CONVENTION ON LONG-RANGE
TRANSBOUNDARY AIR POLLUTION

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

Intercomparison 0620:

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

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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 20th intercomparison of chemical analysis.

Oslo, October 2006

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1. Summary

Intercomparison 0620 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 2006, and included the determination of major ions and metals in natural water samples. The participants were asked to determine pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulphate, calcium, magnesium, sodium, potassium, iron, manganese, cadmium, lead, copper, nickel and zinc.

Two sample sets were prepared for this intercomparison, one for the determination of the major ions, and one for the heavy metals. 133 laboratories were invited to participate in this intercomparison, and the samples were sent to the 73 laboratories who accepted to participate. 67 laboratories submitted results to the Programme Centre before the final statistical treatment of the data. 26 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. 75 % of the result pairs were considered as acceptable, the target limit being the median value ± 20 %, except for pH and conductivity where the special acceptance limits were selected, being ± 0,2 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 74 % of the result pairs were acceptable using this special limit. This is the best results for pH in several years in 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 is necessary to improve the results for pH and alkalinity.

The best results were reported for the analytical variables sodium and sulphate where 88 and 89 % of the results, respectively, were acceptable. The worst results were observed for the heavy metals, especially for lead, zinc and nickel. The main reason for this was the low concentrations of these metals in the samples used, and the fact that a lot of laboratories are using equipment which is not sensitive enough for the low concentrations used in this intercomparison.

The number of participants in the ICP Waters intercomparison has been decreasing the last years, in spite of the fact that more laboratories are invited. The reason for this trend should be discussed and ways to increase the number of participants again should be found.

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 twenteeth intercomparison test, called 0620, included the determination of the major components and some other ions in natural water samples: pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulphate, calcium, magnesium, sodium, potassium, iron, manganese, cadmium, lead, copper, nickel and zinc.

3. Accomplishment of the intercomparison

The preparation of the sample solutions is described in Appendix B. The results of the control analyses performed at the Programme Centre are also summarized in the same place. On the Task Force meeting in Tallinn in October 2005 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 July 6. 2006, and the following day. Most of the participating laboratories received the samples within one week, with some very few exceptions.

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

4. Results

133 laboratories were invited to participate in this intercomparison, and 73 laboratories accepted and therefore received samples. The 67 laboratories which submitted results to the Programme Centre, are representing 26 countries. Some laboratories submitted results a few weeks after the deadline, and a reminder letter was mailed to some few participants. The last results were received in the middle 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, like pH, this may represent a problem as the methods used may produce systematically different results (stirring, non-stirring, and equilibration), and we cannot argue that one method is more correct than the others.

The results are illustrated in Figure 1 - 17, where each laboratory is represented by a small circle and an identification number. Some laboratories with strongly deviating results may be located outside the plot. The great circle in the figures are representing a selected accuracy limit, either the general target limit of ± 20 % of the mean true values for the sample pair, or a special accuracy limit as defined in the sections below. A survey of the results of intercomparison 0620 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. 65 laboratories reported results for pH, 60 % of the laboratories of this group indicated that they read the pH value during stirring the solution, while about 40 % read the pH value in a quiescent solution. The stirring are normally lowering the observed pH result. 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, reported only somewhat higher results than the other laboratories. The information obtained by pH measurement after equilibrating the solution, is different from pH-values read directly, or during stirring the sample. Especially in cases where the difference between the results of the methods are greater than here, it is questionable to establish a "true value" based on the median value for all the reported results for pH, and it should be discussed whether an individual "true value" for each method would be more appropriate.

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

Figure 1 shows that the reported results are rather spread out along the 45 ° line, indicating that the results are influenced by systematic effects on the results. 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. Three laboratories did not answer this question, and the results from these are not corrected.

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), 14 more results located outside the 10 % acceptance circle, would be located within the circle and thus be defined as acceptable. An acceptance limit of ± 10 % seems to be a more reasonable demand.

4.3 Alkalinity

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 5.3. 51 laboratories reported results for alkalinity, and 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. The deviating results in Figure 3 are systematically high. 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, 63 % of the results being acceptable. The alkalinity value varies significantly with the end-point pH used for the titration. In waters containing high concentrations of total inorganic carbon, the equivalence point is close to pH = 5,4. In this case, the relative error introduced by assuming a fixed end-point pH, is negligible. However, at lower alkalinities normally encountered in areas sensitive to acidification, the “total fixed end-point method” may overestimate the true alkalinity or the “equivalence” alkalinity.

4.4 Nitrate + nitrite

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

This time 81 % of the results are evaluated as acceptable, which is about the same as in the intercomparisons the last years. One probable reason for this may be that the concentrations of nitrate-nitrogen were rather high in these intercomparisons. The control analyses at the Programme Centre demonstrated that these samples were stable with respect to the content of nitrate and nitrite, throughout the whole periode of the intercomparison. As nitrite is supposed to be 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. 50 out of 60 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.

82 % acceptable results in this intercomparison is satisfactory.

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 49 of 57 laboratories for the determination of the sulphate content. Three laboratories used a photometric method based on the dissociation of the barium-thorin complex. Only one of the three result pairs was 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. One laboratory used a gravimetric method, the results were acceptable even being a little systematically high.

89 % of the result pairs are acceptable, this is the best result for an analytical variable in this intercomparison.

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. 56 laboratories reported results for calcium, and only 12 of them used the traditional flame atomic absorption spectrometry for the determination. The ICP technique is used by 13 laboratories, and two of these used ICP-MS. An increasing number of laboratories, this time 24, used ion chromatography. Six laboratories used a titrimetric method with EDTA for the determination of calcium, the results being somewhat higher than the other methods. The systematic errors are dominating for this analytical variable, even if there are some examples in Figure 7 being spread out from the 45 degree line.

77 % acceptable result pairs is comparable to the intercomparison last year.

4.8 Magnesium

The magnesium results are presented in Figure 8, and the reported values are given in Table 5.8. The analytical methods used by the participants are the same as for the determination of calcium. 12 laboratories are still using flame atomic absorption spectrometry for the determination of magnesium. ICP atomic emission spectrometry was used by 12 laboratories and ICP-MS by three, and 27 laboratories used ion chromatography. Systematic errors are dominating the results being outside the acceptance limit. This time, 70 % 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, none of the results produced by this method were 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 11 laboratories used flame atomic absorption spectrometry for the determination this time, and ICP-AES was used by 10 laboratories. However, in many laboratories the ion chromatographic technique becomes increasingly more popular in routine determination of the alkaline metals, thus 23 participants used ion chromatography in this intercomparison. Seven laboratories used flame photometry. 88 % of the result pairs are located within the general target accuracy of ± 20 %, which is considered as a very good result.

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 10 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 80 % of the result pairs are considered acceptable, and this is better than the last three years.

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, 77 % of the result pairs are located inside this circle, which is better than for a long time, one possible reason for this is the higher concentrations used for iron in this intercomparison. 35 laboratories submitted results for iron, of which 18 and 8 used ICP-AES and ICP-MS, respectively, while 6 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. 78 % of the result pairs are located inside this circle, which is better than former intercomparisons, probably because the concentrations used this time are somewhat higher than earlier. 36 laboratories submitted results for manganese, of which 18 and 8 used ICP-AES and ICP-MS, respectively, while 3 and 6 used flame and graphite furnace atomic absorption, respectively. Three laboratories had problems with the sensitivity of the method for the sample 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, 74 % of the result pairs are located inside this circle. 34 laboratories submitted results for cadmium, of which 11 and 12 used ICP-AES and ICP-MS, respectively, while 10 used graphite furnace atomic absorption. A laboratory using polarography reported results being comparable to the others. The cadmium concentrations in the samples used this time are a little higher than usual because the samples were spiked. Even then it is obvious that a few laboratories have problems because the method they are using is not sensitive enough for determination of cadmium at this level.

4.14 Lead

The results for lead are illustrated in Figure 14, and the values reported by the participants are given in Table 5.14. The target accuracy is ± 20 %, and is represented by the great circle in Figure 14. Only 52 % of the result pairs are located inside this circle, even if the samples were spiked this time. 33 laboratories submitted results for lead, of which 10 and 12 used ICP-AES and ICP-MS, respectively, while 10 used graphite furnace atomic absorption. Flame atomic absorption is not sensitive enough to determine these low lead concentrations.

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. 77 % 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. 35 laboratories submitted results for copper, of which 12 used ICP-AES and 11 used ICP-MS, while 9 and 2 used graphite furnace and flame atomic absorption, respectively.

4.16 Nickel

The results for nickel are illustrated in Figure 16, and the values reported by the participants are given in Table 5.16. The target accuracy is ± 20 %, and is represented by the great circle in Figure 16. This time, only 63 % 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. 32 laboratories submitted results for nickel, of which 10 and 11 used ICP-AES and ICP-MS, respectively, while 11 used graphite furnace atomic absorption.

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 61 % of the result pairs are located inside this circle. 33 laboratories submitted results for zinc, of which 15 and 10 used ICP-AES and ICP-MS, respectively, while 5 and 2 used flame and graphite furnace atomic absorption, respectively. Generally, the deviating results are affected mainly by systematic errors.

Table 1. Statistical summary of intercomparison 0620

Analytical variable and method	Sample pair	True value 1	True value 2	Total number	Labs excl.	Median 1	Median 2	Sample 1 Average	Sample 1 Std.dev.	Sample 2 Average	Sample 2 Std.dev.	Rel. Std.dev. % 1	Rel. Std.dev. % 2	Rel. error % 1	Rel. error % 2
pH	AB	6,71	7,23	65	2	6,71	7,23	6,72	0,17	7,18	0,20				
No stirring				26	0	6,73	7,23	6,72	0,23	7,19	0,21				
Stirring				38	2	6,70	7,23	6,71	0,12	7,16	0,20				
Equilibration				1	0			6,91		7,42					
Conductivity	AB	2,71	5,69	63	4	2,71	5,69	2,71	0,15	5,65	0,28	5,5	4,9	0,1	-0,7
Alkalinity	AB	0,094	0,291	51	14	0,094	0,291	0,098	0,016	0,295	0,020	16,8	6,6	4,5	1,5
Gran plot titration				21	3	0,096	0,292	0,099	0,015	0,299	0,025	15,0	8,2	5,0	2,9
End point 4,5 and 4,2				17	5	0,090	0,289	0,094	0,016	0,290	0,008	17,5	2,9	-0,1	-0,3
End point 5.6				1	0			0,089		0,281				-5,3	-3,4
End point 5.4				2	0			0,089		0,278				-5,3	-4,5
Other end points				9	5	0,115	0,302	0,116	0,021	0,304	0,015	18,2	4,9	23,4	4,3
Not documented				1	1			0,250		0,450				166	55
Nitrate + nitrite nitrogen	AB	130	209	62	8	130	209	131	12	208	16	9,5	7,6	0,6	-0,3
Autoanalyzer				11	1	133	217	137	12	217	15	9,0	6,9	5,4	3,9
Photometry				7	2	129	200	129	12	200	18	9,6	8,9	-0,9	-4,2
Ion chromatography				37	4	130	210	130	13	208	16	9,7	7,8	-0,1	-0,7
Hydrazine				3	0	130	206	130	2	209	6	1,5	3,1	0,0	-0,2
Cap. electrophoresis				1	0			127		210				-2,3	0,5
Photometry				2	1			140		190				7,7	-9,1
Electrometry				1	0			106		208				-18,5	-0,5
Chloride	AB	1,70	2,98	60	9	1,70	2,98	1,68	0,13	2,97	0,18	7,5	6,2	-1,2	-0,2
Ion chromatography				50	3	1,70	2,96	1,67	0,12	2,96	0,17	7,0	5,8	-1,8	-0,8
Argentometry				3	3			2,99		4,12				75,8	38,3
Manual, Hg				6	3	1,91	3,14	1,80	0,22	3,16	0,29	12,2	9,2	6,1	6,0
Potentiometry				1	0			1,84		3,20				8,2	7,4

Analytical variable and method	Sample pair	True value 1	True value 2	Total number	Labs excl.	Median 1	Median 2	Average Sample 1	Std.dev. Sample 1	Average Sample 2	Std.dev. Sample 2	Rel. Std.dev. % 1	Rel. Std.dev. % 2	Rel. error % 1	Rel. error % 2
Sulphate	AB	2,96	5,13	57	5	2,96	5,13	2,96	0,17	5,09	0,28	5,8	5,6	-0,1	-0,7
Ion chromatography				49	2	2,95	5,14	2,96	0,16	5,12	0,27	5,5	5,2	-0,1	-0,2
Photometry				3	1			2,88		4,53				-2,9	-11,7
Nephelometry				3	2			3,04		4,77				2,7	-7,0
ICP-AES				1	0			2,96		5,22				0,0	1,8
Gravimetry				1	0			3,07		5,19				3,7	1,2
Calcium	AB	2,63	7,23	56	4	2,63	7,23	2,63	0,35	7,21	0,58	13,3	8,1	0,0	-0,2
FAAS				12	0	2,60	7,10	2,58	0,46	6,91	0,58	17,8	8,4	-1,8	-4,4
ICP-AES				11	0	2,60	7,24	2,61	0,10	7,26	0,27	3,7	3,7	-0,8	0,5
EDTA				6	0	2,89	7,30	2,81	0,23	7,33	0,72	8,2	9,8	6,9	1,4
Ion chromatography				24	3	2,70	7,45	2,62	0,41	7,32	0,66	15,6	9,1	-0,5	1,3
ICP-MS				2	1			2,64		7,31				0,4	1,1
Cap. Electrophoresis				1	0			2,60		7,10				-1,1	-1,8
Magnesium	AB	0,37	0,61	56	9	0,37	0,61	0,36	0,03	0,61	0,06	9,5	9,7	-2,1	0,2
FAAS				12	0	0,36	0,61	0,35	0,04	0,62	0,07	11,2	12,1	-3,9	1,9
ICP-AES				11	1	0,37	0,61	0,36	0,04	0,60	0,04	9,8	6,2	-1,2	-0,3
EDTA				6	6			0,76		1,55				107,8	155,7
Ion chromatography				24	1	0,36	0,61	0,36	0,03	0,60	0,06	9,2	10,2	-1,7	-0,4
ICP-MS				2	0			0,37		0,60				-0,1	-0,4
Cap. Electrophoresis				1	1			0,35		1,16				-4,9	91,4
Sodium	AB	1,55	2,30	52	5	1,55	2,30	1,54	0,09	2,30	0,13	5,8	5,5	-0,9	0,1
FAAS				11	1	1,53	2,25	1,51	0,07	2,23	0,12	4,6	5,2	-2,7	-3,0
ICP-AES				10	0	1,49	2,26	1,53	0,13	2,30	0,18	8,7	8,0	-1,5	0,2
AES				6	1	1,50	2,30	1,46	0,09	2,30	0,08	6,2	3,6	-5,5	-0,1
Ion chromatography				23	2	1,57	2,33	1,57	0,06	2,34	0,10	3,7	4,4	1,3	1,7
ICP-MS				1	0			1,56		2,25				0,5	-2,3
Cap. Electrophoresis				1	1			1,49		1,19				-3,9	-48,3

Analytical variable and method		Sample pair	True value 1	True value 2	Total number	Labs excl.	Median 1	Median 2	Sample 1 Average	Sample 1 Std.dev.	Sample 2 Average	Sample 2 Std.dev.	Rel. Std.dev. % 1	Rel. Std.dev. % 2	Rel. error % 1	Rel. error % 2
Potassium		AB	0,295	0,502	51	5	0,295	0,502	0,295	0,029	0,508	0,039	10,0	7,6	0,0	1,1
	FAAS				10	0	0,283	0,500	0,288	0,022	0,502	0,028	7,7	5,6	-2,4	0,0
	ICP-AES				10	0	0,300	0,511	0,308	0,025	0,521	0,035	8,2	6,7	4,2	3,8
	AES				6	3	0,300	0,520	0,297	0,015	0,537	0,029	5,1	5,4	0,6	6,9
	Ion chromatography				23	2	0,293	0,500	0,291	0,034	0,501	0,046	11,8	9,1	-1,5	-0,1
	ICP-MS				1	0			0,278		0,495				-5,8	-1,4
	Cap. Electrophoresis				1	0			0,340		0,490				15,3	-2,4
Iron		CD	539	439	35	4	539	439	531	29	461	53	5,5	11,6	-1,4	4,9
	FAAS				6	1	543	434	539	19	444	36	3,4	8,1	-0,1	1,2
	GFAAS				2	0			481		452				-10,9	3,0
	ICP-AES				18	1	541	439	534	29	456	52	5,4	11,4	-1,0	3,9
	ICP-MS				8	2	542	471	536	29	480	76	5,4	15,8	-0,5	9,3
	Photometry				1	0			526		523				-2,4	19,1
Manganese		CD	20,0	7,8	36	6	20,0	7,8	19,7	1,1	8,0	1,1	5,6	14,3	-1,3	2,1
	FAAS				3	1			20,0		8,0				-0,2	2,3
	GFAAS				6	1	18,7	7,7	19,0	1,9	7,9	1,2	10,0	14,9	-5,0	1,9
	ICP-AES				18	2	20,0	7,9	19,8	1,0	8,0	1,3	4,9	16,0	-1,0	2,4
	ICP-MS				8	1	20,3	7,7	20,1	0,6	7,9	1,1	3,0	14,0	0,4	1,4
	Photometry				1	1			12,0		-5,0				-40	-164
Cadmium		CD	1,88	0,96	34	6	1,88	0,96	1,83	0,19	0,92	0,11	10,4	11,5	-2,2	-3,5
	GFAAS				10	0	1,83	0,94	1,78	0,24	0,90	0,13	13,4	14,2	-5,0	-5,9
	ICP-AES				11	6	1,72	0,83	1,79	0,26	0,89	0,15	14,4	17,1	-4,5	-6,7
	ICP-MS				12	0	1,89	0,97	1,89	0,11	0,95	0,06	5,6	6,5	0,7	-0,3
	Polarography				1	0			1,93		0,93				2,9	-2,7

Analytical variable and method		Sample pair	True value 1	True value 2	Total number	Labs excl.	Median 1	Median 2	Average Sample 1	Std.dev. Sample 1	Average Sample 2	Std.dev. Sample 2	Rel. Std.dev. % 1	Rel. Std.dev. % 2	Rel. error % 1	Rel. error % 2
Lead		CD	6,62	4,06	33	7	6,62	4,06	6,43	0,93	4,01	0,77	14,5	19,1	2,9	-0,7
	GFAAS				10	1	6,60	3,99	6,26	1,16	3,66	0,69	18,5	18,7	-5,4	-9,5
	ICP-AES				10	6	6,06	3,42	6,35	1,61	3,46	0,58	25,4	16,8	-4,1	-14,3
	ICP-MS				12	0	6,66	4,33	6,60	0,48	4,39	0,68	7,3	15,4	-0,3	8,7
	Polarography				1	0			6,24		4,89				-5,7	21,0
Copper		CD	18,39	23,45	35	5	18,39	23,45	18,63	1,57	23,71	1,81	8,5	7,7	1,3	1,1
	FAAS				2	0			19,10		24,60				3,9	4,9
	GFAAS				9	2	18,10	22,70	19,16	2,27	23,26	1,88	11,9	8,1	4,2	-0,8
	ICP-AES				12	3	17,70	22,50	17,97	1,23	22,77	1,62	6,9	7,1	-2,3	-2,2
	ICP-MS				11	0	18,50	24,00	19,03	1,01	24,51	1,81	5,3	7,4	3,5	4,5
	Polarography				1	0			15,65		24,60				-14,9	4,9
Nickel		CD	2,07	3,00	32	9	2,07	3,00	2,08	0,18	2,98	0,26	8,8	8,7	0,6	-0,7
	GFAAS				11	3	2,07	3,11	2,16	0,23	3,11	0,27	10,6	8,6	4,6	3,7
	ICP-AES				10	6	1,94	2,65	1,94	0,04	2,62	0,17	2,3	6,4	-6,2	-12,6
	ICP-MS				11	0	2,10	3,00	2,07	0,15	3,01	0,15	7,4	5,1	0,1	0,4
Zinc		CD	18,3	15,2	33	7	18,3	15,2	18,3	1,7	15,0	1,7	9,2	11,3	0,0	-1,1
	FAAS				5	3			17,7		14,2				-3,3	-6,5
	GFAAS				2	1			20,0		17,0				9,3	11,8
	ICP-AES				15	2	18,0	14,6	18,1	1,4	15,0	1,7	7,8	11,4	-1,2	-1,5
	ICP-MS				10	1	18,5	15,4	18,6	2,1	15,0	1,8	11,3	11,8	1,4	-1,1
	Polarography				1	0			18,4		15,6				0,5	2,6

pH

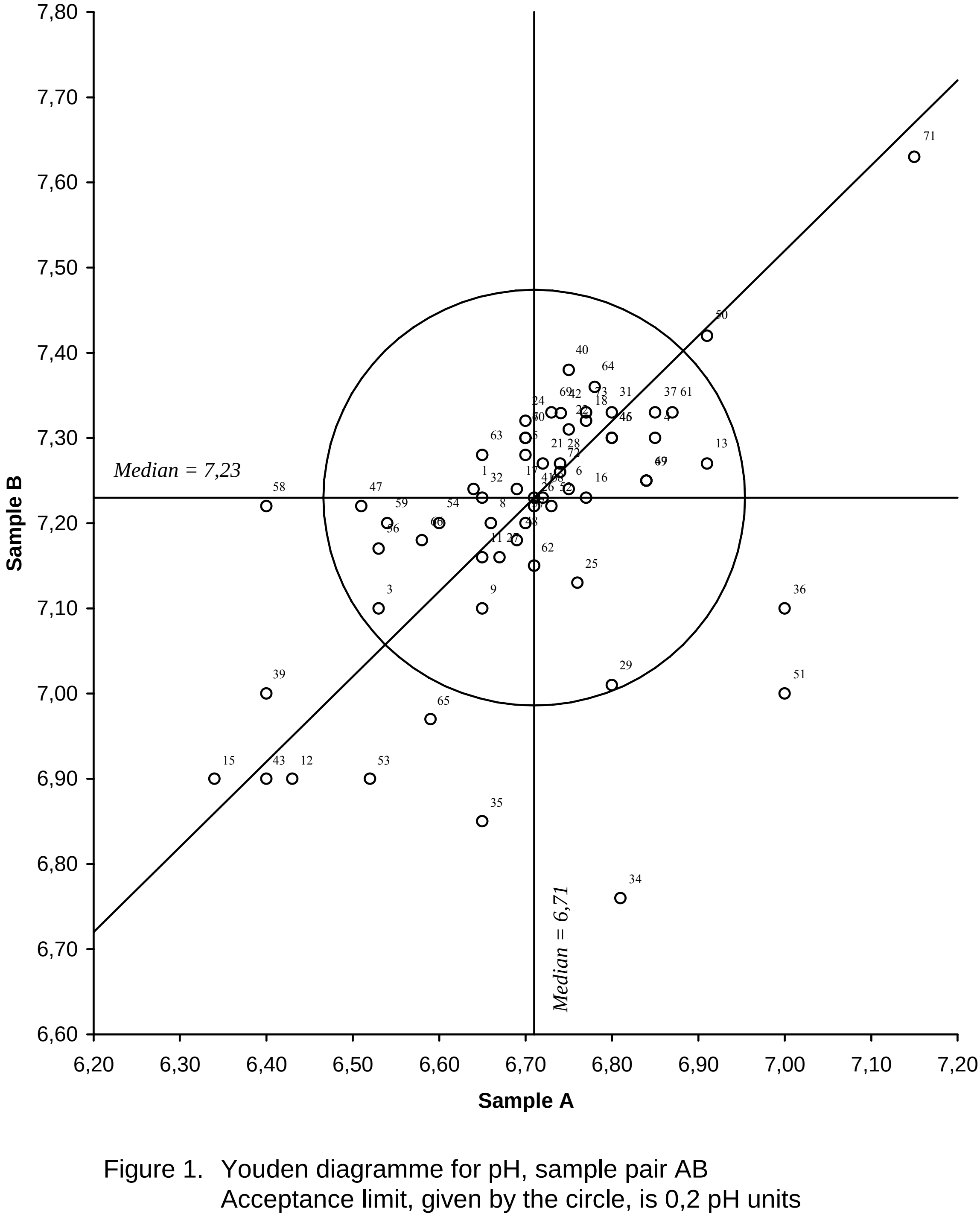

Figure 1. Youden diagramme for pH, sample pair AB
Acceptance limit, given by the circle, is 0,2 pH units

Conductivity

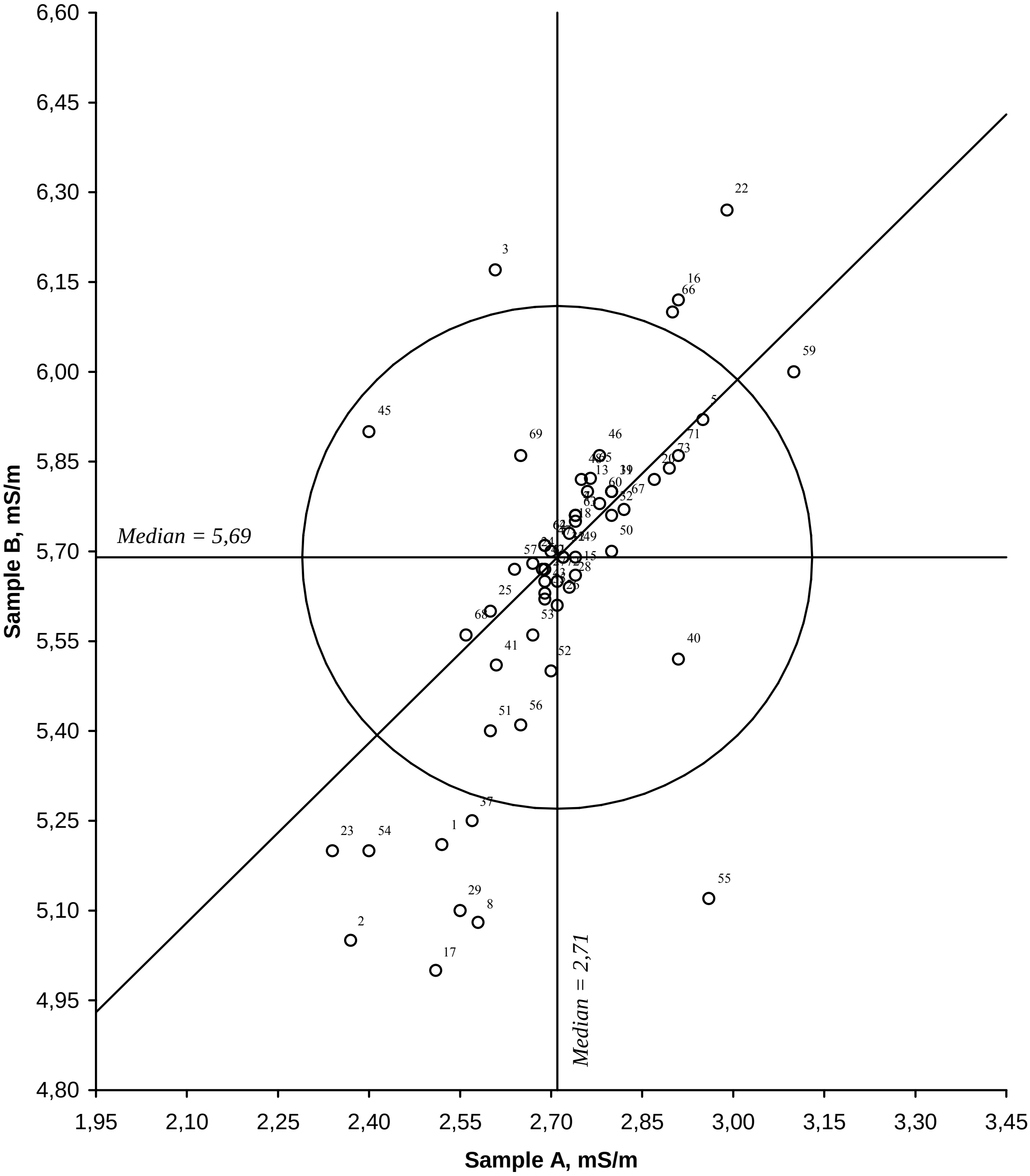

Figure 2. Youden diagramme for conductivity, sample pair AB
Acceptance limit, given by the circle, is 10 %

Alkalinity

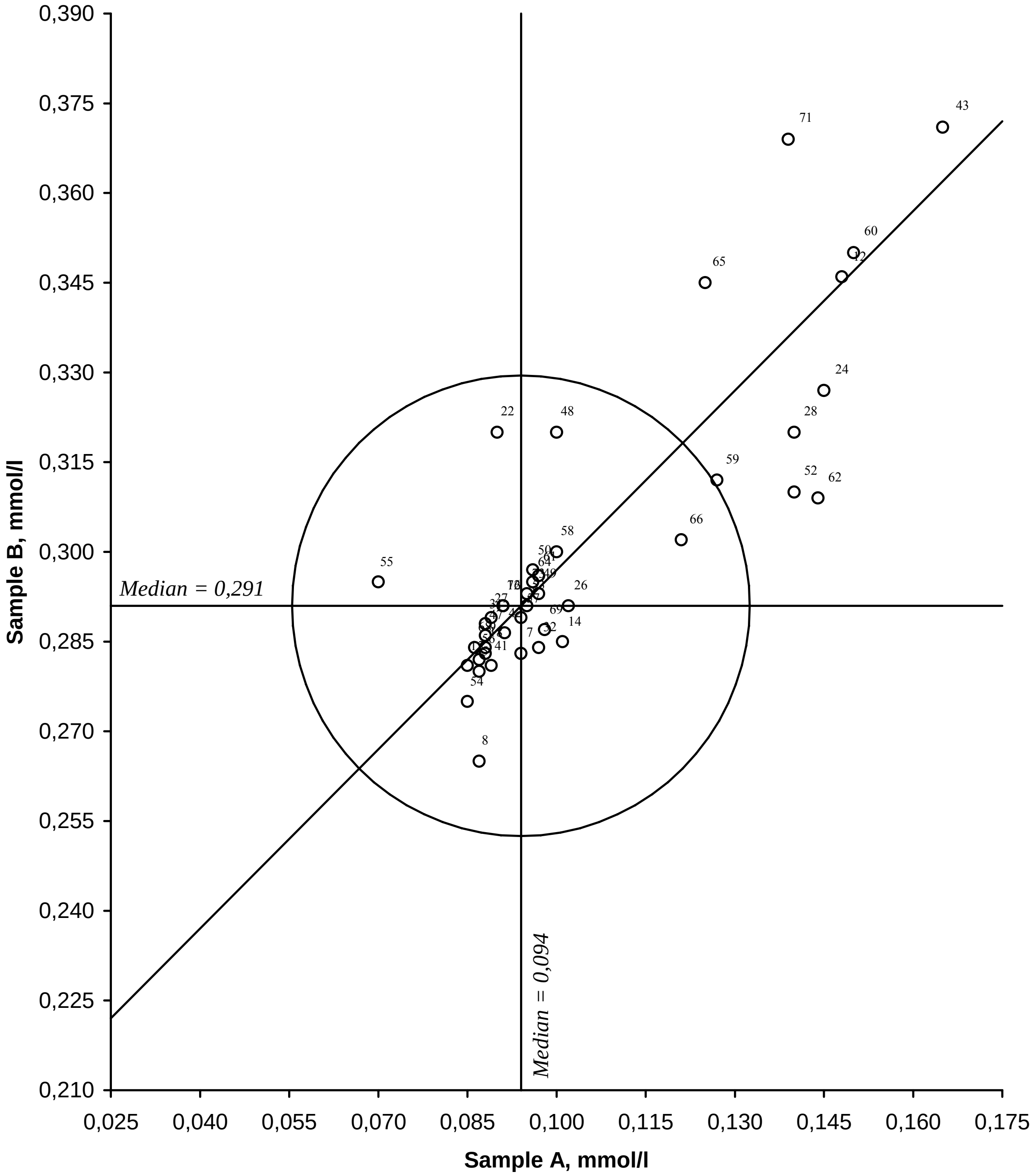

Figure 3. Youden diagramme for alkalinity, sample pair AB
Acceptance limit, given by the circle, is 20 %

Nitrate + nitrite-nitrogen

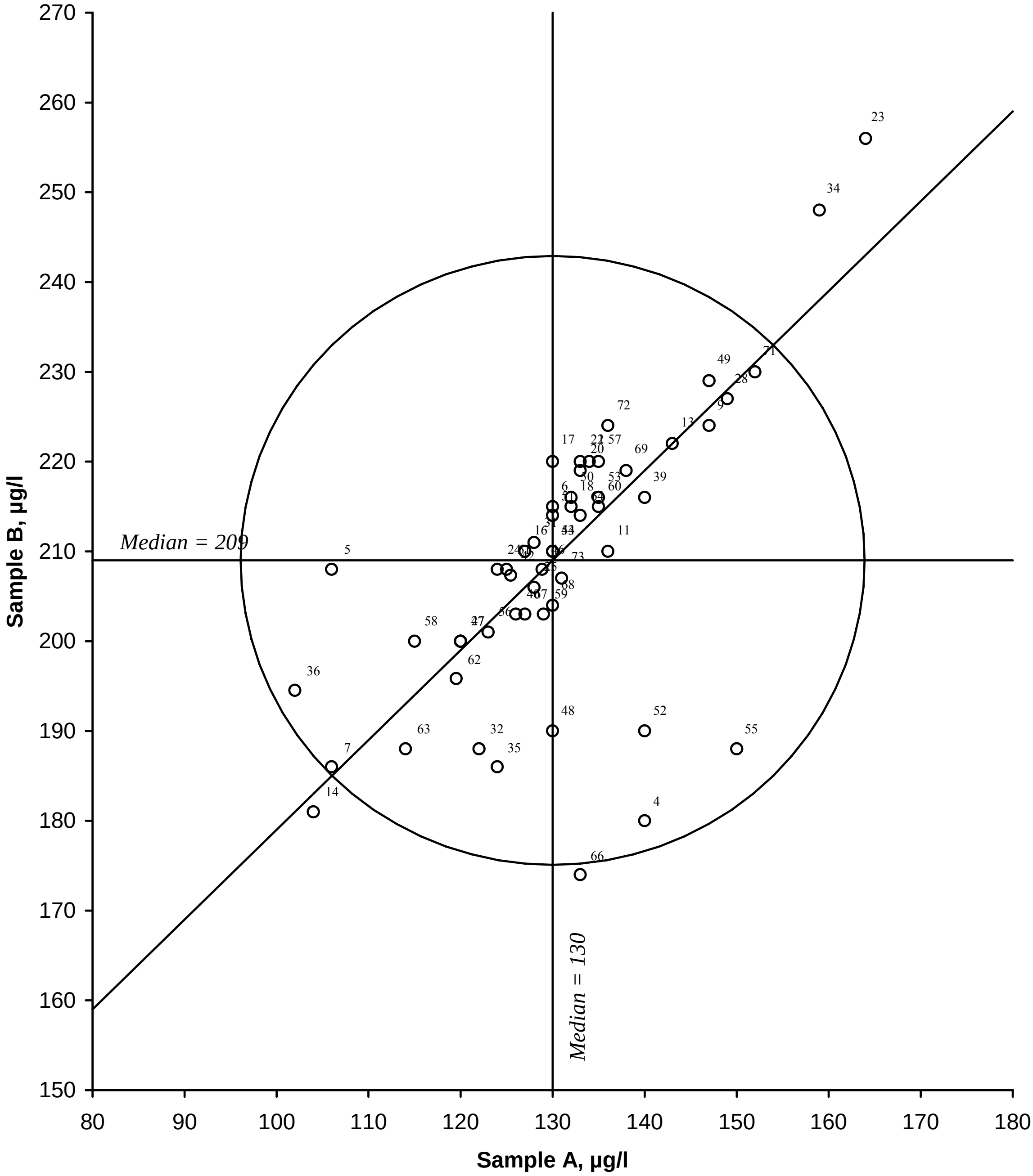

Figure 4. Youden diagramme for nitrate + nitrite-nitrogen, sample pair AB
Acceptance limit, given by the circle, is 20 %

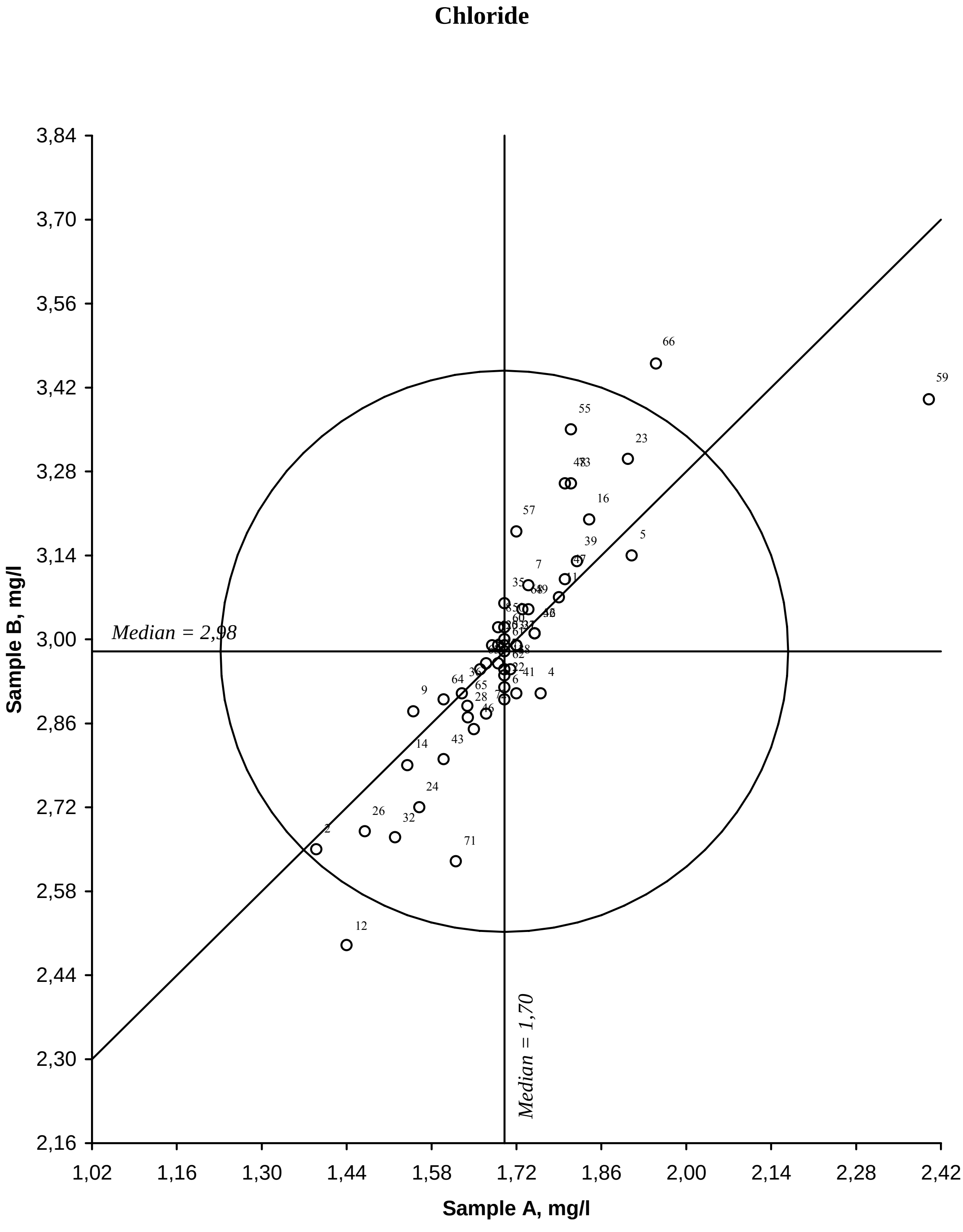

Figure 5. Youden diagramme for chloride, sample pair AB
Acceptance limit, given by the circle, is 20 %

Sulphate

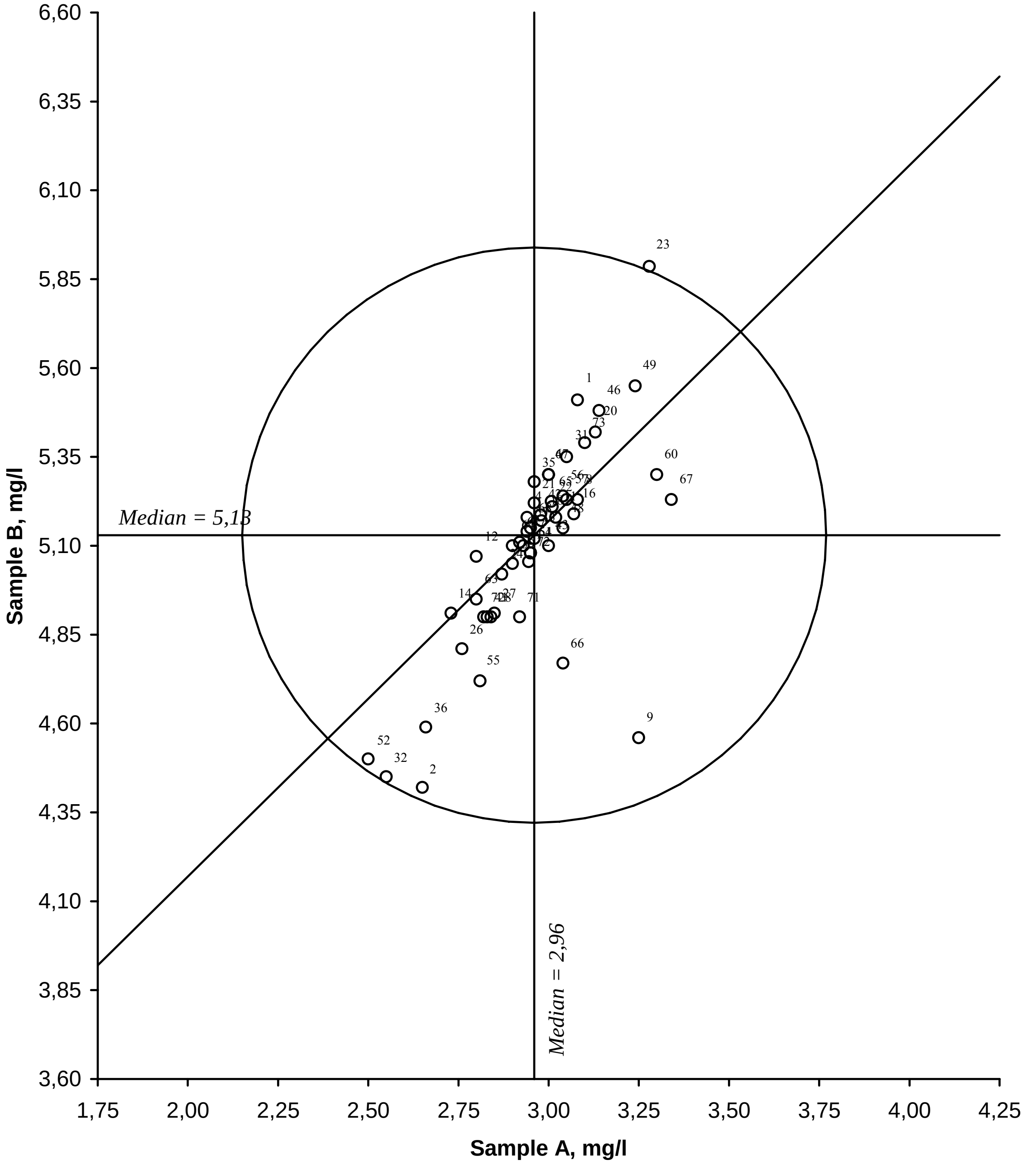

Figure 6. Youden diagramme for sulphate, sample pair AB
Acceptance limit, given by the circle, is 20 %

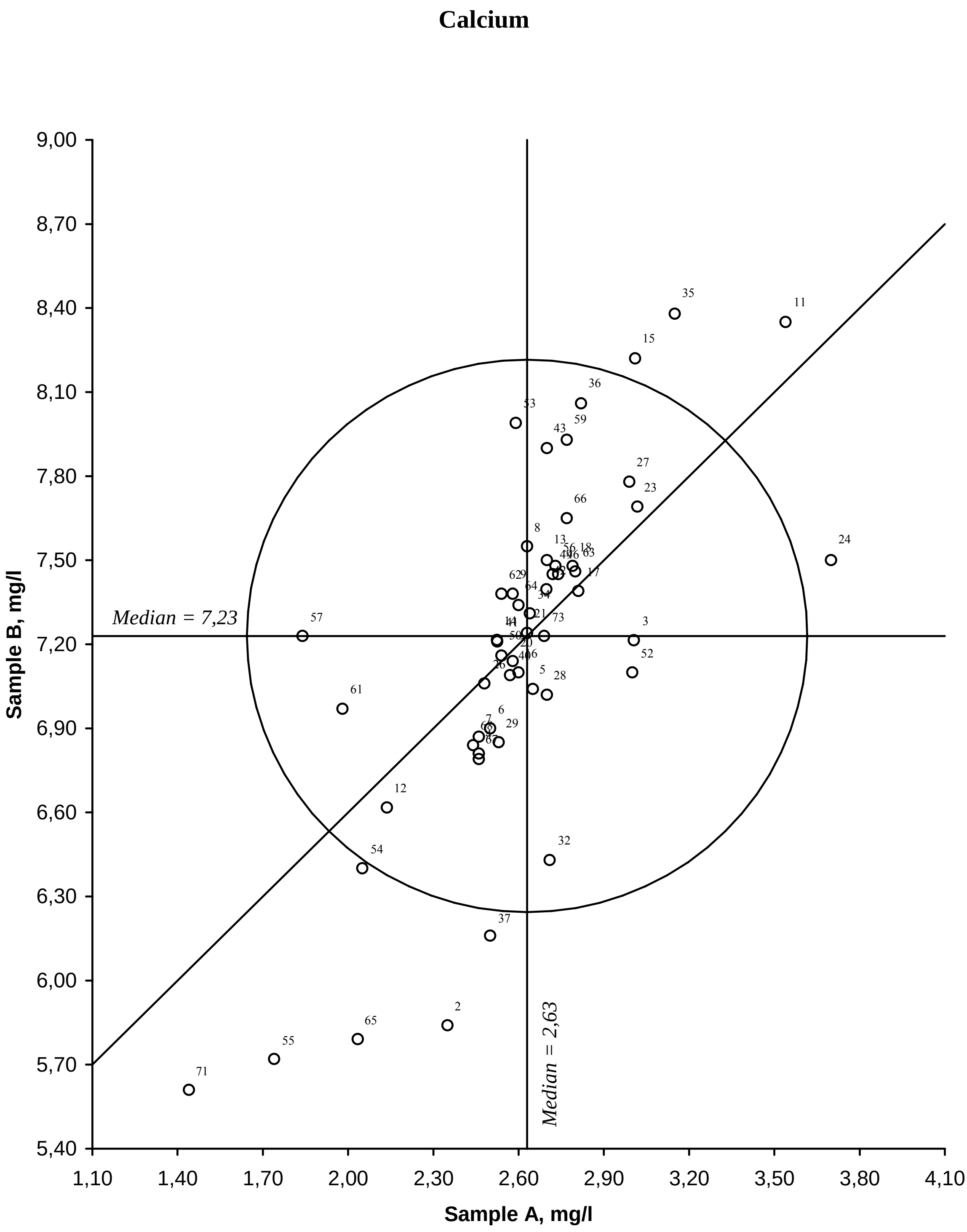

Figure 7. Youden diagramme for calcium, sample pair AB
Acceptance limit, given by the circle, is 20 %

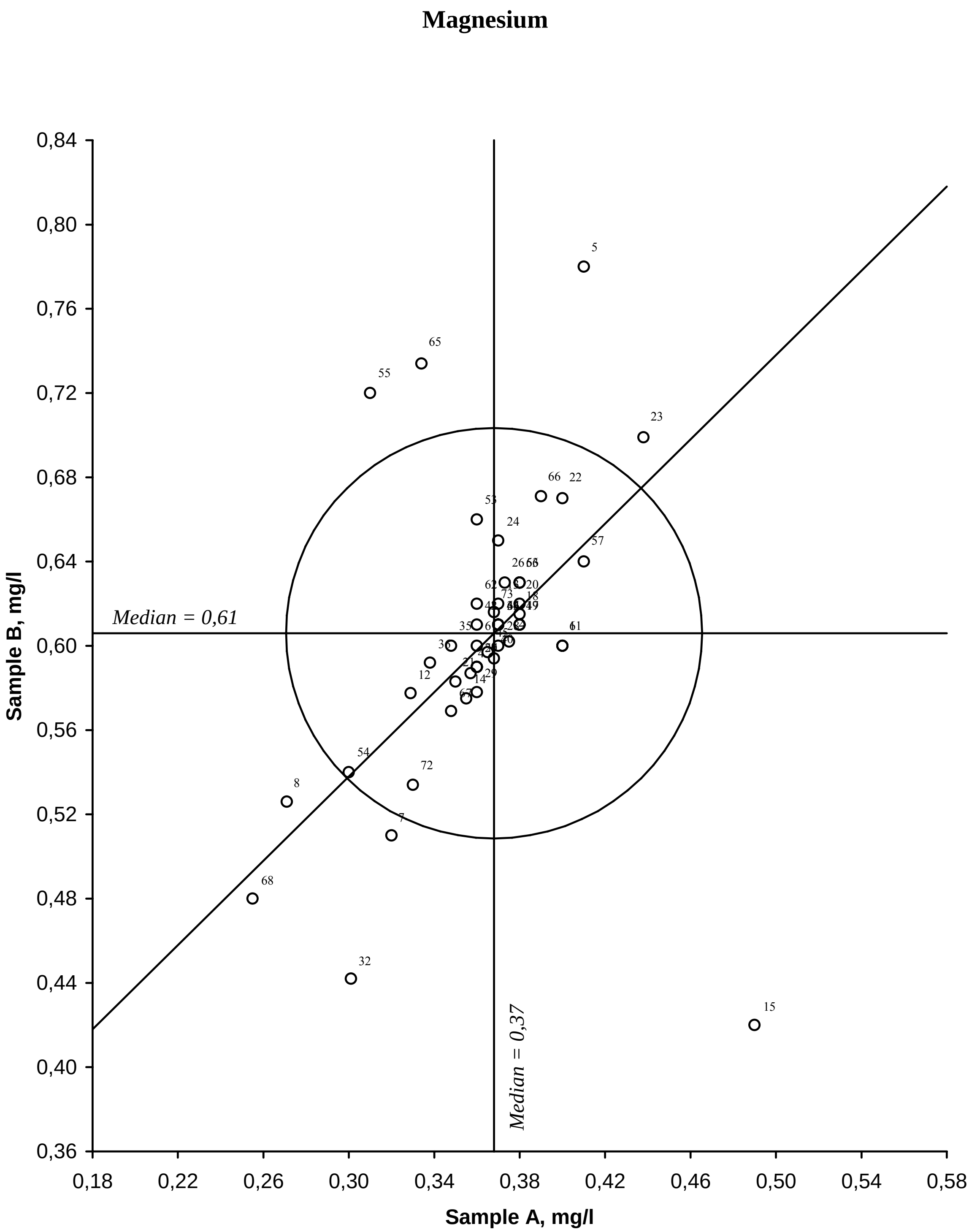

Figure 8. Youden diagramme for magnesium, sample pair AB
Acceptance limit, given by the circle, is 20 %

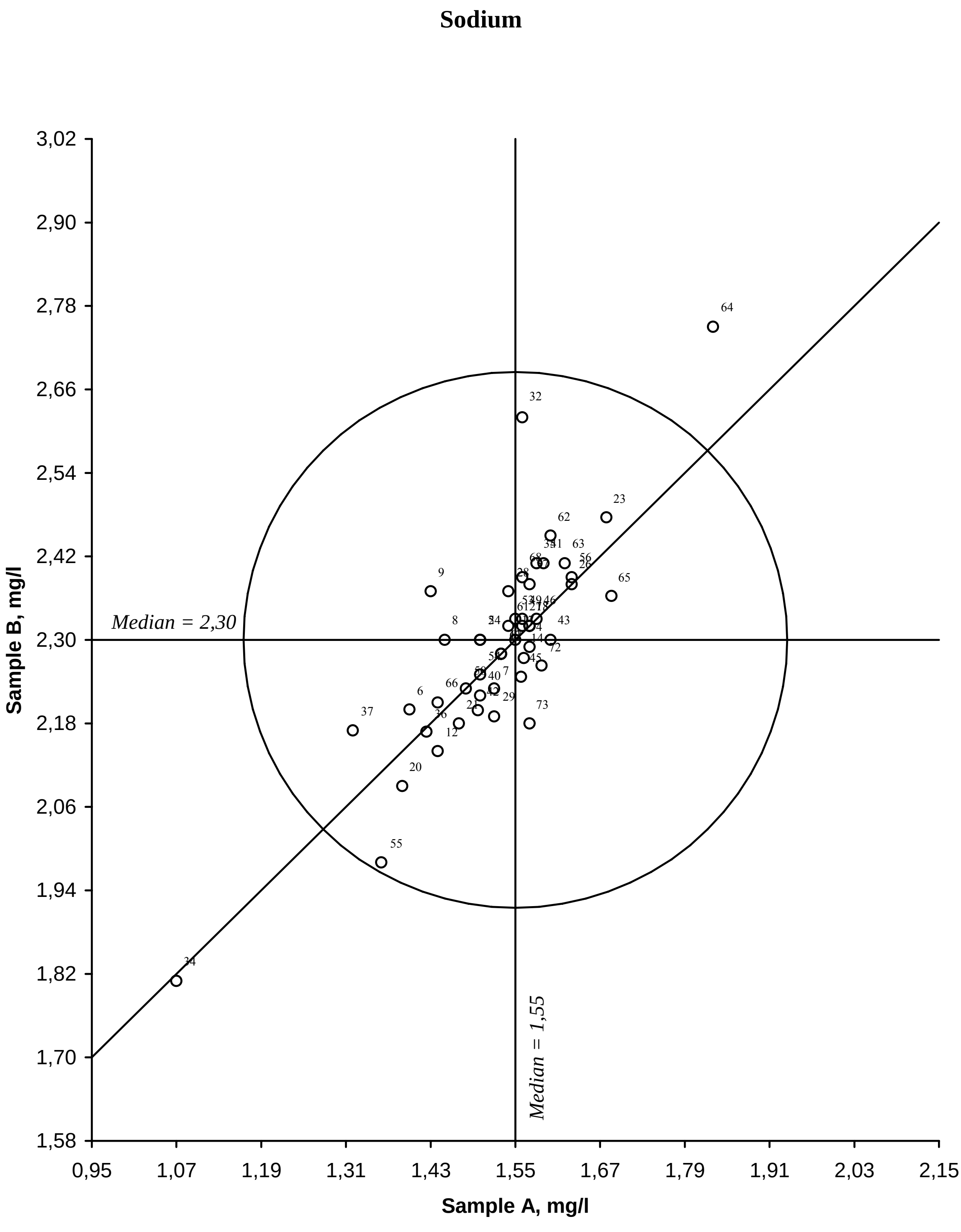

Figure 9. Youden diagramme for sodium, sample pair AB
Acceptance limit, given by the circle, is 20 %

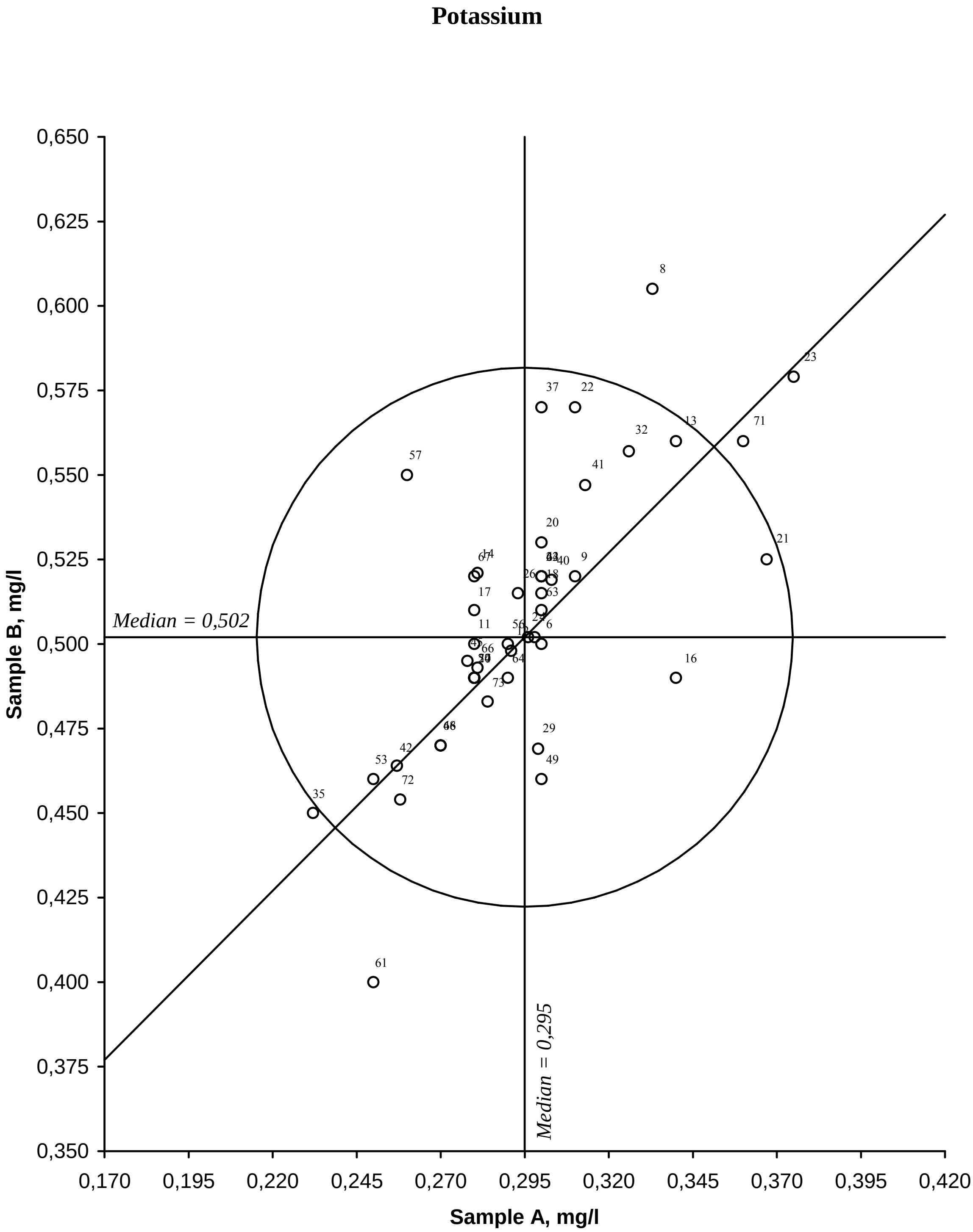

Figure 10. Youden diagramme for potassium, sample pair AB
Acceptance limit, given by the circle, is 20 %

Iron

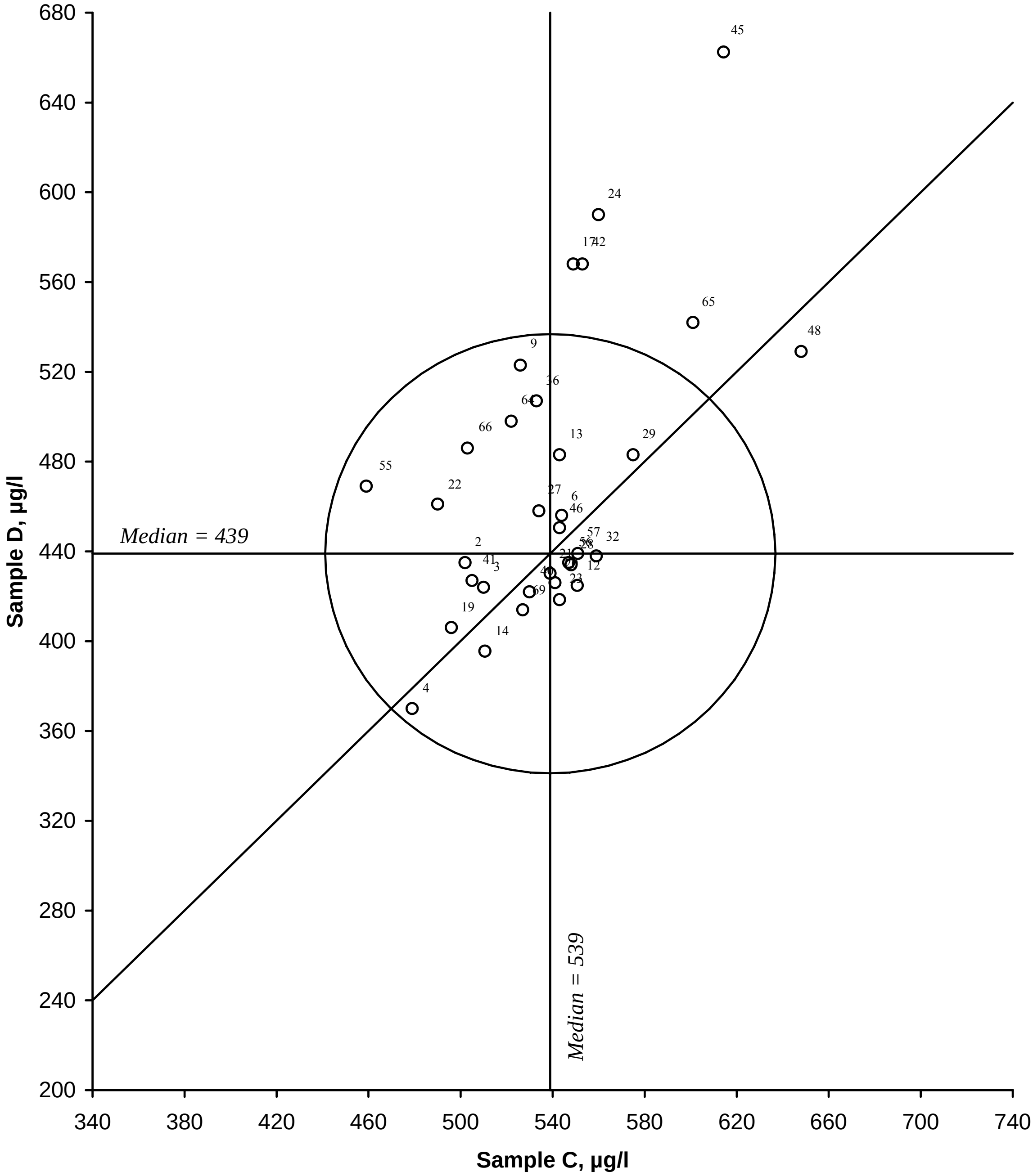

Figure 11. Youden diagramme for iron, sample pair CD
Acceptance limit, given by the circle, is 20 %

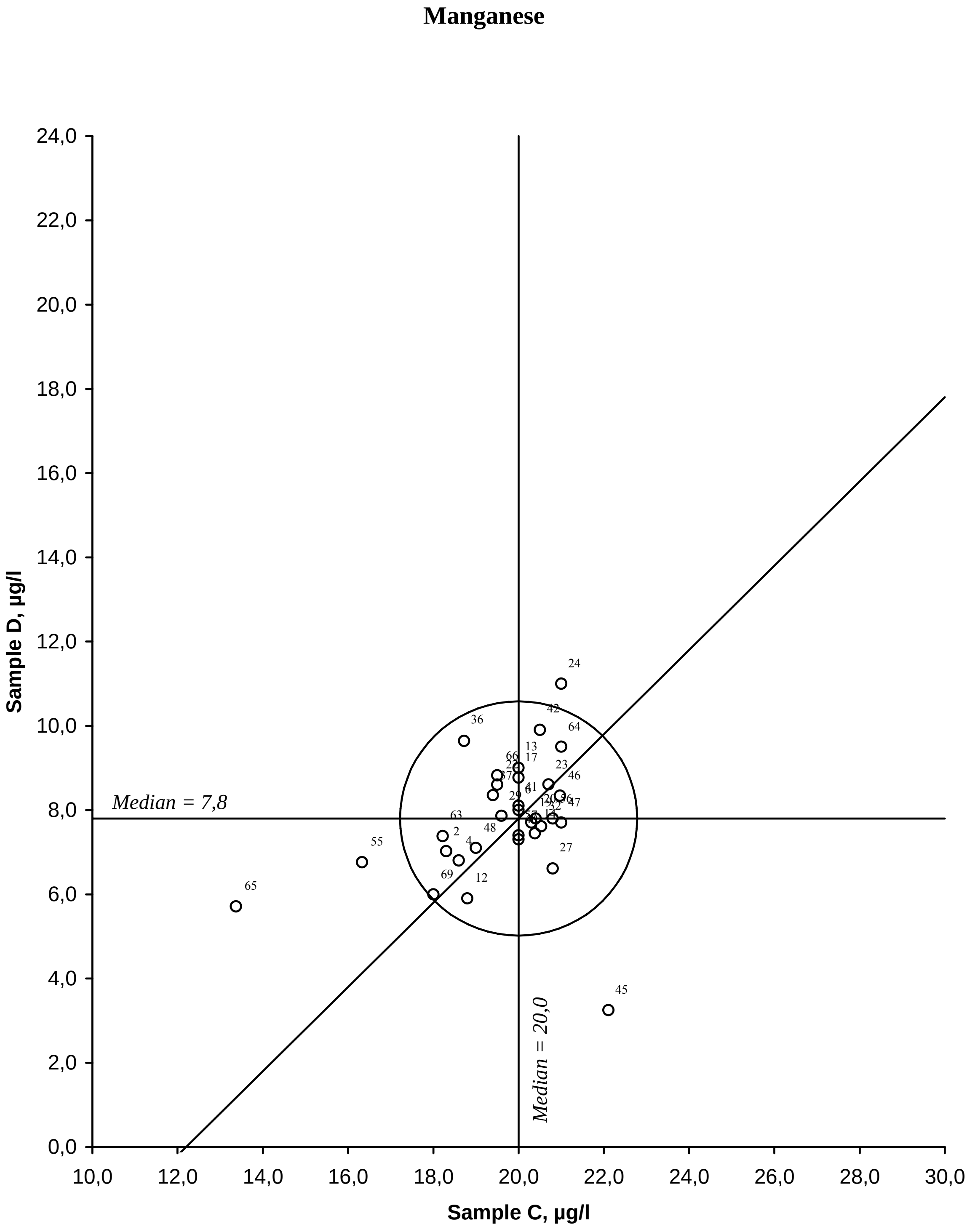

Figure 12. Youden diagramme for manganese, sample pair CD
Acceptance limit, given by the circle, is 20 %

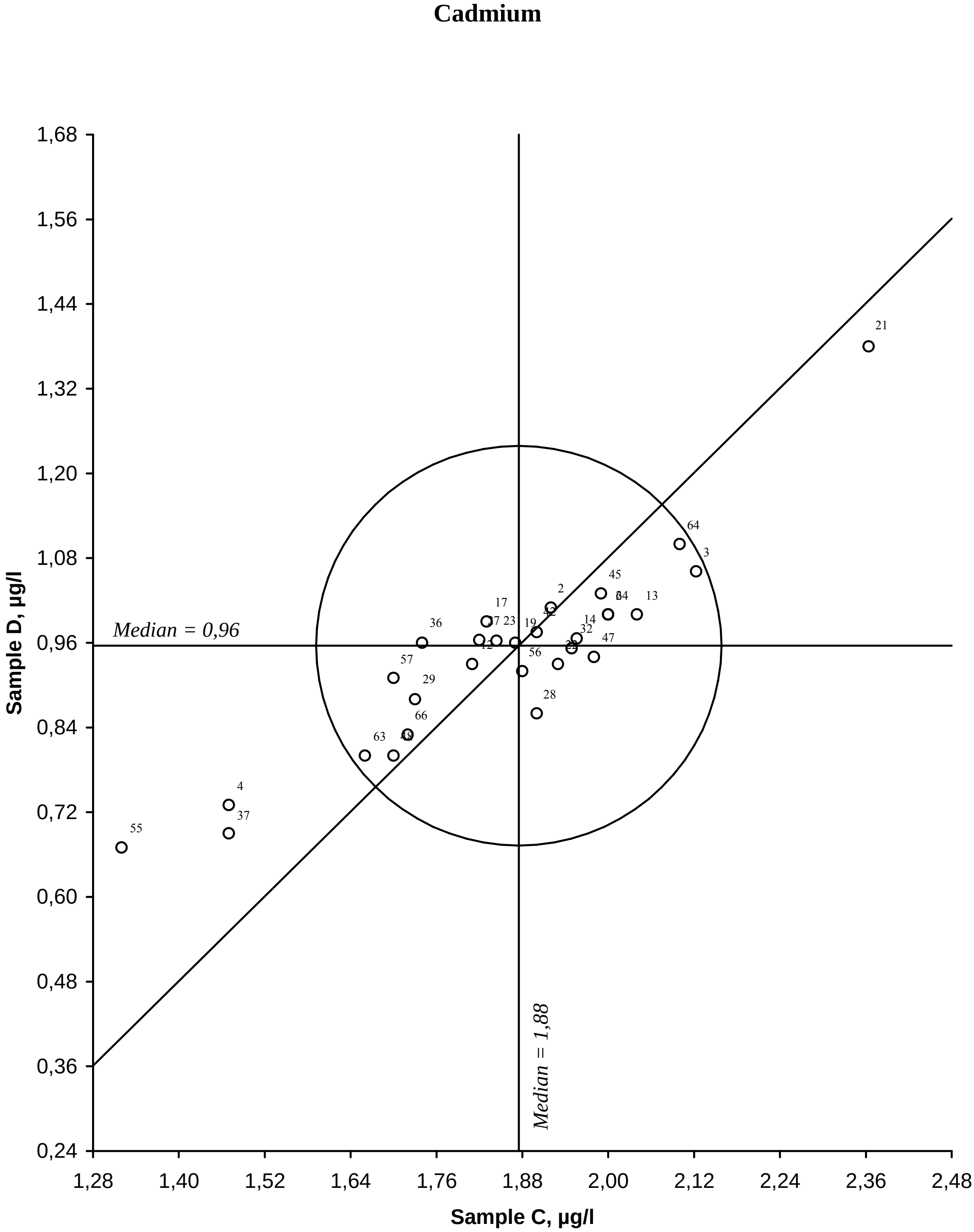

Figure 13. Youden diagramme for cadmium, sample pair CD
Acceptance limit, given by the circle, is 20 %

Lead

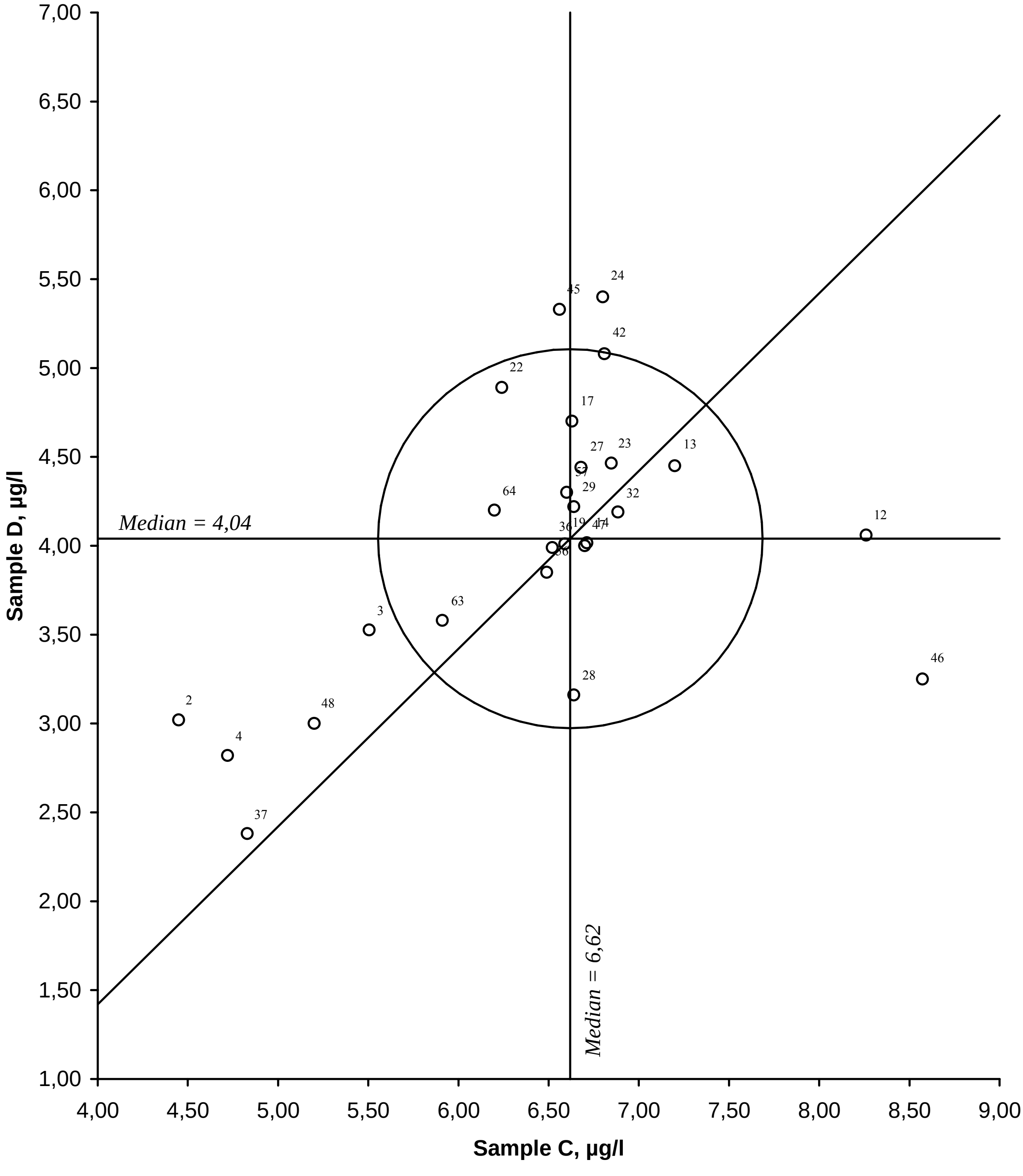

Figure 14. Youden diagramme for lead, sample pair CD
Acceptance limit, given by the circle, is 20 %

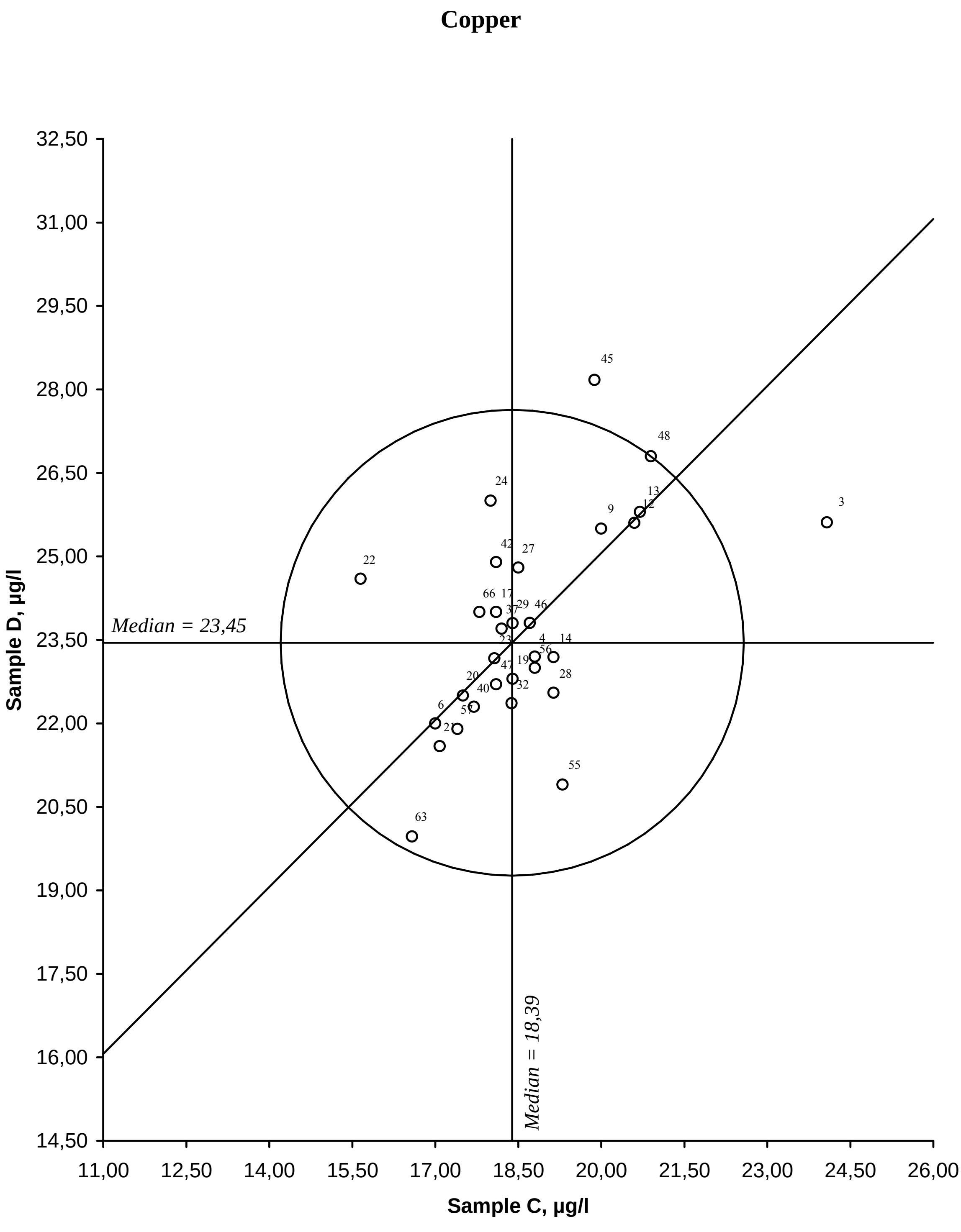

Figure 15. Youden diagramme for copper, sample pair CD
Acceptance limit, given by the circle, is 20 %

Nickel

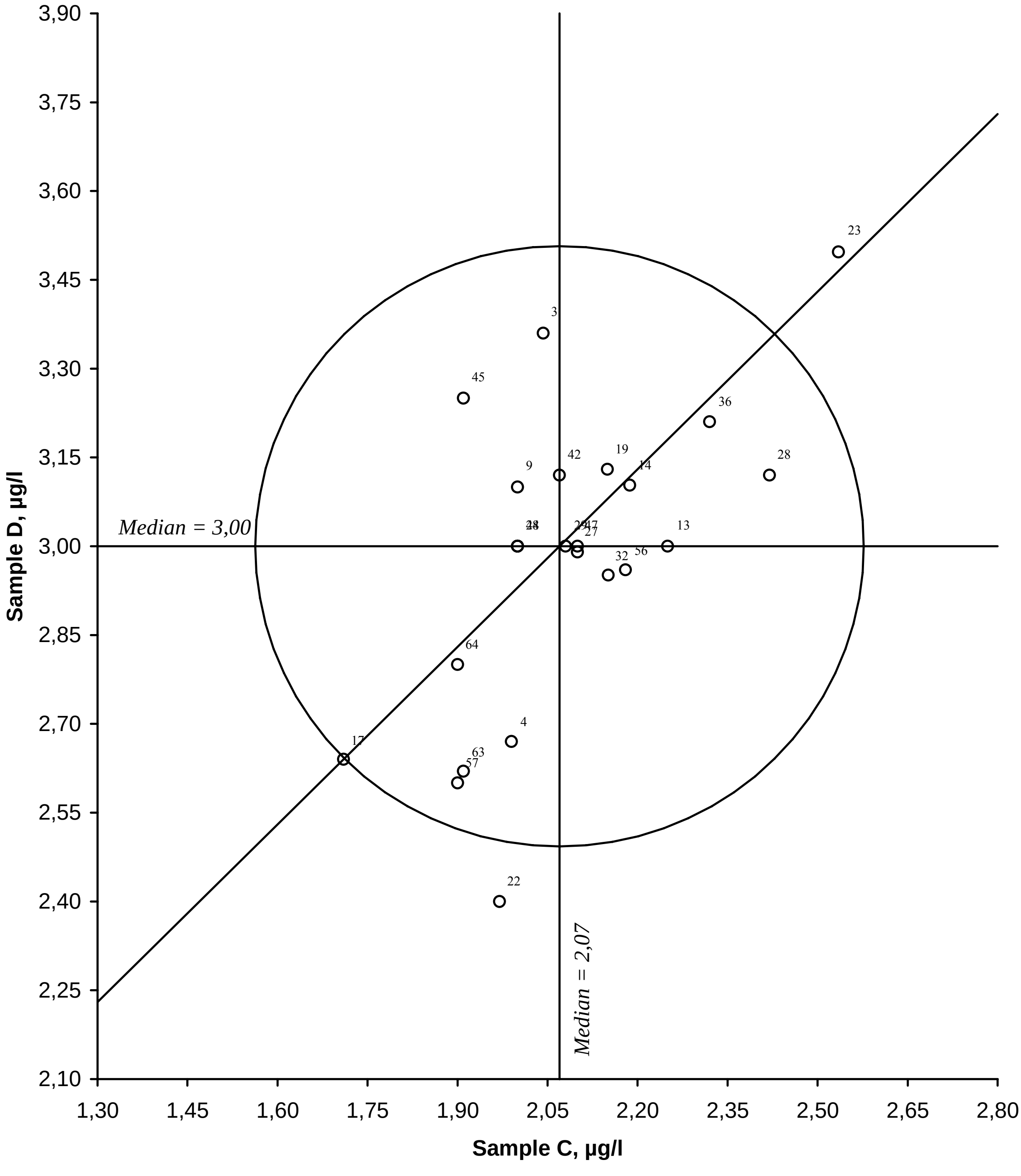

Figure 16. Youden diagramme for nickel, sample pair CD
Acceptance limit, given by the circle, is 20 %

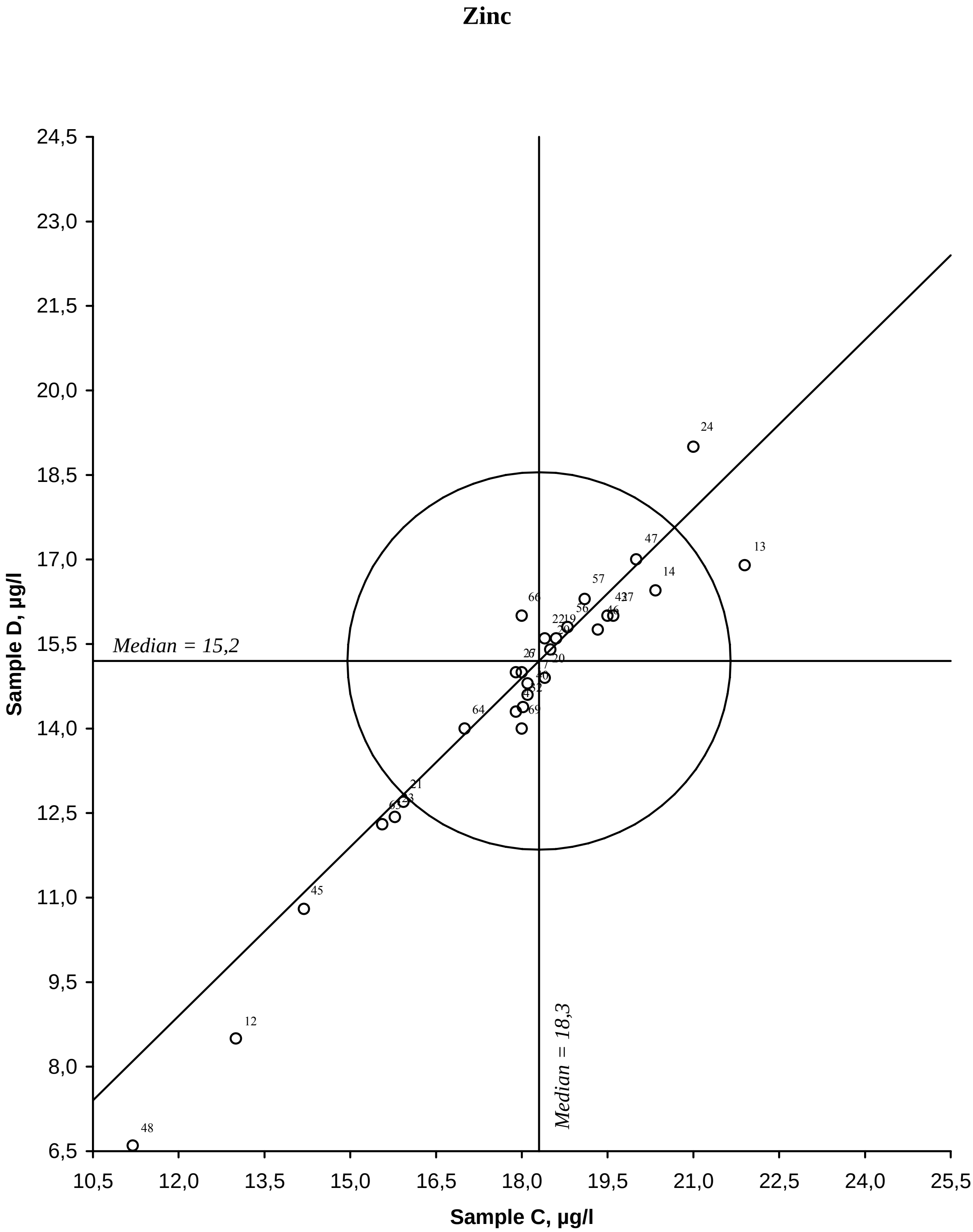

Figure 17. Youden diagramme for zinc, sample pair CD
Acceptance limit, given by the circle, is 20 %

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 0620 is presented, based on the target accuracy (except for pH and conductivity), where the number and percentage of acceptable results are given. 75 % of the results submitted by the participants are acceptable when compared to the acceptance limits given above. By improvement of the routine analytical method, the laboratories should be able to obtain even more accurate and comparable results.

In table 4 the individual results of each laboratory is given, here 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 methods. Of course, one digit more than the statistically significant one 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. With this wider acceptance limit 74 % of the result pairs are evaluated as acceptable.

Problems with poor comparability between the reported results for pH probably arise from the fact that the pH results are strongly affected by the method used, when the measurement is performed in nearly neutral solutions. This problem has been demonstrated through several earlier intercomparisons, and will remain as a problem as long as different methods for pH determination are used by the participating laboratories. This problem is well demonstrated for the equilibration method, which normally gives results quite higher than the other methods. This time there were only minor differences between the pH results produced during stirring the solution and no stirring of the solution, and even when using equilibration of the samples before measurement.

Because of the high precision of the reported results for conductivity in earlier intercomparisons, we have reduced the acceptance limit for this analytical variable from ± 20 % to ± 10 %. Still the number of acceptable results for conductivity is 71 % (Table 2). If we increase the acceptance limit to the target value, the number of acceptable results would increase. It is still a problem that many laboratories report their results in the units they normally use at their laboratory, and they very often do not write the unit used. The unit asked for in this intercomparison is mS/m. Some correspondence with the laboratories was therefore necessary to clarify the right results. In some cases where the laboratory had given the necessary information together with the conductivity results, it was possible to recalculate the result 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 in 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 0620. 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**	**True value**		**Accept. limit**	**Number of pairs**		**% accepatble res. for intercomp.**			
	pair	**1**	**2**	**%**	**N**	**n**	**0620**	**0519**	**0418**	**0317**
pH	AB	6,71	7,23	0,2*	65	48	74	63	57	57
Conductivity, mS/m	AB	2,71	5,69	10	63	45	71	81	80	82
Alkalinity, mmol/l	AB	0,094	0,291	20	51	32	63	63	52	58
Nitrate + nitrite-nitrogen, µg/l	AB	130	209	20	62	50	81	82	81	82
Chloride, mg/l	AB	1,7	2,98	20	60	49	82	86	84	81
Sulphate, mg/l	AB	2,96	5,13	20	57	51	89	81	86	83
Calcium, mg/l	AB	2,63	7,23	20	56	43	77	79	80	77
Magnesium, mg/l	AB	0,368	0,606	20	56	39	70	69	80	79
Sodium, mg/l	AB	1,55	2,3	20	52	46	88	89	87	92
Potassium, mg/l	AB	0,295	0,502	20	51	41	80	73	75	70
Iron, µg/l	CD	539	439	20	35	27	77	57	69	51
Manganese, µg/l	CD	20	7,8	20	36	28	78	65	59	36
Cadmium, µg/l	CD	1,875	0,956	20	34	25	74	18	76	60
Lead, µg/l	CD	6,62	4,04	20	33	17	52	8	78	49
Copper, µg/l	CD	18,39	23,45	20	35	27	77	63	95	83
Nickel, µg/l	CD	2,07	3	20	32	20	63	25	80	68
Zinc, µg/l	CD	18,3	15,2	20	33	20	61	54	82	76
Total					811	608	75	(67)	(77)	(71)

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

For nitrate + nitrite 81 % of the result pairs are acceptable. This is comparable to the results last year, and the nitrate concentrations in this intercomparison are rather high. In some few earlier intercomparisons this analytical variable proved to be unstable, however, this time the control analyses at the Programme Centre demonstrated that the samples were stable with respect to the content of nitrate and nitrite, throughout the whole periode of the intercomparison.

For calcium and magnesium a smaller fraction of the result pairs are acceptable in this intercomparison compared to earlier years, and the fraction of acceptable results are 77 and 70

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

Some heavy metals were included in this intercomparison programme. The best results were obtained for manganese, iron and copper where 78, 77 and 77 % of the results, respectively, are acceptable. This is considered as acceptable, even if there should be possible to achieve better comparability. For some of these elements the concentrations were low, especially for the metals cadmium, lead and nickel which were present down to the trace level. It is obvious that only 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 future.

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

6. Conclusion

67 laboratories submitted results for this intercomparison. The best results were reported for the analytical variables sodium and sulphate where 88 and 89 % of the results, respectively, were acceptable. The worst results were observed for the heavy metals where the concentrations are rather low.

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

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

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

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

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.

The number of participants in this ICP Waters intercomparison has been decreasing during the last years, in spite of the fact that more laboratories are invited. Is some of the reason that the intercomparison is run in the summer time, when many laboratories have vacation, or are there other reasons for this problem? The reason for this trend should be discussed and ways to increase the number of participants again should be found.

7. Literature

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

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

Appendix A.

The participating laboratories

No.	Name of participant	City	Country
1	Zavod za zdravstveno varstvo	Kranj	Slovenia
2	PASci, Institute of Botany	Krakow	Poland
3	Water Sources Laboratory 2	Buchuresti	Romania
4	NRW State Environment Agency	Essen	Germany
5	Primorsky Department for Hydromet. Env. Monitoring	Vladivostok	Russia
6	Centre for Ecology & Hydrology Wallingford	Wallington	United Kingdom
7	Laboratorio Biologico APPA-BZ	Laives (BZ)	Italy
8	SLU, Skoglig marklära	Uppsala	Sweden
9	Northern Water Problems Institute	Petrozavodsk	Russia
11	National Institute of Biology	Ljublana	Slovenia
12	T.G.Masaryk Water Research Institute, Analytical Lab.	Praha	Czech Republic
13	Bayerische Landesamt fur Wasserwirtschaft	München	Germany
14	INP, ENSAT	Castanet Tolosan	France
15	Virumaa Environmental Research Ltd	Jõhvi	Estonia
16	University of Barcelona, High Mountain Res. Center	Vielha, Lleida	Spain
17	Norwegian Institute for Air Research	Kjeller	Norway
18	Universität Innsbruck, Inst für Ökologie	Innsbruck	Austria
19	Umweltbundesamt - Messnetz	Langen	Germany
20	Umweltbundesamt - Dienst-gebaude Langen, Abt. II 5.4	Langen	Germany
21	Institute of soil science and Forest Nutrition	Goettingen	Germany
22	Sezione Protezione Aria, Acqua e Suolo	Bellinzona	Switzerland
23	Vlaamse Milieumaatschappij	Antwerpen	Belgium
24	ZAO "ROSSA"	Moscow	Russia
25	Ontario Ministry of Environment	Etobicoke, Ontario	Canada
26	Shimane Prefectural Institute of Public Health	Shimane	Japan
27	Norwegian Institute for Water Reseearc	Oslo	Norway
28	Environmental Laboratory of Latvian Environment	Riga	Latvia
29	The Environment Agency, NLS Laboratory	Llanelli, Wales	United Kingdom
31	CNR - IRSA	Brugherio	Italy
32	Charles University, Hydrobiol. Station, Velky Palene	Blatna	Czech Republic
34	Aquatische Oecologie en Milieubiologie	Nijmegen	Netherlands
35	EMB, DENR Compound	Quezon City	Philippines
36	CCDR - Alentejo	Vila Nova Santo Andre	Portugal
37	Geological Survey of Estonia	Tallinn	Estonia
39	Amt der Kärntner Landesreg., Abt. 15 Umweltschutz	Klagenfurt	Austria
40	Finnish Forest Research Institute, Central Laboratory	Vantaa	Finland
41	Swedish University of Agricultural Sciences	Uppsala	Sweden
42	Freshwater Laboratory, Fisheries Research Services	Perthshire	Scotland
43	Umweltbundesamt, Analytic 1	Vienna	Austria
45	University of Navarra, Dept. of Chemistry and Soil	Pamplona	Spain
46	Soil Science and Plant Nutrition Department	Firenze	Italy
47	North Ostrobothnia Regional Environmental Centre	Oulu	Finland
48	IASMA Research Center	S.Michele all'Adige	Italy
49	University of Helsinki, Lab. of Geology	Helsinki	Finland
50	Freshwater Institute	Manitoba	Canada
51	ELA Satellite Laboratory	Manitoba	Canada
52	Estonian Environmental Research Center	Pärnu	Estonia
53	Acid Deposition and Oxidant Research Center	Niigata shi	Japan
54	Hydrobiological Institute, ASCR	Ceské Budejovice	Czech Republic
55	Analist Service S.R.L.	Bucarest	Romania

No.	Name of participant	City	Country
56	Finnish Environment Institute Research Laboratory	Helsinki	Finland
57	Tartu Environmental Research	Tartu	Estonia
58	River Biology Laboratory, University of Life Sciences	Tartu	Estonia
59	University of Life Sciences Centre for Limnology	Rannu, Tartu	Estonia
60	Staatliche Umweltbetriebs-gesellschaft	Chemnitz	Germany
61	CNR Istituto Studio degli Ecosistemi	Verbania Pallanza	Italy
62	Environmental Research and Training Centre	Pathumthani	Thailand
63	ISSeP Colfontaine	Wasmes	Belgium
64	University of Maine, Environmental Chemistry Lab.	Orono, Maine	USA
65	Institute of Environmental Engineering	Zabrze	Poland
66	Ecoanalytical Laboratory "ECOANALYT"	Syktyvkar	Russia
67	Environmental Protection Ministry, Joint Research Centre	Vilnius	Lithuania
68	Environment Science centre - Dorset	Dorset, Ontario	Canada
69	Finnish Forest Research Institute, Rovaniemi Res. Station	Rovaniemi	Finland
71	EAWAG, Limnological Research Center	Kastanienbaum	Switzerland
72	IVL, Svenska Miljøinstitutet AB	Göteborg	Sweden
73	Ewica Laboratories	Kouvola	Finland

Number of participating laboratories from the different countries being represented in intercomparison 0620

Country	Labs	Country	Labs	Country	Labs
Austria	3	Japan	2	Russia	4
Belgium	2	Latvia	1	Slovenia	2
Canada	4	Lithuania	1	Spain	2
Czech Republic	3	Netherlands	1	Sweden	3
Estonia	6	Norway	2	Switzerland	2
Finland	6	Philippines	1	Thailand	1
France	1	Poland	2	United Kingdom	3
Germany	6	Portugal	1	USA	1
Italy	5	Romania	2		
				Total	67

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 2005, a few weeks before mailing the samples to the participants. The last sample was analyzed at the end of August 2005. A summary of the control results is presented in Table 3. The control results confirmed that the stability of the sample solutions were acceptable during the intercalibration period for all analytical variables.

Table 3. Summary of the control analyses

Analytical variable	Sample A		Sample B	
	Mean	Std. dev.	Mean	Std. dev.
pH	6,76	0,22	7,22	0,19
Conductivity mS/m	2,71	0,05	5,67	0,06
Alkalinity mmol/l	0,096	0,013	0,297	0,008
Nitrate/nitrite μg/l	112	2,9	172	2,9
Chloride mg/l	1,82	0,08	3,03	0,04
Sulphate mg/l	2,91	0,05	4,95	0,08
Calcium mg/l	2,99	0,08	7,84	0,10
Magnesium mg/l	0,37	0,01	0,061	0,02
Sodium mg/l	1,56	0,03	2,30	0,03
Potassium mg/l	0,28	0,01	0,49	0,01
	Sample C		**Sample D**	
Iron, μg/l	525	8,1	483	25,8
Manganese, μg/l	21,2	1,23	9,37	0,49
Cadmium, μg/l	1,87	0,05	0,97	0,01
Lead, μg/l	6,70	0,09	4,69	0,32
Copper, μg/l	18,4	0,21	24,2	0,74
Nickel, μg/l	2,12	0,04	2,95	0,03
Zinc, μg/l	18,5	0,50	15,4	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 ± 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. no.	pH A	pH B	Conductivity, mS/m A	Conductivity, mS/m B	Alkalinity, mmol/l A	Alkalinity, mmol/l B	Nitrate-N, µg/l A	Nitrate-N, µg/l B
1	6,64	7,24	2,52	5,21			134	220
2	7,40	6,48	2,37	5,05			338	383
3	6,53	7,10	2,608	6,17	0,18	0,37		
4	6,85	7,30	2,74	5,76			140	180
5	6,70	7,28	2,95	5,92	0,087	0,280	106	208
6	6,75	7,24					130	215
7	6,70	7,30	2,74	5,76	0,094	0,283	106	186
8	6,66	7,20	2,58	5,08	0,087	0,265	560	1080
9	6,65	7,10	26,9	56,1	0,088	0,284	147	224
11	6,65	7,16	2,8	5,8	11,9	32,0	136	210
12	6,43	6,90	2,72	5,69	0,148	0,346	610	920
13	6,91	7,27	2,76	5,80			143	222
14	6,6	6,4	1,87	4,11	0,101	0,285	104	181
15	6,34	6,90	2,74	5,66	0,085	0,281		
16	6,77	7,23	2,91	6,12	0,091	0,291	127	210
17	6,69	7,24	2,51	5,00			130	220
18	6,77	7,32	2,73	5,73	0,088	0,283	132	215
19								
20			2,87	5,82			133	219
21	6,72	7,27	2,776	5,69			330	210
22	6,75	7,31	2,99	6,27	0,090	0,32	133	220
23	5,833	6,230	2,34	5,20			164	256
24	6,70	7,32	2,67	5,68	0,145	0,327	124	208
25	6,76	7,13	2,6	5,6			128	206
26	6,71	7,22	2,71	5,61	0,102	0,291	192	249
27	6,67	7,16	2,69	5,65	0,089	0,289	120	200
28	6,74	7,27	2,73	5,64	0,140	0,320	149	227
29	6,80	7,01	2,55	5,10	0,043	0,14	< 200	< 200
31	6,80	7,33	2,72	5,69	0,088	0,288	128	211
32	6,65	7,23	2,80	5,76	0,097	0,284	122	188
34	6,81	6,76			0,19	0,34	159	248
35	6,65	6,85	2,69	5,62	0,054	0,153	124	186
36	7,00	7,10	28,6	58,5	0,37	0,25	102,00	194,52
37	6,85	7,33	2,57	5,25	0,18	0,34	199	264
39	6,40	7,00	2,8	5,8	0,25	0,45	140	216

Lab. no.	pH A	pH B	Conductivity, mS/m A	Conductivity, mS/m B	Alkalinity, mmol/l A	Alkalinity, mmol/l B	Nitrate-N, µg/l A	Nitrate-N, µg/l B
40	6,75	7,38	2,91	5,52			126	203
41	6,71	7,23	2,61	5,51	0,089	0,281		
42	6,741	7,329	2,686	5,670	0,09128	0,28645	125,44	207,34
43	6,4	6,9	2,69	5,63	0,165	0,371	130	210
45	6,8	7,3	2,4	5,9	0,20	0,41		
46	6,8	7,3	2,78	5,86			128,85	208,00
47	6,51	7,22	2,7	5,7	0,088	0,286	120	200
48	6,69	7,18	2,75	5,82	0,100	0,320	130	190
49	6,84	7,25	2,74	5,69	0,097	0,293	147	229
50	6,91	7,42	2,8	5,7	0,096	0,297	132	216
51	7,00	7,00	2,6	5,4			130	214
52	6,73	7,22	2,7	5,5	0,14	0,31	140	190
53	6,52	6,90	2,67	5,56	0,095	0,291	135	216
54	6,6	7,2	2,4	5,2	0,085	0,275	130	210
55	5,22	6,15	2,96	5,12	0,070	0,295	150	188
56	6,53	7,17	2,65	5,41	0,087	0,282	123	201
57	6,70	7,20	2,64	5,67	0,094	0,289	135	220
58	6,4	7,22			0,1	0,3	115	200
59	6,54	7,20	3,1	6,0	0,127	0,312	129	203
60	6,7	7,3	2,78	5,78	0,15	0,35	135	215
61	6,87	7,33	2,69	5,67	0,097	0,296	125	208
62	6,71	7,15	2,69	5,71	0,144	0,309	119,54	195,84
63	6,65	7,28	2,74	5,75			114	188
64	6,78	7,36	2,69	5,71	0,096	0,295	133	214
65	6,59	6,97	2,765	5,822	0,125	0,345	558	451
66	6,58	7,18	2,90	6,10	0,121	0,302	133	174
67	6,84	7,25	2,82	5,77			127	203
68	6,72	7,23	2,56	5,56	0,0862	0,284	130	204
69	6,73	7,33	2,65	5,86	0,098	0,287	138	219
71	7,15	7,63	2,91	5,86	0,139	0,369	152	230
72	6,74	7,26	2,71	5,65	0,091	0,291	136	224
73	6,77	7,33	2,895	5,839	0,095	0,293	131	207

Lab. no.	Chloride, mg/l A	Chloride, mg/l B	Sulphate, mg/l A	Sulphate, mg/l B	Calcium, mg/l A	Calcium, mg/l B	Magnesium, mg/l A	Magnesium, mg/l B
1	1,68	2,99	3,08	5,51				
2	1,39	2,65	2,65	4,42	2,35	5,84	0,375	0,602
3	0,877	2,632			3,006	7,214	0,608	0,729
4	1,76	2,91	2,94	5,18	2,46	6,81	0,357	0,587
5	1,91	3,14	5,1	7,0	2,65	7,04	0,41	0,78
6	1,7	2,9	3,0	5,3	2,5	6,9	0,4	0,6
7	1,74	3,09	2,82	4,90	2,46	6,87	0,32	0,51
8	1,69	3,02	3,08	5,23	2,63	7,55	0,271	0,526
9	1,55	2,88	3,25	4,56	2,58	7,38	0,55	0,91
11	1,79	3,07	3,02	5,18	3,54	8,35	0,4	0,6
12	1,44	2,49	2,80	5,07	2,137	6,617	0,329	0,578
13	1,70	2,95	2,96	5,12	2,70	7,50	0,37	0,62
14	1,54	2,79	2,73	4,91	2,524	7,215	0,355	0,575
15	2,13	4,25	1,2	1,7	3,01	8,22	0,49	0,42
16	1,84	3,20	3,07	5,19	2,60	7,10	0,350	1,16
17	1,69	2,96	2,93	5,10	2,81	7,39	0,38	0,61
18	1,71	2,95	2,98	5,17	2,79	7,48	0,38	0,615
19								
20	1,69	2,99	3,13	5,42	2,58	7,14	0,38	0,62
21	1,69	1,84	2,96	5,22	2,63	7,24	0,350	0,583
22	1,70	2,92	3,01	5,21	3,00	10,91	0,40	0,67
23	1,904	3,301	3,279	5,886	3,018	7,691	0,438	0,699
24	1,56	2,72	2,87	5,02	3,7	7,5	0,37	0,65
25								
26	1,47	2,68	2,76	4,81	2,48	7,06	0,373	0,630
27	1,72	2,99	2,85	4,91	2,99	7,78	0,36	0,59
28	1,64	2,87	2,84	4,90	2,70	7,02	0,37	0,60
29	2,43	3,43	1,60	2,95	2,53	6,85	0,36	0,578
31	1,72	2,99	3,05	5,35				
32	1,52	2,67	2,55	4,45	2,71	6,43	0,301	0,442
34	1,10	1,84			2,64	7,31	0,37	0,61
35	1,70	3,06	2,96	5,28	3,15	8,38	0,348	0,600
36	1,63	2,91	2,66	4,59	2,82	8,06	0,338	0,592
37	5,39	5,73			2,50	6,16	0,82	1,75
39	1,82	3,13	2,9	5,05				
40					2,57	7,09	0,368	0,594
41	1,72	2,91	2,83	4,90	2,525	7,21	0,356	1,18
42	1,75	3,01	2,978	5,187	2,698	7,396	0,360	0,610
43	1,6	2,8	3,0	5,1	2,7	7,9	0,37	0,61
45					1,22	3,36	0,365	0,597

Lab. no.	Chloride, mg/l A	Chloride, mg/l B	Sulphate, mg/l A	Sulphate, mg/l B	Calcium, mg/l A	Calcium, mg/l B	Magnesium, mg/l A	Magnesium, mg/l B
46	1,65	2,85	3,14	5,48	2,74	7,45	0,37	0,61
47	1,8	3,1	3,0	5,3				
48	1,80	3,26	3,04	5,15				
49	1,74	3,05	3,24	5,55	2,72	7,45	0,38	0,61
50	1,70	3,02	4,88	5,02	2,54	7,16	0,36	0,59
51								
52	2,7	4,0	2,5	4,5	3,0	7,1	1,6	5,2
53	1,70	2,99	2,94	5,14	2,59	7,99	0,36	0,66
54	1,67	2,96	2,95	5,08	2,05	6,4	0,30	0,54
55	1,81	3,35	2,81	4,72	1,74	5,72	0,31	0,72
56	1,75	3,01	3,04	5,24	2,73	7,48	0,38	0,63
57	1,72	3,18	3,05	5,23	1,84	7,23	0,41	0,64
58								
59	2,4	3,4	4,2	6,7	2,77	7,93	0,52	0,29
60	1,7	3,0	3,3	5,3				
61	1,70	2,98	2,95	5,08	1,98	6,97	0,36	0,60
62	1,70	2,94	2,92	5,11	2,54	7,38	0,36	0,62
63	1,66	2,95	2,80	4,95	2,80	7,46	0,38	0,63
64	1,6	2,9	2,9	5,1	2,60	7,34	0,37	0,61
65	1,639	2,889	3,007	5,225	2,034	5,791	0,334	0,734
66	1,95	3,46	3,04	4,77	2,77	7,65	0,390	0,671
67	3,86	4,63	3,34	5,23	2,46	6,79	0,348	0,569
68	1,73	3,05	2,95	5,15	2,44	6,84	0,255	0,48
69								
71	1,62	2,63	2,92	4,90	1,44	5,61	0,09	0,23
72	1,67	2,876	2,945	5,055	3,009	9,252	0,330	0,534
73	1,81	3,26	3,10	5,39	2,69	7,23	0,368	0,616

Lab. no.	Sodium, mg/l A	Sodium, mg/l B	Potassium, mg/l A	Potassium, mg/l B	Iron, µg/l C	Iron, µg/l D	Manganese, µg/l C	Manganese, µg/l D
1								
2	1,285	0,852	0,296	0,502	502	435	18,3	7,0
3					510	424	< 14	< 14
4	1,57	2,29	0,298	0,502	479	370	18,6	6,8
5	1,50	2,30	0,38	0,70				
6	1,4	2,2	0,3	0,5	544	456	20,0	8,0
7	1,52	2,23	0,28	0,49				
8	1,45	2,30	0,333	0,605				
9	1,43	2,37	0,31	0,52	526	523	12	< 5
11	1,53	2,28	0,28	0,5				
12	1,44	2,14	0,291	0,498	550,7	424,8	18,8	5,9
13	1,57	2,32	0,34	0,56	543	483	20,0	9,0
14	1,562	2,274	0,281	0,521	510,55	395,52	20,382	7,444
15								
16	1,49	1,19	0,34	0,49				
17	1,55	2,30	0,28	0,51	549	568	20,0	8,77
18	1,57	2,32	0,30	0,515				
19					496	406	20,3	7,7
20	1,39	2,09	0,30	0,53	541	426	20,4	7,8
21	1,47	2,18	0,367	0,525	539	430	20,10	< 10
22	2,13	3,17	0,31	0,57	490	461	19,5	8,6
23	1,679	2,476	0,375	0,579	543,0	418,5	20,70	8,608
24	1,5	2,3	0,30	0,52	560	590	21	11
25								
26	1,63	2,38	0,293	0,515				
27	1,56	2,32	0,28	0,49	534	458	20,8	6,6
28	1,54	2,37	0,45	0,61	548	434	54,8	9,0
29	1,52	2,19	0,299	0,469	575	483	19,6	7,86
31								
32	1,56	2,62	0,326	0,557	559	438	20,53	7,61
34	1,07	1,81	0,02	0,06				
35	1,58	2,41	0,232	0,450				
36	1,424	2,168	0,0	0,565	533	507	18,72	9,64
37	1,32	2,17	0,30	0,57	250	119	19,4	8,35
39								
40	1,50	2,22	0,303	0,519	530	422	20,0	7,3
41	1,59	2,41	0,313	0,547	505	427	20	8,1
42	1,497	2,199	0,257	0,464	553	568	20,5	9,90
43	1,6	2,3	0,30	0,52				
45	1,558	2,247	0,278	0,495	614,32	662,44	22,11	3,25

Lab.	Sodium, mg/l		Potassium, mg/l		Iron, µg/l		Manganese, µg/l	
no.	A	B	A	B	C	D	C	D
46	1,58	2,33	0,27	0,47	543,011	450,531	20,9744	8,3398
47							21,0	7,7
48					648	529	19,0	7,1
49	1,56	2,33	0,30	0,46				
50	1,48	2,23	0,28	0,49				
51								
52								
53	1,55	2,33	0,25	0,46				
54	1,50	2,25	0,28	0,49				
55	1,36	1,98			459	469	16,33	6,76
56	1,63	2,39	0,29	0,50	547	435	20,8	7,80
57	1,57	2,38	0,26	0,55	551	439	20	7,4
58								
59								
60								
61	1,54	2,32	0,25	0,40				
62	1,60	2,45	0,30	0,52				
63	1,62	2,41	0,30	0,51	46,64	38,96	18,22	7,38
64	1,83	2,75	0,29	0,49	522	498	21	9,5
65	1,686	2,363	0,365	0,729	601	542	13,37	5,71
66	1,44	2,21	0,281	0,493	503	486	19,5	8,82
67	1,53	2,28	0,28	0,52				
68	1,56	2,39	0,27	0,47				
69					527	414	18	6
71	0,53	1,22	0,36	0,56				
72	1,587	2,263	0,258	0,454				
73	1,57	2,18	0,284	0,483				

Lab. no.	Cadmium, µg/l C	D	Lead, µg/l C	D	Copper, µg/l C	D	Nickel, µg/l C	D	Zinc, µg/lC C	D
1										
2	1,92	1,01	4,45	3,02	8,41	13,10			8,10	7,50
3	2,123	1,061	5,506	3,526	24,080	25,611	2,043	3,360	-10,0	-10,0
4	1,47	0,73	4,72	2,82	18,8	23,2	1,99	2,67	17,9	14,3
5										
6	2	1	< 10	< 10	17	22	3	4	18	15
7										
8										
9					20,0	25,5	2,0	3,1		
11										
12	1,81	0,93	8,26	4,06	20,6	25,6	< 3	< 3	13,0	8,5
13	2,04	1,00	7,20	4,45	20,7	25,8	2,25	3,00	21,9	16,9
14	1,956	0,966	6,712	4,017	19,138	23,190	2,187	3,103	20,339	16,450
15										
16										
17	1,83	0,99	6,63	4,70	18,1	24,0	1,71	2,64	18,1	14,8
18										
19	1,87	0,96	1,00	4,01	18,4	22,8	2,15	3,13	18,6	15,6
20	< 5	< 5	< 20	< 20	17,5	22,5	< 10	< 10	18,4	14,9
21	2,364	1,380	< 1	< 1	17,08	21,59	< 0,1	< 0,1	15,9	12,7
22	1,93	0,93	6,24	4,89	15,65	24,6	1,97	2,4	18,4	15,6
23	1,844	0,963	6,848	4,465	18,07	23,17	2,535	3,497	15,780	12,430
24	2,0	1,0	6,8	5,4	18	26	2,0	3,0	21	19
25										
26										
27	1,82	0,96	6,68	4,44	18,5	24,8	2,10	2,99	17,9	15,0
28	1,90	0,86	6,64	3,16	19,14	22,55	2,42	3,12	29,21	17,90
29	1,73	0,88	6,64	4,22	18,4	23,8	2,08	3,00	18,5	15,4
31										
32	1,949	0,952	6,884	4,189	18,38	22,36	2,151	2,951	18,02	14,38
34										
35										
36	1,74	0,96	6,52	3,99	10,35	13,20	2,32	3,21	47	67
37	1,47	0,69	4,83	2,38	18,2	23,7	< 5	< 5	19,6	16,0
39										
40	1,70	< 1	< 15	< 15	17,7	22,3	< 10	< 10	18,1	14,6
41										
42	1,90	0,98	6,81	5,08	18,1	24,9	2,07	3,12	19,5	16,0
43										
45	1,99	1,03	6,56	5,33	19,88	28,17	1,91	3,25	14,19	10,80

Lab. no.	Cadmium, µg/l C	D	Lead, µg/l C	D	Copper, µg/l C	D	Nickel, µg/l C	D	Zinc, µg/lC C	D
46	1,0255	0,2392	8,5722	3,2503	18,7093	23,8044	43,7076	44,7984	19,3319	15,7559
47	1,98	0,94	6,70	4,00	18,1	22,7	2,1	3,0	20	17
48	1,7	0,8	5,2	3,0	20,9	26,8	2,0	3,0	11,2	6,6
49										
50										
51										
52										
53										
54										
55	1,32	0,67	44,5	7,33	19,3	20,9	5,22	2,93		
56	1,88	0,92	6,49	3,85	18,8	23,0	2,18	2,96	18,8	15,8
57	1,7	0,91	6,6	4,3	17,4	21,9	1,9	2,6	19,1	16,3
58										
59										
60										
61										
62										
63	1,66	0,80	5,91	3,58	16,58	19,97	1,91	2,62	15,56	12,30
64	2,1	1,1	6,2	4,2	28	35	1,9	2,8	17	14
65	< 5,9	< 5,9	< 42,5	< 42,5	< 18,6	< 18,6	< 13,7	< 13,7	8,49	6,74
66	1,72	0,83			17,8	24,0			18,0	16,0
67										
68										
69	< 24	< 24	< 319	< 319	< 32	< 32			18	14
71										
72										
73										

Table 5.1. Statistics - pH

Sample A

Number of participants	65	Range	1,06
Number of omitted results	2	Variance	0,03
True value	6,71	Standard deviation	0,17
Mean value	6,72	Relative standard deviation	2,6%
Median value	6,71	Relative error	0,1%

Analytical results in ascending order:

55	5,22 U	8	6,66	25	6,76
23	5,83 U	27	6,67	16	6,77
15	6,34	48	6,69	18	6,77
39	6,40	17	6,69	73	6,77
43	6,40	57	6,70	64	6,78
58	6,40	5	6,70	31	6,80
12	6,43	7	6,70	45	6,80
47	6,51	60	6,70	29	6,80
53	6,52	24	6,70	46	6,80
56	6,53	26	6,71	34	6,81
3	6,53	41	6,71	49	6,84
59	6,54	62	6,71	67	6,84
66	6,58	21	6,72	4	6,85
65	6,59	68	6,72	37	6,85
14	6,60	69	6,73	61	6,87
54	6,60	52	6,73	50	6,91
1	6,64	72	6,74	13	6,91
35	6,65	28	6,74	36	7,00
9	6,65	42	6,74	51	7,00
32	6,65	22	6,75	71	7,15
63	6,65	40	6,75	2	7,40
11	6,65	6	6,75		

Sample B

Number of participants	65	Range	1,23
Number of omitted results	2	Variance	0,04
True value	7,23	Standard deviation	0,20
Mean value	7,18	Relative standard deviation	2,8%
Median value	7,23	Relative error	-0,7%

Analytical results in ascending order:

55	6,15 U	66	7,18	13	7,27
23	6,23 U	48	7,18	63	7,28
14	6,40	54	7,20	5	7,28
2	6,48	59	7,20	60	7,30
34	6,76	57	7,20	4	7,30
35	6,85	8	7,20	45	7,30
53	6,90	47	7,22	46	7,30
43	6,90	26	7,22	7	7,30
15	6,90	58	7,22	22	7,31
12	6,90	52	7,22	18	7,32
65	6,97	68	7,23	24	7,32
39	7,00	32	7,23	42	7,33
51	7,00	41	7,23	61	7,33
29	7,01	16	7,23	69	7,33
36	7,10	17	7,24	31	7,33
3	7,10	6	7,24	37	7,33
9	7,10	1	7,24	73	7,33
25	7,13	49	7,25	64	7,36
62	7,15	67	7,25	40	7,38
27	7,16	72	7,26	50	7,42
11	7,16	21	7,27	71	7,63
56	7,17	28	7,27		

U = Omitted result

Table 5.2. Statistics - Conductivity, mS/m

Sample A

Number of participants	63	Range	0,76
Number of omitted results	4	Variance	0,02
True value	2,71	Standard deviation	0,15
Mean value	2,71	Relative standard deviation	5,5%
Median value	2,71	Relative error	0,1%

Analytical results in ascending order:

14	1,87 U	43	2,69	65	2,77
23	2,34	35	2,69	60	2,78
2	2,37	61	2,69	46	2,78
54	2,40	64	2,69	50	2,80
45	2,40	62	2,69	32	2,80
17	2,51	27	2,69	39	2,80
1	2,52	52	2,70	11	2,80
29	2,55	47	2,70	67	2,82
68	2,56	72	2,71	20	2,87
37	2,57	26	2,71	73	2,90
8	2,58	12	2,72	66	2,90
51	2,60	31	2,72	40	2,91
25	2,60	28	2,73	71	2,91
3	2,61	18	2,73	16	2,91
41	2,61	63	2,74	5	2,95
57	2,64	4	2,74	55	2,96
69	2,65	49	2,74	22	2,99
56	2,65	7	2,74	59	3,10
53	2,67	15	2,74	9	26,90 U
24	2,67	48	2,75	21	27,76 U
42	2,69	13	2,76	36	28,60 U

Sample B

Number of participants	63	Range	1,27
Number of omitted results	4	Variance	0,08
True value	5,69	Standard deviation	0,28
Mean value	5,65	Relative standard deviation	4,9%
Median value	5,69	Relative error	-0,7%

Analytical results in ascending order:

14	4,11 U	28	5,64	60	5,78
17	5,00	27	5,65	13	5,80
2	5,05	72	5,65	11	5,80
8	5,08	15	5,66	39	5,80
29	5,10	42	5,67	20	5,82
55	5,12	61	5,67	48	5,82
23	5,20	57	5,67	65	5,82
54	5,20	24	5,68	73	5,84
1	5,21	12	5,69	71	5,86
37	5,25	49	5,69	46	5,86
51	5,40	31	5,69	69	5,86
56	5,41	50	5,70	45	5,90
52	5,50	47	5,70	5	5,92
41	5,51	64	5,71	59	6,00
40	5,52	62	5,71	66	6,10
68	5,56	18	5,73	16	6,12
53	5,56	63	5,75	3	6,17
25	5,60	32	5,76	22	6,27
26	5,61	7	5,76	9	56,10 U
35	5,62	4	5,76	21	56,90 U
43	5,63	67	5,77	36	58,50 U

U = Omitted result

Table 5.3. Statistics - Alkalinity, mmol/l

Sample A

Number of participants	51	Range	0,070
Number of omitted results	14	Variance	0,000
True value	0,094	Standard deviation	0,016
Mean value	0,098	Relative standard deviation	16,8%
Median value	0,094	Relative error	4,5%

Analytical results in ascending order:

29	0,043 U	72	0,091	65	0,125
35	0,054 U	42	0,091	59	0,127
55	0,070	7	0,094	71	0,139
54	0,085	57	0,094	52	0,140
15	0,085	53	0,095	28	0,140
68	0,086	73	0,095	62	0,144 U
8	0,087	64	0,096	24	0,145 U
56	0,087	50	0,096	12	0,148 U
5	0,087	32	0,097	60	0,150 U
18	0,088	49	0,097	43	0,165 U
47	0,088	61	0,097	37	0,180 U
31	0,088	69	0,098	3	0,180 U
9	0,088	58	0,100	34	0,190 U
27	0,089	48	0,100	45	0,200 U
41	0,089	14	0,101	39	0,250 U
22	0,090	26	0,102	36	0,370 U
16	0,091	66	0,121	11	11,900 U

Sample B

Number of participants	51	Range	0,104
Number of omitted results	14	Variance	0,000
True value	0,291	Standard deviation	0,020
Mean value	0,295	Relative standard deviation	6,6%
Median value	0,291	Relative error	1,5%

Analytical results in ascending order:

29	0,140 U	69	0,287	52	0,310
35	0,153 U	31	0,288	59	0,312
36	0,250 U	57	0,289	22	0,320
8	0,265	27	0,289	48	0,320
54	0,275	53	0,291	28	0,320
5	0,280	26	0,291	24	0,327 U
15	0,281	72	0,291	34	0,340 U
41	0,281	16	0,291	37	0,340 U
56	0,282	73	0,293	65	0,345
7	0,283	49	0,293	12	0,346 U
18	0,283	55	0,295	60	0,350 U
9	0,284	64	0,295	71	0,369
68	0,284	61	0,296	3	0,370 U
32	0,284	50	0,297	43	0,371 U
14	0,285	58	0,300	45	0,410 U
47	0,286	66	0,302	39	0,450 U
42	0,286	62	0,309 U	11	32,000 U

U = Omitted result

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

Sample A

Number of participants	62	Range	62
Number of omitted results	8	Variance	155
True value	130	Standard deviation	12
Mean value	131	Relative standard deviation	9,5%
Median value	130	Relative error	0,6%

Analytical results in ascending order:

29	< 200 U	46	129	72	136
36	102	59	129	69	138
14	104	17	130	4	140
7	106	43	130	52	140
5	106	48	130	39	140
63	114	68	130	13	143
58	115	6	130	49	147
62	120	54	130	9	147
47	120	51	130	28	149
27	120	73	131	55	150
32	122	50	132	71	152
56	123	18	132	34	159
35	124	64	133	23	164
24	124	66	133	26	192 U
61	125	20	133	37	199 U
42	125	22	133	21	330 U
40	126	1	134	2	338 U
67	127	57	135	65	558 U
16	127	53	135	8	560 U
25	128	60	135	12	610 U
31	128	11	136		

Sample B

Number of participants	62	Range	82
Number of omitted results	8	Variance	251
True value	209	Standard deviation	16
Mean value	208	Relative standard deviation	7,6%
Median value	209	Relative error	-0,3%

Analytical results in ascending order:

29	< 200 U	25	206	20	219
66	174	73	207	69	219
4	180	42	207	1	220
14	181	46	208	22	220
7	186	61	208	57	220
35	186	5	208	17	220
55	188	24	208	13	222
32	188	21	210 U	9	224
63	188	16	210	72	224
48	190	43	210	28	227
52	190	54	210	49	229
36	195	11	210	71	230
62	196	31	211	34	248
58	200	51	214	26	249 U
27	200	64	214	23	256
47	200	6	215	37	264 U
56	201	60	215	2	383 U
67	203	18	215	65	451 U
59	203	53	216	12	920 U
40	203	39	216	8	1080 U
68	204	50	216		

U = Omitted result

Table 5.5. Statistics - Chloride, mg/l

Sample A

Number of participants	60	Range	0,56
Number of omitted results	9	Variance	0,01
True value	1,70	Standard deviation	0,11
Mean value	1,69	Relative standard deviation	6,5%
Median value	1,70	Relative error	-0,4%

Analytical results in ascending order:

3	0,88 U	20	1,69	7	1,74
34	1,10 U	8	1,69	56	1,75
2	1,39	17	1,69	42	1,75
12	1,44	21	1,69	4	1,76
26	1,47	60	1,70 U	11	1,79
32	1,52	6	1,70	48	1,80
14	1,54	61	1,70	47	1,80
9	1,55	13	1,70	73	1,81
24	1,56	22	1,70	55	1,81
64	1,60	35	1,70	39	1,82
43	1,60	53	1,70	16	1,84
71	1,62	62	1,70	23	1,90
36	1,63	50	1,70	5	1,91
65	1,64	18	1,71	66	1,95
28	1,64	57	1,72	15	2,13 U
46	1,65	31	1,72	59	2,40 U
63	1,66	27	1,72	29	2,43 U
54	1,67	41	1,72	52	2,70 U
72	1,67	68	1,73	67	3,86 U
1	1,68	49	1,74	37	5,39 U

Sample B

Number of participants	60	Range	0,97
Number of omitted results	9	Variance	0,03
True value	2,98	Standard deviation	0,18
Mean value	2,97	Relative standard deviation	6,2%
Median value	2,98	Relative error	-0,2%

Analytical results in ascending order:

34	1,84 U	41	2,91	68	3,05
21	1,84 U	22	2,92	35	3,06
12	2,49	62	2,94	11	3,07
71	2,63	13	2,95	7	3,09
3	2,63 U	63	2,95	47	3,10
2	2,65	18	2,95	39	3,13
32	2,67	17	2,96	5	3,14
26	2,68	54	2,96	57	3,18
24	2,72	61	2,98	16	3,20
14	2,79	20	2,99	48	3,26
43	2,80	1	2,99	73	3,26
46	2,85	31	2,99	23	3,30
28	2,87	53	2,99	55	3,35
72	2,88	27	2,99	59	3,40 U
9	2,88	60	3,00	29	3,43 U
65	2,89	56	3,01	66	3,46
6	2,90	42	3,01	52	4,00 U
64	2,90	50	3,02	15	4,25 U
4	2,91	8	3,02	67	4,63 U
36	2,91	49	3,05	37	5,73 U

U = Omitted result

Table 5.6. Statistics - Sulphate, mg/l

Sample A

Number of participants	57	Range	0,84
Number of omitted results	5	Variance	0,03
True value	2,96	Standard deviation	0,17
Mean value	2,96	Relative standard deviation	5,8%
Median value	2,96	Relative error	-0,1%

Analytical results in ascending order:

15	1,20 U	62	2,92	56	3,04
29	1,60 U	17	2,93	66	3,04
52	2,50	53	2,94	48	3,04
32	2,55	4	2,94	31	3,05
2	2,65	72	2,95	57	3,05
36	2,66	54	2,95	16	3,07
14	2,73	68	2,95	1	3,08
26	2,76	61	2,95	8	3,08
63	2,80	13	2,96	73	3,10
12	2,80	21	2,96	20	3,13
55	2,81	35	2,96	46	3,14
7	2,82	42	2,98	49	3,24
41	2,83	18	2,98	9	3,25
28	2,84	47	3,00	23	3,28
27	2,85	6	3,00	60	3,30
24	2,87	43	3,00	67	3,34
64	2,90	65	3,01	59	4,20 U
39	2,90	22	3,01	50	4,88 U
71	2,92	11	3,02	5	5,10 U

Sample B

Number of participants	57	Range	1,47
Number of omitted results	5	Variance	0,08
True value	5,13	Standard deviation	0,28
Mean value	5,09	Relative standard deviation	5,6%
Median value	5,13	Relative error	-0,7%

Analytical results in ascending order:

15	1,70 U	39	5,05	21	5,22
29	2,95 U	72	5,06	65	5,23
2	4,42	12	5,07	57	5,23
32	4,45	54	5,08	8	5,23
52	4,50	61	5,08	67	5,23
9	4,56	43	5,10	56	5,24
36	4,59	64	5,10	35	5,28
55	4,72	17	5,10	60	5,30
66	4,77	62	5,11	6	5,30
26	4,81	13	5,12	47	5,30
28	4,90	53	5,14	31	5,35
41	4,90	68	5,15	73	5,39
7	4,90	48	5,15	20	5,42
71	4,90	18	5,17	46	5,48
14	4,91	4	5,18	1	5,51
27	4,91	11	5,18	49	5,55
63	4,95	42	5,19	23	5,89
24	5,02	16	5,19	59	6,70 U
50	5,02 U	22	5,21	5	7,00 U

U = Omitted result

Table 5.7. Statistics - Calcium, mg/l

Sample A

Number of participants	56	Range	1,96
Number of omitted results	4	Variance	0,12
True value	2,63	Standard deviation	0,35
Mean value	2,63	Relative standard deviation	13,3%
Median value	2,63	Relative error	0,0%

Analytical results in ascending order:

45	1,22 U	62	2,54	56	2,73
71	1,44 U	50	2,54	46	2,74
55	1,74	40	2,57	66	2,77
57	1,84	9	2,58	59	2,77
61	1,98	20	2,58	18	2,79
65	2,03	53	2,59	63	2,80
54	2,05	64	2,60	17	2,81
12	2,14	16	2,60	36	2,82
2	2,35	21	2,63	27	2,99
68	2,44	8	2,63	52	3,00
4	2,46	34	2,64	22	3,00 U
67	2,46	5	2,65	3	3,01
7	2,46	73	2,69	72	3,01 U
26	2,48	42	2,70	15	3,01
37	2,50	28	2,70	23	3,02
6	2,50	43	2,70	35	3,15
14	2,52	13	2,70	11	3,54
41	2,53	32	2,71	24	3,70
29	2,53	49	2,72		

Sample B

Number of participants	56	Range	2,66
Number of omitted results	4	Variance	0,34
True value	7,23	Standard deviation	0,58
Mean value	7,21	Relative standard deviation	8,1%
Median value	7,23	Relative error	-0,2%

Analytical results in ascending order:

45	3,36 U	40	7,09	63	7,46
71	5,61 U	52	7,10	56	7,48
55	5,72	16	7,10	18	7,48
65	5,79	20	7,14	24	7,50
2	5,84	50	7,16	13	7,50
37	6,16	41	7,21	8	7,55
54	6,40	3	7,21	66	7,65
32	6,43	14	7,22	23	7,69
12	6,62	73	7,23	27	7,78
67	6,79	57	7,23	43	7,90
4	6,81	21	7,24	59	7,93
68	6,84	34	7,31	53	7,99
29	6,85	64	7,34	36	8,06
7	6,87	62	7,38	15	8,22
6	6,90	9	7,38	11	8,35
61	6,97	17	7,39	35	8,38
28	7,02	42	7,40	72	9,25 U
5	7,04	49	7,45	22	10,91 U
26	7,06	46	7,45		

U = Omitted result

Table 5.8. Statistics - Magnesium, mg/l

Sample A

Number of participants	56	Range	0,18
Number of omitted results	9	Variance	0,00
True value	0,37	Standard deviation	0,03
Mean value	0,36	Relative standard deviation	9,5%
Median value	0,37	Relative error	-2,1%

Analytical results in ascending order:

71	0,09 U	42	0,36	56	0,38
68	0,26	62	0,36	49	0,38
8	0,27	29	0,36	63	0,38
54	0,30	27	0,36	20	0,38
32	0,30	50	0,36	17	0,38
55	0,31	61	0,36	66	0,39
7	0,32	45	0,37	6	0,40
12	0,33	73	0,37	22	0,40
72	0,33	40	0,37	11	0,40
65	0,33	46	0,37	5	0,41
36	0,34	28	0,37	57	0,41
67	0,35	34	0,37	23	0,44
35	0,35	43	0,37	15	0,49 U
16	0,35 U	64	0,37	59	0,52 U
21	0,35	13	0,37	9	0,55 U
14	0,36	24	0,37	3	0,61 U
41	0,36 U	26	0,37	37	0,82 U
4	0,36	2	0,38	52	1,60 U
53	0,36	18	0,38		

Sample B

Number of participants	56	Range	0,34
Number of omitted results	9	Variance	0,00
True value	0,61	Standard deviation	0,06
Mean value	0,61	Relative standard deviation	9,7%
Median value	0,61	Relative error	0,2%

Analytical results in ascending order:

71	0,23 U	45	0,60	63	0,63
59	0,29 U	6	0,60	26	0,63
15	0,42 U	28	0,60	56	0,63
32	0,44	61	0,60	57	0,64
68	0,48	35	0,60	24	0,65
7	0,51	11	0,60	53	0,66
8	0,53	2	0,60	22	0,67
72	0,53	46	0,61	66	0,67
54	0,54	49	0,61	23	0,70
67	0,57	42	0,61	55	0,72
14	0,58	34	0,61	3	0,73 U
12	0,58	43	0,61	65	0,73
29	0,58	64	0,61	5	0,78
21	0,58	17	0,61	9	0,91 U
4	0,59	18	0,62	16	1,16 U
50	0,59	73	0,62	41	1,18 U
27	0,59	62	0,62	37	1,75 U
36	0,59	13	0,62	52	5,20 U
40	0,59	20	0,62		

U = Omitted result

Table 5.9. Statistics - Sodium, mg/l

Sample A

Number of participants	52	Range	0,51
Number of omitted results	5	Variance	0,01
True value	1,55	Standard deviation	0,09
Mean value	1,54	Relative standard deviation	5,8%
Median value	1,55	Relative error	-0,9%

Analytical results in ascending order:

71	0,53 U	5	1,50	18	1,57
34	1,07 U	54	1,50	57	1,57
2	1,29 U	7	1,52	73	1,57
37	1,32	29	1,52	46	1,58
55	1,36	67	1,53	35	1,58
20	1,39	11	1,53	72	1,59
6	1,40	61	1,54	41	1,59
36	1,42	28	1,54	62	1,60
9	1,43	53	1,55	43	1,60
12	1,44	17	1,55	63	1,62
66	1,44	45	1,56	56	1,63
8	1,45	49	1,56	26	1,63
21	1,47	27	1,56	23	1,68
50	1,48	32	1,56	65	1,69
16	1,49 U	68	1,56	64	1,83
42	1,50	14	1,56	22	2,13 U
24	1,50	4	1,57		
40	1,50	13	1,57		

Sample B

Number of participants	52	Range	0,77
Number of omitted results	5	Variance	0,02
True value	2,30	Standard deviation	0,13
Mean value	2,30	Relative standard deviation	5,5%
Median value	2,30	Relative error	0,1%

Analytical results in ascending order:

2	0,85 U	45	2,25	49	2,33
16	1,19 U	54	2,25	65	2,36
71	1,22 U	72	2,26	9	2,37
34	1,81 U	14	2,27	28	2,37
55	1,98	67	2,28	57	2,38
20	2,09	11	2,28	26	2,38
12	2,14	4	2,29	56	2,39
36	2,17	24	2,30	68	2,39
37	2,17	5	2,30	41	2,41
73	2,18	17	2,30	63	2,41
21	2,18	43	2,30	35	2,41
29	2,19	8	2,30	62	2,45
42	2,20	61	2,32	23	2,48
6	2,20	13	2,32	32	2,62
66	2,21	18	2,32	64	2,75
40	2,22	27	2,32	22	3,17 U
7	2,23	46	2,33		
50	2,23	53	2,33		

U = Omitted result

Table 5.10. Statistics - Potassium, mg/l

Sample A

Number of participants	51	Range	0,143
Number of omitted results	5	Variance	0,001
True value	0,295	Standard deviation	0,029
Mean value	0,295	Relative standard deviation	10,0%
Median value	0,295	Relative error	0,0%

Analytical results in ascending order:

36	0,000 U	67	0,280	6	0,300
34	0,020 U	66	0,281	63	0,300
35	0,232	14	0,281	37	0,300
61	0,250	73	0,284	40	0,303
53	0,250	64	0,290	22	0,310
42	0,257	56	0,290	9	0,310
72	0,258	12	0,291	41	0,313
57	0,260	26	0,293	32	0,326
68	0,270	2	0,296	8	0,333
46	0,270	4	0,298	13	0,340
45	0,278	29	0,299	16	0,340
50	0,280	20	0,300	71	0,360
54	0,280	49	0,300	65	0,365 U
7	0,280	18	0,300	21	0,367
11	0,280	62	0,300	23	0,375
27	0,280	24	0,300	5	0,380 U
17	0,280	43	0,300	28	0,450 U

Sample B

Number of participants	51	Range	0,205
Number of omitted results	5	Variance	0,001
True value	0,502	Standard deviation	0,039
Mean value	0,508	Relative standard deviation	7,6%
Median value	0,502	Relative error	1,1%

Analytical results in ascending order:

34	0,060 U	66	0,493	24	0,520
61	0,400	45	0,495	14	0,521
35	0,450	12	0,498	21	0,525
72	0,454	6	0,500	20	0,530
53	0,460	11	0,500	41	0,547
49	0,460	56	0,500	57	0,550
42	0,464	2	0,502	32	0,557
29	0,469	4	0,502	13	0,560
68	0,470	63	0,510	71	0,560
46	0,470	17	0,510	36	0,565 U
73	0,483	26	0,515	22	0,570
50	0,490	18	0,515	37	0,570
16	0,490	40	0,519	23	0,579
27	0,490	43	0,520	8	0,605
64	0,490	62	0,520	28	0,610 U
54	0,490	9	0,520	5	0,700 U
7	0,490	67	0,520	65	0,729 U

U = Omitted result

Table 5.11. Statistics - Iron, µg/l

Sample C

Number of participants	35	Range	142
Number of omitted results	4	Variance	848
True value	539	Standard deviation	29
Mean value	531	Relative standard deviation	5,5%
Median value	539	Relative error	-1,4%

Analytical results in ascending order:

63	47 U	9	526	28	548
37	250 U	69	527	17	549
55	459	40	530	12	551
4	479	36	533	57	551
22	490	27	534	42	553
19	496	21	539	32	559
2	502	20	541	24	560
66	503	23	543	29	575
41	505	13	543	65	601
3	510	46	543	45	614 U
14	511	6	544	48	648 U
64	522	56	547		

Sample D

Number of participants	35	Range	220
Number of omitted results	4	Variance	2849
True value	439	Standard deviation	53
Mean value	461	Relative standard deviation	11,6%
Median value	439	Relative error	4,9%

Analytical results in ascending order:

63	39 U	21	430	29	483
37	119 U	28	434	66	486
4	370	2	435	64	498
14	396	56	435	36	507
19	406	32	438	9	523
69	414	57	439	48	529 U
23	419	46	451	65	542
40	422	6	456	17	568
3	424	27	458	42	568
12	425	22	461	24	590
20	426	55	469	45	662 U
41	427	13	483		

U = Omitted result

Table 5.12. Statistics - Manganese, µg/l

Sample C

Number of participants	36	Range	4,7
Number of omitted results	6	Variance	1,2
True value	20,0	Standard deviation	1,1
Mean value	19,7	Relative standard deviation	5,6%
Median value	20,0	Relative error	-1,3%

Analytical results in ascending order:

3	< 14,0 U	22	19,5	20	20,4
9	12,0 U	66	19,5	42	20,5
65	13,4 U	29	19,6	32	20,5
55	16,3	57	20,0	23	20,7
69	18,0	6	20,0	56	20,8
63	18,2	40	20,0 U	27	20,8
2	18,3	13	20,0	46	21,0
4	18,6	41	20,0	24	21,0
36	18,7	17	20,0	64	21,0
12	18,8	21	20,1 U	47	21,0
48	19,0	19	20,3	45	22,1 U
37	19,4	14	20,4	28	54,8 U

Sample D

Number of participants	36	Range	5,1
Number of omitted results	6	Variance	1,3
True value	7,8	Standard deviation	1,1
Mean value	8,0	Relative standard deviation	14,3%
Median value	7,8	Relative error	2,1%

Analytical results in ascending order:

3	< 14,0 U	40	7,3	46	8,3
9	< 5,0 U	63	7,4	37	8,4
21	0,0 U	57	7,4	22	8,6
45	3,3 U	14	7,4	23	8,6
65	5,7 U	32	7,6	17	8,8
12	5,9	19	7,7	66	8,8
69	6,0	47	7,7	28	9,0 U
27	6,6	56	7,8	13	9,0
55	6,8	20	7,8	64	9,5
4	6,8	29	7,9	36	9,6
2	7,0	6	8,0	42	9,9
48	7,1	41	8,1	24	11,0

U = Omitted result

Table 5.13. Statistics - Cadmium, µg/l

Sample C

Number of participants	34	Range	0,80
Number of omitted results	6	Variance	0,04
True value	1,88	Standard deviation	0,19
Mean value	1,83	Relative standard deviation	10,4%
Median value	1,88	Relative error	-2,2%

Analytical results in ascending order:

69	< 24,00 U	29	1,73	32	1,95
65	< 5,90 U	36	1,74	14	1,96
20	< 5,00 U	12	1,81	47	1,98
46	1,03 U	27	1,82	45	1,99
55	1,32	17	1,83	24	2,00
4	1,47	23	1,84	6	2,00
37	1,47	19	1,87	13	2,04
63	1,66	56	1,88	64	2,10
40	1,70 U	42	1,90	3	2,12
57	1,70	28	1,90	21	2,36 U
48	1,70	2	1,92		
66	1,72	22	1,93		

Sample D

Number of participants	34	Range	0,43
Number of omitted results	6	Variance	0,01
True value	0,96	Standard deviation	0,11
Mean value	0,92	Relative standard deviation	11,5%
Median value	0,96	Relative error	-3,5%

Analytical results in ascending order:

69	< 24,00 U	29	0,88	42	0,98
65	< 5,90 U	57	0,91	17	0,99
20	< 5,00 U	56	0,92	24	1,00
40	< 1,00 U	22	0,93	13	1,00
46	0,24 U	12	0,93	6	1,00
55	0,67	47	0,94	2	1,01
37	0,69	32	0,95	45	1,03
4	0,73	19	0,96	3	1,06
48	0,80	36	0,96	64	1,10
63	0,80	23	0,96	21	1,38 U
66	0,83	27	0,96		
28	0,86	14	0,97		

U = Omitted result

Table 5.14. Statistics - Lead, µg/l

Sample C

Number of participants	33	Range	4,12
Number of omitted results	7	Variance	0,87
True value	6,62	Standard deviation	0,93
Mean value	6,43	Relative standard deviation	14,5%
Median value	6,62	Relative error	-2,9%

Analytical results in ascending order:

69	< 319,00 U	63	5,91	27	6,68
65	< 42,50 U	64	6,20	47	6,70
20	< 20,00 U	22	6,24	14	6,71
40	< 15,00 U	56	6,49	24	6,80
6	< 10,00 U	36	6,52	42	6,81
21	0,00 U	45	6,56	23	6,85
2	4,45	19	6,59	32	6,88
4	4,72	57	6,60	13	7,20
37	4,83	17	6,63	12	8,26
48	5,20	29	6,64	46	8,57
3	5,51	28	6,64	55	44,50 U

Sample D

Number of participants	33	Range	3,02
Number of omitted results	7	Variance	0,59
True value	4,04	Standard deviation	0,77
Mean value	4,01	Relative standard deviation	19,1%
Median value	4,04	Relative error	-0,7%

Analytical results in ascending order:

69	< 319,00 U	46	3,25	29	4,22
65	< 42,50 U	3	3,53	57	4,30
20	< 20,00 U	63	3,58	27	4,44
40	< 15,00 U	56	3,85	13	4,45
6	< 10,00 U	36	3,99	23	4,47
21	0,00 U	47	4,00	17	4,70
37	2,38	19	4,01	22	4,89
4	2,82	14	4,02	42	5,08
48	3,00	12	4,06	45	5,33
2	3,02	32	4,19	24	5,40
28	3,16	64	4,20	55	7,33 U

U = Omitted result

Table 5.15. Statistics - Copper, µg/l

Sample C

Number of participants	35	Range	8,43
Number of omitted results	5	Variance	2,48
True value	18,39	Standard deviation	1,57
Mean value	18,63	Relative standard deviation	8,5%
Median value	18,39	Relative error	1,3%

Analytical results in ascending order:

69	< 32,00 U	24	18,00	56	18,80
65	< 18,60 U	23	18,07	14	19,14
2	8,41 U	42	18,10	28	19,14
36	10,35 U	17	18,10	55	19,30
22	15,65	47	18,10	45	19,88
63	16,58	37	18,20	9	20,00
6	17,00	32	18,38	12	20,60
21	17,08	29	18,40	13	20,70
57	17,40	19	18,40	48	20,90
20	17,50	27	18,50	3	24,08
40	17,70	46	18,71	64	28,00 U
66	17,80	4	18,80		

Sample D

Number of participants	35	Range	8,20
Number of omitted results	5	Variance	3,29
True value	23,45	Standard deviation	1,81
Mean value	23,71	Relative standard deviation	7,7%
Median value	23,45	Relative error	1,1%

Analytical results in ascending order:

69	< 32,00 U	28	22,55	22	24,60
65	< 18,60 U	47	22,70	27	24,80
2	13,10 U	19	22,80	42	24,90
36	13,20 U	56	23,00	9	25,50
63	19,97	23	23,17	12	25,60
55	20,90	14	23,19	3	25,61
21	21,59	4	23,20	13	25,80
57	21,90	37	23,70	24	26,00
6	22,00	29	23,80	48	26,80
40	22,30	46	23,80	45	28,17
32	22,36	17	24,00	64	35,00 U
20	22,50	66	24,00		

U = Omitted result

Table 5.16. Statistics - Nickel, µg/l

Sample C

Number of participants	32	Range	0,83
Number of omitted results	9	Variance	0,03
True value	2,07	Standard deviation	0,18
Mean value	2,08	Relative standard deviation	8,8%
Median value	2,07	Relative error	0,6%

Analytical results in ascending order:

65	< 13,70 U	22	1,97	32	2,15
20	< 10,00 U	4	1,99	56	2,18
40	< 10,00 U	9	2,00	14	2,19
37	< 5,00 U	48	2,00	13	2,25
12	< 3,00 U	24	2,00	36	2,32
21	0,00 U	3	2,04	28	2,42
17	1,71	42	2,07	23	2,54
57	1,90	29	2,08	6	3,00 U
64	1,90	27	2,10	55	5,22 U
45	1,91	47	2,10	46	43,71 U
63	1,91	19	2,15		

Sample D

Number of participants	32	Range	1,10
Number of omitted results	9	Variance	0,07
True value	3,00	Standard deviation	0,26
Mean value	2,98	Relative standard deviation	8,7%
Median value	3,00	Relative error	-0,7%

Analytical results in ascending order:

65	< 13,70 U	64	2,80	14	3,10
40	< 10,00 U	55	2,93 U	28	3,12
20	< 10,00 U	32	2,95	42	3,12
37	< 5,00 U	56	2,96	19	3,13
12	< 3,00 U	27	2,99	36	3,21
21	0,00 U	48	3,00	45	3,25
22	2,40	29	3,00	3	3,36
57	2,60	24	3,00	23	3,50
63	2,62	13	3,00	6	4,00 U
17	2,64	47	3,00	46	44,80 U
4	2,67	9	3,10		

U = Omitted result

Table 5.17. Statistics - Zinc, µg/l

Sample C

Number of participants	33	Range	7,7
Number of omitted results	7	Variance	2,9
True value	18,3	Standard deviation	1,7
Mean value	18,3	Relative standard deviation	9,2%
Median value	18,3	Relative error	0,0%

Analytical results in ascending order:

3	< 10,0 U	27	17,9	56	18,8
2	8,1 U	69	18,0	57	19,1
65	8,5 U	6	18,0	46	19,3
48	11,2 U	66	18,0	42	19,5
12	13,0 U	32	18,0	37	19,6
45	14,2	40	18,1	47	20,0
63	15,6	17	18,1	14	20,3
23	15,8	22	18,4	24	21,0
21	15,9	20	18,4	13	21,9
64	17,0	29	18,5	28	29,2 U
4	17,9	19	18,6	36	47,0 U

Sample D

Number of participants	33	Range	8,2
Number of omitted results	7	Variance	2,9
True value	15,2	Standard deviation	1,7
Mean value	15,0	Relative standard deviation	11,3%
Median value	15,2	Relative error	-1,1%

Analytical results in ascending order:

3	< 10,0 U	4	14,3	56	15,8
48	6,6 U	32	14,4	37	16,0
65	6,7 U	40	14,6	66	16,0
2	7,5 U	17	14,8	42	16,0
12	8,5 U	20	14,9	57	16,3
45	10,8	6	15,0	14	16,5
63	12,3	27	15,0	13	16,9
23	12,4	29	15,4	47	17,0
21	12,7	19	15,6	28	17,9 U
64	14,0	22	15,6	24	19,0
69	14,0	46	15,8	36	67,0 U

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

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