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Intercomparison 1125: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn

LRTAP
Long-range Transboundary Air Pollution

Norwegian Institute for Water Research
– an institute in the Environmental Research Alliance of Norway

REPORT

Main Office
Gaustadalléen 21
NO-0349 Oslo, Norway
Phone (47) 22 18 51 00
Telefax (47) 22 18 52 00
Internet: www.niva.no

Regional Office, Sørlandet
Jon Lilletuns vei 3
NO-4879 Grimstad, Norway
Phone (47) 22 18 51 00
Telefax (47) 37 04 45 13

Regional Office, Østlandet
Sandvikaveien 59
NO-2312 Ottestad, Norway
Phone (47) 22 18 51 00
Telefax (47) 62 57 66 53

Regional Office, Vestlandet
Thormøhlens gate 53 D
NO-5006 Bergen Norway
Phone (47) 22 18 51 00
Telefax (47) 55 31 22 14

Regional Office Central
Pirsenteret, Havnegata 9
P.O.Box 1266
NO-7462 Trondheim
Phone (47) 22 18 51 00
Telefax (47) 73 54 63 87

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Abstract

67 laboratories received samples for the intercomparison 1125, and 57 laboratories in 25 countries submitted results. Two sample sets were used, one for the determination of major ions, and one for heavy metals. Based on the general target accuracy of ± 20 %, 83 % of the overall results were considered as acceptable. This is the best result ever. The best results were reported for the analytical variables sodium, cadmium, calcium and iron, with 95, 94, 91 and 91 % acceptable results, respectively. The lowest percentage were observed for lead, total organic carbon and nickel with 67, 69 and 72 % acceptable results. Harmonization of the analytical methods used, and the practical procedures followed, may probably be the most important way to improve the comparability for these parameters.

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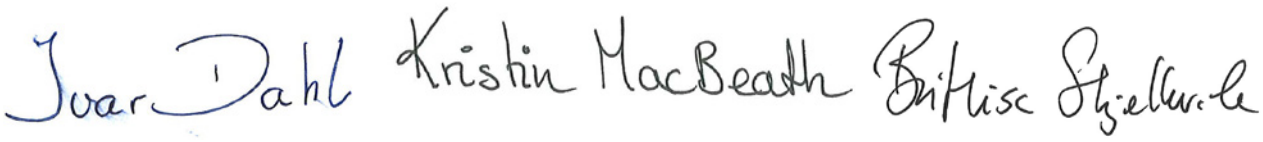

Ivar Dahl
Project Manager

Kristin MacBeath
Research Manager

Brit Lisa Skjelkvåle
Research Director

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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 1125

pH, Conductivity, Alkalinity, NO_3-N, Cl, SO_4, 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 the Norwegian Institute for Water Research (NIVA), while the Climate and Pollution Agency (Klif) leads the programme. The Programme Centres work is supported financially by KLIF.

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 25th intercomparison of chemical analysis.

Oslo, October 2011

Ivar Dahl

Contents

Summary

Intercomparison 1125 was organized as 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 2011, 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. 129 laboratories were invited to participate, and samples were sent to the 67 laboratories who accepted. 57 laboratories submitted results to the Programme Centre before the final statistical treatment of the data. 25 countries were represented in this laboratory group (see Appendix A, page 41).

The median value of the results received from the participants for each variable was selected as "true" value. On average 83 % of the result pairs were considered acceptable, the target limit being the median value ± 20 %, except for pH and conductivity where special acceptance limits were selected, ± 0,2 pH units and ± 10 %, respectively. Due to a mistake at the organizing laboratory there was very big difference in nitrate concentration between the two samples A and B. Sample B should have been spiked to match sample A, but this was not done. As a result sample B was at or below the detection limit for the majority of the participating laboratories. Making a statistical evaluation of the results from sample B or the sample pair as a whole, does not make sense. Instead the evaluation is done just for sample A.

For pH, the accuracy limit was as in earlier intercomparisons extended from the target acceptance limit of ± 0,1 units to ± 0,2 units, and this time 73 % of the result pairs were acceptable using this extended limit. This is much better than in the previous intercomparisons. A total error of ± 0,2 units for pH measurements, however, still seems to be a more reasonable basis for the assessment of the accuracy between laboratories than the target limit of ± 0,1 units.

The best results were reported for the analytical variables sodium, cadmium, calcium and iron where 95, 94, 91 and 91 % of the results, respectively, were acceptable. The worst results were observed for lead (67 %) and total organic carbon (69 %). The main reason for less acceptable results is probably the low concentrations in the samples used for some of the analytical variables and the fact that some laboratories are using equipment which is not sensitive enough for these concentrations. A reduced stability may explain the result for nitrate. More than 80 % acceptable results were obtained for the ten parameters conductivity, chloride, sulfate, calcium, magnesium, sodium, potassium, iron, manganese and cadmium. 70 - 79 % acceptable results were obtained for pH, alkalinity, nitrate, aluminium, copper, nickel and zinc, and 60 – 69 % for total organic carbon and lead.

1. Introduction

As stated in "ICP Waters Programme Manual." (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 twentyfifth intercomparison test, called 1125, included the determination of the major components and metal 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. At the Task Force meeting in Burlington, Canada, in October 2009, 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. It was also decided that total organic carbon and aluminium should be included in this round also.

The samples were mailed from the Programme Centre on July 6th 2011. Most of the participating laboratories received the samples within one week, with a few exceptions. It is important that the delivery address for the samples is given correctly, as one set of samples were not delivered to the destined 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. For different reasons a few laboratories asked for some delay in reporting the results to the Programme Centre, which they were granted. However, the results had to be reported before the start of statistical calculations. Most results were received within the end of August.

3. Results

129 laboratories were invited to participate in this ICP Waters intercomparison. 67 of the laboratories accepted and therefore samples were mailed to them. The 57 laboratories which submitted results to the Programme Centre, are representing 25 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. The participants and their code numbers are listed in Appendix A, which also includes a table summarizing how many laboratories participated from each country (see page 41).

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. Appendix C also gives an estimate for the uncertainty of the assigned true values. This is done according to ISO 13528 (2005). Statistical methods for use in proficiency testing by interlaboratory comparisons.

The results are illustrated in Figure 1 - 18, 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 big circle in the figures are represens a selected accuracy limit, either the general target limit of ± 20 % of the mean true values for the sample pair, or a special accuracy limit as defined in the sections below. A summary of the results of intercomparison 1125 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 information is 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.

49 of the participating laboratories determined pH in the test solutions using their own routine method. 17 reported that they had used electrometry and the others a “not documented” method. Most probably this is also electrometry. In this intercomparison, the laboratories where not asked whether the pH value was read during stirring of the sample or not. It has been observed earlier that this could have a significant influence on the results, especially in

samples with lower total ion strenght than the samples used in this intercomparison (4,5). As a result of this, the practice of establishing a “true value” based on the median value for all the reported results for pH is questionable. Whether an individual “true value” for each method would be more appropriate should therefore be discussed. In the intercomparison 1125 we have used the median value of all the reportede results, after the outliers have been excluded. 73 % of the results were acceptable, that is within the median value ± 0,2 pH units. This is better than in the previous intercomparisons (se table 2).

The main reason for the differences in the reported results is probably connected to the small differences in the analytical methods used by the participants. Random errors are also affecting the results, and to a greater degree for pH than many other variables, illustrated in Figure 1 by the spread of the small circles away from the 45° line for many laboratories.

3.2 **Conductivity**

The conductivity results are presented in Figure 2, where the great circle is representing an accuracy limit of ± 10 %, which is only half of the target accuracy limit given in the Manual (1). The reported results are given in Table 5.2. Some laboratories obviously reported the conductivity results in another unit than the requested one, which was mS/m at 25 °C, as the reported results were at least a factor of ten wrong.

51 laboratories reported results for conductivity, and all participants used an electrometric method for the determination. Most laboratories achieved very good agreement between the results for this variable, and 86 % of the result were within the acceptance limit of ± 10 %. This is somewhat better than the previous intercomparisons. Figure 2 is showing that systematic errors are dominating the results. A proper temperature correction is necessary when determining this variable, as the conductivity is changing by about two percent pr. degree at room temperature. If the accuracy limit was extended to the target value of ± 20 %, defined in the Manual (1), three more results located outside the 10 % acceptance circle, would be located within the circle and thus be defined as acceptable giving 91 % acceptable results. Four laboratories have obviously reported their results in a unit other than mS/m and have been rejected. An acceptance limit of ± 10 % seems to be a more reasonable target acceptance limit.

3.3 **Alkalinity**

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 5.3. 38 laboratories reported results for alkalinity, and 11 of these used a titration to both pH = 4,5 and pH = 4,2. Three participants titrated to pH = 5,4. The rest of the particpants, apart from one, titrated to another end point (either pH = 4,2, 4,5 or 4,8). The last laboratory used a “not documented” method.

In this intercomparison, 79 % of the sample pairs were within the target accuracy of ± 20 %. This is the best results in many years, but the alkalinity of these samples was somewhat higher than usual. It seems that the laboratories which titrated to both pH = 4,5 and 4,2 report somewhat lower results than the laboratories which titrated to either pH = 4,2, 4,5 og 4,8. The

lowest results were obtained by the partipants having titrated to pH = 5.4 but this was done by a low number of laboratories.

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.

The alkalinity value may vary 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.

3.4 **Nitrate + nitrite**

Due to a mistake at the organizing laboratory, the difference in nitrate concentration between the two samples was very big. Sample B should have been spiked to match sample A, but this was not done. As a result, the concentration of sample B was at or below the detection limits for the methods used by the majority of the participating laboratories. Making a statistic evaluation of the results from sample B or the sample pair as a whole, does not make sense. Instead the evaluation was done for sample A only and, as a result of that, it is not possible to present a Youden diagram for this parameter. The evaluation of the results for sample A has been done according to the same statistical priciples as used otherwise. The reported values for both samples are given in Table 5.4, but this discussion and the results in Table 1 considers only sample A.

43 laboratories reported results for this parameter, and ion chromatography is used by 24 of these. The others used different photometric methods apart from two which have used electrometry. Most of these laboratories use an automated version of the cadmium reduction method. There is no significant difference between the results determined by the different methods.

In this intercomparison 74 % of the results are evaluated as acceptable, which is somewhat better than the previous intercomparisons. The stability of the parameter in the sample could be a problem. The samples may be affected by environmental conditions during transport to the laboratories. This has not been examined in this intercomparison.

As nitrite is more or less absent in the sample solutions used here, the results from the photometric and ion chromatographic methods should be directly comparable, This is shown in Table 1.

3.5 **Chloride**

The chloride results are presented in Figure 4, and the reported results from the participants are given in Table 5.5. The target accuracy of ± 20 % is represented by the big circle in figure

4. The majority of the laboratories used ion chromatography as the analytical technique in their determinations of chloride (85 %). The photometric methods seem to give somewhat higher results than ion chromatography, but the number of results are rather low.

As much as 89 % of the result pairs are acceptable in this intercomparison, and this is far better than in the previous year.

3.6 **Sulphate**

The sulphate results are illustrated in Figure 5, and the reported values are given in Table 5.6. The circle represents the target accuracy of ± 20 %. Ion chromatography is used by 89 % of the laboratories for determination of the sulphate content of the samples. Four laboratories used a nephelometric method giving somewhat higher results than ion chromatography. One laboratoriy used ICP-AES for the determination of total sulphur and then recalculated the result to sulphate, the result being somewhat high.

86 % of the result pairs in this intercomparison are acceptable, and this is far better than the previous year.

3.7 **Calcium**

The calcium results are illustrated in Figure 6, and the reported values are given in Table 5.7. The target accuracy is ± 20 %, and is represented by the big circle in the figure. 45 laboratories reported results for calcium. An increasing number of laboratories, this time 22, used ion chromatography, and 10 laboratories used ICP-AES. The traditional flame atomic absorption spectrometry was used by only 8 of the participants in their determination of calcium. Three laboratories used ICP-MS and the last two used a titrimetric method with EDTA and photometry respectively.

As much as 91 % of the result pairs in this intercomparison are acceptable, and this is better than the previous years. The flame atomic absorption methods seem to give somewhat low results in this intercomparison.

3.8 **Magnesium**

The magnesium results are presented in Figure 7, and the reported values are given in Table 5.8. The target accuracy is ± 20 %, and is represented by the big circle in the figure. 45 laboratories reported results for magnesium, and the analytical methods used by the participants are mainly the same as for the determination of calcium. An increasing part of the laboratories, this time 22, used ion chromatography, and 10 laboratories used ICP-AES. The traditional flame atomic absorption spectrometry was used by only 9 of the participants in their determination of magnesium. Three used ICP-MS and the last laboratory used a titrimetric method with EDTA.

As much as 89 % of the result pairs in this intercomparison are acceptable, and this is somewhat better than the previous years.

3.9 **Sodium**

The sodium results are presented in Figure 8, where the big circle represents the general target accuracy of ± 20 %. The reported values are given in Table 5.9. This time 43 laboratories reported results for sodium. An increasing part of the laboratories, 22 in this round, used ion chromatography in their determinations, and 8 laboratories used ICP-AES. The same number used the traditional flame atomic absorption spectrometry. Three used ICP-MS and the last two laboratories used flame atomic emission spectroscopy.

As much as 95 % of the result pairs are located within the general target accuracy of ± 20 %. This determination usually holds a very good quality, and this time it was even better than the previous ones.

3.10 **Potassium**

The potassium results are presented in Figure 9. The big circle represens the target acceptance limit of ± 20 %. The reported values are given in Table 5.10. This time 44 laboratories reported results for potassium, and the methods are very much the same as for sodium. An increasing part of the laboratories, 24 in this intercomparison, used ion chromatography in their determinations, and 8 laboratories used ICP-AES. Seven used the traditional flame atomic absorption spectrometry. Three used ICP-MS and the last two laboratories used flame atomic emission spectroscopy.

82 % of the result pairs are considered acceptable, and this is the same as for the last year, but better than for the previous ones.

3.11 **Total organic carbon**

Total organic carbon was also included in the intercomparison this year, and the results are presented in Figure 10. The big circle represents the target acceptance limit of ± 20 %. The reported values from 29 laboratories are given in Table 5.10. Combustion methods are used by most of the laboratories, only 6 laboratories used UV/peroxodisulfate oxidation method for this determination. No difference in the results for the two techniques was observed in this intercomparison.

Only 69 % of the results were within the targent accuracy of ± 20 %. That is much lower than for the previous two years. There is a high degree of random errors in the data sets, but the difference in concentration between the two samples in the sample pair was quite big so the plot is a little affected by this fact.

3.12 **Aluminium**

The results for aluminium are illustrated in Figure 11, and the values reported by the 29 participants are given in Table 5.12. The target accuracy is ± 20 %, and is represented by the big circle in the figure. 14 and 9 of the laboratories used ICP-AES and ICP-MS, respectively,

while only three used flame atomic absorption. The same number used graphite furnace atomic absortion. As for the other metals the plasma methods are clearly taking over more and more for the atomic absorption methods.

In this round, 76 % of the result pairs are considered acceptable, and this is about the same as for the last two years. ICP-AES gave somewhat higher results than the other methods. The deviating results are mainly affected by systematic errors.

3.13 **Iron**

The results for iron are illustrated in Figure 12, and the values reported by the participants are given in Table 5.13. The target accuracy is ± 20 %, and is represented by the big circle in the figure. 35 laboratories submitted results for iron, of which 17 and 10 used the plasma techniques ICP-AES and ICP-MS respectively, while 6 and 1 used flame and graphite furnace atomic absorption, respectively. The last laboratory used a method based on photometry.

This time, as much as 91 % of the result pairs are considered acceptable, which is very good and much better than the previous intercomparisons. There are no big difference between the different methods. The deviating results are mainly affected by systematic errors.

3.14 **Manganese**

The manganese results are illustrated in Figure 13, and the values reported by the participants are given in Table 5.14. The target accuracy is ± 20 %, and is represented by the big circle in the figure. 37 laboratories submitted results for manganese, of which 17 and 11 used the plasma techniques ICP-AES and ICP-MS respectively, while 7 and 1 used flame and graphite furnace atomic absorption, respectively. The last laboratory used a method based on photometry.

86 % of the result pairs are considered acceptable, which is very good. There are no big difference between the different methods. The deviating results are mainly affected by systematic errors.

3.15 **Cadmium**

The results for cadmium are illustrated in Figure 14, and the values reported by the participants are given in Table 5.15. The target accuracy is ± 20 % and is represented by the big circle in the figure. 32 laboratories submitted results for cadmium and ICP-MS was used by 15 of these. 7 laboratories used graphite furnace atomic absorption, and 6 and 3 used ICP-AES and flame atomic absorption, respectively. The last laboratory reported that they used a potensiometric stripping method.

As much as 94 % of the result pairs are considered acceptable, which is very good and the highest percentage ever. There are no big difference between the different methods. The deviating results are mainly affected by systematic errors.

3.16 **Lead**

The results for lead are illustrated in Figure 15, and the values reported by the participants are given in Table 5.16. The target accuracy is ± 20 %, and is represented by the big circle in the figure. 33 laboratories submitted results for lead and ICP-MS was used by 15 of these. 6 laboratories used graphite furnace atomic absorption, and the same number used ICP-AES. Flame atomic absorption was used by five laboratories and the last one reported that they used a potensiometric stripping method.

67 % of the result of the result pair are considered acceptable, which is about the same fairly low level as int the previous intercomparisons. Flame atomic absorption gave significantly lower results than the rest of the methods, and this method is probably not sensitive enough for the low levels. The most sensitive method, ICP-MS, seems to be the best method for these samples.

3.17 **Copper**

The copper results are illustrated in Figure 16, and the values reported by the participants are given in Table 5.17. The target accuracy is ± 20 %, and is represented by the big circle in the figure. 35 laboratories submitted results for copper and ICP-MS was used by 14 of these. 9 laboratories used graphite furnace atomic absorption, and 8 used ICP-AES. Flame atomic absorption was used by three laboratories and the last one reported that they used a potensiometric stripping method.

77 % of the result pairs are considered acceptable, which is very much better than the previous intercomparisons. However, it is important to have in mind that the concentrations this time were much higher. Apart from flame atomic absorption and potensiometric stripping (low number of results) there was no big difference between the methods.

3.18 **Nickel**

The results for nickel are illustrated in Figure 17, and the values reported by the participants are given in Table 5.18. The target accuracy is ± 20 %, and is represented by the big circle in the figure. 29 laboratories submitted results for nickel and ICP-MS was used by 14 of these. 6 laboratories used graphite furnace atomic absorption, and the same number used ICP-AES. The three last laboratories used flame atomic absorption .

In this round, 77 % of the result pairs are considered acceptable. This is better than the previous year despite the same fairly low concentration levels in the samples.

3.19 **Zinc**

The results for zinc are illustrated in Figure 18, and the values reported by the participants are given in Table 5.19. The target accuracy is ± 20 %, and is represented by the big circle in figure. 34 laboratories submitted results for zinc and ICP-MS had been used by 13 of these. 11 laboratories used ICP-AES, and 7 used flame atomic absorption. Two laboratories used

graphite furnace atomic absortion and the last one reported that they used a potensiometric stripping method.

79 % of the result pairs are considered acceptable. Flame atomic absorption seems to give somewhat lower results than the other methods. Generally, the deviating results are affected mainly by systematic errors, but there are also some rather big random errors despite the fairly high concentration level.

Table 1. Statistical summary for intercomparison 1125

Analytical variable and method	Sample pair	True value 1	True value 2	Total number	Labs. excl.	Median 1	Median 2	Average Sample 1	Std.dev. Sample 1	Average Sample 2	Std.dev. Sample 2	Rel. std.dev. % 1	Rel. std.dev. % 2	Relative err. % 1	Relative err. % 2
pH	AB	7,31	7,40	49	1	7,31	7,40	7,30	0,16	7,37	0,14	2,2	1,9	-0,2	-0,4
Electrometry				17	1	7,34	7,39	7,32	0,20	7,35	0,17	2,7	2,3	0,2	-0,7
Not documented				32	0	7,30	7,41	7,28	0,14	7,38	0,12	1,9	1,6	-0,4	-0,2
Conductivity	AB	8,27	7,13	51	7	8,27	7,13	8,31	0,18	7,17	0,22	2,2	3,1	0,4	0,5
Alkalinity	AB	0,582	0,434	38	6	0,582	0,434	0,584	0,056	0,440	0,047	9,6	10,6	0,3	1,3
End point titration				11	1	0,568	0,426	0,569	0,016	0,427	0,011	2,9	2,5	-2,3	-1,6
End point 5.4				3	1			0,460		0,341				-20,9	-21,4
Other end p.				23	4	0,600	0,451	0,604	0,041	0,456	0,039	6,8	8,5	3,7	5,0
Not documented				1	0			0,597		0,462				2,6	6,5
Nitrate + nitrite-nitrogen	AB	65,0	Not assigned	43	11	65,0		63,2	14,4			22,8		-2,8	
Autoanalyzer				8	2	69,2		64,4	17,4			27,0		-1,0	
Photometry				5	0	62,0		63,4	17,2			27,2		-2,4	
Ion chromatography				24	9	60,7		60,5	15,1			25,0		-6,9	
Flow injection anal.				4	0	71,0		70,0	7,29			10,4		7,7	
Electrometry				2	0	65,5		65,5	0,78			1,2		0,7	
Chloride	AB	3,32	3,06	46	5	3,32	3,06	3,35	0,16	3,07	0,15	4,8	5,0	0,9	0,4
Ion chromatography				39	1	3,31	3,05	3,33	0,15	3,05	0,14	4,5	4,7	0,4	-0,2
Manual, Hg				2	1			3,60		3,40				8,4	11,1
Potentiometry				1	0			3,54		3,30				6,6	7,8
Photometry				2	2			3,70		3,73				11,4	21,9
Electrometry				1	1			3,22		5,15				-3,0	68,3
Photometry HgSCN				1	0			3,65		3,20				9,9	4,6

Analytical variable and method	Sample pair	True value 1	True value 2	Total number	Labs. excl.	Median 1	Median 2	Average Sample 1	Std.dev. Sample 1	Average Sample 2	Std.dev. Sample 2	Rel. std.dev. % 1	Rel. std.dev. % 2	Relative err. % 1	Relative err. % 2
Sulfate	AB	5,13	6,49	44	2	5,13	6,49	5,20	0,42	6,50	0,38	8,2	5,9	1,3	0,2
Ion chromatography				39	1	5,12	6,49	5,17	0,41	6,50	0,38	7,8	5,8	0,7	0,1
Nephelometry				4	1	5,25	6,37	5,52	0,69	6,48	0,58	12,4	8,9	7,6	-0,2
ICP-AES				1	0			5,36		6,80				4,4	4,7
Calcium	AB	8,50	7,20	45	2	8,50	7,20	8,47	0,57	7,21	0,46	6,7	6,3	-0,4	0,1
FAAS				8	0	7,94	6,80	8,02	0,67	6,84	0,40	8,4	5,9	-5,7	-5,0
ICP-AES				10	0	8,65	7,38	8,59	0,43	7,36	0,18	5,0	2,5	1,1	2,2
EDTA				1	0			8,29		6,71				-2,5	-6,8
Ion chromatography				22	1	8,50	7,20	8,59	0,56	7,32	0,47	6,6	6,5	1,0	1,6
ICP-MS				3	0	8,50	7,20	8,51	0,49	7,13	0,72	5,8	10,1	0,1	-0,9
Photometry				1	1			1,26		1,11				-85,2	-84,6
Magnesium	AB	1,98	1,69	45	1	1,98	1,69	2,00	0,14	1,70	0,14	7,1	8,2	1,2	0,6
FAAS				9	1	1,99	1,67	2,04	0,19	1,72	0,18	9,3	10,6	3,2	1,8
ICP-AES				10	0	1,95	1,67	1,97	0,10	1,68	0,07	5,0	4,1	-0,5	-0,7
EDTA				1	0			2,20		2,03				11,1	20,1
Ion chromatography				22	0	2,00	1,70	2,01	0,13	1,70	0,12	6,4	7,0	1,7	0,9
ICP-MS				3	0	1,95	1,66	1,86	0,18	1,59	0,24	9,8	15,0	-6,1	-6,1
Sodium	AB	4,18	3,70	43	2	4,18	3,70	4,17	0,19	3,68	0,17	4,5	4,6	-0,1	-0,4
FAAS				8	0	4,17	3,71	4,19	0,31	3,71	0,26	7,3	7,1	0,1	0,2
ICP-AES				8	0	4,28	3,71	4,26	0,14	3,74	0,11	3,3	2,9	1,9	1,0
AES				2	0			4,17		3,69				-0,2	-0,4
Ion chromatography				22	2	4,15	3,67	4,14	0,17	3,66	0,15	4,0	4,0	-1,0	-1,1
ICP-MS				3	0	4,20	3,70	4,16	0,10	3,65	0,27	2,3	7,4	-0,5	-1,4
Potassium	AB	0,690	0,600	44	4	0,690	0,600	0,695	0,063	0,604	0,053	9,0	8,8	0,8	0,6
FAAS				7	1	0,697	0,597	0,736	0,082	0,637	0,076	11,2	11,9	6,6	6,2
ICP-AES				8	0	0,741	0,632	0,735	0,038	0,637	0,033	5,2	5,2	6,5	6,1
AES				2	0			0,700		0,585				1,4	-2,5
Ion chromatography				24	2	0,665	0,588	0,672	0,059	0,587	0,048	8,8	8,2	-2,7	-2,1
ICP-MS				3	1			0,676		0,569				-2,1	-5,2

Analytical variable and method	Sample pair	True value 1	True value 2	Total number	Labs. excl.	Median 1	Median 2	Average Sample 1	Std.dev. Sample 1	Average Sample 2	Std.dev. Sample 2	Rel. std.dev. % 1	Rel. std.dev. % 2	Relative err. % 1	Relative err. % 2
Total organic carbon	AB	2,75	4,56	29	2	2,75	4,56	2,90	0,41	4,63	0,55	14,2	11,8	5,6	1,6
Combustion				22	2	2,74	4,53	2,88	0,38	4,59	0,54	13,3	11,8	4,6	0,6
UV/peroxodisulphate				6	0	2,71	4,60	2,85	0,39	4,72	0,62	13,8	13,2	3,6	3,5
Other method				1	0			3,81		5,00				38,5	9,6
Aluminium	CD	65,5	96,9	29	3	65,5	96,9	67,3	9,5	98,5	11,9	14,1	12,1	2,7	1,7
FAAS				3	2			91,0		114,0				38,9	17,6
GFAAS				3	1			62,8		100,0				-4,2	3,2
ICP				14	0	67,9	98,5	69,5	9,7	101,6	14,3	14,0	14,1	6,1	4,9
ICP-MS				9	0	63,0	91,2	62,2	3,1	91,7	3,7	5,0	4,0	-5,1	-5,4
Iron	CD	259	290	35	2	259	290	258	17	287	18	6,6	6,2	-0,3	-0,9
FAAS				6	1	250	290	259	16	290	30	6,2	10,3	-0,2	0,1
GFAAS				1	0			277		311				7,1	7,3
ICP-AES				17	0	260	291	260	16	287	14	6,3	4,9	0,2	-1,0
ICP-MS				10	1	254	287	253	21	284	18	8,1	6,4	-2,2	-2,2
Photometry				1	0			258		286				-0,2	-1,4
Manganese	CD	26,1	21,6	37	1	26,1	21,6	26,3	2,0	21,8	2,3	7,7	10,4	0,9	0,7
FAAS				7	1	26,5	23,0	26,5	1,9	22,3	2,0	7,0	8,9	1,6	3,3
GFAAS				1	0			29,8		25,9				14,2	19,9
ICP-AES				17	0	26,3	21,4	26,0	1,4	20,9	1,8	5,4	8,4	-0,2	-3,4
ICP-MS				11	0	26,0	21,6	25,9	2,3	21,9	2,1	9,0	9,5	-0,7	1,4
Photometry				1	0			31,5		27,7				20,6	28,4
Cadmium	CD	3,82	3,80	32	2	3,82	3,80	3,81	0,23	3,76	0,23	6,0	6,1	-0,3	-1,1
FAAS				3	0	3,80	3,65	3,85	0,14	3,65	0,35	3,5	9,6	0,7	-3,9
GFAAS				7	2	3,71	3,56	3,57	0,28	3,62	0,19	7,9	5,3	-6,4	-4,8
ICP-AES				6	0	3,76	3,65	3,79	0,36	3,72	0,38	9,6	10,3	-0,9	-2,1
ICP-MS				15	0	3,90	3,80	3,87	0,09	3,84	0,10	2,3	2,7	1,4	1,1
Pot. Stripping				1	0			4,06		3,77				6,3	-0,8

Analytical variable and method		Sample pair	True value 1	True value 2	Total number	Labs. excl.	Median 1	Median 2	Average Sample 1	Std.dev. Sample 1	Average Sample 2	Std.dev. Sample 2	Rel. std.dev. % 1	Rel. std.dev. % 2	Relative err. % 1	Relative err. % 2
Lead		CD	7,60	6,83	33	4	7,60	6,83	7,39	0,86	6,63	0,70	11,7	10,6	-2,8	-2,9
	FAAS				5	2	6,00	5,71	5,96	0,44	5,52	0,60	7,3	10,8	-21,5	-19,2
	GFAAS				6	1	6,96	6,34	7,11	0,96	6,49	0,49	13,4	7,5	-6,4	-5,0
	ICP-AES				6	1	6,70	5,92	7,12	0,95	6,03	0,69	13,3	11,4	-6,3	-11,8
	ICP-MS				15	0	8,00	7,13	7,91	0,35	7,10	0,29	4,4	4,1	4,0	4,0
	Pot. stripping				1	0			6,60		6,60				-13,2	-3,4
Copper		CD	232	171	35	4	232	171	231	18	171	15	8,0	9,0	-0,6	-0,2
	FAAS				3	1			201		151				-13,4	-12,0
	GFAAS				9	2	232	174	228	20	171	12	8,9	7,2	-1,9	0,0
	ICP-AES				8	1	236	172	238	14	175	14	6,0	8,2	2,4	2,4
	ICP-MS				14	0	232	172	232	17	174	13	7,5	7,6	0,0	1,8
	Pot. stripping				1	0			244		132				5,2	-22,6
Nickel		CD	5,66	5,63	29	1	5,66	5,63	5,74	0,64	5,57	0,65	11,2	11,7	1,4	-1,1
	FAAS				3	0	5,50	4,50	5,53	0,65	4,80	1,08	11,8	22,5	-2,2	-14,7
	GFAAS				6	1	5,34	5,40	5,65	0,68	5,46	0,18	12,1	3,2	-0,2	-2,9
	ICP-AES				6	0	6,05	6,00	5,92	0,94	5,64	0,79	15,9	13,9	4,6	0,2
	ICP-MS				14	0	5,66	5,66	5,74	0,52	5,74	0,53	9,1	9,2	1,4	2,0
Zinc		CD	154	120	34	3	154	120	152	12	119	9	8,1	7,9	-1,3	-1,1
	FAAS				7	2	136	102	135	10	105	8	7,6	8,1	-12,5	-12,1
	GFAAS				2	1			151		119				-1,9	-1,2
	ICP-AES				11	0	155	124	157	13	123	9	8,2	7,5	2,2	2,6
	ICP-MS				13	0	156	122	154	7	121	4	4,4	3,1	-0,1	0,8
	Pot. stripping				1	0			158		107				2,4	-10,9

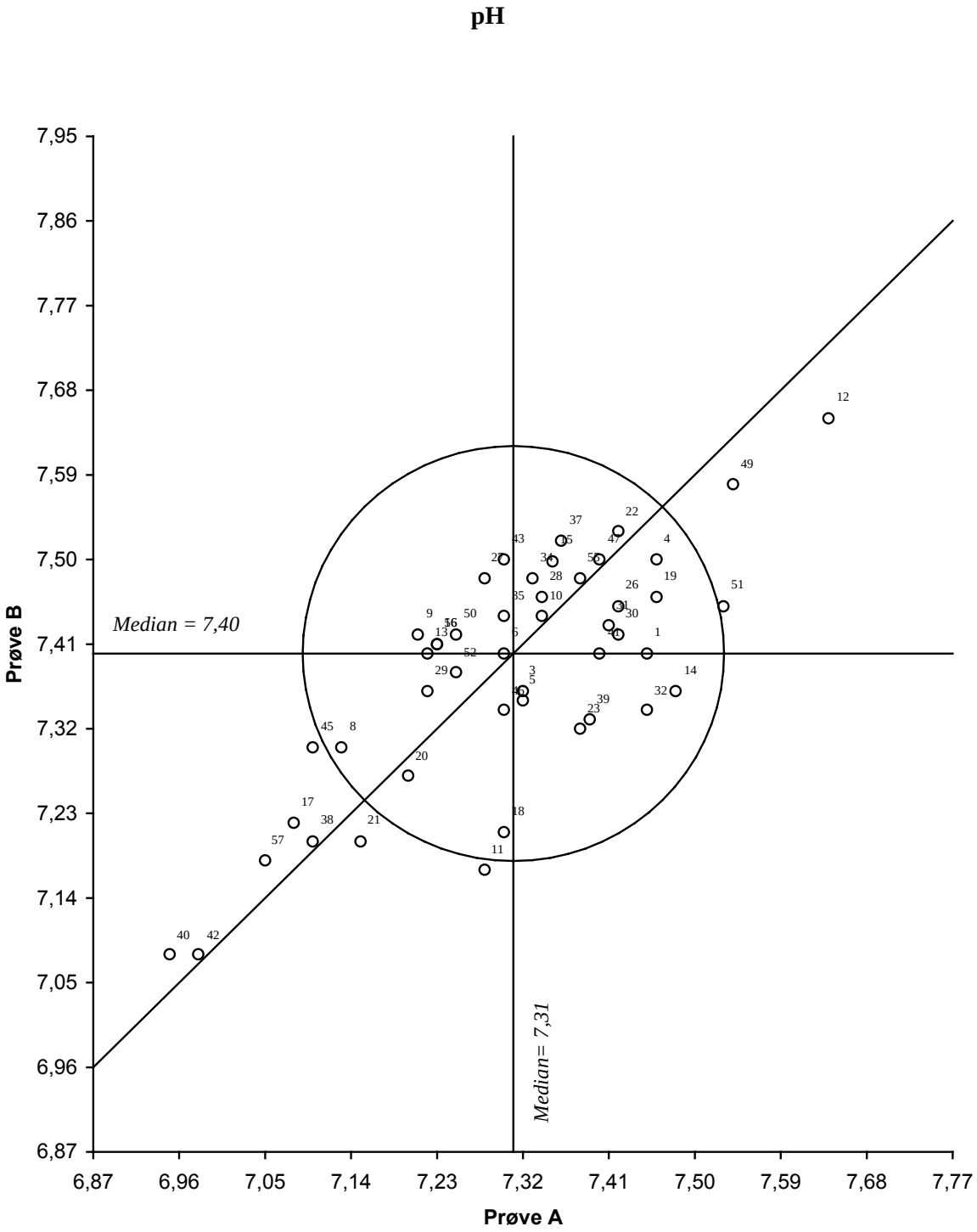

Figure 1. Youdendiagram for pH, Samplepair AB
Acceptable limit , given by circle, is 0,2 pH units

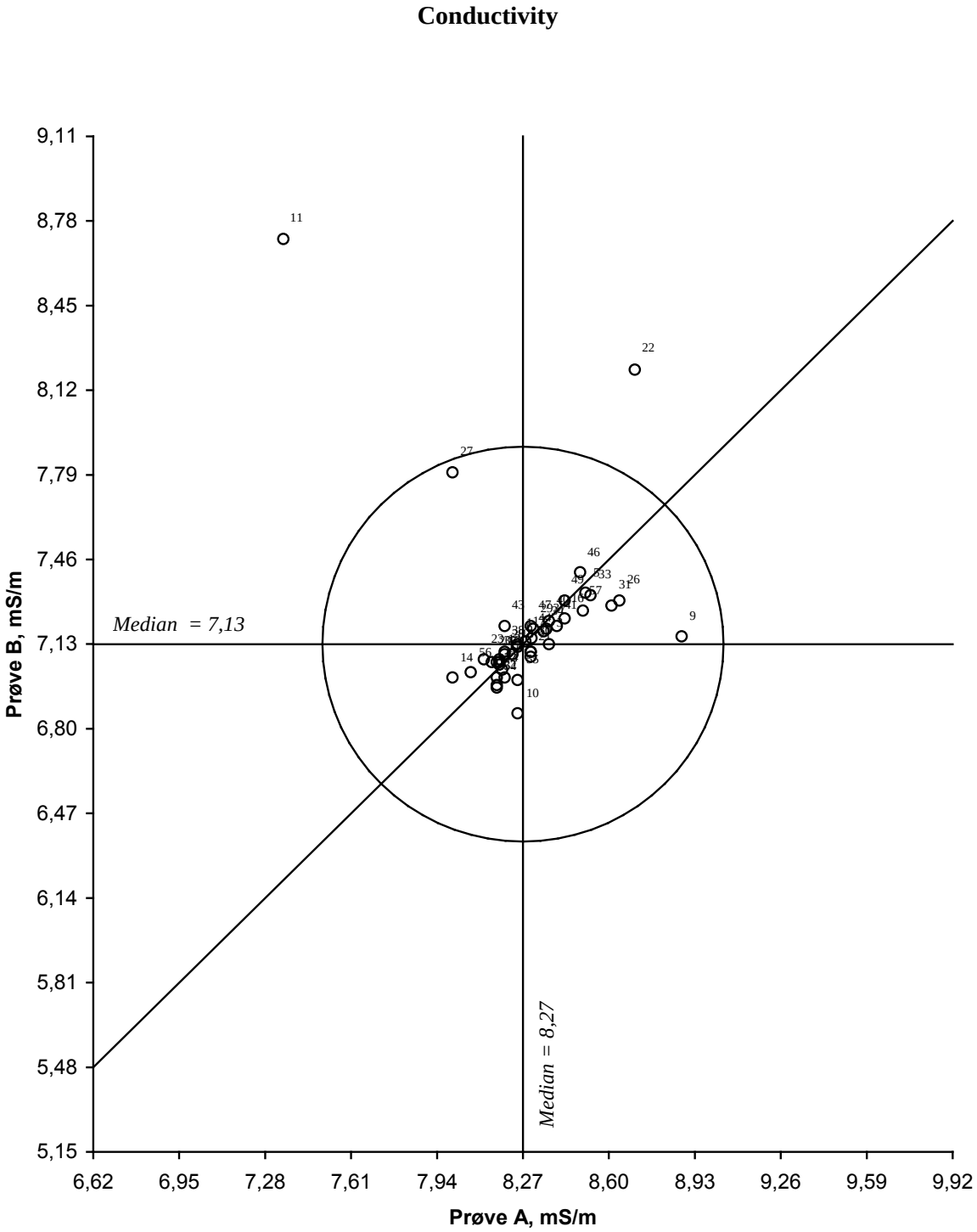

Figure 2. Youdendiagram for conductivity, Samplepair AB
Acceptable limit , given by circle, is 10 %

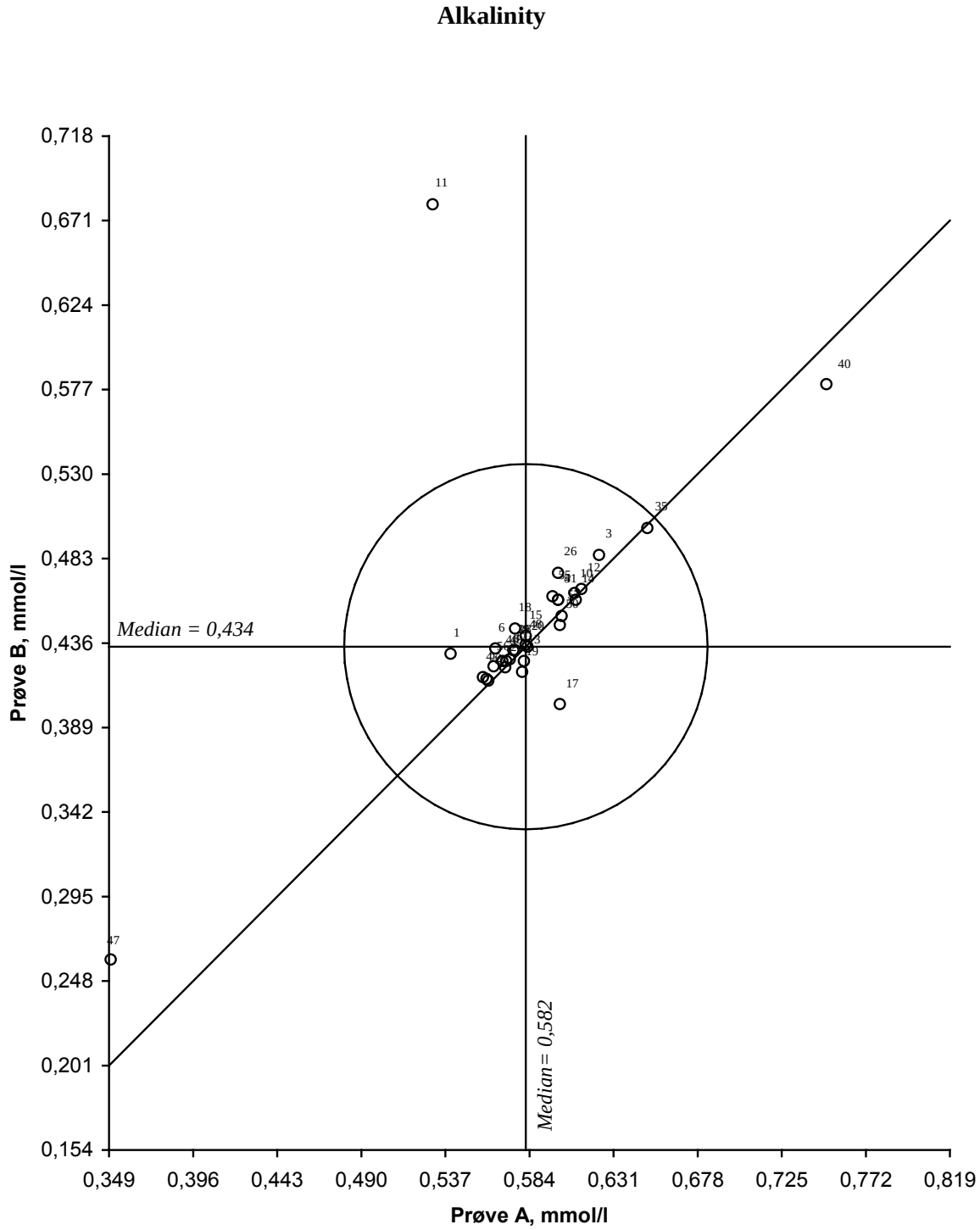

Figure 3. Youdendiagram for alkalinity, Samplepair AB
Acceptable limit , given by circle, is 20 %

Chloride

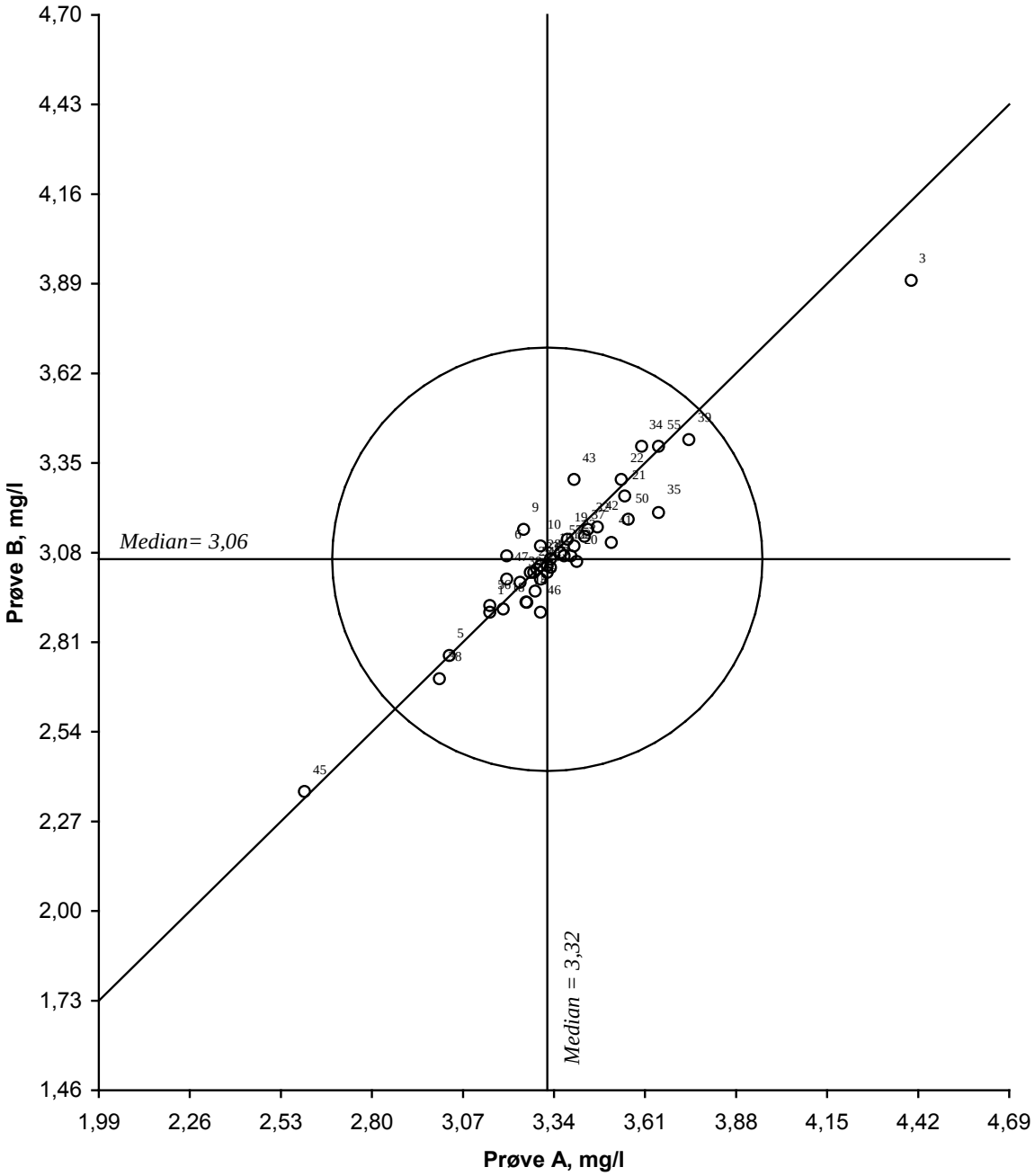

Figure 4. Youdendiagram for chloride, Samplepair AB
Acceptable limit , given by circle, is 20 %

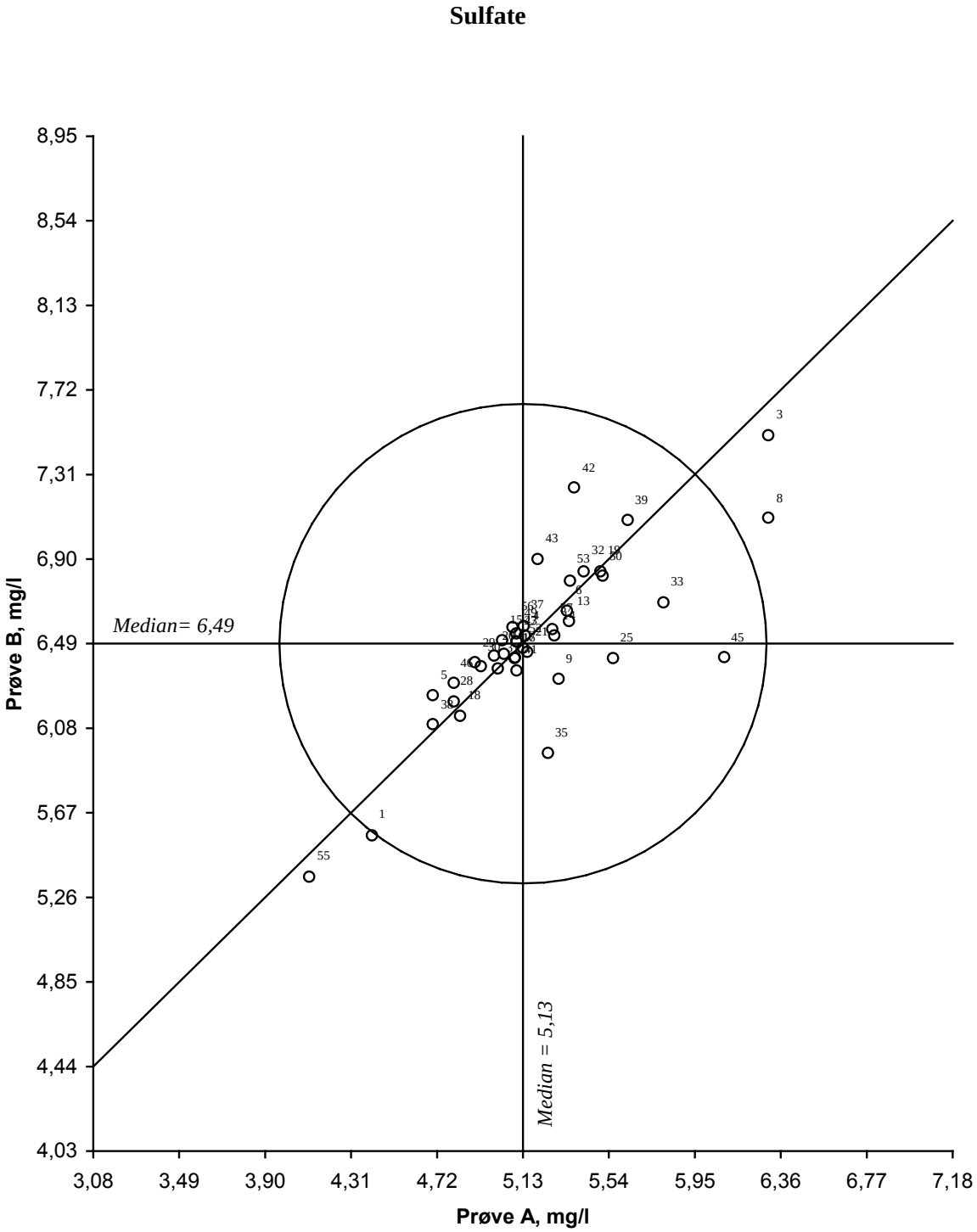

Figure 5. Youdendiagram for sulfate, Samplepair AB
Acceptable limit , given by circle, is 20 %

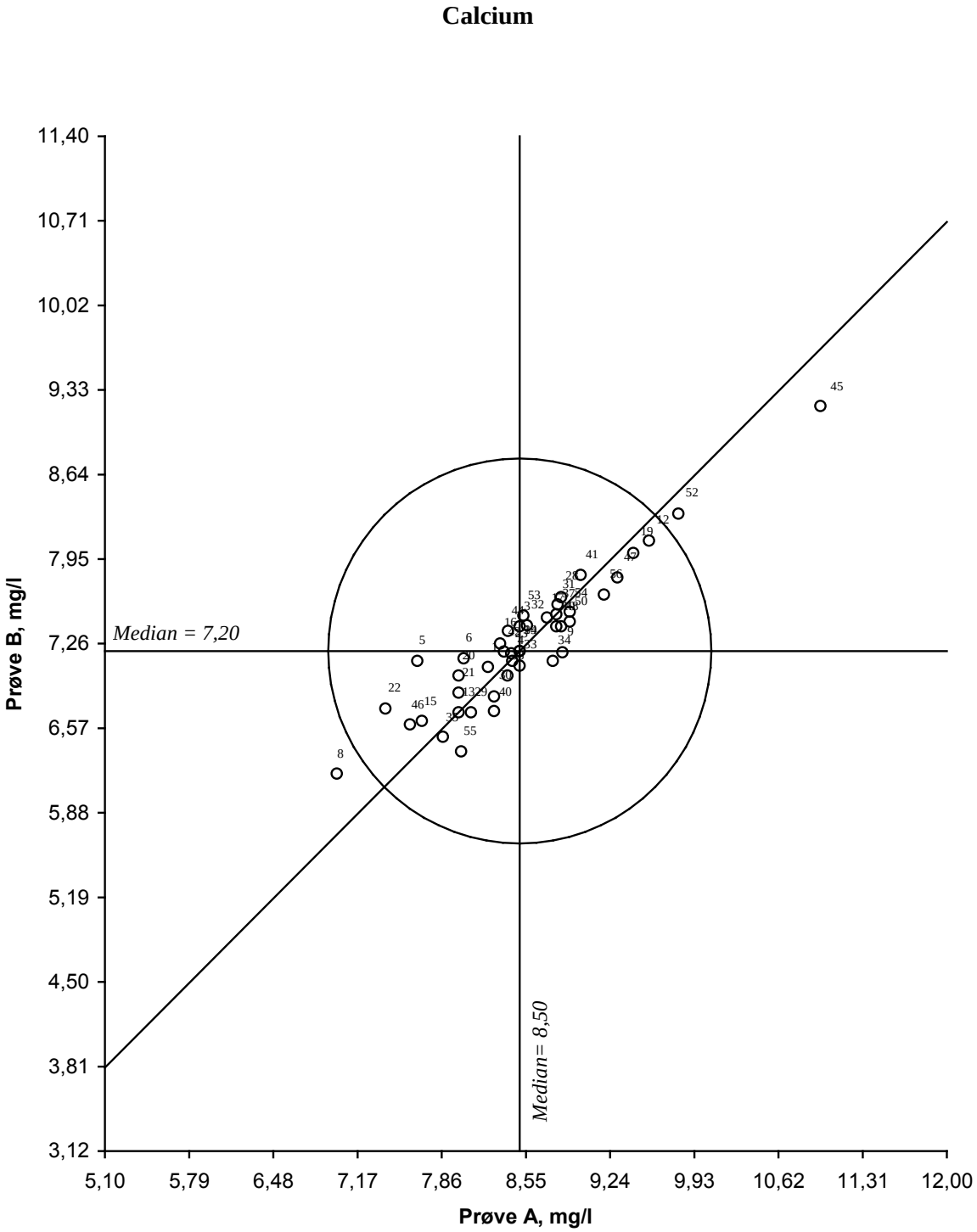

Figure 6. Youdendiagram for calcium, Samplepair AB
Acceptable limit , given by circle, is 20 %

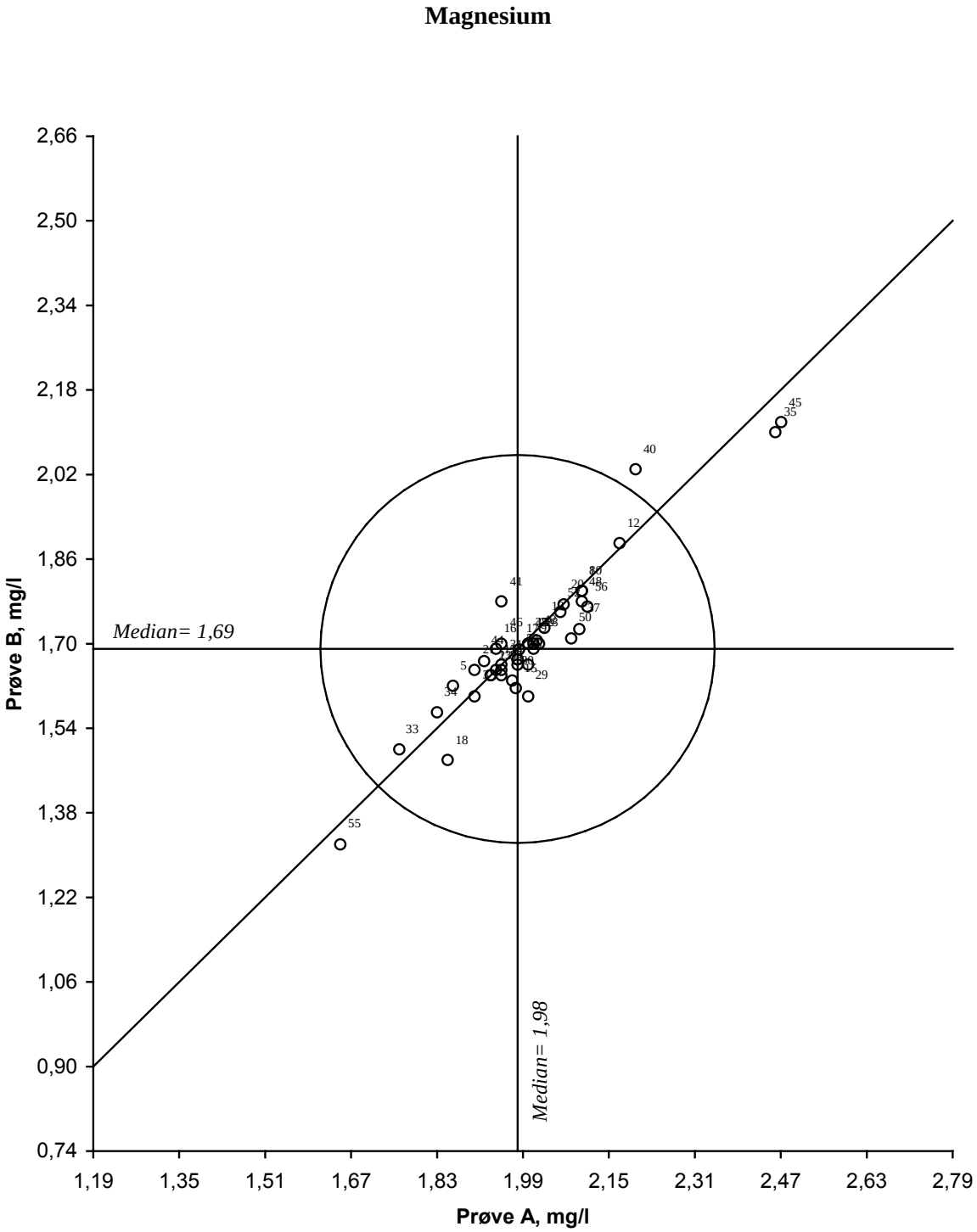

Figure 7. Youdendiagram for magnesium, Samplepair AB
Acceptable limit , given by circle, is 20 %

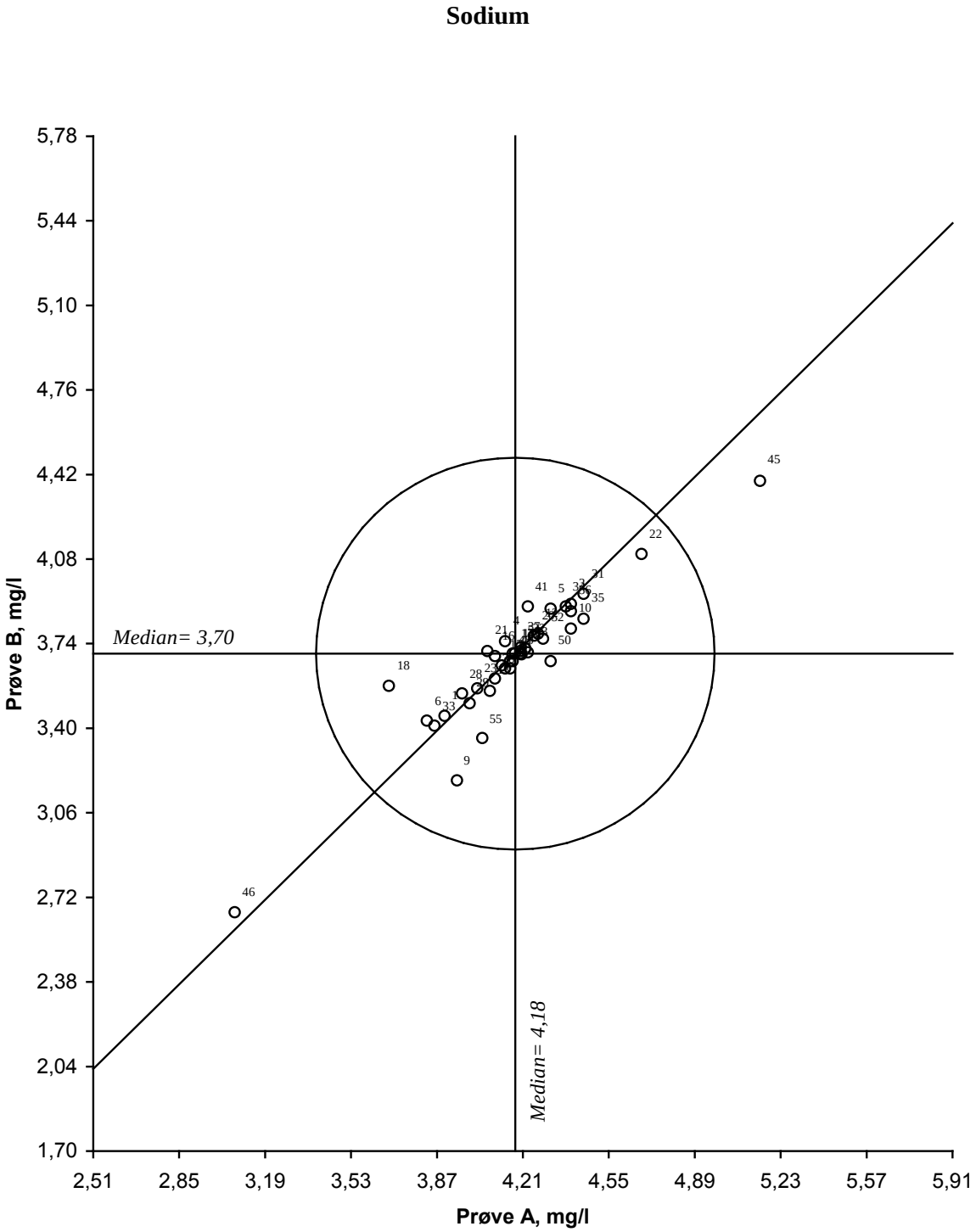

Figure 8. Youdendiagram for sodium, Samplepair AB
Acceptable limit , given by circle, is 20 %

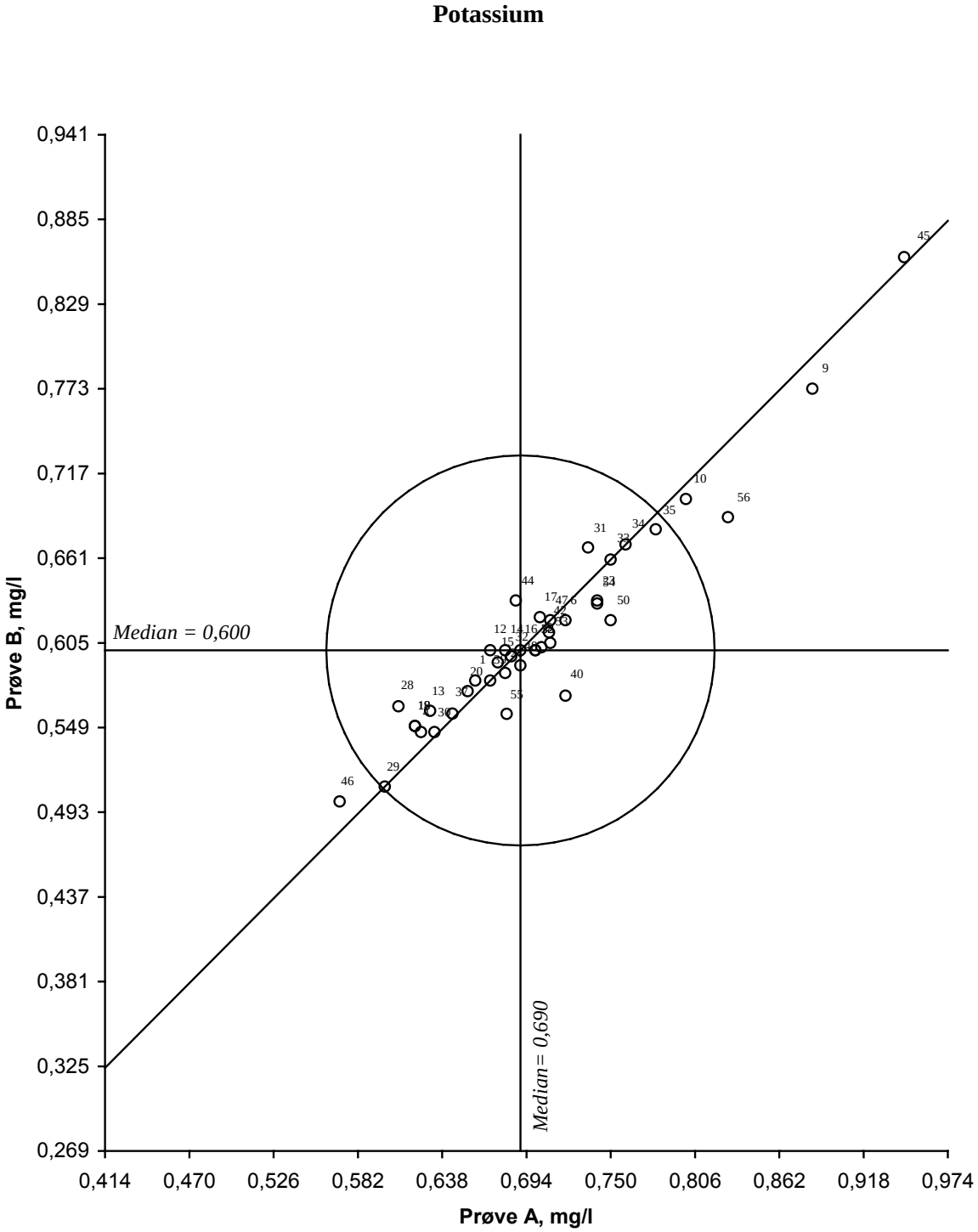

Figure 9. Youdendiagram for potassium, Samplepair AB
Acceptable limit , given by circle, is 20 %

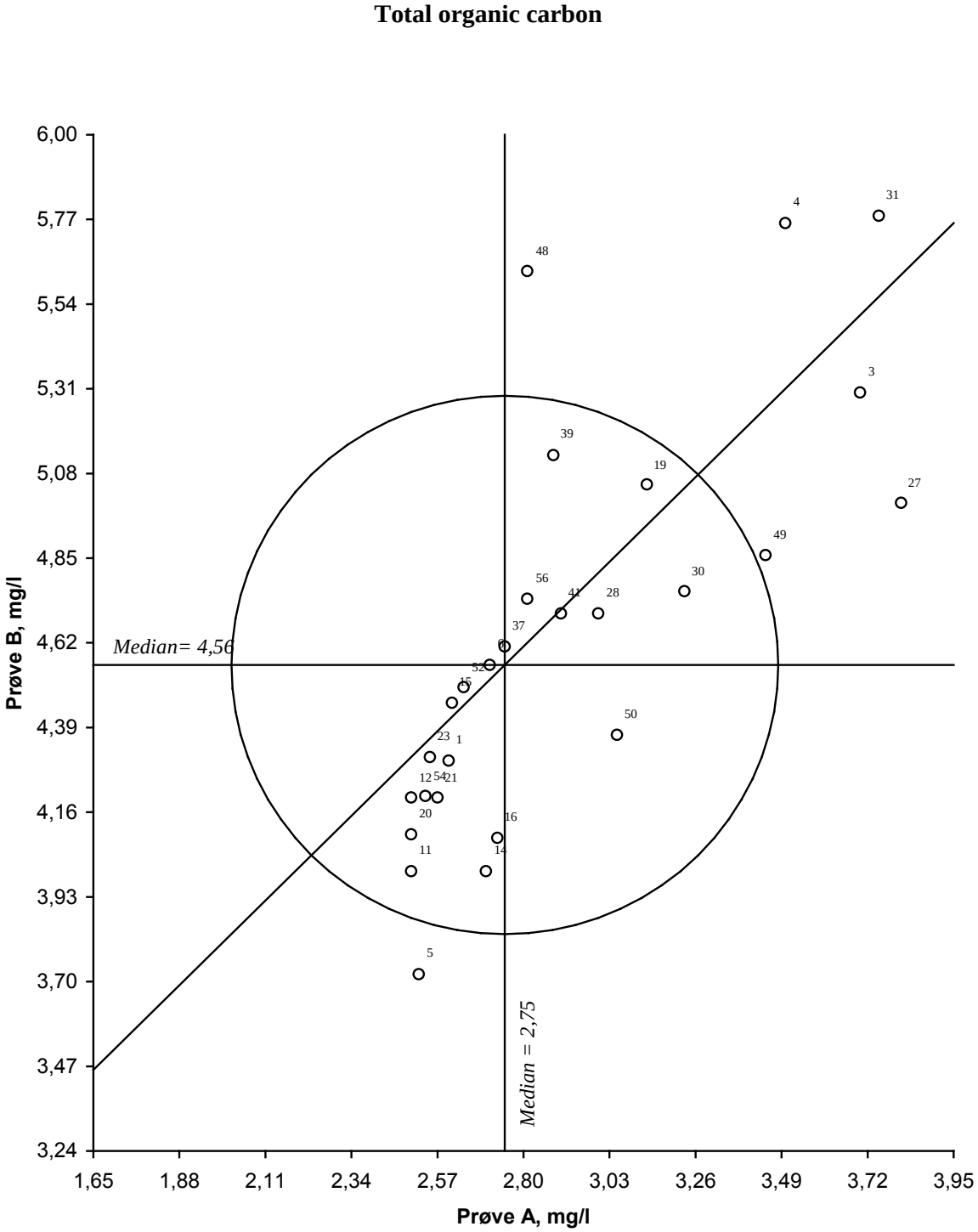

Figure 10. Youdendiagram for total organic carbon, Samplepair AB
Acceptable limit , given by circle, is 20 %

Aluminium

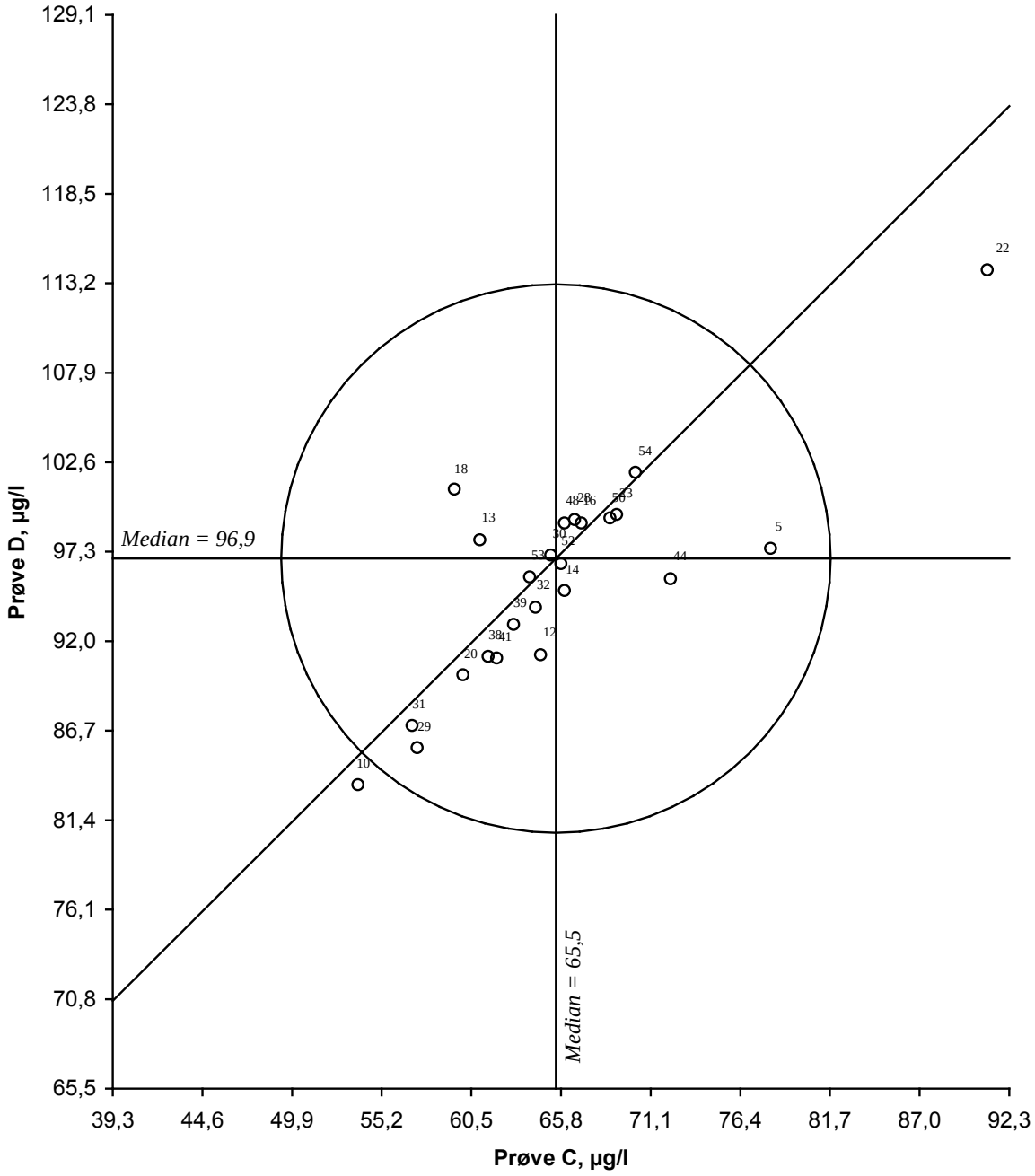

Figure 11. Youdendiagram for aluminium, Samplepair CD
Acceptable limit , given by circle, is 20 %

Iron

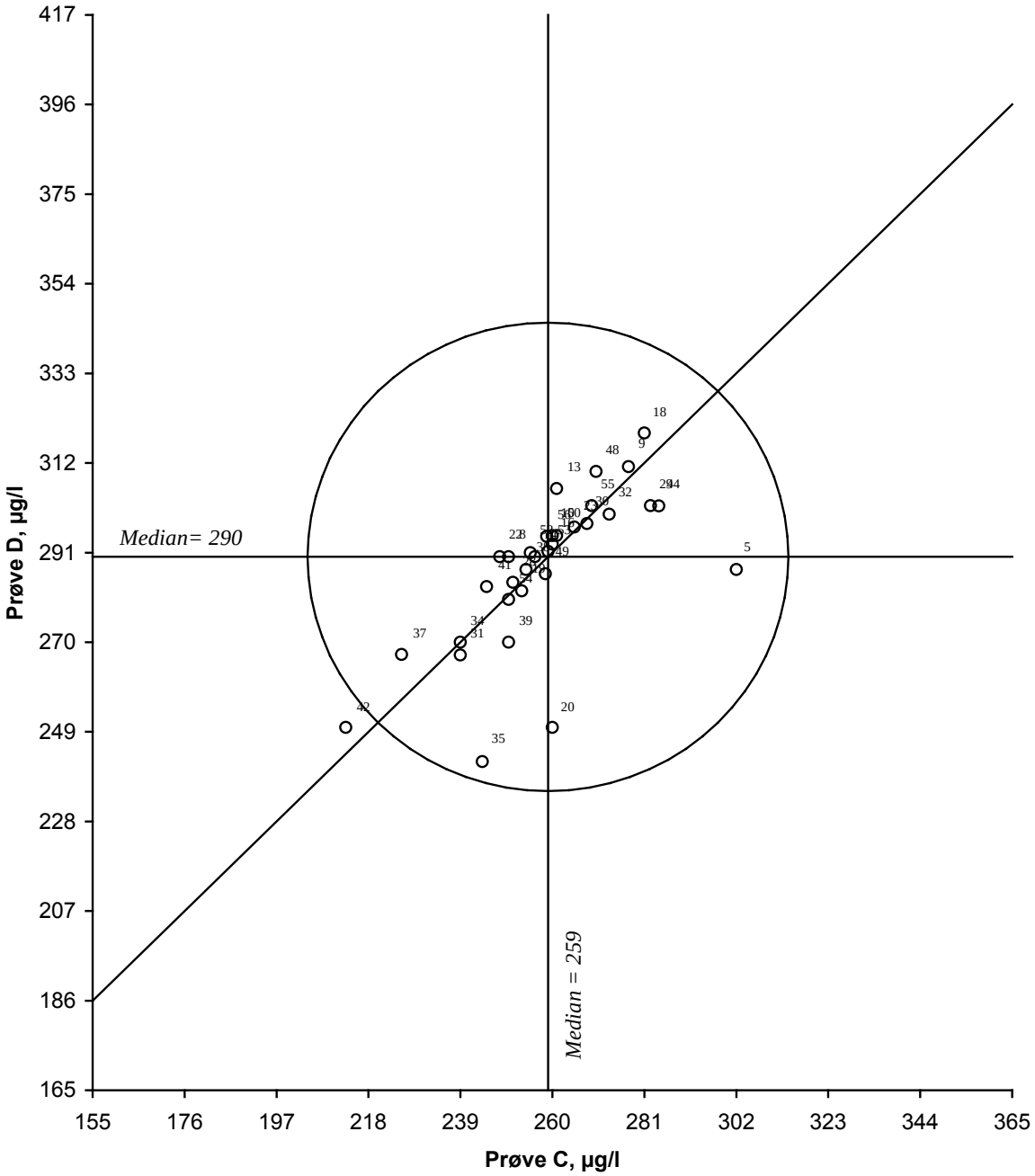

Figure 12. Youdendiagram for iron, Samplepair CD
Acceptable limit , given by circle, is 20 %

Manganese

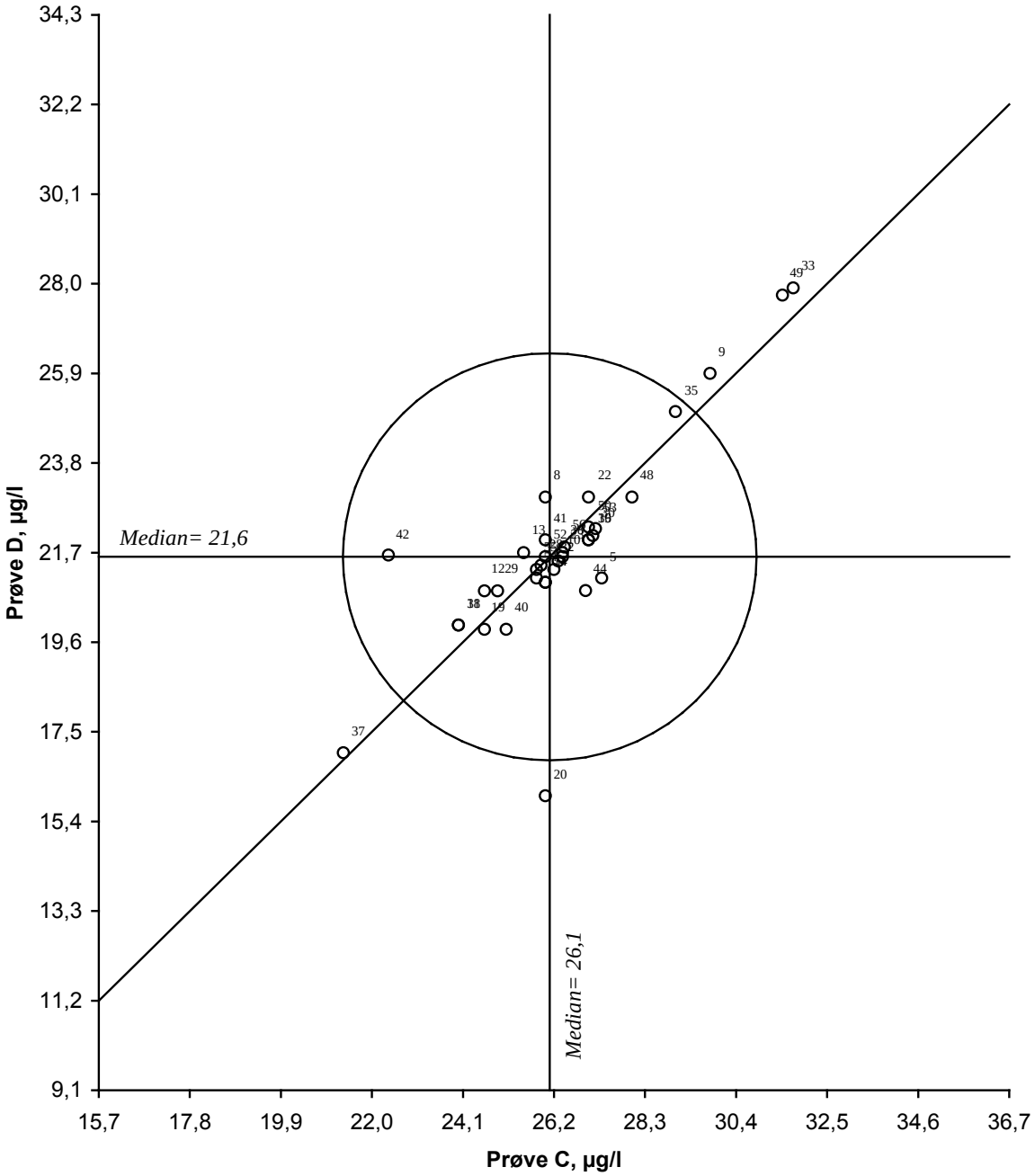

Figure 13. Youdendiagram for manganese, Samplepair CD
Acceptable limit , given by circle, is 20 %

Cadmium

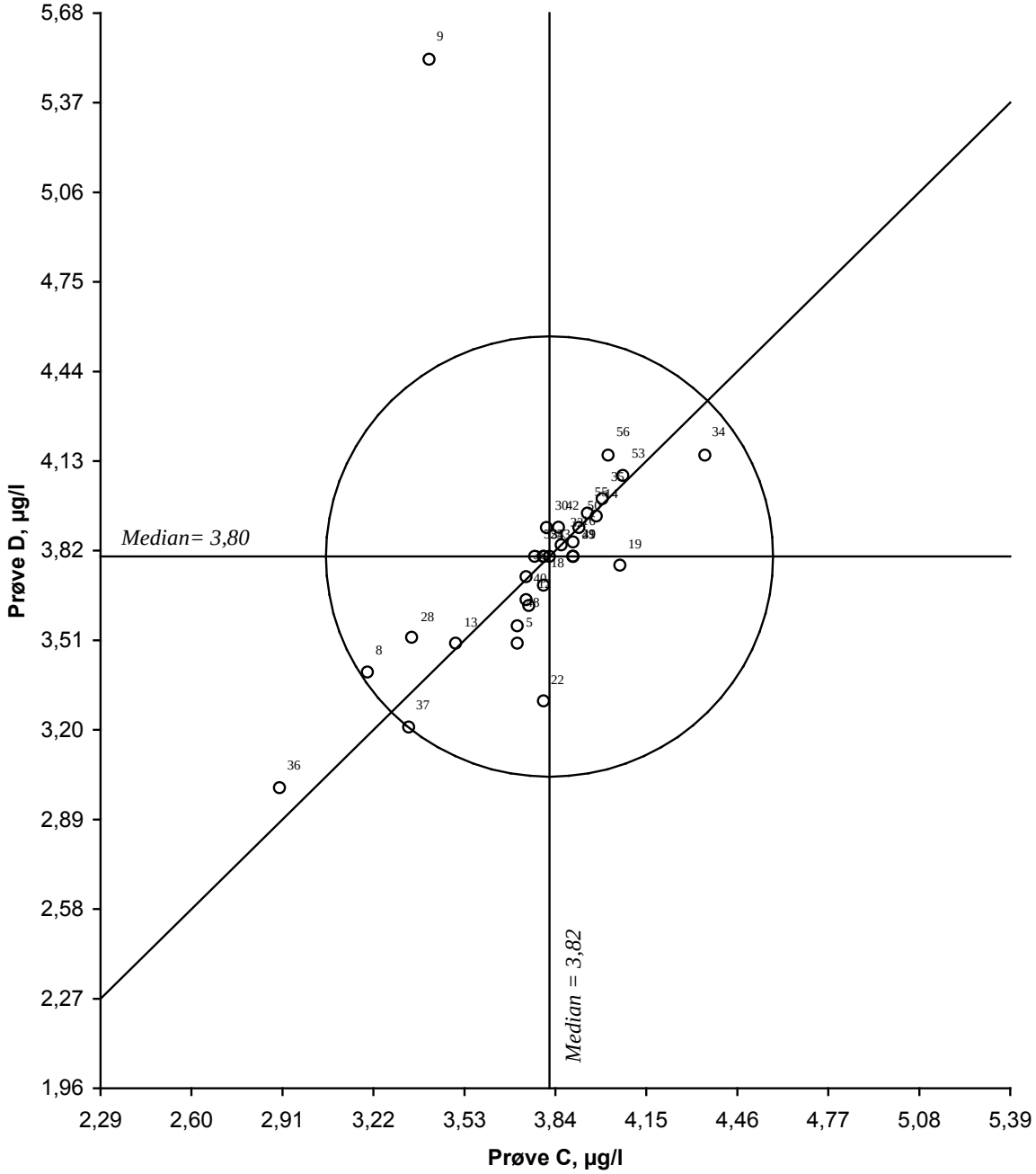

Figure 14. Youdendiagram for cadmium, Samplepair CD
Acceptable limit , given by circle, is 20 %

Lead

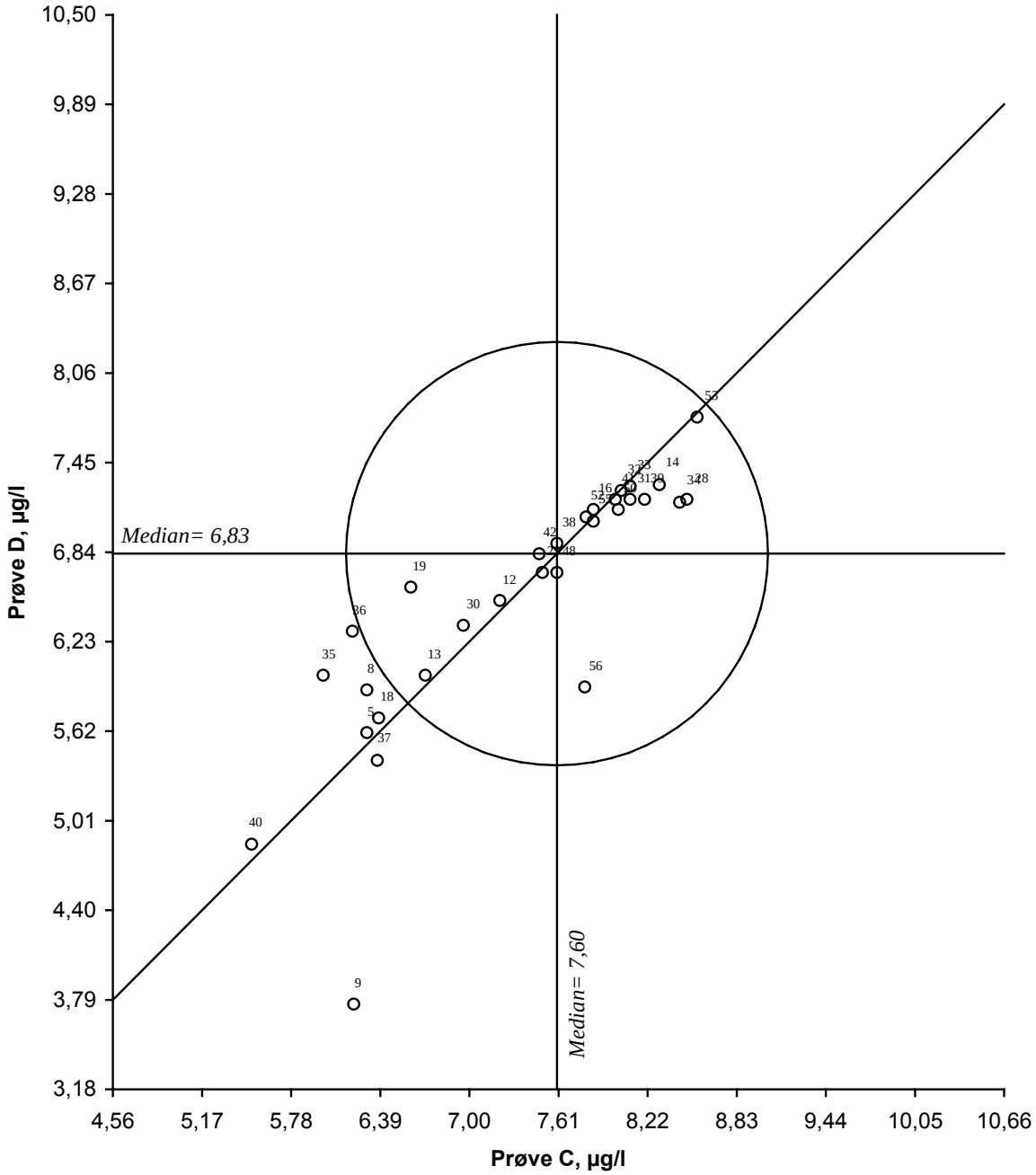

Figure 15. Youdendiagram for lead, Samplepair CD
Acceptable limit , given by circle, is 20 %

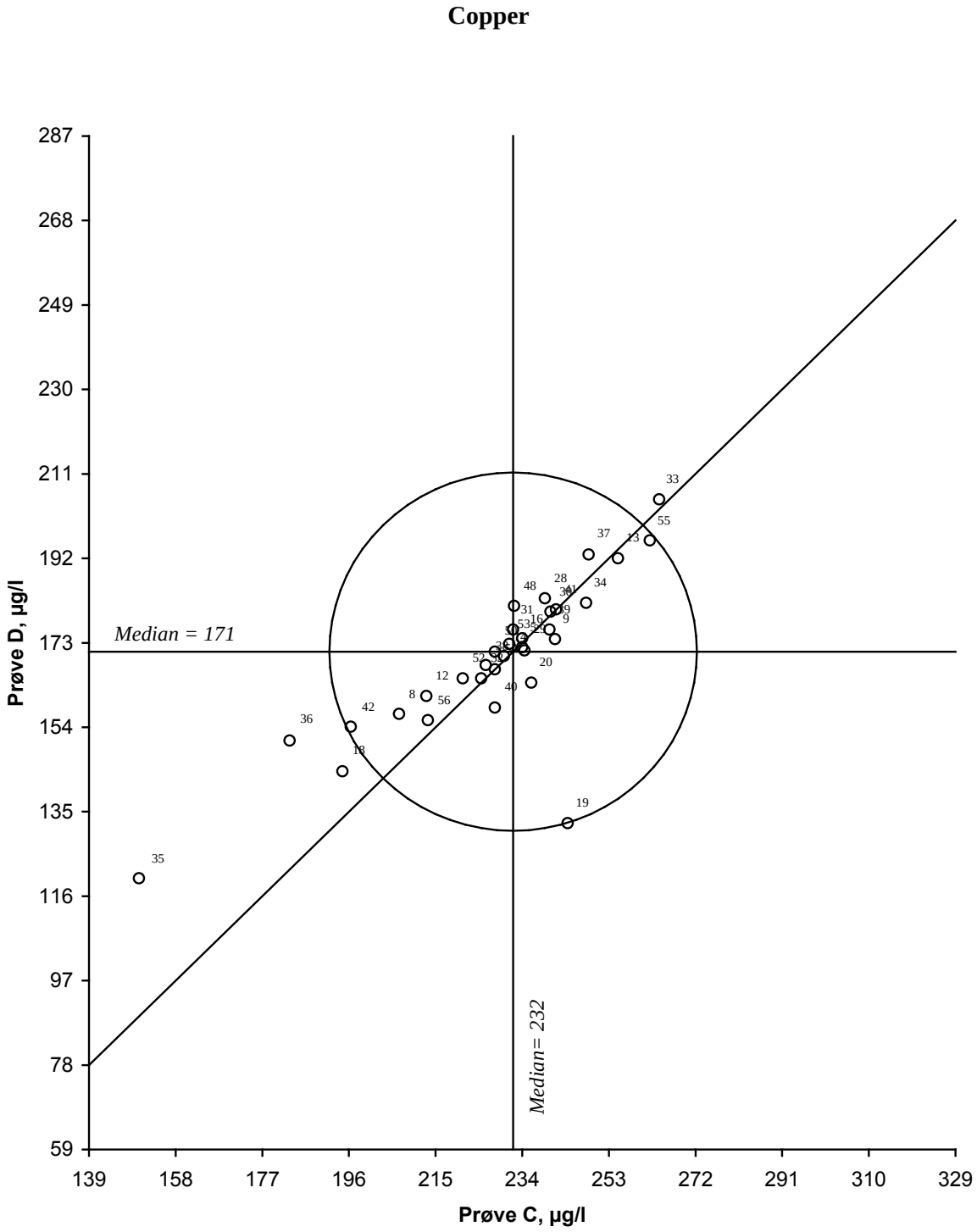

Figure 16. Youdendiagram for copper, Samplepair CD
Acceptable limit , given by circle, is 20 %

Nickel

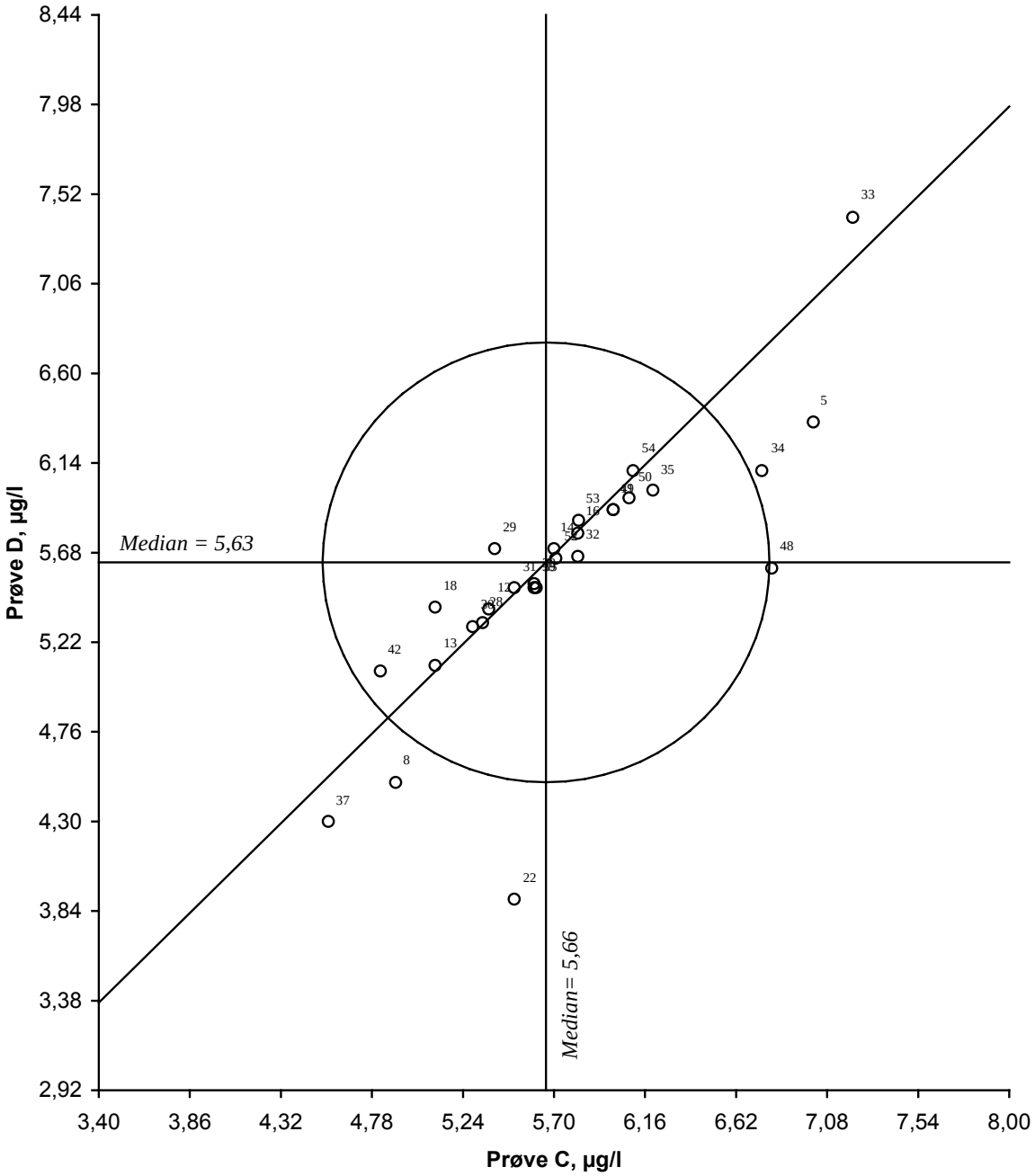

Figure 17. Youdendiagram for nickel, Samplepair CD
Acceptable limit , given by circle, is 20 %

Zinc

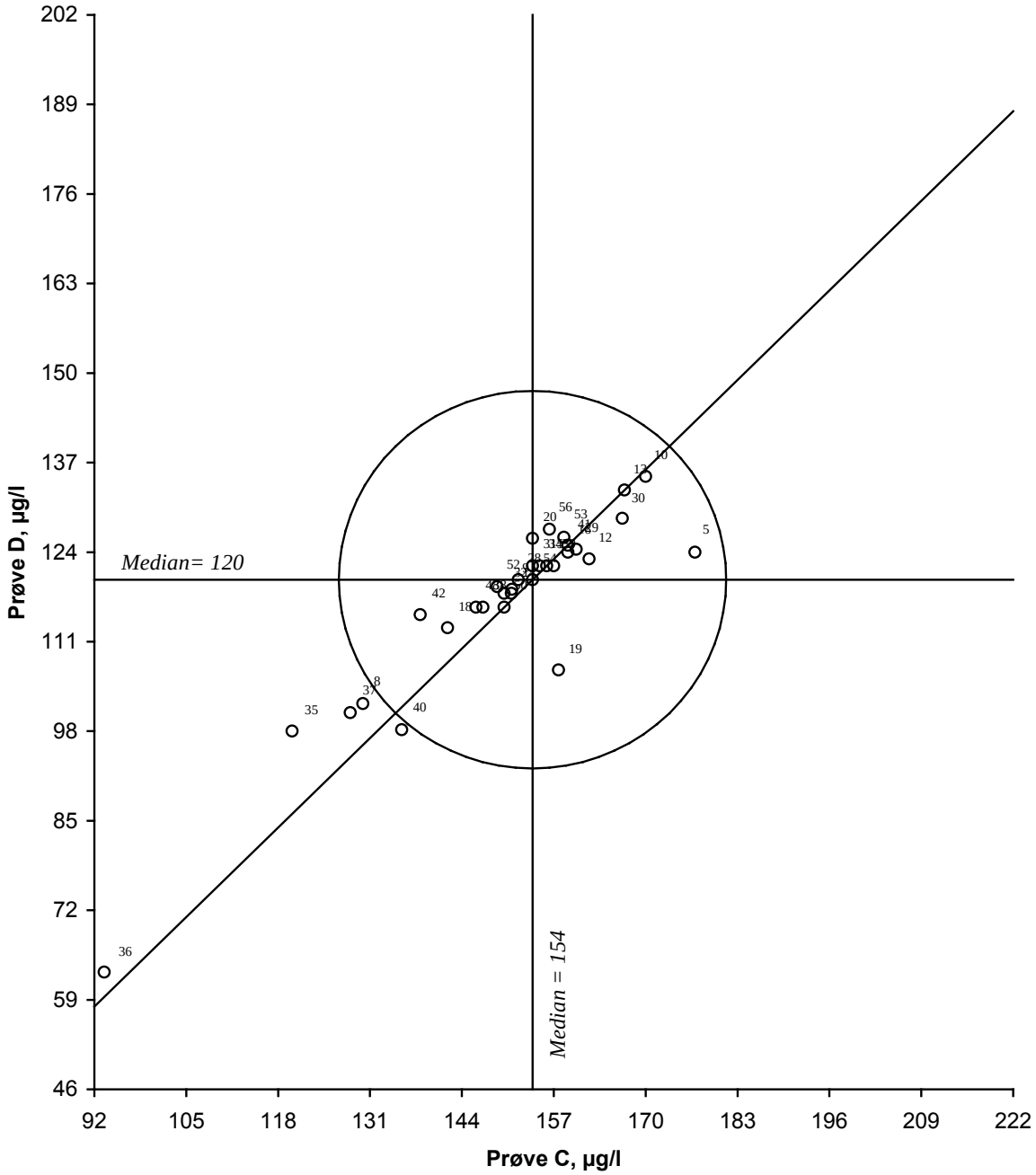

Figure 18. Youdendiagram for zinc, Samplepair CD
Acceptable limit , given by circle, is 20 %

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 correspond 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 1125 is presented with the number and percentage of acceptable results based on the target accuracy (except for pH and conductivity). 83 % of the results submitted by the participants are acceptable when compared to the acceptance limits given in Table 1. This is the highest percentage since these intercomparisons started.

In table 4 (page 47) the individual results of each laboratory are given. The results reported by the laboratory are printed as reported. Some laboratories use far more digits than are statistically significant. This is unnecessary, and each laboratory should determine how many digits are significant for each of their analytical methods. It is however acceptable to report results with one digit more than is statistically significant as this will reduce the round-off error in the statistical calculations.

For pH, the general target accuracy is ± 0,1 pH units (1), and only 47 % of the result pairs are found within these accuracy limits. However, conforming with last years practice, we have chosen to extend the acceptance limit to ± 0,2 pH units. With this wider acceptance limit 73 % of the result pairs are evaluated as acceptable this time. This is a lot better than last year when only 49 % were acceptable.

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 a problem as long as different methods, different working procedures and different instrumental equipment for pH determination are used by the participating laboratories.

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 of ± 20 % to ± 10 %. Even after this, the number of acceptable results for conductivity is as high as 86 % (Table 2). If we increase the acceptance limit to the target value, the number of acceptable results would increase even further. For this parameter, there is still a problem that some laboratories report their results in the units they normally use at their own laboratory instead of mS/m as asked for by the organizer.

Table 2. Evaluation of the results from intercomparison 1125. N is the number of result pairs reported, and n is the number of acceptable results within the given target accuracy.

Parameter and unit	Sample pair	True value 1	True value 2	Accept. limit %	Number of pairs N	Number of pairs n	% acceptable results for intercomparison 1125	1024	0923	0822
pH	AB	7,31	7,40	0,2 *	49	36	**73**	49	61	68
Conductivity, mS/m	AB	8,27	7,13	10 ¤	51	44	**86**	84	71	81
Alkalinity, mmol/l	AB	0,582	0,434	20	38	30	**79**	74	67	35
Nitrate + nitrite-N, µgl	AB	65,0	n.a.	20	43 #	32 #	**74** #	57	58	64
Chloride, mg/l	AB	3,32	3,06	20	46	41	**89**	79	86	85
Sulfate, mg/l	AB	5,13	6,49	20	44	38	**86**	73	77	84
Calcium, mg/l	AB	8,50	7,20	20	45	41	**91**	77	84	85
Magnesium, mg/l	AB	1,98	1,69	20	45	40	**89**	82	88	78
Sodium, mg/l	AB	4,18	3,70	20	43	41	**95**	93	88	91
Potassium, mg/l	AB	0,690	0,600	20	44	36	**82**	82	75	65
Total organic C, mg/l	AB	2,75	4,56	20	29	20	**69**	83	82	-
Aluminium, µg/l	CD	65,5	96,9	20	29	22	**76**	77	77	-
Iron, µg/l	CD	259	290	20	35	32	**91**	81	73	83
Manganese, µg/l	CD	26,1	21,6	20	37	32	**86**	85	67	40
Cadmium, µg/l	CD	3,82	3,80	20	32	30	**94**	88	79	80
Lead, µg/l	CD	7,60	6,83	20	33	22	**67**	73	74	67
Copper, µg/l	CD	232	171	20	35	27	**77**	51	37	20
Nickel, µg/l	CD	5,66	5,63	20	29	21	**72**	66	85	54
Zinc, µg/l	CD	154	120	20	34	27	**79**	82	90	62
Total					741	612	**83**	75	75	69

* The accepatble limit is extended from the target value of ± 0,1 to ± 0,2 pH units
¤ The accepatble limit is reduced from the target value of ± 20 % to ± 10 %
The figures correspond to sample 1 in the sample pair

For alkalinity, as we have observed earlier, the reported results for solutions with low alkalinity values are much more widely spread than solutions with higher concentrations of bicarbonate. The number of acceptable results in this intercomparison was as high as 79 %, and a possible explanation for this may be the rather high concentrations of bicarbonate in the two samples this time.

For nitrate, only 57 % of the result pairs are acceptable. This is too low, and may perhaps be caused by some unstability for this parameter during transport of the samples. Control analyses at the Programme Centre demonstrated that the samples were not stable enough with respect to the content of nitrate, throughout the whole periode of the intercomparison. Also, some participants pointed out that they observed a certain unstability 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. For most of these parameters the results are in fact the best for many years. Total organic carbon, however, had only 69 % acceptable results which is significantly lower than for the two previous intercomparisons.

The best results for heavy metals included in this intercomparison programme were obtained for cadmium and iron where 94 % and 91 % of the results, respectively, are 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 at the trace level.

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

4. Conclusion

57 laboratories submitted results for this intercomparison. The best results were reported for the analytical variables sodium, cadmium, calcium and iron where 95, 94, 91 and 91 % of the results, respectively, were acceptable. The worst results were observed for lead and total organic carbon with only 67 % and 72 %, respectively, acceptable results.

In this intecomparison 83 % of the evaluated results were located within the general target accuracy of ± 20 %, or the special accuracy limit for pH and conductivity (± 0,2 pH units and ± 10 % respectively).. This is the highest percentage acetable results ever since the start of these intercomparisons. The low fraction of acceptable results for some variables may be explained by the rather low concentrations used for these analytical variables and in some cases that the samples were not stable enough. When the concentrations are close to the detection limits for some of the methods used by the participants, it must be expected that the spread of the results will be greater than ± 20 %.

The laboratories which reported results outside this limit should improve their methods to obtain a better accuracy and comparability. Generally, the application of some analytical methods seem 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 obviously report their results in units other than those reguested.

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

Considering the determination of metals in these samples, it is quite clear that the plasma techniques (ICP-AES and ICP-MS) are taking over for atomic absorption methods, which were the dominating methods some years ago. For the major ions, the ion chromatography technique is also clearly growing ahead 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 was far too big of a difference between the concentrations of the two samples for nitrate to use the Youden technique.

5. Literature

1. ICP Waters Programme Centre 2010. ICP Waters Programme manual. ICP Waters report 105/2010. NIVA SNO 6074-2010. 91s.
2. Youden, W.J.: Graphical Diagnosis of Interlaboratory Test Results. Industrial Quality Control. 1959, pp 15 - 24.
3. Youden, W.J., Steiner, E.H.: Statistical Manual of the Association of Official Analytical Chemists. Statistical Techniques for Collaborative Tests. Arlington, 1975.
4. Hindar, A.: The Effect of Stirring on pH Readings in Solutions of Low and High Ionic Strength Measured with Electrodes of Different Condition. Vatten 1984, 40, pp 312 - 19 (in norwegian).
5. Galloway, J.N., Cosby, B.T., Likens, G.E.: Acid Precipitation: Measurement of pH and Alkalinity. Limnol. Oceanogr. 1979, 24, 1161.
6. ISO 13528 (2005).: Statistical methods for use in proficiency testing by interlaboratory comparisons.

Appendix A.

The participating laboratories

No.	Laboratory	Town	Country
1	Institute of Hydrobiology, ASCR	Budejovice	Czech Republic
2	ITMm Stockholm University	Stockholm	Sweden
3	Staatliche Umweltbetriebgesellschaft im UBG	Chemnitz	Germany
4	Freshwater Laboratory	Pitlochry	Scotland
5	T.G.Masaryk Water Research Institute	Prague	Czech Republic
6	Laboratorio Biologico Provinciale	Laives	Italy
7	Environmental Laboratory	Obuasi	Ghana
8	Test Laboratory of Water Quality	Petrozavodsk	Russia
9	Polish Academy of Sciences, Institute of botany	Krakow	Poland
10	SLU, Skoglig Marklæra	Uppsala	Sweden
11	Marklaboratoriet, mv-huset	Uppsala	Sweden
12	Norwegian Institute for Water Research	Oslo	Norway
13	CNR Istituto Studio degli Ecosistemi	Pallanza	Italy
14	ZAO "ROSSA"35-7 Rodnikovaya	Moscow	Russia
15	Adirondac Lakes Survey Corporation	Ray Brook	USA
16	Bayerische Landesamt fur Umwelt	Munchen	Germany
17	Institut fur Zologie, Universitat Innsbruck	Innsbruck	Austria
18	Environmental Pollution Center	Murmansk	Russia
19	Laboratorio Spaas	Bellinzona	Switzerland
20	Centre National de la Recherche Scientifique	Strasbourg	France
21	MOEE, Toronto Laboratory	Etobicoke/Toronto	Canada
22	Laboratory for Monitoring of Atmosphere	Vladivostok	Russia
23	University of Maine. Sawyer Environmental Research Center	Orono	USA
24	Aquatic Chemistry Project, Freshwater Institute	Winnipeg	Canada
25	Institute of Environmental Protection	Warsaw	Poland
26	Laboratory of Hydrochemistry, Vortsjarv	Tartu	Estonia
27	River Biology Laboratory of the EAU Institute	Tartu	Estonia
28	Tartun Environmental Research	Tartu	Estonia
29	Faculty of Applied Science UiTM	Shah Alam	Malaysia
30	Environmental Protection Ministry. Joint Research Centre	Vilnius	Lithuania
31	Bayerische Landesanstalt fur Walt und F.	Freising	Germany
32	University of Helsinki	Helsinki	Finland
33	Institute of Environmental Engineering. Polish Academy of Science	Zabrze	Poland
34	FGU «Baltwodhoz»	St. Petersburg	Russia
35	Hydrochemical Laboratory by Federal State Enterprise on Water Industry	Pskov	Russia
36	Institute of Global Climate and Ecology. USSR Academy of Sciences	Moscow	Russia

No.	Laboratory	Town	Country
37	ISSeP Colfontaine	Wasmes	Belgium
38	Environmental Protection Agency. Richview	Dublin	Ireland
39	Latvian Environmental Laboratory	Riga	Latvia
40	Geological Survey of Estonia	Tallin	Estonia
41	Amt der Karntner Landesregierung	Klagenfurt	Austria
42	Vlaamse MilieuMaatschappij (VMM)	Antwerpen	Belgium
43	North Ostrobothnia Regional Env. Centre	Oulo	Finland
44	Soil Science of Temperate and Boreal syst.	Goettingen	Germany
45	Laboratorio do aguas de Santo Andre	Santo Andre	Portugal
46	Charles University, Hydrobiol. Station	Blatna	Czech Republic
47	IVL AB	Gothenburg	Sweden
48	Chemical Laboratory of CGS	Praha	Czech Republic
49	Finnish Forest Research Institute	Rovaniemi	Finland
50	Finnish Environment Institute. Research Laboratory	Helsinki	Finland
51	Institute of Environmental Protection	Warzaw	Poland
52	Shimane Prefectural Inst. Of Public Health	Shimane	Japan
53	Environment Agency, Starcross Laboratory	Exeter	England
54	Finnish Forest Research Institute	Vantaa	Finland
55	University of Navarra. Laboratorio Integrado de Calidad Ambiental	Pamplona	Spain
56	Institute for Ecology of Industrial Areas	Katowice	Poland
57	CMI, Lab of Water and Waste Water Anal.	Katowice	Poland

Number of participating laboratories from the different countries represented in intercomparison 1125

Country	No. of labs.	Country	No. of labs.	Country	No. of labs.
Austria	2	Ireland	1	Russia	7
Belgium	2	Italy	2	Scotland	1
Canada	2	Japan	1	Spain	1
Czech Republic	4	Latvia	1	Sweden	4
Estonia	4	Lithuania	1	Switzerland	1
Finland	5	Malaysia	1	England	1
France	1	Norway	1	USA	2
Germany	4	Poland	6		
Ghana	1	Portugal	1		
				Number of countries	25

Appendix B.

Preparation of samples

The sample solutions were prepared from water collected from two locations outside Oslo, Norway, one river called Kvisla and one little lake called Ila. 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, the filtrate collected in polyethylene containers, and then stored at room temperature at the laboratory for several weeks 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.

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 represens 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 centre at the intersection of the two straight lines in the diagram (true or median values). The distance between the centre 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 gives the magnitude of the systematic error, while the distance perpendicular to the 45 ° line indicates 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 discover 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 lie outside the true value ± 50 %, are omitted from the statistical calculations. The remaining results are used for the calculation of the mean value (x) and the standard deviation (s). Now the pairs of results where both of the values are lying outside $x \pm 3s$, are omitted. The remaining results are used for a final calculation, the results of which are presented in the tables 5.1 - 5.19. Results being omitted from the calculations are marked with the letter "U".

Estimation of uncertainty of the true values

The median value of the reported results, after exclusion of strongly deviating results, is used as the true value for this intercomparison. Thus the true value is based upon concensus value from the participants, and therefore the estimation of the uncertainty of the true value could be based on the method given in ISO 13528 (2005), Annex C (algorithm A).

For each parameter the median value is determined and an initial value for the robust standard deviation is calculated from the absolute differences between the median value and the result of each participating laboratory according to:

$S^* = 1{,}483 \times$ the median of $|x_i - m|$ $(i = 1, 2 \ldots. p)$

New value for the robust standard deviation is then calculated according to equations C.3-C6 in Annex C. The robust standard deviation is then derived by an interative calculation by updating the values several times using the modified data, until the process converges.

The uncertainty u_X of the assigned value for the true value is then calculated according to chapter 5.6 in ISO 13528:

$$u_X = 1{,}25 x S^* / \sqrt{p}$$

For the estimation of expanded uncertainty U, a coverage factor of two is used:

$U = 2 \times u_X$

It is important to know that there are some limitations in this approach for the estimation of the uncertainty of the true value:

- There may be no real consensus among the participants
- The concensus may be biased by the general use of faulty methodology and this bias will not be reflected in the standard uncertainty of the assigned value using this calculation.

Table 3. Estimation of uncertainty of the assigned true values for

Parameter and unit	Sample	True value	Total no.	Robust std.dev.	Uncertainty	Expanded uncertainty
pH	A	7,31	49	0,155	0,028	0,055
	B	7,40	49	0,131	0,023	0,047
Cond	A	8,27	51	0,228	0,040	0,080
mg/l	B	7,13	51	0,182	0,032	0,064
Alk	A	0,582	38	0,0360	0,0073	0,0146
mmol/l	B	0,434	38	0,0381	0,0077	0,0154
(NO3+NO2)-N	A	65,0	43	25,44	4,85	9,70
µg/l	B	n.a				
Cl	A	3,32	46	0,184	0,034	0,068
mg/l	B	3,06	46	0,182	0,034	0,067
SO4	A	5,13	44	0,355	0,067	0,134
mg/l	B	6,49	44	0,312	0,059	0,117
Ca	A	8,50	45	0,594	0,111	0,221
mg/l	B	7,20	45	0,490	0,091	0,182
Mg	A	1,98	45	0,101	0,019	0,038
mg/l	B	1,69	45	0,088	0,016	0,033
Na	A	4,18	43	0,191	0,036	0,073
mg/l	B	3,70	43	0,172	0,033	0,066
K	A	0,690	44	0,0667	0,0126	0,0251
mg/l	B	0,600	44	0,0587	0,0111	0,0221
TOC	A	2,75	29	0,492	0,114	0,228
mg/l	B	4,56	29	0,570	0,132	0,264
Al	C	65,5	29	9,73	2,26	4,52
µg/l	D	96,9	29	9,07	2,11	4,21
Fe	C	259	35	17,0	3,6	7,2
µg/l	D	290	35	18,4	3,9	7,8
Mn	C	26,1	37	1,55	0,32	0,64
µg/l	D	21,6	37	1,35	0,28	0,56
Cd	C	3,82	32	0,208	0,046	0,092
µg/l	D	3,80	32	0,258	0,057	0,114
Pb	C	7,60	33	1,096	0,238	0,477
µg/l	D	6,83	33	0,871	0,190	0,379
Cu	C	232	35	22,1	4,7	9,4
µg/l	D	171	35	18,4	3,9	7,8
Ni	C	5,66	29	0,636	0,148	0,295
µg/l	D	5,63	29	0,489	0,114	0,227
Zn	C	154	34	13,7	2,9	5,9
µg/l	D	120	34	11,0	2,4	4,7

n.a.: not assigned

Appendix D

Table 4. The results of the participating laboratories.

Lab.	pH		Conductivity, mS/m		Alkalinity, mmol/l		Nitrate-N, µg/l	
no.	A	B	A	B	A	B	A	B
1	7,45	7,40	8,25	7,13	0,540	0,430	71,00	7,00
2					0,571	0,423		
3	7,32	7,36	8,37	7,13	0,623	0,485	110,00	0,00
4	7,46	7,50	8,20	7,00	0,558	0,417	42,28	0,00
5	7,32	7,35	8,51	7,33	0,600	0,460	77,00	22,60
6	7,30	7,40	8,25	7,12	0,565	0,433	15,00	0,00
7	6,81	6,95	12,00	8,00	76,000	77,000		
8	7,13	7,30	0,00	0,00	0,860	0,660		
9	7,21	7,42	8,88	7,16			44,58	0,00
10	7,34	7,44	8,25	6,86	0,609	0,464		
11	7,28	7,17	7,35	8,71	0,530	0,680	62,00	6,00
12	7,64	7,65	8,18	7,06	0,613	0,466	66,00	1,00
13	7,22	7,40	8,18	7,07	0,581	0,426	30,00	5,00
14	7,48	7,36	8,00	7,00	0,610	0,460	30,60	2,20
15	7,35	7,50	822,50	704,80	0,582	0,440	68,11	5,44
16	7,23	7,41	8,43	7,23				
17	7,08	7,22	8,28	7,14	0,601	0,402	36,00	4,00
18	7,30	7,21	8,23	7,09	0,576	0,444	83,10	9,73
19	7,46	7,46	8,18	7,05	0,580	0,420	50,00	10,00
20	7,20	7,27	8,15	7,06	0,583	0,434	56,00	13,00
21	7,15	7,20	8,30	7,08	0,279	0,208	76,00	10,00
22	7,42	7,53	8,70	8,20	0,560	0,416	1420,00	13,00
23	7,38	7,32	8,12	7,07			38,00	5,00
24							46,00	1,00
25							344,00	200,00
26	7,42	7,45	8,64	7,30	0,600	0,475	66,00	5,00
27	7,28	7,48	8,00	7,80			59,00	2,00
28	7,34	7,46	8,20	7,09	0,576	0,432	73,00	11,00
29	7,22	7,36	8,31	7,19				
30	7,42	7,42	8,30	7,10			77,00	11,00
31	7,41	7,43	8,61	7,28			84,90	34,50
32	7,45	7,34	8,17	6,97	0,573	0,427	84,00	22,00
33	6,70	6,97	8,53	7,32			350,00	74,00
34	7,33	7,48	8,35	7,18				
35	7,30	7,44	8330,00	7140,00	0,650	0,500	75,00	38,00
36								
37	7,36	7,52	8,36	7,19			64,18	2,06
38	7,10	7,20	8,20	7,10				
39	7,39	7,33	8,17	7,06	0,575	0,432	41,00	25,00
40	6,95	7,08	8,37	7,22	0,750	0,580		

Lab.	pH		Conductivity, mS/m		Alkalinity, mmol/l		Nitrate-N, µg/l	
no.	A	B	A	B	A	B	A	B
41	7,40	7,40	8,40	7,20	0,600	0,460	32,00	0,00
42	6,98	7,08	83,97	69,90			0,05	0,00
43	7,30	7,50	8,20	7,20	0,561	0,415	78,00	11,00
44			8,30	7,15				
45	7,10	7,30	84,05	72,30	310,000	240,000	64,90	1,56
46	7,30	7,34	8,49	7,41	0,569	0,426	0,07	0,00
47	7,40	7,50	8,30	7,20	0,350	0,260	60,00	0,00
48					0,582	0,435		
49	7,54	7,58	8,43	7,30	0,571	0,426	65,00	6,00
50	7,25	7,42	8,19	7,03	0,601	0,446	65,30	4,10
51	7,53	7,45	8,30	7,10				
52	7,25	7,38	8,17	7,00	0,292	0,220	184,00	156,00
53								
54			8,17	6,96			60,00	10,00
55	7,38	7,48	8,25	6,99	0,597	0,462	43,70	0,00
56	7,23	7,41	8,07	7,02	0,564	0,423	60,70	24,40
57	7,05	7,18	8,50	7,26	0,602	0,451	84,30	7,89

Lab.	Chloride, mg/l		Sulfate, mg/l		Calcium, mg/l		Magnesium, mg/l	
no.	A	B	A	B	A	B	A	B
1	3,15	2,90	4,41	5,56	8,24	7,07	1,93	1,64
2								
3	4,40	3,90	6,30	7,50	8,50	7,40	1,90	1,60
4	3,32	3,04	5,14	6,53	8,44	7,12	1,98	1,67
5	3,03	2,77	4,70	6,24	7,66	7,12	1,86	1,62
6	3,20	3,07	5,34	6,65	8,04	7,14	2,00	1,66
7								
8	4,80	5,10	6,30	7,10	7,00	6,20	2,10	1,80
9	3,25	3,15	5,30	6,32	8,85	7,19	2,01	1,69
10	3,30	3,10	1,80	2,30	8,80	7,40	2,10	1,80
11								
12	3,37	3,07	5,04	6,44	9,56	8,10	2,17	1,89
13	3,32	3,02	5,35	6,60	8,00	6,70	1,94	1,65
14	3,26	2,93	5,28	6,53	8,50	7,20	1,95	1,65
15	3,26	2,93	5,03	6,51	7,70	6,63	1,98	1,62
16	3,33	3,06	5,09	6,42	8,34	7,26	1,94	1,69
17	3,33	3,04	5,09	6,42	8,72	7,47	1,98	1,69
18	3,19	2,91	4,83	6,14	1,26	1,11	1,85	1,48
19	3,38	3,12	5,50	6,84	9,43	8,00	2,03	1,73
20	3,41	3,05	4,99	6,43	8,00	7,00	2,07	1,77
21	3,55	3,25	5,15	6,45	8,00	6,86	1,90	1,65
22	3,54	3,30	6,70	11,50	7,40	6,73	2,81	2,04
23	3,40	3,10	5,10	6,50	8,43	7,18	1,93	1,64
24								
25	3,27	3,02	5,56	6,42				
26								
27								
28	3,30	3,04	4,80	6,21	8,84	7,64	2,02	1,70
29	3,30	3,00	4,90	6,40	8,10	6,70	2,00	1,60
30	3,24	2,99	4,93	6,38	8,29	6,83	1,97	1,63
31	3,28	3,02	5,01	6,37	8,81	7,58	1,95	1,66
32	3,44	3,15	5,42	6,84	8,56	7,41	2,01	1,70
33	3,29	3,03	5,80	6,69	8,50	7,08	1,76	1,50
34	3,60	3,40			8,77	7,12	1,83	1,57
35	3,65	3,20	5,25	5,96	7,87	6,50	2,46	2,10
36								
37	3,43	3,13	5,13	6,58	8,80	7,50	2,09	1,73
38	3,00	2,70	4,70	6,10	8,40	7,00	2,00	1,70
39	3,74	3,42	5,63	7,09	8,50	7,20	1,98	1,66
40	6,10	5,93			8,29	6,71	2,20	2,03
41	3,51	3,11	5,10	6,36	9,00	7,82	1,95	1,78
42	3,47	3,16	5,37	7,25	8,37	7,20	2,02	1,71
43	3,40	3,30	5,20	6,90				
44	3,22	5,15			8,40	7,36	1,92	1,67
45	2,60	2,36	6,09	6,43	10,97	9,20	2,47	2,12
46	3,30	2,90	4,80	6,30	7,60	6,60	1,95	1,70
47	3,20	3,00	5,10	6,50	9,30	7,80	2,00	1,70
48					8,84	7,40	2,10	1,78
49	3,28	2,96	5,10	6,54				
50	3,56	3,18	5,51	6,82	8,91	7,44	2,08	1,71

Lab.	Chloride, mg/l		Sulfate, mg/l		Calcium, mg/l		Magnesium, mg/l	
no.	A	B	A	B	A	B	A	B
51								
52	3,39	3,07	5,13	6,47	9,80	8,32	2,06	1,76
53			5,36	6,80	8,53	7,49	1,98	1,67
54					8,91	7,52	1,95	1,64
55	3,65	3,40	4,11	5,36	8,02	6,38	1,65	1,32
56	3,15	2,92	5,08	6,57	9,19	7,66	2,11	1,77
57	3,36	3,08	5,27	6,56				

Lab.	Sodium, mg/l		Potassium, mg/l		Total organic carbon, mg/l		Aluminum, µg/l	
no.	A	B	A	B	A	B	C	D
1	3,90	3,45	0,660	0,580	2,60	4,30		
2								
3	4,40	3,90	0,880	1,000	3,70	5,30		
4	4,14	3,75	0,624	0,546	3,50	5,76		
5	4,32	3,88	0,704	0,602	2,52	3,72	78,2	97,5
6	3,83	3,43	0,720	0,620	2,71	4,56		
7								
8							112,0	154,0
9	3,95	3,19	0,884	0,773				
10	4,40	3,80	0,800	0,700			53,8	83,5
11					2,50	4,00		
12	4,27	3,78	0,670	0,600	2,50	4,20	64,6	91,2
13	4,08	3,55	0,630	0,560	4,35	4,35	61,0	98,0
14	4,17	3,70	0,680	0,600	2,70	4,00	66,0	95,0
15	4,18	3,70	0,675	0,592	2,61	4,46		
16	4,10	3,69	0,690	0,600	2,73	4,09	67,0	99,0
17	4,13	3,65	0,703	0,622	2716,00	465,00		
18	3,68	3,57	0,620	0,550			59,5	101,0
19	4,14	3,64	0,620	0,550	3,13	5,05	83,1	135,9
20	4,26	3,77	0,655	0,573	2,50	4,10	60,0	90,0
21	4,07	3,71	0,680	0,585	2,57	4,20		
22	4,68	4,10	0,960	1,500			91,0	114,0
23	4,03	3,56	0,741	0,633	2,55	4,31	69,1	99,5
24								
25								
26								
27					3,81	5,00		
28	3,97	3,54	0,609	0,563	3,00	4,70	66,6	99,2
29	4,00	3,50	0,600	0,510			57,3	85,7
30	4,16	3,64	0,633	0,546	3,23	4,76	65,2	97,1
31	4,45	3,94	0,735	0,668	3,75	5,78	57,0	87,0
32	4,22	3,72	0,684	0,596			64,3	94,0
33	3,86	3,41	0,750	0,660				
34	4,38	3,89	0,760	0,670			92,0	131,0
35	4,45	3,84	0,780	0,680			309,0	426,0
36								
37	4,20	3,73	0,645	0,558	2,75	4,61		
38	4,10	3,60	0,700	0,600			61,5	91,1
39	4,20	3,70	0,670	0,580	2,88	5,13	63,0	93,0
40	4,17	3,67	0,720	0,570			34,9	50,3
41	4,23	3,89	0,680	0,000	2,90	4,70	62,0	91,0
42	4,21	3,70	0,709	0,612				
43								
44			0,687	0,633			72,3	95,7
45	5,15	4,39	0,945	0,860				
46	3,07	2,66	0,570	0,500				
47	4,20	3,70	0,710	0,620				
48	4,16	3,67	0,690	0,590	2,81	5,63	66,0	99,0
49					3,45	4,86		

Lab.	Sodium, mg/l		Potassium, mg/l		Total organic carbon, mg/l		Aluminum, µg/l	
no.	A	B	A	B	A	B	C	D
50	4,32	3,67	0,750	0,620	3,05	4,37	68,7	99,3
51								
52	4,29	3,76	0,700	0,600	2,64	4,50	65,8	96,6
53	4,23	3,71	0,710	0,605			64,0	95,8
54	4,20	3,71	0,741	0,631	2,54	4,20	70,2	102,0
55	4,05	3,36	0,681	0,558				
56	4,40	3,87	0,828	0,688	2,81	4,74		
57								

Lab.	Iron, µg/l		Manganese, µg/l		Cadmium, µg/l		Lead, µg/l	
no.	C	D	C	D	C	D	C	D
1								
2								
3								
4								
5	302	287	27,3	21,1	3,71	3,50	6,30	5,61
6								
7	0	0					0,06	0,05
8	250	290	26,0	23,0	3,20	3,40	6,30	5,90
9	277	311	29,8	25,9	3,41	5,52	6,21	3,76
10	260	295	26,3	21,5				
11								
12	0	0	24,6	20,8	3,75	3,63	7,21	6,51
13	261	306	25,5	21,7	3,50	3,50	6,70	6,00
14	256	290	26,0	21,0	3,98	3,94	8,30	7,30
15								
16	260	293	27,0	22,0	3,90	3,85	7,85	7,13
17								
18	281	319	24,0	20,0	3,80	3,70	6,38	5,71
19	253	282	24,6	19,9	4,06	3,77	6,60	6,60
20	260	250	26,0	16,0				
21								
22	248	290	27,0	23,0	3,80	3,30	2,50	5,50
23	265	297	26,4	21,6				
24			32000,0	20000,0				
25								
26								
27								
28	251	284	25,9	21,4	3,35	3,52	8,49	7,20
29	282	302	24,9	20,8	3,90	3,80	7,50	6,70
30	268	298	27,1	22,1	3,81	3,90	6,96	6,34
31	239	267	24,0	20,0	3,80	3,80	8,10	7,20
32	273	300	26,2	21,3	3,86	3,84	8,04	7,26
33			31,7	27,9	3,82	3,80	8,10	7,29
34	239	270	26,0	21,0	4,35	4,15	8,44	7,18
35	244	242	29,0	25,0	4,00	4,00	6,00	6,00
36					2,90	3,00	6,20	6,30
37	226	267	21,3	17,0	3,34	3,21	6,37	5,42
38	254	287	26,4	21,7	3,74	3,73	7,60	6,90
39	250	270	27,0	22,0	3,90	3,80	8,20	7,20
40			25,1	19,9	3,74	3,65	5,51	4,85
41	245	283	26,0	22,0	3,90	3,80	8,00	7,20
42	213	250	22,4	21,6	3,85	3,90	7,48	6,83
43								
44	284	302	26,9	20,8				
45								
46								
47								
48	270	310	28,0	23,0	3,71	3,56	7,60	6,70
49	258	286	31,5	27,7				
50	261	295	27,0	22,3	3,92	3,90	8,02	7,13

Lab.	Iron, µg/l		Manganese, µg/l		Cadmium, µg/l		Lead, µg/l	
no.	C	D	C	D	C	D	C	D
51								
52	255	291	26,0	21,6	3,77	3,80	7,80	7,08
53	259	291	27,2	22,3	4,07	4,08	8,56	7,76
54	250	280	25,8	21,1	3,80	3,80	16,80	14,00
55	269	302	25,8	21,3	3,95	3,95	7,85	7,05
56	259	295	26,4	21,8	4,02	4,15	7,79	5,92
57								

Lab.	Copper, µg/l		Nickel, µg/l		Zinc, µg/l	
no.	C	D	C	D	C	D
1						
2						
3						
4						
5	234	172	7,01	6,35	177	124
6						
7	0	0			0	0
8	207	157	4,90	4,50	130	102
9	241	174	3,15	2,41	151	119
10	750	923			170	135
11						
12	213	161	5,37	5,39	162	123
13	255	192	5,10	5,10	167	133
14	230	170	5,70	5,70	151	118
15						
16	234	174	5,82	5,78	159	124
17						
18	195	144	5,10	5,40	142	113
19	244	132	6,00	5,90	158	107
20	236	164			154	126
21						
22	303	690	5,50	3,90	980	140
23						
24						
25						
26						
27						
28	239	183	5,34	5,32	152	120
29	235	171	5,40	5,70	160	124
30	240	180	5,29	5,30	167	129
31	232	176	5,50	5,50	154	122
32	225	165	5,82	5,66	150	118
33	264	205	7,21	7,40		
34	248	182	6,75	6,10	155	122
35	150	120	6,20	6,00	120	98
36	183	151			93	63
37	249	193	4,56	4,30	128	101
38	226	168	5,60	5,52	147	116
39	240	176	5,60	5,50	157	122
40	228	158			136	98
41	241	181	6,00	5,90	159	125
42	196	154	4,82	5,07	138	115
43						
44						
45						
46						
47						
48	232	181	6,80	5,60	146	116
49						
50	228	171	6,08	5,96	150	116

Lab.	Copper, µg/l		Nickel, µg/l		Zinc, µg/l	
no.	C	D	C	D	C	D
51						
52	221	165	5,71	5,65	149	119
53	231	173	5,83	5,85	158	126
54	228	167	6,10	6,10	154	120
55	262	196	5,61	5,50	156	122
56	213	156			156	127
57						

Table 5.1 Statistics - pH

Sample A

Unit:			
Number of participants	49	Range	0,83
Number of omitted results	1	Variance	0,03
True value	7,31	Standard deviation	0,16
Mean value	7,30	Relative standard deviation	2,2%
Median value	7,31	Relative error	-0,2%

Analytical results in ascending order:

33	6,70	U	52	7,25	39	7,39
7	6,81		11	7,28	41	7,40
40	6,95		27	7,28	47	7,40
42	6,98		35	7,30	31	7,41
57	7,05		43	7,30	22	7,42
17	7,08		18	7,30	30	7,42
45	7,10		46	7,30	26	7,42
38	7,10		6	7,30	1	7,45
8	7,13		3	7,32	32	7,45
21	7,15		5	7,32	4	7,46
20	7,20		34	7,33	19	7,46
9	7,21		10	7,34	14	7,48
29	7,22		28	7,34	51	7,53
13	7,22		15	7,35	49	7,54
56	7,23		37	7,36	12	7,64
16	7,23		55	7,38		
50	7,25		23	7,38		

Sample B

Unit:			
Number of participants	49	Range	0,70
Number of omitted results	1	Variance	0,02
True value	7,40	Standard deviation	0,14
Mean value	7,37	Relative standard deviation	1,9%
Median value	7,40	Relative error	-0,4%

Analytical results in ascending order:

7	6,95		5	7,35	51	7,45
33	6,97	U	29	7,36	26	7,45
40	7,08		14	7,36	28	7,46
42	7,08		3	7,36	19	7,46
11	7,17		52	7,38	27	7,48
57	7,18		41	7,40	55	7,48
21	7,20		6	7,40	34	7,48
38	7,20		13	7,40	15	7,50
18	7,21		1	7,40	4	7,50
17	7,22		16	7,41	43	7,50
20	7,27		56	7,41	47	7,50
8	7,30		30	7,42	37	7,52
45	7,30		50	7,42	22	7,53
23	7,32		9	7,42	49	7,58
39	7,33		31	7,43	12	7,65
46	7,34		35	7,44		
32	7,34		10	7,44		

U = Omitted result

Table 5.2 Statistics - Conductivity

Sample A

Unit: mS/m

Number of participants	51	Range	0,88
Number of omitted results	7	Variance	0,03
True value	8,27	Standard deviation	0,18
Mean value	8,31	Relative standard deviation	2,2%
Median value	8,27	Relative error	0,4%

Analytical results in ascending order:

8	0,00	U	28	8,20	40	8,37		
11	7,35	U	43	8,20	41	8,40		
27	8,00		18	8,23	49	8,43		
14	8,00		6	8,25	16	8,43		
56	8,07		1	8,25	46	8,49		
23	8,12		55	8,25	57	8,50		
20	8,15		10	8,25	5	8,51		
32	8,17		17	8,28	33	8,53		
52	8,17		51	8,30	31	8,61		
39	8,17		47	8,30	26	8,64		
54	8,17		30	8,30	22	8,70		
19	8,18		21	8,30	9	8,88		
13	8,18		44	8,30	7	12,00	U	
12	8,18		29	8,31	42	83,97	U	
50	8,19		34	8,35	45	84,05	U	
38	8,20		37	8,36	15	822,50	U	
4	8,20		3	8,37	35	8330,00	U	

Sample B

Unit: mS/m

Number of participants	51	Range	1,34
Number of omitted results	7	Variance	0,05
True value	7,13	Standard deviation	0,22
Mean value	7,17	Relative standard deviation	3,1%
Median value	7,13	Relative error	0,5%

Analytical results in ascending order:

8	0,00	U	18	7,09	40	7,22		
10	6,86		28	7,09	16	7,23		
54	6,96		30	7,10	57	7,26		
32	6,97		38	7,10	31	7,28		
55	6,99		51	7,10	26	7,30		
52	7,00		6	7,12	49	7,30		
4	7,00		1	7,13	33	7,32		
14	7,00		3	7,13	5	7,33		
56	7,02		17	7,14	46	7,41		
50	7,03		44	7,15	27	7,80		
19	7,05		9	7,16	7	8,00	U	
39	7,06		34	7,18	22	8,20		
12	7,06		29	7,19	11	8,71	U	
20	7,06		37	7,19	42	69,90	U	
23	7,07		41	7,20	45	72,30	U	
13	7,07		43	7,20	15	704,80	U	
21	7,08		47	7,20	35	7140,00	U	

U = Omitted result

Table 5.3 Statistics - Alkalinity

Sample A

Unit: mmol/l

Number of participants	38	Range	0,400
Number of omitted results	6	Variance	0,003
True value	0,582	Standard deviation	0,056
Mean value	0,584	Relative standard deviation	9,6%
Median value	0,582	Relative error	0,3%

Analytical results in ascending order:

21	0,279	U	32	0,573		17	0,601	
52	0,292	U	39	0,575		50	0,601	
47	0,350		28	0,576		57	0,602	
11	0,530	U	18	0,576		10	0,609	
1	0,540		19	0,580		14	0,610	
4	0,558		13	0,581		12	0,613	
22	0,560		48	0,582		3	0,623	
43	0,561		15	0,582		35	0,650	
56	0,564		20	0,583		40	0,750	
6	0,565		55	0,597		8	0,860	U
46	0,569		26	0,600		7	76,000	U
2	0,571		41	0,600		45	310,000	U
49	0,571		5	0,600				

U = Omitted result

Sample B

Unit: mmol/l

Number of participants	38	Range	0,320
Number of omitted results	6	Variance	0,002
True value	0,434	Standard deviation	0,047
Mean value	0,440	Relative standard deviation	10,6%
Median value	0,434	Relative error	1,3%

Analytical results in ascending order:

21	0,208	U	32	0,427		5	0,460	
52	0,220	U	1	0,430		55	0,462	
47	0,260		28	0,432		10	0,464	
17	0,402		39	0,432		12	0,466	
43	0,415		6	0,433		26	0,475	
22	0,416		20	0,434		3	0,485	
4	0,417		48	0,435		35	0,500	
19	0,420		15	0,440		40	0,580	
2	0,423		18	0,444		8	0,660	U
56	0,423		50	0,446		11	0,680	U
46	0,426		57	0,451		7	77,000	U
49	0,426		41	0,460		45	240,000	U
13	0,426		14	0,460				

U = Omitted result

Table 5.4 Statistics - Nitrate + nitrite-nitrogen

Sample A

Unit: µgl

Number of participants	43	Range	48,9
Number of omitted results	11	Variance	
True value	65,0	Standard deviation	14,43
Mean value	63,2	Relative standard deviation	22,8%
Median value	65,0	Relative error	-2,8%

Analytical results in ascending order:

42	0,05	U	27	59,00		21	76,00	
46	0,07	U	47	60,00		30	77,00	
6	15,00	U	54	60,00		5	77,00	
13	30,00	U	56	60,70		43	78,00	
14	30,60	U	11	62,00		18	83,10	
41	32,00	U	37	64,18		32	84,00	
17	36,00		45	64,90		57	84,30	
23	38,00		49	65,00		31	84,90	
39	41,00		50	65,30		3	110,00	U
4	42,28		12	66,00		52	184,00	U
55	43,70		26	66,00		25	344,00	U
9	44,58		15	68,11		33	350,00	U
24	46,00		1	71,00		22	1420,00	U
19	50,00		28	73,00				
20	56,00		35	75,00				

U = Omitted result

Sample B

Unit: µgl

Number of participants	43	Range	0,00
Number of omitted results	41	Variance	0,00
True value	1,00	Standard deviation	0,00
Mean value	1,00	Relative standard deviation	0,0%
Median value	1,00	Relative error	0,0%

Analytical results in ascending order:

4	0,00	U	17	4,00	U	43	11,00	U
3	0,00	U	50	4,10	U	30	11,00	U
6	0,00	U	13	5,00	U	20	13,00	U
46	0,00	U	26	5,00	U	22	13,00	U
9	0,00	U	23	5,00	U	32	22,00	U
55	0,00	U	15	5,44	U	5	22,60	U
41	0,00	U	49	6,00	U	56	24,40	U
42	0,00	U	11	6,00	U	39	25,00	U
47	0,00	U	1	7,00	U	31	34,50	U
12	1,00		57	7,89	U	35	38,00	U
24	1,00		18	9,73	U	33	74,00	U
45	1,56	U	19	10,00	U	52	156,00	U
27	2,00	U	21	10,00	U	25	200,00	U
37	2,06	U	54	10,00	U			
14	2,20	U	28	11,00	U			

U = Omitted result

Table 5.5 Statistics - Chloride

Sample A

Unit: mg/l

Number of participants	46	Range	0,74
Number of omitted results	5	Variance	0,03
True value	3,32	Standard deviation	0,16
Mean value	3,35	Relative standard deviation	4,8%
Median value	3,32	Relative error	0,9%

Analytical results in ascending order:

45	2,60	U	33	3,29		37	3,43	
38	3,00		10	3,30		32	3,44	
5	3,03		28	3,30		42	3,47	
56	3,15		46	3,30		41	3,51	
1	3,15		29	3,30		22	3,54	
18	3,19		13	3,32		21	3,55	
6	3,20		4	3,32		50	3,56	
47	3,20		16	3,33		34	3,60	
44	3,22	U	17	3,33		55	3,65	
30	3,24		57	3,36		35	3,65	
9	3,25		12	3,37		39	3,74	
15	3,26		19	3,38		3	4,40	U
14	3,26		52	3,39		8	4,80	U
25	3,27		23	3,40		40	6,10	U
31	3,28		43	3,40				
49	3,28		20	3,41				

Sample B

Unit: mg/l

Number of participants	46	Range	0,72
Number of omitted results	5	Variance	0,02
True value	3,06	Standard deviation	0,15
Mean value	3,07	Relative standard deviation	5,0%
Median value	3,06	Relative error	0,4%

Analytical results in ascending order:

45	2,36	U	33	3,03		32	3,15	
38	2,70		17	3,04		42	3,16	
5	2,77		28	3,04		50	3,18	
46	2,90		4	3,04		35	3,20	
1	2,90		20	3,05		21	3,25	
18	2,91		16	3,06		43	3,30	
56	2,92		52	3,07		22	3,30	
14	2,93		12	3,07		34	3,40	
15	2,93		6	3,07		55	3,40	
49	2,96		57	3,08		39	3,42	
30	2,99		10	3,10		3	3,90	U
29	3,00		23	3,10		8	5,10	U
47	3,00		41	3,11		44	5,15	U
13	3,02		19	3,12		40	5,93	U
25	3,02		37	3,13				
31	3,02		9	3,15				

U = Omitted result

Table 5.6 Statistics - Sulfate

Sample A

Unit: mg/l

Number of participants	44	Range	2,19
Number of omitted results	2	Variance	0,18
True value	5,13	Standard deviation	0,42
Mean value	5,20	Relative standard deviation	8,2%
Median value	5,13	Relative error	1,3%

Analytical results in ascending order:

10	1,80	U	16	5,09	6	5,34	
55	4,11		17	5,09	13	5,35	
1	4,41		49	5,10	53	5,36	
5	4,70		41	5,10	42	5,37	
38	4,70		23	5,10	32	5,42	
46	4,80		47	5,10	19	5,50	
28	4,80		52	5,13	50	5,51	
18	4,83		37	5,13	25	5,56	
29	4,90		4	5,14	39	5,63	
30	4,93		21	5,15	33	5,80	
20	4,99		43	5,20	45	6,09	
31	5,01		35	5,25	3	6,30	
15	5,03		57	5,27	8	6,30	
12	5,04		14	5,28	22	6,70	U
56	5,08		9	5,30			

U = Omitted result

Sample B

Unit: mg/l

Number of participants	44	Range	2,14
Number of omitted results	2	Variance	0,15
True value	6,49	Standard deviation	0,38
Mean value	6,50	Relative standard deviation	5,9%
Median value	6,49	Relative error	0,2%

Analytical results in ascending order:

10	2,30	U	25	6,42	37	6,58	
55	5,36		17	6,42	13	6,60	
1	5,56		45	6,43	6	6,65	
35	5,96		20	6,43	33	6,69	
38	6,10		12	6,44	53	6,80	
18	6,14		21	6,45	50	6,82	
28	6,21		52	6,47	32	6,84	
5	6,24		23	6,50	19	6,84	
46	6,30		47	6,50	43	6,90	
9	6,32		15	6,51	39	7,09	
41	6,36		4	6,53	8	7,10	
31	6,37		14	6,53	42	7,25	
30	6,38		49	6,54	3	7,50	
29	6,40		57	6,56	22	11,50	U
16	6,42		56	6,57			

U = Omitted result

Table 5.7 Statistics - Calcium

Sample A

Unit: mg/l

Number of participants	45	Range	2,80
Number of omitted results	2	Variance	0,33
True value	8,50	Standard deviation	0,57
Mean value	8,47	Relative standard deviation	6,7%
Median value	8,50	Relative error	-0,4%

Analytical results in ascending order:

18	1,26	U	30	8,29	37	8,80	
8	7,00		16	8,34	10	8,80	
22	7,40		42	8,37	31	8,81	
46	7,60		38	8,40	28	8,84	
5	7,66		44	8,40	48	8,84	
15	7,70		23	8,43	9	8,85	
35	7,87		4	8,44	50	8,91	
13	8,00		14	8,50	54	8,91	
20	8,00		3	8,50	41	9,00	
21	8,00		39	8,50	56	9,19	
55	8,02		33	8,50	47	9,30	
6	8,04		53	8,53	19	9,43	
29	8,10		32	8,56	12	9,56	
1	8,24		17	8,72	52	9,80	
40	8,29		34	8,77	45	10,97	U

U = Omitted result

Sample B

Unit: mg/l

Number of participants	45	Range	2,12
Number of omitted results	2	Variance	0,21
True value	7,20	Standard deviation	0,46
Mean value	7,21	Relative standard deviation	6,3%
Median value	7,20	Relative error	0,1%

Analytical results in ascending order:

18	1,11	U	33	7,08	32	7,41	
8	6,20		4	7,12	50	7,44	
55	6,38		34	7,12	17	7,47	
35	6,50		5	7,12	53	7,49	
46	6,60		6	7,14	37	7,50	
15	6,63		23	7,18	54	7,52	
13	6,70		9	7,19	31	7,58	
29	6,70		42	7,20	28	7,64	
40	6,71		14	7,20	56	7,66	
22	6,73		39	7,20	47	7,80	
30	6,83		16	7,26	41	7,82	
21	6,86		44	7,36	19	8,00	
20	7,00		48	7,40	12	8,10	
38	7,00		10	7,40	52	8,32	
1	7,07		3	7,40	45	9,20	U

U = Omitted result

Table 5.8 Statistics - Magnesium

Sample A

Unit: mg/l

Number of participants	45	Range	0,82
Number of omitted results	1	Variance	0,02
True value	1,98	Standard deviation	0,14
Mean value	2,00	Relative standard deviation	7,1%
Median value	1,98	Relative error	1,2%

Analytical results in ascending order:

55	1,65	54	1,95	28	2,02	
33	1,76	14	1,95	19	2,03	
34	1,83	30	1,97	52	2,06	
18	1,85	15	1,98	20	2,07	
5	1,86	4	1,98	50	2,08	
21	1,90	39	1,98	37	2,09	
3	1,90	53	1,98	48	2,10	
44	1,92	17	1,98	8	2,10	
23	1,93	38	2,00	10	2,10	
1	1,93	47	2,00	56	2,11	
16	1,94	29	2,00	12	2,17	
13	1,94	6	2,00	40	2,20	
46	1,95	32	2,01	35	2,46	
41	1,95	9	2,01	45	2,47	
31	1,95	42	2,02	22	2,81	U

U = Omitted result

Sample B

Unit: mg/l

Number of participants	45	Range	0,80
Number of omitted results	1	Variance	0,02
True value	1,69	Standard deviation	0,14
Mean value	1,70	Relative standard deviation	8,2%
Median value	1,69	Relative error	0,6%

Analytical results in ascending order:

55	1,32	6	1,66	50	1,71	
18	1,48	31	1,66	37	1,73	
33	1,50	39	1,66	19	1,73	
34	1,57	44	1,67	52	1,76	
29	1,60	53	1,67	56	1,77	
3	1,60	4	1,67	20	1,77	
15	1,62	17	1,69	41	1,78	
5	1,62	16	1,69	48	1,78	
30	1,63	9	1,69	10	1,80	
23	1,64	47	1,70	8	1,80	
54	1,64	28	1,70	12	1,89	
1	1,64	38	1,70	40	2,03	
21	1,65	46	1,70	22	2,04	U
14	1,65	32	1,70	35	2,10	
13	1,65	42	1,71	45	2,12	

U = Omitted result

Table 5.9 Statistics - Sodium

Sample A

Unit: mg/l

Number of participants	43	Range	1,00
Number of omitted results	2	Variance	0,04
True value	4,18	Standard deviation	0,19
Mean value	4,17	Relative standard deviation	4,5%
Median value	4,18	Relative error	-0,1%

Analytical results in ascending order:

46	3,07	U	19	4,14		20	4,26	
18	3,68		4	4,14		12	4,27	
6	3,83		30	4,16		52	4,29	
33	3,86		48	4,16		5	4,32	
1	3,90		14	4,17		50	4,32	
9	3,95		40	4,17		34	4,38	
28	3,97		15	4,18		10	4,40	
29	4,00		39	4,20		56	4,40	
23	4,03		54	4,20		3	4,40	
55	4,05		47	4,20		31	4,45	
21	4,07		37	4,20		35	4,45	
13	4,08		42	4,21		22	4,68	
38	4,10		32	4,22		45	5,15	U
16	4,10		41	4,23				
17	4,13		53	4,23				

U = Omitted result

Sample B

Unit: mg/l

Number of participants	43	Range	0,91
Number of omitted results	2	Variance	0,03
True value	3,70	Standard deviation	0,17
Mean value	3,68	Relative standard deviation	4,6%
Median value	3,70	Relative error	-0,4%

Analytical results in ascending order:

46	2,66	U	48	3,67		52	3,76	
9	3,19		40	3,67		20	3,77	
55	3,36		50	3,67		12	3,78	
33	3,41		16	3,69		10	3,80	
6	3,43		42	3,70		35	3,84	
1	3,45		14	3,70		56	3,87	
29	3,50		39	3,70		5	3,88	
28	3,54		47	3,70		41	3,89	
13	3,55		15	3,70		34	3,89	
23	3,56		53	3,71		3	3,90	
18	3,57		21	3,71		31	3,94	
38	3,60		54	3,71		22	4,10	
30	3,64		32	3,72		45	4,39	U
19	3,64		37	3,73				
17	3,65		4	3,75				

U = Omitted result

Table 5.10 Statistics - Potassium

Sample A

Unit: mg/l

Number of participants	44	Range	0,314
Number of omitted results	4	Variance	0,004
True value	0,690	Standard deviation	0,063
Mean value	0,695	Relative standard deviation	9,0%
Median value	0,690	Relative error	0,8%

Analytical results in ascending order:

46	0,570		14	0,680		6	0,720	
29	0,600		21	0,680		31	0,735	
28	0,609		55	0,681		54	0,741	
19	0,620		32	0,684		23	0,741	
18	0,620		44	0,687		33	0,750	
4	0,624		48	0,690		50	0,750	
13	0,630		16	0,690		34	0,760	
30	0,633		52	0,700		35	0,780	
37	0,645		38	0,700		10	0,800	
20	0,655		17	0,703		56	0,828	
1	0,660		5	0,704		3	0,880	U
39	0,670		42	0,709		9	0,884	
12	0,670		53	0,710		45	0,945	U
15	0,675		47	0,710		22	0,960	U
41	0,680	U	40	0,720				

U = Omitted result

Sample B

Unit: mg/l

Number of participants	44	Range	0,273
Number of omitted results	4	Variance	0,003
True value	0,600	Standard deviation	0,053
Mean value	0,604	Relative standard deviation	8,8%
Median value	0,600	Relative error	0,6%

Analytical results in ascending order:

41	0,000	U	21	0,585		17	0,622	
46	0,500		48	0,590		54	0,631	
29	0,510		15	0,592		23	0,633	
30	0,546		32	0,596		44	0,633	
4	0,546		12	0,600		33	0,660	
19	0,550		16	0,600		31	0,668	
18	0,550		52	0,600		34	0,670	
55	0,558		14	0,600		35	0,680	
37	0,558		38	0,600		56	0,688	
13	0,560		5	0,602		10	0,700	
28	0,563		53	0,605		9	0,773	
40	0,570		42	0,612		45	0,860	U
20	0,573		50	0,620		3	1,000	U
39	0,580		6	0,620		22	1,500	U
1	0,580		47	0,620				

U = Omitted result

Table 5.11. Statistics - Total organic carbon

Sample A

Unit: mg/l

Number of participants	29	Range	1,31
Number of omitted results	2	Variance	0,17
True value	2,75	Standard deviation	0,41
Mean value	2,90	Relative standard deviation	14,2%
Median value	2,75	Relative error	5,6%

Analytical results in ascending order:

20	2,50	14	2,70	19	3,13	
12	2,50	6	2,71	30	3,23	
11	2,50	16	2,73	49	3,45	
5	2,52	37	2,75	4	3,50	
54	2,54	48	2,81	3	3,70	
23	2,55	56	2,81	31	3,75	
21	2,57	39	2,88	27	3,81	
1	2,60	41	2,90	13	4,35	U
15	2,61	28	3,00	17	2716,00	U
52	2,64	50	3,05			

U = Omitted result

Sample B

Unit: mg/l

Number of participants	29	Range	2,06
Number of omitted results	2	Variance	0,30
True value	4,56	Standard deviation	0,55
Mean value	4,63	Relative standard deviation	11,8%
Median value	4,56	Relative error	1,6%

Analytical results in ascending order:

5	3,72	13	4,35	U	49	4,86
11	4,00	50	4,37		27	5,00
14	4,00	15	4,46		19	5,05
16	4,09	52	4,50		39	5,13
20	4,10	6	4,56		3	5,30
21	4,20	37	4,61		48	5,63
12	4,20	28	4,70		4	5,76
54	4,20	41	4,70		31	5,78
1	4,30	56	4,74		17	465,00 U
23	4,31	30	4,76			

U = Omitted result

Table 5.12 Statistics - Aluminium

Sample C

Unit: µg/l

Number of participants	29	Range	38,2
Number of omitted results	3	Variance	89,6
True value	65,5	Standard deviation	9,5
Mean value	67,3	Relative standard deviation	14,1%
Median value	65,5	Relative error	2,7%

Analytical results in ascending order:

40	34,9	U	53	64,0	23	69,1
10	53,8		32	64,3	54	70,2
31	57,0		12	64,6	44	72,3
29	57,3		30	65,2	5	78,2
18	59,5		52	65,8	19	83,1
20	60,0		48	66,0	22	91,0
13	61,0		14	66,0	34	92,0
38	61,5		28	66,6	8	112,0
41	62,0		16	67,0	35	309,0
39	63,0		50	68,7		

U = Omitted result

Sample D

Unit: µg/l

Number of participants	29	Range	52,4
Number of omitted results	3	Variance	142,3
True value	96,9	Standard deviation	11,9
Mean value	98,5	Relative standard deviation	12,1%
Median value	96,9	Relative error	1,7%

Analytical results in ascending order:

40	50,3	U	14	95,0	50	99,3
10	83,5		44	95,7	23	99,5
29	85,7		53	95,8	18	101,0
31	87,0		52	96,6	54	102,0
20	90,0		30	97,1	22	114,0
41	91,0		5	97,5	34	131,0
38	91,1		13	98,0	19	135,9
12	91,2		16	99,0	8	154,0
39	93,0		48	99,0	35	426,0
32	94,0		28	99,2		

U = Omitted result

Table 5.13 Statistics - Iron

Sample C

Analytical method: All
Unit: µg/l

Number of participants	35	Range	89
Number of omitted results	2	Variance	293
True value	259	Standard deviation	17
Mean value	258	Relative standard deviation	6,6%
Median value	259	Relative error	-0,3%

Analytical results in ascending order:

12	0	U	28	251	13	261
7	0	U	19	253	23	265
42	213		38	254	30	268
37	226		52	255	55	269
34	239		14	256	48	270
31	239		49	258	32	273
35	244		56	259	9	277
41	245		53	259	18	281
22	248		20	260	29	282
54	250		16	260	44	284
8	250		10	260	5	302
39	250		50	261		

U = Omitted result

Sample D

Unit: µg/l

Number of participants	35	Range	77
Number of omitted results	2	Variance	315
True value	290	Standard deviation	18
Mean value	287	Relative standard deviation	6,2%
Median value	290	Relative error	-0,9%

Analytical results in ascending order:

12	0	U	28	284	50	295
7	0	U	49	286	23	297
35	242		5	287	30	298
42	250		38	287	32	300
20	250		14	290	44	302
31	267		8	290	55	302
37	267		22	290	29	302
34	270		52	291	13	306
39	270		53	291	48	310
54	280		16	293	9	311
19	282		56	295	18	319
41	283		10	295		

U = Omitted result

Table 5.14 Statistics - Manganese

Sample C

Analytical method: All
Unit: µg/l

Number of participants	37	Range	10,4
Number of omitted results	1	Variance	4,1
True value	26,1	Standard deviation	2,0
Mean value	26,3	Relative standard deviation	7,7%
Median value	26,1	Relative error	0,9%

Analytical results in ascending order:

37	21,3	20	26,0	39	27,0
42	22,4	41	26,0	22	27,0
18	24,0	14	26,0	30	27,1
31	24,0	52	26,0	53	27,2
12	24,6	8	26,0	5	27,3
19	24,6	32	26,2	48	28,0
29	24,9	10	26,3	35	29,0
40	25,1	38	26,4	9	29,8
13	25,5	23	26,4	49	31,5
55	25,8	56	26,4	33	31,7
54	25,8	44	26,9	24	32000,0
28	25,9	16	27,0		
34	26,0	50	27,0		

U = Omitted result

Sample D

Unit: µg/l

Number of participants	37	Range	11,9
Number of omitted results	1	Variance	5,2
True value	21,6	Standard deviation	2,3
Mean value	21,8	Relative standard deviation	10,4%
Median value	21,6	Relative error	0,7%

Analytical results in ascending order:

20	16,0	55	21,3	30	22,1
37	17,0	32	21,3	53	22,3
19	19,9	28	21,4	50	22,3
40	19,9	10	21,5	8	23,0
18	20,0	52	21,6	22	23,0
31	20,0	23	21,6	48	23,0
29	20,8	42	21,6	35	25,0
12	20,8	13	21,7	9	25,9
44	20,8	38	21,7	49	27,7
14	21,0	56	21,8	33	27,9
34	21,0	16	22,0	24	20000,0
54	21,1	41	22,0		
5	21,1	39	22,0		

U = Omitted result

Table 5.15 Statistics - Cadmium

Sample C

Unit: µg/l

Number of participants	32	Range	1,15
Number of omitted results	2	Variance	0,05
True value	3,82	Standard deviation	0,23
Mean value	3,81	Relative standard deviation	6,0%
Median value	3,82	Relative error	-0,3%

Analytical results in ascending order:

36	2,90	U	52	3,77		16	3,90
8	3,20		54	3,80		29	3,90
37	3,34		18	3,80		50	3,92
28	3,35		31	3,80		55	3,95
9	3,41	U	22	3,80		14	3,98
13	3,50		30	3,81		35	4,00
48	3,71		33	3,82		56	4,02
5	3,71		42	3,85		19	4,06
38	3,74		32	3,86		53	4,07
40	3,74		41	3,90		34	4,35
12	3,75		39	3,90			

U = Omitted result

Sample D

Unit: µg/l

Number of participants	32	Range	0,94
Number of omitted results	2	Variance	0,05
True value	3,80	Standard deviation	0,23
Mean value	3,76	Relative standard deviation	6,1%
Median value	3,80	Relative error	-1,1%

Analytical results in ascending order:

36	3,00	U	38	3,73		30	3,90
37	3,21		19	3,77		50	3,90
22	3,30		33	3,80		42	3,90
8	3,40		54	3,80		14	3,94
13	3,50		52	3,80		55	3,95
5	3,50		41	3,80		35	4,00
28	3,52		31	3,80		53	4,08
48	3,56		29	3,80		56	4,15
12	3,63		39	3,80		34	4,15
40	3,65		32	3,84		9	5,52
18	3,70		16	3,85			

U = Omitted result

Table 5.16 Statistics - Lead

Sample C

Unit: µg/l

Number of participants	33	Range	3,05
Number of omitted results	4	Variance	0,75
True value	7,60	Standard deviation	0,86
Mean value	7,39	Relative standard deviation	11,7%
Median value	7,60	Relative error	-2,8%

Analytical results in ascending order:

7	0,06	U	13	6,70		41	8,00
22	2,50	U	30	6,96		50	8,02
40	5,51		12	7,21		32	8,04
35	6,00		42	7,48		31	8,10
36	6,20		29	7,50		33	8,10
9	6,21	U	38	7,60		39	8,20
5	6,30		48	7,60		14	8,30
8	6,30		56	7,79		34	8,44
37	6,37		52	7,80		28	8,49
18	6,38		55	7,85		53	8,56
19	6,60		16	7,85		54	16,80

U = Omitted result

Sample D

Unit: µg/l

Number of participants	33	Range	2,91
Number of omitted results	4	Variance	0,49
True value	6,83	Standard deviation	0,70
Mean value	6,63	Relative standard deviation	10,6%
Median value	6,83	Relative error	-2,9%

Analytical results in ascending order:

7	0,05	U	36	6,30		16	7,13
9	3,76	U	30	6,34		34	7,18
40	4,85		12	6,51		28	7,20
37	5,42		19	6,60		41	7,20
22	5,50	U	48	6,70		31	7,20
5	5,61		29	6,70		39	7,20
18	5,71		42	6,83		32	7,26
8	5,90		38	6,90		33	7,29
56	5,92		55	7,05		14	7,30
35	6,00		52	7,08		53	7,76
13	6,00		50	7,13		54	14,00

U = Omitted result

Table 5.17 Statistics - Copper

Sample C

Unit: µg/l

Number of participants	35	Range	81
Number of omitted results	4	Variance	337
True value	232	Standard deviation	18
Mean value	231	Relative standard deviation	8,0%
Median value	232	Relative error	-0,6%

Analytical results in ascending order:

7	0	U	50	228	30	240
35	150	U	40	228	9	241
36	183		14	230	41	241
18	195		53	231	19	244
42	196		31	232	34	248
8	207		48	232	37	249
12	213		5	234	13	255
56	213		16	234	55	262
52	221		29	235	33	264
32	225		20	236	22	303
38	226		28	239	10	750
54	228		39	240		

U = Omitted result

Sample D

Unit: µg/l

Number of participants	35	Range	73
Number of omitted results	4	Variance	236
True value	171	Standard deviation	15
Mean value	171	Relative standard deviation	9,0%
Median value	171	Relative error	-0,2%

Analytical results in ascending order:

7	0	U	32	165	30	180
35	120	U	54	167	41	181
19	132		38	168	48	181
18	144		14	170	34	182
36	151		50	171	28	183
42	154		29	171	13	192
56	156		5	172	37	193
8	157		53	173	55	196
40	158		9	174	33	205
12	161		16	174	22	690
20	164		39	176	10	923
52	165		31	176		

U = Omitted result

Table 5.18 Statistics - Nickel

Sample C

Unit: µg/l

Number of participants	29	Range	2,65
Number of omitted results	1	Variance	0,41
True value	5,66	Standard deviation	0,64
Mean value	5,74	Relative standard deviation	11,2%
Median value	5,66	Relative error	1,4%

Analytical results in ascending order:

9	3,15	U	31	5,50	19	6,00
37	4,56		22	5,50	41	6,00
42	4,82		39	5,60	50	6,08
8	4,90		38	5,60	54	6,10
18	5,10		55	5,61	35	6,20
13	5,10		14	5,70	34	6,75
30	5,29		52	5,71	48	6,80
28	5,34		16	5,82	5	7,01
12	5,37		32	5,82	33	7,21
29	5,40		53	5,83		

U = Omitted result

Sample D

Unit: µg/l

Number of participants	29	Range	3,50
Number of omitted results	1	Variance	0,42
True value	5,63	Standard deviation	0,65
Mean value	5,57	Relative standard deviation	11,7%
Median value	5,63	Relative error	-1,1%

Analytical results in ascending order:

9	2,41	U	31	5,50	53	5,85
22	3,90		39	5,50	19	5,90
37	4,30		55	5,50	41	5,90
8	4,50		38	5,52	50	5,96
42	5,07		48	5,60	35	6,00
13	5,10		52	5,65	54	6,10
30	5,30		32	5,66	34	6,10
28	5,32		29	5,70	5	6,35
12	5,39		14	5,70	33	7,40
18	5,40		16	5,78		

U = Omitted result

Table 5.19 Statistics - Zinc

Sample C

Unit: µg/l

Number of participants	34	Range	57
Number of omitted results	3	Variance	151
True value	154	Standard deviation	12
Mean value	152	Relative standard deviation	8,1%
Median value	154	Relative error	-1,3%

Analytical results in ascending order:

7	0	U	32	150	53	158
36	93	U	14	151	16	159
35	120		9	151	41	159
37	128		28	152	29	160
8	130		20	154	12	162
40	136		54	154	30	167
42	138		31	154	13	167
18	142		34	155	10	170
48	146		55	156	5	177
38	147		56	156	22	980
52	149		39	157		
50	150		19	158		

U = Omitted result

Sample D

Unit: µg/l

Number of participants	34	Range	37
Number of omitted results	3	Variance	87
True value	120	Standard deviation	9
Mean value	119	Relative standard deviation	7,9%
Median value	120	Relative error	-1,1%

Analytical results in ascending order:

7	0	U	32	118	16	124
36	63	U	14	118	29	124
35	98		9	119	41	125
40	98		52	119	20	126
37	101		54	120	53	126
8	102		28	120	56	127
19	107		55	122	30	129
18	113		34	122	13	133
42	115		31	122	10	135
50	116		39	122	22	140
38	116		12	123		
48	116		5	124		

U = Omitted result

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NIVA
Norwegian Institute for Water Research

Gaustadalléen 21 • NO-0349 Oslo, Norway
Telephone: +47 22 18 51 00 • Fax: 22 18 52 00
www.niva.no • post@niva.no

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