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Intercomparison 1226: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn

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

71 laboratories received samples for the intercomparison 1226, and 68 laboratories in 26 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 %, 74 % of the overall results were considered acceptable. This is somewhat lower than last years, but in line with the previous ones. The best results were reported for the analytical variables manganese, copper, sodium and cadmium, with 89, 86, 84 and 84 % acceptable results, respectively. The lowest percentage were observed for alkalinity, nitrate, pH and zinc with 48, 52, 59 and 61 % acceptable results. Nitrate showed clear sign of not being sufficiently stable during the period of analysis. Harmonization of the analytical methods used, and the practical procedures followed, may be the most important way to improve the comparability for these parameters.

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Ivar Dahl
Project Manager

Tomas Adler Blakseth
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 1226:

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
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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 Centre's 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. NIVA is accreditated for organizing interlaboratory studies in accordance with NS-EN ISO/IEC 17043 by the Norwegian Accreditation (NA) (registration no. PT 002).

We hereby report the results from the 26th intercomparison of chemical analysis.

Oslo, September 2012

Ivar Dahl

Contents

Summary

Intercomparison 1226 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 June - August 2012, 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. 130 laboratories were invited to participate, and samples were sent to the 71 laboratories who accepted. 68 laboratories submitted results to the Programme Centre before the final statistical treatment of the data. 26 countries were represented in this laboratory group.

The median value of the results received from the participants for each variable was selected as "true" value. On average 74 % 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.

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 only 59 % of the result pairs were acceptable even when using this extended limit. A total error of ± 0,2 units for pH measurements, therefore 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 manganese, copper, sodium, cadmium and potassium where 89, 86, 84, 84 and 81 % of the results, respectively, were acceptable. The worst results were observed for alkalinity (48 %) and nitrate-nitrogen (52 %). The main reason for unacceptable results is probably the low concentrations in the samples used for some of the analytical variables, and the fact that some laboratories use equipment which is not sufficiently sensitive for these concentrations. It is quite clear that nitrate-nitrogen in especially sample A shows reduced stability and that the evaluation of this variable is questionable.

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

1. Introduction

As stated in the "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 twentysixth intercomparison test, called 1226, 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, as earlier, two sample sets should be included in this intercomparison, one sample pair for the determination of the major ions, and one for the heavy metals. It was also decided that total organic carbon and aluminium should be included in this round also.

The samples were shipped from the Programme Centre on June 18th 2012. With some exceptions the laboratories received the samples within one week. One of the shipped packages was returned to the organizer, but of unknown reasons two laboratories did not receive the samples within time for performing analysis. To ensure that the effect of possible alterations in the solutions is minimized, the participants should analyze the samples as soon as possible, and return the analytical results within August 12th.

3. 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 1 an evaluation of the results of intercomparison 1226 is presented with the number and percentage of acceptable results based on the target accuracy (except for pH and conductivity). In Appendix D, Table 7, the individual results of each laboratory are given. 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.

This year 68 laboratories submitted results for the intercomparison. In this intercomparison 74 % 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 somewhat lower than last year, but in line with the previous ones. The best results were reported for the analytical variables manganese, copper, sodium and cadmium where 89, 86, 84 and 84 % of the results, respectively, were acceptable. The worst results were observed for alkalinity and nitrate-nitrogen with only 48 % and 52 %, respectively, acceptable results.

For pH, the general target accuracy is ± 0,1 pH units (1), and only 22 % of the result pairs are found within these accuracy limits. However, conforming with last years practice, it was chosen to extend the acceptance limit to ± 0,2 pH units. With this wider acceptance limit 59 % of the result pairs are evaluated as acceptable this time. This is lower than last year when 73 % were acceptable, but in line with the previous ones. 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. The samples will also be exposed to different temperature and travel time during shipment. 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.

Due to 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 %. After this, percentage of acceptable result pairs for conductivity is 72 (Table 1). If we increase the acceptance limit to the target value, the number would increase to 84. 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.

For alkalinity, it is observed earlier that the reported results for solutions with low alkalinity values are much more widely spread than are solutions with higher concentrations of bicarbonate. In this intercomparison, the number of acceptable results were only 48 %, but a possible explanation for this could be the lower concentrations of bicarbonate in the two samples this time compared to the two previos years.

For nitrate only 52 % of the result pairs are acceptable. The standard deviation between the results is much higher in sample A compared to sample B. Also the control analyses done at the Program Centre indicates that especially sample A is not sufficiently stable in the period of analysis. Also earlier intercomparisons shows that the stability of this parameter in the samples could be a problem. The samples could be affected by environmental conditions during transport to the laboratories. As a consequence of this, the evaluation of this variable is highly questionable. It also seems that three laboratories reported results in wrong unit, and that also some laboratories possibly have reported their results as nitrate instead of nitrogen.

For the major ions, chloride, sulphate, calcium, magnesium and sodium, the number of acceptable results are usually rather good. This also applies to this intercomparison, but the percentage of acceptable results was still lower than the year before. This could be because the concentrations also were lower this time. However, the determination of total organic carbon showed better performance this year. For the major ions, the ion chromatography technique clearly grow ahead of the traditional methods, the photometric methods for the anions and the atomic absorption or emission methods for the cations.

The best results for heavy metals included in this intercomparison programme were obtained for manganese, copper and cadmium. Some of the elements show a better performance than last year, and some show a decrease in percentage acceptable results. For some of the elements the concentrations were rather low, and it is seems that some laboratories do not have sufficiently sensitive methods to determine heavy metals at trace level. However, the concentrations in these samples are still higher than could be expected in relevant natural 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. It is also a tendency that ICP-MS is increasing at the sacrifice of ICP-AES for the elements with the lowest concentrations.

The low fraction of acceptable results for some variables may in some cases be explained by either rather low concentrations, compared to the methods that have been used, or that the samples were not sufficiently stable. When the concentrations are close to the detection limits for some of the methods used by the participants, it is expected that the spread of the results will be greater than ± 20 %. The low acceptable percentage for conductivity and nitrate-nitrogen can also in part be attributable to results reported in wrong unit.

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 report their results in units other than those requested. In some cases this has been corrected by the laboratory at the Programme Centre after correspondance with the participants.

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.

Table 1. Evaluation of the results from intercomparison 1226.

Determinant and unit	Sample-pair	True value Sample 1	True value Sample 2	Acceptable limit, %	Number of pairs Tot.	Number of pairs Accept.	% acceptable res. for intecalibration 1226	1125	1024	0923
pH	AB	6,53	6,68	0,2 pH	64	38	59	73	49	61
Conductivity, mS/m	AB	2,20	2,35	10	61	44	72	86	84	71
Alkalinity, mmol/l	AB	0,063	0,070	20	48	23	48	79	74	67
Nitrate + nitrite-nitrogen, µg/l	AB	172	178	20	60	31	52	74*	57	58
Chloride, mg/l	AB	1,05	1,23	20	58	46	79	89	79	86
Sulphate, mg/l	AB	3,04	2,79	20	55	44	80	86	73	77
Calcium, mg/l	AB	1,72	2,04	20	56	42	75	91	77	84
Magnesium, mg/l	AB	0,270	0,320	20	57	42	74	89	82	88
Sodium, mg/l	AB	1,73	1,63	20	57	48	84	95	93	88
Potassium, mg/l	AB	0,381	0,350	20	57	46	81	82	82	75
Total organic carbon, mg/l	AB	3,84	4,49	20	42	32	76	69	83	82
Aluminium, µg/l	CD	81,5	84,6	20	39	31	79	76	77	77
Iron, µg/l	CD	70,4	73,0	20	40	28	70	91	81	73
Manganese, µg/l	CD	11,6	15,8	20	44	39	89	86	85	67
Cadmium, µg/l	CD	2,12	1,88	20	44	37	84	94	88	79
Lead, µg/l	CD	8,23	7,40	20	44	34	77	67	73	74
Copper, µg/l	CD	13,9	13,5	20	44	38	86	77	51	37
Nickel, µg/l	CD	8,50	7,20	20	41	32	78	72	66	85
Zinc, µg/l	CD	4,20	5,70	20	38	23	61	79	82	90
Total					949	698	74	83	75	75

* The figure correspond to sample 1 in the sample pair

4. Results

130 laboratories were invited to participate in this ICP Waters intercomparison. 71 of the laboratories accepted and therefore samples were shipped to them. The 68 laboratories which submitted results to the Programme Centre, represents 26 different countries. The participants and their code numbers are listed in Appendix A, which also includes a table summarizing how many laboratories participated from each country.

The analytical results received from the laboratories were treated by the method of Youden (2, 3). A short description of this method, and the statistical treatment of the analytical data, are presented in Appendix C. The purpose of this test is to evaluate the comparability of the analytical results produced by the laboratories participating in the International Cooperative Programme. The real "true value" is not known exactly for the natural water samples used in this intercomparison. Therefore, the median value, determined from the analytical results submitted by the participating laboratories after outliers were excluded, was selected 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. Table 6 in Appendix C 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 - 19, where each laboratory is represented by a small circle and an identification number. Some laboratories with strongly deviating results may be located outside the plot. The big circle in the figures represents 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 1226 is presented in Table 1 and Table 2. The individual results of the participants are presented in Table 7 in Appendix D, sorted in order of increasing identification number. More extensive statistical information is presented in the Tables 8.1 - 8.19 in the same appendix.

4.1 pH

The reported results for pH are graphically presented in Figure 1, where the radius of the circle is 0,2 pH units, and visualizes the degree of comparability between the pH results from the participating laboratories. The values reported by the laboratories are presented in Table 2 and Table 8.1.

64 of the participating laboratories determined pH in the test samples. All the laboratories had used a method based upon electrometry. 11 of the participants used stirring of the sample while reading the result. 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 1226 it was chosen the median value of all the reported results, after the outliers have been excluded. Based upon this 59 % of the results were acceptable, that is within the median value ± 0,2 pH units. This is significantly lower than in the last intercomparison, but in line with the previous ones (se table 1). If the acceptable limit was reduced to the target value of ± 0,1 pH unit, defined in the Manual (1), 24 more result pairs would be located

outside the acceptance circle, giving just 22 % acceptable results. An limit of ± 0,2 pH units seems to be a reasonable target acceptance limit.

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. It is also questionable whether there could be some differences due to instability of the samples during shipment of the samples. However, stability test done at NIVA during the report period, indicate good stability when the samples are kept cool (see Appendix B). The results are also greatly affected by random errors, illustrated in Figure 1 by the spread of the small circles away from the 45° line for many laboratories.

4.2 Conductivity

The conductivity results are presented in Figure 2, where the large circle represents an accuracy limit of ± 10 %, which is only half of the target accuracy limit given in the Manual (1). The values reported by the laboratories are presented in Table 2 and Table 8.2.

61 laboratories reported results for conductivity, and 59 of these used an electrometric method for the determination. The two last ones stated "other method" without specifying. Most laboratories achieved rather good agreement between the results for this variable, and 72 % of the result were within the acceptance limit of ± 10 %. This is, however, somewhat lower than in the previous intercomparison. Figure 2 shows 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. °C at room temperature. If the accuracy limit was extended to the target value of ± 20 %, defined in the Manual (1), seven more result pairs would be located within the circle and thus be defined as acceptable, giving 84 % acceptable results. Four laboratories have most likely reported their results in an unit other than mS/m and have been rejected. An limit of ± 10 % seems to be a reasonable target acceptance limit.

4.3 Alkalinity

The alkalinity results are illustrated in Figure 3, and the reported results are presented in Table 2 and Table 8.3. 47 laboratories reported results for alkalinity, but one of the participants gave results for two different methods. 17 of these used a titration to both pH = 4,5 and pH = 4,2 and 16 used the Gran plot titration method which is the suggested reference method in the manual (1). Eight participants titrated to pH = 5,4, and four of the particpants titrated to another end point. Two laboratories used a colorimetric method.

In this intercomparison, only 48 % of the sample pairs were within the target accuracy of ± 20 %.
This is significantly lower than for the two previous years, but the alkalinity of the samples was also lower this time. It seems that the laboratories which used Gran plot titration reported somewhat higher results than the other participants.

This time there was a great element of random errors in the results. This is illustrated in Figur 3 by the spead of 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 case, the relative error introduced by assuming a fixed end-point pH, is negligible. However, at lower alkalinities normally encountered in areas sensitive to acidification, the “total fixed end-point method” may overestimate the true alkalinity or the “equivalence” alkalinity.

4.4 Nitrate + nitrite-nitrogen

60 laboratories reported results for nitrate + nitrite-nitrogen, and the results are presented in Figure 4, Table 2 and Table 8.4. Ion chromatography was used by 37 participants. The other laboratories used different photometric methods apart from two which had used capillary electrophoresis and two which had stated "other method". Most of the laboratories which had used a photometric method had made used of an automated version of the cadmium reduction method. There is no significant difference between the results determined by the different analytical methods. This is also expected since nitrite is more or less absent in the samples.

In this intercomparison only 52 % of the results are evaluated as acceptable, which is less than the last intercomparison, but more or less in line with the previous ones. However, evaluation of the results from the intercomparison last year was, due to a mistake by the Program Center, done on just one of the samples and not the sample pair. This makes the comparison not quite correct. Table 8.4 in Appendix D shows that the standard deviation between the results is much higher in sample A compared to sample B. Also the control analyses, presented in Appendix B, Table 3 at the Program Centre indicates that especially sample A is not sufficiently stable in the period of analysis. Also earlier intercomparisons shows that the stability of this parameter in the samples could be a problem. The samples could be affected by environmental conditions during transport to the laboratories. As a consequence of this, the evaluation of this variable is highly questionable. It also seems that three laboratories reported results in wrong unit, and that also some laboratories possibly have reported their results as nitrate instead of nitrogen.

4.5 Chloride

58 laboratories reported results for chloride, and the results are presented in Figure 5, Table 2 and Table 8.5. The target accuracy of ± 20 % is represented by the big circle in Figure 5. The majority of the laboratories used ion chromatography as the analytical technique in their determinations of chloride (81 %). The rest had used different photometric methods, argentometry and capillary electrophoresis. Due to the small numbers of other methods it is difficult to evaluate differences between ion chromatography and the rest of the methods.

In this intercomparison 79 % of the results are evaluated as acceptable, which is somewhat less than the last intercomparison but the same as the previous one. The deviating results are mainly affected by systematic errors, but there are also some laboratories with rather large random errors.

4.6 Sulphate

55 laboratories reported results for sulphate, and the results are presented in Figure 6, Table 2 and Table 8.6. The circle in Figure 6 represents the target accuracy of ± 20 %. Most of the laboratories used ion chromatography as the analytical technique in their determinations of sulfate (85 %). Two laboratories used ICP-AES for the determination of total sulphur and then recalculated the result to sulphate. Due to the small numbers of other methods it is not possible to say so much about differences between ion chromatography and the rest of the methods, but it could seems like photometry and nephelometry gave somewhat lower results.

80 % of the result pairs in this intercomparison are acceptable, which is in line with the previous years. The deviating results are mainly affected by systematic errors.

4.7 Calcium

56 laboratories reported results for calcium, and the results are presented in Figure 7, Table 2 and Table 8.7. The circle in Figure 7 represents the target accuracy of ± 20 %. 23 of the laboratories used ion chromatography, and 15 laboratories used ICP-AES. The traditional flame atomic absorption spectrometry was used by 10 of the participants in their determination of calcium. Four laboratories used ICP-MS, and the four last laboratories used different other methods.

75 % of the result pairs in this intercomparison are acceptable, and this is somewhat lower than the previous years. Ion chromatography seems to give somewhat higher results than ICP-AES, but there was also higher standard deviation between the partcipants using this method. The deviating results are mainly affected by systematic errors.

4.8 Magnesium

57 laboratories reported results for magnesium, and the results are presented in Figure 8, Table 2 and Table 8.8. The circle in Figure 8 represents the target accuracy of ± 20 %. The analytical methods used by the participants are mainly the same as for the determination of calcium. 24 of the laboratories used ion chromatography, and 16 used ICP-AES. The traditional flame atomic absorption spectrometry was used by 11 of the participants in their determination of magnesium. Four used ICP-MS and the the two last ones used capillary electrophoresis and photometry, respectively.

74 % of the result pairs in this intercomparison are acceptable, which is somewhat lower than the previous years. Flame atomic absorption seems to give somewhat lower results than the other methods. The deviating results are mainly affected by systematic errors.

4.9 Sodium

57 laboratories reported results for sodium, and the results are presented in Figure 9, Table 2 and Table 8.9. The circle in Figure 9 represents the target accuracy of ± 20 %. 26 in this round used ion chromatography in their determinations, 12 laboratories used ICP-AES, and 10 used the traditional flame atomic absorption spectrometry. Four used ICP-MS and two laboratories used flame atomic emission spectroscopy.

This time, 84 % of the result pairs in this intercomparison are acceptable. This is rather good, but still somewhat lower than the previous years. This determination usually holds a very good quality. There was no significant difference in the results between the different analytical techniques. The deviating results are mainly affected by systematic errors.

4.10 Potassium

57 laboratories reported results for potassium, and the results are presented in Figure 10, Table 2 and Table 8.10. The circle in Figure 10 represents the target accuracy of ± 20 %. The analytical methods and their distribution among the participants were exactly the same as for the determination of sodium.

81 % of the result pairs are considered acceptable, and this is at about the same level as the previous years. The deviating results are mainly affected by systematic errors, but there are also some laboratories with rather large random errors.

4.11 Total organic carbon

42 laboratories reported results for total organic carbon, and the results are presented in Figure 11, Table 2 and Table 8.11. The circle in Figure 11 represents the target accuracy of ± 20 %. Combustion methods are used by most of the laboratories (32), only 6 laboratories used UV/peroxodisulfate oxidation method for this determination. The four last laboratories stated "other method" when reporting. UV/peroxodisulfate oxidation method seems to give somewhat lower results than the other methods but the difference is not significant.

76 % of the results were within the targent accuracy of ± 20 %. That is better than for the last year, but still somewhat lower than the two previous ones. The deviating results are mainly affected by systematic errors.

4.12 Aluminium

37 laboratories reported results for aluminium, but two of the participants gave results for two different methods. The results are presented in Figure 12, Table 2 and Table 8.12. The circle in Figure 12 represents the target accuracy of ± 20 %. 15 of the laboratories used ICP-AES and the same number used ICP-MS. 6 participants used graphite furnace atomic absortion, while only one used flame atomic absorption. The two last laboratories had stated that they used photometry and "other method".

In this round, 79 % of the result pairs are considered acceptable, and this is about the same as for the last years. ICP-MS gave slightly higher results than the other spectroscopy methods. The deviating results are mainly affected by systematic errors.

4.13 Iron

39 laboratories reported results for iron, but one of the participants gave results for two different methods. The results are presented in Figure 13, Table 2 and Table 8.13. The circle in Figure 13 represents the target accuracy of ± 20 %. 17 and 15 of the laboratories used ICP-AES and ICP-MS, respectively. Five participants used graphite furnace atomic absortion, while two used flame atomic absorption. One laboratory used a method based on photometry.

This time 70 % of the result pairs are considered acceptable, which is significantly lower than last year, and also a little lower than the previous intercomparisons. There are no big differences in results between the plasma methods. The deviating results are mainly affected by systematic errors, but there are also some laboratories with rather large random errors.

4.14 Manganese

43 laboratories reported results for manganese, but one of the participants gave results for two different methods. The results are presented in Figure 14, Table 2 and Table 8.14. The circle in Figure 14 represents the target accuracy of ± 20 %. 17 and 16 used the plasma techniques ICP-MS and ICP-AES, respectively, while 8 and 3 used graphite furnace atomic absorption and flame atomic absorption, respectively.

89 % of the result pairs are considered acceptable, which is very good. There are no big differences between the different methods. The deviating results are mainly affected by systematic errors.

4.15 Cadmium

44 laboratories reported results for cadmium, but one of the participants gave results for two different methods. The results are presented in Figure 15, Table 2 and Table 8.15. The circle in Figure 15 represents the target accuracy of ± 20 %. 21 laboratories used ICP-MS, and graphite furnace atomic absorption was used by 13. ICP-AES was used by 7 participants, and the three last ones had used flame atomic absorption, potensiometric stripping and "other method".

84 % of the result pairs are considered acceptable, which is somewhat lower than the last year, but still good. There are no big differences between the different methods, apart from graphite furnace atomic absorption which seems to give a little bit lower results than the plasma techniques. The deviating results are mainly affected by systematic errors, but there are also some laboratories with rather large random errors.

4.16 Lead

43 laboratories reported results for lead, but one of the participants gave results for two different methods. The results are presented in Figure 16, Table 2 and Table 8.16. The circle in Figure 16 represents the target accuracy of ± 20 %. The analytical methods used by the participants are mainly the same as for the determination of cadmium. 21 laboratories used ICP-MS, and graphite furnace atomic absorption was used by 14. ICP-AES was used by 7 participants, and the two last ones had used flame atomic absorption and potensiometric stripping.

77 % of the result pairs are considered acceptable, which is somewhat better than in the previous intercomparisons. There are no significant differences in results between the different methods. The deviating results are mainly affected by systematic errors, but there are also some laboratories with rather large random errors.

4.17 Copper

43 laboratories reported results for copper, but one of the participants gave results for two different methods.The results are presented in Figure 17, Table 2 and Table 8.17. The circle in Figure 17 represents the target accuracy of ± 20 %. 19, 13 and 10 laboratories had used ICP-MS, graphite furnace atomic absorption, and ICP-AES, respectively. The two last ones had used flame atomic absorption and a potensiometric stripping method.

86 % of the result pairs are considered acceptable, which is very good. It has been an significant improvement in the quality of this determination during the last years (table 1). There are no significant differences in results between the different methods, and the deviating results are mainly affected by systematic errors

4.18 Nickel

41 laboratories reported results for nickel, and the results are presented in Figure 18, Table 2 and Table 8.18. The circle in Figure 18 represents the target accuracy of ± 20 %. 18, 14 and 8 laboratories had used ICP-MS, graphite furnace atomic absorption, and ICP-AES, respectively. The last participant had used flame atomic absorption.

In this round, 78 % of the result pairs are considered acceptable. This is better than the two previous year. The deviating results are mainly affected by systematic errors

4.19 Zinc

36 laboratories reported results for zinc, but two of the participants gave results for two different methods. The results are presented in Figure 19, Table 2 and Table 8.19. The circle in Figure 19 represents the target accuracy of ± 20 %. ICP-MS was the most widely used method with 19 participants, and 12 and 5 laboratories had used ICP-AES and graphite furnace atomic absorption, respectively. The two last participants had used flame atomic absortion and a potensiometric stripping method.

Only 61 % of the result pairs are considered acceptable. It has been an significant worsening in the quality of this determination during the last years (table 1). Graphite atomic absorption seems to give somewhat higher results than the plasma methods. Although the deviating results are affected mainly by systematic errors, the values are also highly affected by random errors.

Table 2. Statistical summary for intercomparison 1226

Analysevariable and method	Sample-pair	True value S. 1	True value S. 2	No. of labs. Total	No. of labs. Om.	Median S. 1	Median S. 2	Avg. Sample 1	Std.dev. Sample 1	Avg. Sample 2	Std.dev. Sample 2	Rel..std.dev. % S. 1	Rel..std.dev. % S. 2	Relative error % S. 1	Relative error % S. 2
pH	AB	6,53	6,68	64	3	6,53	6,68	6,50	0,24	6,62	0,22	3,7	3,3	-0,5	-0,9
Electrometry				46	3	6,52	6,69	6,47	0,25	6,61	0,23	3,8	3,5	-1,0	-1,1
Stirring				11	0	6,64	6,69	6,61	0,24	6,67	0,25	3,6	3,7	1,2	-0,1
Equilibration				6	0	6,62	6,67	6,57	0,13	6,68	0,05	2,0	0,7	0,7	0,0
Other method				1	0			6,14		6,42				-6,0	-3,9
Conductivity, mS/m	AB	2,20	2,35	61	8	2,20	2,35	2,21	0,14	2,33	0,14	6,2	6,2	0,3	-0,7
Electrometry				59	8	2,20	2,35	2,21	0,14	2,34	0,14	6,2	6,2	0,3	-0,6
Other method				2	0			2,18		2,28				-0,9	-3,2
Alkalinity, mmol/l	AB	0,063	0,070	48	14	0,063	0,070	0,067	0,013	0,072	0,012	19,5	16,7	6,3	2,9
End point titration				17	6	0,061	0,069	0,066	0,013	0,069	0,010	20,3	14,0	4,5	-0,9
Gran plot titration				16	2	0,067	0,075	0,067	0,014	0,073	0,014	20,7	18,7	6,8	4,9
End point 5.4				7	2	0,060	0,070	0,066	0,012	0,071	0,005	18,8	6,5	4,9	1,5
End point				3	1			0,079		0,083				24,6	17,9
Colorimetry				2	2			0,067		0,074				6,3	5,0
Other method				2	1			0,063		0,067				-0,3	-4,4
End point 5.6				1	0			0,059		0,070				-6,0	-0,1
Nitrate + nitrite-nitrogen, µg/l	AB	172	178	60	19	172	178	161	29	178	16	17,9	8,8	-6,6	-0,2
Ion chromatography				37	13	170	177	157	32	177	18	20,4	10,1	-9,0	-0,5
Photometry				8	3	176	180	159	36	177	17	22,5	9,8	-7,8	-0,5
Flow injection anal.				6	1	173	173	175	5	175	5	2,7	3,0	1,5	-1,9
Autoanalyzer				3	0	172	182	174	7	179	5	4,2	2,6	1,1	0,7
Cap. electrophoresis				2	1			170		172				-1,2	-3,4
Other method				2	1			183		186				6,4	4,5
Hydrazine				1	0			170		170				-1,2	-4,5
Photometry				1	0			119		207				-30,8	16,3
Chloride, mg/l	AB	1,05	1,23	58	4	1,05	1,23	1,04	0,11	1,24	0,10	10,2	8,3	-0,7	0,7
Ion chromatography				47	0	1,05	1,23	1,05	0,10	1,25	0,10	9,6	7,7	0,0	1,2
Argentometry				2	1			0,90		1,38				-14,3	12,2
Cap. electrophoresis				2	1			1,00		1,21				-4,8	-2,0
Manual, Hg				2	0			1,12		1,26				6,7	2,4
AA				1	0			0,95		1,02				-9,5	-17,1
Other method				1	1			1,56		1,84				48,6	49,6
Photometry				1	0			1,05		1,24				0,0	0,8
Photometry HgSCN				1	0			0,78		1,02				-25,7	-17,1
Potentiometry				1	1			0,00		0,00				-100	-100
Sulphate, mg/l	AB	3,04	2,79	55	3	3,04	2,79	3,00	0,29	2,80	0,23	9,7	8,3	-1,3	0,4
Ion chromatography				47	2	3,04	2,79	3,01	0,27	2,79	0,24	9,1	8,6	-0,9	0,0
Cap. electrophoresis				2	0			3,02		2,81				-0,7	0,7
ICP-AES				2	0			3,09		2,86				1,5	2,6
Photometry				2	0			2,49		2,90				-18,1	3,9
Nephelometry				1	1			2,30		3,60				-24,3	29,0
Other method				1	0			3,25		2,92				6,9	4,7

Om.: Sample pair omitted from the calculations

Analysevariable and method	Sample-pair	True value S. 1	True value S. 2	No. of labs. Total	No. of labs. Om.	Median S. 1	Median S. 2	Avg. Sample 1	Std.dev. Sample 1	Avg. Sample 2	Std.dev. Sample 2	Rel..std.dev. % S. 1	Rel..std.dev. % S. 2	Relative error % S. 1	Relative error % S. 2
Calcium, mg/l	AB	1,72	2,04	56	3	1,72	2,04	1,72	0,23	2,06	0,26	13,4	12,6	0,0	1,2
Ion chromatography				23	0	1,80	2,16	1,76	0,29	2,14	0,33	16,3	15,3	2,0	5,0
ICP-AES				15	0	1,69	2,01	1,71	0,11	2,02	0,11	6,4	5,3	-0,5	-0,8
FAAS				10	2	1,76	2,03	1,76	0,10	2,02	0,15	6,0	7,5	2,4	-0,9
ICP-MS				4	0	1,64	1,92	1,64	0,20	2,04	0,30	12,1	14,8	-4,7	-0,2
Cap. Electrophoresis				1	0			1,02		1,47				-40,7	-27,9
EDTA				1	0			1,85		2,10				7,6	2,9
Other method				1	0			1,63		1,92				-5,4	-5,9
Photometry				1	1			0,00		0,00				-100	-100
Magnesium, mg/l	AB	0,270	0,320	57	2	0,270	0,320	0,272	0,042	0,322	0,037	15,5	11,6	0,8	0,8
Ion chromatography				24	1	0,270	0,330	0,276	0,040	0,327	0,037	14,4	11,4	2,4	2,3
ICP-AES				16	0	0,270	0,319	0,276	0,029	0,316	0,023	10,4	7,3	2,1	-1,3
FAAS				11	0	0,250	0,300	0,247	0,052	0,313	0,050	20,8	16,1	-8,4	-2,3
ICP-MS				4	0	0,272	0,320	0,274	0,023	0,333	0,044	8,3	13,3	1,3	4,1
Cap. Electrophoresis				1	0			0,390		0,380				44,4	18,8
Photometry				1	1			0,000		0,000				-100	-100
Sodium, mg/l	AB	1,73	1,63	57	3	1,73	1,63	1,71	0,13	1,63	0,15	7,7	9,0	-1,2	0,3
Ion chromatography				26	3	1,73	1,64	1,74	0,09	1,65	0,08	5,1	5,0	0,5	1,3
ICP-AES				12	0	1,68	1,60	1,69	0,08	1,61	0,11	5,0	6,7	-2,1	-1,0
FAAS				10	0	1,73	1,64	1,70	0,17	1,64	0,21	9,8	12,8	-1,5	0,3
ICP-MS				4	0	1,67	1,58	1,74	0,19	1,70	0,28	11,1	16,6	0,4	4,4
AES				2	0			1,61		1,54				-6,9	-5,8
Other method				2	0			1,52		1,52				-12,4	-7,1
Cap. Electrophoresis				1	0			1,79		1,68				3,5	3,1
Potassium, mg/l	AB	0,381	0,350	57	6	0,381	0,350	0,379	0,035	0,347	0,029	9,3	8,5	-0,2	-0,9
Ion chromatography				26	1	0,381	0,350	0,374	0,035	0,343	0,032	9,3	9,3	-1,6	-2,0
ICP-AES				12	1	0,391	0,350	0,384	0,041	0,347	0,021	10,8	6,1	1,1	-0,9
FAAS				10	2	0,380	0,348	0,388	0,043	0,352	0,034	11,2	9,6	2,0	0,6
ICP-MS				4	1	0,374	0,340	0,371	0,010	0,335	0,023	2,8	7,0	-2,3	-4,2
AES				2	0			0,390		0,350				2,6	0,0
Other method				2	1			0,410		0,410				7,9	17,1
Cap. Electrophoresis				1	0			0,375		0,361				-1,3	3,1
Total organic carbon, mg/l	AB	3,84	4,49	42	2	3,84	4,49	3,91	0,46	4,56	0,44	11,8	9,7	1,8	1,6
Combustion				32	1	3,81	4,50	3,92	0,43	4,59	0,42	10,9	9,1	2,2	2,2
UV/peroxodisulphate				6	1	3,57	4,15	3,86	0,80	4,44	0,70	20,6	15,7	0,6	-1,0
Other method				4	0	3,95	4,49	3,88	0,25	4,47	0,32	6,6	7,1	1,0	-0,4
Aluminium, µg/l	CD	81,5	84,6	39	2	81,5	84,6	80,5	8,6	82,2	9,3	10,7	11,3	-1,3	-2,8
ICP-AES				15	0	78,6	80,0	79,3	7,9	79,9	8,2	10,0	10,2	-2,7	-5,6
ICP-MS				15	0	83,2	85,1	83,3	6,2	85,4	6,6	7,5	7,8	2,2	0,9
GFAAS				6	0	74,0	77,5	77,8	13,9	78,9	15,6	17,9	19,7	-4,5	-6,7
FAAS				1	0			70,8		90,0				-13,1	6,4
Other method				1	1			42,4		43,4				-47,9	-48,7
Photometry				1	1			118,0		107,0				44,8	26,5

Om.: Sample pair omitted from the calculations

Analysevariable and method	Sample-pair	True value S. 1	True value S. 2	No. of labs. Total	No. of labs. Om.	Median S. 1	Median S. 2	Avg. Sample 1	Std.dev. Sample 1	Avg. Sample 2	Std.dev. Sample 2	Rel..std.dev. % S. 1	Rel..std.dev. % S. 2	Relative error % S. 1	Relative error % S. 2
Iron, µg/l	CD	70,4	73,0	40	5	70,4	73,0	71,2	9,7	72,9	8,3	13,6	11,4	1,1	-0,1
ICP-AES				17	0	70,0	72,9	71,2	3,5	73,5	5,0	5,0	6,9	1,1	0,7
ICP-MS				15	1	70,3	73,7	69,5	10,2	72,6	9,8	14,6	13,5	-1,3	-0,6
GFAAS				5	3			61,1		63,4				-13,3	-13,2
FAAS				2	0			93,5		79,5				32,8	8,9
Photometry				1	1			115,0		225,0				63,4	208,2
Manganese, µg/l	CD	11,6	15,8	44	4	11,6	15,8	11,6	0,8	15,7	1,0	6,7	6,2	-0,2	-0,7
ICP-MS				17	0	11,6	15,9	11,5	0,7	15,8	1,0	6,5	6,6	-0,5	-0,1
ICP-AES				16	0	11,5	15,7	11,4	0,5	15,6	0,5	4,6	3,2	-1,3	-1,1
GFAAS				8	4	11,5	16,0	11,4	1,5	16,2	1,6	12,9	9,8	-1,4	2,8
FAAS				3	0	12,5	14,0	12,6	0,3	14,8	1,4	2,8	9,4	8,7	-6,3
Cadmium, µg/l	CD	2,12	1,88	44	0	2,12	1,88	2,11	0,20	1,86	0,21	9,5	11,0	-0,3	-1,1
ICP-MS				21	0	2,12	1,89	2,15	0,13	1,91	0,15	6,0	7,6	1,5	1,5
GFAAS				13	0	2,01	1,73	2,05	0,24	1,77	0,23	11,6	13,2	-3,5	-5,9
ICP-AES				7	0	2,20	1,90	2,17	0,23	1,86	0,15	10,8	8,1	2,5	-1,1
FAAS				1	0			2,30		2,30				8,5	22,3
Other method				1	0			1,60		1,40				-24,5	-25,5
Pot. stripping				1	0			2,15		2,05				1,6	9,0
Lead, µg/l	CD	8,23	7,40	44	4	8,23	7,40	8,30	0,71	7,38	0,71	8,6	9,6	0,9	-0,3
ICP-MS				21	0	8,20	7,38	8,18	0,64	7,36	0,70	7,9	9,4	-0,6	-0,5
GFAAS				14	4	8,27	7,59	8,45	0,73	7,51	0,89	8,6	11,9	2,7	1,5
ICP-AES				7	0	8,49	7,40	8,44	0,94	7,19	0,55	11,2	7,6	2,5	-2,9
FAAS				1	0			7,85		7,15				-4,6	-3,4
Pot. stripping				1	0			9,00		8,00				9,3	8,1
Copper, µg/l	CD	13,9	13,5	44	3	13,9	13,5	13,8	1,1	13,3	1,2	8,3	8,9	-1,0	-1,8
ICP-MS				19	1	14,0	13,5	14,1	0,7	13,6	0,8	4,8	5,7	1,5	0,9
GFAAS				13	2	14,2	13,6	13,6	1,5	12,9	1,6	10,8	12,6	-2,1	-4,1
ICP-AES				10	0	13,7	13,2	13,4	1,4	13,0	1,2	10,5	9,4	-3,4	-3,6
FAAS				1	0			13,5		13,7				-2,9	1,5
Pot. stripping				1	0			13,0		11,9				-6,8	-11,7
Nickel, µg/l	CD	8,50	7,20	41	0	8,50	7,20	8,36	1,00	7,27	1,10	12,0	15,2	-1,6	0,9
ICP-MS				18	0	8,52	7,22	8,56	0,61	7,37	0,68	7,2	9,3	0,7	2,3
GFAAS				14	0	8,18	7,12	7,94	1,36	6,87	1,44	17,2	21,0	-6,6	-4,6
ICP-AES				8	0	8,68	7,40	8,64	0,92	7,61	1,15	10,7	15,1	1,6	5,8
FAAS				1	0			8,60		8,20				1,2	13,9
Zinc, µg/l	CD	4,20	5,70	38	6	4,24	5,70	4,22	0,81	5,84	0,87	19,2	15,0	0,5	2,4
ICP-MS				19	1	4,20	5,73	4,17	0,81	5,87	0,93	19,3	15,8	-0,8	3,0
ICP-AES				12	3	4,19	5,64	4,03	0,81	5,58	0,85	20,1	15,2	-4,0	-2,1
GFAAS				5	1	4,91	6,25	4,96	0,68	6,35	0,71	13,7	11,2	18,0	11,4
FAAS				1	1			13,00		12,50				209,5	119,3
Pot. stripping				1	0			3,89		5,51				-7,4	-3,3

Om.: Sample pair omitted from the calculations

pH

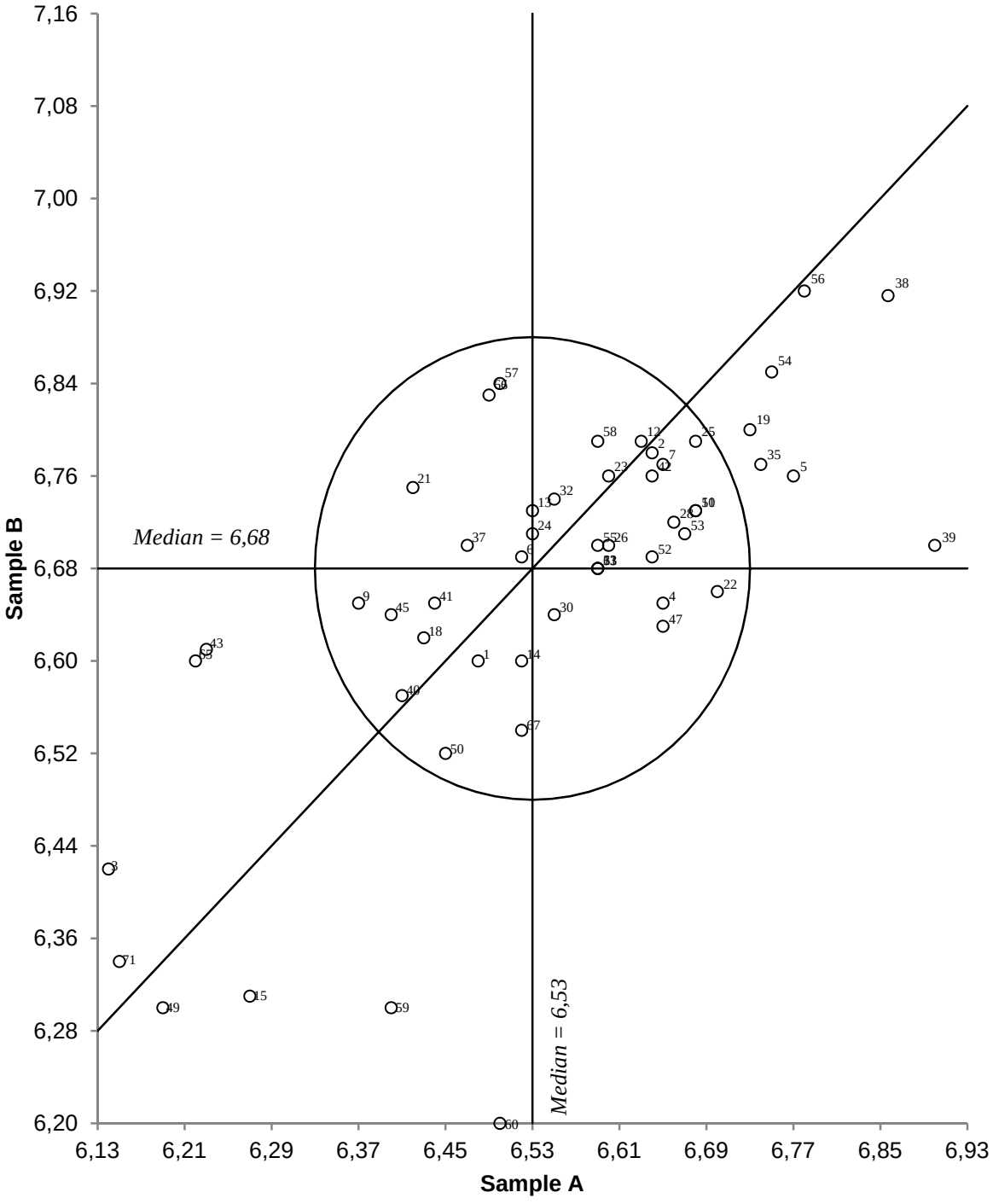

Figure 1. Youdendiagram for pH, Samplepair AB
Acceptable limit , given by circle, is 0,2 pH units

Conductivity

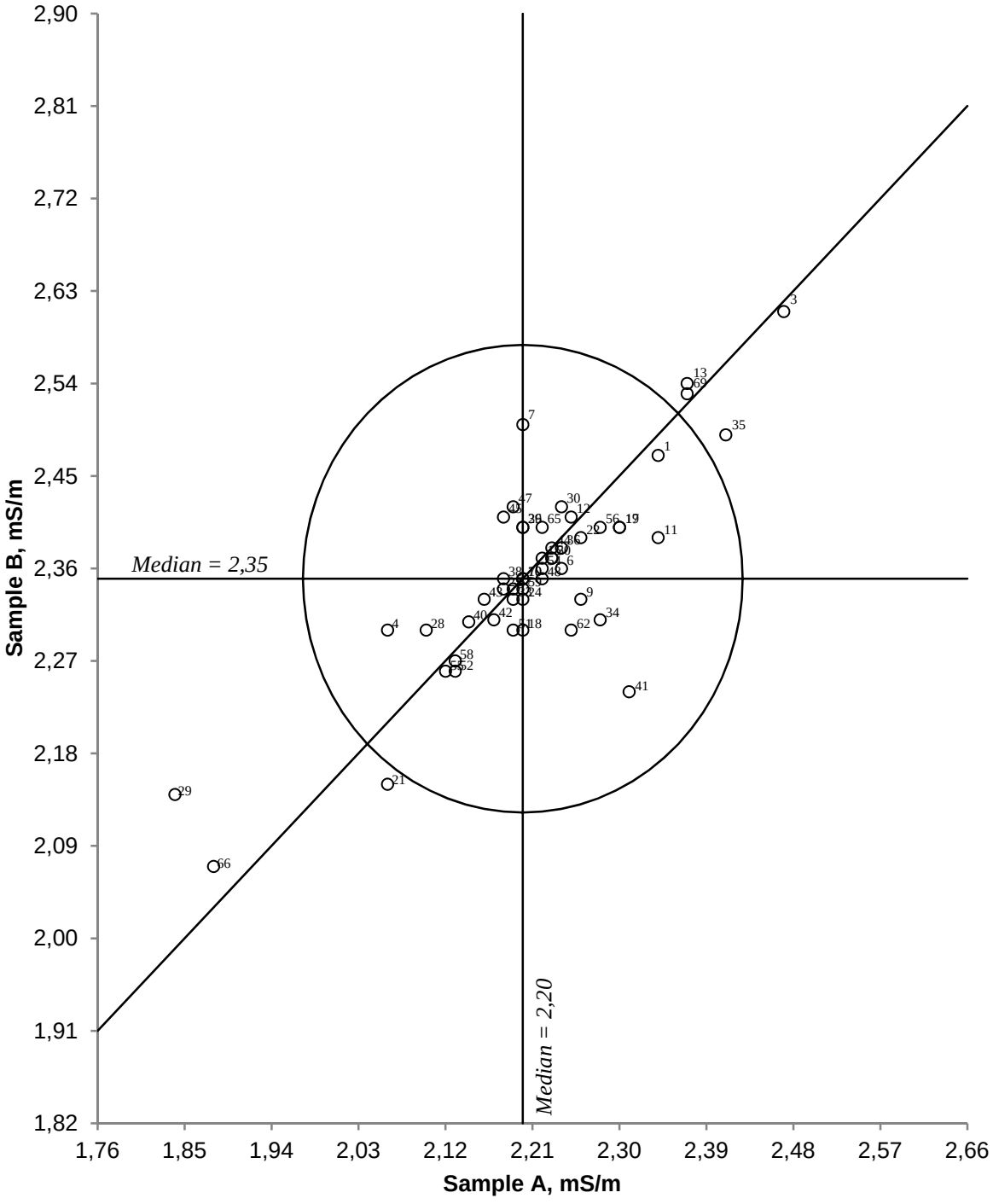

Figure 2. Youdendiagram for conductivity, Samplepair AB
Acceptable limit , given by circle, is 10 %

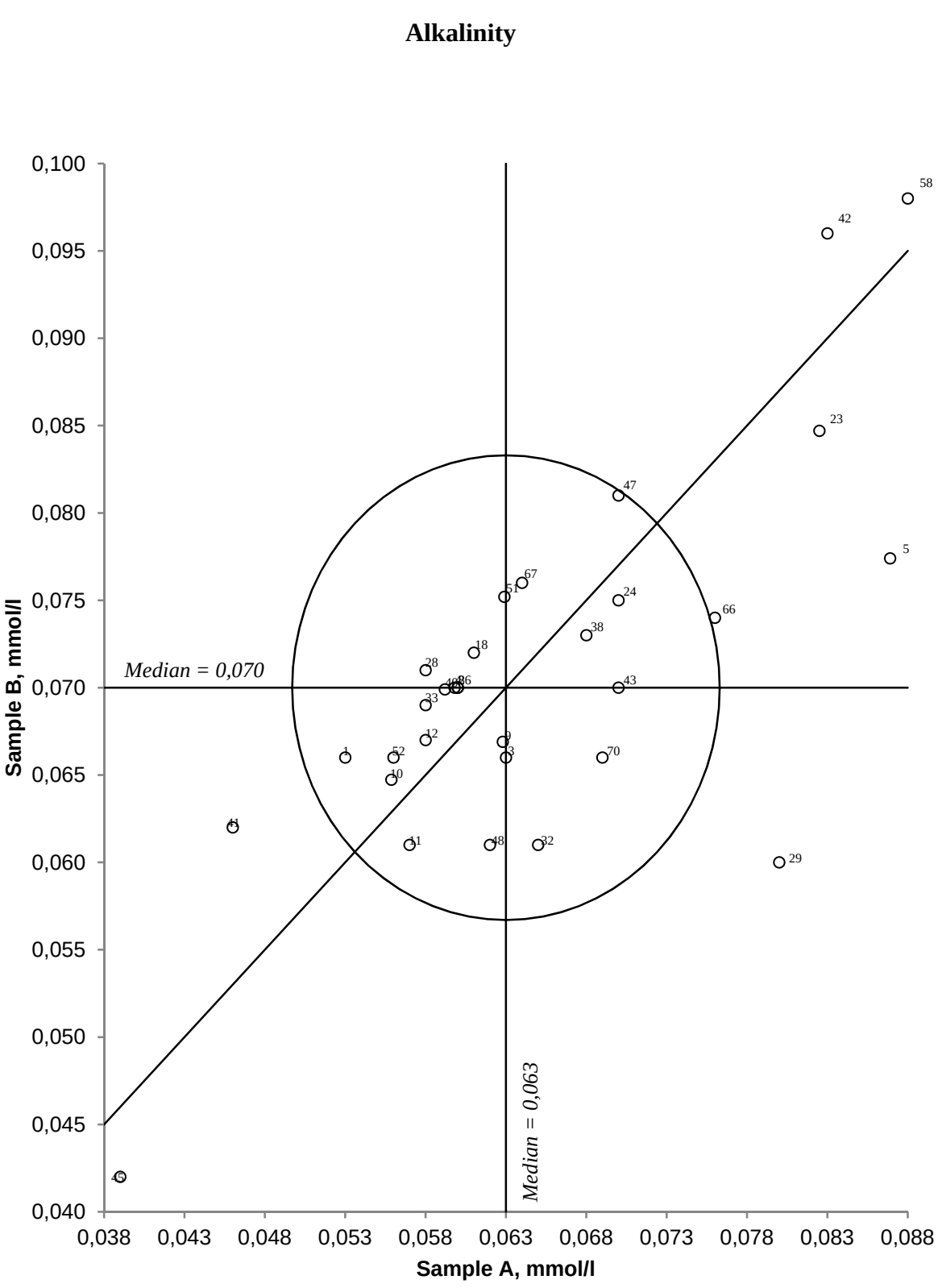

Figure 3. Youdendiagram for alkalinity, Samplepair AB
Acceptable limit , given by circle, is 20 %

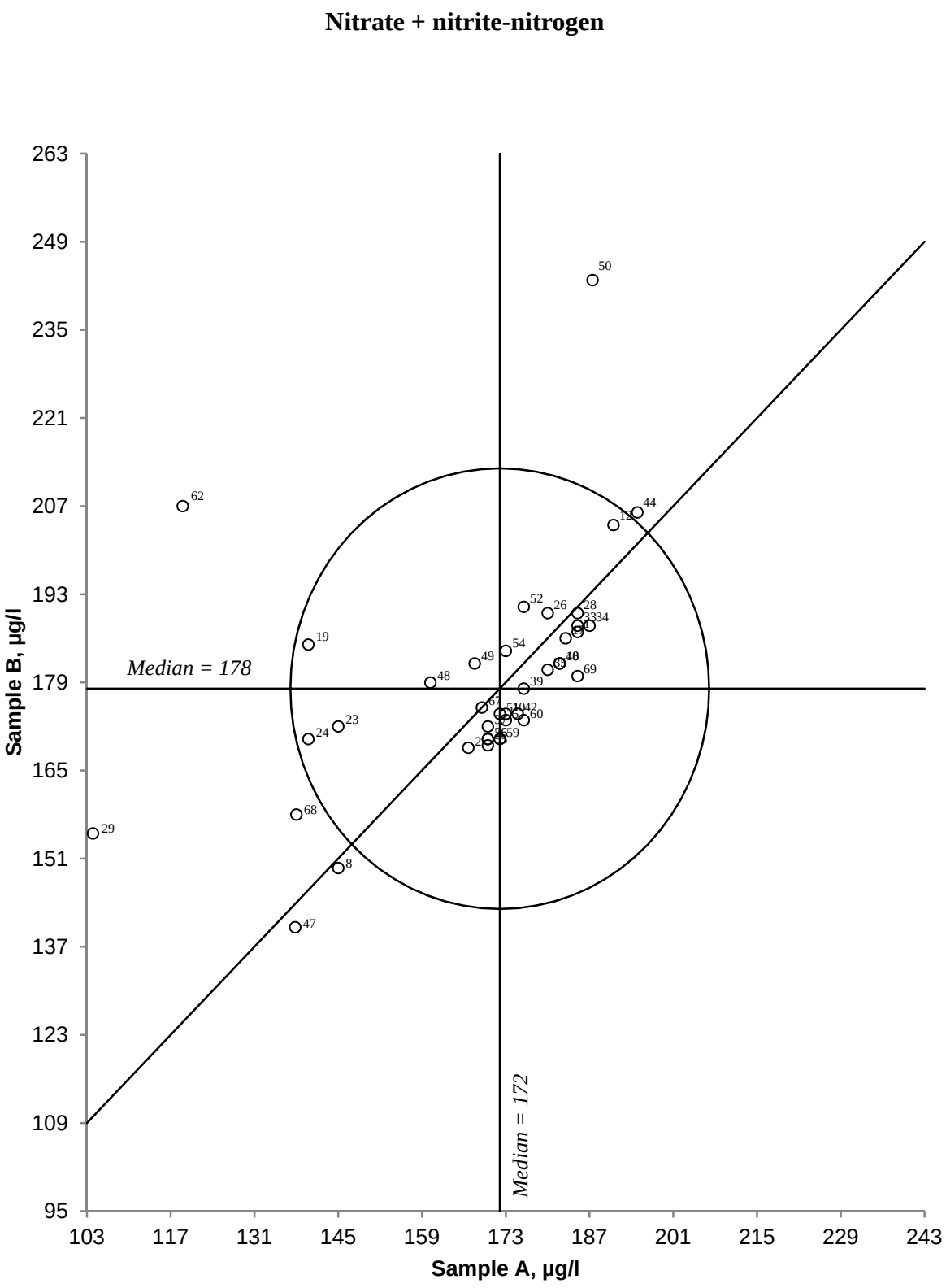

Figure 4. Youdendiagram for nitrate + nitrite-nitrogen, Samplepair AB
Acceptable limit , given by circle, is 20 %

Chloride

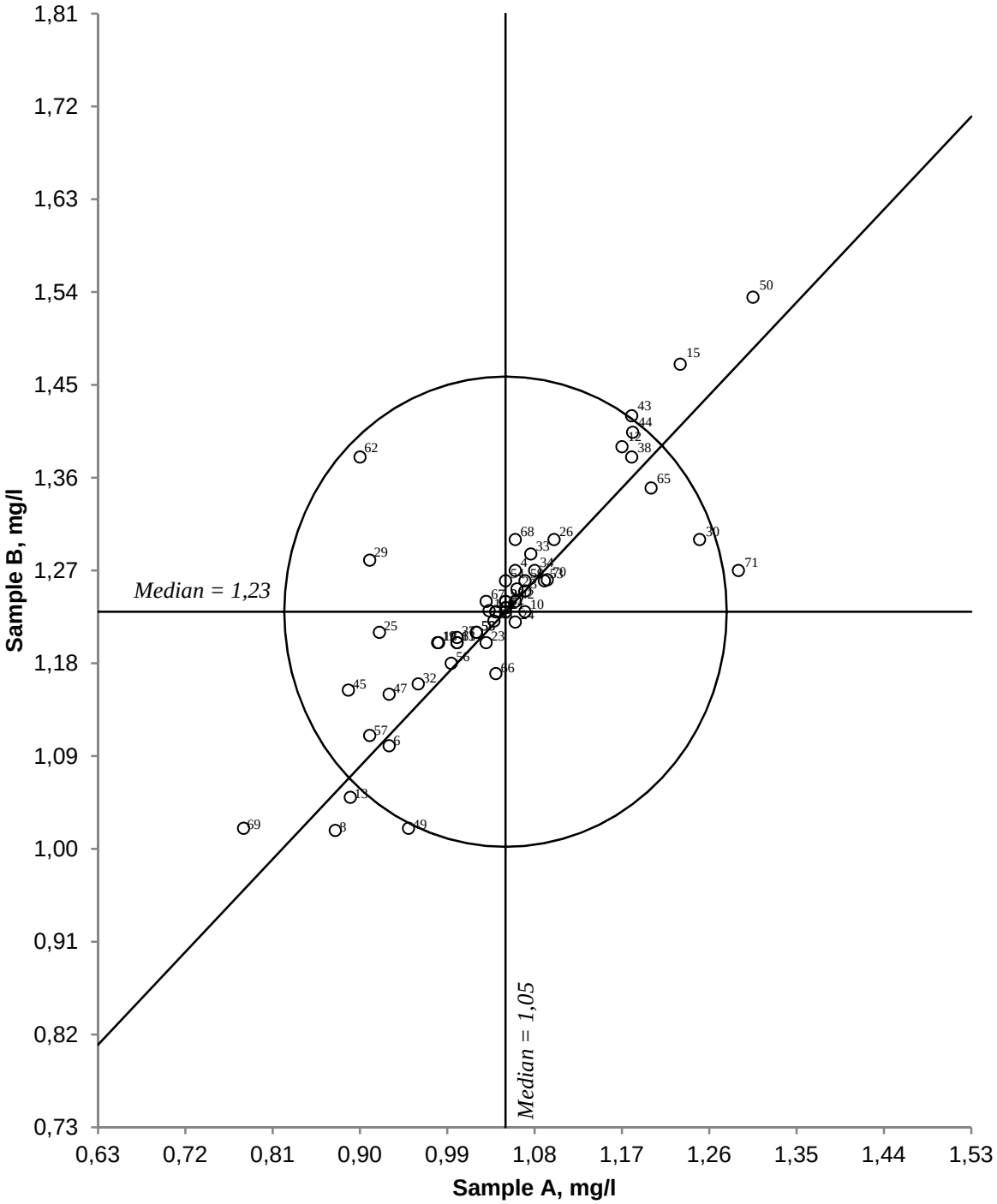

Figure 5. Youdendiagram for chloride, Samplepair AB
Acceptable limit , given by circle, is 20 %

Sulphate

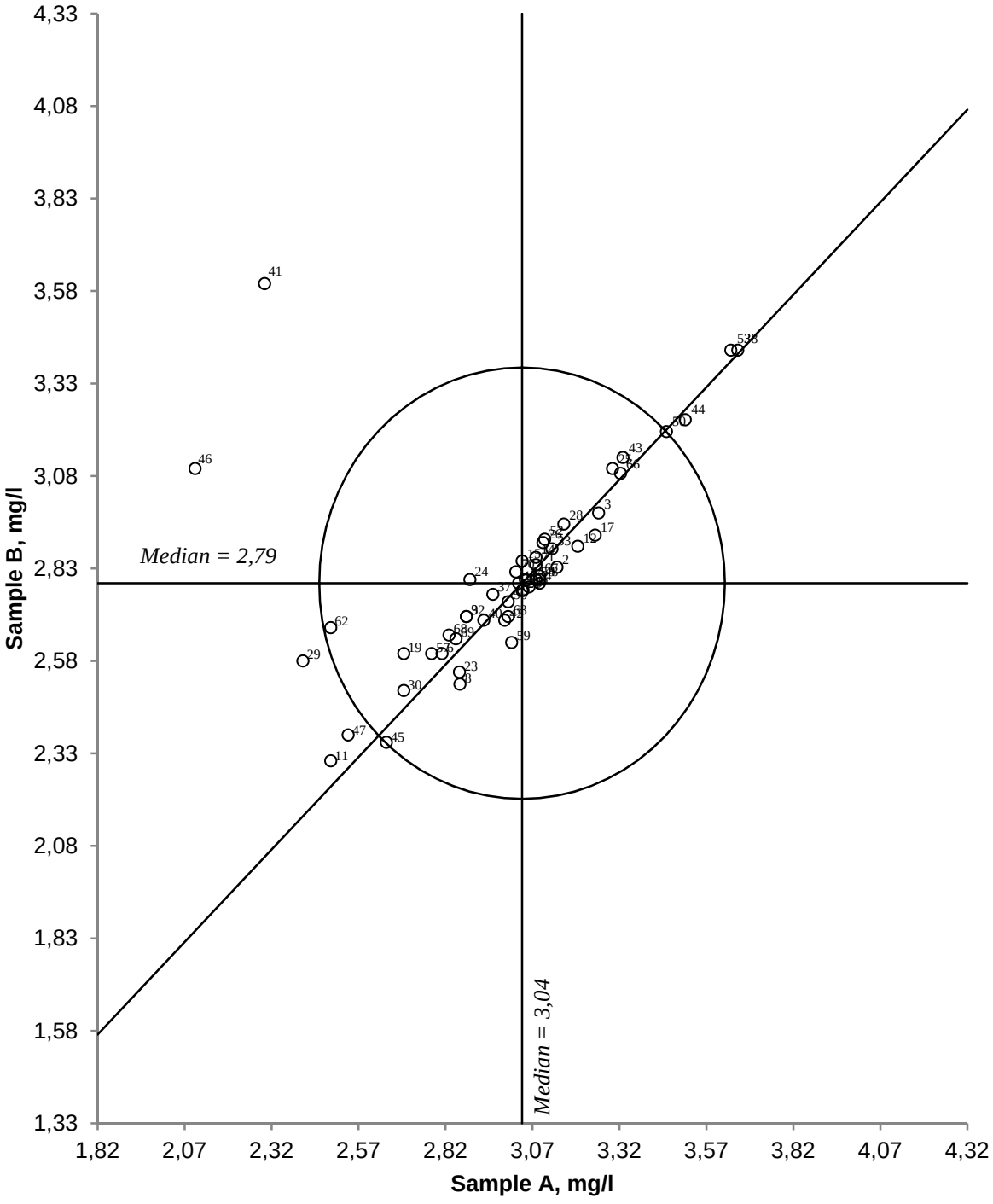

Figure 6. Youdendiagram for sulphate, Samplepair AB
Acceptable limit , given by circle, is 20 %

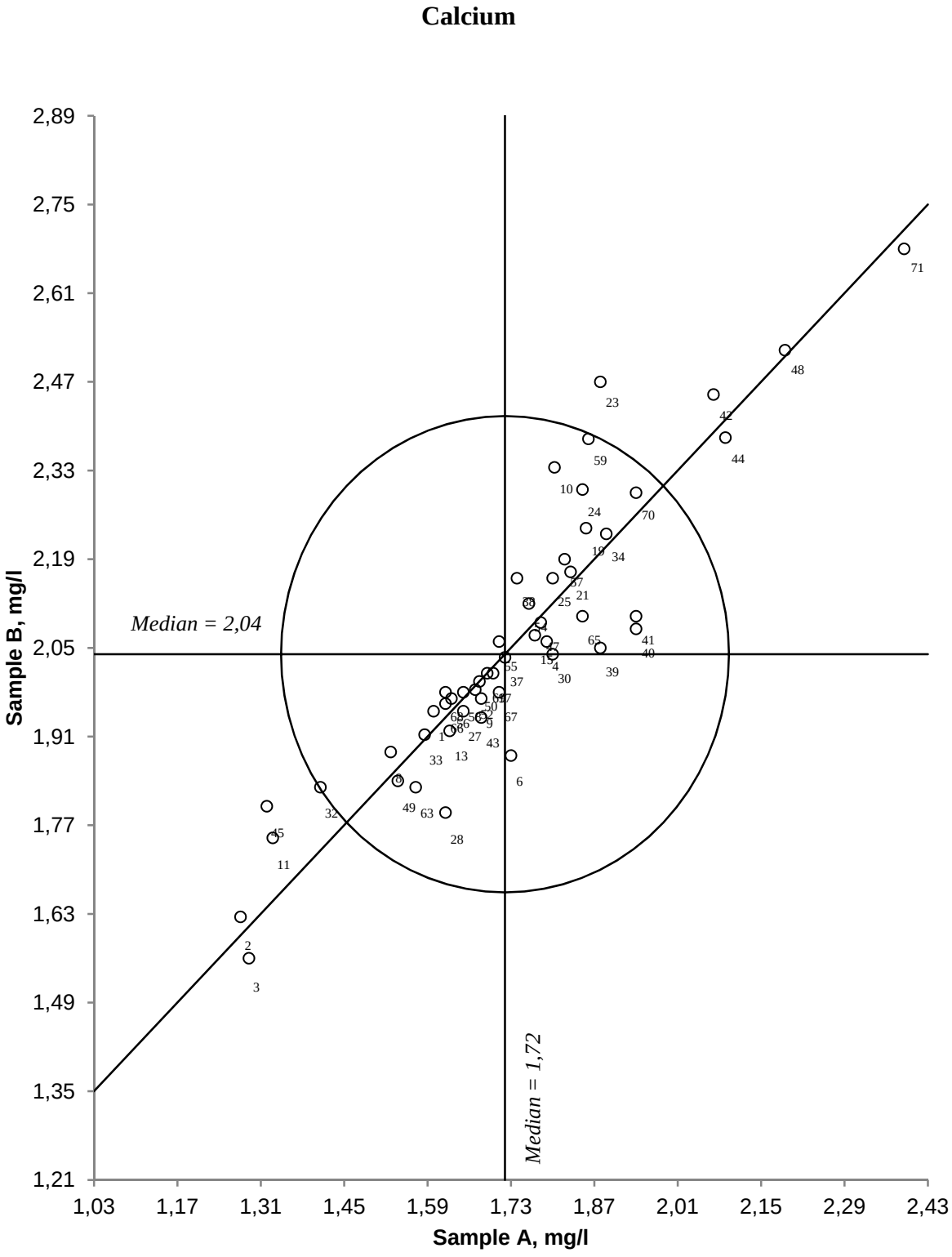

Figure 7. Youdendiagram for calcium, Samplepair AB
Acceptable limit , given by circle, is 20 %

Magnesium

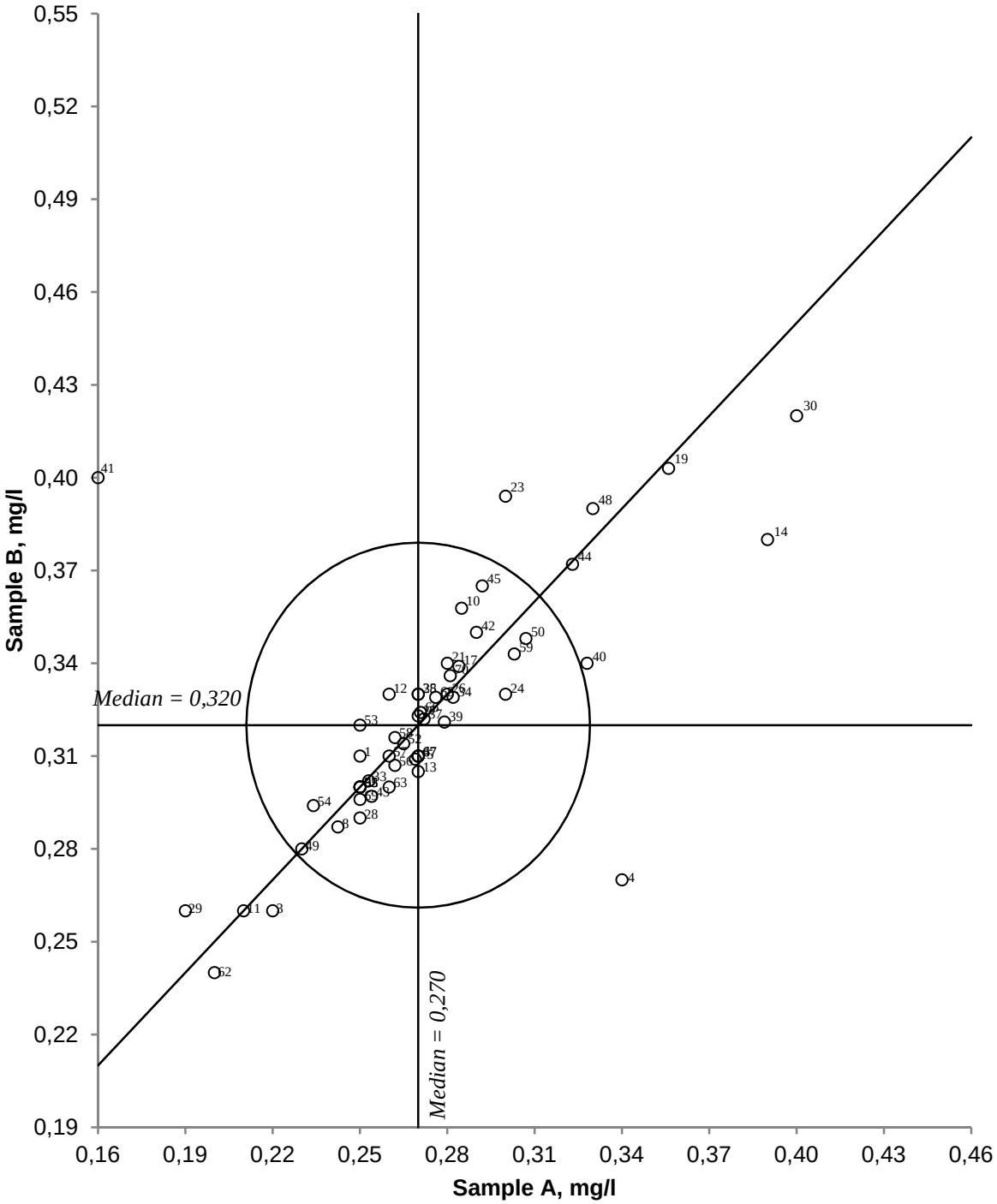

Figure 8. Youdendiagram for magnesium, Samplepair AB
Acceptable limit , given by circle, is 20 %

Sodium

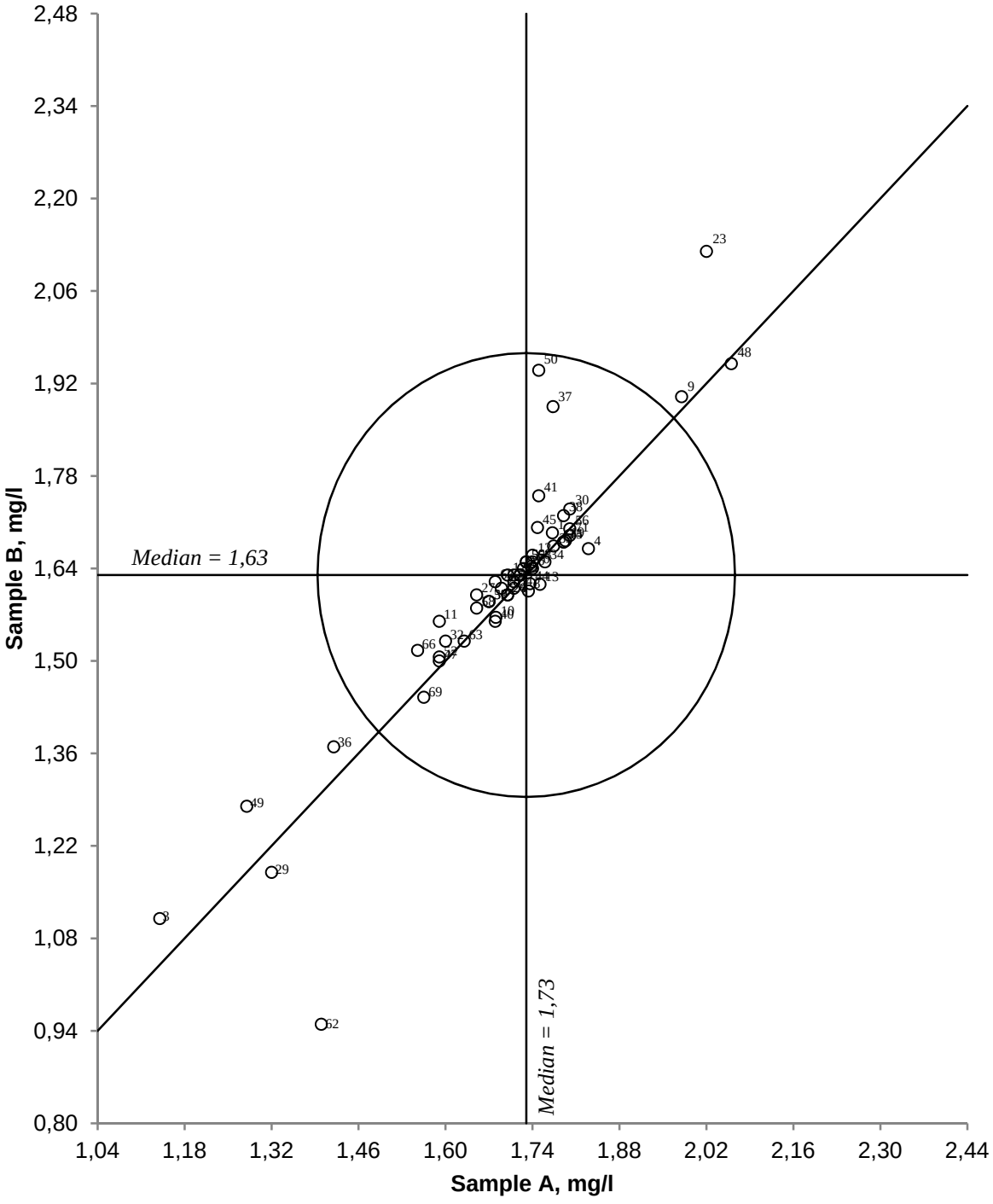

Figure 9. Youdendiagram for sodium, Samplepair AB
Acceptable limit , given by circle, is 20 %

Potassium

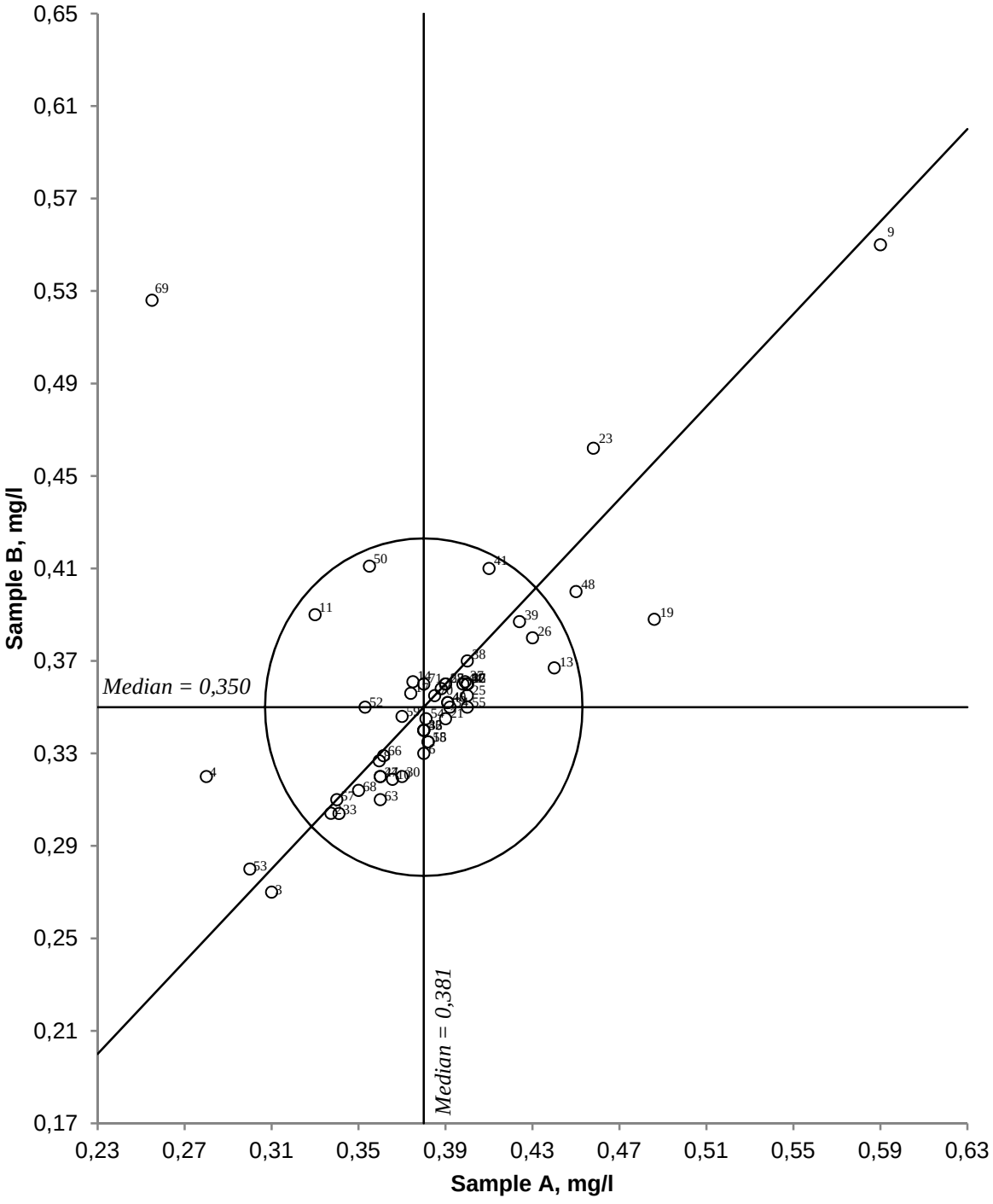

Figure 10. Youdendiagram for potassium, Samplepair AB
Acceptable limit , given by circle, is 20 %

Total organic carbon

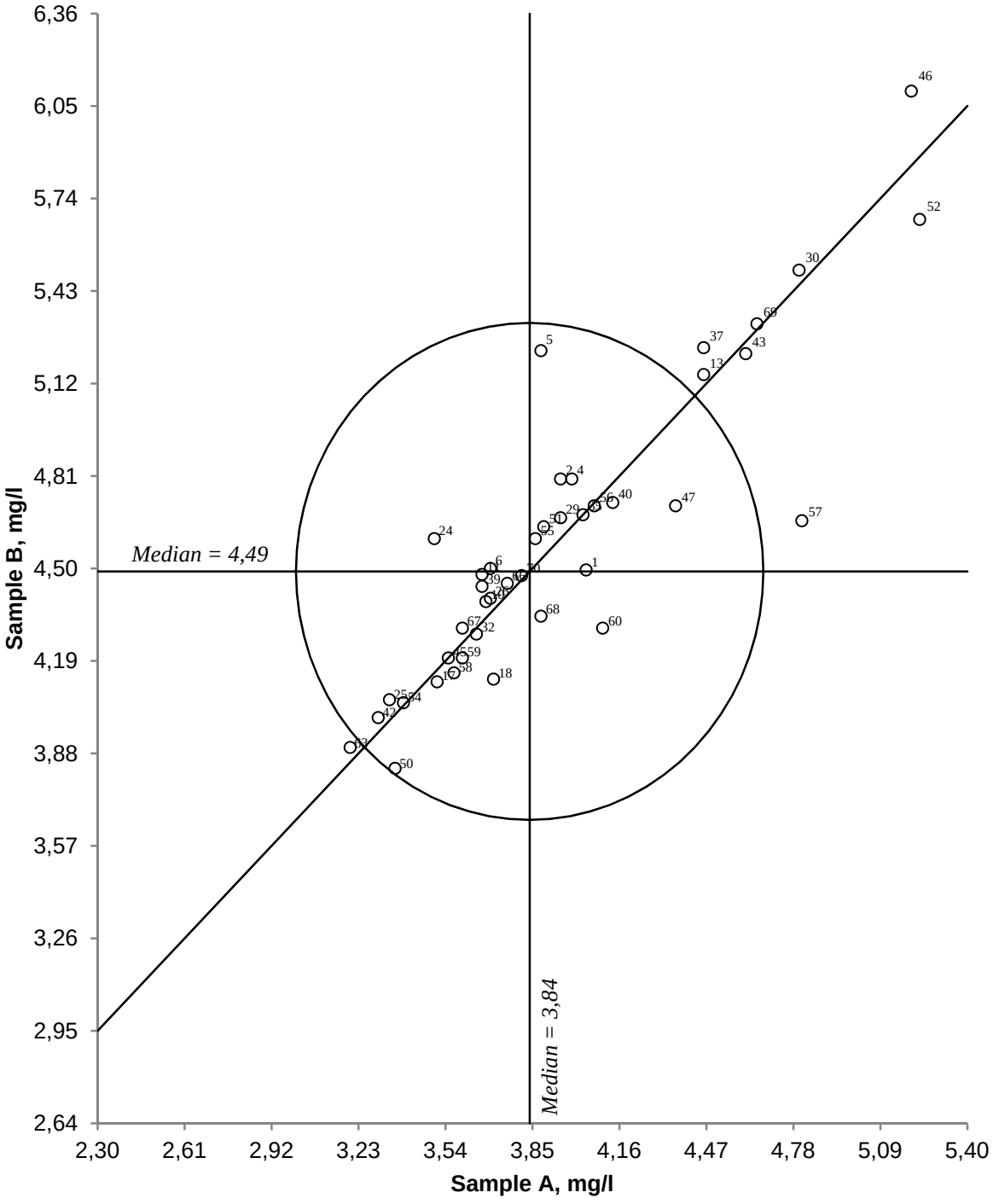

Figure 11. Youdendiagram for total organic carbon, Samplepair AB
Acceptable limit , given by circle, is 20 %

Aluminium

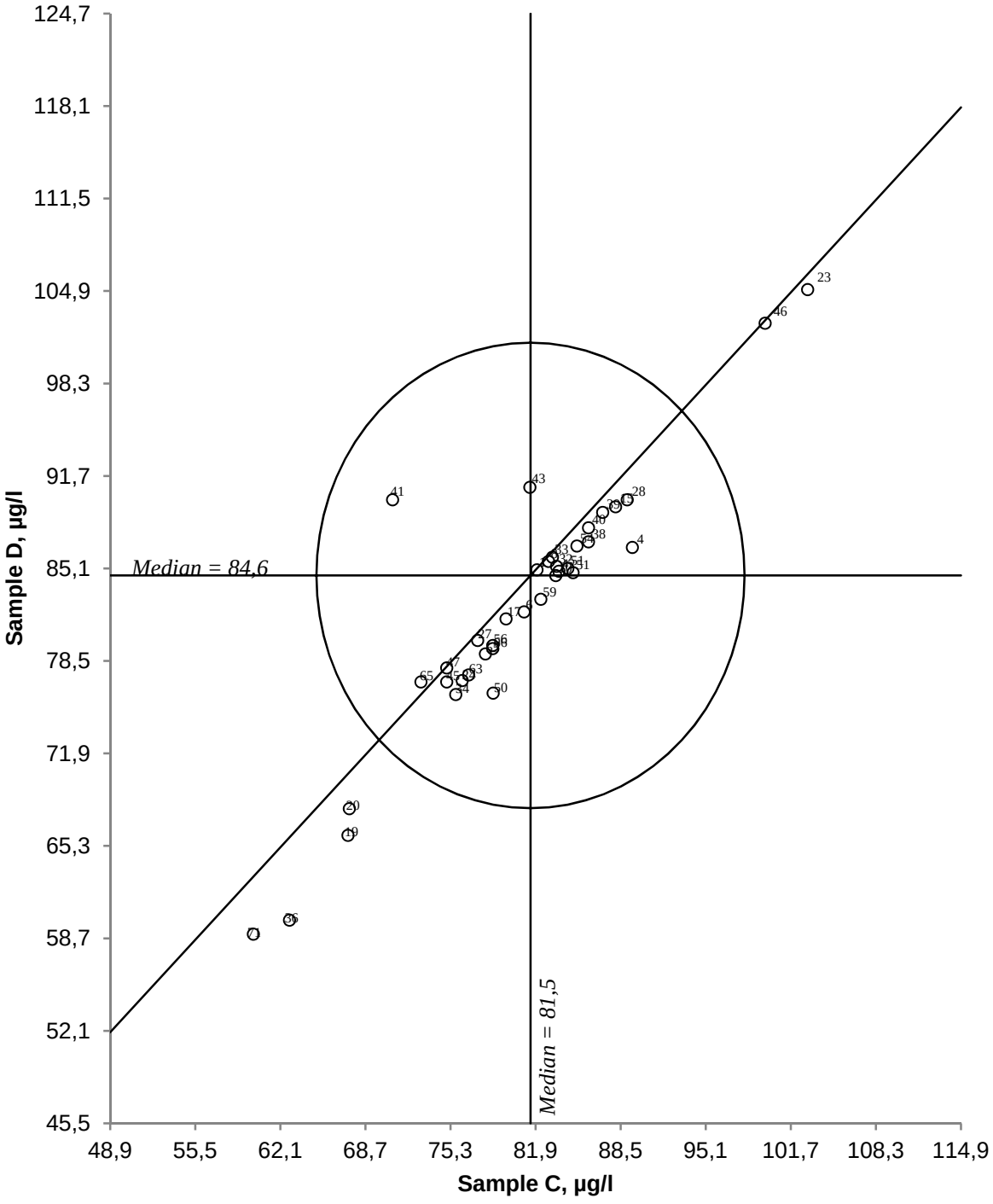

Figure 12..Youdendiagram for aluminium, Samplepair CD
Acceptable limit , given by circle, is 20 %

Iron

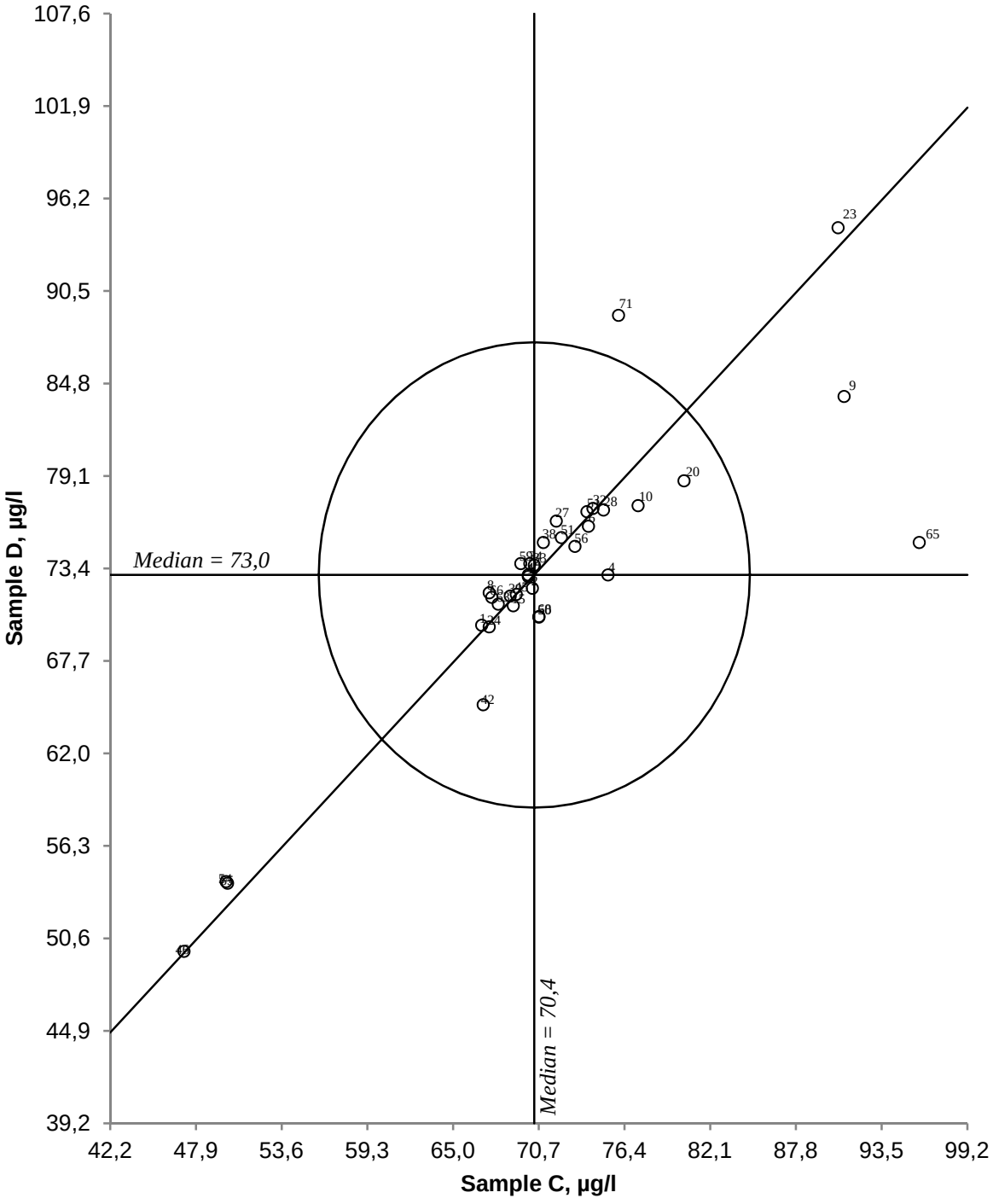

Figure 13. Youdendiagram for iron, Samplepair CD
Acceptable limit , given by circle, is 20 %

Manganese

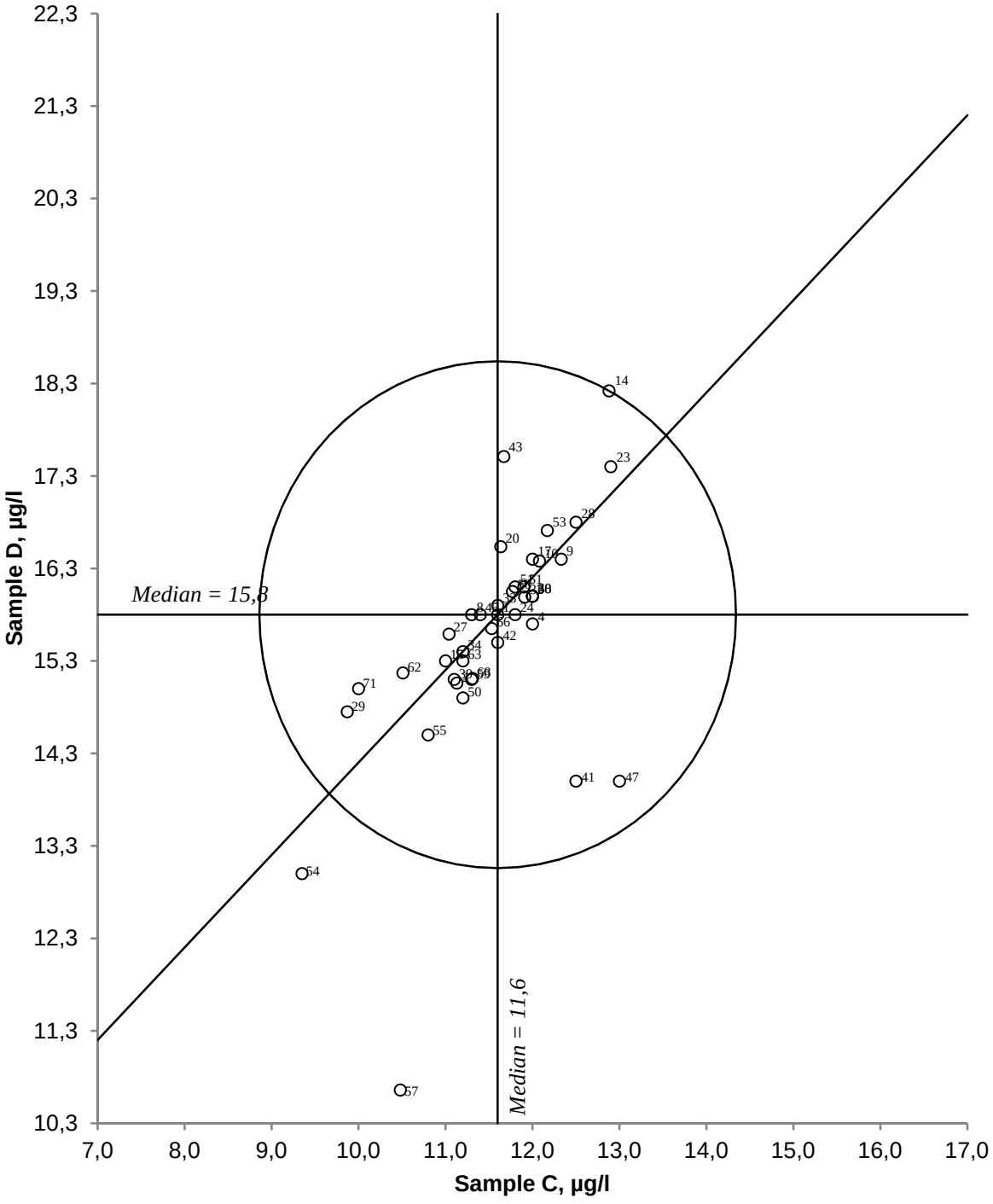

Figure 14. Youdendiagram for manganese, Samplepair CD
Acceptable limit , given by circle, is 20 %

Cadmium

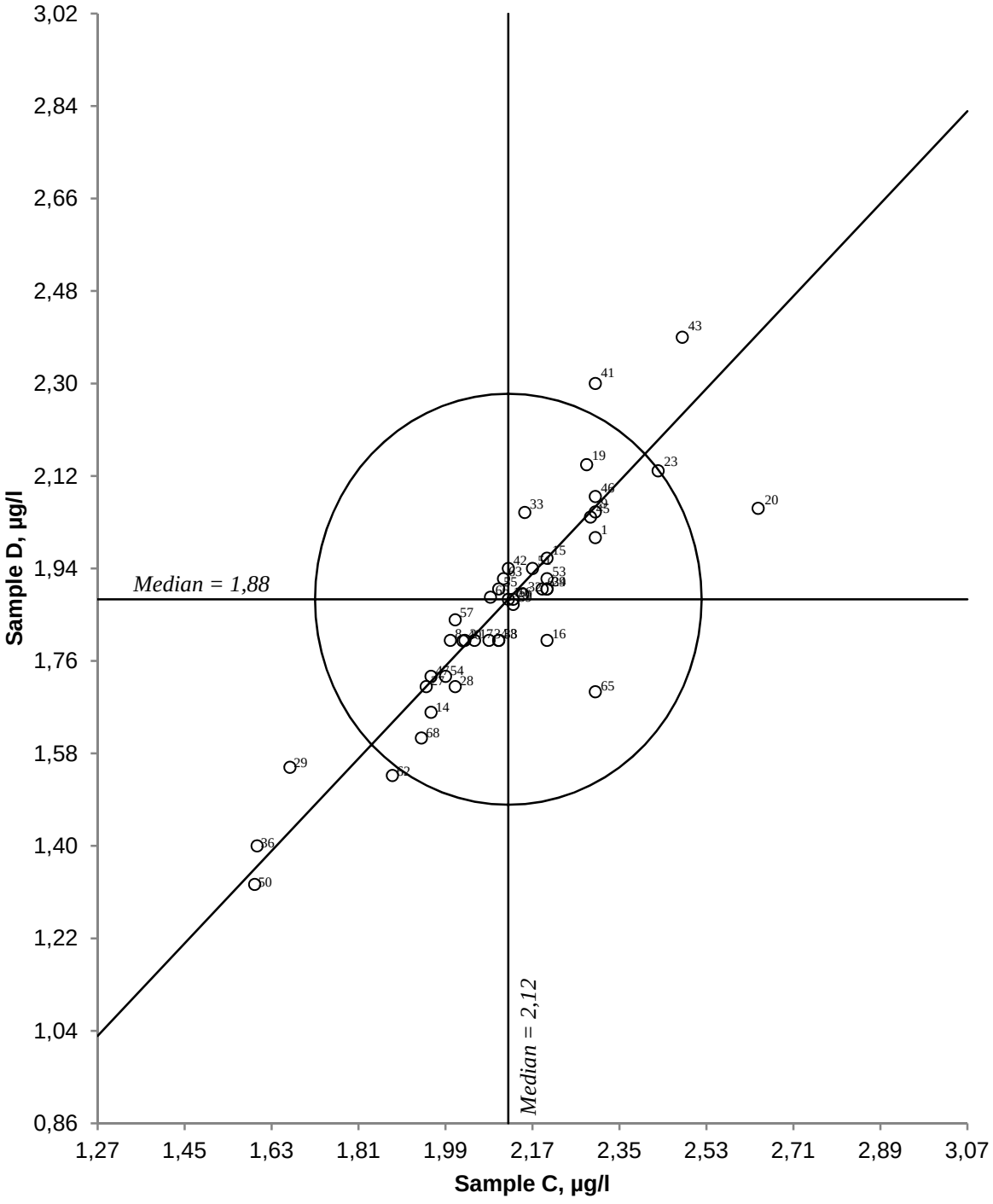

Figure 15. Youdendiagram for cadmium, Samplepair CD
Acceptable limit , given by circle, is 20 %

Lead

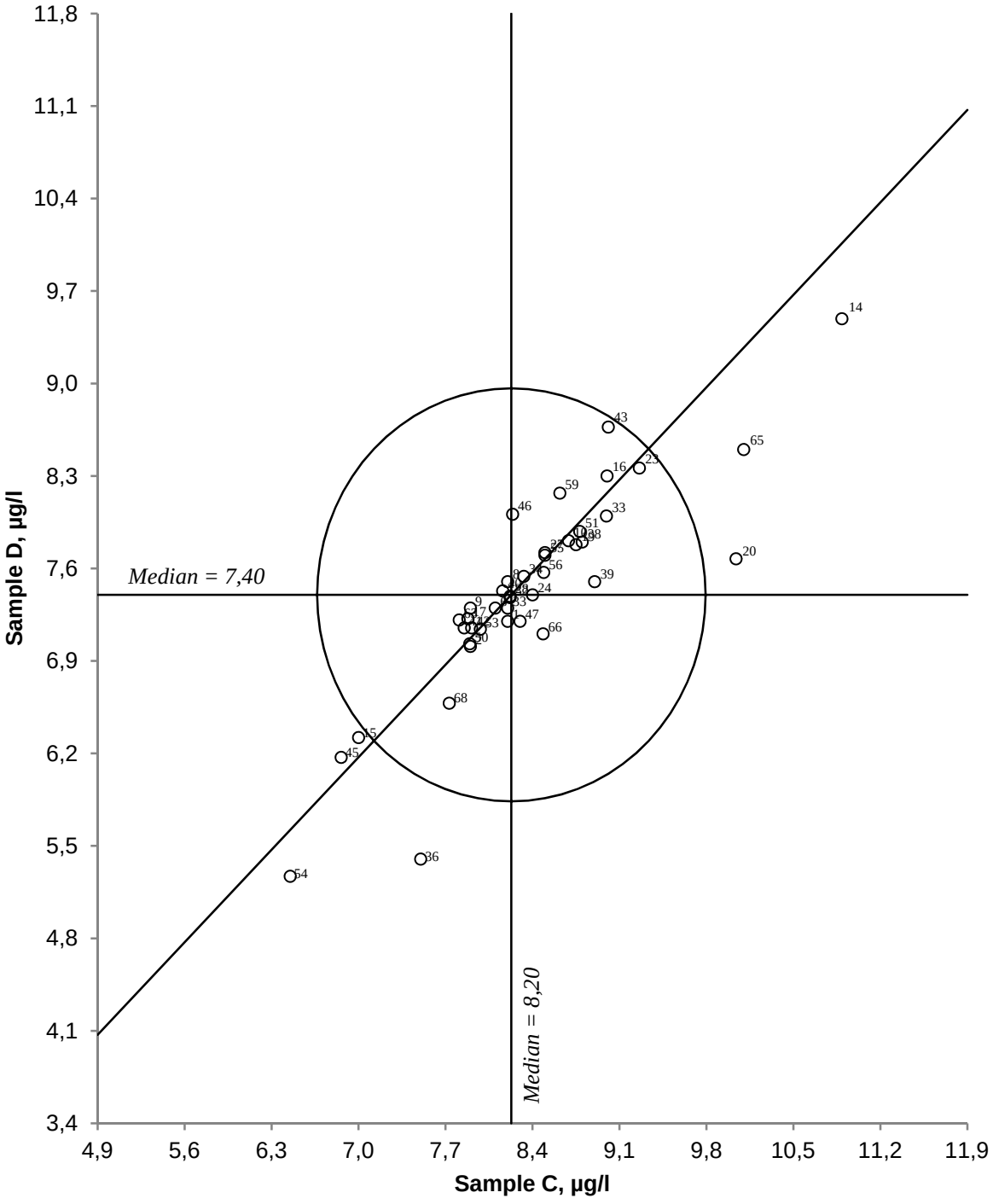

Figure 16. Youdendiagram for lead, Samplepair CD
Acceptable limit , given by circle, is 20 %

Copper

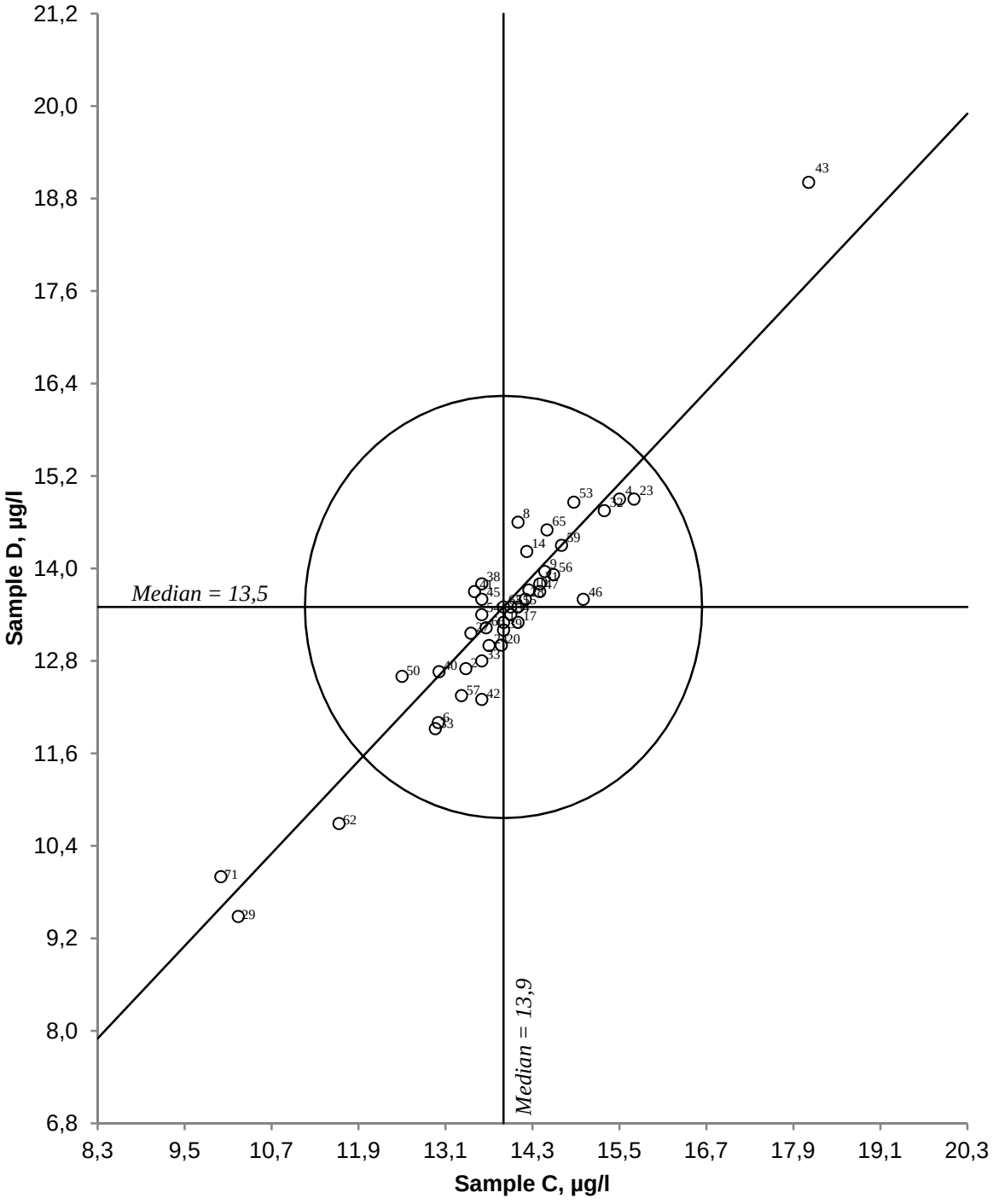

Figure 17. Youdendiagram for copper, Samplepair CD
Acceptable limit , given by circle, is 20 %

Nickel

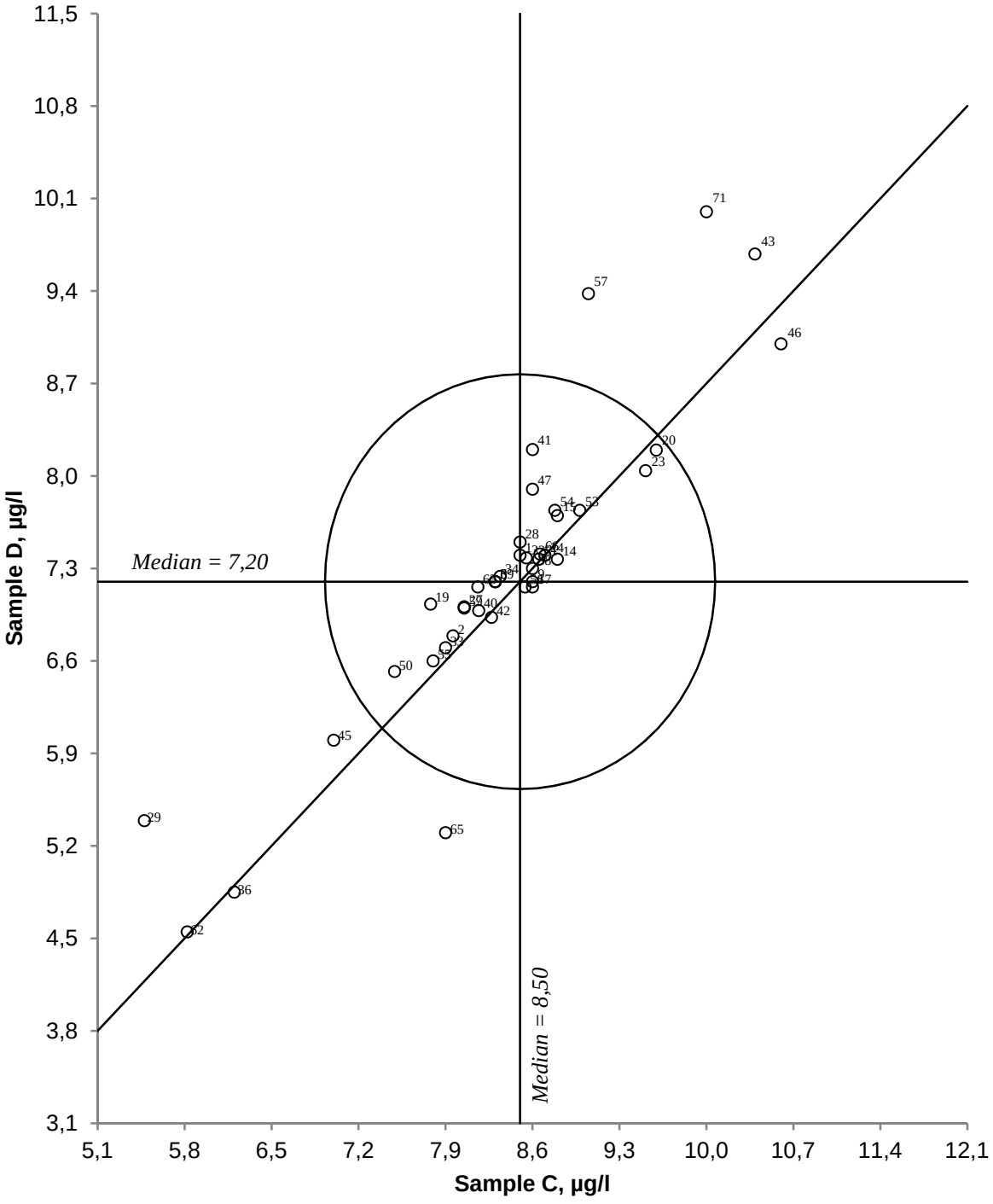

Figure 18. Youdendiagram for nickel, Samplepair CD
Acceptable limit , given by circle, is 20 %

Zinc

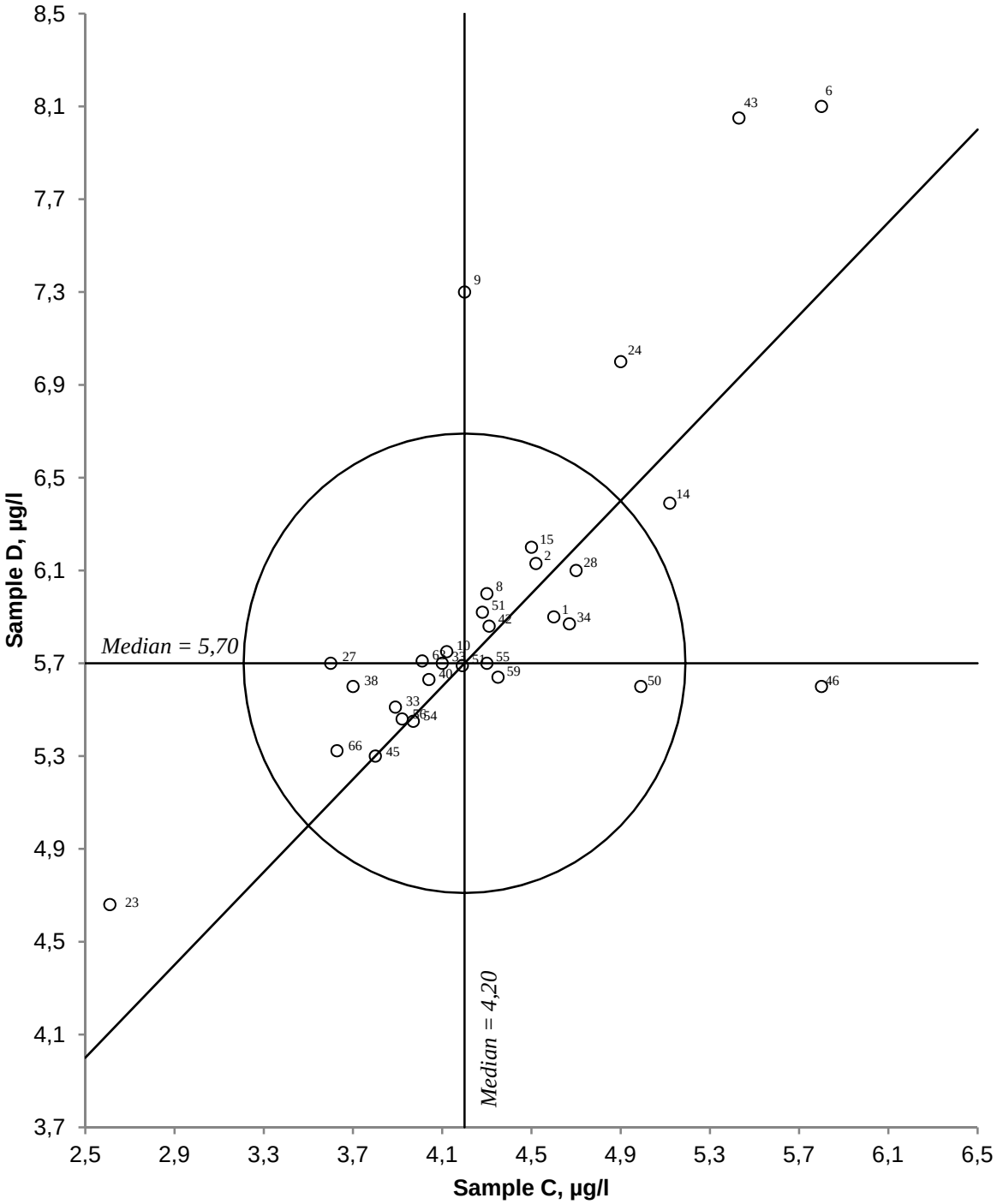

Figure 19. Youdendiagram for zinc, Samplepair CD
Acceptable limit , given by circle, is 20 %

5. Literature

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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	Laboratoire d'Ecologie Fonctionnelle et Environnement (ECOLAB)	Castanet Tolosan	France
2	ISSeP Colfontaine Zoning Schweitzer	Colfontaine	Belgium
3	Charles University, Hydrobiol. Station Velky Palenec	Blatna	Czech Republic
4	SLU, Mark och miljö	Uppsala	Sweden
5	Marklaboratoriet, pl4 Institusjonen for mark och mil	Uppsala	Sweden
6	ZAO "ROSSA"35-7 Rodnikovaya	Moscow	Russian Federation
7	Institute of Environmental Protection-Puszcza Borecka station	Warszawa	Poland
8	EPA, Dublin Inspectorate McCumiskey Hs,	Dublin	Ireland
9	Northern Water Problems Institute	Petrozavodsk	Russian Federation
10	ITM Stockholm University	Stockholm	Sweden
11	Laboratorio Biologico Provinciale	Laives	Italy
12	CNR-IRSA Water Research Institute	Gallarate	Italy
13	Forest Nutrition and Water Resources Department of Ecology, Technis	Freising	Germany
14	Hydrochemical Laboratory by Federal State Enterprise on Water Industry	Pskov	Russian Federation
15	FGU «Baltwodhoz»	Saint-Petersburg	Russian Federation
16	Institute of Global Climate and Ecology (IGCE) Roshydromet and RAS Russian Academy of Sciences	Moscow	Russian Federation
17	Environment Agency Starcross Laboratory,	Exeter	United Kingdom
18	Finnish Forest Research Institute Rovaniemi Research Station	Rovaniemi	Finland
19	Polish Academy of Sciences Institute of Botany	Krakow	Poland
20	Lab di Microanalysis University of Florence	Firenze	Italy
21	Earth Science Department - University of Florence Soil Solution Lab.	Firenze	Italy
22	Innovation Center Iceland	Reykjavik	Iceland
23	Laboratorio Integrado de Calidad Ambiental University of Navarra	Pamplona	Spain
24	CNR Istituto Studio degli Ecosistemi	Pallanza	Italy
25	MOEE, DORSET Laboratory	Dorset	Canada
26	IVL AB	Gothenburg	Sweden
27	Insitute of Industrial Ecology Problems of the North (INEP) Group ICP methods of analysis	Murmansk	Russian Federation
28	Kola Science Center Inst. North Industrial Ecol. p	Apatity	Russian Federation
29	Water Sources Laboratory 2	Bucuresti	Romania
30	Staatliche Betriebgesellschaft für Umwelt und Landwirtschaft (BfUL)	Chemnitz	Germany
32	Latvian Environmental Laboratory	Riga	Latvia
33	Laboratorio Spaas	Bellinzona	Switzerland

No.	Laboratory	Town	Country
34	NILU, Avd. uorganisk analyse	Kjeller	Norway
35	Tallinn Technical University Institute of Environmental Eng	Tallinn	Estonia
36	Geological Survey of Estonia	Tallinn	Estonia
37	Institute of Environmental Protection Warsaw Monitoring Laboratory	Warszawa	Poland
38	University of Helsinki Lab. of Geology and Geography	Helsinki	Finland
39	Finnish Forest Research Institute Vantaa Laboratory	Vantaa	Finland
40	Swedish University for Agricultural Sciences Aquatic Sciences and Assesment	Uppsala	Sweden
41	Center for Environmental Monitoring, Primorsky Dept. for Hydrometeorology & Environmental Monitoring Primorsky CEM	Vladivostok	Russian Federation
42	Norsk institutt for vannforskning	Oslo	Norway
43	Limnological Institute of Russian Academy of Sciences -Siberian Branch LIN SB RAS	Irkutsk	Russian Federation
44	Vlaamse MilieuMaatschappij (VMM) Lucht, Milieu en Communicatie	Antwerpen	Belgium
45	Centre National de la Recherche Scientifique LhyGeS	Strasbourg	France
46	ENGEES, Laboratoire LEE	Strasbourg	France
47	Chemical Laboratory, Czech Geological Survey	Praha	Czech Republic
48	Environmental Research and Training Center Thailand	Klong Luang	Thailand
49	Radbouduniversiteit afd. Ecologie t.a.v. G. Verheggen	Nijmegen	Netherlands
50	T.G.Masaryk Water Research Institute Analytical Laboratory	Praha	Czech Republic
51	Finnish Environment Institute SYKE Laboratory Center	Helsinki	Finland
52	Marine Scotland Science Freshwater Laboratory	Pitlochry	United Kingdom
53	Institute of Environmental Engineering Polish Academy of Science	Zabrze	Poland
54	Asia Center for Air Pollution Research	Niigata-shi	Japan
55	Bayerische Landesanstalt fur Wald und Forstwirtschaft Abteilung 2 - Klima und Boden	Freising	Germany
56	Environmental Protection Agency Environmental Research Departm	Vinius	Lithuania
57	EMC (PUSARPEDAL)	Tangerang	Indonesia
58	US Environmental Protection Agency, Western Ecology Division	Corvallis	United States
59	Estonian Environmental Research Centre Ltd Tartu Branch	Tartu	Estonia
60	River Biology Laboratory of the EAU Institute	Tartu	Estonia
62	Analist Service S.R.L.	Bucuresti	Romania
63	Bayerische Landesamt fur Umwelt	München	Germany
65	Test Laboratory of Water Quality (Vodokanal)	Petrozav	Russian Federation
66	Institute of Biology Komi SC UB RAS	Syktyvkar	Russian Federation
67	Biology Centre ASCR Institute of Hydrobiology	Ceske Budejovice	Czech Republic

No.	Laboratory	Town	Country
68	Institute for Ecology of Industrial Areas	Katowice	Poland
69	Büsgen-Institute - Soil Science of Temperate Ecosystems	Goettingen	Germany
70	Institut fur Ökologie	Innsbruck	Austria
71	University of Innsbruck Institute of Meteorology and Geophysics	Innsbruck	Austria

Number of participating laboratories from the different countries represented in intercomparison 1226

Country	No. of labs.	Country	No. of labs.	Country	No. of labs.
Austria	2	Indonesia	1	Romania	2
Belgium	2	Ireland	1	Russian Federation	11
Canada	1	Italy	5	Spain	1
Czech Republic	4	Japan	1	Sweden	5
Estonia	4	Latvia	1	Switzerland	1
Finland	4	Lithuania	1	Thailand	1
France	3	Netherlands	1	United Kingdom	2
Germany	5	Norway	2	United States	1
Iceland	1	Poland	5		
				Number of countries	26

Appendix B.

Preparation of samples

The sample solutions were prepared from water collected from river, Skjerselva, just outside the city of Oslo in Norway. The water was collected in 25 liter plastic containers and brought to the laboratory and stored for about two weeks. The water was then filtrated through 0,45 μm membrane filter, the filtrate collected in polyethylene containers, and then stored at room temperature about one more week 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. Some days before shipping the samples to the participants, the samples were transferred to 500 ml (sample set AB) or 250 ml acid washed (sample set CD) high density polyethylene bottles with screw cap. These samples were stored at room temperature until they were shiped to the participating laboratories.

Sample control analyses

During the intercomparison period, three sets of samples were randomly selected from the batch for control analyses. The determinations were carried out by the laboratory at the Programme Centre, the first sample set being analyzed in June 2012 at about the same time as the samples were shipped to the participants. The last sample set was analyzed in the second half of August 2012. A summary of the control results is presented in Table 3. The control results confirmed that the stability and homogeneity of the sample solutions were acceptable during the intercalibration period for all analytical variables except for nitrate in sample A

Table 3. Summary of the control analyses (n=3)

Analytical variable	**Sample A**		**Sample B**	
	Mean	Std. dev.	Mean	Std. dev.
pH	6,61	0,05	6,74	0,03
Conductivity mS/m	2,18	0,01	2,31	0,00
Alkalinity mmol/l	0,084	0,003	0,096	0,004
Nitrate-nitrogen μg/l	122	49	172	9,2
Chloride mg/l	1,07	0,01	1,26	0,02
Sulphate mg/l	3,00	0,01	2,74	0,05
Calcium mg/l	2,08	0,02	2,46	0,02
Magnesium mg/l	0,28	0,02	0,34	0,02
Sodium mg/l	1,70	0,05	1,62	0,05
Potassium mg/l	0,39	0,02	0,36	0,01
Total organic carbon, mg/l	3,4	0,12	4,0	0,06
Analytical variable	**Sample C**		**Sample D**	
	Mean	Std. dev.	Mean	Std. dev.
Aluminium, μg/l	82,9	1,3	84,0	3,0
Iron, μg/l	67	67	1	2
Manganese, μg/l	11,6	0,1	15,5	0,2
Cadmium, μg/l	2,13	0,01	1,88	0,06
Lead, μg/l	7,88	0,17	7,09	0,21
Copper, μg/l	14,1	0,4	13,3	0,8
Nickel, μg/l	8,36	0,10	7,05	0,13
Zinc, μg/l	4,36	0,13	5,98	0,13

Stability

Sample set AB was tested further for stability of pH, conductivity and alkalinity within the actual periode of the reporting window. The determinations were carried out by the laboratory at the Programme Centre. The sets were testet approximately at the date for shipment of the samples to the participants, halfway to the deadline for reporting and finally at the deadline. The samples were kept refrigerated over this period of time. The results are reported in the tables below.

Table 4. Stability tests for sample A

Set	Date	No. of replicates	pH		Conductivity mS/m		Alkalinity mmol/l	
			Average	Std. dev.	Average	Std. dev.	Average	Std. dev.
1	17.06.12	5	6,68	0,027	2,16	0,007	0,084	0,0007
2	20.07.12	5	6,59	0,023	2,18	0,000	0,081	0,0004
3	21.08.12	5	6,66	0,019	2,18	0,005	0,089	0,0004

Table 5. Stability tests for sample B

Set	Date	No. of replicates	pH		Conductivity mS/m		Alkalinity mmol/l	
			Average	Std. dev.	Average	Std. dev.	Average	Std. dev.
1	17.06.12	5	6,77	0,009	2,31	0,004	0,096	0,0004
2	20.07.12	5	6,72	0,011	2,31	0,004	0,092	0,0004
3	21.08.12	5	6,76	0,007	2,32	0,005	0,099	0,0005

The difference of results are within the uncertainties of the measurements at the laboratory. No sign of trends in the results could be observed, which indicates that the samples are stable for these analytical parameters within the relevant periode of time.

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 represent 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 one or 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 8.1 - 8.19. Results being omitted from the calculations are marked with the letter "O".

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 $|x_i - m|$ $\quad (i = 1, 2 \ldots. p)$

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 6. Estimation of uncertainty of the assigned true values

Parameter and unit	Sample	True value	Total no.	Robust std.dev.	Uncertainty	Expanded uncertainty
pH	A	6,53	61	0,233	0,037	0,075
	B	6,68	61	0,172	0,028	0,055
Conductivity	A	2,20	53	0,084	0,014	0,029
mS/m	B	2,35	54	0,081	0,014	0,027
Alkalinity	A	0,063	35	0,0146	0,0031	0,0062
mmol/l	B	0,070	37	0,0119	0,0024	0,0049
Nitrate + nitrite-nitrogen	A	172	42	23,0	4,4	8,9
µg/l	B	178	42	14,3	2,8	5,5
Chloride	A	1,05	54	0,101	0,017	0,034
mg/l	B	1,23	54	0,078	0,013	0,027
Sulfate	A	3,04	53	0,252	0,043	0,087
mg/l	B	2,79	52	0,206	0,036	0,071
Calcium	A	1,72	55	0,194	0,033	0,065
mg/l	B	2,04	52	0,215	0,037	0,075
Magnesium	A	0,270	56	0,0320	0,0054	0,0107
mg/l	B	0,320	54	0,0316	0,0054	0,0108
Sodium	A	1,73	55	0,087	0,015	0,029
mg/l	B	1,63	55	0,088	0,015	0,030
Potassium	A	0,381	52	0,0294	0,0051	0,0102
mg/l	B	0,350	52	0,0290	0,0050	0,0100
Total organic carbon	A	3,84	41	0,466	0,091	0,182
mg/l	B	4,49	40	0,441	0,087	0,174
Aluminum	C	81,5	37	7,00	1,44	2,88
µg/l	D	84,6	38	7,09	1,44	2,88
Iron	C	70,4	35	4,67	0,99	1,97
µg/l	D	73,0	35	4,05	0,85	1,71
Manganese	C	11,6	41	0,70	0,14	0,27
µg/l	D	15,8	41	0,85	0,17	0,33
Cadmium	C	2,12	44	0,160	0,030	0,060
µg/l	D	1,88	44	0,177	0,033	0,067
Lead	C	8,23	40	0,564	0,111	0,223
µg/l	D	7,40	41	0,580	0,113	0,226
Copper	C	13,9	42	0,74	0,14	0,28
µg/l	D	13,5	42	0,99	0,19	0,38
Nickel	C	8,50	41	0,636	0,124	0,248
µg/l	D	7,20	41	0,711	0,139	0,278
Zinc	C	4,24	32	0,624	0,138	0,276
µg/l	D	5,70	31	0,446	0,100	0,200

Appendix D

Table 7. The results of the participating laboratories.

Lab.	pH		Conductivity, mS/m		Alkalinity, mmol/l		Nitrate + nitrite-nitrogen, µg/l		Chloride, mg/l		Sulphate, mg/l		Calcium, mg/l		Magnesium, mg/l	
nr.	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
1	6,48	6,60	2,34	2,47	0,053	0,066	185	187	1,03	1,23	3,05	2,80	1,60	1,95	0,250	0,310
2	6,64	6,78	2,23	2,37			167	169	1,06	1,25	3,14	2,83	1,28	1,63	0,135	0,164
3	6,14	6,42	2,47	2,61	0,063	0,066	94	208	1,07	1,25	3,26	2,98	1,29	1,56	0,220	0,260
4	6,65	6,65	2,06	2,30	0,060	0,070			1,06	1,27	3,09	2,79	1,79	2,06	0,340	0,270
5	6,77	6,76	3,51	3,05	0,087	0,077	173	173								
6	6,52	6,69	2,24	2,36	0,120	0,120	0	160	0,93	1,10	2,81	2,60	1,73	1,88	0,270	0,310
7	6,65	6,77	2,20	2,50												
8	5,90	6,00	0,00	0,00	0,060	0,070	145	150	0,87	1,02	2,86	2,52	1,53	1,89	0,242	0,287
9	6,37	6,65	2,26	2,33	0,063	0,067	102	193	1,05	1,24	2,88	2,70	1,68	1,97	0,250	0,300
10	6,68	6,73	2,20	2,35	0,056	0,065	173	174	1,07	1,23	3,03	2,79	1,80	2,34	0,285	0,358
11	6,59	6,68	2,34	2,39	0,057	0,061	100	164	1,00	1,20	2,49	2,31	1,33	1,75	0,210	0,260
12	6,63	6,79	2,25	2,41	0,058	0,067	191	204	1,17	1,39	3,20	2,89			0,260	0,330
13	6,53	6,73	2,37	2,54	1,400	1,730	92	140	0,89	1,05	0,90	0,82	1,63	1,92	0,270	0,305
14	6,52	6,60	24,50	26,50	0,090	0,110	45	196	1,71	1,69	3,08	2,86	1,02	1,47	0,390	0,380
15	6,27	6,31	2,22	2,37	0,101	0,105	79	184	1,23	1,47	3,04	2,85	1,77	2,07	0,269	0,309
16																
17	7,14	7,17	2,30	2,40	0,030	0,034	183	186			3,25	2,92	1,70	2,01	0,284	0,339
18	6,43	6,62	2,20	2,30	0,061	0,072	182	182	0,98	1,20	1,16	1,05				
19	6,73	6,80	2,30	2,40			140	185	0,98	1,20	2,70	2,60	1,86	2,24	0,356	0,403
20																
21	6,42	6,75	2,06	2,15			85	188	1,05	1,23	3,04	2,77	1,83	2,17	0,280	0,340
22	6,70	6,66	2,26	2,39	0,029	0,033										
23	6,60	6,76	1,65	1,77	0,083	0,085	145	172	1,03	1,20	2,86	2,55	1,88	2,47	0,300	0,394
24	6,53	6,71	2,20	2,33	0,070	0,075	140	170	1,06	1,22	2,89	2,80	1,85	2,30	0,300	0,330
25	6,68	6,79	2,18	2,34	0,090	0,092	170	170	0,92	1,21	3,30	3,10	1,80	2,16	0,270	0,330
26	6,60	6,70	2,20	2,40	0,060	0,070	180	190	1,10	1,30	3,10	2,90	1,80	2,90	0,280	0,330
27													1,65	1,95	0,270	0,323
28	6,66	6,72	2,10	2,30	0,058	0,071	185	190	1,05	1,24	3,16	2,95	1,62	1,79	0,250	0,290
29	5,56	5,32	1,84	2,14	0,080	0,060	104	155	0,91	1,28	2,41	2,58	1,28	1,07	0,190	0,260
30	6,55	6,64	2,24	2,42	0,135	0,134	0	0	1,25	1,30	2,70	2,50	1,80	2,04	0,400	0,420
32	6,55	6,74	22,60	24,00	0,065	0,061	0	0	0,96	1,16	2,88	2,70	1,41	1,83	0,250	0,300
33	6,59	6,68	2,19	2,33	0,058	0,069	185	188	1,08	1,29	3,13	2,88	1,59	1,91	0,253	0,302
34	6,03	6,24	2,28	2,31			187	188	1,08	1,27			1,89	2,23	0,282	0,329
35	6,74	6,77	2,41	2,49			180	181	1,04	1,22	3,04	2,77				
36	6,06	6,08	2,24	2,38					2,94	2,73						

Lab.	pH		Conductivity, mS/m		Alkalinity, mmol/l		Nitrate + nitrite-nitrogen, µg/l		Chloride, mg/l		Sulphate, mg/l		Calcium, mg/l		Magnesium, mg/l	
nr.	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
37	6,47	6,70					170	172	1,00	1,21	2,96	2,76	1,72	2,04	0,272	0,322
38	6,86	6,92	2,18	2,35	0,068	0,073	722	827	1,18	1,38	3,66	3,42	1,74	2,16	0,270	0,330
39	6,90	6,70	2,20	2,40			176	178					1,88	2,05	0,279	0,321
40	6,41	6,57	2,14	2,31	0,059	0,070	182	182	1,04	1,23	2,93	2,69	1,94	2,08	0,328	0,340
41	6,44	6,65	2,31	2,24	0,046	0,062	510	840	1,56	1,84	2,30	3,60	1,94	2,10	0,160	0,400
42	6,64	6,76	2,17	2,31	0,083	0,096	175	174	1,06	1,24	2,99	2,69	2,07	2,45	0,290	0,350
43	6,23	6,61	2,16	2,33	0,070	0,070	27	185	1,18	1,42	3,33	3,13	1,68	1,94	0,254	0,297
44	5,99	6,13	2,23	2,38			195	206	1,18	1,40	3,51	3,23	2,09	2,38	0,323	0,372
45	6,40	6,64	2,18	2,41	0,039	0,042	78	137	0,89	1,15	2,65	2,36	1,32	1,80	0,292	0,365
46	1,19	1,19	0,31	0,31	0,104	0,113	372	346	0,00	0,00	2,10	3,10	0,00	0,00	0,000	0,000
47	6,65	6,63	2,19	2,42	0,070	0,081	138	140	0,93	1,15	2,54	2,38	1,78	2,09	0,270	0,310
48	6,09	6,22	2,22	2,35	0,062	0,061	160	179	1,04	1,23	3,09	2,80	2,19	2,52	0,330	0,390
49	6,19	6,30			0,500	0,100	168	182	0,95	1,02			1,54	1,84	0,230	0,280
50	6,45	6,52	2,23	2,37	0,129	0,132	188	243	1,31	1,54	3,46	3,20	1,68	2,00	0,307	0,348
51	6,68	6,73	2,19	2,30	0,063	0,075	172	174								
52	6,64	6,69	2,13	2,26	0,056	0,066	176	191	1,05	1,23	3,11	2,91	1,67	1,98	0,265	0,314
53	6,67	6,71					720	722	1,09	1,26	3,64	3,42			0,250	0,320
54	6,75	6,85	2,22	2,36	0,031	0,036	173	184	1,05	1,26	3,05	2,80	1,76	2,12	0,234	0,294
55	6,59	6,70	2,12	2,26			170	169	1,02	1,21	3,06	2,78	1,71	2,06	0,250	0,300
56	6,78	6,92	2,28	2,40			170	170	0,99	1,18	3,00	2,74	1,63	1,97	0,262	0,307
57	6,50	6,84	3,24	3,24	0,116	0,102	265	450	0,91	1,11	2,78	2,60	1,82	2,19	0,260	0,310
58					0,088	0,098										
58	6,59	6,79	2,13	2,27	0,120	0,124	48	177	1,02	1,21	3,08	2,80	1,65	1,98	0,262	0,316
59	6,40	6,30	2,20	2,34	0,092	0,104	172	170	1,07	1,26	3,01	2,63	1,86	2,38	0,303	0,343
60	6,50	6,20	2,50	1,80			176	173								
62	5,51	5,04	2,25	2,30	0,090	0,070	119	207	0,90	1,38	2,49	2,67	1,39	0,99	0,200	0,240
63	6,59	6,68	0,22	0,23			0	0	1,00	1,20	3,00	2,70	1,57	1,83	0,260	0,300
65	6,22	6,60	2,22	2,40					1,20	1,35			1,85	2,10	0,250	0,300
66	6,49	6,83	1,88	2,07	0,076	0,074	57	174	1,04	1,17	3,32	3,09	1,62	1,96	0,271	0,324
67	6,52	6,54	2,19	2,34	0,064	0,076	169	175	1,03	1,24	3,09	2,81	1,71	1,98	0,270	0,310
68							138	158	1,06	1,30	2,83	2,65	1,62	1,98	0,276	0,329
69	6,09	6,35	2,37	2,53			185	180	0,78	1,02	2,85	2,64	1,69	2,01	0,250	0,296
70	6,12	6,58	2,20	2,35	0,069	0,066	49	187	1,09	1,26	3,02	2,82	1,94	2,30	0,281	0,336
71	6,15	6,34	1,23	1,23	0,109	0,074	397	214	1,29	1,27	3,08	2,84	2,39	2,68		

Lab.	Sodium, mg/l		Potassium, mg/l		Total organic carbon, mg/l		Aluminium, µg/l		Iron, µg/l		Manganese, µg/l		Cadmium, µg/l		Lead, µg/l	
nr.	A	B	A	B	A	B	C	D	C	D	C	D	C	D	C	D
1	1,77	1,69	0,388	0,358	4,04	4,50	82,0	85,0	66,9	69,9	11,6	15,8	2,30	2,00	8,20	7,20
2	1,73	1,64	0,337	0,304	3,95	4,80			70,3	72,2	11,1	15,1	2,03	1,80	7,90	7,01
3	1,14	1,11	0,310	0,270												
4	1,83	1,67	0,280	0,320	3,99	4,80	89,4	86,6	75,3	73,0	12,0	15,7				
5					3,88	5,23										
6	1,74	1,64	0,380	0,330	3,70	4,50	81,0	82,0	74,0	76,0	12,0	16,0	2,19	1,90	8,10	7,30
7																
8	1,73	1,61	0,360	0,327			82,9	85,6	67,4	71,9	11,3	15,8	2,00	1,80	8,20	7,50
9	1,98	1,90	0,590	0,550			118,0	107,0	91,0	84,0	12,3	16,4	2,30	2,05	7,90	7,30
10	1,68	1,57	0,366	0,319	3,68	4,39	83,5	84,6	77,3	77,3	12,1	16,4	2,12	1,88	8,69	7,81
11	1,59	1,56	0,330	0,390	3,67	4,48										
12	1,74	1,66	0,400	0,360												
13	1,75	1,62	0,440	0,367	4,46	5,15										
14	1,79	1,68	0,375	0,361					133,2	121,8	12,9	18,2	1,96	1,66	10,89	9,49
15	1,79	1,68	0,382	0,335			88,1	89,5	69,0	71,1	11,0	15,3	2,20	1,96	7,00	6,32
16													2,20	1,80	9,00	8,30
17	1,70	1,63	0,374	0,356	3,51	4,12	79,6	81,5	70,0	72,9	12,0	16,4	2,05	1,80	7,88	7,22
18					3,71	4,13										
19	1,79	1,68	0,486	0,388			67,3	66,1	10,2	15,2	50,3	58,7	2,28	2,14	8,75	7,78
20							67,4	68,0	80,4	78,8	11,6	16,5	2,64	2,06	10,04	7,67
21	1,71	1,63	0,390	0,345												
22																
23	2,02	2,12	0,458	0,462	8,54	8,93	103,0	105,0	90,6	94,4	12,9	17,4	2,43	2,13	9,26	8,36
24	1,70	1,60	0,360	0,320	3,50	4,60	76,2	77,1	67,4	69,8	11,8	15,8	2,20	1,90	8,40	7,40
25	1,72	1,63	0,400	0,355	3,34	4,06										
26	1,70	1,60	0,430	0,380	3,70	4,40										
27	1,65	1,60	0,400	0,360			77,4	80,0	71,9	76,3	11,0	15,6	1,95	1,71	8,50	7,72
28	1,69	1,61	0,390	0,360			89,0	90,0	75,0	77,0	12,5	16,8	2,01	1,71	8,22	7,39
29	1,32	1,18	0,720	0,580	3,95	4,67					9,9	14,8	1,67	1,55	2,36	2,46
30	1,80	1,73	0,370	0,320	4,80	5,50										
32	1,60	1,53	0,380	0,340	3,65	4,28	83,5	85,3	74,3	77,1	11,9	16,0	2,15	1,89	8,22	7,38
33							42,4	43,4					2,15	2,05	9,00	8,00
33	1,77	1,67	0,341	0,304			83,2	85,9	70,4	73,6	11,6	15,9	2,10	1,80	2,10	1,80
34	1,76	1,65	0,392	0,350			75,7	76,1	70,1	73,7	11,2	15,4	2,08	1,80	8,33	7,54
35					4,03	4,68										
36	1,42	1,37	0,380	0,340			62,8	60,0					1,60	1,40	7,50	5,40
37	1,77	1,89	0,399	0,361	4,46	5,24										
38	1,79	1,72	0,400	0,370			86,0	87,0	71,0	75,0	12,0	16,0	2,10	1,80	8,80	7,80
39	1,67	1,59	0,424	0,387	3,67	4,44	87,1	89,1	68,8	71,7	11,1	15,1	2,20	1,90	8,90	7,50
40	1,68	1,56	0,391	0,352	4,14	4,72	86,0	88,0	70,0	73,0	12,0	16,0	2,03	1,80	8,16	7,43
41	1,75	1,75	0,410	0,410			70,8	90,0	115,0	225,0	12,5	14,0	2,30	2,30	7,85	7,15
42	1,72	1,63	0,400	0,360	3,30	4,00	83,7	84,9	67,0	65,0	11,6	15,5	2,12	1,94	7,91	7,15

Lab.	Sodium, mg/l		Potassium, mg/l		Total organic carbon, mg/l		Aluminium, µg/l		Iron, µg/l		Manganese, µg/l		Cadmium, µg/l		Lead, µg/l	
nr.	A	B	A	B	A	B	C	D	C	D	C	D	C	D	C	D
43	1,71	1,62	0,380	0,340	4,61	5,22	81,5	90,9	4,6	5,1	11,7	17,5	2,48	2,39	9,01	8,67
44	1,74	1,62	0,398	0,360												
45	1,75	1,70	0,391	0,352	3,55	4,20	75,0	77,0	69,2	71,8	11,4	15,8	2,29	2,04	6,86	6,17
46					5,20	6,10	99,7	102,6	47,1	49,8	7,8	10,1	2,30	2,08	8,24	8,01
47	1,59	1,50	0,360	0,320	4,36	4,71	75,0	78,0			13,0	14,0	1,96	1,73	8,30	7,20
48	2,06	1,95	0,450	0,400												
49	1,28	1,28	0,760	0,590												
50	1,75	1,94	0,355	0,411	3,36	3,83	78,6	76,2	70,7	70,4	11,2	14,9	1,60	1,33	7,90	7,03
51							84,4	85,1	73,9	76,9	11,9	16,1	2,17	1,94	8,78	7,88
51					3,89	4,64	84,8	84,8	72,2	75,1	11,8	16,1				
52	1,59	1,51	0,353	0,350	5,23	5,67										
53	0,34	0,32	0,300	0,280							12,2	16,7	2,20	1,92	7,98	7,14
54	1,71	1,61	0,381	0,345	3,39	4,05	85,1	86,7	49,9	54,1	9,4	13,0	1,99	1,73	6,45	5,27
55	1,73	1,65	0,400	0,350	3,86	4,60	78,0	79,0	50,0	54,0	10,8	14,5	2,10	1,90	8,50	7,70
56	1,80	1,70	0,400	0,360	4,07	4,71	78,6	79,6	73,1	74,8	11,8	16,1	2,13	1,88	8,49	7,57
57	1,67	1,59	0,340	0,310	4,81	4,66					10,5	10,7	2,01	1,84	15,60	14,82
58	1,65	1,58	0,382	0,335	3,57	4,15										
59	1,73	1,65	0,370	0,346	3,60	4,20	82,3	82,9	69,5	73,7	11,3	15,1	2,13	1,87	8,62	8,17
60					4,10	4,30										
62	1,40	0,95	0,750	0,510					33,4	37,0	10,5	15,2	1,88	1,54	2,45	2,25
63	1,63	1,53	0,360	0,310	3,20	3,90	76,7	77,5	68,0	71,2	11,2	15,3	2,11	1,92	7,81	7,21
65							73,0	77,0	96,0	75,0	22,0	28,0	2,30	1,70	10,10	8,50
66	1,56	1,52	0,362	0,329	3,76	4,45	78,6	79,4	67,6	71,6	11,5	15,7	2,08	1,88	8,49	7,11
67	1,68	1,62	0,390	0,360	3,60	4,30										
68	1,74	1,65	0,350	0,314	3,88	4,34			70,7	70,4	11,3	15,1	1,94	1,61	7,73	6,58
69	1,57	1,45	0,255	0,526	4,65	5,32										
70	1,74	1,64	0,385	0,355	3,81	4,48										
71	1,80	1,69	0,380	0,360			60,0	59,0	76,0	89,0	10,0	15,0				

Lab.	Copper, µg/l		Nickel, µg/l		Zinc, µg/l		Lab.	Copper, µg/l		Nickel, µg/l		Zinc, µg/l	
nr.	C	D	C	D	C	D	nr.	C	D	C	D	C	D
1	13,9	13,3	8,50	7,40	4,60	5,90	36			6,20	4,85		
2	13,4	12,7	7,96	6,79	4,52	6,13	37						
3							38	13,6	13,8	8,60	7,30	3,70	5,60
4	15,5	14,9			8,70	8,90	39	13,9	13,2	8,30	7,20		
5							40	13,0	12,7	8,17	6,98	4,04	5,63
6	13,0	12,0	8,30	7,20	5,80	8,10	41	13,5	13,7	8,60	8,20	13,00	12,50
7							42	13,6	12,3	8,27	6,93	4,31	5,86
8	14,1	14,6	8,30	7,20	4,30	6,00	43	18,1	19,0	10,39	9,68	5,43	8,05
9	14,5	14,0	8,60	7,20	4,20	7,30	44						
10	14,3	13,7			4,12	5,75	45	13,6	13,6	7,00	6,00	3,80	5,30
11							46	15,0	13,6	10,60	9,00	5,80	5,60
12							47	14,4	13,7	8,60	7,90		
13							48						
14	14,2	14,2	8,80	7,37	5,12	6,39	49						
15	14,1	13,5	8,80	7,70	4,50	6,20	50	12,5	12,6	7,49	6,52	4,99	5,60
16	6,9	6,7					51	14,4	13,8	8,65	7,37	4,19	5,69
17	14,1	13,3	8,60	7,16	0,00	5,66	51					4,28	5,92
18							52						
19	13,9	22,2	7,78	7,03	6,70	5,26	53	14,9	14,9	8,98	7,74		
20	13,9	13,0	9,60	8,20	7,46	7,14	54	13,6	13,4	8,78	7,74	3,97	5,45
21							55	14,0	13,5	7,80	6,60	4,30	5,70
22							56	14,6	13,9	8,54	7,16	3,92	5,46
23	15,7	14,9	9,51	8,04	2,61	4,66	57	13,3	12,4	9,05	9,38		
24	13,7	13,0	8,70	7,40	4,90	7,00	58						
25							59	14,7	14,3	8,05	7,00	4,35	5,64
26							60						
27	13,5	13,2	8,05	7,01	3,60	5,70	62	11,6	10,7	5,82	4,55		
28	14,2	13,6	8,50	7,50	4,70	6,10	63	13,9	13,5	8,16	7,16	4,01	5,71
29	10,2	9,5	5,48	5,39			65	14,5	14,5	7,90	5,30		
30							66	13,7	13,2	8,66	7,41	3,63	5,32
32	15,3	14,8	8,55	7,38	2,34	4,22	67						
33	13,0	11,9			3,89	5,51	68					2,34	3,79
33	13,6	12,8	7,90	6,70	4,10	5,70	69						
34	14,0	13,4	8,34	7,24	4,67	5,87	70						
35							71	10,0	10,0	10,00	10,00	21,00	10,00

Table 8.1. Statistics - pH

Sample A

Analytical method: All
Unit:

Number of participants	64	Range	1,24
Number of omitted results	3	Variance	0,06
True value	6,53	Standard deviation	0,24
Mean value	6,50	Relative standard deviation	3,7%
Median value	6,53	Relative error	-0,5%

Analytical results in ascending order:

46	1,19	O	41	6,44	42	6,64
62	5,51	O	50	6,45	2	6,64
29	5,56	O	37	6,47	52	6,64
8	5,90		1	6,48	7	6,65
44	5,99		66	6,49	47	6,65
34	6,03		60	6,50	4	6,65
36	6,06		57	6,50	28	6,66
48	6,09		67	6,52	53	6,67
69	6,09		6	6,52	51	6,68
70	6,12		14	6,52	25	6,68
3	6,14		24	6,53	10	6,68
71	6,15		13	6,53	22	6,70
49	6,19		32	6,55	19	6,73
65	6,22		30	6,55	35	6,74
43	6,23		58	6,59	54	6,75
15	6,27		33	6,59	5	6,77
9	6,37		63	6,59	56	6,78
45	6,40		55	6,59	38	6,86
59	6,40		11	6,59	39	6,90
40	6,41		26	6,60	17	7,14
21	6,42		23	6,60		
18	6,43		12	6,63		

O = Omitted result

Table 8.1. Statistics - pH

Sample B

Analytical method: All
Unit:

Number of participants	64	Range	1,17
Number of omitted results	3	Variance	0,05
True value	6,68	Standard deviation	0,22
Mean value	6,62	Relative standard deviation	3,3%
Median value	6,68	Relative error	-0,9%

Analytical results in ascending order:

46	1,19	O	43	6,61		10	6,73
62	5,04	O	18	6,62		13	6,73
29	5,32	O	47	6,63		32	6,74
8	6,00		30	6,64		21	6,75
36	6,08		45	6,64		42	6,76
44	6,13		41	6,65		23	6,76
60	6,20		9	6,65		5	6,76
48	6,22		4	6,65		35	6,77
34	6,24		22	6,66		7	6,77
49	6,30		63	6,68		2	6,78
59	6,30		33	6,68		58	6,79
15	6,31		11	6,68		25	6,79
71	6,34		52	6,69		12	6,79
69	6,35		6	6,69		19	6,80
3	6,42		55	6,70		66	6,83
50	6,52		37	6,70		57	6,84
67	6,54		39	6,70		54	6,85
40	6,57		26	6,70		38	6,92
70	6,58		24	6,71		56	6,92
14	6,60		53	6,71		17	7,17
65	6,60		28	6,72			
1	6,60		51	6,73			

O = Omitted result

Table 8.2. Statistics - Conductivity

Sample A

Analytical method: All
Unit: mS/m

Number of participants	61	Range	0,85
Number of omitted results	8	Variance	0,02
True value	2,20	Standard deviation	0,14
Mean value	2,21	Relative standard deviation	6,2%
Median value	2,20	Relative error	0,3%

Analytical results in ascending order:

8	0,00	O	47	2,19		62	2,25	
63	0,22	O	67	2,19		9	2,26	
46	0,31	O	70	2,20		22	2,26	
71	1,23	O	24	2,20		56	2,28	
23	1,65		59	2,20		34	2,28	
29	1,84		10	2,20		19	2,30	
66	1,88		18	2,20		17	2,30	
21	2,06		26	2,20		41	2,31	
4	2,06		7	2,20		11	2,34	
28	2,10		39	2,20		1	2,34	
55	2,12		15	2,22		69	2,37	
58	2,13		48	2,22		13	2,37	
52	2,13		65	2,22		35	2,41	
40	2,14		54	2,22		3	2,47	
43	2,16		50	2,23		60	2,50	
42	2,17		2	2,23		57	3,24	O
25	2,18		44	2,23		5	3,51	O
45	2,18		36	2,24		32	22,60	O
38	2,18		6	2,24		14	24,50	O
33	2,19		30	2,24				
51	2,19		12	2,25				

O = Omitted result

Table 8.2. Statistics - Conductivity

Sample B

Analytical method: All
Unit: mS/m

Number of participants	61	Range	0,84
Number of omitted results	8	Variance	0,02
True value	2,35	Standard deviation	0,14
Mean value	2,33	Relative standard deviation	6,2%
Median value	2,35	Relative error	-0,7%

Analytical results in ascending order:

8	0,00	O	43	2,33		65	2,40	
63	0,23	O	33	2,33		19	2,40	
46	0,31	O	24	2,33		17	2,40	
71	1,23	O	9	2,33		39	2,40	
23	1,77		25	2,34		56	2,40	
60	1,80		59	2,34		12	2,41	
66	2,07		67	2,34		45	2,41	
29	2,14		48	2,35		30	2,42	
21	2,15		38	2,35		47	2,42	
41	2,24		10	2,35		1	2,47	
52	2,26		70	2,35		35	2,49	
55	2,26		54	2,36		7	2,50	
58	2,27		6	2,36		69	2,53	
62	2,30		50	2,37		13	2,54	
28	2,30		15	2,37		3	2,61	
51	2,30		2	2,37		5	3,05	O
18	2,30		36	2,38		57	3,24	O
4	2,30		44	2,38		32	24,00	O
40	2,31		22	2,39		14	26,50	O
34	2,31		11	2,39				
42	2,31		26	2,40				

O = Omitted result

Table 8.3. Statistics - Alkalinity

Sample A

Analytical method: All
Unit: mmol/l

Number of participants	48	Range	0,053
Number of omitted results	14	Variance	0,000
True value	0,063	Standard deviation	0,013
Mean value	0,067	Relative standard deviation	19,5%
Median value	0,063	Relative error	6,3%

Analytical results in ascending order:

22	0,029	O	18	0,061		5	0,087	
17	0,030	O	48	0,062		58	0,088	
54	0,031	O	9	0,063		62	0,090	
45	0,039		51	0,063		14	0,090	O
41	0,046		3	0,063		25	0,090	
1	0,053		67	0,064		59	0,092	
10	0,056		32	0,065		15	0,101	O
52	0,056		38	0,068		46	0,104	O
11	0,057		70	0,069		71	0,109	O
12	0,058		24	0,070		57	0,116	O
28	0,058		43	0,070		58	0,120	O
33	0,058		47	0,070		6	0,120	O
40	0,059		66	0,076		50	0,129	O
4	0,060		29	0,080		30	0,135	O
26	0,060		23	0,083		49	0,500	O
8	0,060		42	0,083		13	1,400	O

O = Omitted result

Table 8.3. Statistics - Alkalinity

Sample B

Analytical method: All
Unit: mmol/l

Number of participants	48	Range	0,062
Number of omitted results	14	Variance	0,000
True value	0,070	Standard deviation	0,012
Mean value	0,072	Relative standard deviation	16,7%
Median value	0,070	Relative error	2,9%

Analytical results in ascending order:

22	0,033	O	33	0,069		47	0,081	
17	0,034	O	40	0,070		23	0,085	
54	0,036	O	4	0,070		25	0,092	
45	0,042		8	0,070		42	0,096	
29	0,060		26	0,070		58	0,098	
48	0,061		43	0,070		49	0,100	O
11	0,061		62	0,070		57	0,102	O
32	0,061		28	0,071		59	0,104	
41	0,062		18	0,072		15	0,105	O
10	0,065		38	0,073		14	0,110	O
3	0,066		71	0,074	O	46	0,113	O
1	0,066		66	0,074		6	0,120	O
52	0,066		24	0,075		58	0,124	O
70	0,066		51	0,075		50	0,132	O
9	0,067		67	0,076		30	0,134	O
12	0,067		5	0,077		13	1,730	O

O = Omitted result

Table 8.4. Statistics - Nitrate + nitrite-nitrogen

Sample A

Analytical method: All
Unit: µg/l

Number of participants	60	Range	103
Number of omitted results	19	Variance	826
True value	172	Standard deviation	29
Mean value	161	Relative standard deviation	17,9%
Median value	172	Relative error	-6,6%

Analytical results in ascending order:

6	0	O	24	140	39	176	
32	0	O	19	140	26	180	
30	0	O	8	145	35	180	
63	0	O	23	145	40	182	
43	27	O	48	160	18	182	
14	45	O	2	167	17	183	
58	48	O	49	168	1	185	
70	49	O	67	169	33	185	
66	57	O	25	170	69	185	
45	78	O	37	170	28	185	
15	79	O	55	170	34	187	
21	85	O	56	170	50	188	O
13	92		51	172	12	191	
3	94		59	172	44	195	
11	100		5	173	57	265	O
9	102		54	173	46	372	O
29	104		10	173	71	397	O
62	119		42	175	41	510	O
47	138		60	176	53	720	O
68	138		52	176	38	722	O

O = Omitted result

Table 8.4. Statistics - Nitrate + nitrite-nitrogen

Sample B

Analytical method: All
Unit: µg/l

Number of participants	60	Range	69
Number of omitted results	19	Variance	246
True value	178	Standard deviation	16
Mean value	178	Relative standard deviation	8,8%
Median value	178	Relative error	-0,2%

Analytical results in ascending order:

32	0	O	60	173		1	187	
63	0	O	66	174	O	21	188	O
30	0	O	42	174		33	188	
45	137	O	10	174		34	188	
13	140		51	174		26	190	
47	140		67	175		28	190	
8	150		58	177	O	52	191	
29	155		39	178		9	193	
68	158		48	179		14	196	O
6	160	O	69	180		12	204	
11	164		35	181		44	206	
2	169		49	182		62	207	
55	169		40	182		3	208	
25	170		18	182		71	214	O
24	170		15	184	O	50	243	O
59	170		54	184		46	346	O
56	170		43	185	O	57	450	O
23	172		19	185		53	722	O
37	172		17	186		38	827	O
5	173		70	187	O	41	840	O

O = Omitted result

Table 8.5. Statistics - Chloride

Sample A

Analytical method: All
Unit: mg/l

Number of participants	58	Range	0,53
Number of omitted results	4	Variance	0,01
True value	1,05	Standard deviation	0,11
Mean value	1,04	Relative standard deviation	10,2%
Median value	1,05	Relative error	-0,7%

Analytical results in ascending order:

46	0,00	O	55	1,02		3	1,07	
69	0,78		23	1,03		33	1,08	
8	0,87		67	1,03		34	1,08	
45	0,89		1	1,03		53	1,09	
13	0,89		35	1,04		70	1,09	
62	0,90		40	1,04		26	1,10	
57	0,91		66	1,04		12	1,17	
29	0,91		48	1,04		38	1,18	
25	0,92		52	1,05		43	1,18	
6	0,93		54	1,05		44	1,18	
47	0,93		28	1,05		65	1,20	
49	0,95		9	1,05		15	1,23	
32	0,96		21	1,05		30	1,25	
19	0,98		4	1,06		71	1,29	
18	0,98		68	1,06		50	1,31	
56	0,99		24	1,06		41	1,56	O
63	1,00		42	1,06		14	1,71	O
11	1,00		2	1,06		36	2,94	O
37	1,00		10	1,07				
58	1,02		59	1,07				

O = Omitted result

Table 8.5. Statistics - Chloride

Sample B

Analytical method: All
Unit: mg/l

Number of participants	58	Range	0,52
Number of omitted results	4	Variance	0,01
True value	1,23	Standard deviation	0,10
Mean value	1,24	Relative standard deviation	8,3%
Median value	1,23	Relative error	0,7%

Analytical results in ascending order:

46	0,00	O	55	1,21		34	1,27	
8	1,02		24	1,22		4	1,27	
49	1,02		35	1,22		29	1,28	
69	1,02		21	1,23		33	1,29	
13	1,05		10	1,23		26	1,30	
6	1,10		40	1,23		30	1,30	
57	1,11		48	1,23		68	1,30	
47	1,15		1	1,23		65	1,35	
45	1,15		52	1,23		62	1,38	
32	1,16		67	1,24		38	1,38	
66	1,17		42	1,24		12	1,39	
56	1,18		28	1,24		44	1,40	
11	1,20		9	1,24		43	1,42	
19	1,20		3	1,25		15	1,47	
23	1,20		2	1,25		50	1,54	
18	1,20		54	1,26		14	1,69	O
63	1,20		53	1,26		41	1,84	O
37	1,21		59	1,26		36	2,73	O
58	1,21		70	1,26				
25	1,21		71	1,27				

O = Omitted result

Table 8.6. Statistics - Sulphate

Sample A

Analytical method: All
Unit: mg/l

Number of participants	55	Range	1,56
Number of omitted results	3	Variance	0,09
True value	3,04	Standard deviation	0,29
Mean value	3,00	Relative standard deviation	9,7%
Median value	3,04	Relative error	-1,3%

Analytical results in ascending order:

13	0,90	O	24	2,89	4	3,09
18	1,16	O	40	2,93	48	3,09
46	2,10		37	2,96	26	3,10
41	2,30	O	42	2,99	52	3,11
29	2,41		56	3,00	33	3,13
11	2,49		63	3,00	2	3,14
62	2,49		59	3,01	28	3,16
47	2,54		70	3,02	12	3,20
45	2,65		10	3,03	17	3,25
30	2,70		21	3,04	3	3,26
19	2,70		15	3,04	25	3,30
57	2,78		35	3,04	66	3,32
6	2,81		1	3,05	43	3,33
68	2,83		54	3,05	50	3,46
69	2,85		55	3,06	44	3,51
23	2,86		14	3,08	53	3,64
8	2,86		71	3,08	38	3,66
32	2,88		58	3,08		
9	2,88		67	3,09		

O = Omitted result

Table 8.6. Statistics - Sulphate

Sample B

Analytical method: All
Unit: mg/l

Number of participants	55	Range	1,11
Number of omitted results	3	Variance	0,05
True value	2,79	Standard deviation	0,23
Mean value	2,80	Relative standard deviation	8,3%
Median value	2,79	Relative error	0,4%

Analytical results in ascending order:

13	0,82	O	9	2,70		14	2,86	
18	1,05	O	63	2,70		33	2,88	
11	2,31		56	2,74		12	2,89	
45	2,36		37	2,76		26	2,90	
47	2,38		21	2,77		52	2,91	
30	2,50		35	2,77		17	2,92	
8	2,52		55	2,78		28	2,95	
23	2,55		4	2,79		3	2,98	
29	2,58		10	2,79		66	3,09	
6	2,60		1	2,80		46	3,10	
19	2,60		48	2,80		25	3,10	
57	2,60		24	2,80		43	3,13	
59	2,63		54	2,80		50	3,20	
69	2,64		58	2,80		44	3,23	
68	2,65		67	2,81		53	3,42	
62	2,67		70	2,82		38	3,42	
42	2,69		2	2,83		41	3,60	O
40	2,69		71	2,84				
32	2,70		15	2,85				

O = Omitted result

Table 8.7. Statistics - Calcium

Sample A

Analytical method: All
Unit: mg/l

Number of participants	56	Range	1,37
Number of omitted results	3	Variance	0,05
True value	1,72	Standard deviation	0,23
Mean value	1,72	Relative standard deviation	13,4%
Median value	1,72	Relative error	0,0%

Analytical results in ascending order:

46	0,00	O	27	1,65	30	1,80
14	1,02		58	1,65	10	1,80
2	1,28		52	1,67	57	1,82
29	1,28	O	50	1,68	21	1,83
3	1,29		9	1,68	24	1,85
45	1,32		43	1,68	65	1,85
11	1,33		69	1,69	19	1,86
62	1,39	O	17	1,70	59	1,86
32	1,41		55	1,71	23	1,88
8	1,53		67	1,71	39	1,88
49	1,54		37	1,72	34	1,89
63	1,57		6	1,73	70	1,94
33	1,59		38	1,74	40	1,94
1	1,60		54	1,76	41	1,94
66	1,62		15	1,77	42	2,07
68	1,62		47	1,78	44	2,09
28	1,62		4	1,79	48	2,19
13	1,63		25	1,80	71	2,39
56	1,63		26	1,80		

O = Omitted result

Table 8.7. Statistics - Calcium

Sample B

Analytical method: All
Unit: mg/l

Number of participants	56	Range	1,43
Number of omitted results	3	Variance	0,07
True value	2,04	Standard deviation	0,26
Mean value	2,06	Relative standard deviation	12,6%
Median value	2,04	Relative error	1,2%

Analytical results in ascending order:

46	0,00	O	66	1,96	65	2,10
62	0,99	O	56	1,97	54	2,12
29	1,07	O	9	1,97	38	2,16
14	1,47		68	1,98	25	2,16
3	1,56		67	1,98	21	2,17
2	1,63		58	1,98	57	2,19
11	1,75		52	1,98	34	2,23
28	1,79		50	2,00	19	2,24
45	1,80		17	2,01	70	2,30
63	1,83		69	2,01	24	2,30
32	1,83		37	2,04	10	2,34
49	1,84		30	2,04	59	2,38
6	1,88		39	2,05	44	2,38
8	1,89		55	2,06	42	2,45
33	1,91		4	2,06	23	2,47
13	1,92		15	2,07	48	2,52
43	1,94		40	2,08	71	2,68
27	1,95		47	2,09	26	2,90
1	1,95		41	2,10		

O = Omitted result

Table 8.8. Statistics - Magnesium

Sample A

Analytical method: All
Unit: mg/l

Number of participants	57	Range	0,240
Number of omitted results	2	Variance	0,002
True value	0,270	Standard deviation	0,042
Mean value	0,272	Relative standard deviation	15,5%
Median value	0,270	Relative error	0,8%

Analytical results in ascending order:

46	0,000	O	43	0,254	21	0,280
2	0,135	O	63	0,260	26	0,280
41	0,160		57	0,260	70	0,281
29	0,190		12	0,260	34	0,282
62	0,200		56	0,262	17	0,284
11	0,210		58	0,262	10	0,285
3	0,220		52	0,265	42	0,290
49	0,230		15	0,269	45	0,292
54	0,234		13	0,270	24	0,300
8	0,242		47	0,270	23	0,300
9	0,250		67	0,270	59	0,303
55	0,250		27	0,270	50	0,307
32	0,250		38	0,270	44	0,323
1	0,250		6	0,270	40	0,328
53	0,250		25	0,270	48	0,330
65	0,250		66	0,271	4	0,340
28	0,250		37	0,272	19	0,356
69	0,250		68	0,276	14	0,390
33	0,253		39	0,279	30	0,400

O = Omitted result

Table 8.8. Statistics - Magnesium

Sample B

Analytical method: All
Unit: mg/l

Number of participants	57	Range	0,180
Number of omitted results	2	Variance	0,001
True value	0,320	Standard deviation	0,037
Mean value	0,322	Relative standard deviation	11,6%
Median value	0,320	Relative error	0,8%

Analytical results in ascending order:

46	0,000	O	13	0,305	12	0,330
2	0,164	O	56	0,307	24	0,330
62	0,240		15	0,309	38	0,330
11	0,260		57	0,310	70	0,336
29	0,260		6	0,310	17	0,339
3	0,260		67	0,310	21	0,340
4	0,270		1	0,310	40	0,340
49	0,280		47	0,310	59	0,343
8	0,287		52	0,314	50	0,348
28	0,290		58	0,316	42	0,350
54	0,294		53	0,320	10	0,358
69	0,296		39	0,321	45	0,365
43	0,297		37	0,322	44	0,372
63	0,300		27	0,323	14	0,380
65	0,300		66	0,324	48	0,390
55	0,300		68	0,329	23	0,394
9	0,300		34	0,329	41	0,400
32	0,300		25	0,330	19	0,403
33	0,302		26	0,330	30	0,420

O = Omitted result

Table 8.9. Statistics - Sodium

Sample A

Analytical method: All
Unit: mg/l

Number of participants	57	Range	0,78
Number of omitted results	3	Variance	0,02
True value	1,73	Standard deviation	0,13
Mean value	1,71	Relative standard deviation	7,7%
Median value	1,73	Relative error	-1,2%

Analytical results in ascending order:

53	0,34	O	10	1,68	45	1,75
3	1,14	O	28	1,69	50	1,75
49	1,28		17	1,70	41	1,75
29	1,32		26	1,70	13	1,75
62	1,40	O	24	1,70	34	1,76
36	1,42		21	1,71	1	1,77
66	1,56		43	1,71	37	1,77
69	1,57		54	1,71	33	1,77
11	1,59		25	1,72	38	1,79
47	1,59		42	1,72	15	1,79
52	1,59		2	1,73	14	1,79
32	1,60		59	1,73	19	1,79
63	1,63		55	1,73	71	1,80
27	1,65		8	1,73	30	1,80
58	1,65		44	1,74	56	1,80
39	1,67		70	1,74	4	1,83
57	1,67		68	1,74	9	1,98
40	1,68		12	1,74	23	2,02
67	1,68		6	1,74	48	2,06

O = Omitted result

Table 8.9. Statistics - Sodium

Sample B

Analytical method: All
Unit: mg/l

Number of participants	57	Range	0,94
Number of omitted results	3	Variance	0,02
True value	1,63	Standard deviation	0,15
Mean value	1,63	Relative standard deviation	9,0%
Median value	1,63	Relative error	0,3%

Analytical results in ascending order:

53	0,32	O	24	1,60	34	1,65
62	0,95	O	27	1,60	12	1,66
3	1,11	O	8	1,61	4	1,67
29	1,18		54	1,61	33	1,67
49	1,28		28	1,61	14	1,68
36	1,37		13	1,62	15	1,68
69	1,45		44	1,62	19	1,68
47	1,50		67	1,62	71	1,69
52	1,51		43	1,62	1	1,69
66	1,52		42	1,63	56	1,70
63	1,53		21	1,63	45	1,70
32	1,53		25	1,63	38	1,72
40	1,56		17	1,63	30	1,73
11	1,56		2	1,64	41	1,75
10	1,57		6	1,64	37	1,89
58	1,58		70	1,64	9	1,90
57	1,59		55	1,65	50	1,94
39	1,59		68	1,65	48	1,95
26	1,60		59	1,65	23	2,12

O = Omitted result

Table 8.10. Statistics - Potassium

Sample A

Analytical method: All
Unit: mg/l

Number of participants	57	Range	0,206
Number of omitted results	6	Variance	0,001
True value	0,381	Standard deviation	0,035
Mean value	0,379	Relative standard deviation	9,3%
Median value	0,381	Relative error	-0,4%

Analytical results in ascending order:

69	0,255	O	17	0,374		37	0,399	
4	0,280		14	0,375		27	0,400	
53	0,300		32	0,380		56	0,400	
3	0,310		36	0,380		12	0,400	
11	0,330		6	0,380		25	0,400	
2	0,337		71	0,380		55	0,400	
57	0,340		43	0,380		38	0,400	
33	0,341		54	0,381		42	0,400	
68	0,350		15	0,382		41	0,410	
52	0,353		58	0,382		39	0,424	
50	0,355		70	0,385		26	0,430	
8	0,360		1	0,388		13	0,440	
63	0,360		67	0,390		48	0,450	
24	0,360		28	0,390		23	0,458	O
47	0,360		21	0,390		19	0,486	
66	0,362		45	0,391		9	0,590	O
10	0,366		40	0,391		29	0,720	O
59	0,370		34	0,392		62	0,750	O
30	0,370		44	0,398		49	0,760	O

O = Omitted result

Table 8.10. Statistics - Potassium

Sample B

Analytical method: All
Unit: mg/l

Number of participants	57	Range	0,141
Number of omitted results	6	Variance	0,001
True value	0,350	Standard deviation	0,029
Mean value	0,347	Relative standard deviation	8,5%
Median value	0,350	Relative error	-0,9%

Analytical results in ascending order:

3	0,270	32	0,340	56	0,360	
53	0,280	54	0,345	27	0,360	
33	0,304	21	0,345	37	0,361	
2	0,304	59	0,346	14	0,361	
57	0,310	34	0,350	13	0,367	
63	0,310	55	0,350	38	0,370	
68	0,314	52	0,350	26	0,380	
10	0,319	45	0,352	39	0,387	
47	0,320	40	0,352	19	0,388	
24	0,320	25	0,355	11	0,390	
4	0,320	70	0,355	48	0,400	
30	0,320	17	0,356	41	0,410	
8	0,327	1	0,358	50	0,411	
66	0,329	42	0,360	23	0,462	O
6	0,330	67	0,360	62	0,510	O
15	0,335	28	0,360	69	0,526	O
58	0,335	44	0,360	9	0,550	O
36	0,340	12	0,360	29	0,580	O
43	0,340	71	0,360	49	0,590	O

O = Omitted result

Table 8.11. Statistics - Total organic carbon

Sample A

Analytical method: All
Unit: mg/l

Number of participants	42	Range	2,03
Number of omitted results	2	Variance	0,21
True value	3,84	Standard deviation	0,46
Mean value	3,91	Relative standard deviation	11,8%
Median value	3,84	Relative error	1,8%

Analytical results in ascending order:

63	3,20	10	3,68	1	4,04	
42	3,30	6	3,70	56	4,07	
25	3,34	26	3,70	60	4,10	
50	3,36	18	3,71	40	4,14	
54	3,39	66	3,76	47	4,36	
24	3,50	70	3,81	37	4,46	
17	3,51	55	3,86	13	4,46	
45	3,55	68	3,88	43	4,61	
58	3,57	5	3,88	69	4,65	
59	3,60	51	3,89	30	4,80	
67	3,60	2	3,95	57	4,81	
32	3,65	29	3,95	46	5,20	O
11	3,67	4	3,99	52	5,23	
39	3,67	35	4,03	23	8,54	O

O = Omitted result

Table 8.11. Statistics - Total organic carbon

Sample B

Analytical method: All
Unit: mg/l

Number of participants	42	Range	1,84
Number of omitted results	2	Variance	0,19
True value	4,49	Standard deviation	0,44
Mean value	4,56	Relative standard deviation	9,7%
Median value	4,49	Relative error	1,6%

Analytical results in ascending order:

50	3,83	10	4,39	47	4,71	
63	3,90	26	4,40	56	4,71	
42	4,00	39	4,44	40	4,72	
54	4,05	66	4,45	2	4,80	
25	4,06	70	4,48	4	4,80	
17	4,12	11	4,48	13	5,15	
18	4,13	1	4,50	43	5,22	
58	4,15	6	4,50	5	5,23	
45	4,20	24	4,60	37	5,24	
59	4,20	55	4,60	69	5,32	
32	4,28	51	4,64	30	5,50	
67	4,30	57	4,66	52	5,67	
60	4,30	29	4,67	46	6,10	O
68	4,34	35	4,68	23	8,93	O

O = Omitted result

Table 8.12. Statistics - Aluminium

Sample C

Analytical method: All
Unit: µg/l

Number of participants	39	Range	43,0
Number of omitted results	2	Variance	74,0
True value	81,5	Standard deviation	8,6
Mean value	80,5	Relative standard deviation	10,7%
Median value	81,5	Relative error	-1,3%

Analytical results in ascending order:

33	42,4	O	55	78,0		42	83,7	
71	60,0		66	78,6		51	84,4	
36	62,8		56	78,6		51	84,8	
19	67,3		50	78,6		54	85,1	
20	67,4		17	79,6		38	86,0	
41	70,8		6	81,0		40	86,0	
65	73,0		43	81,5		39	87,1	
45	75,0		1	82,0		15	88,1	
47	75,0		59	82,3		28	89,0	
34	75,7		8	82,9		4	89,4	
24	76,2		33	83,2		46	99,7	
63	76,7		10	83,5		23	103,0	
27	77,4		32	83,5		9	118,0	O

O = Omitted result

Table 8.12. Statistics - Aluminium

Sample D

Analytical method: All
Unit: µg/l

Number of participants	39	Range	46,0
Number of omitted results	2	Variance	86,7
True value	84,6	Standard deviation	9,3
Mean value	82,2	Relative standard deviation	11,3%
Median value	84,6	Relative error	-2,8%

Analytical results in ascending order:

33	43,4	O	66	79,4	33	85,9	
71	59,0		56	79,6	4	86,6	
36	60,0		27	80,0	54	86,7	
19	66,1		17	81,5	38	87,0	
20	68,0		6	82,0	40	88,0	
34	76,1		59	82,9	39	89,1	
50	76,2		10	84,6	15	89,5	
45	77,0		51	84,8	28	90,0	
65	77,0		42	84,9	41	90,0	
24	77,1		1	85,0	43	90,9	
63	77,5		51	85,1	46	102,6	
47	78,0		32	85,3	23	105,0	
55	79,0		8	85,6	9	107,0	O

O = Omitted result

Table 8.13. Statistics - Iron

Sample C

Analytical method: All
Unit: µg/l

Number of participants	40	Range	48,9
Number of omitted results	5	Variance	93,7
True value	70,4	Standard deviation	9,7
Mean value	71,2	Relative standard deviation	13,6%
Median value	70,4	Relative error	1,1%

Analytical results in ascending order:

43	4,6	O	45	69,2		6	74,0	
19	10,2	O	59	69,5		32	74,3	
62	33,4	O	40	70,0		28	75,0	
46	47,1		17	70,0		4	75,3	
54	49,9		34	70,1		71	76,0	
55	50,0		2	70,3		10	77,3	
1	66,9		33	70,4		20	80,4	
42	67,0		50	70,7		23	90,6	
24	67,4		68	70,7		9	91,0	
8	67,4		38	71,0		65	96,0	
66	67,6		27	71,9		41	115,0	O
63	68,0		51	72,2		14	133,2	O
39	68,8		56	73,1				
15	69,0		51	73,9				

O = Omitted result

Table 8.13. Statistics - Iron

Sample D

Analytical method: All
Unit: µg/l

Number of participants	40	Range	44,6
Number of omitted results	5	Variance	68,8
True value	73,0	Standard deviation	8,3
Mean value	72,9	Relative standard deviation	11,4%
Median value	73,0	Relative error	-0,1%

Analytical results in ascending order:

43	5,1	O	39	71,7		6	76,0	
19	15,2	O	45	71,8		27	76,3	
62	37,0	O	8	71,9		51	76,9	
46	49,8		2	72,2		28	77,0	
55	54,0		17	72,9		32	77,1	
54	54,1		40	73,0		10	77,3	
42	65,0		4	73,0		20	78,8	
24	69,8		33	73,6		9	84,0	
1	69,9		59	73,7		71	89,0	
50	70,4		34	73,7		23	94,4	
68	70,4		56	74,8		14	121,8	O
15	71,1		38	75,0		41	225,0	O
63	71,2		65	75,0				
66	71,6		51	75,3				

O = Omitted result

Table 8.14. Statistics - Manganese

Sample C

Analytical method: All
Unit: µg/l

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

Analytical results in ascending order:

46	7,8	O	59	11,3		17	12,0	
54	9,4		68	11,3		38	12,0	
29	9,9		45	11,4		6	12,0	
71	10,0		66	11,5		40	12,0	
57	10,5	O	42	11,6		10	12,1	
62	10,5		1	11,6		53	12,2	
55	10,8		33	11,6		9	12,3	
15	11,0		20	11,6		28	12,5	
27	11,0		43	11,7		41	12,5	
39	11,1		56	11,8		14	12,9	
2	11,1		24	11,8		23	12,9	
50	11,2		51	11,8		47	13,0	
63	11,2		51	11,9		65	22,0	O
34	11,2		32	11,9		19	50,3	O
8	11,3		4	12,0				

O = Omitted result

Table 8.14. Statistics - Manganese

Sample D

Analytical method: All
Unit: µg/l

Number of participants	44	Range	5,2
Number of omitted results	4	Variance	0,9
True value	15,8	Standard deviation	1,0
Mean value	15,7	Relative standard deviation	6,2%
Median value	15,8	Relative error	-0,7%

Analytical results in ascending order:

46	10,1	O	15	15,3		56	16,1	
57	10,7	O	34	15,4		51	16,1	
54	13,0		42	15,5		51	16,1	
41	14,0		27	15,6		10	16,4	
47	14,0		66	15,7		17	16,4	
55	14,5		4	15,7		9	16,4	
29	14,8		1	15,8		20	16,5	
50	14,9		24	15,8		53	16,7	
71	15,0		45	15,8		28	16,8	
2	15,1		8	15,8		23	17,4	
39	15,1		33	15,9		43	17,5	
59	15,1		32	16,0		14	18,2	
68	15,1		40	16,0		65	28,0	O
62	15,2		38	16,0		19	58,7	O
63	15,3		6	16,0				

O = Omitted result

Table 8.15. Statistics - Cadmium

Sample C

Analytical method: All
Unit: µg/l

Number of participants	44	Range	1,04
Number of omitted results	0	Variance	0,04
True value	2,12	Standard deviation	0,20
Mean value	2,11	Relative standard deviation	9,5%
Median value	2,12	Relative error	-0,3%

Analytical results in ascending order:

50	1,60	34	2,08	15	2,20
36	1,60	66	2,08	39	2,20
29	1,67	38	2,10	16	2,20
62	1,88	33	2,10	53	2,20
68	1,94	55	2,10	19	2,28
27	1,95	63	2,11	45	2,29
47	1,96	10	2,12	65	2,30
14	1,96	42	2,12	9	2,30
54	1,99	56	2,13	41	2,30
8	2,00	59	2,13	46	2,30
57	2,01	32	2,15	1	2,30
28	2,01	33	2,15	23	2,43
40	2,03	51	2,17	43	2,48
2	2,03	6	2,19	20	2,64
17	2,05	24	2,20		

O = Omitted result

Table 8.15. Statistics - Cadmium

Sample D

Analytical method: All
Unit: µg/l

Number of participants	44	Range	1,07
Number of omitted results	0	Variance	0,04
True value	1,88	Standard deviation	0,21
Mean value	1,86	Relative standard deviation	11,0%
Median value	1,88	Relative error	-1,1%

Analytical results in ascending order:

50	1,33	33	1,80	53	1,92
36	1,40	38	1,80	42	1,94
62	1,54	34	1,80	51	1,94
29	1,55	17	1,80	15	1,96
68	1,61	57	1,84	1	2,00
14	1,66	59	1,87	45	2,04
65	1,70	10	1,88	33	2,05
28	1,71	56	1,88	9	2,05
27	1,71	66	1,88	20	2,06
47	1,73	32	1,89	46	2,08
54	1,73	24	1,90	23	2,13
40	1,80	6	1,90	19	2,14
16	1,80	55	1,90	41	2,30
8	1,80	39	1,90	43	2,39
2	1,80	63	1,92		

O = Omitted result

Table 8.16. Statistics - Lead

Sample C

Analytical method: All
Unit: µg/l

Number of participants	44	Range	3,65
Number of omitted results	4	Variance	0,51
True value	8,23	Standard deviation	0,71
Mean value	8,30	Relative standard deviation	8,6%
Median value	8,23	Relative error	0,9%

Analytical results in ascending order:

29	2,36	O	6	8,10		59	8,62	
62	2,45	O	40	8,16		10	8,69	
54	6,45		1	8,20		19	8,75	
45	6,86		33	8,20		51	8,78	
15	7,00		8	8,20		38	8,80	
36	7,50		28	8,22		39	8,90	
68	7,73		32	8,22		33	9,00	
63	7,81		46	8,24		16	9,00	
41	7,85		47	8,30		43	9,01	
17	7,88		34	8,33		23	9,26	
50	7,90		24	8,40		20	10,04	
9	7,90		66	8,49		65	10,10	
2	7,90		56	8,49		14	10,89	O
42	7,91		55	8,50		57	15,60	O
53	7,98		27	8,50				

O = Omitted result

Table 8.16. Statistics - Lead

Sample D

Analytical method: All
Unit: µg/l

Number of participants	44	Range	3,40
Number of omitted results	4	Variance	0,50
True value	7,40	Standard deviation	0,71
Mean value	7,38	Relative standard deviation	9,6%
Median value	7,40	Relative error	-0,3%

Analytical results in ascending order:

62	2,25	O	63	7,21		27	7,72	
29	2,46	O	17	7,22		19	7,78	
54	5,27		6	7,30		38	7,80	
36	5,40		33	7,30		10	7,81	
45	6,17		9	7,30		51	7,88	
15	6,32		32	7,38		33	8,00	
68	6,58		28	7,39		46	8,01	
2	7,01		24	7,40		59	8,17	
50	7,03		40	7,43		16	8,30	
66	7,11		39	7,50		23	8,36	
53	7,14		8	7,50		65	8,50	
41	7,15		34	7,54		43	8,67	
42	7,15		56	7,57		14	9,49	O
1	7,20		20	7,67		57	14,82	O
47	7,20		55	7,70				

O = Omitted result

Table 8.17. Statistics - Copper

Sample C

Analytical method: All
Unit: µg/l

Number of participants	44	Range	5,7
Number of omitted results	3	Variance	1,3
True value	13,9	Standard deviation	1,1
Mean value	13,8	Relative standard deviation	8,3%
Median value	13,9	Relative error	-1,0%

Analytical results in ascending order:

16	6,9	O	54	13,6		14	14,2	
71	10,0		38	13,6		10	14,3	
29	10,2		66	13,7		47	14,4	
62	11,6		24	13,7		51	14,4	
50	12,5		20	13,9		9	14,5	
33	13,0		19	13,9	O	65	14,5	
6	13,0		1	13,9		56	14,6	
40	13,0		63	13,9		59	14,7	
57	13,3		39	13,9		53	14,9	
2	13,4		55	14,0		46	15,0	
27	13,5		34	14,0		32	15,3	
41	13,5		15	14,1		4	15,5	
42	13,6		8	14,1		23	15,7	
45	13,6		17	14,1		43	18,1	O
33	13,6		28	14,2				

O = Omitted result

Table 8.17. Statistics - Copper

Sample D

Analytical method: All
Unit: µg/l

Number of participants	44	Range	5,4
Number of omitted results	3	Variance	1,4
True value	13,5	Standard deviation	1,2
Mean value	13,3	Relative standard deviation	8,9%
Median value	13,5	Relative error	-1,8%

Analytical results in ascending order:

16	6,7	O	39	13,2		38	13,8	
29	9,5		66	13,2		51	13,8	
71	10,0		1	13,3		56	13,9	
62	10,7		17	13,3		9	14,0	
33	11,9		34	13,4		14	14,2	
6	12,0		54	13,4		59	14,3	
42	12,3		63	13,5		65	14,5	
57	12,4		15	13,5		8	14,6	
50	12,6		55	13,5		32	14,8	
40	12,7		45	13,6		53	14,9	
2	12,7		28	13,6		23	14,9	
33	12,8		46	13,6		4	14,9	
24	13,0		41	13,7		43	19,0	O
20	13,0		47	13,7		19	22,2	O
27	13,2		10	13,7				

O = Omitted result

Table 8.18. Statistics - Nickel

Sample C

Analytical method: All
Unit: µg/l

Number of participants	41	Range	5,12
Number of omitted results	0	Variance	1,01
True value	8,50	Standard deviation	1,00
Mean value	8,36	Relative standard deviation	12,0%
Median value	8,50	Relative error	-1,6%

Analytical results in ascending order:

29	5,48	42	8,27	51	8,65
62	5,82	8	8,30	66	8,66
36	6,20	39	8,30	24	8,70
45	7,00	6	8,30	54	8,78
50	7,49	34	8,34	15	8,80
19	7,78	28	8,50	14	8,80
55	7,80	1	8,50	53	8,98
33	7,90	56	8,54	57	9,05
65	7,90	32	8,55	23	9,51
2	7,96	17	8,60	20	9,60
27	8,05	9	8,60	71	10,00
59	8,05	47	8,60	43	10,39
63	8,16	41	8,60	46	10,60
40	8,17	38	8,60		

O = Omitted result

Table 8.18. Statistics - Nickel

Sample D

Analytical method: All
Unit: µg/l

Number of participants	41	Range	5,45
Number of omitted results	0	Variance	1,21
True value	7,20	Standard deviation	1,10
Mean value	7,27	Relative standard deviation	15,2%
Median value	7,20	Relative error	0,9%

Analytical results in ascending order:

62	4,55	63	7,16	66	7,41
36	4,85	56	7,16	28	7,50
65	5,30	17	7,16	15	7,70
29	5,39	8	7,20	54	7,74
45	6,00	6	7,20	53	7,74
50	6,52	39	7,20	47	7,90
55	6,60	9	7,20	23	8,04
33	6,70	34	7,24	20	8,20
2	6,79	38	7,30	41	8,20
42	6,93	14	7,37	46	9,00
40	6,98	51	7,37	57	9,38
59	7,00	32	7,38	43	9,68
27	7,01	24	7,40	71	10,00
19	7,03	1	7,40		

O = Omitted result

Table 8.19. Statistics - Zinc

Sample C

Analytical method: All
Unit: µg/l

Number of participants	38	Range	3,46
Number of omitted results	6	Variance	0,66
True value	4,24	Standard deviation	0,81
Mean value	4,22	Relative standard deviation	19,2%
Median value	4,24	Relative error	-0,5%

Analytical results in ascending order:

17	0,00	O	33	4,10	28	4,70	
68	2,34		10	4,12	24	4,90	
32	2,34		51	4,19	50	4,99	
23	2,61		9	4,20	14	5,12	
27	3,60		51	4,28	43	5,43	
66	3,63		8	4,30	6	5,80	
38	3,70		55	4,30	46	5,80	
45	3,80		42	4,31	19	6,70	O
33	3,89		59	4,35	20	7,46	O
56	3,92		15	4,50	4	8,70	O
54	3,97		2	4,52	41	13,00	O
63	4,01		1	4,60	71	21,00	O
40	4,04		34	4,67			

O = Omitted result

Table 8.19. Statistics - Zinc

Sample D

Analytical method: All
Unit: µg/l

Number of participants	38	Range	4,31
Number of omitted results	6	Variance	0,76
True value	5,70	Standard deviation	0,87
Mean value	5,84	Relative standard deviation	15,0%
Median value	5,70	Relative error	2,4%

Analytical results in ascending order:

68	3,79		59	5,64		28	6,10	
32	4,22		17	5,66	O	2	6,13	
23	4,66		51	5,69		15	6,20	
19	5,26	O	27	5,70		14	6,39	
45	5,30		33	5,70		24	7,00	
66	5,32		55	5,70		20	7,14	O
54	5,45		63	5,71		9	7,30	
56	5,46		10	5,75		43	8,05	
33	5,51		42	5,86		6	8,10	
50	5,60		34	5,87		4	8,90	O
46	5,60		1	5,90		71	10,00	O
38	5,60		51	5,92		41	12,50	O
40	5,63		8	6,00				

O = 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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