0,52				
52	1,511	2,613	0,292	0,585	22,68	118	15,40	6,072
53	1,58	2,61	0,23	0,47				
54							15,3	5,5
55								
56	1,98	2,89	5,57	2,30	31	131	15,8	5,9
57								
58	1,53	2,46	0,36	0,61	51,3	177	15,3	5,7
59	1,20	2,20	0,38	0,50			16,0	6,0
60	1,6	2,7	0,26	0,52	40	126	15,5	5,6
61					38,070	154,340	15,024	3,6064
62	1,58	2,68	0,29	0,57				
63	1,46	2,24	0,38	0,47	45	140	15,51	5,18
64							15,5	5,4
65	1,58	2,59	0,24	0,53				
66	1,54	2,56	0,27	0,56	30	120	12,5	4,51
67	1,5	2,5	0,3	0,8	30	129	16	6
68	1,77	2,7	< 0,6	< 0,6	40	129	16,7	5,93
69								
70	1,52	2,61	0,240	0,49	30,73	142,90	16,40	6,4
71	1,63	2,76	0,27	0,55	27	118	15,3	5,34
72	1,65	2,77	0,206	0,474			8,24	2,75

Lab.	Cadmium, µg/l		Lead, µg/l		Copper, µg/l		Nickel, µg/l		Zinc, µg/l	
no.	C	D	C	D	C	D	C	D	C	D
1	1,2	5,9	3,2	5,9	20,2	20,8	6,6	3,5	5,5	12,3
2	1,40	6,00	5,5	8,0	21,5	20,0	5,7	2,8	< 10	15,0
3										
4										
5	1,5	6	6,5	9,3	19,5	21	6,05	3,48	< 5	10,6
6										
7										
8	1,05	4,22	5,26	7,31	18,03	18,66	6,29	3,67	1,82	4,53
9										
10	1,02	5,10	10,4	12,3	16,8	15,5			4,8	10,7
11	1,57	6,55	4,2	6,6	19,0	19,3	5,7	2,6	10,7	16,7
12	1,40	6,00	5,88	9,00	19,4	20,4	5,80	3,21	< 5	12,7
13	0,91	3,42	7,70	9,30	19,90	19,0	7,21	4,10	15,12	11,15
14										
15	1,5	6,5	< 1	< 1	26	25	7	4	9,0	12,8
16										
17	1,60	6,75	6,73	10,1	20,3	21,3	7,00	3,85	6,23	12,8
18	1,54	6,53	6,52	9,82	19,1	20,2	6,86	3,69	5,66	13,18
19										
20	1,42	7,08	6,17	10,05	19,75	23,93	6,85	4,07	6,36	15,42
21	1,58	7,07	4,00	5,59	20,31	20,99	6,43	3,22	5,56	12,49
22	1,4	6,6	6,2	10	24,0	24,0	7,5	4,2	12	17
23	1,24	5,51	3,39	7,74	10,0	9,42	10,9	7,33	-	5,33
24										
25	1,55	6,73	6,58	9,96	20,1	21,0	6,84	3,82	5,99	12,6
26										
27	1,42	6,32	6,50	13,21	19,18	20,19	5,54	2,88	6,14	11,67
28										
29										
30										
31										
32										
33										
34	0,94	4,6			18	19	5,7	8,2	5,6	11,8
35	1,93	6,92	5,93	9,23	19,9	20,8	7,34	3,86	3,87	7,49
36										
37										
38	1,4	6,2	< 15	< 15	19,2	19,6	< 10	< 10	6,3	12,1
39										
40										

Lab.	Cadmium, µg/l		Lead, µg/l		Copper, µg/l		Nickel, µg/l		Zinc, µg/l	
no.	C	D	C	D	C	D	C	D	C	D
41	1,48	6,00	6,00	9,1	18	20	6,14	3,54	5,46	11,2
42	1,4	6,3	5,5	8,5	19	20	6	3	6,0	11,0
43	1,16	3,9	7,3	10,1	10,4	11,46	20,2	54,7	9,2	11,0
44	1,49	6,33	5,86	9,05	19,3	21,2	9,31	3,40	6,0	12,6
45										
46	1,70	6,77	6,82	10,20	21,1	22,2	7,24	3,96	6,23	14,05
47	1,57	6,92	6,03	9,30	18,7	19,7	5,90	3,38	4,1	10,8
48	1,517	6,568	6,513	9,601	20,19	20,62	6,676	3,519	6,222	12,57
49	1,66	7,05	6,45	9,85	19,7	20,65	6,55	3,80	4,25	11,65
50	1,46	5,80	5,51	8,37	17,36	16,76	5,39	2,90	3,07	7,85
51										
52	1,516	6,199	6,456	9,727	18,60	19,48	7,367	3,842	6,032	13,02
53	1,48	6,79	6,40	9,23	18,38	18,23			5,71	11,66
54	1,50	6,45	6,24	9,27	19,20	20,30	6,5	3,8	6,0	12,6
55										
56	1,54	6,47	5,9	9,0	20,1	21,5	6,5	3,5	6,7	12,2
57										
58	1,4	6,3	6,0	9,2	20,5	21,8	5,7	2,8	6,0	12,6
59	1,28	5,67	5,0	6,2	20,4	21,9	5,6	5,0	5,0	13,0
60	1,60	6,7	6,2	9,4	19,5	20,7	6,9	4,0	5,2	11,8
61	3,3524	8,0145	3,2999	3,4027	23,377	23,592	21,806	18,009	8,4248	15,828
62										
63	1,42	6,44	4,33	2,76	16,65	18,60	5,03	2,62		
64	1,54	6,53	6,52	9,82	19,1	20,2	6,86	3,69	5,66	13,18
65										
66	1,43	6,07	7,01	10,6	20,9	21,4	6,93	3,86	5,50	11,2
67	1,5	6	< 10	< 10	20	20	7	4	7	18
68	1,48	6,3	7,06	10,8	20,2	20,9	7,01	4,19	6,27	13,0
69										
70	1,75	7,64	6,73	10,15	20,10	21,46	6,78	3,61	7,87	17,48
71	1,24	5,41			18,6	19,2	9	8	6,05	12,9
72	0,80	3,53	6,02	5,02	13,8	13,8	4,95	3,71	7,08	9,81

Table 5.1. Statistics - pH
Sample A

Number of participants	69		Range		1,52
Number of omitted results	1		Variance		0,07
True value	6,69		Standard deviation		0,26
Mean value	6,65		Relative standard deviation		3,9%
Median value	6,69		Relative error		-0,6%

Analytical results in ascending order:

9	5,81	U	6	6,60		1	6,74
31	5,93		68	6,60		69	6,75
20	5,99		5	6,62		8	6,76
72	6,03		56	6,63		3	6,77
27	6,05		45	6,65		18	6,78
52	6,27		65	6,65		29	6,79
33	6,28		14	6,65		22	6,79
38	6,35		40	6,65		71	6,80
23	6,36		16	6,65		28	6,82
13	6,37		25	6,68		24	6,82
30	6,38		53	6,68		4	6,83
42	6,42		37	6,69		51	6,83
35	6,43		19	6,69		50	6,85
36	6,45		60	6,70		41	6,85
57	6,50		47	6,71		66	6,85
64	6,53		7	6,71		59	6,90
21	6,54		32	6,71		34	6,92
15	6,54		62	6,72		48	6,96
63	6,55		58	6,72		46	6,97
55	6,58		67	6,72		44	6,98
12	6,59		70	6,73		49	7,02
11	6,59		26	6,74		10	7,15
2	6,60		17	6,74		43	7,45

Sample B

Number of participants	69		Range		1,49
Number of omitted results	1		Variance		0,08
True value	7,25		Standard deviation		0,29
Mean value	7,18		Relative standard deviation		4,0%
Median value	7,25		Relative error		-0,9%

Analytical results in ascending order:

72	6,35		2	7,16		8	7,30
31	6,43		19	7,18		3	7,30
27	6,50		9	7,19	U	29	7,30
52	6,64		16	7,20		60	7,32
33	6,66		55	7,20		53	7,32
57	6,70		42	7,20		58	7,33
15	6,78		32	7,22		48	7,33
23	6,79		40	7,22		17	7,34
35	6,80		47	7,23		56	7,34
63	6,84		34	7,24		41	7,35
20	6,89		65	7,25		69	7,36
22	6,90		45	7,25		1	7,36
13	6,92		37	7,25		4	7,40
36	6,97		26	7,25		50	7,40
64	7,08		46	7,25		51	7,44
21	7,08		30	7,28		25	7,45
11	7,09		6	7,28		28	7,46
5	7,09		67	7,28		66	7,51
49	7,10		12	7,28		44	7,52
68	7,10		59	7,28		62	7,55
18	7,12		7	7,29		24	7,60
14	7,15		70	7,30		43	7,81
38	7,15		71	7,30		10	7,84

U = Omitted result

Table 5.2. Statistics - Conductivity

SampleA, mS/m

Number of participants	66	Range	1,00
Number of omitted results	3	Variance	0,03
True value	2,84	Standard deviation	0,17
Mean value	2,84	Relative standard deviation	6,0%
Median value	2,84	Relative error	0,1%

Analytical results in ascending order:

46	2,28	U	11	2,80		64	2,88	
24	2,41		40	2,80		66	2,88	
55	2,50		9	2,80		3	2,89	
10	2,54		48	2,81		2	2,90	
58	2,56		1	2,82		45	2,90	
36	2,62		26	2,82		68	2,90	
7	2,65		8	2,83		13	2,90	
35	2,66		37	2,83		49	2,90	
31	2,67		65	2,84		43	2,91	
32	2,71		51	2,84		21	2,92	
25	2,74		17	2,84		41	2,92	
62	2,75		72	2,84		4	2,95	
6	2,75		16	2,84		38	2,98	
33	2,76		47	2,84		29	3,01	
14	2,76		53	2,84		63	3,05	
59	2,76		15	2,85		57	3,07	
27	2,76		69	2,85		18	3,22	
71	2,77		20	2,86		28	3,24	
42	2,78		70	2,87		44	3,34	
19	2,78		52	2,87		60	3,41	
5	2,78		50	2,87		12	3,85	U
23	2,79		22	2,87		56	4,66	U

Sample B

Number of participants	66	Range	1,55
Number of omitted results	3	Variance	0,07
True value	6,60	Standard deviation	0,27
Mean value	6,55	Relative standard deviation	4,1%
Median value	6,60	Relative error	-0,7%

Analytical results in ascending order:

46	4,11	U	42	6,50		47	6,66	
32	5,61		56	6,50	U	66	6,68	
24	5,83		40	6,50		15	6,69	
58	6,11		31	6,51		68	6,70	
18	6,13		41	6,54		65	6,70	
7	6,17		63	6,57		64	6,71	
36	6,18		5	6,58		52	6,72	
11	6,20		9	6,59		3	6,72	
55	6,20		72	6,59		50	6,73	
27	6,24		57	6,59		70	6,76	
10	6,24		43	6,60		20	6,76	
33	6,31		48	6,60		17	6,76	
25	6,31		45	6,60		62	6,77	
35	6,35		22	6,60		2	6,78	
8	6,38		13	6,62		38	6,80	
71	6,45		51	6,62		69	6,84	
6	6,46		14	6,62		29	6,90	
59	6,47		49	6,63		60	6,92	
23	6,47		37	6,64		44	6,92	
19	6,48		53	6,64		28	7,10	
16	6,49		26	6,65		4	7,16	
21	6,50		1	6,66		12	9,54	U

U = Omitted result

Table 5.3. Statistics - Alkalinity

Sample A, mmol/l

Number of participants	48	Range	0,065
Number of omitted results	9	Variance	0,000
True value	0,106	Standard deviation	0,020
Mean value	0,114	Relative standard deviation	17,3%
Median value	0,106	Relative error	7,1%

Analytical results in ascending order:

14	0,049	U	2	0,102		56	0,115	
49	0,065	U	4	0,103		45	0,127	
24	0,070	U	6	0,103		9	0,130	
31	0,091		66	0,104		5	0,140	
17	0,092		28	0,105		35	0,142	
26	0,095		48	0,105		60	0,145	
70	0,095		51	0,106		33	0,148	
53	0,096		8	0,107		57	0,150	
25	0,099		16	0,108		30	0,150	
37	0,100		64	0,109		27	0,155	
19	0,100		29	0,109		63	0,156	
21	0,100		1	0,109		69	0,171	U
68	0,100		71	0,109		47	0,175	U
3	0,100		11	0,110		13	0,183	U
7	0,100		32	0,113	U	23	0,274	U
65	0,101		42	0,114		43	2,080	U

Sample B

Number of participants	48	Range	0,123
Number of omitted results	9	Variance	0,001
True value	0,356	Standard deviation	0,024
Mean value	0,360	Relative standard deviation	6,8%
Median value	0,356	Relative error	1,1%

Analytical results in ascending order:

14	0,136	U	48	0,349		45	0,375	
32	0,175	U	51	0,350		19	0,380	
49	0,190	U	37	0,350		9	0,380	
24	0,200	U	28	0,352		30	0,380	
11	0,300		56	0,354		35	0,382	
65	0,325		66	0,354		5	0,385	
26	0,330		6	0,354		60	0,393	
7	0,332		70	0,356		27	0,396	
31	0,332		71	0,356		57	0,400	
21	0,340		29	0,358		33	0,408	
2	0,343		42	0,358		69	0,419	U
25	0,343		68	0,360		47	0,421	U
8	0,345		1	0,360		63	0,423	
17	0,345		3	0,367		13	0,487	U
16	0,345		64	0,367		23	0,776	U
4	0,346		53	0,368		43	2,280	U

U = Omitted result

Table 5.4. Statistics - Nitrate-nitrogen

Sample A, µg/l

Number of participants	64	Range	99	
Number of omitted results	15	Variance	429	
True value	160	Standard deviation	21	
Mean value	154	Relative standard deviation	13,4%	
Median value	160	Relative error	-3,6%	

Analytical results in ascending order:

35	< 10	U	50	145	6	164	
5	< 1	U	17	151	48	164	
24	0	U	12	153	68	164	
23	28	U	41	153	52	166	
64	29	U	71	154	60	166	
42	32	U	26	155	22	166	
43	37	U	18	155	67	167	
62	57	U	46	157	31	168	
32	66	U	36	157	15	170	
56	80	U	25	158	27	174	U
33	97		51	158	65	174	
57	103		66	160	8	175	
9	110		47	160	45	179	
14	115		1	160	20	180	
55	120		4	160	70	193	
10	124		28	161	58	196	
29	131		49	162	30	368	U
11	133		3	162	72	409	U
16	136		39	162	13	536	U
2	138		69	162	44	721	U
40	144		37	162			
53	144		38	163			

Sample B

Number of participants	64	Range	153	
Number of omitted results	15	Variance	756	
True value	255	Standard deviation	27	
Mean value	252	Relative standard deviation	10,9%	
Median value	255	Relative error	-1,3%	

Analytical results in ascending order:

24	0	U	18	249	1	262	
5	1	U	55	250	38	263	
43	58	U	65	251	51	264	
35	88	U	28	251	48	265	
23	98	U	69	251	60	265	
32	127	U	12	252	47	270	
64	134	U	71	252	67	270	
27	142	U	15	253	56	270	U
62	156	U	68	253	22	271	
33	175		6	254	20	274	
11	185		25	255	52	275	
10	190		41	255	45	279	
14	196		4	255	58	281	
53	212		66	255	8	293	
26	220		49	256	46	296	
9	220		36	257	70	328	
40	235		2	258	72	425	U
50	235		39	258	30	515	U
29	238		42	260	U	44	1081	U
16	239		37	261	13	1131	U
57	240		31	261			
17	246		3	262			

U = Omitted result

Table 5.5. Statistics - Chloride

Sample A, mg/l

Number of participants	66	Range	1,19
Number of omitted results	6	Variance	0,04
True value	1,86	Standard deviation	0,21
Mean value	1,88	Relative standard deviation	11,1%
Median value	1,86	Relative error	1,3%

Analytical results in ascending order:

23	< 0,10	U	25	1,82		33	1,91	
48	0,05	U	11	1,82		9	1,91	
13	1,31		6	1,82		52	1,91	
10	1,41	U	39	1,83		26	1,93	
49	1,42		14	1,84		37	1,94	
24	1,62		51	1,84		35	1,95	
12	1,64		44	1,85		68	1,95	
15	1,66		69	1,85		66	1,98	
5	1,68		29	1,86		45	1,99	
4	1,71		42	1,86		53	1,99	
2	1,73		31	1,86		64	2,03	
47	1,74		17	1,86		16	2,06	
22	1,74		62	1,87		32	2,10	
8	1,75		20	1,87		63	2,27	
65	1,75		28	1,87		30	2,28	
50	1,78		3	1,87		70	2,36	
41	1,79		71	1,87		57	2,40	
46	1,79		56	1,88		34	2,40	
1	1,80		36	1,88		59	2,45	U
18	1,80		58	1,89		19	2,50	
60	1,81		7	1,89		72	3,04	U
27	1,81		67	1,90		43	3,10	U

Sample B

Number of participants	66	Range	1,67
Number of omitted results	6	Variance	0,06
True value	3,41	Standard deviation	0,25
Mean value	3,41	Relative standard deviation	7,5%
Median value	3,41	Relative error	0,1%

Analytical results in ascending order:

48	0,10	U	25	3,36		7	3,44	
10	2,38	U	56	3,37		20	3,44	
13	2,55		17	3,37		53	3,44	
49	2,73		3	3,37		31	3,47	
23	2,98	U	33	3,38		35	3,48	
5	3,02		69	3,39		34	3,50	
72	3,04	U	41	3,40		71	3,51	
12	3,04		1	3,40		52	3,54	
24	3,10		67	3,40		11	3,56	
15	3,11		36	3,41		29	3,58	
4	3,19		22	3,41		66	3,59	
39	3,22		68	3,41		26	3,61	
65	3,24		58	3,41		2	3,62	
47	3,27		60	3,41		64	3,62	
46	3,29		37	3,41		19	3,70	
62	3,29		9	3,42		32	3,70	
44	3,30		30	3,42		57	3,80	
50	3,31		28	3,43		16	3,98	
18	3,32		8	3,43		63	4,02	
27	3,34		51	3,43		70	4,22	
14	3,34		45	3,43		59	5,71	U
6	3,35		42	3,43		43	6,20	U

U = Omitted result

Table 5.6. Statistics - Sulfate

Sample A, mg/l

Number of participants	64	Range	1,04
Number of omitted results	9	Variance	0,03
True value	2,72	Standard deviation	0,17
Mean value	2,71	Relative standard deviation	6,4%
Median value	2,72	Relative error	-0,5%

Analytical results in ascending order:

48	0,06	U	68	2,66		11	2,79	
6	0,93	U	71	2,67		67	2,80	
7	0,94	U	65	2,68		20	2,80	
4	0,98	U	42	2,68		13	2,82	
10	1,44	U	33	2,69		69	2,82	
34	2,20		9	2,70		36	2,82	
49	2,29		56	2,70		17	2,83	
41	2,44		66	2,71		64	2,84	
3	2,45		62	2,71		28	2,84	
12	2,46		18	2,72		26	2,86	
59	2,47	U	14	2,72		52	2,89	
16	2,48		5	2,72		58	2,91	
2	2,49		37	2,72		45	2,91	
29	2,53		51	2,73		22	2,93	
47	2,55		31	2,73		53	2,98	
24	2,56		1	2,73		32	3,00	
8	2,56		25	2,74		27	3,24	
19	2,58		35	2,74		70	3,98	U
63	2,59		60	2,74		72	4,70	U
15	2,60		39	2,74		43	9,27	U
44	2,61		46	2,76				
50	2,65		23	2,76				

Sample B

Number of participants	64	Range	2,21
Number of omitted results	9	Variance	0,11
True value	5,75	Standard deviation	0,34
Mean value	5,74	Relative standard deviation	5,9%
Median value	5,75	Relative error	-0,2%

Analytical results in ascending order:

48	0,12	U	65	5,62		17	5,82	
59	1,23	U	18	5,66		58	5,85	
7	1,94	U	66	5,66		71	5,86	
6	1,99	U	2	5,67		19	5,87	
4	2,13	U	9	5,68		29	5,96	
10	3,84	U	42	5,69		28	5,97	
72	4,40	U	50	5,69		32	6,00	
13	4,40		69	5,71		67	6,00	
12	4,95		5	5,72		36	6,01	
49	4,98		62	5,73		64	6,01	
41	5,31		33	5,74		27	6,05	
35	5,40		46	5,75		45	6,06	
3	5,43		31	5,75		26	6,07	
15	5,49		53	5,76		52	6,07	
24	5,50		37	5,76		22	6,08	
16	5,53		51	5,76		11	6,16	
44	5,53		25	5,76		8	6,46	
47	5,58		39	5,77		63	6,61	
56	5,59		60	5,77		70	8,00	U
14	5,60		1	5,79		43	18,54	U
34	5,60		20	5,79				
68	5,62		23	5,82				

U = Omitted result

Table 5.7. Statistics - Calcium

Sample A, mg/l

Number of participants	65	Range	1,18
Number of omitted results	7	Variance	0,05
True value	2,81	Standard deviation	0,23
Mean value	2,84	Relative standard deviation	8,0%
Median value	2,81	Relative error	1,1%

Analytical results in ascending order:

59	1,95	U	39	2,77		52	2,94	
32	2,40		21	2,78		30	2,96	
26	2,40		25	2,78		27	2,96	
5	2,49		47	2,78		42	2,96	
12	2,57		1	2,79		50	2,98	
56	2,58		11	2,79		66	2,99	
46	2,59		67	2,80		37	3,03	
17	2,59		18	2,81		57	3,10	
60	2,60		29	2,81		34	3,10	
19	2,60		36	2,83		68	3,10	
53	2,60		38	2,84		33	3,10	
31	2,62		23	2,85		35	3,15	
58	2,64		14	2,86	U	72	3,19	
51	2,68		43	2,86	U	8	3,20	
16	2,69		28	2,87		24	3,22	
15	2,69		6	2,88		4	3,34	
10	2,70		22	2,88		2	3,58	
9	2,71		71	2,88		41	3,74	U
44	2,72		20	2,89		49	5,30	U
62	2,75		48	2,91		13	5,36	U
45	2,76		65	2,91		63	6,00	U
70	2,77		7	2,92				

Sample B

Number of participants	65	Range	2,37
Number of omitted results	7	Variance	0,21
True value	8,53	Standard deviation	0,46
Mean value	8,57	Relative standard deviation	5,4%
Median value	8,53	Relative error	0,4%

Analytical results in ascending order:

14	0,71	U	11	8,36		27	8,85	
59	5,85	U	44	8,37		42	8,87	
43	6,10	U	1	8,41		37	8,88	
46	7,32		10	8,41		45	8,88	
26	7,70		18	8,42		66	8,89	
38	7,76		31	8,44		8	8,90	
47	7,84		36	8,44		48	8,92	
32	8,00		22	8,47		7	8,92	
58	8,01		28	8,50		4	8,95	
12	8,09		39	8,52		35	8,98	
15	8,14		68	8,53		52	8,99	
5	8,16		67	8,60		30	9,22	
72	8,17		53	8,60		24	9,26	
60	8,20		20	8,62		33	9,46	
19	8,21		23	8,64		6	9,49	
9	8,23		56	8,64		29	9,50	
16	8,24		71	8,69		51	9,69	
17	8,24		65	8,75		41	10,30	U
25	8,32		57	8,76		63	10,75	U
62	8,34		2	8,79		49	10,88	U
70	8,35		34	8,80		13	15,11	U
21	8,35		50	8,80				

U = Omitted result

Table 5.8. Statistics - Magnesium

Sample A, mg/l

Number of participants	65	Range	0,18
Number of omitted results	11	Variance	0,00
True value	0,40	Standard deviation	0,03
Mean value	0,40	Relative standard deviation	8,1%
Median value	0,40	Relative error	0,3%

Analytical results in ascending order:

68	< 0,50	U	38	0,40		51	0,42	
43	< 0,10	U	28	0,40		37	0,43	
57	0,30		45	0,40		22	0,43	
63	0,30	U	65	0,40		52	0,43	
13	0,33		1	0,40		31	0,43	
6	0,34		34	0,40	U	66	0,43	
53	0,35		67	0,40		71	0,43	
32	0,35		26	0,40		62	0,43	
8	0,36		16	0,40		20	0,43	
5	0,36		48	0,40		4	0,43	
29	0,36		21	0,41		11	0,44	
46	0,37		18	0,41		12	0,44	
58	0,37		47	0,41		2	0,44	
70	0,38		14	0,41	U	24	0,45	
60	0,38		42	0,41		41	0,48	
23	0,38		44	0,42		19	0,49	U
15	0,39		9	0,42		10	0,54	U
33	0,39		27	0,42		56	0,55	U
25	0,39		50	0,42		59	0,59	U
17	0,39		30	0,42		49	0,63	U
36	0,39		7	0,42		72	1,78	U
39	0,39		35	0,42				

Sample B

Number of participants	65	Range	0,22
Number of omitted results	11	Variance	0,00
True value	0,69	Standard deviation	0,05
Mean value	0,69	Relative standard deviation	6,7%
Median value	0,69	Relative error	-0,2%

Analytical results in ascending order:

63	0,36	U	27	0,68		66	0,73	
6	0,57		36	0,69		50	0,73	
57	0,57		1	0,69		11	0,73	
60	0,59		42	0,69		62	0,73	
13	0,60		16	0,69		52	0,73	
23	0,63		21	0,69		24	0,74	
46	0,63		48	0,69		7	0,74	
53	0,64		28	0,70		12	0,74	
58	0,64		18	0,70		30	0,74	
29	0,64		65	0,70		56	0,74	U
70	0,65		2	0,70		31	0,75	
8	0,65		71	0,70		10	0,76	U
15	0,66		67	0,70		41	0,79	
25	0,67		47	0,70		51	0,79	
39	0,67		35	0,70		49	0,89	U
33	0,68		9	0,70		34	0,90	U
45	0,68		44	0,71		59	1,18	U
5	0,68		68	0,71	U	19	1,56	U
38	0,68		22	0,71		72	1,70	U
32	0,68		37	0,71		43	1,79	U
26	0,68		4	0,72		14	8,76	U
17	0,68		20	0,72				

U = Omitted result

Table 5.9. Statistics - Sodium

Sample A, mg/l

Number of participants	62	Range	0,45
Number of omitted results	4	Variance	0,01
True value	1,59	Standard deviation	0,09
Mean value	1,59	Relative standard deviation	5,5%
Median value	1,59	Relative error	0,1%

Analytical results in ascending order:

59	1,20	U	21	1,55		6	1,61	
23	1,24	U	9	1,56		37	1,62	
5	1,42		13	1,56		1	1,62	
29	1,46		42	1,56		27	1,62	
11	1,46		49	1,56		14	1,63	
63	1,46		65	1,58		71	1,63	
47	1,47		53	1,58		31	1,63	
15	1,49		62	1,58		36	1,65	
38	1,50		20	1,59		72	1,65	
67	1,50		28	1,59		4	1,66	
22	1,51		35	1,59		50	1,68	
52	1,51		45	1,60		24	1,69	
70	1,52		32	1,60		33	1,70	
39	1,53		44	1,60		30	1,76	
58	1,53		16	1,60		48	1,77	
2	1,53		60	1,60		68	1,77	
17	1,54		8	1,60		41	1,80	
10	1,54		26	1,60		7	1,87	
46	1,54		18	1,60		56	1,98	U
66	1,54		51	1,61		43	7,48	U
25	1,54		12	1,61				

Sample B

Number of participants	62	Range	0,84
Number of omitted results	4	Variance	0,02
True value	2,67	Standard deviation	0,14
Mean value	2,66	Relative standard deviation	5,4%
Median value	2,67	Relative error	-0,2%

Analytical results in ascending order:

23	2,00	U	27	2,60		68	2,70	
59	2,20	U	26	2,60		49	2,71	
63	2,24		70	2,61		51	2,72	
5	2,45		53	2,61		30	2,76	
15	2,46		52	2,61		71	2,76	
58	2,46		17	2,63		72	2,77	
46	2,47		20	2,64		50	2,77	
47	2,49		44	2,64		4	2,77	
67	2,50		13	2,65		36	2,78	
38	2,52		9	2,67		12	2,80	
22	2,54		28	2,67		35	2,83	
6	2,54		10	2,67		24	2,84	
11	2,56		45	2,68		16	2,84	
21	2,56		37	2,68		33	2,84	
66	2,56		62	2,68		56	2,89	U
39	2,57		1	2,68		41	2,92	
2	2,59		14	2,69		48	2,94	
29	2,59		18	2,69		7	2,96	
65	2,59		31	2,70		8	3,08	
25	2,60		32	2,70		43	5,18	U
42	2,60		60	2,70				

U = Omitted result

Table 5.10. Statistics - Potassium

Sample A, mg/l

Number of participants	61	Range	0,175
Number of omitted results	5	Variance	0,001
True value	0,280	Standard deviation	0,037
Mean value	0,283	Relative standard deviation	13,2%
Median value	0,280	Relative error	1,0%

Analytical results in ascending order:

43	< 1,000	U	39	0,270		44	0,295	
68	< 0,600	U	4	0,273		45	0,300	
9	0,205		25	0,273		67	0,300	U
72	0,206		33	0,274		8	0,300	
53	0,230		22	0,276		31	0,306	
17	0,230		16	0,280		11	0,310	
6	0,238		37	0,280		10	0,310	
65	0,240		26	0,280		20	0,310	
70	0,240		28	0,280		48	0,313	
21	0,248		1	0,280		35	0,320	
51	0,250		36	0,280		41	0,320	
29	0,250		14	0,280		46	0,328	
32	0,250		23	0,283		2	0,330	
42	0,250		18	0,287		58	0,360	
49	0,250		50	0,290		13	0,371	
47	0,260		62	0,290		63	0,380	
60	0,260		12	0,290		59	0,380	
27	0,260		24	0,290		30	0,510	U
5	0,265		38	0,292		56	5,570	U
71	0,270		15	0,292				
66	0,270		52	0,292				

Sample B

Number of participants	61	Range	0,215
Number of omitted results	5	Variance	0,002
True value	0,556	Standard deviation	0,048
Mean value	0,549	Relative standard deviation	8,8%
Median value	0,556	Relative error	-1,3%

Analytical results in ascending order:

43	< 1,000	U	11	0,540		44	0,575	
68	< 0,600	U	42	0,540		31	0,578	
8	0,460		46	0,541		50	0,580	
9	0,469		1	0,550		24	0,580	
53	0,470		26	0,550		28	0,584	
63	0,470		71	0,550		52	0,585	
27	0,474		15	0,554		20	0,590	
72	0,474		4	0,554		35	0,590	
23	0,476		22	0,556		45	0,600	
49	0,480		21	0,556		2	0,610	
70	0,490		5	0,559		41	0,610	
12	0,490		33	0,560		58	0,610	
6	0,491		47	0,560		38	0,625	
59	0,500		18	0,560		48	0,626	
25	0,507		66	0,560		10	0,630	
17	0,510		14	0,560		13	0,675	
60	0,520		39	0,560		30	0,700	U
51	0,520		37	0,565		67	0,800	U
65	0,530		16	0,570		56	2,300	U
29	0,530		36	0,570				
32	0,530		62	0,570				

U = Omitted result

Table 5.12. Statistics - Manganese

Sample C, µg/l

Number of participants	44	Range	5,7
Number of omitted results	8	Variance	1,4
True value	15,4	Standard deviation	1,2
Mean value	15,4	Relative standard deviation	7,6%
Median value	15,4	Relative error	0,0%

Analytical results in ascending order:

72	8,2	U	61	15,0		67	16,0	
23	11,6	U	47	15,1		38	16,2	
10	12,0	U	41	15,1		17	16,2	
66	12,5		44	15,2		70	16,4	
50	13,1		54	15,3		48	16,6	
8	13,2		71	15,3		68	16,7	
1	13,7	U	58	15,3		15	17,0	
34	14,0		52	15,4		46	17,0	
35	14,1		13	15,5		22	17,2	
20	14,3		60	15,5		12	18,2	
5	14,5		64	15,5		2	19,0	U
27	15,0		63	15,5		39	20,0	U
21	15,0		25	15,7		49	20,2	U
11	15,0		56	15,8		43	28,9	U
42	15,0		59	16,0				

Sample D

Number of participants	44	Range	3,0
Number of omitted results	8	Variance	0,4
True value	5,7	Standard deviation	0,6
Mean value	5,5	Relative standard deviation	11,3%
Median value	5,7	Relative error	-2,8%

Analytical results in ascending order:

1	< 10,0	U	27	5,3		15	6,0	
23	1,9	U	71	5,3		46	6,0	
10	2,1	U	44	5,4		67	6,0	
72	2,8	U	64	5,4		59	6,0	
61	3,6		54	5,5		52	6,1	
66	4,5		60	5,6		20	6,2	
34	4,6		25	5,7		13	6,3	
50	4,8		38	5,7		70	6,4	
8	5,0		47	5,7		22	6,5	
41	5,0		58	5,7		35	6,6	
42	5,0		21	5,8		49	7,2	U
5	5,0		17	5,8		2	8,0	U
11	5,0		48	5,9		43	13,0	U
63	5,2		56	5,9		39	20,0	U
12	5,2		68	5,9				

U = Omitted result

Table 5.13. Statistics - Cadmium

Sample C, µg/l

Number of participants	44	Range	1,13
Number of omitted results	1	Variance	0,05
True value	1,48	Standard deviation	0,22
Mean value	1,42	Relative standard deviation	15,9%
Median value	1,48	Relative error	-4,2%

Analytical results in ascending order:

72	0,80	58	1,40	48	1,52	
13	0,91	20	1,42	56	1,54	
34	0,94	63	1,42	64	1,54	
10	1,02	27	1,42	25	1,55	
8	1,05	66	1,43	47	1,57	
43	1,16	50	1,46	11	1,57	
1	1,20	41	1,48	21	1,58	
71	1,24	68	1,48	17	1,60	
23	1,24	53	1,48	60	1,60	
59	1,28	44	1,49	49	1,66	
2	1,40	5	1,50	46	1,70	
38	1,40	67	1,50	70	1,75	
12	1,40	54	1,50	35	1,93	
22	1,40	15	1,50	61	3,35	U
42	1,40	52	1,52			

Sample D

Number of participants	44	Range	4,22
Number of omitted results	1	Variance	0,88
True value	6,30	Standard deviation	0,94
Mean value	6,08	Relative standard deviation	15,4%
Median value	6,30	Relative error	-3,4%

Analytical results in ascending order:

13	3,42	67	6,00	48	6,57	
72	3,53	66	6,07	22	6,60	
43	3,90	52	6,20	60	6,70	
8	4,22	38	6,20	25	6,73	
34	4,60	68	6,30	17	6,75	
10	5,10	58	6,30	46	6,77	
71	5,41	42	6,30	53	6,79	
23	5,51	27	6,32	35	6,92	
59	5,67	44	6,33	47	6,92	
50	5,80	63	6,44	49	7,05	
1	5,90	54	6,45	21	7,07	
5	6,00	56	6,47	20	7,08	
12	6,00	15	6,50	70	7,64	
41	6,00	64	6,53	61	8,01	U
2	6,00	11	6,55			

U = Omitted result

Table 5.14. Statistics - Lead

Sample C, µg/l

Number of participants	42	Range	4,5
Number of omitted results	6	Variance	1,0
True value	6,2	Standard deviation	1,0
Mean value	6,0	Relative standard deviation	16,7%
Median value	6,2	Relative error	-3,6%

Analytical results in ascending order:

38	< 15,0	U	44	5,9		52	6,5	
67	< 10,0	U	12	5,9		27	6,5	
15	< 1,0	U	56	5,9		5	6,5	
1	3,2		35	5,9		48	6,5	
61	3,3	U	58	6,0		64	6,5	
23	3,4		41	6,0		25	6,6	
21	4,0		72	6,0		17	6,7	
11	4,2		47	6,0		70	6,7	
63	4,3	U	20	6,2		46	6,8	
59	5,0		60	6,2		66	7,0	
8	5,3		22	6,2		68	7,1	
42	5,5		54	6,2		43	7,3	
2	5,5		53	6,4		13	7,7	
50	5,5		49	6,5		10	10,4	U

Sample D

Number of participants	42	Range	8,2
Number of omitted results	6	Variance	2,6
True value	9,3	Standard deviation	1,6
Mean value	9,0	Relative standard deviation	17,8%
Median value	9,3	Relative error	-3,5%

Analytical results in ascending order:

38	< 15,0	U	42	8,5		52	9,7	
67	< 10,0	U	12	9,0		64	9,8	
15	< 1,0	U	56	9,0		49	9,9	
63	2,8	U	44	9,1		25	10,0	
61	3,4	U	41	9,1		22	10,0	
72	5,0		58	9,2		66	10,0	
21	5,6		35	9,2		20	10,1	
1	5,9		53	9,2		43	10,1	
59	6,2		54	9,3		17	10,1	
11	6,6		5	9,3		70	10,2	
8	7,3		47	9,3		46	10,2	
23	7,7		13	9,3		68	10,8	
2	8,0		60	9,4		10	12,3	U
50	8,4		48	9,6		27	13,2	

U = Omitted result

Table 5.15. Statistics - Copper

Sample C, µg/l

Number of participants	44	Range	12,2
Number of omitted results	2	Variance	3,8
True value	19,6	Standard deviation	1,9
Mean value	19,6	Relative standard deviation	9,9%
Median value	19,6	Relative error	0,1%

Analytical results in ascending order:

23	10,0	U	64	19,1	56	20,1
43	10,4	U	27	19,2	48	20,2
72	13,8		38	19,2	68	20,2
63	16,7		54	19,2	1	20,2
10	16,8		44	19,3	17	20,3
50	17,4		12	19,4	21	20,3
41	18,0		60	19,5	59	20,4
34	18,0		5	19,5	58	20,5
8	18,0		49	19,7	66	20,9
53	18,4		20	19,8	46	21,1
52	18,6		35	19,9	2	21,5
71	18,6		13	19,9	61	23,4
47	18,7		67	20,0	22	24,0
42	19,0		25	20,1	15	26,0
11	19,0		70	20,1		

Sample D

Number of participants	44	Range	11,2
Number of omitted results	2	Variance	4,2
True value	20,5	Standard deviation	2,0
Mean value	20,3	Relative standard deviation	10,1%
Median value	20,5	Relative error	-0,7%

Analytical results in ascending order:

23	9,4	U	67	20,0	25	21,0
43	11,5	U	42	20,0	5	21,0
72	13,8		2	20,0	44	21,2
10	15,5		41	20,0	17	21,3
50	16,8		27	20,2	66	21,4
53	18,2		64	20,2	70	21,5
63	18,6		54	20,3	56	21,5
8	18,7		12	20,4	58	21,8
34	19,0		48	20,6	59	21,9
13	19,0		49	20,7	46	22,2
71	19,2		60	20,7	61	23,6
11	19,3		35	20,8	20	23,9
52	19,5		1	20,8	22	24,0
38	19,6		68	20,9	15	25,0
47	19,7		21	21,0		

U = Omitted result

Table 5.16. Statistics - Nickel

Sample C, µg/l

Number of participants	42	Range	2,55
Number of omitted results	7	Variance	0,47
True value	6,55	Standard deviation	0,69
Mean value	6,42	Relative standard deviation	10,7%
Median value	6,55	Relative error	-1,9%

Analytical results in ascending order:

38	< 10,00	U	41	6,14		17	7,00	
72	4,95		8	6,29		67	7,00	
63	5,03		21	6,43		15	7,00	
50	5,39		56	6,50		68	7,01	
27	5,54		54	6,50		13	7,21	
59	5,60		49	6,55		46	7,24	
58	5,70		1	6,60		35	7,34	
11	5,70		48	6,68		52	7,37	
34	5,70	U	70	6,78		22	7,50	
2	5,70		25	6,84		71	9,00	U
12	5,80		20	6,85		44	9,31	U
47	5,90		64	6,86		23	10,90	U
42	6,00		60	6,90		43	20,20	U
5	6,05		66	6,93		61	21,81	U

Sample D

Number of participants	42	Range	2,40
Number of omitted results	7	Variance	0,27
True value	3,69	Standard deviation	0,52
Mean value	3,60	Relative standard deviation	14,4%
Median value	3,69	Relative error	-2,5%

Analytical results in ascending order:

38	< 10,00	U	56	3,50		46	3,96	
11	2,60		48	3,52		15	4,00	
63	2,62		41	3,54		60	4,00	
2	2,80		70	3,61		67	4,00	
58	2,80		8	3,67		20	4,07	
27	2,88		64	3,69		13	4,10	
50	2,90		72	3,71		68	4,19	
42	3,00		49	3,80		22	4,20	
12	3,21		54	3,80		59	5,00	
21	3,22		25	3,82		23	7,33	U
47	3,38		52	3,84		71	8,00	U
44	3,40	U	17	3,85		34	8,20	U
5	3,48		66	3,86		61	18,01	U
1	3,50		35	3,86		43	54,70	U

U = Omitted result

Table 5.17. Statistics - Zinc

Sample C, µg/l

Number of participants	43	Range	5,9
Number of omitted results	9	Variance	1,4
True value	6,0	Standard deviation	1,2
Mean value	5,9	Relative standard deviation	19,8%
Median value	6,0	Relative error	-1,4%

Analytical results in ascending order:

2	< 10,0	U	21	5,6		68	6,3	
12	< 5,0	U	34	5,6		38	6,3	
5	< 5,0	U	64	5,7		20	6,4	
23	< 1,0	U	53	5,7		56	6,7	
8	1,8	U	25	6,0		67	7,0	
50	3,1		58	6,0		72	7,1	
35	3,9		54	6,0		70	7,9	
47	4,1		42	6,0		61	8,4	
49	4,3		44	6,0		15	9,0	
10	4,8		52	6,0		43	9,2	U
59	5,0		71	6,1		11	10,7	U
60	5,2		27	6,1		22	12,0	U
41	5,5		48	6,2		13	15,1	U
66	5,5		17	6,2				
1	5,5		46	6,2				

Sample D

Number of participants	43	Range	10,5
Number of omitted results	9	Variance	4,5
True value	12,5	Standard deviation	2,1
Mean value	12,4	Relative standard deviation	17,0%
Median value	12,5	Relative error	-0,7%

Analytical results in ascending order:

8	4,5	U	27	11,7		71	12,9	
23	5,3	U	60	11,8		68	13,0	
35	7,5		34	11,8		59	13,0	
50	7,9		38	12,1		52	13,0	
72	9,8		56	12,2		64	13,2	
5	10,6	U	1	12,3		46	14,1	
10	10,7		21	12,5		2	15,0	U
47	10,8		48	12,6		20	15,4	
43	11,0	U	54	12,6		61	15,8	
42	11,0		58	12,6		11	16,7	U
13	11,2	U	25	12,6		22	17,0	U
66	11,2		44	12,6		70	17,5	
41	11,2		12	12,7	U	67	18,0	
49	11,7		17	12,8				
53	11,7		15	12,8				

U = Omitted result

Appendix E.

Intercomparison reports from ICP Waters

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. Intercalibration 8802. pH, K_{25}, HCO_3, NO_3, SO, Cl, Ca, Mg, Na, K. Programme Centre, NIVA, Oslo.

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.

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.

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.

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.

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.

Hovind, H. 1994. Intercomparison 9408. pH, k_{25}, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, TOC and COD-Mn. Programme Centre, NIVA, Oslo. NIVA-Report SNO 3142-94.

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.

Hovind, H. 1996. Intercomparison 9610. pH, K_{25}, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium -

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

Hovind, H. 1997. Intercomparison 9711. 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 3716-97.

Hovind, H. 1998. Intercomparison 9812. pH, K_{25}, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC and COD-Mn. NIVA-Report SNO 3939-98, ICP-Waters Report 49/1998.

Hovind, H. 1999. Intercomparison 9913. pH, K_{25}, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC and COD-Mn. NIVA-Report SNO 4093-99, ICP Waters Report 51/1999.

Hovind, H. 2000. Intercomparison 0014. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-Report SNO 4281-2000, ICP Waters Report 55/2000.

Hovind, H. 2000. Trends in intercomparisons 8701-9812: pH, K_{25}, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K and aluminium - reactive and nonlabile, TOC, COD-Mn. NIVA-Report SNO 4281-2000, ICP Waters Report 56/2000.

Hovind, H. 2001. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-Report SNO 4416-2002, ICP Waters report 64/2001.

Hovind. H. 2002. Intercomparison 0216. pH, K_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-Report SNO 4558-2002, ICP Waters Report 68/2002.

Hovind, 2003. Intercomparison 0317. pH, K25, HCO3, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-report SNO 4715-2003, ICP Waters report 74/2003.

Hovind, 2004. Intercomparison 0418. pH, K25, HCO3, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-report SNO 4875-2004, ICP Waters report 78/2004.

Hovind, 2005. Intercomparison 0519. pH, K25, HCO3, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-report SNO 5068-2005, ICP Waters report 82/2005.

Hovind, 2006. Intercomparison 0620. pH, K25, HCO3, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA-report SNO 5285-20065, ICP Waters report 86/2006.