

# Convention on Long-Range Transboundary Air Pollution

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



ICP Waters Report 98/2009

## **Intercomparison 0923:**

pH, Cond,  $\text{HCO}_3$ ,  $\text{NO}_3 + \text{NO}_2$ ,  $\text{Cl}$ ,  $\text{SO}_4$ ,  
Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb,  
Cu, Ni and Zn.



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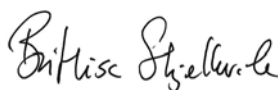
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<p>Abstract</p> <p>72 laboratories received samples for the intercomparison 0923, and 68 laboratories in 29 countries submitted results. Two sample sets were used, one for the determination of major ions, and one for heavy metals. Based on the general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

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

**Intercomparison 0923**

pH, Cond, HCO<sub>3</sub>, NO<sub>3</sub>-N,  
Cl, SO<sub>4</sub>, Ca, Mg, Na, K, TOC,  
Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn

Prepared by the ICP Waters Programme Centre  
Norwegian Institute for Water Research  
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## Preface

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

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

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

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

We here report the results from the 23rd intercomparison of chemical analysis.

Oslo, October 2009

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## Summary

Intercomparison 0923 was organized as a part of the between-laboratory quality control programme, as stated in "Manual for Chemical and Biological Monitoring" (1), by the International Cooperative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes (ICP Waters).

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

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

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

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

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

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

## **1. Introduction**

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

The between-laboratory control carried out by the Programme Centre is based on the "round robin" concept and the procedure of Youden (2, 3), which is briefly described in Appendix C. This twentythird intercomparison test, called 0923, included the determination of the major components and some other ions in natural water samples: pH, conductivity, alkalinity, nitrate, chloride, sulphate, calcium, magnesium, sodium, potassium, total organic carbon, aluminium, iron, manganese, cadmium, lead, copper, nickel and zinc.

## **2. Accomplishment of the intercomparison**

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

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

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

### 3. Results

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

The analytical results received from the laboratories were treated by the method of Youden (2, 3). A short description of this method, and the statistical treatment of the analytical data, is presented in Appendix C. The purpose of this test is to evaluate the comparability of the analytical results produced by the laboratories participating in the International Cooperative Programme. The real "true value" is not known exactly for the natural water samples used in this intercomparison. Therefore, we selected the median value, determined from the analytical results submitted by the participating laboratories after outliers were excluded, as the "true value" for each analytical variable. The median value is considered to be an acceptable estimate of the true value for this purpose, as long as most of the participants are using essentially the same analytical method. For certain variables, for instance pH, this may represent a problem as the different methods used may produce systematically different results (stirring, non-stirring, and equilibration of the test solution), and we cannot argue that one method is more correct than the others.

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

#### 3.1 pH

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

The participating laboratories determined pH in the test solutions using their own routine method. An electrometric method was used by all laboratories. 64 laboratories reported results for pH, 25 of the laboratories of this group indicated that they read the pH value during stirring the solution, while about 35 read the pH value in a quiescent solution. The stirring are normally lowering the observed pH result. However, in this intercomparison the median values are not significantly different in the stirred samples compared to the non-stirred samples (see Table 1).



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

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

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

### 3.2 Conductivity

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

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

### 3.3 Alkalinity

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

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

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

### 3.4 Nitrate + nitrite

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

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

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

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

### 3.5 Chloride

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

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

### 3.6 Sulphate

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

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

### 3.7 Calcium

The calcium results are illustrated in Figure 7, and the reported values are given in Table 5.7. The target accuracy is  $\pm 20\%$ , and is represented by the great circle in Figure 7. 57 laboratories reported results for calcium, and only 12 of them used the traditional flame atomic absorption spectrometry for the determination. The ICP technique is used by 15 laboratories, and three of these used ICP-MS. An increasing part of the laboratories, this time 26, used ion chromatography. Three laboratories used a titrimetric method with EDTA for the determination of calcium. One laboratory using capillary electrophoresis reported acceptable results.

84 % acceptable result pairs is a good result.

### 3.8 Magnesium

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

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

### **3.9 Sodium**

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

### **3.10 Potassium**

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

### **3.11 Total organic carbon**

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

### 3.12 Aluminium

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

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

### 3.13 Iron

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

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

### 3.14 Manganese

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

### 3.15 Cadmium

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

### 3.16 Lead

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

### 3.17 Copper

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

### 3.18 Nickel

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

### 3.19 Zinc

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

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Table 1. Statistical summary for intercomparison 0923

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

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



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

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

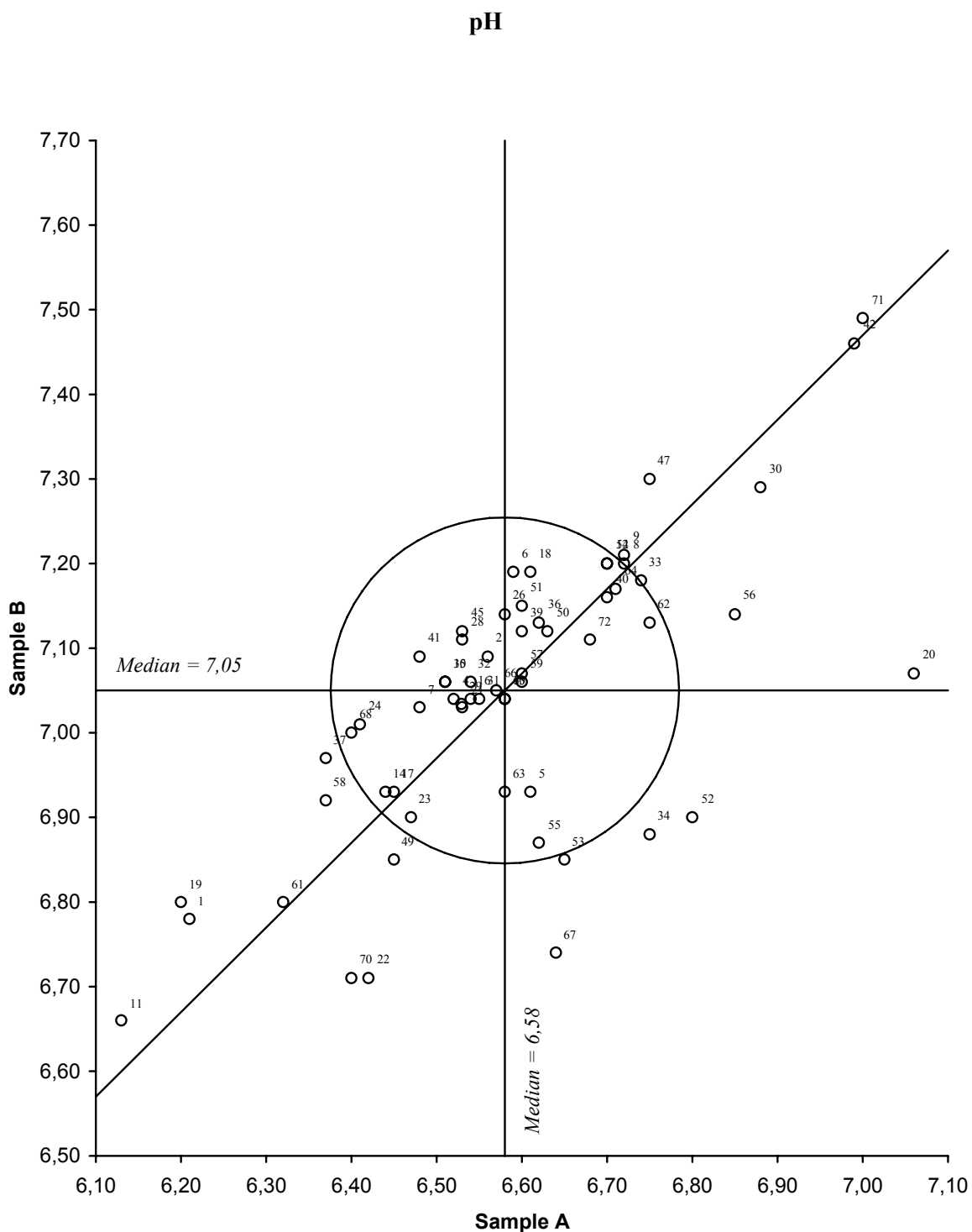


Figure 1. Youden diagram for pH, sample pair AB  
 Acceptance limit, given by the circle, is 0,2 pH units

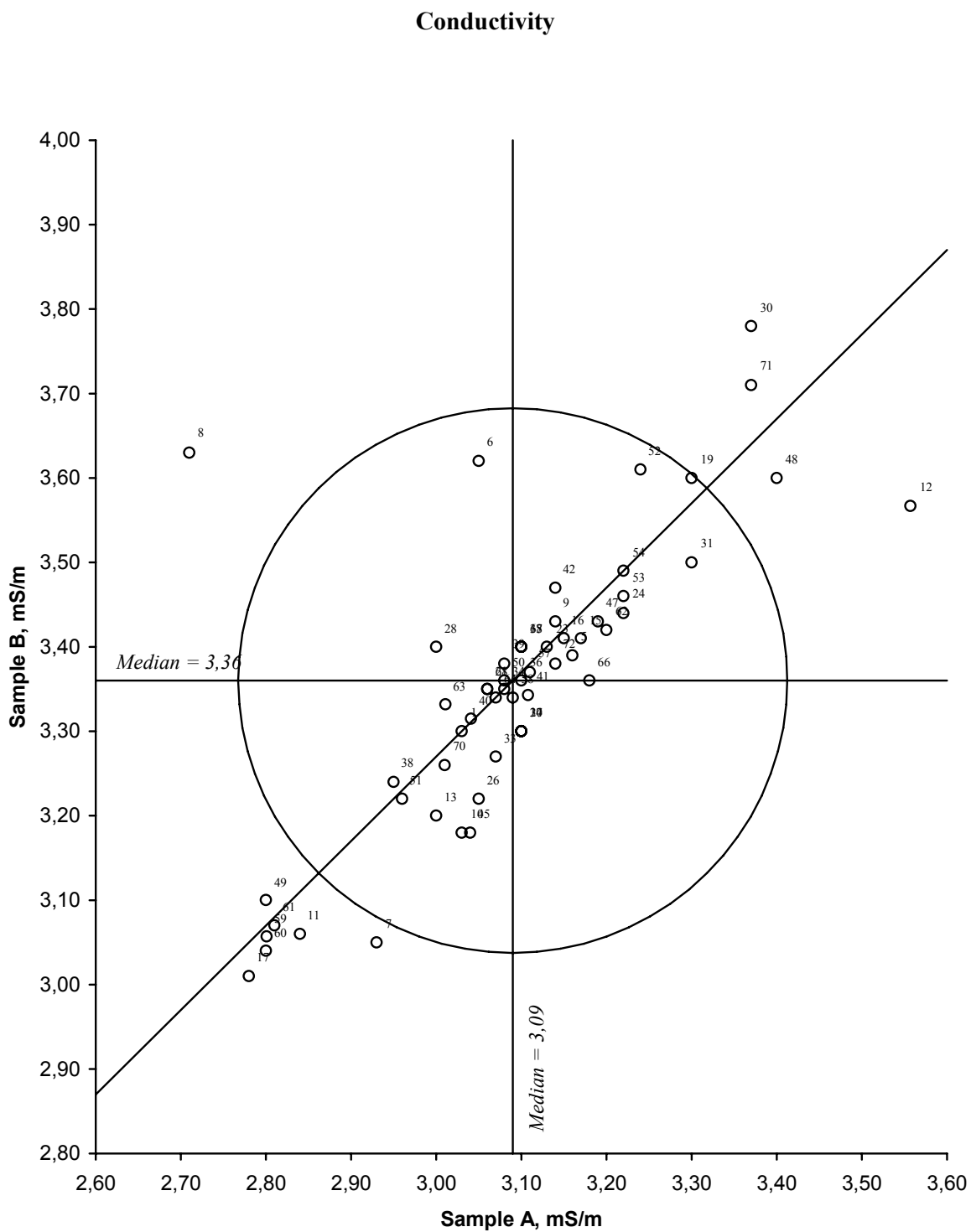


Figure 2. Youden diagram for conductivity, sample pair AB  
 Acceptance limit, given by circle, is 10 %

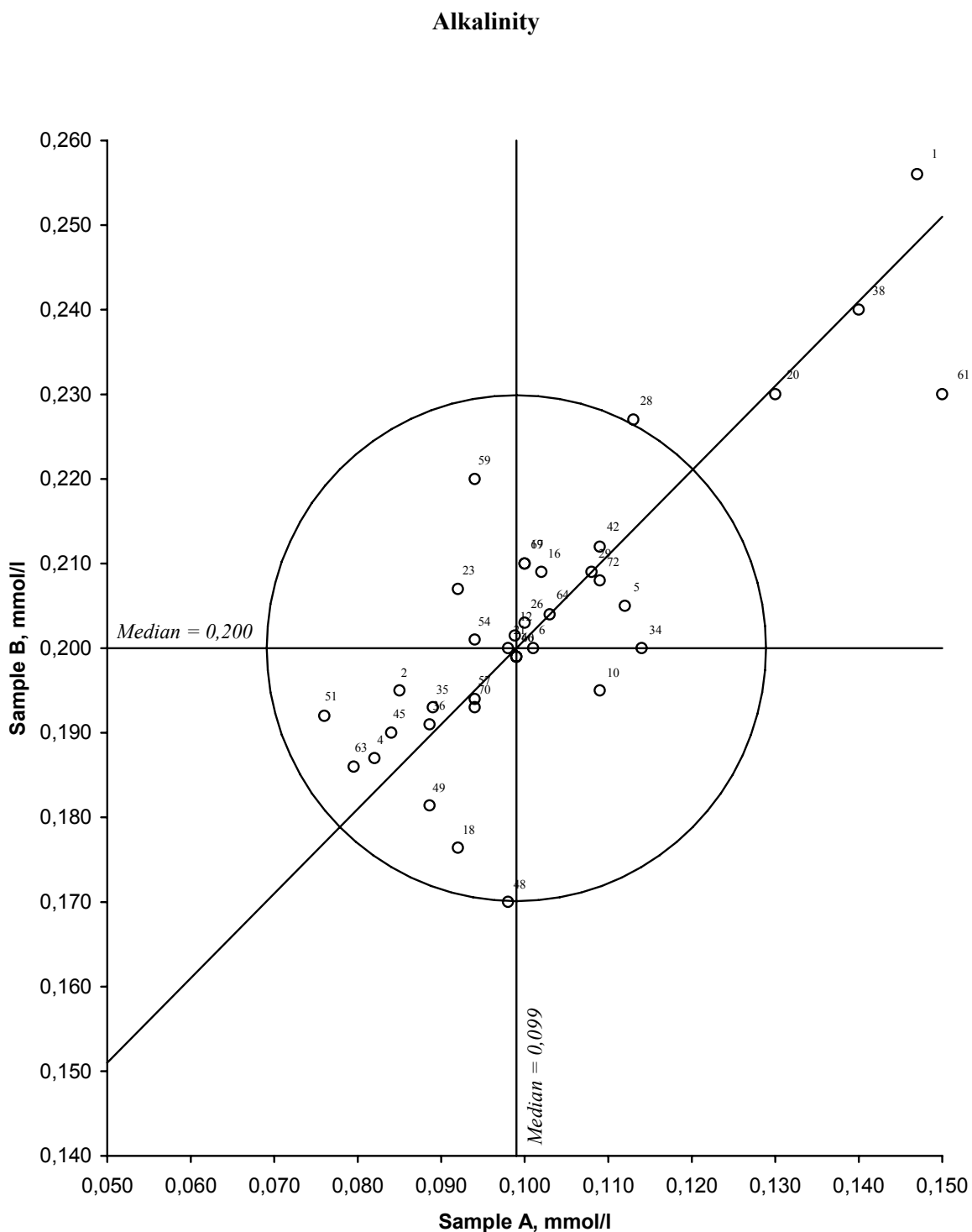


Figure 3. Youden diagram for alkalinity, sample pair AB  
 Acceptance limit, given by circle, is 20 %

Nitrate + nitrite-nitrogen

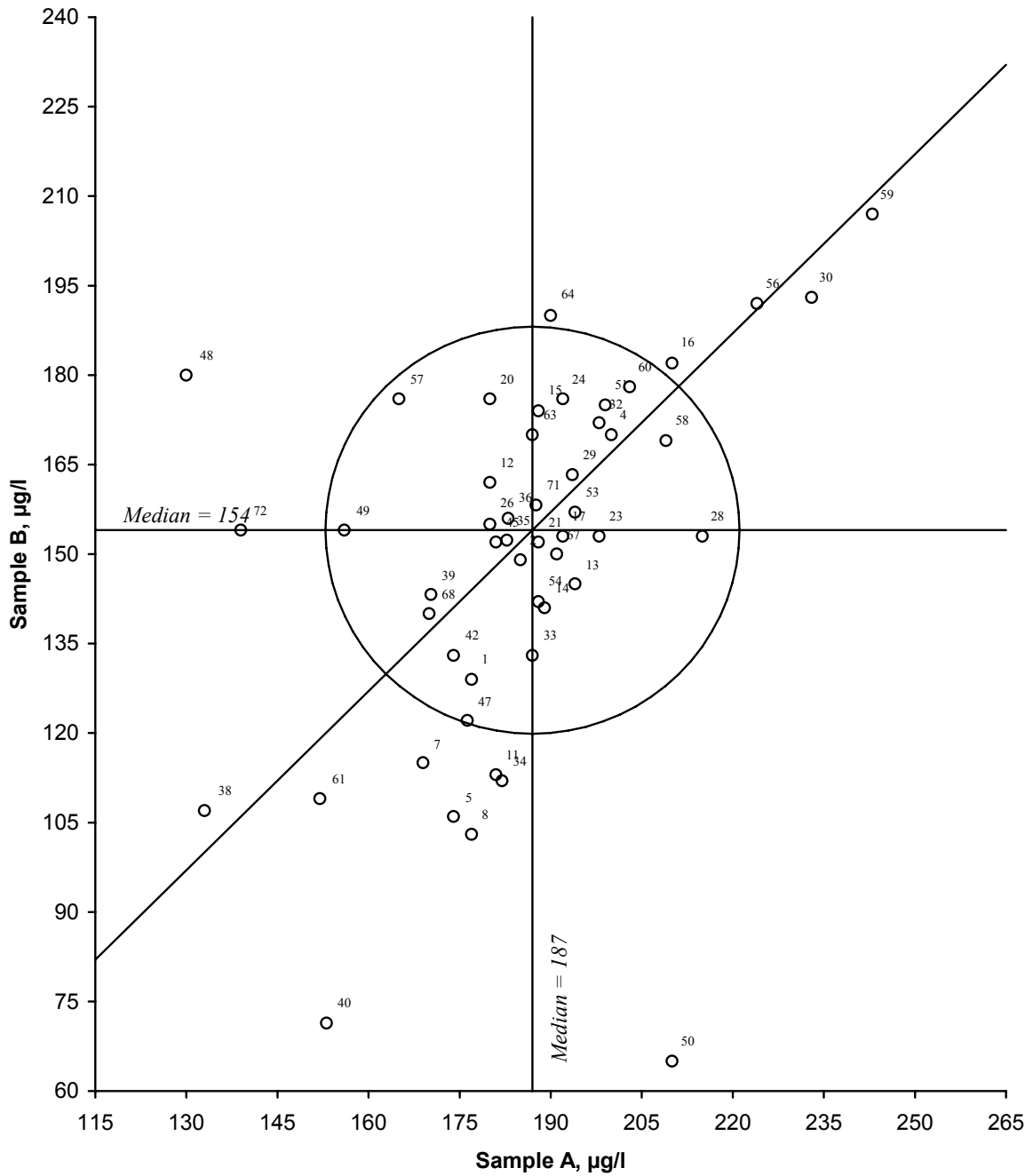


Figure 4. Youden diagram for nitrate + nitrite-nitrogen, sample pair AB  
Acceptance limit, given by the circle, is 20 %

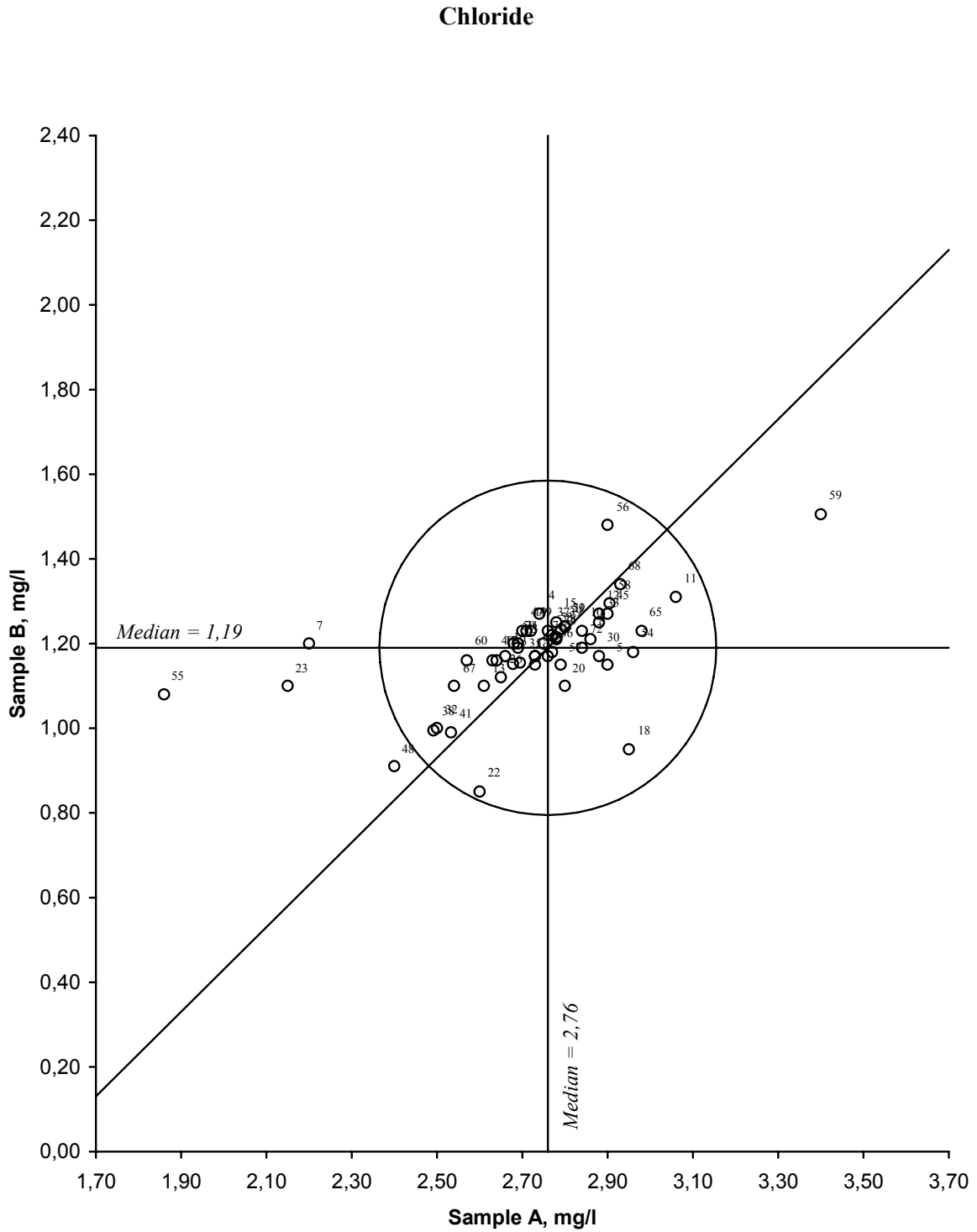


Figure 5. Youden diagram for chloride, sample pair AB  
Acceptance limit, given by the circle, is 20 %

Sulfate

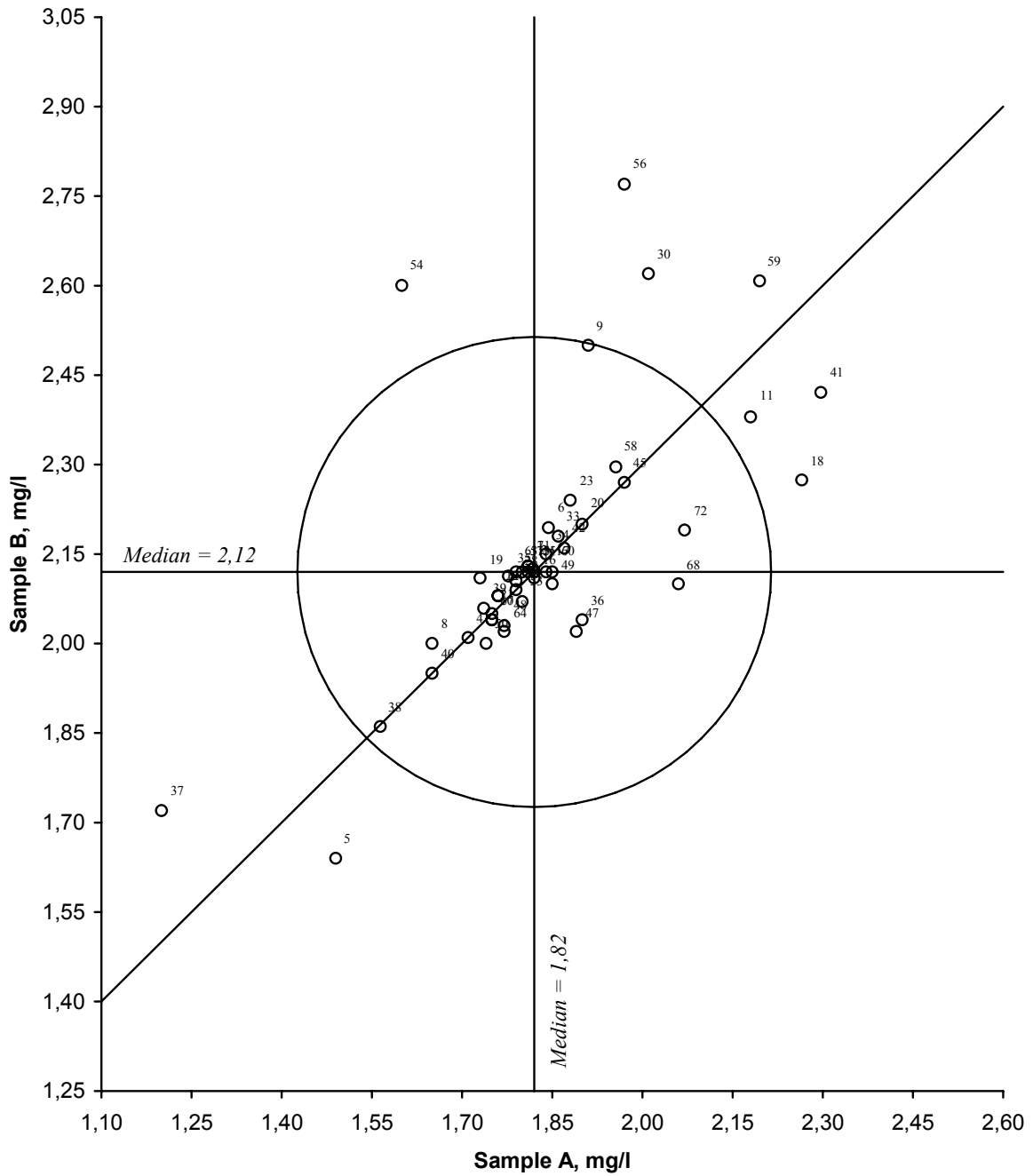


Figure 6. Youden diagram for sulfate, sample pair AB  
 Acceptance limit, given by the circle, is 20 %



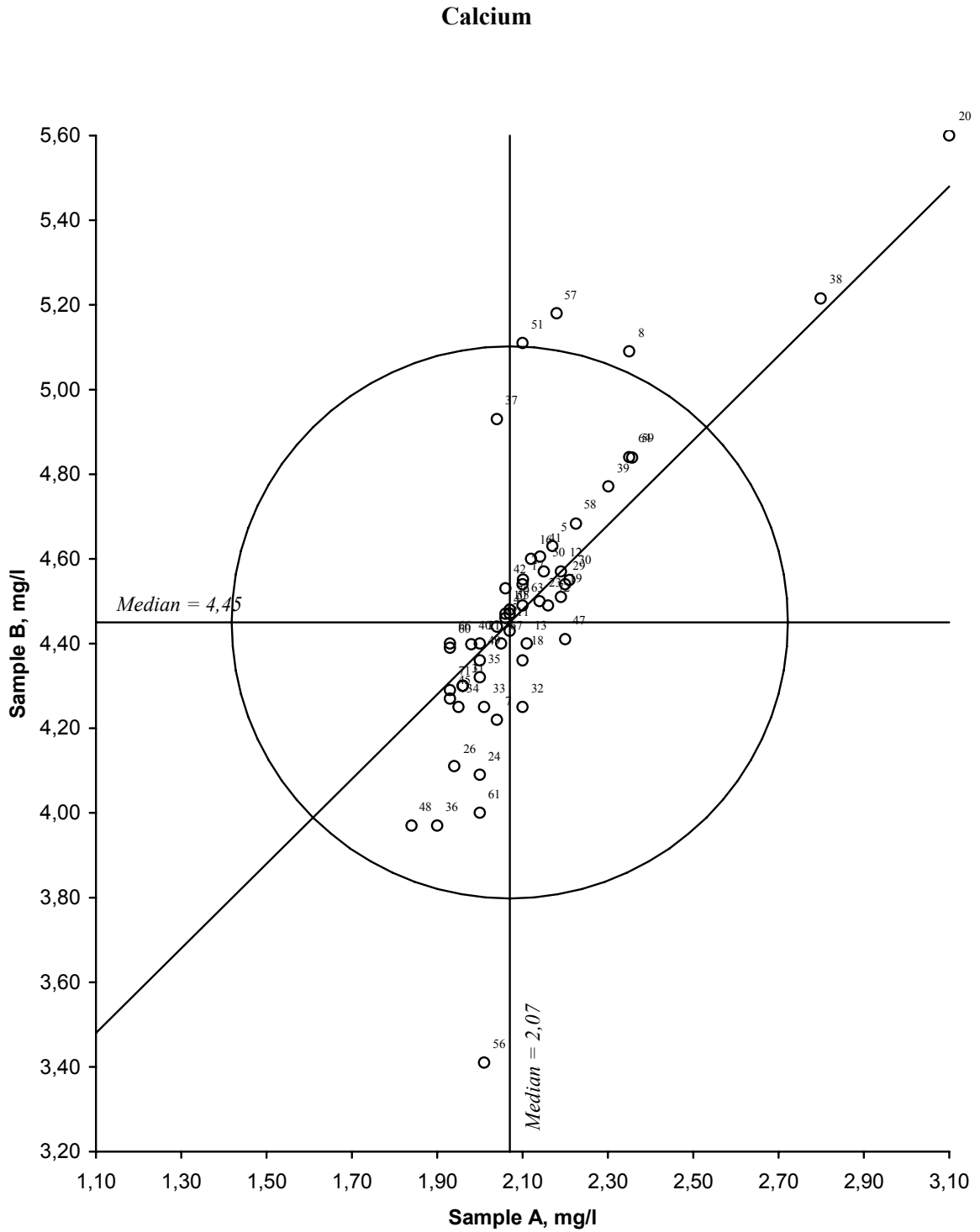


Figure 7. Youden diagram for calcium, sample pair AB  
 Acceptance limit, given by the circle, is 20 %

**Magnesium**

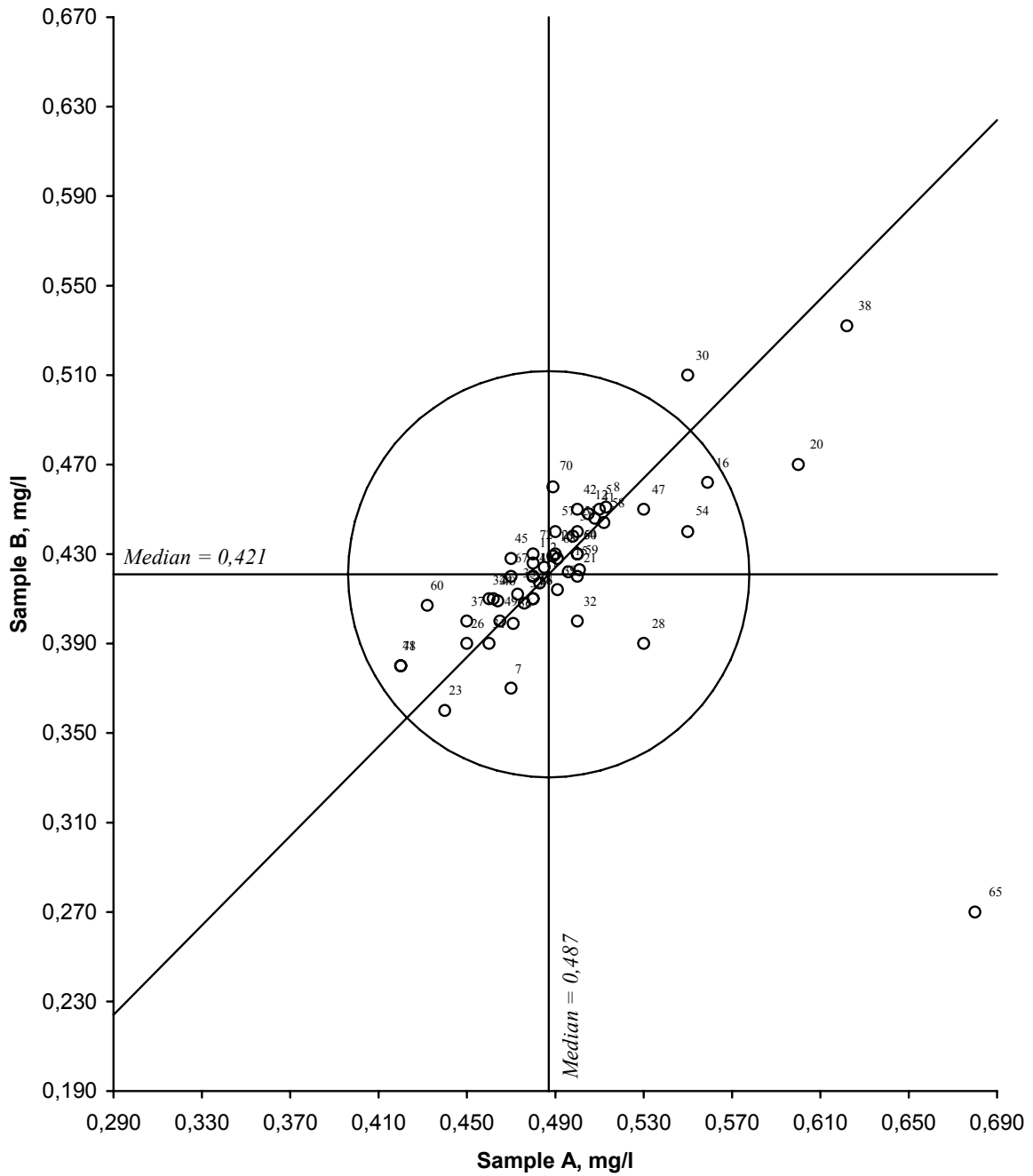


Figure 8. Youden diagram for magnesium, sample pair AB  
 Acceptance limit, given by the circle, is 20 %

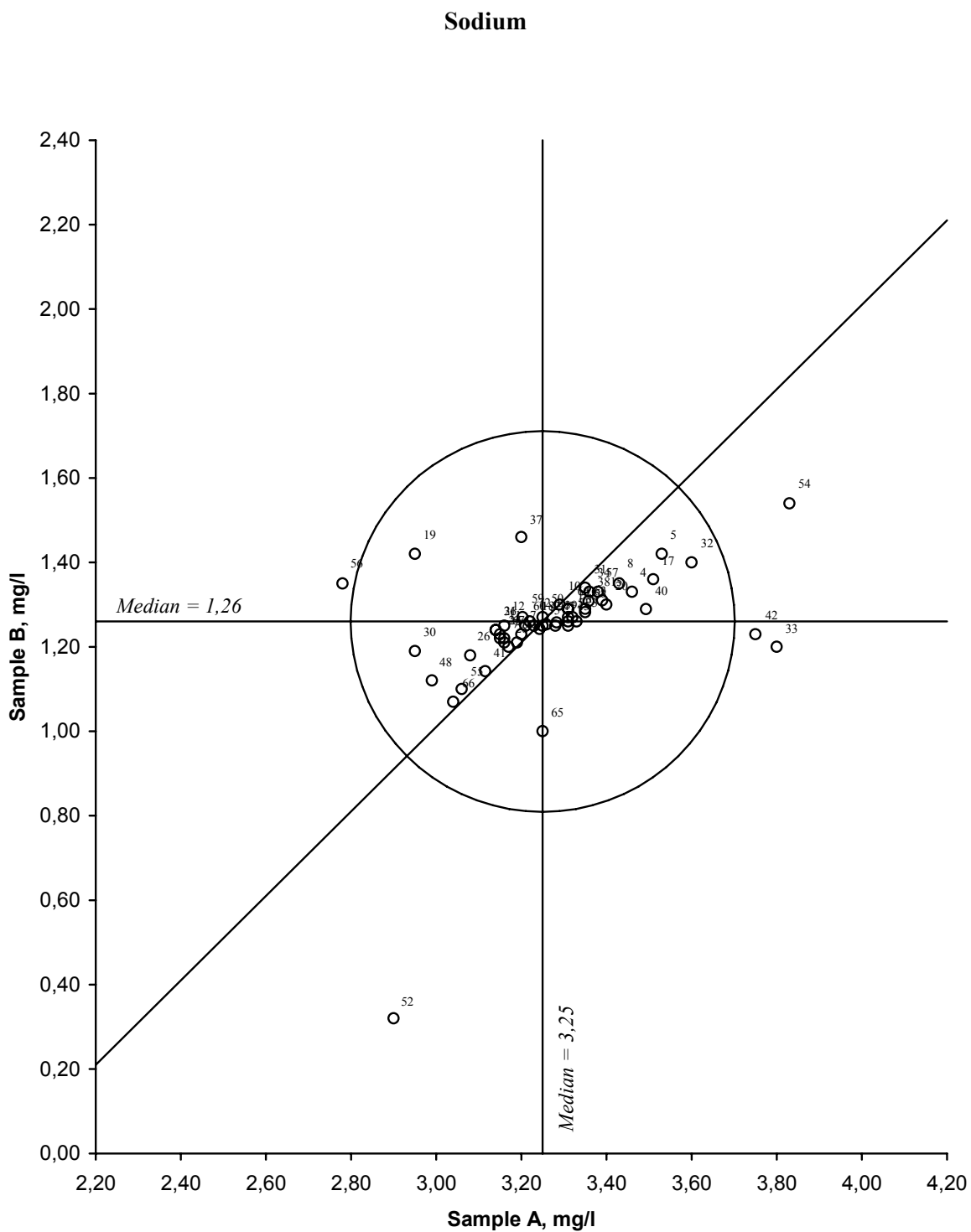


Figure 9. Youdendiagram for sodium, sample pair AB  
 Acceptance limit, given by the circle, is 20 %

**Potassium**

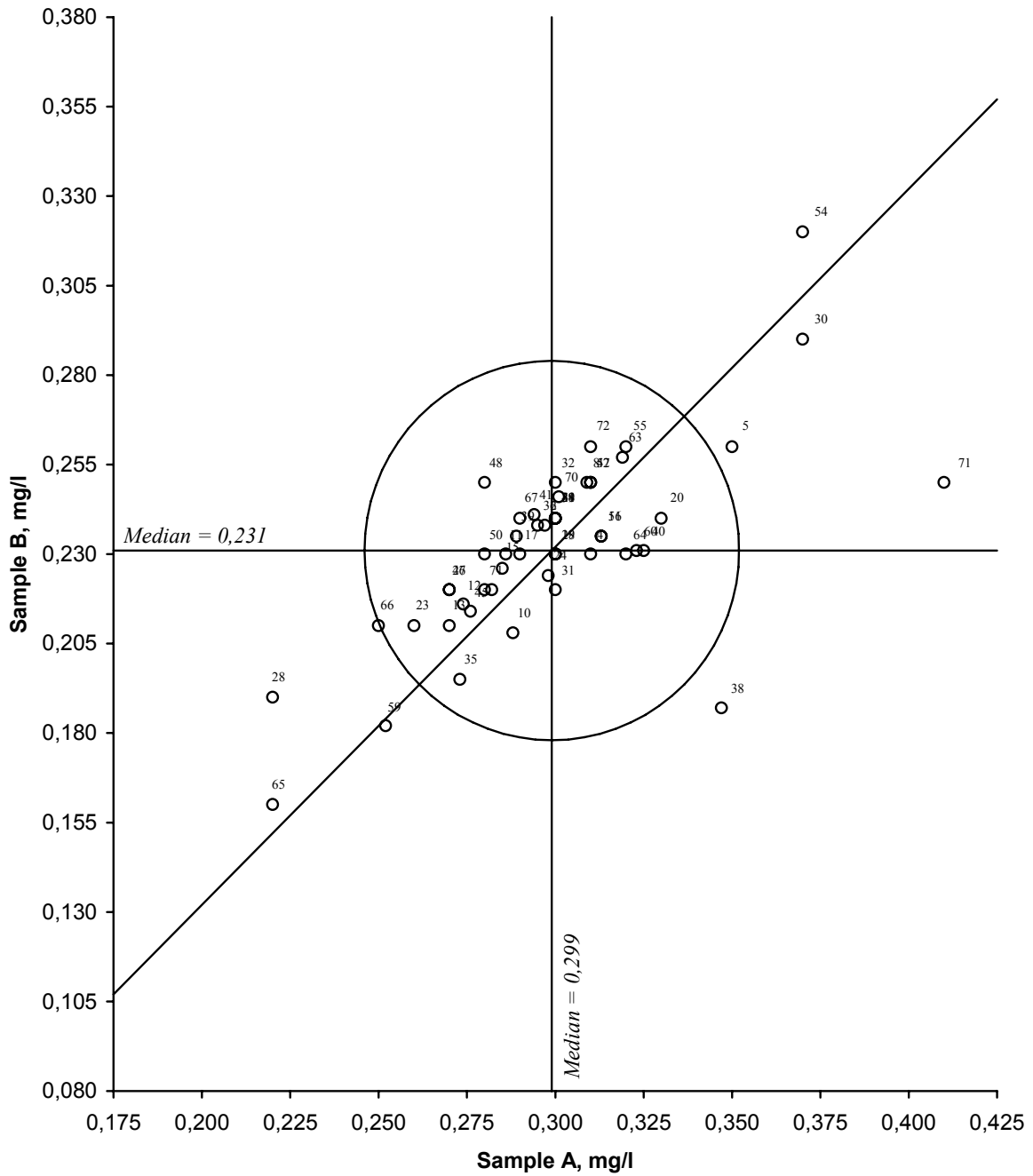


Figure 10. Youden diagram for potassium, sample pair AB  
 Acceptance limit, given by the circle, is 20 %

**Total organic carbon**

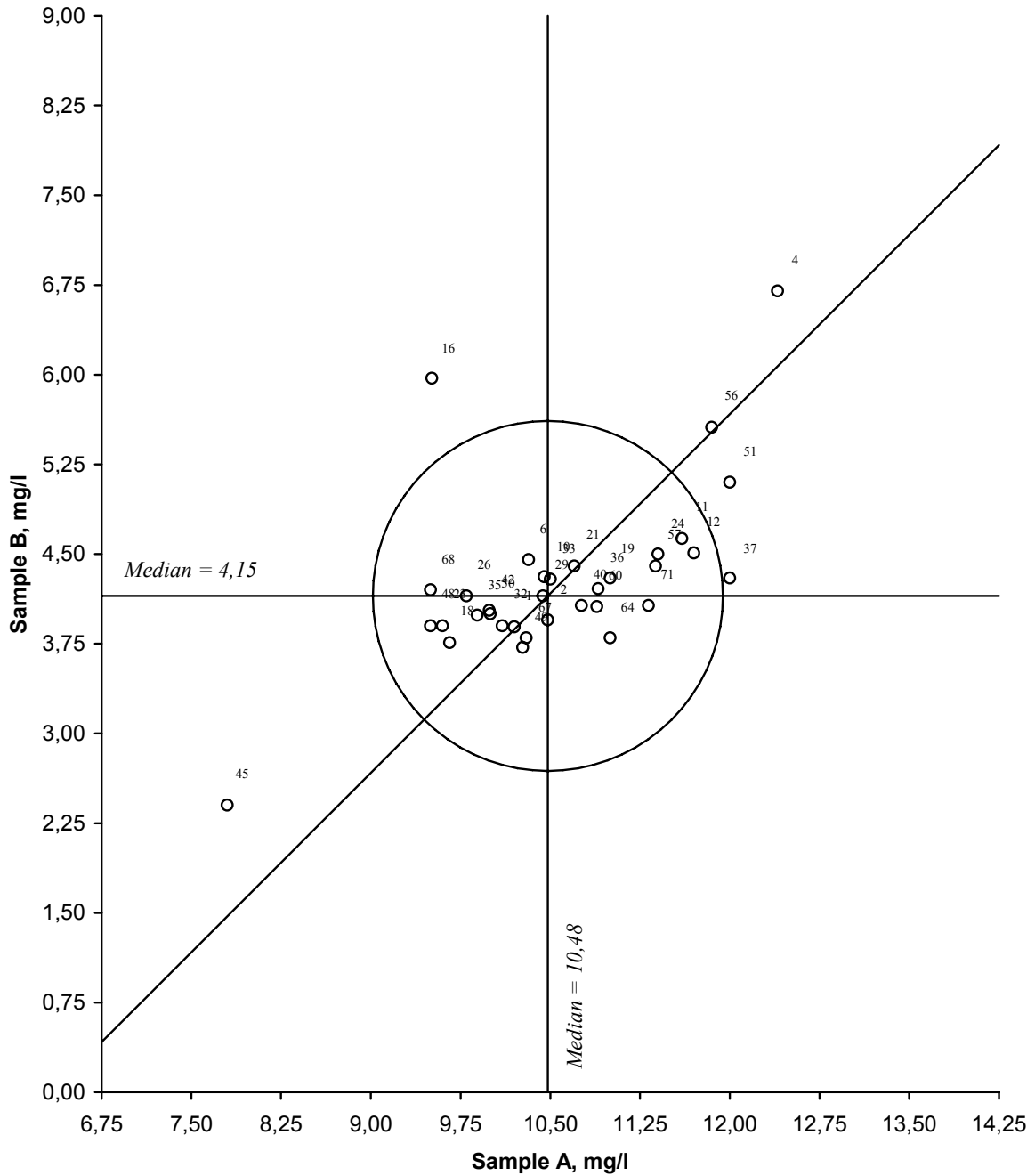


Figure 11. Youden diagram for total organic carbon, sample pair AB  
 Acceptance limit, given by the circle, is 20 %

**Aluminium**

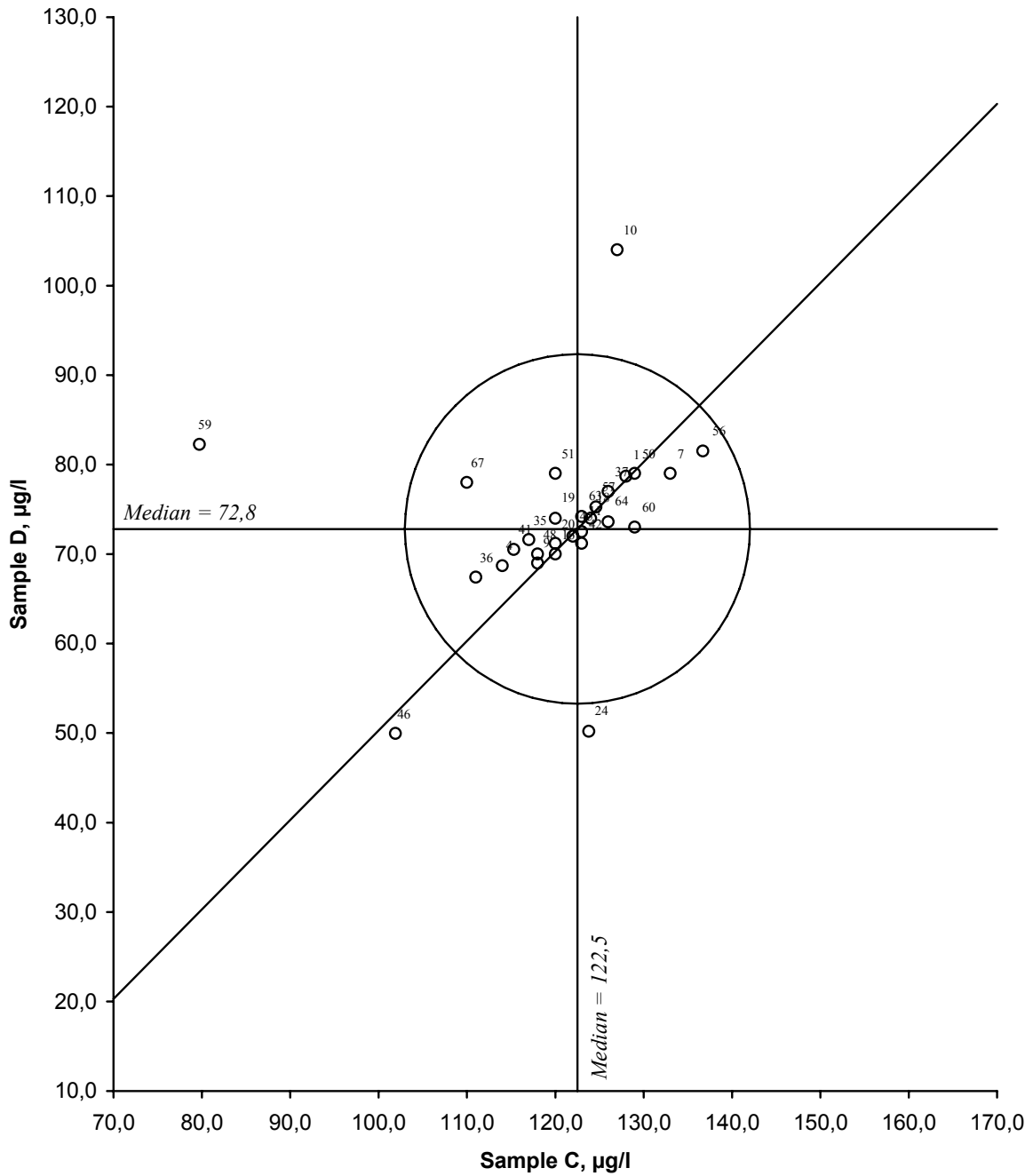


Figure 12. Youdendiagram for aluminium, sample pair CD  
 Acceptance limit, given by the circle, is 20 %

**Iron**

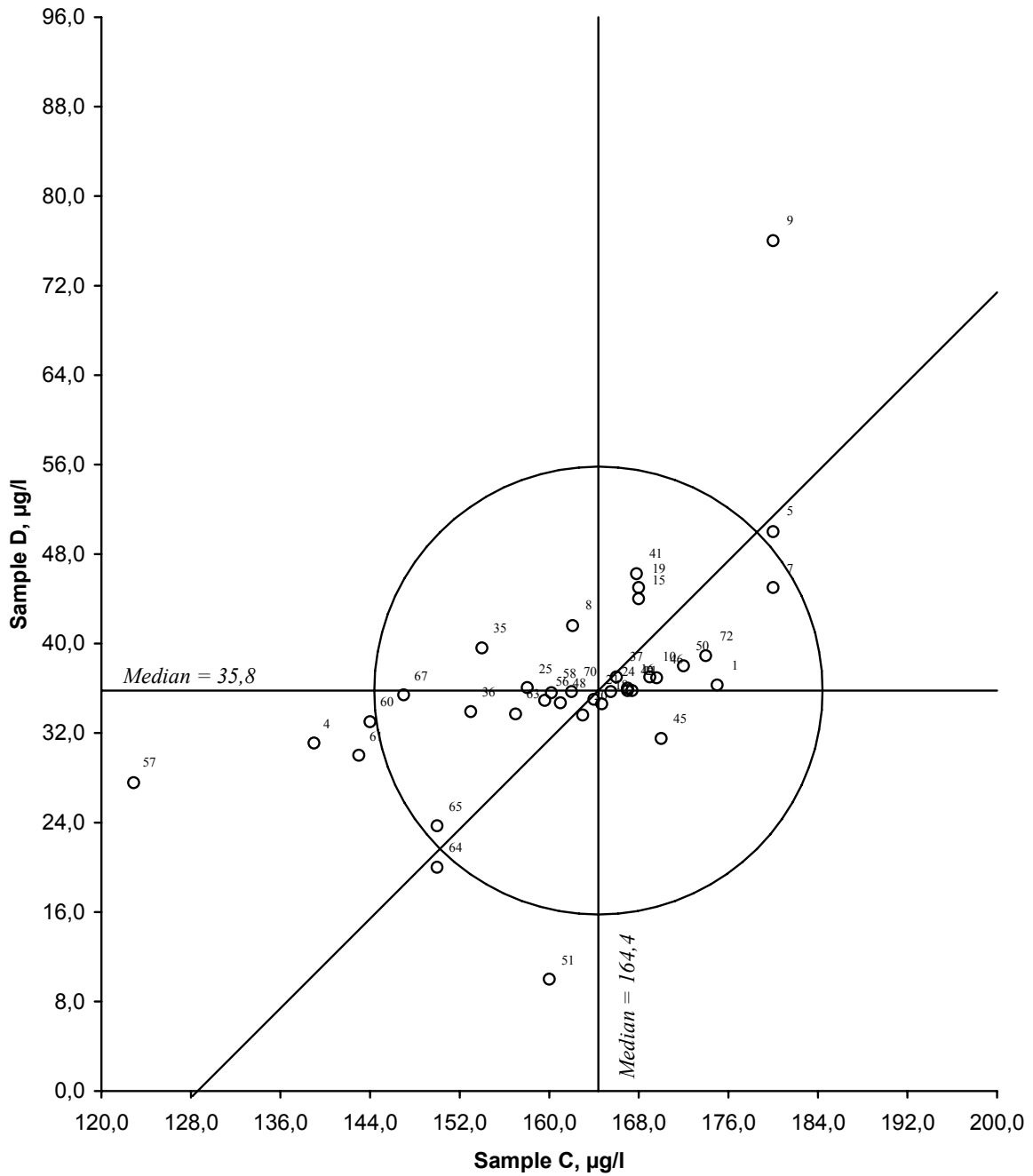


Figure 13. Youden diagram for iron, sample pair CD  
 Acceptance limit, given by the circle, is 20 %

**Manganese**

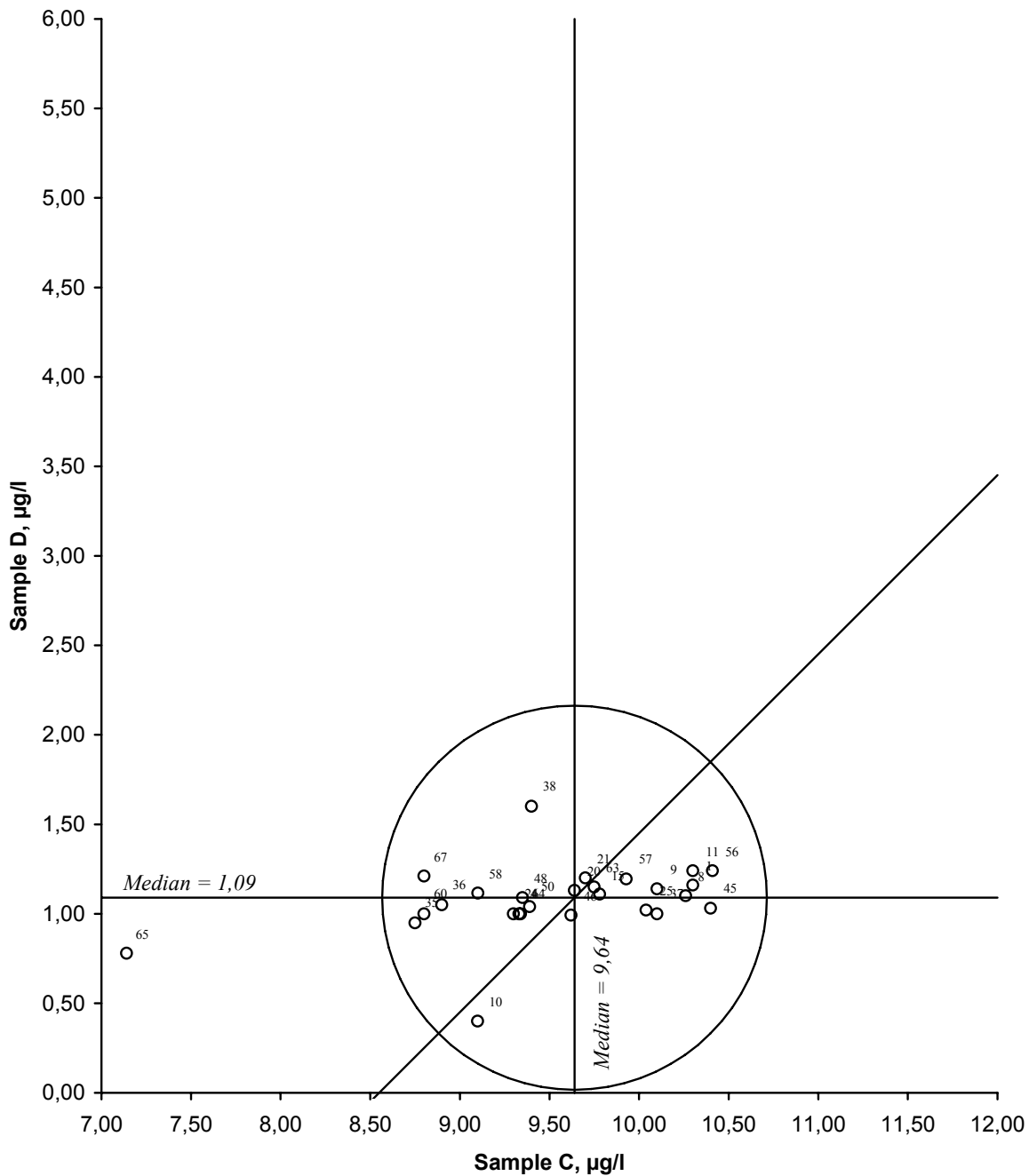


Figure 14. Youden diagram for manganese, sample pair CD  
 Acceptance limit, given by the circle, is 20 %



**Cadmium**

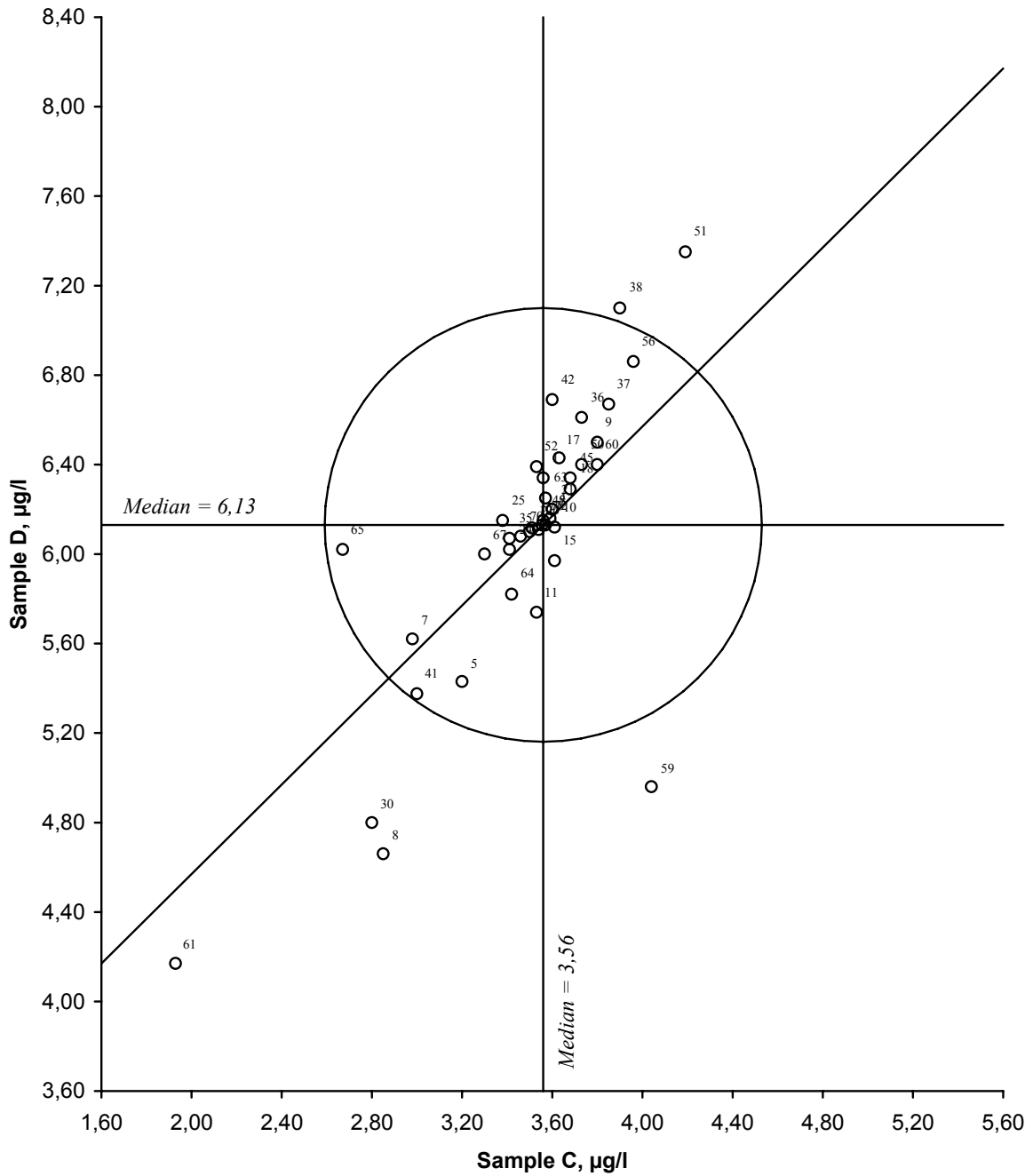


Figure 15. Youden diagram for cadmium, sample pair CD  
 Acceptance limit, given by the circle, is 20 %

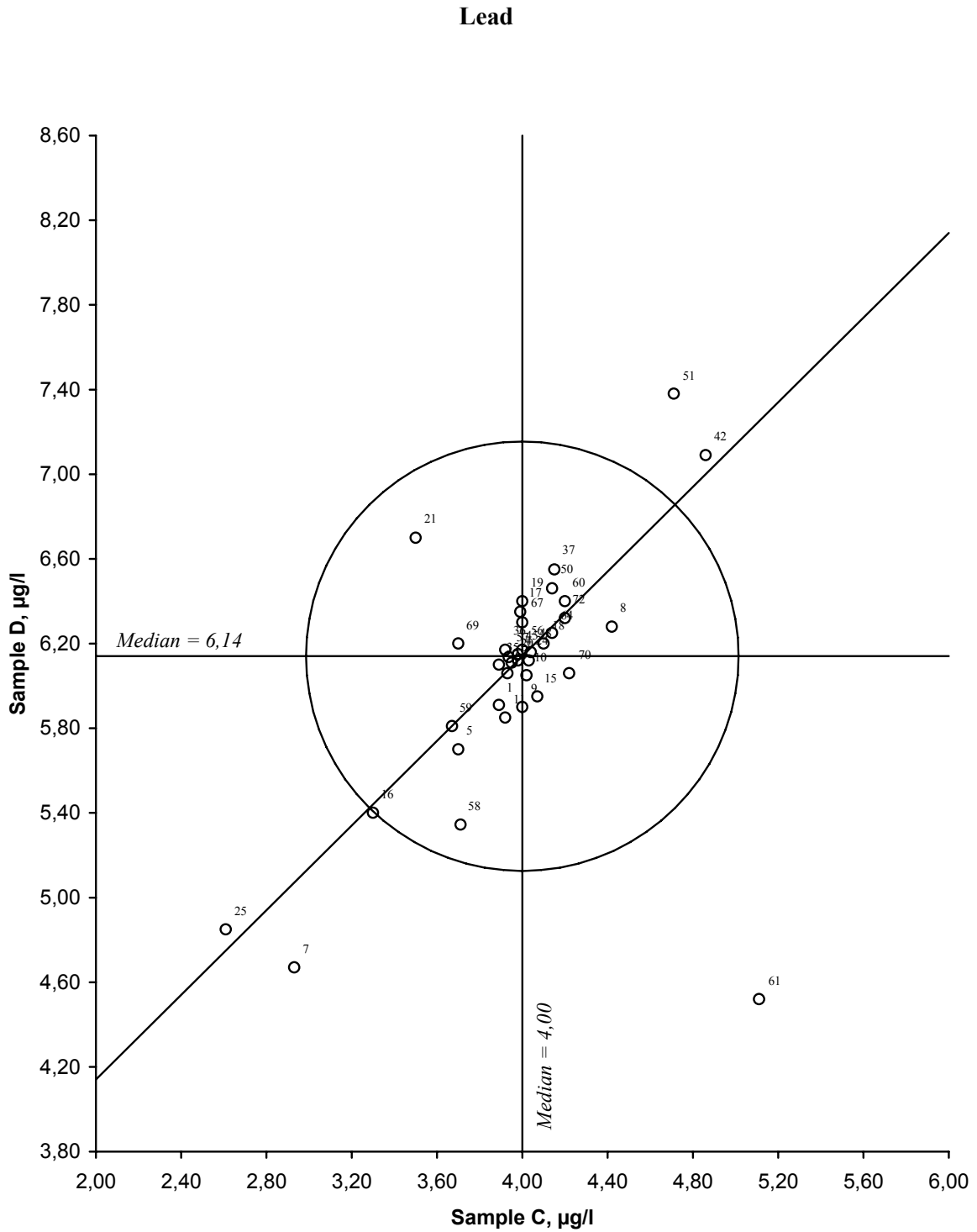


Figure 16. Youden diagram for lead, sample pair CD  
 Acceptance limit, given by the circle, is 20 %

Copper

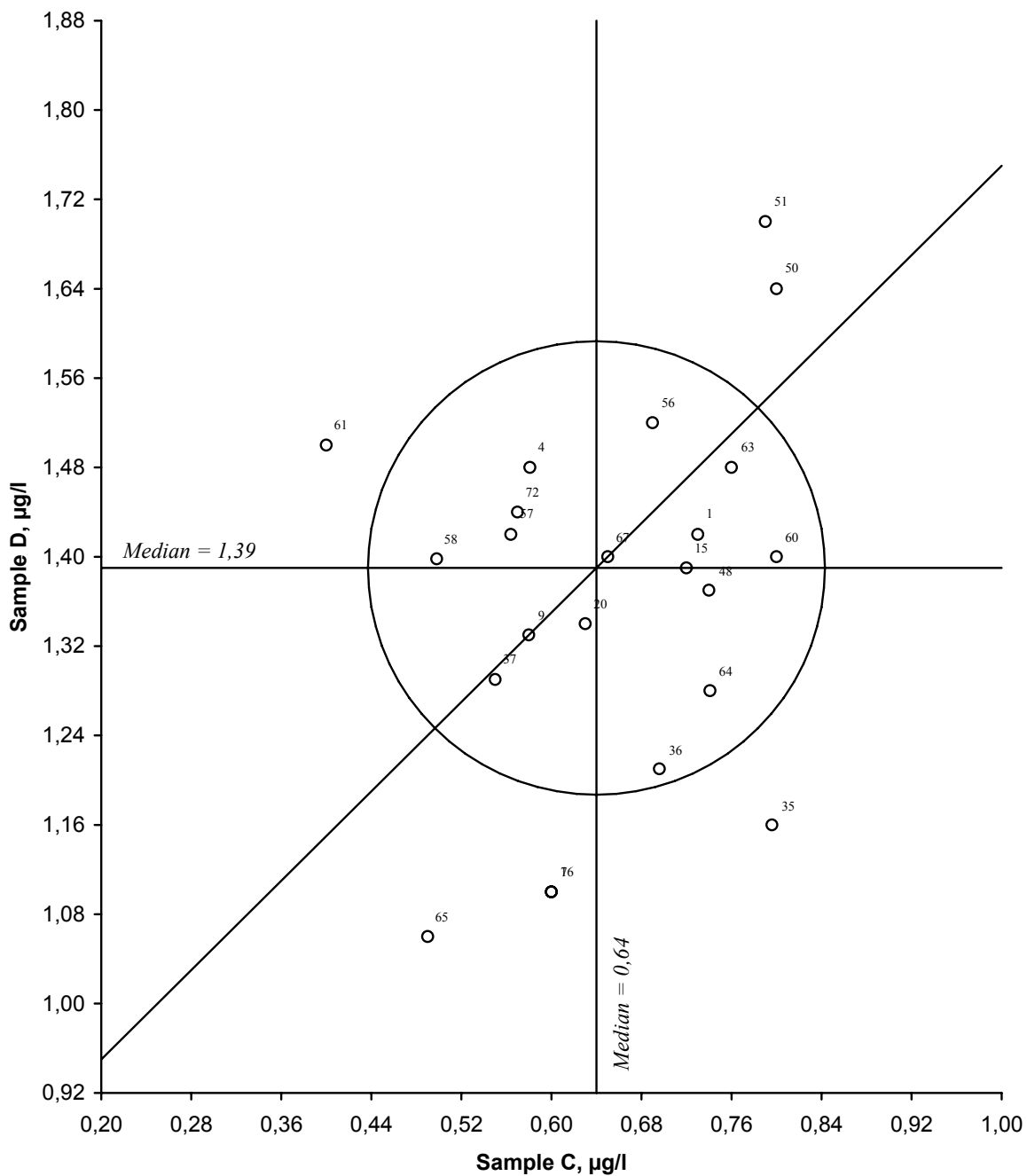


Figure 17. Youdendiagram for copper, sample pair CD  
 Acceptance limit, given by the circle, is 20 %

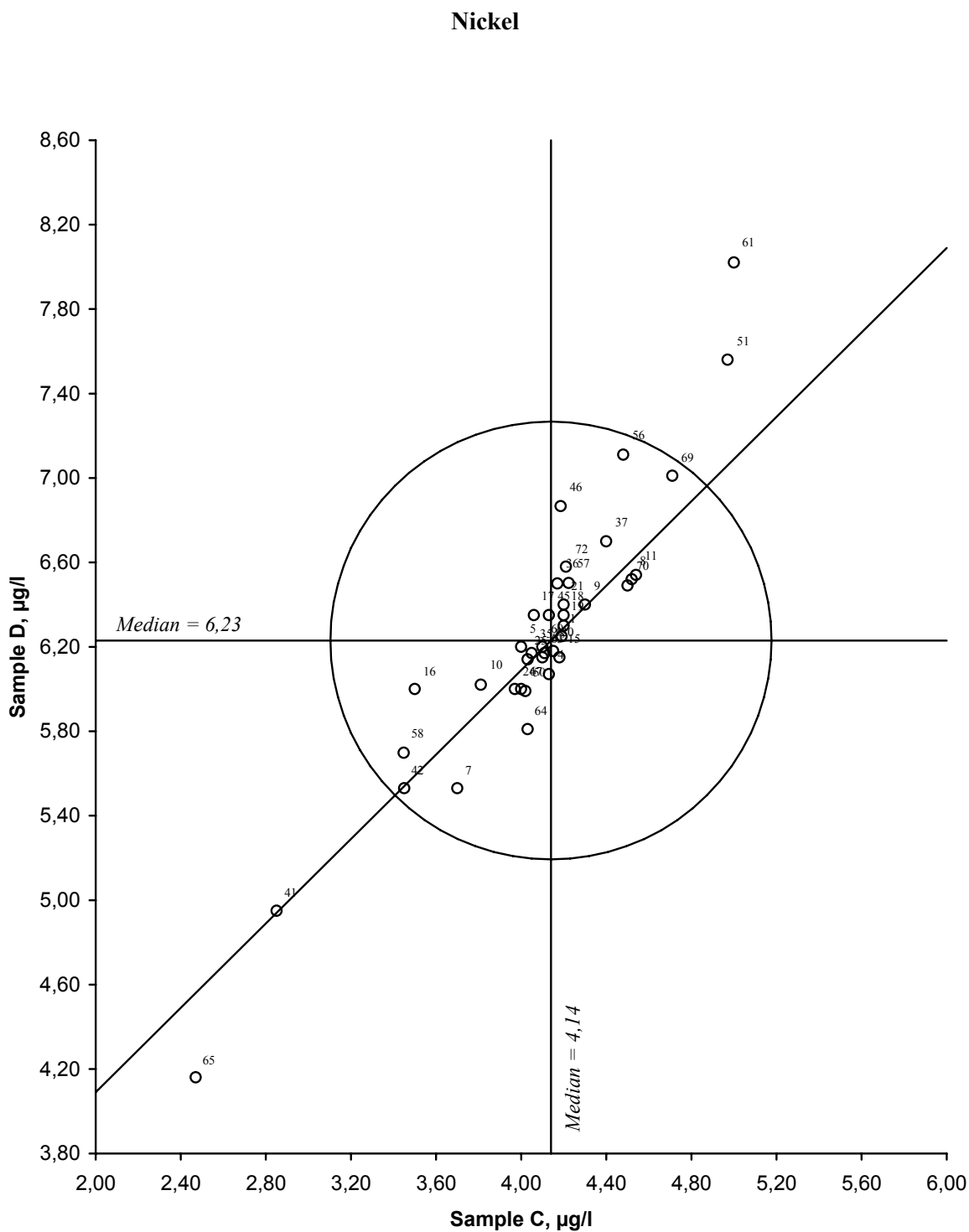


Figure 18. Youden diagram for nickel, sample pair CD  
 Acceptance limit, given by the circle, is 20 %

Zinc

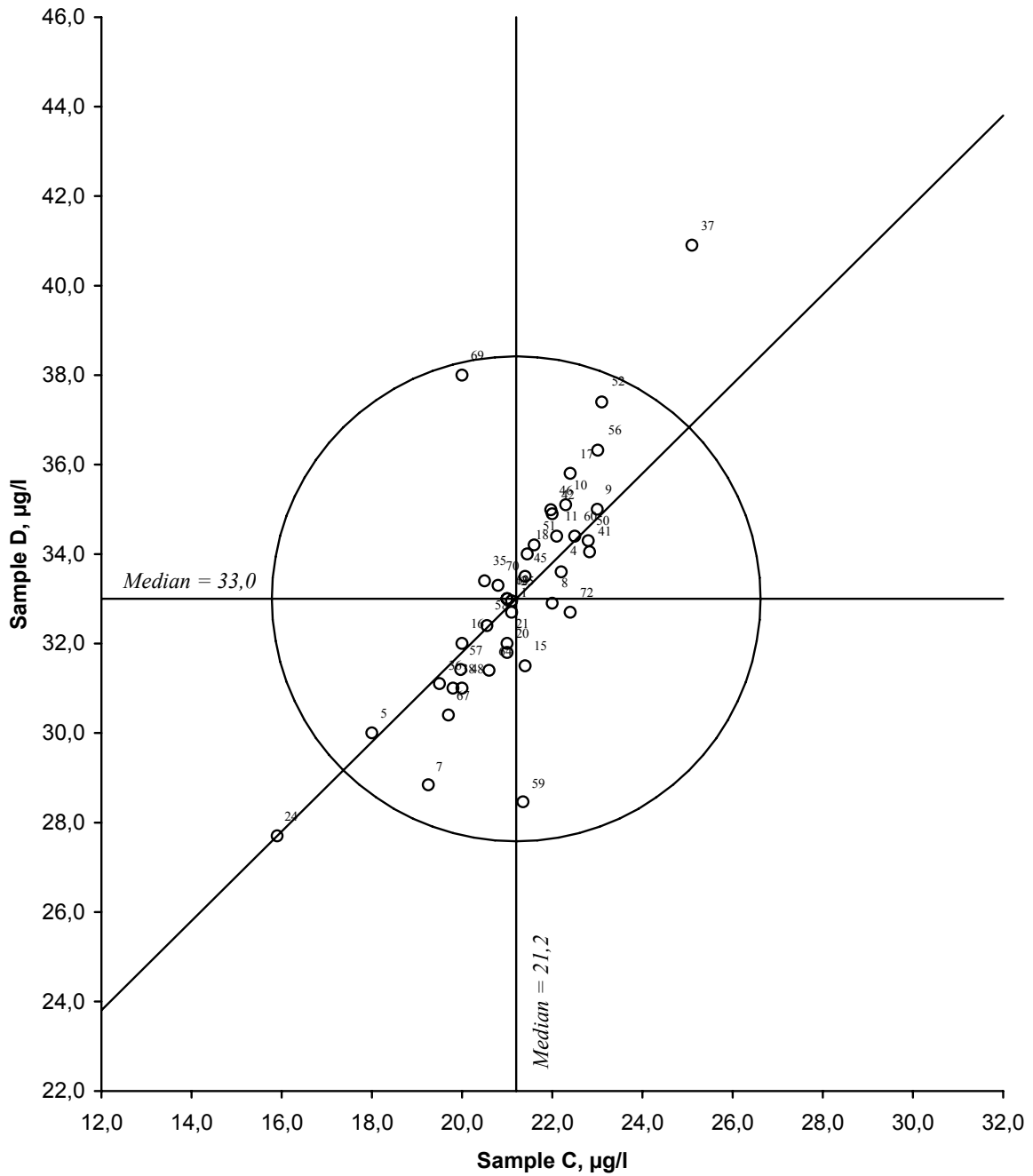


Figure 19. Youden diagram for zinc, sample pair CD  
 Acceptance limit, given by the circle, is 20 %

## 4. Discussion

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

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

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

For pH, the general target accuracy is  $\pm 0,1$  pH units (1), and less than 50 % of the result pairs are found within these accuracy limits. However, we have chosen to extend the acceptance limit to  $\pm 0,2$  pH units. Even with this wider acceptance limit only 61 % of the result pairs are evaluated as acceptable this time.

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

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

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

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

\* Acceptance limit for pH is given in pH units

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

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

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

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

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

## 4. Conclusion

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

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



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  $\pm 0,2$  pH units seems to be a reasonable assessment of the accuracy for pH measurements, when near neutral water samples - which are not in CO<sub>2</sub> equilibrium - are analyzed.

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

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

## 5. Literature

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## Appendix A.

### The participating laboratories

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

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

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

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

## Appendix B.

### Preparation of samples

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

### Sample control analyses

During the intercomparison period, four sets of samples were randomly selected from the batch for control analyses. The determinations were carried out by the laboratory at the Programme Centre, the first sample set being analyzed in June 2009, a few weeks before mailing the samples to the participants. The last sample was analyzed medio August 2009. A summary of the control results is presented in Table 3. The control results confirmed that the stability of the sample solutions were acceptable during the intercalibration period for all analytical variables. Even nitrate proved to be stable in these solutions when stored at 4 °C.

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

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

## Appendix C.

### Treatment of analytical data

The intercomparison was carried out by the method of Youden. This procedure requires two samples to be analyzed, and every laboratory shall report only one result for each sample and analytical variable. In a coordinate system the result of sample B is plotted against the result of sample A (see Figures 1 - 19).

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

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

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

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

## Appendix D

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

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

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

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



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

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

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

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

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

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

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

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

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

Analytical results in ascending order:

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

**Sample B**

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

Analytical results in ascending order:

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

U = Omitted result



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

**Sample A**

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

Analytical results in ascending order:

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

**Sample B**

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

Analytical results in ascending order:

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

U = Omitted result

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

**Sample A**

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

Analytical results in ascending order:

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

**Sample B**

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

Analytical results in ascending order:

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

U = Omitted result

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

**Sample A**

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

Analytical results in ascending order:

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

**Sample B**

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

Analytical results in ascending order:

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

U = Omitted result

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

Number of participants	59	Range	1,25
Number of omitted results	4	Variance	0,04
True value	2,76	Standard deviation	0,19
Mean value	2,74	Relative standard deviation	7,1%
Median value	2,76	Relative error	-0,6%
Analytical results in ascending order:			
55	1,86 U	47	2,70
23	2,15	19	2,71
7	2,20	49	2,72
48	2,40	9	2,73
38	2,49	42	2,73
32	2,50	64	2,73
41	2,53	4	2,74
67	2,54	71	2,75
60	2,57	37	2,76
22	2,60	1	2,76
13	2,61	36	2,77
40	2,63	53	2,77
17	2,64	34	2,78
26	2,65	15	2,78
16	2,66	28	2,78
2	2,68	57	2,79
50	2,68	39	2,79
63	2,69	29	2,80
21	2,69	51	2,80
35	2,70	20	2,80
		72	2,84
		10	2,84
		8	2,86
		30	2,88
		12	2,88
		33	2,88
		5	2,90
		45	2,90
		56	2,90
		58	2,91
		68	2,93
		18	2,95
		54	2,96
		65	2,98
		11	3,06
		59	3,40
		6	3,90 U
		61	5,10 U
		52	5,90 U

**Sample B**

Number of participants	59	Range	0,66
Number of omitted results	4	Variance	0,01
True value	1,19	Standard deviation	0,11
Mean value	1,18	Relative standard deviation	9,6%
Median value	1,19	Relative error	-0,6%
Analytical results in ascending order:			
22	0,85	42	1,17
48	0,91	64	1,17
18	0,95	16	1,17
41	0,99	1	1,17
38	1,00	30	1,17
32	1,00	36	1,18
55	1,08 U	54	1,18
23	1,10	72	1,19
13	1,10	63	1,19
67	1,10	21	1,20
20	1,10	71	1,20
26	1,12	7	1,20
5	1,15	50	1,20
9	1,15	34	1,21
57	1,15	8	1,21
2	1,15	28	1,22
35	1,16	53	1,22
17	1,16	65	1,23
40	1,16	37	1,23
60	1,16	49	1,23
		47	1,23
		10	1,23
		19	1,23
		39	1,23
		51	1,24
		29	1,24
		15	1,25
		33	1,25
		12	1,27
		4	1,27
		45	1,27
		58	1,30
		11	1,31
		68	1,34
		56	1,48
		59	1,51
		6	2,51 U
		61	3,60 U
		52	3,70 U

U = Omitted result

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

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

Analytical results in ascending order:

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

**Sample B**

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

Analytical results in ascending order:

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

U = Omitted result

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

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

Analytical results in ascending order:

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

**Sample B**

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

Analytical results in ascending order:

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

U = Omitted result

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

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

Analytical results in ascending order:

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

**Sample B**

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

Analytical results in ascending order:

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

U = Omitted result

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

Number of participants	58		Range		1,02	
Number of omitted results	4		Variance		0,03	
True value	3,25		Standard deviation		0,18	
Mean value	3,27		Relative standard deviation		5,6%	
Median value	3,25		Relative error		0,5%	
Analytical results in ascending order:						
	29	0,85 U	7	3,20	58	3,35
	56	2,78	59	3,20	31	3,35
	52	2,90 U	60	3,21	63	3,35
	30	2,95	72	3,22	38	3,36
	19	2,95	18	3,23	34	3,36
	48	2,99	35	3,24	57	3,38
	66	3,04	49	3,25	15	3,39
	55	3,06	65	3,25	20	3,40
	26	3,08	50	3,25	8	3,43
	41	3,12	2	3,26	4	3,46
	21	3,14	47	3,28	40	3,49
	36	3,14	39	3,28	17	3,51
	24	3,15	10	3,29	5	3,53
	11	3,15	16	3,31	32	3,60
	67	3,16	1	3,31	42	3,75
	12	3,16	45	3,31	33	3,80
	70	3,16	51	3,31	54	3,83 U
	28	3,17	64	3,31	61	8,70 U
	13	3,19	71	3,32		
	37	3,20	23	3,33		

**Sample B**

Number of participants	58		Range		0,46	
Number of omitted results	4		Variance		0,01	
True value	1,26		Standard deviation		0,08	
Mean value	1,26		Relative standard deviation		6,6%	
Median value	1,26		Relative error		0,1%	
Analytical results in ascending order:						
	52	0,32 U	35	1,24	16	1,29
	65	1,00	12	1,25	10	1,30
	66	1,07	18	1,25	20	1,30
	55	1,10	49	1,25	38	1,31
	48	1,12	45	1,25	15	1,31
	41	1,14	60	1,25	57	1,33
	26	1,18	47	1,25	4	1,33
	30	1,19	2	1,25	34	1,33
	33	1,20	39	1,26	31	1,34
	28	1,20	23	1,26	8	1,35
	70	1,21	51	1,26	56	1,35
	13	1,21	72	1,26	17	1,36
	24	1,22	59	1,27	32	1,40
	29	1,22 U	71	1,27	19	1,42
	67	1,22	50	1,27	5	1,42
	42	1,23	1	1,27	37	1,46
	11	1,23	58	1,28	54	1,54 U
	7	1,23	40	1,29	61	7,10 U
	36	1,24	63	1,29		
	21	1,24	64	1,29		

U = Omitted result



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

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

Analytical results in ascending order:

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

**Sample B**

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

Analytical results in ascending order:

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

U = Omitted result

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

**Sample A**

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

Analytical results in ascending order:

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

**Sample B**

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

Analytical results in ascending order:

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

U = Omitted result

**Table 5.12. Statistics - Aluminium**

**Sample C**

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

Analytical results in ascending order:

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

**Sample D**

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

Analytical results in ascending order:

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

U = Omitted result

**Table 5.13. Statistics - Iron**

**Sample C**

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

Analytical results in ascending order:

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

**Sample D**

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

Analytical results in ascending order:

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

U = Omitted result

**Table 5.14. Statistics - Manganese**

**Sample C**

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

Analytical results in ascending order:

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

**Sample D**

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

Analytical results in ascending order:

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

U = Omitted result

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

**Sample C**

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

Analytical results in ascending order:

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

**Sample D**

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

Analytical results in ascending order:

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

U = Omitted result

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

**Sample C**

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

Analytical results in ascending order:

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

**Sample D**

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

Analytical results in ascending order:

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

U = Omitted result

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

**Sample C**

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

Analytical results in ascending order:

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

**Sample D**

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

Analytical results in ascending order:

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

U = Omitted result



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

**Sample C**

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

Analytical results in ascending order:

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

**Sample D**

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

Analytical results in ascending order:

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

U = Omitted result

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

**Sample C**

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

Analytical results in ascending order:

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

**Sample D**

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

Analytical results in ascending order:

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

U = Omitted resultat