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Intercomparison 1529:
pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn

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

Convention on Long-Range Transboundary Air Pollution

Norwegian Institute for Water Research

– an institute in the Environmental Research Alliance of Norway

REPORT

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Abstract

81 laboratories were invited to participate in the current intercomparison. Of these, 40 from 19 different countries accepted the invitation and 39 of them submitted results to the Organization. Two sample sets were prepared: one for the determination of major ions and one for heavy metals. Based on the general target accuracy of ± 20 % or the special accuracy limit for pH and conductivity (± 0,2 pH units and ± 10 % respectively), 88 % 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: chloride, sulphate, calcium, magnesium, sodium, potassium, cadmium, copper and nickel, with acceptance rate of 90% or higher.
For pH, only 64 percent of the reported results fulfilled the acceptance criteria. 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.
Participants may have observed higher concentrations in the sample set AB if compared to previous intercalibrations. This sample set has been spiked with NaCl, KNO_3, NaCl and $CaCl_2$ and $MgSO_4$ salts. The purpose was to compare results for freshwaters with higher content of salts than the naturally occurring in Norwegian lakes and rivers.

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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 1529:

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

Prepared by the ICP Waters Programme Centre
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Preface

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

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 29th intercomparison of chemical analysis.

Oslo, September 2015

Dr. Carlos Escudero-Oñate

Contents

Summary

The Intercomparison 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 2015, 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. 81 laboratories were invited to participate, and samples were sent to the 40 laboratories who accepted. All of them, except one, submitted results to the Programme Centre before the final statistical treatment of the data. 19 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 88 % of the result pairs were considered acceptable, the target limit being the median value ± 20 %, except for pH and conductivity, where special acceptance limits were selected, ± 0,2 pH units and ± 10 %, respectively.

For pH, the accuracy limit was, as in earlier intercomparisons, extended from the target acceptance limit of ± 0,1 units to ± 0,2 units, and 64 % of the result pairs were acceptable 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 chloride, sulphate, calcium, magnesium, sodium, potassium and cadmium, with 90% or more of the results accepted. Remarkable also is the general improvement in the quality of the results if compared to the last 3 edition.

Noticeable is the improvement on the quality of the results provided by the participants in the analysis of the variable nitrate+nitrite-N compared to previous intercomparisons, since 88% of the results fulfilled the target accuracy. This excellent result compared to these obtained in previous editions is probably due to the higher concentration of this variable since the sample set AB was spiked, among others, with a nitrate salt. From the data obtained from previous editions, it might be stated that the main error on the determination of this variable is due to its low concentration in the natural freshwater samples.

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-ninth intercomparison test, called 1529, 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 2015. 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 save their 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 1529 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 39 laboratories submitted results to the intercomparison. If results for the different variables are averaged, 88 % 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 the best from the last 4 editions. As previously stated, the best acceptance (≥90%) was observed in the determination of chloride, sulphate, calcium, magnesium, sodium, potassium, calcium, cadmium, copper and nickel. The lowest acceptable results were reported for pH (64%). 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.

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 been spiked and then, the concentrations of some of the variables are still higher than could be expected 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 laboratories which reported results outside this limit should improve their methods to obtain a better accuracy and then be able to get a better score in the intercomparison assay. 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 the target detection limit that should be achieved by the participating laboratories.

Table 1. Evaluation of the results from intercomparison 1529.

				Acceptable Limit	Number of pairs		Acceptable results for intecalibration (%)			
Variable	Sample pair	Sample 1	Sample 2	%	Total	Accept.	1529	1428	1327	1226
pH	AB	7,14	7,14	2,86	36	23	64	68	52	59
Conductivity,	AB	24,6	22,1	10	35	31	89	93	78	72
Alkalinity,	AB	0,237	0,210	20	28	21	75	26	63	48
Nitrate + nitrite-nitrogen,	AB	1201	1086	20	33	29	88	14	0	52
Chloride,	AB	43,0	38,6	20	32	31	97	93	78	79
Sulphate,	AB	25,32	22,63	20	32	31	97	87	77	80
Calcium,	AB	15,42	13,78	20	33	32	97	97	85	75
Magnesium,	AB	5,96	5,30	20	33	33	100	87	82	74
Sodium,	AB	17,27	15,25	20	33	32	97	97	91	84
Potassium,	AB	3,17	2,78	20	33	32	97	97	70	81
Total organic carbon,	AB	2,81	2,425	20	23	16	70	82	78	76
Aluminium,	CD	163,0	147,9	20	27	25	89	78	89	79
Iron,	CD	93,28	83,21	20	30	25	81	74	72	70
Manganese,	CD	23,09	20,8	20	30	26	84	88	78	89
Cadmium,	CD	5,305	4,745	20	30	30	100	84	85	84
Lead,	CD	5,28	4,82	20	30	23	77	80	71	77
Copper,	CD	16,72	15,28	20	30	28	93	88	84	86
Nickel,	CD	11,00	9,80	20	29	28	97	92	83	78
Zinc,	CD	21,86	19,99	20	29	25	83	79	60	61
Total					586	521	88	80	73	74

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

81 laboratories were invited to participate in this ICP Waters intercomparison. 40 laboratories of 19 different countries accepted and therefore samples were shipped to them. At the end of the program, almost 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 6 in Appendix C provides an estimate for the 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 a selected accuracy limit, either the general target limit of ± 20 % of the mean true values for the sample pair, or a special accuracy limit as defined in the sections below.

A summary of the results of intercomparison 1529 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 shows 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.

36 participants determined pH in the test samples A and B. 34 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, 64 % of the results were acceptable, that is within the median value ± 0,2 pH units. The acceptance has decreased in 4% if compared to the previous edition (Table 1).

The most probable reason for the differences in the reported results could be due to the slight differences in the analytics that the different participants employed. It is also questionable whether there could be some differences due to instability of the samples during their shipment. Stability tests performed 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.

35 laboratories have reported results for conductivity in the current edition. All the participants reported the use of electrometric methods. Most laboratories achieved rather good agreement between the results for this variable, and an excellent 89 % of the results were within the acceptance limit of ± 10 %.

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.

28 laboratories reported results for alkalinity. From them, 8 used Gran plot titration method, which is the suggested reference method in the manual (1), while 9 made use of end point titration. 4 participants employed end point titration to pH 5,4. 75 % of them provided results that were within the target accuracy of ± 20 %. This percentage is notably higher than the last year edition and the best of the last four rounds of intercalibration.

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.

The distribution of the results in the Youden's chart indicates that the analysis is affected mainly by systematic error.

4.4 Nitrate + nitrite-nitrogen

33 laboratories reported results for nitrate + nitrite-nitrogen and the results are presented in Tables 2 and 5.4. Ion chromatography is the preferred technique for the determination of this variable in the samples, as it was used by 20 participants. Remarkable is the excellent quality on the results provided by the participants if compared to previous editions. In the current round of the intercomparison, the sample set AB has been spiked with a nitrate salt to provide a concentration about 1000 µg/L. This

level is much higher than those reported in previous editions, indicating then that an important source of error is due to the low concentration. The participants are encouraged to check their analytical performance to improve their Limits of Quantification in the determination of nitrate+nitrite.

The Youden plot demonstrates that the slight deviation in the results is mainly due to systematic error.

4.5 Chloride

32 laboratories reported results for chloride and, from them, 31 were accepted. 97% of the participants provided results that fulfilled the acceptance criteria. 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 24 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

32 laboratories reported results for sulphate. From them 97% fulfilled the target accuracy. This percentage is the best of the last 4 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 and 1 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 4.5 %.

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

4.7 Calcium

33 laboratories reported results for calcium from which 97 % fulfilled the target accuracy. This percentage is in line with the last edition. The results are presented in Figure 7, Table 2 and Table 5.7. The circle in Figure 7 represents the target accuracy of ± 20 %.

14 laboratories used ICP-AES and 12 ion chromatography. Flame atomic absorption spectrometry was used by 4 of the participants in their determination of calcium. Only 2 laboratories used ICP-MS. 1 participant made use of an electrophoretic technique.

The results are mainly affected by slight systematic and random error, but almost all the results where within the 20% target accuracy stablished in the Youden calculations.

4.8 Magnesium

33 laboratories reported results for magnesium and 100 % of the results were considered as acceptable according to the criteria of the intercomparison.

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 %. 12 of the laboratories used ICP-AES and 12, ion chromatography. Flame atomic absorption spectrometry was used by 4 of the participants in their determination of this variable. 3 of the laboratories reported the use of ICP-MS, 1 capillary electrophoresis and 1 participant reported the use of other method.

It worth note that the slight deviation of the results is mainly to a contribution of both, random and systematic error, as it can be observed in Figure 8.

4.9 Sodium

33 laboratories reported results for sodium. 97 % of the results fulfilled the target accuracy stablished in the intercomparision. This is in agreement with the percentage of acceptance of 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, 11 participants analysed sodium by ICP-AES and 2 ICP-MS. Ion chromatography techniques are nearly as extended as plasma techniques, as 13 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. 1 participant reported the use of emission in flame. Just 1 laboratory reported the use of capillary electrophoresis and 1 indicated the use of other method different than the aforementioned.

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 set results provided by the participants.

4.10 Potassium

33 laboratories reported results for potassium. From these results, 97 % were acceptable. Regarding the analytical techniques, a similar 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 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

23 laboratories reported results for total organic carbon. From them, 70 % 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 (16) while 5 reported the use of UV/peroxodisulfate oxidation method for this determination. 2 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

27 laboratories reported results for aluminium. From these all were accepted according to the target accuracy criteria (89% 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, 11 laboratories used ICP-MS and 10, ICP-AES. 5 participants reported the use of graphite furnace. Only one participant reported the use of a photometric method. From these techniques, the lowest relative standard deviation 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

30 laboratories provided results for iron and 89% fulfilled the target accuracy criteria. 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 %.

13 and 11 of the laboratories used ICP-AES and ICP-MS, respectively. 5 participants reported the use of atomic absorption techniques: 2 employed GFASS and 3 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

30 participants reported results in the analysis of manganese. From these, 84% fulfilled the acceptance criteria. 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 a photometric method. From them, 13 and 11 participants used ICP-AES and ICP-MS, respectively, while 2 and 3 used graphite furnace atomic absorption and flame atomic absorption respectively. No relevant differences were detected in between the different techniques.

The analysis is mainly affected by systematic error, as shown in the characteristic Youden chart.

4.15 Cadmium

30 laboratories reported results for cadmium in the set of samples C and D. All the results were acceptable, according to the target accuracy.

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 24 participants reported its use. From them, 15 detected mass (ICP-MS) and 9 emitted radiation (ICP-AES). The preferred method employed by the participants that used atomic absorption techniques was the graphite furnace (GFAAS). The use of this technique was reported by 6 of the participants. In the current edition, any participant reported the use of non-atomic techniques.

According to the Youden chart, the deviating results seem to be affected by both systematic and random error.

4.16 Lead

30 laboratories reported results for lead in samples C and D. From these, 77 were. This percentage is 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 24 participants have communicated the use of ICP. From them, 15 used mass detection (ICP-MS) and 9, emitted radiation (ICP-AES). The preferred method employed by the participants that used atomic absorption techniques was the graphite furnace (GFAAS).

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

4.17 Copper

30 laboratories reported results for copper in sample set C and D. From them, 93% were acceptable. 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 random error with slight contribution of systematic error.

By analysis, almost all the participants employed atomic based techniques, being plasma the most widely used with 15 of the participants using mass detectors and 9 using emitted light. Noteworthy also is the important contribution of the atomic absorption techniques, as 5 participants employed GFAAS and 1 FAAS.

4.18 Nickel

29 laboratories reported results for nickel in samples C and D. From these, 97% were classified as acceptable according to the target accuracy of the assay.

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 %.

By analysis type, it is remarkable the use of atomic based techniques. From them, plasma is the most widely used, with 24 participants. 15 employed ICP-MS while only 9 reported the use of ICP-AES. The 5 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

29 laboratories reported results in the determination of zinc in sample set C and D. From these results, 83% fulfilled the acceptance criteria.

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 14 participants, followed by emission in plasma (ICP-AES) that was used by 10 of the laboratories. From the techniques based on atomic absorption spectroscopy 2 laboratories made use of the graphite furnace (GFAAS) while 3 participants reported the use of flame atomic absorption spectroscopy (FAAS). In the current edition none of the participants reported results achieved with non-atomic techniques.

Table 2. Statistical summary for intercomparison 1529

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	7,14	7,14	36	0	7,14	7,14	7,11	0,21	7,10	0,20	3,0	2,8	-0,4	-0,5
Electrometry				34	0	7,14	7,14	7,11	0,22	7,10	0,20	3,1	2,8	-0,4	-0,6
Stirring				2	0			7,20		7,15				0,8	0,1
Conductivity	AB	24,60	22,10	35	5	24,60	22,10	24,60	0,40	22,12	0,29	1,6	1,3	0,0	0,1
Electrometry				35	5	24,60	22,10	24,60	0,40	22,12	0,29	1,6	1,3	0,0	0,1
Alkalinity	AB	0,237	0,210	28	0	0,237	0,210	0,245	0,035	0,221	0,032	14,4	14,5	3,5	5,0
End point titration				9	0	0,270	0,252	0,270	0,040	0,245	0,035	14,8	14,4	14,2	16,6
Gran plot titration				8	0	0,237	0,208	0,230	0,039	0,202	0,032	17,1	15,8	-2,9	-4,1
End point 5.4				4	0	0,229	0,212	0,230	0,009	0,218	0,023	4,0	10,5	-2,9	3,8
Other method				3	0	0,236	0,210	0,235	0,003	0,214	0,009	1,1	4,3	-0,7	1,5
Colorimetry				2	0			0,250		0,216				5,7	2,7
End point				1	0			0,227		0,204				-4,0	-3,0
End point 5.6				1	0			0,235		0,211				-0,8	0,1
Nitrate+Nitrite-N	AB	1201	1086	33	1	1201	1086	1218	93	1091	87	7,7	8,0	1,4	0,5
Ion chromatography				20	1	1221	1096	1212	93	1089	90	7,7	8,3	0,9	0,3
Autoanalyzer				5	0	1167	1072	1218	90	1102	71	7,4	6,5	1,4	1,5
Photometry				5	0	1174	1045	1245	128	1096	119	10,3	10,9	3,6	0,9
Cap. electrophoresis				1	0			1149		1017				-4,4	-6,3
Flow injection anal.				1	0			1200		1080				-0,1	-0,5
Other method				1	0			1292		1148				7,5	5,7
Chloride	AB	43,0	38,6	32	1	43,0	38,6	43,0	2,1	38,8	1,6	4,8	4,2	0,1	0,6
Ion chromatography				24	1	43,1	38,8	43,1	2,0	39,1	1,7	4,6	4,3	0,3	1,2
Other method				2	0			41,5		37,1				-3,5	-4,0
Photometry				2	0			43,6		39,3				1,4	1,8
AA				1	0			48,0		40,0				11,6	3,6
Cap. electrophoresis				1	0			41,0		37,4				-4,6	-3,1
Photometry HgSCN				1	0			42,7		38,3				-0,7	-0,8
Potentiometry				1	0			40,3		36,8				-6,3	-4,6
Sulphate	AB	25,32	22,63	32	1	25,32	22,63	24,85	1,17	22,35	1,16	4,7	5,2	-1,9	-1,2
Ion chromatography				26	0	25,36	22,70	24,94	1,10	22,42	0,91	4,4	4,1	-1,5	-0,9
ICP-AES				3	1			24,67		21,67				-2,6	-4,2
Photometry				2	0			24,10		22,58				-4,8	-0,2
Cap. electrophoresis				1	0			24,21		21,49				-4,4	-5,0
Calcium	AB	15,42	13,78	33	3	15,42	13,78	15,40	0,53	13,85	0,50	3,4	3,6	-0,1	0,5
ICP-AES				14	0	15,23	13,71	15,26	0,42	13,71	0,42	2,7	3,0	-1,0	-0,5
Ion chromatography				12	1	15,58	13,88	15,64	0,54	14,04	0,53	3,5	3,8	1,4	1,9
FAAS				4	0	15,22	13,77	15,26	0,81	13,84	0,72	5,3	5,2	-1,0	0,4
ICP-MS				2	1			15,43		13,79				0,1	0,1
Cap. Electrophoresis				1	1			19,99		13,51				29,7	-2,0

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		pair	S. 1	S. 2	Total	Om	S. 1
Magnesium	AB	5,96	5,30	33	1	5,96	5,30	5,94	0,24	5,32	0,21	4,0	3,9	-0,2	0,4
ICP-AES				12	0	5,96	5,28	6,00	0,19	5,37	0,19	3,1	3,5	0,8	1,5
Ion chromatography				12	1	6,07	5,38	6,01	0,18	5,36	0,12	3,0	2,3	1,0	1,2
FAAS				4	0	5,88	5,23	5,90	0,31	5,22	0,23	5,2	4,5	-1,0	-1,4
ICP-MS				3	0	5,46	4,86	5,63	0,35	5,02	0,32	6,2	6,3	-5,5	-5,1
Cap. Electrophoresis				1	0			5,65		5,54				-5,1	4,6
Other method				1	0			5,90		5,20				-0,9	-1,8
Sodium	AB	17,27	15,25	33	3	17,27	15,25	17,20	0,62	15,29	0,42	3,6	2,8	-0,4	0,3
Ion chromatography				13	1	17,24	15,25	17,19	0,56	15,31	0,40	3,3	2,6	-0,4	0,5
ICP-AES				11	0	17,50	15,37	17,36	0,63	15,27	0,46	3,6	3,0	0,6	0,2
FAAS				4	1	16,80	15,16	17,00	0,35	15,25	0,41	2,0	2,7	-1,5	0,1
ICP-MS				2	1			17,05		15,26				-1,2	0,1
AES				1	0			18,05		16,11				4,5	5,7
Cap. Electrophoresis				1	0			15,64		15,05				-9,4	-1,3
Other method				1	0			16,90		14,80				-2,1	-2,9
Potassium	AB	3,17	2,78	33	1	3,17	2,78	3,12	0,18	2,77	0,13	5,6	4,9	-1,4	-0,5
Ion chromatography				13	0	3,17	2,78	3,14	0,16	2,79	0,13	5,1	4,7	-0,9	0,2
ICP-AES				9	0	3,18	2,78	3,17	0,15	2,78	0,11	4,7	3,9	0,0	0,2
FAAS				4	0	3,22	2,82	3,13	0,25	2,74	0,18	8,0	6,7	-1,3	-1,3
AES				3	0	3,12	2,78	3,11	0,16	2,78	0,14	5,0	4,9	-1,7	-0,1
ICP-MS				2	0			3,00		2,68				-5,2	-3,6
Cap. Electrophoresis				1	0			2,76		2,56				-12,8	-7,9
Other method				1	1			2,70		2,20				-14,7	-20,9
Total Organic Carbon	AB	2,81	2,43	23	1	2,81	2,43	2,86	0,39	2,55	0,36	13,5	14,1	1,8	5,3
Combustion				16	1	2,90	2,50	2,99	0,37	2,65	0,37	12,3	14,1	6,3	9,3
UV/peroxodisulphate				5	0	2,45	2,31	2,56	0,33	2,33	0,25	12,8	10,8	-9,0	-4,0
Other method				2	0			2,67		2,40				-4,9	-1,2
Aluminium	CD	163,0	147,9	27	0	163,0	147,9	161,7	13,6	145,2	13,2	8,4	9,1	-0,8	-1,8
ICP-MS				11	0	162,0	146,8	163,8	9,1	148,2	11,6	5,5	7,8	0,5	0,2
ICP-AES				10	0	167,2	150,4	163,3	15,3	146,4	13,0	9,4	8,9	0,2	-1,0
GFAAS				5	0	160,0	143,0	157,5	18,7	138,1	17,9	11,9	12,9	-3,4	-6,6
Photometry				1	0			144,0		137,0				-11,7	-7,4
Iron	CD	93,28	83,21	30	1	93,28	83,21	92,18	9,27	83,98	8,21	10,1	9,8	-1,2	0,9
ICP-AES				13	0	93,32	82,50	93,49	5,97	84,35	6,39	6,4	7,6	0,2	1,4
ICP-MS				11	1	92,90	83,58	90,59	5,88	82,10	5,84	6,5	7,1	-2,9	-1,3
FAAS				3	0	101,00	98,00	106,00	9,54	98,13	8,20	9,0	8,4	13,6	17,9
GFAAS				2	0			84,42		77,26				-9,5	-7,2
Photometry				1	0			65,00		69,00				-30,3	-17,1
Manganese	CD	23,09	20,80	30	1	23,09	20,80	22,99	1,41	20,99	1,71	6,2	8,1	-0,4	0,9
ICP-MS				13	0	23,01	20,87	22,83	0,94	20,90	1,41	4,1	6,8	-1,1	0,5
ICP-AES				11	0	22,95	20,75	22,86	1,03	20,69	0,73	4,5	3,5	-1,0	-0,5
FAAS				3	0	23,90	20,60	24,16	1,23	22,12	3,03	5,1	13,7	4,6	6,3
GFAAS				2	0			22,98		21,49				-0,5	3,3
Photometry				1	1			28,00		30,00				21,3	44,2

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		pair	S. 1	S. 2	Total	Om	S. 1
Cadmium	CD	5,31	4,75	30	0	5,31	4,75	5,31	0,26	4,80	0,30	4,9	6,2	0,2	1,2
ICP-MS				15	0	5,26	4,84	5,30	0,22	4,87	0,27	4,1	5,6	-0,1	2,6
ICP-AES				9	0	5,21	4,70	5,26	0,25	4,77	0,24	4,8	4,9	-0,8	0,5
GFAAS				6	0	5,48	4,68	5,43	0,37	4,68	0,42	6,9	9,0	2,3	-1,4
Lead	CD	5,28	4,82	30	2	5,28	4,82	5,37	0,51	4,96	0,45	9,6	9,1	1,7	3,0
ICP-MS				15	0	5,34	4,86	5,40	0,27	4,97	0,34	5,0	6,9	2,3	3,2
ICP-AES				9	1	5,19	4,77	5,18	0,66	4,89	0,57	12,7	11,6	-1,8	1,6
GFAAS				6	1	5,20	4,80	5,57	0,80	5,06	0,63	14,4	12,5	5,5	5,0
Copper	CD	16,72	15,28	30	2	16,72	15,28	16,70	0,87	15,22	0,84	5,2	5,5	-0,1	-0,4
ICP-MS				15	0	16,92	15,48	16,88	0,66	15,42	0,72	3,9	4,7	1,0	0,9
ICP-AES				9	0	16,46	15,17	16,73	1,18	15,16	1,04	7,0	6,9	0,1	-0,7
GFAAS				5	2	16,10	14,60	15,84	0,53	14,40	0,44	3,4	3,1	-5,2	-5,8
FAAS				1	0			16,26		15,15				-2,7	-0,8
Nickel	CD	11,00	9,80	29	2	11,00	9,80	10,92	0,40	9,78	0,48	3,7	4,9	-0,8	-0,2
ICP-MS				15	1	11,06	9,92	11,05	0,25	9,98	0,25	2,3	2,5	0,4	1,8
ICP-AES				9	0	11,05	9,80	10,99	0,34	9,87	0,38	3,1	3,9	-0,1	0,7
GFAAS				5	1	10,30	8,79	10,29	0,44	8,90	0,27	4,2	3,1	-6,5	-9,2
Zinc	CD	21,86	19,99	29	1	21,86	19,99	21,83	1,55	19,95	1,78	7,1	8,9	-0,1	-0,2
ICP-MS				14	0	22,05	20,18	22,21	1,26	20,35	1,66	5,7	8,2	1,6	1,8
ICP-AES				10	0	21,80	19,64	21,55	0,73	19,58	0,62	3,4	3,2	-1,4	-2,0
FAAS				3	1			21,32		18,82				-2,5	-5,9
GFAAS				2	0			21,09		20,13				-3,5	0,7

*Om.: Sample pair omitted from the calculations

pH

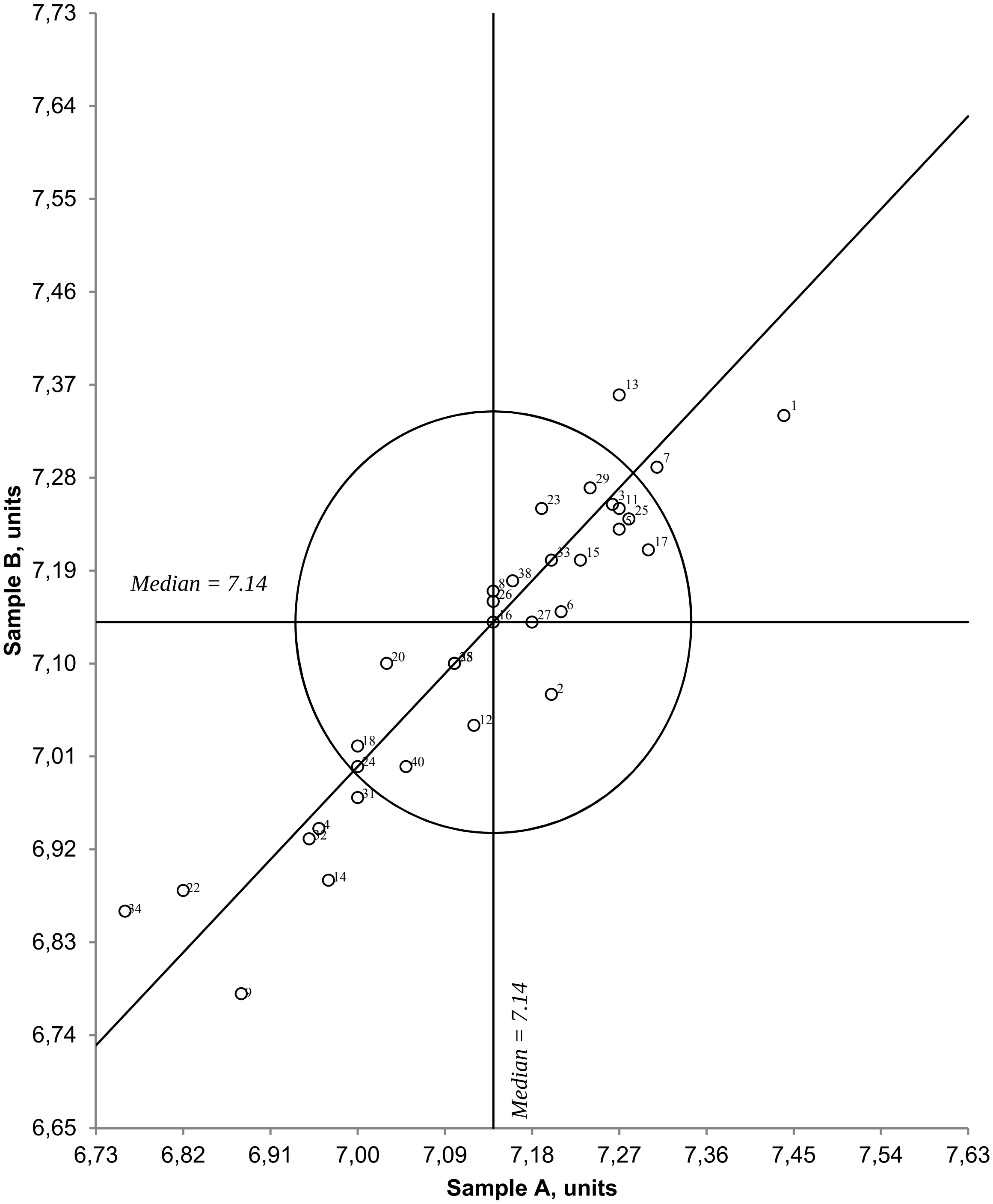

Figure 1. Youden diagram for pH, sample pair AB
Acceptable limit, given by circle, is 2.86 %

Conductivity

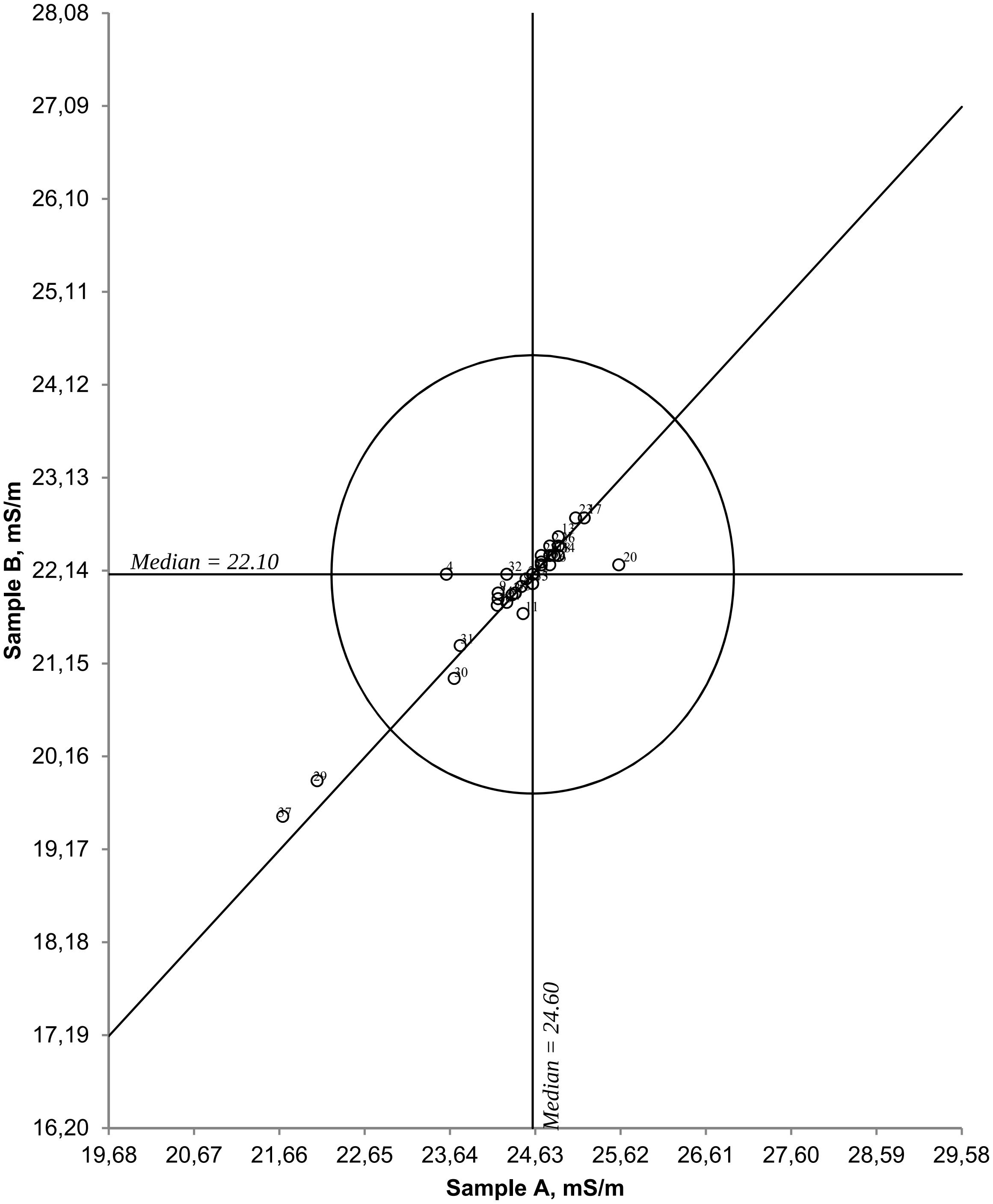

Figure 2. Youden diagram for conductivity, sample pair AB
Acceptable limit, given by circle, is 10 %

Alkalinity

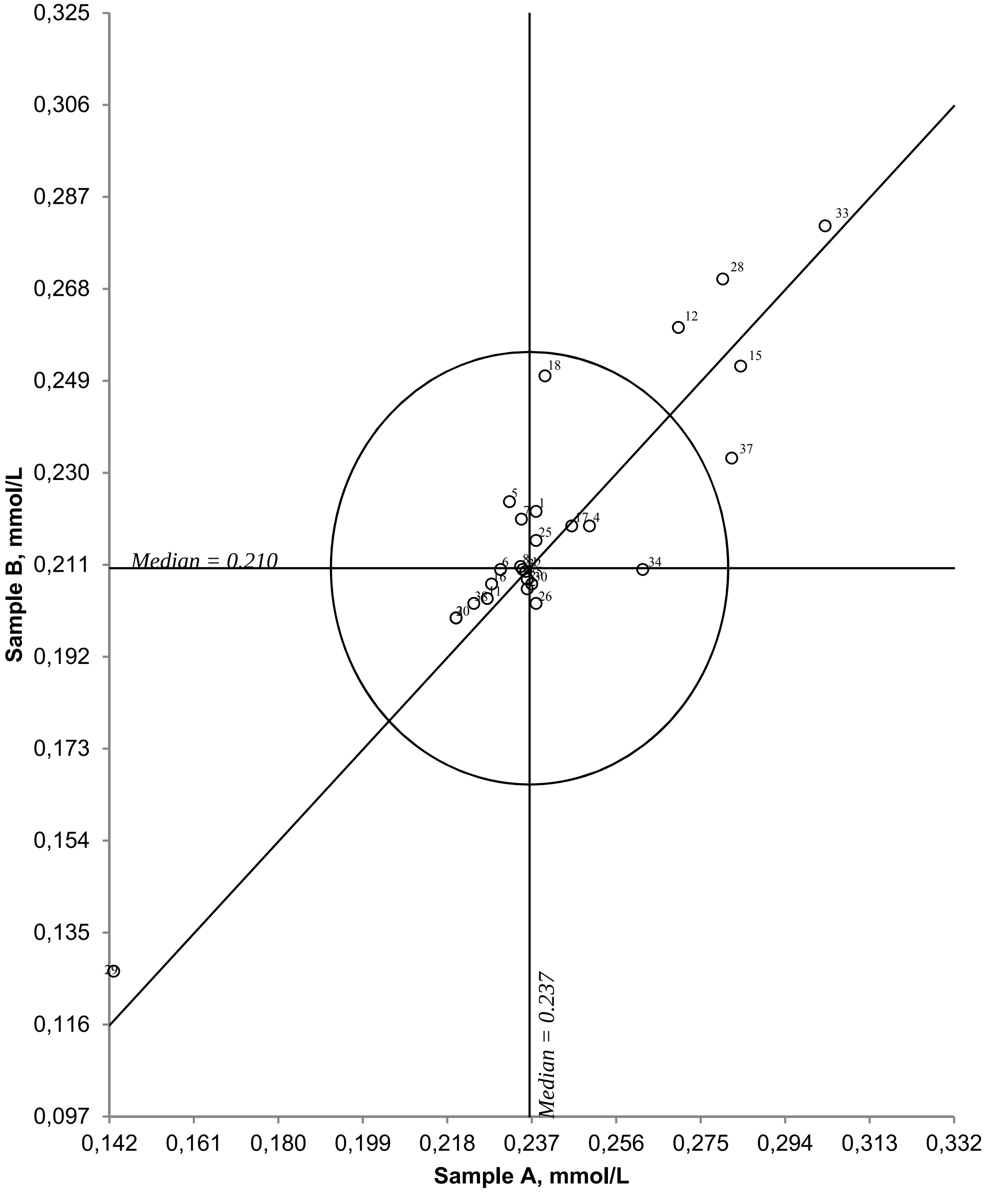

Figure 3. Youden diagram for alkalinity, sample pair AB
Acceptable limit, given by circle, is 20 %

Nitrate + nitrite-nitrogen

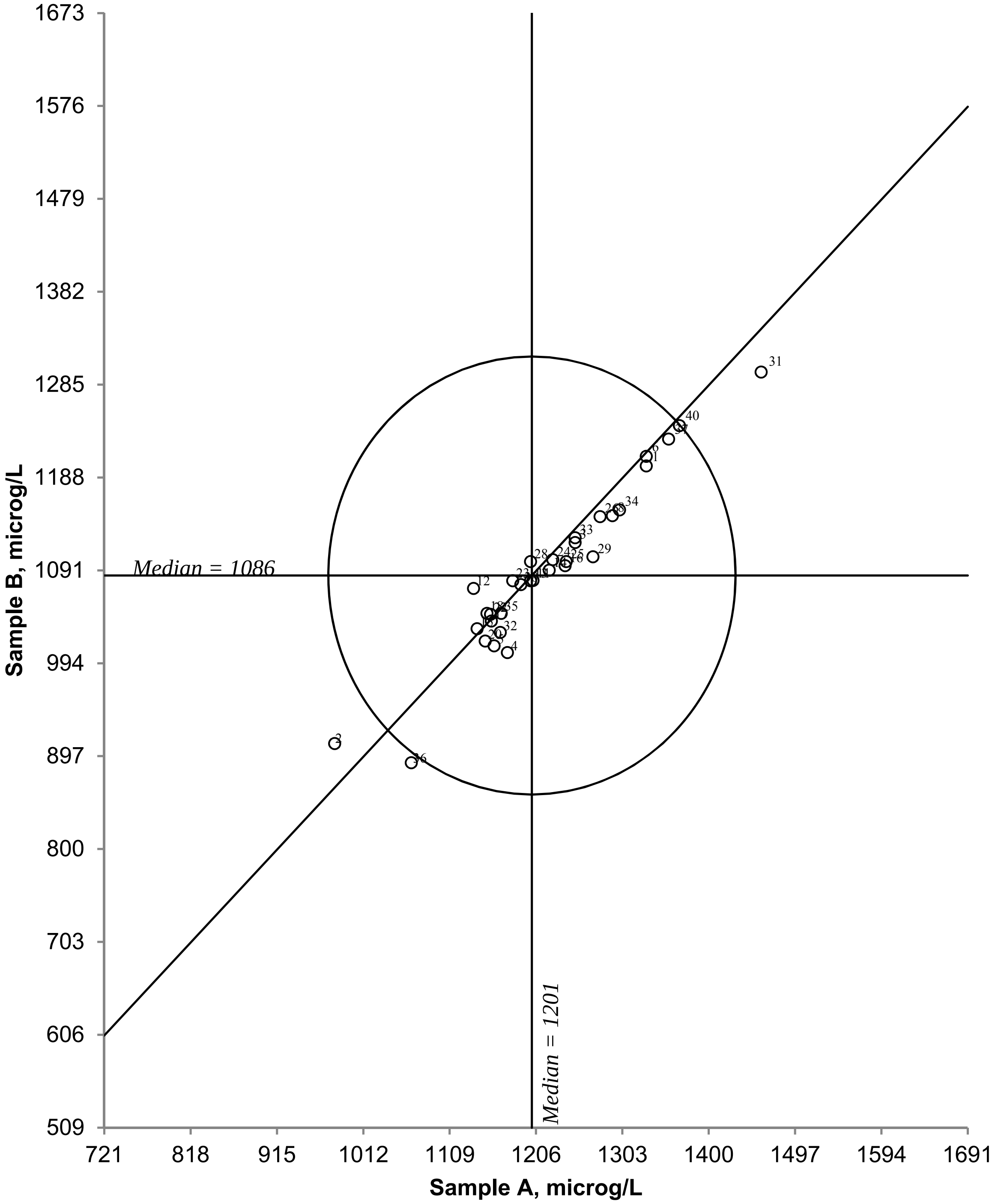

Figure 4. Youden diagram for nitrate + nitrite-nitrogen, sample pair AB
Acceptable limit, given by circle, is 20 %

Chloride

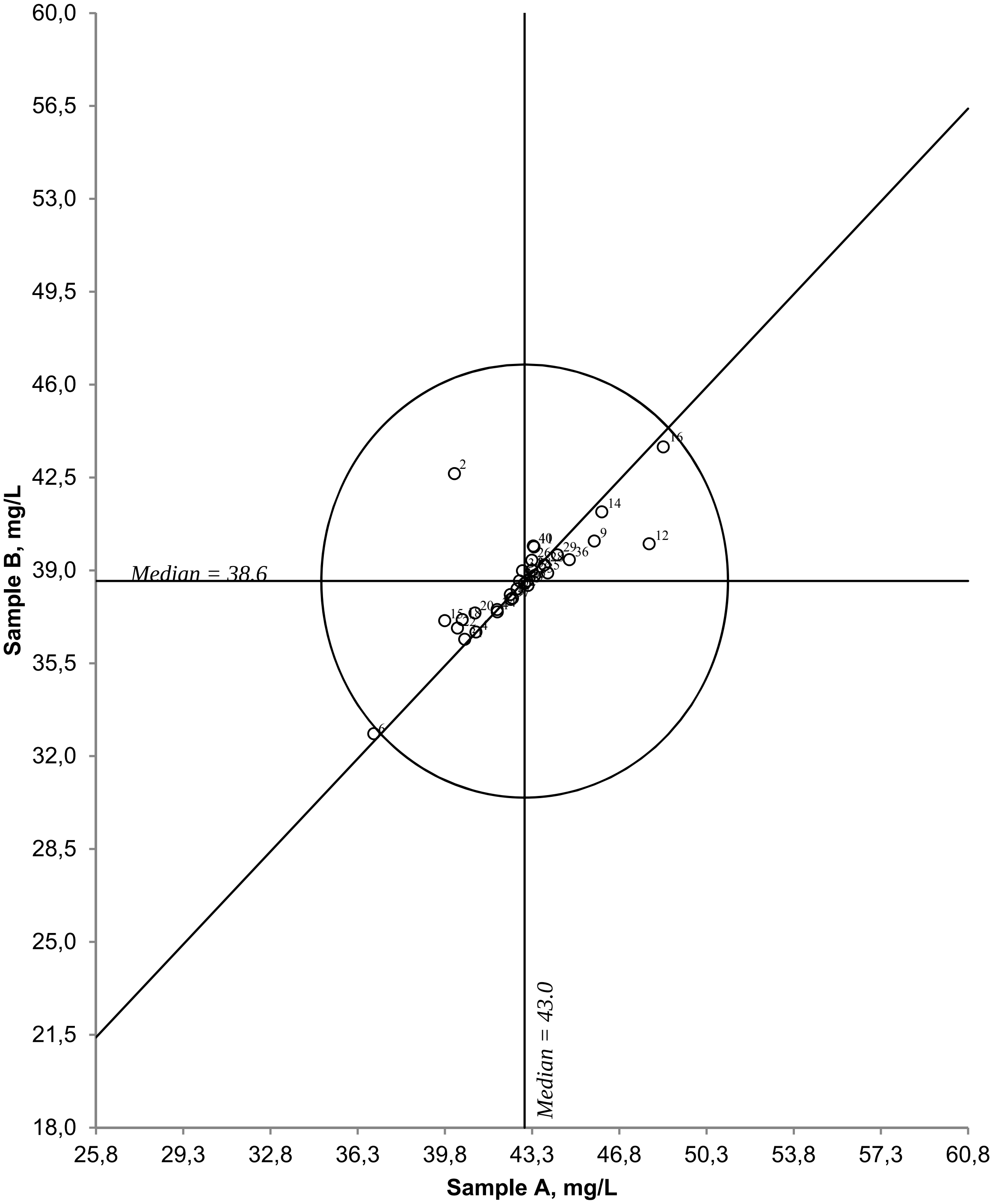

Figure 5. Youden diagram for chloride, sample pair AB
Acceptable limit, given by circle, is 20 %

Sulphate

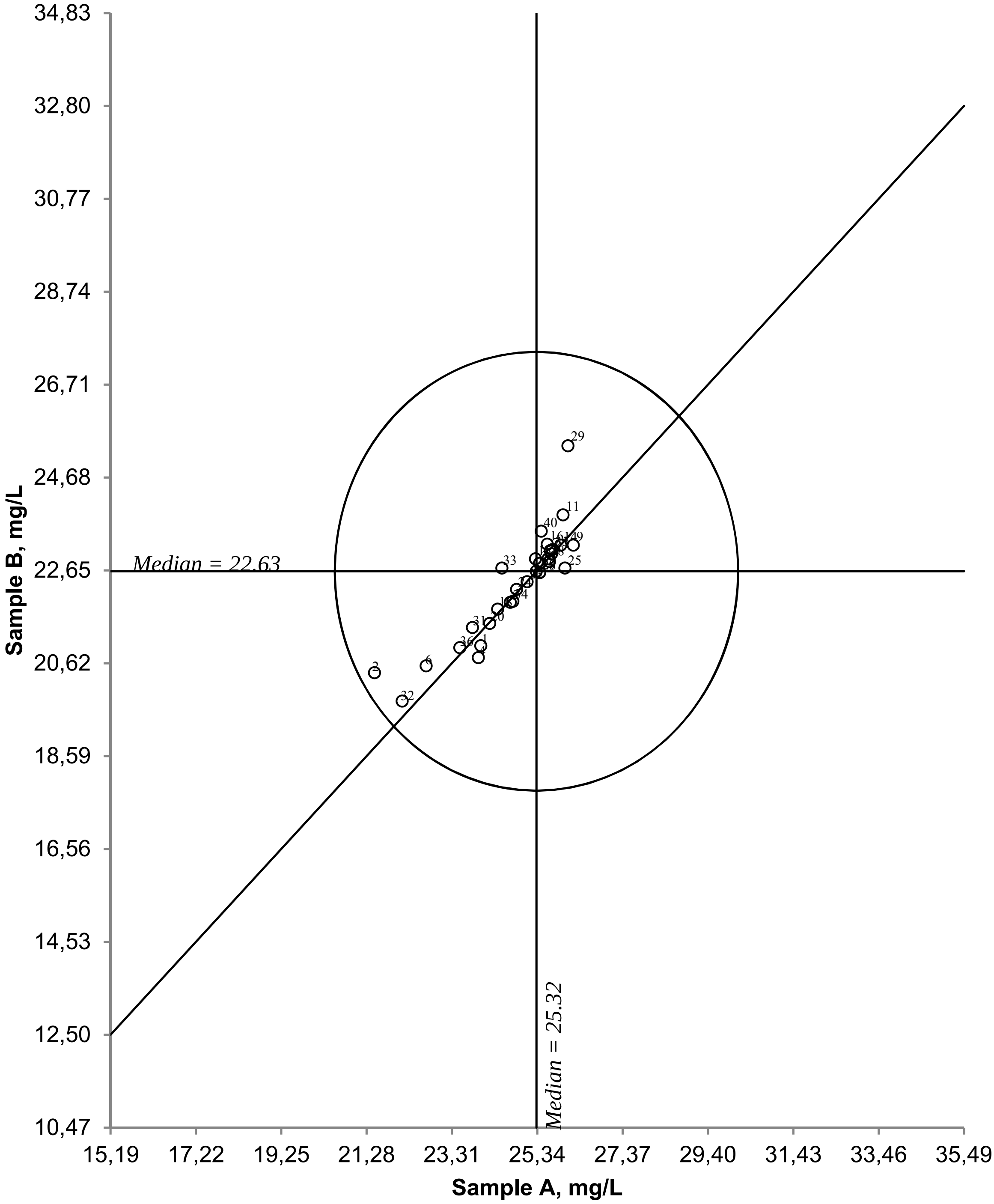

Figure 6. Youden diagram for sulphate, sample pair AB
Acceptable limit, given by circle, is 20 %

Calcium

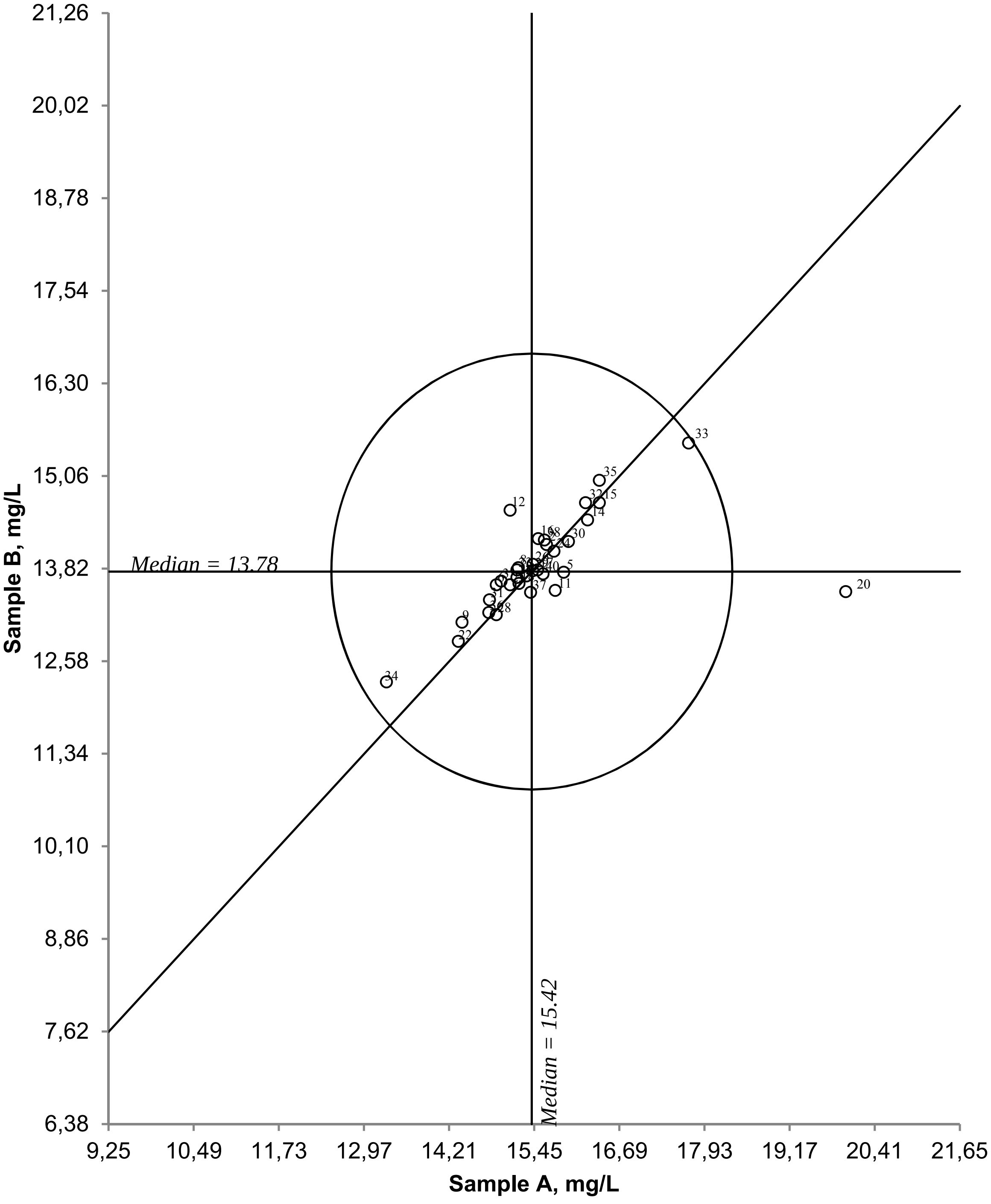

Figure 7. Youden diagram for calcium, sample pair AB
Acceptable limit, given by circle, is 20 %

Magnesium

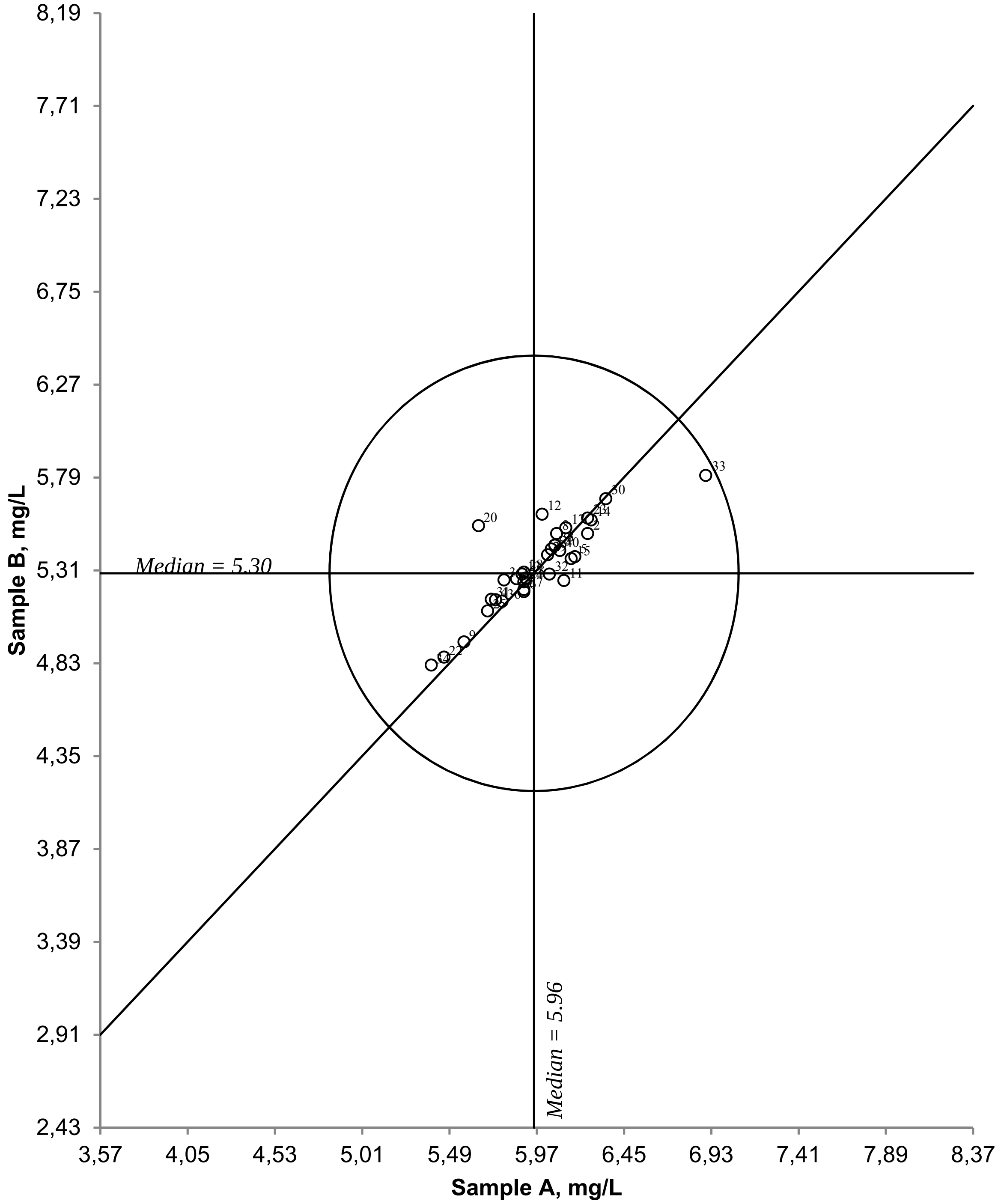

Figure 8. Youden diagram for magnesium, sample pair AB
Acceptable limit, given by circle, is 20 %

Sodium

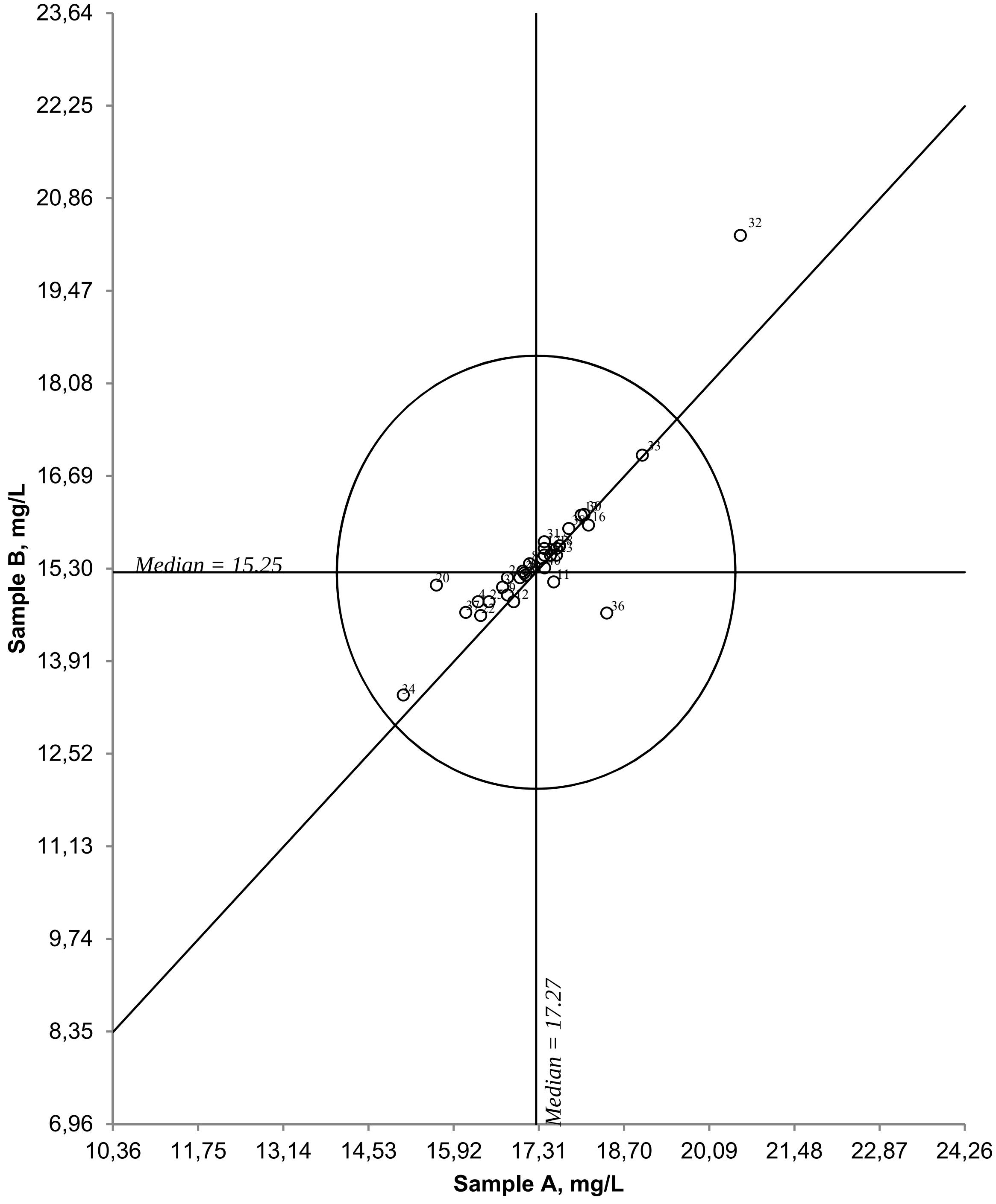

Figure 9. Youden diagram for sodium, sample pair AB
Acceptable limit, given by circle, is 20 %

Potassium

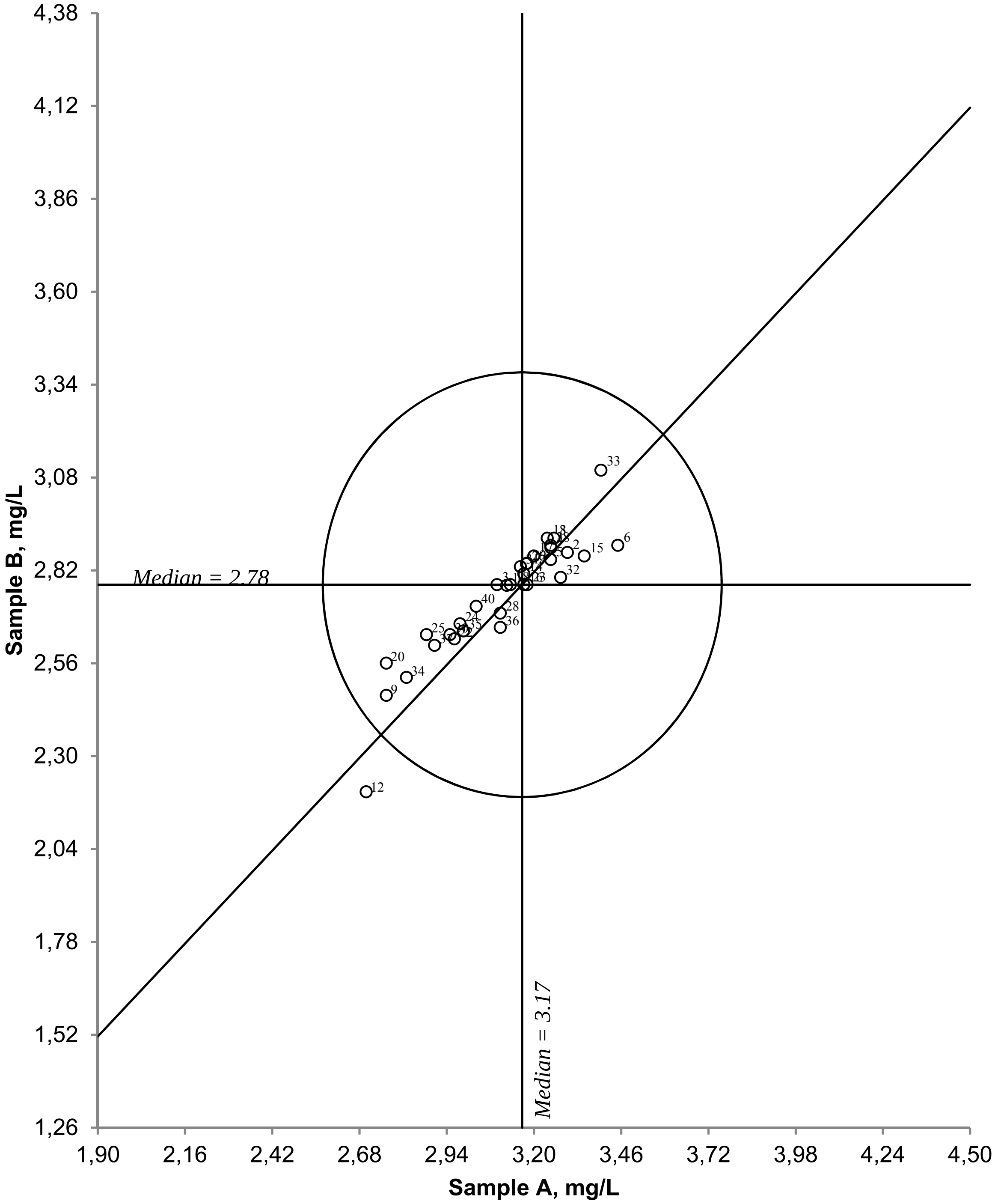

Figure 10. Youden diagram for potassium, sample pair AB
Acceptable limit, given by circle, is 20 %

Total organic carbon

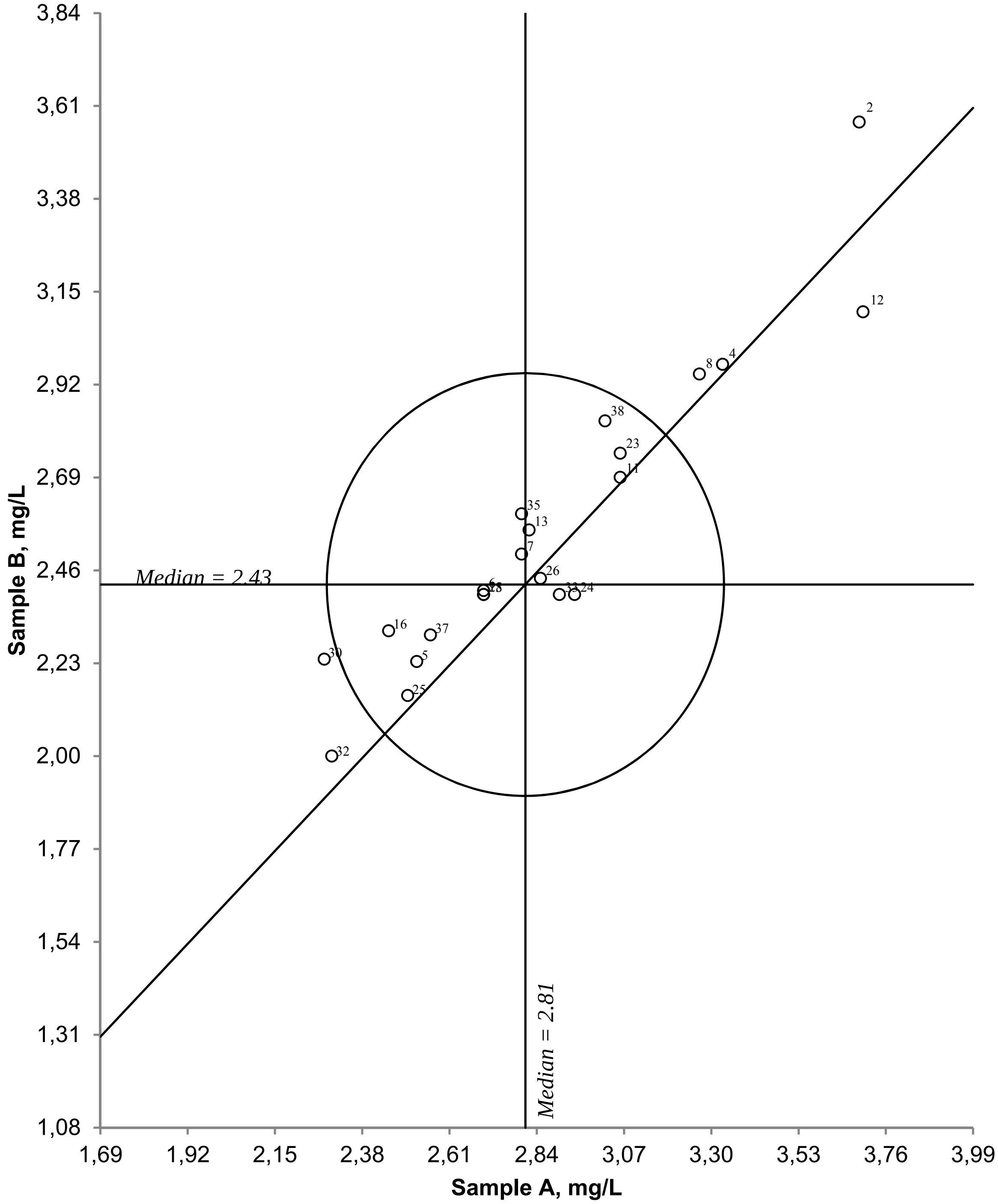

Figure 11. Youden diagram for total organic carbon, sample pair AB
Acceptable limit, given by circle, is 20 %

Aluminium

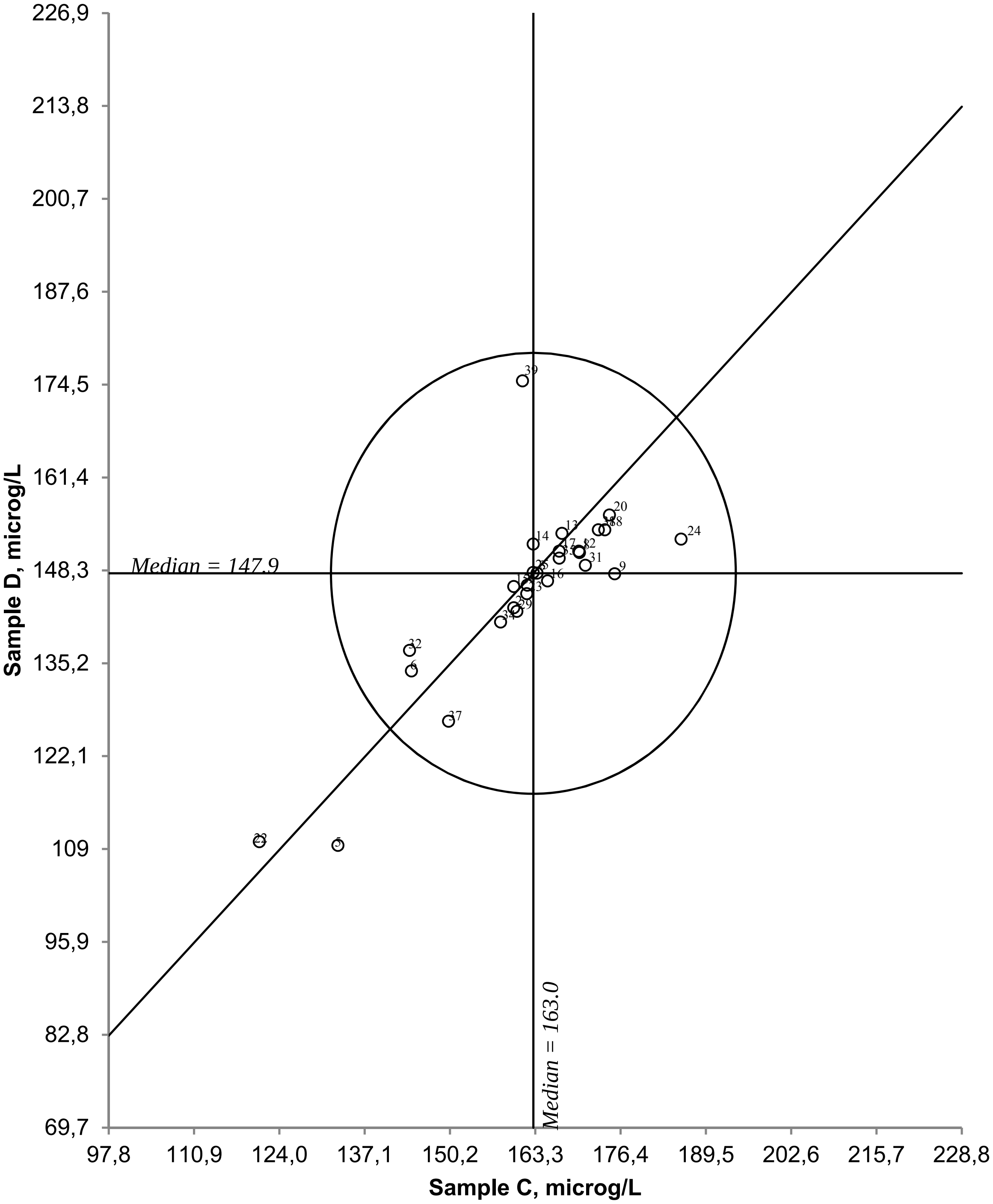

Figure 12. Youden diagram for aluminium, sample pair CD
Acceptable limit, given by circle, is 20 %

Iron

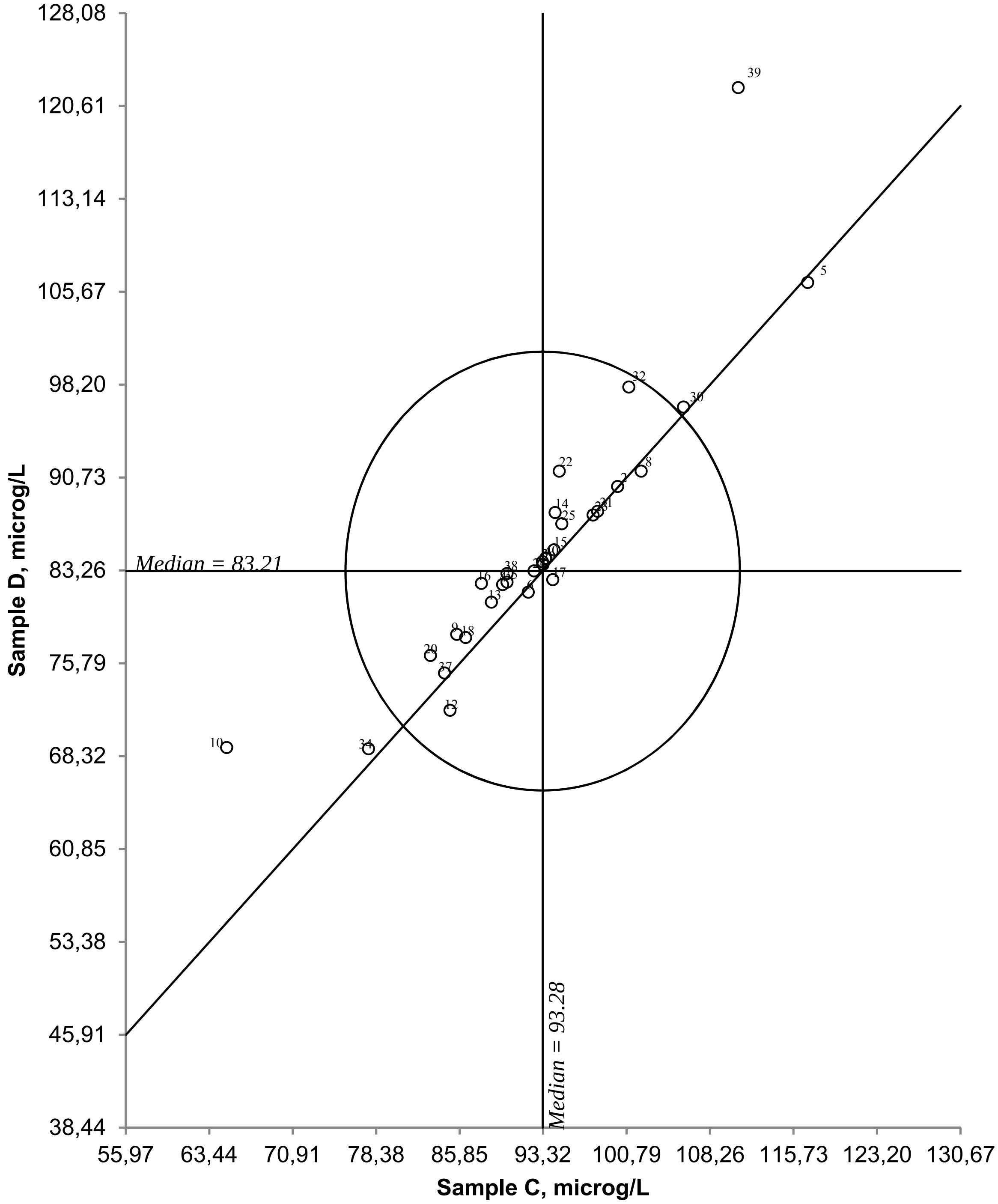

Figure 13. Youden diagram for iron, sample pair CD
Acceptable limit, given by circle, is 20 %

Manganese

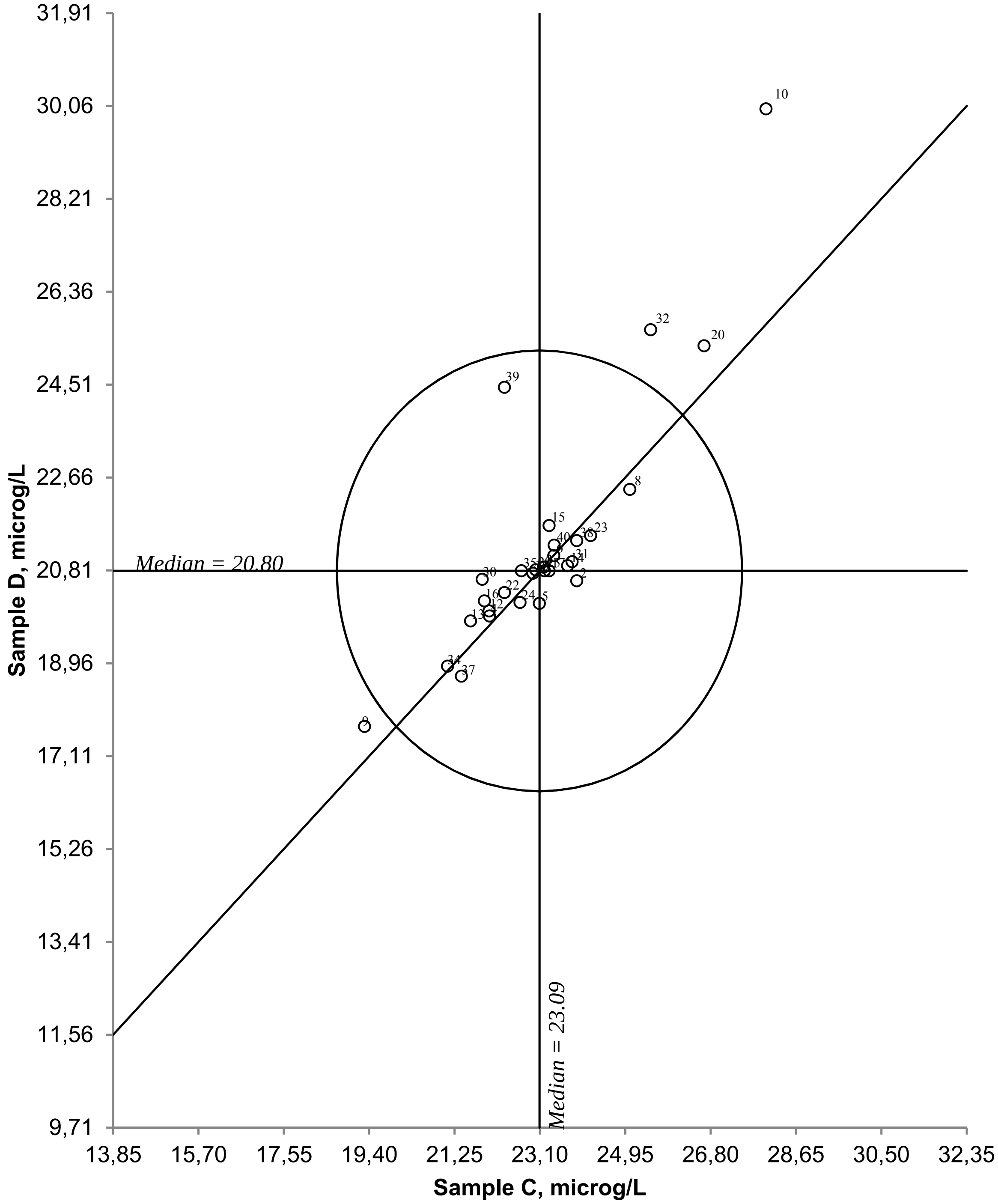

Figure 14. Youden diagram for manganese, sample pair CD
Acceptable limit, given by circle, is 20 %

Cadmium

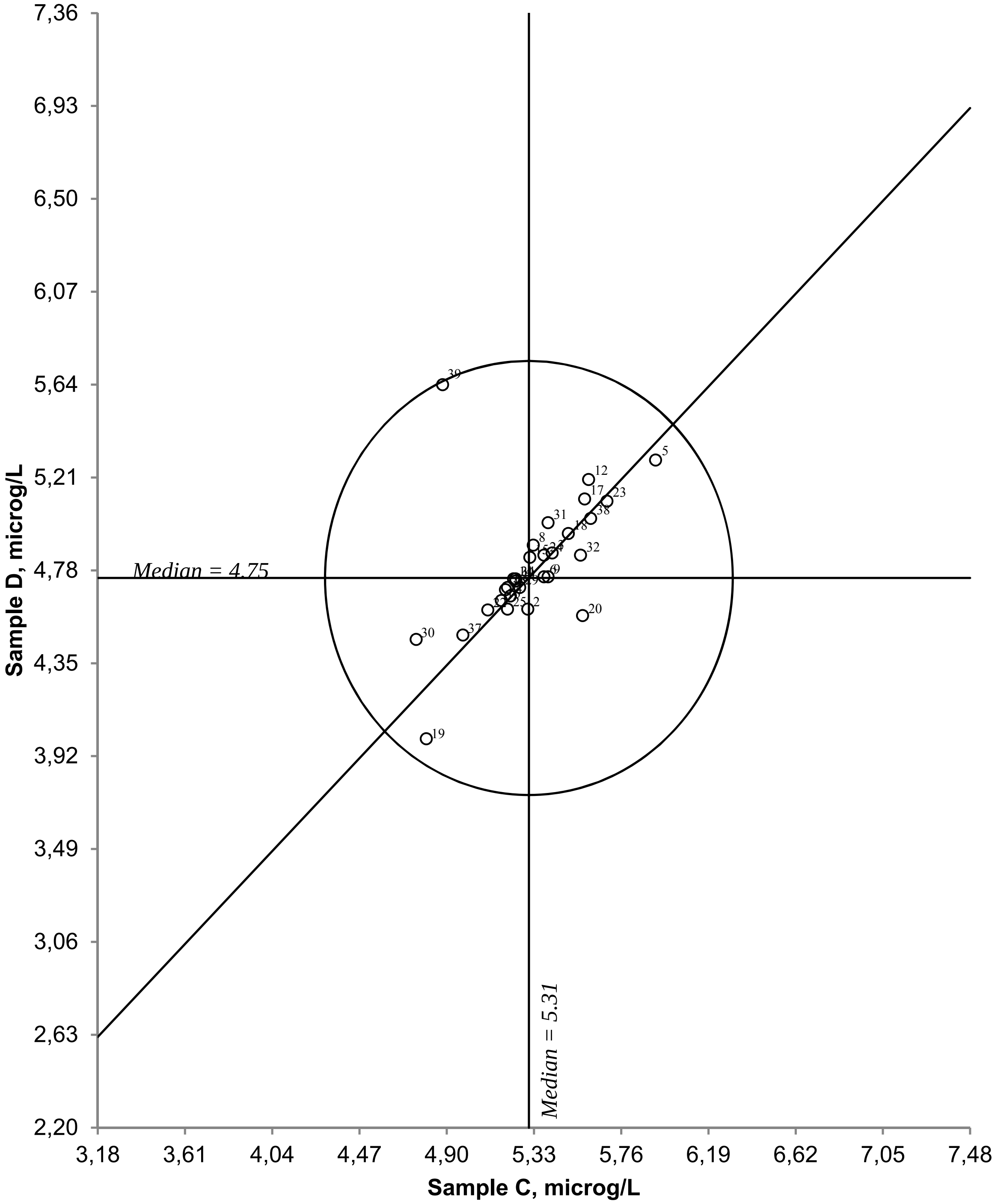

Figure 15. Youden diagram for cadmium, sample pair CD
Acceptable limit, given by circle, is 20 %

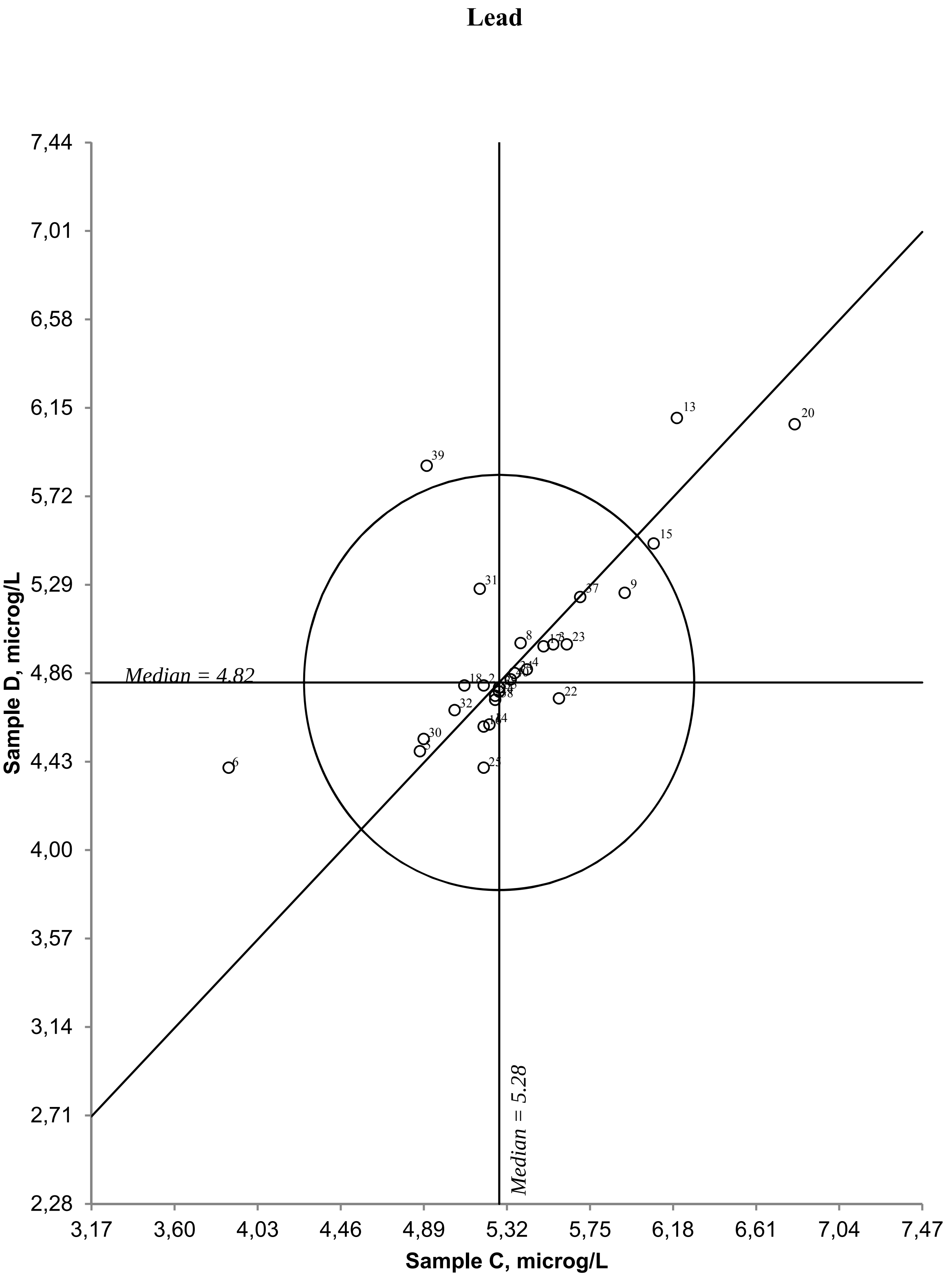

Figure 16. Youden diagram for lead, sample pair CD
Acceptable limit, given by circle, is 20 %

Copper

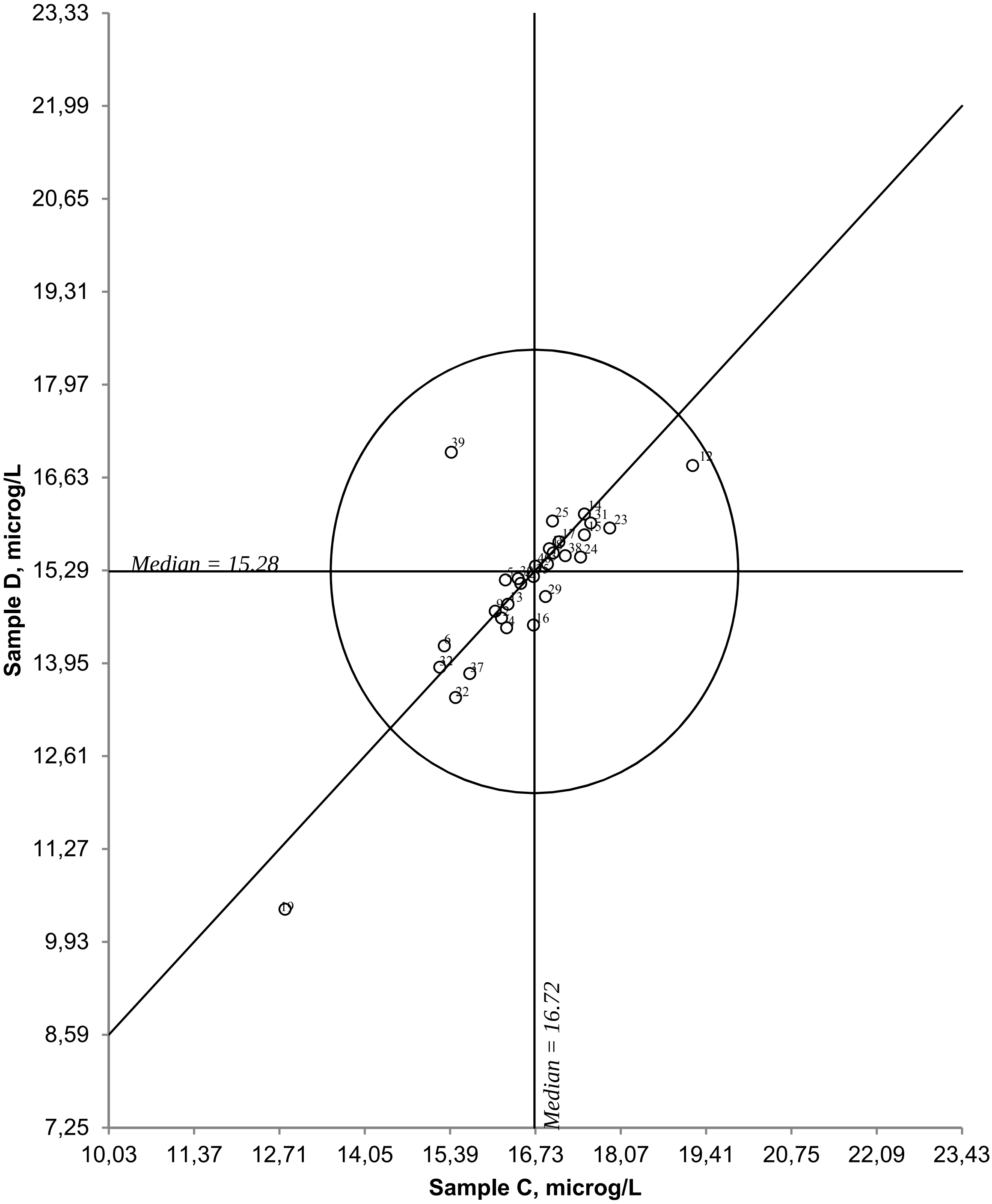

Figure 17. Youden diagram for copper, sample pair CD
Acceptable limit, given by circle, is 20 %

Nickel

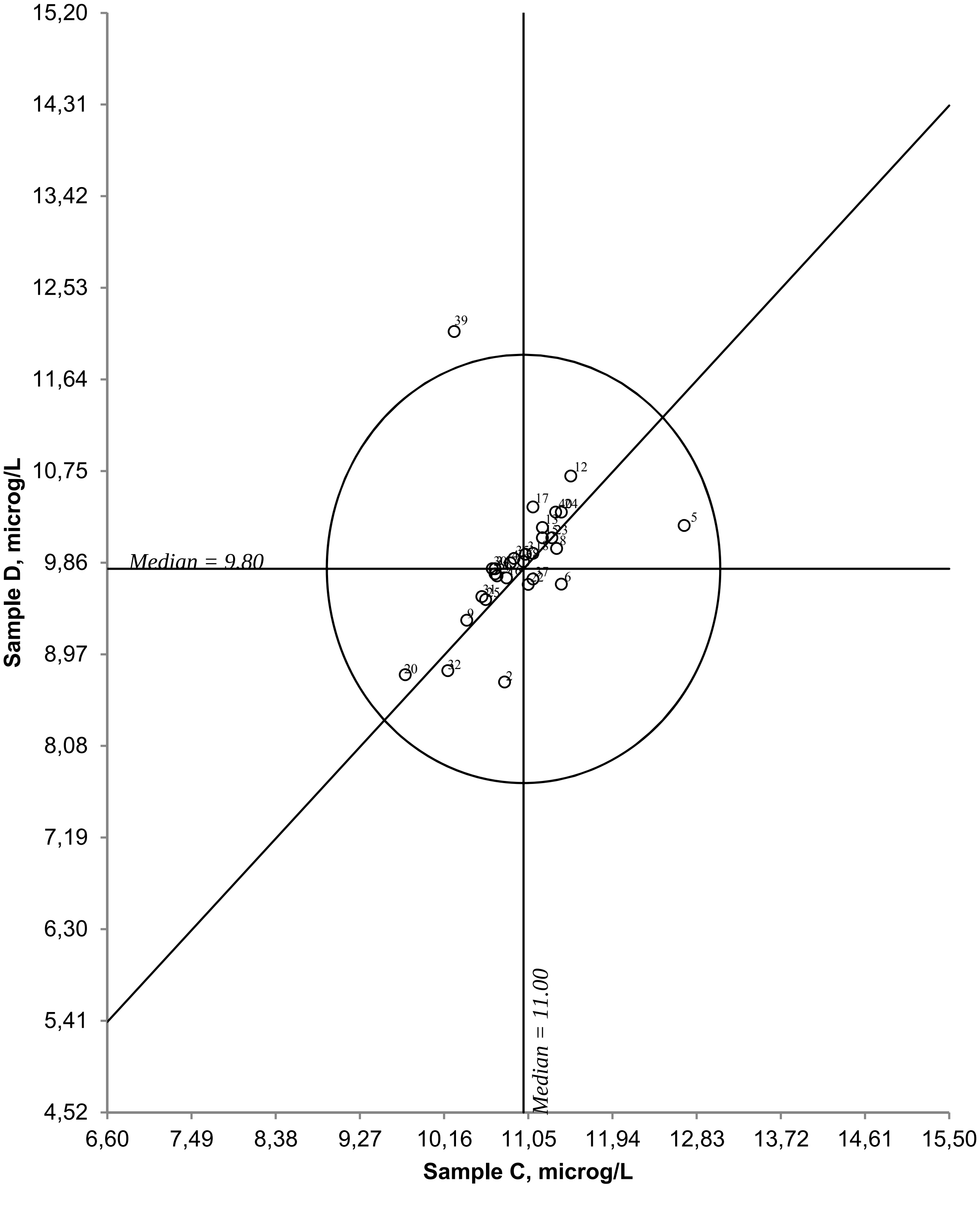

Figure 18. Youden diagram for nickel, sample pair CD
Acceptable limit, given by circle, is 20 %

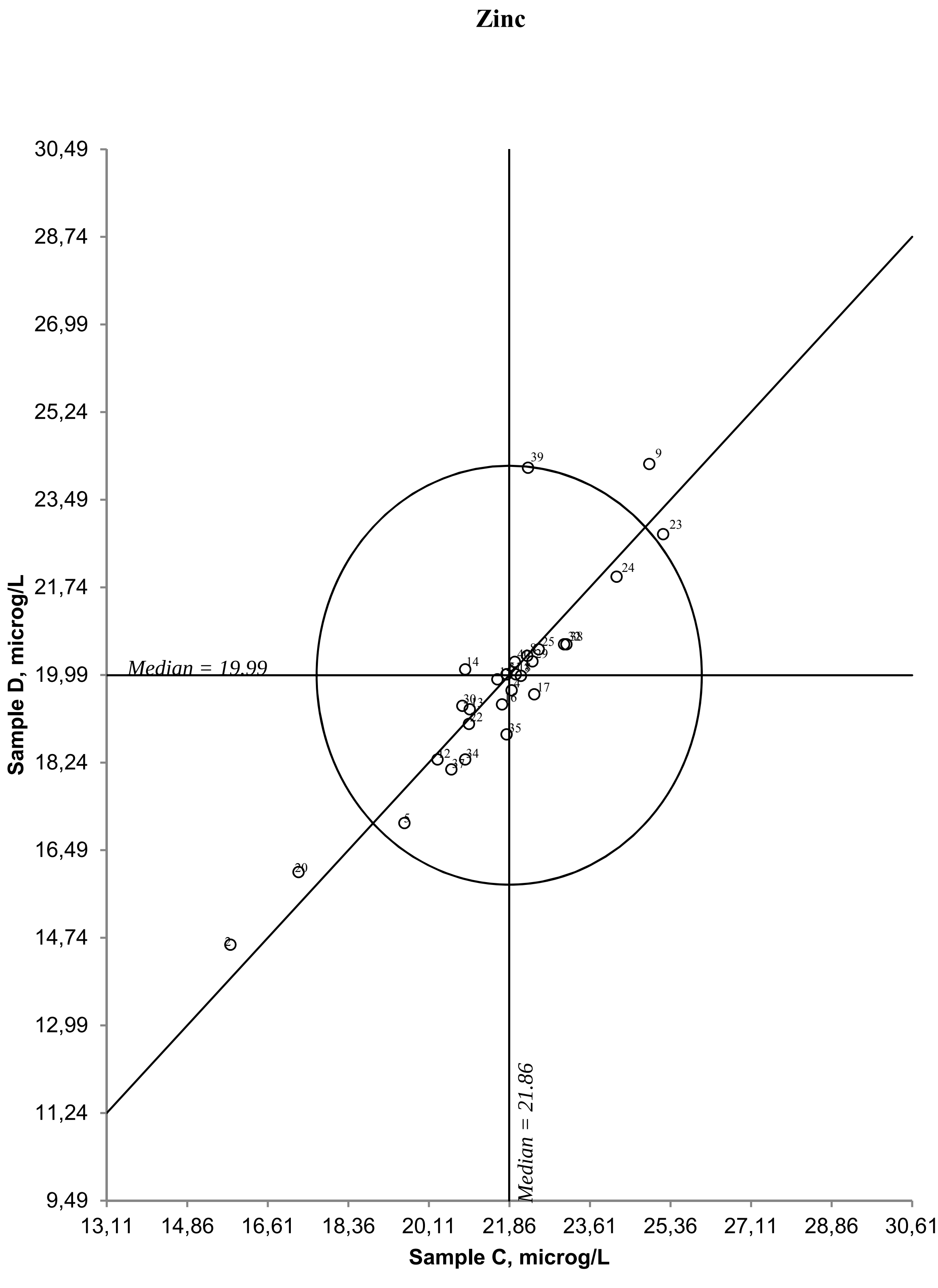

Figure 19. Youden diagram for zinc, sample pair CD
Acceptable limit, given by circle, is 20 %

5. Literature

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

Appendix A.

The participating laboratories

No	Laboratory	Town	Country
1	EPA Regional Inspectorate Castlebar OEA	John Moore Road, Castlebar, Ireland.	Ireland
2	Chemical Laboratory, Czech Geological Survey	Geologická 6, 152 00 Prague	Czech Republic
3	University of Helsinki Lab. of Geology and Geography	P.O.Box 64 00014 university of Helsinki	Finland
4	Institute of Biology Komi SC UB RAS	Kommunisticheskaya st.,28 Syktyvkar,167982,Russia	Russian Federation
5	Environmental Pollution Monitoring Center Laboratory of surface and sea	Verkhnerostinskoe sh,51,MUGMS,Murmansk,Russia	Russian Federation
6	Latvian Environmental Laboratory	165 Maskavas str., Riga LV-1019	Latvia
7	Stockholms universitet, ACES	106 91 Stockholm	Sweden
8	Swedish University for Agricultural Sciences Aquatic Sciences and Assesment	Box 7050 750 07 UPPSALA	Sweden
9	Polish Academy of Sciences Institute of Botany	PAN Instytut Botaniki 31-512 Kraków ul. Lubicz 46	Poland
10	Institute for Public Health Pancevo	Pasterova 2 26000 Pancevo	Serbia
11	Marine Scotland Science Freshwater Laboratory	Faskally, Pitlochry, Perthshire, PH16 5BB, Scotland.	United Kingdom
12	Radbouduniversiteit afd. Ecologie t.a.v. G. Verheggen	Postbus 9010 6500 GL Nijmegen	Netherlands
13	Natural Resources Institute Finland Vantaa	Jokiniemenkuja 1 FIN-01370 Vantaa	Finland
14	NILU, Avd. uorganisk analyse	Postboks 100 2027 Kjeller	Norway
15	Norsk institutt for vannforskning	Gaustadalléen 21 0439 OSLO	Norway
16	Ufficio del Monitoraggio Ambientale - Laboratorio	Via Mirasole 22 6500 Bellinzona	Switzerland
17	Finnish Environment Institute SYKE Laboratory Center	Hakuninmaantie 6 FI-00430 HELSINKI	Finland
18	FGU «Baltwodhoz»	Saint-Petersburg, V.O. Sredny pr. 26	Russian Federation
19	Institute of Global Climate and Ecology (IGCE) Roshydromet and RAS Russian Academy of Sciences	20-B, Glebovskaya St., Moscow, 107258	Russian Federation

No	Laboratory	Town	Country
20	Hydrochemical Laboratory by Federal State Enterprise on Water Industry	10 A Stahanovskaya str., Pskov, 180004	Russian Federation
21	Institute of Botany PAS	PAN Instytut Botaniki 31-512 Kraków ul. Lubicz 46	Poland
22	Büsgen-Institute - Soil Science of Temperate Ecosystems	D-37077 Goettingen Buesgenweg 2	Germany
23	Bayerisches Landesamt fuer Umwelt	Ref 71 Bürgerm-Ulrich-Str. 160 D-86179 Augsburg	Germany
24	Bayerische Landesanstalt fur Wald und Forstwirtschaft Abteilung 2 - Boden und Klima	Hans-Carl-von-Carlowitz-Platz 1 D-85354 Freising	Germany
25	CNR Istituto Studio degli Ecosistemi	Largo Tonolli 50 I-28922 VERBANIA Pallanza	Italy
26	Institut fur Ökologie	Technikerstrasse 25 6020 Innsbruck Austria	Austria
27	Institute of Environmental Protection-Puszcza Borecka station	Kolektorska 4	Poland
28	Staatliche Betriebgesellschaft für Umwelt und Landwirtschaft (BfUL)	Haus5, FB53 Waldheimer Str. 219 D-01683 Nossen	Germany
29	Natural Resources Wales , Llanelli Laboratory	19 Penyfai Lane Furnace Llanelli Carmarthenshire	United Kingdom
30	Institute for Ecology of Industrial Areas	Kossutha str. 6 40-844 Katowice	Poland
31	Insitute of Industrial Ecology Problems of the North (INEP) Group ICP methods of analysis	184209 Apatity, Akademgorodok 14A, Murmansk reg.	Russian Federation
32	Northern Water Problems Institute	A.Nevskogo, 50, Petrozavodsk 185030	Russian Federation
33	Staatliche Betriebgesellschaft für Umwelt und Landwirtschaft (BfUL)	Stephanplatz 3 D-09010 Chemnitz	Germany
34	EPA, Dublin Inspectorate McCumiskey Hs,	Richview, Clonskeagh Road, Dublin 14, Ireland.	Ireland
35	Estonian Environment Research Centre	Marja 4 D 10617 Tallinn Estonia	Estonia
36	Forest Nutrition and Water Resources Department of Ecology, Technis	H.C.v.Carlowitz-Platz 2 D-85354 Freising Germany	Germany
37	Laboratoire d'Ecologie Fonctionnelle et Environnement (ECOLAB)	Avenue Agrobiopole 31326 Castanet Tolosan	France

No	Laboratory	Town	Country
38	IVL Svenska miljöinstitutet AB	P.O. Box 53021 SE-400 14 Gothenburg	Sweden
39	Servei d'Anàlisi Química i Estructural	STR-UdG Pic de Peguera, 15 17003-Girona	Spain
40	ISSeP Colfontaine Zoning Schweitzer	Rue de la Platinerie B-7340 COLFONTAINE	Belgium

Number of participating laboratories from the different countries represented in intercomparison 1529

Country	No. of labs.	Country	No. of labs.
Austria	1	Netherlands	1
Belgium	1	Norway	2
Czech Republic	1	Poland	4
Estonia	1	Russia	7
Finland	3	Serbia	1
France	1	Spain	1
Germany	6	Sweden	3
Ireland	2	Switzerland	1
Italy	1	United Kingdom	2
Latvia	1		

Total: 19 countries

Appendix B.

Preparation of samples

The sample solutions were prepared from water collected in Isdammen lake (Latitude: 59.955745; Longitude: 10.823742; Altitude: 245 m) just outside the city of Oslo in Norway. The water, collected in 25 litre plastic containers, was brought to the laboratory and stored for about two weeks. The water was then filtrated through 0,45 µm cellulose acetate membrane. The filtrate was collected in polyethylene containers and stored at room temperature one more week to equilibrate. Small aliquots were taken from the filtrate to determine the background concentrations of the analytical variables of interest.

In the current edition, no modification of natural pH was performed, however, the sample set AB was spiked with salts to increase the concentration of Na^+, K^+, Ca^{2+}, Mg^{2+} Cl^-, NO_3^- and SO_4^{2-}. 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 they were delivered 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 $|x_i - m|$ $(i = 1, 2 \ldots. p)$

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	7,14	36	0,177	0,037	0,074
	B	7,14	36	0,180	0,038	0,075
Conductivity	A	24,60	32	0,397	0,088	0,176
mS/m	B	22,10	31	0,289	0,065	0,130
Alkalinity	A	0,237	28	0,0226	0,0053	0,0107
mmol/l	B	0,210	26	0,0165	0,0040	0,0081
Nitrate + nitrite-nitrogen	A	1201	32	83,8	18,5	37,0
µg N/l	B	1086	32	76,3	16,9	33,7
Chloride	A	43,0	32	1,97	0,44	0,87
mg/l	B	38,6	31	1,39	0,31	0,62
Sulphate	A	25,32	31	0,981	0,220	0,440
mg/l	B	22,63	31	1,104	0,248	0,496
Calcium	A	15,42	32	0,610	0,135	0,270
mg/l	B	13,78	33	0,560	0,122	0,244
Magnesium	A	5,96	32	0,238	0,053	0,105
mg/l	B	5,30	33	0,206	0,045	0,089
Sodium	A	17,27	32	0,693	0,153	0,306
mg/l	B	15,25	32	0,507	0,112	0,224
Potassium	A	3,17	33	0,194	0,042	0,084
mg/l	B	2,78	32	0,130	0,029	0,057
Total organic carbon	A	2,81	22	0,375	0,100	0,200
mg/l	B	2,43	20	0,267	0,075	0,149
Aluminium	C	163,0	27	10,17	2,45	4,89
µg/l	D	147,9	27	7,69	1,85	3,70
Iron	C	93,28	30	7,618	1,739	3,477
µg/l	D	83,21	29	7,242	1,681	3,362
Manganese	C	23,09	30	1,295	0,296	0,591
µg/l	D	20,80	29	0,985	0,229	0,457
Cadmium	C	5,31	30	0,245	0,056	0,112
µg/l	D	4,75	30	0,242	0,055	0,110
Lead	C	5,28	28	0,360	0,085	0,170
µg/l	D	4,82	28	0,361	0,085	0,171
Copper	C	16,72	28	0,849	0,201	0,401
µg/l	D	15,28	29	0,890	0,207	0,413
Nickel	C	11,00	28	0,404	0,095	0,191
µg/l	D	9,80	28	0,401	0,095	0,190
Zinc	C	21,86	28	1,140	0,269	0,538
µg/l	D	19,99	29	1,421	0,330	0,660

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	7,44	7,34	24,60	22,10	0,238	0,222	1330	1200	41,9	37,4	24,00	21,00				
2	7,20	7,07	24,80	22,40	0,236	0,206	980	910	40,2	42,6	21,47	20,41	15,63	14,14	6,25	5,50
3	7,26	7,25	24,90	22,30	0,220	0,200	1250	1120	42,5	38,0	25,63	22,84	14,97	13,65	5,79	5,26
4	6,96	6,94	23,60	22,10	0,250	0,219	1174	1005	41,1	36,7	23,94	20,74	15,34	13,72	5,74	5,16
5	7,27	7,23	24,80	22,30	0,232	0,224	1159	1012	43,9	38,9	24,70	21,95	15,88	13,77	6,18	5,38
6	7,21	7,15	239,00	215,00	0,230	0,210	1330	1210	37,0	32,8	22,70	20,56	14,90	13,60	5,90	5,20
7	7,31	7,29	24,70	22,20	0,235	0,220			42,4	38,1	25,65	23,08				
8	7,14	7,17	24,47	21,97	0,235	0,211	1292	1148	43,1	38,4	25,68	23,01	15,22	13,83	6,08	5,50
9	6,88	6,78	24,20	21,90			1	1	45,8	40,1	26,20	23,20	14,40	13,10	5,57	4,94
10																
11	7,27	7,25	24,49	21,68	0,227	0,204	1203	1080	43,4	39,9	25,95	23,86	15,76	13,53	6,12	5,26
12	7,12	7,04			0,270	0,260	1136	1072	48,0	40,0			15,10	14,60	6,00	5,60
13	7,27	7,36	24,90	22,50			1200	1080					15,20	13,70	5,89	5,29
14	6,97	6,89	255,00	213,00			1221	1091	46,1	41,2	25,90	23,20	16,23	14,47	6,27	5,57
15	7,23	7,20	24,60	22,00	0,284	0,252	1140	1030	39,8	37,1	25,30	22,90	16,40	14,70	6,16	5,37
16	7,14	7,14	24,19	21,77	0,228	0,207	1239	1096	48,6	43,7	25,58	23,22	15,51	14,22	6,05	5,42
17	7,30	7,21	25,20	22,70	0,246	0,219	1156	1038					15,50	13,80	6,13	5,53
18	7,00	7,02	24,85	22,30	0,240	0,250	1151	1046	40,5	37,1	24,40	21,80	15,23	13,62	5,91	5,27
19																
20	7,03	7,10	25,60	22,20	0,220	0,200	1149	1017	41,0	37,4	24,21	21,49	19,99	13,51	5,65	5,54

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
22	6,82	6,88	24,53	22,05			1155	1045	40,3	36,8	8,07	7,19	14,35	12,84	5,46	4,86
23	7,19	7,25	25,10	22,70			1180	1080	43,4	38,8	25,10	22,40	15,20	13,80	6,25	5,58
24	7,00	7,00	24,20	21,84			1225	1102	41,9	37,5	24,85	22,23	15,74	14,05	5,90	5,25
25	7,28	7,24	24,36	21,88	0,238	0,216	1240	1100	43,1	38,6	26,00	22,70	15,10	13,60	5,70	5,10
26	7,14	7,16	24,80	22,20	0,238	0,203	1278	1147	43,3	39,4	25,39	22,80	15,43	13,88	5,86	5,27
27	7,18	7,14	24,30	21,80												
28	7,10	7,10	24,70	22,30	0,280	0,270	1200	1100	43,8	39,2	25,40	22,60	14,90	13,20	5,90	5,30
29	7,24	7,27	22,10	19,90	0,143	0,127	1270	1105	44,3	39,6	26,07	25,37	15,43	13,79	6,03	5,39
30	6,70	6,73	23,69	20,99	0,237	0,207							15,95	14,18	6,35	5,68
31	7,00	6,97	23,76	21,34	0,235	0,210	1459	1298	40,6	36,4	23,80	21,40	14,80	13,40	5,72	5,16
32	6,95	6,93	24,30	22,10	0,236	0,210	1166	1026	42,7	38,3	22,13	19,79	16,20	14,70	6,04	5,29
33	7,20	7,20	24,60	22,00	0,303	0,281	1250	1125	43,0	38,5	24,50	22,70	17,70	15,50	6,90	5,80
34	6,76	6,86	24,90	22,30	0,262	0,210	1300	1154	42,9	39,0	24,76	21,97	13,30	12,30	5,39	4,82
35	7,10	7,10	24,60	22,10	0,236	0,208	1167	1046	42,8	38,6	25,70	23,10	16,40	15,00	6,07	5,44
36	7,71	7,60	24,90	22,40	0,350	0,300	1066	890	44,8	39,4	23,50	20,96	14,79	13,23	5,78	5,15
37	6,55	6,60	21,70	19,52	0,282	0,233	1355	1228	42,5	37,9	25,32	22,63	15,40	13,50	5,90	5,21
38	7,16	7,18	24,40	21,90	0,224	0,203	1189	1076	43,3	39,0	25,60	22,90	15,60	14,20	6,07	5,44
39																
40	7,05	7,00	24,70	22,23			1367	1242	43,4	39,9	25,44	23,50	15,58	13,75	6,10	5,41

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	16,80	15,16	3,30	2,87	3,69	3,57	160,0	143,0	100,00	90,00
3	16,72	15,02	3,09	2,78			163,6	147,9	93,28	83,95
4	16,32	14,80	3,25	2,88	3,33	2,97	162,1	146,2	89,70	82,10
5	17,65	15,64	3,25	2,85	2,52	2,23	133,0	109,5	117,00	106,40
6	17,50	15,50	3,45	2,89	2,70	2,41	144,3	134,1	92,00	81,50
7					2,80	2,50				
8	17,16	15,37	3,26	2,91	3,27	2,95	170,1	150,8	102,10	91,23
9	16,80	14,90	2,76	2,47			175,5	147,8	85,60	78,10
10									65,00	69,00
11	17,56	15,10	3,12	2,78	3,06	2,69				
12	16,90	14,80	2,70	2,20	3,70	3,10	170,0	151,0	85,00	72,00
13	18,00	16,10	3,24	2,91	2,82	2,56	167,4	153,5	88,70	80,70
14	17,37	15,45	3,17	2,81			163,0	152,0	94,40	87,90
15	17,10	15,20	3,35	2,86	2,70	2,40	160,0	146,0	94,30	84,90
16	18,12	15,95	3,17	2,78	2,45	2,31	165,2	146,8	87,80	82,20
17	17,40	15,60	3,20	2,86			167,0	151,0	94,20	82,50
18	17,60	15,60	3,13	2,78			174,0	154,0	86,40	77,85
19										
20	15,64	15,05	2,76	2,56			174,7	156,1	83,24	76,41

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
22	16,36	14,59	2,96	2,63	1,12	0,73	120,9	110,0	94,77	91,23
23	17,60	15,50	3,18	2,78	3,06	2,75	162,0	145,0	97,80	87,70
24	17,07	15,23	2,98	2,67	2,94	2,40	185,7	152,7	92,51	83,21
25	16,50	14,80	2,88	2,64	2,50	2,15	163,0	148,0	95,00	87,00
26	17,00	15,16	3,18	2,84	2,85	2,44				
27										
28	17,10	15,20	3,10	2,70	2,70	2,40				
29	17,05	15,26	3,18	2,84			160,5	142,5	93,32	83,72
30	18,05	16,11	2,95	2,64	2,28	2,24			105,90	96,39
31	17,40	15,70	3,16	2,83			171,0	149,0	98,20	88,00
32	20,60	20,30	3,28	2,80	2,30	2,00	144,0	137,0	101,00	98,00
33	19,00	17,00	3,40	3,10	2,90	2,40				
34	15,10	13,40	2,82	2,52			158,0	141,0	77,70	68,90
35	17,40	15,50	2,99	2,65	2,80	2,60	167,0	150,0	90,10	82,30
36	18,42	14,63	3,10	2,66						
37	16,12	14,64	2,90	2,61	2,56	2,30	150,0	127,0	84,50	75,00
38	17,80	15,90	3,25	2,89	3,02	2,83	173,0	154,0	90,10	83,00
39							161,4	175,0	110,79	122,07
40	17,41	15,31	3,03	2,72					93,55	84,22

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												
2	23,90	20,60	5,30	4,60	5,20	4,80	16,20	14,60	10,80	8,70	15,80	14,60
3	23,18	20,87	5,42	4,86	5,56	5,00	16,92	15,38	11,02	9,94	22,11	19,97
4	22,01	19,90	5,21	4,66	5,42	4,88	16,28	14,46	10,86	9,86	21,91	19,68
5	23,09	20,15	5,93	5,29	4,87	4,48	16,26	15,15	12,70	10,22	19,58	17,03
6	23,40	21,10	5,38	4,75	3,88	4,40	15,30	14,20	11,40	9,65	21,80	20,00
7												
8	25,05	22,42	5,33	4,90	5,39	5,01	17,01	15,54	11,35	10,00	22,25	20,37
9	19,30	17,70	5,40	4,75	5,93	5,25	16,10	14,70	10,40	9,30	24,90	24,20
10	28,00	30,00										
11												
12	22,00	20,00	5,60	5,20	8,50	7,60	19,20	16,80	11,50	10,70	20,30	18,30
13	21,60	19,80	5,20	4,70	6,20	6,10	16,30	14,80	11,20	10,20	21,00	19,30
14	23,70	20,90	5,23	4,74	5,23	4,61	17,50	16,10	10,70	9,75	20,90	20,10
15	23,30	21,70	5,31	4,84	6,08	5,49	17,50	15,80	11,20	10,10	21,60	19,90
16	21,90	20,20	5,17	4,64	5,20	4,60	16,70	14,50	10,82	9,71	21,70	19,40
17	23,30	20,80	5,58	5,11	5,51	4,99	17,10	15,70	11,10	10,40	22,40	19,60
18	22,95	20,75	5,50	4,95	5,10	4,80	16,95	15,60	11,10	9,95	22,00	20,00
19			4,80	4,00	2,90	2,60	12,80	10,40				
20	26,66	25,28	5,57	4,57	6,81	6,07	7,73	6,82	9,75	8,77	17,28	16,05

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
22	22,33	20,37	5,10	4,60	5,59	4,74	15,48	13,45	11,05	9,65	20,98	19,01
23	24,20	21,50	5,69	5,10	5,63	5,00	17,90	15,90	11,30	10,10	25,20	22,80
24	22,67	20,17	5,38	4,85	5,26	4,75	17,44	15,48	11,40	10,35	24,19	21,95
25	23,20	20,80	5,20	4,60	5,20	4,40	17,00	16,00	10,60	9,50	22,50	20,50
26												
27												
28												
29	23,01	20,82	5,26	4,70	5,28	4,79	16,89	14,91	10,72	9,73	22,36	20,26
30	21,85	20,63	4,75	4,46	4,89	4,54	16,46	15,17	10,67	9,80	20,84	19,37
31	23,80	20,98	5,40	5,00	5,18	5,27	17,60	15,97	10,56	9,53	21,80	20,00
32	25,50	25,60	5,56	4,85	5,05	4,68	15,23	13,89	10,20	8,81	23,05	20,60
33												
34	21,10	18,90	5,24	4,74	5,36	4,86	16,50	15,10	10,70	9,80	20,90	18,30
35	22,70	20,80	5,19	4,69	5,28	4,77	16,70	15,20	10,90	9,90	21,80	18,80
36												
37	21,40	18,70	4,98	4,48	5,70	5,23	15,70	13,80	11,10	9,70	20,60	18,10
38	23,90	21,40	5,61	5,02	5,26	4,73	17,20	15,50	11,00	9,87	23,10	20,60
39	22,33	24,45	4,88	5,64	4,91	5,87	15,41	16,99	10,27	12,10	22,27	24,13
40	23,41	21,31	5,24	4,73	5,34	4,83	16,73	15,35	11,34	10,35	21,98	20,25

Table 5.1. Statistics
pH

Sample A

Analytical method: All
Unit: units

Number of participants	36	Range	1,16
Number of omitted results	0	Variance	0,05
True value	7,14	Standard deviation	0,21
Mean value	7,11	Relative standard deviation	3,0%
Median value	7,14	Relative error	-0,4%

Analytical results in ascending order:

37	6,55	40	7,05	6	7,21
30	6,70	28	7,10	15	7,23
34	6,76	35	7,10	29	7,24
22	6,82	12	7,12	3	7,26
9	6,88	26	7,14	5	7,27
32	6,95	16	7,14	11	7,27
4	6,96	8	7,14	13	7,27
14	6,97	38	7,16	25	7,28
24	7,00	27	7,18	17	7,30
18	7,00	23	7,19	7	7,31
31	7,00	33	7,20	1	7,44
20	7,03	2	7,20	36	7,71

O = Omitted result

Table 5.1. Statistics
pH

Sample B

Analytical method: All
Unit: units

Number of participants	36	Range	1,00
Number of omitted results	0	Variance	0,04
True value	7,14	Standard deviation	0,20
Mean value	7,10	Relative standard deviation	2,8%
Median value	7,14	Relative error	-0,5%

Analytical results in ascending order:

37	6,60	12	7,04	33	7,20
30	6,73	2	7,07	17	7,21
9	6,78	35	7,10	5	7,23
34	6,86	28	7,10	25	7,24
22	6,88	20	7,10	23	7,25
14	6,89	27	7,14	11	7,25
32	6,93	16	7,14	3	7,25
4	6,94	6	7,15	29	7,27
31	6,97	26	7,16	7	7,29
24	7,00	8	7,17	1	7,34
40	7,00	38	7,18	13	7,36
18	7,02	15	7,20	36	7,60

Table 5.2. Statistics
Conductivity

Sample A

Analytical method: All
Unit: mS/m

Number of participants	35	Range	2,00
Number of omitted results	5	Variance	0,16
True value	24,60	Standard deviation	0,40
Mean value	24,60	Relative standard deviation	1,6%
Median value	24,60	Relative error	0,0%

Analytical results in ascending order:

37	21,70 O	8	24,47	26	24,80
29	22,10 O	11	24,49	18	24,85
4	23,60	22	24,53	36	24,90
30	23,69 O	1	24,60	34	24,90
31	23,76	35	24,60	3	24,90
16	24,19	15	24,60	13	24,90
9	24,20	33	24,60	23	25,10
24	24,20	28	24,70	17	25,20
27	24,30	40	24,70	20	25,60
32	24,30	7	24,70	6	239,00 O
25	24,36	2	24,80	14	255,00 O
38	24,40	5	24,80		

O = Omitted result

Table 5.2. Statistics
Conductivity

Sample B

Analytical method: All
Unit: mS/m

Number of participants	35	Range	1,36
Number of omitted results	5	Variance	0,09
True value	22,10	Standard deviation	0,29
Mean value	22,12	Relative standard deviation	1,3%
Median value	22,10	Relative error	0,1%

Analytical results in ascending order:

37	19,52 O	15	22,00	18	22,30
29	19,90 O	33	22,00	3	22,30
30	20,99 O	22	22,05	28	22,30
31	21,34	35	22,10	5	22,30
11	21,68	4	22,10	36	22,40
16	21,77	1	22,10	2	22,40
27	21,80	32	22,10	13	22,50
24	21,84	20	22,20	23	22,70
25	21,88	7	22,20	17	22,70
38	21,90	26	22,20	14	213,00 O
9	21,90	40	22,23	6	215,00 O
8	21,97	34	22,30		

O = Omitted result

Table 5.3. Statistics
Alkalinity

Sample A

Analytical method: All
Unit: mmol/L

Number of participants	28	Range	0,207
Number of omitted results	0	Variance	0,001
True value	0,237	Standard deviation	0,035
Mean value	0,245	Relative standard deviation	14,4%
Median value	0,237	Relative error	3,5%

Analytical results in ascending order:

29	0,143	31	0,235	4	0,250
3	0,220	32	0,236	34	0,262
20	0,220	35	0,236	12	0,270
38	0,224	2	0,236	28	0,280
11	0,227	30	0,237	37	0,282
16	0,228	1	0,238	15	0,284
6	0,230	25	0,238	33	0,303
5	0,232	26	0,238	36	0,350
8	0,235	18	0,240		
7	0,235	17	0,246		

O = Omitted result

Table 5.3. Statistics
Alkalinity

Sample B

Analytical method: All
Unit: mmol/L

Number of participants	28	Range	0,173
Number of omitted results	0	Variance	0,001
True value	0,210	Standard deviation	0,032
Mean value	0,221	Relative standard deviation	14,5%
Median value	0,210	Relative error	5,0%

Analytical results in ascending order:

29	0,127	32	0,210	5	0,224
3	0,200	31	0,210	37	0,233
20	0,200	34	0,210	18	0,250
38	0,203	6	0,210	15	0,252
26	0,203	8	0,211	12	0,260
11	0,204	25	0,216	28	0,270
2	0,206	17	0,219	33	0,281
16	0,207	4	0,219	36	0,300
30	0,207	7	0,220		
35	0,208	1	0,222		

O = Omitted result

Table 5.4. Statistics
Nitrate + nitrite-nitrogen

Sample A

Analytical method: All
Unit: microg/L

Number of participants	33	Range	479
Number of omitted results	1	Variance	8685
True value	1201	Standard deviation	93
Mean value	1218	Relative standard deviation	7,7%
Median value	1201	Relative error	1,4%

Analytical results in ascending order:

9	1 O	35	1167	3	1250
2	980	4	1174	33	1250
36	1066	23	1180	29	1270
12	1136	38	1189	26	1278
15	1140	28	1200	8	1292
20	1149	13	1200	34	1300
18	1151	11	1203	6	1330
22	1155	14	1221	1	1330
17	1156	24	1225	37	1355
5	1159	16	1239	40	1367
32	1166	25	1240	31	1459

O = Omitted result

Table 5.4. Statistics
Nitrate + nitrite-nitrogen

Sample B

Analytical method: All
Unit: microg/L

Number of participants	33	Range	408
Number of omitted results	1	Variance	7531
True value	1086	Standard deviation	87
Mean value	1091	Relative standard deviation	8,0%
Median value	1086	Relative error	0,5%

Analytical results in ascending order:

9	1 O	35	1046	29	1105
36	890	12	1072	3	1120
2	910	38	1076	33	1125
4	1005	23	1080	26	1147
5	1012	13	1080	8	1148
20	1017	11	1080	34	1154
32	1026	14	1091	1	1200
15	1030	16	1096	6	1210
17	1038	28	1100	37	1228
22	1045	25	1100	40	1242
18	1046	24	1102	31	1298

O = Omitted result

Table 5.5. Statistics
Chloride

Sample A

Analytical method: All
Unit: mg/L

Number of participants	32	Range	8,8
Number of omitted results	1	Variance	4,3
True value	43,0	Standard deviation	2,1
Mean value	43,0	Relative standard deviation	4,8%
Median value	43,0	Relative error	0,1%

Analytical results in ascending order:

6	37,0 O	37	42,5	11	43,4
15	39,8	3	42,5	23	43,4
2	40,2	32	42,7	28	43,8
22	40,3	35	42,8	5	43,9
18	40,5	34	42,9	29	44,3
31	40,6	33	43,0	36	44,8
20	41,0	25	43,1	9	45,8
4	41,1	8	43,1	14	46,1
24	41,9	26	43,3	12	48,0
1	41,9	38	43,3	16	48,6
7	42,4	40	43,4		

O = Omitted result

Table 5.5. Statistics
Chloride

Sample B

Analytical method: All
Unit: mg/L

Number of participants	32	Range	7,3
Number of omitted results	1	Variance	2,6
True value	38,6	Standard deviation	1,6
Mean value	38,8	Relative standard deviation	4,2%
Median value	38,6	Relative error	0,6%

Analytical results in ascending order:

6	32,8 O	7	38,1	26	39,4
31	36,4	32	38,3	36	39,4
4	36,7	8	38,4	29	39,6
22	36,8	33	38,5	11	39,9
15	37,1	25	38,6	40	39,9
18	37,1	35	38,6	12	40,0
20	37,4	23	38,8	9	40,1
1	37,4	5	38,9	14	41,2
24	37,5	34	39,0	2	42,6
37	37,9	38	39,0	16	43,7
3	38,0	28	39,2		

O = Omitted result

Table 5.6. Statistics
Sulphate

Sample A

Analytical method: All
Unit: mg/L

Number of participants	32	Range	4,73
Number of omitted results	1	Variance	1,37
True value	25,32	Standard deviation	1,17
Mean value	24,85	Relative standard deviation	4,7%
Median value	25,32	Relative error	-1,9%

Analytical results in ascending order:

22	8,07 O	5	24,70	38	25,60
2	21,47	34	24,76	3	25,63
32	22,13	24	24,85	7	25,65
6	22,70	23	25,10	8	25,68
36	23,50	15	25,30	35	25,70
31	23,80	37	25,32	14	25,90
4	23,94	26	25,39	11	25,95
1	24,00	28	25,40	25	26,00
20	24,21	29	25,40	29	26,07
18	24,40	40	25,44	9	26,20
33	24,50	16	25,58		

O = Omitted result

Table 5.6. Statistics
Sulphate

Sample B

Analytical method: All
Unit: mg/L

Number of participants	32	Range	5,58
Number of omitted results	1	Variance	1,34
True value	22,63	Standard deviation	1,16
Mean value	22,35	Relative standard deviation	5,2%
Median value	22,63	Relative error	-1,2%

Analytical results in ascending order:

22	7,19 O	34	21,97	38	22,90
32	19,79	24	22,23	8	23,01
2	20,41	23	22,40	7	23,08
6	20,56	29	22,60	35	23,10
4	20,74	28	22,60	9	23,20
36	20,96	37	22,63	14	23,20
1	21,00	25	22,70	16	23,22
31	21,40	33	22,70	40	23,50
20	21,49	26	22,80	11	23,86
18	21,80	3	22,84	29	25,37
5	21,95	15	22,90		

O = Omitted result

Table 5.7. Statistics
Calcium

Sample A

Analytical method: All
Unit: mg/L

Number of participants	33	Range	2,05
Number of omitted results	3	Variance	0,28
True value	15,42	Standard deviation	0,53
Mean value	15,40	Relative standard deviation	3,4%
Median value	15,42	Relative error	-0,1%

Analytical results in ascending order:

34	13,30 O	13	15,20	2	15,63
22	14,35	8	15,22	24	15,74
9	14,40	18	15,23	11	15,76
36	14,79	4	15,34	5	15,88
31	14,80	37	15,40	30	15,95
28	14,90	29	15,43	32	16,20
6	14,90	26	15,43	14	16,23
3	14,97	17	15,50	15	16,40
25	15,10	16	15,51	35	16,40
12	15,10	40	15,58	33	17,70 O
23	15,20	38	15,60	20	19,99 O

O = Omitted result

Table 5.7. Statistics
Calcium

Sample B

Analytical method: All
Unit: mg/L

Number of participants	33	Range	2,16
Number of omitted results	3	Variance	0,25
True value	13,78	Standard deviation	0,50
Mean value	13,85	Relative standard deviation	3,6%
Median value	13,78	Relative error	0,5%

Analytical results in ascending order:

34	12,30 O	18	13,62	24	14,05
22	12,84	3	13,65	2	14,14
9	13,10	13	13,70	30	14,18
28	13,20	4	13,72	38	14,20
36	13,23	40	13,75	16	14,22
31	13,40	5	13,77	14	14,47
37	13,50	29	13,79	12	14,60
20	13,51 O	23	13,80	32	14,70
11	13,53	17	13,80	15	14,70
6	13,60	8	13,83	35	15,00
25	13,60	26	13,88	33	15,50 O

O = Omitted result

Table 5.8. Statistics
Magnesium

Sample A

Analytical method: All
Unit: mg/L

Number of participants	33	Range	0,96
Number of omitted results	1	Variance	0,06
True value	5,96	Standard deviation	0,24
Mean value	5,94	Relative standard deviation	4,0%
Median value	5,96	Relative error	-0,2%

Analytical results in ascending order:

34	5,39	37	5,90	8	6,08
22	5,46	6	5,90	40	6,10
9	5,57	28	5,90	11	6,12
20	5,65	24	5,90	17	6,13
25	5,70	18	5,91	15	6,16
31	5,72	12	6,00	5	6,18
4	5,74	29	6,03	23	6,25
36	5,78	32	6,04	2	6,25
3	5,79	16	6,05	14	6,27
26	5,86	35	6,07	30	6,35
13	5,89	38	6,07	33	6,90 O

O = Omitted result

Table 5.8. Statistics
Magnesium

Sample B

Analytical method: All
Unit: mg/L

Number of participants	33	Range	0,86
Number of omitted results	1	Variance	0,04
True value	5,30	Standard deviation	0,21
Mean value	5,32	Relative standard deviation	3,9%
Median value	5,30	Relative error	0,4%

Analytical results in ascending order:

34	4,82	3	5,26	35	5,44
22	4,86	26	5,27	38	5,44
9	4,94	18	5,27	2	5,50
25	5,10	32	5,29	8	5,50
36	5,15	13	5,29	17	5,53
4	5,16	28	5,30	20	5,54
31	5,16	15	5,37	14	5,57
6	5,20	5	5,38	23	5,58
37	5,21	29	5,39	12	5,60
24	5,25	40	5,41	30	5,68
11	5,26	16	5,42	33	5,80 O

O = Omitted result

Table 5.9. Statistics
Sodium

Sample A

Analytical method: All
Unit: mg/L

Number of participants	33	Range	2,78
Number of omitted results	3	Variance	0,39
True value	17,27	Standard deviation	0,62
Mean value	17,20	Relative standard deviation	3,6%
Median value	17,27	Relative error	-0,4%

Analytical results in ascending order:

34	15,10 O	29	17,05	11	17,56
20	15,64	24	17,07	23	17,60
37	16,12	15	17,10	18	17,60
4	16,32	28	17,10	5	17,65
22	16,36	8	17,16	38	17,80
25	16,50	14	17,37	13	18,00
3	16,72	17	17,40	30	18,05
2	16,80	35	17,40	16	18,12
9	16,80	31	17,40	36	18,42
12	16,90	40	17,41	33	19,00 O
26	17,00	6	17,50	32	20,60 O

O = Omitted result

Table 5.9. Statistics
Sodium

Sample B

Analytical method: All
Unit: mg/L

Number of participants	33	Range	1,52
Number of omitted results	3	Variance	0,18
True value	15,25	Standard deviation	0,42
Mean value	15,29	Relative standard deviation	2,8%
Median value	15,25	Relative error	0,3%

Analytical results in ascending order:

34	13,40 O	26	15,16	6	15,50
22	14,59	2	15,16	18	15,60
36	14,63	15	15,20	17	15,60
37	14,64	28	15,20	5	15,64
12	14,80	24	15,23	31	15,70
25	14,80	29	15,26	38	15,90
4	14,80	40	15,31	16	15,95
9	14,90	8	15,37	13	16,10
3	15,02	14	15,45	30	16,11
20	15,05	35	15,50	33	17,00 O
11	15,10	23	15,50	32	20,30 O

O = Omitted result

Table 5.10. Statistics
Potassium

Sample A

Analytical method: All
Unit: mg/L

Number of participants	33	Range	0,69
Number of omitted results	1	Variance	0,03
True value	3,17	Standard deviation	0,18
Mean value	3,12	Relative standard deviation	5,6%
Median value	3,17	Relative error	-1,4%

Analytical results in ascending order:

12	2,70 O	3	3,09	17	3,20
9	2,76	36	3,10	13	3,24
20	2,76	28	3,10	5	3,25
34	2,82	11	3,12	38	3,25
25	2,88	18	3,13	4	3,25
37	2,90	31	3,16	8	3,26
30	2,95	16	3,17	32	3,28
22	2,96	14	3,17	2	3,30
24	2,98	26	3,18	15	3,35
35	2,99	23	3,18	33	3,40
40	3,03	29	3,18	6	3,45

O = Omitted result

Table 5.10. Statistics
Potassium

Sample B

Analytical method: All
Unit: mg/L

Number of participants	33	Range	0,63
Number of omitted results	1	Variance	0,02
True value	2,78	Standard deviation	0,13
Mean value	2,77	Relative standard deviation	4,9%
Median value	2,78	Relative error	-0,5%

Analytical results in ascending order:

12	2,20 O	28	2,70	29	2,84
9	2,47	40	2,72	5	2,85
34	2,52	11	2,78	15	2,86
20	2,56	18	2,78	17	2,86
37	2,61	3	2,78	2	2,87
22	2,63	23	2,78	4	2,88
25	2,64	16	2,78	38	2,89
30	2,64	32	2,80	6	2,89
35	2,65	14	2,81	8	2,91
36	2,66	31	2,83	13	2,91
24	2,67	26	2,84	33	3,10

O = Omitted result

Table 5.11. Statistics
Total organic carbon

Sample A

Analytical method: All
Unit: mg/L

Number of participants	23	Range	1,42
Number of omitted results	1	Variance	0,15
True value	2,81	Standard deviation	0,39
Mean value	2,86	Relative standard deviation	13,5%
Median value	2,81	Relative error	1,8%

Analytical results in ascending order:

22	1,12 O	28	2,70	38	3,02
30	2,28	15	2,70	11	3,06
32	2,30	35	2,80	23	3,06
16	2,45	7	2,80	8	3,27
25	2,50	13	2,82	4	3,33
5	2,52	26	2,85	2	3,69
37	2,56	33	2,90	12	3,70
6	2,70	24	2,94		

O = Omitted result

Table 5.11. Statistics
Total organic carbon

Sample B

Analytical method: All
Unit: mg/L

Number of participants	23	Range	1,57
Number of omitted results	1	Variance	0,13
True value	2,43	Standard deviation	0,36
Mean value	2,55	Relative standard deviation	14,1%
Median value	2,43	Relative error	5,3%

Analytical results in ascending order:

22	0,73 O	33	2,40	11	2,69
32	2,00	15	2,40	23	2,75
25	2,15	24	2,40	38	2,83
5	2,23	6	2,41	8	2,95
30	2,24	26	2,44	4	2,97
37	2,30	7	2,50	12	3,10
16	2,31	13	2,56	2	3,57
28	2,40	35	2,60		

O = Omitted result

Table 5.12. Statistics
Aluminium

Sample C

Analytical method: All
Unit: microg/L

Number of participants	27	Range	64,8
Number of omitted results	0	Variance	184,9
True value	163,0	Standard deviation	13,6
Mean value	161,7	Relative standard deviation	8,4%
Median value	163,0	Relative error	-0,8%

Analytical results in ascending order:

22	120,9	39	161,4	13	167,4
5	133,0	23	162,0	12	170,0
32	144,0	4	162,1	8	170,1
6	144,3	25	163,0	31	171,0
37	150,0	14	163,0	38	173,0
34	158,0	3	163,6	18	174,0
2	160,0	16	165,2	20	174,7
15	160,0	17	167,0	9	175,5
29	160,5	35	167,0	24	185,7

O = Omitted result

Table 5.12. Statistics
Aluminium

Sample D

Analytical method: All
Unit: microg/L

Number of participants	27	Range	65,5
Number of omitted results	0	Variance	175,3
True value	147,9	Standard deviation	13,2
Mean value	145,2	Relative standard deviation	9,1%
Median value	147,9	Relative error	-1,8%

Analytical results in ascending order:

5	109,5	15	146,0	17	151,0
22	110,0	4	146,2	12	151,0
37	127,0	16	146,8	14	152,0
6	134,1	9	147,8	24	152,7
32	137,0	3	147,9	13	153,5
34	141,0	25	148,0	18	154,0
29	142,5	31	149,0	38	154,0
2	143,0	35	150,0	20	156,1
23	145,0	8	150,8	39	175,0

O = Omitted result

Table 5.13. Statistics
Iron

Sample C

Analytical method: All
Unit: microg/L

Number of participants	30	Range	52,00
Number of omitted results	1	Variance	85,85
True value	93,28	Standard deviation	9,27
Mean value	92,18	Relative standard deviation	10,1%
Median value	93,28	Relative error	-1,2%

Analytical results in ascending order:

10	65,00	38	90,10	22	94,77
34	77,70	35	90,10	25	95,00
20	83,24	6	92,00	23	97,80
37	84,50	24	92,51	31	98,20
12	85,00	3	93,28	2	100,00
9	85,60	29	93,32	32	101,00
18	86,40	40	93,55	8	102,10
16	87,80	17	94,20	30	105,90
13	88,70	15	94,30	39	110,79 O
4	89,70	14	94,40	5	117,00

O = Omitted result

Table 5.13. Statistics
Iron

Sample D

Analytical method: All

Unit: microg/L

Number of participants	30	Range	37,50
Number of omitted results	1	Variance	67,35
True value	83,21	Standard deviation	8,21
Mean value	83,98	Relative standard deviation	9,8%
Median value	83,21	Relative error	0,9%

Analytical results in ascending order:

34	68,90	16	82,20	23	87,70
10	69,00	35	82,30	14	87,90
12	72,00	17	82,50	31	88,00
37	75,00	38	83,00	2	90,00
20	76,41	24	83,21	8	91,23
18	77,85	29	83,72	22	91,23
9	78,10	3	83,95	30	96,39
13	80,70	40	84,22	32	98,00
6	81,50	15	84,90	5	106,40
4	82,10	25	87,00	39	122,07 O

O = Omitted result

Table 5.14. Statistics
Manganese

Sample C

Analytical method: All

Unit: microg/L

Number of participants	30	Range	7,36
Number of omitted results	1	Variance	2,00
True value	23,09	Standard deviation	1,41
Mean value	22,99	Relative standard deviation	6,2%
Median value	23,09	Relative error	-0,4%

Analytical results in ascending order:

9	19,30	24	22,67	40	23,41
34	21,10	35	22,70	14	23,70
37	21,40	18	22,95	31	23,80
13	21,60	29	23,01	38	23,90
30	21,85	5	23,09	2	23,90
16	21,90	3	23,18	23	24,20
12	22,00	25	23,20	8	25,05
4	22,01	17	23,30	32	25,50
39	22,33	15	23,30	20	26,66
22	22,33	6	23,40	10	28,00 O

O = Omitted result

Table 5.14. Statistics
Manganese

Sample D

Analytical method: All
Unit: microg/L

Number of participants	30	Range	7,90
Number of omitted results	1	Variance	2,92
True value	20,80	Standard deviation	1,71
Mean value	20,99	Relative standard deviation	8,1%
Median value	20,80	Relative error	0,9%

Analytical results in ascending order:

9	17,70	2	20,60	6	21,10
37	18,70	30	20,63	40	21,31
34	18,90	18	20,75	38	21,40
13	19,80	25	20,80	23	21,50
4	19,90	17	20,80	15	21,70
12	20,00	35	20,80	8	22,42
5	20,15	29	20,82	39	24,45
24	20,17	3	20,87	20	25,28
16	20,20	14	20,90	32	25,60
22	20,37	31	20,98	10	30,00 O

O = Omitted result

Table 5.15. Statistics
Cadmium

Sample C

Analytical method: All
Unit: microg/L

Number of participants	30	Range	1,18
Number of omitted results	0	Variance	0,07
True value	5,31	Standard deviation	0,26
Mean value	5,31	Relative standard deviation	4,9%
Median value	5,31	Relative error	0,2%

Analytical results in ascending order:

30	4,75	14	5,23	31	5,40
19	4,80	34	5,24	3	5,42
39	4,88	40	5,24	18	5,50
37	4,98	29	5,26	32	5,56
22	5,10	2	5,30	20	5,57
16	5,17	15	5,31	17	5,58
35	5,19	8	5,33	12	5,60
13	5,20	6	5,38	38	5,61
25	5,20	24	5,38	23	5,69
4	5,21	9	5,40	5	5,93

O = Omitted result

Table 5.15. Statistics
Cadmium

Sample D

Analytical method: All
Unit: microg/L

Number of participants	30	Range	1,64
Number of omitted results	0	Variance	0,09
True value	4,75	Standard deviation	0,30
Mean value	4,80	Relative standard deviation	6,2%
Median value	4,75	Relative error	1,2%

Analytical results in ascending order:

19	4,00	29	4,70	3	4,86
30	4,46	13	4,70	8	4,90
37	4,48	40	4,73	18	4,95
20	4,57	34	4,74	31	5,00
22	4,60	14	4,74	38	5,02
25	4,60	6	4,75	23	5,10
2	4,60	9	4,75	17	5,11
16	4,64	15	4,84	12	5,20
4	4,66	32	4,85	5	5,29
35	4,69	24	4,85	39	5,64

O = Omitted result

Table 5.16. Statistics
Lead

Sample C

Analytical method: All
Unit: microg/L

Number of participants	30	Range	2,93
Number of omitted results	2	Variance	0,26
True value	5,28	Standard deviation	0,51
Mean value	5,37	Relative standard deviation	9,6%
Median value	5,28	Relative error	1,7%

Analytical results in ascending order:

19	2,90 O	2	5,20	17	5,51
6	3,88	14	5,23	3	5,56
5	4,87	24	5,26	22	5,59
30	4,89	38	5,26	23	5,63
39	4,91	29	5,28	37	5,70
32	5,05	35	5,28	9	5,93
18	5,10	40	5,34	15	6,08
31	5,18	34	5,36	13	6,20
25	5,20	8	5,39	20	6,81
16	5,20	4	5,42	12	8,50 O

O = Omitted result

Table 5.16. Statistics
Lead

Sample D

Analytical method: All
Unit: microg/L

Number of participants	30	Range	1,70
Number of omitted results	2	Variance	0,21
True value	4,82	Standard deviation	0,45
Mean value	4,96	Relative standard deviation	9,1%
Median value	4,82	Relative error	3,0%

Analytical results in ascending order:

19	2,60 O	24	4,75	3	5,00
25	4,40	35	4,77	8	5,01
6	4,40	29	4,79	37	5,23
5	4,48	2	4,80	9	5,25
30	4,54	18	4,80	31	5,27
16	4,60	40	4,83	15	5,49
14	4,61	34	4,86	39	5,87
32	4,68	4	4,88	20	6,07
38	4,73	17	4,99	13	6,10
22	4,74	23	5,00	12	7,60 O

O = Omitted result

Table 5.17. Statistics
Copper

Sample C

Analytical method: All
Unit: microg/L

Number of participants	30	Range	3,97
Number of omitted results	2	Variance	0,76
True value	16,72	Standard deviation	0,87
Mean value	16,70	Relative standard deviation	5,2%
Median value	16,72	Relative error	-0,1%

Analytical results in ascending order:

20	7,73 O	4	16,28	25	17,00
19	12,80 O	13	16,30	8	17,01
32	15,23	30	16,46	17	17,10
6	15,30	34	16,50	38	17,20
39	15,41	16	16,70	24	17,44
22	15,48	35	16,70	14	17,50
37	15,70	40	16,73	15	17,50
9	16,10	29	16,89	31	17,60
2	16,20	3	16,92	23	17,90
5	16,26	18	16,95	12	19,20

O = Omitted result

Table 5.17. Statistics
Copper

Sample D

Analytical method: All
Unit: microg/L

Number of participants	30	Range	3,54
Number of omitted results	2	Variance	0,71
True value	15,28	Standard deviation	0,84
Mean value	15,22	Relative standard deviation	5,5%
Median value	15,28	Relative error	-0,4%

Analytical results in ascending order:

20	6,82 O	13	14,80	8	15,54
19	10,40 O	29	14,91	18	15,60
22	13,45	34	15,10	17	15,70
37	13,80	5	15,15	15	15,80
32	13,89	30	15,17	23	15,90
6	14,20	35	15,20	31	15,97
4	14,46	40	15,35	25	16,00
16	14,50	3	15,38	14	16,10
2	14,60	24	15,48	12	16,80
9	14,70	38	15,50	39	16,99

O = Omitted result

Table 5.18. Statistics
Nickel

Sample C

Analytical method: All
Unit: microg/L

Number of participants	29	Range	1,75
Number of omitted results	2	Variance	0,16
True value	11,00	Standard deviation	0,40
Mean value	10,92	Relative standard deviation	3,7%
Median value	11,00	Relative error	-0,8%

Analytical results in ascending order:

20	9,75	2	10,80	13	11,20
32	10,20	16	10,82	15	11,20
39	10,27 O	4	10,86	23	11,30
9	10,40	35	10,90	40	11,34
31	10,56	38	11,00	8	11,35
25	10,60	3	11,02	24	11,40
30	10,67	22	11,05	6	11,40
34	10,70	18	11,10	12	11,50
14	10,70	17	11,10	5	12,70 O
29	10,72	37	11,10		

O = Omitted result

Table 5.18. Statistics
Nickel

Sample D

Analytical method: All
Unit: microg/L

Number of participants	29	Range	2,00
Number of omitted results	2	Variance	0,23
True value	9,80	Standard deviation	0,48
Mean value	9,78	Relative standard deviation	4,9%
Median value	9,80	Relative error	-0,2%

Analytical results in ascending order:

2	8,70	29	9,73	15	10,10
20	8,77	14	9,75	23	10,10
32	8,81	30	9,80	13	10,20
9	9,30	34	9,80	5	10,22 O
25	9,50	4	9,86	40	10,35
31	9,53	38	9,87	24	10,35
22	9,65	35	9,90	17	10,40
6	9,65	3	9,94	12	10,70
37	9,70	18	9,95	39	12,10 O
16	9,71	8	10,00		

O = Omitted result

Table 5.19. Statistics
Zinc

Sample C

Analytical method: All
Unit: microg/L

Number of participants	29	Range	7,92
Number of omitted results	1	Variance	2,40
True value	21,86	Standard deviation	1,55
Mean value	21,83	Relative standard deviation	7,1%
Median value	21,86	Relative error	-0,1%

Analytical results in ascending order:

2	15,80 O	15	21,60	39	22,27
20	17,28	16	21,70	29	22,36
5	19,58	6	21,80	17	22,40
12	20,30	31	21,80	25	22,50
37	20,60	35	21,80	32	23,05
30	20,84	4	21,91	38	23,10
14	20,90	40	21,98	24	24,19
34	20,90	18	22,00	9	24,90
22	20,98	3	22,11	23	25,20
13	21,00	8	22,25		

O = Omitted result

Table 5.19. Statistics
Zinc

Sample D

Analytical method: All
Unit: microg/L

Number of participants	29	Range	8,15
Number of omitted results	1	Variance	3,16
True value	19,99	Standard deviation	1,78
Mean value	19,95	Relative standard deviation	8,9%
Median value	19,99	Relative error	-0,2%

Analytical results in ascending order:

2	14,60 O	16	19,40	29	20,26
20	16,05	17	19,60	8	20,37
5	17,03	4	19,68	25	20,50
37	18,10	15	19,90	38	20,60
12	18,30	3	19,97	32	20,60
34	18,30	6	20,00	24	21,95
35	18,80	18	20,00	23	22,80
22	19,01	31	20,00	39	24,13
13	19,30	14	20,10	9	24,20
30	19,37	40	20,25		

O = Omitted result

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