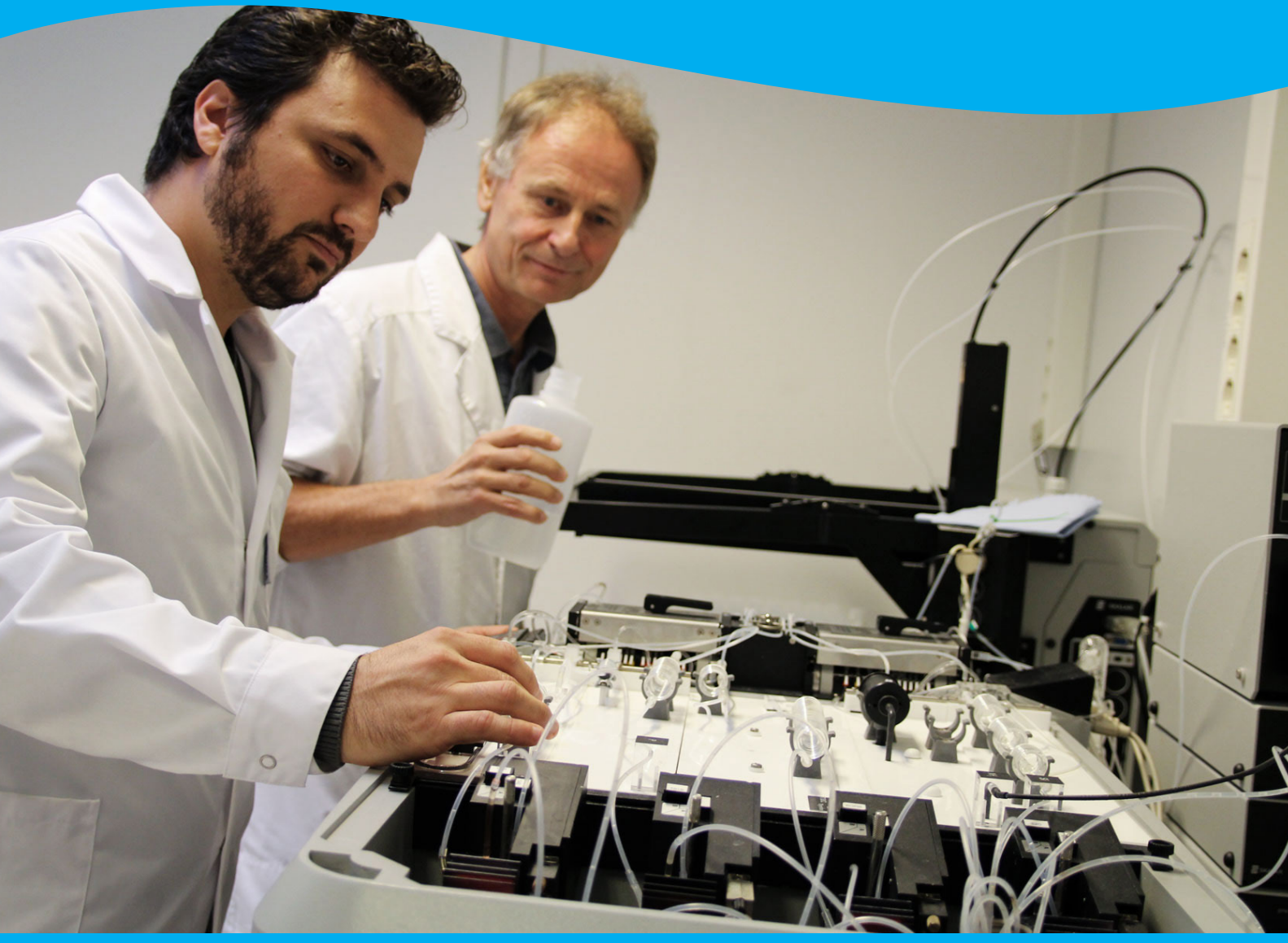
RAPPORT L.NR. 6569-2013

ICP Waters Report 116/2013

Intercomparison 1327: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn



International Cooperative Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes

Convention on Long-Range Transboundary Air Pollution

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

REPORT

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Title	Serial No.	Date
Intercomparison 1327: pH, Conductivity, Alkalinity, NO_3-N, Cl, SO_4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn	6569-2013	25.09.2013
	Report No. / Project No.: 116/2013 / 10300	Pages / Price: 91
Author(s): Dr. Carlos Escudero-Oñate	Topic group: Analytical chemistry	Distribution: Open
	Geographical area: Europe, North America, Asia	Printed: NIVA

Client(s)	Client ref.
Norwegian Environmental Agency United Nations Economic Commission for Europe (UNECE)	

Abstract

In the current ICP Waters Intercomparison program, 106 laboratories were invited to participate. 66 accepted the invitation and 60 laboratories from 28 countries submitted results. Two sample sets were used, one for the determination of major ions and one for heavy metals. Based on the general target accuracy of ± 20 %, 76 % of the overall results were considered acceptable. This is slightly better than last year, but in line with previous editions. The best results were reported for the analytical variables sodium, calcium, aluminium, cadmium, copper and nickel with 91, 85, 89, 85, 84 and 83 % acceptable results respectively. The lowest percentage of acceptable results was observed for pH and Zn, where only a 52 and 60 % of the reported results were acceptable respectively. The improvement of quality in the determination of alkalinity in the current edition is noteworthy, with 63% of acceptable results compared to the previous one with only 48 %. Nitrate showed clear signs of not being sufficiently stable and extremely different results were reported from participants. Harmonization of the analytical methods used and of the practical procedures followed, may be the most important way to improve the comparability for these parameters.

4 keywords, Norwegian	4 keywords, English
1. Prøvningssammenligning	1. Intercomparison
2. Sur nedbør	2. Acid precipitation
3. Kvalitetskontroll	3. Quality Control
4. Overvåking	4. Monitoring

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ISBN 978-82-577-6304-6

CONVENTION ON LONG-RANGE
TRANSBOUNDARY AIR POLLUTION

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

Intercomparison 1327:

pH, Conductivity, Alkalinity, NO_3-N, Cl, SO_4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn

Prepared by the ICP Waters Programme Centre
Norwegian Institute for Water Research
Oslo, September 2013

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 have been published over the years.

The ICP Waters Programme Centre is hosted by the Norwegian Institute for Water Research (NIVA), while the Norwegian Environmental Agency leads the programme. The Programme Centre's work is supported financially by the Norwegian Environmental Agency.

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

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

We hereby report the results from the 27th intercomparison of chemical analysis.

Oslo, September 2013

Dr. Carlos Escudero-Oñate

Contents

Summary

Intercomparison 1327 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 2013, 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. 106 laboratories were invited to participate, and samples were sent to the 66 laboratories who accepted. 60 laboratories submitted results to the Programme Centre before the final statistical treatment of the data. 29 countries were represented in the current intercomparison program.

The median value of the results received from the participants for each variable was selected as "true" value. On average, 76 % 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 52 % 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 sodium, calcium, aluminium, cadmium, copper and nickel with 91, 85, 89, 85, 84 and 83 % acceptable results respectively. The case of Al is also remarkable, where the number of acceptable results increases by 10% compared to the last year’s edition.

The lowest percentage of acceptable results was observed for pH and Zn, where only 52 and 60 % of the reported results were acceptable. It is worthy to note the improvement of quality in the determination of alkalinity in the current edition, with 63% of acceptable results, compared to the previous one with only 48 %.

More than 80 % of the reported results were accepted for: calcium, magnesium, sodium, aluminium, cadmium, copper and nickel. 70 - 79 % acceptable results were obtained for conductivity, chloride, sulphate, potassium, TOC, iron, manganese and lead while only 60 – 69 % where accepted for alkalinity and zinc. Nitrate demonstrated to be unstable, as unacceptable differences in the results were communicated by the different participants.

The potential explanation to the unacceptable results could be the low concentrations of some of the variables, forcing the laboratories to work close or even under their quantification limits. Some of the laboratories reported the absence of instrumental or analytical techniques sensitive enough to deal with these concentrations.

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 twentyseventh intercomparison test, called 1327, 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 that were delivered to the different participating laboratories is presented in Appendix B of this document. 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 heavy metals. It was decided that total organic carbon and aluminium should also be included.

The samples were shipped from the Programme Centre on July the 18th of 2013. With some exceptions, the laboratories received the samples within one week. Two of the shipped packages were returned back to the organizer. Despite samples being sent with a declaration of absence of commercial value and description of only testing samples, in some cases, delays in the reception of the samples were reported by the laboratories. Further research in the origin of the trouble demonstrated that delay was due to troubles in the customs in some of the countries.

To ensure the integrity and minimal degradation of the samples, participants were encouraged to analyze them as soon as possible and register the analytical results in the Organization’s database before August the 23th.

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 is the greater, i.e. fixed or relative acceptance limits.

In Table 1, an evaluation of the results of intercomparison 1327 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 presented. 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.

In the current edition 60 laboratories submitted results to the intercomparison. If results for the different variables are averaged, 76 % of them 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 result is only slightly higher than last year, but in line with the previous ones. As previously stated, the best results were obtained in the determination of sodium, calcium, aluminium, cadmium, copper and nickel. The worstresults,were reported in the determination of pH and Zn concentration.

pH results may be strongly affected by the method used when the measurement is performed in solutions close to neutral. 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, from the last edition the Organization decided to reduce the acceptance limit for this analytical variable from the target value of ± 20 % to ± 10 % and this criterion was still used in the current one.

In the case of nitrate analysis it is worthwhile to note the high number of laboratories that reported a 0 concentration in addition to the high dispersion in determination of this variable reported by the different participants. Due to these extremely different results, the Program Centre decided not to plot the Youden chart for this variable. However, the stability of the sample was evaluated by the Organizerduring the intercomparison and the results showed that nitrate was not stable (Appendix B, Table 3). This seems to show quite clearly that uncontrolled variables in the shipping are negatively influencing the nitrate concentration.

Earlier intercomparisons indicated also that the stability of this parameter could be a problem for its determination. The conclusion is that the evaluation of this variable is highly questionable. It seems also that some of the participants reported results in wrong concentration units and that also some of them 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. The determination of total organic carbon showed better performance this year compared to the last two. For the major ions, the ion chromatography technique clearly grows ahead of the traditional methods, the photometric methods for the anions and the atomic absorption or emission methods for the cations.

The best percentage of acceptable results for heavy metals in this intercomparison programme was obtained for copper and cadmium. The increase of this percentage is also relevant in the case of aluminium if compared to the last 3 years editions.

Despite some of the determinations having achieved a better performance than last year, some of them have shown a decrease in percentage of acceptable results. It has to be taken into account that even though the concentrations in these samples are higher than could be expected in relevant natural samples, some of the laboratories do not have available methods sensitive enough to determine heavy metals at trace level.

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 in the determination of some of the variables may in some cases be explained by either low concentration, 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 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 attributed 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 1327.

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 1327	1226	1125	1024
pH	AB	6,57	6,5	0,2 pH(±)	56	29	52	59	73	49
Conductivity, mS/m	AB	1,92	1,86	10	55	43	78	72	86	84
Alkalinity, mmol/l	AB	0,097	0,092	20	43	27	63	48	79	74
Chloride, mg/l	AB	0,9	0,92	20	51	40	78	79	89	79
Sulphate, mg/l	AB	1,3	1,25	20	52	40	77	80	86	73
Calcium, mg/l	AB	2,19	2,01	20	55	47	85	75	91	77
Magnesium, mg/l	AB	0,27	0,25	20	55	45	82	74	89	82
Sodium, mg/l	AB	1,01	1,09	20	54	49	91	84	95	93
Potassium, mg/l	AB	0,185	0,198	20	53	37	70	81	82	82
Total organic carbon, mg/l	AB	4,45	4,26	20	36	28	78	76	69	83
Aluminium, µg/l	CD	92,6	91,3	20	35	31	89	79	76	77
Iron, µg/l	CD	34,3	31,2	20	36	26	72	70	91	81
Manganese, µg/l	CD	6,2	6,97	20	36	28	78	89	86	85
Cadmium, µg/l	CD	1,53	1,76	20	39	33	85	84	94	88
Lead, µg/l	CD	3	3,28	20	35	25	71	77	67	73
Copper, µg/l	CD	10	10,5	20	38	32	84	86	77	51
Nickel, µg/l	CD	4,05	4,19	20	36	30	83	78	72	66
Zinc, µg/l	CD	3,96	4,3	20	35	21	60	61	79	82
Total					800	611	76	74	83	75

4. Results

106 laboratories were invited to participate in this ICP Waters intercomparison. 66 laboratories from 29 different countries accepted and therefore samples were shipped to them. At the end of the program, 60 laboratories had submitted results to the Programme Centre. The participants and their code numbers are listed in Appendix A, which also includes a table summarizing the number of laboratories that participated in each of the countries.

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 excluding outliers- 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 Figures 1 - 18, where each laboratory is represented by a small circle and an identification number. Some laboratories with strongly deviating results may be located outside the plot. The big circle in the figures 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. As previously stated, in the current edition Youden’s chart for nitrate has been omitted due to the high divergences between the participants and from the target expected value.

A summary of the results of intercomparison 1327 is presented in Tables 1 and 2. The individual results of the participants are presented in Table 7 in Appendix D, sorted by 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 the Youden graph (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 and the statistical calculations are presented in Table 2 and Table 8.1.

56 of the participants determined pH in the test samples A and B. All the laboratories had used a method based upon electrometry. Ten 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 strength than the samples used in this intercomparison (4,5). Despite differences in between both stirring and non stirring are slight, better accuracy and lower relative standard deviation was achieved in stirred samples.

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 current edition of the intercomparison, as last year, the median value of all the reported results after excluding the outliers was chosen. Based upon this, 52 % of the results were acceptable, that is, within the median value ± 0,2 pH units. This is slightly lower than in the last intercomparison, where 59 % of the results fulfilled the acceptability criteria (Table 1).

The most probable reason for the differences in the reported results could be due to the slight differences in the analytics that the different participants employed. It is also questionable whether there could be some differences due to instability of the samples during their shipment. Stability tests performed by the Organizer during the report period put into evidence the stability of the samples, if preserved at 4 ºC and in the dark (See Appendix B).

The presence of important systematic errors in the determination of pH is also noteworthy, as illustrated in Figure 1 by the spread of the results away from the 45° line for many laboratories in the characteristic elliptical distribution.

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.

In the current intercomparison, 55 laboratories have reported results for conductivity. From them, 51 used an electrometric method while only four laboratories reported the use of "other method" without further specification. Most laboratories achieved rather good agreement with the results for this variable, and 78 % of the results were within the acceptance limit of ± 10 %. These results are slightly better than in the last year edition and a little bit lower than in previous ones.

In the current edition it can be concluded that systematic errors have taken place, as is shown in the distribution of the results in Figure 2. It has to be pointed out that an accurate temperature control or proper temperature correction is necessary when determining this variable, as the conductivity changes by about two percent pr. °C at room temperature.

4.3 Alkalinity

The Youden chart obtained in the determination of the alkalinity in samples A and B is illustrated in Figure 3. The statistical results are presented in Tables 2 and 8.3.

43 laboratories reported results for alkalinity. From them, 14 used Gran plot titration method, which is the suggested reference method in the manual (1), while 11 made use of end point titration. Four participants employed end point titration to pH 5,4 while only one reported titration until 5,6. Six of the laboratories titrated to another end point and seven reported the use of other method for the determination of the alkalinity

From the 43 reporting laboratories, only 27 of the sample pairs - 63 % of them - were within the target accuracy of ± 20 %. This percentage is notably higher than the last year edition but lower than in the editions of 2011 and 2010.

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 cases, 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.

In the current edition it can be concluded that both slight systematic and random errors have taken place as is shown by the distribution of the results in Figure 3.

4.4 Nitrate + nitrite-nitrogen

39 laboratories reported results for nitrate + nitrite-nitrogen and the results are presented in Tables 2 and 8.4. Ion chromatography was by far the most used by the participants (24). As shown in Table 8.4, an important number of laboratories reported a zero concentration for this variable. According to the extremely different results reported by many of the participants, the Program Centre decided not to plot the Youden chart for nitrate.

The stability study carried out by the Organizer shows that Nitrate concentration is stable during the period of the interlab (Appendix B, Table 3). It seems clear then that transport and storage of the samples in uncontrolled conditions has a significant influence in this parameter.

Earlier intercomparisons also indicate that the stability of this parameter can influence its determination. Our conclusion is that the evaluation of this variable is highly questionable. It seems also that some of the participants reported results in wrong units and that also some of them possibly have reported their results as nitrate instead of nitrogen.

4.5 Chloride

51 laboratories reported results for chloride and, from them, 40 were accepted. The results are presented in Figure 4, Table 2 and Table 8.5. The target accuracy of ± 20 % is represented by the circle in Figure 4.

Ion chromatography appears as the most widely employed technique, with 41 of the participants reporting its use. Other techniques such as argentometry, photometry, AA, capillary electrophoresis and others using Hg were employed to a lesser extent.

Most of the laboratories used ion chromatography as the analytical technique in their determination of chloride (81 %). Other participants reported the use of different photometric methods, argentometry and capillary electrophoresis. It has to be mentioned that the three results provided by the argentometric technique were extremely high and had to be omitted for calculations so it seems that this technique is not useful for the determination of chloride in the low concentrations of the samples. Despite this, 78 % of the results reported by the different laboratories were acceptable, in line with previous editions of the intercomparison program. From the data obtained in the current edition it can be concluded that IC provided accurate results with relative standard deviations lower than 7 %.

The deviations from the established true value are mainly due to systematic errors, but some laboratories presented results affected with important random errors.

4.6 Sulphate

52 laboratories reported results for sulphate. Of these, 40 were accepted, in other words, 77 % of the total. This percentage is similar to that observed in previous editions. The results obtained for the analysis of sulphate are presented in Figure 5, Table 2 and Table 8.6.

The circle in Figure 5 represents the target accuracy of ± 20 %. As in the case of chloride, most of the laboratories (41 participants) used ion chromatography as the analytical technique in their

determinations of sulfate. Four of the participants reported the use of ICP-AES for the determination of this variable, three made use of photometry, two nephelometry, one electrophoresis and one participant used other method.

Due to the small number of methods other than ion chromatography, it is not possible to discuss much about differences between them, but it can be concluded that both, IC and ICP-AES provided accurate results with relative standard deviations lower than 11 %.

According to the Youden chart obtained for this variable it can be concluded that the deviations in the results are mainly due to systematic errors.

4.7 Calcium

55 laboratories reported results for calcium from which 47 were accepted (85 % of total). This percentage is 10 % higher than that observed in the last edition. The results are presented in Figure 6, Table 2 and Table 8.7. The circle in Figure 6 represents the target accuracy of ± 20 %.

23 of the laboratories used ion chromatography and 17 ICP-AES. The traditional flame atomic absorption spectrometry was used by seven of the participants in their determination of calcium. Only three laboratories used ICP-MS and three more complexing titrations with EDTA. One of the participants made use of electrophoretic techniques and another participant reported other method.

In the current edition, more accurate results have been obtained by ICP-AES than by ion chromatography, with also lower standard deviation.

The deviating results are mainly affected by systematic errors, despite some laboratories exhibiting random errors.

4.8 Magnesium

55 laboratories reported results for magnesium. Of these, 45 were acceptable (a 82 % of the total). This percentage is in line with the acceptable results reported in previous editions.

The characteristic Youden chart obtained in the current edition is presented in Figure 7. Statistical results can be found in Tables 2 and 8.8. The circle in Figure 7 represents the target accuracy of ± 20 %. The analytical methods used by the participants are mainly the same as for the determination of calcium. 23 of the laboratories used ion chromatography, and 17 used ICP-AES. The traditional flame atomic absorption spectrometry was used by seven of the participants in their determination of this variable. Three of the laboratories reported the use of ICP-MS, two participants employed EDTA complexing titration, one capillary electrophoresis and one participant used a different method.

In the current edition, excellent results have been reported by ion chromatography, ICP-AES and FAAS, however, the lowest relative standard deviations have been obtained by the plasma emission technique.

The deviations in the results are mainly due to systematic errors, as is shown in Figure 8.

4.9 Sodium

54 laboratories reported results for sodium and from them, 49 pairs were accepted, involving an excellent 91 % of the total. This is in agreement with the percentage of acceptance of previous editions.

The characteristic Youden chart is presented in Figure 8. Tables 2 and 8.9 summarize the statistical treatment of the data. The circle in Figure 8 represents the target accuracy of ± 20 %. 24 in this round used ion chromatography in their determinations, 15 laboratories used ICP-AES, and four used the traditional flame atomic absorption spectrometry. Three used ICP-MS, one laboratory used capillary electrophoresis and one participant reported the use of a technique different to these previously mentioned.

This determination usually holds a very good quality and there was no significant difference in the results obtained by the different analytical techniques.

When checking the Youden chart obtained in the determination of sodium, it is clear that the deviating results are mainly affected by systematic errors.

4.10 Potassium

53 laboratories reported results for potassium. From these results, 37 where considered as acceptable, involving 70 % of the total. This is a significant decrease in acceptable results by 10% compared with results from the last three intercomparisons.

The Youden graph obtained for the determination of potassium in this round is presented in Figure 9. Statistical results for this variable are presented in Tables 2 and 8.10. The circle in Figure 9 represents the target accuracy of ± 20 %. The analytical methods and their distribution is almost the same as in the determination of sodium among the participants.

As in the case of sodium, the deviating results have a strong component of systematic errors, however, in this case, an important component of random error appears in some of the results reported by the laboratories.

4.11 Total organic carbon

36 laboratories reported results for total organic carbon. Of these, 78 % of the results were within the target accuracy of ± 20 % (28 laboratories).

The results of the Youden test are presented in Figure 10, while the statistics are presented in Tables 2 and 8.11. The circle in Figure 10 represents the target accuracy of ± 20 %. Combustion methods are used by most of the laboratories (26), only seven laboratories used UV/peroxodisulfate oxidation method for this determination. The last three laboratories stated "other method" when reporting. Not significant differences were observed in the results provided by the combustion and the UV/peroxodisulfate methods. The UV/peroxodisulfate oxidation method seems to provide slightly lower results than the combustion method, but the difference is not significant.

Youden’s chart demonstrates that the deviating results are mainly affected by systematic errors.

4.12 Aluminium

35 laboratories reported results for aluminium. Of these, 31 where accepted according to the target accuracy criteria, which means 89 % (10 % more than in the last year edition). The results of the Youden test are presented in Figure 11, where the circle represents the target accuracy of ± 20 %. The statistics of the analytics are presented in Tables 2 and 8.12.

In the current edition, 13 of the laboratories used ICP-MS and 12 used ICP-AES. Nine participants used graphite furnace atomic absorption, while only one reported the use of a photometric method.

The ICP-MS technique provided the best results, however, no significant differences were observed between the plasma and the graphite furnace techniques. From these techniques, the highest relative standard deviation in the results was observed for the graphite furnace.

According to the distribution of the results in the Youden chart, deviating results are mainly affected by systematic error.

4.13 Iron

From the 66 participants, only 36 laboratories reported results in the determination of iron. From these laboratories, 26 provided acceptable results (72 % of total). The results of the Youden test are presented in Figure 12. The statistical calculations are presented in Table 2 and Table 8.13. The circle in Figure 12 represents the target accuracy of ± 20 %.

Fourteen and thirteen of the laboratories used ICP-AES and ICP-MS, respectively. Four participants used graphite furnace atomic absorption, while three used flame atomic absorption. One laboratory used a method based on photometry and another reported the use of other method.

There are no important differences in the results obtained by the plasma methods and graphite furnace. However, graphite furnace was observed to provide the highest relative standard deviation in the results.

The Youden chart puts into evidence that deviating results are mainly affected by systematic errors, however there are also some laboratories with rather large random errors.

4.14 Manganese

Only 36 participants reported results in the analysis of manganese. From these, only 28 fulfilled the acceptance criteria. This involves 78 % of acceptance, which is notably lower than in the last three years' editions. The Youden chart is presented in Figure 13 and the statistical results in Tables 2 and 8.14. The circle in Figure 13 represents the target accuracy of ± 20 %.

All the laboratories have reported the use of atomic techniques. Fourteen and twelve participants used ICP-MS and ICP-AES, respectively, while seven and two used graphite furnace atomic absorption and flame atomic absorption respectively. No significant differences were detected between the different techniques.

According to the distribution of the Youden chart, deviating results are mainly affected by systematic errors.

4.15 Cadmium

39 laboratories reported results for cadmium in the set of samples C and D. From these, 33 of the results were acceptable, according to the target accuracy. This involves 85 % of them, which is in line with the previous edition of the intercomparison, but quite lower if compared with the acceptance percentage of the editions of 2011 and 2010.

The Youden graph for cadmium is presented in Figure 14 while the statistical calculations for this variable are presented in Tables 2 and 8.15. The circle in Figure 14 represents the target accuracy of ± 20 %.

Plasma techniques have been the most employed, as 26 participants reported its use. From them, 17 detected mass (ICP-MS) and 9 emitted radiation (ICP-AES). The preferred method employed by the participants that used atomic absorption techniques was the graphite furnace (GFAAS). The use of this technique was reported by 9 of the participants. One of the laboratories reported the use of polarography for the quantification of Cd. All the methods provided similar results, without significative differences.

The deviating results are mainly affected by systematic errors, however a few laboratories also have important random errors.

4.16 Lead

35 laboratories reported results for lead in samples C and D. From these, 25 were accepted involving 71 % of the results. This percentage of acceptance was slightly lower than in the last year edition, but in line with previous intercomparisons. The Youden chart is presented in Figure 15 and statistical results in the determination of this variable can be found in Tables 2 and 8.16.

The circle in Figure 15 represents the target accuracy of ± 20 %. In this case, all the laboratories have reported the use of atomic techniques. Again, plasma techniques have been the most employed, as 24 participants have communicated the use of ICP. From them, 18 used mass detection (ICP-MS) and 6, emitted radiation (ICP-AES). The preferred method employed by the participants using atomic absorption techniques was the graphite furnace (GFAAS). It is worthy to note that from the laboratories employing ICP techniques, all the results were acceptable, while from those employing GFAAS, three of the results had to be omitted for the statistical calculations.

As is shown in the characteristic Youden chart, the deviating results are mainly affected by systematic errors, but there are also some laboratories with rather large random errors.

4.17 Copper

38 laboratories reported results for copper in sample set C and D. From them, 32 were acceptable (84 % of the total). The Youden chart is presented in Figure 16 and statistical results in the determination of this variable in Tables 2 and 8.17. The circle in the figure represents the target accuracy of ± 20 %. Figure 16 shows that only two of the results are outside the target accuracy and deviations can be assigned mainly to systematic error.

For the analysis, almost all the participants employed atomic based techniques, plasma being the most widely used with 17 of the participants using mass detectors and 9 using emitted light. The contribution of the atomic absorption techniques is also important as eight participants employed GFAAS while only three made use of FAAS. Only one of the participants employed an electrochemical technique based on polarography.

4.18 Nickel

36 laboratories reported results for nickel in samples C and D. From these results, only 30 where acceptable, involving 83 % of the total. This percentage of acceptable results is the highest since2010 and indicates a clear improvement in the quality of the results in the last four years.

Nickel's Youden chart is presented in Figure 17 and the statistical results in Tables 2 and 8.17. The circle in the figure represents the target accuracy of ± 20 %. The Youden chart shows that the determination of nickel in the samples is affected mainly by systematic error.

Atomic based techniques is the most widely used technique for this analysis. From them, plasma is the most widely used with 24 participants. 17 employed ICP-MS while only seven used ICP-AES. From the laboratories that did atomic absorption based techniques, ten of them employed graphite furnace while only one performed the analytics in flame absorption mode.

4.19 Zinc

35 laboratories reported results in the determination of zinc in sample set C and D. From these labs, only 21 were accepted, involving 60 % of the total. These results are in line with the percentage of last year's edition but lower than in the editions of 2011 and 2010. It has to be mentioned also that the determination of this variable has exhibited a worsening trend from the 2010 edition, going from 82 % of acceptable results reported in 2010 till 60 % in the current edition.

The Youden chart is presented in Figure 18 and statistical results in Tables 2 and 8.19. The circle in Figure 18 represents the target accuracy of ± 20 %. In the determination of Zn, deviations in the results are mainly due to the presence of systematic errors with some contribution of random errors.

Plasma techniques are, by far, the most widely employed by the laboratories.Of the plasma techniques, ICP-MS was the most widely used, with 17 participants, followed by emission in plasma (ICP-AES) used by nine of the laboratories. From the techniques based on atomic absorption spectroscopy five laboratories made use of the graphite furnace (GFAAS) and four of absorption in flame (FAAS). In the current edition, nobody reported results with a non-atomic technique.

Table 2. Statistical summary for intercomparison 1327

Analytical variable and method	Sample pair	TRUE S. 1	Value S. 2	No. of lab. Total	Om.	Median S. 1	S. 2	Avg/Std.av. Sample 1		Avg/Std.av. Sample 2		Rel.std.av. % S. 1	S. 2	Relative error % S. 1	S. 2
pH	AB	6,57	6,50	56	0	6,57	6,50	6,54	0,23	6,49	0,22	3,5	3,4	-0,5	-0,2
Electrometry				42	0	6,57	6,49	6,55	0,24	6,50	0,23	3,7	3,5	-0,3	0,1
Stirring				10	0	6,58	6,53	6,58	0,13	6,50	0,13	2,0	2,0	0,1	0,0
Equilibration				2	0			6,41		6,34				-2,4	-2,5
Other method				2	0			6,29		6,30				-4,3	-3,1
Conductivity	AB	1,92	1,86	55	8	1,92	1,86	1,92	0,07	1,86	0,08	3,9	4,2	0,2	0,1
Electrometry				51	7	1,92	1,86	1,93	0,07	1,87	0,08	3,9	4,1	0,4	0,3
Other method				4	1	1,86	1,80	1,86	0,03	1,80	0,04	1,9	2,5	-3,1	-3,4
Alkalinity	AB	0,097	0,092	43	10	0,097	0,092	0,099	0,014	0,093	0,012	14,1	12,9	1,7	1,6
Gran plot titration				14	2	0,098	0,096	0,097	0,012	0,094	0,011	12,2	11,7	-0,2	2,0
End point titration				11	4	0,098	0,092	0,104	0,013	0,097	0,012	12,6	12,2	7,5	5,3
Other method				7	3	0,094	0,089	0,099	0,029	0,087	0,021	29,6	23,8	2,3	-5,4
End point				6	0	0,099	0,093	0,100	0,011	0,095	0,013	11,2	14,0	2,7	2,7
End point 5.4				4	1	0,091	0,092	0,093	0,004	0,092	0,002	4,1	1,7	-4,5	-0,4
End point 5.6				1	0			0,092		0,090				-5,7	-2,7
Nitrate + nitrite-nitrogen	AB	10	2	39	2	10	2	25	30	5	10	119,8	181,7		
Ion chromatography				24	1	6	1	27	33	4	6	122,9	174,9		
Autoanalyzer				5	0	11	2	17	22	6	9	126,7	147,3		
Flow injection anal.				4	0	16	5	21	23	6	7	107,8	118,3		
Photometry				3	1			24		26					
Photometry				2	0			5		5					
Hydrazine				1	0			69		0					
Chloride	AB	0,900	0,920	51	6	0,900	0,920	0,895	0,083	0,910	0,074	9,3	8,2	-0,6	-1,1
Ion chromatography				41	2	0,900	0,920	0,885	0,059	0,904	0,063	6,7	6,9	-1,6	-1,8
Argentometry				3	3			2,407		2,153				167,4	134,1
Photometry				2	0			1,065		1,013				18,3	10,1
AA				1	0			0,670		0,790				-25,6	-14,1
Cap. electrophoresis				1	1			0,644		0,617				-28,4	-32,9
Manual, Hg				1	0			1,100		1,100				22,2	19,6
Other method				1	0			0,833		0,842				-7,4	-8,5
Photometry HgSCN				1	0			1,000		0,940				11,1	2,2
Sulphate	AB	1,300	1,250	52	4	1,301	1,250	1,303	0,109	1,261	0,125	8,3	9,9	0,2	0,9
Ion chromatography				41	2	1,290	1,240	1,284	0,107	1,234	0,111	8,3	9,0	-1,2	-1,3
ICP-AES				4	0	1,405	1,333	1,388	0,093	1,362	0,143	6,7	10,5	6,7	8,9
Photometry				3	2			1,450		1,510				11,5	20,8
Nephelometry				2	0			1,380		1,430				6,2	14,4
Cap. electrophoresis				1	0			1,270		1,220				-2,3	-2,4
Other method				1	0			1,430		1,390				10,0	11,2

Om.: Sample pair omitted from the calculations

Analytical variable and method	Sample pair	TRUE S. 1	TRUE S. 2	No. of lab. Total	No. of lab. Om.	Median S. 1	Median S. 2	Avg/Std.av. Sample 1		Avg/Std.av. Sample 2		Rel.std.av. % S. 1	Rel.std.av. % S. 2	Relative error % S. 1	Relative error % S. 2
Calcium	AB	2,19	2,01	55	2	2,19	2,01	2,20	0,20	2,03	0,21	9,0	10,1	0,3	1,0
Ion chromatography				23	2	2,17	2,01	2,17	0,25	2,02	0,24	11,7	12,0	-1,0	0,3
ICP-AES				17	0	2,19	2,00	2,20	0,16	2,01	0,14	7,1	7,0	0,7	0,2
FAAS				7	0	2,20	1,94	2,21	0,08	1,95	0,09	3,8	4,5	0,8	-3,1
EDTA				3	0	2,18	2,10	2,19	0,04	2,23	0,28	1,6	12,3	0,0	11,1
ICP-MS				3	0	2,20	2,10	2,38	0,31	2,23	0,32	13,2	14,3	8,5	10,8
Cap. Electrophoresis				1	0			2,10		2,09				-4,0	4,1
Other method				1	0			2,16		1,94				-1,4	-3,5
Magnesium	AB	0,270	0,250	55	6	0,270	0,250	0,270	0,022	0,252	0,023	8,0	9,0	-0,2	0,7
Ion chromatography				23	3	0,259	0,247	0,265	0,030	0,250	0,032	11,3	12,7	-1,9	-0,1
ICP-AES				17	1	0,277	0,260	0,276	0,013	0,258	0,012	4,8	4,5	2,1	3,0
FAAS				7	0	0,272	0,250	0,275	0,011	0,248	0,018	4,0	7,2	1,7	-0,8
ICP-MS				3	1			0,255		0,249				-5,7	-0,4
EDTA				2	1			0,270		0,250				0,0	0,0
Other method				2	0			0,262		0,237				-3,1	-5,2
Cap. Electrophoresis				1	0			0,272		0,266				0,7	6,4
Sodium	AB	1,010	1,090	54	2	1,010	1,090	1,003	0,060	1,079	0,075	6,0	6,9	-0,7	-1,0
Ion chromatography				24	1	1,010	1,102	1,012	0,050	1,095	0,055	5,0	5,0	0,2	0,5
ICP-AES				15	0	1,000	1,100	0,997	0,051	1,077	0,060	5,1	5,6	-1,3	-1,2
AES				5	0	1,010	1,040	1,004	0,034	1,058	0,050	3,4	4,7	-0,6	-2,9
FAAS				4	0	1,075	1,110	1,073	0,046	1,153	0,114	4,3	9,9	6,2	5,7
ICP-MS				3	1			0,963		1,005				-4,7	-7,8
Other method				2	0			0,884		0,960				-12,5	-11,9
Cap. Electrophoresis				1	0			0,926		0,920				-8,3	-15,6
Potassium	AB	0,185	0,198	53	7	0,185	0,198	0,183	0,022	0,196	0,026	11,8	13,4	-0,9	-1,0
Ion chromatography				22	2	0,170	0,180	0,170	0,019	0,184	0,026	10,9	14,0	-8,1	-7,1
ICP-AES				16	2	0,189	0,202	0,187	0,014	0,199	0,015	7,7	7,3	1,0	0,4
AES				4	0	0,201	0,200	0,202	0,016	0,197	0,008	8,0	4,0	9,1	-0,6
FAAS				4	1	0,200	0,210	0,198	0,013	0,220	0,026	6,3	12,0	7,2	11,1
ICP-MS				4	1	0,188	0,200	0,203	0,033	0,223	0,049	16,1	22,1	9,5	12,8
Other method				2	1			0,184		0,191				-0,5	-3,5
Cap. Electrophoresis				1	0			0,223		0,244				20,5	23,2
Total organic carbon	AB	4,45	4,26	36	4	4,45	4,26	4,55	0,41	4,39	0,41	9,0	9,3	2,3	3,1
Combustion				26	3	4,48	4,30	4,56	0,44	4,41	0,40	9,5	9,2	2,5	3,5
UV/peroxodisulphate				7	0	4,31	4,10	4,49	0,35	4,30	0,45	7,8	10,5	1,0	0,9
Other method				3	1			4,66		4,51				4,7	5,9
Aluminium	CD	92,6	91,3	35	4	92,6	91,3	92,9	4,3	91,3	3,8	4,7	4,2	0,3	0,0
ICP-MS				13	1	92,7	91,0	93,2	3,7	91,0	3,4	4,0	3,7	0,7	-0,4
ICP-AES				12	1	93,8	91,4	93,4	3,6	91,2	3,3	3,9	3,6	0,8	-0,1
GFAAS				9	1	91,4	90,8	91,8	6,2	91,9	5,3	6,8	5,8	-0,9	0,7
Photometry				1	1			65,0		61,0				-29,8	-33,2

Om.: Sample pair omitted from the calculations

Analytical variable and method	Sample pair	TRUE S. 1	Value S. 2	No. of lab. Total	Om.	Median S. 1	S. 2	Avg/Std.av. Sample 1		Avg/Std.av. Sample 2		Rel.std.av. % S. 1	S. 2	Relative error % S. 1	S. 2
Iron	CD	34,3	31,2	36	5	34,3	31,2	35,2	2,9	32,3	2,9	8,1	9,0	2,6	3,7
ICP-AES				14	0	34,6	30,9	34,7	1,2	31,0	1,2	3,4	3,9	1,3	-0,5
ICP-MS				13	3	33,9	30,8	33,9	2,2	31,8	2,4	6,6	7,4	-1,2	2,0
GFAAS				4	1	36,8	39,4	37,2	6,2	36,7	5,3	16,6	14,3	8,5	17,5
FAAS				3	1			40,6		36,4				18,4	16,7
Other method				1	0			34,3		31,0				0,0	-0,6
Photometry				1	0			38,4		36,1				11,8	15,8
Manganese	CD	6,20	6,97	36	4	6,20	6,97	6,18	0,62	6,90	0,52	10,1	7,5	-0,3	-1,0
ICP-MS				14	2	6,18	7,02	6,06	0,57	6,87	0,55	9,4	8,0	-2,2	-1,4
ICP-AES				12	0	6,16	6,87	6,17	0,47	6,91	0,38	7,7	5,5	-0,5	-0,9
GFAAS				7	0	6,98	7,00	6,40	0,95	6,87	0,74	14,9	10,7	3,2	-1,4
FAAS				2	1			6,20		7,30				0,0	4,7
Other method				1	1			0,00		0,00				- 100,0	- 100,0
Cadmium	CD	1,53	1,76	39	2	1,53	1,76	1,52	0,13	1,72	0,14	8,5	8,0	-0,4	-2,1
ICP-MS				17	0	1,53	1,77	1,52	0,15	1,76	0,15	9,7	8,4	-0,4	-0,2
GFAAS				12	1	1,61	1,73	1,57	0,11	1,70	0,12	6,8	6,8	2,4	-3,6
ICP-AES				9	1	1,48	1,73	1,48	0,11	1,71	0,13	7,1	7,7	-3,0	-2,6
Polarography				1	0			1,36		1,52				-11,1	-13,6
Lead	CD	3,00	3,28	35	3	3,00	3,28	3,02	0,39	3,30	0,33	13,0	10,1	0,7	0,5
ICP-MS				18	0	3,03	3,31	3,09	0,34	3,34	0,28	10,9	8,5	3,0	1,9
GFAAS				11	3	2,96	3,18	3,06	0,54	3,22	0,39	17,7	12,2	2,1	-1,8
ICP-AES				6	0	2,75	3,19	2,76	0,24	3,25	0,43	8,8	13,2	-7,9	-0,8
Copper	CD	10,00	10,50	38	5	10,00	10,50	9,84	0,60	10,41	0,77	6,1	7,4	-1,6	-0,9
ICP-MS				17	2	10,10	10,80	10,08	0,43	10,84	0,49	4,3	4,5	0,8	3,2
ICP-AES				9	2	10,00	10,40	9,98	0,44	10,40	0,36	4,4	3,4	-0,2	-0,9
GFAAS				8	0	9,26	10,16	9,44	0,78	9,90	0,98	8,3	9,9	-5,6	-5,7
FAAS				3	1			9,47		9,53				-5,3	-9,3
Polarography				1	0			9,30		9,71				-7,0	-7,5
Nickel	CD	4,05	4,19	36	2	4,05	4,19	4,12	0,48	4,22	0,47	11,6	11,1	1,8	0,8
ICP-MS				17	1	4,05	4,17	4,05	0,26	4,16	0,28	6,3	6,7	0,1	-0,6
GFAAS				10	0	4,07	4,29	4,24	0,77	4,26	0,65	18,2	15,2	4,7	1,6
ICP-AES				7	1	4,10	4,19	4,19	0,40	4,40	0,62	9,5	14,1	3,4	5,0
FAAS				1	0			4,08		4,20				0,7	0,2
Other method				1	0			3,72		3,83				-8,1	-8,6
Zinc	CD	3,96	4,30	35	6	3,96	4,30	3,90	0,57	4,22	0,69	14,7	16,4	-1,6	-1,8
ICP-MS				17	3	3,94	4,31	3,96	0,47	4,30	0,62	11,8	14,4	0,0	0,0
ICP-AES				9	2	3,93	4,30	3,80	0,40	4,23	0,52	10,6	12,3	-4,2	-1,7
GFAAS				5	1	3,04	3,51	3,35	0,86	3,85	1,38	25,6	35,9	-15,4	-10,5
FAAS				4	0	4,19	4,36	4,41	0,53	4,32	0,35	12,1	8,1	11,3	0,4

Om.: Sample pair omitted from the calculations

pH

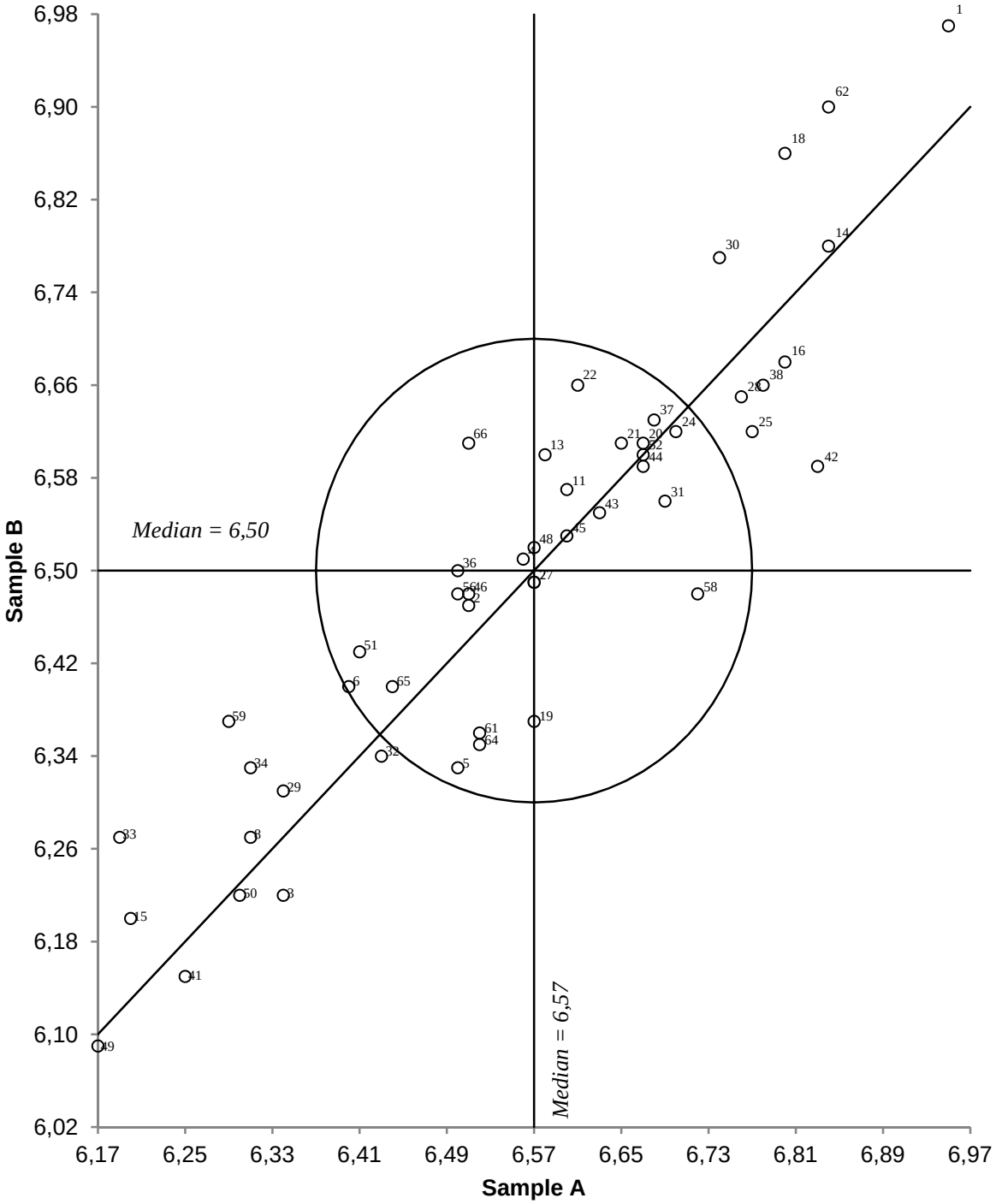

Figure 1. Youden diagram for pH, sample pair AB
Acceptable limit, given by circle, is 0,2 pH units.

Conductivity

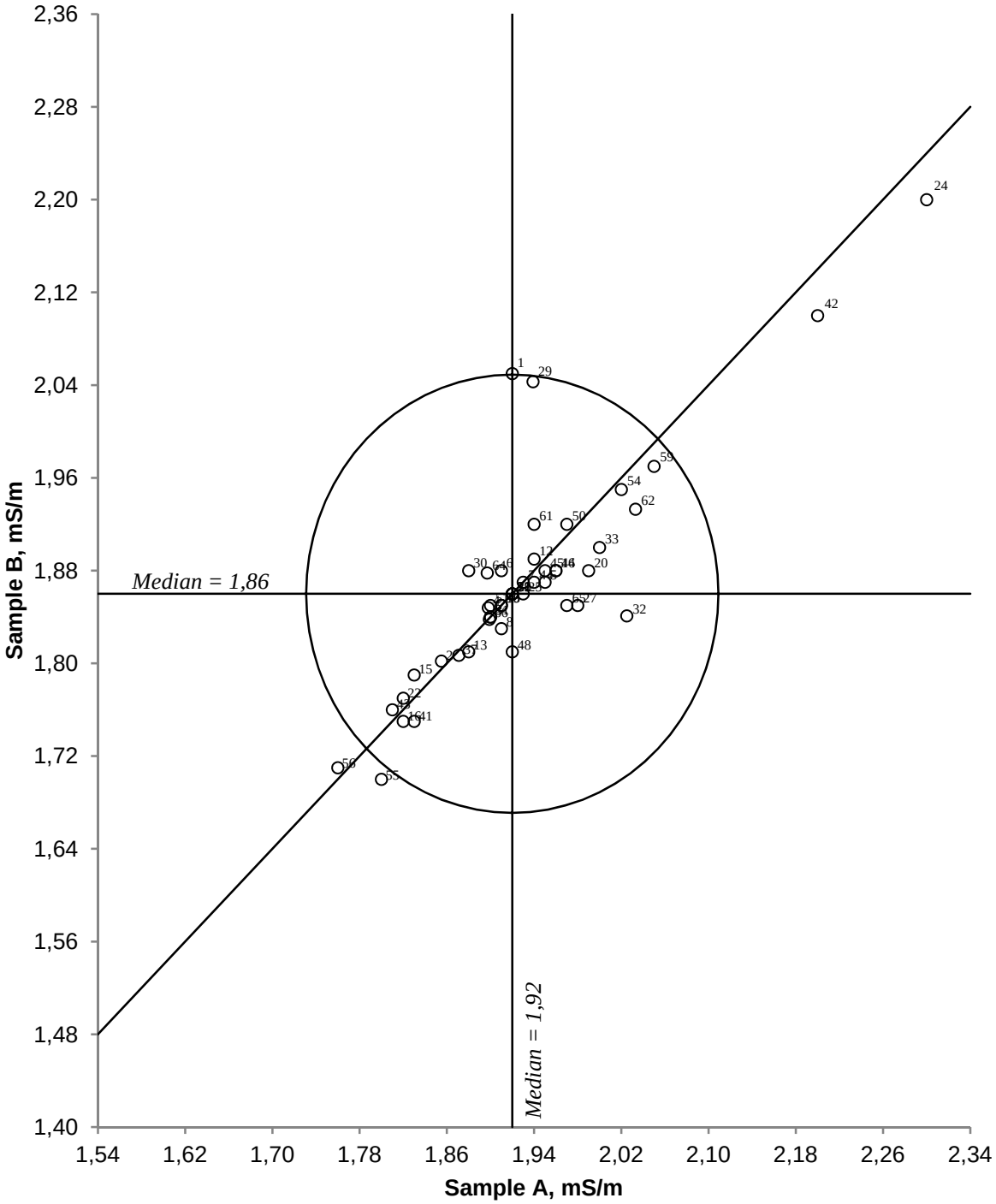

Figure 2. Youden diagram for conductivity, sample pair AB
Acceptable limit, given by circle, is 10 %

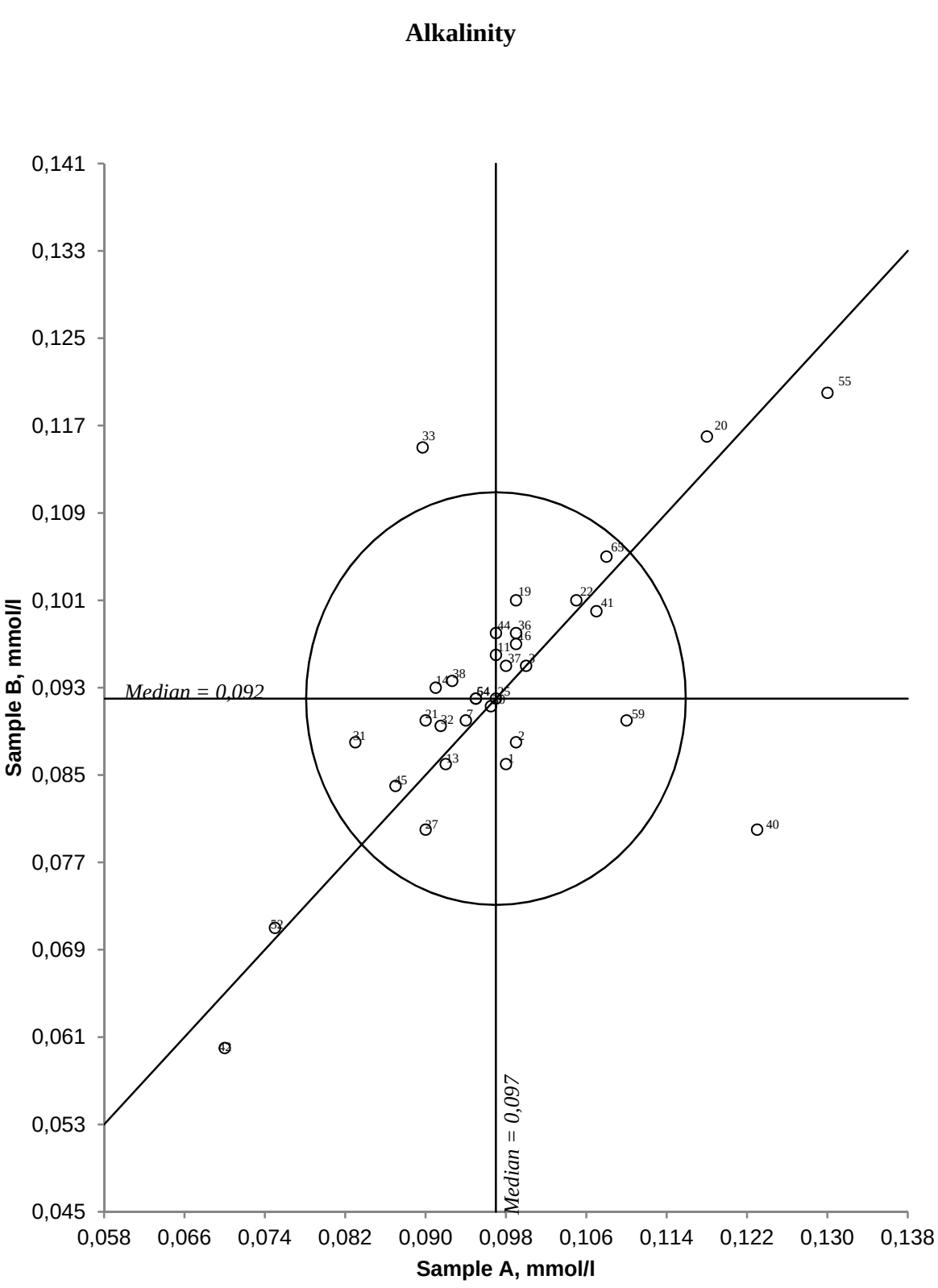

Figure 3. Youden diagram for alkalinity, sample pair AB
Acceptable limit, given by circle, is 20 %

Chloride

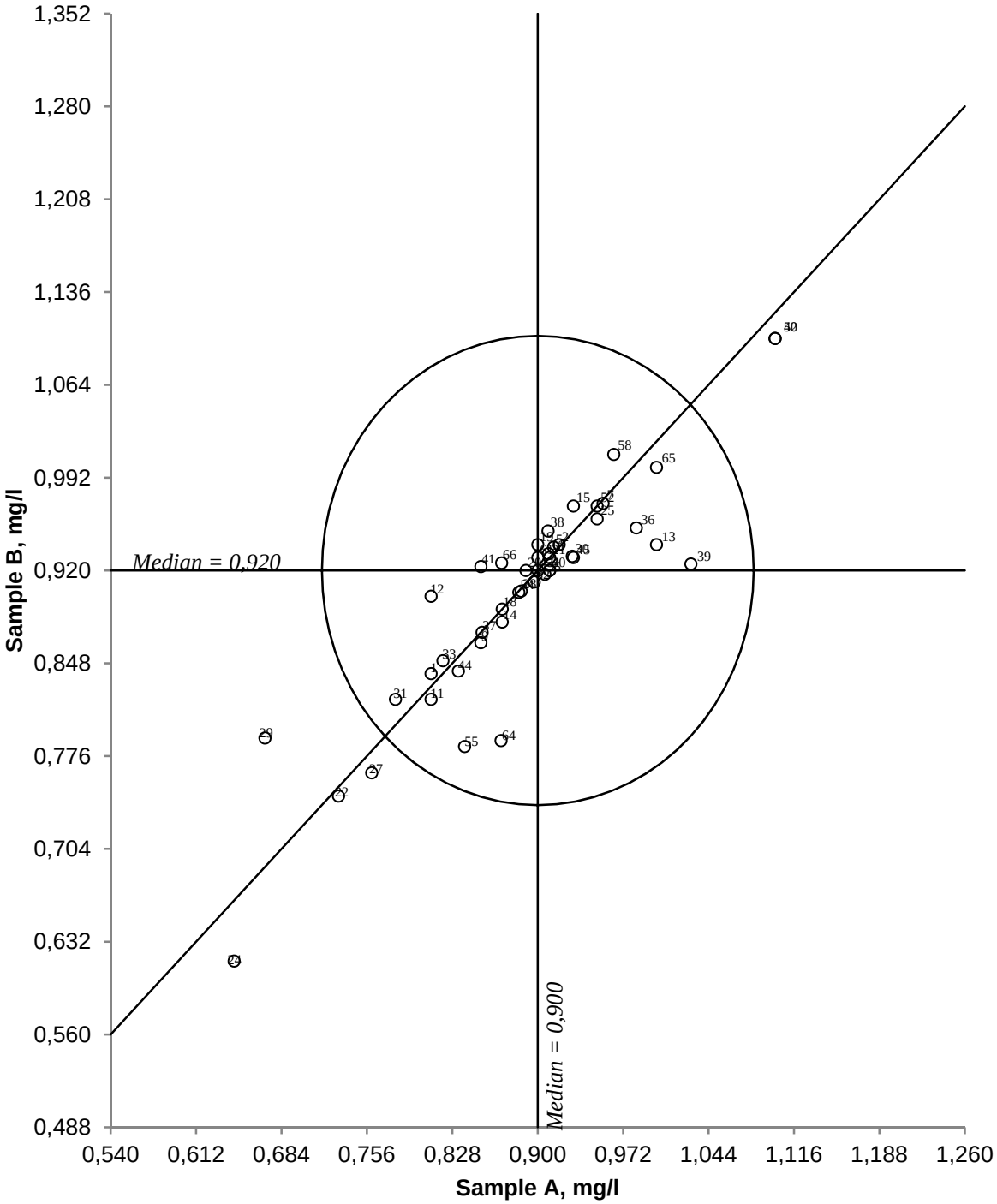

Figure 4. Youden diagram for chloride, sample pair AB
Acceptable limit, given by circle, is 20 %

Sulphate

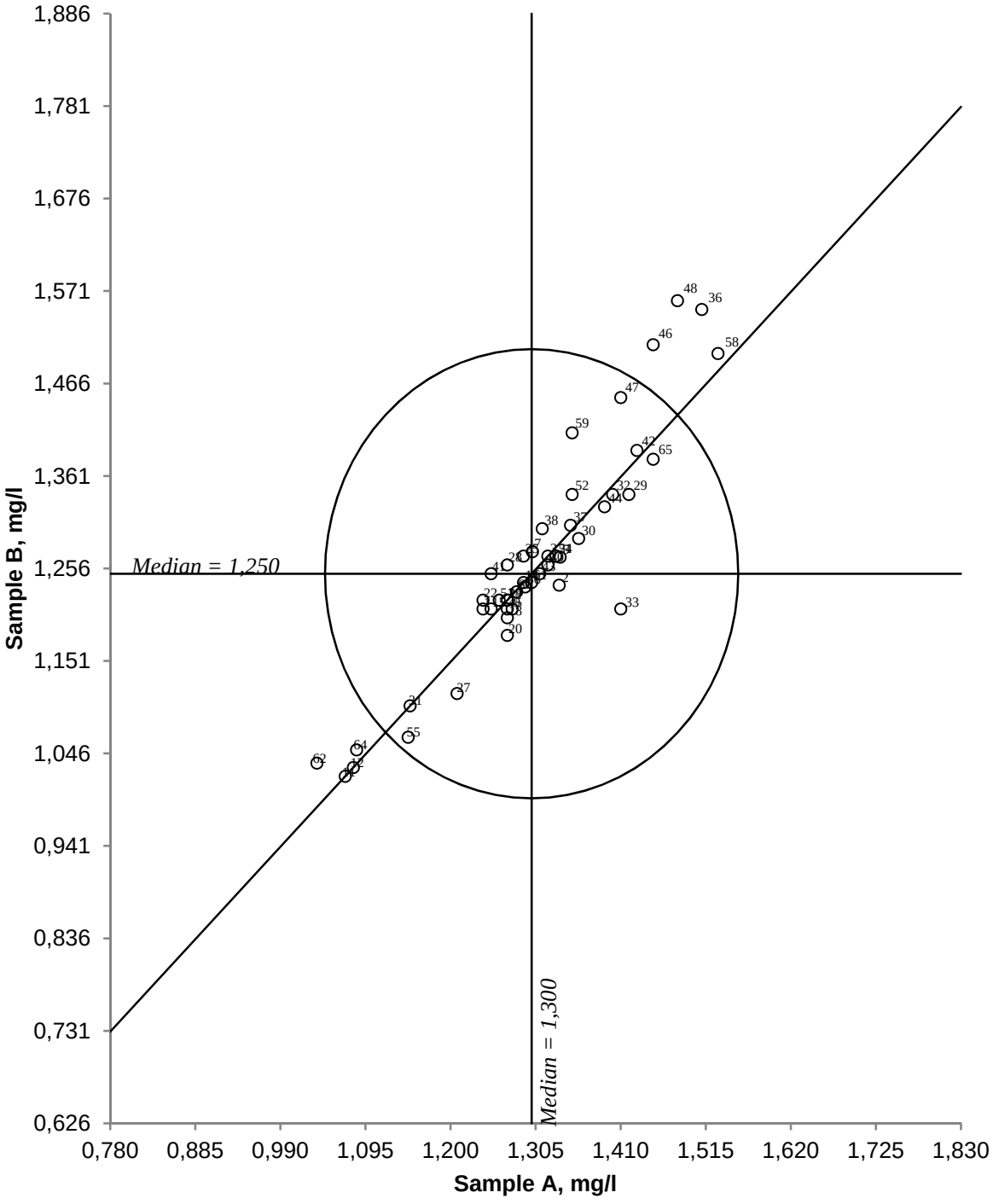

Figure 5. Youden diagram for sulphate, sample pair AB
Acceptable limit, given by circle, is 20 %

Calcium

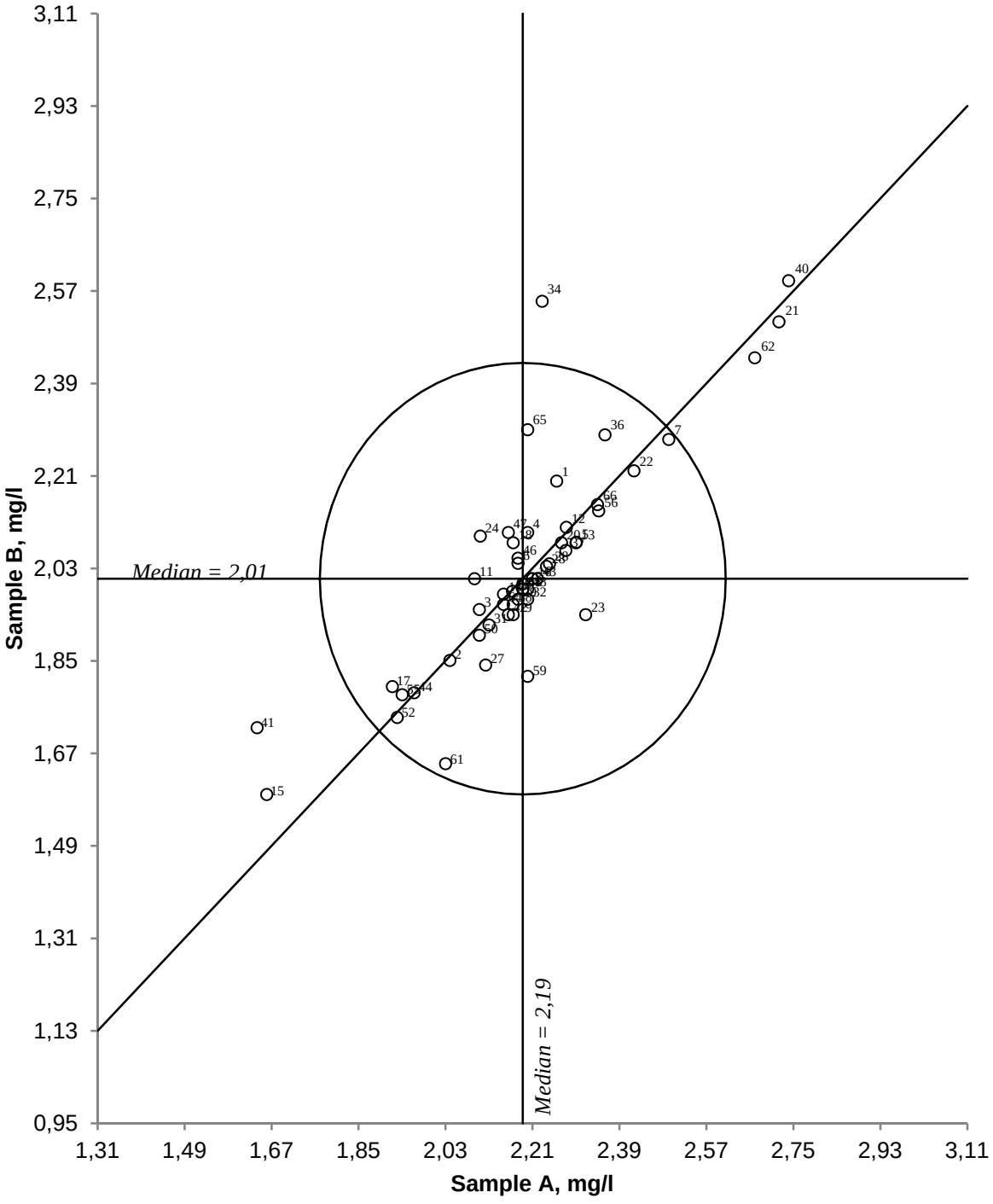

Figure 6. Youden diagram for calcium, sample pair AB
Acceptable limit, given by circle, is 20 %

Magnesium

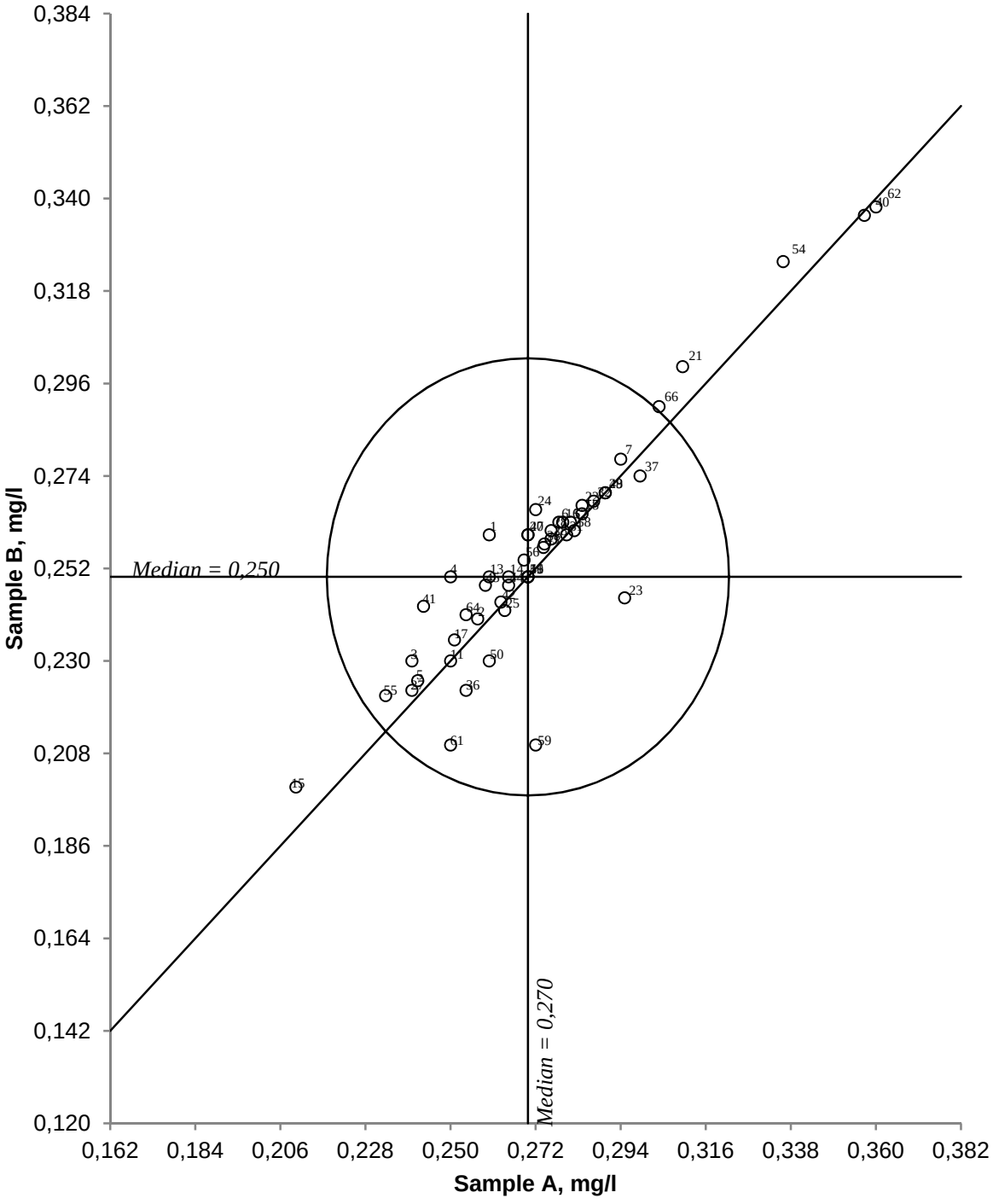

Figure 7. Youden diagram for magnesium, sample pair AB
Acceptable limit, given by circle, is 20 %

Sodium

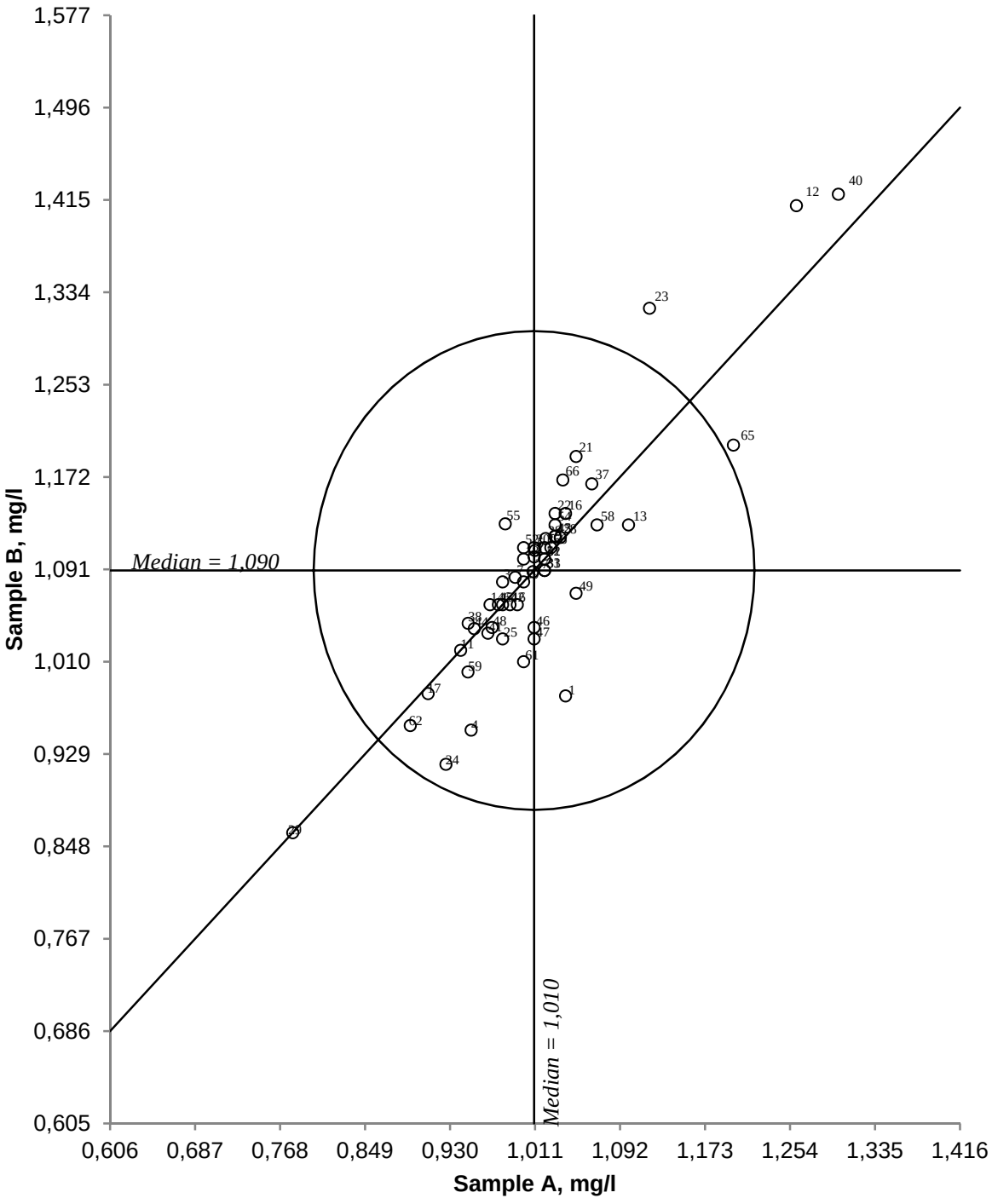

Figure 8. Youden diagram for sodium, sample pair AB
Acceptable limit, given by circle, is 20 %

Potassium

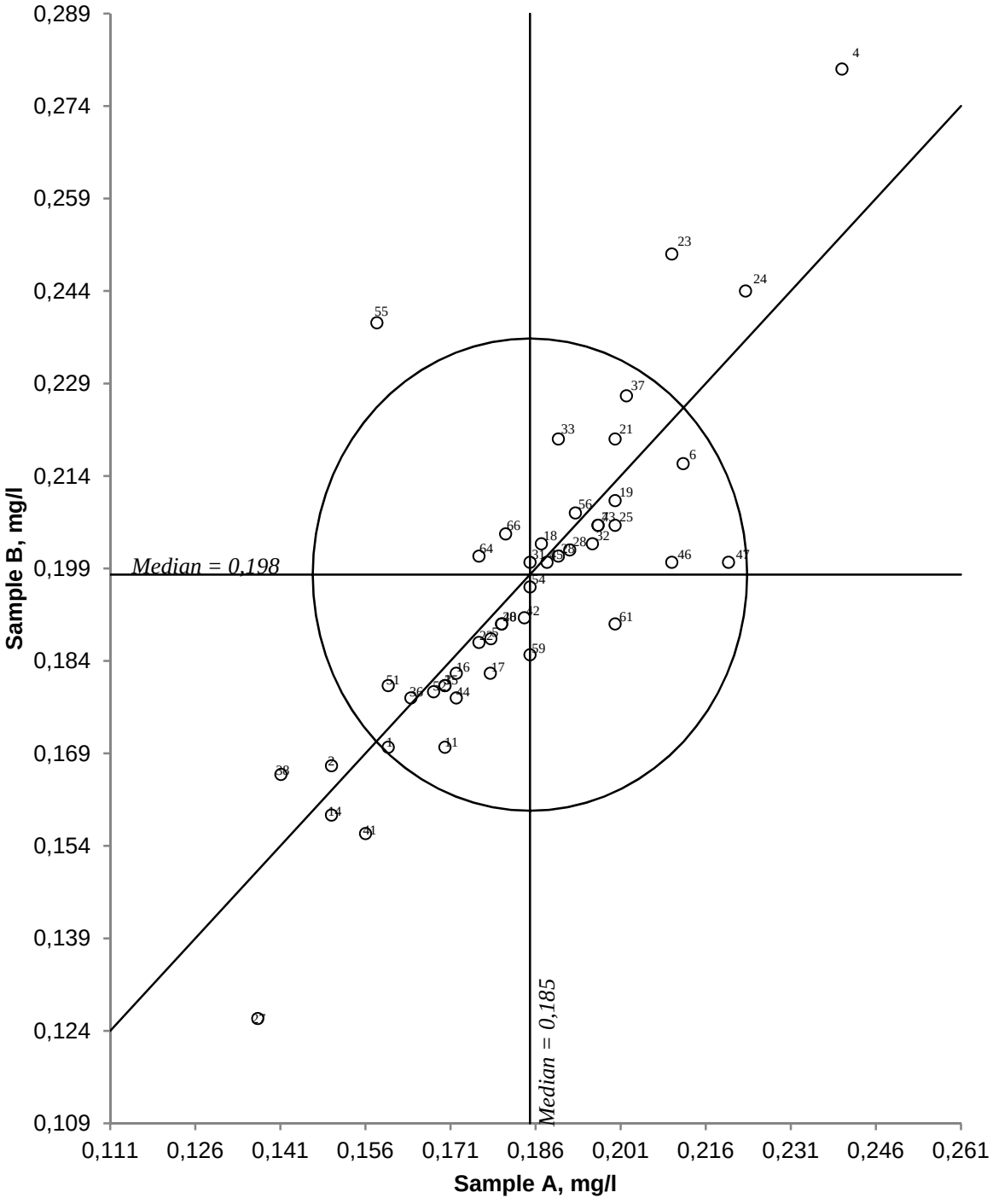

Figure 9. Youden diagram for potassium, sample pair AB
Acceptable limit, given by circle, is 20 %

Total organic carbon

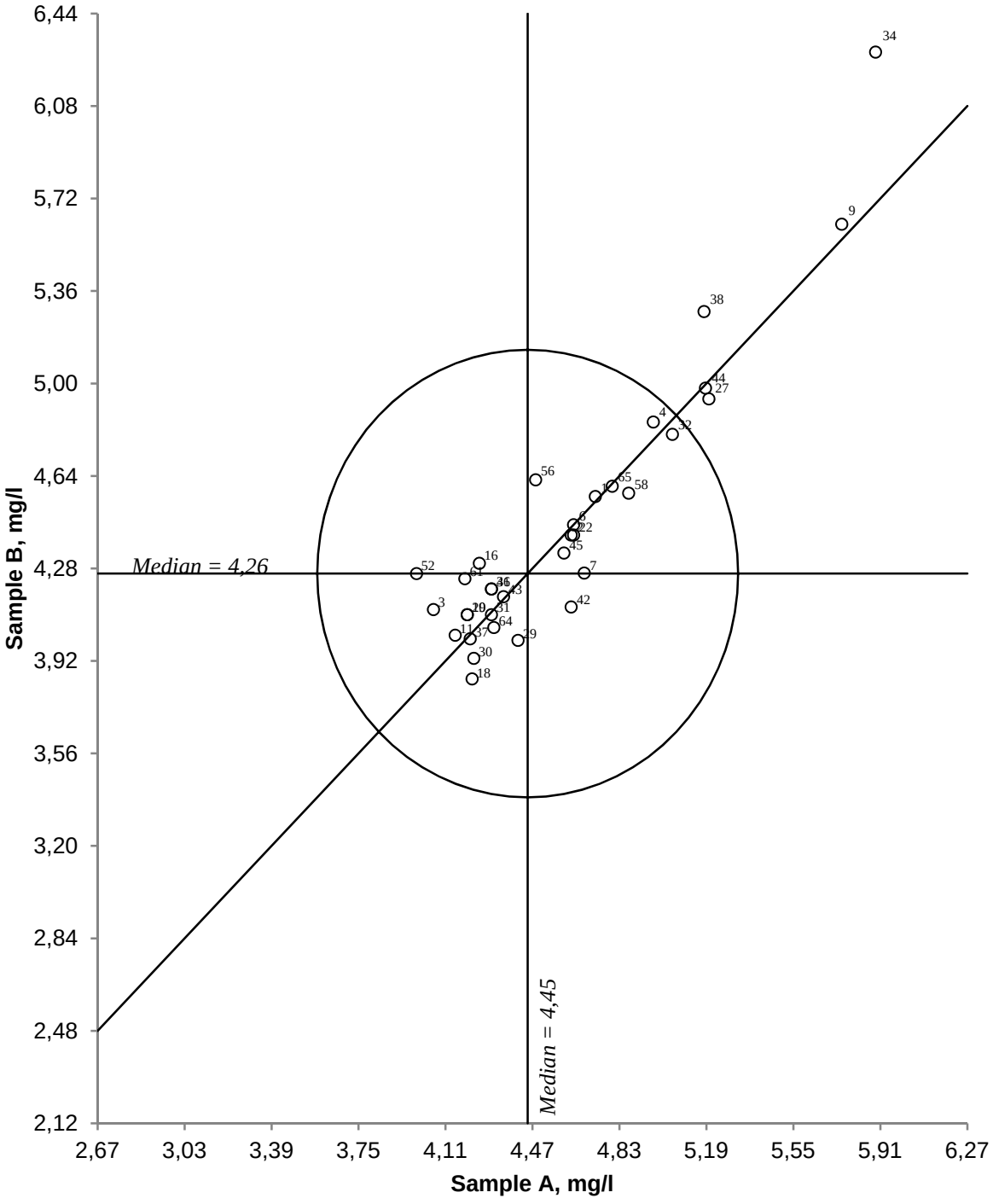

Figure 10. Youdendiagram for total organic carbon, sample pair AB
Acceptable limit, given by circle, is 20 %

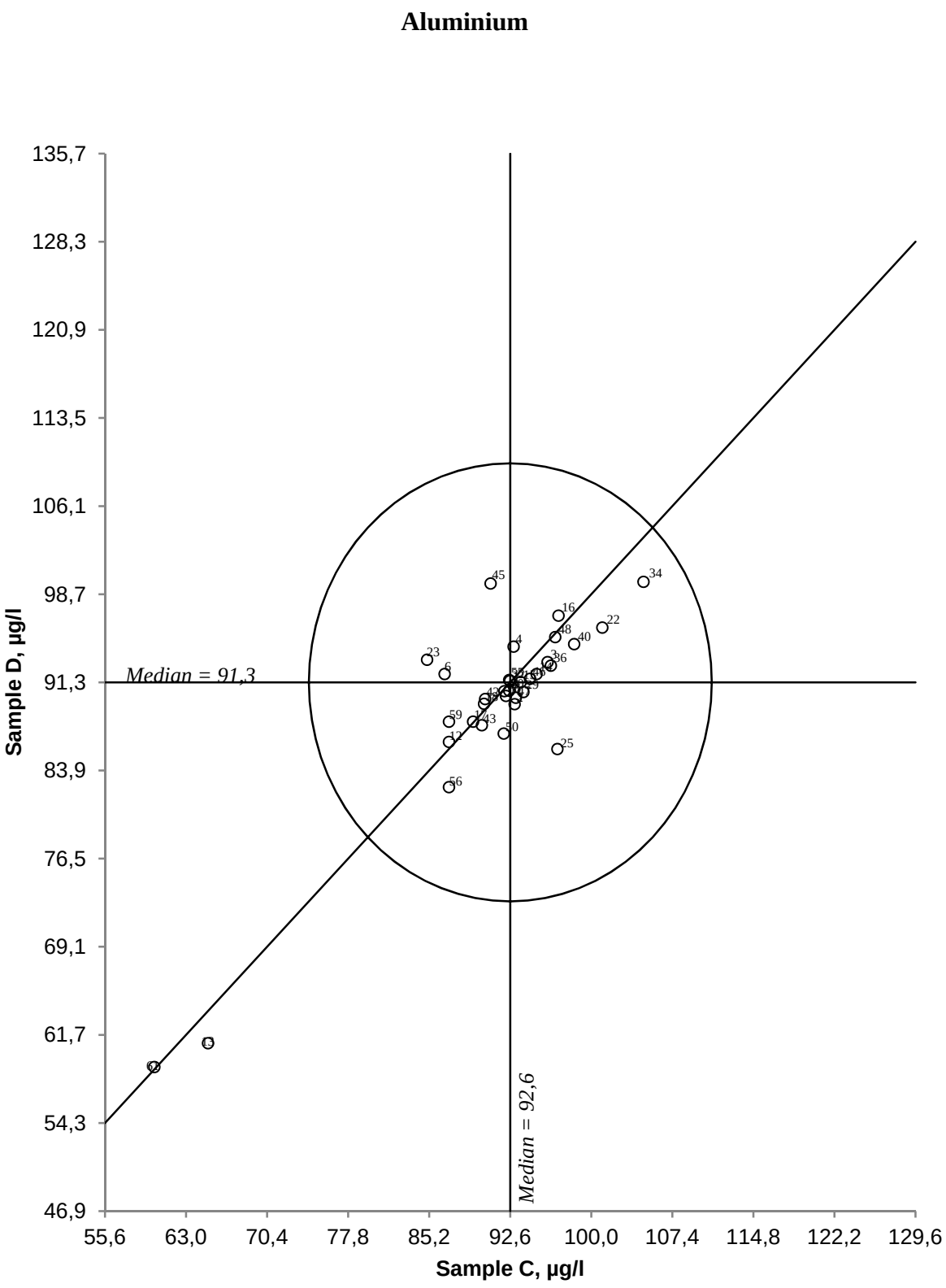

Figure 11. Youden diagram for aluminium, sample pair CD
Acceptable limit, given by circle, is 20 %

Iron

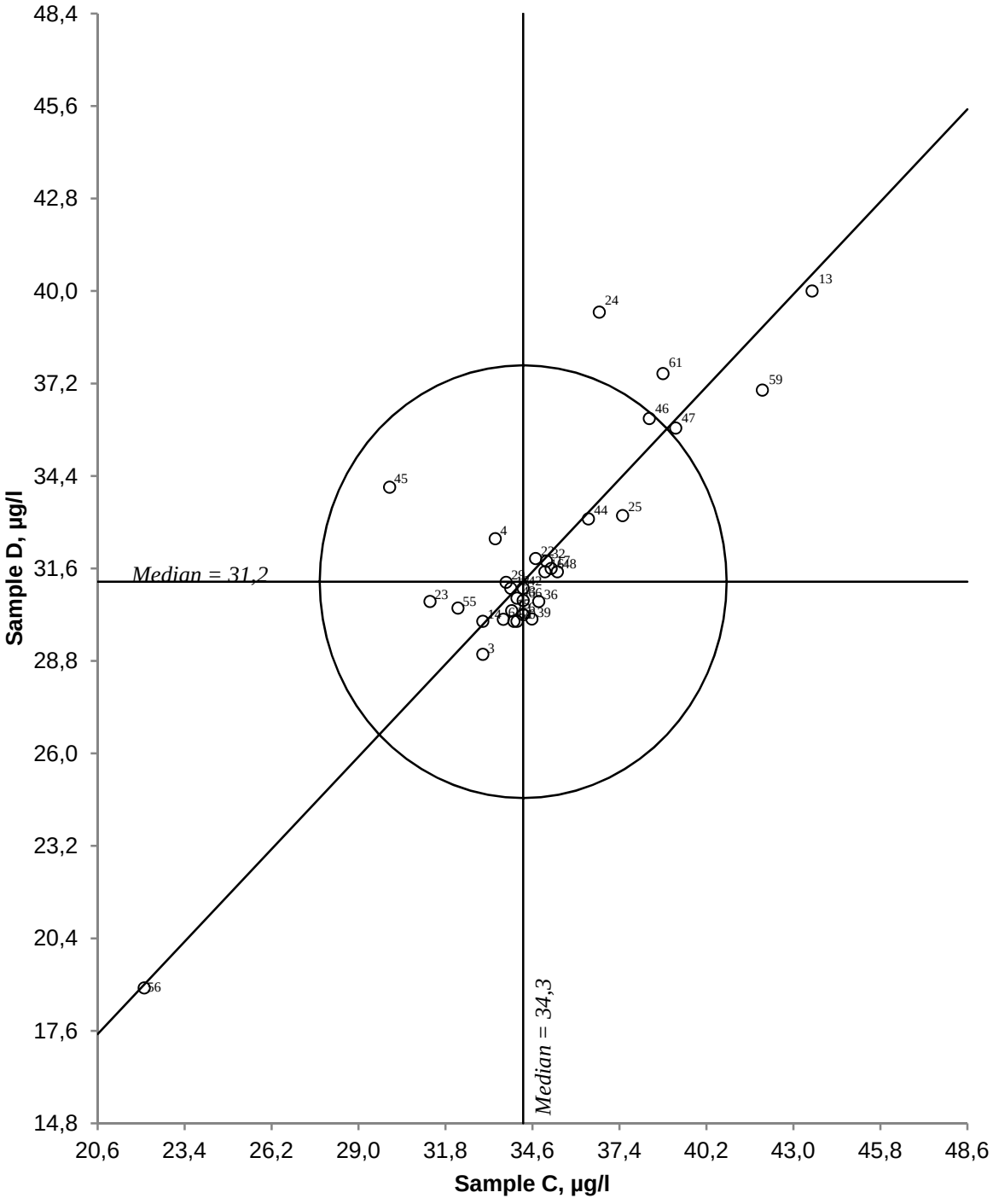

Figure 12. Youden diagram for iron, sample pair CD
Acceptable limit, given by circle, is 20 %

Manganese

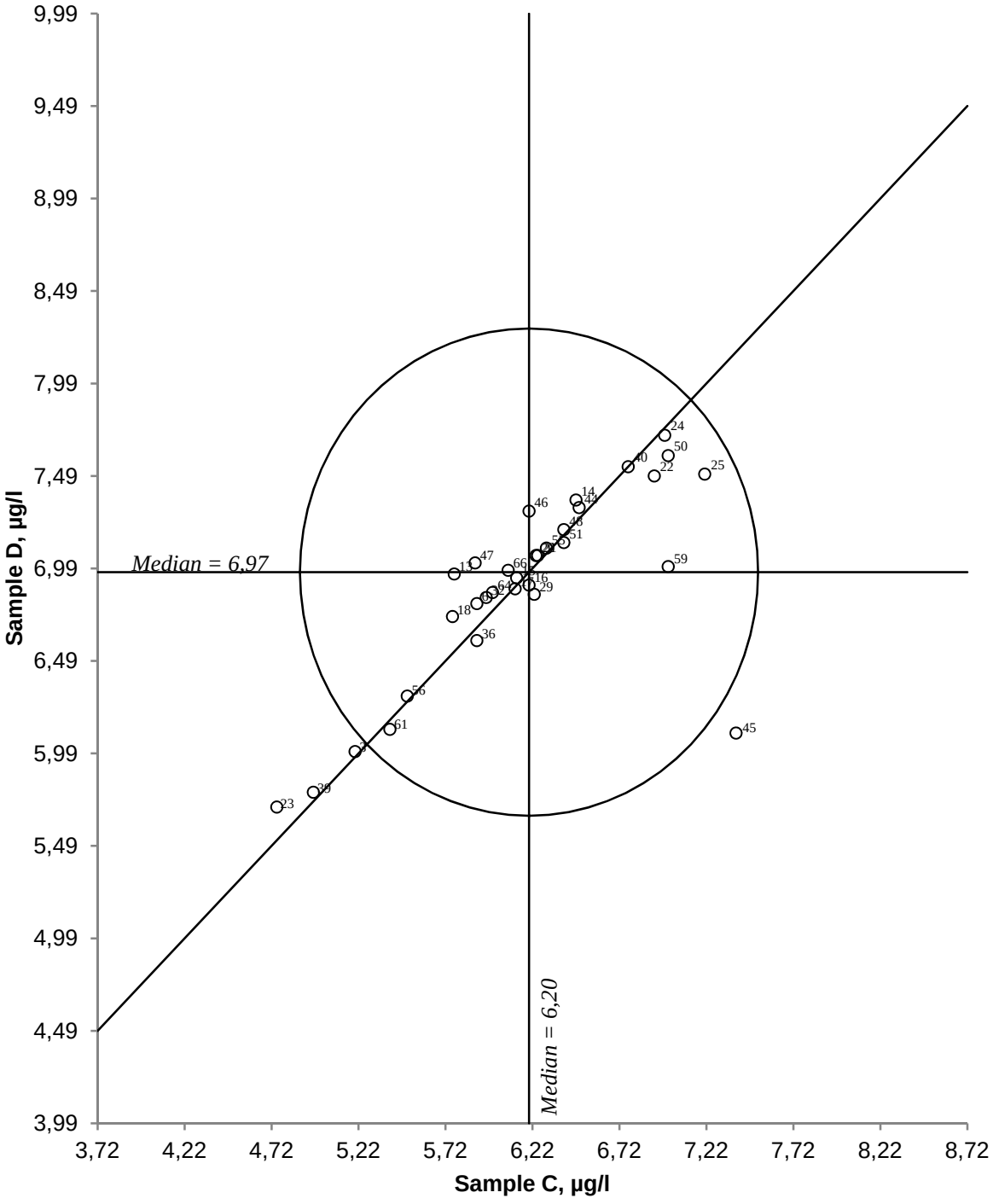

Figure 13. Youden diagram for manganese, sample pair CD
Acceptable limit, given by circle, is 20 %

Cadmium

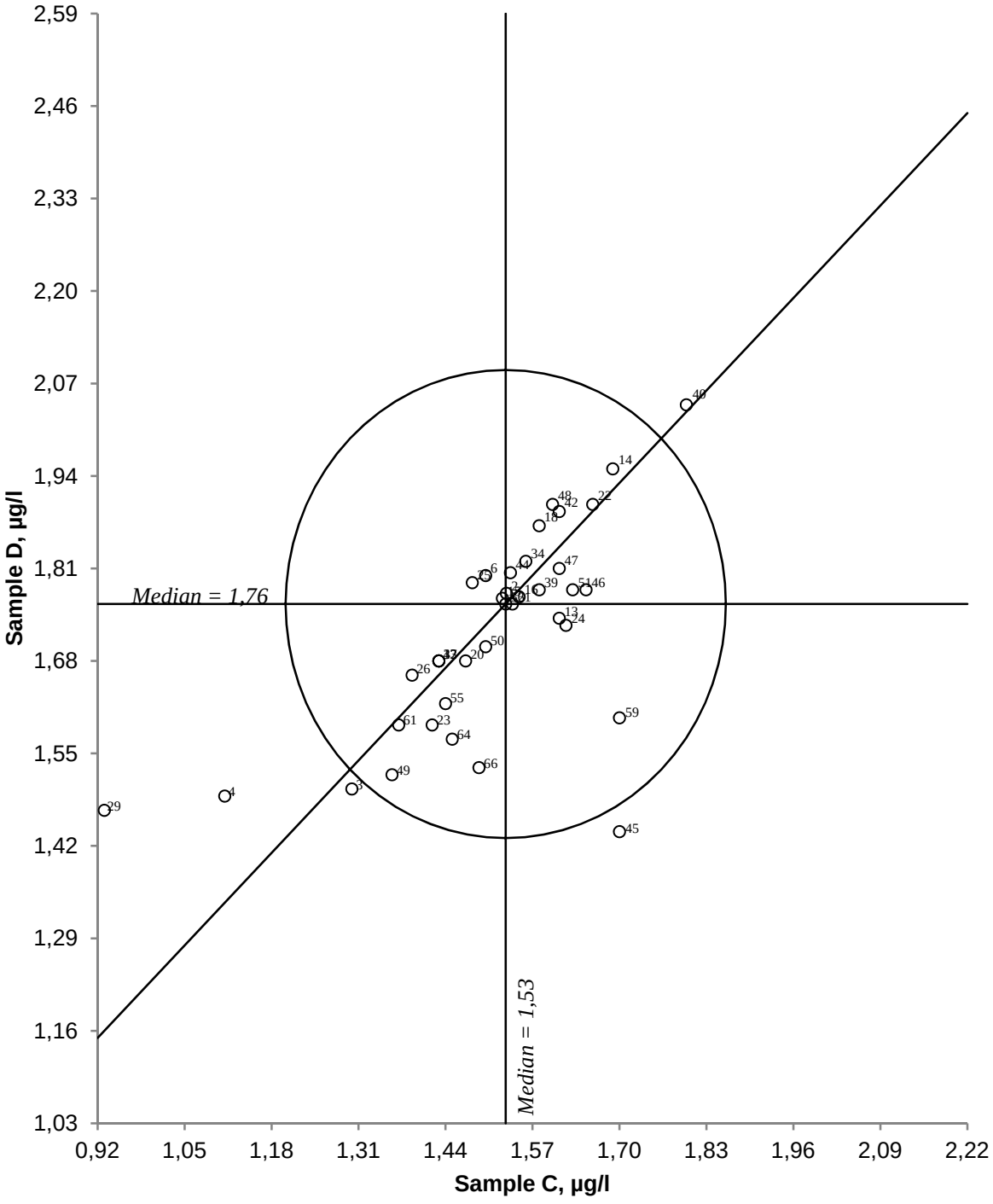

Figure 14. Youden diagram for cadmium, sample pair CD
Acceptable limit, given by circle, is 20 %

Lead

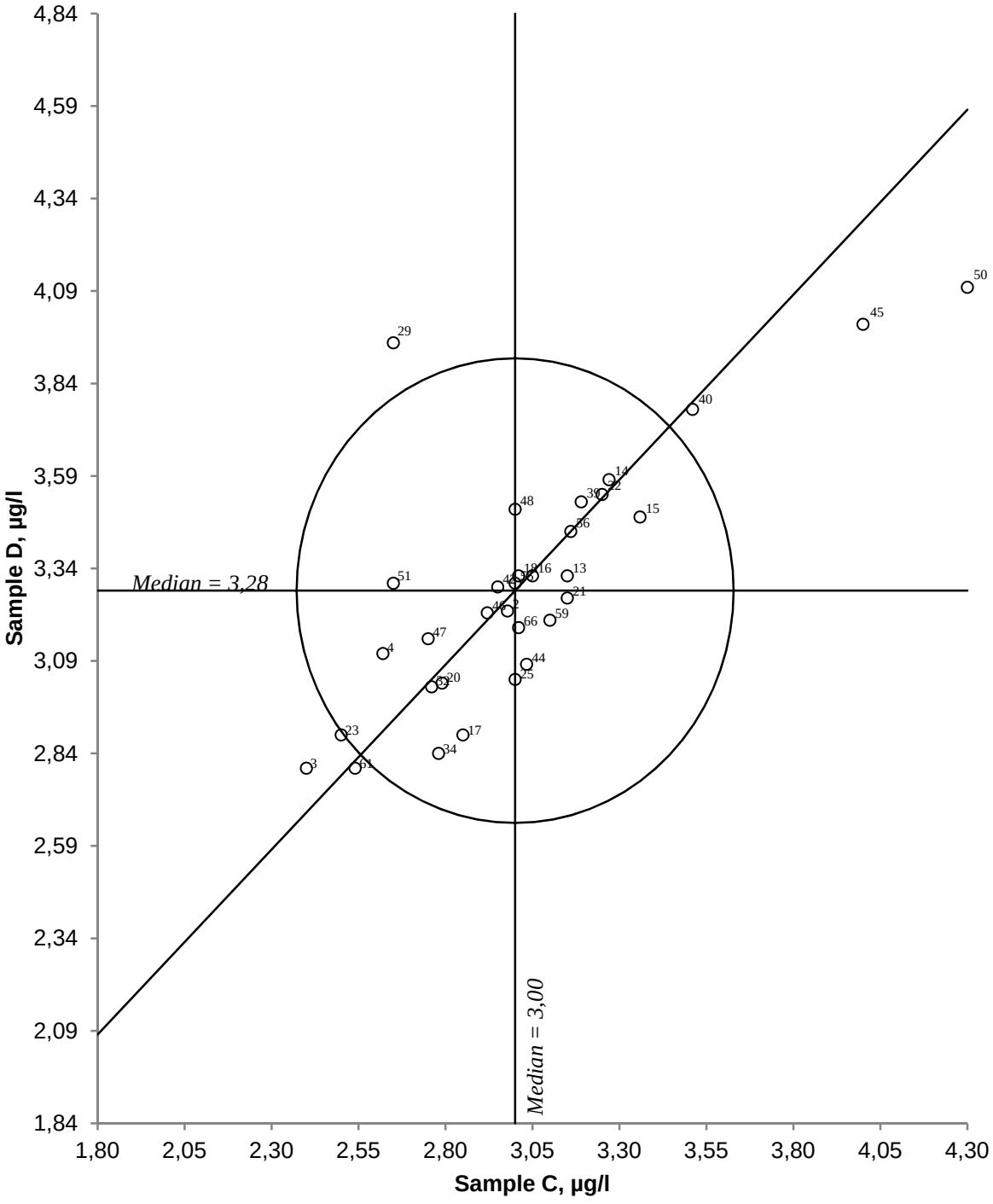

Figure 15. Youden diagram for lead, sample pair CD
Acceptable limit, given by circle, is 20 %

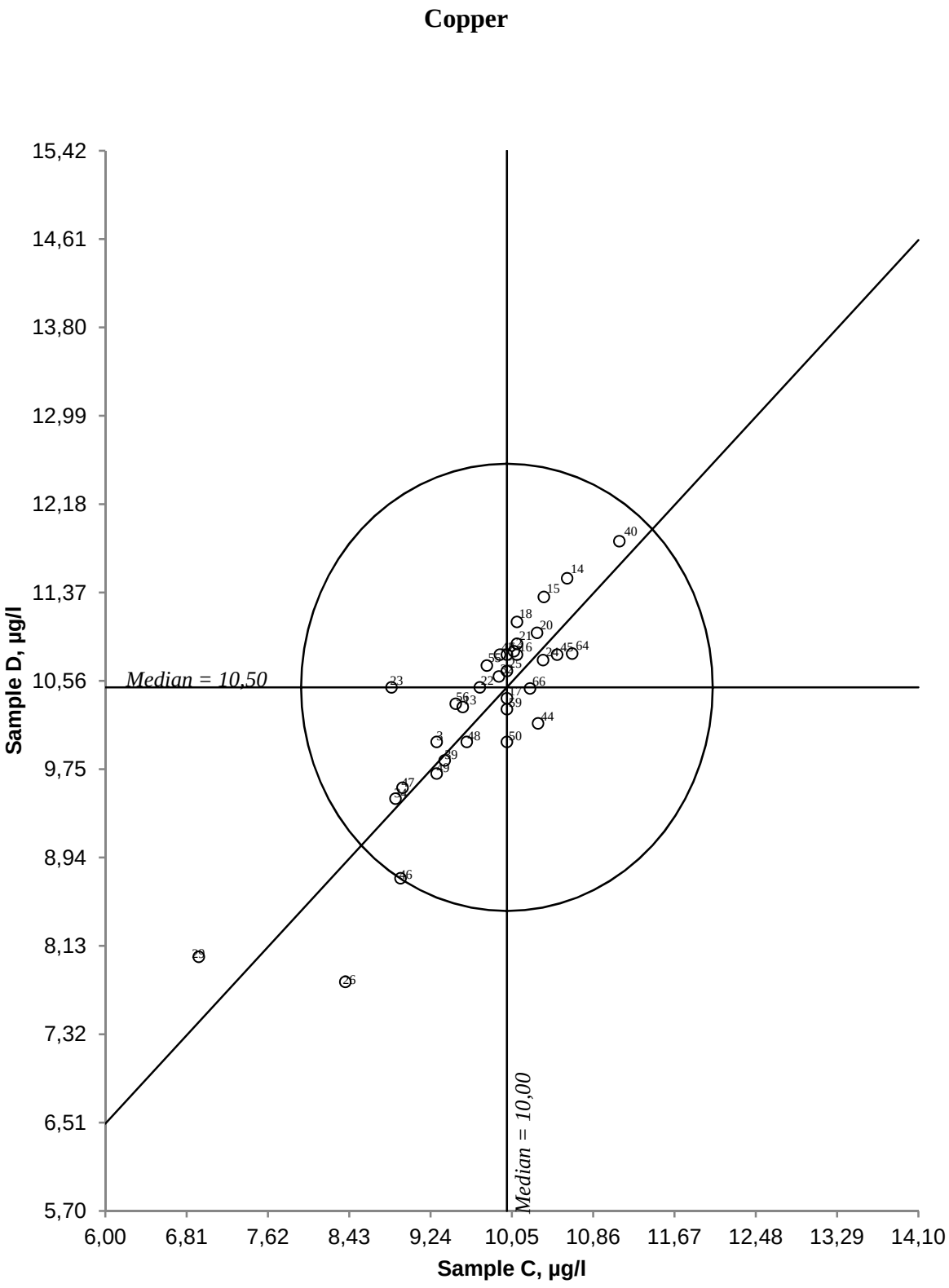

Figure 16. Youden diagram for copper, sample pair CD
Acceptable limit, given by circle, is 20 %

Nickel

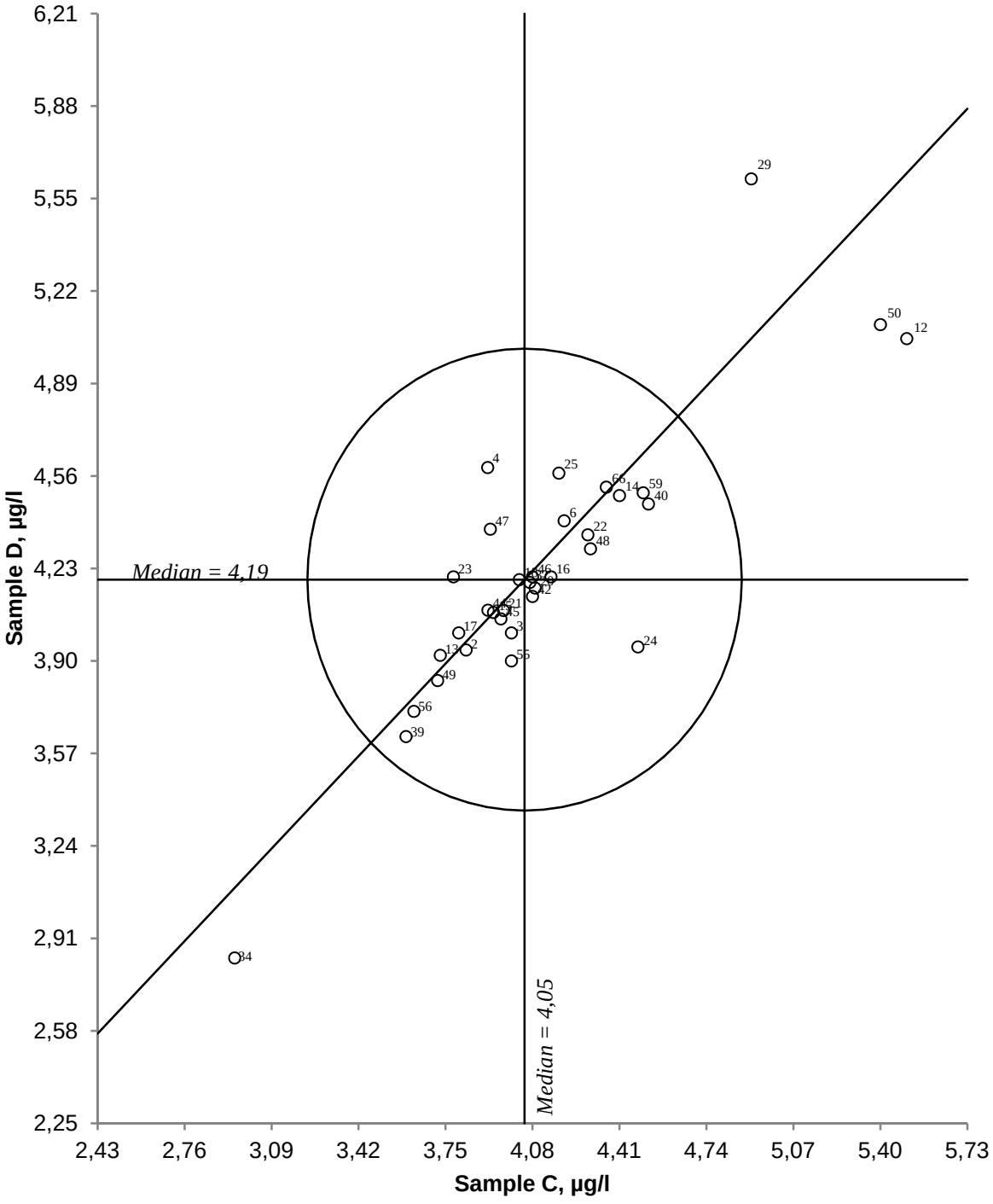

Figure 17. Youden diagram for nickel, sample pair CD
Acceptable limit, given by circle, is 20 %

Zinc

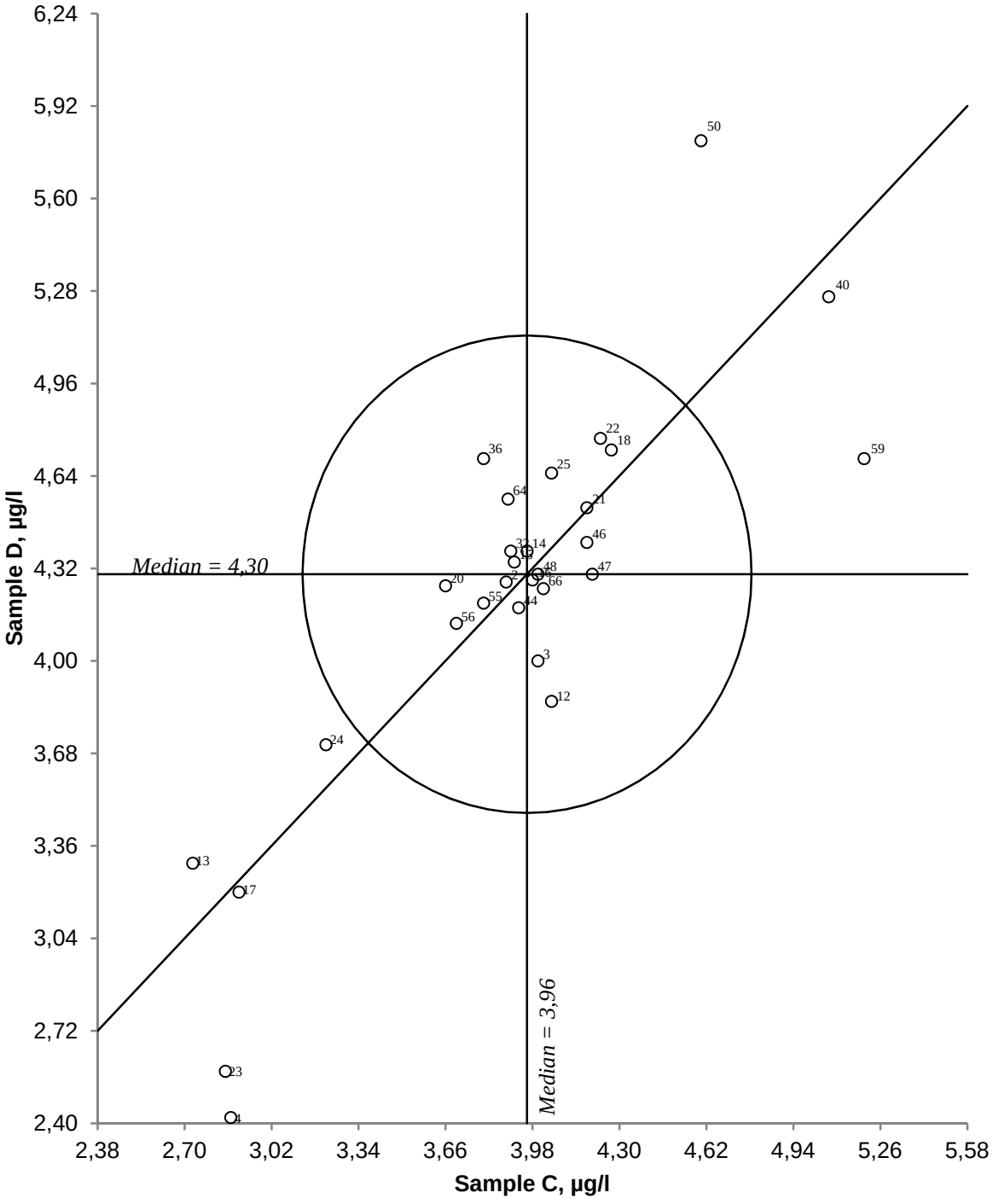

Figure 18. Youden diagram for zinc, sample pair CD
Acceptable limit, given by circle, is 20 %

5. Literature

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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	EMC (PUSARPEDAL)	Tangerang, Banten 15314	Indonesia
2	Ufficio del Monitoraggio Ambientale - Laboratorio	Via Mirasole 22 6500 Bellinzona	Switzerland
3	CNR Istituto Studio degli Ecosistemi	Largo Tonolli 50 I-28922 VERBANIA Pallanza	Italy
4	Laboratorios Echevarne	Provença 312, bajos 08037 Barcelona	Spain
5	ISSeP Colfontaine Zoning Schweitzer	Rue de la Platinerie B-7340 COLFONTAINE	Belgium
6	Finnish Forest Research Institute Vantaa Laboratory	Jokiniemenkuja 1 FIN-01370 Vantaa	Finland
7	Institut fur Ökologie	Technikerstrasse 25 6020 Innsbruck Austria	Austria
8	Institute of Environmental Protection-Puszcza Borecka station	Kolektorska 4	Poland
9	Tallinn Technical University Institute of Environmental Eng	Ehitajate tee 5, 19086 Tallinn	Estonia
10	Geological Survey of Estonia	Kadaka Tee 82, Tallinn 12618	Estonia
11	Laboratorio Biologico Provinciale APPA Bolzano	Via Sottomonte 2 IT-39055 Laives	Italy
12	Environmental Pollution Monitoring Center Laboratory of surface and sea	Verkhnerostinskoe sh,51,MUGMS,Murmansk,Russia	Russian Federation
13	Northern Water Problems Institute	A.Nevskogo, 50, Petrozavodsk 185003	Russian Federation
14	University of Helsinki Lab. of Geology and Geography	P.O.Box 64 00014 university of Helsinki	Finland
15	NILU, Avd. uorganisk analyse	Postboks 100 2027 Kjeller	Norway
16	Finnish Environment Institute SYKE Laboratory Center	Hakuninmaantie 6 FI-00430 HELSINKI	Finland
17	Insitute of Industrial Ecology Problems of the North (INEP) Group ICP methods of analysis	184209 Apatity, Akademgorodok 14A, Murmansk reg.	Russian Federation
18	Bayerisches Landesamt fur Umwelt	Ref 73 Bürgerm-Ulrich-Str. 160 D-86179 Augsburg	Germany
19	Biology Centre ASCR Institute of Hydrobiology	Na Sadakach 7 370 05 Ceske Budejovice	Czech Republic
20	Norsk institutt for vannforskning	Gaustadalléen 21 0349 OSLO	Norway
21	IVL AB	P.O. Box 53021 SE-400 14 Gothenburg	Sweden
22	Shimane Prefectural Inst. Of Public Health and Environmental Science	Shimane 690-0122	Japan
23	Polish Academy of Sciences Institute of Botany	Lubicz Str. 46 Krakow	Poland

No	*Laboratory*	*Town*	*Country*
24	Hydrochemical Laboratory by Federal State Enterprise on Water Industry	10 A Stahanovskaya str., Pskov, 180004	Russia
25	FGU «Baltwodhoz»	Saint-Petersburg, Vasilievsky ostrov	Russia
26	Institute of Global Climate and Ecology (IGCE) Roshydromet and RAS Russian Academy of Sciences	20-B, Glebovskaya St., Moscow, 107258	Russia
27	Environmental Protection Agency Environmental Research Departm	A. Goustauto str. 9, LT-01108 Vilnius	Lithuania
28	Institute of Environmental Protection Warsaw Monitoring Laboratory	POLAND 00-548 Warszawa Krucza 5/11D	Poland
29	Radbouduniversiteit afd. Ecologie t.a.v. G. Verheggen	Postbus 9010 6500 GL Nijmegen	Netherlands
30	Finnish Forest Research Institute Rovaniemi Research Station	Etelaranta 55 (P.O.Box 16), FI-96301 Rovaniemi	Finland
31	MOEE, DORSET Laboratory	P.O. Box 39 Dorset, Ontario Canada P0A 1E0	Canada
32	Swedish University for Agricultural Sciences Aquatic Sciences and Assesment	Box 7050 750 07 UPPSALA	Sweden
33	National Institute of Biology, LFTER	Vecna pot 111 1000 Ljubljana SLOVENIJA	Slovenia
34	ANAR - ABA Arges-Vedea, SGA Ilfov-Bucuresti Laborator de Calitatea Apei	Spl.Independentei294,Sector6,Bucuresti, CP:060031	Romania
35	River Biology Laboratory of the EAU Institute	51014 Tartu Kreutzwaldi1	Estonia
36	Estonian Environmental Research Centre Ltd Tartu Branch	Vaksali 17A 50410 Tartu ESTONIA	Estonia
37	US Environmental Protection Agency, Western Ecology Division	US EPA 200 SW 35th St. Corvallis, OR 97333 USA	United States
38	Marine Scotland Science Freshwater Laboratory	Faskally,Pitlochry,Perthshire,PH16 5BB, Scotland.	United Kingdom
39	Vlaamse MilieuMaatschappij (VMM) Dienst Laboratorium	Raymonde de Larochelaan 1,9051 Sint-Denijs-Westrem	Belgium
40	Laboratorio Integrado de Calidad Ambiental University of Navarra	Irunlarrea 1, 31080, Pamplona	Spain
41	Centre National de la Recherche Scientifique LHyGeS	1 Rue Blessig 67000 STRASBOURG	France
42	NLS Starcross laboratory Staplake Mount	Starcross, Exeter, Devon, EX6 8FD	United Kingdom
43	University of Maine Sawyer Environmental Research	5764 Sawyer Research Center Orono, ME 04469-5764	United States
44	Institute of Biology Komi SC UB RAS	Kommunisticheskaya st.,28 Syktyvkar,167982,Russia	Russia
45	Latvian Environmental Laboratory	165 Maskavas str., Riga LV-1019	Latvia

No	*Laboratory*	*Town*	*Country*
46	Institute for Public Health Kralevo	Slobodana Penezica 16 36000 Kralevo	Serbia
47	Institute for Public Health Pozarevac	Jovana Serbanovica, 14, 12000 Pozarevac	Serbia
48	Institute for Public Health Uzice	Dr Veselina Marinkovica 4 31000 Uzice Serbia	Serbia
49	Institute for Public Health Pancevo	Pasterova 2 26000 Pancevo	Serbia
50	Test Laboratory of Water Quality (Vodokanal)	Gogolja St. 60, 185035 Petrozav¿dsk Vodokanal	Russia
51	Büsgen-Institute - Soil Science of Temperate Ecosystems	D-37077 Goettingen Buesgenweg 2	Germany
52	Japan Sanitation Center Asia Center for Air Pollution Research	1182 Sowa, Nishi-ku, Niigata city 950-2144	Japan
53	Laboratoire d'Ecologie Fonctionnelle et Environnement (ECOLAB)	Avenue Agrobiopole 31326 Castanet Tolosan	France
54	Environmental Research and Training Center Thailand	Technopolis, Klong Luang, Pathumthani 12120	Thailand
55	EPA, Dublin Inspectorate McCumiskey Hs,	Richview,Clonskeagh Road, Dublin 14.	Ireland
56	Bayerische Landesanstalt fur Wald und Forstwirtschaft Abteilung 2 - Klima und Boden	Hans-Carl-von-Carlowitz-Platz 1 D-85354 Freising	Germany
57	Lab di Microanalysis University of Florence	Via della Lastruccia,13 50019SestoF.no Firenze	Italy
58	Marklaboratoriet, pl4 Institusjonen for mark och mil	Mark o miljö Marklab Box 7014 750 07 UPPSALA	Sweden
59	Public Health Institute Nis Dept. of Sanitary Chemistry	Bulevar Dr Zoran Djindjic 50 18000 Nis	Serbia
60	Analist Service S.R.L.	Aviator Petre Cretu nr. 15 Sector 1 Bucuresti	Romania
61	Charles University, Hydrobiol. Station Velky Palenec	Tchorovice 71, P.O.Box 47 CZ-38801 BLATNA	Czech Republic
62	Forest Nutrition and Water Resources Department of Ecology, Technis	H.C.v.Carlowitz-Platz 2 D-85354 Freising Germany	Germany
63	Environmental Laboratory	AngloGold Ashanti Ltd Box 10, Obuasi, A/R Ghana	Ghana
64	Institute for Ecology of Industrial Areas	Kossutha str. 6 40-844 Katowice	Poland
65	Staatliche Betriebgesellschaft für Umwelt und Landwirtschaft (BfUL)	Stephanplatz 3 D-09112 Chemnitz	Germany
66	Department of Chemistry Malaysia	JKM Sultan Road 46661 Petaling Jaya,Sel,malaysia	Malaysia

Number of participating laboratories from the different countries represented in intercomparison 1327

Country	No. of labs.	Country	No. of labs.	Country	No. of labs.
Austria	1	Ireland	1	Russia	8
Belgium	2	Italy	3	Serbia	5
Canada	1	Japan	2	Slovenia	1
Czech Republic	2	Latvia	1	Spain	2
Estonia	4	Lithuania	1	Sweden	3
Finland	4	Malaysia	1	Switzerland	1
France	2	Netherlands	1	Thailand	1
Germany	5	Norway	2	United Kingdom	2
Ghana	1	Poland	4	United States	2
Indonesia	1	Romania	2		

Total: 29 countries

Appendix B.

Preparation of samples

The sample solutions were prepared from water collected from river Langlielva, just outside the city of Oslo in Norway. The water, collected in 25 liter plastic containers was brought to the laboratory and stored for about two weeks. The water was then filtrated through 0,45 μm cellulose acetate membrane. The filtrate was collected in polyethylene containers and stored at room temperature one more week to equilibrate. Small aliquots were taken from the filtrate to determine the background concentrations of the analytical variables of interest. The samples were prepared by spiking the filtrated water with stock solutions of stoichiometric compounds containing the major ions, or heavy metals.
The samples C and D were prepared for the determination of metals and preserved by addition of 5 ml concentrated nitric acid pr. liter sample. A few days before shipping the samples to the participants, they 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 delivered 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 July 2013 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 2013. 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 B.

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

Analytical variable	Sample A		Sample B	
	Mean	Std. dev.	Mean	Std. dev.
pH	6,78	0,06	6,74	0,06
Conductivity mS/m	1,96	0,01	1,90	0,02
Alkalinity mmol/l	0,12	0,00	0,11	0,00
Nitrate-nitrogen μg/l	113,33	2,89	95,67	16,17
Chloride mg/l	0,91	0,01	0,93	0,01
Sulphate mg/l	1,29	0,02	1,25	0,00
Calcium mg/l	2,27	0,04	2,07	0,04
Magnesium mg/l	0,27	0,01	0,25	0,01
Sodium mg/l	1,01	0,02	1,10	0,02
Potassium mg/l	0,18	0,01	0,19	0,01
Total organic carbon, mg/l	4,27	0,06	4,07	0,06

Analytical variable	Sample C		Sample D	
	Mean	Std. dev.	Mean	Std. dev.
Aluminium, μg/l	92,4	4,0	87,1	1,2
Iron, μg/l	33,0	1,3	29,9	0,1
Manganese, μg/l	6,2	0,14	6,8	0,34
Cadmium, μg/l	1,5	0,04	1,7	0,05
Lead, μg/l	2,8	0,05	3,1	0,04
Copper, μg/l	10,0	0,21	10,4	0,21
Nickel, μg/l	4,0	0,12	3,9	0,04
Zinc, μg/l	3,8	0,02	4,2	0,07

Stability

Sample set AB was tested further for stability of pH, conductivity and alkalinity within the actual period of the reporting window. The determinations were carried out by the laboratory at the Programme Centre. The sets were tested 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	Replicates	pH		Conductivity (mS/m)		Alkalinity (mmol/l)	
			Average	Std. dev.	Average	Std. dev.	Average	Std. dev.
1	30.07.13	5	6,74	0,019	1,96	0,005	0,114	0,0045
2	14.08.13	5	6,83	0,004	1,96	0,010	0,116	0,0000
3	12.09.13	5	6,84	0,039	1,96	0,005	0,120	0,0007

Table 5. Stability tests for sample B

Set	Date	Replicates	pH		Conductivity (mS/m)		Alkalinity (mmol/l)	
			Average	Std. dev.	Average	Std. dev.	Average	Std. dev.
1	30.07.13	5	6,74	0,074	1,95	0,094	0,113	0,0100
2	14.08.13	5	6,76	0,011	1,88	0,000	0,112	0,0005
3	12.09.13	5	6,81	0,008	1,91	0,015	0,116	0,0009

The differences in between the results obtained are within the uncertainties of the measurements at the laboratory. No sign of trends in the results were observed, which indicates that the samples are stable for these analytical parameters within the relevant period 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 each laboratory shall report only one result per 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).

TheYouden's chart allows the 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 Youden's diagram provides then important information about the size and type of analytical error, making it easier to ascertain which the source of error is.

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 consensus 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 iterative 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 consensus 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	6,57	56	0,244	0,041	0,082
	B	6,50	56	0,220	0,037	0,073
Conductivity (mS/m)	A	1,92	47	0,064	0,012	0,023
	B	1,86	48	0,059	0,011	0,021
Alkalinity (mmol/l)	A	0,097	34	0,0103	0,0022	0,0044
	B	0,092	32	0,0089	0,0020	0,0039
Chloride(mg/l)	A	0,900	46	0,0742	0,0137	0,0274
	B	0,920	45	0,0640	0,0119	0,0238
Sulphate(mg/l)	A	1,300	48	0,0971	0,0175	0,0350
	B	1,250	48	0,1068	0,0193	0,0386
Calcium (mg/l)	A	2,19	53	0,127	0,022	0,044
	B	2,01	53	0,173	0,030	0,060
Magnesium (mg/l)	A	0,270	53	0,0230	0,0039	0,0079
	B	0,250	51	0,0211	0,0037	0,0074
Sodium (mg/l)	A	1,010	52	0,0436	0,0075	0,0151
	B	1,090	52	0,0622	0,0108	0,0216
Potassium (mg/l)	A	0,185	47	0,0214	0,0039	0,0078
	B	0,198	50	0,0260	0,0046	0,0092
Total organic carbon (mg/l)	A	4,45	33	0,427	0,093	0,186
	B	4,26	33	0,374	0,081	0,163
Aluminium (µg/l)	C	92,6	31	4,18	0,94	1,88
	D	91,3	31	3,58	0,80	1,61
Iron (µg/l)	C	34,3	31	2,22	0,50	1,00
	D	31,2	31	2,27	0,51	1,02
Manganese (µg/l)	C	6,20	32	0,618	0,136	0,273
	D	6,97	32	0,503	0,111	0,222
Cadmium (µg/l)	C	1,53	37	0,120	0,025	0,049
	D	1,76	38	0,150	0,030	0,061
Lead (µg/l)	C	3,00	34	0,343	0,074	0,147
	D	3,28	32	0,320	0,071	0,142
Copper (µg/l)	C	10,00	36	0,697	0,145	0,291
	D	10,50	35	0,682	0,144	0,288
Nickel (µg/l)	C	4,05	34	0,338	0,073	0,145
	D	4,19	34	0,329	0,070	0,141
Zinc (µg/l)	C	3,96	31	0,527	0,118	0,237
	D	4,30	31	0,542	0,122	0,244

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	6,95	6,97	1,92	2,05	0,098	0,086			0,810	0,840	1,240	1,210	2,26	2,20	0,260	0,260
2	6,51	6,47	1,86	1,80	0,099	0,088	0	0	0,918	0,940	1,334	1,237	2,04	1,85	0,257	0,240
3	6,34	6,22	1,90	1,84	0,100	0,095	6	5	0,910	0,920	1,320	1,270	2,10	1,95	0,240	0,230
4	6,56	6,51	1,90	1,85									2,20	2,10	0,250	0,250
5	6,50	6,33	1,95	1,87			74	0	0,913	0,938	1,335	1,269	2,30	2,08	0,242	0,225
6	6,40	6,40	1,91	1,88									2,18	2,04	0,278	0,263
7	6,57	6,49	1,93	1,87	0,094	0,090	2	2	0,955	0,972	1,301	1,275	2,49	2,28	0,294	0,278
8	6,31	6,27	1,91	1,83												
9							24	23	0,852	0,864	1,276	1,210				
11	6,60	6,57	1,92	1,86	0,097	0,096	6	3	0,810	0,820	1,070	1,020	2,09	2,01	0,250	0,230
12	6,07	5,99	1,94	1,89	0,184	0,180	0	0	0,810	0,900	1,080	1,030	2,28	2,11	0,410	0,350
13	6,58	6,60	1,88	1,81	0,092	0,086	2	2	1,000	0,940			2,30	2,08	0,260	0,250
14	6,84	6,78	1,96	1,88	0,091	0,093	29	18	0,870	0,880	1,290	1,240	2,15	1,98	0,265	0,250
15	6,20	6,20	1,83	1,79					0,930	0,970	1,250	1,210	1,66	1,59	0,210	0,200
16	6,80	6,68	1,82	1,75	0,099	0,097	56	20	0,909	0,933	2,150	1,270	2,21	2,01	0,279	0,263
17													1,92	1,80	0,251	0,235
18	6,80	6,86	2,43	1,92			0	0	0,870	0,890	1,270	1,200	2,17	2,08	0,284	0,265
19	6,57	6,37	1,91	1,85	0,099	0,101	74	2	0,900	0,940	1,270	1,220	2,17	1,94	0,270	0,250
20	6,67	6,61	1,99	1,88	0,118	0,116	50	1	0,890	0,920	1,270	1,180	2,27	2,08	0,270	0,260
21	6,65	6,61	1,92	1,86	0,090	0,090			0,910	0,930	1,330	1,270	2,72	2,51	0,310	0,300
22	6,61	6,66	1,82	1,77	0,105	0,101			0,732	0,745	1,240	1,220	2,42	2,22	0,284	0,267
23	6,99	6,82	7,50	5,80			102	0	2,100	2,410	2,470	2,370	2,32	1,94	0,295	0,245
24	6,70	6,62	2,30	2,20	0,272	0,260			0,644	0,617	1,270	1,220	2,10	2,09	0,272	0,266
25	6,77	6,62	1,93	1,86	0,097	0,092			0,950	0,960	1,290	1,270	2,19	2,00	0,264	0,242
26																
27	6,57	6,49	1,98	1,85	0,090	0,080	21	0	0,760	0,763	1,208	1,114	2,11	1,84	0,240	0,223
28	6,76	6,65							0,886	0,904	1,270	1,260	2,25	2,04	0,276	0,261
29	6,34	6,31	1,94	2,04	0,185	0,175	13	7	0,670	0,790	1,420	1,340	2,18	1,97	0,290	0,270
30	6,74	6,77	1,88	1,88	0,097	0,091	53	15	0,929	0,931	1,358	1,290				
31	6,69	6,56	1,90	1,84	0,083	0,088	69	0	0,780	0,820	1,150	1,100	2,12	1,92	0,280	0,260
32	6,43	6,34	2,03	1,84	0,092	0,090	8	2	0,897	0,911	1,400	1,340	2,20	1,97	0,287	0,268
33	6,19	6,27	2,00	1,90	0,090	0,115	2	2	0,820	0,850	1,410	1,210	3,74	3,86	0,350	0,390

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
34	6,31	6,33	0,02	0,02	9,060	9,060	47	49	2,120	1,760	14,490	13,620	2,23	2,55	0,774	0,967
36	6,50	6,50	1,91	1,85	0,099	0,098	11	10	0,983	0,953	1,510	1,550	2,36	2,29	0,254	0,223
37	6,68	6,63	1,87	1,81	0,098	0,095	2	2	0,853	0,872	1,348	1,305	2,28	2,07	0,299	0,274
38	6,78	6,66	19,20	18,50	0,093	0,094	0	0	0,909	0,951	1,313	1,301	2,17	1,99	0,274	0,258
39	6,12	6,10	1,92	1,86			0	0	1,029	0,925	1,882	2,005				
40	6,91	6,99	28,59	10,39	0,123	0,080	0	0	0,910	0,920	1,320	1,260	2,74	2,59	0,357	0,336
41	6,25	6,15	1,83	1,75	0,107	0,100	10	10	0,852	0,923	1,250	1,250	1,64	1,72	0,243	0,243
42	6,83	6,59	2,20	2,10	0,070	0,060	0	0	1,100	1,100	1,430	1,390	2,16	1,94	0,263	0,244
43	6,63	6,55	1,81	1,76	0,050	0,047			0,900	0,920	1,310	1,250	2,22	2,01	0,274	0,257
44	6,67	6,59	1,94	1,87	0,097	0,098	104	108	0,833	0,842	1,390	1,326	1,97	1,79	0,265	0,248
45	6,60	6,53	1,95	1,88	0,087	0,084	39	14	0,930	0,930	1,270	1,210	2,19	1,99	0,259	0,248
46	6,51	6,48	1,96	1,88	0,140	0,110					1,450	1,510	2,18	2,05	0,270	0,250
47											1,410	1,450	2,16	2,10	0,270	0,260
48	6,57	6,52	1,92	1,81	0,170	0,160			3,500	3,000	1,480	1,560	2,20	1,99	0,290	0,270
49	6,17	6,09	0,09	0,07	0,260	0,270										
50	6,30	6,22	1,97	1,92					1,100	1,100			2,10	1,90	0,260	0,230
51	6,41	6,43	1,90	1,85			10	10			1,260	1,220	2,19	1,99	0,270	0,250
52	6,67	6,60	1,92	1,86	0,075	0,071	128	131	0,950	0,970	1,350	1,340	1,93	1,74	0,281	0,263
54	6,10	6,27	2,02	1,95	0,095	0,092	0	0	0,884	0,903	1,330	1,270	3,34	3,16	0,336	0,325
55	6,11	6,20	1,80	1,70	0,130	0,120	11	0	0,838	0,783	1,148	1,064	1,94	1,78	0,233	0,222
56	6,50	6,48	1,76	1,71			77	2	0,906	0,917	1,292	1,235	2,35	2,14	0,269	0,254
58	6,72	6,48	3,23	2,05	0,153	0,104	0	0	0,964	1,010	1,530	1,500	2,17	1,96	0,282	0,261
59	6,29	6,37	2,05	1,97	0,110	0,090			1,600	1,700	1,350	1,410	2,20	1,82	0,272	0,210
61	6,52	6,36	1,94	1,92	102,000	96,000	50	0	0,900	0,930	1,300	1,240	2,03	1,65	0,250	0,210
62	6,84	6,90	2,03	1,93	0,172	0,169	80	0	81,000	86,000	1,035	1,035	2,67	2,44	0,360	0,338
64	6,52	6,35	1,90	1,88	0,095	0,092			0,869	0,788	1,084	1,050	2,15	1,96	0,254	0,241
65	6,44	6,40	1,97	1,85	0,108	0,105	0	0	1,000	1,000	1,450	1,380	2,20	2,30	0,370	0,400
66	6,51	6,61	1,90	1,84					0,870	0,926	1,282	1,230	2,34	2,15	0,304	0,291

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	1,040	0,980	0,160	0,170	4,73	4,56										
2	1,010	1,102	0,150	0,167	4,63	4,41	93,0	89,5	0,0	0,0	0,00	0,00	1,53	1,78	2,98	3,23
3	0,980	1,080	0,170	0,180	4,06	4,12	96,0	93,0	33,0	29,0	5,20	6,00	1,30	1,50	2,40	2,80
4	0,950	0,950	0,240	0,280	4,97	4,85	92,9	94,3	33,4	32,5	39,80	36,60	1,11	1,49	2,62	3,11
5	1,011	1,108	0,178	0,188												
6	0,994	1,060	0,212	0,216	4,64	4,45	86,6	92,0	34,3	30,2	5,90	6,80	1,50	1,80		
7	0,992	1,084	0,197	0,206	4,68	4,26										
8																
9					5,75	5,62										
11	0,940	1,020	0,170	0,170	4,15	4,02										
12	1,260	1,410	0,270	0,360			87,0	86,3	0,0	35,2	0,00	5,98	3,35	2,35	5,61	7,40
13	1,100	1,130	0,280	0,160			65,0	61,0	43,6	40,0	5,77	6,96	1,61	1,74	3,15	3,32
14	0,968	1,060	0,150	0,159			95,0	92,0	33,0	30,0	6,47	7,36	1,69	1,95	3,27	3,58
15	1,030	1,120	0,170	0,180			93,6	91,3	33,9	30,3	6,13	6,94	1,53	1,77	3,36	3,48
16	1,040	1,140	0,172	0,182	4,25	4,30	97,0	96,9	35,0	31,5	6,20	6,90	1,55	1,77	3,05	3,32
17	0,909	0,982	0,178	0,182			89,2	88,0	35,2	31,6	6,12	6,88	1,43	1,68	2,85	2,89
18	1,000	1,100	0,187	0,203	4,22	3,85	90,2	89,5	33,9	31,0	5,76	6,73	1,58	1,87	3,01	3,32
19	1,000	1,080	0,200	0,210	4,20	4,10										
20	1,010	1,110	0,180	0,190	4,20	4,10	92,5	90,6	34,1	30,0	6,24	7,06	1,47	1,68	2,79	3,03
21	1,050	1,190	0,200	0,220							6,25	7,06	1,54	1,76	3,15	3,26
22	1,030	1,140	0,176	0,187	4,64	4,41	101,0	95,9	34,7	31,9	6,92	7,49	1,66	1,90	3,25	3,54
23	1,120	1,320	0,210	0,250			85,0	93,2	31,3	30,6	4,75	5,70	1,42	1,59	2,50	2,89
24	0,926	0,920	0,223	0,244			149,6	146,1	36,8	39,4	6,98	7,71	1,62	1,73	4,20	4,91
25	0,980	1,030	0,200	0,206			96,9	85,7	37,5	33,2	7,21	7,50	1,48	1,79	3,00	3,04
26													1,39	1,66	1,55	1,77
27	1,009	1,089	0,137	0,126	5,20	4,94										
28	1,035	1,119	0,192	0,202												
29	0,780	0,860	0,160	0,330	4,41	4,00	93,8	90,5	33,8	31,2	6,23	6,85	0,93	1,47	2,65	3,95
30					4,23	3,93										
31	1,020	1,090	0,185	0,200	4,30	4,10										
32	1,020	1,100	0,196	0,203	5,05	4,80	92,6	91,4	35,1	31,8	5,95	6,83	1,43	1,68	2,76	3,02
33	1,020	1,090	0,190	0,220												

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
34					5,89	6,29	104,8	99,7					1,56	1,82	2,78	2,84
36	1,020	1,110	0,164	0,178	4,30	4,20	96,3	92,7	34,8	30,6	5,90	6,60				
37	1,065	1,166	0,202	0,227	4,21	4,01										
38	0,947	1,044	0,141	0,166	5,18	5,28										
39									34,6	30,1	4,96	5,78	1,58	1,78	3,19	3,52
40	1,300	1,420	0,288	0,303	8,12	7,21	98,4	94,5	61,2	55,5	6,77	7,54	1,80	2,04	3,51	3,77
41	0,966	1,035	0,156	0,156	4,30	4,20										
42	0,987	1,060	0,184	0,191	4,63	4,13	90,3	89,9	34,3	31,0	0,00	0,00	1,61	1,89	2,95	3,29
43	1,030	1,120	0,197	0,206	4,35	4,17	90,0	87,7	34,1	30,7			1,43	1,68		
44	0,953	1,039	0,172	0,178	5,19	4,98	92,1	90,6	36,4	33,1	6,49	7,32	1,54	1,80	3,03	3,08
45	0,976	1,060	0,188	0,200	4,60	4,34	90,8	99,6	30,0	34,1	7,39	6,10	1,70	1,44	4,00	4,00
46	1,010	1,040	0,210	0,200			94,4	91,6	38,4	36,1	6,20	7,30	1,65	1,78	2,92	3,22
47	1,010	1,030	0,220	0,200			93,1	90,0	39,2	35,9	5,89	7,02	1,61	1,81	2,75	3,15
48	0,970	1,040	0,180	0,190			96,7	95,1	35,4	31,5	6,40	7,20	1,60	1,90	3,00	3,50
49	1,050	1,070											1,36	1,52		
50							92,0	87,0	90,0	75,0	7,00	7,60	1,50	1,70	4,30	4,10
51	1,020	1,100	0,160	0,180	6,68	6,49	193,0	187,0	34,0	30,0	6,40	7,13	1,63	1,78	2,65	3,30
52	1,000	1,110	0,168	0,179	3,99	4,26										
54	1,030	1,130	0,185	0,196												
55	0,983	1,131	0,158	0,239			92,5	91,5	32,2	30,4	6,30	7,10	1,44	1,62	3,00	3,30
56	1,026	1,110	0,193	0,208	4,48	4,63	87,0	82,5	22,1	18,9	5,50	6,30	1,53	1,76	3,16	3,44
58	1,070	1,130	0,315	0,266	4,87	4,57										
59	0,947	1,001	0,185	0,185	2,40	2,60	87,0	88,0	42,0	37,0	7,00	7,00	1,70	1,60	3,10	3,20
61	1,000	1,010	0,200	0,190	4,19	4,24	60,1	59,0	38,8	37,5	5,40	6,12	1,37	1,59	2,54	2,80
62	0,892	0,954	0,066	0,065												
64	0,980	1,060	0,176	0,201	4,31	4,05			33,7	30,1	5,99	6,86	1,45	1,57		
65	1,200	1,200	0,270	0,280	4,80	4,60										
66	1,037	1,169	0,181	0,205			92,2	90,2	34,3	30,6	6,08	6,98	1,49	1,53	3,01	3,18

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							31						
2	10,07	10,83	3,83	3,94	3,88	4,27	32	9,92	10,60	4,07	4,18	3,90	4,38
3	9,30	10,00	4,00	4,00	4,00	4,00	33						
4	31,80	28,80	3,91	4,59	2,87	2,42	34	8,89	9,48	2,95	2,84		
5							36					3,80	4,70
6	10,00	10,80	4,20	4,40			37						
7							38						
8							39	9,38	9,83	3,60	3,63	6,78	5,63
9							40	11,12	11,84	4,52	4,46	5,07	5,26
11							41						
12	0,00	9,82	5,50	5,05	4,05	3,86	42	9,93	10,80	4,08	4,13	0,00	0,00
13	9,56	10,32	3,73	3,92	2,73	3,30	43						
14	10,60	11,50	4,41	4,49	3,96	4,38	44	10,31	10,17	3,91	4,08	3,93	4,18
15	10,37	11,33	3,93	4,07	3,91	4,34	45	10,50	10,80	3,96	4,05	5,44	7,30
16	10,10	10,80	4,15	4,20	3,98	4,28	46	8,94	8,75	4,08	4,20	4,18	4,41
17	10,00	10,40	3,80	4,00	2,90	3,20	47	8,96	9,58	3,92	4,37	4,20	4,30
18	10,10	11,10	4,03	4,19	4,27	4,73	48	9,60	10,00	4,30	4,30	4,00	4,30
19							49	9,30	9,71	3,72	3,83		
20	10,30	11,00	4,09	4,16	3,66	4,26	50	10,00	10,00	5,40	5,10	4,60	5,80
21	10,10	10,90	3,97	4,08	4,18	4,53	51	12,70	20,50	0,00	0,00	0,16	0,00
22	9,73	10,50	4,29	4,35	4,23	4,77	52						
23	8,85	10,50	3,78	4,20	2,85	2,58	54						
24	10,36	10,75	4,48	3,95	3,22	3,71	55	9,80	10,70	4,00	3,90	3,80	4,20
25	10,00	10,65	4,18	4,57	4,05	4,65	56	9,49	10,35	3,63	3,72	3,70	4,13
26	8,39	7,80					58						
27							59	10,00	10,30	4,50	4,50	5,20	4,70
28							61	12,60	17,30	2,03	2,04	15,30	19,10
29	6,93	8,03	4,91	5,62	5,74	6,89	62						
30							64	10,65	10,81			3,89	4,56
							65						
							66	10,23	10,49	4,36	4,52	4,02	4,25

Table 8.1. Statistics pH

Sample A

Analytical method: All

Unit:

Number of participants	56	Range	0,92
Number of omitted results	0	Variance	0,05
True value	6,57	Standard deviation	0,23
Mean value	6,54	Relative standard deviation	3,5%
Median value	6,57	Relative error	-0,5%

Analytical results in ascending order:

12	6,07	5	6,50	52	6,67
54	6,10	36	6,50	20	6,67
55	6,11	46	6,51	37	6,68
39	6,12	66	6,51	31	6,69
49	6,17	2	6,51	24	6,70
33	6,19	64	6,52	58	6,72
15	6,20	61	6,52	30	6,74
41	6,25	4	6,56	28	6,76
59	6,29	7	6,57	25	6,77
50	6,30	27	6,57	38	6,78
34	6,31	48	6,57	16	6,80
8	6,31	19	6,57	18	6,80
29	6,34	13	6,58	42	6,83
3	6,34	45	6,60	14	6,84
6	6,40	11	6,60	62	6,84
51	6,41	22	6,61	40	6,91
32	6,43	43	6,63	1	6,95
65	6,44	21	6,65	23	6,99
56	6,50	44	6,67		

O = Omitted result

Table 8.1. Statistics
pH

Sample B

Analytical method: All
Unit:

Number of participants	56	Range	1,00
Number of omitted results	0	Variance	0,05
True value	6,50	Standard deviation	0,22
Mean value	6,49	Relative standard deviation	3,4%
Median value	6,50	Relative error	-0,2%

Analytical results in ascending order:

12	5,99	65	6,40	52	6,60
49	6,09	6	6,40	66	6,61
39	6,10	51	6,43	21	6,61
41	6,15	2	6,47	20	6,61
55	6,20	46	6,48	24	6,62
15	6,20	56	6,48	25	6,62
3	6,22	58	6,48	37	6,63
50	6,22	27	6,49	28	6,65
33	6,27	7	6,49	38	6,66
54	6,27	36	6,50	22	6,66
8	6,27	4	6,51	16	6,68
29	6,31	48	6,52	30	6,77
34	6,33	45	6,53	14	6,78
5	6,33	43	6,55	23	6,82
32	6,34	31	6,56	18	6,86
64	6,35	11	6,57	62	6,90
61	6,36	42	6,59	1	6,97
19	6,37	44	6,59	40	6,99
59	6,37	13	6,60		

O = Omitted result

Table 8.2. Statistics Conductivity

Sample A

Analytical method: All

Unit: mS/m

Number of participants	55	Range	0,44
Number of omitted results	8	Variance	0,01
True value	1,92	Standard deviation	0,07
Mean value	1,92	Relative standard deviation	3,9%
Median value	1,92	Relative error	0,2%

Analytical results in ascending order:

34	0,02	O	6	1,91	14	1,96	
49	0,09	O	36	1,91	65	1,97	
56	1,76		19	1,91	50	1,97	
55	1,80		8	1,91	27	1,98	
43	1,81		52	1,92	20	1,99	
16	1,82		1	1,92	33	2,00	
22	1,82		39	1,92	54	2,02	
41	1,83		48	1,92	32	2,03	
15	1,83		21	1,92	62	2,03	
2	1,86		11	1,92	59	2,05	
37	1,87		25	1,93	42	2,20	
30	1,88		7	1,93	24	2,30	O
13	1,88		29	1,94	18	2,43	O
64	1,90		12	1,94	58	3,23	O
4	1,90		61	1,94	23	7,50	O
66	1,90		44	1,94	38	19,20	O
3	1,90		5	1,95	40	28,59	O
31	1,90		45	1,95			
51	1,90		46	1,96			

O = Omitted result

Table 8.2. Statistics Conductivity

Sample B

Analytical method: All

Unit: mS/m

Number of participants	55	Range	0,40
Number of omitted results	8	Variance	0,01
True value	1,86	Standard deviation	0,08
Mean value	1,86	Relative standard deviation	4,2%
Median value	1,86	Relative error	0,1%

Analytical results in ascending order:

34	0,02	O	36	1,85	6	1,88	
49	0,07	O	27	1,85	12	1,89	
55	1,70		19	1,85	33	1,90	
56	1,71		65	1,85	50	1,92	
41	1,75		51	1,85	18	1,92	O
16	1,75		21	1,86	61	1,92	
43	1,76		25	1,86	62	1,93	
22	1,77		39	1,86	54	1,95	
15	1,79		52	1,86	59	1,97	
2	1,80		11	1,86	29	2,04	
37	1,81		5	1,87	1	2,05	
13	1,81		7	1,87	58	2,05	O
48	1,81		44	1,87	42	2,10	
8	1,83		64	1,88	24	2,20	O
66	1,84		45	1,88	23	5,80	O
31	1,84		46	1,88	40	10,39	O
3	1,84		14	1,88	38	18,50	O
32	1,84		20	1,88			
4	1,85		30	1,88			

O = Omitted result

Table 8.3. Statistics
Alkalinity

Sample A

Analytical method: All
Unit: mmol/l

Number of participants	43	Range	0,070
Number of omitted results	10	Variance	0,000
True value	0,097	Standard deviation	0,014
Mean value	0,099	Relative standard deviation	14,1%
Median value	0,097	Relative error	1,7%

Analytical results in ascending order:

43	0,050	O	30	0,097		20	0,118	
42	0,070		44	0,097		40	0,123	
52	0,075		11	0,097		55	0,130	
31	0,083		25	0,097		46	0,140	
45	0,087		37	0,098		58	0,153	O
33	0,090		1	0,098		48	0,170	O
27	0,090		16	0,099		62	0,172	O
21	0,090		2	0,099		12	0,184	O
14	0,091		19	0,099		29	0,185	O
32	0,092		36	0,099		49	0,260	O
13	0,092		3	0,100		24	0,272	O
38	0,093		22	0,105		34	9,060	O
7	0,094		41	0,107		61	102,000	O
64	0,095		65	0,108				
54	0,095		59	0,110				

O = Omitted result

Table 8.3. Statistics
Alkalinity

Sample B

Analytical method: All
Unit: mmol/l

Number of participants	43	Range	0,060
Number of omitted results	10	Variance	0,000
True value	0,092	Standard deviation	0,012
Mean value	0,093	Relative standard deviation	12,9%
Median value	0,092	Relative error	1,6%

Analytical results in ascending order:

43	0,047	O	64	0,092		65	0,105	
42	0,060		54	0,092		46	0,110	
52	0,071		25	0,092		33	0,115	
27	0,080		14	0,093		20	0,116	
40	0,080		38	0,094		55	0,120	
45	0,084		3	0,095		48	0,160	O
1	0,086		37	0,095		62	0,169	O
13	0,086		11	0,096		29	0,175	O
31	0,088		16	0,097		12	0,180	O
2	0,088		36	0,098		24	0,260	O
32	0,090		44	0,098		49	0,270	O
7	0,090		41	0,100		34	9,060	O
59	0,090		22	0,101		61	96,000	O
21	0,090		19	0,101				
30	0,091		58	0,104	O			

O = Omitted result

Table 8.4. Statistics
Nitrate + nitrite-nitrogen

Sample A

Analytical method: All
Unit: µg/l

Number of participants	39	Range	102
Number of omitted results	2	Variance	901
True value	10	Standard deviation	30
Mean value	25	Relative standard deviation	119,8%
Median value	10	Relative error	150,5%

Analytical results in ascending order:

39	0	13	2	34	47	
12	0	3	6	20	50	
54	0	11	6	61	50	
18	0	32	8	30	53	
40	0	51	10	16	56	
65	0	41	10	31	69	
42	0	55	11	19	74	
2	0	36	11	5	74	
58	0	29	13	56	77	
38	0	27	21	62	80	
37	2	9	24	23	102	
33	2	14	29	44	104	O
7	2	45	39	52	128	O

O = Omitted result

Table 8.4. Statistics
Nitrate + nitrite-nitrogen

Sample B

Analytical method: All

Unit: µg/l

Number of participants	39	Range	49
Number of omitted results	2	Variance	95
True value	2	Standard deviation	10
Mean value	5	Relative standard deviation	181,7%
Median value	2	Relative error	182,8%

Analytical results in ascending order:

42	0	31	0	3	5	
61	0	39	0	29	7	
2	0	62	0	41	10	
23	0	27	0	36	10	
18	0	20	1	51	10	
12	0	37	2	45	14	
40	0	32	2	30	15	
5	0	7	2	14	18	
38	0	33	2	16	20	
54	0	13	2	9	23	
58	0	19	2	34	49	
65	0	56	2	44	108	O
55	0	11	3	52	131	O

O = Omitted result

Table 8.5. Statistics Chloride

Sample A

Analytical method: All

Unit: mg/l

Number of participants	51	Range	0,430
Number of omitted results	6	Variance	0,007
True value	0,900	Standard deviation	0,083
Mean value	0,895	Relative standard deviation	9,3%
Median value	0,900	Relative error	-0,6%

Analytical results in ascending order:

24	0,644	O	18	0,870	15	0,930	
29	0,670		54	0,884	45	0,930	
22	0,732		28	0,886	52	0,950	
27	0,760		20	0,890	25	0,950	
31	0,780		32	0,897	7	0,955	
12	0,810		61	0,900	58	0,964	
1	0,810		19	0,900	36	0,983	
11	0,810		43	0,900	65	1,000	
33	0,820		56	0,906	13	1,000	
44	0,833		38	0,909	39	1,029	
55	0,838		16	0,909	50	1,100	
41	0,852		3	0,910	42	1,100	
9	0,852		40	0,910	59	1,600	O
37	0,853		21	0,910	23	2,100	O
64	0,869		5	0,913	34	2,120	O
66	0,870		2	0,918	48	3,500	O
14	0,870		30	0,929	62	81,000	O

O = Omitted result

Table 8.5. Statistics Chloride

Sample B

Analytical method: All

Unit: mg/l

Number of participants	51	Range	0,355
Number of omitted results	6	Variance	0,006
True value	0,920	Standard deviation	0,074
Mean value	0,910	Relative standard deviation	8,2%
Median value	0,920	Relative error	-1,1%

Analytical results in ascending order:

24	0,617	O	28	0,904	2	0,940	
22	0,745		32	0,911	19	0,940	
27	0,763		56	0,917	38	0,951	
55	0,783		3	0,920	36	0,953	
64	0,788		40	0,920	25	0,960	
29	0,790		20	0,920	15	0,970	
31	0,820		43	0,920	52	0,970	
11	0,820		41	0,923	7	0,972	
1	0,840		39	0,925	65	1,000	
44	0,842		66	0,926	58	1,010	
33	0,850		45	0,930	50	1,100	
9	0,864		21	0,930	42	1,100	
37	0,872		61	0,930	59	1,700	O
14	0,880		30	0,931	34	1,760	O
18	0,890		16	0,933	23	2,410	O
12	0,900		5	0,938	48	3,000	O
54	0,903		13	0,940	62	86,000	O

O = Omitted result

Table 8.6. Statistics Sulphate

Sample A

Analytical method: All

Unit: mg/l

Number of participants	52	Range	0,495
Number of omitted results	4	Variance	0,012
True value	1,300	Standard deviation	0,109
Mean value	1,303	Relative standard deviation	8,3%
Median value	1,301	Relative error	0,2%

Analytical results in ascending order:

62	1,035	9	1,276	30	1,358	
11	1,070	66	1,282	44	1,390	
12	1,080	14	1,290	32	1,400	
64	1,084	25	1,290	33	1,410	
55	1,148	56	1,292	47	1,410	
31	1,150	61	1,300	29	1,420	
27	1,208	7	1,301	42	1,430	
1	1,240	43	1,310	65	1,450	
22	1,240	38	1,313	46	1,450	
41	1,250	3	1,320	48	1,480	
15	1,250	40	1,320	36	1,510	
51	1,260	54	1,330	58	1,530	
28	1,270	21	1,330	39	1,882	O
19	1,270	2	1,334	16	2,150	O
20	1,270	5	1,335	23	2,470	O
24	1,270	37	1,348	34	14,490	O
45	1,270	59	1,350			
18	1,270	52	1,350			

O = Omitted result

Table 8.6. Statistics
Sulphate

Sample B

Analytical method: All

Unit: mg/l

Number of participants	52	Range	0,540
Number of omitted results	4	Variance	0,016
True value	1,250	Standard deviation	0,125
Mean value	1,261	Relative standard deviation	9,9%
Median value	1,250	Relative error	0,9%

Analytical results in ascending order:

11	1,020	66	1,230		37	1,305	
12	1,030	56	1,235		44	1,326	
62	1,035	2	1,237		32	1,340	
64	1,050	14	1,240		29	1,340	
55	1,064	61	1,240		52	1,340	
31	1,100	41	1,250		65	1,380	
27	1,114	43	1,250		42	1,390	
20	1,180	28	1,260		59	1,410	
18	1,200	40	1,260		47	1,450	
1	1,210	5	1,269		58	1,500	
9	1,210	3	1,270		46	1,510	
45	1,210	25	1,270		36	1,550	
33	1,210	54	1,270		48	1,560	
15	1,210	21	1,270		39	2,005	O
24	1,220	16	1,270	O	23	2,370	O
22	1,220	7	1,275		34	13,620	O
19	1,220	30	1,290				
51	1,220	38	1,301				

O = Omitted result

Table 8.7. Statistics Calcium

Sample A

Analytical method: All

Unit: mg/l

Number of participants	55	Range	1,10
Number of omitted results	2	Variance	0,04
True value	2,19	Standard deviation	0,20
Mean value	2,20	Relative standard deviation	9,0%
Median value	2,19	Relative error	0,3%

Analytical results in ascending order:

41	1,64	58	2,17	1	2,26	
15	1,66	18	2,17	20	2,27	
17	1,92	19	2,17	37	2,28	
52	1,93	29	2,18	12	2,28	
55	1,94	6	2,18	13	2,30	
44	1,97	46	2,18	5	2,30	
61	2,03	51	2,19	23	2,32	
2	2,04	45	2,19	66	2,34	
11	2,09	25	2,19	56	2,35	
50	2,10	32	2,20	36	2,36	
3	2,10	48	2,20	22	2,42	
24	2,10	4	2,20	7	2,49	
27	2,11	65	2,20	62	2,67	
31	2,12	59	2,20	21	2,72	
64	2,15	16	2,21	40	2,74	
14	2,15	43	2,22	54	3,34	O
42	2,16	34	2,23	33	3,74	O
47	2,16	28	2,24			
38	2,17	28	2,25			

O = Omitted result

Table 8.7. Statistics Calcium

Sample B

Analytical method: All

Unit: mg/l

Number of participants	55	Range	1,00
Number of omitted results	2	Variance	0,04
True value	2,01	Standard deviation	0,21
Mean value	2,03	Relative standard deviation	10,1%
Median value	2,01	Relative error	1,0%

Analytical results in ascending order:

15	1,59	29	1,97	24	2,09	
61	1,65	14	1,98	4	2,10	
41	1,72	38	1,99	47	2,10	
52	1,74	45	1,99	12	2,11	
55	1,78	51	1,99	56	2,14	
44	1,79	48	1,99	66	2,15	
17	1,80	25	2,00	1	2,20	
59	1,82	43	2,01	22	2,22	
27	1,84	16	2,01	7	2,28	
2	1,85	11	2,01	36	2,29	
50	1,90	28	2,03	65	2,30	
31	1,92	28	2,04	62	2,44	
23	1,94	6	2,04	21	2,51	
19	1,94	46	2,05	34	2,55	
42	1,94	37	2,07	40	2,59	
3	1,95	20	2,08	54	3,16	O
58	1,96	18	2,08	33	3,86	O
64	1,96	13	2,08			
32	1,97	5	2,08			

O = Omitted result

Table 8.8. Statistics
Magnesium

Sample A

Analytical method: All
Unit: mg/l

Number of participants	55	Range	0,126
Number of omitted results	6	Variance	0,000
True value	0,270	Standard deviation	0,022
Mean value	0,270	Relative standard deviation	8,0%
Median value	0,270	Relative error	-0,2%

Analytical results in ascending order:

15	0,210	44	0,265	18	0,284	
55	0,233	14	0,265	22	0,284	
27	0,240	56	0,269	32	0,287	
3	0,240	19	0,270	48	0,290	
5	0,242	47	0,270	29	0,290	
41	0,243	20	0,270	7	0,294	
61	0,250	46	0,270	23	0,295	
4	0,250	51	0,270	37	0,299	
11	0,250	24	0,272	66	0,304	
17	0,251	59	0,272	21	0,310	
36	0,254	43	0,274	54	0,336	
64	0,254	38	0,274	33	0,350	O
2	0,257	28	0,276	40	0,357	O
45	0,259	28	0,276	62	0,360	O
13	0,260	6	0,278	65	0,370	O
1	0,260	16	0,279	12	0,410	O
50	0,260	31	0,280	34	0,774	O
42	0,263	52	0,281			
25	0,264	58	0,282			

O = Omitted result

Table 8.8. Statistics
Magnesium

Sample B

Analytical method: All
Unit: mg/l

Number of participants	55	Range	0,125
Number of omitted results	6	Variance	0,001
True value	0,250	Standard deviation	0,023
Mean value	0,252	Relative standard deviation	9,0%
Median value	0,250	Relative error	0,7%

Analytical results in ascending order:

15	0,200	46	0,250	18	0,265	
61	0,210	14	0,250	24	0,266	
59	0,210	4	0,250	22	0,267	
55	0,222	51	0,250	32	0,268	
27	0,223	19	0,250	48	0,270	
36	0,223	13	0,250	29	0,270	
5	0,225	56	0,254	37	0,274	
11	0,230	43	0,257	7	0,278	
3	0,230	38	0,258	66	0,291	
50	0,230	28	0,259	21	0,300	
17	0,235	1	0,260	54	0,325	
2	0,240	47	0,260	40	0,336	O
64	0,241	20	0,260	62	0,338	O
25	0,242	31	0,260	12	0,350	O
41	0,243	58	0,261	33	0,390	O
42	0,244	28	0,261	65	0,400	O
23	0,245	6	0,263	34	0,967	O
44	0,248	52	0,263			
45	0,248	16	0,263			

O = Omitted result

Table 8.9. Statistics Sodium

Sample A

Analytical method: All

Unit: mg/l

Number of participants	54	Range	0,420
Number of omitted results	2	Variance	0,004
True value	1,010	Standard deviation	0,060
Mean value	1,003	Relative standard deviation	6,0%
Median value	1,010	Relative error	-0,7%

Analytical results in ascending order:

29	0,780	7	0,992	56	1,026	
62	0,892	6	0,994	22	1,030	
17	0,909	52	1,000	54	1,030	
24	0,926	61	1,000	43	1,030	
11	0,940	18	1,000	15	1,030	
59	0,947	19	1,000	28	1,035	
38	0,947	27	1,009	66	1,037	
4	0,950	46	1,010	16	1,040	
44	0,953	2	1,010	1	1,040	
41	0,966	20	1,010	21	1,050	
14	0,968	47	1,010	49	1,050	
48	0,970	5	1,011	37	1,065	
45	0,976	33	1,020	58	1,070	
64	0,980	32	1,020	13	1,100	
3	0,980	31	1,020	23	1,120	
25	0,980	51	1,020	65	1,200	
55	0,983	36	1,020	12	1,260	O
42	0,987	28	1,021	40	1,300	O

O = Omitted result

Table 8.9. Statistics
Sodium

Sample B

Analytical method: All
Unit: mg/l

Number of participants	54	Range	0,460
Number of omitted results	2	Variance	0,006
True value	1,090	Standard deviation	0,075
Mean value	1,079	Relative standard deviation	6,9%
Median value	1,090	Relative error	-1,0%

Analytical results in ascending order:

29	0,860	42	1,060	36	1,110	
24	0,920	45	1,060	28	1,118	
4	0,950	14	1,060	28	1,119	
62	0,954	49	1,070	43	1,120	
1	0,980	19	1,080	15	1,120	
17	0,982	3	1,080	58	1,130	
59	1,001	7	1,084	54	1,130	
61	1,010	27	1,089	13	1,130	
11	1,020	31	1,090	55	1,131	
25	1,030	33	1,090	22	1,140	
47	1,030	18	1,100	16	1,140	
41	1,035	51	1,100	37	1,166	
44	1,039	32	1,100	66	1,169	
48	1,040	2	1,102	21	1,190	
46	1,040	5	1,108	65	1,200	
38	1,044	56	1,110	23	1,320	
64	1,060	52	1,110	12	1,410	O
6	1,060	20	1,110	40	1,420	O

O = Omitted result

Table 8.10. Statistics Potassium

Sample A

Analytical method: All

Unit: mg/l

Number of participants	53	Range	0,103
Number of omitted results	7	Variance	0,000
True value	0,185	Standard deviation	0,022
Mean value	0,183	Relative standard deviation	11,8%
Median value	0,185	Relative error	-0,9%

Analytical results in ascending order:

62	0,066	O	64	0,176		43	0,197	
27	0,137		17	0,178		25	0,200	
38	0,141		5	0,178		21	0,200	
2	0,150		48	0,180		61	0,200	
14	0,150		20	0,180		19	0,200	
41	0,156		66	0,181		37	0,202	
55	0,158		42	0,184		46	0,210	
1	0,160		31	0,185		23	0,210	
29	0,160	O	54	0,185		6	0,212	
51	0,160		59	0,185		47	0,220	
36	0,164		18	0,187		24	0,223	
52	0,168		45	0,188		4	0,240	
15	0,170		33	0,190		12	0,270	O
3	0,170		28	0,190		65	0,270	O
11	0,170		28	0,192		13	0,280	O
16	0,172		56	0,193		40	0,288	O
44	0,172		32	0,196		58	0,315	O
22	0,176		7	0,197				

O = Omitted result

Table 8.10. Statistics
Potassium

Sample B

Analytical method: All
Unit: mg/l

Number of participants	53	Range	0,154
Number of omitted results	7	Variance	0,001
True value	0,198	Standard deviation	0,026
Mean value	0,196	Relative standard deviation	13,4%
Median value	0,198	Relative error	-1,0%

Analytical results in ascending order:

62	0,065	O	22	0,187		25	0,206	
27	0,126		5	0,188		43	0,206	
41	0,156		61	0,190		56	0,208	
14	0,159		20	0,190		19	0,210	
13	0,160	O	48	0,190		6	0,216	
38	0,166		42	0,191		21	0,220	
2	0,167		54	0,196		33	0,220	
1	0,170		46	0,200		37	0,227	
11	0,170		45	0,200		55	0,239	
44	0,178		47	0,200		24	0,244	
36	0,178		31	0,200		23	0,250	
52	0,179		64	0,201		58	0,266	O
15	0,180		28	0,201		4	0,280	
3	0,180		28	0,202		65	0,280	O
51	0,180		18	0,203		40	0,303	O
17	0,182		32	0,203		29	0,330	O
16	0,182		66	0,205		12	0,360	O
59	0,185		7	0,206				

O = Omitted result

Table 8.11. Statistics
Total organic carbon

Sample A

Analytical method: All
Unit: mg/l

Number of participants	36	Range	1,76
Number of omitted results	4	Variance	0,17
True value	4,45	Standard deviation	0,41
Mean value	4,55	Relative standard deviation	9,0%
Median value	4,45	Relative error	2,3%

Analytical results in ascending order:

59	2,40	O	31	4,30	1	4,73	
52	3,99		36	4,30	65	4,80	
3	4,06		64	4,31	58	4,87	
11	4,15		43	4,35	4	4,97	
61	4,19		29	4,41	32	5,05	
20	4,20		56	4,48	38	5,18	
19	4,20		45	4,60	44	5,19	
37	4,21		2	4,63	27	5,20	
18	4,22		42	4,63	9	5,75	
30	4,23		6	4,64	34	5,89	O
16	4,25		22	4,64	51	6,68	O
41	4,30		7	4,68	40	8,12	O

O = Omitted result

Table 8.11. Statistics
Total organic carbon

Sample B

Analytical method: All
Unit: mg/l

Number of participants	36	Range	1,77
Number of omitted results	4	Variance	0,17
True value	4,26	Standard deviation	0,41
Mean value	4,39	Relative standard deviation	9,3%
Median value	4,26	Relative error	3,1%

Analytical results in ascending order:

59	2,60	O	43	4,17		58	4,57	
18	3,85		41	4,20		65	4,60	
30	3,93		36	4,20		56	4,63	
29	4,00		61	4,24		32	4,80	
37	4,01		52	4,26		4	4,85	
11	4,02		7	4,26		27	4,94	
64	4,05		16	4,30		44	4,98	
19	4,10		45	4,34		38	5,28	
20	4,10		2	4,41		9	5,62	
31	4,10		22	4,41		34	6,29	O
3	4,12		6	4,45		51	6,49	O
42	4,13		1	4,56		40	7,21	O

O = Omitted result

Table 8.12. Statistics
Aluminium

Sample C

Analytical method: All
Unit: µg/l

Number of participants	35	Range	19,8
Number of omitted results	4	Variance	18,8
True value	92,6	Standard deviation	4,3
Mean value	92,9	Relative standard deviation	4,7%
Median value	92,6	Relative error	0,3%

Analytical results in ascending order:

61	60,1	O	50	92,0		14	95,0	
13	65,0	O	44	92,1		3	96,0	
23	85,0		66	92,2		36	96,3	
6	86,6		20	92,5		48	96,7	
56	87,0		55	92,5		25	96,9	
59	87,0		32	92,6		16	97,0	
12	87,0		4	92,9		40	98,4	
17	89,2		2	93,0		22	101,0	
43	90,0		47	93,1		34	104,8	
18	90,2		15	93,6		24	149,6	O
42	90,3		29	93,8		51	193,0	O
45	90,8		46	94,4				

O = Omitted result

Table 8.12. Statistics
Aluminium

Sample D

Analytical method: All
Unit: µg/l

Number of participants	35	Range	17,2
Number of omitted results	4	Variance	14,5
True value	91,3	Standard deviation	3,8
Mean value	91,3	Relative standard deviation	4,2%
Median value	91,3	Relative error	0,0%

Analytical results in ascending order:

61	59,0	O	47	90,0	3	93,0	
13	61,0	O	66	90,2	23	93,2	
56	82,5		29	90,5	4	94,3	
25	85,7		44	90,6	40	94,5	
12	86,3		20	90,6	48	95,1	
50	87,0		15	91,3	22	95,9	
43	87,7		32	91,4	16	96,9	
17	88,0		55	91,5	45	99,6	
59	88,0		46	91,6	34	99,7	
2	89,5		6	92,0	24	146,1	O
18	89,5		14	92,0	51	187,0	O
42	89,9		36	92,7			

O = Omitted result

Table 8.13. Statistics
Iron

Sample C

Analytical method: All
Unit: µg/l

Number of participants	36	Range	13,6
Number of omitted results	5	Variance	8,1
True value	34,3	Standard deviation	2,9
Mean value	35,2	Relative standard deviation	8,1%
Median value	34,3	Relative error	2,6%

Analytical results in ascending order:

12	0,0	O	15	33,9	17	35,2	
2	0,0	O	51	34,0	48	35,4	
56	22,1	O	43	34,1	44	36,4	
45	30,0		20	34,1	24	36,8	
23	31,3		6	34,3	25	37,5	
55	32,2		42	34,3	46	38,4	
14	33,0		66	34,3	61	38,8	
3	33,0		39	34,6	47	39,2	
4	33,4		22	34,7	59	42,0	
64	33,7		36	34,8	13	43,6	
29	33,8		16	35,0	40	61,2	O
18	33,9		32	35,1	50	90,0	O

O = Omitted result

Table 8.13.
Statistics Iron

Sample D

Analytical method: All
Unit: µg/l

Number of participants	36	Range	11,0
Number of omitted results	5	Variance	8,6
True value	31,2	Standard deviation	2,9
Mean value	32,3	Relative standard deviation	9,0%
Median value	31,2	Relative error	3,7%

Analytical results in ascending order:

2	0,0	O	36	30,6	44	33,1	
56	18,9	O	66	30,6	25	33,2	
3	29,0		43	30,7	45	34,1	
14	30,0		42	31,0	12	35,2	O
20	30,0		18	31,0	47	35,9	
51	30,0		29	31,2	46	36,1	
64	30,1		16	31,5	59	37,0	
39	30,1		48	31,5	61	37,5	
6	30,2		17	31,6	24	39,4	
15	30,3		32	31,8	13	40,0	
55	30,4		22	31,9	40	55,5	O
23	30,6		4	32,5	50	75,0	O

O = Omitted result

Table 8.14. Statistics Manganese

Sample C

Analytical method: All

Unit: µg/l

Number of participants	36	Range	2,64
Number of omitted results	4	Variance	0,39
True value	6,20	Standard deviation	0,62
Mean value	6,18	Relative standard deviation	10,1%
Median value	6,20	Relative error	-0,3%

Analytical results in ascending order:

12	0,00	O	36	5,90		48	6,40	
2	0,00	O	32	5,95		51	6,40	
42	0,00	O	64	5,99		14	6,47	
23	4,75		66	6,08		44	6,49	
39	4,96		17	6,12		40	6,77	
3	5,20		15	6,13		22	6,92	
61	5,40		46	6,20		24	6,98	
56	5,50		16	6,20		59	7,00	
18	5,76		29	6,23		50	7,00	
13	5,77		20	6,24		25	7,21	
47	5,89		21	6,25		45	7,39	
6	5,90		55	6,30		4	39,80	O

O = Omitted result

Table 8.14. Statistics
Manganese

Sample D

Analytical method: All
Unit: µg/l

Number of participants	36	Range	2,01
Number of omitted results	4	Variance	0,27
True value	6,97	Standard deviation	0,52
Mean value	6,90	Relative standard deviation	7,5%
Median value	6,97	Relative error	-1,0%

Analytical results in ascending order:

2	0,00	O	32	6,83	55	7,10	
42	0,00	O	29	6,85	51	7,13	
23	5,70		64	6,86	48	7,20	
39	5,78		17	6,88	46	7,30	
12	5,98	O	16	6,90	44	7,32	
3	6,00		15	6,94	14	7,36	
45	6,10		13	6,96	22	7,49	
61	6,12		66	6,98	25	7,50	
56	6,30		59	7,00	40	7,54	
36	6,60		47	7,02	50	7,60	
18	6,73		20	7,06	24	7,71	
6	6,80		21	7,06	4	36,60	O

O = Omitted result

Table 8.15. Statistics
Cadmium

Sample C

Analytical method: All
Unit: µg/l

Number of participants	39	Range	0,69
Number of omitted results	2	Variance	0,02
True value	1,53	Standard deviation	0,13
Mean value	1,52	Relative standard deviation	8,5%
Median value	1,53	Relative error	-0,4%

Analytical results in ascending order:

29	0,93	O	25	1,48		48	1,60	
4	1,11		66	1,49		13	1,61	
3	1,30		50	1,50		42	1,61	
49	1,36		6	1,50		47	1,61	
61	1,37		15	1,53		24	1,62	
26	1,39		56	1,53		51	1,63	
23	1,42		2	1,53		46	1,65	
32	1,43		44	1,54		22	1,66	
17	1,43		21	1,54		14	1,69	
43	1,43		16	1,55		45	1,70	
55	1,44		34	1,56		59	1,70	
64	1,45		18	1,58		40	1,80	
20	1,47		39	1,58		12	3,35	O

O = Omitted result

Table 8.15. Statistics
Cadmium

Sample D

Analytical method: All
Unit: µg/l

Number of participants	39	Range	0,60
Number of omitted results	2	Variance	0,02
True value	1,76	Standard deviation	0,14
Mean value	1,72	Relative standard deviation	8,0%
Median value	1,76	Relative error	-2,1%

Analytical results in ascending order:

45	1,44		20	1,68		39	1,78	
29	1,47	O	17	1,68		25	1,79	
4	1,49		43	1,68		6	1,80	
3	1,50		50	1,70		44	1,80	
49	1,52		24	1,73		47	1,81	
66	1,53		13	1,74		34	1,82	
64	1,57		21	1,76		18	1,87	
23	1,59		56	1,76		42	1,89	
61	1,59		15	1,77		22	1,90	
59	1,60		16	1,77		48	1,90	
55	1,62		2	1,78		14	1,95	
26	1,66		51	1,78		40	2,04	
32	1,68		46	1,78		12	2,35	O

O = Omitted result

Table 8.16. Statistics Lead

Sample C

Analytical method: All

Unit: µg/l

Number of participants	35	Range	1,90
Number of omitted results	3	Variance	0,15
True value	3,00	Standard deviation	0,39
Mean value	3,02	Relative standard deviation	13,0%
Median value	3,00	Relative error	0,7%

Analytical results in ascending order:

26	1,55	O	46	2,92		13	3,15	
3	2,40		42	2,95		56	3,16	
23	2,50		2	2,98		39	3,19	
61	2,54		48	3,00		22	3,25	
4	2,62		55	3,00		14	3,27	
29	2,65		25	3,00		15	3,36	
51	2,65		66	3,01		40	3,51	
47	2,75		18	3,01		45	4,00	
32	2,76		44	3,03		24	4,20	O
34	2,78		16	3,05		50	4,30	
20	2,79		59	3,10		12	5,61	O
17	2,85		21	3,15				

O = Omitted result

Table 8.16. Statistics
Lead

Sample D

Analytical method: All
Unit: µg/l

Number of participants	35	Range	1,30
Number of omitted results	3	Variance	0,11
True value	3,28	Standard deviation	0,33
Mean value	3,30	Relative standard deviation	10,1%
Median value	3,28	Relative error	0,5%

Analytical results in ascending order:

26	1,77	O	66	3,18		15	3,48	
61	2,80		59	3,20		48	3,50	
3	2,80		46	3,22		39	3,52	
34	2,84		2	3,23		22	3,54	
23	2,89		21	3,26		14	3,58	
17	2,89		42	3,29		40	3,77	
32	3,02		55	3,30		29	3,95	
20	3,03		51	3,30		45	4,00	
25	3,04		16	3,32		50	4,10	
44	3,08		13	3,32		24	4,91	O
4	3,11		18	3,32		12	7,40	O
47	3,15		56	3,44				

O = Omitted result

Table 8.17. Statistics Copper

Sample C

Analytical method: All

Unit: µg/l

Number of participants	38	Range	2,73
Number of omitted results	5	Variance	0,36
True value	10,00	Standard deviation	0,60
Mean value	9,84	Relative standard deviation	6,1%
Median value	10,00	Relative error	-1,6%

Analytical results in ascending order:

12	0,00	O	22	9,73	66	10,23	
29	6,93	O	55	9,80	20	10,30	
26	8,39		32	9,92	44	10,31	
23	8,85		42	9,93	24	10,36	
34	8,89		17	10,00	15	10,37	
46	8,94		50	10,00	45	10,50	
47	8,96		59	10,00	14	10,60	
3	9,30		25	10,00	64	10,65	
49	9,30		6	10,00	40	11,12	
39	9,38		2	10,07	61	12,60	O
56	9,49		21	10,10	51	12,70	O
13	9,56		18	10,10	4	31,80	O
48	9,60		16	10,10			

O = Omitted result

Table 8.17. Statistics
Copper

Sample D

Analytical method: All
Unit: µg/l

Number of participants	38	Range	4,04
Number of omitted results	5	Variance	0,59
True value	10,50	Standard deviation	0,77
Mean value	10,41	Relative standard deviation	7,4%
Median value	10,50	Relative error	-0,9%

Analytical results in ascending order:

26	7,80		13	10,32		6	10,80	
29	8,03	O	56	10,35		64	10,81	
46	8,75		17	10,40		2	10,83	
34	9,48		66	10,49		21	10,90	
47	9,58		23	10,50		20	11,00	
49	9,71		22	10,50		18	11,10	
12	9,82	O	32	10,60		15	11,33	
39	9,83		25	10,65		14	11,50	
3	10,00		55	10,70		40	11,84	
50	10,00		24	10,75		61	17,30	O
48	10,00		42	10,80		51	20,50	O
44	10,17		45	10,80		4	28,80	O
59	10,30		16	10,80				

O = Omitted result

Table 8.18. Statistics
Nickel

Sample C

Analytical method: All
Unit: µg/l

Number of participants	36	Range	2,55
Number of omitted results	2	Variance	0,23
True value	4,05	Standard deviation	0,48
Mean value	4,12	Relative standard deviation	11,6%
Median value	4,05	Relative error	1,8%

Analytical results in ascending order:

51	0,00	O	47	3,92	25	4,18
61	2,03	O	15	3,93	6	4,20
34	2,95		45	3,96	22	4,29
39	3,60		21	3,97	48	4,30
56	3,63		55	4,00	66	4,36
49	3,72		3	4,00	14	4,41
13	3,73		18	4,03	24	4,48
23	3,78		32	4,07	59	4,50
17	3,80		42	4,08	40	4,52
2	3,83		46	4,08	29	4,91
4	3,91		20	4,09	50	5,40
44	3,91		16	4,15	12	5,50

O = Omitted result

Table 8.18. Statistics
Nickel

Sample D

Analytical method: All
Unit: µg/l

Number of participants	36	Range	2,78
Number of omitted results	2	Variance	0,22
True value	4,19	Standard deviation	0,47
Mean value	4,22	Relative standard deviation	11,1%
Median value	4,19	Relative error	0,8%

Analytical results in ascending order:

51	0,00	O	45	4,05	22	4,35
61	2,04	O	15	4,07	47	4,37
34	2,84		21	4,08	6	4,40
39	3,63		44	4,08	40	4,46
56	3,72		42	4,13	14	4,49
49	3,83		20	4,16	59	4,50
55	3,90		32	4,18	66	4,52
13	3,92		18	4,19	25	4,57
2	3,94		23	4,20	4	4,59
24	3,95		46	4,20	12	5,05
3	4,00		16	4,20	50	5,10
17	4,00		48	4,30	29	5,62

O = Omitted result

Table 8.19. Statistics
Zinc

Sample C

Analytical method: All
Unit: µg/l

Number of participants	35	Range	2,47
Number of omitted results	6	Variance	0,33
True value	3,96	Standard deviation	0,57
Mean value	3,90	Relative standard deviation	14,7%
Median value	3,96	Relative error	-1,6%

Analytical results in ascending order:

42	0,00	O	64	3,89		21	4,18	
51	0,16	O	32	3,90		47	4,20	
13	2,73		15	3,91		22	4,23	
23	2,85		44	3,93		18	4,27	
4	2,87		14	3,96		50	4,60	
17	2,90		16	3,98		40	5,07	
24	3,22		3	4,00		59	5,20	
20	3,66		48	4,00		45	5,44	O
56	3,70		66	4,02		29	5,74	O
55	3,80		12	4,05		39	6,78	O
36	3,80		25	4,05		61	15,30	O
2	3,88		46	4,18				

O = Omitted result

Table 8.19. Statistics
Zinc

Sample D

Analytical method: All
Unit: µg/l

Number of participants	35	Range	3,38
Number of omitted results	6	Variance	0,48
True value	4,30	Standard deviation	0,69
Mean value	4,22	Relative standard deviation	16,4%
Median value	4,30	Relative error	-1,8%

Analytical results in ascending order:

51	0,00	O	66	4,25	25	4,65	
42	0,00	O	20	4,26	36	4,70	
4	2,42		2	4,27	59	4,70	
23	2,58		16	4,28	18	4,73	
17	3,20		48	4,30	22	4,77	
13	3,30		47	4,30	40	5,26	
24	3,71		15	4,34	39	5,63	O
12	3,86		32	4,38	50	5,80	
3	4,00		14	4,38	29	6,89	O
56	4,13		46	4,41	45	7,30	O
44	4,18		21	4,53	61	19,10	O
55	4,20		64	4,56			

O = Omitted result

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