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Intercomparison 1630:
pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni and Zn

The international Cooperative Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP Waters)
Convention on Long-Range Transboundary Air Pollution

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REPORT

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Abstract

89 laboratories were invited to participate in the current intercomparison. Of these, 35 from 20 different countries accepted the invitation and all of them submitted results to the ICP Waters. 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), 81% of the overall results were considered acceptable. This is in line with previous editions. The best results were reported for the analytical variables: sulphate, calcium, sodium, iron, manganese, cadmium and nickel with acceptance rate of 90% or higher.

For pH, only 56 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.

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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 1630:
pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni and Zn

Prepared by the ICP Waters Programme Centre
Norwegian Institute for Water Research
Oslo, September 2016

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 30th intercomparison of chemical analysis.

Oslo, September 2016

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 2016, 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. 89 laboratories were invited to participate, and samples were sent to the 35 laboratories who accepted. All of them, except one, submitted results to the Programme Centre before the final statistical treatment of the data. 20 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 81% 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 56 % 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 sulphate, calcium, sodium, iron, manganese, cadmium and nickel, 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 editions.

Good quality was observed as well for the variable nitrate+nitrite-N; 71% of the results provided by the participants fulfilled the target accuracy. This excellent result is in line with the previous editions but much better than the quality of the results provided in 2014 and 2013.

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 thirty intercomparison test, called 1630, included the determination of 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 Monte Verità, Switzerland, it was decided that pH of the samples should reflect acidified waters while concentrations of major components should vary between years. The samples for this year's intercomparison were prepared with this in mind.

The samples were shipped from the Programme Centre the week 21 of 2016. 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 analyse 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 1630 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 35 laboratories submitted results to the intercomparison. If results for the different variables are averaged, 81 % 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 in line with previous editions. As previously stated, the best acceptance (≥90%) was observed in the determination of sulphate, calcium, sodium, iron, manganese, cadmium and nickel. The lowest acceptable results were reported for alkalinity (46%) and pH (56%). 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 analysed.

Due to the high precision of the reported results for conductivity in earlier intercomparisons, from the 2012 edition the Organization decided to reduce the acceptance limit for this analytical variable from the target value of ± 20 % to ± 10 % and this criterion was still used in the current one.

In the case of the determination of trace metals, some of the analyses have achieved a better acceptability than last year. This is the case of Fe, Mn and Pb. However, in some other cases (Al, Cd, Cu, Ni and Zn) the percentage of acceptable results has decreased if compared to the 1529 edition. It has to be taken into account that, despite samples have been spiked and then, the concentrations of trace metals is still higher than could be expected in natural samples, some of the laboratories do not have available methods sensitive enough to determine these elements.

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 analysed 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.

The author of the current report suggests that the Task Force should discuss which concentration levels of heavy metals would be most useful for ICP Waters in the coming intercomparisons. It could also be useful to consider whether absolute acceptance limits for some parameters should be used instead of the relative one (± 20 %) that was used here. If the Task Force decide that absolute acceptance limits should be applied, it would be advisable to indicate the target detection limit that should be achieved by the participating laboratories. Since the intercomparison targets the scenario of acidification of freshwater bodies, the Programme Centre aims for keep on performing intercalibrations with slightly acidified solutions.

Table 1. Evaluation of the results from intercomparison 1630

				Acceptable Limit	Number of pairs		Acceptable results for intecalibration (%)			
Variable	**Sample pair**	**Sample 1**	**Sample 2**	**%**	**Total**	**Accept.**	**1630**	**1529**	**1428**	**1327**
pH	AB	6.00	6.04	3,3	32	18	56	64	68	52
Conductivity,	AB	4.08	4.59	10	30	23	77	89	93	78
Alkalinity,	AB	0.042	0.046	20	24	11	46	75	26	63
Nitrate + nitrite-nitrogen,	AB	276	309	20	31	22	71	88	14	0
Chloride,	AB	2.45	2.81	20	30	26	87	97	93	78
Sulphate,	AB	8.07	9.2	20	30	27	90	97	87	77
Calcium,	AB	3.9	4.42	20	30	28	93	97	97	85
Magnesium,	AB	0.41	0.47	20	28	25	89	100	87	82
Sodium,	AB	1.87	2.14	20	28	27	96	97	97	91
Potassium,	AB	0.43	0.49	20	28	24	86	97	97	70
Total organic carbon,	AB	4.09	4.65	20	21	17	81	70	82	78
Aluminium,	CD	255	270	20	23	18	78	89	78	89
Iron,	CD	186	190	20	22	20	91	81	74	72
Manganese,	CD	48	51.7	20	23	21	91	84	88	78
Cadmium,	CD	6.87	7.73	20	21	19	90	100	84	85
Lead,	CD	7.23	8.34	20	21	18	86	77	80	71
Copper,	CD	24.6	28	20	22	19	86	93	88	84
Nickel,	CD	10.2	11.5	20	21	19	90	97	92	83
Zinc,	CD	34.4	38.1	20	21	17	81	83	79	60
Total					**486**	**399**	**81**	88	80	73

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 1630 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.

32 participants determined pH in the test samples A and B. 25 laboratories used a method based upon electrometry. As stated in previous intercomparisons, stirring has been observed that could have a significant influence on the results, especially in samples with lower total ion strength than the samples used in this intercomparison (4, 5). As a result of this, the practice of establishing a “true value” based on the median value for all the reported results for pH is questionable. Whether an individual “true value” for each method would be more appropriate should therefore be discussed. In this intercomparison it was chosen the median value of all the reported results after excluding the outliers. Based upon this, 56 % of the results were acceptable, that is within the median value ± 0.2 pH units. The acceptance has decreased in 8% 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.

30 laboratories have reported results for conductivity in the current edition. 29 participants reported the use of electrometric methods. Most laboratories achieved rather good agreement between the results for this variable, 77 % 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.

24 laboratories reported results for alkalinity. From them, 9 used Gran plot titration method, which is the suggested reference method in the manual (1), while 8 made use of end point titration. 2 participants employed end point titration to pH 5.4. 46% of them provided results that were within the target accuracy of ± 20%.

It is 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

31 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 15 participants. An overall good quality was observed in the result set provided by the participants if compared to Editions 1428 and 1327.

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

4.5 Chloride

30 laboratories reported results for chloride and, from them, 26 were accepted. 87% 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 21 of the participants reporting its use. Other techniques such as photometry, capillary electrophoresis and others were employed in much lower extension. A high accuracy in the results provided by the participants was in general observed, as it might be observed in characteristic Youden plot. Just slight systematic error has been detected in the analytics.

4.6 Sulphate

30 laboratories reported results for the variable sulphate in the current intercomparison. From them 90% fulfilled the target accuracy. 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 sulphate. 4 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 2%.

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

30 laboratories reported results for calcium from which 93% fulfilled the target accuracy. This percentage is in line with the last editions. The results are presented in Figure 7, Table 2 and Table 5.7. The circle in Figure 7 represents the target accuracy of ± 20%.

9 laboratories used ICP-AES and 9 ion chromatography. Flame atomic absorption spectrometry was used by 6 participants in their determination of calcium. 4 laboratories used ICP-MS. 1 participant made use of an electrophoretic technique and another determined the variable using complexometric techniques with EDTA.

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

4.8 Magnesium

28 laboratories reported results for magnesium and 89% 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 %. 9 of the laboratories reported the use of ICP-AES and 9, ion chromatography. Flame atomic absorption spectrometry was used by 6 of the participants in their determination of this variable. 3 of the laboratories reported the use of ICP-MS and 1, capillary electrophoresis.

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

4.9 Sodium

28 laboratories reported results for sodium. 96% of the results fulfilled the target accuracy stablished in the intercomparison. This is in agreement with the percentage of acceptance observed in previous editions.

The characteristics Youden chart is presented in Figure 9. Tables 2 and 5.9 summarize the statistical treatment of the data. The circle in Figure 9 represents the target accuracy of ± 20 %. In this round of the intercomparison, 9 participants analysed sodium by ICP-AES and 3 by ICP-MS. Ion chromatography techniques are nearly as extended as plasma techniques, as 9 of the participants reported the use of ion chromatography in this analytical determination. Among the flame techniques, atomic absorption is the preferred, as it was used by 4 laboratories. 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 accuracy of the set results provided by the participants. Just slight random error affects the quality of the results.

4.10 Potassium

28 laboratories reported results for potassium. From these results, 86% were acceptable. Regarding the analytical techniques used by the participants, 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.

4.11 Total organic carbon

21 laboratories reported results for total organic carbon. From them, 81% of the results were within the target accuracy of ± 20%.

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 (13) while 6 reported the use of UV/peroxodisulfate oxidation method for this determination. 2 laboratories reported the use of other method. 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

23 laboratories reported results for aluminium. From these all were accepted according to the target accuracy criteria (78% 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, 10 laboratories used ICP-MS and 7, ICP-AES. 3 participants reported the use of graphite furnace. 2 participants reported the use of a photometric method and 1 used FAAS in the determination of this variable. From these techniques, the lowest relative standard deviation in the results was observed for the ICP-AES 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. The magnitude of the errors is not very relevant and almost all the results are found within the 20% target accuracy.

4.13 Iron

22 laboratories provided results for iron and 91% 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%.

9 and 8 of the laboratories used ICP-AES and ICP-MS, respectively. 4 participants reported the use of atomic absorption techniques: 2 employed GFASS and 2 FAAS. 1 laboratory reported the use of a photometry-based method.

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

4.14 Manganese

23 participants reported results in the analysis of manganese. From these, 91% 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, 9 and 9 participants used ICP-AES and ICP-MS, respectively, while 3 and 1 used graphite furnace atomic absorption and flame atomic absorption respectively. No relevant differences were detected in between the different techniques. Just 1 participant reported the use of a photometry-based method in the analysis of Mn. Noteworthy is the excellent precision and accuracy shown by the result set.

4.15 Cadmium

21 laboratories reported results for cadmium in the set of samples C and D. 90% of 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 16 participants reported its use. From them, 11 detected mass (ICP-MS) and 5 emitted radiation (ICP-AES). The preferred method employed by the participants that used atomic absorption techniques was the graphite furnace (GFAAS). The use of this technique was reported by 5 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 just slight systematic error.

4.16 Lead

21 laboratories reported results for lead in samples C and D. From these, 86% were acceptable. 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 15 participants have communicated the use of ICP. From them, 11 used mass detection (ICP-MS) and 4, 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 show a slight systematic error.

4.17 Copper

22 laboratories reported results for copper in sample set C and D. From them, 86% 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.

By analysis, almost all the participants employed atomic based techniques, being plasma the most widely used with 11 of the participants using mass detectors and 6 using emitted light. Relevant is also the contribution of atomic absorption techniques to the characterization of Cu in the samples, as 5 participants employed GFAAS.

4.18 Nickel

21 laboratories reported results for nickel in samples C and D. From these, 90% 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 17 participants. 11 employed ICP-MS while only 6 reported the use of ICP-AES. The 4 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 random error.

4.19 Zinc

21 laboratories reported results in the determination of zinc in sample set C and D. From these results, 81% fulfilled the acceptance criteria, in line with previous editions.

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 11 participants, followed by emission in plasma (ICP-AES) that was used by 6 of the laboratories. From the techniques based on atomic absorption spectroscopy 3 laboratories made use of the graphite furnace (GFAAS) while just 1 participant 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 1630

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	6.00	6.04	32	0	6.00	6.04	6.04	0.25	6.05	0.24	4.2	3.9	0.7	0.2
Electrometry				25	0	5.98	6.04	6.04	0.24	6.05	0.22	4.0	3.6	0.7	0.1
Stirring				4	0	5.96	5.97	5.89	0.17	5.90	0.19	2.8	3.2	-1.8	-2.4
Equilibration				2	0			6.37		6.44				6.1	6.6
Other method				1	0			6.05		6.04				0.8	0.0
Conductivity	AB	4.08	4.59	30	4	4.08	4.59	4.06	0.18	4.53	0.19	4.3	4.2	-0.5	-1.4
Electrometry				29	4	4.07	4.58	4.06	0.18	4.52	0.19	4.4	4.3	-0.6	-1.4
Other method				1	0			4.10		4.60				0.5	0.2
Alkalinity	AB	0.042	0.046	24	8	0.042	0.046	0.041	0.007	0.046	0.005	16.7	11.1	-1.4	-1.1
Gran plot titration				9	1	0.043	0.047	0.044	0.008	0.046	0.006	19.1	13.6	4.5	-0.2
End point titration				8	3	0.040	0.046	0.039	0.005	0.046	0.004	13.2	9.2	-8.0	-0.3
End point				2	2			0.079		0.083				86.9	80.4
Other method				2	1			0.040		0.044				-3.8	-3.5
Colorimetry				1	1			2.400		0.800				5614.3	1639.1
End point 5.4				1	0			0.036		0.040				-14.3	-13.0
End point 5.6				1	0			0.042		0.047				0.0	2.2
Nitrate+Nitrite-N	AB	276	309	31	3	276	309	279	31	317	36	10.9	11.4	1.1	2.4
Ion chromatography				15	1	273	305	280	41	317	46	14.5	14.5	1.4	2.5
Photometry				6	1	277	310	277	9	323	27	3.4	8.4	0.5	4.6
Autoanalyzer				3	0	277	309	274	7	300	17	2.7	5.6	-0.6	-3.1
Flow injection anal.				3	1			269		315				-2.5	1.8
Other method				2	0			291		330				5.4	6.8
Cap. electrophoresis				1	0			290		315				5.1	1.9
Hydrazine				1	0			272		308				-1.4	-0.3
Chloride	AB	2.5	2.8	30	3	2.5	2.8	2.5	0.2	2.8	0.2	7.0	7.2	0.3	0.0
Ion chromatography				21	0	2.4	2.8	2.4	0.2	2.8	0.2	6.5	6.3	-0.1	-0.6
Other method				3	0	2.7	3.0	2.6	0.2	2.9	0.3	7.2	8.8	5.4	3.3
Photometry				2	1			2.5		2.9				1.6	1.8
AA				1	1			1.0		1.2				-60.8	-57.7
Argentometry				1	1			1.4		1.8				-42.9	-35.9
Cap. electrophoresis				1	0			2.6		3.2				6.1	13.9
Potentiometry				1	0			2.1		2.4				-14.6	-13.4
Sulphate	AB	8.07	9.20	30	2	8.07	9.20	8.08	0.35	9.30	0.53	4.4	5.7	0.1	1.0
Ion chromatography				22	0	8.04	9.21	8.10	0.38	9.28	0.41	4.7	4.4	0.4	0.8
ICP-AES				4	0	7.94	9.19	7.92	0.29	9.09	0.33	3.6	3.7	-1.9	-1.2
Photometry				2	1			8.17		8.72				1.2	-5.2
Cap. electrophoresis				1	0			8.10		11.10				0.4	20.7
Other method				1	1			13.00		14.40				61.1	56.5
Calcium	AB	3.90	4.42	30	1	3.90	4.42	3.93	0.22	4.51	0.27	5.6	6.1	0.7	2.0
ICP-AES				9	0	3.91	4.40	3.96	0.17	4.47	0.16	4.4	3.6	1.6	1.2
Ion chromatography				9	0	4.06	4.66	4.03	0.23	4.59	0.24	5.6	5.3	3.3	3.9
FAAS				6	0	3.89	4.40	3.81	0.27	4.57	0.47	7.0	10.2	-2.4	3.3
ICP-MS				4	0	3.88	4.41	3.89	0.09	4.43	0.14	2.3	3.3	-0.3	0.2
Cap. Electrophoresis				1	0			3.60		4.10				-7.7	-7.2
EDTA				1	1			3.20		5.60				-17.9	26.7

Analytical variable and method	Sample	TRUE Value		No. lab.		Median		Avg/Std.av.		Avg/Std.av.		Rel.std.av. %		Relative error %	
	pair	S. 1	S. 2	Total	Om	S. 1	S. 2	Sample 1		Sample 2		S. 1	S. 2	S. 1	S. 2
Magnesium	AB	0.41	0.47	28	2	0.41	0.47	0.40	0.02	0.46	0.02	5.6	5.1	-1.6	-1.9
ICP-AES				9	0	0.42	0.47	0.41	0.02	0.47	0.02	5.4	4.6	-0.5	-0.9
Ion chromatography				9	1	0.40	0.46	0.40	0.03	0.45	0.03	6.5	5.9	-2.8	-4.2
FAAS				6	1	0.41	0.47	0.40	0.03	0.47	0.03	7.3	6.2	-2.2	-0.9
ICP-MS				3	0	0.41	0.47	0.41	0.01	0.47	0.01	1.8	2.3	-0.2	-0.5
Cap. Electrophoresis				1	0			0.40		0.46				-2.4	-2.1
Sodium	AB	1.87	2.14	28	1	1.87	2.14	1.88	0.06	2.16	0.10	3.3	4.4	0.7	1.0
ICP-AES				9	0	1.86	2.15	1.87	0.06	2.13	0.11	3.0	4.9	0.2	-0.5
Ion chromatography				9	0	1.88	2.14	1.88	0.06	2.17	0.09	3.0	3.9	0.7	1.2
FAAS				4	1	1.86	2.11	1.85	0.08	2.13	0.06	4.4	2.9	-1.2	-0.4
ICP-MS				3	0	1.84	2.12	1.89	0.09	2.14	0.06	4.9	2.7	1.2	-0.2
AES				1	0			1.87		2.23				0.0	4.2
Cap. Electrophoresis				1	0			1.93		2.36				3.2	10.3
Other method				1	0			2.00		2.30				7.0	7.5
Potassium	AB	0.43	0.49	28	1	0.43	0.49	0.42	0.03	0.49	0.05	7.7	9.6	-1.9	0.3
Ion chromatography				9	0	0.40	0.47	0.40	0.03	0.45	0.03	8.2	7.6	-7.6	-7.4
ICP-AES				8	0	0.44	0.50	0.44	0.03	0.50	0.03	7.1	5.4	1.5	2.3
FAAS				4	0	0.43	0.51	0.43	0.01	0.53	0.05	2.8	9.8	-0.1	7.6
ICP-MS				3	0	0.43	0.48	0.42	0.02	0.48	0.01	4.2	2.8	-2.7	-2.6
AES				2	0			0.44		0.55				1.2	12.4
Cap. Electrophoresis				1	1			0.59		0.71				37.2	44.9
Other method				1	0			0.48		0.53				11.6	8.2
Total Organic Carbon	AB	4.09	4.65	21	0	4.09	4.65	4.00	0.56	4.45	0.64	14.1	14.4	-2.2	-4.3
Combustion				13	0	4.00	4.72	4.01	0.60	4.48	0.75	15.0	16.6	-2.0	-3.6
UV/peroxodisulphate				6	0	4.10	4.53	4.01	0.14	4.46	0.24	3.5	5.4	-2.0	-4.0
Other method				2	0			3.91		4.18				-4.4	-10.2
Aluminium	CD	255	270	23	3	255	270	252	21	271	24	8.3	8.7	-1.1	0.4
ICP-MS				10	0	253	268	247	19	263	15	7.7	5.6	-3.0	-2.7
ICP-AES				7	1	270	284	259	22	273	24	8.6	8.6	1.5	1.3
GFAAS				3	0	274	285	259	30	278	36	11.6	12.9	1.4	3.0
Photometry				2	2			329		343				29.0	27.0
FAAS				1	0			240		320				-5.9	18.5
Iron	CD	186.0	190.0	22	1	186.00	190.00	187.88	10.18	192.94	12.92	5.4	6.7	1.0	1.5
ICP-AES				9	1	186.00	189.50	186.96	8.46	189.02	7.26	4.5	3.8	0.5	-0.5
ICP-MS				8	0	186.00	189.50	188.15	12.03	190.22	11.39	6.4	6.0	1.2	0.1
FAAS				2	0			193.00		212.50				3.8	11.8
GFAAS				2	0			188.75		201.40				1.5	6.0
Photometry				1	0			181.00		190.00				-2.7	0.0
Manganese	CD	48.00	51.70	23	2	48.00	51.70	48.33	1.63	51.99	1.60	3.4	3.1	0.7	0.6
ICP-AES				9	1	47.74	51.10	48.16	1.75	51.42	1.48	3.6	2.9	0.3	-0.5
ICP-MS				9	0	48.50	52.19	48.67	1.06	52.47	1.34	2.2	2.5	1.4	1.5
GFAAS				3	0	48.20	53.10	48.67	2.63	52.83	2.21	5.4	4.2	1.4	2.2
FAAS				1	0			45.60		49.70				-5.0	-3.9
Photometry				1	1			82.00		78.00				70.8	50.9

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	6.87	7.73	21	2	6.87	7.73	6.92	0.34	7.86	0.47	5.0	6.0	0.7	1.7
ICP-MS				11	0	6.87	7.74	7.00	0.33	7.98	0.45	4.8	5.7	1.8	3.3
GFAAS				5	1	6.99	7.62	6.92	0.46	7.79	0.67	6.7	8.6	0.8	0.7
ICP-AES				5	1	6.70	7.62	6.69	0.18	7.61	0.21	2.6	2.8	-2.6	-1.6
Lead	CD	7.23	8.34	21	2	7.23	8.34	7.20	0.60	8.34	0.55	8.3	6.6	-0.4	0.0
ICP-MS				11	0	7.40	8.44	7.51	0.37	8.57	0.40	5.0	4.6	3.9	2.8
GFAAS				6	1	6.90	8.05	6.67	0.62	7.76	0.56	9.2	7.2	-7.8	-7.0
ICP-AES				4	1	6.70	8.34	6.93	0.65	8.48	0.37	9.4	4.4	-4.1	1.7
Copper	CD	24.60	28.00	22	3	24.60	28.00	24.91	1.40	28.08	1.16	5.6	4.1	1.3	0.3
ICP-MS				11	1	24.60	28.00	24.51	0.78	27.98	0.83	3.2	3.0	-0.4	-0.1
ICP-AES				6	1	24.75	27.60	25.41	1.87	27.78	1.27	7.3	4.6	3.3	-0.8
GFAAS				5	1	25.18	28.28	25.31	2.04	28.69	1.79	8.1	6.2	2.9	2.5
Nickel	CD	10.20	11.50	21	1	10.20	11.50	10.16	0.57	11.51	0.79	5.6	6.9	-0.4	0.1
ICP-MS				11	0	10.40	11.60	10.31	0.38	11.57	0.36	3.7	3.1	1.1	0.6
ICP-AES				6	1	10.10	11.20	9.95	0.68	11.70	1.21	6.9	10.3	-2.5	1.8
GFAAS				4	0	9.69	10.73	10.00	0.86	11.11	1.14	8.6	10.2	-1.9	-3.4
Zinc	CD	34.4	38.1	21	1	34.4	38.1	34.4	3.0	38.5	3.8	8.6	9.9	-0.1	1.1
ICP-MS				11	0	35.0	39.0	35.4	2.7	40.0	3.4	7.6	8.4	2.9	5.0
ICP-AES				6	1	33.9	38.9	34.4	1.8	38.8	1.5	5.1	3.9	-0.1	1.8
GFAAS				3	0	34.3	36.7	32.1	3.9	35.2	3.9	12.3	11.0	-6.6	-7.6
FAAS				1	0			29.5		30.6				-14.2	-19.7

*Om.: Sample pair omitted from the calculations

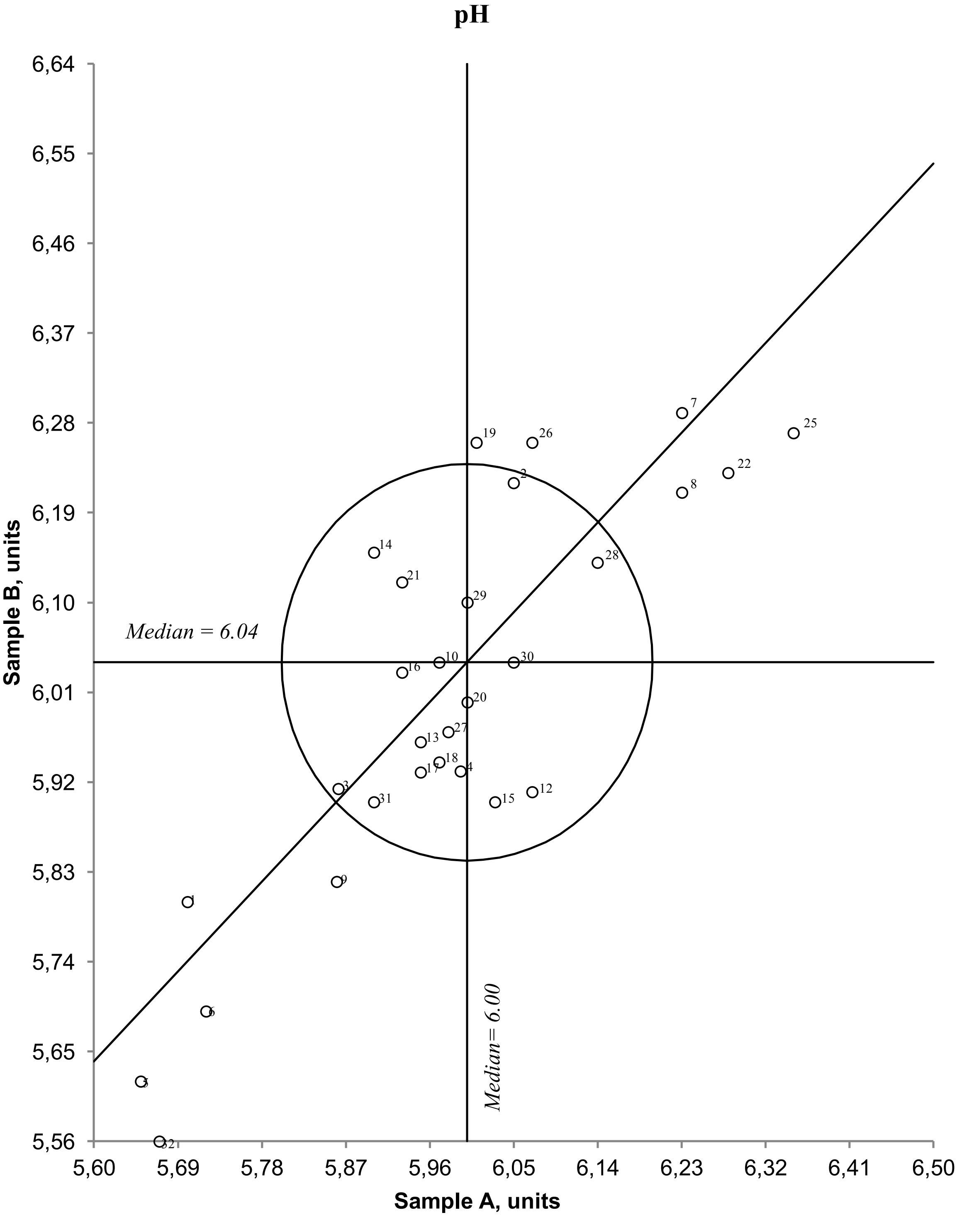

Figure 1. Youden diagram for pH, sample pair AB
Acceptable limit, given by circle, is 3.3 %

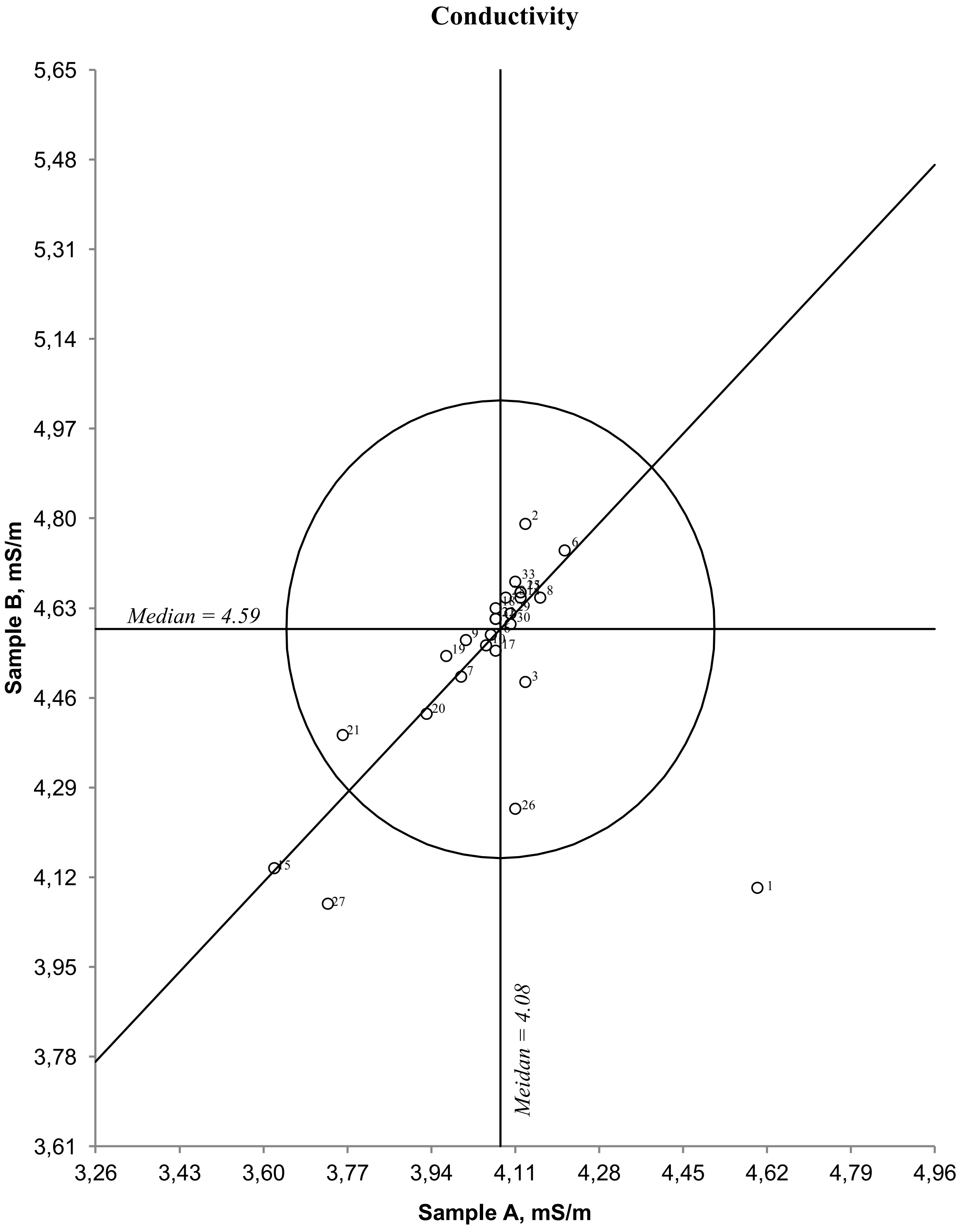

Figure 2. Youden diagram for conductivity, sample pair AB
Acceptable limit, given by circle, is 10 %

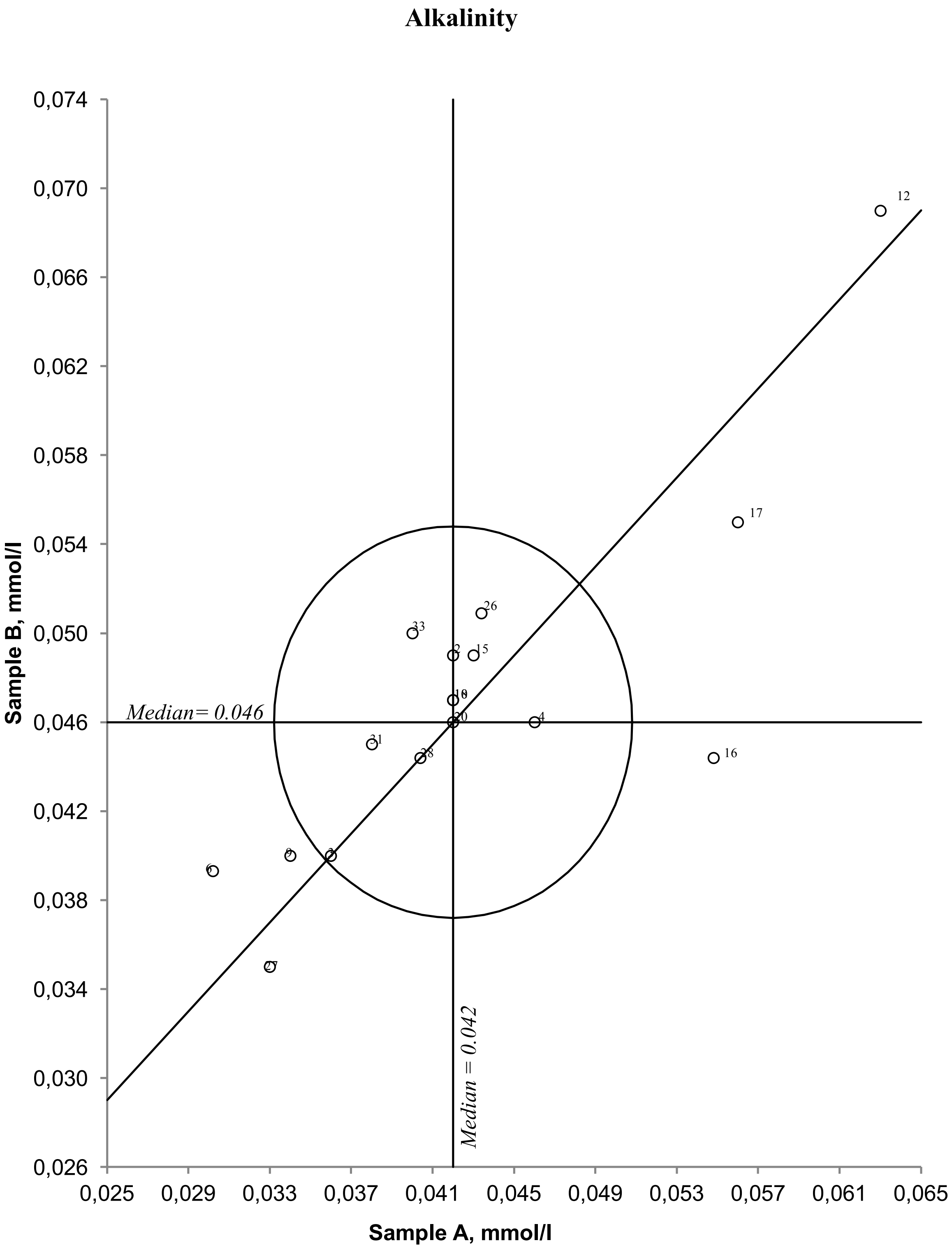

Figure 3. Youden diagram for alkalinity, sample pair AB
Acceptable limit, given by circle, is 20 %

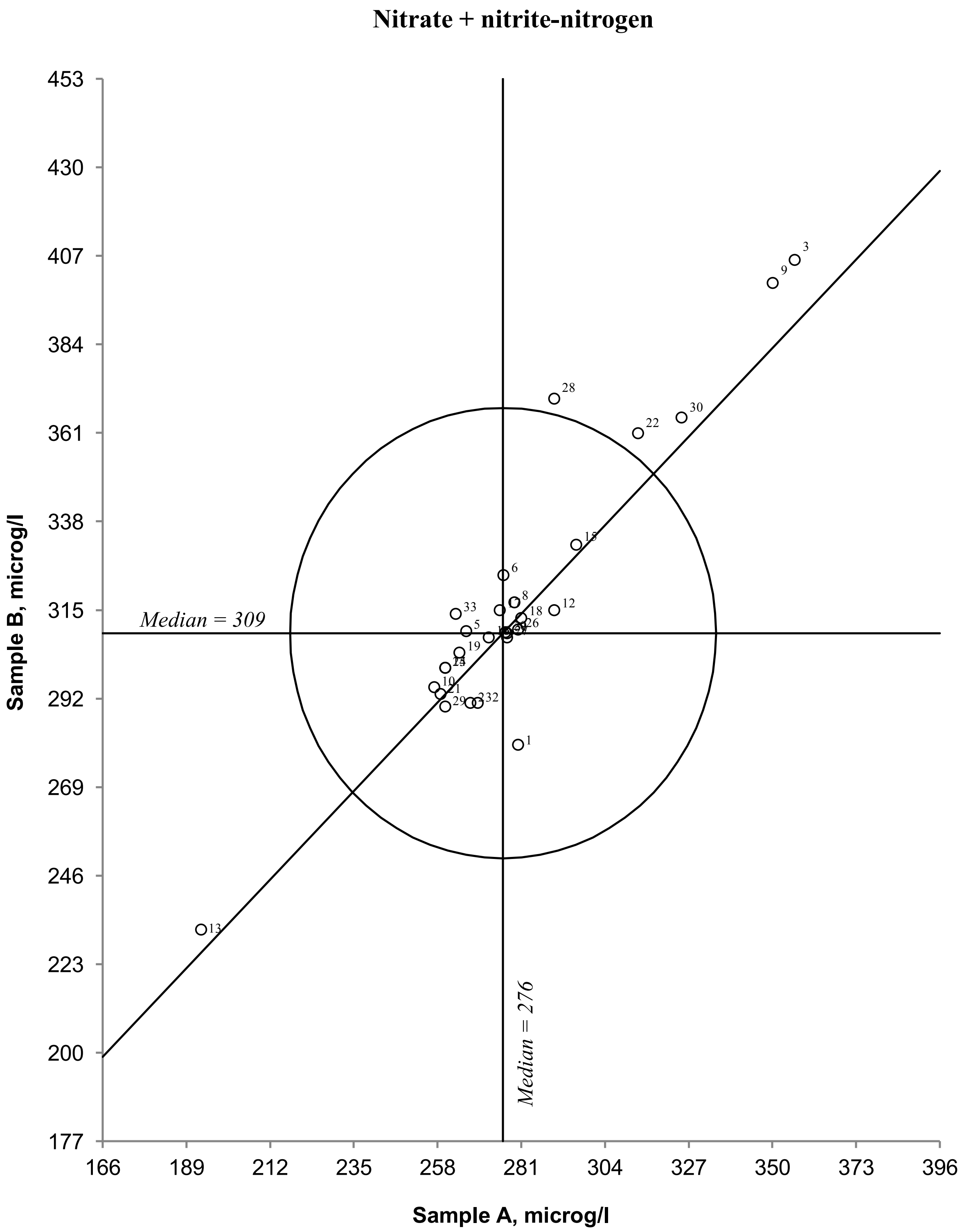

Figure 4. Youden diagram for nitrate + nitrite-nitrogen, sample pair AB
Acceptable limit, given by circle, is 20 %

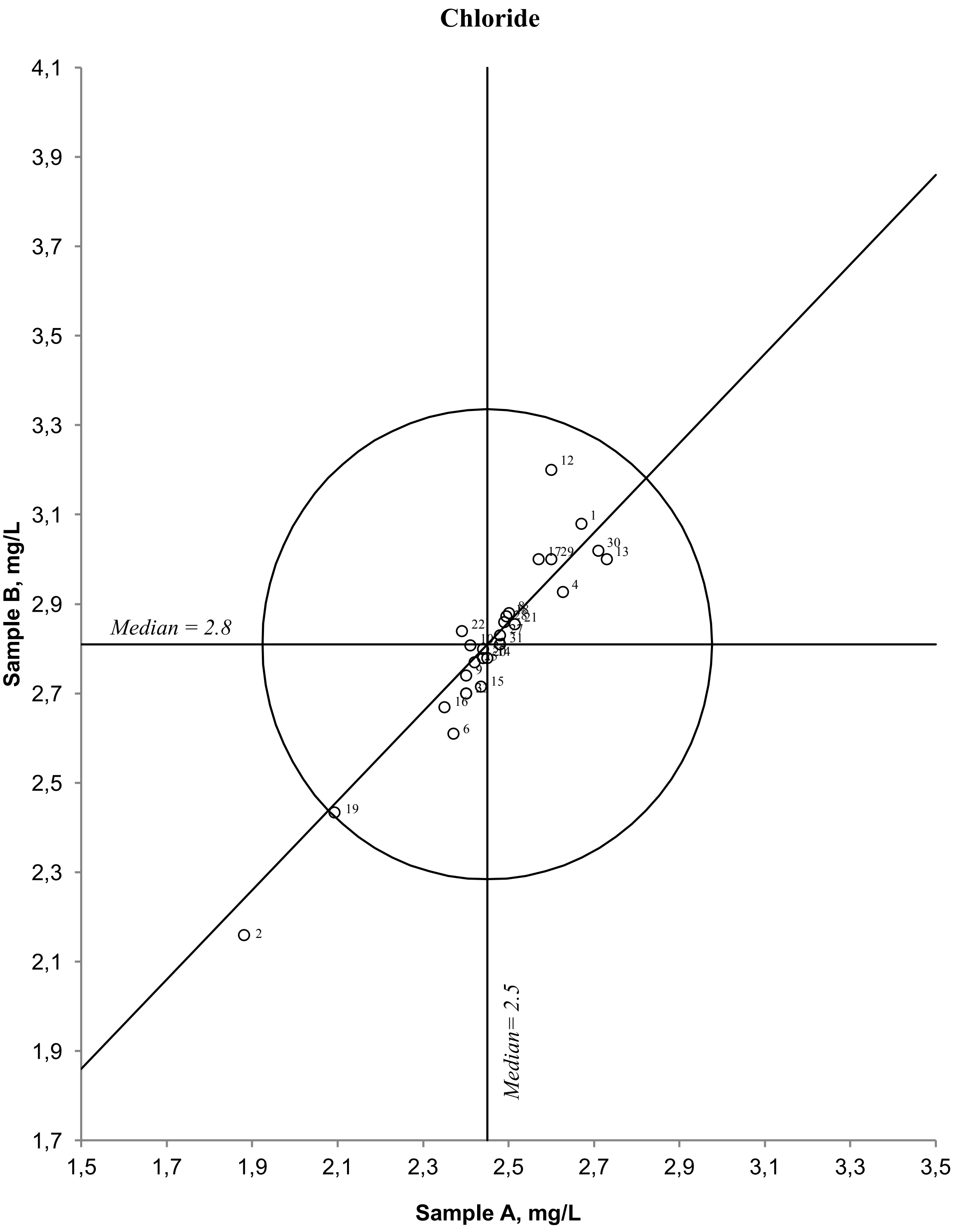

Figure 5. Youden diagram for chloride, sample pair AB
Acceptable limit, given by circle, is 20 %

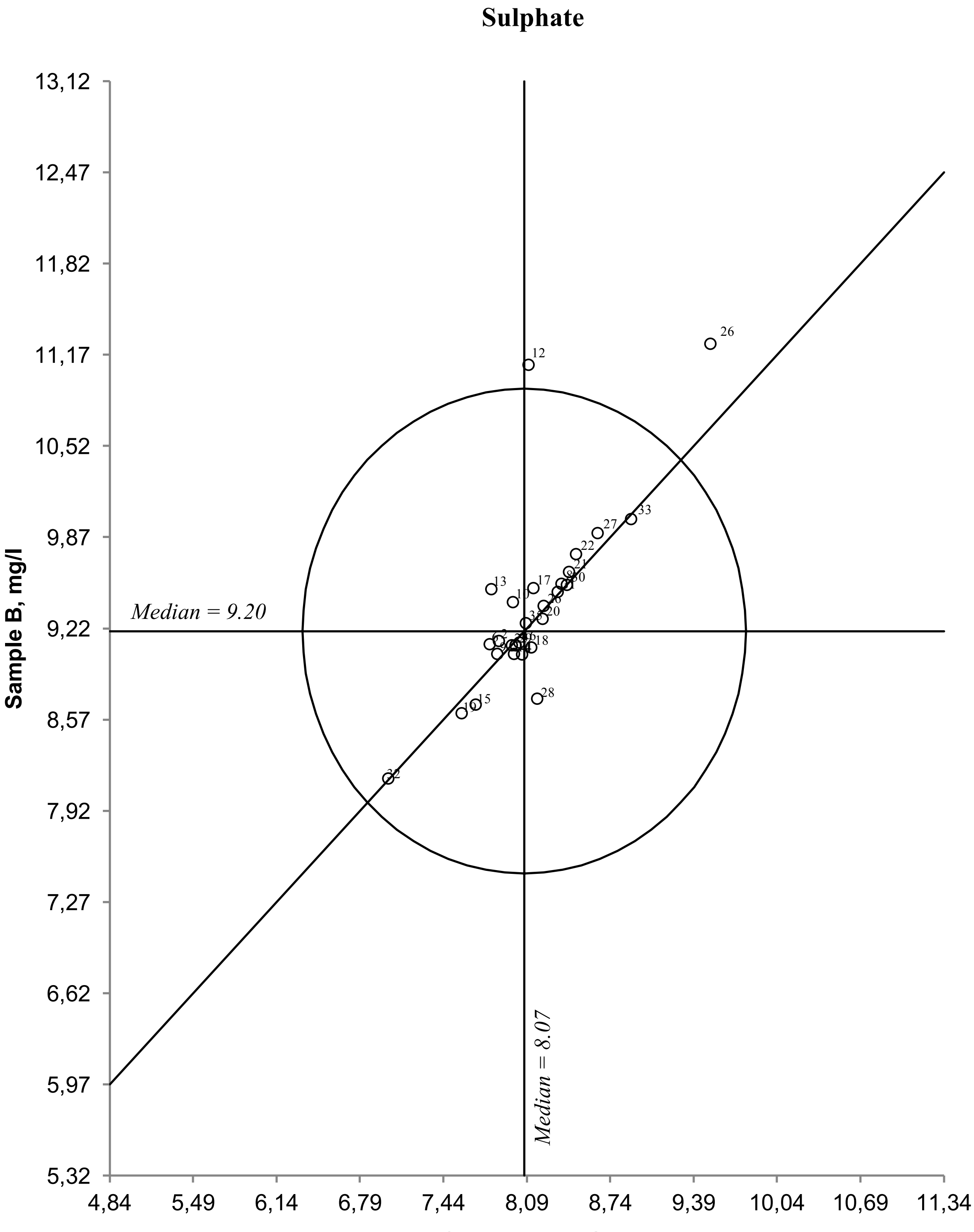

Figure 6. Youden diagram for sulphate, sample pair AB
Acceptable limit, given by circle, is 20 %

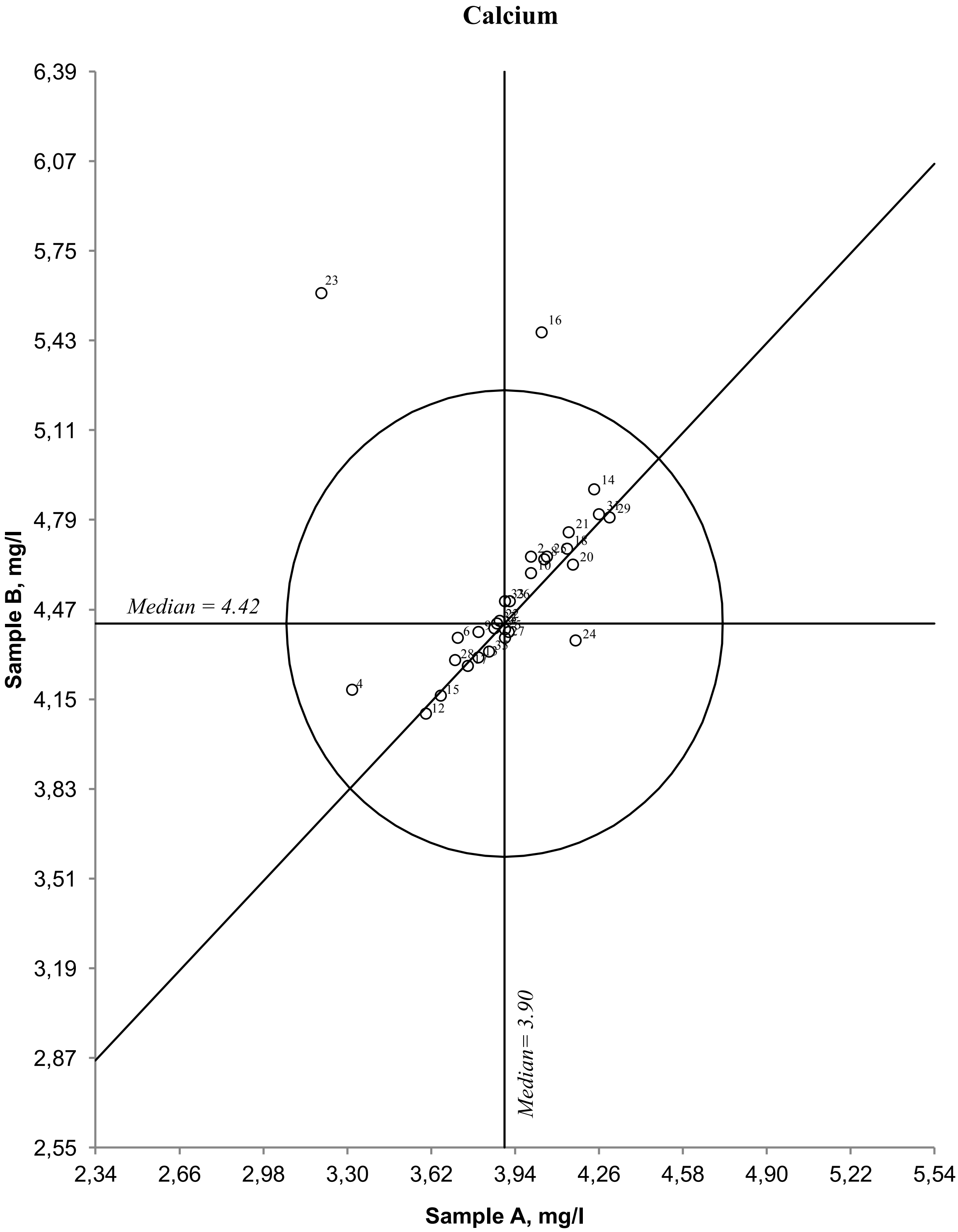

Figure 7. Youden diagram for calcium, sample pair AB
Acceptable limit, given by circle, is 20 %

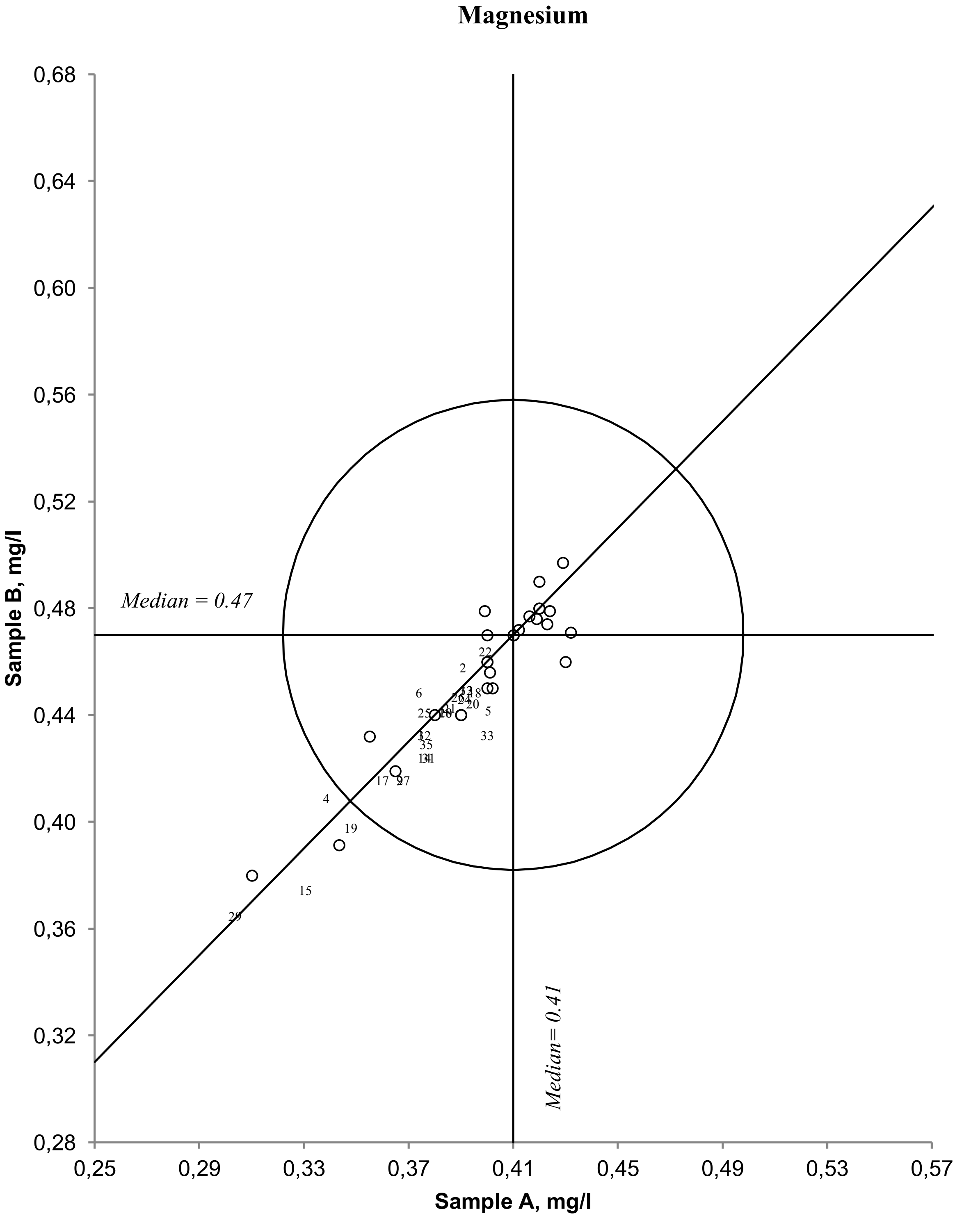

Figure 8. Youden diagram for magnesium, sample pair AB
Acceptable limit, given by circle, is 20 %

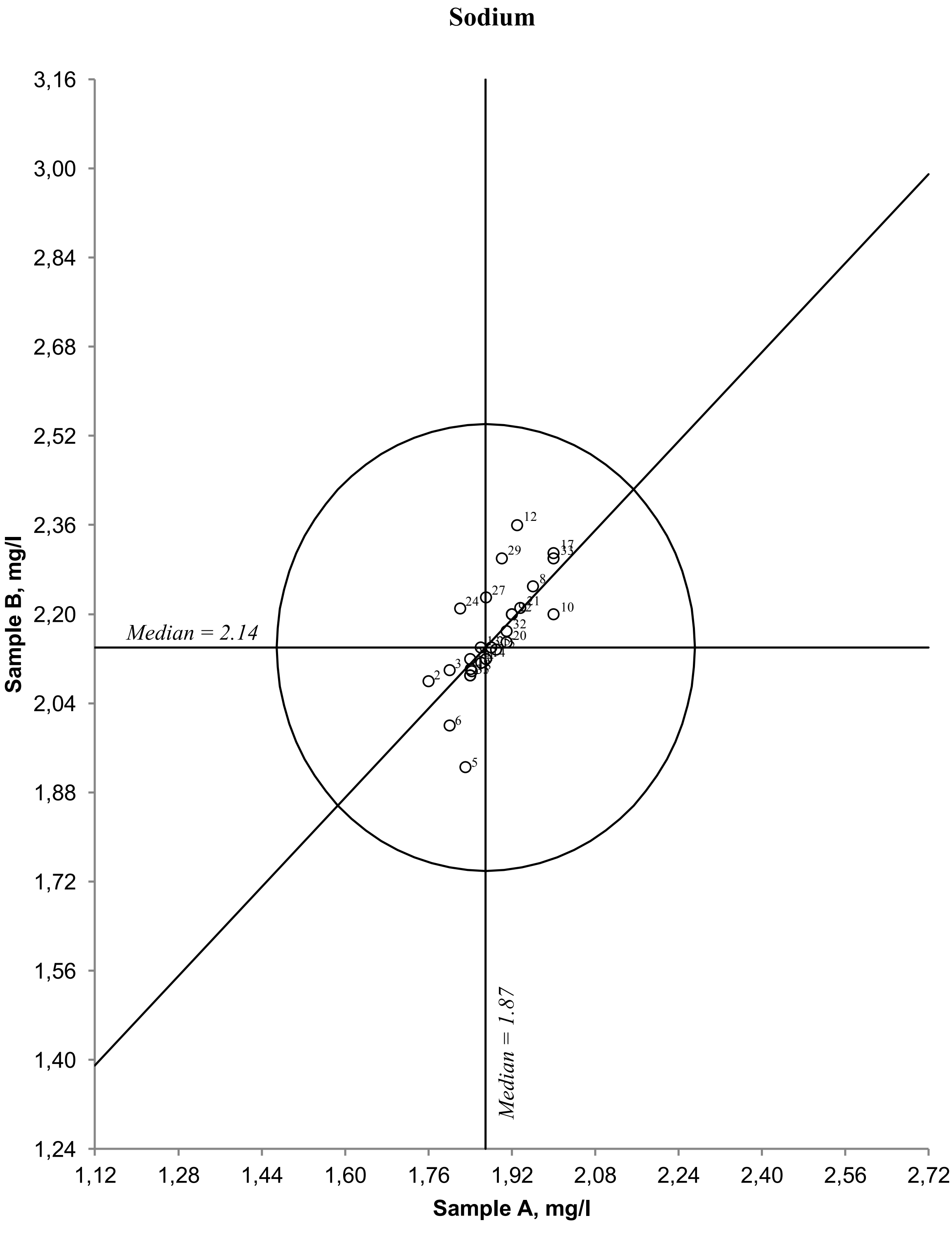

Figure 9. Youden diagram for sodium, sample pair AB
Acceptable limit, given by circle, is 20 %

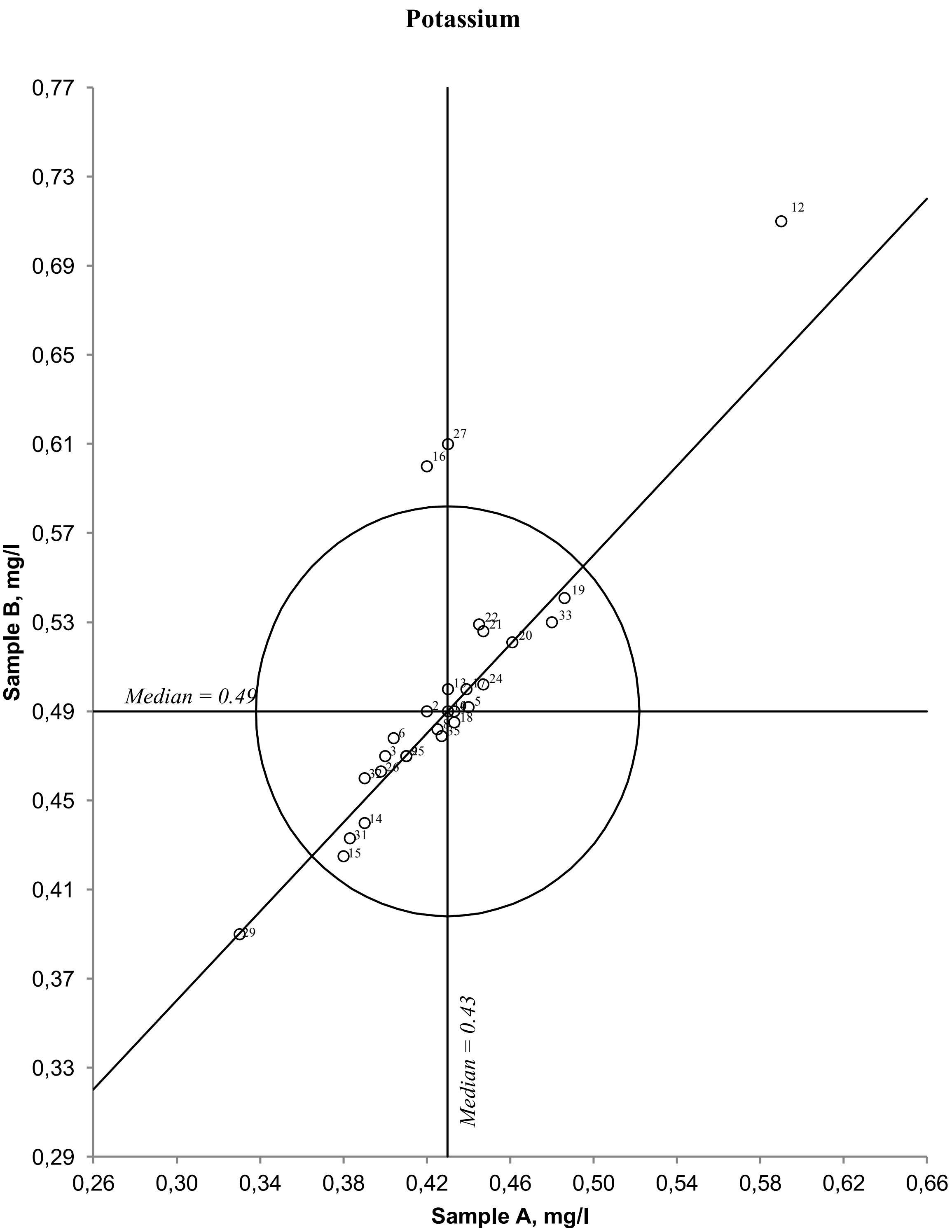

Figure 10. Youden diagram for potassium, sample pair AB
Acceptable limit, given by circle, is 20 %

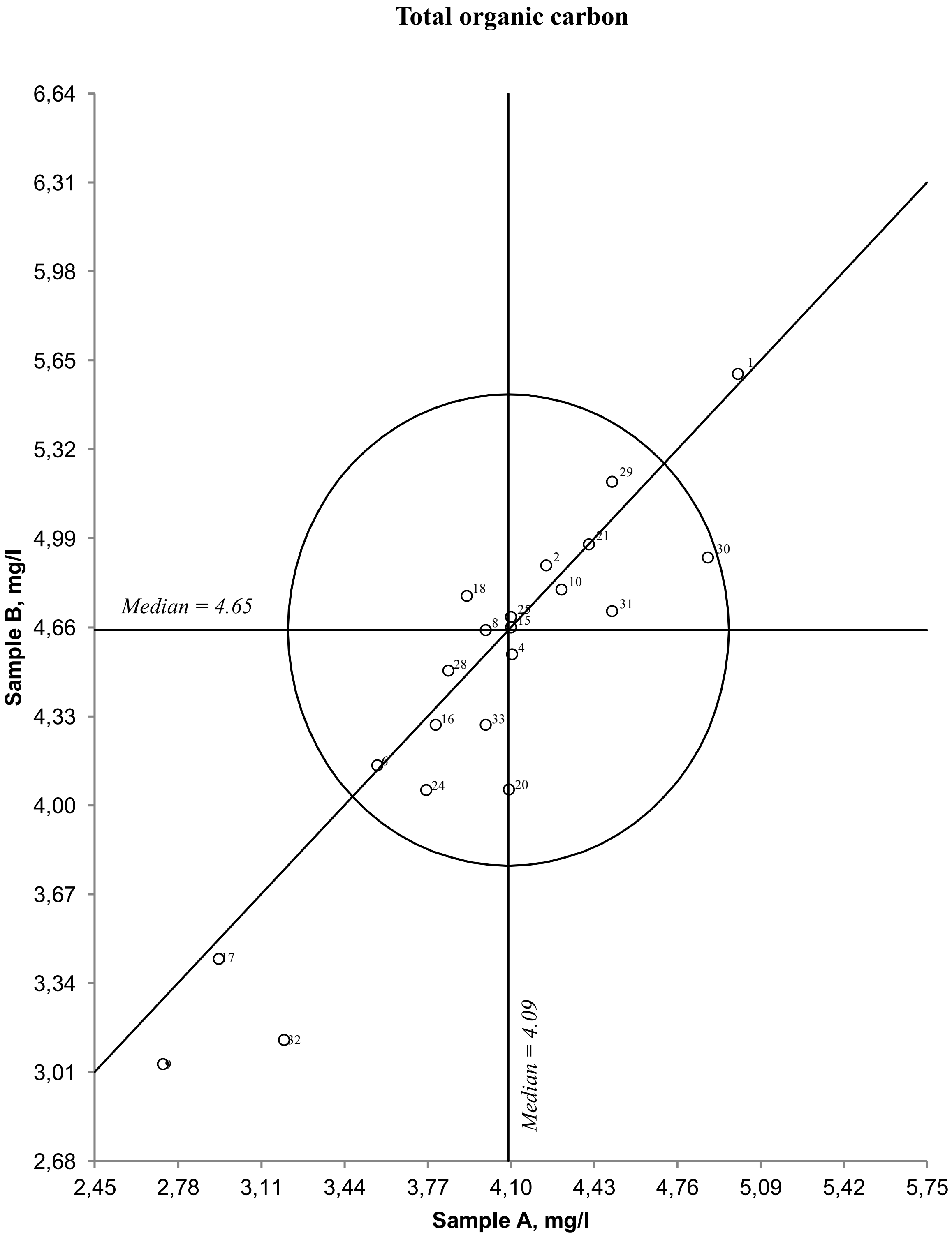

Figure 11. Youden diagram for total organic carbon, sample pair AB
Acceptable limit, given by circle, is 20 %

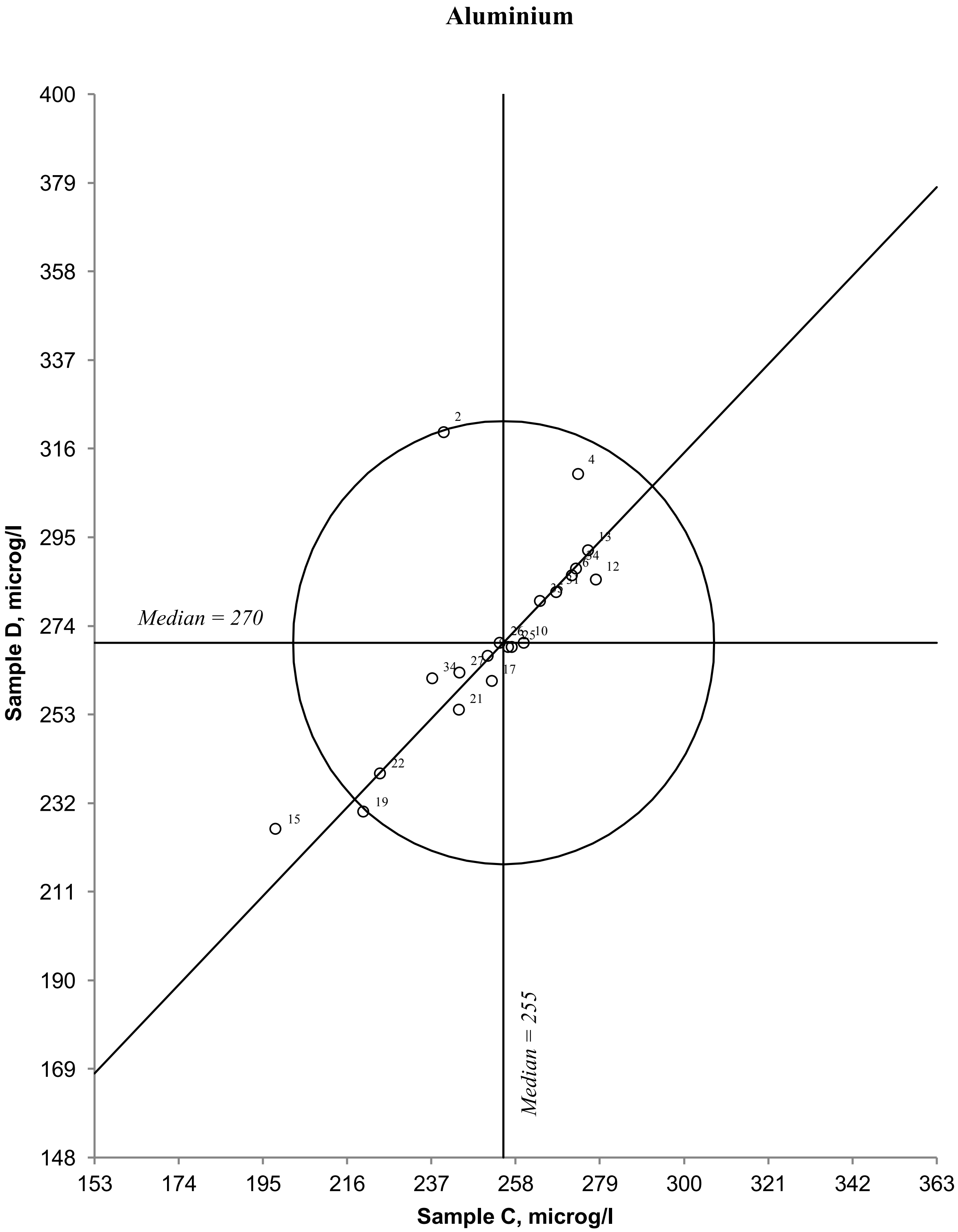

Figure 12. Youden diagram for aluminium, sample pair CD
Acceptable limit, given by circle, is 20 %

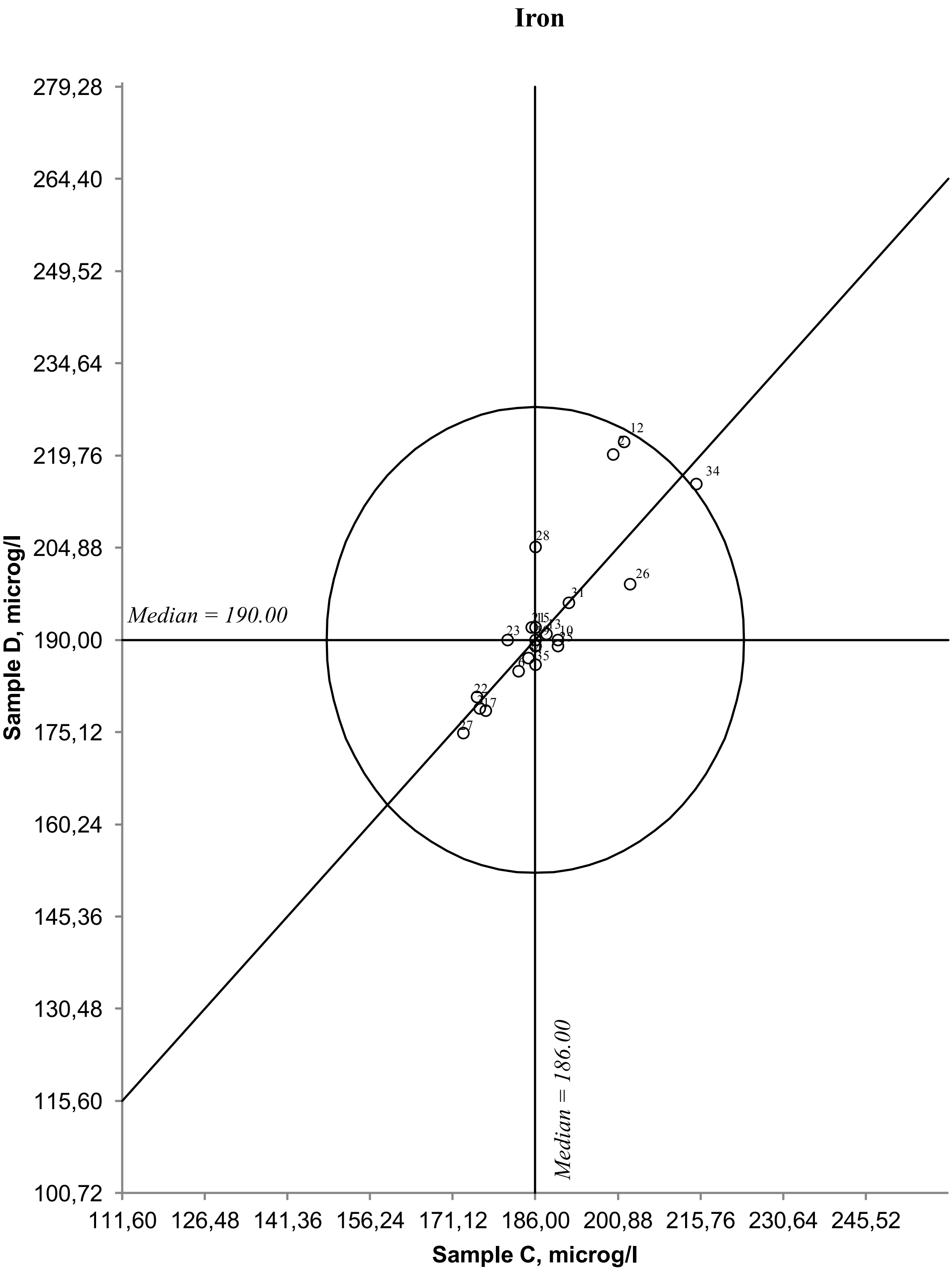

Figure 13. Youden diagram for iron, sample pair CD
Acceptable limit, given by circle, is 20 %

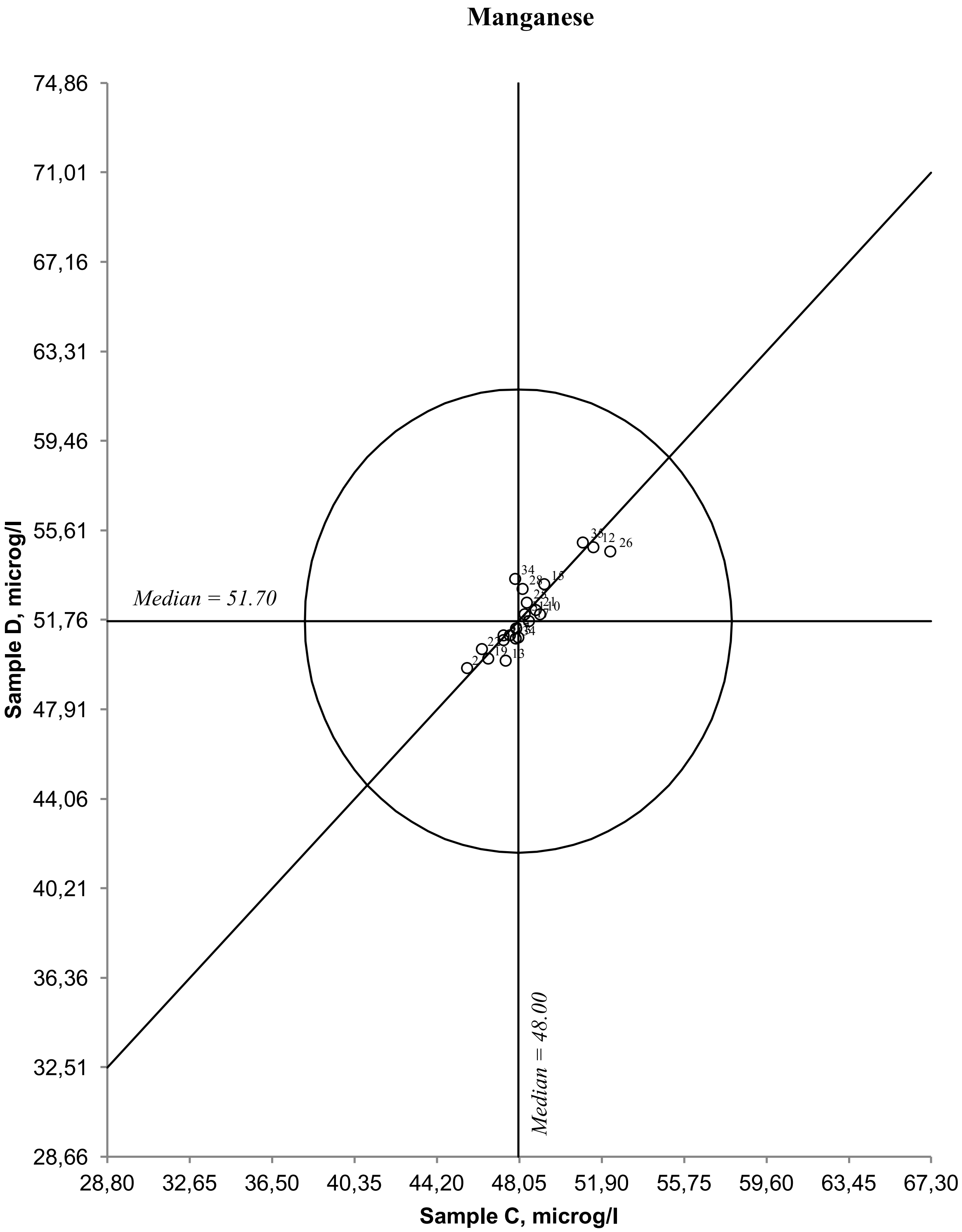

Figure 14. Youden diagram for manganese, sample pair CD
Acceptable limit, given by circle, is 20 %

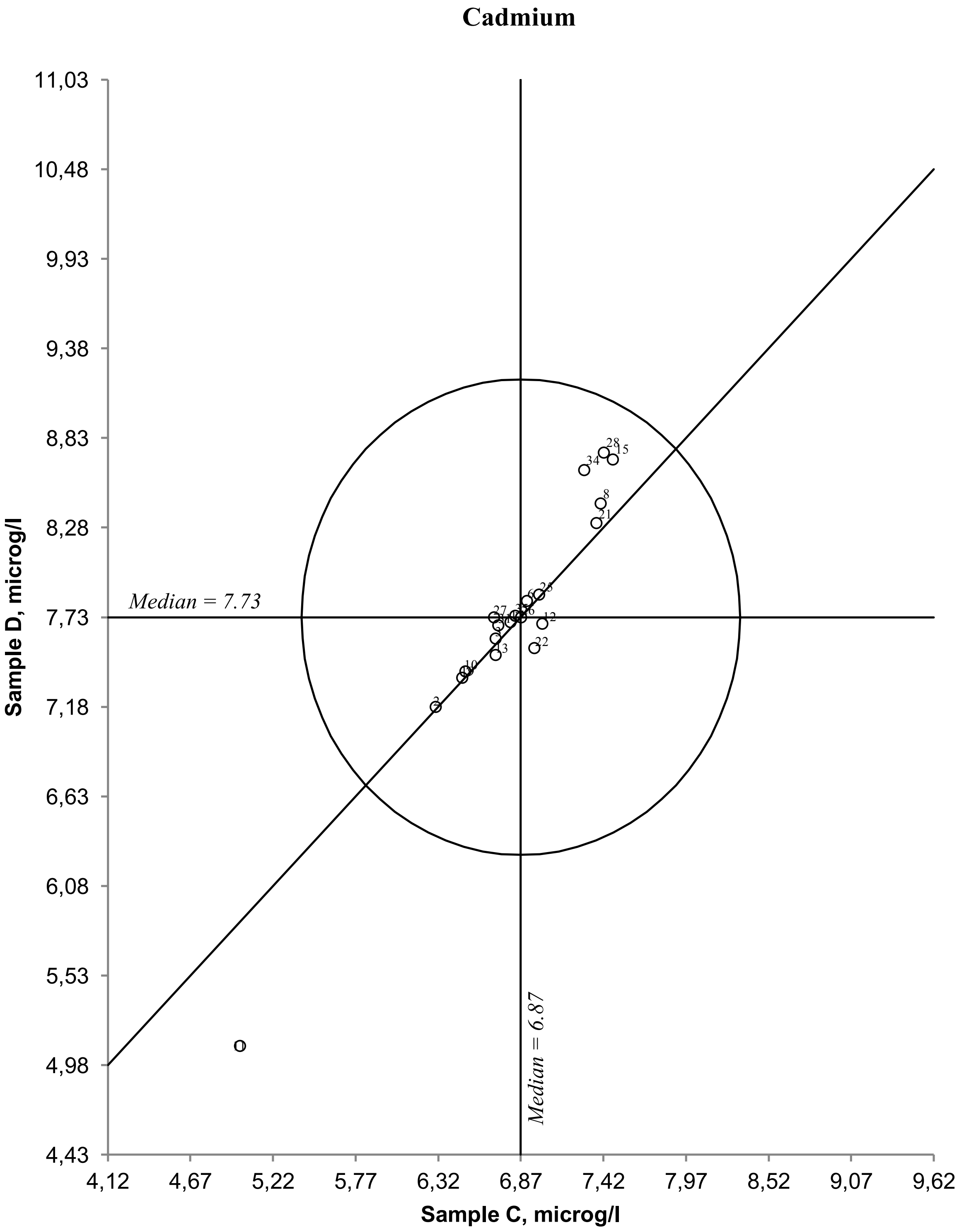

Figure 15. Youden diagram for cadmium, sample pair CD
Acceptable limit, given by circle, is 20 %

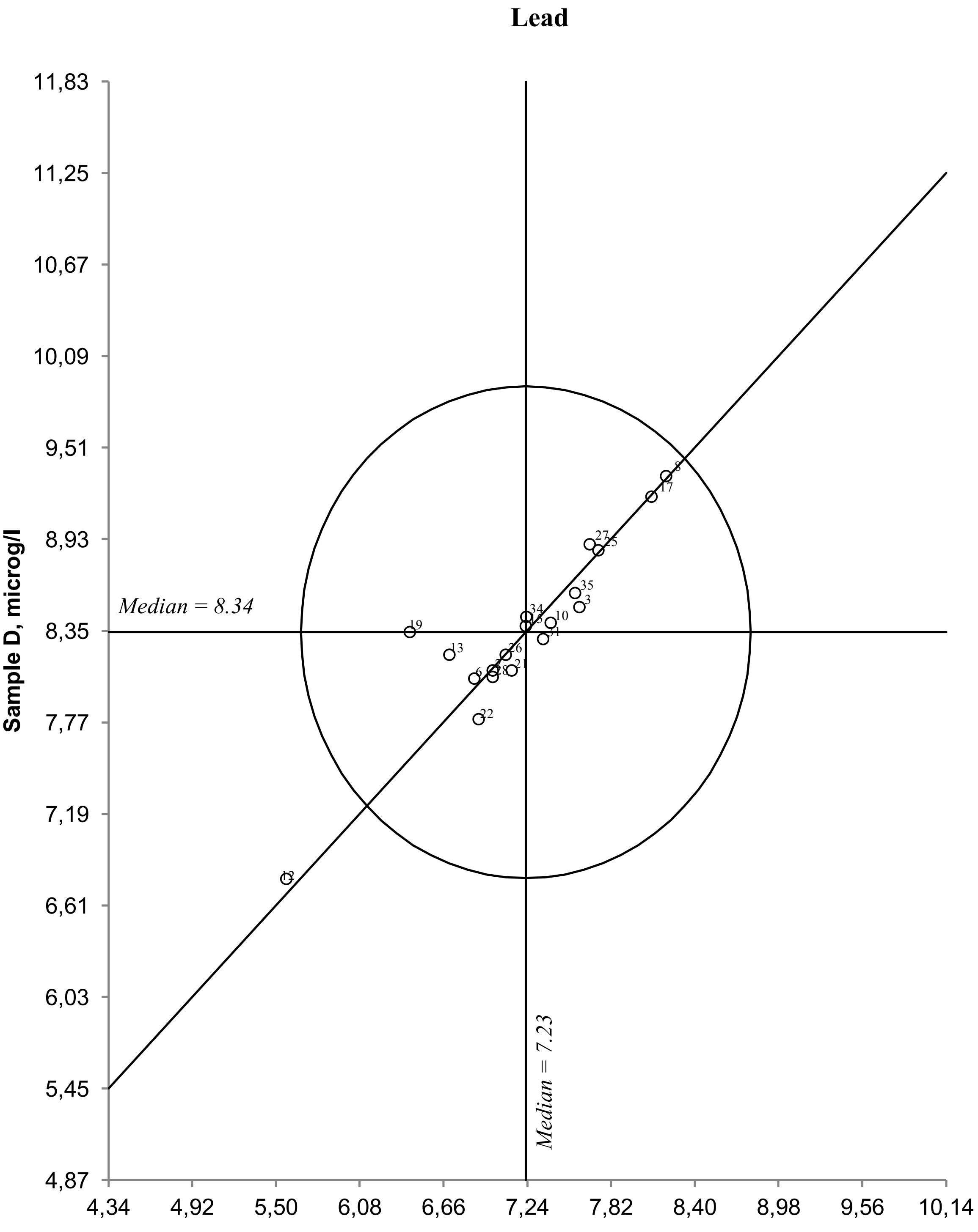

Figure 16. Youden diagram for lead, sample pair CD
Acceptable limit, given by circle, is 20 %

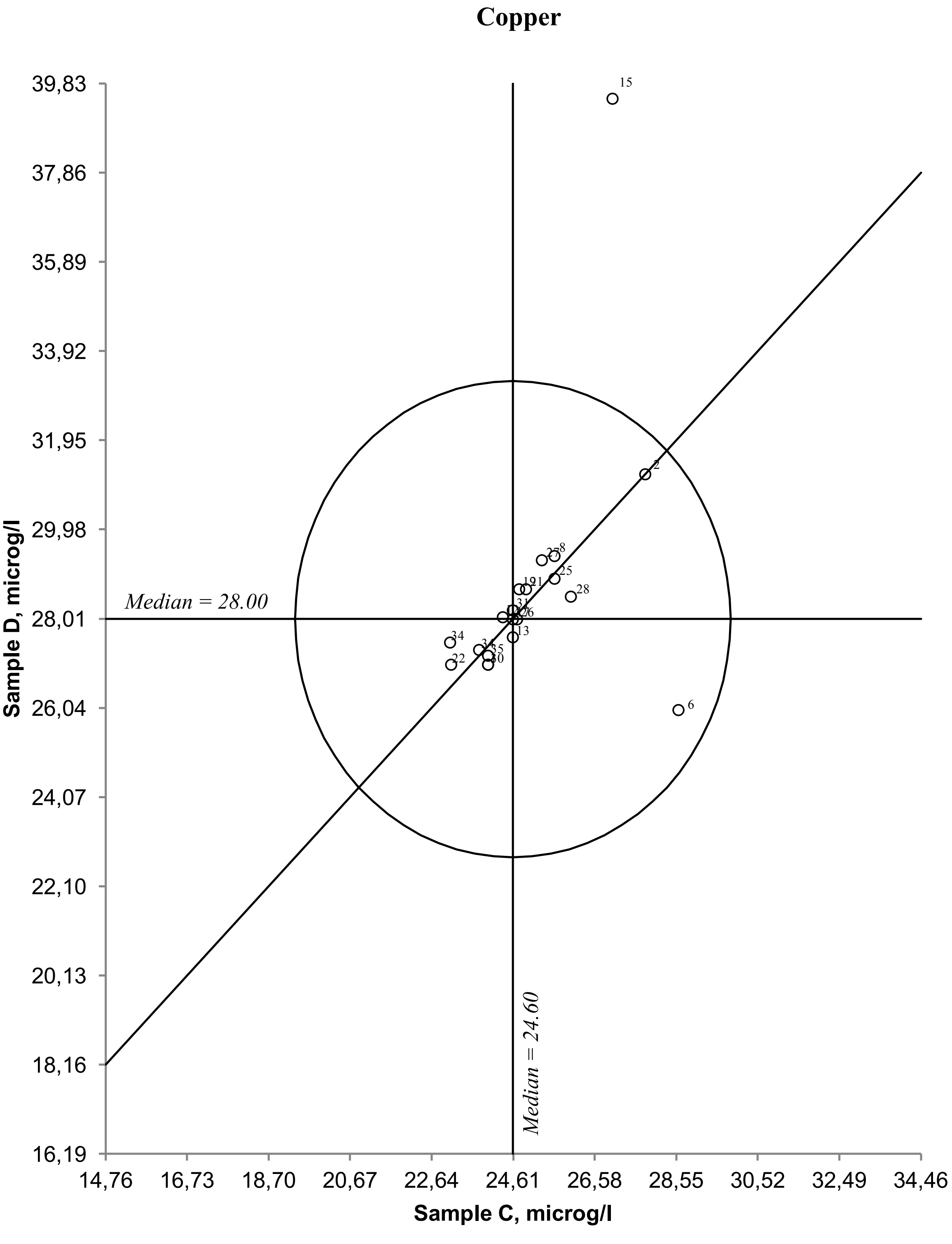

Figure 17. Youden diagram for copper, sample pair CD
Acceptable limit, given by circle, is 20 %

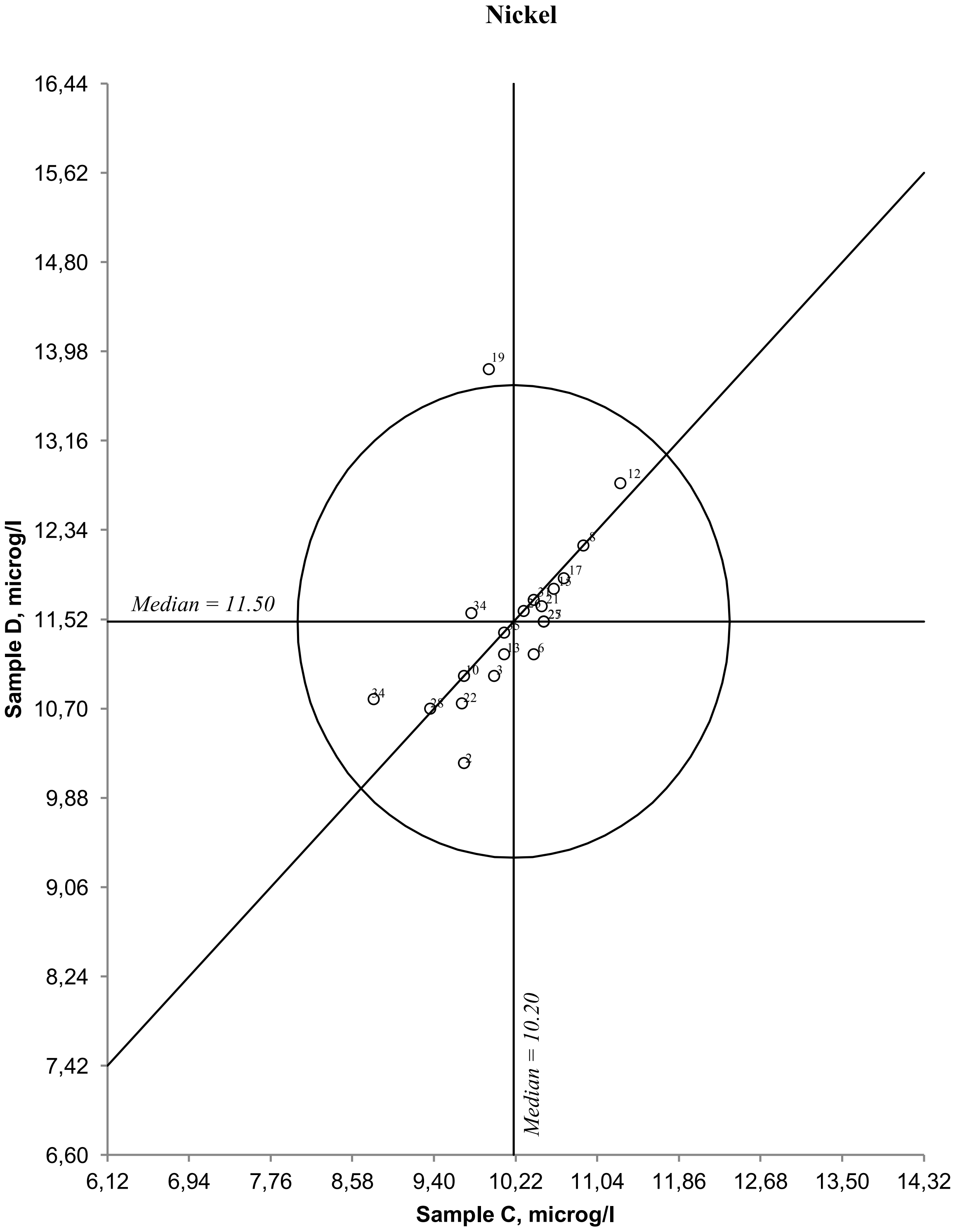

Figure 18. Youden diagram for nickel, sample pair CD
Acceptable limit, given by circle, is 20 %

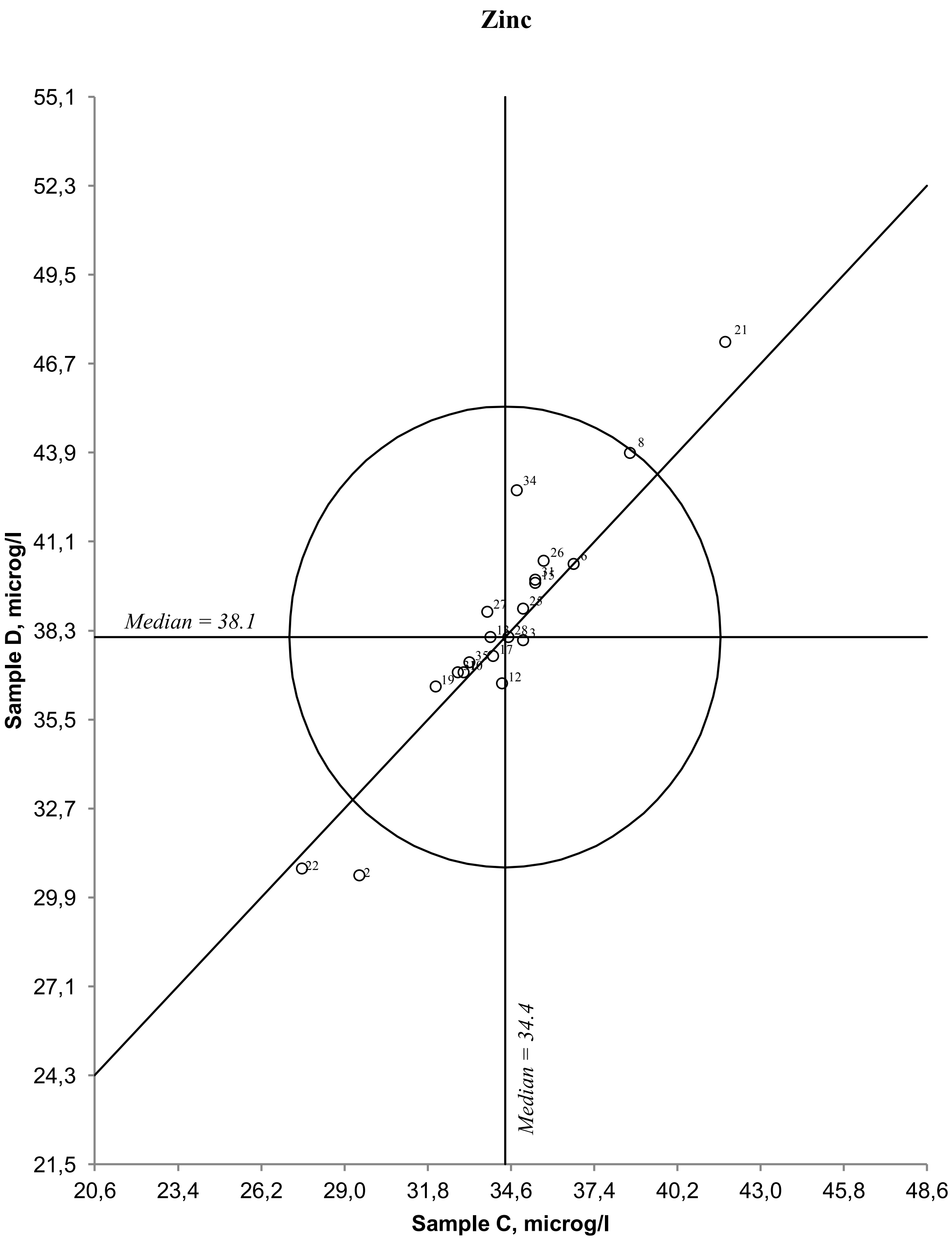

Figure 19. Youden diagram for zinc, sample pair CD
Acceptable limit, given by circle, is 20 %

5. Literature

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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	Adirondack Lakes Survey Corporation	PO Box 296 Route 86 Ray Brook, NY 12977	United States
5	Radbouduniversiteit afd. Ecologie t.a.v. G. Verheggen	Postbus 9010 6500 GL Nijmegen The Netherlands	Netherlands
6	Institute of Biology Komi SC UB RAS	Kommunisticheskaya st.,28 Syktyvkar,167982,Russia	Russian Federation
7	Institute of Environmental Protection-Puszcza Borecka station	Kolektorska 4, 01692, Warszawa, Poland	Poland
8	Bayerisches Landesamt fuer Umwelt	Ref 71 Bürgerm-Ulrich-Str. 160 D-86179 Augsburg	Germany
9	CNR Istituto Studio degli Ecosistemi	Largo Tonolli 50 I-28922 VERBANIA Pallanza	Italy
10	Swedish University for Agricultural Sciences Aquatic Sciences and Assesment	Box 7050 750 07 UPPSALA	Sweden
11	Institute of Global Climate and Ecology (IGCE) Roshydromet and RAS Russian Academy of Sciences	20-B, Glebovskaya St., Moscow, 107258	Russian Federation
12	Hydrochemical Laboratory by Federal State Enterprise on Water Industry	10 A Stahanovskaya str., Pskov, 180004	Russian Federation
13	FGU «Baltwodhoz»	Saint-Petersburg, V.O. Sredny pr. 26	Russian Federation
14	Staatliche Betriebgesellschaft für Umwelt und Landwirtschaft (BfUL)	Haus5, FB53 Waldheimer Str. 219 D-01683 Nossen	Germany
15	Ufficio del Monitoraggio Ambientale - Laboratorio	Via Mirasole 226500 Bellinzona	Switzerland
16	MOEECC, DORSET Laboratory	P.O. Box 39 Dorset, Ontario Canada P0A 1E0	Canada
17	Laboratoire d'Ecologie Fonctionnelle et Environnement (ECOLAB)	Avenue Agrobiopole 31326 Castanet Tolosan	France
18	Institut fur Ökologie	Technikerstrasse 25 6020 Innsbruck Austria	Austria
19	Büsgen-Institute - Soil Science of Temperate Ecosystems	D-37077 Goettingen Buesgenweg 2	Germany

No	Laboratory	Town	Country
20	Marine Scotland Science Freshwater Laboratory	Faskally, Pitlochry,Perthshire, PH16 5BB, Scotland.	United Kingdom
21	Bayerische Landesanstalt fur Wald und Forstwirtschaft Abteilung 2 - Boden und Klima	Hans-Carl-von-Carlowitz-Platz 1 D-85354 Freising	Germany
22	Polish Academy of Sciences Institute of Botany	PAN Instytut Botaniki 31-512 Kraków ul. Lubicz 46	Poland
23	Institute for Public Health Pancevo	Pasterova 2 26000 Pancevo	Serbia
24	Natural Resources Institute Finland Vantaa	Jokiniemenkuja 1 FIN-01370 Vantaa	Finland
25	Norsk institutt for vannforskning	Gaustadalléen 21 0439 OSLO	Norway
26	Natural Resources Wales , Llanelli Laboratory	19 Penyfai Lane Furnace Llanelli Carmarthenshire	United Kingdom
27	Insitute of Industrial Ecology Problems of the North (INEP) Group ICP methods of analysis	184209 Apatity, Akademgorodok 14A, Murmansk reg.	Russian Federation
28	Northern Water Problems Institute	A.Nevskogo, 50, Petrozavodsk 185030	Russian Federation
29	Staatliche Betriebgesellschaft für Umwelt und Landwirtschaft (BfUL)	Stephanplatz 3 D-09010 Chemnitz	Germany
30	Kilkenny Lab, Environmental Protection agency		Ireland
31	Estonian Environment Research Centre	Marja 4 D 10617 Tallinn Estonia	Estonia
32	Forest Nutrition and Water Resources Department of Ecology, Technis	H.C.v.Carlowitz-Platz 2 D-85354 Freising Germany	Germany
33	Environmental Protection Agency Research Department	A.Gostauto 9 01108 Vilnius	Lithuania
34	Servei d'Anàlisi Química i Estructural	STR-UdG Pic de Peguera, 15 17003-Girona	Spain
35	Environment Agency Starcross Laboratory,	Staplake Mount, Starcross, Devon, UK, EX6 8FD	United Kingdom

Number of participating laboratories from the different countries represented in intercomparison 1630

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

Total: 20 countries

Appendix B

Preparation of samples

The sample solutions were prepared from water collected in Hakadals verk, a Nittedal's municipality in Akershus county (Latitude: 60.1213875; Longitude: 10.823947; Altitude: 164 m). 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, sample set AB was obtained lowering the natural pH of the effluent by addition of HCl and H_2SO_4 diluted solutions. 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 analysed, 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).

The Youden'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	6.00	32	0.212	0.047	0.094
	B	6.04	32	0.224	0.049	0.099
Conductivity	A	4.08	26	0.089	0.022	0.044
(mS/m)	B	4.59	27	0.151	0.036	0.072
Alkalinity	A	0.042	17	0.0080	0.0024	0.0048
(mmol/l)	B	0.046	17	0.0057	0.0017	0.0035
Nitrate + nitrite-nitrogen	A	276	28	17.2	4.1	8.1
(µg N/l)	B	309	28	23.4	5.5	11.0
Chloride	A	2.5	27	0.12	0.03	0.06
(mg/l)	B	2.8	26	0.15	0.04	0.07
Sulphate	A	8.07	28	0.289	0.068	0.136
(mg/l)	B	9.20	29	0.447	0.104	0.207
Calcium	A	3.90	30	0.228	0.052	0.104
(mg/l)	B	4.42	29	0.239	0.055	0.111
Magnesium	A	0.41	27	0.019	0.005	0.009
(mg/l)	B	0.47	27	0.023	0.005	0.011
Sodium	A	1.87	28	0.064	0.015	0.030
(mg/l)	B	2.14	27	0.092	0.022	0.044
Potassium	A	0.43	27	0.029	0.007	0.014
(mg/l)	B	0.49	27	0.039	0.009	0.019
Total organic carbon	A	4.09	21	0.506	0.138	0.276
(mg/l)	B	4.65	21	0.541	0.148	0.295
Aluminium	C	255	21	19.3	5.3	10.5
(µg/l)	D	270	20	22.4	6.3	12.5
Iron	C	186.00	22	9.397	2.504	5.008
(µg/l)	D	190.00	21	10.986	2.997	5.994
Manganese	C	48.00	22	1.234	0.329	0.658
(µg/l)	D	51.70	21	1.679	0.458	0.916
Cadmium	C	6.87	20	0.372	0.104	0.208
(µg/l)	D	7.73	19	0.502	0.144	0.288
Lead	C	7.23	20	0.596	0.166	0.333
(µg/l)	D	8.34	19	0.429	0.123	0.246
Copper	C	24.60	21	1.191	0.325	0.650
(µg/l)	D	28.00	20	1.134	0.317	0.634
Nickel	C	10.20	21	0.540	0.147	0.295
(µg/l)	D	11.50	20	0.613	0.171	0.343
Zinc	C	34.4	21	1.83	0.50	1.00
(µg/l)	D	38.1	20	2.76	0.77	1.54

Appendix D

Table 4. The results of the participating laboratories

Lab. nr.	pH		Conductivity, mS/m		Alkalinity, mmol/l		Nitrate + nitrite-nitrogen, µg N/l		Chloride, mg/l		Sulphate, mg/l		Calcium, mg/l		Magnesium, mg/l	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
1	5.70	5.80	4.60	4.10	0.084	0.088	280	280	2.7	3.1						
2	6.05	6.22	4.13	4.79	0.042	0.049	267	291	1.9	2.2	7.87	9.13	4.00	4.66	0.42	0.49
3	5.86	5.91	4.13	4.49	0.036	0.040	356	406	2.4	2.7	8.00	9.10	3.90	4.40	0.40	0.46
4	6.68	6.66	403.18	455.46	0.046	0.046	29	33	2.6	2.9	8.05	9.04	3.32	4.19	0.36	0.43
5	5.65	5.62			0.079	0.084	266	310	1.0	1.2			3.91	4.39	0.43	0.47
6	5.72	5.69	4.21	4.74	0.030	0.039	276	324	2.4	2.6	7.80	9.11	3.72	4.37	0.40	0.48
7	6.23	6.29	4.00	4.50												
8	6.23	6.21	4.16	4.65			279	317	2.5	2.9	8.36	9.54	4.05	4.65		
9	5.86	5.82	4.01	4.57	0.034	0.040	350	400	2.4	2.7	7.86	9.04	3.80	4.39	0.39	0.44
10	5.97	6.04	4.05	4.56	0.042	0.047	257	295	2.4	2.8	7.98	9.41	4.00	4.60	0.41	0.47
11																
12	6.07	5.91	5.09	5.20	0.063	0.069	290	315	2.6	3.2	8.10	11.10	3.60	4.10	0.40	0.46
13	5.95	5.96	4.12	4.66			193	232	2.7	3.0	7.81	9.50	3.80	4.30	0.42	0.48
14	5.90	6.15	4.12	4.65			260	300	2.5	2.8	7.99	9.04	4.24	4.90	0.40	0.45
15	6.03	5.90	3.62	4.14	0.043	0.049	296	332	2.4	2.7	7.69	8.68	3.66	4.16	0.34	0.39
16	5.93	6.03	4.06	4.58	0.055	0.044	272	308	2.4	2.7	8.03	9.12	4.04	5.46	0.43	1.81
17	5.95	5.93	4.07	4.55	0.056	0.055	275	315	2.6	3.0	8.14	9.51	3.76	4.27	0.38	0.44
18	5.97	5.94	4.07	4.63	0.042	0.047	281	313	2.5	2.9	8.12	9.09	4.14	4.69	0.42	0.48
19	6.01	6.26	3.97	4.54			264	304	2.1	2.4	7.58	8.62	3.86	4.40	0.37	0.42
20	6.00	6.00	3.93	4.43	0.042	0.046	277	309	2.4	2.8	8.21	9.29	4.16	4.63	0.42	0.47
21	5.93	6.12	3.76	4.39			259	293	2.5	2.9	8.42	9.62	4.14	4.75	0.41	0.47
22	6.28	6.23	4.07	4.61			313	361	2.4	2.8	8.47	9.75	3.88	4.43	0.43	0.50
23	6.70	6.33	0.06	0.05	0.100	0.080			1.4	1.8	13.00	14.40	3.20	5.60		
24							67	90					4.17	4.36	0.42	0.48
25	6.35	6.27	4.12	4.66	0.083	0.087	260	300	2.4	2.8	7.97	9.10	4.06	4.66	0.40	0.47
26	6.07	6.26	4.11	4.25	0.043	0.051	280	310	1.2	1.5	9.52	11.25	3.92	4.50	0.42	0.48
27	5.98	5.97	3.73	4.07	0.033	0.035	277	308	2.5	2.8	8.64	9.90	3.90	4.37	0.39	0.44
28	6.14	6.14	4.09	4.65	0.040	0.044	290	370	2.5	2.9	8.17	8.72	3.71	4.29	0.41	0.47
29	6.00	6.10	4.10	4.62	0.074	0.079	260	290	2.6	3.0	8.00	9.10	4.30	4.80	0.31	0.38
30	6.05	6.04	4.10	4.60	2.400	0.800	325	365	2.7	3.0	8.40	9.53				
31	5.90	5.90	4.07	4.61	0.038	0.045	277	309	2.5	2.8	8.33	9.48	4.26	4.81	0.40	0.45
32	5.67	5.56	40.70	48.00	0.180	0.180	269	291	2.4	2.8	7.01	8.15	3.87	4.42	0.42	0.48
33	6.53	6.47	4.11	4.68	0.040	0.050	263	314	2.4	2.7	8.90	10.00	3.90	4.50	0.43	0.46
34																
35							0	0			8.08	9.26	3.84	4.32	0.40	0.46

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					5.00	5.60				
2	1.76	2.08	0.42	0.49	4.24	4.89	240	320	200	220
3	1.80	2.10	0.40	0.47			256	269	176	179
4	1.86	2.11	0.43	0.49	4.10	4.56	274	310		
5	1.83	1.93	0.44	0.49						
6	1.80	2.00	0.40	0.48	3.57	4.15	272	286	183	185
7										
8	1.96	2.25	0.43	0.48	4.00	4.65	251	267	186	189
9	1.92	2.20	0.41	0.47	2.72	3.04				
10	2.00	2.20	0.43	0.49	4.30	4.80	260	270	190	190
11										
12	1.93	2.36	0.59	0.71			278	285	202	222
13	1.86	2.14	0.43	0.50			276	292	188	191
14	1.87	2.12	0.39	0.44						
15	1.89	2.14	0.38	0.43	4.10	4.66	198	226	186	192
16	1.94	3.55	0.42	0.60	3.80	4.30				
17	2.00	2.31	0.44	0.50	2.94	3.43	252	261	177	179
18	1.84	2.10	0.43	0.49	3.92	4.78				
19	1.84	2.10	0.49	0.54			220	230	186	190
20	1.91	2.15	0.46	0.52	4.09	4.06				
21	1.94	2.21	0.45	0.53	4.41	4.97	244	254	185	192
22	1.92	2.20	0.45	0.53			224	239	176	181
23							510	530	181	190
24	1.82	2.21	0.45	0.50	3.76	4.06	268	0	181	0
25	1.88	2.14	0.41	0.47	4.10	4.70	257	269	190	189
26	1.84	2.12	0.40	0.46			254	270	203	199
27	1.87	2.23	0.43	0.61			244	263	173	175
28					3.85	4.50	148	156	186	205
29	1.90	2.30	0.33	0.39	4.50	5.20				
30					4.88	4.92				
31	1.84	2.09	0.38	0.43	4.50	4.72	268	282	192	196
32	1.91	2.17	0.39	0.46	3.20	3.13				
33	2.00	2.30	0.48	0.53	4.00	4.30				
34							273	288	215	215
35	1.84	2.09	0.43	0.48			264	280	186	186

Lab. nr.	Manganese µg/l		Cadmium µg/l		Lead µg/l		Copper µg/l		Nickel µg/l		Zinc µg/l	
	A	B	A	B	A	B	A	B	C	D	C	D
1												
2	45.60	49.70	6.30	7.18	7.00	8.10	27.80	31.20	9.70	10.20	29.5	30.6
3	48.00	51.00	6.70	7.60	7.60	8.50	24.00	27.00	10.00	11.00	35.0	38.0
4												
5												
6	47.30	51.10	6.91	7.83	6.87	8.05	28.60	26.00	10.40	11.20	36.7	40.4
7												
8	47.90	51.40	7.40	8.43	8.20	9.33	25.60	29.40	10.90	12.20	38.6	43.9
9												
10	49.00	52.00	6.50	7.40	7.40	8.40	24.00	27.00	9.70	11.00	33.0	37.0
11			5.00	5.10	3.53	4.10	14.20	13.60				
12	51.50	54.90	7.01	7.69	5.57	6.78	24.35	28.05	11.27	12.77	34.3	36.7
13	47.40	50.00	6.70	7.50	6.70	8.20	24.60	27.60	10.10	11.20	33.9	38.1
14												
15	49.20	53.30	7.48	8.70	7.23	8.38	27.00	39.50	10.60	11.80	35.4	39.8
16												
17	48.50	51.70	6.80	7.70	8.10	9.20	24.60	28.00	10.70	11.90	34.0	37.5
18												
19	46.60	50.10	6.48	7.36	6.42	8.34	24.75	28.66	9.95	13.82	32.1	36.6
20												
21	48.82	52.19	7.37	8.31	7.13	8.10	24.92	28.66	10.48	11.64	41.8	47.4
22	46.30	50.50	6.96	7.54	6.90	7.79	23.10	27.00	9.68	10.75	27.6	30.8
23	82.00	78.00										
24	47.20	0.00	7.00	0.00	8.90	0.00	24.60	0.00	10.70	0.00	34.0	0.0
25	48.40	52.50	6.99	7.87	7.73	8.86	25.60	28.90	10.50	11.50	35.0	39.0
26	52.30	54.70	6.87	7.73	7.09	8.20	24.70	28.00	10.30	11.60	35.7	40.5
27	47.60	51.10	6.69	7.73	7.67	8.90	25.30	29.30	10.50	11.50	33.8	38.9
28	48.20	53.10	7.42	8.74	7.00	8.06	26.00	28.50	9.36	10.70	34.5	38.1
29												
30												
31	48.30	52.00	6.72	7.68	7.35	8.30	24.60	28.20	10.40	11.70	35.4	39.9
32												
33												
34	47.88	53.54	7.29	8.63	7.23	8.44	23.78	27.32	9.77	11.58	34.8	42.7
35	51.00	55.10	6.83	7.74	7.57	8.59	24.00	27.20	10.10	11.40	33.2	37.3

Table 5.1. Statistics
pH
Sample A
Analytical method: All
Unit: units

Number of participants	32	Range	1.05
Number of omitted results	0	Variance	0.06
True value	6.00	Standard deviation	0.25
Mean value	6.04	Relative standard deviation	4.2%
Median value	6.00	Relative error	0.7%

Analytical results in ascending order:

5	5.65	17	5.95	12	6.07
32	5.67	18	5.97	26	6.07
1	5.70	10	5.97	28	6.14
6	5.72	27	5.98	8	6.23
9	5.86	4	5.99	7	6.23
3	5.86	29	6.00	22	6.28
14	5.90	20	6.00	25	6.35
31	5.90	19	6.01	33	6.53
16	5.93	15	6.03	4	6.68
21	5.93	2	6.05	23	6.70
13	5.95	30	6.05		

O = Omitted result

Table 5.1. Statistics
pH
Sample B
Analytical method: All
Unit: units

Number of participants	32	Range	1.10
Number of omitted results	0	Variance	0.06
True value	6.04	Standard deviation	0.24
Mean value	6.05	Relative standard deviation	3.9%
Median value	6.04	Relative error	0.2%

Analytical results in ascending order:

32	5.56	18	5.94	8	6.21
5	5.62	13	5.96	2	6.22
6	5.69	27	5.97	22	6.23
1	5.80	20	6.00	19	6.26
9	5.82	16	6.03	26	6.26
15	5.90	10	6.04	25	6.27
31	5.90	30	6.04	7	6.29
12	5.91	29	6.10	23	6.33
3	5.91	21	6.12	33	6.47
17	5.93	28	6.14	4	6.66
4	5.93	14	6.15		

O = Omitted result

Table 5.2. Statistics
Conductivity
Sample A

Analytical method: All
Unit: mS/m

Number of participants	30	Range	0.98
Number of omitted results	4	Variance	0.03
True value	4.08	Standard deviation	0.18
Mean value	4.06	Relative standard deviation	4.3%
Median value	4.08	Relative error	-0.5%

Analytical results in ascending order:

23	0.06 O	17	4.07	14	4.12
15	3.62	18	4.07	25	4.12
27	3.73	22	4.07	2	4.13
21	3.76	31	4.07	3	4.13
20	3.93	28	4.09	8	4.16
19	3.97	30	4.10	6	4.21
7	4.00	29	4.10	1	4.60
9	4.01	33	4.11	12	5.09 O
10	4.05	26	4.11	32	40.70 O
16	4.06	13	4.12	4	403.18 O

O = Omitted result

Table 5.2. Statistics
Conductivity
Sample B

Analytical method: All
Unit: mS/m

Number of participants	30	Range	0.72
Number of omitted results	4	Variance	0.04
True value	4.59	Standard deviation	0.19
Mean value	4.53	Relative standard deviation	4.2%
Median value	4.59	Relative error	-1.4%

Analytical results in ascending order:

23	0.05 O	17	4.55	28	4.65
27	4.07	10	4.56	14	4.65
1	4.10	9	4.57	13	4.66
15	4.14	16	4.58	25	4.66
26	4.25	30	4.60	33	4.68
21	4.39	22	4.61	6	4.74
20	4.43	31	4.61	2	4.79
3	4.49	29	4.62	12	5.20 O
7	4.50	18	4.63	32	48.00 O
19	4.54	8	4.65	4	455.46 O

O = Omitted result

Table 5.3. Statistics
Alkalinity
Sample A

Analytical method: All

Unit: mmol/l

Number of participants	24	Range	0.026
Number of omitted results	8	Variance	0.000
True value	0.042	Standard deviation	0.007
Mean value	0.041	Relative standard deviation	16.7%
Median value	0.042	Relative error	-1.4%

Analytical results in ascending order:

6	0.030	2	0.042	12	0.063 O
27	0.033	20	0.042	29	0.074 O
9	0.034	10	0.042	5	0.079 O
3	0.036	15	0.043	25	0.083 O
31	0.038	26	0.043	1	0.084 O
33	0.040	4	0.046	23	0.100 O
28	0.040	16	0.055	32	0.180 O
18	0.042	17	0.056	30	2.400 O

O = Omitted result

Table 5.3. Statistics
Alkalinity
Sample B

Analytical method: All

Unit: mmol/l

Number of participants	24	Range	0.020
Number of omitted results	8	Variance	0.000
True value	0.046	Standard deviation	0.005
Mean value	0.046	Relative standard deviation	11.1%
Median value	0.046	Relative error	-1.1%

Analytical results in ascending order:

27	0.035	20	0.046	12	0.069 O
6	0.039	10	0.047	29	0.079 O
3	0.040	18	0.047	23	0.080 O
9	0.040	15	0.049	5	0.084 O
28	0.044	2	0.049	25	0.087 O
16	0.044	33	0.050	1	0.088 O
31	0.045	26	0.051	32	0.180 O
4	0.046	17	0.055	30	0.800 O

O = Omitted result

Table 5.4. Statistics
Nitrate + nitrite-nitrogen
Sample A

Analytical method: All

Unit: microg/l

Number of participants	31	Range	163
Number of omitted results	3	Variance	931
True value	276	Standard deviation	31
Mean value	279	Relative standard deviation	10.9%
Median value	276	Relative error	1.1%

Analytical results in ascending order:

35	0 O	5	266	26	280
4	29 O	2	267	18	281
24	67 O	32	269	12	290
13	193	16	272	28	290
10	257	17	275	15	296
21	259	6	276	22	313
29	260	20	277	30	325
25	260	27	277	9	350
14	260	31	277	3	356
33	263	8	279		
19	264	1	280		

O = Omitted result

Table 5.4. Statistics
Nitrate + nitrite-nitrogen
Sample B

Analytical method: All

Unit: microg/l

Number of participants	31	Range	174
Number of omitted results	3	Variance	1297
True value	309	Standard deviation	36
Mean value	317	Relative standard deviation	11.4%
Median value	309	Relative error	2.4%

Analytical results in ascending order:

35	0 O	14	300	12	315
4	33 O	19	304	8	317
24	90 O	16	308	6	324
13	232	27	308	15	332
1	280	31	309	22	361
29	290	20	309	30	365
2	291	5	310	28	370
32	291	26	310	9	400
21	293	18	313	3	406
10	295	33	314		
25	300	17	315		

O = Omitted result

Table 5.5. Statistics
Chloride
Sample A

Analytical method: All

Unit: mg/L

Number of participants	30	Range	0.9
Number of omitted results	3	Variance	0.0
True value	2.5	Standard deviation	0.2
Mean value	2.5	Relative standard deviation	7.0%
Median value	2.5	Relative error	0.3%

Analytical results in ascending order:

5	1.0 O	3	2.4	18	2.5
26	1.2 O	10	2.4	8	2.5
23	1.4 O	25	2.4	21	2.5
2	1.9	15	2.4	17	2.6
19	2.1	20	2.4	29	2.6
16	2.4	32	2.4	12	2.6
6	2.4	14	2.5	4	2.6
22	2.4	31	2.5	1	2.7
33	2.4	27	2.5	30	2.7
9	2.4	28	2.5	13	2.7

O = Omitted result

Table 5.5. Statistics
Chloride
Sample B

Analytical method: All

Unit: mg/L

Number of participants	30	Range	1.0
Number of omitted results	3	Variance	0.0
True value	2.8	Standard deviation	0.2
Mean value	2.8	Relative standard deviation	7.2%
Median value	2.8	Relative error	0.0%

Analytical results in ascending order:

5	1.2 O	9	2.7	28	2.9
26	1.5 O	25	2.8	18	2.9
23	1.8 O	20	2.8	8	2.9
2	2.2	14	2.8	4	2.9
19	2.4	32	2.8	17	3.0
6	2.6	10	2.8	29	3.0
16	2.7	31	2.8	13	3.0
33	2.7	27	2.8	30	3.0
3	2.7	22	2.8	1	3.1
15	2.7	21	2.9	12	3.2

O = Omitted result

Table 5.6. Statistics
Sulphate
Sample A

Analytical method: All

Unit: mg/l

Number of participants	30	Range	1.89
Number of omitted results	2	Variance	0.13
True value	8.07	Standard deviation	0.35
Mean value	8.08	Relative standard deviation	4.4%
Median value	8.07	Relative error	0.1%

Analytical results in ascending order:

32	7.01	3	8.00	26	8.22
19	7.58	29	8.00	31	8.33
15	7.69	16	8.03	8	8.36
6	7.80	4	8.05	30	8.40
13	7.81	35	8.08	21	8.42
9	7.86	12	8.10	22	8.47
2	7.87	18	8.12	27	8.64
25	7.97	17	8.14	33	8.90
10	7.98	28	8.17	26	9.52 O
14	7.99	20	8.21	23	13.00 O

O = Omitted result

Table 5.6. Statistics
Sulphate
Sample B

Analytical method: All

Unit: mg/l

Number of participants	30	Range	2.95
Number of omitted results	2	Variance	0.28
True value	9.20	Standard deviation	0.53
Mean value	9.30	Relative standard deviation	5.7%
Median value	9.20	Relative error	1.0%

Analytical results in ascending order:

32	8.15	3	9.10	17	9.51
19	8.62	6	9.11	30	9.53
15	8.68	16	9.12	8	9.54
28	8.72	2	9.13	21	9.62
4	9.04	35	9.26	22	9.75
14	9.04	20	9.29	27	9.90
9	9.04	26	9.38	33	10.00
18	9.09	10	9.41	12	11.10
25	9.10	31	9.48	26	11.25 O
29	9.10	13	9.50	23	14.40 O

O = Omitted result

Table 5.7. Statistics
Calcium
Sample A

Analytical method: All
Unit: mg/l

Number of participants	30	Range	0.98
Number of omitted results	1	Variance	0.05
True value	3.90	Standard deviation	0.22
Mean value	3.93	Relative standard deviation	5.6%
Median value	3.90	Relative error	0.7%

Analytical results in ascending order:

23	3.20 O	19	3.86	16	4.04
4	3.32	32	3.87	8	4.05
12	3.60	22	3.88	25	4.06
15	3.66	27	3.90	18	4.14
28	3.71	3	3.90	21	4.14
6	3.72	33	3.90	20	4.16
17	3.76	5	3.91	24	4.17
13	3.80	26	3.92	14	4.24
9	3.80	2	4.00	31	4.26
35	3.84	10	4.00	29	4.30

O = Omitted result

Table 5.7. Statistics
Calcium
Sample B

Analytical method: All
Unit: mg/l

Number of participants	30	Range	1.36
Number of omitted results	1	Variance	0.08
True value	4.42	Standard deviation	0.27
Mean value	4.51	Relative standard deviation	6.1%
Median value	4.42	Relative error	2.0%

Analytical results in ascending order:

12	4.10	9	4.39	8	4.65
15	4.16	5	4.39	2	4.66
4	4.19	3	4.40	25	4.66
17	4.27	19	4.40	18	4.69
28	4.29	32	4.42	21	4.75
13	4.30	22	4.43	29	4.80
35	4.32	33	4.50	31	4.81
24	4.36	26	4.50	14	4.90
27	4.37	10	4.60	16	5.46
6	4.37	20	4.63	23	5.60 O

O = Omitted result

Table 5.8. Statistics
Magnesium
Sample A

Analytical method: All

Unit: mg/l

Number of participants	28	Range	0.09
Number of omitted results	2	Variance	0.00
True value	0.41	Standard deviation	0.02
Mean value	0.40	Relative standard deviation	5.6%
Median value	0.41	Relative error	-1.6%

Analytical results in ascending order:

29	0.31 O	12	0.40	13	0.42
15	0.34	25	0.40	2	0.42
4	0.36	35	0.40	20	0.42
19	0.37	31	0.40	18	0.42
17	0.38	28	0.41	16	0.43 O
27	0.39	10	0.41	22	0.43
9	0.39	21	0.41	33	0.43
6	0.40	26	0.42	5	0.43
3	0.40	24	0.42		
14	0.40	32	0.42		

O = Omitted result

Table 5.8. Statistics
Magnesium
Sample B

Analytical method: All

Unit: mg/l

Number of participants	28	Range	0.11
Number of omitted results	2	Variance	0.00
True value	0.47	Standard deviation	0.02
Mean value	0.46	Relative standard deviation	5.1%
Median value	0.47	Relative error	-1.9%

Analytical results in ascending order:

29	0.38 O	12	0.46	26	0.48
15	0.39	3	0.46	18	0.48
19	0.42	33	0.46	6	0.48
4	0.43	10	0.47	32	0.48
9	0.44	25	0.47	13	0.48
27	0.44	28	0.47	2	0.49
17	0.44	5	0.47	22	0.50
14	0.45	21	0.47	16	1.81 O
31	0.45	20	0.47		
35	0.46	24	0.48		

O = Omitted result

Table 5.9. Statistics
Sodium
Sample A

Analytical method: All

Unit: mg/l

Number of participants	28	Range	0.24
Number of omitted results	1	Variance	0.00
True value	1.87	Standard deviation	0.06
Mean value	1.88	Relative standard deviation	3.3%
Median value	1.87	Relative error	0.7%

Analytical results in ascending order:

2	1.76	13	1.86	22	1.92
3	1.80	4	1.86	12	1.93
6	1.80	27	1.87	21	1.94
24	1.82	14	1.87	16	1.94 O
5	1.83	25	1.88	8	1.96
35	1.84	15	1.89	10	2.00
31	1.84	29	1.90	33	2.00
26	1.84	20	1.91	17	2.00
19	1.84	32	1.91		
18	1.84	9	1.92		

O = Omitted result

Table 5.9. Statistics
Sodium
Sample B

Analytical method: All

Unit: mg/l

Number of participants	28	Range	0.43
Number of omitted results	1	Variance	0.01
True value	2.14	Standard deviation	0.10
Mean value	2.16	Relative standard deviation	4.4%
Median value	2.14	Relative error	1.0%

Analytical results in ascending order:

5	1.93	26	2.12	21	2.21
6	2.00	15	2.14	27	2.23
2	2.08	25	2.14	8	2.25
35	2.09	13	2.14	33	2.30
31	2.09	20	2.15	29	2.30
18	2.10	32	2.17	17	2.31
3	2.10	10	2.20	12	2.36
19	2.10	9	2.20	16	3.55 O
4	2.11	22	2.20		
14	2.12	24	2.21		

O = Omitted result

Table 5.10. Statistics
Potassium
Sample A

Analytical method: All
Unit: mg/l

Number of participants	28	Range	0.16
Number of omitted results	1	Variance	0.00
True value	0.43	Standard deviation	0.03
Mean value	0.42	Relative standard deviation	7.7%
Median value	0.43	Relative error	-1.9%

Analytical results in ascending order:

29	0.33	16	0.42	5	0.44
15	0.38	2	0.42	22	0.45
31	0.38	8	0.43	24	0.45
14	0.39	35	0.43	21	0.45
32	0.39	13	0.43	20	0.46
26	0.40	10	0.43	33	0.48
3	0.40	27	0.43	19	0.49
6	0.40	18	0.43	12	0.59 O
25	0.41	4	0.43		
9	0.41	17	0.44		

O = Omitted result

Table 5.10. Statistics
Potassium
Sample B

Analytical method: All
Unit: mg/l

Number of participants	28	Range	0.22
Number of omitted results	1	Variance	0.00
True value	0.49	Standard deviation	0.05
Mean value	0.49	Relative standard deviation	9.6%
Median value	0.49	Relative error	0.3%

Analytical results in ascending order:

29	0.39	35	0.48	20	0.52
15	0.43	8	0.48	21	0.53
31	0.43	18	0.49	22	0.53
14	0.44	2	0.49	33	0.53
32	0.46	4	0.49	19	0.54
26	0.46	10	0.49	16	0.60
25	0.47	5	0.49	27	0.61
3	0.47	13	0.50	12	0.71 O
9	0.47	17	0.50		
6	0.48	24	0.50		

O = Omitted result

Table 5.11. Statistics
Total organic carbon
Sample A

Analytical method: All

Unit: mg/l

Number of participants	21	Range	2.28
Number of omitted results	0	Variance	0.32
True value	4.09	Standard deviation	0.56
Mean value	4.00	Relative standard deviation	14.1%
Median value	4.09	Relative error	-2.2%

Analytical results in ascending order:

9	2.72	18	3.92	2	4.24
17	2.94	8	4.00	10	4.30
32	3.20	33	4.00	21	4.41
6	3.57	20	4.09	29	4.50
24	3.76	25	4.10	31	4.50
16	3.80	15	4.10	30	4.88
28	3.85	4	4.10	1	5.00

O = Omitted result

Table 5.11. Statistics
Total organic carbon
Sample B

Analytical method: All

Unit: mg/l

Number of participants	21	Range	2.56
Number of omitted results	0	Variance	0.41
True value	4.65	Standard deviation	0.64
Mean value	4.45	Relative standard deviation	14.4%
Median value	4.65	Relative error	-4.3%

Analytical results in ascending order:

9	3.04	16	4.30	18	4.78
32	3.13	28	4.50	10	4.80
17	3.43	4	4.56	2	4.89
24	4.06	8	4.65	30	4.92
20	4.06	15	4.66	21	4.97
6	4.15	25	4.70	29	5.20
33	4.30	31	4.72	1	5.60

O = Omitted result

Table 5.12. Statistics
Aluminium
Sample C

Analytical method: All

Unit: microg/l

Number of participants	23	Range	80
Number of omitted results	3	Variance	436
True value	255	Standard deviation	21
Mean value	252	Relative standard deviation	8.3%
Median value	255	Relative error	-1.1%

Analytical results in ascending order:

28	148 O	8	251	24	268 O
15	198	17	252	6	272
19	220	26	254	34	273
22	224	3	256	4	274
34	237	25	257	13	276
2	240	10	260	12	278
21	244	35	264	23	510 O
27	244	31	268		

O = Omitted result

Table 5.12. Statistics
Aluminium
Sample D

Analytical method: All

Unit: microg/l

Number of participants	23	Range	94
Number of omitted results	3	Variance	555
True value	270	Standard deviation	24
Mean value	271	Relative standard deviation	8.7%
Median value	270	Relative error	0.4%

Analytical results in ascending order:

28	156 O	8	267	6	286
15	226	25	269	34	288
19	230	3	269	13	292
22	239	26	270	4	310
21	254	10	270	2	320
17	261	35	280	23	530 O
34	262	31	282	24	O
27	263	12	285		

O = Omitted result

Table 5.13. Statistics
Iron
Sample C

Analytical method: All
Unit: microg/l

Number of participants	22	Range	41.92
Number of omitted results	1	Variance	103.60
True value	186.00	Standard deviation	10.18
Mean value	187.88	Relative standard deviation	5.4%
Median value	186.00	Relative error	1.0%

Analytical results in ascending order:

27	173.00	21	185.30	25	190.00
22	175.50	8	186.00	31	192.00
3	176.00	15	186.00	2	200.00
17	177.00	19	186.00	12	202.00
24	180.70 O	28	186.00	26	203.00
23	181.00	35	186.00	34	214.92
6	183.00	13	188.00		
34	184.68	10	190.00		

O = Omitted result

Table 5.13. Statistics
Iron
Sample D

Analytical method: All
Unit: microg/l

Number of participants	22	Range	47.00
Number of omitted results	1	Variance	166.91
True value	190.00	Standard deviation	12.92
Mean value	192.94	Relative standard deviation	6.7%
Median value	190.00	Relative error	1.5%

Analytical results in ascending order:

27	175.00	25	189.00	26	199.00
17	178.60	10	190.00	28	205.00
3	179.00	19	190.00	34	215.15
22	180.80	23	190.00	2	220.00
6	185.00	13	191.00	12	222.00
35	186.00	21	192.00	24	O
34	187.14	15	192.00		
8	189.00	31	196.00		

O = Omitted result

Table 5.14. Statistics
Manganese
Sample C

Analytical method: All

Unit: microg/l

Number of participants	23	Range	6.70
Number of omitted results	2	Variance	2.66
True value	48.00	Standard deviation	1.63
Mean value	48.33	Relative standard deviation	3.4%
Median value	48.00	Relative error	0.7%

Analytical results in ascending order:

2	45.60	34	47.84	21	48.82
22	46.30	34	47.88	10	49.00
19	46.60	8	47.90	15	49.20
24	47.20 O	3	48.00	35	51.00
31	47.30	28	48.20	12	51.50
6	47.30	31	48.30	26	52.30
13	47.40	25	48.40	23	82.00 O
27	47.60	17	48.50		

O = Omitted result

Table 5.14. Statistics
Manganese
Sample D

Analytical method: All

Unit: microg/l

Number of participants	23	Range	5.40
Number of omitted results	2	Variance	2.57
True value	51.70	Standard deviation	1.60
Mean value	51.99	Relative standard deviation	3.1%
Median value	51.70	Relative error	0.6%

Analytical results in ascending order:

2	49.70	27	51.10	15	53.30
13	50.00	8	51.40	34	53.54
19	50.10	17	51.70	26	54.70
22	50.50	10	52.00	12	54.90
31	50.90	31	52.00	35	55.10
34	50.96	21	52.19	23	78.00 O
3	51.00	25	52.50	24	O
6	51.10	28	53.10		

O = Omitted result

Table 5.15. Statistics
Cadmium
Sample C

Analytical method: All

Unit: microg/l

Number of participants	21	Range	1.18
Number of omitted results	2	Variance	0.12
True value	6.87	Standard deviation	0.34
Mean value	6.92	Relative standard deviation	5.0%
Median value	6.87	Relative error	0.7%

Analytical results in ascending order:

11	5.00 O	31	6.72	24	7.00 O
2	6.30	17	6.80	12	7.01
19	6.48	35	6.83	34	7.29
10	6.50	26	6.87	21	7.37
27	6.69	6	6.91	8	7.40
3	6.70	22	6.96	28	7.42
13	6.70	25	6.99	15	7.48

O = Omitted result

Table 5.15. Statistics
Cadmium
Sample D

Analytical method: All

Unit: microg/l

Number of participants	21	Range	1.56
Number of omitted results	2	Variance	0.22
True value	7.73	Standard deviation	0.47
Mean value	7.86	Relative standard deviation	6.0%
Median value	7.73	Relative error	1.7%

Analytical results in ascending order:

11	5.10 O	31	7.68	25	7.87
2	7.18	12	7.69	21	8.31
19	7.36	17	7.70	8	8.43
10	7.40	27	7.73	34	8.63
13	7.50	26	7.73	15	8.70
22	7.54	35	7.74	28	8.74
3	7.60	6	7.83	24	O

O = Omitted result

Table 5.16. Statistics
Lead
Sample C

Analytical method: All

Unit: microg/l

Number of participants	21	Range	2.63
Number of omitted results	2	Variance	0.36
True value	7.23	Standard deviation	0.60
Mean value	7.20	Relative standard deviation	8.3%
Median value	7.23	Relative error	-0.4%

Analytical results in ascending order:

11	3.53 O	2	7.00	35	7.57
12	5.57	26	7.09	3	7.60
19	6.42	21	7.13	27	7.67
13	6.70	15	7.23	25	7.73
6	6.87	34	7.23	17	8.10
22	6.90	31	7.35	8	8.20
28	7.00	10	7.40	24	8.90 O

O = Omitted result

Table 5.16. Statistics
Lead
Sample D

Analytical method: All

Unit: microg/l

Number of participants	21	Range	2.55
Number of omitted results	2	Variance	0.30
True value	8.34	Standard deviation	0.55
Mean value	8.34	Relative standard deviation	6.6%
Median value	8.34	Relative error	0.0%

Analytical results in ascending order:

11	4.10 O	13	8.20	3	8.50
12	6.78	26	8.20	35	8.59
22	7.79	31	8.30	25	8.86
6	8.05	19	8.34	27	8.90
28	8.06	15	8.38	17	9.20
2	8.10	10	8.40	8	9.33
21	8.10	34	8.44	24	O

O = Omitted result

Table 5.17. Statistics
Copper
Sample C

Analytical method: All

Unit: microg/l

Number of participants	22	Range	5.53
Number of omitted results	3	Variance	1.96
True value	24.60	Standard deviation	1.40
Mean value	24.91	Relative standard deviation	5.6%
Median value	24.60	Relative error	1.3%

Analytical results in ascending order:

11	14.20 O	13	24.60	8	25.60
34	23.07	31	24.60	25	25.60
22	23.10	17	24.60	28	26.00
34	23.78	24	24.60 O	15	27.00 O
10	24.00	26	24.70	2	27.80
35	24.00	19	24.75	6	28.60
3	24.00	21	24.92		
12	24.35	27	25.30		

O = Omitted result

Table 5.17. Statistics
Copper
Sample D

Analytical method: All

Unit: microg/l

Number of participants	22	Range	5.20
Number of omitted results	3	Variance	1.35
True value	28.00	Standard deviation	1.16
Mean value	28.08	Relative standard deviation	4.1%
Median value	28.00	Relative error	0.3%

Analytical results in ascending order:

11	13.60 O	13	27.60	25	28.90
6	26.00	17	28.00	27	29.30
10	27.00	26	28.00	8	29.40
22	27.00	12	28.05	2	31.20
3	27.00	31	28.20	15	39.50 O
35	27.20	28	28.50	24	O
34	27.32	19	28.66		
34	27.49	21	28.66		

O = Omitted result

Table 5.18. Statistics
Nickel
Sample C

Analytical method: All

Unit: microg/l

Number of participants	21	Range	2.48
Number of omitted results	1	Variance	0.32
True value	10.20	Standard deviation	0.57
Mean value	10.16	Relative standard deviation	5.6%
Median value	10.20	Relative error	-0.4%

Analytical results in ascending order:

34	8.79	3	10.00	27	10.50
28	9.36	13	10.10	25	10.50
22	9.68	35	10.10	15	10.60
2	9.70	26	10.30	24	10.70 O
10	9.70	31	10.40	17	10.70
34	9.77	6	10.40	8	10.90
19	9.95	21	10.48	12	11.27

O = Omitted result

Table 5.18. Statistics
Nickel
Sample D

Analytical method: All

Unit: microg/l

Number of participants	21	Range	3.62
Number of omitted results	1	Variance	0.63
True value	11.50	Standard deviation	0.79
Mean value	11.51	Relative standard deviation	6.9%
Median value	11.50	Relative error	0.1%

Analytical results in ascending order:

2	10.20	13	11.20	31	11.70
28	10.70	35	11.40	15	11.80
22	10.75	27	11.50	17	11.90
34	10.79	25	11.50	8	12.20
10	11.00	34	11.58	12	12.77
3	11.00	26	11.60	19	13.82
6	11.20	21	11.64	24	O

O = Omitted result

Table 5.19. Statistics
Zinc
Sample C

Analytical method: All

Unit: microg/l

Number of participants	21	Range	14.3
Number of omitted results	1	Variance	8.7
True value	34.4	Standard deviation	3.0
Mean value	34.4	Relative standard deviation	8.6%
Median value	34.4	Relative error	-0.1%

Analytical results in ascending order:

22	27.6	13	33.9	3	35.0
2	29.5	17	34.0	31	35.4
19	32.1	24	34.0 O	15	35.4
31	32.8	12	34.3	26	35.7
10	33.0	28	34.5	6	36.7
35	33.2	34	34.8	8	38.6
27	33.8	25	35.0	21	41.8

O = Omitted result

Table 5.19. Statistics
Zinc
Sample D

Analytical method: All

Unit: microg/l

Number of participants	21	Range	16.8
Number of omitted results	1	Variance	14.4
True value	38.1	Standard deviation	3.8
Mean value	38.5	Relative standard deviation	9.9%
Median value	38.1	Relative error	1.1%

Analytical results in ascending order:

2	30.6	17	37.5	31	39.9
22	30.8	3	38.0	6	40.4
19	36.6	13	38.1	26	40.5
12	36.7	28	38.1	34	42.7
31	37.0	27	38.9	8	43.9
10	37.0	25	39.0	21	47.4
35	37.3	15	39.8	24	O

O = Omitted result

6. Reports and publications from the ICP Waters Programme

All reports from the ICP Waters programme from 2000 up to present are listed below. Reports before year 2000 can be listed on request. All reports are available from the Programme Centre. Reports and recent publications are also accessible through the ICP Waters website; http://www.icp-waters.no/

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