

ICP Waters Report 141/2019

Intercomparison 1933: pH, Conductivity, Alkalinity, $\text{NO}_3\text{-N}$, Cl , SO_4 , Ca, Mg, Na, K, TOC, Tot-P, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn



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

Convention on Long-Range Transboundary Air Pollution



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Summary

A total of 36 laboratories from 19 different countries accepted the invitation to join the ICP-Waters chemical intercomparison, and 33 laboratories from 16 different countries successfully reported results. Two sets of samples were prepared and successfully distributed to the participants: one for the determination of ions and one for the metals. In general, the results were good with an overall acceptance of 75% ($\pm 20\%$ of the "true value", and for pH and conductivity ± 0.2 pH units and $\pm 10\%$, respectively). The highest acceptance ratios were found for the ions: sodium, chlorine, calcium, and magnesium, all being higher than 90%. The lowest acceptance ratio was found for total phosphorus with only 35% of the results being accepted. However, the concentration of total phosphorus was relatively low, and this parameter was only recently introduced into the test. For several of the parameters a relatively high number of different techniques had been used, which can lead to systematic errors in the results. This was investigated for pH and alkalinity, but no clear connections could be found between the systematic error in the results and the techniques employed. General trends in the choice of techniques continue to shift towards plasma from atomic absorption, and to mass detection from ionic emission. This is especially promising for the determination of metals at low levels.

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CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR
POLLUTION

INTERNATIONAL COOPERATIVE PROGRAMME ON
ASSESSMENT AND MONITORING EFFECTS OF AIR POLLUTION
ON RIVERS AND LAKES

**Intercomparison 1933:
pH, Conductivity, Alkalinity, NO₃-N, Cl, SO₄, Ca,
Mg, Na, K, TOC, Total-P, Al, Fe, Mn, Cd, Pb, Cu,
Ni, and Zn**

Prepared at the ICP Waters Programme Centre
Norwegian Institute for Water Research
Oslo, December 2019

Preface

The International Cooperative Programme on Assessment and Monitoring of the 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 (CLRTAP) in July 1985. Since then, ICP Waters has been an important contributor to document the effects of implementing the Protocols under the Convention. ICP Waters has prepared numerous assessments, reports and publications that address the effects of long-range transported air pollution.

ICP Waters and its Programme Centre is chaired and hosted by the Norwegian Institute for Water Research (NIVA), respectively. A programme subcentre is established at NORCE (previously known as Uni Research), Bergen. ICP Waters is supported financially by the Norwegian Environment Agency and the Trust Fund of the UNECE LRTAP Convention.

The main aim of the ICP Waters programme is to assess, on a regional basis, the degree and geographical extent of the impact of atmospheric pollution, in particular acidification, on surface waters. More than 20 countries in Europe and North America participate in the programme on a regular basis.

An objective of the ICP Waters programme is to establish and maintain an international network of surface water monitoring sites and promote international harmonisation of monitoring practices. A tool in this work are inter-laboratory quality assurance tests. Here biases between analyses carried out by the individual participants of the programme are identified and controlled.

Here we report the results from the 33rd intercomparison of chemical analyses.



Cathrine Brecke Gundersen

ICP Waters Programme Centre
Oslo, December 2019

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Summary

The chemical inter-laboratory comparison is an important tool for the ICP Waters to ensure consistency and comparability of the surface water monitoring results among the programme participants. The test is conducted yearly and is based on the “round robin” principle. In short, the same water sample is distributed to all the participating laboratories which analyse the sample for a set of variables with their method of choice. The results are then compiled and analysed using the Youden test statistic. The “true value” for each variable is calculated as the median of the reported results after excluding extreme observations. Two different sets of samples are prepared and distributed: one for the determination of ions and the other for metals.

The 1933 edition of the test, referring to the 33rd version, was conducted in the period from April to December 2019. A total of 36 laboratories representing 19 different countries signed up, and among these, 33 laboratories representing 16 different countries successfully reported results to the database. The participants were invited to determine pH, conductivity, alkalinity, nitrate+nitrite nitrogen, chloride, sulphate, calcium, magnesium, sodium, potassium, total organic carbon, total phosphorus, aluminium, iron, manganese, cadmium, lead, copper, nickel, and zinc. The acceptance limit was for most parameters at $\pm 20\%$ of the “true value”, except for pH and conductivity (± 0.2 pH units and $\pm 10\%$ respectively).

In general, the acceptance ratios for the 33rd edition were good and comparable to the results from the recent years. Overall, 75% of the results was within the target threshold (median of the various parameter acceptance ratios). The highest acceptances were accomplished for some of the ions, with a maximum of 100% for sodium, and followed by chloride, calcium, and magnesium, all with acceptances above 90%. The poorest acceptance ratio, at 35% was obtained for total phosphorus. In the Youden chart, the distribution of the results for total phosphorus clearly showed both systematic and random effects. The systematic effect was likely caused by the use of five different techniques while the random effect resulted from the relatively low concentration in the samples. Total phosphorus, as a parameter, was only recently included in the intercomparison test, and we expect the results to improve in the coming years. Other relatively low acceptance ratios were for pH and aluminium, both at 60%. pH is typically one of the more challenging parameters to determine, and especially when the pH is close to neutral like it was this year. pH could have been influenced by other factors such as different types handling and storage practices among the laboratories. With regards to aluminium, the low acceptance ratio was likely caused by the level in the sample being close to the quantification limit.

For several of the parameters there was a relatively large range in the different types of analytical techniques applied for analysis. Up to seven different were reported to have been used for alkalinity, while as many as six different were used for the determination of nitrate+nitrite nitrogen, sodium, and potassium. For alkalinity there was a systematic effect in the distribution of the results in the Youden chart. However, due to the few participants per technique, it was not possible to state whether the systematic error resulted from this. The systematic effect was not as strong for sodium and potassium, and for nitrate+nitrite nitrogen the effect was likely masked by additional random effects. The use of different techniques can challenge the unity of the results from the different laboratories, and the effect is typically higher when the level of analyte is low.

Despite the different techniques used, some overall patterns for the different variables could be found. For the determination of anions (nitrate+nitrite nitrogen, chloride, and sulphate), ion chromatography

was the technique of choice, while for the cations (calcium, magnesium, sodium, and potassium) the preferred technique varied between ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy), ion chromatography, and FAAS (Flame Atomic Absorption Spectroscopy). For the determination of metals (aluminium, iron, manganese, lead, copper, nickel, and zinc), ICP-MS (Inductively Coupled Plasma-Mass Spectrometer) was most commonly employed. This confirms the trends observed in the last years, that plasma techniques are taking over for the more traditional atomic absorption techniques, and that the much more sensitive mass detector is replacing the optical emission spectroscopy detector.

With regards to the determination of metals, the trend of moving towards the more sensitive mass detector is an encouraging observation. It has previously been discussed at what concentration levels the metals should be at in the samples of the chemical intercomparison test. The overall aim should be to obtain high acceptance ratio for most of the parameters at levels as close to the low expected natural conditions as possible. The acceptance ratio for most metals was very good this year despite most metals being presented at relatively low concentration.

For certain of the parameters, low acceptance ratios are typically re-occurring in the intercomparison test. In this edition, the potential effect from using different techniques was investigated for pH and alkalinity by colour-coding the points in the Youden charts according to the techniques used. For pH the different practices of stirring and non-stirring of the sample did not appear to have caused systematic errors in the result, and the poor acceptance ratio was instead attributed to the close-to-neutral pH. For alkalinity, the large number of different methods used made it difficult to assess the effect from this due to the resulting low number of participants per method.

Some of the laboratories report their results with far more digits than what is likely statistically significant. Please consider the uncertainty of your analytical method and report results with number of digits accordingly.

1 Introduction

The international cooperative programme for assessment and monitoring of the effects of air pollution on rivers and lakes (ICP Waters) works to assess the degree to which atmospheric pollution has affected surface waters. The programme was established in 1985 under the Executive Body of the United Nations Economic Commission for Europe (UNECE). The Focal Centres in each country contributes with data from their national monitoring programmes.

To ensure that the results across the entire ICP Waters are consistent and comparable, inter-laboratory quality controls are necessary, as stated in the "ICP Waters Programme Manual" (1). In a multi laboratory programme, typical causes of inconsistency include the use of different types of analytical techniques, errors in the calibration procedure, etc. The between-laboratory control carried out by the Programme Centre of ICP Waters is based on the "round robin" concept meaning that the same sample is analysed by the different participating laboratories using their analytical principle and method of choice. The analytical results are analysed using the Youden test statistics (2, 3) that assesses the consistency of the results between the laboratories, and can also indicate whether the results are affected by a systematic effect (e.g. different analytical techniques give slightly different results) or only by random errors (typically at levels close to the limit of quantification). The Youden test is briefly described in Annex C. The levels of the variables should be set to be as close to the expected natural levels as possible, and that the range from year-to-year shall cover the variation among countries of the participating laboratories.

Several factors can contribute to the acceptance ratio and these should be considered when evaluating the results, and when considering measures to improve the results from individual laboratories. For example, different methods used by different laboratories may give systematic different results (higher or lower). Based on the method used by most of the participating laboratories, the "true value" may be biased. Such systematic effect will be evident in the distribution of the results in the Youden chart, by the points residing *along* the 45° angled line. One other cause of poor acceptance ratio is when the concentration in the sample is low, and close to the limit of quantification of the method used. This will most often appear in the Youden chart as a horizontal distribution of the results *across* the 45° angled line.

This thirty-third chemical intercomparison test, called 1933, covered the determination of the following constituents of natural surface waters: pH, conductivity, alkalinity, nitrate+nitrite nitrogen, chloride, sulphate, calcium, magnesium, sodium, potassium, total organic carbon, total phosphorus, aluminium, iron, manganese, cadmium, lead, copper, nickel, and zinc. While most of these variables have been part of the test since it started, total organic carbon and aluminium was included in 2009, and total phosphorus in 2017.

2 Procedures of the intercomparison

Two different sets of samples were prepared by the Programme Centre and distributed to the participating laboratories: one pair for the determination of major ions and one pair for the determination of metals (as agreed upon at the Task Force meeting in Burlington, Canada, 2009). The procedure for the preparation of the two sample sets is presented in Annex B. The samples were shipped from the Programme Centre during week 26, and there were no reported delays or other issues with the shipment. To ensure the integrity and minimal degradation of the samples, the participants were encouraged to conduct the analyses as soon as possible after reception.

The analytical results were treated by the Youden method (2, 3) to evaluate the comparability of the analytical results produced by the laboratories participating in the International Cooperative Programme, and to assess potential systematic and/or random error in the distribution of the results. For each variable, the “true value” was calculated as the median of the reported results, after excluding extreme observations. This way of setting the “true value” is considered acceptable as long as the participants mainly use the same analytical techniques. However, this is not always the case, and for parameters such as pH and alkalinity different techniques/methods are frequently used and producing strong systematic bias in the results. Since not one method can be argued to be better than another, this issue has persisted in the inter-laboratory harmonisation.

The criteria for acceptable results were for most variables $\pm 20\%$ of the “true value”, as outlined in the Manual for Chemical and Biological Monitoring (1). Exceptions from this were pH and conductivity, for which the acceptance limits were set to ± 0.2 pH units and $\pm 10\%$, respectively. For pH the acceptance limit was extended due to overall poor acceptance ratios, while for conductivity the limit was reduced due to the overall good results for this parameter.

3 Results and Discussion

In the 33rd edition of the chemical intercomparison test, a total of 36 laboratories (representing 19 different countries) registered to participate, and 33 of the laboratories representing 16 different countries successfully registered results. Information about the laboratories is provided in Appendix A, both by the identity of the laboratories (Table 3) and by a summary of the different countries represented (Table 4). There was no report of delayed delivery of samples or other issues with the customs, which has previously been encountered.

In Table 1, the results from the 33rd chemical intercomparison test is summarised, constituting for each parameter: the number of participants, the acceptance ratio, and the acceptance ratio from the three previous years for comparison. In general, the results were good with an overall median acceptance at 75% with the general target accuracy of $\pm 20\%$, or the special accuracy limit for pH and conductivity (± 0.2 pH units and $\pm 10\%$ respectively).

Throughout this chapter the results for each variable will be presented and discussed on the basis of the acceptance ratio (Table 1) and the visual distribution of the results in the Youden chart (Figures 1-19). In the Youden chart, each laboratory is presented by one point, and the distribution of points can indicate the occurrence of random and/or systematic errors in the distribution of the results among the laboratories. For two of the parameters for which systematic error have frequently been encountered in previous editions (pH and alkalinity), the points in the chart have been colour-coded depending on the techniques used. The acceptance limit (typically $\pm 20\%$ of the mean true values for the sample pair) is indicated in the charts as a circle. Note that laboratories with results that strongly deviated from the others has been excluded from the calculations and from the charts. Information on the different analytical techniques used by the laboratories is shown in Table 2.

For more detailed information on the uncertainty of the "true values" see Table 5 (Appendix C). The calculation has been performed according to ISO 13528 (2005), "Statistical methods for use in proficiency testing by interlaboratory comparisons". The individual results reported by the laboratories are listed in Table 6 (Appendix D), and more detailed statistics for each parameter is presented in Tables 7.1 to 7.20 (Appendix D).

Table 1. Summary of the results including the true values, number of participating laboratories, and acceptance rate in the 1933 edition and the three previous years (1832, 1731, and 1630) for each variable.

Variable	Sample pair	True value		limit, % *	Number of pairs		Acceptable results for intercalibration (%)			
		Sample 1	Sample 2		Tot.	Accept.	19-33	18-32	17-31	16-30
pH	AB	6.91	6.88	2.9	30	18	60	81	53	56
Conductivity (mS/m)	AB	6.70	6.71	10	29	23	79	85	77	77
Alkalinity (mmol/L)	AB	0.211	0.208	20	20	13	65	0	17	46
Nitrate + nitrite-nitrogen (µg/L)	AB	114.6	116.4	20	29	20	69	85	35	71
Chloride (mg/L)	AB	9.3	9.4	20	29	27	93	81	82	87
Sulphate (mg/L)	AB	3.32	3.34	20	28	21	75	96	90	90
Calcium (mg/L)	AB	5.70	5.70	20	28	26	93	93	83	93
Magnesium (mg/L)	AB	0.65	0.65	20	28	27	96	82	93	89
Sodium (mg/L)	AB	5.09	5.06	20	26	26	100	86	86	96
Potassium (mg/L)	AB	0.91	0.89	20	26	23	88	82	69	86
Total organic carbon (mg/L)	AB	6.83	6.96	20	20	16	80	74	81	81
Total phosphorus (µg/L)	AB	24.2	23.6	20	23	8	35	33	21	-
Aluminium (µg/L)	CD	49.3	48.2	20	20	12	60	57	82	75
Iron (µg/L)	CD	108.9	106.8	20	23	19	83	95	74	87
Manganese (µg/L)	CD	3.68	3.37	20	20	15	75	91	100	84
Cadmium (µg/L)	CD	0.98	0.97	20	21	17	81	88	92	90
Lead (µg/L)	CD	2.31	2.22	20	21	16	76	65	88	86
Copper (µg/L)	CD	12.5	11.2	20	23	18	78	84	95	86
Nickel (µg/L)	CD	4.47	4.31	20	21	17	81	87	100	90
Zinc (µg/L)	CD	14.30	14.25	20	21	14	67	91	96	77
Total					502	376	75	(79)	(76)	(81)

3.1 pH

Results for pH were reported by 30 laboratories of which 60% were within the acceptable limit (Table 1 and Figure 1). The acceptance threshold was ± 0.2 pH units of the “true value”. With the pH of the samples being close to neutral, which is inherently challenging to determine accurately, the acceptance ratio was considered acceptable.

The distribution of the results from the participating laboratories is illustrated by a Youden chart in Figure 1. Most of the points fall along the 45° angled line, indicating systematic effects that can typically result from the use of different techniques. In Figure 1 the points have been colour-coded according to the type of technique used (e.g. stirring or non-stirring). If the use of different techniques had caused the systematic effect in the distribution of the results, the points of same colour would cluster together in the chart, but this was not the case. Most laboratories used electrometric techniques, but with different techniques (Table 2). Stirring of the sample during measurements was conducted by 13 of the laboratories (red in Figure 1) while nine laboratories did not use stirring (yellow), and another five laboratories used the equilibration technique (blue). Two laboratories reported to have used another unidentified technique (green).

The acceptance ratio for pH has, during the previous editions, often been low compared to most of the other parameters. Although the use of different techniques was not the cause of the relatively poor accuracy this year, the different practices of e.g. stirring- or not stirring has previously been found to affect the result, and especially for samples of low ionic strength (4, 5). Moreover, pH is typically influenced by factors such as different practices of sample storage and handling, and it must be stressed that this parameter should be determined as soon as possible after the samples have arrived at the laboratory.

3.2 Conductivity

Measurements of conductivity has typically been very consistent between the laboratories, and this was also the case for the 33rd edition. Conductivity was reported by 29 laboratories, and with an acceptance ratio of 79% (Table 1). Note that for conductivity the acceptance limit is set at $\pm 10\%$ of the “true value” (1).

Most of the participants, constituting 27 laboratories, used electrometric techniques for the determination of conductivity while two laboratories reported to have used other unidentified methods (Table 2). The unity of the conductivity results was confirmed by the Youden chart, in Figure 3, in which the results from the laboratories were centred around the origo of the coordinate system. Only a few laboratories lied either lower or higher than the consensus of the other laboratories. One plausible explanation for the few deviating laboratories could be the lack of accurate temperature correction during determination. Conductivity is highly temperature dependent and will vary by 2% for each degree at the temperatures round room temperature.

3.3 Alkalinity

Alkalinity was reported by 20 of the participating laboratories, producing an acceptance ratio of 65% ($\pm 20\%$ of the “true value”, Table 1). This can be considered as a good achievement compared to previous years (alkalinity was not included in the 1832 edition due to the low pH of samples A and B). A total of seven different techniques had been employed to determine alkalinity (Table 2), and the points in the Youden chart in Figure 3 have been colour-coded accordingly. The distribution of the results shows some systematic error. The cause of this could be the use of different methods, but due to the few numbers of participating laboratories per type of method, it is not possible to state whether this was the cause of the error. According to Table 2, most laboratories used either Gran plot titration or two-end-points titration, employed by six and five laboratories, respectively. Single-end-point titration was used by a total of five laboratories, but with different pH-end points (pH 5.4, 5.6, or other). Two laboratories had used a colorimetric method, while the remaining two laboratories had used another unidentified method.

3.4 Nitrate + nitrite-nitrogen

A total of 29 laboratories reported results for nitrate+nitrite nitrogen, and of which 69% was within the acceptance limit ($\pm 20\%$ of the “true value”). This was within the normal variation of acceptance ratios from the previous recent years (Table 1). Regarding analytical techniques (Table 2), most laboratories reported to have used ion chromatography (14 laboratories), while the remaining laboratories had used different techniques including photometry (total of 12 laboratories with autoanalyzer, manual or other method), hydrazine reduction (two laboratories), or capillary electrophoresis (one laboratory). The Youden plot of nitrate+nitrite-nitrogen demonstrated only a slight systematic error that might result from the use of different techniques (Figure 3).

3.5 Chloride

For chloride, the acceptance ratio was very high, amounting to 93% for the 29 participating laboratories ($\pm 20\%$ of the “true value”, Table 1). According to Table 2, ion chromatography was the technique of choice for most laboratories (19 participants), while other laboratories used techniques such as automated photometry (six participants), capillary electrophoresis (one participant), electrometry (one participant), or another unidentified method (two participants). The distribution of the results in the Youden diagram was very good, and with only a very weak systematic effect (Figure 4).

3.6 Sulphate

Results for sulphate was reported by 28 laboratories, and from which 75% had results within the target value ($\pm 20\%$ of the “true value”, Table 1). In comparison to the recent years, the acceptance ratio was considered a little low (Table 1). This was likely caused by the relatively low sulphate concentrations in this year's samples ($\sim 3 \text{ mg L}^{-1}$). The preferred technique for sulphate determination was ion chromatography (19 participants), followed by ICP-OES (three participants), photometry (two participants), and nephelometry (one participant). The Youden chart in Figure 6 demonstrates excellent precision of the results, with only a weak systematic effect.

3.7 Calcium

Like the results from the three previous years, the acceptance ratio for calcium was high at 93% ($\pm 20\%$ of the “true value”), for the 28 reporting laboratories (Table 1). Different techniques had been used for the determination of calcium (Table 2), which constituted ion chromatography (eight participants), ICP-OES (eight participants), FAAS (six participants), ICP-MS (five participants), and capillary electrophoresis (one laboratory). Despite the widespread use of different analytical techniques, the unity of the results for calcium was very good, and with only a weak systematic effect evident in the Youden diagram (Figure 7).

3.8 Magnesium

According to Table 1, magnesium results were reported by 28 laboratories and with an acceptance ratio at 96% ($\pm 20\%$ of the “true value”). This was an improvement from the previous years and especially considering that the concentration this year was not especially high ($\sim 0.6 \text{ mg L}^{-1}$). Different techniques had been used for the determination of magnesium (Table 2): ICP-OES by eight participants, FAAS and ion chromatography by seven participants each, respectively, ICP-MS by five participants, and capillary electrophoresis by one participant. Despite the different techniques used, the participants have generated a very precise dataset which is illustrated in the Youden diagram in Figure 8.

3.9 Sodium

The most precise results of this year’s chemical intercomparison was provided for the determination of sodium. All of the 26 laboratories that submitted results were within the acceptance limit ($\pm 20\%$ of the “true value”, Table 1). This was higher than-, but still comparable to the results from the recent years. This could partly be explained by the concentration of sodium in the samples being slightly higher this year ($\sim 5 \text{ mg L}^{-1}$). Ion chromatography was the technique of choice for most laboratories (nine participants), while also ICP-OES (six participants), FAAS (five participants), and ICP-MS (four participants) was frequently employed (Table 2). Capillary electrophoresis and flame photometry were reported used by one laboratory each. The good agreement of the sodium results between the laboratories was confirmed by the distribution in the Youden chart showing very little sign of spread in the data (Figure 9).

3.10 Potassium

For potassium, 26 laboratories reported results from which 88% were within the acceptable threshold ($\pm 20\%$ of the “true value”, Table 1). This was in accordance with the results from the recent previous years. Regarding the choice of analytical techniques (Table 2), the same distribution was evident as for sodium: Most laboratories used ion chromatography (nine participants), and followed by ICP-OES (six participants), FAAS (five participants), ICP-MS (four participants), and capillary electrophoresis and flame photometry (one laboratory each, respectively). Looking at the Youden chart for potassium in Figure 10, the precision among the laboratories is very good.

3.11 Total organic carbon

Results for total organic carbon was reported by 20 laboratories, among which 80% was within the target threshold at $\pm 20\%$ of the “true value” (Table 1). This was comparable to the results from the three previous years. Two main- and different analytical techniques have been employed: combustion method used by 13 laboratories and UV/peroxodisulphate used by four laboratories. Another three laboratories reported to have used other unidentified methods. The results for total organic carbon was influenced by some systematic effect (Figure 11), which could result from the different techniques used for its determination.

3.12 Total Phosphorus

Total phosphorus was only recently included in the chemical intercomparison (in 2017), and it was pleasant to see that as many as 23 laboratories reported results (Table 1). The acceptance ratio was the lowest among the variables this year, amounting to only 35%. This was comparable to the results from the two previous years. According to table 2, most laboratories used photometry for the determination of total phosphorus (13 participants), followed by ICP-OES (four participants), ICP-MS (one participant), and ion chromatography (one participant). Other unidentified methods were reported to have been used by four of the laboratories. In Figure 12, the distribution of the total phosphorus results can be seen affected by both systematic and random effects. This was likely a result from the combination the different techniques and that the concentration was relatively low.

3.13 Aluminium

Aluminium results were reported by 20 laboratories from which only 60% were accepted according to the target criteria ($\pm 20\%$ of the “true value”, Table 1). Considering the importance of aluminium in an acid-rain perspective, this was considered a little low, but still comparable to the results from the recent years. Only three different techniques have been used for the determination of aluminium: ICP-MS (eight participants), ICP-OES (seven participants), and GFAAS (five participants). In the Youden chart for aluminium, there was some systematic effect on the distribution, and particularly three laboratories have reported values lower than the consensus of the other laboratories.

3.14 Iron

Results for iron showed a relatively high acceptance ratio at 83% for the 23 laboratories that had provided results (Table 1). This was comparable to the results from the previous years. Atomic techniques had been most frequently used, detecting either mass, light emission or absorption, and constituted: ICP-MS by nine laboratories, ICP-OES by seven laboratories, and GFAAS and FAAS by three laboratories each. Photometry was used by one laboratory (Table 2). The Youden chart for iron showed some systematic effects in the distribution of the results (Figure 14).

3.15 Manganese

The acceptance ratio for manganese was at 75% for the results provided by 20 laboratories. This was a lower acceptance than from the three previous years. This was likely caused by the relatively low concentration in this year's sample ($\sim 3 \mu\text{g L}^{-1}$). The types of analytical techniques used for manganese determination were like that used for aluminium: Nine laboratories used ICP-MS, seven used ICP-OES, and four used GFAAS (Table 2). The Youden chart for manganese, in Figure 15, showed both some systematic and random effects, likely as a result of the relatively low concentration in the sample.

3.16 Cadmium

Cadmium was determined by 21 laboratories from which 81% of the results were accepted (Table 1). This was a good result, although the acceptance ratio was a little lower than in the three previous years. The cadmium concentration in this year's sample was relatively low ($\sim 1.0 \mu\text{g L}^{-1}$). Plasma techniques were most frequently employed, represented by ten laboratories using ICP-MS and four using ICP-OES (Table 2). The atomic absorption technique GFAAS was used by six laboratories, while the one remaining laboratory had used another unidentified method. Looking at the Youden chart for cadmium in Figure 16, three laboratories reported results that were lower than the others. Except from those, there was little spread in the accepted data for cadmium concentration.

3.17 Lead

For lead, the results were comparable to the results from the previous years. Results were reported by 21 laboratories from which 76% were within the acceptance limit ($\pm 20\%$ of the "true value", Table 1). According to Table 2 almost all the laboratories reported to have used atomic techniques with detection of either mass, emission or absorption. Ten laboratories used ICP-MS, three used ICP-OES, six used GFAAS, and one used FAAS. One laboratory reported to have used another unidentified method. Looking at the Youden distribution of the results in Table 17, there was only some very weak systematic effect.

3.18 Copper

The acceptance ratio for copper was at 78% for the total of 23 laboratories reporting results (Table 1). This was a little lower than-, but still comparable to the results from the previous years. Copper was by most of the laboratories determined using ICP-MS (11 participants), followed by GFAAS (seven participants), and ICP-OES (five participants). See Table 2. The distribution of the results in the Youden chart in Figure 18 looks good, and with only a small random effect.

3.19 Nickel

Results for nickel was reported by 22 laboratories for which 87% of were classified as acceptable according to the target limit ($\pm 20\%$ of the "true value", Table 1). The analytical techniques employed for the determination of nickel constituted ICP-MS by 11 laboratories, and GFAAS and ICP-OES by five laboratories each, respectively (Table 2). The Youden chart of nickel in Figure 19 confirms good precision of the results, and only with a weak systematic effect for a few of the laboratories.

3.20 Zinc

Zinc in the sample was determined by 21 laboratories from which 67% fulfilled the acceptance criteria of being $\pm 20\%$ of the “true value” (Table 1). This is considered as low if compared to the results reported in the three last editions. A few different techniques had been used among the different laboratories to measure zinc (Table 2). ICP-MS was the most frequently employed analytical technique, used by 11 laboratories. ICP-OES was used by six laboratories, and GFAAS and FAAS was used by three and one laboratories, respectively. The low acceptance rate for zinc was accompanied by both systematic and random error in the distribution of the results presented in the Youden chart in Figure 20.

Table 2. Statistical summary of the results from the 33rd edition, including information of the different analytical techniques used by the laboratories.

Variable and technique/method	Sample pair	True value		No. lab.		Median		Sample 1		Sample 2		Rel.std.av. %		Relative error %	
		S. 1	S. 2	Total	U	S. 1	S. 2	Average	Stdev	Average	Stdev	S. 1	S. 2	S. 1	S. 2
pH	AB	6.91	6.88	30	0	6.91	6.88	6.90	0.18	6.88	0.17	2.6	2.5	-0.1	-0.1
Elec., stirring				13	0	6.91	6.87	6.91	0.18	6.87	0.21	2.5	3.0	-0.1	-0.1
Elec., non-stirring				9	0	6.93	6.92	6.93	0.21	6.91	0.17	3.0	2.4	0.3	0.5
Elec., equilibration				5	0	6.89	6.86	6.84	0.22	6.83	0.17	3.2	2.5	-1.0	-0.8
Other method				3	0	6.91	6.88	6.91	0.10	6.84	0.08	1.4	1.2	0.0	-0.5
Conductivity	AB	6.70	6.71	29	4	6.70	6.71	6.63	0.25	6.66	0.24	3.8	3.6	-1.0	-0.8
Electrometry				27	3	6.70	6.72	6.63	0.25	6.65	0.25	3.8	3.7	-1.1	-0.8
Other method				2	1			6.70		6.70				0.0	-0.1
Alkalinity	AB	0.211	0.208	20	1	0.211	0.208	0.216	0.034	0.209	0.031	15.9	14.9	2.2	0.4
Gran plot titration				6	0	0.209	0.209	0.208	0.010	0.207	0.011	4.6	5.5	-1.5	-0.5
Two end points titration				5	1	0.241	0.209	0.237	0.040	0.220	0.033	16.9	15.1	12.4	5.9
One end point(other)titr.				3	0	0.232	0.228	0.232	0.018	0.234	0.024	7.8	10.3	10.0	12.3
Colorimetry				2	0			0.166		0.163				-21.6	-21.6
Other method				2	0			0.245		0.210				16.1	1.0
One end point(pH5.4)titr.				1	0			0.185		0.194				-12.3	-6.7
One end point(pH5.6)titr.				1	0			0.201		0.202				-4.7	-2.9
Nitrate + nitrite-nitrogen	AB	115	116	29	5	115	116	115	11	117	14	9.2	12.3	0.4	0.4
Ion chromatography				14	2	114	113	113	10	112	11	9.1	10.2	-1.6	-3.5
Auto.,photometry, Cd red				4	0	120	118	119	4	118	5	3.5	4.4	3.4	1.2
Manual.,photometry,Cd red				4	0	112	119	116	12	128	26	10.3	20.3	1.6	10.3
Photometry, other method				4	3			137		134				19.5	15.1
Hydrazine reduction				2	0			111		114				-2.9	-2.2
Cap. electrophoresis				1	0			108		111				-5.8	-4.6
Chloride	AB	9.3	9.4	29	1	9.3	9.4	9.3	0.5	9.4	0.5	5.8	5.5	-0.3	0.0
Ion chromatography				19	0	9.3	9.3	9.2	0.3	9.3	0.3	3.7	3.5	-1.6	-1.0
Photometry, autoanalyzer				6	1	9.7	9.7	9.5	1.1	9.5	1.0	11.2	10.8	2.1	1.3
Other method				2	0			9.3		9.4				-0.4	0.0
Cap. electrophoresis				1	0			9.9		10.0				6.1	6.9
Electrometry				1	0			9.9		10.0				6.4	6.4
Sulphate	AB	3.32	3.34	28	4	3.32	3.34	3.28	0.25	3.27	0.28	7.6	8.7	-1.1	-2.0
Ion chromatography				21	2	3.32	3.34	3.25	0.19	3.25	0.22	5.7	6.9	-2.0	-2.7
ICP-OES				3	1			3.64		3.61				9.5	8.4
Photometry				2	0			3.19		3.19				-4.0	-4.4
Cap. electrophoresis				1	0			3.30		3.20				-0.6	-4.0
Nephelometry				1	1			9.50		10.60				186.1	217.8
Calcium	AB	5.70	5.70	28	1	5.70	5.70	5.66	0.36	5.71	0.43	6.3	7.6	-0.7	0.2
ICP-OES				8	0	5.65	5.75	5.63	0.26	5.66	0.29	4.6	5.1	-1.2	-0.8
Ion chromatography				8	0	5.89	5.91	5.80	0.27	5.89	0.36	4.7	6.2	1.8	3.3
FAAS				6	0	5.49	5.53	5.34	0.48	5.32	0.55	9.1	10.4	-6.4	-6.6
ICP-MS				5	1	5.79	5.85	5.83	0.18	5.91	0.24	3.2	4.1	2.3	3.7
Cap. Electrophoresis				1	0			6.10		6.30				7.0	10.5
Magnesium	AB	0.65	0.65	28	0	0.65	0.65	0.64	0.04	0.64	0.04	5.8	6.2	-1.1	-0.6
ICP-OES				8	0	0.66	0.66	0.65	0.04	0.65	0.04	5.4	6.6	-0.5	0.4
FAAS				7	0	0.62	0.62	0.62	0.04	0.62	0.04	7.0	6.9	-4.1	-4.4
Ion chromatography				7	0	0.65	0.65	0.66	0.03	0.66	0.03	3.8	4.4	1.7	2.8
ICP-MS				5	0	0.64	0.65	0.64	0.05	0.64	0.04	7.4	5.6	-1.5	-0.5
Cap. Electrophoresis				1	0			0.63		0.61				-3.2	-5.5

Variable and methods	Sample pair	True value		No. lab.		Median		Sample 1		Sample 2		Rel.std.av. %		Relative error %	
		S. 1	S. 2	Total	U	S. 1	S. 2	Average	Stdev	Average	Stdev	S. 1	S. 2	S. 1	S. 2
Sodium	AB	5.09	5.06	26	0	5.09	5.06	5.06	0.25	5.05	0.26	4.9	5.2	-0.7	0.0
Ion chromatography				9	0	5.14	5.15	5.14	0.26	5.17	0.30	5.1	5.8	0.9	2.3
ICP-OES				6	0	4.93	4.97	4.94	0.20	4.95	0.23	4.1	4.6	-3.0	-2.1
FAAS				5	0	5.10	5.16	5.02	0.26	5.04	0.30	5.2	6.0	-1.5	-0.3
ICP-MS				4	0	5.07	5.06	5.02	0.30	4.98	0.25	5.9	4.9	-1.4	-1.5
Cap. Electrophoresis				1	0			5.40		5.00				6.1	-1.1
Flame photometry				1	0			5.05		5.03				-0.8	-0.5
Potassium	AB	0.91	0.89	26	2	0.91	0.89	0.92	0.06	0.89	0.04	6.9	4.2	0.7	-0.1
Ion chromatography				9	1	0.92	0.91	0.91	0.09	0.90	0.05	10.1	6.0	0.2	0.2
ICP-OES				6	0	0.91	0.89	0.91	0.03	0.89	0.02	3.2	2.2	-0.6	-0.4
FAAS				5	1	0.94	0.90	0.94	0.06	0.90	0.03	6.3	3.5	3.6	0.5
ICP-MS				4	0	0.90	0.89	0.90	0.03	0.89	0.04	3.8	4.9	-1.0	-0.7
Cap. Electrophoresis				1	0			1.01		0.91				10.8	1.7
Flame photometry				1	0			0.89		0.88				-2.3	-1.6
Total organic carbon	AB	6.83	6.96	20	0	6.83	6.96	6.87	0.71	6.94	0.72	10.4	10.4	0.6	-0.3
Combustion				13	0	7.04	7.09	6.86	0.63	6.94	0.68	9.2	9.8	0.5	-0.4
UV/peroxodisulphate				4	0	6.55	6.79	7.00	1.23	7.16	1.14	17.6	15.9	2.5	2.8
Other method				3	0	6.56	6.61	6.71	0.25	6.66	0.20	3.8	3.1	-1.8	-4.4
Total phosphorus	AB	24.20	23.60	23	3	24.20	23.60	23.87	4.87	24.06	4.76	20.4	19.8	-1.4	2.0
Photometry				13	1	24.30	24.05	23.79	3.95	24.34	4.01	16.6	16.5	-1.7	3.1
ICP-OES				4	0	19.78	21.77	21.29	4.60	21.72	4.41	21.6	20.3	-12.0	-8.0
Other method				4	0	27.58	26.48	26.69	7.23	25.57	7.40	27.1	28.9	10.3	8.3
ICP-MS				1	1			41.00		41.00				69.4	73.7
Ion chromatography				1	1			0.00		0.00				100.0	100.0
Aluminium	CD	49	48	20	3	49	48	47	9	47	9	19.0	19.3	-4.1	-2.2
ICP-MS				8	0	49	48	48	3	49	5	6.5	9.9	-1.8	0.7
ICP-OES				7	2	50	50	53	10	52	10	19.4	18.6	7.4	8.3
GFAAS				5	1	35	35	38	10	38	10	25.4	26.4	-23.2	-21.3
Iron	CD	108.90	106.80	23	0	108.90	106.80	111.56	13.69	107.87	15.62	12.3	14.5	2.4	1.0
ICP-MS				9	0	108.90	106.10	108.81	9.09	106.02	10.09	8.3	9.5	-0.1	-0.7
ICP-OES				7	0	111.50	107.60	112.41	19.11	105.79	23.31	17.0	22.0	3.2	-0.9
FAAS				3	0	105.00	103.00	109.27	9.36	107.73	10.72	8.6	9.9	0.3	0.9
GFAAS				3	0	112.70	109.30	121.97	18.08	117.40	18.99	14.8	16.2	12.0	9.9
Photometry				1	0			106.00		111.00				-2.7	3.9
Manganese	CD	3.68	3.37	20	1	3.68	3.37	3.78	0.44	3.40	0.50	11.7	14.7	2.8	1.1
ICP-MS				9	0	3.64	3.29	3.60	0.21	3.33	0.26	5.7	7.9	-2.0	-1.1
ICP-OES				7	1	3.74	3.37	3.78	0.55	3.26	0.69	14.4	21.1	2.9	-3.0
GFAAS				4	0	4.18	3.86	4.18	0.51	3.78	0.54	12.3	14.2	13.7	12.3
Cadmium	CD	0.98	0.97	21	1	0.98	0.97	0.96	0.09	0.94	0.12	9.7	13.0	-1.8	-3.0
ICP-MS				10	0	1.01	0.98	1.01	0.05	0.98	0.05	4.7	4.8	2.5	0.9
GFAAS				6	1	0.95	0.94	0.89	0.12	0.89	0.15	13.2	16.3	-9.0	-8.1
ICP-OES				4	0	0.94	0.94	0.95	0.13	0.90	0.22	13.3	24.2	-3.6	-7.8
Other method				1	0			0.97		0.99				-1.3	2.0
Lead	CD	2.31	2.22	21	3	2.31	2.22	2.31	0.17	2.23	0.29	7.2	13.0	0.1	0.4
ICP-MS				10	0	2.32	2.26	2.31	0.12	2.24	0.10	5.2	4.3	0.1	0.8
GFAAS				6	3	2.43	2.50	2.38	0.16	2.38	0.24	6.6	10.1	2.9	7.0
ICP-OES				3	0	2.34	2.20	2.38	0.30	2.16	0.74	12.5	34.1	2.9	-2.9
FAAS				1	0			2.02		1.98				-12.6	-10.8
Other method				1	0			2.22		2.19				-3.9	-1.4
Copper	CD	12.50	11.20	23	4	12.50	11.20	12.58	0.82	11.21	0.63	6.6	5.6	0.7	0.1
ICP-MS				11	1	12.40	11.05	12.44	0.68	11.18	0.52	5.4	4.6	-0.5	-0.2
GFAAS				7	1	12.57	11.75	12.61	0.88	11.56	0.42	7.0	3.7	0.9	3.2
ICP-OES				5	2	12.56	11.00	13.02	1.31	10.58	0.95	10.1	8.9	4.2	-5.5

Variable and methods	Sample pair	True value		No. lab.		Median		Sample 1		Sample 2		Rel.std.av. %		Relative error %	
		S. 1	S. 2	Total	U	S. 1	S. 2	Average	Stdev	Average	Stdev	S. 1	S. 2	S. 1	S. 2
Nickel	CD	4.47	4.31	21	2	4.47	4.31	4.37	0.39	4.14	0.52	9.0	12.6	-2.1	-3.9
ICP-MS				11	0	4.51	4.46	4.54	0.09	4.42	0.11	2.1	2.5	1.6	2.6
GFAAS				5	0	3.99	3.90	4.13	0.66	3.76	0.58	15.9	15.4	-7.7	-12.9
ICP-OES				5	2	4.30	4.10	4.18	0.33	3.76	0.85	7.9	22.5	-6.6	-12.7
Zinc	CD	14.30	14.25	21	1	14.30	14.25	14.52	1.53	13.86	2.24	10.5	16.2	1.5	-2.7
ICP-MS				11	0	15.10	14.80	15.05	1.00	15.11	1.24	6.7	8.2	5.2	6.0
ICP-OES				6	1	13.91	13.71	14.10	1.60	12.77	2.29	11.4	17.9	-1.4	-10.4
GFAAS				3	0	14.30	10.25	13.69	2.86	11.38	2.92	20.9	25.7	-4.3	-20.1
FAAS				1	0			13.21		13.04				-7.6	-8.5

*Om.: Sample pair omitted from the calculations

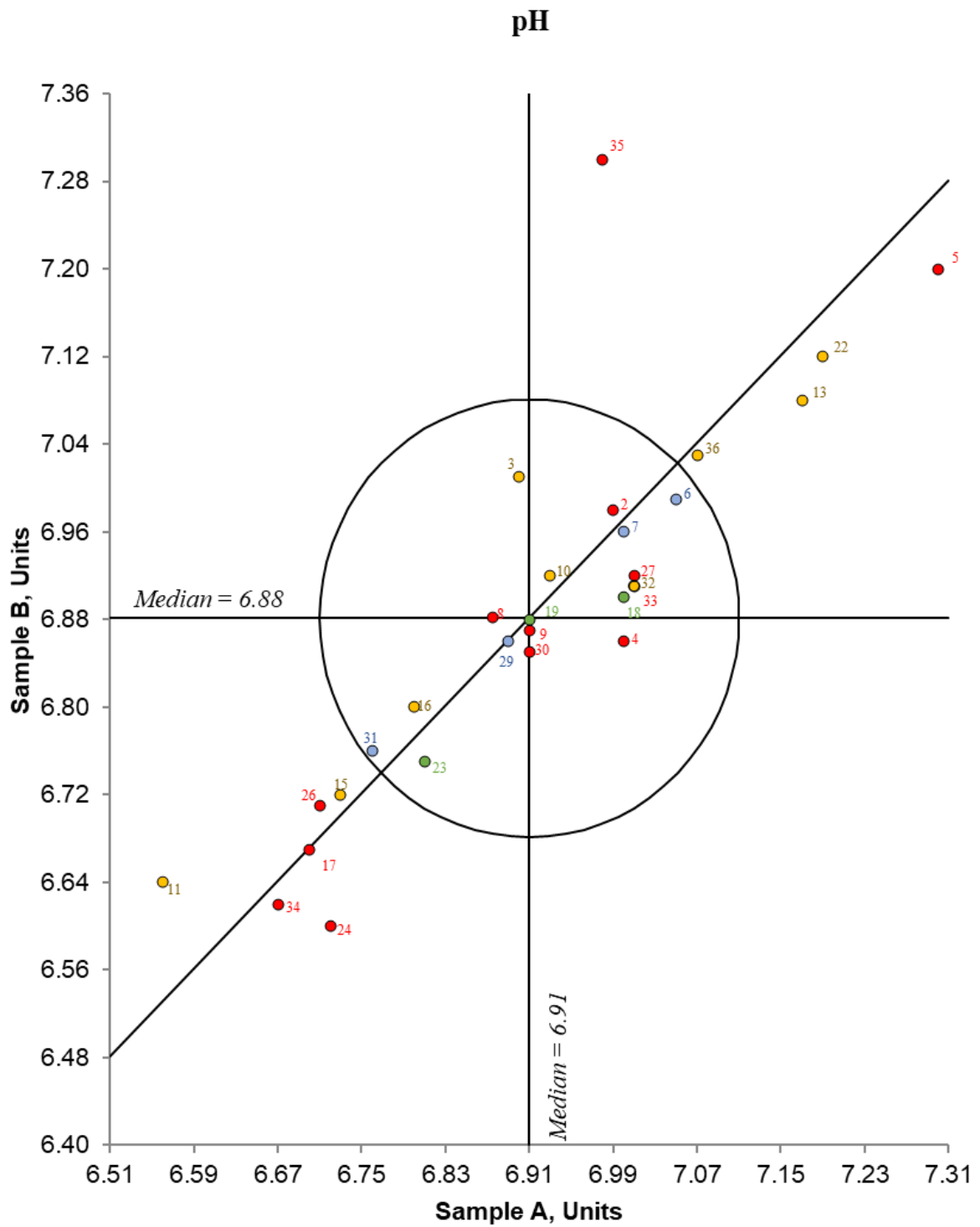


Figure 1. Youden diagram for pH. Sample pair AB. Acceptable limit, given by circle, is 2.9%. The colours indicate the type of technique/method used: red used elec., with stirring (n=13), yellow used elec., non-stirring (n=9), blue used elec., equilibration (n=5), and green used other method (n=3).

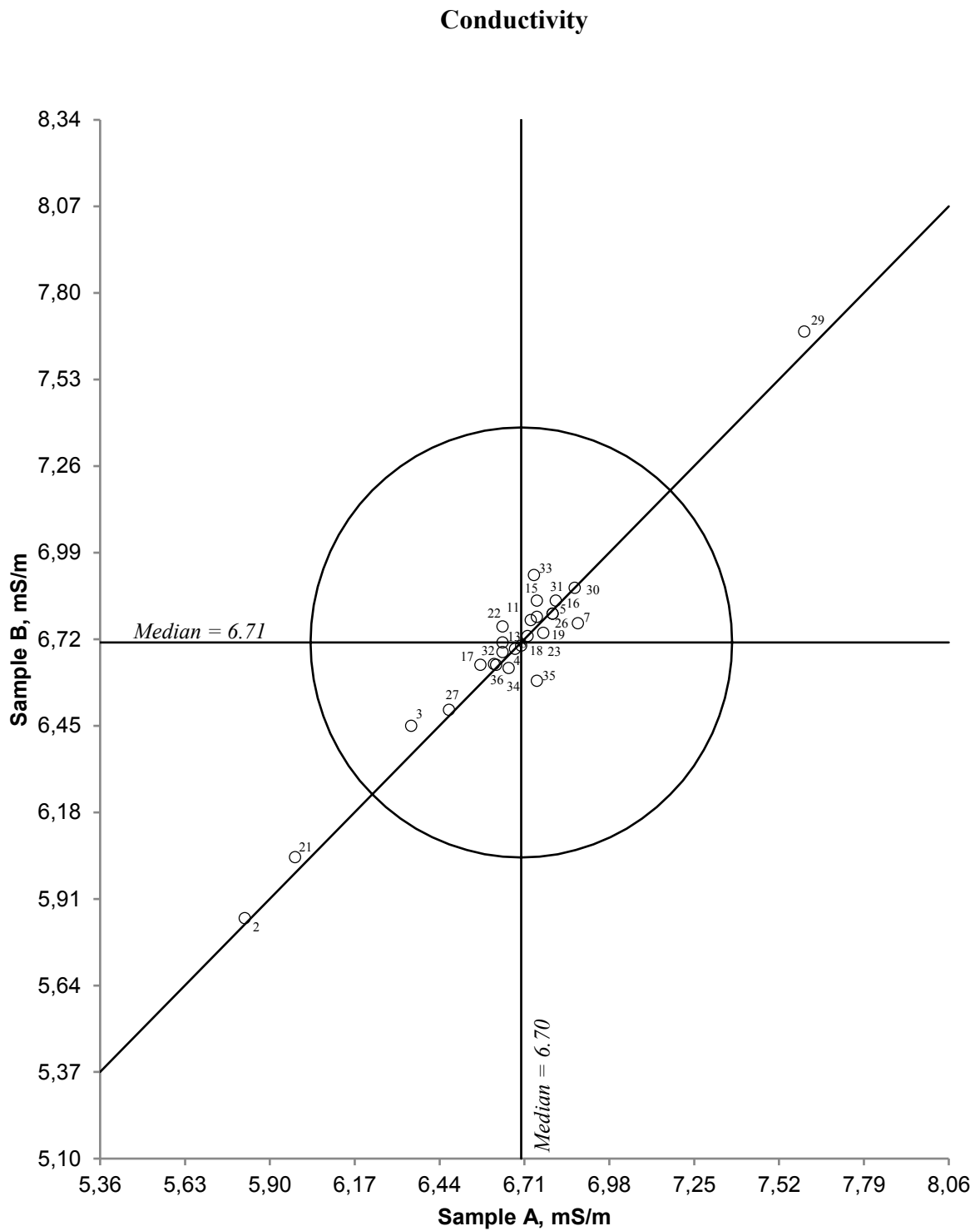


Figure 2. Youden diagram for conductivity. Sample pair AB. Acceptable limit, given by circle, is 10%.

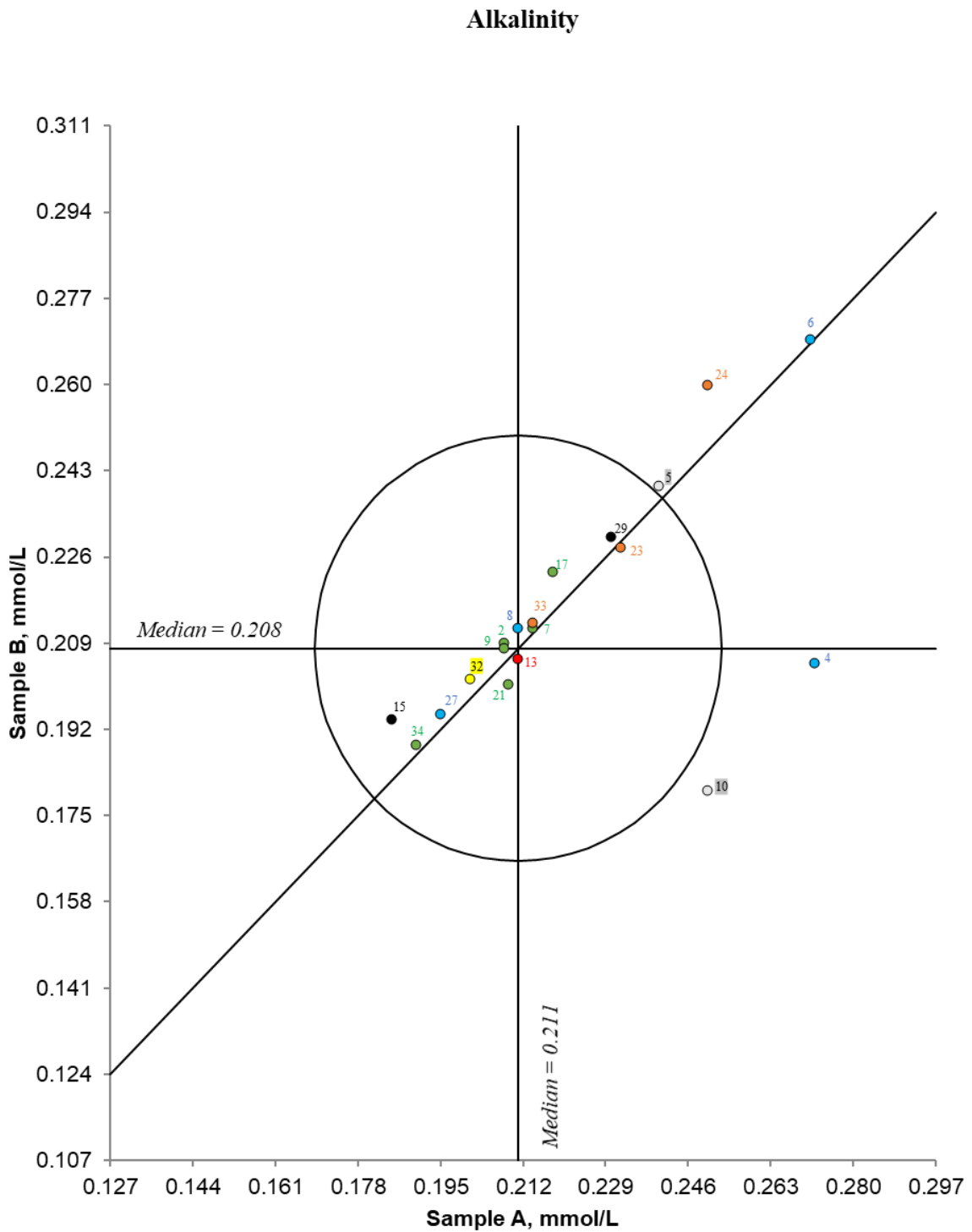


Figure 3. Youden diagram for alkalinity. Sample pair AB. Acceptable limit, given by circle, is 20%. The colours indicate the type of technique/method used: green used Gran plot (n=6), blue used two end points titration (n=4), orange used one end point (other) titration (n=3), red used colorimetry (n=2), grey used other method (n=2), black used one end point (5.4) titration (n=2), and yellow used one end point (5.6) titration (n=1).

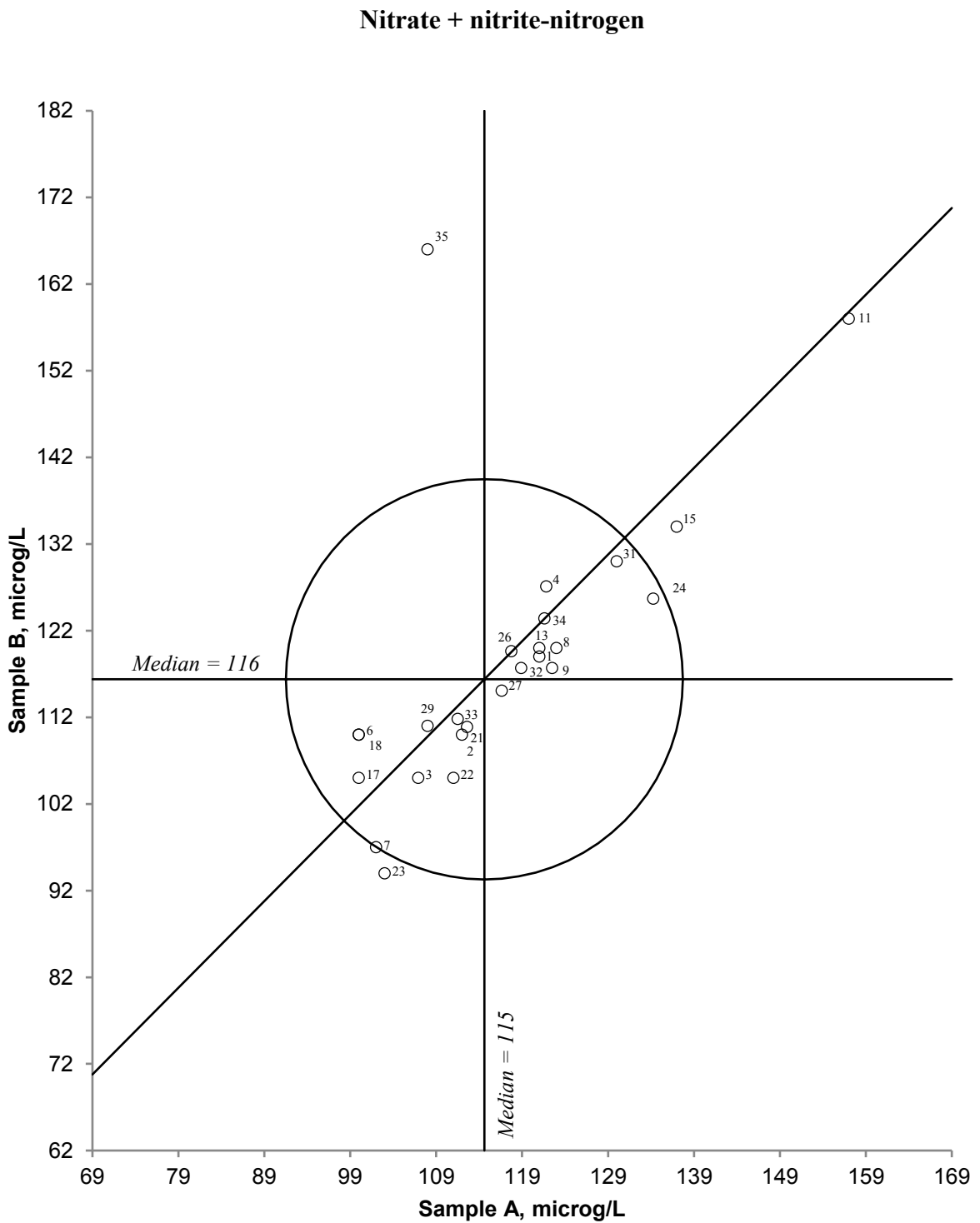


Figure 4. Youden diagram for NO₃ + NO₂-N. Sample pair AB. Acceptable limit, given by circle, is 20%.

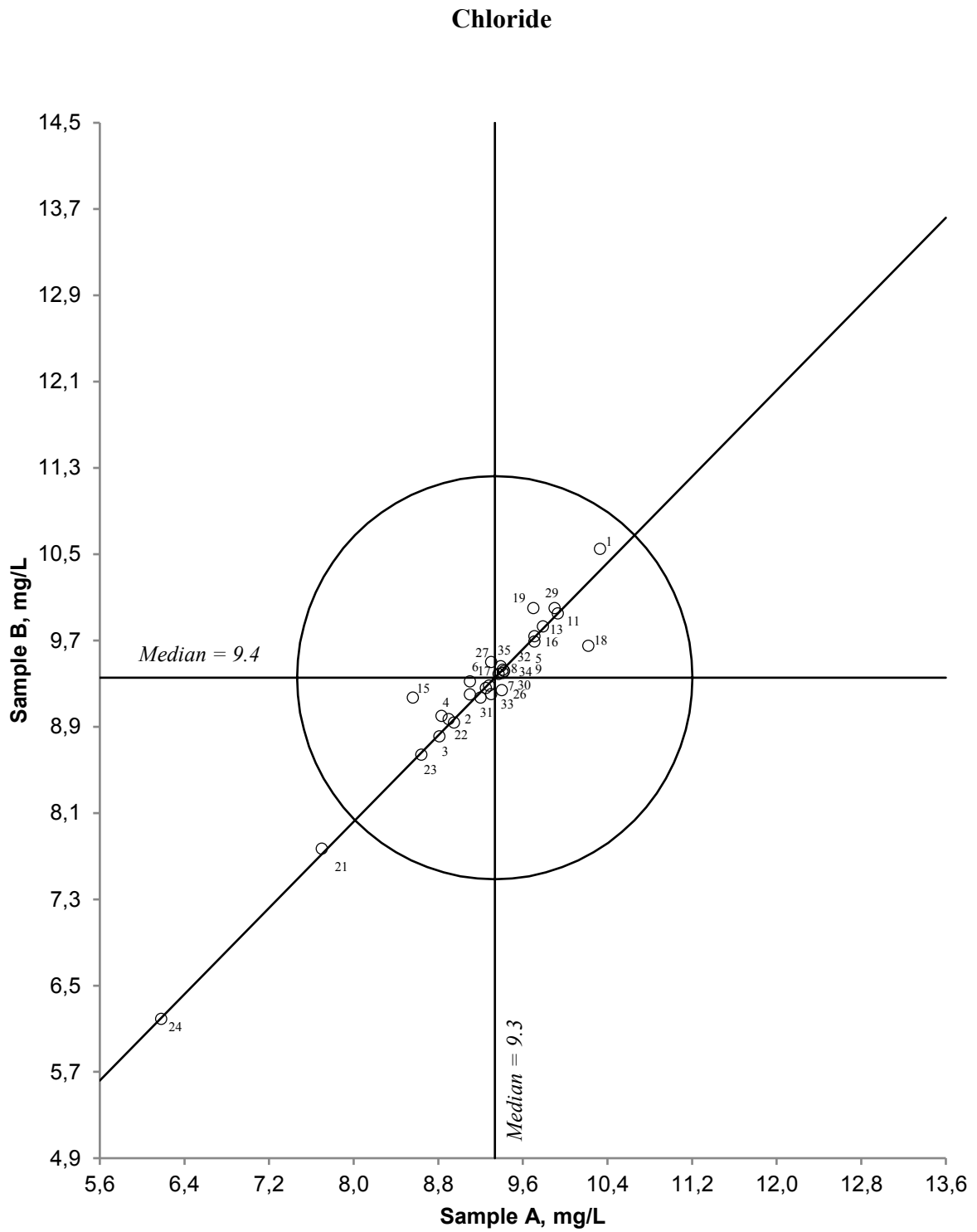


Figure 5. Youden diagram for Chloride. Sample pair AB. Acceptable limit, given by circle, is 20%.

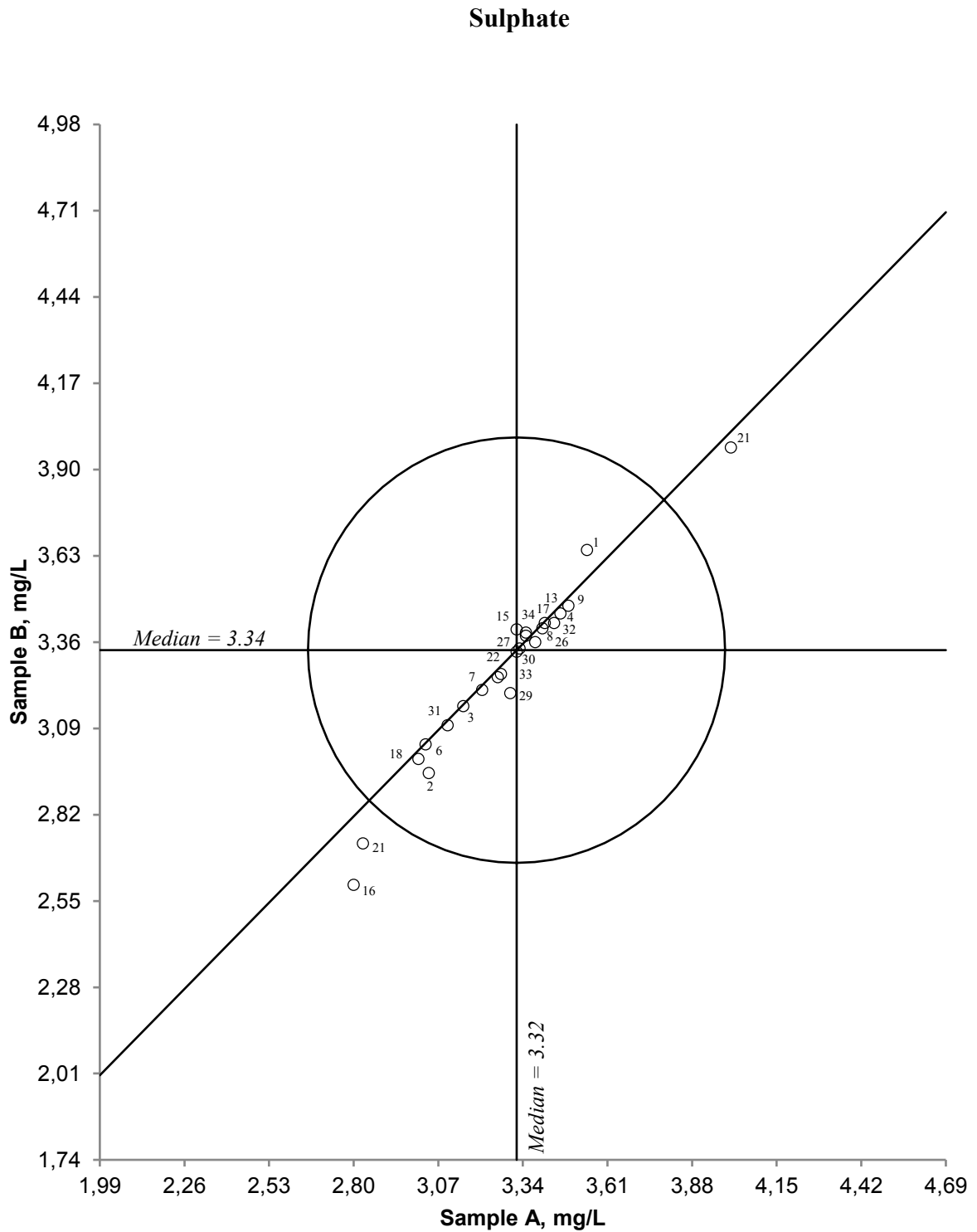


Figure 6. Youden diagram for Sulphate. Sample pair AB. Acceptable limit, given by circle, is 20%.

Calcium

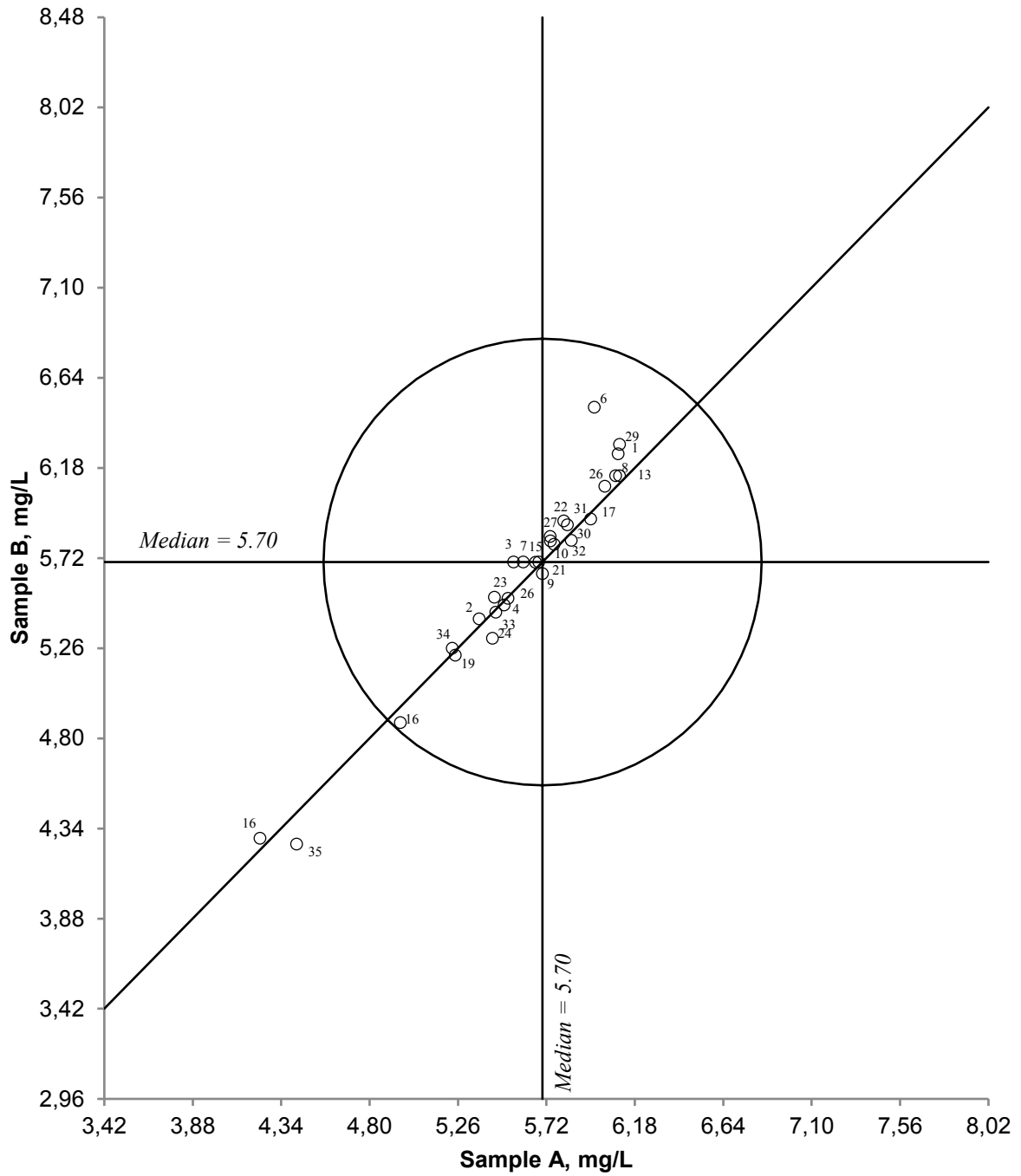


Figure 7. Youden diagram for Calcium. Sample pair AB. Acceptable limit, given by circle, is 20%.

Magnesium

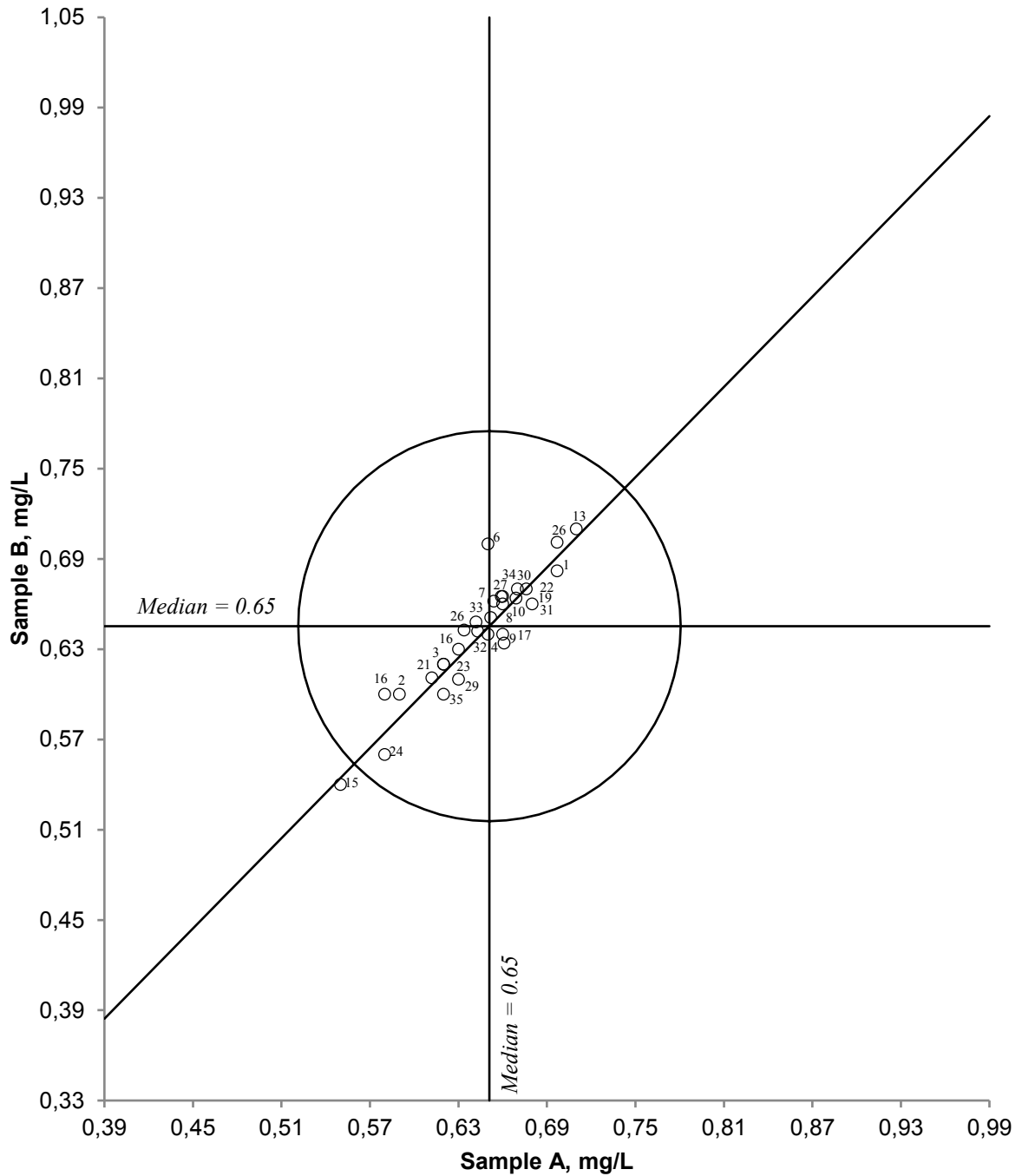


Figure 8. Youden diagram for Magnesium. Sample pair AB. Acceptable limit, given by circle, is 20%.

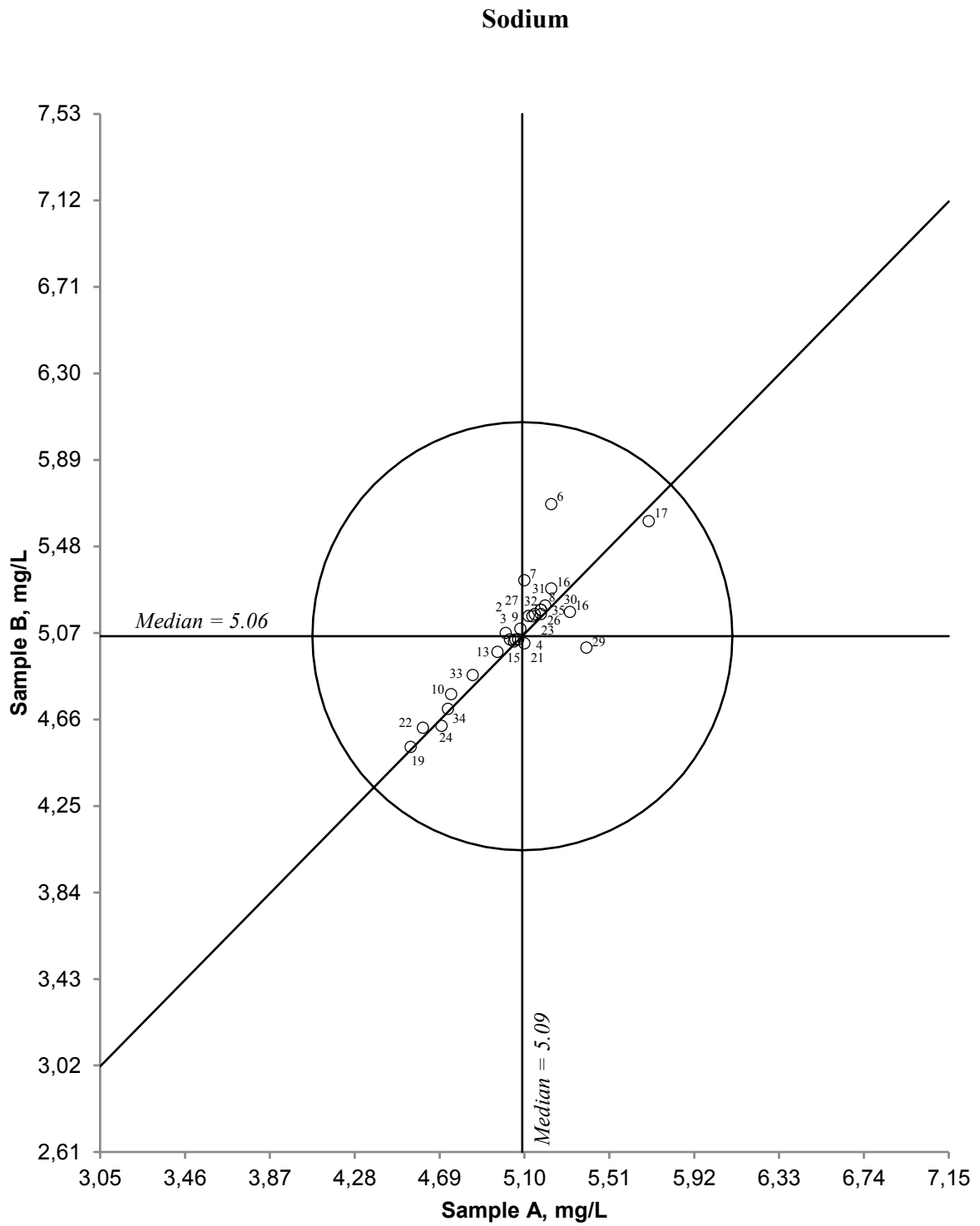


Figure 9. Youden diagram for Sodium. Sample pair AB. Acceptable limit, given by circle, is 20%.

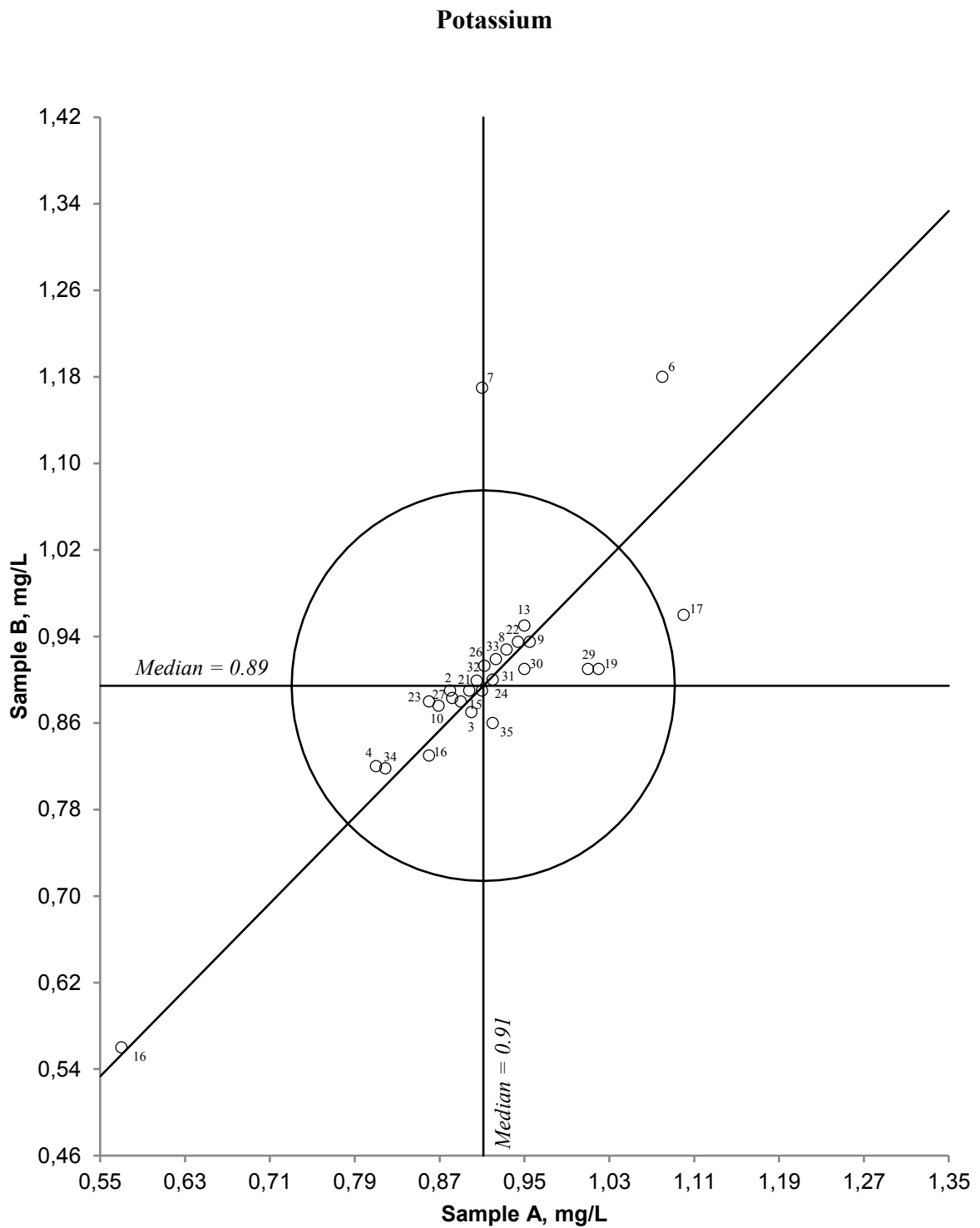


Figure 10. Youden diagram for Potassium. Sample pair AB. Acceptable limit, given by circle, is 20%.

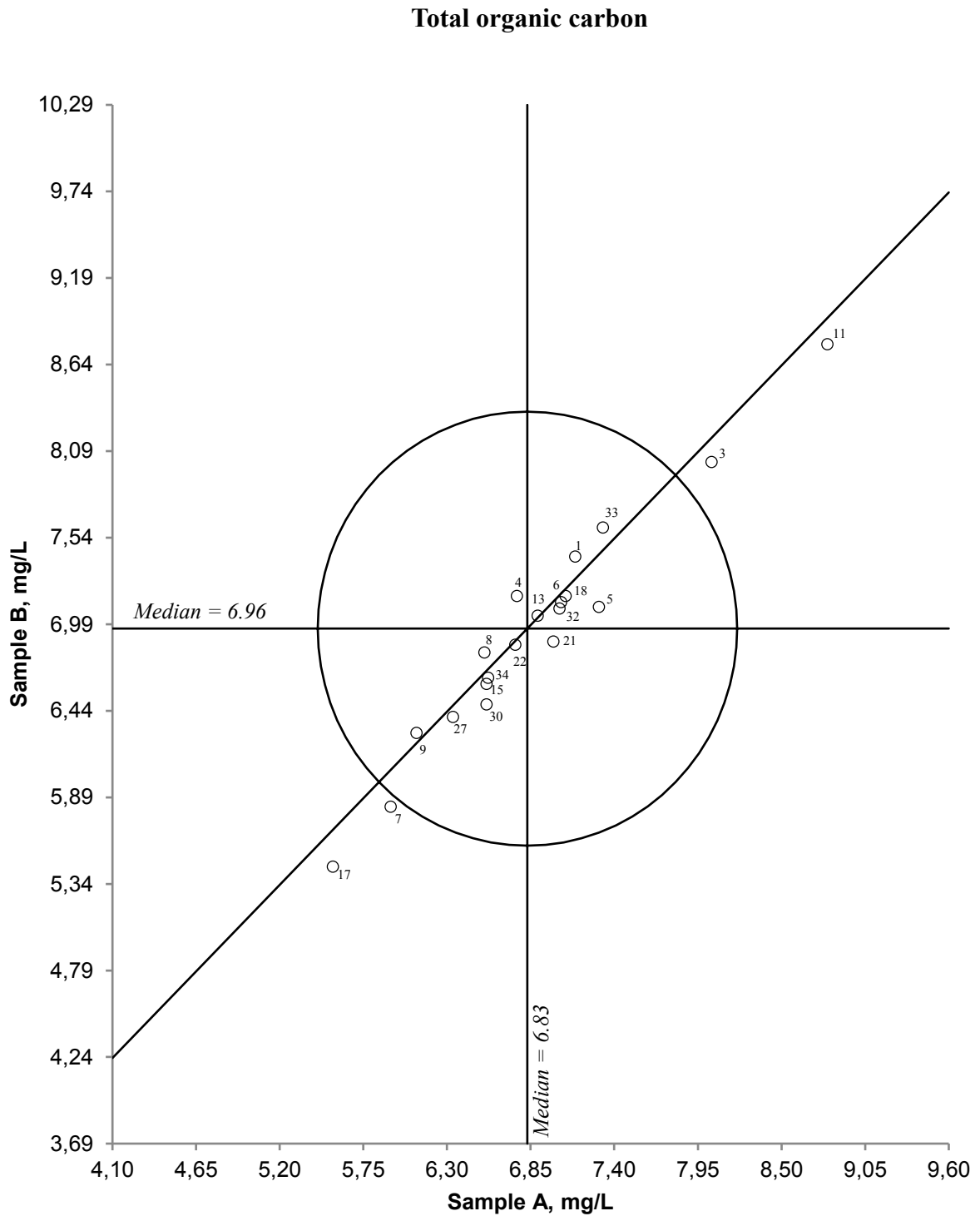


Figure 11. Youden diagram for TOC. Sample pair AB. Acceptable limit, given by circle, is 20%.

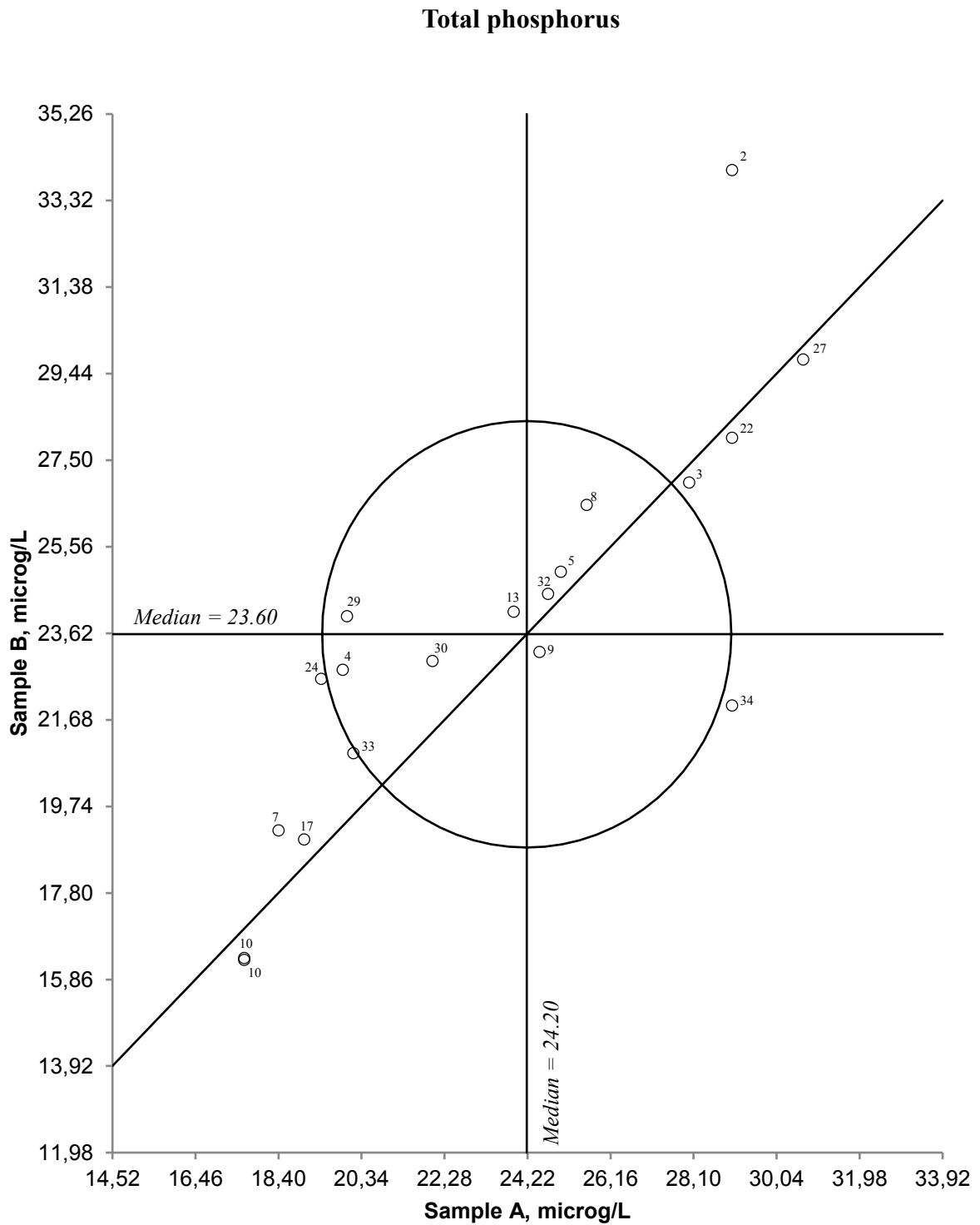


Figure 12. Youden diagram for total phosphorus. Sample pair AB. Acceptable limit, given by circle, is 20%.

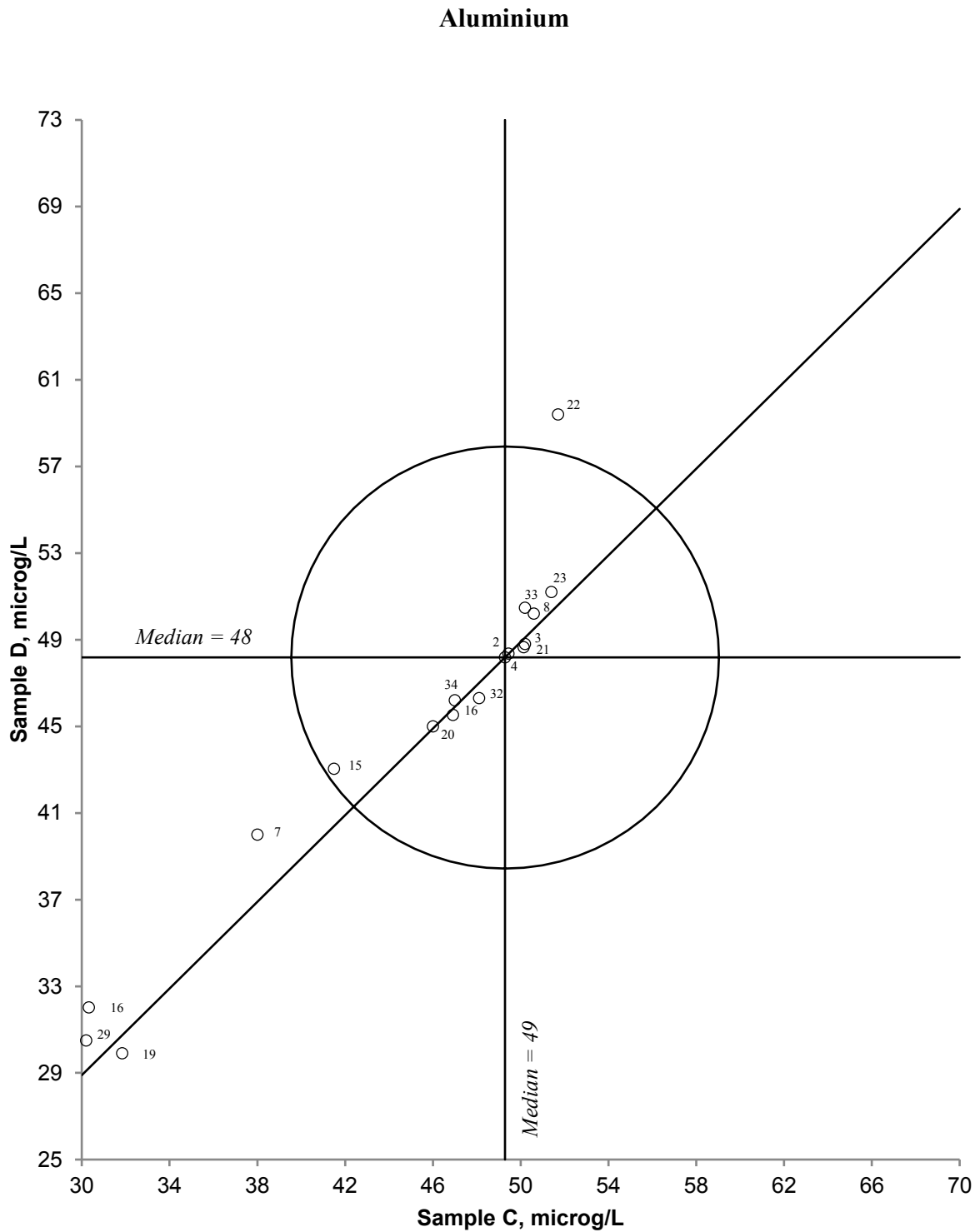


Figure 13. Youden diagram for Aluminium. Sample pair CD. Acceptable limit, given by circle, is 20%.

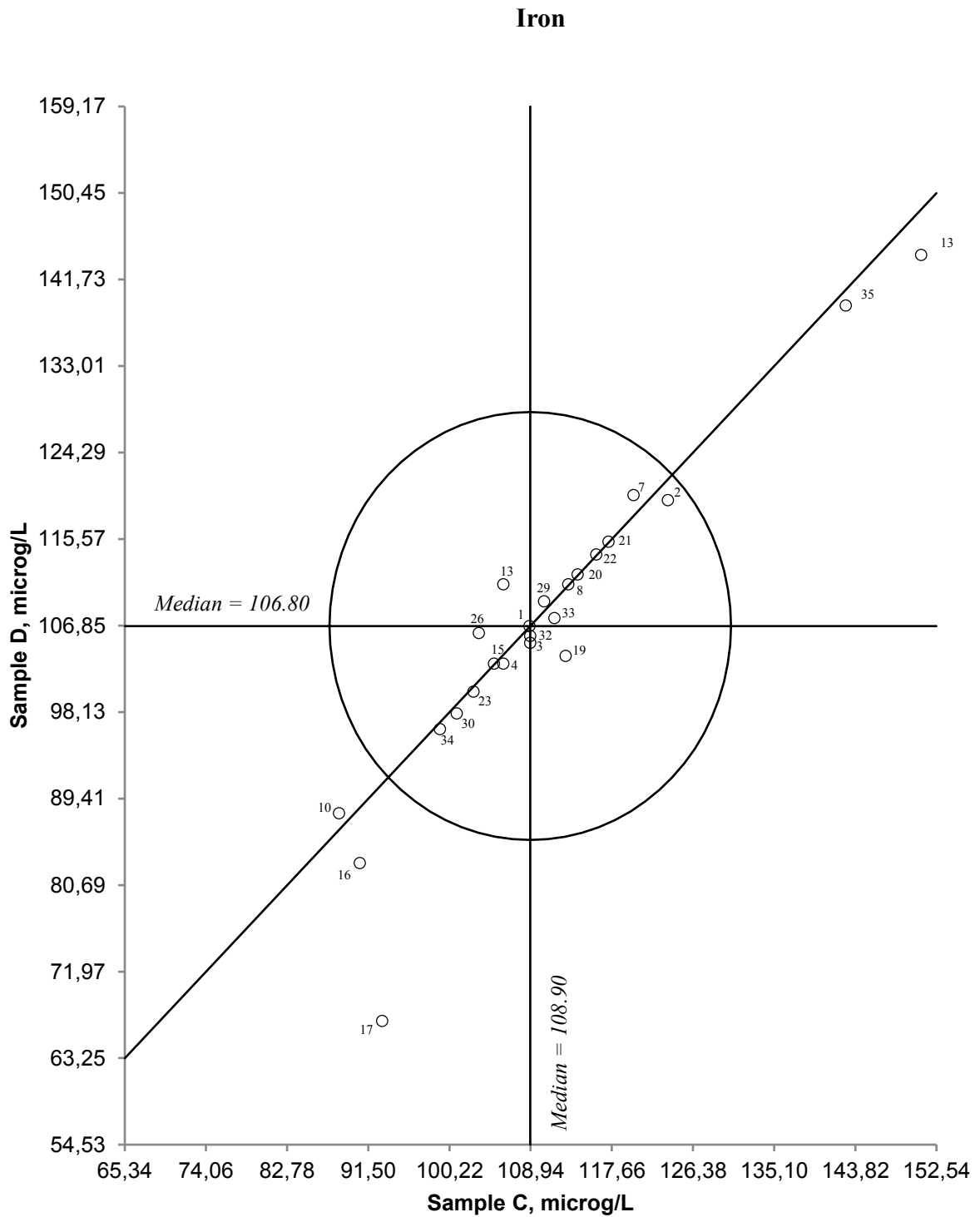


Figure 14. Youden diagram for Iron. Sample pair CD. Acceptable limit, given by circle, is 20%.

Manganese

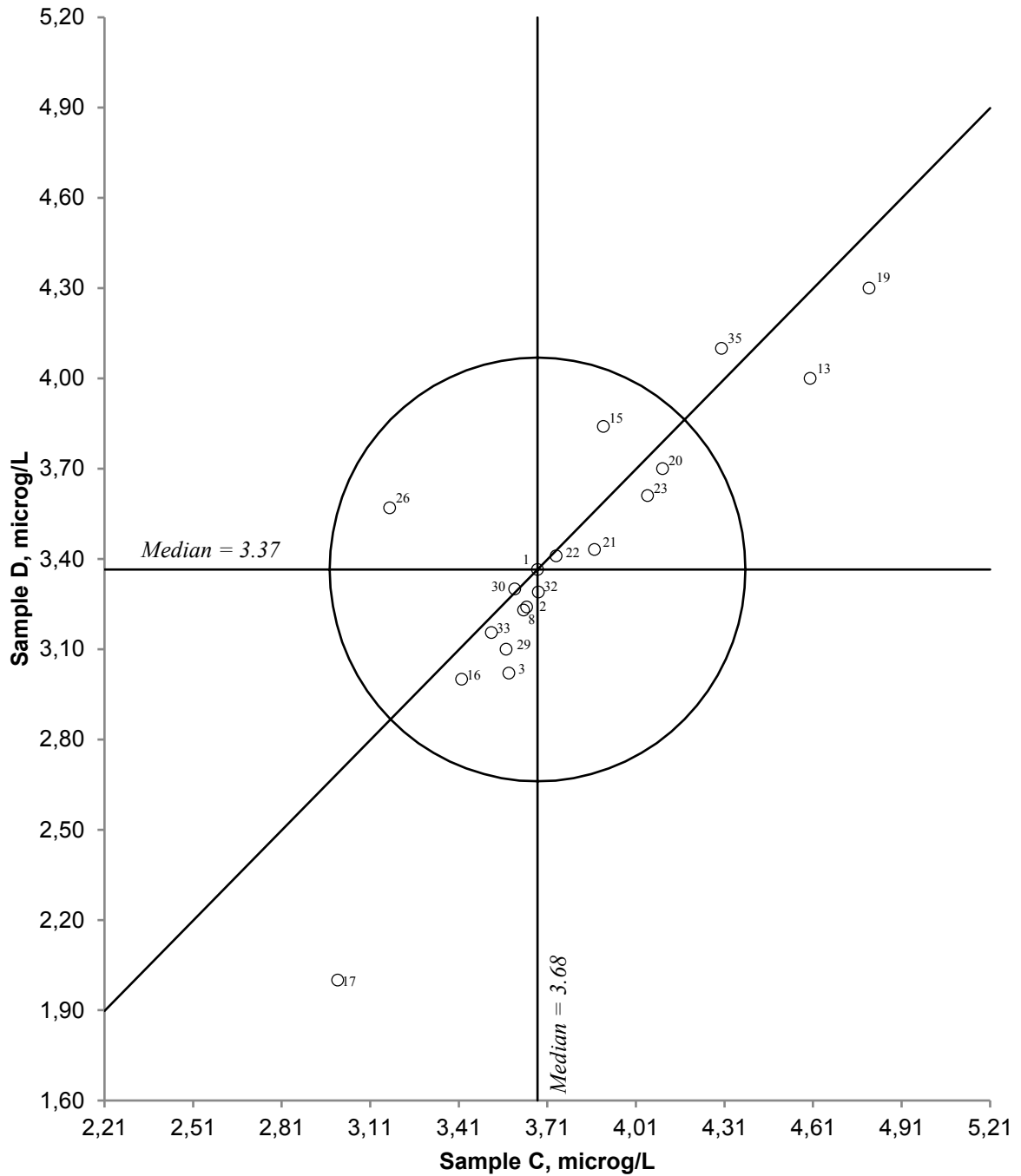


Figure 15. Youden diagram for Manganese. Sample pair CD. Acceptable limit, given by circle, is 20%.

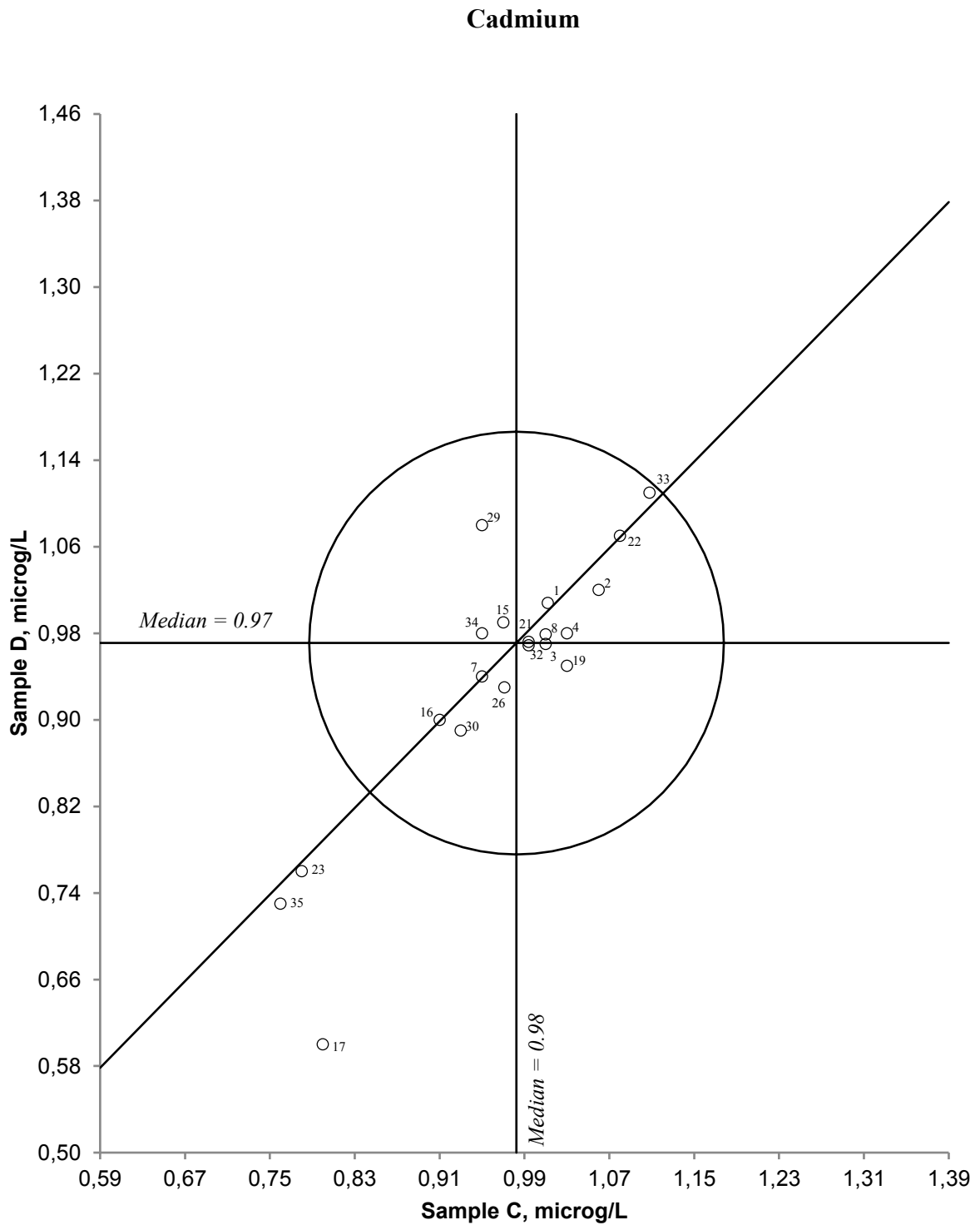


Figure 16. Youden diagram for Cadmium. Sample pair CD. Acceptable limit, given by circle, is 20%.

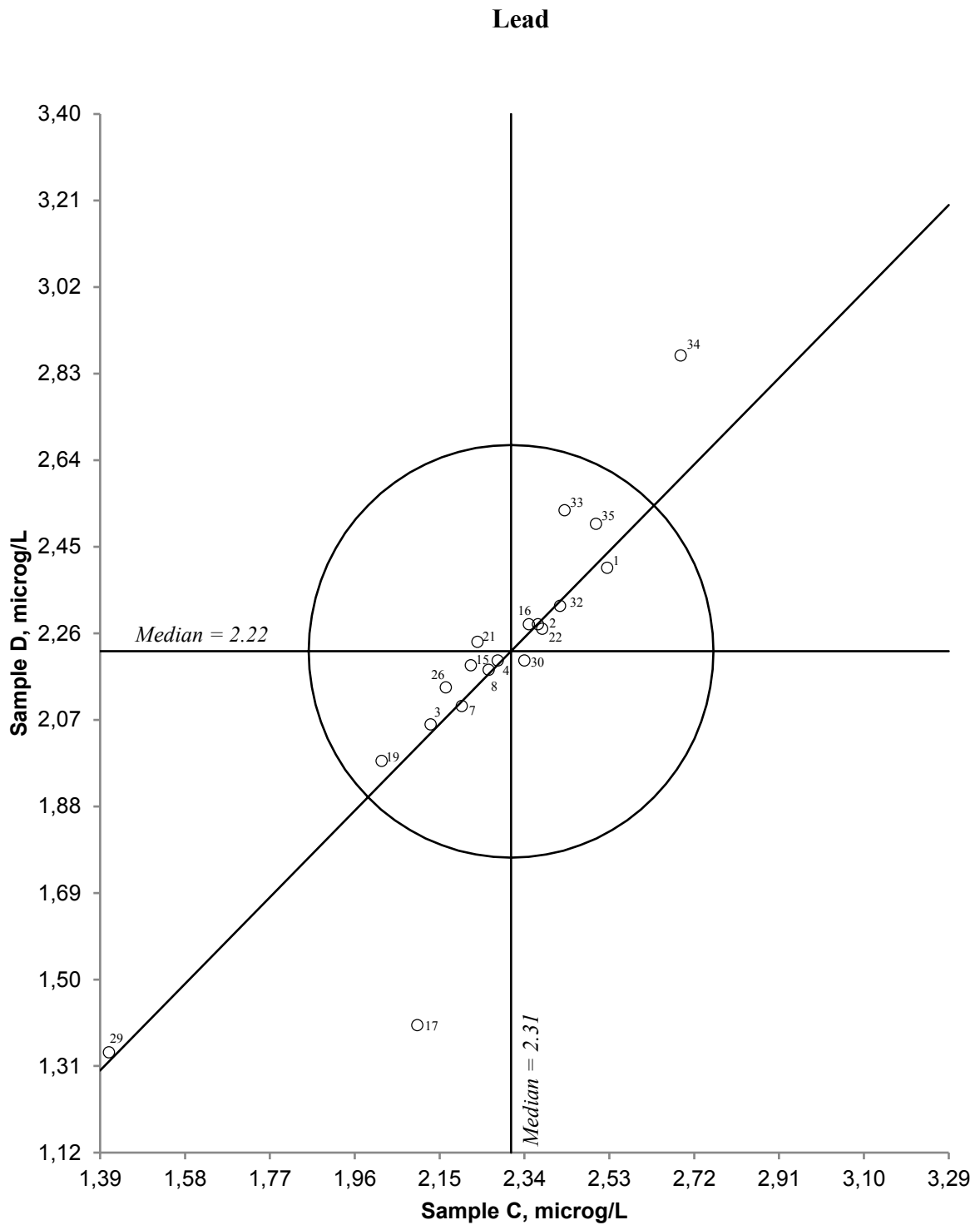


Figure 17. Youden diagram for Lead. Sample pair CD. Acceptable limit, given by circle, is 20%.

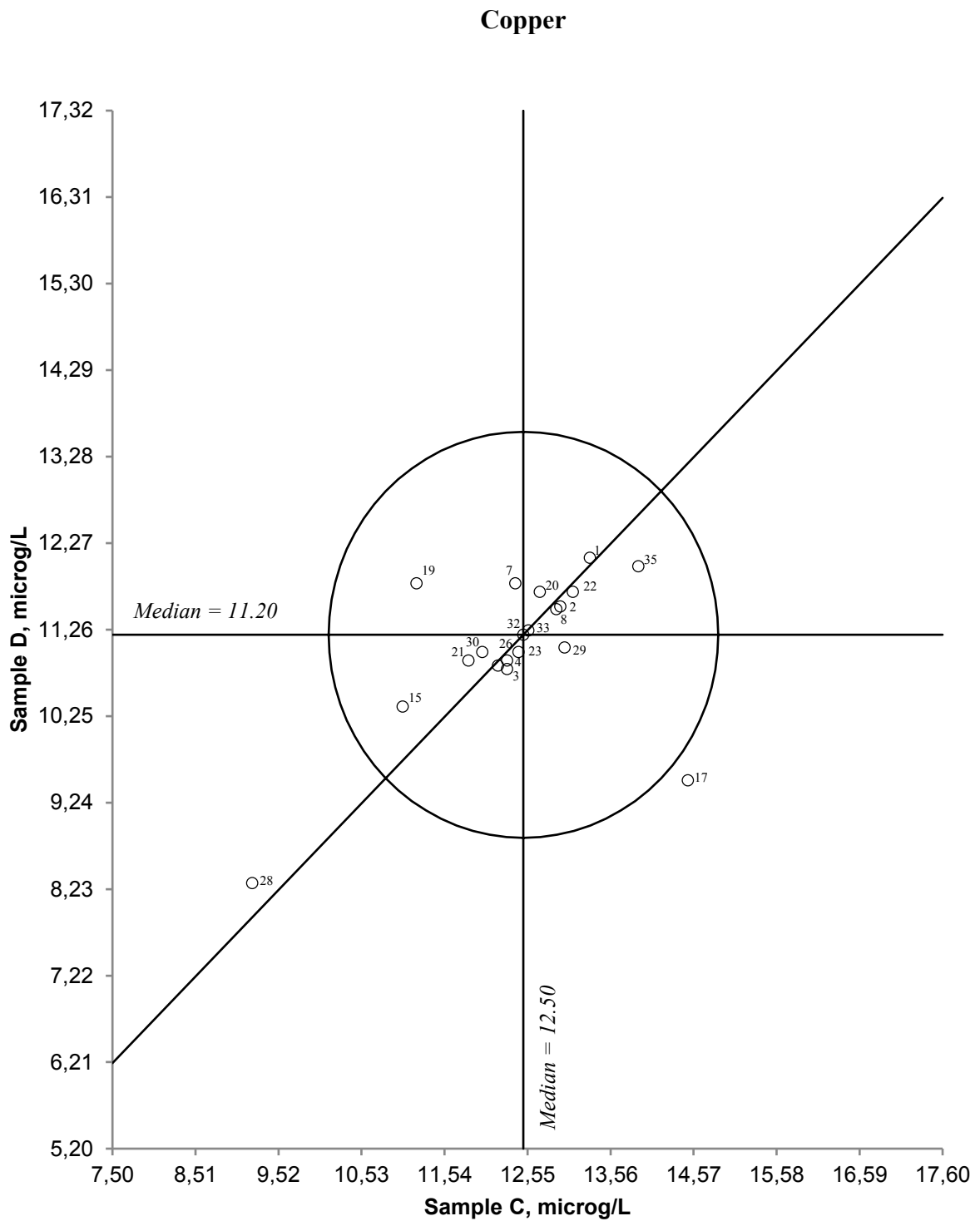


Figure 18. Youden diagram for Copper. Sample pair CD. Acceptable limit, given by circle, is 20%.

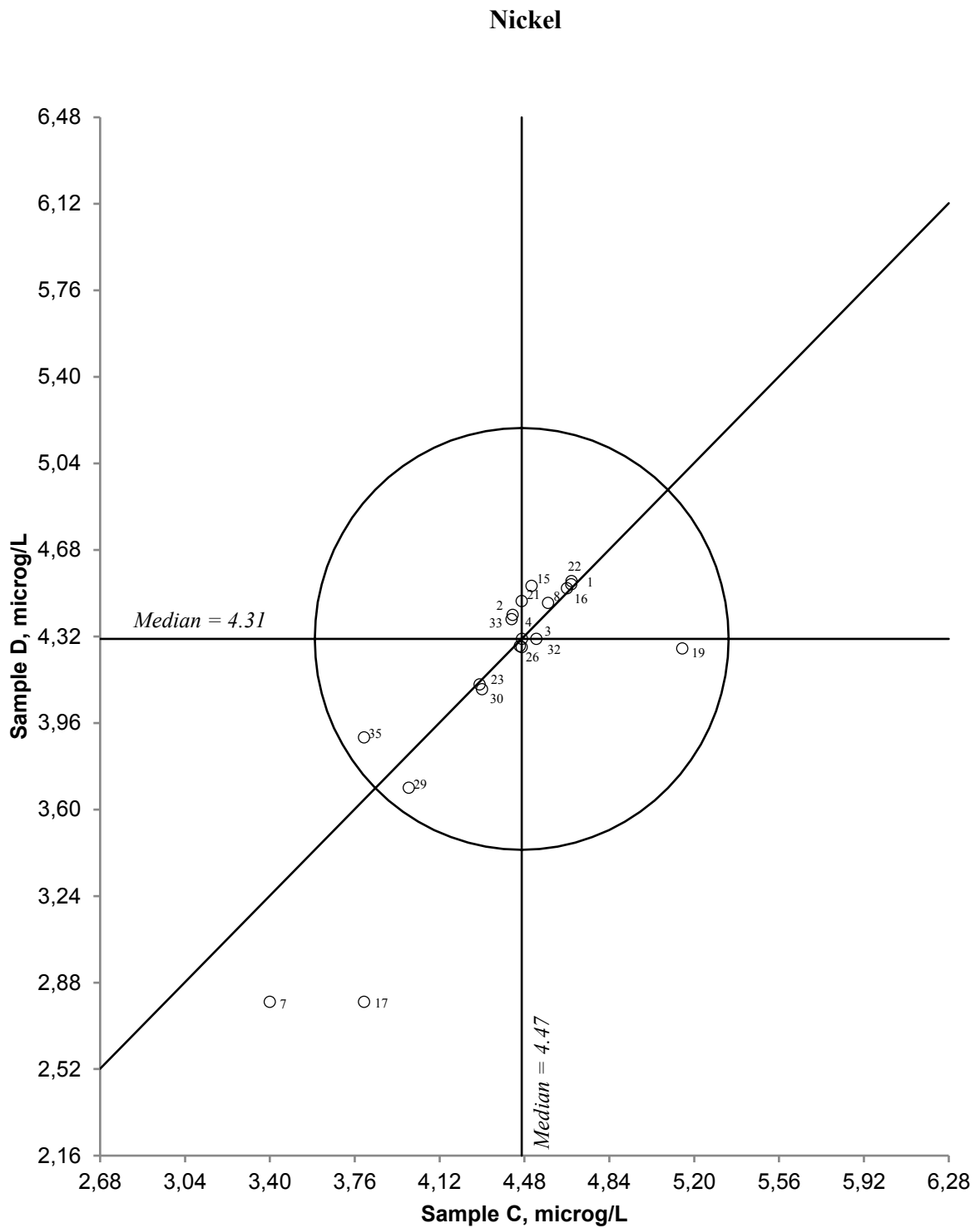


Figure 19. Youden diagram for Nickel. Sample pair CD. Acceptable limit, given by circle, is 20%.

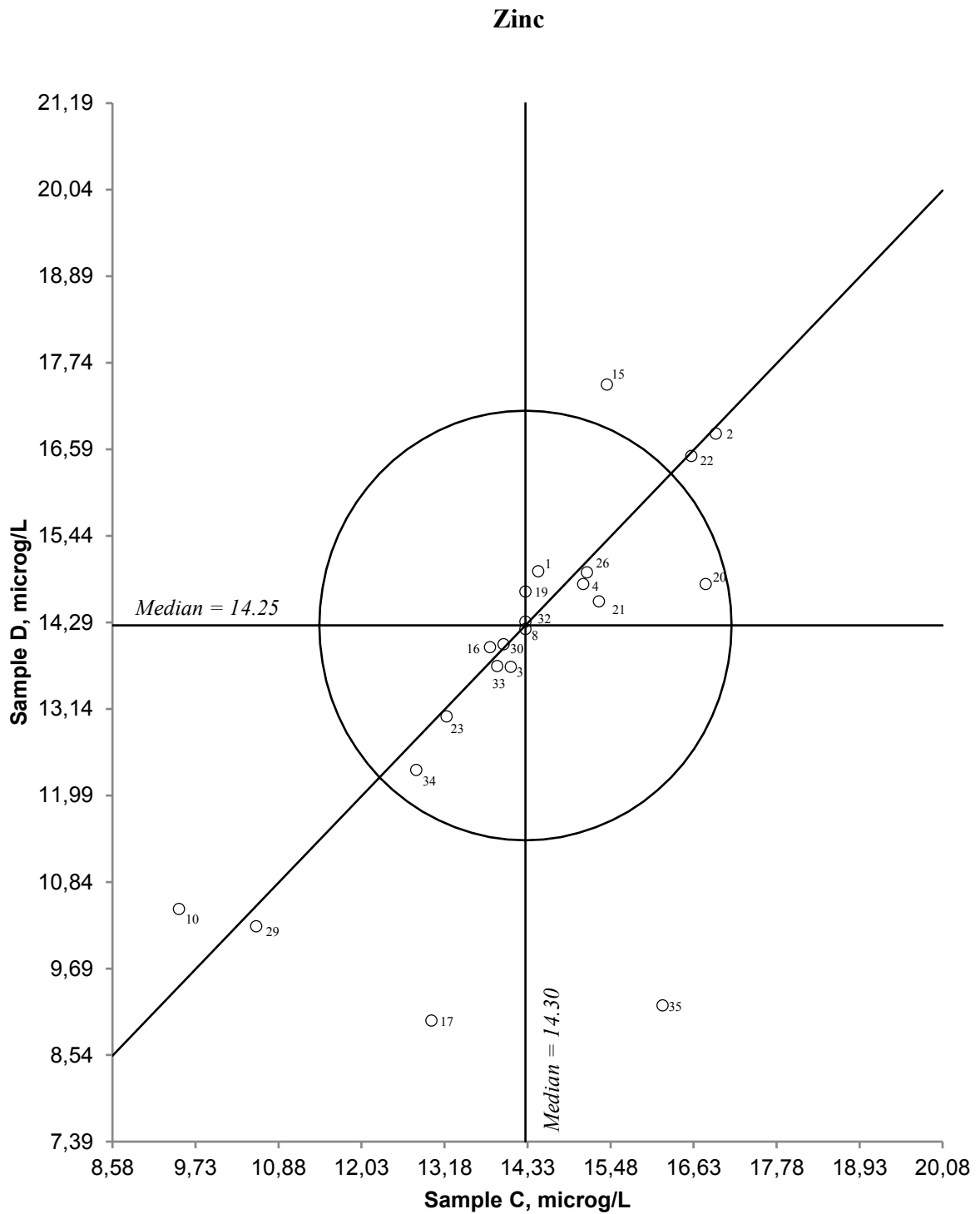


Figure 20. Youden diagram for Zinc. Sample pair CD. Acceptable limit, given by circle, is 20%.

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Appendix A. The participating laboratories

Table 3. Information of the participating laboratories including name, address, and country.

ILC Participating laboratories			
No	Name of Laboratory	Address	Country
1	Vlaamse MilieuMaatschappij (VMM) Dienst Laboratorium	Raymonde de Larocheaan 1,9051 Sint-Denijs-Westrem	Belgium
2	Insitute of Industrial Ecology Problems of the North (INEP) Center for the collective use	184209 Apatity, Akademgorodok 14A, Murmansk reg.	Russian Federation
3	Bayerische Landesanstalt fuer Wald und Forstwirtschaft Abteilung 2 - Boden und Klima	Hans-Carl-von-Carlowitz-Platz 1 D-85354 Freising	Germany
4	Ufficio del Monitoraggio Ambientale - Laboratorio	Via Mirasole 22 6500 Bellinzona	Switzerland
5	EPA Regional Inspectorate Castlebar OEA	John Moore Road, Castlebar, co mayo Ireland.	Ireland
6	Staatliche Betriebgesellschaft für Umwelt und Landwirtschaft (BfUL)	Dresdner Straße 183 D-09131 Chemnitz	Germany
7	Chemical Laboratory, Czech Geological Survey	Geologická 6, 152 00 Prague	Czech Republic
8	Estonian Environment Research Centre	Marja 4 D 10617 Tallinn Estonia	Estonia
9	MOEECC, DORSET Laboratory	P.O. Box 39 Dorset, Ontario Canada P0A 1E0	Canada
10	Forest Nutrition and Water Resources Department of Ecology, Technis	H.C.v.Carlowitz-Platz 2 D-85354 Freising Germany	Germany
11	Büsgen-Institute - Soil Science of Temperate Ecosystems	D-37077 Goettingen Buesgenweg 2	Germany
12	University of Helsinki Lab. of Geology and Geography	P.O.Box 64 00014 University of Helsinki	Finland
13	Institut für Ökologie	Technikerstr. 25 6020 Innsbruck Austria Europe	Austria
14	Institute for Public Health Pancevo	6 Oktobar No 9 26000 Pancevo	Serbia
15	Limnological Institute of Russian Academy of Sciences -Siberian Branch LIN SB RAS	Ulanbaatorskaya str. 3 Irkutsk 664033	Russian Federation
16	EPA, Dublin Inspectorate McCumiskey Hs,	Kieran Gordon	Ireland
17	CNR Institute of Water Research (IRSA)	Largo Tonolli 50 I-28922 VERBANIA Pallanza	Italy
18	Kilkenny Lab, Environmental Protection agency	Environmental Protection Agency, Seville Lodge,	Ireland

ILC_Participating laboratories			
No	Name of Laboratory	Address	Country
19	Polish Academy of Sciences Institute of Botany	PAN Instytut Botaniki 31-512 Kraków ul. Lubicz 46	Poland
20	Environmental Protection Agency Environmental Research Departm	A. Gostauto str. 9, LT-01108 Vilnius	Lithuania
21	Natural Resources Wales Analytical Services (NRWAS)	As per delivery address below	United Kingdom
22	Bayerisches Landesamt fuer Umwelt	Ref 71 Bürgerme-Ulrich-Str. 160 D-86179 Augsburg	Germany
23	Environmental Pollution Monitoring Center Laboratory of surface and sea	Verkhne-Rostinskoe sh,51,MUGMS,Murmansk,183034	Russian Federation
24	Radbouduniversiteit afd. Ecologie t.a.v. G. Verheggen	Postbus 9010 6500 GL Nijmegen The Netherlands	Netherlands
25	Norsk institutt for vannforskning	Gaustadalléen 21 NO-0349 OSLO	Norway
26	ISSeP Colfontaine Zoning Schweitzer	Rue de la Platinerie B-7340 COLFONTAINE	Belgium
27	Marine Scotland Science Freshwater Laboratory	Faskally,Pitlochry,Perthshire,PH16 5BB, Scotland.	United Kingdom
28	Yu.A.Izrael Institute of Global Climate and Ecology (IGCE) Roshydromet	20-B, Glebovskaya St., Moscow, 107258, RUSSIA	Russian Federation
29	Hydrochemical Laboratory by Federal State Enterprise on Water Industry	10 A Stahanovskaya str., Pskov, 180004	Russian Federation
30	FGU «Baltwodhoz»	199004, Saint-Petersburg, V.O. Sredny pr. 26	Russian Federation
31	Staatliche Betriebsgesellschaft für Umwelt und Landwirtschaft (BfUL)	Haus5, FB53 Waldheimer Str. 219 D-01683 Nossen	Germany
32	Swedish University for Agricultural Sciences Aquatic Sciences and Assesment	Box 7050 750 07 UPPSALA	Sweden
33	Institute of Biology of Komi Science Centre of the Ural Branch of the Russian Academy of Sciences IB FRC Komi SC UB RAS	Kommunisticheskaya st.,28 Syktyvkar,167982,Russia	Russian Federation
34	Laboratoire d'écologie fonctionnelle et environnement (EcoLab)	Avenue Agrobiopole 31326 Castanet Tolosan	France
35	Center for Environmental Monitoring, Primorsky Dept. for Hydrometeorology & Environmental Monitoring Primorsky CEM	Mordovtseva str. 3 Vladivostok 690091 RUSSIA	Russian Federation
36	Institute of Environmental Protection-Puszcza Borecka station	Kolektorska 4, 01-692, Warszawa, Poland	Poland

Table 4. Overview of the different countries represented by the participating laboratories.

Country	No. of labs.	Country	No. of labs.
Austria	1	Lithuania	1
Belgium	2	Netherlands	1
Canada	1	Norway	1
Czech Republic	1	Poland	2
Estonia	1	Russia	8
Finland	1	Serbia	1
France	1	Sweden	1
Germany	6	Switzerland	1
Ireland	3	United Kingdom	2
Italy	1		

Total: 19 countries

Appendix B. Preparation of the samples

Both sample sets AB and CD were prepared using water from lake Ulsrudvannet, Oslo, Norway. The lake is in a forested area to the east of Oslo city and is a popular recreational area during summer. The lake was selected for being a natural brown humic lake typically associated with higher levels of some of the parameters of interest to this intercomparison. The lake has previously been part of studies of water quality, and thus, some information was available on the chemical characteristics of this lake (www.vannmiljø.no).

The water was collected during the end of May 2019 and transported to the laboratory using two 25 L plastic containers. The water was allowed to settle for about two weeks prior to filtration through 0.45 µm cellulose acetate membrane filters. Then, the filtrate could settle for one week until the below mentioned additions were made to produce sample sets AB and CD.

To produce sample set AB, some amount of nitrogen and phosphorus was added using the chemicals potassium nitrate (KNO_3) and phytic acid ($\text{C}_6\text{H}_{18}\text{O}_{24}\text{P}_6$). This addition was conducted as close as possible to the day of sample shipment to avoid biodegradation of these nutrients. Sample set CD was created by spiking with standard solution of the metals: aluminium, iron, manganese, cadmium, lead, copper, nickel, and zinc. The water was conserved by adding nitric acid to a concentration of 0.5% (v/v). Like the previous year the levels were relatively low this year and considered realistic to the expected environmental levels. A few days before shipping, the water prepared for sample set AB was distributed to 500 mL bottles and the water for sample set CD to 250 mL bottles. The samples were stored cold until they were shipped to the participating laboratories.

Appendix C. Statistical treatment of the results

Initial treatment of the analytical results

The results were assessed for the presence of potential outliers which was conducted in two subsequent steps. First, if one or both values in a sample set (AB or CD) was deviating with more than 50% from the true value, that pair of results was omitted. The remaining values were used to calculate the mean and the standard deviation of the distribution. Second, those pairs of results in which one or both values were more than three times the standard deviation higher or lower than the mean value was omitted. The remaining results were used for the final calculation for which the results are presented in Tables 7.1 - 7.20. Note that the results omitted from the second step have been marked with the letter "O".

Estimation the “true value” and uncertainty

For each variable, the “true value” is the median of the reported results after excluding strongly deviating values (i.e. outliers). Thus, the true value is the consensus value from the participants and the corresponding uncertainty is based on the method given in ISO 13528 (2005), Annex C (algorithm A).

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:

$$S^* = 1,483 \times \text{the median of } |x_i - m| \quad (i = 1, 2 \dots p)$$

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:

$$u_x = 1,25 \times S^* / \sqrt{p}$$

For the estimation of expanded uncertainty U, a coverage factor of two is used:

$$U = 2 \times u_x$$

It is important to note that there are some limitations to this approach for estimating 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.

The Youden statistical test

The measurement results reported to the intercomparison test was assessed using the method of Youden. This procedure requires that two samples are analyzed for each parameter (e.g. A and B) and that each laboratory reports only one result for each sample and analytical variable. The results for sample A and B are plotted in a coordinate system in which the “true value” of sample A constitutes the x-axis and the “true value” of sample B the y-axis. Then, by plotting the individual results from each laboratory in the chart, producing one point for each laboratory (result from sample A along the x-axis and result from sample B along the y-axis), the distribution of the results among the laboratories is visualized (see Figures 1 - 20). Patterns in the distribution of the results can reveal systematic and/or random errors among the participating laboratories.

For example, if the results are affected by random errors only, the points will be spread randomly around the origo of the Youden chart. However, if systematic effects are influencing the results (e.g. from the use of different deviating analytical methods), the points in the chart will be distributed in a characteristic elliptical pattern along a 45° line in the chart. 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 is indicated in the Youden chart by a circle around the origo. The distance from the center of the circle and the point of an individual laboratory is a measure of the absolute error of the result. 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. Thus, the location of the point of each laboratory in the Youden’s diagram provides important information of the size and type of analytical error (random or systematic) present in the dataset, making it possible to indicate what is the source of deviation from the consensus of the participating laboratories.

Table 5. Uncertainty of the calculated “true value” for each parameter.

Parameter and unit	Sample	True value	Total no.	Robust std.dev.	Uncertainty	Expanded uncertainty
pH	A	6.91	30	0.179	0.041	0.082
	B	6.88	30	0.178	0.041	0.081
Conductivity (mS/m)	A	6.70	25	0.134	0.034	0.067
	B	6.71	25	0.138	0.034	0.069
Alkalinity (mmol/L)	A	0.211	20	0.0312	0.0087	0.0174
	B	0.208	20	0.0238	0.0067	0.0133
Nitrate + nitrite-nitrogen (µg/L)	A	115	25	11.5	2.9	5.7
	B	116	25	12.0	3.0	6.0
Chloride (mg/L)	A	9.3	28	0.49	0.11	0.23
	B	9.4	28	0.43	0.10	0.20
Sulphate (mg/L)	A	3.32	24	0.207	0.053	0.106
	B	3.34	24	0.231	0.059	0.118
Calcium (mg/L)	A	5.70	27	0.313	0.075	0.150
	B	5.70	28	0.392	0.093	0.185
Magnesium (mg/L)	A	0.65	28	0.037	0.009	0.017
	B	0.65	28	0.038	0.009	0.018
Sodium (mg/L)	A	5.09	26	0.233	0.057	0.114
	B	5.06	26	0.227	0.056	0.111
Potassium (mg/L)	A	0.91	26	0.054	0.013	0.027
	B	0.89	24	0.036	0.009	0.018
Total organic carbon (mg/L)	A	6.83	20	0.558	0.156	0.312
	B	6.96	20	0.585	0.164	0.327
Total phosphorus (µg/L)	A	24.20	20	5.253	1.468	2.937
	B	23.60	20	4.759	1.330	2.660
Aluminium (µg/L)	C	49	18	7.4	2.2	4.4
	D	48	18	8.2	2.4	4.8
Iron (µg/L)	C	108.90	23	9.695	2.527	5.054
	D	106.80	23	9.795	2.553	5.106
Manganese (µg/L)	C	3.68	19	0.401	0.115	0.230
	D	3.37	19	0.419	0.120	0.240
Cadmium (µg/L)	C	0.98	20	0.080	0.022	0.045
	D	0.97	20	0.088	0.025	0.049
Lead (µg/L)	C	2.31	20	0.203	0.057	0.113
	D	2.22	20	0.251	0.070	0.140
Copper (µg/L)	C	12.50	20	0.856	0.239	0.479
	D	11.20	19	0.581	0.166	0.333
Nickel (µg/L)	C	4.47	19	0.315	0.090	0.180
	D	4.31	20	0.311	0.087	0.174
Zinc (µg/L)	C	14.30	20	1.494	0.417	0.835
	D	14.25	20	1.894	0.529	1.059

Appendix D. Results reported by the participating laboratories

Table 6. Results reported by the participating laboratories.

Lab. nr.	pH, Units		Conductivity, mS/m		Alkalinity, mmol/L		Nitrate + nitrite- nitrogen, microg/L		Chloride, mg/L		Sulphate, mg/L	
	A	B	A	B	A	B	A	B	A	B	A	B
1							121	119	10.3	10.6	3.55	3.65
2	6.99	6.98	5.82	5.85	0.208	0.209	112	110	9.0	8.9	3.04	2.95
3	6.90	7.01	6.35	6.45			107	105	8.8	8.8	3.15	3.16
4	7.00	6.86	6.64	6.68	0.272	0.205	122	127	8.8	9.0	3.44	3.42
5	7.30	7.20	6.80	6.80	0.240	0.240	100	190	9.7	9.7		
6	7.05	6.99	68.40	68.10	0.271	0.269	100	110	9.1	9.3	3.03	3.04
7	7.00	6.96	6.88	6.77	0.214	0.212	102	97	9.4	9.2	3.21	3.21
8	6.88	6.88	6.68	6.69	0.211	0.212	123	120	9.4	9.4	3.38	3.36
9	6.91	6.87	0.67	0.68	0.208	0.208	123	118	9.4	9.4	3.49	3.47
10	6.93	6.92	67.30	67.70	0.250	0.180	381	382			1.17	1.16
11	6.56	6.64	6.73	6.78			157	158	9.9	10.0		
13	7.17	7.08	6.64	6.71	0.211	0.206	121	120	9.8	9.8	3.46	3.45
15	6.73	6.72	6.75	6.84	0.185	0.194	137	134	8.6	9.2	3.32	3.40
16	6.80	6.80	6.80	6.80	0.120	0.120	0	0	9.7	9.7	2.80	2.60
17	6.70	6.67	6.57	6.64	0.218	0.223	100	105	9.2	9.2	3.35	3.39
18	7.00	6.90	6.70	6.70			100	110	10.2	9.7	3.01	2.99
19	6.91	6.88	6.77	6.74					9.7	10.0	30.00	32.00
20												
21	6.50	6.57	5.98	6.04	0.209	0.201	113	111	7.7	7.8	4.00	3.97
22	7.19	7.12	6.64	6.76			111	105	8.9	9.0	3.26	3.25
23	6.81	6.75	6.72	6.73	0.232	0.228	103	94	8.6	8.6	1.43	1.43
24	6.72	6.60			0.250	0.260	134	126	6.2	6.2		
26	6.71	6.71	6.75	6.79			118	120	9.3	9.3	3.40	3.40
27	7.01	6.92	6.47	6.50	0.195	0.195	117	115	9.3	9.3	3.32	3.33
28												
29	6.89	6.86	7.60	7.68			108	111	9.9	10.0	3.30	3.20
30	6.91	6.85	6.87	6.88			0	0	9.4	9.4	3.33	3.34
31	6.76	6.76	6.81	6.84			130	130	9.1	9.2	3.10	3.10
32	7.01	6.91	6.61	6.64	0.201	0.202	119	118	9.4	9.5	3.41	3.42
33	7.01	6.91	6.74	6.92	0.214	0.213	112	112	9.3	9.2	3.27	3.26
34	6.67	6.62	6.66	6.63	0.190	0.189	122	123	9.4	9.4	3.35	3.38
35	6.98	7.30	6.75	6.59	0.130	0.100	108	166	9.3	9.5	9.50	10.60
36	7.07	7.03	6.62	6.64								

Lab. nr.	Calcium, mg/L		Magnesium, mg/L		Sodium, mg/L		Potassium, mg/L		Total organic carbon, mg/L		Total phosphorus, microg/L	
	A	B	A	B	A	B	A	B	A	B	A	B
1	6.09	6.25	0.70	0.68					7.14	7.42	41.00	41.00
2	5.37	5.41	0.59	0.60	5.15	5.16	0.88	0.89			29.00	34.00
3	5.55	5.70	0.62	0.62	5.01	5.07	0.90	0.87	8.04	8.02	28.00	27.00
4	5.50	5.48	0.65	0.64	5.07	5.04	0.81	0.82	6.76	7.17	19.90	22.80
5									7.30	7.10	25.00	25.00
6	5.97	6.49	0.65	0.70	5.23	5.68	1.08	1.18	7.05	7.13	34.00	33.00
7	5.60	5.70	0.66	0.66	5.10	5.32	0.91	1.17	5.93	5.83	18.40	19.20
8	6.08	6.14	0.65	0.65	5.18	5.18	0.93	0.93	6.55	6.81	25.60	26.50
9	5.70	5.64	0.66	0.63	5.10	5.02	0.96	0.94	6.10	6.30	24.50	23.20
10	5.74	5.81	0.65	0.66	4.75	4.78	0.87	0.88			17.60	16.34
11									8.80	8.77		
13	6.10	6.14	0.71	0.71	4.97	4.98	0.95	0.95	6.90	7.04	23.90	24.10
15	5.68	5.70	0.55	0.54	5.05	5.03	0.89	0.88	6.56	6.61		
16	4.23	4.29	0.58	0.60	5.32	5.17	0.86	0.83				
17	5.95	5.92	0.66	0.64	5.70	5.60	1.10	0.96	5.55	5.45	19.00	19.00
18									7.08	7.17		
19	5.25	5.22	0.67	0.66	4.55	4.53	1.02	0.91				
20												
21	5.66	5.70	0.61	0.61	5.06	5.04	0.90	0.89	7.00	6.88	55.30	52.50
22	5.81	5.91	0.68	0.67	4.61	4.62	0.94	0.94	6.75	6.86	29.00	28.00
23	5.45	5.52	0.62	0.62	5.03	5.04	0.86	0.88				
24	5.44	5.31	0.58	0.56	4.70	4.63	0.91	0.89			19.40	22.60
26	6.02	6.09	0.70	0.70	5.14	5.15	0.91	0.91			0.00	0.00
27	5.74	5.83	0.66	0.67	5.12	5.15	0.88	0.88	6.34	6.40	30.66	29.76
28												
29	6.10	6.30	0.63	0.61	5.40	5.00	1.01	0.91			20.00	24.00
30	5.85	5.81	0.67	0.67	5.20	5.20	0.95	0.91	6.56	6.48	22.00	23.00
31	5.83	5.89	0.68	0.66	5.18	5.18	0.92	0.90				
32	5.76	5.79	0.64	0.65	5.08	5.09	0.91	0.90	7.04	7.09	24.70	24.50
33	5.46	5.44	0.64	0.64	4.85	4.87	0.92	0.92	7.33	7.60	20.15	20.93
34	5.23	5.26	0.66	0.67	4.73	4.71	0.82	0.82	6.57	6.65	29.00	22.00
35	4.42	4.26	0.62	0.60	5.18	5.16	0.92	0.86				
36												

Lab. nr.	Aluminium, microg/L		Iron, microg/L		Manganese, microg/L		Cadmium, microg/L		Lead, microg/L		Copper, microg/L		Nickel, microg/L		Zinc, microg/L	
	C	D	C	D	C	D	C	D	C	D	C	D	C	D	C	D
1			108.80	106.80	3.68	3.37	1.01	1.01	2.53	2.40	13.31	12.10	4.68	4.54	14.48	14.97
2	49	48	123.70	119.50	3.64	3.24	1.06	1.02	2.37	2.28	12.95	11.53	4.43	4.41	16.94	16.80
3	50	49	108.90	105.10	3.58	3.02	1.01	0.97	2.13	2.06	12.30	10.80	4.53	4.31	14.10	13.70
4	49	48	106.00	103.00			1.03	0.98	2.28	2.20	12.30	10.90	4.47	4.31	15.10	14.80
5																
6																
7	38	40	120.00	120.00			0.95	0.94	2.20	2.10	12.40	11.80	3.40	2.80		
8	51	50	113.00	111.00	3.63	3.23	1.01	0.98	2.26	2.18	12.90	11.50	4.58	4.46	14.30	14.20
9																
10																
11																
13	86	85	150.90	144.20	4.60	4.00					23.70	22.70	6.40	6.20	24.50	24.00
15	41	43	105.00	103.00	3.90	3.84	0.97	0.99	2.22	2.19	11.03	10.36	4.51	4.53	15.43	17.45
16	47	46	90.59	82.91	3.42	3.00	0.91	0.90	2.35	2.28	0.03	0.03	4.66	4.52	13.81	13.96
17	33	24	93.00	67.00	3.00	2.00	0.80	0.60	2.10	1.40	14.50	9.50	3.80	2.80	13.00	9.00
18																
19	32	30	112.70	103.80	4.80	4.30	1.03	0.95	2.02	1.98	11.20	11.80	5.15	4.27	14.30	14.70
20	46	45	114.00	112.00	4.10	3.70					12.70	11.70			16.80	14.80
21	50	49	117.30	115.30	3.87	3.43	0.99	0.97	2.24	2.24	11.83	10.90	4.47	4.47	15.32	14.57
22	52	59	116.00	114.00	3.74	3.41	1.08	1.07	2.38	2.27	13.10	11.70	4.68	4.55	16.60	16.50
23	51	51	102.80	100.20	4.05	3.61	0.78	0.76	1.10	1.01	12.44	11.00	4.29	4.12	13.21	13.04
24																
26			103.38	106.10	3.18	3.57	0.97	0.93	2.16	2.14	12.19	10.84	4.47	4.28	15.15	14.96
27																
28							0.44	0.48	1.46	1.07	9.20	8.30				
29	30	31	110.40	109.30	3.57	3.10	0.95	1.08	1.41	1.34	13.00	11.05	3.99	3.69	10.57	10.25
30	71	69	101.00	98.00	3.60	3.30	0.93	0.89	2.34	2.20	12.00	11.00	4.30	4.10	14.00	14.00
31																
32	48	46	108.90	105.80	3.68	3.29	0.99	0.97	2.42	2.32	12.50	11.20	4.46	4.28	14.30	14.30
33	50	50	111.50	107.60	3.52	3.16	1.11	1.11	2.43	2.53	12.56	11.25	4.43	4.39	13.91	13.71
34	47	46	99.20	96.40	1.26	0.91	0.95	0.98	2.69	2.87	5.01	3.70	0.71	0.50	12.79	12.33
35	82	76	142.80	139.10	4.30	4.10	0.76	0.73	2.50	2.50	13.90	12.00	3.80	3.90	16.20	9.20
36																

Table 7.1. Statistics - pH**Sample A**

Analytical method: All
Unit: Units

Number of participants	30	Range	0.80
Number of omitted results	0	Variance	0.03
True value	6.91	Standard deviation	0.18
Mean value	6.90	Relative standard deviation	2.6%
Median value	6.91	Relative error	-0.1%

Analytical results in ascending order:

21	6.50	8	6.88	7	7.00
11	6.56	29	6.89	18	7.00
34	6.67	3	6.90	32	7.01
17	6.70	30	6.91	33	7.01
26	6.71	9	6.91	27	7.01
24	6.72	19	6.91	6	7.05
15	6.73	10	6.93	36	7.07
31	6.76	35	6.98	13	7.17
16	6.80	2	6.99	22	7.19
23	6.81	4	7.00	5	7.30

O = Omitted result

Sample B

Analytical method: All
Unit: Units

Number of participants	30	Range	0.73
Number of omitted results	0	Variance	0.03
True value	6.88	Standard deviation	0.17
Mean value	6.88	Relative standard deviation	2.5%
Median value	6.88	Relative error	-0.1%

Analytical results in ascending order:

21	6.57	30	6.85	27	6.92
24	6.60	29	6.86	7	6.96
34	6.62	4	6.86	2	6.98
11	6.64	9	6.87	6	6.99
17	6.67	19	6.88	3	7.01
26	6.71	8	6.88	36	7.03
15	6.72	18	6.90	13	7.08
23	6.75	33	6.91	22	7.12
31	6.76	32	6.91	5	7.20
16	6.80	10	6.92	35	7.30

O = Omitted result

Table 7.2. Statistics - Conductivity**Sample A**

Analytical method: All

Unit: mS/m

Number of participants	29	Range	1.06
Number of omitted results	4	Variance	0.06
True value	6.70	Standard deviation	0.25
Mean value	6.63	Relative standard deviation	3.8%
Median value	6.70	Relative error	-1.0%

Analytical results in ascending order:

9	0.67	O	4	6.64	19	6.77
2	5.82		34	6.66	16	6.80
21	5.98		8	6.68	5	6.80
3	6.35		18	6.70	31	6.81
27	6.47		23	6.72	30	6.87
17	6.57		11	6.73	7	6.88
32	6.61		33	6.74	29	7.60
36	6.62		15	6.75	10	67.30
22	6.64		26	6.75	6	68.40
13	6.64		35	6.75		

O = Omitted result

Sample B

Analytical method: All

Unit: mS/m

Number of participants	29	Range	1.07
Number of omitted results	4	Variance	0.06
True value	6.71	Standard deviation	0.24
Mean value	6.66	Relative standard deviation	3.6%
Median value	6.71	Relative error	-0.8%

Analytical results in ascending order:

9	0.68	O	4	6.68	5	6.80
2	5.85		8	6.69	16	6.80
21	6.04		18	6.70	31	6.84
3	6.45		13	6.71	15	6.84
27	6.50		23	6.73	30	6.88
35	6.59		19	6.74	33	6.92
34	6.63		22	6.76	29	7.68
36	6.64		7	6.77	10	67.70
17	6.64		11	6.78	6	68.10
32	6.64		26	6.79		

O = Omitted result

Table 7.3. Statistics - Alkalinity**Sample A**

Analytical method: All
Unit: mmol/L

Number of participants	20	Range	0.152
Number of omitted results	1	Variance	0.001
True value	0.211	Standard deviation	0.034
Mean value	0.216	Relative standard deviation	15.9%
Median value	0.211	Relative error	2.2%

Analytical results in ascending order:

16	0.120		2	0.208	23	0.232
35	0.130	O	21	0.209	5	0.240
15	0.185		8	0.211	10	0.250
34	0.190		13	0.211	24	0.250
27	0.195		7	0.214	6	0.271
32	0.201		33	0.214	4	0.272
9	0.208		17	0.218		

O = Omitted result

Sample B

Analytical method: All
Unit: mmol/L

Number of participants	20	Range	0.149
Number of omitted results	1	Variance	0.001
True value	0.208	Standard deviation	0.031
Mean value	0.209	Relative standard deviation	14.9%
Median value	0.208	Relative error	0.4%

Analytical results in ascending order:

35	0.100	O	32	0.202	33	0.213
16	0.120		4	0.205	17	0.223
10	0.180		13	0.206	23	0.228
34	0.189		9	0.208	5	0.240
15	0.194		2	0.209	24	0.260
27	0.195		7	0.212	6	0.269
21	0.201		8	0.212		

O = Omitted result

Table 7.4. Statistics - Nitrate + nitrite-nitrogen*Sample A*

Analytical method: All

Unit: microg/L

Number of participants	29	Range	37
Number of omitted results	5	Variance	112
True value	115	Standard deviation	11
Mean value	115	Relative standard deviation	9.2%
Median value	115	Relative error	0.4%

Analytical results in ascending order:

16	0	O	29	108	34	122
30	0	O	22	111	4	122
18	100		33	112	9	123
17	100		2	112	8	123
6	100		21	113	31	130
5	100	O	27	117	24	134
7	102		26	118	15	137
23	103		32	119	11	157
3	107		13	121	10	381
35	108		1	121		

O = Omitted result

Sample B

Analytical method: All

Unit: microg/L

Number of participants	29	Range	72
Number of omitted results	5	Variance	205
True value	116	Standard deviation	14
Mean value	117	Relative standard deviation	12.3%
Median value	116	Relative error	0.4%

Analytical results in ascending order:

16	0	O	21	111	34	123
30	0	O	29	111	24	126
23	94		33	112	4	127
7	97		27	115	31	130
3	105		32	118	15	134
17	105		9	118	11	158
22	105		1	119	35	166
6	110		26	120	5	190
2	110		8	120	10	382
18	110		13	120		

O = Omitted result

Table 7.5. Statistics - Chloride**Sample A**

Analytical method: All
Unit: mg/L

Number of participants	29	Range	2.6
Number of omitted results	1	Variance	0.3
True value	9.3	Standard deviation	0.5
Mean value	9.3	Relative standard deviation	5.8%
Median value	9.3	Relative error	-0.3%

Analytical results in ascending order:

24	6.2	O	17	9.2	9	9.4
21	7.7		26	9.3	19	9.7
15	8.6		27	9.3	5	9.7
23	8.6		33	9.3	16	9.7
3	8.8		35	9.3	13	9.8
4	8.8		30	9.4	29	9.9
22	8.9		32	9.4	11	9.9
2	9.0		7	9.4	18	10.2
31	9.1		8	9.4	1	10.3
6	9.1		34	9.4		

O = Omitted result

Sample B

Analytical method: All
Unit: mg/L

Number of participants	29	Range	2.8
Number of omitted results	1	Variance	0.3
True value	9.4	Standard deviation	0.5
Mean value	9.4	Relative standard deviation	5.5%
Median value	9.4	Relative error	0.0%

Analytical results in ascending order:

24	6.2	O	33	9.2	35	9.5
21	7.8		7	9.2	18	9.7
23	8.6		26	9.3	5	9.7
3	8.8		27	9.3	16	9.7
2	8.9		6	9.3	13	9.8
22	9.0		30	9.4	11	10.0
4	9.0		8	9.4	29	10.0
15	9.2		9	9.4	19	10.0
17	9.2		34	9.4	1	10.6
31	9.2		32	9.5		

O = Omitted result

Table 7.6. Statistics - Sulphate*Sample A*

Analytical method: All

Unit: mg/L

Number of participants	28	Range	1.20
Number of omitted results	4	Variance	0.06
True value	3.32	Standard deviation	0.25
Mean value	3.28	Relative standard deviation	7.6%
Median value	3.32	Relative error	-1.1%

Analytical results in ascending order:

10	1.17	O	22	3.26	32	3.41
23	1.43	O	33	3.27	4	3.44
16	2.80		29	3.30	13	3.46
21	2.83		15	3.32	9	3.49
18	3.01		27	3.32	1	3.55
6	3.03		30	3.33	21	4.00
2	3.04		17	3.35	35	9.50
31	3.10		34	3.35	19	30.00
3	3.15		8	3.38		
7	3.21		26	3.40		

O = Omitted result

Sample B

Analytical method: All

Unit: mg/L

Number of participants	28	Range	1.37
Number of omitted results	4	Variance	0.08
True value	3.34	Standard deviation	0.28
Mean value	3.27	Relative standard deviation	8.7%
Median value	3.34	Relative error	-2.0%

Analytical results in ascending order:

10	1.16	O	7	3.21	32	3.42
23	1.43	O	22	3.25	4	3.42
16	2.60		33	3.26	13	3.45
21	2.73		27	3.33	9	3.47
2	2.95		30	3.34	1	3.65
18	2.99		8	3.36	21	3.97
6	3.04		34	3.38	35	10.60
31	3.10		17	3.39	19	32.00
3	3.16		15	3.40		
29	3.20		26	3.40		

O = Omitted result

Table 7.7. Statistics - Calcium**Sample A**

Analytical method: All
Unit: mg/L

Number of participants	28	Range	1.68
Number of omitted results	1	Variance	0.13
True value	5.70	Standard deviation	0.36
Mean value	5.66	Relative standard deviation	6.3%
Median value	5.70	Relative error	-0.7%

Analytical results in ascending order:

16	4.23	O	3	5.55	30	5.85
35	4.42		7	5.60	17	5.95
34	5.23		21	5.66	6	5.97
19	5.25		15	5.68	26	6.02
2	5.37		9	5.70	8	6.08
24	5.44		27	5.74	1	6.09
23	5.45		10	5.74	29	6.10
33	5.46		32	5.76	13	6.10
4	5.50		22	5.81		
26	5.52		31	5.83		

O = Omitted result

Sample B

Analytical method: All
Unit: mg/L

Number of participants	28	Range	2.23
Number of omitted results	1	Variance	0.19
True value	5.70	Standard deviation	0.43
Mean value	5.71	Relative standard deviation	7.6%
Median value	5.70	Relative error	0.2%

Analytical results in ascending order:

35	4.26		9	5.64	22	5.91
16	4.29	O	21	5.70	17	5.92
19	5.22		7	5.70	26	6.09
34	5.26		15	5.70	13	6.14
24	5.31		3	5.70	8	6.14
2	5.41		32	5.79	1	6.25
33	5.44		10	5.81	29	6.30
4	5.48		30	5.81	6	6.49
26	5.52		27	5.83		
23	5.52		31	5.89		

O = Omitted result

Table 7.8. Statistics - Magnesium**Sample A**

Analytical method: All
Unit: mg/L

Number of participants	28	Range	0.16
Number of omitted results	0	Variance	0.00
True value	0.65	Standard deviation	0.04
Mean value	0.64	Relative standard deviation	5.8%
Median value	0.65	Relative error	-1.1%

Analytical results in ascending order:

15	0.55	32	0.64	9	0.66
16	0.58	33	0.64	19	0.67
24	0.58	6	0.65	30	0.67
2	0.59	4	0.65	22	0.68
21	0.61	8	0.65	31	0.68
35	0.62	10	0.65	1	0.70
23	0.62	27	0.66	26	0.70
3	0.62	34	0.66	13	0.71
29	0.63	7	0.66		
26	0.63	17	0.66		

O = Omitted result

Sample B

Analytical method: All
Unit: mg/L

Number of participants	28	Range	0.17
Number of omitted results	0	Variance	0.00
True value	0.65	Standard deviation	0.04
Mean value	0.64	Relative standard deviation	6.2%
Median value	0.65	Relative error	-0.6%

Analytical results in ascending order:

15	0.54	4	0.64	34	0.67
24	0.56	17	0.64	27	0.67
35	0.60	33	0.64	30	0.67
16	0.60	26	0.64	22	0.67
2	0.60	32	0.65	1	0.68
29	0.61	8	0.65	6	0.70
21	0.61	7	0.66	26	0.70
23	0.62	31	0.66	13	0.71
3	0.62	10	0.66		
9	0.63	19	0.66		

O = Omitted result

Table 7.9. Statistics - Sodium**Sample A**

Analytical method: All
Unit: mg/L

Number of participants	26	Range	1.15
Number of omitted results	0	Variance	0.06
True value	5.09	Standard deviation	0.25
Mean value	5.06	Relative standard deviation	4.9%
Median value	5.09	Relative error	-0.7%

Analytical results in ascending order:

19	4.55	15	5.05	8	5.18
22	4.61	21	5.06	35	5.18
24	4.70	4	5.07	31	5.18
34	4.73	32	5.08	30	5.20
10	4.75	9	5.10	6	5.23
33	4.85	7	5.10	16	5.32
13	4.97	27	5.12	29	5.40
3	5.01	26	5.14	17	5.70
23	5.03	2	5.15		

O = Omitted result

Sample B

Analytical method: All
Unit: mg/L

Number of participants	26	Range	1.15
Number of omitted results	0	Variance	0.07
True value	5.06	Standard deviation	0.26
Mean value	5.05	Relative standard deviation	5.2%
Median value	5.06	Relative error	0.0%

Analytical results in ascending order:

19	4.53	15	5.03	35	5.16
22	4.62	21	5.04	16	5.17
24	4.63	23	5.04	8	5.18
34	4.71	4	5.04	31	5.18
10	4.78	3	5.07	30	5.20
33	4.87	32	5.09	7	5.32
13	4.98	26	5.15	17	5.60
29	5.00	27	5.15	6	5.68
9	5.02	2	5.16		

U = Omitted result

Table 7.10. Statistics - Potassium**Sample A**

Analytical method: All

Unit: mg/L

Number of participants	26	Range	0.29
Number of omitted results	2	Variance	0.00
True value	0.91	Standard deviation	0.06
Mean value	0.92	Relative standard deviation	6.9%
Median value	0.91	Relative error	0.7%

Analytical results in ascending order:

4	0.81	3	0.90	22	0.94
34	0.82	32	0.91	13	0.95
16	0.86	24	0.91	30	0.95
23	0.86	7	0.91	9	0.96
10	0.87	26	0.91	29	1.01
2	0.88	35	0.92	19	1.02
27	0.88	31	0.92	6	1.08
15	0.89	33	0.92	17	1.10
21	0.90	8	0.93		

O = Omitted result

Sample B

Analytical method: All

Unit: mg/L

Number of participants	26	Range	0.14
Number of omitted results	2	Variance	0.00
True value	0.89	Standard deviation	0.04
Mean value	0.89	Relative standard deviation	4.2%
Median value	0.89	Relative error	-0.1%

Analytical results in ascending order:

34	0.82	24	0.89	33	0.92
4	0.82	21	0.89	8	0.93
16	0.83	2	0.89	22	0.94
35	0.86	32	0.90	9	0.94
3	0.87	31	0.90	13	0.95
10	0.88	29	0.91	17	0.96
23	0.88	19	0.91	7	1.17
15	0.88	30	0.91	6	1.18
27	0.88	26	0.91		

O = Omitted result

Table 7.11. Statistics – Total organic carbon**Sample A**

Analytical method: All

Unit: mg/L

Number of participants	20	Range	3.25
Number of omitted results	0	Variance	0.51
True value	6.83	Standard deviation	0.71
Mean value	6.87	Relative standard deviation	10.4%
Median value	6.83	Relative error	0.6%

Analytical results in ascending order:

17	5.55	34	6.57	18	7.08
7	5.93	22	6.75	1	7.14
9	6.10	4	6.76	5	7.30
27	6.34	13	6.90	33	7.33
8	6.55	21	7.00	3	8.04
30	6.56	32	7.04	11	8.80
15	6.56	6	7.05		

O = Omitted result

Sample B

Analytical method: All

Unit: mg/L

Number of participants	20	Range	3.32
Number of omitted results	0	Variance	0.52
True value	6.96	Standard deviation	0.72
Mean value	6.94	Relative standard deviation	10.4%
Median value	6.96	Relative error	-0.3%

Analytical results in ascending order:

17	5.45	8	6.81	18	7.17
7	5.83	22	6.86	4	7.17
9	6.30	21	6.88	1	7.42
27	6.40	13	7.04	33	7.60
30	6.48	32	7.09	3	8.02
15	6.61	5	7.10	11	8.77
34	6.65	6	7.13		

O = Omitted result

Table 7.12. Statistics – Total phosphorus**Sample A**

Analytical method: All
Unit: microg/L

Number of participants	23	Range	16.40
Number of omitted results	3	Variance	23.71
True value	24.20	Standard deviation	4.87
Mean value	23.87	Relative standard deviation	20.4%
Median value	24.20	Relative error	-1.4%

Analytical results in ascending order:

26	0.00	O	33	20.15	22	29.00
10	17.60		30	22.00	34	29.00
10	17.60		13	23.90	2	29.00
7	18.40		9	24.50	27	30.66
17	19.00		32	24.70	6	34.00
24	19.40		5	25.00	1	41.00
4	19.90		8	25.60	21	55.30
29	20.00		3	28.00		O

O = Omitted result

Sample B

Analytical method: All
Unit: microg/L

Number of participants	23	Range	17.70
Number of omitted results	3	Variance	22.69
True value	23.60	Standard deviation	4.76
Mean value	24.06	Relative standard deviation	19.8%
Median value	23.60	Relative error	2.0%

Analytical results in ascending order:

26	0.00	O	4	22.80	3	27.00
10	16.30		30	23.00	22	28.00
10	16.34		9	23.20	27	29.76
17	19.00		29	24.00	6	33.00
7	19.20		13	24.10	2	34.00
33	20.93		32	24.50	1	41.00
34	22.00		5	25.00	21	52.50
24	22.60		8	26.50		O

O = Omitted result

Table 7.13. Statistics - Aluminium**Sample C**

Analytical method: All
Unit: microg/L

Number of participants	20	Range	41
Number of omitted results	3	Variance	81
True value	49	Standard deviation	9
Mean value	47	Relative standard deviation	19.0%
Median value	49	Relative error	-4.1%

Analytical results in ascending order:

29	30	34	47	8	51	
19	32	32	48	23	51	
17	33	O	2	49	22	52
7	38	4	49	30	71	
15	41	21	50	35	82	O
20	46	33	50	13	86	O
16	47	3	50			

O = Omitted result

Sample D

Analytical method: All
Unit: microg/L

Number of participants	20	Range	39
Number of omitted results	3	Variance	83
True value	48	Standard deviation	9
Mean value	47	Relative standard deviation	19.3%
Median value	48	Relative error	-2.2%

Analytical results in ascending order:

17	24	O	34	46	33	50
19	30	32	46	23	51	
29	31	2	48	22	59	
7	40	4	48	30	69	
15	43	21	49	35	76	O
20	45	3	49	13	85	O
16	46	8	50			

O = Omitted result

Table 7.14. Statistics - Iron**Sample C**

Analytical method: All
Unit: microg/L

Number of participants	23	Range	60.31
Number of omitted results	0	Variance	187.47
True value	108.90	Standard deviation	13.69
Mean value	111.56	Relative standard deviation	12.3%
Median value	108.90	Relative error	2.4%

Analytical results in ascending order:

16	90.59	13	106.00	20	114.00
17	93.00	1	108.80	22	116.00
34	99.20	3	108.90	21	117.30
30	101.00	32	108.90	7	120.00
23	102.80	29	110.40	2	123.70
26	103.38	33	111.50	35	142.80
15	105.00	19	112.70	13	150.90
4	106.00	8	113.00		

O = Omitted result

Sample D

Analytical method: All
Unit: microg/L

Number of participants	23	Range	77.20
Number of omitted results	0	Variance	244.12
True value	106.80	Standard deviation	15.62
Mean value	107.87	Relative standard deviation	14.5%
Median value	106.80	Relative error	1.0%

Analytical results in ascending order:

17	67.00	3	105.10	20	112.00
16	82.91	32	105.80	22	114.00
34	96.40	26	106.10	21	115.30
30	98.00	1	106.80	2	119.50
23	100.20	33	107.60	7	120.00
15	103.00	29	109.30	35	139.10
4	103.00	8	111.00	13	144.20
19	103.80	13	111.00		

O = Omitted result

Table 7.15. Statistics - Manganese**Sample C**

Analytical method: All
Unit: microg/L

Number of participants	20	Range	1.80
Number of omitted results	1	Variance	0.20
True value	3.68	Standard deviation	0.44
Mean value	3.78	Relative standard deviation	11.7%
Median value	3.68	Relative error	2.8%

Analytical results in ascending order:

34	1.26	O	30	3.60	15	3.90
17	3.00		8	3.63	23	4.05
26	3.18		2	3.64	20	4.10
16	3.42		1	3.68	35	4.30
33	3.52		32	3.68	13	4.60
29	3.57		22	3.74	19	4.80
3	3.58		21	3.87		

O = Omitted result

Sample D

Analytical method: All
Unit: microg/L

Number of participants	20	Range	2.30
Number of omitted results	1	Variance	0.25
True value	3.37	Standard deviation	0.50
Mean value	3.40	Relative standard deviation	14.7%
Median value	3.37	Relative error	1.1%

Analytical results in ascending order:

34	0.91	O	2	3.24	23	3.61
17	2.00		32	3.29	20	3.70
16	3.00		30	3.30	15	3.84
3	3.02		1	3.37	13	4.00
29	3.10		22	3.41	35	4.10
33	3.16		21	3.43	19	4.30
8	3.23		26	3.57		

O = Omitted result

Table 7.16. Statistics - Cadmium**Sample C**

Analytical method: All
Unit: microg/L

Number of participants	21	Range	0.35
Number of omitted results	1	Variance	0.01
True value	0.98	Standard deviation	0.09
Mean value	0.96	Relative standard deviation	9.7%
Median value	0.98	Relative error	-1.8%

Analytical results in ascending order:

28	0.44	O	29	0.95	8	1.01
35	0.76		7	0.95	1	1.01
23	0.78		15	0.97	19	1.03
17	0.80		26	0.97	4	1.03
16	0.91		32	0.99	2	1.06
30	0.93		21	0.99	22	1.08
34	0.95		3	1.01	33	1.11

O = Omitted result

Sample D

Analytical method: All
Unit: microg/L

Number of participants	21	Range	0.51
Number of omitted results	1	Variance	0.01
True value	0.97	Standard deviation	0.12
Mean value	0.94	Relative standard deviation	13.0%
Median value	0.97	Relative error	-3.0%

Analytical results in ascending order:

28	0.48	O	7	0.94	4	0.98
17	0.60		19	0.95	15	0.99
35	0.73		21	0.97	1	1.01
23	0.76		3	0.97	2	1.02
30	0.89		32	0.97	22	1.07
16	0.90		8	0.98	29	1.08
26	0.93		34	0.98	33	1.11

O = Omitted result

Table 7.17. Statistics - Lead**Sample C**

Analytical method: All
Unit: microg/L

Number of participants	21	Range	0.67
Number of omitted results	3	Variance	0.03
True value	2.31	Standard deviation	0.17
Mean value	2.31	Relative standard deviation	7.2%
Median value	2.31	Relative error	0.1%

Analytical results in ascending order:

23	1.10	O	7	2.20	2	2.37
29	1.41	O	15	2.22	22	2.38
28	1.46	O	21	2.24	32	2.42
19	2.02		8	2.26	33	2.43
17	2.10		4	2.28	35	2.50
3	2.13		30	2.34	1	2.53
26	2.16		16	2.35	34	2.69

O = Omitted result

Sample D

Analytical method: All
Unit: microg/L

Number of participants	21	Range	1.47
Number of omitted results	3	Variance	0.08
True value	2.22	Standard deviation	0.29
Mean value	2.23	Relative standard deviation	13.0%
Median value	2.22	Relative error	0.4%

Analytical results in ascending order:

23	1.01	O	26	2.14	2	2.28
28	1.07	O	8	2.18	16	2.28
29	1.34	O	15	2.19	32	2.32
17	1.40		4	2.20	1	2.40
19	1.98		30	2.20	35	2.50
3	2.06		21	2.24	33	2.53
7	2.10		22	2.27	34	2.87

O = Omitted result

Table 7.18. Statistics - Copper**Sample C**

Analytical method: All
Unit: microg/L

Number of participants	23	Range	3.47
Number of omitted results	4	Variance	0.68
True value	12.50	Standard deviation	0.82
Mean value	12.58	Relative standard deviation	6.6%
Median value	12.50	Relative error	0.7%

Analytical results in ascending order:

16	0.03	O	3	12.30	2	12.95
34	5.01	O	4	12.30	29	13.00
28	9.20	O	7	12.40	22	13.10
15	11.03		23	12.44	1	13.31
19	11.20		32	12.50	35	13.90
21	11.83		33	12.56	17	14.50
30	12.00		20	12.70	13	23.70
26	12.19		8	12.90		O

O = Omitted result

Sample D

Analytical method: All
Unit: microg/L

Number of participants	23	Range	2.60
Number of omitted results	4	Variance	0.39
True value	11.20	Standard deviation	0.63
Mean value	11.21	Relative standard deviation	5.6%
Median value	11.20	Relative error	0.1%

Analytical results in ascending order:

16	0.03	O	4	10.90	22	11.70
34	3.70	O	23	11.00	20	11.70
28	8.30	O	30	11.00	7	11.80
17	9.50		29	11.05	19	11.80
15	10.36		32	11.20	35	12.00
3	10.80		33	11.25	1	12.10
26	10.84		8	11.50	13	22.70
21	10.90		2	11.53		O

O = Omitted result

Table 7.19. Statistics - Nickel**Sample C**

Analytical method: All
Unit: microg/L

Number of participants	21	Range	1.75
Number of omitted results	2	Variance	0.15
True value	4.47	Standard deviation	0.39
Mean value	4.37	Relative standard deviation	9.0%
Median value	4.47	Relative error	-2.1%

Analytical results in ascending order:

34	0.71	O	33	4.43	3	4.53
7	3.40		2	4.43	8	4.58
35	3.80		32	4.46	16	4.66
17	3.80		21	4.47	1	4.68
29	3.99		26	4.47	22	4.68
23	4.29		4	4.47	19	5.15
30	4.30		15	4.51	13	6.40
						O

O = Omitted result

Sample D

Analytical method: All
Unit: microg/L

Number of participants	21	Range	1.75
Number of omitted results	2	Variance	0.27
True value	4.31	Standard deviation	0.52
Mean value	4.14	Relative standard deviation	12.6%
Median value	4.31	Relative error	-3.9%

Analytical results in ascending order:

34	0.50	O	19	4.27	8	4.46
7	2.80		26	4.28	21	4.47
17	2.80		32	4.28	16	4.52
29	3.69		3	4.31	15	4.53
35	3.90		4	4.31	1	4.54
30	4.10		33	4.39	22	4.55
23	4.12		2	4.41	13	6.20
						O

O = Omitted result

Table 7.20. Statistics - Zinc**Sample C**

Analytical method: All
Unit: microg/L

Number of participants	21	Range	6.37
Number of omitted results	1	Variance	2.34
True value	14.30	Standard deviation	1.53
Mean value	14.52	Relative standard deviation	10.5%
Median value	14.30	Relative error	1.5%

Analytical results in ascending order:

29	10.57	3	14.10	21	15.32
34	12.79	19	14.30	15	15.43
17	13.00	8	14.30	35	16.20
23	13.21	32	14.30	22	16.60
16	13.81	1	14.48	20	16.80
33	13.91	4	15.10	2	16.94
30	14.00	26	15.15	13	24.50

O = Omitted result

Sample D

Analytical method: All
Unit: microg/L

Number of participants	21	Range	8.45
Number of omitted results	1	Variance	5.04
True value	14.25	Standard deviation	2.24
Mean value	13.86	Relative standard deviation	16.2%
Median value	14.25	Relative error	-2.7%

Analytical results in ascending order:

17	9.00	16	13.96	4	14.80
35	9.20	30	14.00	26	14.96
29	10.25	8	14.20	1	14.97
34	12.33	32	14.30	22	16.50
23	13.04	21	14.57	2	16.80
3	13.70	19	14.70	15	17.45
33	13.71	20	14.80	13	24.00

O = Omitted result

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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- Anker Halvorsen, G., Johannessen, A. and Landås, T.S. 2016. Biological intercalibration: Invertebrates 2016. NIVA report SNO 7089-2016. **ICP Waters report 130/2016.**
- Escudero-Oñate, C. 2016. Intercomparison 1630: pH, Conductivity, Alkalinity, NO₃-N, Cl, SO₄, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA report SNO 7081-2016. **ICP Waters report 129/2016.**

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