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Intercomparison 1428: pH, Conductivity, Alkalinity, NO_3-N, Cl, SO_4, 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

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REPORT

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Abstract

In the current edition of the ICP Waters Intercomparison program, 64 laboratories were invited to participate. 33 from 12 different countries accepted the invitation and all the participants submitted results to the Organization. Two sample sets were prepared: one for the determination of major ions and one for heavy metals. This year a slightly acidic sample was prepared to make the intercomparison more relevant for monitoring of acidic waters. The samples of the set AB where slightly spiked with hydrochloric acid to get a pH close to 6. The detailed procedure is described in Appendix B of the document. Based on the general target accuracy of ± 20 % or the special accuracy limit for pH and conductivity (± 0,2 pH units and ± 10 % respectively),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: conductivity, chloride, calcium, potassium and sodium, with acceptances of 90% or higher.

The lowest percentage of acceptable results was observed for alkalinity and nitrate+nitrite-N, where only 26 and 14% of the reported results were acceptable respectively. As observed in earlier intercomparisons, nitrate showed clear signs of unstability and a large variation in values were reported from the participating laboratories. 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.

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CONVENTION ON LONG-RANGE
TRANSBOUNDARY AIR POLLUTION

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

Intercomparison 1428:

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 2014

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 Environment Agency leads the programme. The Programme Centre's work is supported financially by the Norwegian Environment Agency and UNECE.

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 28th intercomparison of chemical analysis.

Oslo, September 2014

Dr. Carlos Escudero-Oñate

Contents

Summary

The Intercomparison 1428 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 the period April-September 2014, 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. 64 laboratories were invited to participate, and samples were sent to the 33 laboratories who accepted. All of them submitted results to the Programme Centre before the final statistical treatment of the data. 12 countries are 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. 68 % 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 in terms of acceptance were obtained for conductivity, alkalinity, chloride, calcium, sodium and potassium, with 90% or more of the results accepted. Remarkable also is the general improvement in the quality of the results if compared to the previous edition.

Concerning are the results obtained for alkalinity and nitrate+nitrite-N as only 26 and 14% of the results were considered as acceptable according to the accuracy stablished in the intercalibration. As in previous editions, the variable nitrate+nitrite-N has demonstrated clear signs of unstability as evidenced by the disperse results reported by the different participants.

1. Introduction

The international cooperative programme on assessment and monitoring of effects of air pollution on rivers and lakes (ICP Waters) was established under the Executive Body of the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP) in July 1985. Since then, ICP Waters has been an important contributor to document the effects of implementing the Protocols under the Convention. Numerous assessments, workshops, reports and publications covering the effects of long-range transported air pollution has been published over the years.

ICP Waters operates from the middle of a monitoring hierarchy that is designed to evaluate the environmental effects of air pollutants on surface waters chemistry and biology, and predict future ecosystem changes occurring under different deposition scenarios. Lower in the hierarchy is a series of national networks that employ progressively less comprehensive and frequent sampling but greater spatial coverage, culminating in one-time regional surveys. Achieving the Programme objectives requires that both the temporally intensive and regionally extensive data are collected on a continually basis.

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 twenty-eighth intercomparison test, called 1428, 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 the week 17 of 2014. With some exceptions, the participants received the samples within one week. Despite samples were 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 as soon as possible.

3. Discussion

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

In Table 1 an evaluation of the results of intercomparison 1428 is presented with the number and percentage of acceptable results based on the target accuracy (except for pH and conductivity). In Appendix D, Table 4, 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 33 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 slightly higher than last year, but in line with the previous ones. As previously stated, the best acceptance (≥90%) was observed in the determination of conductivity, chloride, calcium, sodium and potassium. The lowest acceptable results were reported for alkalinity, nitrate+nitrate-N (26 and 14% accepted respectively).

pH results may be strongly affected by the method used when the measurement is performed in solutions close to the neutrality. 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 2012 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 worth noting the high number of laboratories that reported values of concentration close to 0 and the noticeable dispersion in the results. As stated in previous intercomparisons, the stability of the sample could be an important issue. Uncontrolled variables in the delivery process seem to negatively influencing the nitrate concentration. The conclusion that we get is that the evaluation of this variable is highly questionable and the obtained values reported as true have to be taken as indicative. The organization strongly encourages checking carefully the units when reporting. 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.

Regarding heavy metals characterization, the best percentage of acceptable results in this intercomparison programme was obtained for nickel, cadmium, copper and manganese (≥80%).

Despite some of the determinations have achieved a better performance than last year, some of them have shown a decrease on its percentage of acceptable results. It has to be taken into account that despite samples have where spiked and then, the concentrations of some of the variables are still 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.

As it had been observed in the last years, the current edition confirms that plasma techniques (ICP-AES and ICP-MS) are taking over for atomic absorption methods, which were the dominating methods some years ago. There's also a general trend to use ICP-MS instead of ICP-AES for the determination of trace heavy metals.

The low fraction of acceptable results in the determination of some of the variables may in some cases be explained by either rather 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 attributable to results reported in wrong units. The laboratories which reported results outside this limit should improve their methods to obtain a better accuracy. In general terms, the use of some analytical methods seems to be less suited for the water samples analyzed in this programme, as the detection limits of some methods applied by participants are too high. This is especially true for some manual methods and some of the methods used for the determination of metals, especially when the concentration is very low. It is important that methods with detection limits low enough are used by the participating laboratories.

It should be further discussed which concentration levels for the heavy metals would be most useful for ICP Waters in the coming intercomparisons as well as 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 1428.

				Acceptable Limit	Number of pairs		Acceptable results for intecalibration (%)			
Variable	Sample pair	Sample 1	Sample 2	%	Total	Accept.	1428	1327	1226	1125
pH	AB	5,81	5,9	3,416	31	21	68	52	59	73
Conductivity,	AB	5,26	4,79	10	30	27	90	78	72	86
Alkalinity,	AB	0,021	0,022	20	19	5	26	63	48	79
Nitrate + nitrite-nitrogen,	AB	105,4	77	20	29	4	14	0	52	21
Chloride,	AB	10,47	9,6	20	29	26	90	78	79	89
Sulphate,	AB	2,86	2,61	20	30	25	83	77	80	86
Calcium,	AB	5,07	4,59	20	31	29	94	85	75	91
Magnesium,	AB	0,345	0,317	20	31	26	84	82	74	89
Sodium,	AB	2,73	2,51	20	30	28	93	91	84	95
Potassium,	AB	0,55	0,511	20	30	28	93	70	81	82
Total organic carbon,	AB	4,8	4,36	20	17	13	76	78	76	69
Aluminium,	CD	190	184	20	22	17	74	89	79	76
Iron,	CD	90,6	87,3	20	22	16	70	72	70	91
Manganese,	CD	39,3	38,2	20	23	20	83	78	89	86
Cadmium,	CD	5,3	4,8	20	25	20	80	85	84	94
Lead,	CD	7,79	7,2	20	25	19	76	71	77	67
Copper,	CD	23,4	24,2	20	25	21	84	84	86	77
Nickel,	CD	10,6	9,99	20	24	21	88	83	78	72
Zinc,	CD	38,4	38,1	20	24	18	75	60	61	79
Total					497	384	76	(72)	(74)	(79)

Units: Conductivity: mS/m
Alkalinity: mmol/l
Nitrate+nitrite-N: µg N/l
Chloride, Sulphate, Calcium, Magnesium, Sodium, Potassium, TOC: mg/l
Aluminium, Iron, Manganese, Cadmium, Lead, Copper, Nickel and Zinc: µg/l

4. Results

64 laboratories were invited to participate in this ICP Waters intercomparison. 33 laboratories of 12 different countries accepted and therefore samples were delivered to them. At the end of the program, all the laboratories that agreed to participate had submitted results to the Programme Centre. The participants and the numerical identity used in the report are listed in Appendix A. In the same appendix, a table summarizing the number of laboratories that participated in each one of the countries can be also found.

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 3 in Appendix C provides an estimated uncertainty of the assigned true values. This calculation is performed according to ISO 13528 (2005), "Statistical methods for use in proficiency testing by interlaboratory comparisons".

The results are illustrated in Figures 1 - 19, where each laboratory is represented by a small circle and an identification number. Some laboratories with strongly deviating results may be located outside the plot. The big circle in the figure, centred in the intersection of the median axes, represents the selected accuracy limit, either the general target limit of ± 20 % of the mean true values for the sample pair or a special accuracy limit as defined in the sections below.

A summary of the results of intercomparison 1428 is presented in Tables 1 and 2. The individual results of the participants are presented in Table 4 in Appendix D, sorted by increasing identification number. More extensive statistical information is presented in the Tables 5.1 - 5.19 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 5.1.

31 of the participants determined pH in the test samples A and B. 25 laboratories used a method based upon electrometry. As stated in previous intercomparisons, stirring has been observed that 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). 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 this intercomparison it was chosen the median value of all the reported results after excluding the outliers. Based upon this, 68 % of the results were acceptable, that is within the median value ± 0,2 pH

units. The acceptance has increased in16% if compared to the previous edition, where only 52 % 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 inestability of the samples during their shipment. Stability tests performed at NIVA in previous years have demonstrated that samples are stable if stored in the dark at 4 ºC.

Noteworthy is also the presence of important systematic errors in the determination of pH, 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 Youden chart for conductivity results is 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 5.2.

30 laboratories have reported results for conductivity in the current edition. From them, 28 used an electrometric method while only 2 laboratories reported the use of "other method" without further specification. Most laboratories achieved rather good agreement between the results for this variable, and an excellent 90 % of the results were within the acceptance limit of ± 10 %. These results are much better than the reported in the last year edition and provide the maximum acceptance from the last 4 intercomparisons.

In the current edition it can be concluded that conductivity is affected mainly by systematic errors, as it can be observed 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 is changing 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 5.3.

19 laboratories reported results for alkalinity. From them, 9 used Gran plot titration method, which is the suggested reference method in the manual (1), while 5 made use of end point titration. 1 participant employed end point titration to pH 5,4 while only 1 reported titration until 5,6. 1 participant reported the use of other method for the determination of the alkalinity

From the 19 reporting laboratories, only 5 of the sample pairs (19 % of them) provided results that were within the target accuracy of ± 20 %. This percentage is notably lower than the last year edition and the lowest of the last four intercalibrations.

It worth note that the alkalinity value may vary significantly with the end-point pH used for the titration. In waters containing high concentrations of total inorganic carbon, the equivalence point is close to pH = 5,4. In such case, the relative error introduced by assuming a fixed end-point pH, is negligible. However, at lower alkalinities normally encountered in areas sensitive to acidification, the “total fixed end-point method” may overestimate the true alkalinity or the “equivalence” alkalinity.

Despite of the low amount of valid data for this variable, the distribution of them in the Youden’s chart indicates that the analysis is affected mainly by random error.

4.4 Nitrate + nitrite-nitrogen

29 laboratories reported results for nitrate + nitrite-nitrogen and the results are presented in Tables 2 and 5.4. Ion chromatography seems to be the preferred technique for the determination of this variable in the samples, as it was used by 16 of the 29 laboratories. It is noticeable the high dispersion in the analysis of this variable, as it may be observed in Figure 4 and also in Table 5.4. As it happened in previous editions of the intercomparison, this dispersion is indicative of the effect of uncontrolled variables during the delivery that negatively influence the nitrate and nitrite concentration. Taking into account these results, it might be concluded that the evaluation of this variable is highly questionable and the values calculated as true might be considered just as indicative.

4.5 Chloride

29 laboratories reported results for chloride and, from them, 26 were accepted (90% of total). The results are presented in Figure 5, Table 2 and Table 5.5. The target accuracy of ± 20 % is represented by the circle in Figure 5.

Ion chromatography appears as the most widely employed technique, with 22 of the participants reporting its use. Other techniques such as photometry, capillary electrophoresis and others using Hg were employed in much lower extension. It is remarkable in the current year edition the high accuracy of the results provided by the participants, as demonstrated in the characteristic Youden plot. Just slight random error affected the analytics.

4.6 Sulphate

30 laboratories reported results for sulphate. From them, 25 where accepted, that involves a 83 % of the total. This percentage is similar to the observed in previous editions. The results obtained for the analysis of sulphate are presented in Figure 6, Table 2 and Table 5.6.

The circle in Figure 6 represents the target accuracy of ± 20 %. As in the case of chloride, most of the laboratories (22 participants) used ion chromatography as the analytical technique in their determinations of sulfate. 3 participants reported the use of ICP-AES for the determination of this variable, 2 made use of photometry, 2 nephelometry and 1 capillary electrophoresis.

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 9 %.

As in the case of chloride, the Youden chart demonstrates the excellent accuracy of the results provided by the participants. Just slight random error inside the 20% deviation from the target value was detected.

4.7 Calcium

31 laboratories reported results for calcium from which 29 were accepted (94 % of total). This percentage is a 9 % higher than the observed in the last edition and the best of the last 4 rounds of the intercomparison. The results are presented in Figure 7, Table 2 and Table 5.7. The circle in Figure 7 represents the target accuracy of ± 20 %.

11 laboratories used ICP-AES and 9 ion chromatography. Flame atomic absorption spectrometry was used by 6 of the participants in their determination of calcium. Only 2 laboratories used ICP-MS and 2 reported the use of other methods. 1 participant made use of electrophoretic techniques.

The results are mainly affected by slight systematic but within the 20% target accuracy stablished in the Youden calculations.

4.8 Magnesium

31 laboratories reported results for magnesium. 26 of them where considered as acceptable according to the criteria of the intercomparison (84 % of the total). This percentage is similar to the acceptable results reported in previous editions.

The characteristic Youden chart obtained in the current edition is presented in Figure 8. Statistical results can be found in Tables 2 and 5.8. The circle in Figure 8 represents the target accuracy of ± 20 %. The analytical methods used by the participants are exactly the same as for the determination of calcium. 11 of the laboratories used ICP-AES and 9, ion chromatography. Flame atomic absorption spectrometry was used by 6 of the participants in their determination of this variable. 2 of the laboratories reported the use of ICP-MS, 1 capillary electrophoresis and 2 participants reported the use of other method.

In the current edition good quality results have been reported by the participants, with relative standard deviations lower than 7%. Remarkable is the quality of the results obtained by the emission in plasma technique, which provided a relative standard deviation lower than 4% for both samples.

It worth note that the slight deviation of the results is mainly to systematic errors, as it can be observed in Figure 8.

4.9 Sodium

30 laboratories reported results for sodium and from them 28 pairs were accepted. That involves an excellent 93 % of the total. This is in agreement with the percentage of acceptance reported in previous editions.

The characteristics Youden chart is presented in Figure 9. Tables 2 and 5.9 summarize the statistical treatment of the data. The circle in Figure 9 represents the target accuracy of ± 20 %. In this round of the intercomparison, 10 participants analysed sodium by ICP-AES and 2 ICP-MS. Ion chromatography techniques are nearly as extended as plasma techniques, as 9 of the participants reported the use of ion chromatography in this analytical determination. Among the flame techniques, atomic absorption is the preferred, as it was used by 4 laboratories. 2 participants reported the use of emission in flame. Just 1 laboratory reported the use of capillary electrophoresis and 2 indicated the use of other method different than the previously mentioned.

As in previous editions, the determination of sodium holds a very good quality and there were no strong differences in the results obtained by the different analytical techniques.

When checking the Youden chart obtained in the determination of sodium, it is noticeable the high precision and exactitude of the result set provided by the participants.

4.10 Potassium

30 laboratories reported results for potassium. From these results, 28 where considered as acceptable, involving a 93 % of the total. This acceptance is the highest achieved in the last 4 years. Regarding the analytical techniques, the same distribution as in the case of the analysis of sodium was evidenced.

The Youden graphic obtained for the determination of potassium in this round is presented in Figure 10. Statistics results for this variable are presented in Tables 2 and 5.10. The circle in Figure 10 represents the target accuracy of ± 20 %.

The Youden chart points out that the deviating results are affected by systematic and random error. However, its magnitude seems not to be very important and all the results almost lie within the target 20 % accuracy.

4.11 Total organic carbon

17 laboratories reported results for total organic carbon. From them, 76 % of the results were within the target accuracy of ± 20 % (13 laboratories).

The results of the Youden test are presented in Figure 11, while the statistics can be found in Tables 2 and 5.11. The circle in Figure 11 represents the target accuracy of ± 20 %. Combustion methods are used by most of the laboratories (10) while 4 reported the use of UV/peroxodisulfate oxidation method for this determination. 3 last laboratories reported the use of other method when reporting. Not significant differences were observed in the results provided by the combustion and the UV/peroxodisulfate methods.

The distribution of the results in the Youden's chart demonstrates that the deviating results are mainly affected by systematic error.

4.12 Aluminium

22 laboratories reported results for aluminium. From these 17 where accepted according to the target accuracy criteria (74% of total). The results of the Youden test are presented in Figure 12, where the circle represents the target accuracy of ± 20 %. The statistics of the analytics are presented in Tables 2 and 5.12.

In the current edition, 9 laboratories used ICP-MS and 7, ICP-AES. 4 participants reported the use of atomic absorption techniques. 2 of them, graphite furnace and the other 2, flame atomic absorption. Only one participant reported the use of a photometric method. From these techniques, the lowest relative error in the results was observed for the ICP-MS technique.

According to the distribution of the results in the Youden chart it can be stated that the deviating results are mainly affected by systematic error with slight contribution also of random error.

4.13 Iron

22 laboratories provided results for iron and 16 pair were acceptable (70% of total). The results of the Youden test are presented in Figure 13. The statistics calculations are presented in Table 2 and Table 8.13. The circle in Figure 13 represents the target accuracy of ± 20%.

9 and 7 of the laboratories used ICP-AES and ICP-MS, respectively. 4 participants reported the use of atomic absorption techniques: 2 employed GFASS and 2 FAAS. One laboratory reported the use photometry and another one used a method different than the previously mentioned.

The Youden chart puts into evidence that deviating results are mainly affected by systematic error.

4.14 Manganese

23 participants reported results in the analysis of manganese. From these, 20 fulfilled the acceptance criteria. This involves a 83 % of acceptance, higher than in the last but in line with previous editions. The Youden chart is presented in Figure 14 and the statistical results in Tables 2 and 5.14. The circle in the figure represents the target accuracy of ± 20 %.

Almost all the participants reported the use of atomic techniques. Only 1 participant reported the use of other method. From them, 9 and 8 participants used ICP-AES and ICP-MS, respectively, while 4 and 1 used graphite furnace atomic absorption and flame atomic absorption respectively. No relevant differences were detected in between the different techniques.

Despite systematic error is affecting the analysis of manganese it is of a small magnitude as demonstrates the short distance from the diagonal.

4.15 Cadmium

25 laboratories reported results for cadmium in the set of samples C and D. From these, 20 of the results were acceptable, according to the target accuracy. This involves a 80 % of them, the lowest of the last 4 editions.

The Youden graph for cadmium is presented in Figure 15 while the statistical calculations for this variable are presented in Tables 2 and 5.15. The circle in Figure 15 represents the target accuracy of ± 20 %.

Plasma techniques have been the most employed, as 17 participants reported its use. From them, 12 detected mass (ICP-MS) and 5 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 8 of the participants. In the current edition, any participant reported the use of non-atomic techniques. Noteworthy is also the quality of the results provided by the plasma techniques, as all of them fulfilled the acceptance criteria.

According to the Youden chart, the deviating results seem to be mainly affected by systematic errors.

4.16 Lead

25 laboratories reported results for lead in samples C and D. From these, 19 where accepted involving a 76 % of the results. This percentage of acceptance was slightly higher than in the last year edition, but in line with previous intercomparisons. Youden chart is presented in Figure 16 and statistical results in the determination of this variable in Tables 2 and 5.16.

The circle in Figure 16 represents the target accuracy of ± 20 %. In this case, all the laboratories have reported the use of atomic techniques. Plasma techniques have been the most employed, as 15 participants have communicated the use of ICP. From them, 12 used mass detection (ICP-MS) and 6, emitted radiation (ICP-AES). The preferred method employed by the participants that used atomic absorption techniques was the graphite furnace (GFAAS). It is remarkable the fact that from the laboratories that employed ICP techniques, all the results were acceptable, while from these that employed GFAAS, 2 of the results had to be omitted for statistics calculation.

As it can be observed in the characteristic Youden chart, the results exhibit a clear systematic error.

4.17 Copper

25 laboratories reported results for copper in sample set C and D. From them, 21 were acceptable (84 % of the total). Youden chart is presented in Figure 17 and statistical results in the determination of this variable in Tables 2 and 5.17. The circle in the figure represents the target accuracy of ± 20 %. As it can be seen in the figure, almost all the results lied in the target accuracy stablished and the deviation in the results can be assigned mainly to systematic error.

By analysis, almost all the participants employed atomic based techniques, being plasma the most widely used with 13 of the participants using mass detectors and 5 using emitted light. Noteworthy also is the important contribution of the atomic absorption techniques, as 8 participants employed GFAAS.

4.18 Nickel

24 laboratories reported results for nickel in samples C and D. From these, 21 where classified as acceptable according to the target accuracy of the assay. This involves 88% of the total. The percentage of acceptable reaches its maximum from 2011 and indicates a clear improvement in the quality of the results in the last 4 years.

Nickel's Youden chart is presented in Figure 18 and statistical results in Tables 2 and 5.18. The circle in the figure represents the target accuracy of ± 20 %. It can be observed that the determination of nickel in the samples is affected mainly by systematic error.

By analysis type, it is remarkable the use of atomic based techniques. From them, plasma is the most widely used, with 24 participants. 12 employed ICP-MS while only 6 reported the use of ICP-AES. All the laboratories that reported the use of atomic absorption based techniques employed graphite furnace. In this edition, any participant analysed nickel by flame absorption mode.

The distribution of the results in the Youden chart puts into evidence that the analysis is mainly affected by systematic error.

4.19 Zinc

24 laboratories reported results in the determination of zinc in sample set C and D. From these results, 18 were accepted (75 % of the total). These results involve an increase of the acceptability of 15% if compared to the last year edition and an increase to almost the acceptance reported in the edition of 2011.

The Youden chart is presented in Figure 19 and statistical results in Tables 2 and 5.19. The circle in Figure 19 represents the target accuracy of ± 20 %. The elliptic distribution of the results in the Youden chart demonstrates that the determination of Zn is mainly affected by systematic error.

Plasma techniques are, by far, the most widely employed by the laboratories. From them, ICP-MS demonstrated to be the most widely used, with 12 participants, followed by emission in plasma (ICP-AES) that was used by 6 of the laboratories. From the techniques based on atomic absorption spectroscopy 4 laboratories made use of the graphite furnace (GFAAS) while only 2 participants reported the use of flame atomic absorption spectroscopy (FAAS). In the current edition any participant reported results derived from the analysis with a non-atomic technique.

Table 2. Statistical summary for intercomparison 1428

Analytical variable and method	Sample	TRUE Value		No. lab.		Median		Avg/Std.av.		Avg/Std.av.		Rel.std. av. %		Relative error %	
	pair	S. 1	S. 2	Total	Om	S. 1	S. 2	Sample 1		Sample 2		S. 1	S. 2	S. 1	S. 2
pH	AB	5,81	5,90	31	2	5,81	5,90	5,82	0,16	5,93	0,13	2,7	2,1	0,2	0,4
Electrometry				25	2	5,84	5,90	5,82	0,17	5,93	0,14	2,9	2,3	0,2	0,5
Stirring				4	0	5,81	5,91	5,85	0,12	5,93	0,10	2,1	1,7	0,7	0,6
Other method				2	0			5,80		5,86				-0,3	-0,8
Conductivity	AB	5,26	4,79	30	2	5,25	4,79	5,25	0,14	4,77	0,12	2,6	2,5	-0,3	-0,4
Electrometry				28	1	5,26	4,79	5,25	0,13	4,78	0,12	2,5	2,4	-0,1	-0,2
Other method				2	1			5,02		4,60				-4,6	-4,0
Alkalinity	AB	0,021	0,022	19	10	0,021	0,022	0,020	0,004	0,023	0,004	21,7	17,7	-3,9	3,8
Gran plot titration				9	5	0,018	0,022	0,018	0,006	0,023	0,005	33,4	23,9	-12,0	2,4
End point titration				5	3			0,023		0,025				8,1	13,6
End point 5.4				1	0			0,019		0,018				-7,6	-16,4
End point				2	0			0,022		0,024				2,4	6,8
End point 5.6				1	1			0,045		0,039				114,3	77,3
Other method				1	1			0,009		0,021				-59,5	-2,7
Nitrate+nitrite-Nitrogen	AB	105,4	77,0	29	13	108,4	88,5	106,2	18,4	83,5	21,8	17,3	26,1	0,8	8,5
Ion chromatography				16	9	100,0	64,6	96,8	15,6	65,9	17,7	16,1	26,8	-8,2	-14,5
Photometry				4	1	114,0	90,0	125,6	23,8	89,2	14,8	19,0	16,6	19,2	15,8
Autoanalyzer				3	1			113,5		108,5				7,6	40,8
Photometry				3	0	107,0	103,1	102,2	16,3	97,7	15,7	16,0	16,1	-3,1	26,9
Cap. electrophoresis				1	1			0,1		0,1				-99,9	-99,9
Flow injection anal.				1	1			109,5		9,7				3,9	-87,4
Hydrazine				1	0			112,0		98,0				6,3	27,3
Chloride	AB	10,47	9,60	29	3	10,47	9,58	10,39	0,33	9,54	0,36	3,2	3,7	-0,8	-0,7
Ion chromatography				22	1	10,50	9,60	10,45	0,24	9,55	0,34	2,3	3,5	-0,2	-0,5
Other method				2	0			10,04		9,16				-4,2	-4,6
Cap. electrophoresis				1	0			10,88		10,22				3,9	6,5
Manual, Hg				1	1			12,50		10,10				19,4	5,2
Photometry				1	1			8,73		7,66				-16,6	-20,2
Photometry HgSCN				1	0			9,36		9,19				-10,6	-4,3
Potentiometry				1	0			10,43		9,65				-0,4	0,5
Sulphate	AB	2,86	2,61	30	4	2,85	2,61	2,84	0,14	2,60	0,15	5,0	5,7	-0,7	-0,5
Ion chromatography				22	0	2,85	2,61	2,82	0,13	2,58	0,15	4,5	5,6	-1,5	-1,2
ICP-AES				3	1			3,09		2,82				8,1	7,9
Nephelometry				2	2			6,95		6,30				143,0	141,4
Photometry				2	1			2,91		2,59				1,7	-0,8
Cap. electrophoresis				1	0			2,75		2,57				-3,9	-1,6
Calcium	AB	5,07	4,59	31	1	5,08	4,59	5,07	0,19	4,61	0,18	3,8	4,0	0,1	0,4
ICP-AES				11	0	5,10	4,59	5,13	0,12	4,64	0,11	2,4	2,4	1,1	1,1
Ion chromatography				9	0	5,15	4,67	5,12	0,24	4,69	0,21	4,6	4,6	1,1	2,1
FAAS				6	1	5,13	4,60	5,05	0,23	4,55	0,23	4,5	5,0	-0,5	-1,0
ICP-MS				2	0			4,87		4,56				-3,9	-0,7
Other method				2	0			4,97		4,36				-2,0	-5,0
Cap. Electrophoresis				1	0			4,82		4,46				-4,9	-2,8

Analytical variable and method	Sample	TRUE Value		No. lab.		Median		Avg/Std.av.		Avg/Std.av.		Rel.std.av. %		Relative error %	
	pair	S. 1	S. 2	Total	Om	S. 1	S. 2	Sample 1		Sample 2		S. 1	S. 2	S. 1	S. 2
Magnesium	AB	0,345	0,317	31	4	0,344	0,316	0,345	0,014	0,316	0,014	4,0	4,5	0,1	-0,3
ICP-AES				11	0	0,346	0,317	0,346	0,013	0,314	0,012	3,8	3,8	0,3	-0,9
Ion chromatography				9	2	0,341	0,312	0,343	0,017	0,313	0,011	4,8	3,6	-0,6	-1,1
FAAS				6	2	0,346	0,327	0,350	0,016	0,325	0,021	4,7	6,5	1,3	2,6
ICP-MS				2	0			0,336		0,308				-2,8	-3,0
Other method				2	0			0,349		0,310				1,0	-2,2
Cap. Electrophoresis				1	0			0,357		0,343				3,5	8,2
Sodium	AB	2,73	2,51	30	1	2,72	2,51	2,70	0,09	2,48	0,12	3,4	4,7	-1,2	-1,1
ICP-AES				10	0	2,74	2,48	2,70	0,11	2,46	0,12	3,9	4,7	-1,2	-2,1
Ion chromatography				9	0	2,73	2,53	2,72	0,07	2,50	0,07	2,6	2,8	-0,2	-0,4
FAAS				4	1	2,72	2,52	2,64	0,19	2,44	0,17	7,3	6,9	-3,3	-2,7
AES				2	0			2,72		2,64				-0,3	5,0
ICP-MS				2	0			2,66		2,43				-2,6	-3,4
Other method				2	0			2,68		2,39				-2,0	-4,8
Cap. Electrophoresis				1	0			2,71		2,65				-0,8	5,5
Potassium	AB	0,550	0,511	30	1	0,550	0,510	0,548	0,033	0,513	0,028	6,0	5,5	-0,3	0,5
ICP-AES				10	0	0,551	0,514	0,556	0,024	0,514	0,025	4,3	4,9	1,1	0,6
Ion chromatography				10	0	0,549	0,506	0,542	0,028	0,508	0,029	5,1	5,7	-1,4	-0,6
FAAS				4	0	0,553	0,517	0,542	0,066	0,523	0,038	12,2	7,2	-1,5	2,4
AES				2	0			0,542		0,538				-1,5	5,3
ICP-MS				2	0			0,534		0,499				-2,9	-2,4
Cap. Electrophoresis				1	1			0,556		0,619				1,1	21,1
Other method				1	0			0,600		0,500				9,1	-2,2
Total Organic Carbon	AB	4,80	4,36	17	0	4,77	4,34	4,80	0,51	4,36	0,51	10,7	11,6	-0,1	-0,1
Combustion				10	0	4,82	4,39	4,94	0,42	4,50	0,41	8,6	9,0	2,9	3,3
UV/peroxodisulphate				4	0	4,44	4,10	4,42	0,58	3,97	0,60	13,1	15,2	-8,0	-8,9
Other method				3	0	4,82	4,34	4,82	0,65	4,38	0,60	13,5	13,7	0,4	0,5
Aluminium	CD	190	184	22	2	191	184	187	15	183	12	8,2	6,7	-1,7	-0,5
ICP-MS				9	0	188	184	187	12	181	10	6,2	5,4	-1,3	-1,7
ICP-AES				7	0	193	186	196	7	188	5	3,4	2,9	3,1	2,2
GFAAS				5	2	164	196	168	25	184	27	15,0	14,5	-11,6	-0,2
Photometry				1	0			175		166				-7,9	-9,8
Iron	CD	90,6	87,3	22	0	90,7	87,1	90,6	11,7	87,8	10,9	12,9	12,4	0,0	0,6
ICP-AES				9	0	90,7	89,1	90,8	4,3	88,7	4,1	4,8	4,6	0,2	1,6
ICP-MS				7	0	87,7	84,7	84,2	11,1	81,5	11,9	13,2	14,6	-7,1	-6,6
FAAS				2	0			96,7		91,1				6,7	4,3
GFAAS				2	0			84,9		85,5				-6,3	-2,1
Other method				1	0			111,0		97,0				22,5	11,1
Photometry				1	0			112,0		113,0				23,6	29,4
Manganese	CD	39,3	38,2	23	0	39,4	38,3	39,2	2,8	38,4	2,8	7,2	7,4	-0,1	0,5
ICP-AES				9	0	39,7	38,7	39,5	2,0	38,5	2,0	5,1	5,2	0,5	0,9
ICP-MS				8	0	39,3	38,2	39,6	3,4	39,0	3,2	8,6	8,3	0,8	2,0
GFAAS				4	0	38,1	37,8	37,7	3,2	36,8	3,7	8,6	9,9	-4,0	-3,7
FAAS				1	0			36,7		35,8				-6,6	-6,3
Other method				1	0			42,8		41,8				8,9	9,4

Analytical variable and method	Sample	TRUE Value		No. lab.		Median		Avg/Std.av.		Avg/Std.av.		Rel.std.av. %		Relative error %	
	pair	S. 1	S. 2	Total	Om	S. 1	S. 2	Sample 1		Sample 2		S. 1	S. 2	S. 1	S. 2
Cadmium	CD	5,30	4,80	25	3	5,32	4,80	5,30	0,34	4,75	0,37	6,4	7,8	0,0	-1,0
ICP-MS				12	0	5,35	4,83	5,35	0,37	4,77	0,41	6,8	8,7	1,0	-0,6
GFAAS				8	3	5,15	4,80	5,08	0,34	4,65	0,37	6,6	7,9	-4,2	-3,0
ICP-AES				5	0	5,30	4,80	5,40	0,21	4,81	0,32	3,8	6,6	2,0	0,2
Lead	CD	7,79	7,20	25	2	7,79	7,20	7,85	0,55	7,24	0,66	7,0	9,1	0,7	0,5
ICP-MS				12	0	7,85	7,41	7,83	0,38	7,39	0,43	4,8	5,8	0,5	2,6
GFAAS				10	2	7,70	6,88	7,63	0,64	6,85	0,79	8,4	11,5	-2,1	-4,8
ICP-AES				3	0	8,42	7,36	8,51	0,45	7,69	0,71	5,3	9,2	9,2	6,8
Copper	CD	23,4	24,2	25	3	23,4	24,2	23,5	1,4	24,2	1,6	5,8	6,5	0,6	0,1
ICP-MS				13	0	23,4	24,2	23,2	1,3	24,2	1,4	5,5	5,9	-0,9	0,1
GFAAS				8	2	23,7	23,3	24,1	1,6	23,8	2,1	6,8	8,8	2,9	-1,6
ICP-AES				4	1	23,5	24,6	24,0	1,0	25,0	1,1	4,1	4,4	2,4	3,3
Nickel	CD	10,60	9,99	24	0	10,65	9,98	10,62	0,80	10,02	0,72	7,5	7,2	0,2	0,3
ICP-MS				12	0	11,10	10,06	10,91	0,49	10,12	0,46	4,5	4,6	3,0	1,3
GFAAS				7	0	10,00	9,40	9,81	0,57	9,43	0,61	5,8	6,5	-7,4	-5,6
ICP-AES				5	0	10,60	10,30	11,06	0,93	10,62	0,84	8,4	7,9	4,3	6,3
Zinc	CD	38,4	38,1	24	3	38,4	38,2	38,6	3,1	38,4	3,7	8,0	9,6	0,5	0,8
ICP-MS				12	1	38,5	38,4	38,9	2,7	38,9	3,2	6,9	8,1	1,4	2,2
ICP-AES				6	0	38,4	38,5	39,9	3,3	40,0	3,9	8,2	9,9	3,9	5,1
GFAAS				4	1	35,1	32,8	35,9	3,0	34,4	2,8	8,4	8,1	-6,5	-9,8
FAAS				2	1			35,3		35,1				-8,1	-7,9

*Om.: Sample pair omitted from the calculations

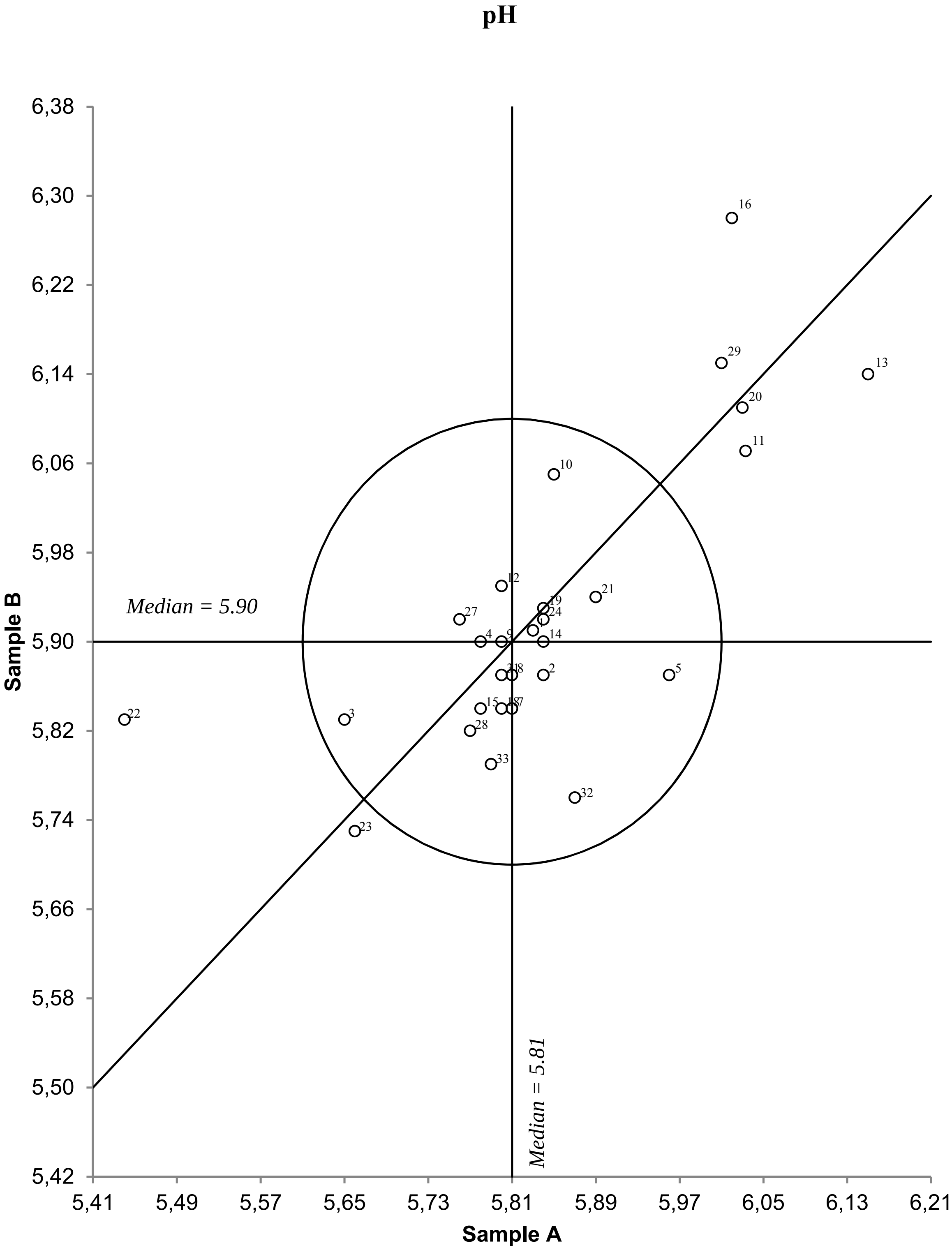

Figure 1. Youden diagram for pH, sample pair AB
Acceptable limit, given by circle, is 3.416 %

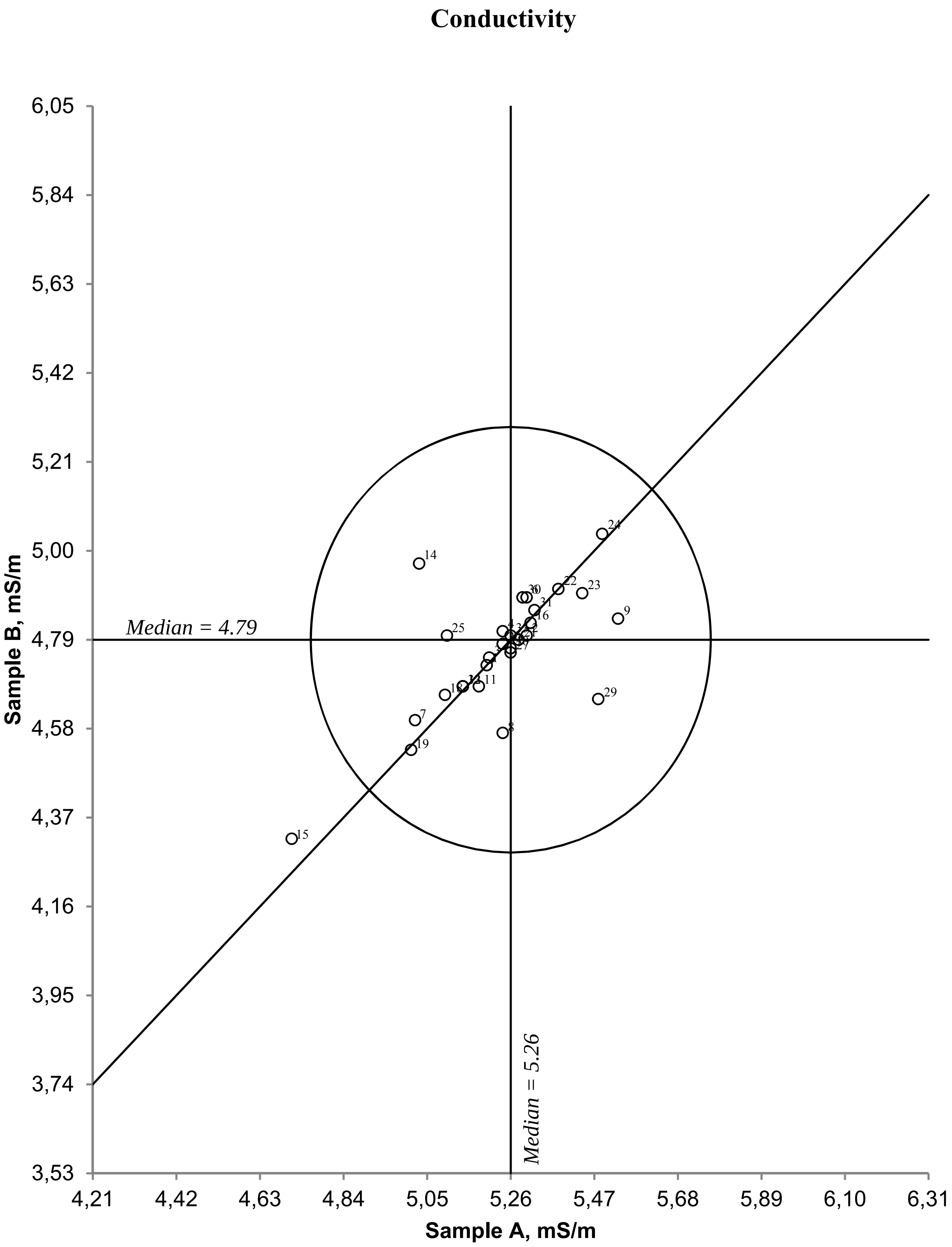

Figure 2. Youden diagram for conductivity, sample pair AB
Acceptable limit, given by circle, is 10 %

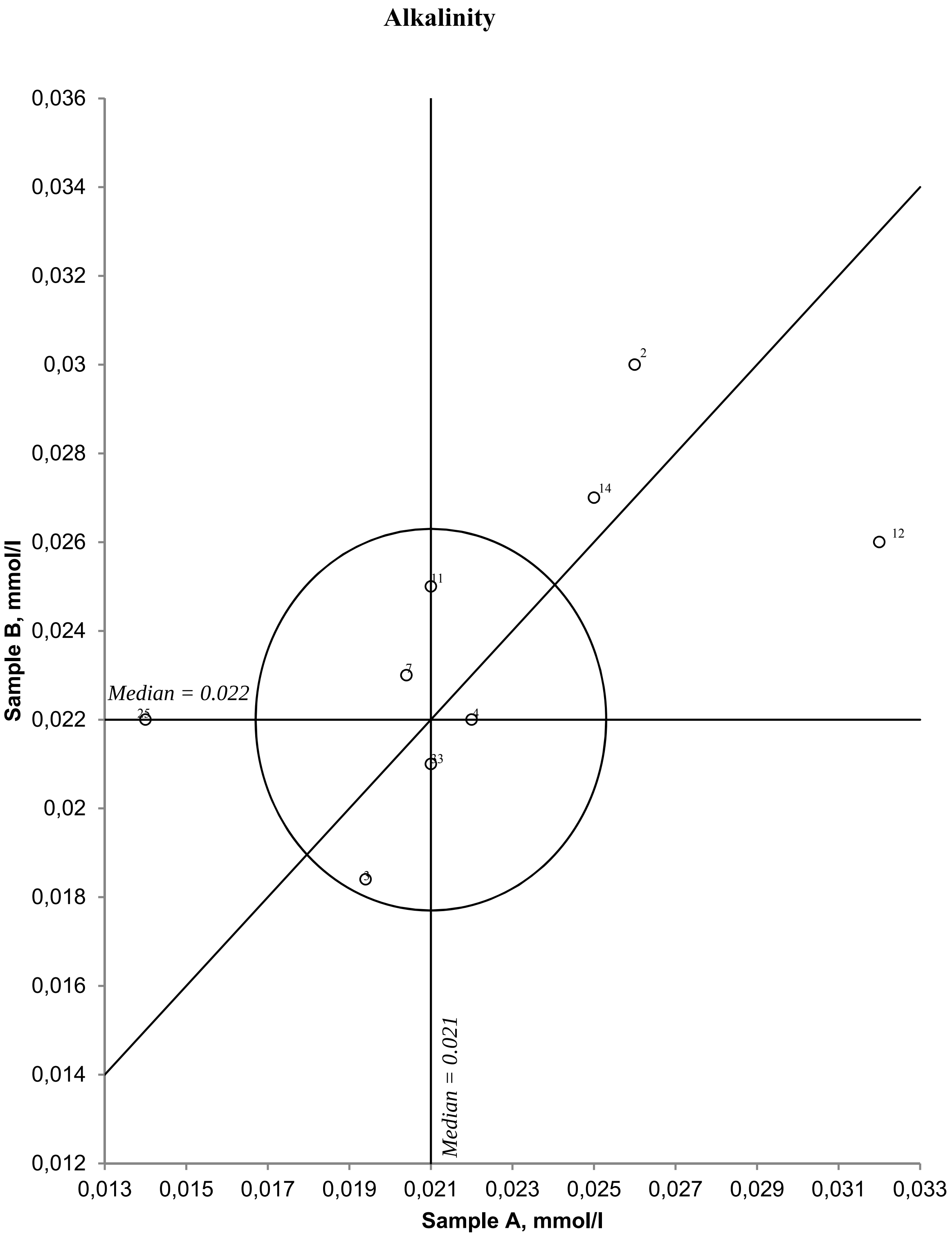

Figure 3. Youden diagram for alkalinity, sample pair AB
Acceptable limit, given by circle, is 20 %

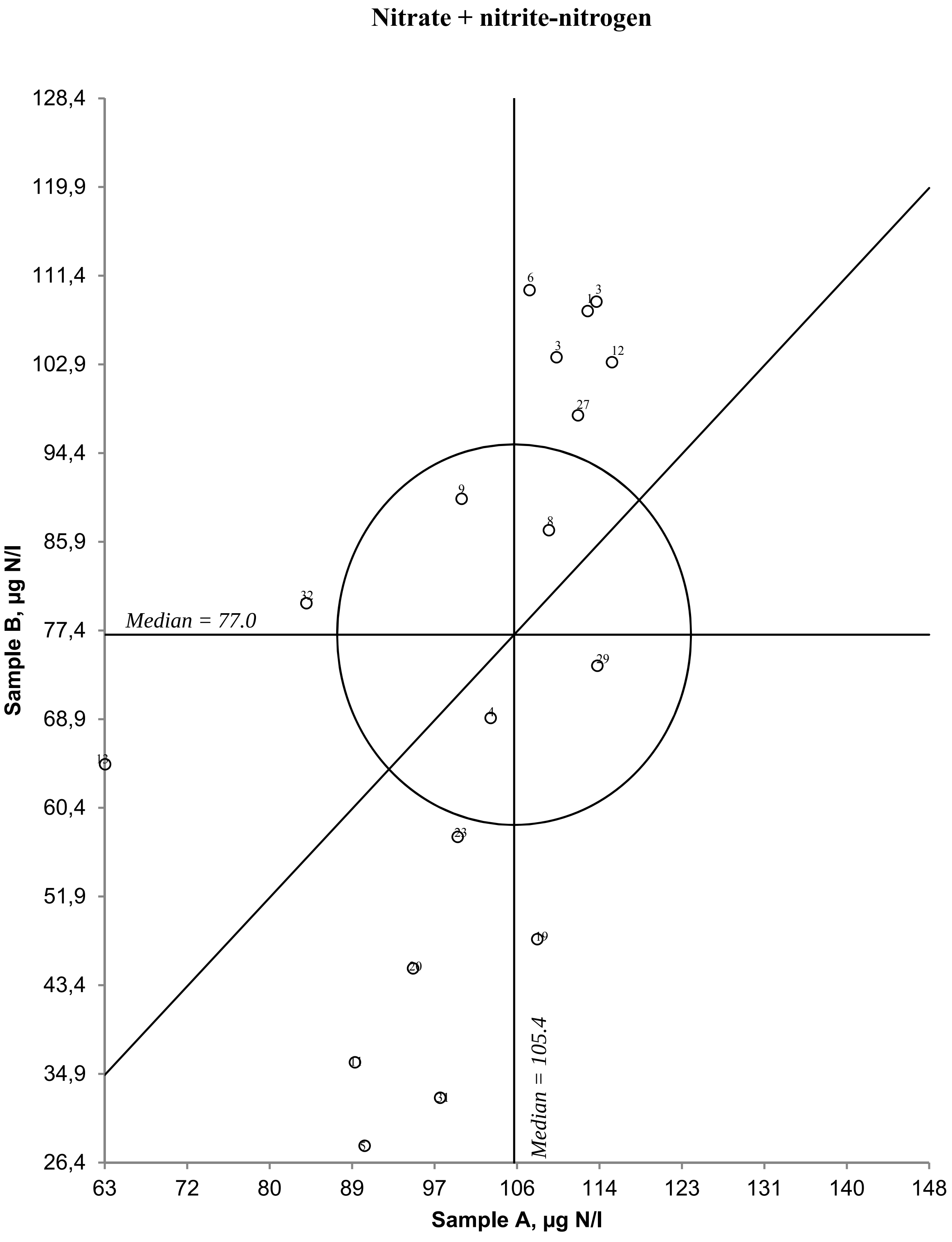

Figure 4. Youden diagram for nitrate + nitrite-nitrogen, sample pair AB
Acceptable limit, given by circle, is 20 %

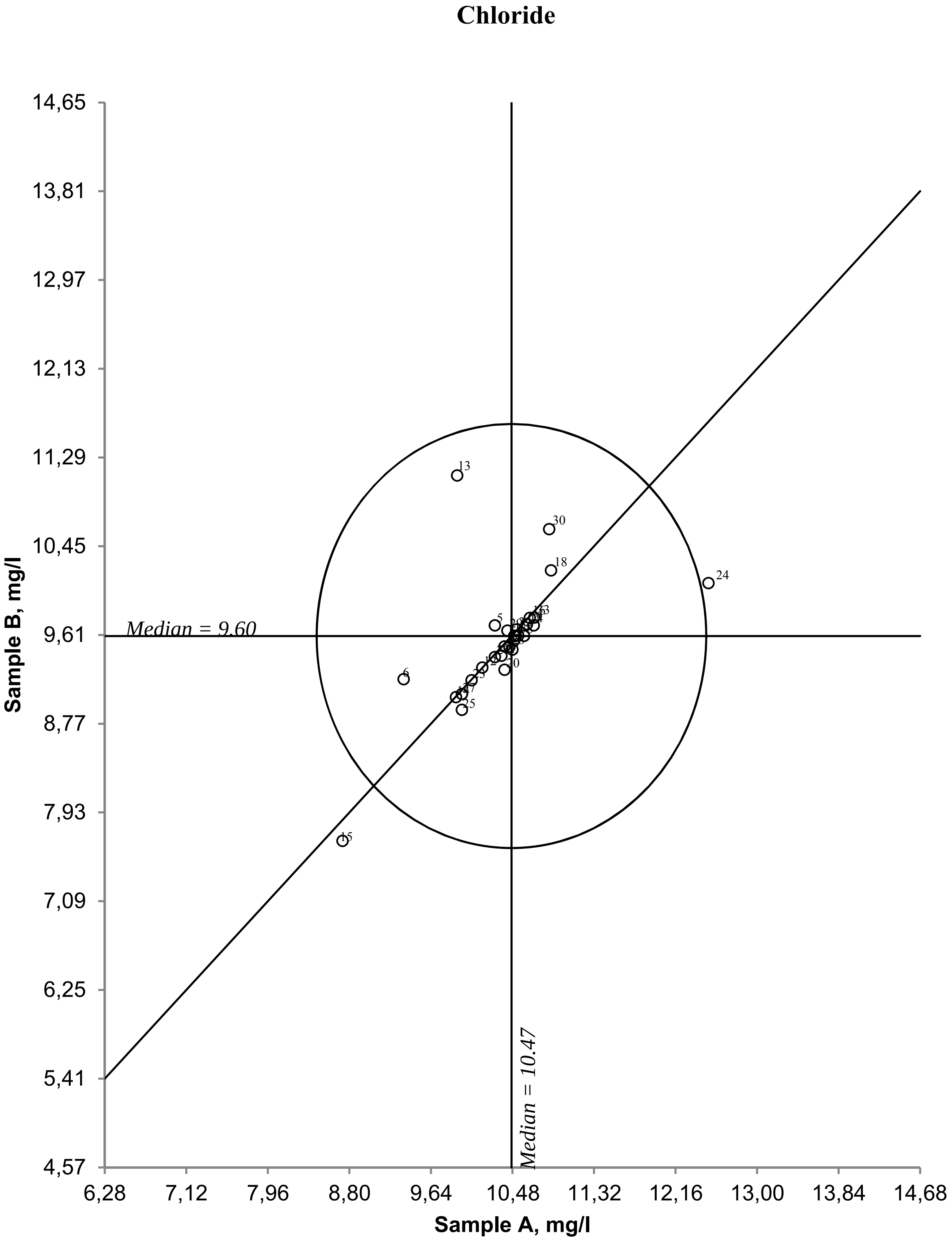

Figure 5. Youden diagram for chloride, sample pair AB
Acceptable limit, given by circle, is 20 %

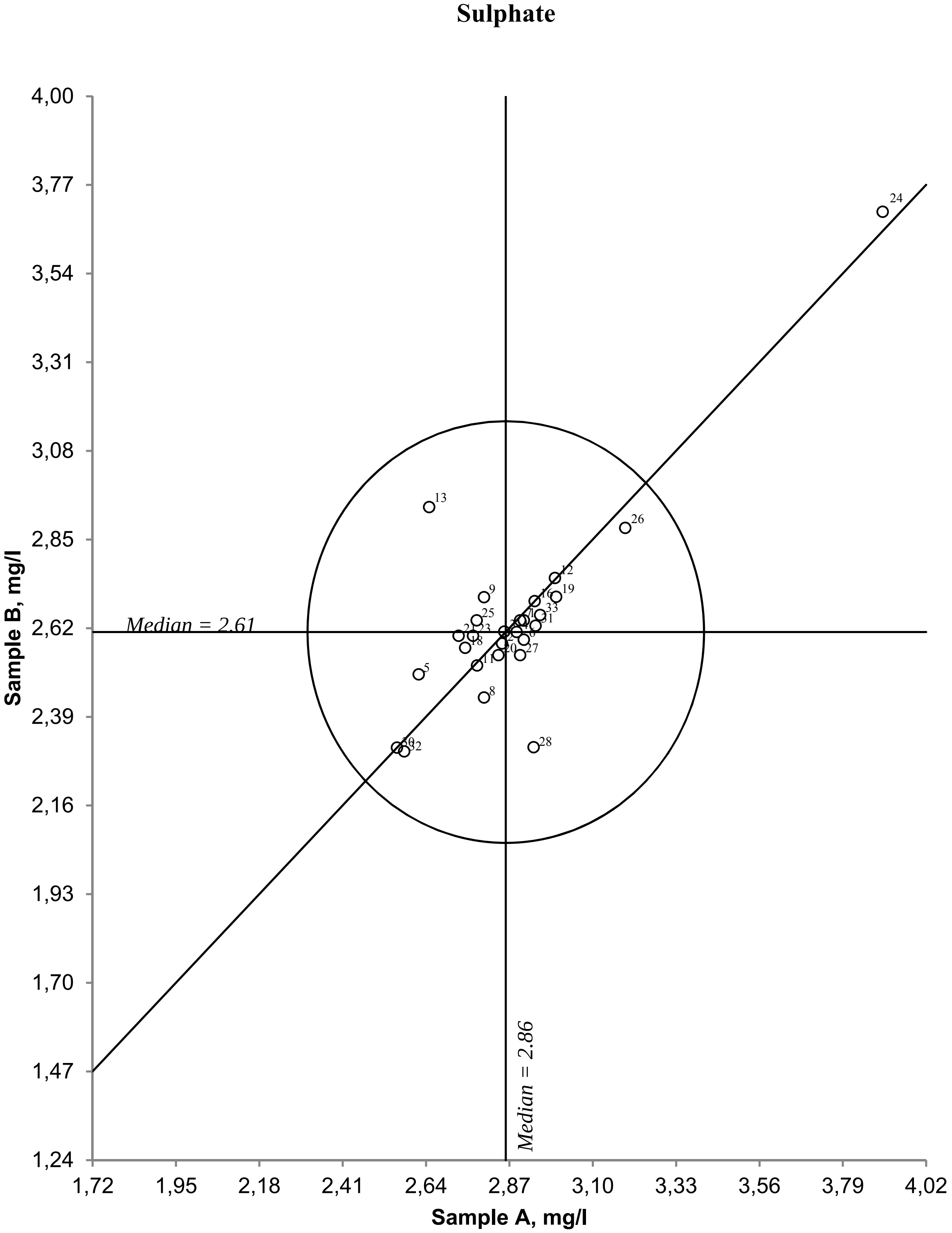

Figure 6. Youden diagram for sulphate, sample pair AB
Acceptable limit, given by circle, is 20 %

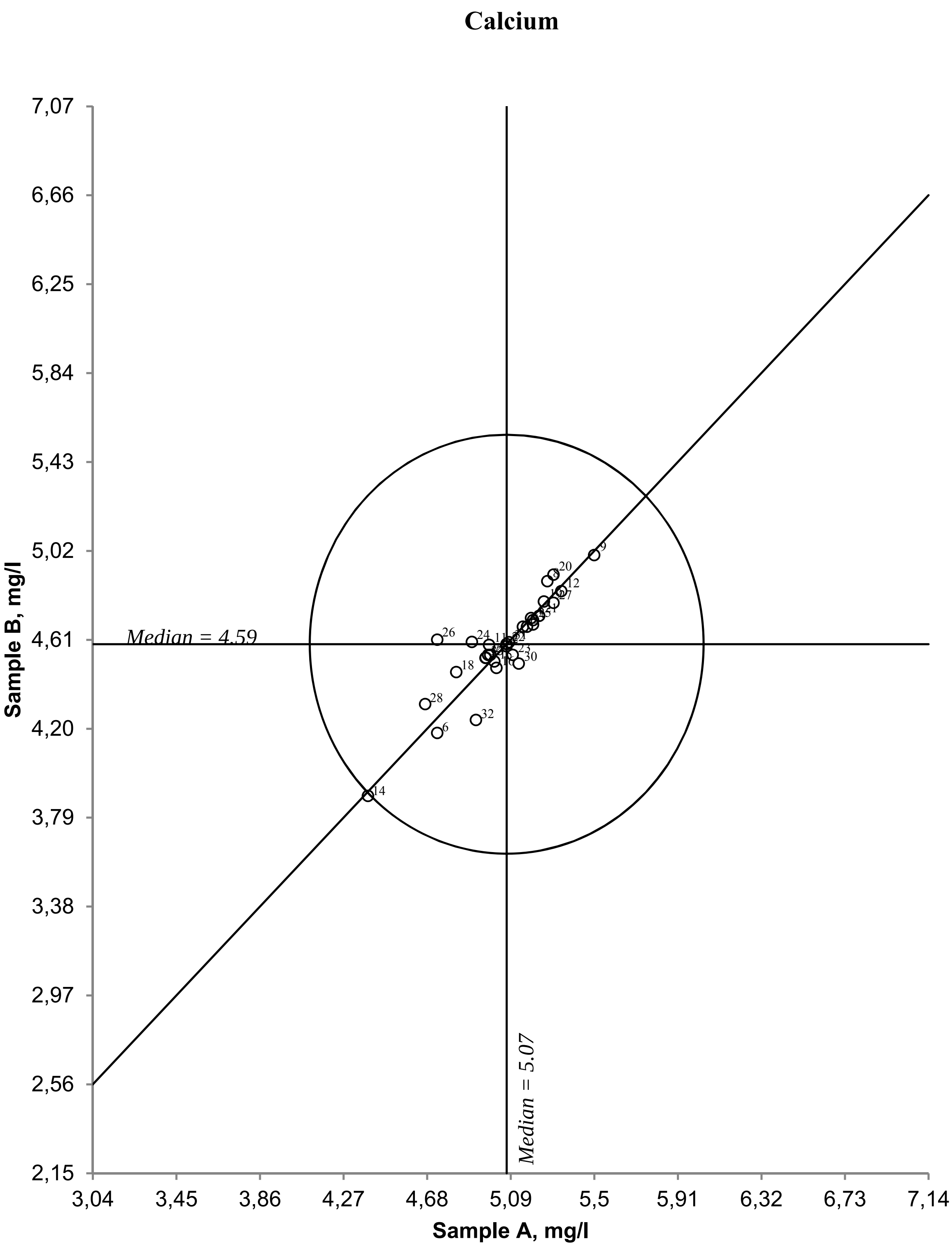

Figure 7. Youden diagram for calcium, sample pair AB
Acceptable limit, given by circle, is 20 %

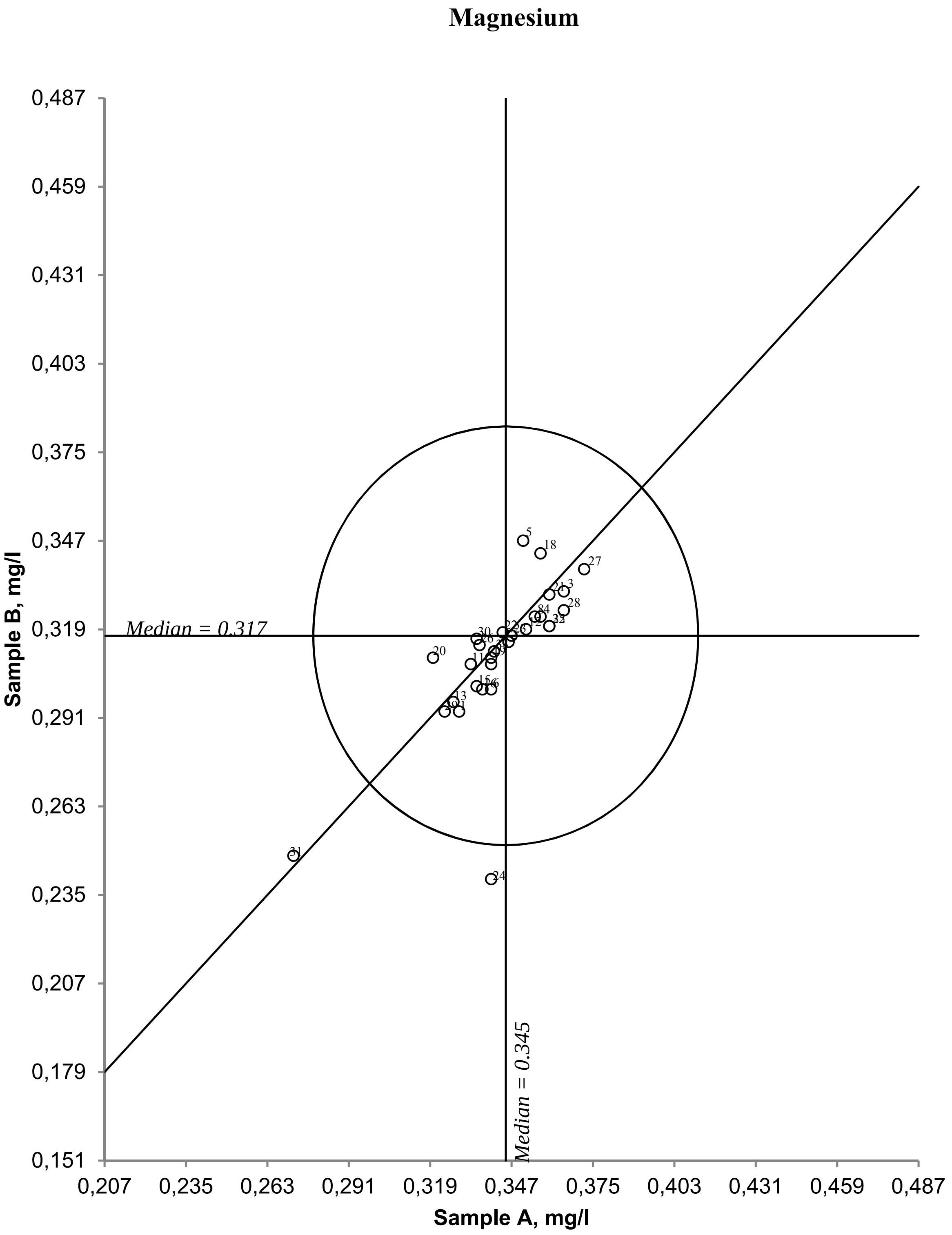

Figure 8. Youden diagram for magnesium, sample pair AB
Acceptable limit, given by circle, is 20 %

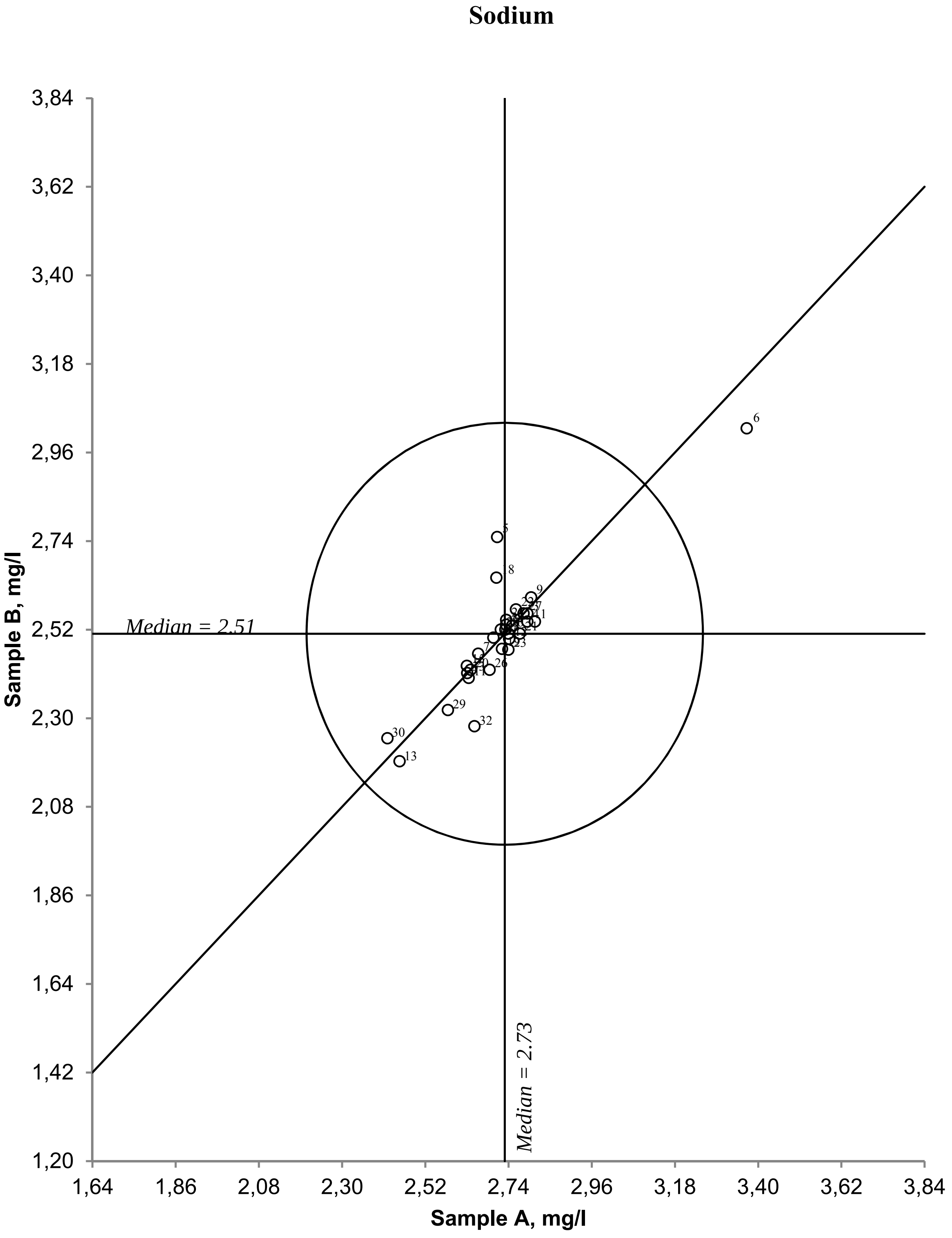

Figure 9. Youden diagram for sodium, sample pair AB
Acceptable limit, given by circle, is 20 %

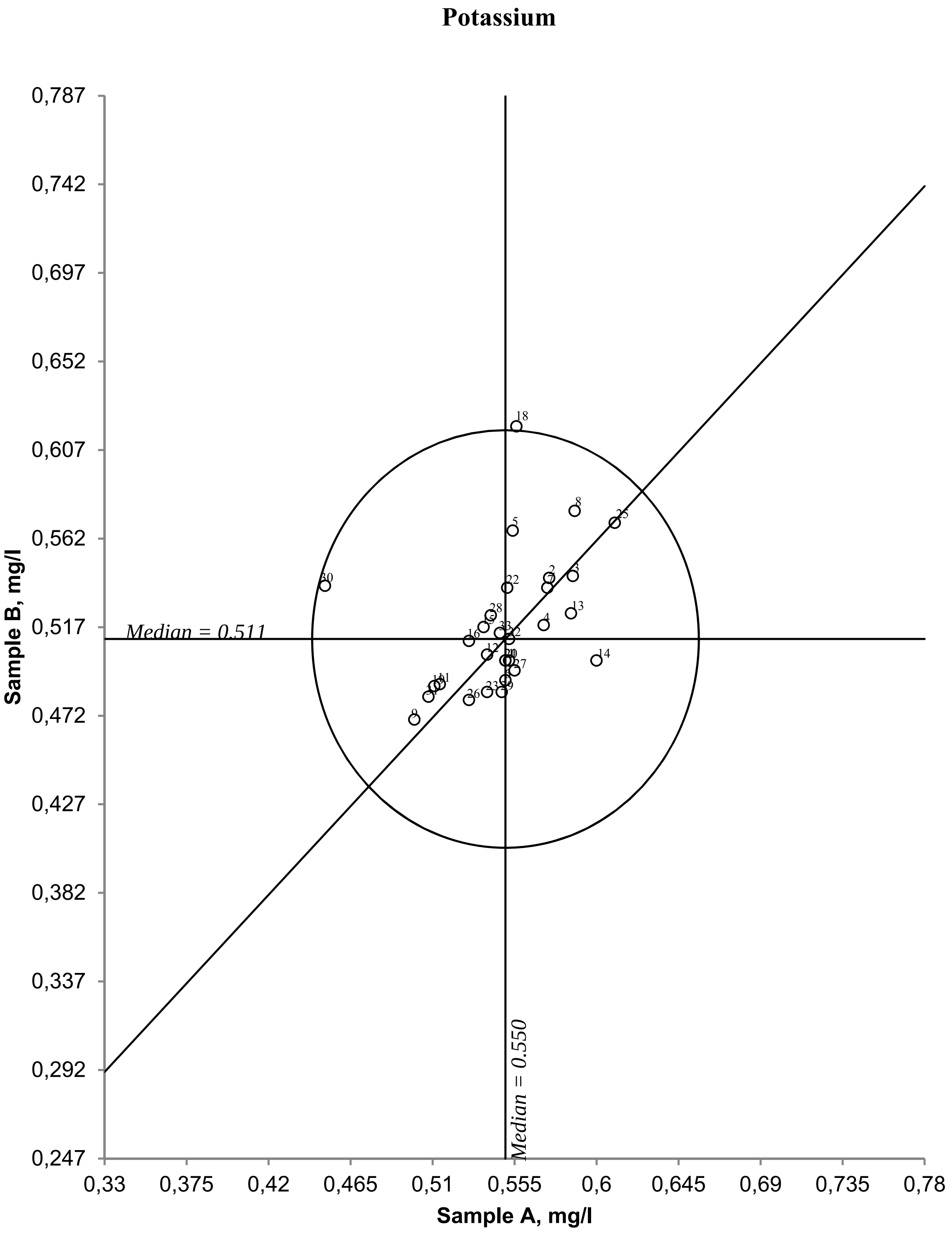

Figure 10. Youden diagram for potassium, sample pair AB
Acceptable limit, given by circle, is 20 %

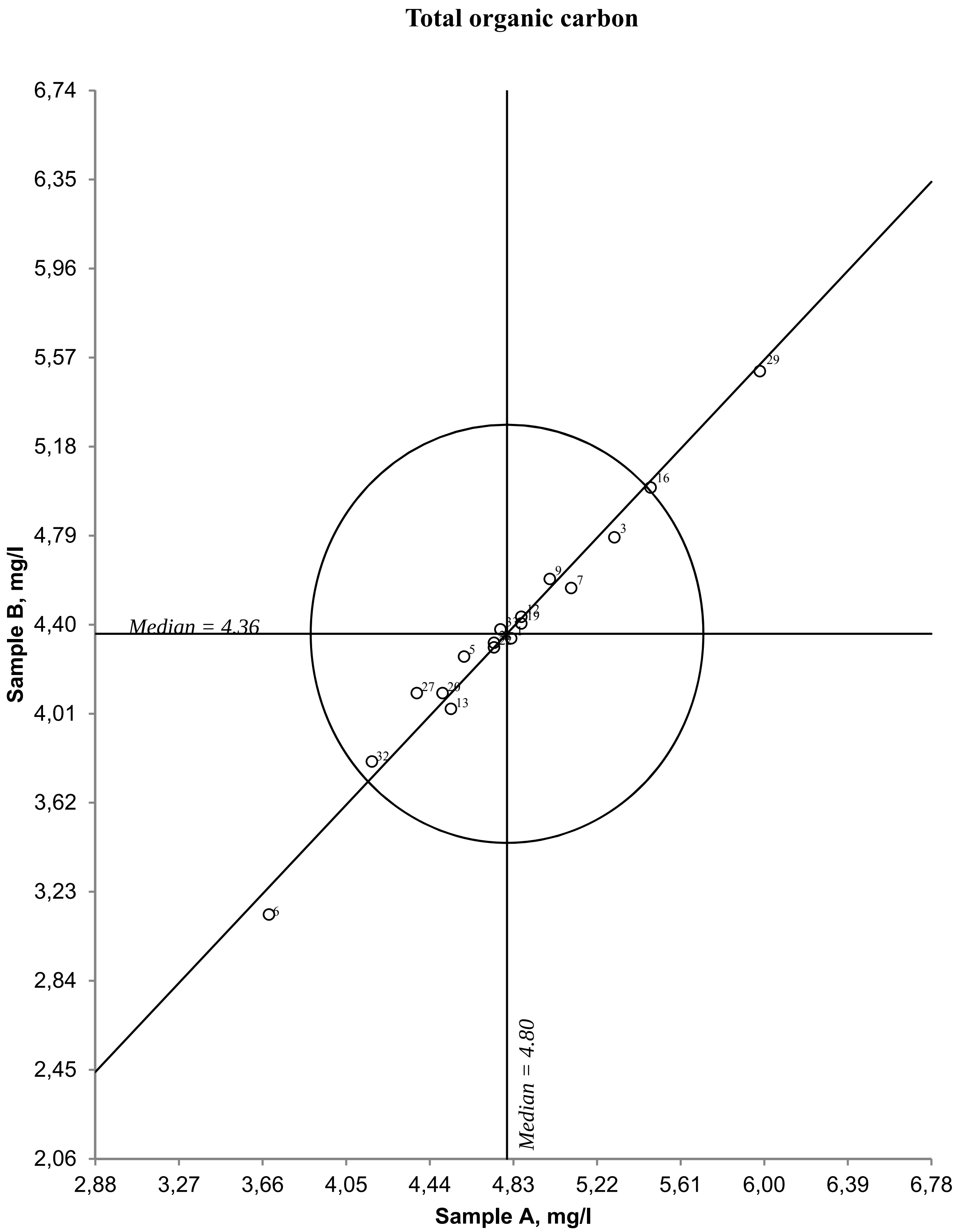

Figure 11. Youden diagram for total organic carbon, sample pair AB
Acceptable limit, given by circle, is 20 %

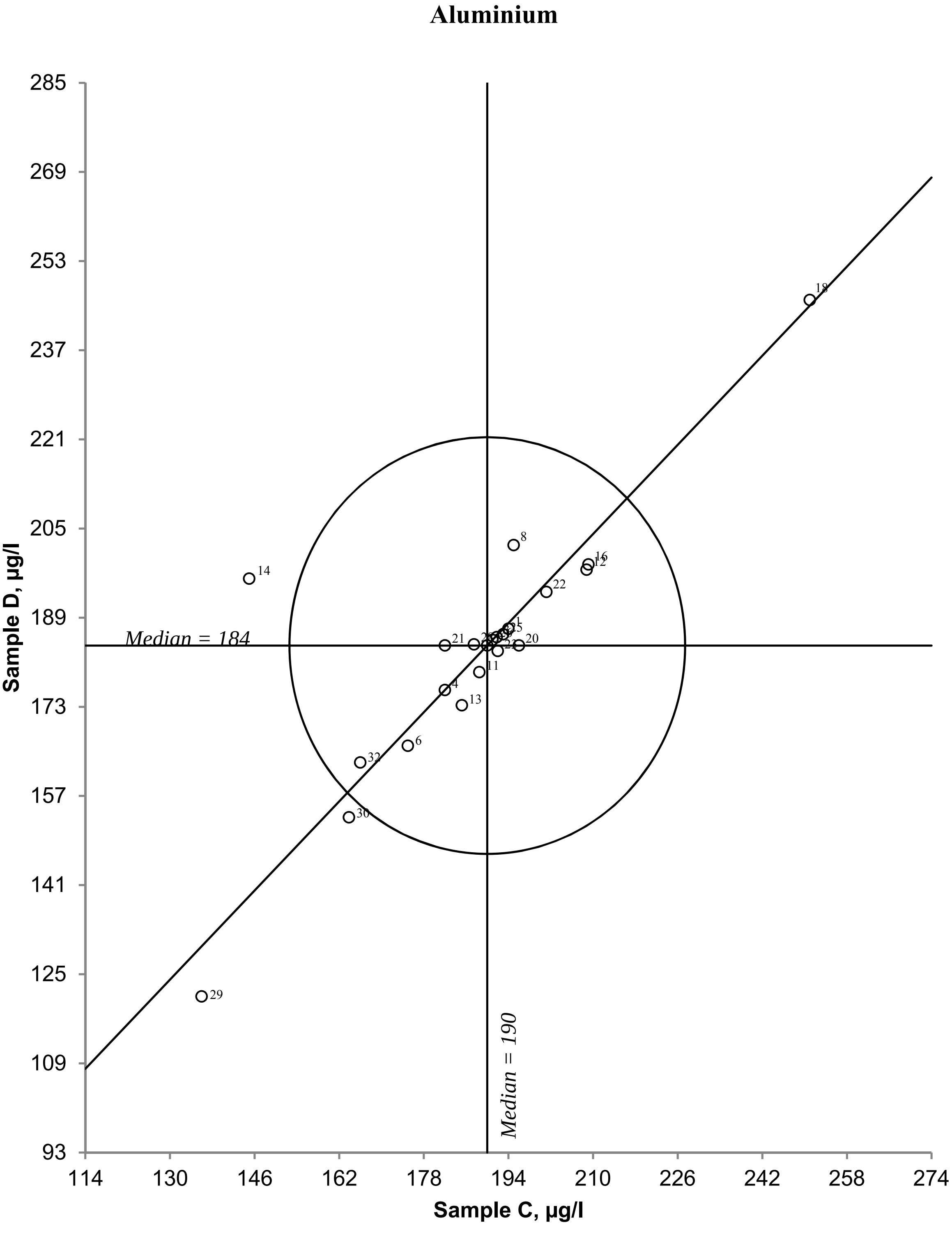

Figure 12. Youden diagram for aluminium, sample pair CD
Acceptable limit, given by circle, is 20 %

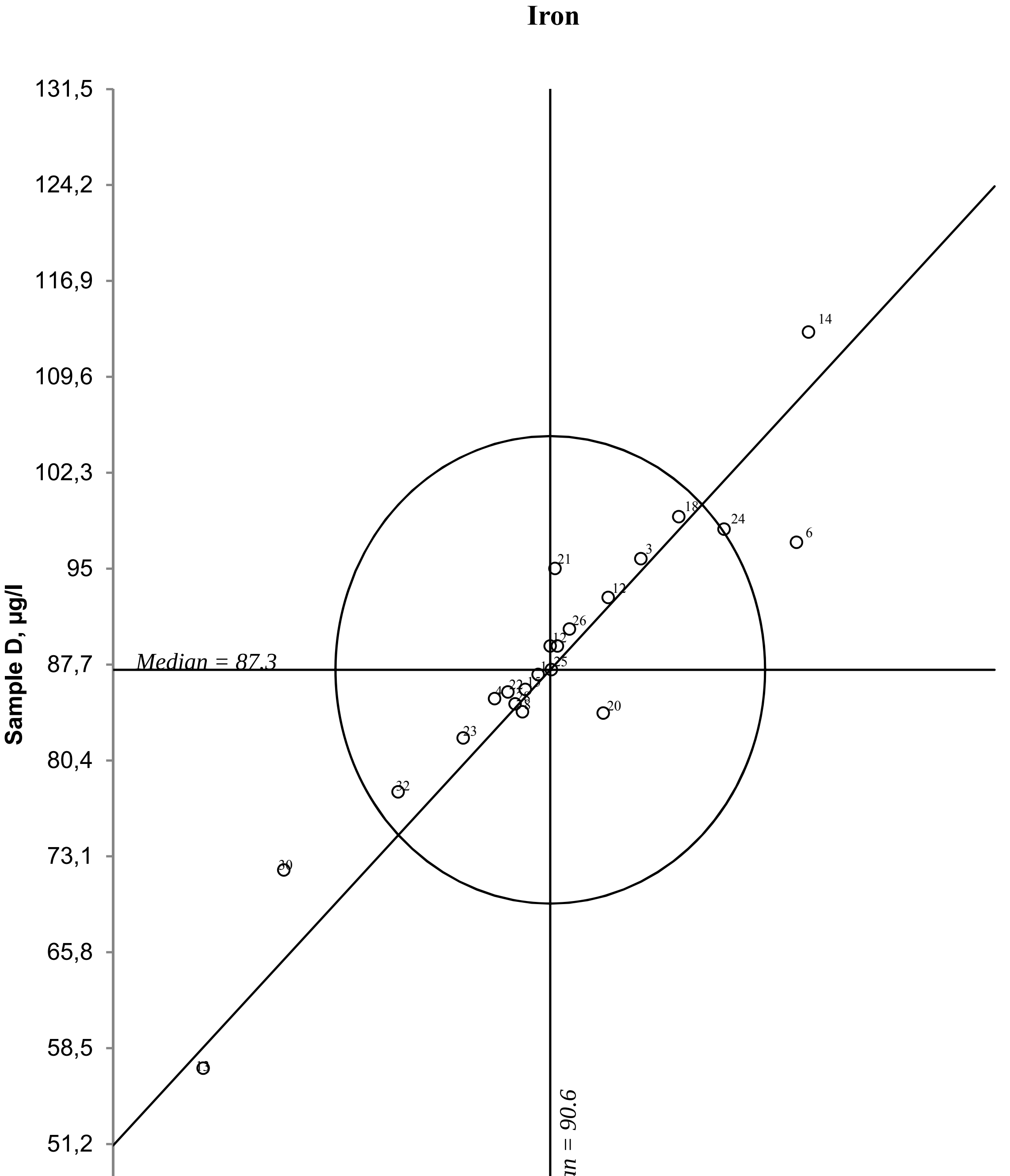

Figure 13. Youden diagram for iron, sample pair CD
Acceptable limit, given by circle, is 20 %

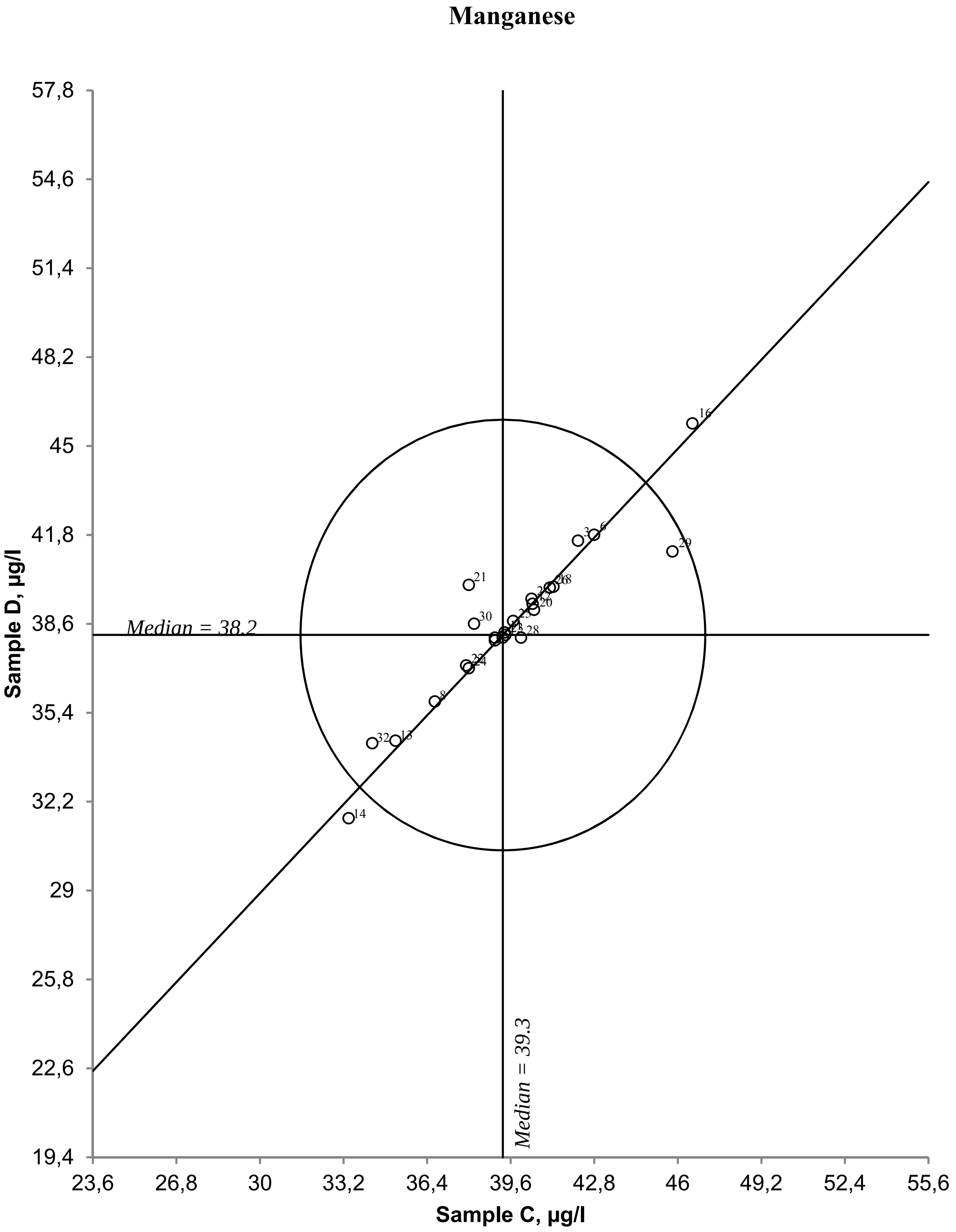

Figure 14. Youden diagram for manganese, sample pair CD
Acceptable limit, given by circle, is 20 %

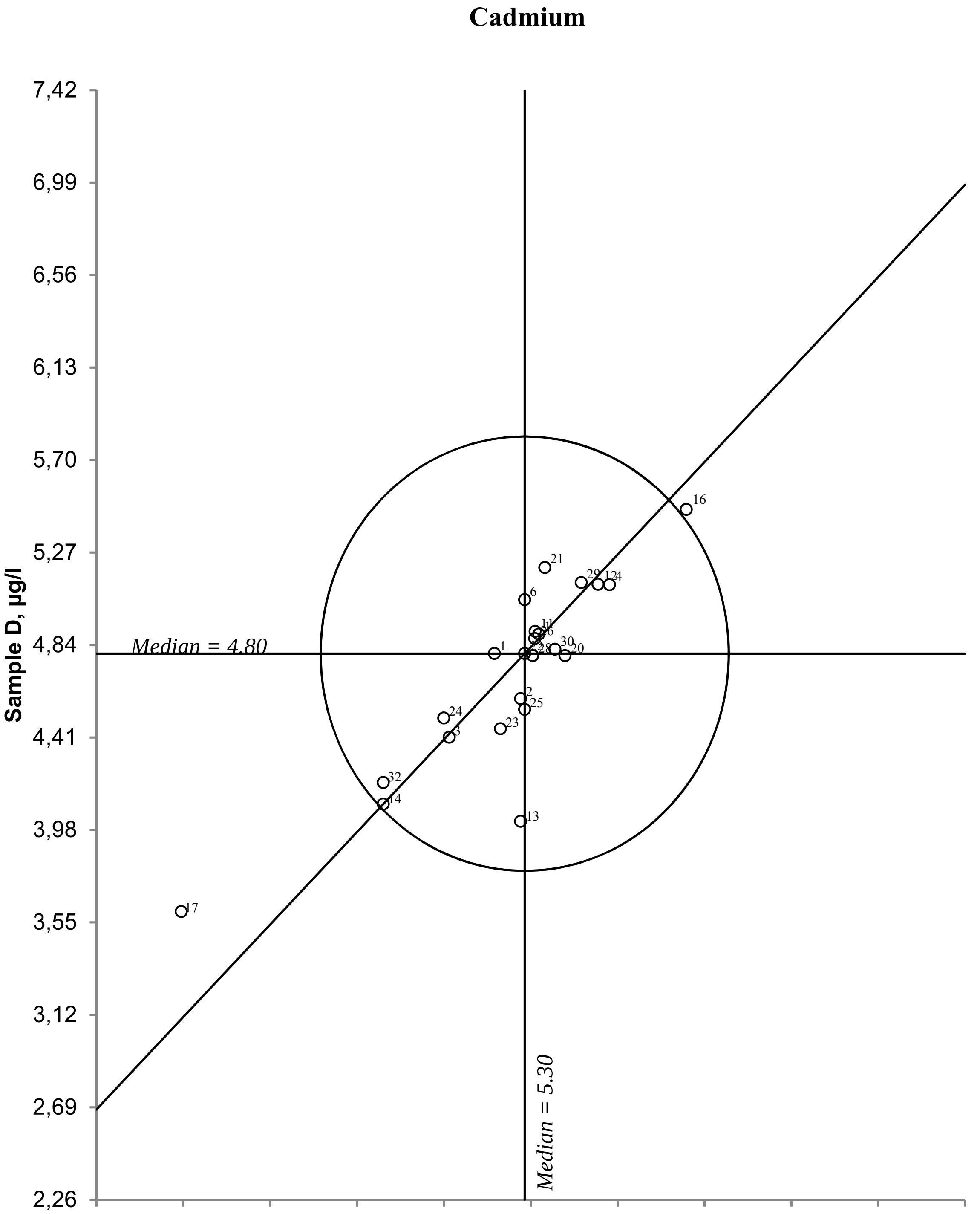

Figure 15. Youden diagram for cadmium, sample pair CD
Acceptable limit, given by circle, is 20 %

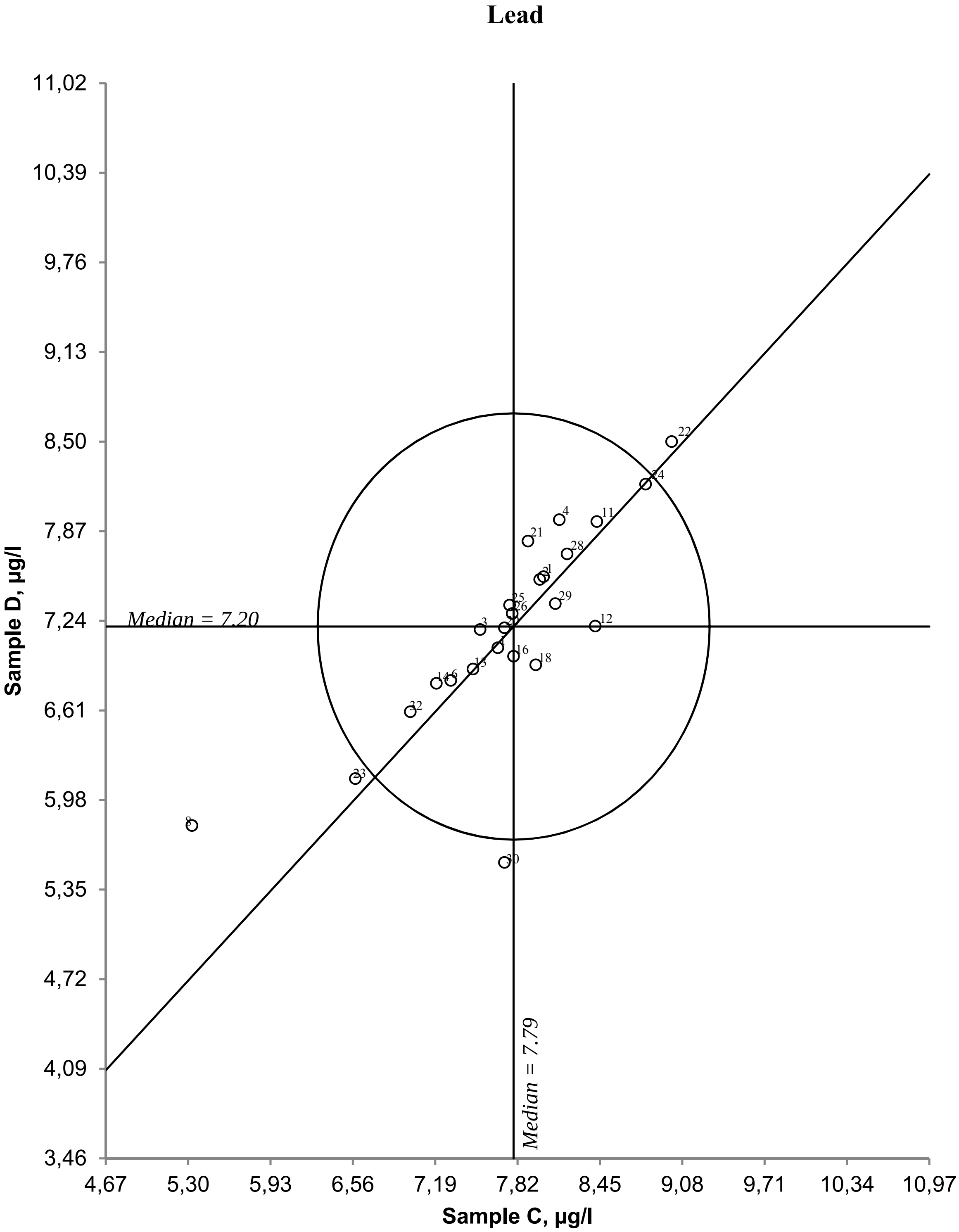

Figure 16. Youden diagram for lead, sample pair CD
Acceptable limit, given by circle, is 20 %

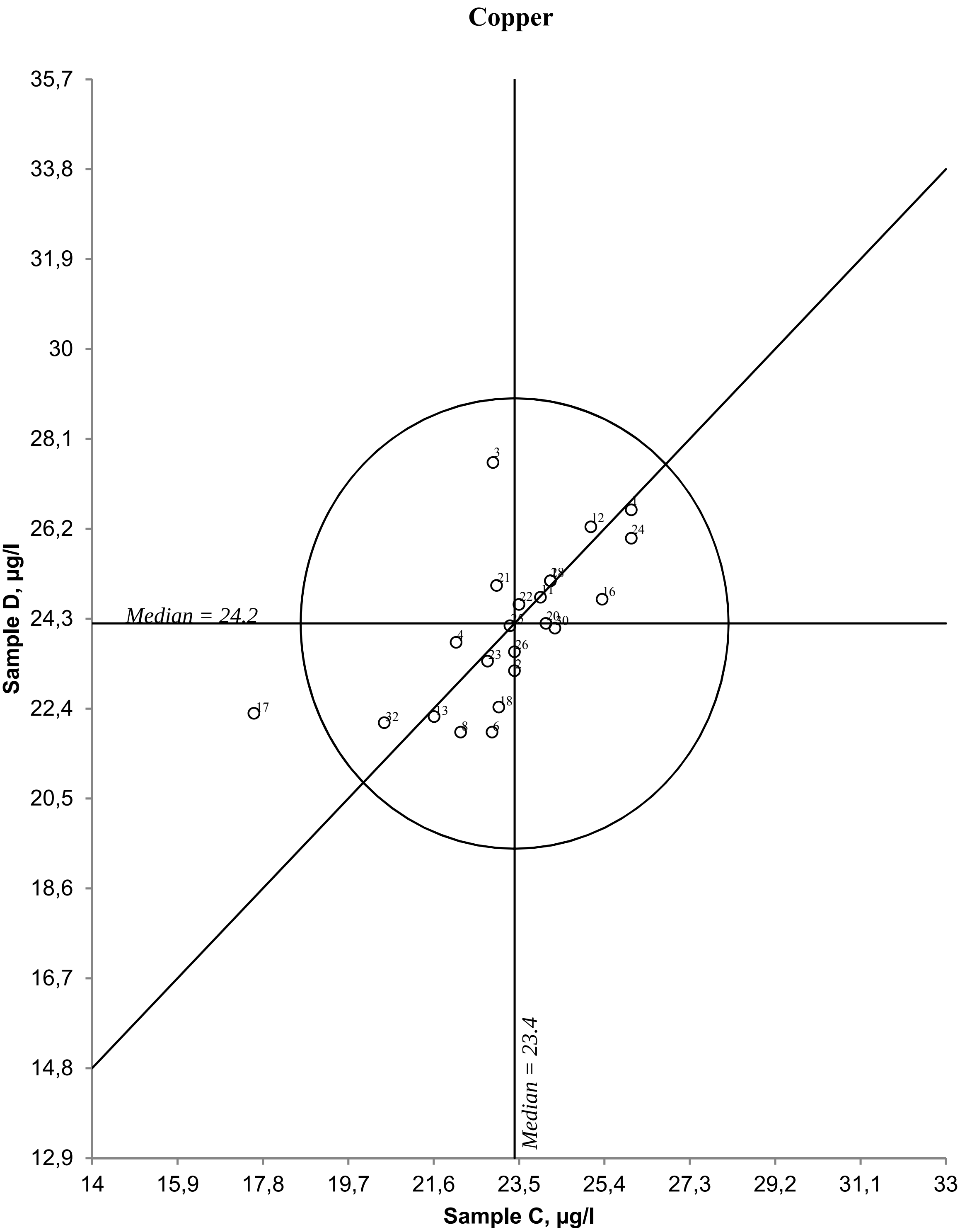

Figure 17. Youden diagram for copper, sample pair CD
Acceptable limit, given by circle, is 20 %

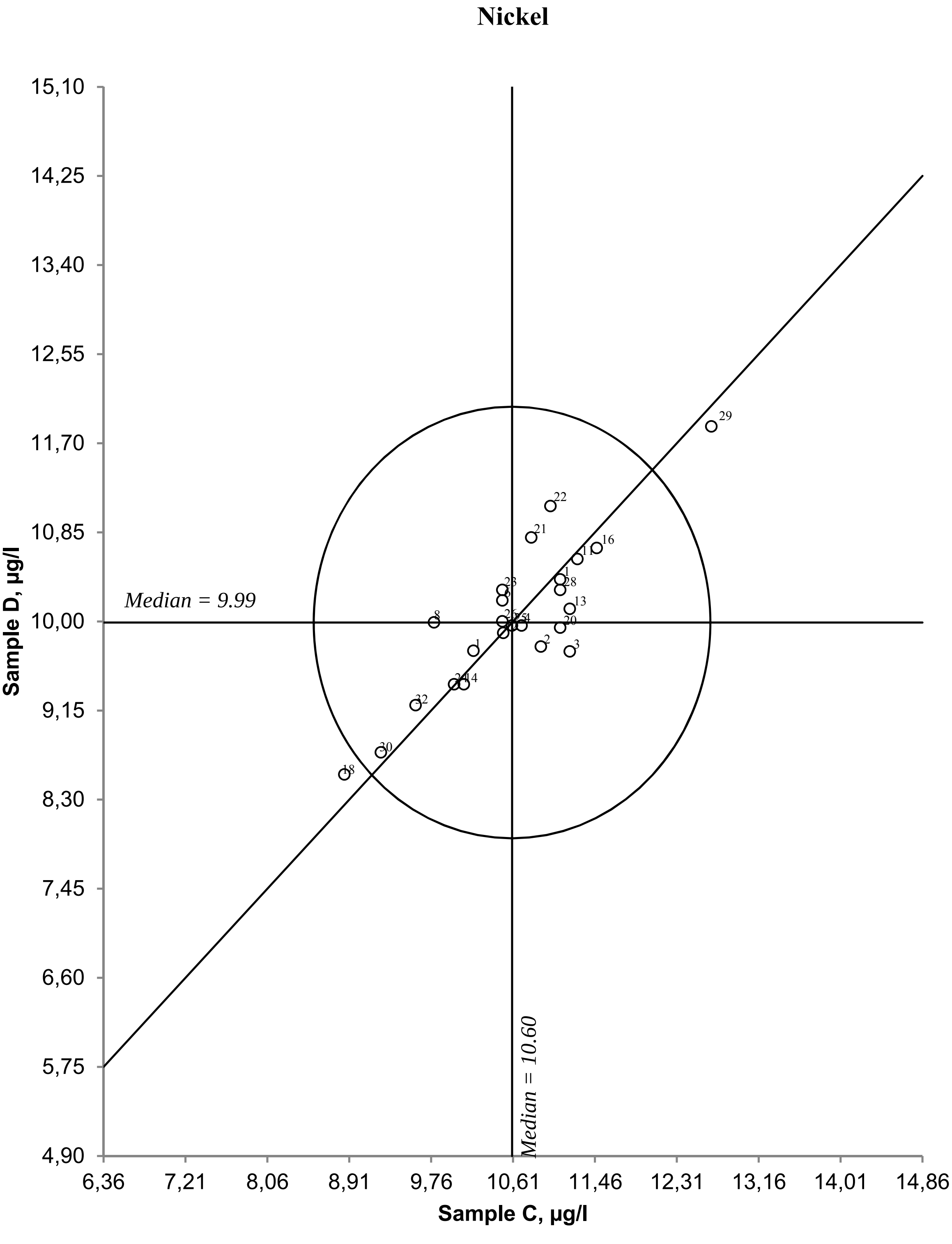

Figure 18. Youden diagram for nickel, sample pair CD
Acceptable limit, given by circle, is 20 %

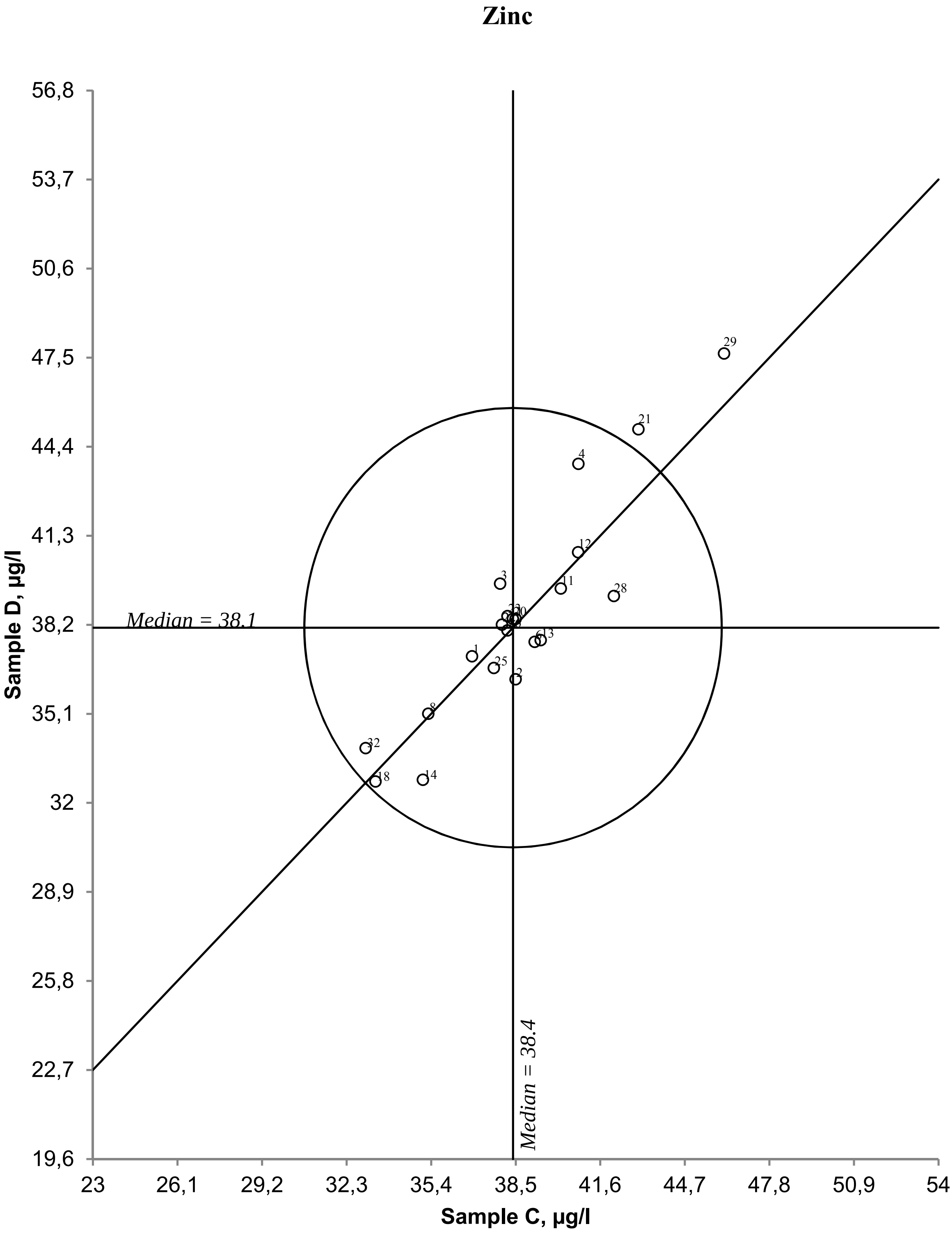

Figure 19. Youden diagram for zinc, sample pair CD
Acceptable limit, given by circle, is 20 %

5. Literature

1. ICP Waters Programme Centre 2010. ICP Waters Programme manual. ICP Waters report 105/2010. NIVA SNO 6074-2010. 91p.

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

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

6. ISO 13528 (2005): Statistical methods for use in proficiency testing by interlaboratory comparisons.

Appendix A.

The participating laboratories

No	Laboratory	Town	Country
1	Estonian Environment Research Centre	Marja 4 D 10617 Tallinn	Estonia
2	Finnish Environment Institute SYKE Laboratory Center	Hakuninmaantie 6 FI-00430 HELSINKI	Finland
3	Swedish University for Agricultural Sciences Aquatic Sciences and Assessment	Box 7050 750 07 UPPSALA	Sweden
4	IVL AB	P.O. Box 53021 SE-400 14 Gothenburg	Sweden
5	Institute of Environmental Protection Warsaw Monitoring Laboratory	POLAND Krucza 5/11D 00-548 Warszawa	Poland
6	Northern Water Problems Institute	A.Nevskogo, 50, Petrozavodsk 185003	Russian Federation
7	Marine Scotland Science Freshwater Laboratory	Faskally, Pitlochry, Perthshire, PH16 5BB, Scotland.	United Kingdom
8	Environmental Pollution Monitoring Center Laboratory of surface and sea	Verkhnerostinskoe sh,51,MUGMS,Murmansk	Russian Federation
9	Staatliche Betriebgesellschaft für Umwelt und Landwirtschaft (BfUL)	Stephanplatz 3 D-09112 Chemnitz	Germany
10	Institute of Environmental Protection-Puszcza Borecka station	Kolektorska 4	Poland
11	University of Helsinki Lab. of Geology and Geography	P.O.Box 64 00014 University of Helsinki	Finland
12	Institute of Biology Komi SC UB RAS	Kommunisticheskaya st.,28 Syktyvkar,167982	Russian Federation
13	Trent University	ERS, 1600 West Bank Drive Peterborough, ON K9J7B8	Canada
14	Center for Environmental Monitoring, Primorsky Dept. for Hydrometeorology & Environmental Monitoring Primorsky CEM	Mordovtseva str. 3 Vladivostok 690990	Russian Federation
15	Natural Resources Wales, Llanelli Laboratory	19 Penyfai Lane Furnace Llanelli Carmarthenshire	United Kingdom
16	Limnological Institute of Russian Academy of Sciences -Siberian Branch LIN SB RAS	Ulanbaatorskaya str. 3 Irkutsk 664033	Russian Federation
17	Institute of Global Climate and Ecology (IGCE) Roshydromet and RAS Russian Academy of Sciences	20-B, Glebovskaya St., Moscow, 107258	Russian Federation
18	Hydrochemical Laboratory by Federal State Enterprise on Water Industry	10 A Stahanovskaya str., Pskov, 180004	Russian Federation
19	Bayerische Landesanstalt fur Wald und Forstwirtschaft Abteilung 2 - Klima und Boden	Hans-Carl-von-Carlowitz-Platz 1, D-85354 Freising	Germany

No	Laboratory	Town	Country
20	Norsk institutt for vannforskning	Gaustadalléen 21 0439 OSLO	Norway
21	Bayerisches Landesamt fur Umwelt	Ref 73 Bürgerm-Ulrich-Str. 160 D-86179 Augsburg	Germany
22	Finnish Forest Research Institute Vantaa Laboratory	Jokiniemenkuja 1 FIN-01370 Vantaa	Finland
23	Regional Laboratory for Analytical Control and Analysis (RLAC&A)	199004, 26, Srednii pr, V.O. St. Petersburg	Russian Federation
24	Test Laboratory of Water Quality (Vodokanal)	Gogolja St. 60, 185035 Petrozavodsk Vodokanal	Russian Federation
25	Insitute of Industrial Ecology Problems of the North (INEP) Group ICP methods of analysis	184209 Apatity, Akademgorodok 14A, Murmansk reg.	Russian Federation
26	Environment Agency Starcross Laboratory,	Staplake Mount, Starcross, Devon, UK, EX6 8FD	United Kingdom
27	MOEE, DORSET Laboratory	P.O. Box 39, Dorset, Ontario P0A 1E0	Canada
28	NILU, Avd. uorganisk analyse	Postboks 100 2027 Kjeller	Norway
29	Büsgen-Institute - Soil Science of Temperate Ecosystems	D-37077 Goettingen Buesgenweg 2	Germany
30	Institute of Botany PAS	PAN Instytut Botaniki 31-512 Kraków ul. Lubicz 46	Poland
31	ISSeP Colfontaine Zoning Schweitzer	Rue de la Platinerie B-7340 COLFONTAINE	Belgium
32	Laboratoire d'Ecologie Fonctionnelle et Environnement (ECOLAB)	Avenue Agrobiopole 31326 Castanet Tolosan	France
33	Institut fur Ökologie	Technikerstrasse 25 6020 Innsbruck	Austria

Number of participating laboratories from the different countries represented in intercomparison 1428

Country	No. of labs.	Country	No. of labs.
Austria	1	Germany	4
Belgium	1	Norway	2
Canada	2	Poland	3
Estonia	1	Russia	10
Finland	3	Sweden	2
France	1	United Kingdom	3

Total: 12 countries

Appendix B.

Preparation of samples

The sample solutions were prepared from water collected in the lake Steinbruvannet (Latitude: 59.9781667; Longitude: 10.883093700000018; Altitude: 265 m) just outside the city of Oslo, in Norway. The water, collected in 25 litre plastic containers, was brought to the laboratory, stored for about two weeks and 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.

In the current edition, an important modification of the pH of was also carried out. The water, with an initial pH about 7, was spiked with HCl to get a solution with a pH about 6. Due to the natural buffering capacity of the water taken, the pH had to be measured periodically and re-adjusted with additional amounts of diluted acid until a pH about 6 that remained stable for 2 days was observed.

The samples for the set CD were prepared by spiking the filtered water with stock solutions of stoichiometric compounds containing heavy metals and preserved by addition of 5 ml concentrated nitric acid pr. litre 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 their deliver to the participating laboratories.

Appendix C.

Treatment of analytical data

The intercomparison was carried out by the method of Youden. This procedure requires two samples to be analyzed, and 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 ± 3s, are omitted. The remaining results are used for a final calculation, the results of which are presented in the tables 5.1 - 5.19. Results being omitted from the calculations are marked with the letter "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 3. Estimation of uncertainty of the assigned true values

Parameter and unit	Sample	True value	Total no.	Robust std.dev.	Uncertainty	Expanded uncertainty
pH	A	5,81	30	0,137	0,031	0,062
	B	5,90	30	0,131	0,030	0,060
Conductivity	A	5,26	28	0,145	0,034	0,069
mS/m	B	4,79	28	0,122	0,029	0,057
Alkalinity	A	0,021	9	0,0050	0,0021	0,0041
mmol/l	B	0,022	10	0,0044	0,0017	0,0035
Nitrate + nitrite-nitrogen	A	105,4	26	13,29	3,26	6,52
µg N/l	B	77,0	23	42,73	11,14	22,27
Chloride	A	10,47	28	0,345	0,082	0,163
mg/l	B	9,60	28	0,350	0,083	0,166
Sulphate	A	2,86	27	0,141	0,034	0,068
mg/l	B	2,61	26	0,115	0,028	0,056
Calcium	A	5,07	31	0,207	0,046	0,093
mg/l	B	4,59	30	0,163	0,037	0,075
Magnesium	A	0,345	28	0,0147	0,0035	0,0070
mg/l	B	0,317	28	0,0155	0,0037	0,0073
Sodium	A	2,73	29	0,072	0,017	0,034
mg/l	B	2,51	29	0,093	0,022	0,043
Potassium	A	0,550	29	0,0276	0,0064	0,0128
mg/l	B	0,511	29	0,0282	0,0065	0,0131
Total organic carbon	A	4,80	17	0,451	0,137	0,273
mg/l	B	4,36	17	0,387	0,117	0,235
Aluminium	C	190	21	14,5	3,9	7,9
µg/l	D	184	20	12,1	3,4	6,8
Iron	C	90,6	22	9,62	2,56	5,13
µg/l	D	87,3	22	8,11	2,16	4,32
Manganese	C	39,3	23	2,38	0,62	1,24
µg/l	D	38,2	23	2,27	0,59	1,19
Cadmium	C	5,30	23	0,321	0,084	0,167
µg/l	D	4,80	23	0,424	0,111	0,221
Lead	C	7,79	24	0,551	0,141	0,281
µg/l	D	7,20	24	0,656	0,167	0,335
Copper	C	23,4	23	1,44	0,38	0,75
µg/l	D	24,2	23	1,70	0,44	0,89
Nickel	C	10,60	24	0,697	0,178	0,356
µg/l	D	9,99	24	0,623	0,159	0,318
Zinc	C	38,4	22	3,25	0,87	1,73
µg/l	D	38,1	21	3,27	0,89	1,78

Appendix D

Table 4. The results of the participating laboratories.

Lab. nr.	pH		Conductivity, mS/m		Alkalinity, mmol/l		Nitrate + nitrite-nitrogen, µg N/l		Chloride, mg/l		Sulphate, mg/l		Calcium, mg/l		Magnesium, mg/l	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
1	5,83	5,91	5,20	4,73	0,066	0,065	113,0	108,0	10,50	9,56	2,91	2,64	5,15	4,67	0,329	0,293
2	5,84	5,87	5,30	4,80	0,026	0,030	102,0	25,0	10,40	9,50	2,85	2,58	5,07	4,58	0,346	0,315
3	5,65	5,83	5,21	4,75	0,019	0,018	113,9	108,9	10,54	9,60	2,86	2,61	5,20	4,68	0,365	0,331
4	5,78	5,90	5,24	4,81	0,022	0,022	103,0	69,0	10,70	9,70	2,89	2,61	5,19	4,71	0,357	0,323
5	5,96	5,87					90,0	28,0	10,30	9,70	2,62	2,50	5,17	4,67	0,351	0,347
6	5,40	6,03	5,30	4,89	0,009	0,021	107,0	110,0	9,36	9,19	2,91	2,59	4,73	4,18	0,340	0,300
7	5,81	5,84	5,02	4,60	0,020	0,023	107,8	0,0	10,48	9,47	2,90	2,64	4,98	4,54	0,340	0,308
8	5,81	5,87	5,24	4,57			109,0	87,0	10,60	9,60	2,80	2,44	5,27	4,88	0,355	0,323
9	5,80	5,90	5,53	4,84	0,045	0,039	100,0	90,0	10,50	9,60	2,80	2,70	5,50	5,00	0,750	0,730
10	5,85	6,05	5,26	4,77												
11	6,03	6,07	5,18	4,68	0,021	0,025	89,0	36,0	10,52	9,60	2,78	2,52	4,98	4,59	0,333	0,308
12	5,80	5,95	5,14	4,68	0,032	0,026	115,5	103,1	10,17	9,30	3,00	2,75	5,34	4,83	0,352	0,319
13	6,15	6,14	5,14	4,68	0,035	0,029	63,2	64,6	9,91	11,12	2,65	2,93	4,97	4,53	0,327	0,296
14	5,84	5,90	5,03	4,97	0,025	0,027	250,0	310,0	9,90	9,02	10,00	8,90	4,39	3,89	1,200	0,890
15	5,78	5,84	4,71	4,32	0,013	0,017	153,0	90,0	8,73	7,66	1,44	1,38	5,01	4,51	0,335	0,301
16	6,02	6,28	5,31	4,83	0,040	0,042	76,8	0,2	10,66	9,77	2,94	2,69	5,02	4,48	0,337	0,300
17																
18	5,80	5,84	5,10	4,66	0,050	0,052	0,1	0,1	10,88	10,22	2,75	2,57	4,82	4,46	0,357	0,343
19	5,84	5,93	5,01	4,53			107,8	47,8	10,63	9,71	3,00	2,70	5,25	4,79	0,340	0,310
20	6,03	6,11	5,24	4,78	0,058	0,059	95,0	45,0	10,40	9,28	2,84	2,55	5,30	4,91	0,320	0,310
21	5,89	5,94	5,28	4,79			0,1	0,1	10,30	9,40	2,73	2,60	5,23	4,72	0,360	0,330
22	5,44	5,83	5,38	4,91			109,5	9,7					5,07	4,59	0,344	0,318
23	5,66	5,73	5,44	4,90			99,6	57,6	10,06	9,18	2,77	2,60	5,10	4,54	0,347	0,317
24	5,84	5,92	5,49	5,04					12,50	10,10	3,90	3,70	4,90	4,60	0,340	0,240
25	5,37	5,32	5,10	4,80	0,014	0,022			9,96	8,90	2,78	2,64	5,20	4,70	0,360	0,320
26											3,19	2,88	4,73	4,61	0,336	0,314
27	5,76	5,92	5,26	4,76	0,033	0,032	112,0	98,0	9,96	9,05	2,90	2,55	5,30	4,78	0,372	0,338
28	5,77	5,82	53,50	47,90			117,0	24,1	10,45	9,50	2,94	2,31	4,67	4,31	0,365	0,325
29	6,01	6,15	5,48	4,65			114,0	74,0	10,43	9,65	0,83	0,75	4,99	4,54	0,324	0,293
30	6,47	6,38	5,29	4,89			68,0	2,9	10,86	10,61	2,56	2,31	5,13	4,50	0,335	0,316
31	5,80	5,87	5,32	4,86			97,8	32,6	10,37	9,41	2,94	2,63	5,08	4,60	0,272	0,247
32	5,87	5,76	5,14	4,68	0,074	0,060	84,0	80,0	10,52	9,66	2,58	2,30	4,92	4,24	0,360	0,320
33	5,79	5,79	5,26	4,80	0,021	0,021	110,0	18,0	10,71	9,77	2,96	2,65	4,97	4,53	0,341	0,312

Lab. Nr	Sodium, mg/l		Potassium, mg/l		Total organic carbon, mg/l		Aluminium, µg/l		Iron, µg/l	
	A	B	A	B	A	B	C	D	C	D
1	2,81	2,54	0,552	0,500	4,82	4,34	194	187	90,6	89,1
2	2,75	2,53	0,574	0,542			190	184	91,2	89,1
3	2,79	2,56	0,587	0,543	5,30	4,78	192	186	98,1	95,8
4	2,79	2,54	0,571	0,518			182	176	86,0	85,1
5	2,71	2,75	0,554	0,566	4,60	4,26				
6	3,37	3,02	0,550	0,490	3,69	3,13	175	166	111,0	97,0
7	2,66	2,46	0,573	0,537	5,10	4,56				
8	2,74	2,51	0,588	0,576			195	202	88,3	84,1
9	2,80	2,60	0,500	0,470	5,00	4,60				
10										
11	2,64	2,40	0,514	0,488			189	179	89,6	86,9
12	2,74	2,50	0,540	0,503	4,87	4,43	209	198	95,4	92,8
13	2,45	2,19	0,586	0,524	4,54	4,03	185	173	61,9	57,0
14	2,70	2,50	0,600	0,500			145	196	112,0	113,0
15	2,63	2,43	0,538	0,517					88,5	85,8
16	2,73	2,52	0,530	0,510	5,47	5,00	209	199		
17										
18	2,71	2,65	0,556	0,619			251	246	101,3	99,0
19	2,72	2,47	0,511	0,487	4,87	4,41				
20	2,64	2,42	0,550	0,500	4,50	4,10	196	184	95,0	84,0
21	2,77	2,51	0,550	0,500	4,74	4,32	182	184	91,0	95,0
22	2,76	2,57	0,551	0,537	4,74	4,30	201	194	87,1	85,6
23	2,74	2,47	0,540	0,484			192	183	83,4	82,1
24							320	210	105,0	98,0
25	2,72	2,52	0,610	0,570			193	186	90,7	87,3
26	2,69	2,42	0,530	0,480			191	185	92,2	90,4
27	2,78	2,56	0,555	0,495	4,38	4,10				
28	2,73	2,54	0,542	0,523			188	184	87,7	84,7
29	2,58	2,32	0,548	0,484	5,98	5,51				
30	2,42	2,25	0,451	0,538			164	153	68,5	72,1
31	2,73	2,53	0,508	0,482						
32	2,65	2,28	0,552	0,511	4,17	3,80	166	163	78,0	78,0
33	2,63	2,41	0,547	0,514	4,77	4,38				

Lab. Nr	Manganese, µg/l		Cadmium, µg/l		Lead, µg/l		Copper, µg/l		Nickel, µg/l		Zinc, µg/l	
	C	D	C	D	C	D	C	D	C	D	C	D
1	39,0	38,1	5,37	4,89	8,02	7,55	26,0	26,6	11,10	10,40	38,5	38,4
2	40,4	39,5	5,28	4,59	7,99	7,53	23,4	23,2	10,90	9,76	38,5	36,3
3	42,2	41,6	4,93	4,41	7,53	7,18	22,9	27,6	11,20	9,71	37,9	39,6
4	39,3	38,1	5,72	5,12	8,14	7,95	22,1	23,8	10,70	9,96	40,8	43,8
5												
6	42,8	41,8	5,30	5,05	7,31	6,82	22,9	21,9	10,50	10,20	39,2	37,6
7												
8	36,7	35,8	2,98	2,81	5,33	5,80	22,2	21,9	9,79	9,99	35,3	35,1
9												
10												
11	39,4	38,3	5,35	4,90	8,43	7,94	24,0	24,8	11,28	10,60	40,2	39,5
12	40,4	39,3	5,66	5,12	8,42	7,20	25,1	26,2	10,51	9,89	40,8	40,7
13	35,2	34,4	5,28	4,02	7,48	6,90	21,6	22,2	11,20	10,12	39,4	37,7
14	33,4	31,6	4,60	4,10	7,20	6,80	2550,0	34,8	10,10	9,40	35,1	32,8
15												
16	46,6	45,8	6,10	5,47	7,79	6,99	25,4	24,7	11,48	10,70	66,0	55,7
17			3,60	3,60	4,00	4,00	17,6	22,3				
18	41,2	39,9	11,92	11,36	7,96	6,93	23,1	22,4	8,86	8,54	33,4	32,7
19												
20	40,5	39,1	5,50	4,79	7,72	7,19	24,1	24,2	11,10	9,94	38,4	38,4
21	38,0	40,0	5,40	5,20	7,90	7,80	23,0	25,0	10,80	10,80	43,0	45,0
22	37,9	37,1	5,30	4,80	9,00	8,50	23,5	24,6	11,00	11,10	38,0	38,2
23	39,4	38,2	5,18	4,45	6,58	6,13	22,8	23,4	10,50	10,30	38,2	38,5
24	38,0	37,0	4,90	4,50	8,80	8,20	26,0	26,0	10,00	9,40	29,0	64,0
25	39,7	38,7	5,30	4,54	7,76	7,35	23,3	24,2	10,60	9,96	37,7	36,7
26	41,1	39,9	5,35	4,87	7,78	7,29	23,4	23,6	10,50	10,00	38,2	38,0
27												
28	40,0	38,1	5,34	4,79	8,20	7,71	24,2	25,1	11,10	10,30	42,1	39,2
29			5,58	5,13	8,11	7,36	33,3	47,0	12,67	11,86	46,1	47,6
30	38,2	38,6	5,45	4,82	7,72	5,54	24,3	24,1	9,24	8,75	9,8	10,2
31												
32	34,3	34,3	4,60	4,20	7,00	6,60	20,5	22,1	9,60	9,20	33,0	33,9
33												

Table 5.1. Statistics
pH

Sample A

Analytical method: All
Unit:

Number of participants	31	Range	0,75
Number of omitted results	2	Variance	0,02
True value	5,81	Standard deviation	0,16
Mean value	5,82	Relative standard deviation	2,7%
Median value	5,81	Relative error	0,2%

Analytical results in ascending order:

25	5,37	O	9	5,80		32	5,87	
6	5,40		18	5,80		21	5,89	
22	5,44		12	5,80		5	5,96	
3	5,65		8	5,81		29	6,01	
23	5,66		7	5,81		16	6,02	
27	5,76		1	5,83		20	6,03	
28	5,77		24	5,84		11	6,03	
15	5,78		19	5,84		13	6,15	
4	5,78		14	5,84		30	6,47	O
33	5,79		2	5,84				
31	5,80		10	5,85				

O = Omitted result

Table 5.1. Statistics
pH

Sample B

Analytical method: All
Unit:

Number of participants	31	Range	0,55
Number of omitted results	2	Variance	0,02
True value	5,90	Standard deviation	0,13
Mean value	5,93	Relative standard deviation	2,1%
Median value	5,90	Relative error	0,4%

Analytical results in ascending order:

25	5,32	O	2	5,87		12	5,95	
23	5,73		8	5,87		6	6,03	
32	5,76		5	5,87		10	6,05	
33	5,79		9	5,90		11	6,07	
28	5,82		4	5,90		20	6,11	
22	5,83		14	5,90		13	6,14	
3	5,83		1	5,91		29	6,15	
15	5,84		24	5,92		16	6,28	
18	5,84		27	5,92		30	6,38	O
7	5,84		19	5,93				
31	5,87		21	5,94				

O = Omitted result

Table 5.2. Statistics
Conductivity

Sample A

Analytical method: All

Unit: mS/m

Number of participants	30	Range	0,52
Number of omitted results	2	Variance	0,02
True value	5,26	Standard deviation	0,14
Mean value	5,25	Relative standard deviation	2,6%
Median value	5,25	Relative error	-0,3%

Analytical results in ascending order:

15	4,71	O	1	5,20		2	5,30	
19	5,01		3	5,21		6	5,30	
7	5,02		20	5,24		16	5,31	
14	5,03		8	5,24		31	5,32	
18	5,10		4	5,24		22	5,38	
25	5,10		10	5,26		23	5,44	
32	5,14		27	5,26		29	5,48	
12	5,14		33	5,26		24	5,49	
13	5,14		21	5,28		9	5,53	
11	5,18		30	5,29		28	53,50	O

O = Omitted result

Table 5.2. Statistics Conductivity

Sample B

Analytical method: All

Unit: mS/m

Number of participants	30		Range	0,51
Number of omitted results	2		Variance	0,01
True value	4,79		Standard deviation	0,12
Mean value	4,77		Relative standard deviation	2,5%
Median value	4,79		Relative error	-0,4%

Analytical results in ascending order:

15	4,32	O	1	4,73	16	4,83	
19	4,53		3	4,75	9	4,84	
8	4,57		27	4,76	31	4,86	
7	4,60		10	4,77	6	4,89	
29	4,65		20	4,78	30	4,89	
18	4,66		21	4,79	23	4,90	
32	4,68		2	4,80	22	4,91	
13	4,68		25	4,80	14	4,97	
11	4,68		33	4,80	24	5,04	
12	4,68		4	4,81	28	47,90	O

O = Omitted result

Table 5.3. Statistics Alkalinity

Sample A

Analytical method: All
Unit: mmol/l

Number of participants	19	Range	0,013
Number of omitted results	10	Variance	0,000
True value	0,021	Standard deviation	0,004
Mean value	0,020	Relative standard deviation	21,7%
Median value	0,021	Relative error	-3,9%

Analytical results in ascending order:

6	0,009	O	4	0,022		9	0,045	O
15	0,013		14	0,025		18	0,050	O
25	0,014		2	0,026		20	0,058	O
3	0,019		12	0,032	O	1	0,066	O
7	0,020		27	0,033	O	32	0,074	O
33	0,021		13	0,035	O			
11	0,021		16	0,040	O			

O = Omitted result

Table 5.3. Statistics
Alkalinity

Sample B

Analytical method: All

Unit: mmol/l

Number of participants	19	Range	0,013
Number of omitted results	10	Variance	0,000
True value	0,022	Standard deviation	0,004
Mean value	0,023	Relative standard deviation	17,7%
Median value	0,022	Relative error	3,8%

Analytical results in ascending order:

15	0,017		11	0,025		16	0,042	O
3	0,018		12	0,026	O	18	0,052	O
33	0,021		14	0,027		20	0,059	O
6	0,021	O	13	0,029	O	32	0,060	O
25	0,022		2	0,030		1	0,065	O
4	0,022		27	0,032	O			
7	0,023		9	0,039	O			

O = Omitted result

Table 5.4. Statistics
Nitrate + nitrite-nitrogen

Sample A

Analytical method: All

Unit: µg N/l

Number of participants	29	Range	89,8
Number of omitted results	13	Variance	337,1
True value	105,4	Standard deviation	18,4
Mean value	106,2	Relative standard deviation	17,3%
Median value	108,4	Relative error	0,8%

Analytical results in ascending order:

18	0,1	O	23	99,6		33	110,0	O
21	0,1	O	9	100,0		27	112,0	
13	63,2		2	102,0	O	1	113,0	
30	68,0	O	4	103,0		3	113,9	
16	76,8	O	6	107,0		29	114,0	
32	84,0		19	107,8		12	115,5	
11	89,0	O	7	107,8	O	28	117,0	O
5	90,0	O	8	109,0		15	153,0	
20	95,0		22	109,5	O	14	250,0	O
31	97,8	O	3	109,8				

O = Omitted result

Table 5.4. Statistics
Nitrate + nitrite-nitrogen

Sample B

Analytical method: All

Unit: µg N/l

Number of participants	29	Range	65,0
Number of omitted results	13	Variance	476,0
True value	77,0	Standard deviation	21,8
Mean value	83,5	Relative standard deviation	26,1%
Median value	88,5	Relative error	8,5%

Analytical results in ascending order:

7	0,0	O	31	32,6	O	9	90,0	
18	0,1	O	11	36,0	O	15	90,0	
21	0,1	O	20	45,0		27	98,0	
16	0,2	O	19	47,8		12	103,1	
30	2,9	O	23	57,6		3	103,6	
22	9,7	O	13	64,6		1	108,0	
33	18,0	O	4	69,0		3	108,9	
28	24,1	O	29	74,0		6	110,0	
2	25,0	O	32	80,0		14	310,0	O
5	28,0	O	8	87,0				

O = Omitted result

Table 5.5. Statistics Chloride

Sample A

Analytical method: All

Unit: mg/l

Number of participants	29	Range	1,52
Number of omitted results	3	Variance	0,11
True value	10,47	Standard deviation	0,33
Mean value	10,39	Relative standard deviation	3,2%
Median value	10,47	Relative error	-0,8%

Analytical results in ascending order:

15	8,73	O	31	10,37		3	10,54	
6	9,36		2	10,40		8	10,60	
14	9,90		20	10,40		19	10,63	
13	9,91	O	29	10,43		16	10,66	
25	9,96		28	10,45		4	10,70	
27	9,96		7	10,48		33	10,71	
23	10,06		9	10,50		30	10,86	
12	10,17		1	10,50		18	10,88	
5	10,30		11	10,52		24	12,50	O
21	10,30		32	10,52				

O = Omitted result

Table 5.5. Statistics Chloride

Sample B

Analytical method: All

Unit: mg/l

Number of participants	29	Range	1,71
Number of omitted results	3	Variance	0,13
True value	9,60	Standard deviation	0,36
Mean value	9,54	Relative standard deviation	3,7%
Median value	9,58	Relative error	-0,7%

Analytical results in ascending order:

15	7,66	O	7	9,47		4	9,70	
25	8,90		28	9,50		5	9,70	
14	9,02		2	9,50		19	9,71	
27	9,05		1	9,56		16	9,77	
23	9,18		11	9,60		33	9,77	
6	9,19		8	9,60		24	10,10	O
20	9,28		9	9,60		18	10,22	
12	9,30		3	9,60		30	10,61	
21	9,40		29	9,65		13	11,12	O
31	9,41		32	9,66				

O = Omitted result

Table 5.6. Statistics Sulphate

Sample A

Analytical method: All

Unit: mg/l

Number of participants	30	Range	0,63
Number of omitted results	4	Variance	0,02
True value	2,86	Standard deviation	0,14
Mean value	2,84	Relative standard deviation	5,0%
Median value	2,85	Relative error	-0,7%

Analytical results in ascending order:

29	0,83	O	11	2,78		1	2,91	
15	1,44	O	8	2,80		28	2,94	
30	2,56		9	2,80		16	2,94	
32	2,58		20	2,84		31	2,94	
5	2,62		2	2,85		33	2,96	
13	2,65		3	2,86		12	3,00	
21	2,73		4	2,89		19	3,00	
18	2,75		27	2,90		26	3,19	
23	2,77		7	2,90		24	3,90	O
25	2,78		6	2,91		14	10,00	O

O = Omitted result

Table 5.6. Statistics
Sulphate

Sample B

Analytical method: All
Unit: mg/l

Number of participants	30	Range	0,63
Number of omitted results	4	Variance	0,02
True value	2,61	Standard deviation	0,15
Mean value	2,60	Relative standard deviation	5,7%
Median value	2,61	Relative error	-0,5%

Analytical results in ascending order:

29	0,75	O	18	2,57	25	2,64	
15	1,38	O	2	2,58	33	2,65	
32	2,30		6	2,59	16	2,69	
30	2,31		21	2,60	9	2,70	
28	2,31		23	2,60	19	2,70	
8	2,44		4	2,61	12	2,75	
5	2,50		3	2,61	26	2,88	
11	2,52		31	2,63	13	2,93	
20	2,55		1	2,64	24	3,70	O
27	2,55		7	2,64	14	8,90	O

O = Omitted result

Table 5.7. Statistics Calcium

Sample A

Analytical method: All

Unit: mg/l

Number of participants	31	Range	0,83
Number of omitted results	1	Variance	0,04
True value	5,07	Standard deviation	0,19
Mean value	5,07	Relative standard deviation	3,8%
Median value	5,08	Relative error	0,1%

Analytical results in ascending order:

14	4,39	O	29	4,99	25	5,20
28	4,67		15	5,01	3	5,20
6	4,73		16	5,02	21	5,23
26	4,73		22	5,07	19	5,25
18	4,82		2	5,07	8	5,27
24	4,90		31	5,08	27	5,30
32	4,92		23	5,10	20	5,30
13	4,97		30	5,13	12	5,34
33	4,97		1	5,15	9	5,50
7	4,98		5	5,17		
11	4,98		4	5,19		

O = Omitted result

Table 5.7. Statistics
Calcium

Sample B

Analytical method: All
Unit: mg/l

Number of participants	31	Range	0,82
Number of omitted results	1	Variance	0,03
True value	4,59	Standard deviation	0,18
Mean value	4,61	Relative standard deviation	4,0%
Median value	4,59	Relative error	0,4%

Analytical results in ascending order:

14	3,89	O	29	4,54	25	4,70
6	4,18		23	4,54	4	4,71
32	4,24		2	4,58	21	4,72
28	4,31		11	4,59	27	4,78
18	4,46		22	4,59	19	4,79
16	4,48		31	4,60	12	4,83
30	4,50		24	4,60	8	4,88
15	4,51		26	4,61	20	4,91
13	4,53		1	4,67	9	5,00
33	4,53		5	4,67		
7	4,54		3	4,68		

O = Omitted result

Table 5.8. Statistics
Magnesium

Sample A

Analytical method: All

Unit: mg/l

Number of participants	31	Range	0,052
Number of omitted results	4	Variance	0,000
True value	0,345	Standard deviation	0,014
Mean value	0,345	Relative standard deviation	4,0%
Median value	0,344	Relative error	0,1%

Analytical results in ascending order:

31	0,272	O	24	0,340	O	18	0,357	
20	0,320		6	0,340		25	0,360	
29	0,324		19	0,340		21	0,360	
13	0,327		33	0,341		32	0,360	
1	0,329		22	0,344		28	0,365	
11	0,333		2	0,346		3	0,365	
15	0,335		23	0,347		27	0,372	
30	0,335		5	0,351		9	0,750	O
26	0,336		12	0,352		14	1,200	O
16	0,337		8	0,355				
7	0,340		4	0,357				

O = Omitted result

Table 5.8. Statistics
Magnesium

Sample B

Analytical method: All

Unit: mg/l

Number of participants	31	Range	0,054
Number of omitted results	4	Variance	0,000
True value	0,317	Standard deviation	0,014
Mean value	0,316	Relative standard deviation	4,5%
Median value	0,316	Relative error	-0,3%

Analytical results in ascending order:

24	0,240	O	20	0,310		4	0,323	
31	0,247	O	33	0,312		28	0,325	
1	0,293		26	0,314		21	0,330	
29	0,293		2	0,315		3	0,331	
13	0,296		30	0,316		27	0,338	
16	0,300		23	0,317		18	0,343	
6	0,300		22	0,318		5	0,347	
15	0,301		12	0,319		9	0,730	O
7	0,308		32	0,320		14	0,890	O
11	0,308		25	0,320				
19	0,310		8	0,323				

O = Omitted result

Table 5.9. Statistics
Sodium

Sample A

Analytical method: All
Unit: mg/l

Number of participants	30	Range	0,39
Number of omitted results	1	Variance	0,01
True value	2,73	Standard deviation	0,09
Mean value	2,70	Relative standard deviation	3,4%
Median value	2,72	Relative error	-1,2%

Analytical results in ascending order:

30	2,42	14	2,70	12	2,74	
13	2,45	18	2,71	2	2,75	
29	2,58	5	2,71	22	2,76	
15	2,63	25	2,72	21	2,77	
33	2,63	19	2,72	27	2,78	
11	2,64	16	2,73	3	2,79	
20	2,64	31	2,73	4	2,79	
32	2,65	28	2,73	9	2,80	
7	2,66	8	2,74	1	2,81	
26	2,69	23	2,74	6	3,37	O

O = Omitted result

Table 5.9. Statistics Sodium

Sample B

Sample B

Analytical method: All

Unit: mg/l

Number of participants	30	Range	0,56
Number of omitted results	1	Variance	0,01
True value	2,51	Standard deviation	0,12
Mean value	2,48	Relative standard deviation	4,7%
Median value	2,51	Relative error	-1,1%

Analytical results in ascending order:

13	2,19	23	2,47	4	2,54	
30	2,25	19	2,47	1	2,54	
32	2,28	12	2,50	28	2,54	
29	2,32	14	2,50	27	2,56	
11	2,40	8	2,51	3	2,56	
33	2,41	21	2,51	22	2,57	
26	2,42	16	2,52	9	2,60	
20	2,42	25	2,52	18	2,65	
15	2,43	2	2,53	5	2,75	
7	2,46	31	2,53	6	3,02	O

O = Omitted result

Table 5.10. Statistics
Potassium

Sample A

Analytical method: All

Unit: mg/l

Number of participants	30	Range	0,159
Number of omitted results	1	Variance	0,001
True value	0,550	Standard deviation	0,033
Mean value	0,548	Relative standard deviation	6,0%
Median value	0,550	Relative error	-0,3%

Analytical results in ascending order:

30	0,451	28	0,542	27	0,555	
9	0,500	33	0,547	18	0,556	O
31	0,508	29	0,548	4	0,571	
19	0,511	20	0,550	7	0,573	
11	0,514	6	0,550	2	0,574	
16	0,530	21	0,550	13	0,586	
26	0,530	22	0,551	3	0,587	
15	0,538	32	0,552	8	0,588	
23	0,540	1	0,552	14	0,600	
12	0,540	5	0,554	25	0,610	

O = Omitted result

Table 5.10. Statistics Potassium

Sample B

Analytical method: All

Unit: mg/l

Number of participants	30	Range	0,106
Number of omitted results	1	Variance	0,001
True value	0,511	Standard deviation	0,028
Mean value	0,513	Relative standard deviation	5,5%
Median value	0,510	Relative error	0,5%

Analytical results in ascending order:

9	0,470	1	0,500	13	0,524	
26	0,480	20	0,500	22	0,537	
31	0,482	21	0,500	7	0,537	
23	0,484	12	0,503	30	0,538	
29	0,484	16	0,510	2	0,542	
19	0,487	32	0,511	3	0,543	
11	0,488	33	0,514	5	0,566	
6	0,490	15	0,517	25	0,570	
27	0,495	4	0,518	8	0,576	
14	0,500	28	0,523	18	0,619	O

O = Omitted result

Table 5.11. Statistics Total organic carbon

Sample A

Analytical method: All
Unit: mg/l

Number of participants	17	Range	2,29
Number of omitted results	0	Variance	0,27
True value	4,80	Standard deviation	0,51
Mean value	4,80	Relative standard deviation	10,7%
Median value	4,77	Relative error	-0,1%

Analytical results in ascending order:

6	3,69	22	4,74	9	5,00
32	4,17	21	4,74	7	5,10
27	4,38	33	4,77	3	5,30
20	4,50	1	4,82	16	5,47
13	4,54	12	4,87	29	5,98
5	4,60	19	4,87		

O = Omitted result

Table 5.11. Statistics Total organic carbon

Sample B

Analytical method: All

Unit: mg/l

Number of participants	17	Range	2,38
Number of omitted results	0	Variance	0,26
True value	4,36	Standard deviation	0,51
Mean value	4,36	Relative standard deviation	11,6%
Median value	4,34	Relative error	-0,1%

Analytical results in ascending order:

6	3,13	22	4,30	7	4,56
32	3,80	21	4,32	9	4,60
13	4,03	1	4,34	3	4,78
27	4,10	33	4,38	16	5,00
20	4,10	19	4,41	29	5,51
5	4,26	12	4,43		

O = Omitted result

Table 5.12. Statistics Aluminium

Sample C

Analytical method: All

Unit: µg/l

Number of participants	22	Range	64
Number of omitted results	2	Variance	232
True value	190	Standard deviation	15
Mean value	187	Relative standard deviation	8,2%
Median value	191	Relative error	-1,7%

Analytical results in ascending order:

14	145	11	189	20	196	
30	164	2	190	22	201	
32	166	26	191	12	209	
6	175	3	192	16	209	
4	182	23	192	18	251	O
21	182	25	193	24	320	O
13	185	1	194			
28	188	8	195			

O = Omitted result

Table 5.12. Statistics Aluminium

Sample D

Analytical method: All

Unit: µg/l

Number of participants	22	Range	49
Number of omitted results	2	Variance	151
True value	184	Standard deviation	12
Mean value	183	Relative standard deviation	6,7%
Median value	184	Relative error	-0,5%

Analytical results in ascending order:

30	153	20	184	14	196	
32	163	21	184	12	198	
6	166	28	184	16	199	
13	173	26	185	8	202	
4	176	3	186	24	210	O
11	179	25	186	18	246	O
23	183	1	187			
2	184	22	194			

O = Omitted result

Table 5.13. Statistics
Iron

Sample C

Analytical method: All
Unit: µg/l

Number of participants	22	Range	50,1
Number of omitted results	0	Variance	136,8
True value	90,6	Standard deviation	11,7
Mean value	90,6	Relative standard deviation	12,9%
Median value	90,7	Relative error	0,0%

Analytical results in ascending order:

13	61,9	15	88,5	12	95,4
30	68,5	11	89,6	3	98,1
32	78,0	1	90,6	18	101,3
23	83,4	25	90,7	24	105,0
4	86,0	21	91,0	6	111,0
22	87,1	2	91,2	14	112,0
28	87,7	26	92,2		
8	88,3	20	95,0		

O = Omitted result

Table 5.13. Statistics Iron

Sample D

Analytical method: All

Unit: µg/l

Number of participants	22	Range	56,0
Number of omitted results	0	Variance	118,1
True value	87,3	Standard deviation	10,9
Mean value	87,8	Relative standard deviation	12,4%
Median value	87,1	Relative error	0,6%

Analytical results in ascending order:

13	57,0	22	85,6	21	95,0
30	72,1	15	85,8	3	95,8
32	78,0	11	86,9	6	97,0
23	82,1	25	87,3	24	98,0
20	84,0	2	89,1	18	99,0
8	84,1	1	89,1	14	113,0
28	84,7	26	90,4		
4	85,1	12	92,8		

O = Omitted result

Table 5.14. Statistics Manganese

Sample C

Analytical method: All
Unit: µg/l

Number of participants	23	Range	13,2
Number of omitted results	0	Variance	8,0
True value	39,3	Standard deviation	2,8
Mean value	39,2	Relative standard deviation	7,2%
Median value	39,4	Relative error	-0,1%

Analytical results in ascending order:

14	33,4	1	39,0	12	40,4
32	34,3	1	39,0	20	40,5
13	35,2	4	39,3	26	41,1
8	36,7	11	39,4	18	41,2
22	37,9	23	39,4	3	42,2
24	38,0	25	39,7	6	42,8
21	38,0	28	40,0	16	46,6
30	38,2	2	40,4		

O = Omitted result

Table 5.14. Statistics Manganese

Sample D

Analytical method: All

Unit: µg/l

Number of participants	23	Range	14,2
Number of omitted results	0	Variance	8,0
True value	38,2	Standard deviation	2,8
Mean value	38,4	Relative standard deviation	7,4%
Median value	38,3	Relative error	0,5%

Analytical results in ascending order:

14	31,6	4	38,1	2	39,5
32	34,3	1	38,1	26	39,9
13	34,4	23	38,2	18	39,9
8	35,8	11	38,3	21	40,0
24	37,0	30	38,6	3	41,6
22	37,1	25	38,7	6	41,8
1	38,0	20	39,1	16	45,8
28	38,1	12	39,3		

O = Omitted result

Table 5.15. Statistics Cadmium

Sample C

Analytical method: All

Unit: µg/l

Number of participants	25	Range	1,50
Number of omitted results	3	Variance	0,12
True value	5,30	Standard deviation	0,34
Mean value	5,30	Relative standard deviation	6,4%
Median value	5,32	Relative error	0,0%

Analytical results in ascending order:

8	2,98	O	13	5,28		30	5,45	
17	3,60	O	22	5,30		20	5,50	
32	4,60		6	5,30		29	5,58	
14	4,60		25	5,30		12	5,66	
24	4,90		28	5,34		4	5,72	
3	4,93		26	5,35		16	6,10	
1	5,15		11	5,35		18	11,92	O
23	5,18		1	5,37				
2	5,28		21	5,40				

O = Omitted result

Table 5.15. Statistics
Cadmium

Sample D

Analytical method: All

Unit: µg/l

Number of participants	25	Range	1,45
Number of omitted results	3	Variance	0,14
True value	4,80	Standard deviation	0,37
Mean value	4,75	Relative standard deviation	7,8%
Median value	4,80	Relative error	-1,0%

Analytical results in ascending order:

8	2,81	O	2	4,59		6	5,05	
17	3,60	O	20	4,79		4	5,12	
13	4,02		28	4,79		12	5,12	
14	4,10		22	4,80		29	5,13	
32	4,20		1	4,80		21	5,20	
3	4,41		30	4,82		16	5,47	
23	4,45		26	4,87		18	11,36	O
24	4,50		1	4,89				
25	4,54		11	4,90				

O = Omitted result

Table 5.16. Statistics Lead

Sample C

Analytical method: All

Unit: µg/l

Number of participants	25	Range	2,42
Number of omitted results	2	Variance	0,30
True value	7,79	Standard deviation	0,55
Mean value	7,85	Relative standard deviation	7,0%
Median value	7,79	Relative error	0,7%

Analytical results in ascending order:

17	4,00	O	20	7,72	29	8,11
8	5,33	O	30	7,72	4	8,14
23	6,58		25	7,76	28	8,20
32	7,00		26	7,78	12	8,42
14	7,20		16	7,79	11	8,43
6	7,31		21	7,90	24	8,80
13	7,48		18	7,96	22	9,00
3	7,53		2	7,99		
1	7,67		1	8,02		

O = Omitted result

Table 5.16. Statistics Lead

Sample D

Analytical method: All

Unit: µg/l

Number of participants	25	Range	2,96
Number of omitted results	2	Variance	0,43
True value	7,20	Standard deviation	0,66
Mean value	7,24	Relative standard deviation	9,1%
Median value	7,20	Relative error	0,5%

Analytical results in ascending order:

17	4,00	O	16	6,99		1	7,55
30	5,54		1	7,05		28	7,71
8	5,80	O	3	7,18		21	7,80
23	6,13		20	7,19		11	7,94
32	6,60		12	7,20		4	7,95
14	6,80		26	7,29		24	8,20
6	6,82		25	7,35		22	8,50
13	6,90		29	7,36			
18	6,93		2	7,53			

O = Omitted result

Table 5.17. Statistics Copper

Sample C

Analytical method: All

Unit: µg/l

Number of participants	25	Range	5,5
Number of omitted results	3	Variance	1,8
True value	23,4	Standard deviation	1,4
Mean value	23,5	Relative standard deviation	5,8%
Median value	23,4	Relative error	0,6%

Analytical results in ascending order:

17	17,6	O	18	23,1	30	24,3	
32	20,5		25	23,3	12	25,1	
13	21,6		2	23,4	16	25,4	
4	22,1		26	23,4	1	26,0	
8	22,2		22	23,5	24	26,0	
23	22,8		11	24,0	29	33,3	O
6	22,9		20	24,1	14	2550,0	O
3	22,9		28	24,2			
21	23,0		1	24,2			

O = Omitted result

Table 5.17. Statistics Copper

Sample D

Analytical method: All

Unit: µg/l

Number of participants	25	Range	5,7
Number of omitted results	3	Variance	2,5
True value	24,2	Standard deviation	1,6
Mean value	24,2	Relative standard deviation	6,5%
Median value	24,2	Relative error	0,1%

Analytical results in ascending order:

6	21,9		4	23,8		28	25,1	
8	21,9		30	24,1		24	26,0	
32	22,1		25	24,2		12	26,2	
13	22,2		20	24,2		1	26,6	
17	22,3	O	22	24,6		3	27,6	
18	22,4		16	24,7		14	34,8	O
2	23,2		11	24,8		29	47,0	O
23	23,4		21	25,0				
26	23,6		1	25,1				

O = Omitted result

Table 5.18. Statistics Nickel

Sample C

Analytical method: All

Unit: µg/l

Number of participants	24	Range	3,81
Number of omitted results	0	Variance	0,64
True value	10,60	Standard deviation	0,80
Mean value	10,62	Relative standard deviation	7,5%
Median value	10,65	Relative error	0,2%

Analytical results in ascending order:

18	8,86	23	10,50	1	11,10
30	9,24	26	10,50	20	11,10
32	9,60	12	10,51	28	11,10
8	9,79	25	10,60	3	11,20
24	10,00	4	10,70	13	11,20
14	10,10	21	10,80	11	11,28
1	10,20	2	10,90	16	11,48
6	10,50	22	11,00	29	12,67

O = Omitted result

Table 5.18. Statistics
Nickel

Sample D

Analytical method: All

Unit: µg/l

Number of participants	24	Range	3,32
Number of omitted results	0	Variance	0,51
True value	9,99	Standard deviation	0,72
Mean value	10,02	Relative standard deviation	7,2%
Median value	9,98	Relative error	0,3%

Analytical results in ascending order:

18	8,54	12	9,89	28	10,30
30	8,75	20	9,94	23	10,30
32	9,20	25	9,96	1	10,40
14	9,40	4	9,96	11	10,60
24	9,40	8	9,99	16	10,70
3	9,71	26	10,00	21	10,80
1	9,72	13	10,12	22	11,10
2	9,76	6	10,20	29	11,86

O = Omitted result

Table 5.19. Statistics
Zinc

Sample C

Analytical method: All

Unit: µg/l

Number of participants	24	Range	13,1
Number of omitted results	3	Variance	9,4
True value	38,4	Standard deviation	3,1
Mean value	38,6	Relative standard deviation	8,0%
Median value	38,4	Relative error	0,5%

Analytical results in ascending order:

30	9,8	O	3	37,9		13	39,4	
24	29,0	O	22	38,0		11	40,2	
32	33,0		26	38,2		12	40,8	
18	33,4		23	38,2		4	40,8	
14	35,1		20	38,4		28	42,1	
8	35,3		1	38,5		21	43,0	
1	36,9		2	38,5		29	46,1	
25	37,7		6	39,2		16	66,0	O

O = Omitted result

Table 5.19. Statistics
Zinc

Sample D

Analytical method: All

Unit: µg/l

Number of participants	24	Range	14,9
Number of omitted results	3	Variance	13,6
True value	38,1	Standard deviation	3,7
Mean value	38,4	Relative standard deviation	9,6%
Median value	38,2	Relative error	0,8%

Analytical results in ascending order:

30	10,2	O	6	37,6	11	39,5	
18	32,7		13	37,7	3	39,6	
14	32,8		26	38,0	12	40,7	
32	33,9		22	38,2	4	43,8	
8	35,1		1	38,4	21	45,0	
2	36,3		20	38,4	29	47,6	
25	36,7		23	38,5	16	55,7	O
1	37,1		28	39,2	24	64,0	O

O = Omitted result

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