NIVA REPORT SNO 7681-2021

ICP Waters Report 147/2021

Intercomparison 2135: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Tot-P, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn

Photo: Anne Lise Ribeiro

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

Convention on Long-Range Transboundary Air Pollution

LRTAP Long-range Transboundary Air Pollution

Norwegian Institute for Water Research

REPORT

Main Office
Økernveien 94
NO-0579 Oslo, Norway
Phone (47) 22 18 51 00

NIVA Region South
Jon Lilletuns vei 3
NO-4879 Grimstad, Norway
Phone (47) 22 18 51 00

NIVA Region East
Sandvikaveien 59
NO-2312 Ottestad, Norway
Phone (47) 22 18 51 00

NIVA Region West
Thormøhlensgate 53 D
NO-5006 Bergen Norway
Phone (47) 22 18 51 00

NIVA Denmark
Njalsgade 76, 4th floor
DK 2300 Copenhagen S, Denmark
Phone (45) 39 17 97 33

Internet: www.niva.no

Title	Serial number	Date
Intercomparison 2135: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Tot-P, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn	NIVA 7681-2021 ICP Waters report 147/2021	09.12.2021
Author(s) Tina Bryntesen	Topic group Environmental monitoring	Distribution Open
	Geographical area Europe, North America, Russian Federation	Pages 38 + appendix

Client(s)	Client's contact person
Norwegian Ministry of Climate and Environment United Nations Economic Commission for Europe (UNECE)	Eli Marie Åsen
Client's publication: ICP Waters report	Printed NIVA Project number 10300

Summary

Thirty-two laboratories from 17 countries accepted the invitation to join the ICP Waters chemical intercomparison and thirty of these successfully reported their 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 not as good as previous years, with an overall acceptance rate of 65% (± 20% of the "true value", and for pH and conductivity ± 0.2 pH units and ± 10%, respectively). The lower acceptance rates can be explained by low concentrations of most of the analytes this year. The highest acceptance rates (> 80%) were obtained for some of the ions, with a maximum of 91% for sulphate. The lowest acceptance rates were for lead and total phosphorus, at 24% and 29% respectively. For lead, an error causing shipment of unpreserved metal samples to the participants may have biased the results and contributed to the low acceptance rate. 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.

Four keywords	Fire emneord
1. Intercomparison	1. Laboratoriesammenligning
2. Acid precipitation	2. Sur nedbør
3. Quality control	3. Kvalitetskontroll
4. ICP Waters	4. ICP Waters

This report is quality assured in accordance with NIVA's quality system and approved by:

Tina Bryntesen	*Øyvind Garmo*	*Sondre Meland*
Main Author	Quality Assurance	Research Manager

ISBN 978-82-577-7417-2
NIVA-report ISSN 1894-7948

CONVENTION OF LONG-RANGE TRANSBOUNDARY AIR POLLUTION

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

Intercomparison 2135
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 2021

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, Bergen. ICP Waters is supported financially by the Norwegian Ministry of Climate and Environment 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 35th intercomparison of chemical analyses.

Oslo, December 2021

Tina Bryntesen
ICP Waters Programme Centre

Table of contents

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 with their methods of choice analyse the sample for a set repertoire of parameters. Then, the results are compiled and analysed using the Youden statistical test. The "true value" for each parameter 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 2135 edition of the test was conducted in the period from May to November 2021. A total of 32 laboratories representing 17 different countries signed up and among these, 30 laboratories representing 16 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 typically at $\pm$ 20% of the "true value", except for pH and conductivity ($\pm$ 0.2 pH units and $\pm$ 10%, respectively).

Overall, the acceptance rates for the 2135 edition were lower than the results from recent years. 65% of the results were within the target threshold (the median of all the parameter acceptance rates). Several different factors can influence the acceptance rate, such as the concentration of the analyte in the sample and the choice of analytical techniques among the laboratories. This year, the concentrations of many analytes were very low, which likely was a strong contributor to the lower acceptance rates.

The highest acceptance rates (>80%) were obtained for some of the ions, with a maximum of 91% for sulphate, then 89% and 83% for sodium and chloride, respectively. The poorest acceptance rates were obtained for lead and total phosphorus, with 24% and 29%, respectively. For lead, the results may be biased and the true values could be higher than what the statistics show. For total phosphorous, the results are also spread out systematically, with a grouping at a concentration level higher than the estimated true values. Even though most participants determined total phosphorus using the same principle, there may be some differences in the methods, giving rise to systematic differences in the measured values.

For several of the parameters, different analytical techniques had been used by the various laboratories. The use of different techniques can give systematically different results, with the effect typically being more severe for low analyte concentrations. For several of the ions, five and six different techniques had been used, while for the metals the number of different techniques was at three to five. Some overall patterns in preferred techniques could be found: Ion chromatography was preferred for the determination of the negatively charged ions, and ion chromatography or some form of plasma technique (ICP-OES/ICP-MS) were most frequently employed for the positively charged ions. For all the metals, the sensitive ICP-MS was the preferred technique. 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.

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) to assess 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 affect 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 systematically 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 distribution of the results *perpendicular to* the 45° angled line.

This thirty-fifth chemical intercomparison test, called 2135, 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 if 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. This issue has persisted in the inter-laboratory harmonisation.

The criteria for acceptable results were for most variables ± 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 ± 10%, respectively.

3 Results and Discussion

In the 2135 edition of the chemical intercomparison test, a total of 32 laboratories (representing 17 different countries) registered to participate, and 30 of the laboratories representing 16 different countries successfully registered their results. Information about the participating laboratories is provided in Appendix A, both by the identity of the laboratories (Table A. 1) and by a summary of the different countries represented (Table A. 2). 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 2135 chemical intercomparison test are summarised, constituting for each parameter: the number of participants, the acceptance ratio, and for comparison the acceptance ratio from the three previous years. Overall, the results were not as good as the previous years, with the median of the acceptance ratio indicating that 65% of the results were within the general target accuracy of 20%, or the special accuracy limit for pH and conductivity ($\pm$ 0.2 pH units and $\pm$ 10% respectively). The lower acceptance ratios of this year can mostly be explained by the samples having low concentrations of analytes, in many cases lower than what has been seen the last 20 years. In addition, the sample pair for metals was due to an error not acidified before shipment. If participants have not acidified the sample directly in the bottle, there is the potential of underestimating the metal concentration in the sample due to elements adhering to the bottle walls, which again can lead to a bias in the reported results.

Throughout this chapter the results for each variable will be presented and discussed based on acceptance ratio (Table 1) and the visual distribution of the results in the Youden chart (Figures 1-20). In the Youden chart, the results from each laboratory is presented as one point, and the distribution of points can indicate the occurrence of random and/or systematic errors among the laboratories. The acceptance limit (typically $\pm$ 20 % of the mean true values for the sample pair) is illustrated in the charts as a circle. Note that laboratories with results that strongly deviated from the others has been excluded from the charts. Information on the different analytical techniques used by the laboratories is shown in Table 2. Factors that are typically found to influence the degree of compliance among the laboratories are low parameter values, the use of several different analytical methods for the determination of the same parameter, both leading to increased variability in the results.

For more detailed information on the uncertainty of the “true values” see Table C. 1 (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 D.1 (Appendix D), and more detailed statistics for each parameter is presented in Tables D.2.1 to D.2.20 (Appendix D).

Table 1. Summary of the results including the true values, number of participating laboratories, and acceptance rate in the 2135 edition and the three previous years (2034, 1933, and 1832) for each parameter

Parameter	Sample	True value		Acceptable	Number of pairs		Acceptable results for intercalibration (%)			
(unit)	pair	Sample 1	Sample 2	limit, % *	Tot.	Accept.	2135	2034	1933	1832
pH	AB	6.31	6.38	3,15	26	17	65	75	60	81
Conductivity (mS/m)	AB	1.21	1.1	10	25	16	64	80	79	85
Alkalinity (mmol/L)	AB	0.036	0.032	20	19	8	42	44	62	0
Nitrate+nitrite-nitrogen (µg/L)	AB	84.5	77.3	20	20	10	50	47	69	85
Chloride (mg/L)	AB	1.11	1.01	20	23	19	83	90	93	81
Sulphate (mg/L)	AB	0.747	0.675	20	23	21	91	76	75	96
Calcium (mg/L)	AB	1.00	0.91	20	29	20	69	89	90	93
Magnesium (mg/L)	AB	0.170	0.154	20	28	20	71	95	93	82
Sodium (mg/L)	AB	0.835	0.762	20	28	25	89	100	96	86
Potassium (mg/L)	AB	0.151	0.14	20	27	20	74	95	85	82
Total organic carbon (mg/L)	AB	2.51	2.40	20	17	12	71	73	80	74
Total phosphorous (µg/L)	AB	13.8	13.0	20	21	6	29	41	35	33
Aluminium (µg/L)	CD	52.3	47.2	20	18	12	67	80	55	57
Iron (µg/L)	CD	11.2	10.9	20	18	10	56	94	76	95
Manganese (µg/L)	CD	2.67	2.96	20	17	11	65	93	71	91
Cadmium (µg/L)	CD	0.507	0.465	20	18	10	56	94	77	88
Lead (µg/L)	CD	1.63	1.26	20	17	4	24	88	73	65
Copper (µg/L)	CD	5.58	4.72	20	20	14	70	94	75	84
Nickel (µg/L)	CD	2.72	2.45	20	18	13	72	94	77	87
Zinc (µg/L)	CD	14.1	12.9	20	18	13	72	80	61	91
Total					430	281	65	(81)	(75)	(79)

3.1 pH

Values of pH were reported by 26 laboratories, among which 65% were within the acceptable limit (± 0.2 pH units of the "true value", Table 1). This was a relatively good accomplishment. During previous years, pH has typically been associated with poor acceptance ratio and this has been attributed to the use of different measuring methods. E.g. the different practices of stirring or not stirring the sample during determination can give a systematic error, and this is especially the case for samples with lower total ionic strength (4, 5). This year, the number of laboratories using each of the different was relatively evenly distributed and this may have contributed to unity in the reported results, e.g. no heavy bias towards one measurement technique (Table 2). The most used method was electrometric determination with stirring (11 laboratories), without stirring (8 laboratories), and with equilibration (5 laboratories). The last 2 participants reported to have used an unspecified method. The Youden chart showed that random error dominates the distribution of the results for pH (Figure 1).

It is important to remember that pH is a very sensitive parameter to determine, and that sample storage and handling, as well as the use of different analytical techniques can affect the results. This parameter should be determined as soon as possible after the samples have arrived at the laboratory.

3.2 Conductivity

In this 2135 edition, conductivity was measured by 25 laboratories and showed an acceptance rate of 64%. This is a low acceptance rate for conductivity, and much lower than the last years (Table 1). The last years, the conductivity has normally been around 6 mS/m, so the poor acceptance rate can be explained by samples having a low conductivity with values at only 1.10 and 1.21 mS/m. As the acceptance limit is set at 10% for this parameter, small variations will lead to results being outside of the acceptance limit.

All the 25 laboratories reported to have used electrometry for the determination of conductivity (Table 2). The Youden chart (Figure 2) shows a significant systematic distribution of the points. Conductivity is highly temperature dependent, and improper temperature correction may lead to deviating results. Conductivity will vary by 2% for each degree at the temperatures around room temperature.

3.3 Alkalinity

Alkalinity was reported by 19 of the participating laboratories, producing an acceptance ratio of 42% (± 20% of the "true value", Table 1). Gran plot titration method, which is the suggested reference method in the manual (1) was used by 6 laboratories. End point titration was used by 7 participants and of these, 2 used titration to 5.4 and 5.6 respectively, while the rest did not specify the end point. Two end points titration was used by 4 laboratories and the remaining 2 reported to have used colorimetry and an unspecified method.

The Youden chart (Figure 3) shows that the results are distributed along the 45° line, indicating systematic differences. It is also worth noting that there is a separate grouping of results from labs having reported results around 0.050 to 0.070 mmol/L. 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 = 4.5. In such case, the relative error introduced by assuming affixed end-point pH of 4.5, 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

3.4 Nitrate + nitrite-nitrogen

A total of 20 laboratories reported results for nitrate+nitrite nitrogen of which 50% of the results were within the acceptance limit (± 20% of the "true value", Table 1). This was similar to the acceptance rate from last year, but lower than the years before. This can be due to the concentration in the samples.

Regarding the choice of analytical techniques and methods (Table 2), ion chromatography was the most commonly used (13 laboratories), followed by automatized photometry with Cd reduction (4 laboratories), manual photometry with Cd reduction (2 laboratories) and an unspecified method (1 laboratory).

The Youden chart for nitrate+nitrite-nitrogen (Figure 4) indicates a strong systematic distribution of the results.

3.5 Chloride

For chloride an acceptance rate of 83% (± 20% of the "true value") was achieved by the 23 participating laboratories (Table 1). According to Table 2, ion chromatography was the technique of choice by most of the participants (19 laboratories). The last 4 participants had used photometry with autoanalyzer, capillary electrophoresis, electrometry, and an unspecified method.

The distribution of the results in the Youden diagram (Figure 5) shows that most results have only small systematic errors.

3.6 Sulphate

Results for sulphate was reported by 23 laboratories, producing an acceptance rate at 91% (± 20% of the "true value", Table 1). This is the highest acceptance rate this year, and a very good result, especially when considering that the sulphate concentrations were relatively low. The preferred technique for sulphate determination was ion chromatography (19 participants), followed by ICP-OES (3 participants), and capillary electrophoresis (1 participant)

The Youden chart in Figure 6 demonstrates good precision of the results, with only a weak systematic effect.

3.7 Calcium

The acceptance rate for calcium was low this year, at only 69% (± 20% of the "true value", Table 1), for the 29 reporting laboratories. This parameter has normally had a high acceptance rate, around 90%. The low result this year is likely due to the calcium concentration being very low, around 1 mg/L, while it has been around 3-6 mg/L the last years.

The different techniques that had been used for the determination of calcium (Table 2) constituted ICP-OES (10 laboratories), ion chromatography (9 laboratories), FAAS and ICP-MS (4 laboratories each), and finally capillary electrophoresis and EDTA titration (1 laboratory each). Despite the use of several different analytical techniques, and the low concentration, the Youden diagram in Figure 7 shows that many participants have good precision. The remaining results are dominated by systematic errors.

3.8 Magnesium

Levels of magnesium was reported by 28 laboratories. The acceptance ratio was 71%, which is lower than normal for this parameter, but still quite good considering the low concentrations in the samples (~ 0.15 mg/L). The different techniques and methods that had been used for the determination of magnesium are listed in Table 2, and constituted ICP-OES (10 laboratories), ion chromatography (9 laboratories), FAAS and ICP-MS (4 laboratories each), and capillary electrophoresis (1 laboratory).

The Youden diagram in Figure 8 shows that many participants have reported very precise results, and the distribution of the rest of the results is dominated by systematic errors.

3.9 Sodium

An acceptance rate of 89% was achieved for sodium this year, and results were provided by 28 laboratories. Sodium has typically showed high acceptance rates during the previous years. This year,

the sodium concentration was at a very low level (0.7 – 0.9 mg/L), which has not been seen in this intercomparison test since at least before 2000. Considering this, a result at 89% acceptance rate is very good. Six different techniques had been used by the laboratories for the determination of sodium: ICP-OES and ion chromatography (10 laboratories each), ICP-MS (4 laboratories), FAAS (2 laboratories), capillary electrophoresis (1 laboratory) and flame photometry (1 laboratory).

The good agreement of the sodium concentrations between the laboratories was confirmed by the distribution in the Youden chart, showing only a small, mostly systematic, variation in the results (Figure 9).

3.10 Potassium

For potassium, 27 laboratories reported results from which 74% were within the acceptable threshold (± 20% of the "true value", Table 1). This is an acceptance rate which is lower than the previous years but can likely be explained by the relatively low concentrations of potassium in the sample (approximately 0.15 mg/l). Five different techniques had been used by the laboratories for the determination of potassium: ICP-OES and ion chromatography (10 laboratories each), ICP-MS (4 laboratories), FAAS (2 laboratories), and flame photometry (1 laboratory).

The Youden diagram in Figure 10 shows that the spread of the results is dominated by systematic errors, both within and outside of the ± 20% acceptance limit.

3.11 Total organic carbon

Concentrations of total organic carbon was reported by 17 laboratories, among which 71% were within the target threshold (± 20% of the "true value", Table 1). This was comparable to the results from the previous years.

Most of the laboratories (13 laboratories) had used the technique of combustion for the determination of total organic carbon, while 3 laboratories had used the UV/peroxodisulphate technique, and 1 laboratory had used an unspecified method. There was no apparent bias in the results depending on the method used for analysis. The Youden chart for total organic carbon showed a mix of both systematic and random errors in the distribution of the results (Figure 11).

3.12 Total phosphorus

Total phosphorus was reported by 21 laboratories (Table 1). The acceptance rate was one of the lowest among the parameters this year, at 29%. The acceptance rate of this parameter has been low since it was included in the chemical intercomparison (in 2017). A few participants have reported that the results were below their LOQ.

According to Table 2, most participants used photometry for the determination of total phosphorus (13 participants), followed by ICP-OES (5 participants). The last 3 participants used ICP-MS, ion chromatography, and another unspecified method. Of the 5 result pairs measured by ICP-OES, 3 were omitted due to the results being very low, and the other 2 result pairs are also underestimated. The spread of the results in the Youden chart (Figure 12) shows mainly systematic errors, and a grouping of results at a concentration around 40% higher than the "true values". This could be due to differences in the applied methods, even if both groups used photometry.

3.13 Aluminium

Concentrations of aluminium were reported by 18 laboratories, producing an acceptance rate at 67% (± 20% of the "true value", Table 1). This is lower than last year, which had one sample with a higher concentration, but comparable to the previous years with similar aluminium concentrations as this year.

Three techniques were used for the determination of aluminium (Table 2): ICP-MS (10 laboratories), ICP-OES (6 laboratories), and GFAAS (2 laboratories). The Youden chart for aluminium (Figure 13) shows that most of the errors were systematic.

3.14 Iron

Results reported for iron showed an acceptance ratio at only 56% for the 18 reporting laboratories (± 20% of the "true value", Table 1). This is lower than for the previous years but can likely be explained by the iron concentration being only around 10 µg/L, a concentration level not seen in this intercomparison test for the last 20 years.

Four techniques were used for the determination of iron (Table 2), constituting ICP-MS (9 laboratories), ICP-OES (6 laboratories), GFAAS (2 laboratories), and photometry (1 laboratory). The Youden chart (Figure 14) shows that the spread of the results is highly random in nature. When evaluating their results, the participants should consider the error in absolute values in addition to the relative error, especially if the true values are close to their quantification limits.

3.15 Manganese

The acceptance rate for manganese was at 65% for the 17 laboratories providing results (± 20% of the "true value", Table 1). This is lower than the previous years and again likely related to the low manganese concentration in the samples.

For the determination of manganese, 10 laboratories had used ICP-MS, 6 had used ICP-OES and the last laboratory had used GFAAS (Table 2). The Youden chart in Figure 15 showed mostly random errors.

3.16 Cadmium

Cadmium was determined by 18 of the participating laboratories, providing results with an acceptance rate of 56% (± 20% of the "true value", Table 1). The concentration of cadmium (approximately 0.5 µg/L) is lower than what has been seen in a while but results around 1 µg/L have given acceptance rates around 80% in previous intercomparison tests. It may still be that participants normally do not analyse many results lower than 1 µg/L, resulting in lower precision on that concentration level.

ICP-MS was the determination method used by most of the participants (12 laboratories), followed by GFAAS (4 laboratories) and ICP-OES (2 laboratories). The Youden chart (Figure 16) shows both systematic and random errors.

3.17 Lead

Lead showed the poorest acceptance rate this year, with 17 laboratories producing an acceptance rate of only 24%. While the concentration is low at 1.2 – 1.6 µg/L, the same concentration level was seen in intercomparison 1832, which produced an acceptance rate of 65%.

According to Table 2, the most used method for determination of lead was ICP-MS (11 laboratories), followed by GFAAS and ICP-OES (3 laboratories each). Looking at the Youden chart (Figure 17), the results are spread out over a relatively large area, causing only a few participants to be marked as accepted.

Due to an error, the CD sample set was not acidified before shipment, and the lower biased values may be due to laboratories removing a sample aliquot without acidifying the sample inside the original bottle. Lead sticking to the bottle walls can lower the lead concentration in the water, which again leads to a negative bias in the results. The amount of lead added when preparing the sample sets indicate that the higher results are more likely to be the real values. Participants should consider this when evaluating their results.

3.18 Copper

The acceptance rate for copper was at 70% for the results provided by 20 laboratories (± 20% of the "true value", Table 1). This was good and comparable to the results from the previous years when considering the relatively low concentration. For determination, 12 participants had used ICP-MS, 5 had used ICP-OES and the last 3 had used GFAAS.

The distribution of the results in the Youden chart in Figure 18 shows a dominance of systematic errors, but random effects can also be seen.

3.19 Nickel

Results for nickel was reported by 18 laboratories for which 72% of were classified as acceptable according to the target limit (± 20% of the "true value", Table 1). This is a relatively good result considering the concentration level of nickel in the samples. For determination, 12 participants had used ICP-MS, 5 had used ICP-OES and the last participant had used GFAAS. The Youden chart (Figure 19) shows that systematic errors are dominating the spread of the results.

3.20 Zinc

Concentration of zinc in the samples were determined by 18 laboratories from which 72% fulfilled the acceptance criteria (± 20% of the "true value", Table 1). This is slightly lower than the previous years, when comparing with the concentration levels.

For determination, 11 participants had used ICP-MS, 5 had used ICP-OES and 2 had used GFAAS. The Youden chart in Figure 20 shows that many participants have very precise results, but there are some outliers which are affecting the acceptance rate. The 2 laboratories that had used GFAAS are both outliers in the lower left quadrant, which may indicate a systematic effect due to the method used. Most of the errors seen in the results are systematic.

Table 2. Statistical summary of the results from the 2135 edition, including information of the different analytical techniques used by the laboratories.

Parameter	Sample	True value		No. Lab		Median		Sample 1		Sample 2		Rel. Stdev. Av%		Rel. Error %	
and method	pair	S1	S2	Total	U	S1	S2	Ave.	Stdev	Ave.	Stdev	S1	S2	S1	S2
pH	AB	6,31	6,38	26	1	6.31	6.38	6.33	0.23	6.31	0.20	3.6	3.2	0.3	-1.1
Elec., stirring				11	1	6.30	6.29	6.27	0.23	6.24	0.18	3.6	2.8	-0.7	-2.2
Elec., non-stirring				8	0	6.37	6.34	6.41	0.29	6.36	0.29	4.5	4.5	1.5	-0.4
Elec., equilibration				5	0	6.25	6.39	6.27	0.10	6.35	0.08	1.6	1.3	-0.7	-0.4
Other method				2	0			6.48		6.41				2.6	0.4
Conductivity	AB	1,21	1,10	25	3	1.21	1.10	1.19	0.08	1.08	0.06	6.8	5.5	-1.8	-1.9
Electrometry				25	3	1.21	1.10	1.19	0.08	1.08	0.06	6.8	5.5	-1.8	-1.9
Alkalinity	AB	0,036	0,032	19	8	0.036	0.032	0.036	0.006	0.032	0.005	17.1	14.4	-0.1	1.1
Gran plot titration				6	1	0.037	0.034	0.038	0.005	0.035	0.004	12.3	11.6	6.6	9.3
One end point(other)titr.				5	4			0.023		0.026				-36.1	-18.8
Two end points titration				4	2			0.036		0.030				0.0	-7.8
Colorimetry				1	0			0.043		0.038				19.4	18.8
One end point(pH5.4)titr.				1	0			0.031		0.028				-13.9	-12.5
One end point(pH5.6)titr.				1	0			0.035		0.030				-2.8	-6.3
Other method				1	1			52.8		47.2				>100	>100
Nitrate + nitrite-nitrogen	AB	84,5	77,3	20	6	84.5	77.3	79.4	15.1	72.9	13.0	19.1	17.9	-6.1	-5.7
Ion chromatography				13	3	86.0	77.5	79.7	15.2	73.6	12.4	19.1	16.8	-5.7	-4.8
Auto.,photometry, Cd red				4	1	78.0	70.0	72.8	15.5	65.5	14.8	21.3	22.7	-13.9	-15.3
Manual.,photometry,Cd red				2	2			1.7		1.7				-98.0	-97.9
Other method				1	0			96.0		88.0				13.6	13.8
Chloride	AB	1,11	1,01	23	0	1.11	1.01	1.11	0.11	1.01	0.09	10.0	9.2	-0.4	-0.4
Ion chromatography				19	0	1.11	1.01	1.11	0.07	1.02	0.08	6.7	7.8	-0.1	0.5
Cap. electrophoresis				1	0			1.42		1.15				27.9	13.9
Electrometry				1	0			1.03		0.95				-6.8	-6.4
Other method				1	0			1.03		0.96				-7.2	-5.2
Photometry, autoanalyzer				1	0			0.86		0.79				-22.5	-21.8
Sulphate	AB	0,747	0,675	23	1	0.747	0.675	0.747	0.071	0.667	0.048	9.4	7.2	0.0	-1.2
Ion chromatography				19	1	0.744	0.680	0.746	0.073	0.671	0.047	9.8	7.0	-0.1	-0.5
ICP-OES				3	0	0.747	0.666	0.740	0.074	0.661	0.052	10.0	7.8	-1.0	-2.1
Cap. electrophoresis				1	0			0.790		0.600				5.8	-11.1
Calcium	AB	1,00	0,91	29	2	1.00	0.91	0.97	0.16	0.91	0.13	16.9	14.2	-2.6	-0.4
ICP-OES				10	0	1.01	0.91	1.00	0.07	0.92	0.08	6.6	8.5	-0.2	0.8
Ion chromatography				9	1	1.01	0.91	1.00	0.22	0.92	0.20	21.8	21.2	0.3	1.1
FAAS				4	0	0.95	0.87	0.97	0.11	0.90	0.09	11.6	10.1	-3.0	-1.4
ICP-MS				4	0	1.01	0.92	0.98	0.14	0.93	0.05	14.9	5.9	-2.4	1.7
Cap. Electrophoresis				1	0			0.51		0.64				-49.0	-29.7
EDTA titration				1	1			2.00		1.60				100.0	75.8
Magnesium	AB	0,170	0,154	28	2	0.170	0.154	0.166	0.019	0.153	0.021	11.6	13.6	-2.3	-1.0
ICP-OES				10	0	0.171	0.156	0.172	0.014	0.157	0.023	8.0	14.4	1.4	2.0
Ion chromatography				9	1	0.169	0.154	0.163	0.029	0.149	0.026	17.6	17.3	-4.1	-3.5
FAAS				4	0	0.161	0.146	0.161	0.012	0.147	0.008	7.2	5.7	-5.6	-4.4
ICP-MS				4	0	0.163	0.158	0.162	0.017	0.154	0.017	10.2	11.1	-4.6	0.0
Cap. Electrophoresis				1	1			3.490		6.170				>100	>100

Table 2. cont.

Parameter	Sample	True value		No. Lab		Median		Sample 1		Sample 2		Rel. Stdev. Av%		Rel. Error %	
and method	pair	S1	S2	Total	U	S1	S2	Ave.	Stdev	Ave.	Stdev	S1	S2	S1	S2
Sodium	AB	0,835	0,762	28	3	0.835	0.762	0.839	0.053	0.766	0.042	6.3	5.5	0.4	0.6
ICP-OES				10	1	0.835	0.764	0.814	0.052	0.755	0.036	6.4	4.8	-2.5	-0.9
Ion chromatography				10	1	0.826	0.753	0.846	0.053	0.773	0.047	6.3	6.1	1.3	1.4
ICP-MS				4	0	0.876	0.791	0.884	0.052	0.797	0.046	5.9	5.8	5.8	4.5
FAAS				2	0			0.817		0.736				-2.2	-3.5
Cap. Electrophoresis				1	1			1.090		1.390				30.5	82.4
Flame photometry				1	0			0.850		0.750				1.8	-1.6
Potassium	AB	0,151	0,140	27	2	0.151	0.140	0.151	0.020	0.143	0.021	13.2	14.7	-0.3	2.0
ICP-OES				10	1	0.155	0.148	0.156	0.020	0.154	0.023	13.0	15.0	3.1	10.0
Ion chromatography				10	0	0.145	0.131	0.141	0.022	0.131	0.019	15.3	14.2	-6.3	-6.3
ICP-MS				4	0	0.156	0.146	0.159	0.014	0.148	0.012	8.7	7.8	5.0	5.7
FAAS				2	1			0.160		0.150				6.0	7.1
Flame photometry				1	0			0.155		0.130				2.6	-7.1
Total organic carbon	AB	2,51	2,40	17	0	2.51	2.40	2.55	0.43	2.49	0.43	16.7	17.3	1.7	3.5
Combustion				13	0	2.49	2.45	2.48	0.38	2.44	0.39	15.3	15.8	-1.4	1.8
UV/peroxodisulphate				3	0	2.60	2.40	2.85	0.65	2.71	0.70	22.7	25.8	13.4	12.9
Other method				1	0			2.67		2.37				6.4	-1.2
Total phosphorous	AB	13,8	13,0	21	6	13.8	13.0	13.7	3.8	13.0	3.3	27.7	25.1	-0.4	0.4
Photometry				13	2	14.1	13.2	14.1	4.3	13.8	3.3	30.6	24.1	2.5	6.3
ICP-OES				5	3			11.4		9.3				-17.8	-28.8
ICP-MS				1	1			22.0		24.0				59.4	84.6
Ion chromatography				1	0			12.9		12.3				-6.9	-5.5
Other method				1	0			15.0		13.0				8.7	0.0
Aluminium	CD	52,3	47,2	18	0	52.5	47.2	50.4	9.0	46.4	7.8	17.8	16.9	-3.6	-1.7
ICP-MS				10	0	53.0	47.7	53.2	5.0	48.4	4.7	9.4	9.8	1.8	2.6
ICP-OES				6	0	52.0	48.0	49.2	9.9	46.4	8.4	20.2	18.0	-5.8	-1.7
GFAAS				2	0			39.8		36.2				-23.8	-23.3
Iron	CD	11,2	10,9	18	0	11.2	10.9	11.3	2.1	11.1	2.0	18.8	18.3	0.7	1.6
ICP-MS				9	0	11.7	10.4	11.8	1.9	11.2	1.8	15.7	16.0	5.6	3.1
ICP-OES				6	0	9.6	10.8	9.7	2.1	10.2	2.3	22.0	23.0	-13.8	-6.8
GFAAS				2	0			12.9		11.5				15.2	5.5
Photometry				1	0			12.8		14.2				14.3	30.3
Manganese	CD	2,67	2,96	17	2	2.67	2.96	2.61	0.37	2.84	0.36	14.3	12.8	-2.1	-4.0
ICP-MS				10	0	2.69	2.98	2.66	0.26	2.98	0.16	9.7	5.4	-0.4	0.6
ICP-OES				6	2	2.24	2.76	2.31	0.35	2.68	0.53	15.3	20.0	-13.4	-9.5
GFAAS				1	0			3.38		2.15				26.6	-27.4
Cadmium	CD	0,507	0,465	18	0	0.507	0.465	0.496	0.064	0.462	0.058	12.9	12.6	-2.1	-0.7
ICP-MS				12	0	0.515	0.469	0.512	0.054	0.466	0.041	10.5	8.8	1.0	0.3
GFAAS				4	0	0.435	0.410	0.441	0.048	0.453	0.106	10.9	23.5	-13.1	-2.6
ICP-OES				2	0			0.514		0.455				1.3	-2.3
Lead	CD	1,63	1,26	17	3	1.63	1.26	1.54	0.40	1.22	0.28	26.3	22.6	-5.8	-2.8
ICP-MS				11	1	1.69	1.29	1.59	0.39	1.23	0.29	24.3	23.5	-2.2	-2.8
GFAAS				3	1			1.78		1.45				9.3	14.8
ICP-OES				3	1			1.00		1.00				-38.7	-20.6

Table 2. cont.

Parameter	Sample	True value		No. Lab		Median		Sample 1		Sample 2		Rel. Stdev. Av%		Rel. Error %	
and method	pair	S1	S2	Total	U	S1	S2	Ave.	Stdev	Ave.	Stdev	S1	S2	S1	S2
Copper	CD	5,58	4,72	20	1	5.58	4.72	5.21	1.05	4.39	0.83	20.1	18.8	-6.6	-6.9
ICP-MS				12	0	5.80	4.84	5.51	0.83	4.58	0.71	15.1	15.5	-1.2	-2.9
ICP-OES				5	0	4.70	3.89	4.41	1.39	3.84	1.04	31.6	27.0	-20.9	-18.6
GFAAS				3	1			5.43		4.64				-2.7	-1.8
Nickel	CD	2,72	2,45	18	0	2.72	2.45	2.64	0.29	2.36	0.36	10.9	15.1	-3.1	-3.7
ICP-MS				12	0	2.74	2.45	2.70	0.25	2.45	0.19	9.2	7.7	-0.9	0.2
ICP-OES				5	0	2.70	2.00	2.49	0.38	2.11	0.58	15.2	27.3	-8.6	-14.0
GFAAS				1	0			2.67		2.50				-1.8	2.0
Zinc	CD	14,1	12,9	18	1	14.1	12.9	13.6	2.2	12.5	1.9	16.1	14.9	-3.4	-3.3
ICP-MS				11	0	14.2	13.0	14.4	1.5	13.3	1.1	10.6	8.7	2.5	2.7
ICP-OES				5	1	13.9	12.5	13.4	2.0	12.2	1.4	15.1	11.2	-5.1	-5.3
GFAAS				2	0			9.5		8.7				-32.5	-32.4

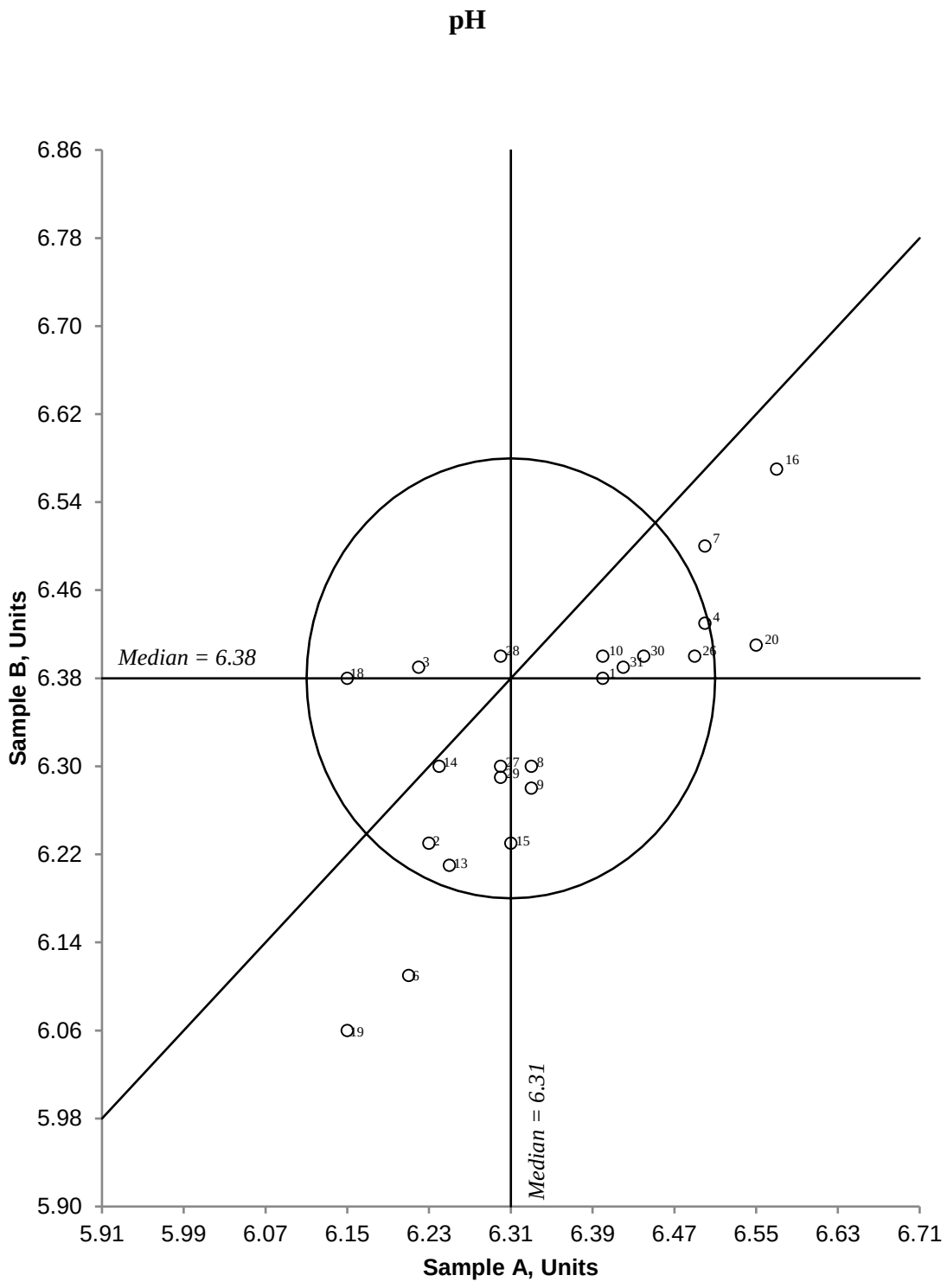

Figure 1. Youden diagram for pH. Sample pair AB. Acceptance limit, given by circle, is 0.2 pH units. (3,15%)

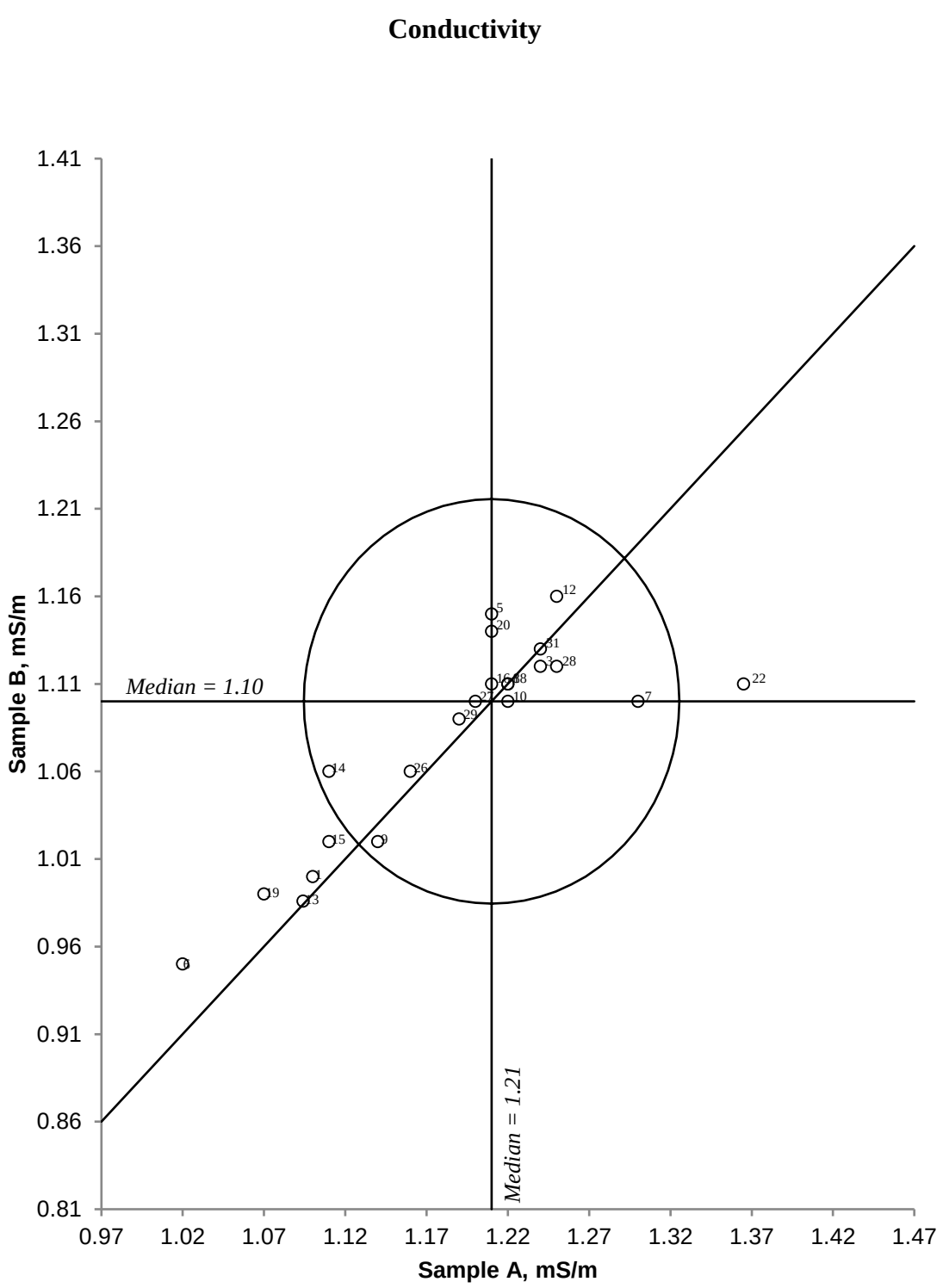

Figure 2. Youden diagram for conductivity. Sample pair AB. Acceptance limit, given by circle, is 10%.

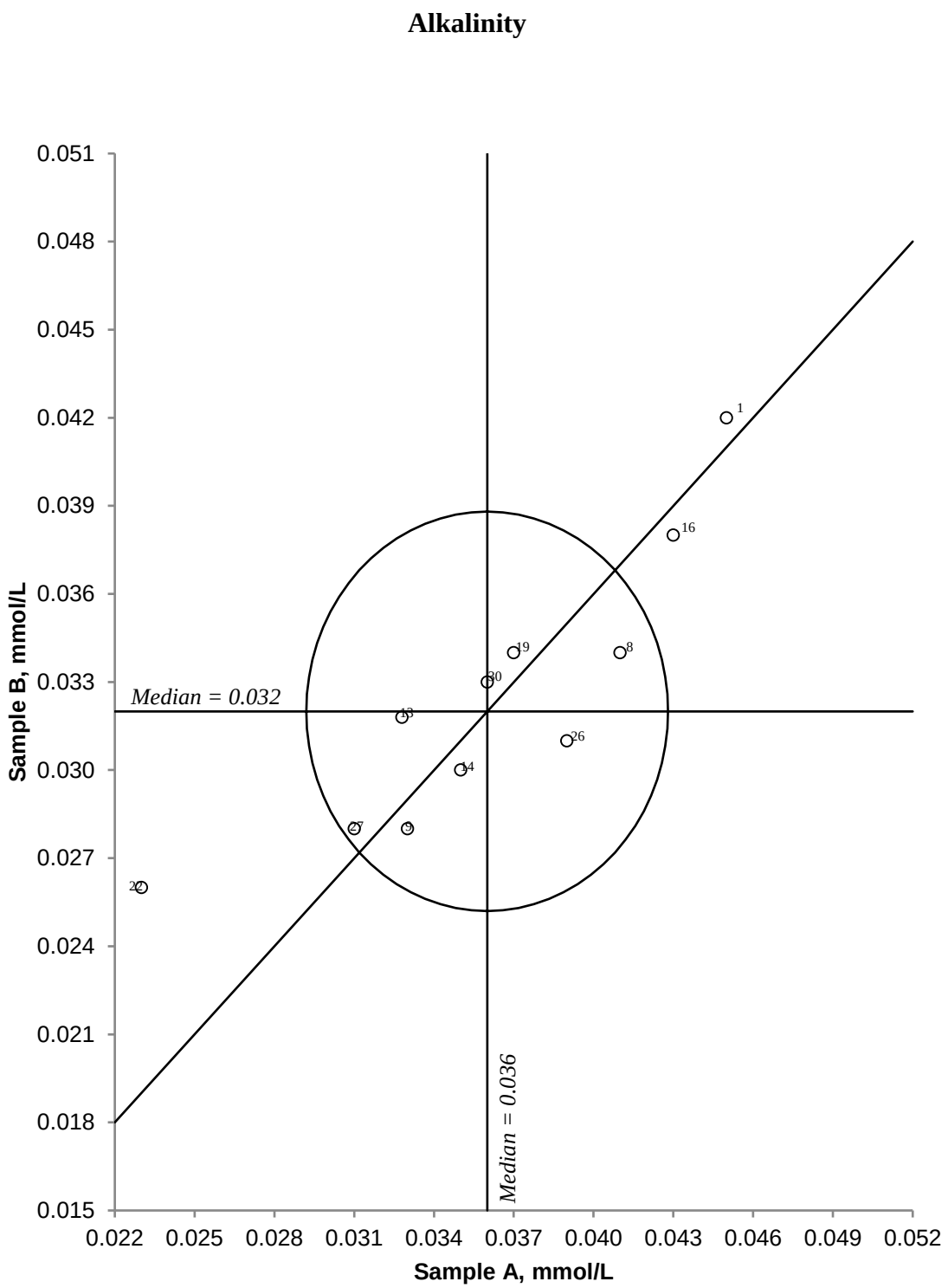

Figure 3. Youden diagram for alkalinity. Sample pair AB. Acceptance limit, given by circle, is 20%.

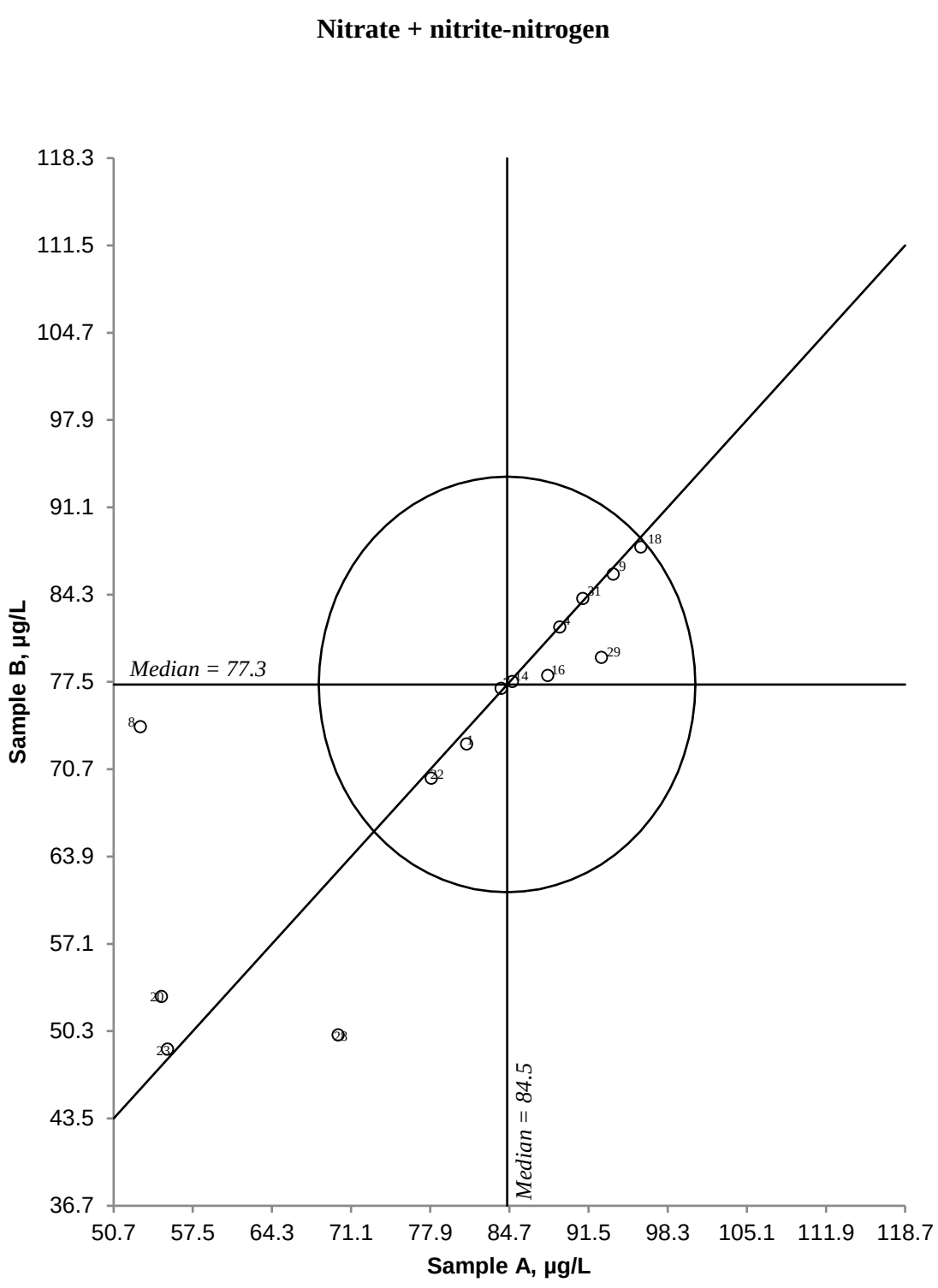

Figure 4. Youden diagram for nitrate+nitrite-nitrogen. Sample pair AB. Acceptance limit, given by circle, is 20%.

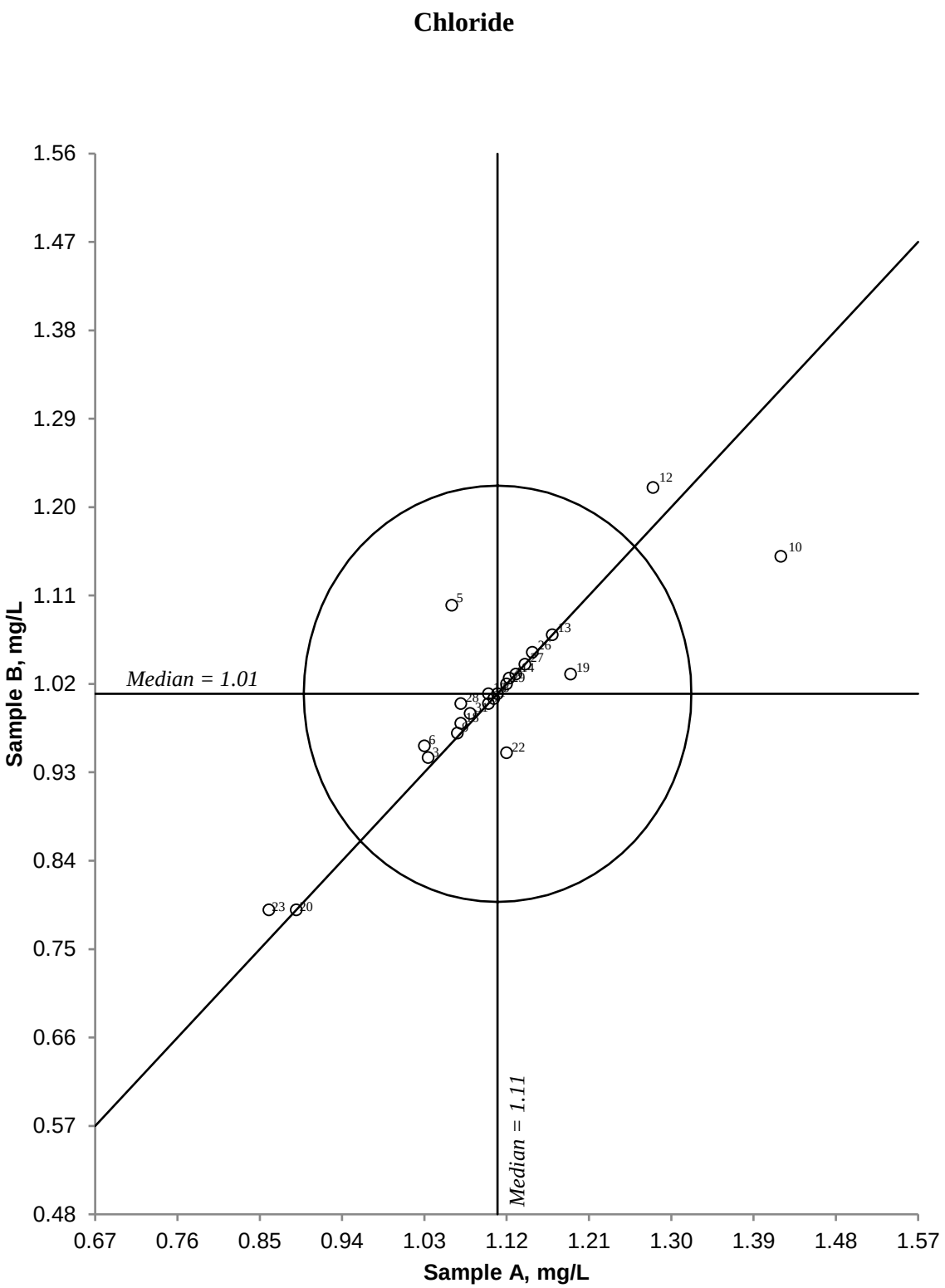

Figure 5. Youden diagram for chloride. Sample pair AB. Acceptance limit, given by circle, is 20%.

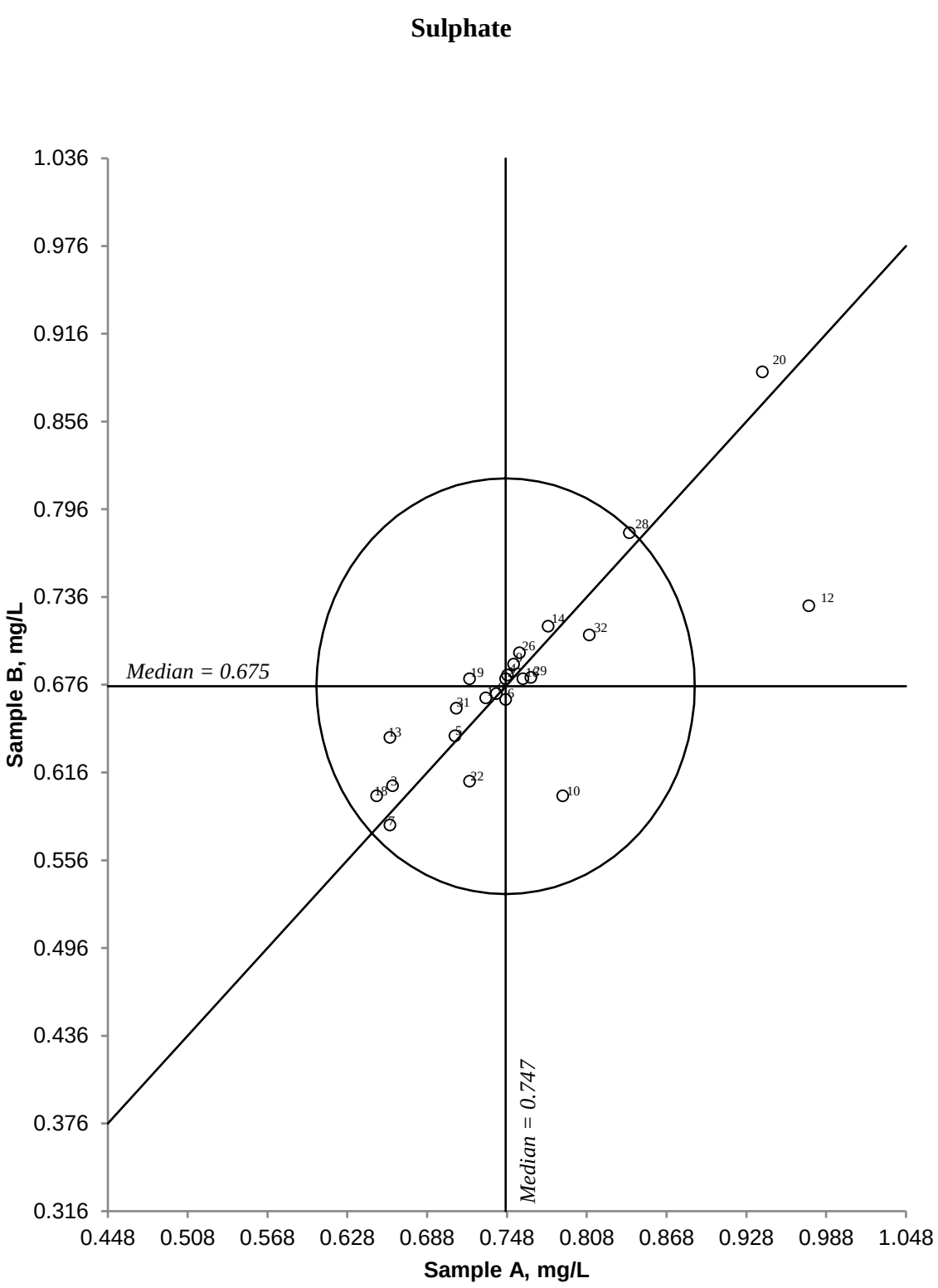

Figure 6. Youden diagram for sulphate. Sample pair AB. Acceptance limit, given by circle, is 20%.

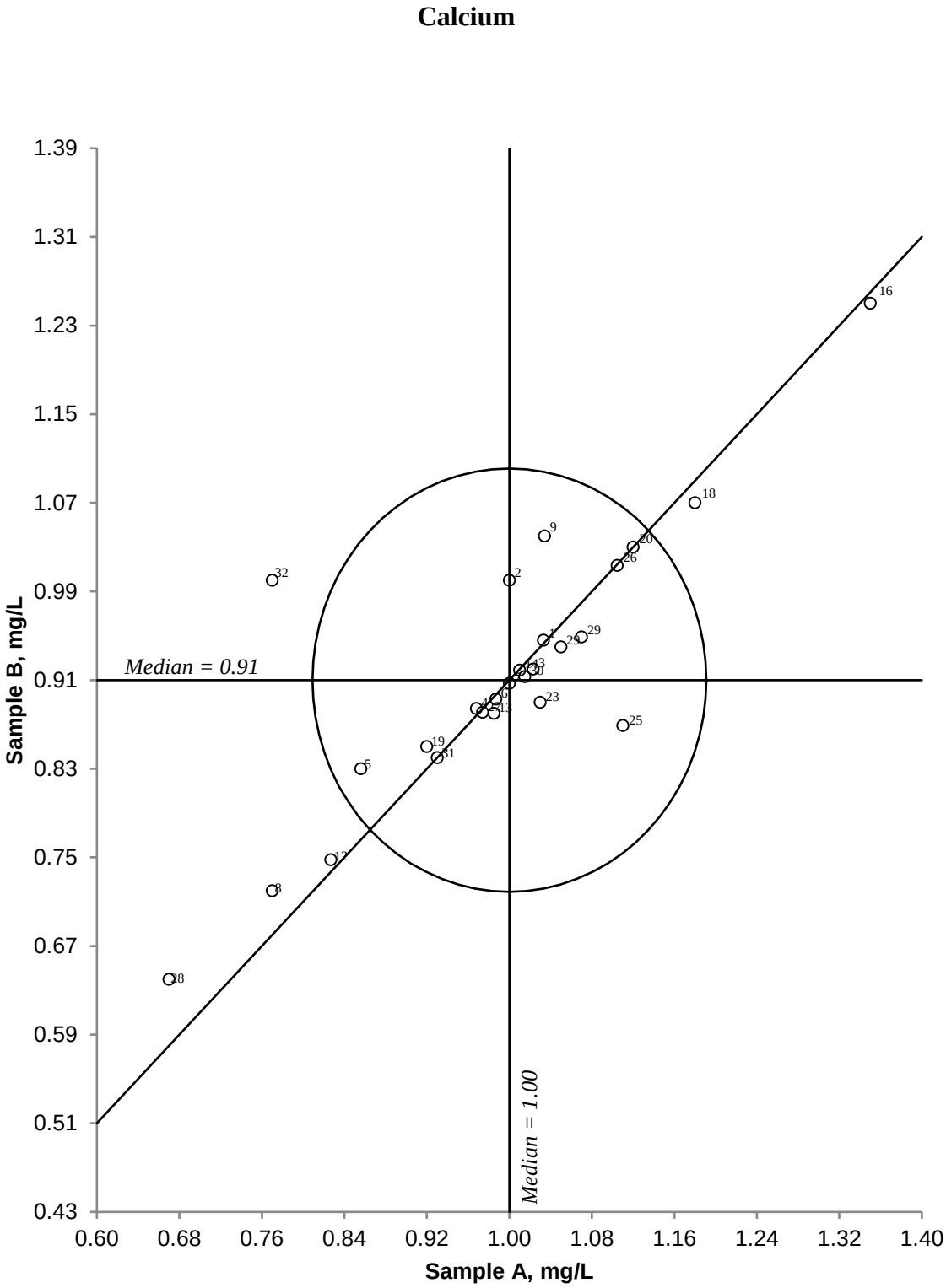

Figure 7. Youden diagram for calcium. Sample pair AB. Acceptance limit, given by circle, is 20%.

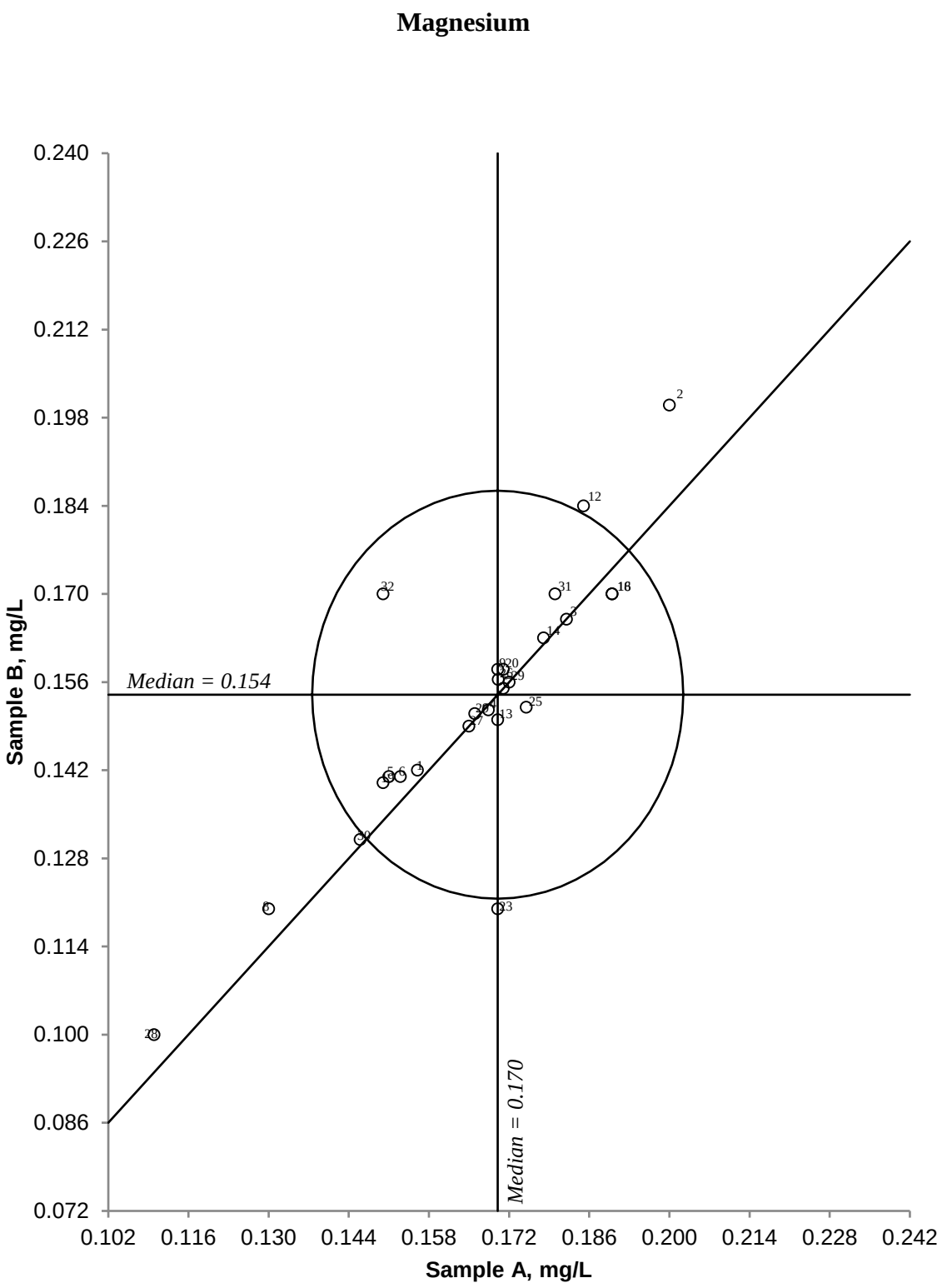

Figure 8. Youden diagram for magnesium. Sample pair AB. Acceptance limit, given by circle, is 20%.

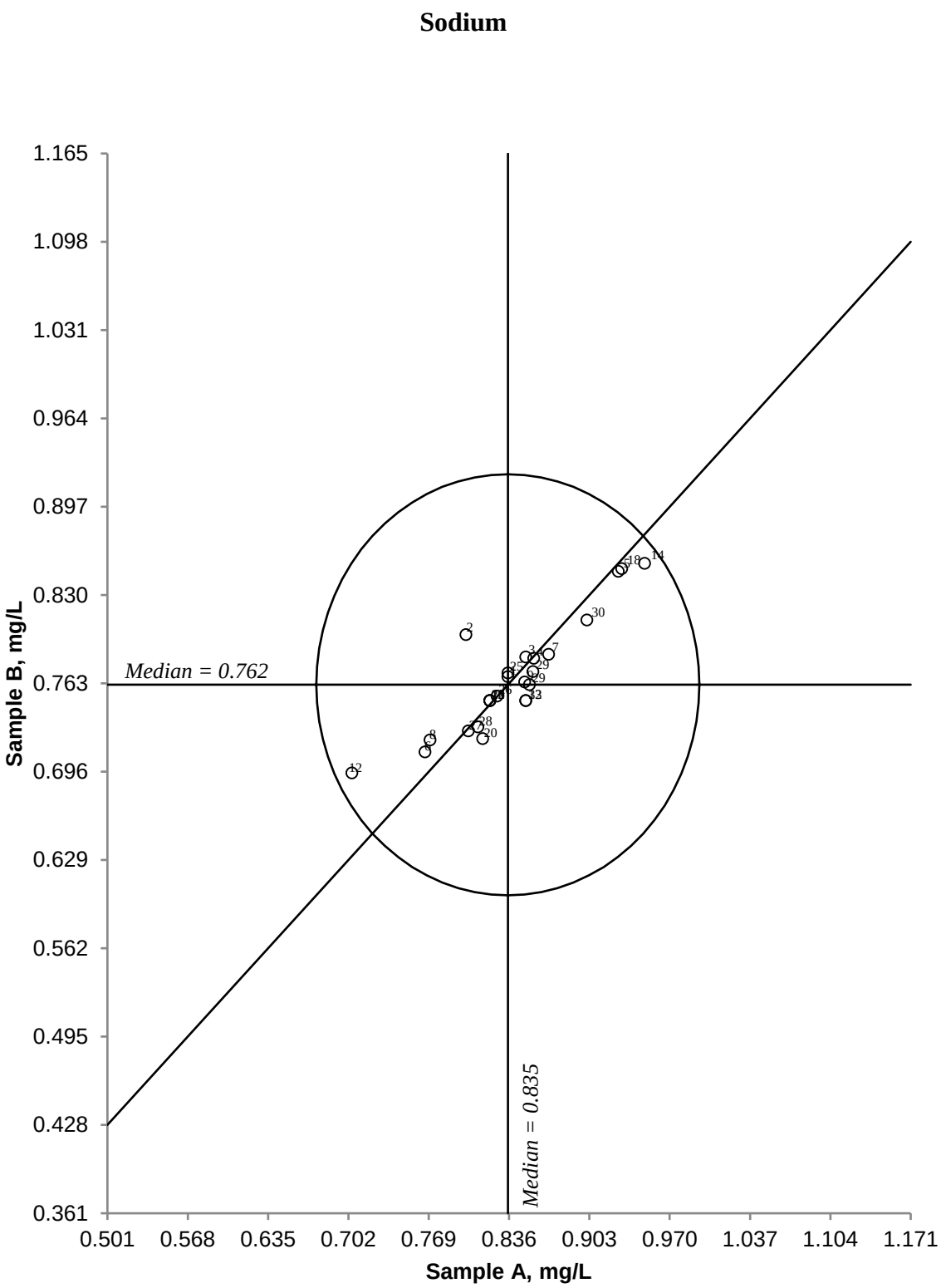

Figure 9. Youden diagram for sodium. Sample pair AB. Acceptance limit, given by circle, is 20%.

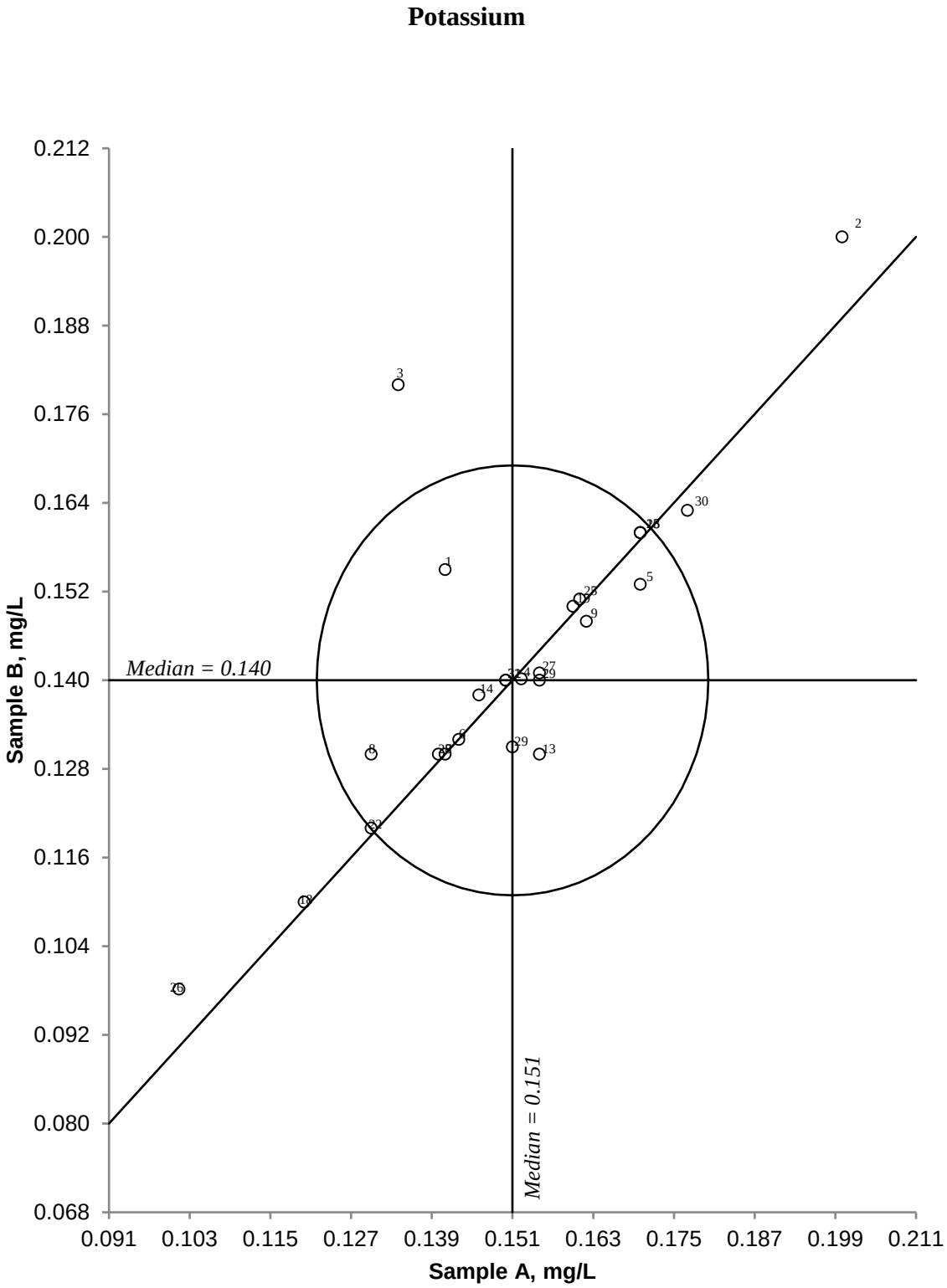

Figure 10. Youden diagram for potassium. Sample pair AB. Acceptance limit, given by circle, is 20%.

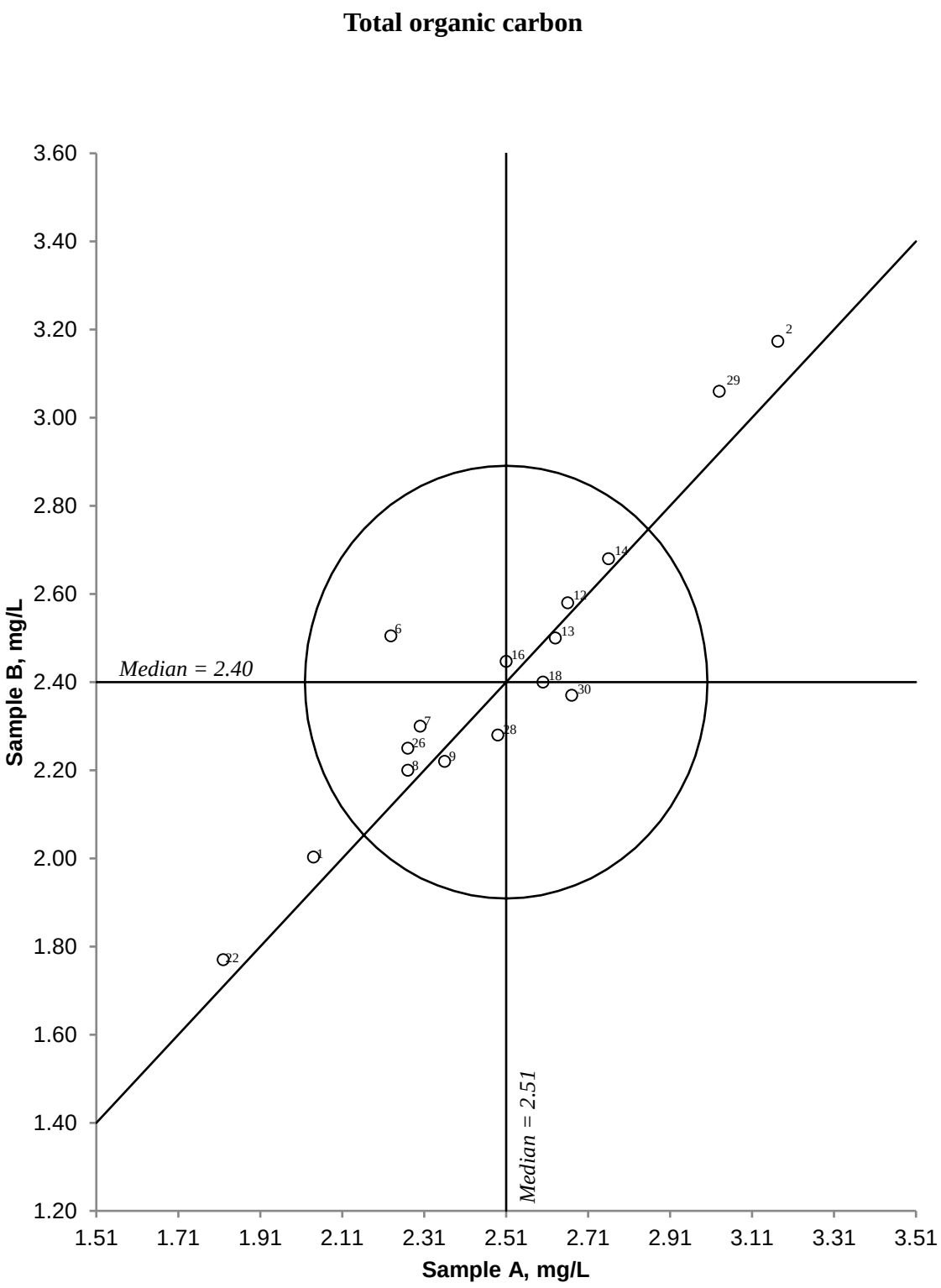

Figure 11. Youden diagram for total organic carbon. Sample pair AB. Acceptance limit, given by circle, is 20%.

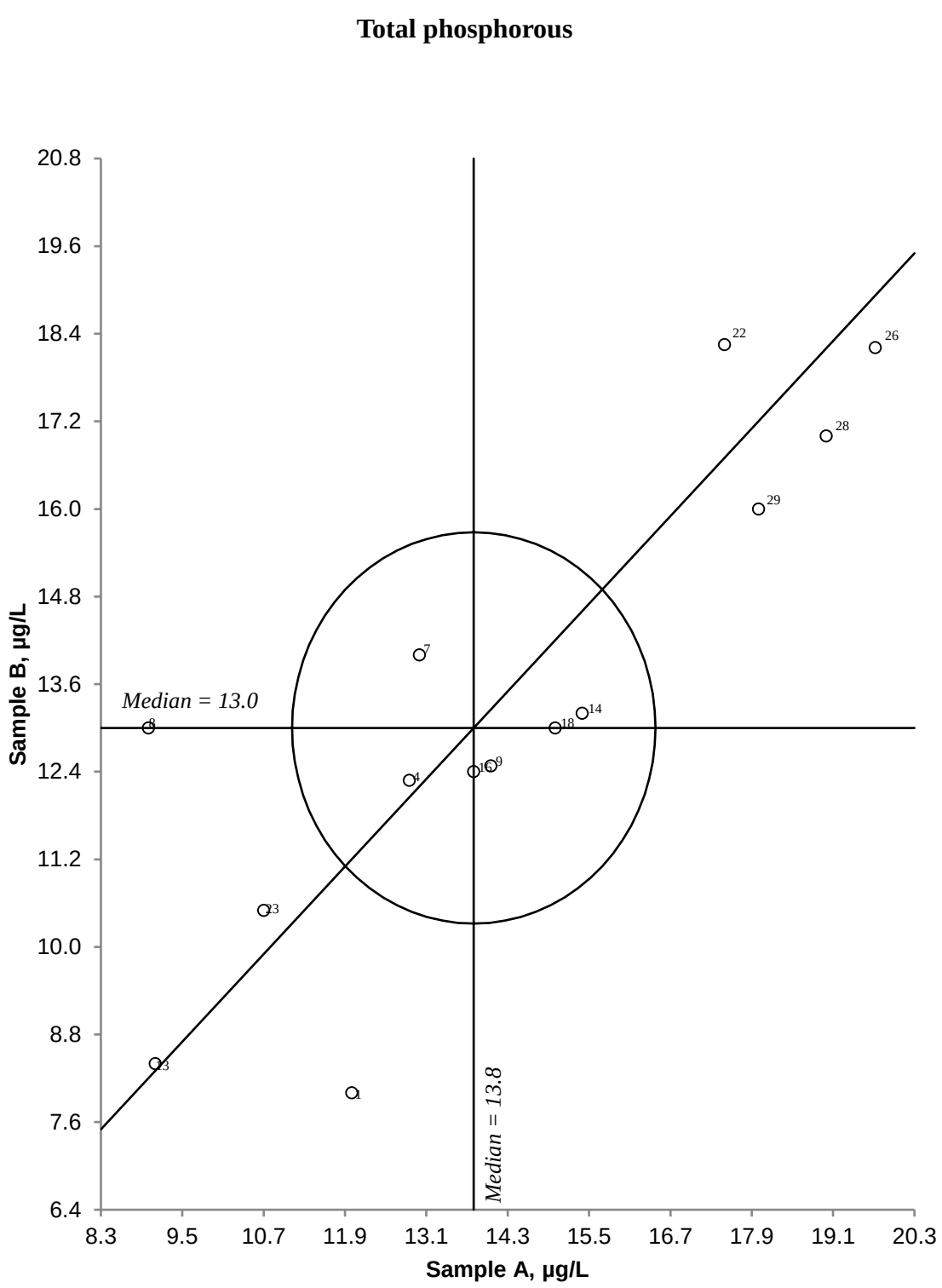

Figure 12. Youden diagram for total phosphorous. Sample pair AB. Acceptance limit, given by circle, is 20%.

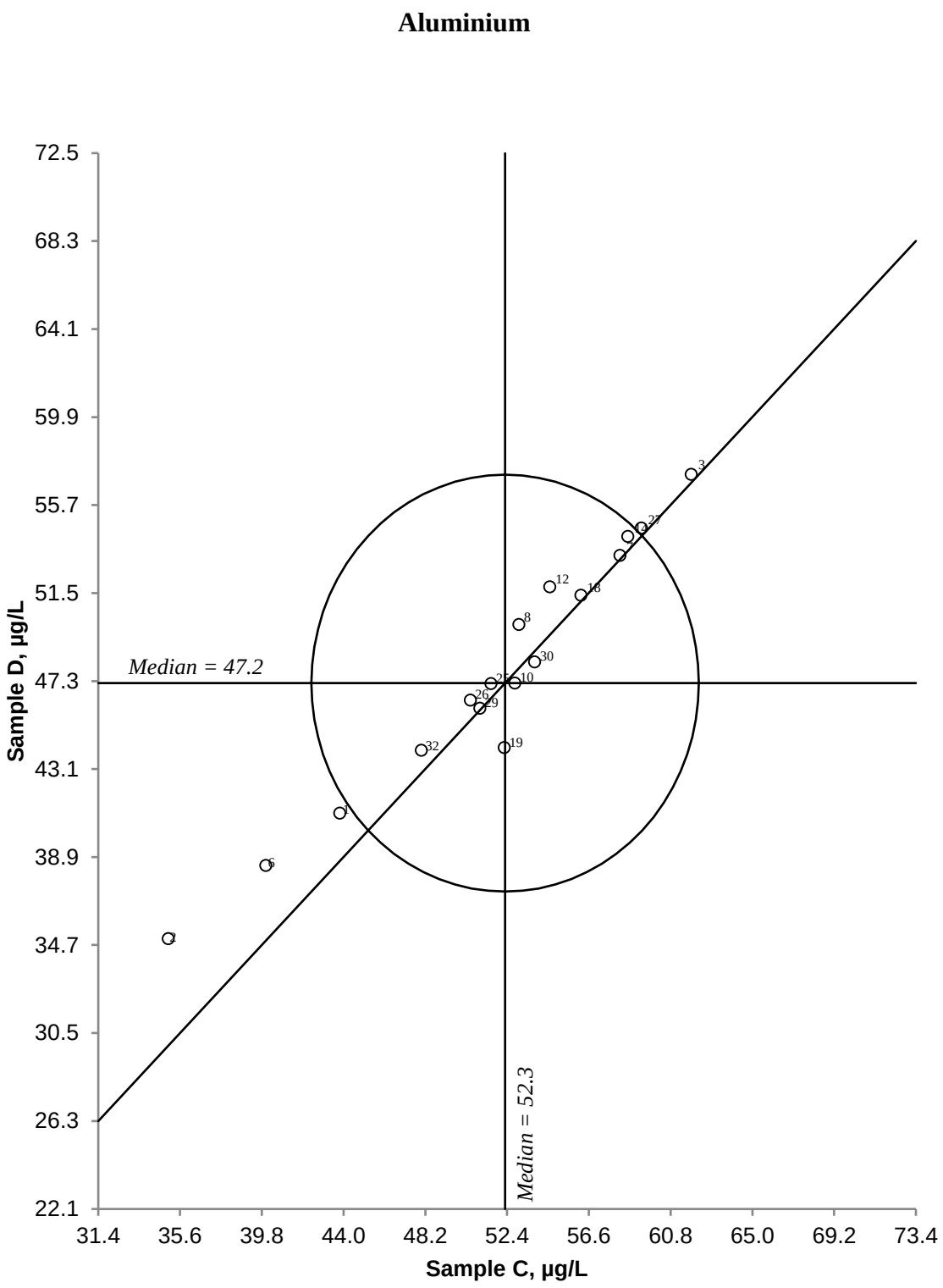

Figure 13. Youden diagram for aluminum. Sample pair CD. Acceptance limit, given by circle, is 20%.

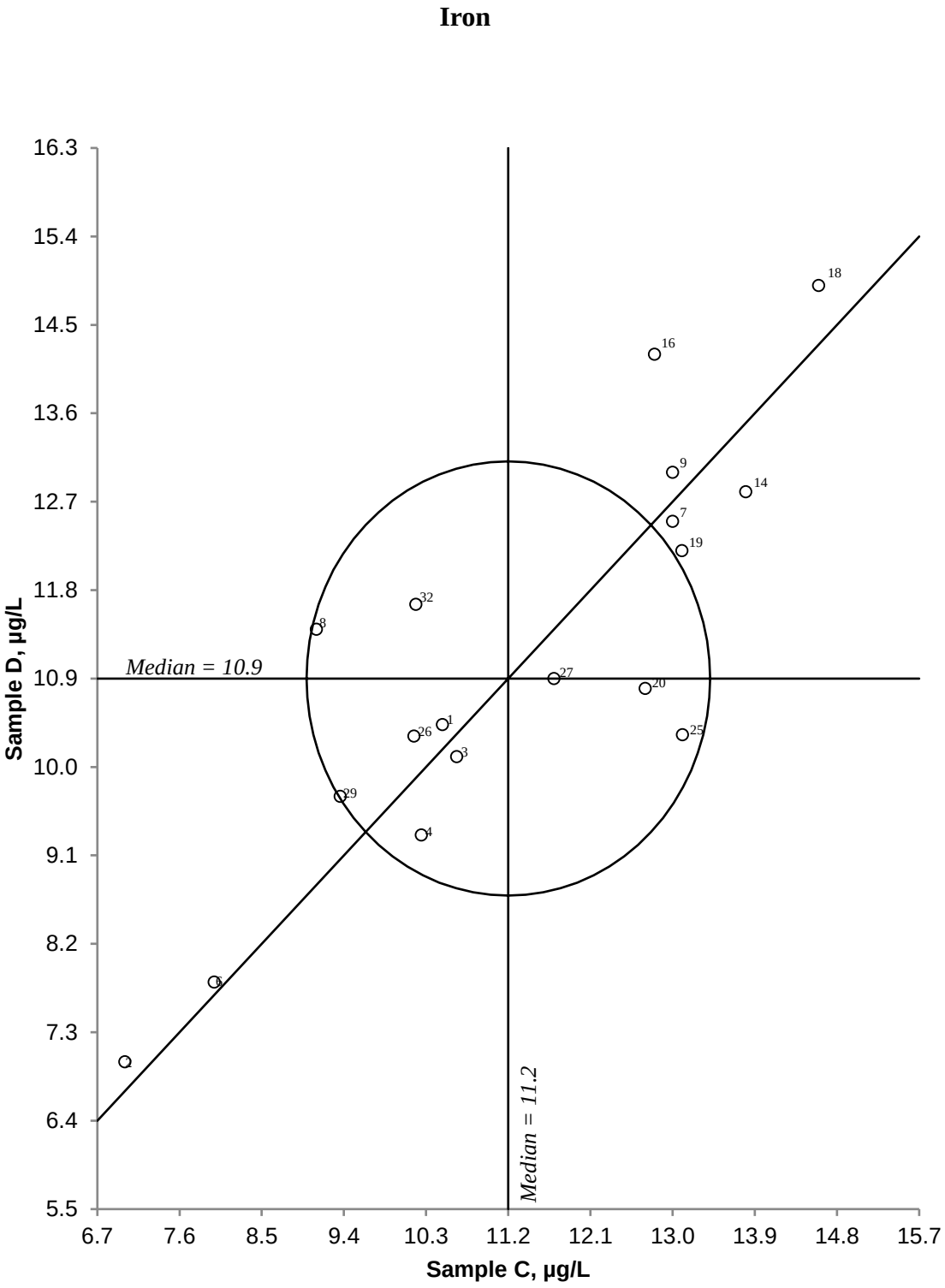

Figure 14. Youden diagram for iron. Sample pair CD. Acceptance limit, given by circle, is 20%.

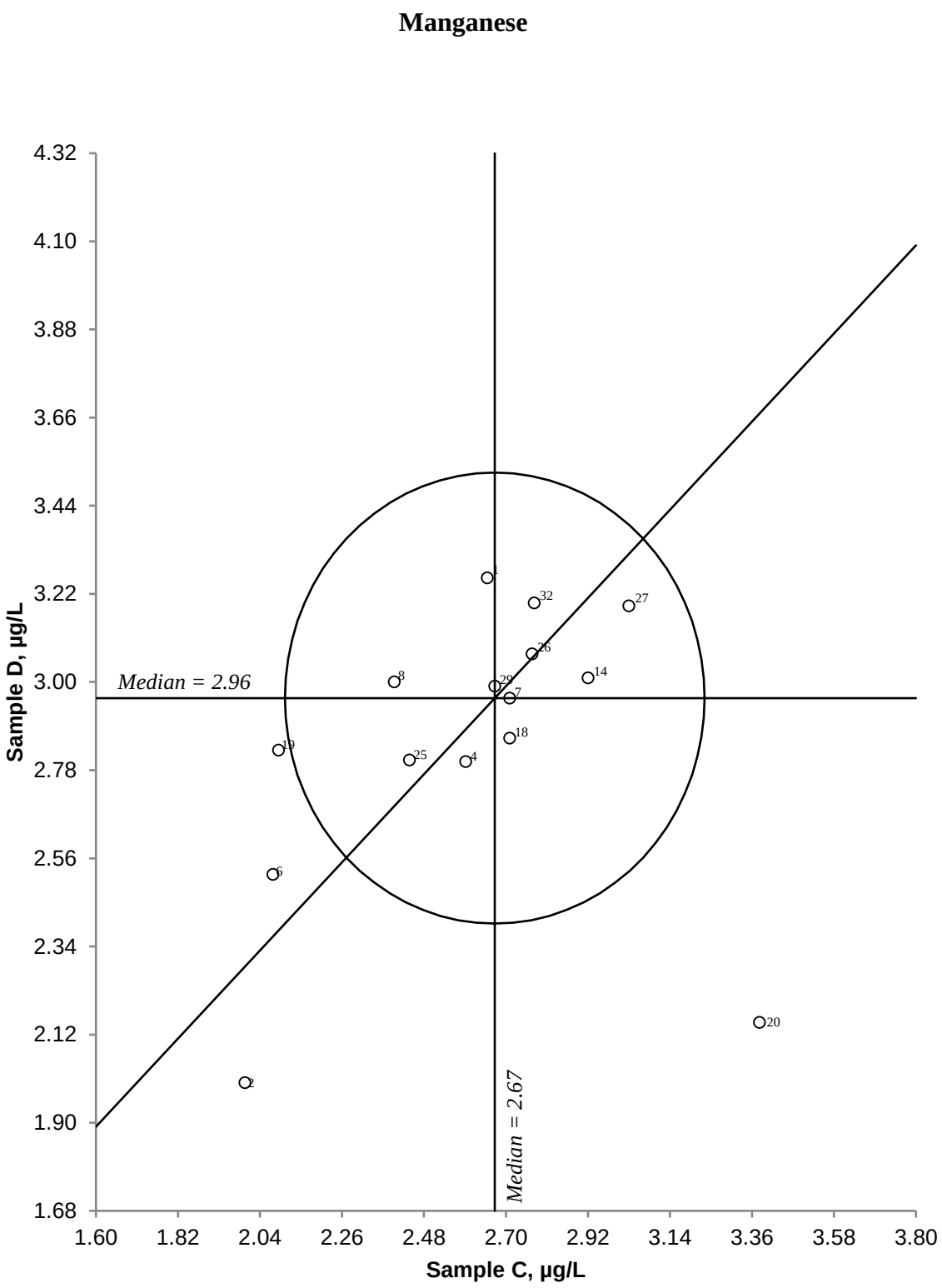

Figure 15. Youden diagram for manganese. Sample pair CD. Acceptance limit, given by circle, is 20%.

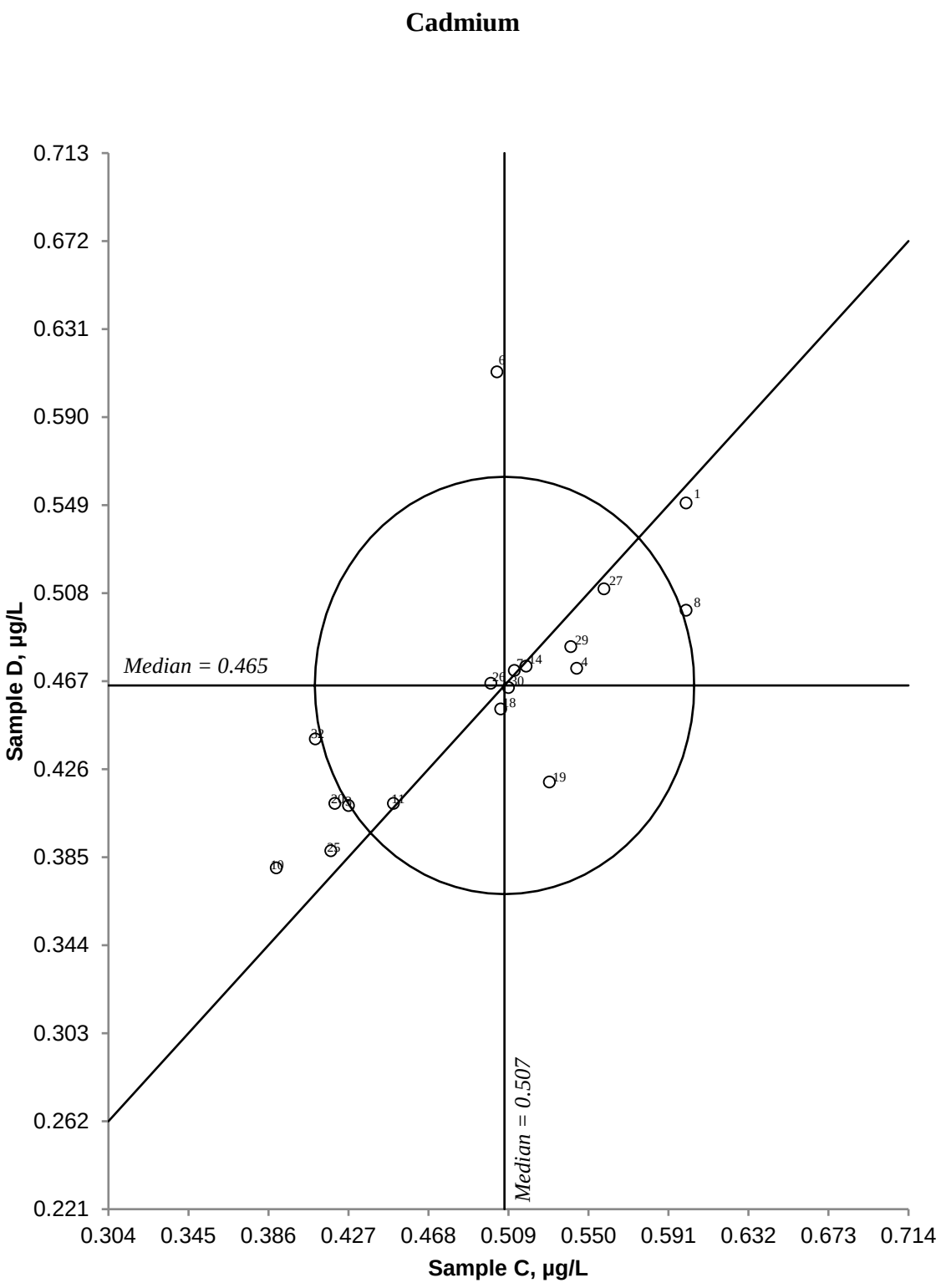

Figure 16. Youden diagram for cadmium. Sample pair CD. Acceptance limit, given by circle, is 20%.

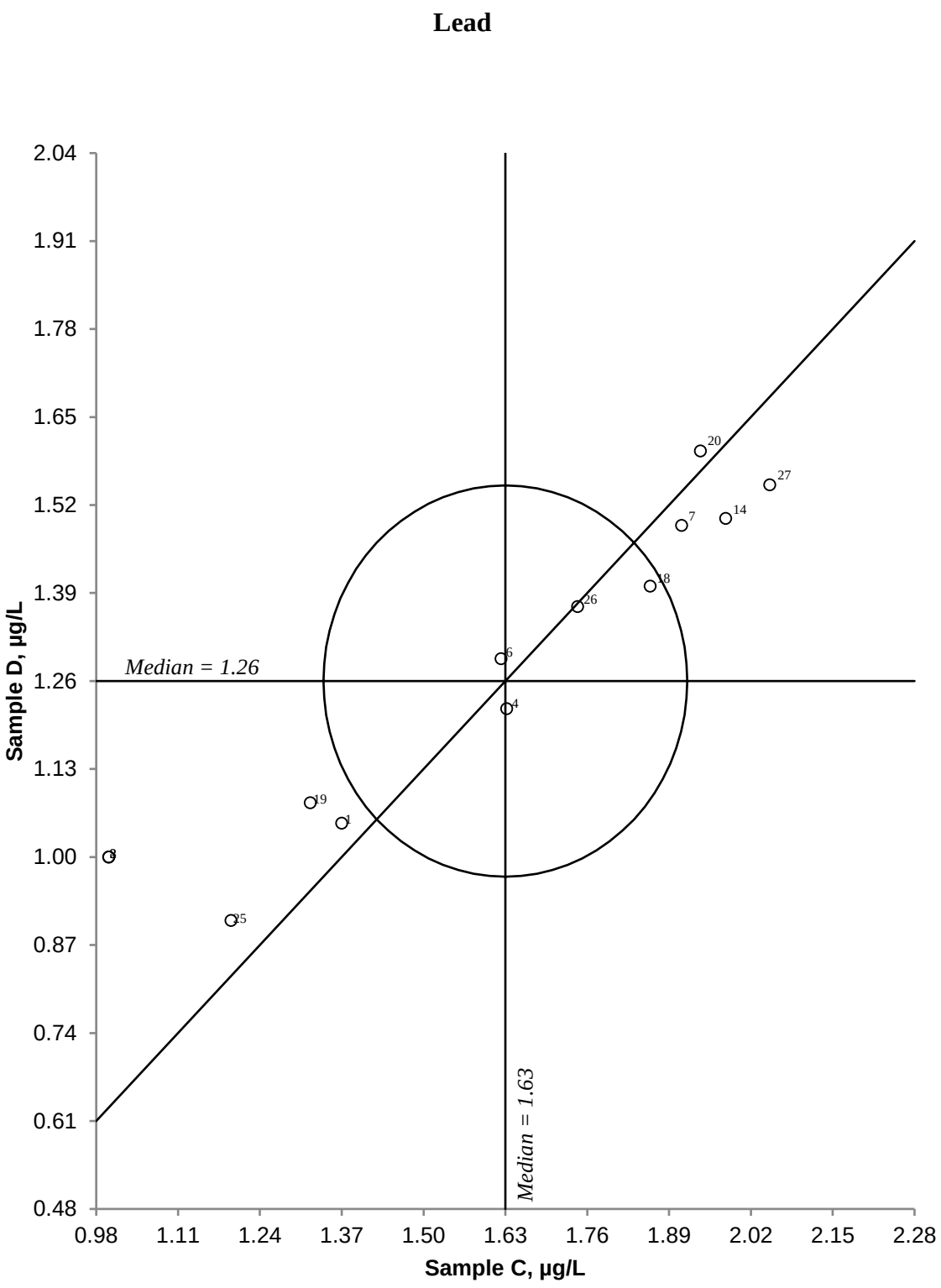

Figure 17. Youden diagram for lead. Sample pair CD. Acceptance limit, given by circle, is 20%.

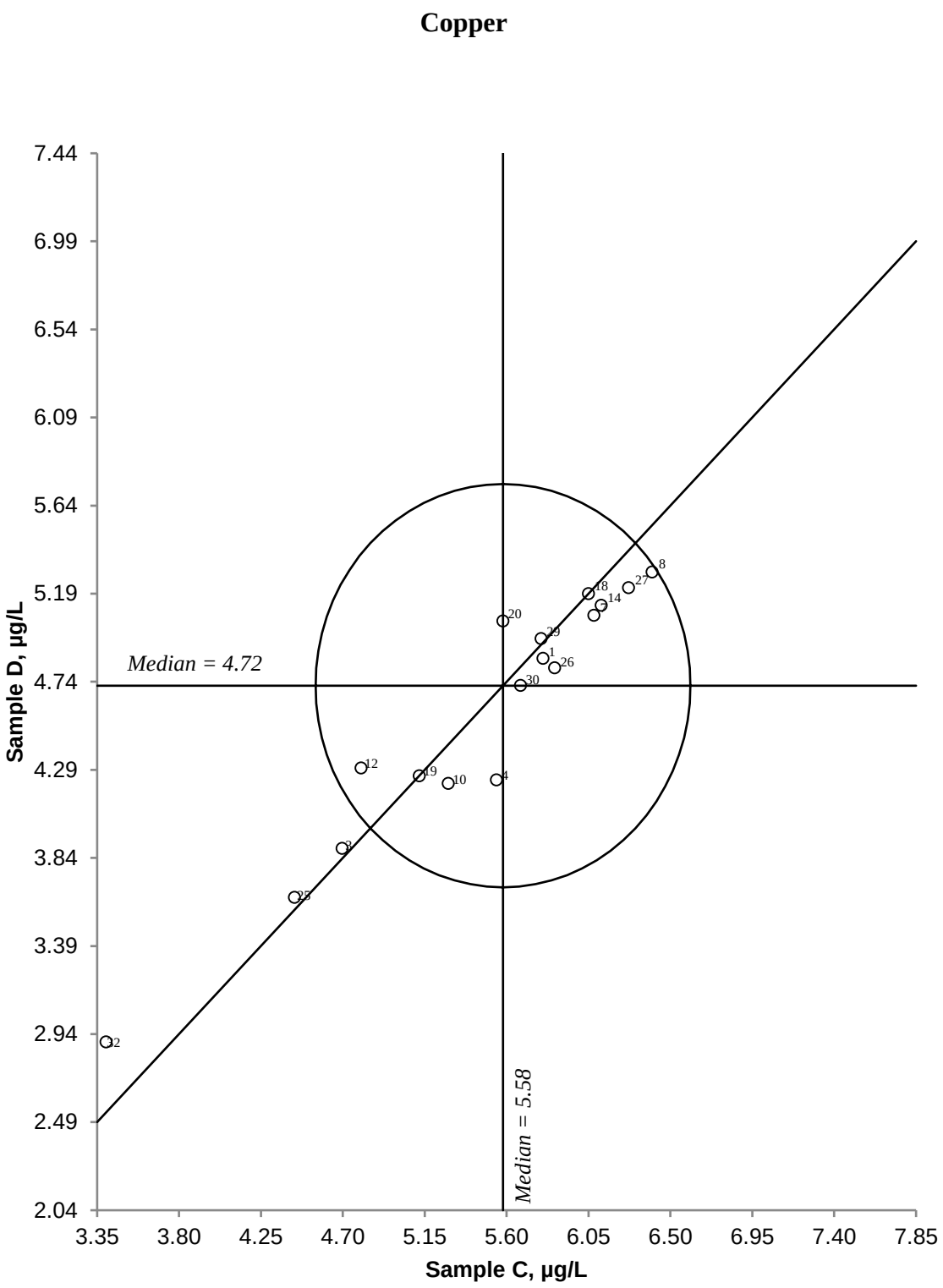

Figure 18. Youden diagram for copper. Sample pair CD. Acceptance limit, given by circle, is 20%.

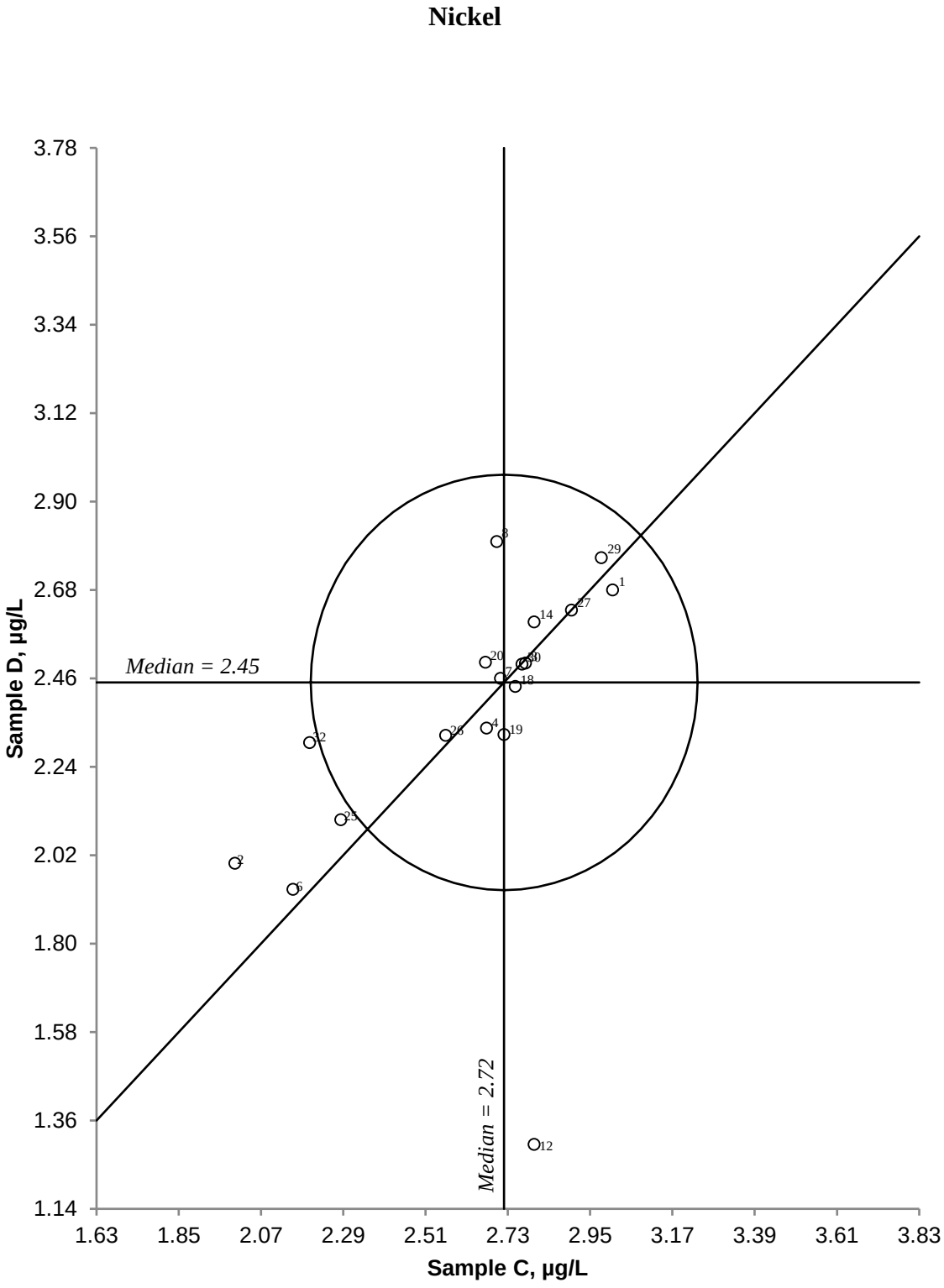

Figure 19. Youden diagram for nickel. Sample pair CD. Acceptance limit, given by circle, is 20%.

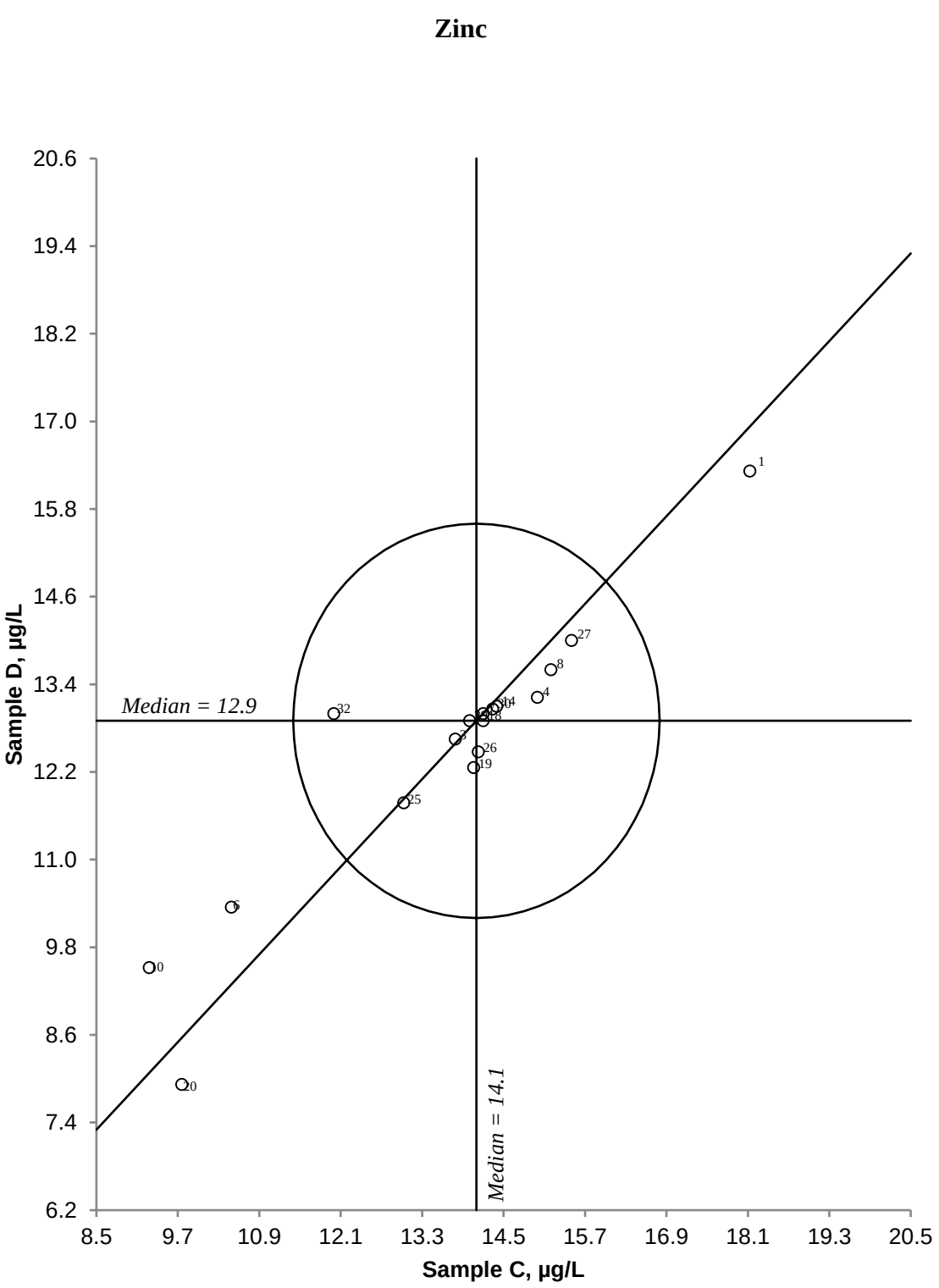

Figure 20. Youden diagram for zinc. Sample pair CD. Acceptance limit, given by circle, is 20%.

4 Literature

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

2. Youden, W.J.: Graphical Diagnosis of Interlaboratory Test Results. Industrial Quality Control. 1959, pp 15 - 24.

3. Youden, W.J., Steiner, E.H.: Statistical Manual of the Association of Official Analytical Chemists. Statistical Techniques for Collaborative Tests. Arlington, 1975.

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

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

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

Appendix A. The participating laboratories

Table A. 1. Information of the participating laboratories including name, address, and country.

No	Name of Laboratory	Address	Country
1	Bayerische Landesanstalt fuer Wald und Forstwirtschaft Abteilung 2 - Boden und Klima	Hans-Carl-von-Carlowitz-Platz 1 D-85354 Freising	Germany
2	Centre for Hidrographic Studies	Paseo Bajo Virgen del Puerto, 3, 28005 Madrid	Spain
3	Büsgen-Institute - Soil Science of Temperate Ecosystems	D-37077 Goettingen Buesgenweg 2	Germany
4	ISSeP Colfontaine Zoning Schweitzer	Rue de la Platinerie B-7340 COLFONTAINE	Belgium
5	Environmental Pollution Monitoring Center Laboratory of surface and sea	Verkhne-Rostinskoe sh,51,MUGMS,Murmansk,183034	Russian Federation
6	Institute of Biology of FRC Komi Science Centre of the Ural Branch of the RAS IB FRC Komi SC UB RAS	Kommunisticheskaya st.,28 Syktyvkar,167982,Russia	Russian Federation
7	Bayerisches Landesamt fuer Umwelt	Ref 71 Bürgerm-Ulrich-Str. 160 D-86179 Augsburg	Germany
8	CNR Institute of Water Research (IRSA)	Largo Tonolli 50 I-28922 VERBANIA Pallanza	Italy
9	Marine Scotland Science Freshwater Laboratory	Faskally,Pitlochry,Perthshire,PH16 5BB, Scotland.	United Kingdom
10	Hydrochemical Laboratory by Federal State Enterprise on Water Industry	10 A Stahanovskaya str., Pskov, 180004	Russian Federation
11	Yu.A.Izrael Institute of Global Climate and Ecology (IGCE) Roshydromet	20-B, Glebovskaya St., Moscow, 107258, RUSSIA	Russian Federation
12	Regional Laboratory for Analytical Control and Analysis Filial "Baltwodhoz"	199004,26,Srednii prospekt, St.Petersburg, Russia	Russian Federation
13	Chemical Laboratory, Czech Geological Survey	Geologická 6, 152 00 Prague	Czech Republic
14	Swedish University for Agricultural Sciences Aquatic Sciences and Assesment	Box 7050 750 07 UPPSALA	Sweden
15	Institute of Environmental Protection-Puszcza Borecka station	Kolektorska 4, 01-692, Warszawa, Poland	Poland
16	Institut fur Ökologie	Technikerstr. 25 6020 Innsbruck Austria Europe	Austria
17	Forest Nutrition and Water Resources Department of Ecology, Technis	H.C.v.Carlowitz-Platz 2 D-85354 Freising Germany	Germany
18	Norsk institutt for vannforskning	Økernveien 94 NO-0579 OSLO	Norway

Table A. 1. cont.

No	Name of Laboratory	Address	Country
19	Insitute of Industrial Ecology Problems of the North (INEP) Center for the collective use	184209 Apatity, Akademgorodok 14A, Murmansk reg.	Russian Federation
20	Polish Academy of Sciences Institute of Botany	PAN Instytut Botaniki 31-512 Kraków ul. Lubicz 46	Poland
21	Institute for Public Health Pancevo	6 Oktobar No 9 26000 Pancevo	Serbia
22	Laboratoire d'écologie fonctionnelle et environnement (EcoLab)	Avenue Agrobiopole 31326 Castanet Tolosan	France
23	Radbouduniversiteit afd. Ecologie t.a.v. G. Verheggen	Postbus 9010 6500 GL Nijmegen The Netherlands	Netherlands
24	Environment Agency EQMD/SWQMC	38Albi¿oara str,Chisinau Moldova MD-2005	Moldova, Republic Of
25	Vlaamse MilieuMaatschappij (VMM) Dienst Laboratorium	Raymonde de Larochelaan 1,9051 Sint-Denijs-Westrem	Belgium
26	Ufficio del Monitoraggio Ambientale - Laboratorio	Via Mirasole 22 6500 Bellinzona	Switzerland
27	IVL Svenska miljöinstitutet AB	P.O. Box 53021 SE-400 14 Gothenburg	Sweden
28	Staatliche Betriebgesellschaft für Umwelt und Landwirtschaft (BfUL)	Dresdner Straße 183 D-09131 Chemnitz	Germany
29	Estonian Environment Research Centre	Marja 4 D 10617 Tallinn Estonia	Estonia
30	Natural Resources Wales Analytical Services (NRWAS)	As per delivery address below	United Kingdom
31	Staatliche Betriebsgesellschaft für Umwelt und Landwirtschaft (BfUL)	Haus5, FB53 Waldheimer Str. 219 D-01683 Nossen	Germany
32	NLS Starcross laboratory Staplake Mount	Starcross labortory, Exeter, EX68FD	United Kingdom

Table A. 2. Overview of the different countries represented by the participating laboratories.

Country	No. of labs.	Country	No. of labs.
Austria	1	Netherlands	1
Belgium	2	Norway	1
Czech Republic	1	Poland	2
Estonia	1	Russia	6
France	1	Serbia	1
Germany	6	Spain	1
Italy	1	Sweden	2
Moldova, Republic Of	1	Switzerland	1
		United Kingdom	3

Total: 17 countries

Appendix B. Preparation of the samples

Both sample sets, AB and CD, were prepared using water from Maridalsvannet (Lake Maridal) outside of Oslo, Norway. The lake is a drinking water source and has relatively low levels of the parameters of interest in the intercomparison test. This water was then diluted approximately 1:2 using deionized water from the laboratory, in order to mimic water coming from a mountain lake.

The water was collected during the 19th of May 2021 and transported to the laboratory using two 25 L plastic containers. The water was allowed to settle for approximately 24 hours before filtration through 0.45 µm cellulose acetate membrane filters. Then, the filtrate settled for three weeks until the below mentioned additions were made to produce sample sets AB and CD.

To produce sample set AB, some amount of phosphorous was added in the form of phosphate, using monopotassium phosphate (KH_2PO_4). This addition was conducted as close as possible to the day of sample shipment to avoid biodegradation. Sample set CD was created by spiking with standard solution of the metals: lead, cadmium, copper, nickel, and zinc. Aluminum, iron and manganese were found to be present in high enough values without spiking the samples. By an error, sample set CD was not conserved by adding nitric acid. This should normally have been done to a concentration of 0.5% (v/v), and the error can potentially have impacted some of the results, and most likely the results for lead. 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 D.2.1 – D.2.20. 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:

$S^* = 1.483 \times$ the median of $|x_i - m|$ $\quad (i = 1, 2 \ldots. p)$

New value for the robust standard deviation is then calculated according to equations C.3-C6 in Annex C. The robust standard deviation is then derived by an iterative calculation by updating the values several times using the modified data, until the process converges.

The uncertainty u_x of the assigned value for the true value is then calculated according to chapter 5.6 in ISO 13528:

$$\mu_X = 1.25\ x\ S^* / \sqrt{p}$$

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

$U = 2 \times u_X$

It is important to 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 C. 1. 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	6.31	25	0.168	0.042	0.084
Units	B	6.38	25	0.151	0.038	0.075
Conductivity	A	1.21	23	0.080	0.021	0.042
(mS/m)	B	1.10	23	0.068	0.018	0.035
Alkalinity	A	0.036	12	0.0069	0.0025	0.0050
(mmol/L)	B	0.032	11	0.0046	0.0017	0.0035
Nitrate + nitrite-nitrogen	A	84.5	15	15.53	5.01	10.02
(µg/L)	B	77.3	14	13.84	4.62	9.25
Chloride	A	1.11	23	0.064	0.017	0.033
(mg/L)	B	1.01	23	0.060	0.016	0.031
Sulphate	A	0.747	23	0.0641	0.0167	0.0334
(mg/L)	B	0.675	22	0.0485	0.0129	0.0259
Calcium	A	1.00	27	0.133	0.032	0.064
(mg/L)	B	0.91	27	0.110	0.026	0.053
Magnesium	A	0.170	26	0.0169	0.0041	0.0083
(mg/L)	B	0.154	26	0.0178	0.0044	0.0087
Sodium	A	0.835	28	0.0576	0.0136	0.0272
(mg/L)	B	0.762	26	0.0418	0.0102	0.0205
Potassium	A	0.151	26	0.0187	0.0046	0.0092
(mg/L)	B	0.140	25	0.0172	0.0043	0.0086
Total organic carbon	A	2.51	17	0.398	0.121	0.242
(mg/L)	B	2.40	17	0.379	0.115	0.230
Total phosphorous	A	13.8	15	4.27	1.38	2.76
(µg/L)	B	13.0	14	3.39	1.13	2.26
Aluminium	C	52.3	18	7.68	2.26	4.53
(µg/L)	D	47.2	18	6.99	2.06	4.12
Iron	C	11.2	18	2.30	0.68	1.35
(µg/L)	D	10.9	18	2.06	0.61	1.21
Manganese	C	2.67	15	0.391	0.126	0.253
(µg/L)	D	2.96	15	0.292	0.094	0.189
Cadmium	C	0.507	18	0.0724	0.0213	0.0427
(µg/L)	D	0.465	18	0.0539	0.0159	0.0318
Lead	C	1.63	15	0.462	0.149	0.298
(µg/L)	D	1.26	12	0.343	0.124	0.248
Copper	C	5.58	19	0.923	0.265	0.529
(µg/L)	D	4.72	19	0.818	0.235	0.469
Nickel	C	2.72	18	0.286	0.084	0.168
(µg/L)	D	2.45	18	0.298	0.088	0.175
Zinc	C	14.1	17	1.89	0.57	1.14
(µg/L)	D	12.9	17	1.17	0.36	0.71

Appendix D. Results reported by the participating laboratories

Table D. 1. Results reported by the participating laboratories.

Lab.	pH, Units		Conductivity, mS/m		Alkalinity, mmol/L		Nitrate + nitrite-nitrogen, µg/L		Chloride, mg/L		Sulphate, mg/L		Calcium, mg/L	
nr.	A	B	A	B	A	B	A	B	A	B	A	B	A	B
1	6.40	6.38	1.10	1.00	0.045	0.042	81.0	72.7	1.11	1.01	0.732	0.667	1.03	0.95
2	6.23	6.23	0.83	0.83	0.052	0.052							1.00	1.00
3	6.22	6.39	1.24	1.12			36.0	26.0	1.03	0.95	0.662	0.607	1.02	0.92
4	6.50	6.43	12.18	11.16			89.0	81.8	1.12	1.03	0.749	0.683	0.97	0.88
5	5.95	5.79	1.21	1.15					1.06	1.10	0.709	0.641	0.86	0.83
6	6.21	6.11	1.02	0.95	0.059	0.054	3.3	3.3	1.03	0.96	0.747	0.666	0.99	0.89
7	6.50	6.50	1.30	1.10			84.0	77.0	1.10	1.00	0.660	0.580	1.00	0.91
8	6.33	6.30	1.22	1.11	0.041	0.034	53.0	74.0	1.11	1.01	0.740	0.670	0.77	0.72
9	6.33	6.28	1.14	1.02	0.033	0.028	93.6	85.9	1.07	0.97	0.753	0.690	1.03	1.04
10	6.40	6.40	1.22	1.10	52.800	47.200			1.42	1.15	0.790	0.600	0.51	0.64
11														
12	6.94	6.77	1.25	1.16			19.4	12.0	1.28	1.22	0.975	0.730	0.83	0.75
13	6.25	6.21	1.09	0.99	0.033	0.032			1.17	1.07	0.660	0.640	0.99	0.88
14	6.24	6.30	1.11	1.06	0.035	0.030	85.0	77.5	1.13	1.03	0.779	0.716	1.01	0.92
15	6.31	6.23	1.11	1.02										
16	6.57	6.57	1.21	1.11	0.043	0.038	88.0	78.0	1.10	1.01	0.760	0.680	1.35	1.25
18	6.15	6.38	1.22	1.11	0.066	0.070	96.0	88.0	1.07	0.98	0.650	0.600	1.18	1.07
19	6.15	6.06	1.07	0.99	0.037	0.034	0.0	0.0	1.19	1.03	0.720	0.680	0.92	0.85
20	6.55	6.41	1.21	1.14			54.8	53.0	0.89	0.79	0.940	0.890	1.12	1.03
21					1.100	1.700							2.00	1.60
22	5.10	5.10	1.37	1.11	0.023	0.026	78.0	70.0	1.12	0.95	0.720	0.610	2.13	2.01
23	5.71	5.87			0.060	0.070	55.3	48.9	0.86	0.79			1.03	0.89
25													1.11	0.87
26	6.49	6.40	1.16	1.06	0.039	0.031	0.1	0.1	1.15	1.05	0.757	0.698	1.10	1.01
27	6.30	6.30	1.20	1.10	0.031	0.028	85.0	0.0	1.14	1.04	0.747	0.680	0.97	0.88
28	6.30	6.40	1.25	1.12	0.099	0.089	70.0	50.0	1.07	1.00	0.840	0.780	0.67	0.64
29	6.30	6.29	1.19	1.09	0.061	0.059	92.6	79.4	1.12	1.02	0.766	0.681	1.07	0.95
30	6.44	6.40	1.11	1.64	0.036	0.033							1.02	0.91
31	6.42	6.39	1.24	1.13			91.0	84.0	1.08	0.99	0.710	0.660	0.93	0.84
32											0.810	0.710	0.77	1.00

Table D. 1. cont.

Lab.	Magnesium, mg/L		Sodium, mg/L		Potassium, mg/L		Total organic carbon, mg/L		Total phosphorous, µg/L		Aluminium, µg/L		Iron, µg/L	
nr.	A	B	A	B	A	B	A	B	A	B	C	D	C	D
1	0.156	0.142	0.835	0.768	0.141	0.155	2.04	2.00	12.0	8.0	43.8	41.0	10.5	10.4
2	0.200	0.200	0.800	0.800	0.200	0.200	3.17	3.17			35.0	35.0	7.0	7.0
3	0.182	0.166	0.850	0.783	0.134	0.180	3.58	3.51	0.5	0.9	61.9	57.2	10.6	10.1
4	0.168	0.152	0.857	0.782	0.152	0.140			12.9	12.3			10.2	9.3
5	0.151	0.141	0.927	0.848	0.170	0.153								
6	0.153	0.141	0.766	0.711	0.143	0.132	2.23	2.51	1.3	2.4	40.0	38.5	8.0	7.8
7	0.171	0.155	0.869	0.785	0.141	0.130	2.30	2.30	13.0	14.0	58.2	53.3	13.0	12.5
8	0.130	0.120	0.770	0.720	0.130	0.130	2.27	2.20	9.0	13.0	53.0	50.0	9.1	11.4
9	0.170	0.158	0.849	0.764	0.162	0.148	2.36	2.22	14.1	12.5			13.0	13.0
10	3.490	6.170	1.090	1.390							52.8	47.2		
11														
12	0.185	0.184	0.705	0.695	0.296	0.288	2.66	2.58	5.0	6.5	54.6	51.8		
13	0.170	0.150	0.850	0.750	0.155	0.130	2.63	2.50	9.1	8.4				
14	0.178	0.163	0.949	0.854	0.146	0.138	2.76	2.68	15.4	13.2	58.6	54.2	13.8	12.8
15														
16	0.190	0.170	0.820	0.750	0.170	0.160	2.51	2.45	13.8	12.4			12.8	14.2
18	0.190	0.170	0.930	0.850	0.120	0.110	2.60	2.40	15.0	13.0	56.2	51.4	14.6	14.9
19	0.150	0.140	0.820	0.750	0.160	0.150			7.0	9.0	52.3	44.1	13.1	12.2
20	0.171	0.158	0.814	0.721	0.226	0.214					26.9	25.2	12.7	10.8
21														
22	0.280	0.260	0.820	0.750	0.130	0.120	1.82	1.77	17.5	18.3				
23	0.170	0.120	0.590	0.350	0.170	0.160			10.7	10.5				
25	0.175	0.152	0.835	0.771	0.161	0.151			22.0	24.0	51.6	47.2	13.1	10.3
26	0.170	0.156	0.826	0.753	0.101	0.098	2.27	2.25	19.7	18.2	50.5	46.4	10.2	10.3
27	0.165	0.149	0.802	0.727	0.155	0.141			0.0	0.0	59.3	54.6	11.7	10.9
28	0.110	0.100	0.810	0.730	0.140	0.130	2.49	2.28	19.0	17.0				
29	0.172	0.156	0.856	0.772	0.155	0.140	3.03	3.06	18.0	16.0	51.0	46.0	9.4	9.7
30	0.146	0.131	0.901	0.811	0.177	0.163	2.67	2.37	25.0	26.2	53.8	48.2		
31	0.180	0.170	0.890	0.081	0.150	0.140								
32	0.150	0.170	0.850	0.750	0.150	0.140					48.0	44.0	10.2	11.7

Table D. 1. cont.

Lab.	Manganese, µg/L		Cadmium, µg/L		Lead, µg/L		Copper, µg/L		Nickel, µg/L		Zinc, µg/L	
nr.	C	D	C	D	C	D	C	D	C	D	C	D
1	2.65	3.26	0.600	0.550	1.37	1.05	5.80	4.86	3.01	2.68	18.1	16.3
2	2.00	2.00			1.00	1.00	3.00	3.00	2.00	2.00		
3	1.24	1.38	0.427	0.409	1.08	0.47	4.70	3.89	2.78	2.50	13.8	12.6
4	2.59	2.80	0.544	0.473	1.63	1.22	5.54	4.24	2.67	2.34	15.0	13.2
5												
6	2.08	2.52	0.503	0.611	1.62	1.29	3.16	2.72	2.16	1.94	10.5	10.4
7	2.71	2.96	0.512	0.472	1.91	1.49	6.08	5.08	2.71	2.46	14.2	13.0
8	2.40	3.00	0.600	0.500	1.00	1.00	6.40	5.30	2.70	2.80	15.2	13.6
9												
10			0.390	0.380			5.28	4.22			9.3	9.5
11			0.450	0.410	0.55	0.18	19.10	2.49				
12	1.00	3.00					4.80	4.30	2.80	1.30	6.1	5.4
13												
14	2.92	3.01	0.518	0.474	1.98	1.50	6.12	5.13	2.80	2.60	14.4	13.1
15												
16												
18	2.71	2.86	0.505	0.454	1.86	1.40	6.05	5.19	2.75	2.44	14.2	12.9
19	2.09	2.83	0.530	0.420	1.32	1.08	5.12	4.26	2.72	2.32	14.1	12.3
20	3.38	2.15	0.420	0.410	1.94	1.60	5.58	5.05	2.67	2.50	9.8	7.9
21												
22												
23												
25	2.44	2.81	0.418	0.388	1.19	0.91	4.43	3.64	2.28	2.11	13.0	11.8
26	2.77	3.07	0.500	0.466	1.75	1.37	5.86	4.81	2.56	2.32	14.1	12.5
27	3.03	3.19	0.558	0.510	2.05	1.55	6.27	5.22	2.90	2.63	15.5	14.0
28												
29	2.67	2.99	0.541	0.483	0.88	0.69	5.79	4.96	2.98	2.76	14.0	12.9
30			0.509	0.464			5.68	4.72	2.77	2.50	14.3	13.1
31												
32	2.78	3.20	0.410	0.440	0.72	0.56	3.40	2.90	2.20	2.30	12.0	13.0

Table D.2.1. Statistics - pH

Sample A

Analytical method: All

Unit: Units

Number of participants	26	Range	1.23
Number of omitted results	1	Variance	0.05
True value	6.31	Standard deviation	0.23
Mean value	6.33	Relative standard deviation	3.6%
Median value	6.31	Relative error	0.3%

Analytical results in ascending order:

22	5.10	O	13	6.25	31	6.42
23	5.71		28	6.30	30	6.44
5	5.95		27	6.30	26	6.49
18	6.15		29	6.30	7	6.50
19	6.15		15	6.31	4	6.50
6	6.21		9	6.33	20	6.55
3	6.22		8	6.33	16	6.57
2	6.23		1	6.40	12	6.94
14	6.24		10	6.40		

O = Omitted result

Sample B

Analytical method: All

Unit: Units

Number of participants	26	Range	0.98
Number of omitted results	1	Variance	0.04
True value	6.38	Standard deviation	0.20
Mean value	6.31	Relative standard deviation	3.2%
Median value	6.38	Relative error	-1.1%

Analytical results in ascending order:

22	5.10	O	29	6.29	30	6.40
5	5.79		8	6.30	28	6.40
23	5.87		14	6.30	10	6.40
19	6.06		27	6.30	20	6.41
6	6.11		1	6.38	4	6.43
13	6.21		18	6.38	7	6.50
15	6.23		31	6.39	16	6.57
2	6.23		3	6.39	12	6.77
9	6.28		26	6.40		

O = Omitted result

Table D.2.2. Statistics - Conductivity

Sample A

Analytical method: All
Unit: mS/m

Number of participants	25	Range	0.35
Number of omitted results	3	Variance	0.01
True value	1.21	Standard deviation	0.08
Mean value	1.19	Relative standard deviation	6.8%
Median value	1.21	Relative error	-1.8%

Analytical results in ascending order:

2	0.83	O	26	1.16	3	1.24	
6	1.02		29	1.19	31	1.24	
19	1.07		27	1.20	28	1.25	
13	1.09		5	1.21	12	1.25	
1	1.10		16	1.21	7	1.30	
30	1.11	O	20	1.21	22	1.37	
14	1.11		10	1.22	4	12.18	O
15	1.11		18	1.22			
9	1.14		8	1.22			

O = Omitted result

Sample B

Analytical method: All
Unit: mS/m

Number of participants	25	Range	0.21
Number of omitted results	3	Variance	0.00
True value	1.10	Standard deviation	0.06
Mean value	1.08	Relative standard deviation	5.5%
Median value	1.10	Relative error	-1.9%

Analytical results in ascending order:

2	0.83	O	29	1.09	3	1.12	
6	0.95		10	1.10	31	1.13	
13	0.99		7	1.10	20	1.14	
19	0.99		27	1.10	5	1.15	
1	1.00		22	1.11	12	1.16	
9	1.02		18	1.11	30	1.64	O
15	1.02		16	1.11	4	11.16	O
26	1.06		8	1.11			
14	1.06		28	1.12			

O = Omitted result

Table D.2.3. Statistics - Alkalinity

Sample A

Analytical method: All

Unit: mmol/L

Number of participants	19	Range	0.022
Number of omitted results	8	Variance	0.000
True value	0.036	Standard deviation	0.006
Mean value	0.036	Relative standard deviation	17.1%
Median value	0.036	Relative error	-0.1%

Analytical results in ascending order:

22	0.023	26	0.039	29	0.061	O
27	0.031	8	0.041	18	0.066	O
13	0.033	16	0.043	28	0.099	O
9	0.033	1	0.045	21	1.100	O
14	0.035	2	0.052 O	10	52.800	O
30	0.036	6	0.059 O			
19	0.037	23	0.060 O			

O = Omitted result

Sample B

Analytical method: All

Unit: mmol/L

Number of participants	19	Range	0.016
Number of omitted results	8	Variance	0.000
True value	0.032	Standard deviation	0.005
Mean value	0.032	Relative standard deviation	14.4%
Median value	0.032	Relative error	1.1%

Analytical results in ascending order:

22	0.026	19	0.034	18	0.070	O
9	0.028	8	0.034	23	0.070	O
27	0.028	16	0.038	28	0.089	O
14	0.030	1	0.042	21	1.700	O
26	0.031	2	0.052 O	10	47.200	O
13	0.032	6	0.054 O			
30	0.033	29	0.059 O			

O = Omitted result

Table D.2.4. Statistics - Nitrate + nitrite-nitrogen

Sample A

Analytical method: All

Unit: µg/L

Number of participants	20	Range	43.0
Number of omitted results	6	Variance	229.2
True value	84.5	Standard deviation	15.1
Mean value	79.4	Relative standard deviation	19.1%
Median value	84.5	Relative error	-6.1%

Analytical results in ascending order:

19	0.0	O	23	55.3		16	88.0
26	0.1	O	28	70.0		4	89.0
6	3.3	O	22	78.0		31	91.0
12	19.4	O	1	81.0		29	92.6
3	36.0	O	7	84.0		9	93.6
8	53.0		14	85.0		18	96.0
20	54.8		27	85.0	O		

O = Omitted result

Sample B

Analytical method: All

Unit: µg/L

Number of participants	20	Range	39.1
Number of omitted results	6	Variance	170.1
True value	77.3	Standard deviation	13.0
Mean value	72.9	Relative standard deviation	17.9%
Median value	77.3	Relative error	-5.7%

Analytical results in ascending order:

27	0.0	O	28	50.0		16	78.0
19	0.0	O	20	53.0		29	79.4
26	0.1	O	22	70.0		4	81.8
6	3.3	O	1	72.7		31	84.0
12	12.0	O	8	74.0		9	85.9
3	26.0	O	7	77.0		18	88.0
23	48.9		14	77.5			

O = Omitted result

Table D.2.5. Statistics - Chloride

Sample A

Analytical method: All

Unit: mg/L

Number of participants	23	Range	0.56
Number of omitted results	0	Variance	0.01
True value	1.11	Standard deviation	0.11
Mean value	1.11	Relative standard deviation	10.0%
Median value	1.11	Relative error	-0.4%

Analytical results in ascending order:

23	0.86	31	1.08	14	1.13
20	0.89	7	1.10	27	1.14
6	1.03	16	1.10	26	1.15
3	1.03	1	1.11	13	1.17
5	1.06	8	1.11	19	1.19
9	1.07	22	1.12	12	1.28
18	1.07	29	1.12	10	1.42
28	1.07	4	1.12		

O = Omitted result

Sample B

Analytical method: All

Unit: mg/L

Number of participants	23	Range	0.43
Number of omitted results	0	Variance	0.01
True value	1.01	Standard deviation	0.09
Mean value	1.01	Relative standard deviation	9.2%
Median value	1.01	Relative error	-0.4%

Analytical results in ascending order:

23	0.79	7	1.00	19	1.03
20	0.79	28	1.00	27	1.04
3	0.95	1	1.01	26	1.05
22	0.95	8	1.01	13	1.07
6	0.96	16	1.01	5	1.10
9	0.97	29	1.02	10	1.15
18	0.98	4	1.03	12	1.22
31	0.99	14	1.03		

O = Omitted result

Table D.2.6. Statistics - Sulphate

Sample A

Analytical method: All

Unit: mg/L

Number of participants	23	Range	0.325
Number of omitted results	1	Variance	0.005
True value	0.747	Standard deviation	0.071
Mean value	0.747	Relative standard deviation	9.4%
Median value	0.747	Relative error	0.0%

Analytical results in ascending order:

18	0.650	1	0.732	29	0.766	
13	0.660	8	0.740	14	0.779	
7	0.660	6	0.747	10	0.790	
3	0.662	27	0.747	32	0.810	
5	0.709	4	0.749	28	0.840	
31	0.710	9	0.753	20	0.940	O
19	0.720	26	0.757	12	0.975	
22	0.720	16	0.760			

O = Omitted result

Sample B

Analytical method: All

Unit: mg/L

Number of participants	23	Range	0.200
Number of omitted results	1	Variance	0.002
True value	0.675	Standard deviation	0.048
Mean value	0.667	Relative standard deviation	7.2%
Median value	0.675	Relative error	-1.2%

Analytical results in ascending order:

7	0.580	6	0.666	9	0.690	
10	0.600	1	0.667	26	0.698	
18	0.600	8	0.670	32	0.710	
3	0.607	19	0.680	14	0.716	
22	0.610	27	0.680	12	0.730	
13	0.640	16	0.680	28	0.780	
5	0.641	29	0.681	20	0.890	O
31	0.660	4	0.683			

O = Omitted result

Table D.2.7. Statistics - Calcium

Sample A

Analytical method: All

Unit: mg/L

Number of participants	29	Range	0.84
Number of omitted results	2	Variance	0.03
True value	1.00	Standard deviation	0.16
Mean value	0.97	Relative standard deviation	16.9%
Median value	1.00	Relative error	-2.6%

Analytical results in ascending order:

10	0.51	13	0.99	29	1.05	
28	0.67	6	0.99	29	1.07	
8	0.77	7	1.00	26	1.10	
32	0.77	2	1.00	25	1.11	
12	0.83	14	1.01	20	1.12	
5	0.86	30	1.02	18	1.18	
19	0.92	3	1.02	16	1.35	
31	0.93	23	1.03	21	2.00	O
4	0.97	1	1.03	22	2.13	O
27	0.97	9	1.03			

O = Omitted result

Sample B

Analytical method: All

Unit: mg/L

Number of participants	29	Range	0.61
Number of omitted results	2	Variance	0.02
True value	0.91	Standard deviation	0.13
Mean value	0.91	Relative standard deviation	14.2%
Median value	0.91	Relative error	-0.4%

Analytical results in ascending order:

10	0.64	4	0.88	2	1.00	
28	0.64	23	0.89	32	1.00	
8	0.72	6	0.89	26	1.01	
12	0.75	7	0.91	20	1.03	
5	0.83	30	0.91	9	1.04	
31	0.84	14	0.92	18	1.07	
19	0.85	3	0.92	16	1.25	
25	0.87	29	0.94	21	1.60	O
13	0.88	1	0.95	22	2.01	O
27	0.88	29	0.95			

O = Omitted result

Table D.2.8. Statistics - Magnesium

Sample A

Analytical method: All

Unit: mg/L

Number of participants	28	Range	0.090
Number of omitted results	2	Variance	0.000
True value	0.170	Standard deviation	0.019
Mean value	0.166	Relative standard deviation	11.6%
Median value	0.170	Relative error	-2.3%

Analytical results in ascending order:

28	0.110	4	0.168	31	0.180	
8	0.130	9	0.170	3	0.182	
30	0.146	23	0.170	12	0.185	
32	0.150	13	0.170	16	0.190	
19	0.150	26	0.170	18	0.190	
5	0.151	7	0.171	2	0.200	
6	0.153	20	0.171	22	0.280	O
1	0.156	29	0.172	10	3.490	O
27	0.165	25	0.175			
29	0.166	14	0.178			

O = Omitted result

Sample B

Analytical method: All

Unit: mg/L

Number of participants	28	Range	0.100
Number of omitted results	2	Variance	0.000
True value	0.154	Standard deviation	0.021
Mean value	0.153	Relative standard deviation	13.6%
Median value	0.154	Relative error	-1.0%

Analytical results in ascending order:

28	0.100	29	0.151	16	0.170	
8	0.120	4	0.152	31	0.170	
23	0.120	25	0.152	18	0.170	
30	0.131	7	0.155	32	0.170	
19	0.140	29	0.156	12	0.184	
5	0.141	26	0.156	2	0.200	
6	0.141	20	0.158	22	0.260	O
1	0.142	9	0.158	10	6.170	O
27	0.149	14	0.163			
13	0.150	3	0.166			

O = Omitted result

Table D.2.9. Statistics - Sodium

Sample A

Analytical method: All

Unit: mg/L

Number of participants	28	Range	0.244
Number of omitted results	3	Variance	0.003
True value	0.835	Standard deviation	0.053
Mean value	0.839	Relative standard deviation	6.3%
Median value	0.835	Relative error	0.4%

Analytical results in ascending order:

23	0.590	O	22	0.820		4	0.857	
12	0.705		26	0.826		7	0.869	
6	0.766		1	0.835		31	0.890	O
8	0.770		25	0.835		30	0.901	
2	0.800		9	0.849		5	0.927	
27	0.802		32	0.850		18	0.930	
28	0.810		13	0.850		14	0.949	
20	0.814		3	0.850		10	1.090	O
16	0.820		29	0.853				
19	0.820		29	0.856				

O = Omitted result

Sample B

Analytical method: All

Unit: mg/L

Number of participants	28	Range	0.159
Number of omitted results	3	Variance	0.002
True value	0.762	Standard deviation	0.042
Mean value	0.766	Relative standard deviation	5.5%
Median value	0.762	Relative error	0.6%

Analytical results in ascending order:

31	0.081	O	16	0.750		3	0.783	
23	0.350	O	22	0.750		7	0.785	
12	0.695		13	0.750		2	0.800	
6	0.711		26	0.753		30	0.811	
8	0.720		29	0.762		5	0.848	
20	0.721		9	0.764		18	0.850	
27	0.727		1	0.768		14	0.854	
28	0.730		25	0.771		10	1.390	O
19	0.750		29	0.772				
32	0.750		4	0.782				

O = Omitted result

Table D.2.10. Statistics - Potassium

Sample A

Analytical method: All
Unit: mg/L

Number of participants	27	Range	0.099
Number of omitted results	2	Variance	0.000
True value	0.151	Standard deviation	0.020
Mean value	0.151	Relative standard deviation	13.2%
Median value	0.151	Relative error	-0.3%

Analytical results in ascending order:

26	0.101	14	0.146	25	0.161	
18	0.120	31	0.150	9	0.162	
8	0.130	32	0.150	5	0.170	
22	0.130	29	0.151	16	0.170	
3	0.134	4	0.152	23	0.170	
28	0.140	13	0.155	30	0.177	
7	0.141	29	0.155	2	0.200	
1	0.141	27	0.155	20	0.226	O
6	0.143	19	0.160	12	0.296	O

O = Omitted result

Sample B

Analytical method: All
Unit: mg/L

Number of participants	27	Range	0.102
Number of omitted results	2	Variance	0.000
True value	0.140	Standard deviation	0.021
Mean value	0.143	Relative standard deviation	14.7%
Median value	0.140	Relative error	2.0%

Analytical results in ascending order:

26	0.098	14	0.138	5	0.153	
18	0.110	29	0.140	1	0.155	
22	0.120	31	0.140	23	0.160	
28	0.130	32	0.140	16	0.160	
7	0.130	4	0.140	30	0.163	
8	0.130	27	0.141	3	0.180	
13	0.130	9	0.148	2	0.200	
29	0.131	19	0.150	20	0.214	O
6	0.132	25	0.151	12	0.288	O

O = Omitted result

Table D.2.11. Statistics - Total organic carbon

Sample A

Analytical method: All

Unit: mg/L

Number of participants	17	Range	1.76
Number of omitted results	0	Variance	0.18
True value	2.51	Standard deviation	0.43
Mean value	2.55	Relative standard deviation	16.7%
Median value	2.51	Relative error	1.7%

Analytical results in ascending order:

22	1.82	9	2.36	30	2.67
1	2.04	28	2.49	14	2.76
6	2.23	16	2.51	29	3.03
26	2.27	18	2.60	2	3.17
8	2.27	13	2.63	3	3.58
7	2.30	12	2.66		

O = Omitted result

Sample B

Analytical method: All

Unit: mg/L

Number of participants	17	Range	1.74
Number of omitted results	0	Variance	0.18
True value	2.40	Standard deviation	0.43
Mean value	2.49	Relative standard deviation	17.3%
Median value	2.40	Relative error	3.5%

Analytical results in ascending order:

22	1.77	7	2.30	12	2.58
1	2.00	30	2.37	14	2.68
8	2.20	18	2.40	29	3.06
9	2.22	16	2.45	2	3.17
26	2.25	13	2.50	3	3.51
28	2.28	6	2.51		

O = Omitted result

Table D.2.12. Statistics - Total phosphorous

Sample A

Analytical method: All

Unit: µg/L

Number of participants	21	Range	12.7
Number of omitted results	6	Variance	14.5
True value	13.8	Standard deviation	3.8
Mean value	13.7	Relative standard deviation	27.7%
Median value	13.8	Relative error	-0.4%

Analytical results in ascending order:

27	0.0	O	23	10.7	14	15.4	
3	0.5	O	1	12.0	22	17.5	
6	1.3	O	4	12.9	29	18.0	
12	5.0	O	7	13.0	28	19.0	
19	7.0		16	13.8	26	19.7	
8	9.0		9	14.1	25	22.0	O
13	9.1		18	15.0	30	25.0	O

O = Omitted result

Sample B

Analytical method: All

Unit: µg/L

Number of participants	21	Range	10.3
Number of omitted results	6	Variance	10.7
True value	13.0	Standard deviation	3.3
Mean value	13.0	Relative standard deviation	25.1%
Median value	13.0	Relative error	0.4%

Analytical results in ascending order:

27	0.0	O	23	10.5	7	14.0	
3	0.9	O	4	12.3	29	16.0	
6	2.4	O	16	12.4	28	17.0	
12	6.5	O	9	12.5	26	18.2	
1	8.0		18	13.0	22	18.3	
13	8.4		8	13.0	25	24.0	O
19	9.0		14	13.2	30	26.2	O

O = Omitted result

Table D.2.13. Statistics - Aluminium

Sample C

Analytical method: All

Unit: µg/L

Number of participants	18	Range	35.0
Number of omitted results	0	Variance	80.5
True value	52.3	Standard deviation	9.0
Mean value	50.4	Relative standard deviation	17.8%
Median value	52.5	Relative error	-3.6%

Analytical results in ascending order:

20	26.9	29	51.0	12	54.6
2	35.0	25	51.6	18	56.2
6	40.0	19	52.3	7	58.2
1	43.8	10	52.8	14	58.6
32	48.0	8	53.0	27	59.3
26	50.5	30	53.8	3	61.9

O = Omitted result

Sample D

Analytical method: All

Unit: µg/L

Number of participants	18	Range	32.0
Number of omitted results	0	Variance	61.5
True value	47.2	Standard deviation	7.8
Mean value	46.4	Relative standard deviation	16.9%
Median value	47.2	Relative error	-1.7%

Analytical results in ascending order:

20	25.2	29	46.0	18	51.4
2	35.0	26	46.4	12	51.8
6	38.5	25	47.2	7	53.3
1	41.0	10	47.2	14	54.2
32	44.0	30	48.2	27	54.6
19	44.1	8	50.0	3	57.2

O = Omitted result

Table D.2.14. Statistics - Iron

Sample C

Analytical method: All

Unit: µg/L

Number of participants	18	Range	7.6
Number of omitted results	0	Variance	4.5
True value	11.2	Standard deviation	2.1
Mean value	11.3	Relative standard deviation	18.8%
Median value	11.2	Relative error	0.7%

Analytical results in ascending order:

2	7.0	4	10.2	9	13.0
6	8.0	1	10.5	7	13.0
8	9.1	3	10.6	19	13.1
29	9.4	27	11.7	25	13.1
26	10.2	20	12.7	14	13.8
32	10.2	16	12.8	18	14.6

O = Omitted result

Sample D

Analytical method: All

Unit: µg/L

Number of participants	18	Range	7.9
Number of omitted results	0	Variance	4.1
True value	10.9	Standard deviation	2.0
Mean value	11.1	Relative standard deviation	18.3%
Median value	10.9	Relative error	1.6%

Analytical results in ascending order:

2	7.0	25	10.3	19	12.2
6	7.8	1	10.4	7	12.5
4	9.3	20	10.8	14	12.8
29	9.7	27	10.9	9	13.0
3	10.1	8	11.4	16	14.2
26	10.3	32	11.7	18	14.9

O = Omitted result

Table D.2.15. Statistics - Manganese

Sample C

Analytical method: All

Unit: µg/L

Number of participants	17	Range	1.38
Number of omitted results	2	Variance	0.14
True value	2.67	Standard deviation	0.37
Mean value	2.61	Relative standard deviation	14.3%
Median value	2.67	Relative error	-2.1%

Analytical results in ascending order:

12	1.00	O	25	2.44		26	2.77
3	1.24	O	4	2.59		32	2.78
2	2.00		1	2.65		14	2.92
6	2.08		29	2.67		27	3.03
19	2.09		7	2.71		20	3.38
8	2.40		18	2.71			

O = Omitted result

Sample D

Analytical method: All

Unit: µg/L

Number of participants	17	Range	1.26
Number of omitted results	2	Variance	0.13
True value	2.96	Standard deviation	0.36
Mean value	2.84	Relative standard deviation	12.8%
Median value	2.96	Relative error	-4.0%

Analytical results in ascending order:

3	1.38	O	19	2.83		14	3.01
2	2.00		18	2.86		26	3.07
20	2.15		7	2.96		27	3.19
6	2.52		29	2.99		32	3.20
4	2.80		12	3.00	O	1	3.26
25	2.81		8	3.00			

O = Omitted result

Table D.2.16. Statistics - Cadmium

Sample C

Analytical method: All

Unit: µg/L

Number of participants	18	Range	0.210
Number of omitted results	0	Variance	0.004
True value	0.507	Standard deviation	0.064
Mean value	0.496	Relative standard deviation	12.9%
Median value	0.507	Relative error	-2.1%

Analytical results in ascending order:

10	0.390	26	0.500	19	0.530
32	0.410	6	0.503	29	0.541
25	0.418	18	0.505	4	0.544
20	0.420	30	0.509	27	0.558
3	0.427	7	0.512	8	0.600
11	0.450	14	0.518	1	0.600

O = Omitted result

Sample D

Analytical method: All

Unit: µg/L

Number of participants	18	Range	0.231
Number of omitted results	0	Variance	0.003
True value	0.465	Standard deviation	0.058
Mean value	0.462	Relative standard deviation	12.6%
Median value	0.465	Relative error	-0.7%

Analytical results in ascending order:

10	0.380	32	0.440	14	0.474
25	0.388	18	0.454	29	0.483
3	0.409	30	0.464	8	0.500
11	0.410	26	0.466	27	0.510
20	0.410	7	0.472	1	0.550
19	0.420	4	0.473	6	0.611

O = Omitted result

Table D.2.17. Statistics - Lead

Sample C

Analytical method: All

Unit: µg/L

Number of participants	17	Range	1.17
Number of omitted results	3	Variance	0.16
True value	1.63	Standard deviation	0.40
Mean value	1.54	Relative standard deviation	26.3%
Median value	1.63	Relative error	-5.8%

Analytical results in ascending order:

11	0.55	O	25	1.19		18	1.86
32	0.72	O	19	1.32		7	1.91
29	0.88		1	1.37		20	1.94
2	1.00		6	1.62		14	1.98
8	1.00		4	1.63		27	2.05
3	1.08	O	26	1.75			

O = Omitted result

Sample D

Analytical method: All

Unit: µg/L

Number of participants	17	Range	0.92
Number of omitted results	3	Variance	0.08
True value	1.26	Standard deviation	0.28
Mean value	1.22	Relative standard deviation	22.6%
Median value	1.26	Relative error	-2.8%

Analytical results in ascending order:

11	0.18	O	2	1.00		18	1.40
3	0.47	O	1	1.05		7	1.49
32	0.56	O	19	1.08		14	1.50
29	0.69		4	1.22		27	1.55
25	0.91		6	1.29		20	1.60
8	1.00		26	1.37			

O = Omitted result

Table D.2.18. Statistics - Copper

Sample C

Analytical method: All

Unit: µg/L

Number of participants	20	Range	3.40
Number of omitted results	1	Variance	1.10
True value	5.58	Standard deviation	1.05
Mean value	5.21	Relative standard deviation	20.1%
Median value	5.58	Relative error	-6.6%

Analytical results in ascending order:

2	3.00	10	5.28	18	6.05	
6	3.16	4	5.54	7	6.08	
32	3.40	20	5.58	14	6.12	
25	4.43	30	5.68	27	6.27	
3	4.70	29	5.79	8	6.40	
12	4.80	1	5.80	11	19.10	O
19	5.12	26	5.86			

O = Omitted result

Sample D

Analytical method: All

Unit: µg/L

Number of participants	20	Range	2.58
Number of omitted results	1	Variance	0.68
True value	4.72	Standard deviation	0.83
Mean value	4.39	Relative standard deviation	18.8%
Median value	4.72	Relative error	-6.9%

Analytical results in ascending order:

11	2.49	O	4	4.24	20	5.05
6	2.72		19	4.26	7	5.08
32	2.90		12	4.30	14	5.13
2	3.00		30	4.72	18	5.19
25	3.64		26	4.81	27	5.22
3	3.89		1	4.86	8	5.30
10	4.22		29	4.96		

O = Omitted result

Table D.2.19. Statistics - Nickel

Sample C

Analytical method: All

Unit: µg/L

Number of participants	18	Range	1.01
Number of omitted results	0	Variance	0.08
True value	2.72	Standard deviation	0.29
Mean value	2.64	Relative standard deviation	10.9%
Median value	2.72	Relative error	-3.1%

Analytical results in ascending order:

2	2.00	4	2.67	3	2.78
6	2.16	8	2.70	14	2.80
32	2.20	7	2.71	12	2.80
25	2.28	19	2.72	27	2.90
26	2.56	18	2.75	29	2.98
20	2.67	30	2.77	1	3.01

O = Omitted result

Sample D

Analytical method: All

Unit: µg/L

Number of participants	18	Range	1.50
Number of omitted results	0	Variance	0.13
True value	2.45	Standard deviation	0.36
Mean value	2.36	Relative standard deviation	15.1%
Median value	2.45	Relative error	-3.7%

Analytical results in ascending order:

12	1.30	19	2.32	20	2.50
6	1.94	4	2.34	14	2.60
2	2.00	18	2.44	27	2.63
25	2.11	7	2.46	1	2.68
32	2.30	30	2.50	29	2.76
26	2.32	3	2.50	8	2.80

O = Omitted result

Table D.2.20. Statistics - Zinc

Sample C

Analytical method: All

Unit: µg/L

Number of participants	18	Range	8.9
Number of omitted results	1	Variance	4.8
True value	14.1	Standard deviation	2.2
Mean value	13.6	Relative standard deviation	16.1%
Median value	14.1	Relative error	-3.4%

Analytical results in ascending order:

12	6.1	O	3	13.8	30	14.3
10	9.3		29	14.0	14	14.4
20	9.8		19	14.1	4	15.0
6	10.5		26	14.1	8	15.2
32	12.0		18	14.2	27	15.5
25	13.0		7	14.2	1	18.1

O = Omitted result

Sample D

Analytical method: All

Unit: µg/L

Number of participants	18	Range	8.4
Number of omitted results	1	Variance	3.4
True value	12.9	Standard deviation	1.9
Mean value	12.5	Relative standard deviation	14.9%
Median value	12.9	Relative error	-3.3%

Analytical results in ascending order:

12	5.4	O	26	12.5	30	13.1
20	7.9		3	12.6	14	13.1
10	9.5		18	12.9	4	13.2
6	10.4		29	12.9	8	13.6
25	11.8		32	13.0	27	14.0
19	12.3		7	13.0	1	16.3

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/

Thrane, J.E., de Wit, H. and Austnes, K. 2021. Effects of nitrogen on nutrient-limitation in oligotrophic northern surface waters. NIVA report SNO 7680-2021. **ICP Waters report 146/2021.**

Garmo, Ø., Furuseth, I.S., and Austnes, K. (editors) 2021. Proceedings of the 37th Task Force meeting of the ICP Waters Programme held on-line, April 28-29, 2021. NIVA report SNO 7657-2021. **ICP Waters report 145/2021**

Velle, G., Birkeland, I.B., Johannessen, A. and Landås, T.S. 2020. Biological intercalibration: Invertebrates 2020. NIVA SNO 7556-2020. **ICP Waters report 144/2020**

Gundersen, C.B. and Bryntesen, T. 2021. Intercomparison 2034: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Tot-P, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA SNO 7621-2021. **ICP Waters report 143/2021.**

Gundersen, C.B. 2020. Intercomparison 2034: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Tot-P, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA SNO 7549-2020. **ICP Waters report 143/2020.** *Obs! This report has been revised (see ICP Waters 143/2021 above).*

Garmo, Ø., Arle, J., Austnes, K. de Wit, H., Fölster, J., Houle, D., Hruška, J., Indriksone, I., Monteith, D., Rogora, M., Sample, J.E., Steingruber, S., Stoddard, J.L., Talkop, R., Trodd, W., Ulańczyk, R.P. and Vuorenmaa, J. 2020. Trends and patterns in surface water chemistry in Europe and North America between 1990 and 2016, with particular focus on changes in land use as a confounding factor for recovery. NIVA report SNO 7479-2020. **ICP Waters report 142/2020**

Gundersen, C.B. 2019. Intercomparison 1933: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Tot-P, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA SNO 7445-2019. **ICP Waters report 141/2019.**

Velle, G., Birkeland, I.B., Johannessen, A. and Landås, T.S. 2019. Biological intercalibration: Invertebrates 2019. NIVA SNO 7433-2019. **ICP Waters report 140/2019**

Garmo, Ø., Austnes, K. and Vuorenmaa, J. (editors) 2019. Proceedings of the 35th Task Force meeting of the ICP Waters Programme in Helsinki, June 4-6, 2019. NIVA report SNO 7437-2019. **ICP Waters report 139/2019**

Velle, G., Johannessen, A. and Landås, T.S. 2018. Biological intercalibration: Invertebrates 2018. NIVA report SNO 7314-2018. **ICP Waters report 138/2018**

Escudero-Oñate, C. 2018. Intercomparison 1832: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Tot-P, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA report SNO 7316-2018. **ICP Waters report 137/2018.**

Garmo, Ø., Ulańczyk, R. and de Wit, H. (eds.) 2018. Proceedings of the 34th Task Force meeting of the ICP Waters Programme in Warsaw, May 7-9, 2018. NIVA report SNO 7298-2018. **ICP Waters report 136/2018.**

Austnes, K. Aherne, J., Arle, J., Čičendajeva, M., Couture, S., Fölster, J., Garmo, Ø., Hruška, J., Monteith, D., Posch, M., Rogora, M., Sample, J., Skjelkvåle, B.L., Steingruber, S., Stoddard, J.L., Ulańczyk, R., van Dam, H., Velasco, M.T., Vuorenmaa, J., Wright, R.F., de Wit, H. 2018. Regional assessment of the current extent of acidification of surface waters in Europe and North America. NIVA report SNO 7268-2018. **ICP Waters report 135/2018**

Escudero-Oñate, C. 2017. Intercomparison 1731: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA report SNO7207-2017. **ICP Waters report 134/2017**.

Halvorsen, G.A., Johannessen, A. and Landås, T.S. 2017. Biological intercalibration: Invertebrates 2017. NIVA report SNO 7198-2017. **ICP Waters report 133/2017**.

Braaten, H.F.V., Åkerblom, S., de Wit, H.A., Skotte, G., Rask, M., Vuorenmaa, J., Kahilainen, K.K., Malinen, T., Rognerud, S., Lydersen, E., Amundsen, P.A., Kashulin, N., Kashulina, T., Terentyev, P., Christensen, G., Jackson-Blake, L., Lund, E. and Rosseland, B.O. 2017. Spatial and temporal trends of mercury in freshwater fish in Fennoscandia (1965-2015). NIVA report SNO 7179-2017. **ICP Waters report 132/2017**.

Garmo, Ø., de Wit, H. and Fölster, J. (eds.) 2017. Proceedings of the 33rd Task Force meeting of the ICP Waters Programme in Uppsala, May 9-11, 2017. NIVA report SNO 7178-2017. **ICP Waters report 131/2017**.

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.**

De Wit, H. and Valinia, S. (eds.) 2016. Proceedings of the 32st Task Force meeting of the ICP Waters Programme in Asker, Oslo, May 24-26, 2016. NIVA report SNO 7090-2016. **ICP Waters report 128/2016**.

Velle, G., Mahlum, S., Monteith, D.T., de Wit, H., Arle, J., Eriksson, L., Fjellheim, A., Frolova, M., Fölster, J., Grudule, N., Halvorsen, G.A., Hildrew, A., Hruška, J., Indriksone, I., Kamasová, L., Kopáček, J., Krám, P., Orton, S., Senoo, T., Shilland, E.M., Stuchlík, E., Telford, R.J., Ungermanová, L., Wiklund, M.-L. and Wright, R.F. 2016. Biodiversity of macro-invertebrates in acid-sensitive waters: trends and relations to water chemistry and climate. NIVA report SNO 7077-2016. NIVA report SNO 7077-2016. **ICP Waters report 127/2016**.

De Wit, H., Valinia, S. and Steingruber, S. 2015. Proceedings of the 31st Task Force meeting of the ICP Waters Programme in Monte Verità, Switzerland 6th –8th October, 2015. NIVA report SNO 7003-2016. **ICP Waters report 126/2015**.

De Wit, H., Hettelingh, J.P. and Harmens, H. 2015. Trends in ecosystem and health responses to long-range transported atmospheric pollutants. NIVA report SNO 6946-2015. **ICP Waters report 125/2015**.

Fjellheim, A., Johannessen, A. and Landås, T.S. 2015. Biological intercalibration: Invertebrates 1915. NIVA report SNO 6940-2015. **ICP Waters report 124/2015**.

Escudero-Oñate, C. 2015 Intercomparison 1529: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA report SNO 6910-2015. **ICP Waters report 123/2015**.

de Wit, H., Wathne, B. M. (eds.) 2015. Proceedings of the 30th Task Force meeting of the ICP Waters Programme in Grimstad, Norway 14th –16th October, 2014. NIVA report SNO 6793-2015. **ICP Waters report 122/2015**.

Fjellheim, A., Johannessen, A. and Landås, T.S. 2014. Biological intercalibration: Invertebrates 1814. NIVA report SNO 6761-2014. **ICP Waters Report 121/2014**.

Escuedero-Oñate. 2014. Intercomparison 1428: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA report SNO 6718-2014. **ICP Waters Report 120/2014**.

De Wit, H. A., Garmo Ø. A. and Fjellheim A. 2015. Chemical and biological recovery in acid-sensitive waters: trends and prognosis. **ICP Waters Report 119/2014**.

Fjellheim, A., Johannessen, A. and Landås, T.S. 2013. Biological intercalibration: Invertebrates 1713. NIVA report SNO 6662-2014. **ICP Waters Report 118/2014**.

de Wit, H., Bente M. Wathne, B. M. and Hruśka, J. (eds.) 2014. Proceedings of the 29th Task Force meeting of the ICP Waters Programme in Český Krumlov, Czech Republic 1st –3rd October, 2013. NIVA report SNO 6643-2014. **ICP Waters report 117/2014**.

Escuedero-Oñate, C. 2013. Intercomparison 1327: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA report SNO 6569-2013. **ICP Waters Report 116/2013**.

Holen, S., R.F. Wright and Seifert, I. 2013. Effects of long-range transported air pollution (LTRAP) on freshwater ecosystem services. NIVA report SNO 6561-2013. **ICP Waters Report 115/2013**.

Velle, G., Telford, R.J., Curtis, C., Eriksson, L., Fjellheim, A., Frolova, M., Fölster J., Grudule N., Halvorsen G.A., Hildrew A., Hoffmann A., Indriksone I., Kamasová L., Kopáček J., Orton S., Krám P., Monteith D.T., Senoo T., Shilland E.M., Stuchlík E., Wiklund M.L., de Wit, H. and Skjelkvaale B.L. 2013. Biodiversity in freshwaters. Temporal trends and response to water chemistry. NIVA report SNO 6580-2013. **ICP Waters Report 114/2013**.

Fjellheim, A., Johannessen, A. and Landås, T.S. 2013. Biological intercalibration: Invertebrates 1612. **ICP Waters Report 113/2012**.

Skjelkvåle, B.L., Wathne, B.M., de Wit, H. and Rogora, M. (eds.) 2013. Proceedings of the 28th Task Force meeting of the ICP Waters Programme in Verbania Pallanza, Italy, October 8 – 10, 2012. NIVA report SNO 6472-2013. **ICP Waters Report 112/2013**.

Dahl, I. 2012. Intercomparison 1226: pH, Conductivity, Alkalinity, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA report SNO 6412-2012. **ICP Waters report 111/2012**.

Skjelkvåle, B.L., Wathne B. M. and Moiseenko, T. (eds.) 2012. Proceedings of the 27th meeting of the ICP Waters Programme Task Force in Sochi, Russia, October 19 – 21, 2011. NIVA report SNO 6300-2012. **ICP Waters report 110/2012**.

Fjellheim, A., Johannessen, A., Svanevik Landås, T. 2011. Biological intercalibration: Invertebrates 1511. NIVA report SNO 6264-2011. **ICP Waters report 109/2011**.

Wright, R.F., Helliwell, R., Hruska, J., Larssen, T., Rogora, M., Rzychoń, D., Skjelkvåle, B.L. and Worsztynowicz, A. 2011. Impacts of Air Pollution on Freshwater Acidification under Future Emission Reduction Scenarios; ICP Waters contribution to WGE report. NIVA report SNO 6243-2011. **ICP Waters report 108/2011**.

Dahl, I and Hagebø, E. 2011. Intercomparison 1125: pH, Cond, HCO3, NO3-N, Cl, SO4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA report SNO 6222-2011. **ICP Waters report 107/2011**.

Skjelkvåle B.L. and de Wit, H. (eds.) 2011. Trends in precipitation chemistry, surface water chemistry and aquatic biota in acidified areas in Europe and North America from 1990 to 2008. NIVA report SNO 6218-2011. **ICP Waters report 106/2011**.

ICP Waters Programme Centre 2010. ICP Waters Programme manual. NIVA SNO 6074-2010. **ICP Waters report 105/2010**.

Skjelkvåle, B.L., Wathne B. M. and Vuorenmaa J. (eds.) 2010. Proceedings of the 26th meeting of the ICP Waters Programme Task Force in Helsinki, Finland, October 4 – 6, 2010. NIVA report SNO 6097-2010. **ICP Waters report 104/2010**.

Fjellheim, A. 2010. Biological intercalibration: Invertebrates 1410. NIVA report SNO 6087-2010. NIVA report SNO 6087-2010. **ICP Waters report 103/2010**.

Hovind, H. 2010. Intercomparison 1024: pH, Cond, HCO_3, NO_3-N, Cl, SO_4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA report SNO 6029-2010. **ICP Waters report 102/2010**.

De Wit, H.A. and Lindholm M. 2010. Nutrient enrichment effects of atmospheric N deposition on biology in oligotrophic surface waters – a review. NIVA report SNO 6007 - 2010. **ICP Waters report 101/2010**.

Skjelkvåle, B.L., De Wit, H. and Jeffries, D. (eds.) 2010. Proceedings of presentations of national activities to the 25th meeting of the ICP Waters Programme Task Force in Burlington, Canada, October 19-21 2009. NIVA report SNO 5995 - 2010. **ICP Waters report 100/2010**.

Fjellheim, A. 2009. Biological intercalibration: Invertebrates 1309. NIVA report SNO 5883-2009, **ICP Waters report 99/2009**.

Hovind, H. 2009. Intercomparison 0923: pH, Cond, HCO_3, NO_3-N, Cl, SO_4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA report SNO 5845-2009. **ICP Waters report 98/2009**.

Ranneklev, S.B., De Wit, H., Jenssen, M.T.S. and Skjelkvåle, B.L. 2009. An assessment of Hg in the freshwater aquatic environment related to long-range transported air pollution in Europe and North America. NIVA report SNO 5844-2009. **ICP Waters report 97/2009**.

Skjelkvåle, B.L., Jenssen, M. T. S. and De Wit, H (eds.) 2009. Proceedings of the 24th meeting of the ICP Waters Programme Task Force in Budapest, Hungary, October 6 – 8, 2008. NIVA report SNO 5770-2009. **ICP Waters report 96/2009**.

Fjellheim, A and Raddum, G.G. 2008. Biological intercalibration: Invertebrates 1208. NIVA report SNO 5706-2008, **ICP Waters report 95/2008**.

Skjelkvåle, B.L., and De Wit, H. (eds.) 2008. ICP Waters 20 year with monitoring effects of long-range transboundary air pollution on surface waters in Europe and North-America. NIVA report SNO 5684-2008. **ICP Waters report 94/2008**.

Hovind, H. 2008. Intercomparison 0822: pH, Cond, HCO_3, NO_3-N, Cl, SO_4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA report SNO 5660-2008. **ICP Waters report 93/2008**.

De Wit, H. Jenssen, M. T. S. and Skjelkvåle, B.L. (eds.) 2008. Proceedings of the 23rd meeting of the ICP Waters Programme Task Force in Nancy, France, October 8 – 10, 2007. NIVA report SNO 5567-2008. **ICP Waters report 92/2008**.

Fjellheim, A and Raddum, G.G. 2008. Biological intercalibration: Invertebrates 1107. NIVA report SNO 5551–2008. **ICP Waters report 91/2008**.

Hovind, H. 2007. Intercomparison 0721: pH, Cond, HCO3, NO3-N, Cl, SO4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni, and Zn. NIVA report SNO 5486-2007. **ICP Waters report 90/2007**.

Wright, R.F., Posch, M., Cosby, B. J., Forsius, M., and Skjelkvåle, B. L. 2007. Review of the Gothenburg Protocol: Chemical and biological responses in surface waters and soils. NIVA report SNO 5475-2007. **ICP Waters report 89/2007**.

Skjelkvåle, B.L., Forsius, M., Wright, R.F., de Wit, H., Raddum, G.G., and Sjøeng, A.S.M. 2006. Joint Workshop on Confounding Factors in Recovery from Acid Deposition in Surface Waters, 9-10 October 2006, Bergen, Norway; Summary and Abstracts. NIVA report SNO 5310-2006. **ICP Waters report 88/2006**.

De Wit, H. and Skjelkvåle, B.L. (eds) 2007. Trends in surface water chemistry and biota; The importance of confounding factors. NIVA report SNO 5385-2007. **ICP Waters report 87/2007**.

Hovind, H. 2006. Intercomparison 0620. pH, K25, HCO3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA report SNO 5285-2006. **ICP Waters report 86/2006**.

Raddum, G.G. and Fjellheim, A. 2006. Biological intercalibration 1006: Invertebrate fauna. NIVA report SNO 5314-2006, **ICP Waters report 85/2006**.

De Wit, H. and Skjelkvåle, B.L. (eds.) 2006. Proceedings of the 21th meeting of the ICP Waters Programme Task Force in Tallinn, Estonia, October 17-19, 2005. NIVA report SNO 5204-2006, **ICP Waters report 84/2006**.

Wright, R.F., Cosby, B.J., Høgåsen, T., Larssen, T. and Posch, M. 2005. Critical Loads, Target Load Functions and Dynamic Modelling for Surface Waters and ICP Waters Sites. NIVA report SNO 5166-2005. **ICP Waters report 83/2006**.

Hovind, H. 2005. Intercomparison 0317. pH, K25, HCO3, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA report SNO 5068-2005. **ICP Waters report 82/2005**.

Raddum, G.G. 2005. Intercalibration 0307: Invertebrate fauna. NIVA report SNO 5067-2005. **ICP Waters report 81/2005**.

De Wit, H. and Skjelkvåle, B.L (eds.) 2005. Proceedings of the 20th meeting of the ICP Waters Programme Task Force in Falun, Sweden, October 18-20, 2004. NIVA report SNO 5018-2005. **ICP Waters report 80/2005**.

Fjeld, E., Le Gall, A.-C. and Skjelkvåle, B.L. 2005. An assessment of POPs related to long-range air pollution in the aquatic environment. NIVA report SNO 5107-2005. **ICP Waters report 79/2005**.

Skjelkvåle et al. 2005. Regional scale evidence for improvements in surface water chemistry 1990-2001. Environmental Pollution, 137: 165-176

Hovind, H. 2004. Intercomparison 0418. pH, K25, HCO3, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA report SNO 4875-2004. **ICP Waters report 78/2004**.

Raddum, G.G. 2004. Intercalibration: Invertebrate fauna 09/04. NIVA report SNO 4863-2004. **ICP Waters report 77/2004**.

Skjelkvåle, B.L. (ed) 2004. Proceedings of the 19th meeting of the ICP Waters Programme Task Force in Lugano, Switzerland, October 18-20, 2003. NIVA report SNO 4858-2004. **ICP Waters report 76/2004.**

Raddum, G.G, et al. 2004. Recovery from acidification of invertebrate fauna in ICP Water sites in Europe and North America. NIVA report SNO 4864-2004. **ICP Waters report 75/2004.**

Hovind, H. 2003. Intercomparison 0317. pH, K25, HCO3, NO3 + NO2, Cl, SO4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA report SNO 4715-2003. **ICP Waters report 74/2003.**

Skjelkvåle, B.L. (ed) 2003. The 15-year report: Assessment and monitoring of surface waters in Europe and North America; acidification and recovery, dynamic modelling and heavy metals. NIVA report SNO 4716-2003. **ICP Waters report 73/2003.**

Raddum.G.G. 2003. Intercalibration 0307: Invertebrate fauna. NIVA report SNO 4659-2003. **ICP Waters report 72/2003**.

Skjelkvåle, B.L. (ed.) 2003. Proceedings of the 18th meeting of the ICP Waters Programme Task Force in Moscow, October 7-9, 2002. NIVA report SNO 4658-2003. **ICP Waters report 71/2003**.

Wright, R.F. and Lie, M.C. 2002.Workshop on models for Biological Recovery from Acidification in a Changing Climate. 9-11 september 2002 in Grimstad, Norway. Workshop report. NIVA report 4589-2002.

Jenkins, A. Larssen, Th., Moldan, F., Posch, M. and Wrigth, R.F. 2002. Dynamic Modelling of Surface Waters: Impact of emission reduction - possibilities and limitations. NIVA report SNO 4598-2002. **ICP Waters report 70/2002**.

Halvorsen, G.A, Heergaard, E. and Raddum, G.G. 2002. Tracing recovery from acidification - a multivariate approach. NIVA report SNO 4564-2002. **ICP Waters report 69/2002**.

Hovind. H. 2002. Intercomparison 0216. pH, K_{25}, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA report SNO 4558-2002. **ICP Waters Report 68/2002**.

Skjelkvåle, B.L. and Ulstein, M. (eds) 2002. Proceedings from the Workshop on Heavy Metals (Pb, Cd and Hg) in Surface Waters; Monitoring and Biological Impact. March 18-20, 2002, Lillehammer, Norway. NIVA report SNO 4563-2002. **ICP Waters report 67/2002**.

Raddum.G.G. 2002. Intercalibration 0206: Invertebrate fauna. NIVA report SNO 4494-2002. **ICP Waters report 66/2002**.

Bull, K.R. Achermann, B., Bashkin, V., Chrast, R. Fenech, G., Forsius, M., Gregor H.-D., Guardans, R., Haussmann, T., Hayes, F., Hettelingh, J.-P., Johannessen, T., Kryzanowski, M., Kucera, V., Kvaeven, B., Lorenz, M., Lundin, L., Mills, G., Posch, M., Skjelkvåle, B.L. and Ulstein, M.J. 2001. Coordinated Effects Monitoring and Modelling for Developing and Supporting International Air Pollution Control Agreements. Water Air Soil Poll. 130:119-130.

Hovind, H. 2001. Intercomparison 0115: pH, K_{25}, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA report SNO 4416-2002. **ICP Waters report 64/2001**.

Lyulko, I. Berg, P. and Skjelkvåle, B.L. (eds.) 2001. National presentations from the 16th meeting of the ICP Waters Programme Task Force in Riga, Latvia, October 18-20, 2000. NIVA report SNO 4411-2001. **ICP Waters report 63/2001**.

Raddum.G.G. 2000. Intercalibration 0005: Invertebrate fauna. NIVA report SNO 4384-2001. **ICP Waters report 62/2001**.

Raddum, G.G. and Skjekvåle B.L. 2000. Critical Load of Acidifying Compounds to Invertebrates In Different Ecoregions of Europe. Water Air Soil Poll. 130:825-830.

Stoddard, J. Traaen, T and Skjelkvåle, B.L. 2001. Assessment of Nitrogen leaching at ICP-Waters sites (Europe and North America). Water Air Soil Poll. 130:825-830.

Skjelkvåle, B.L. Stoddard J.L. and Andersen, T. 2001. Trends in surface waters acidification in Europe and North America (1989-1998). Water Air Soil Poll.130:781-786.

Kvaeven, B. Ulstein, M.J., Skjelkvåle, B.L., Raddum, G.G. and Hovind. H. 2001. ICP Waters – An international programme for surface water monitoring. Water Air Soil Poll.130:775-780.

Wright, R.F. 2001. Note on: Effect of year-to-year variations in climate on trends in acidification. NIVA report SNO 4328-2001. **ICP Waters report 57/2001**.

Hovind, H. 2000. Trends in intercomparisons 8701-9812: pH, K_{25}, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K and aluminium - reactive and nonlabile, TOC, COD-Mn. NIVA report SNO 4281-2000, **ICP Waters Report 56/2000**.

Hovind, H. 2000. Intercomparison 0014. pH, K_{25}, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn. Fe, Mn, Cd, Pb, Cu, Ni and Zn. NIVA report SNO 4281-2000. **ICP Waters Report 55/2000**.

Skjelkvåle, B.L., Olendrzynski, K., Stoddard, J., Traaen, T.S, Tarrason, L., Tørseth, K., Windjusveen, S. and Wright, R.F. 2001. Assessment of trends and leaching in Nitrogen at ICP Waters Sites (Europe And North America). NIVA report SNO 4383-2001. **ICP Waters report 54/2001.**

Stoddard, J. L., Jeffries, D. S., Lükewille, A., Clair, T. A., Dillon, P. J., Driscoll, C. T., Forsius, M., Johannessen, M., Kahl, J. S., Kellogg, J. H., Kemp, A., Mannio, J., Monteith, D., Murdoch, P. S., Patrick, S., Rebsdorf, A., Skjelkvåle, B. L., Stainton, M. P., Traaen, T. S., van Dam, H., Webster, K. E., Wieting, J., and Wilander, A. 1999. Regional trends in aquatic recovery from acidification in North America and Europe 1980-95. Nature 401:575- 578.

Skjelkvåle, B. L., Andersen, T., Halvorsen, G. A., Raddum, G.G., Heegaard, E., Stoddard, J. L., and Wright, R. F. 2000. The 12-year report; Acidification of Surface Water in Europe and North America; Trends, biological recovery and heavy metals. NIVA report SNO 4208/2000. **ICP Waters report 52/2000**.

Reports before year 2000 can be listed on request.

NIVA: Norway's leading centre of competence in aquatic environments

NIVA provides government, business and the public with a basis for preferred water management through its contracted research, reports and development work. A characteristic of NIVA is its broad scope of professional disciplines and extensive contact network in Norway and abroad. Our solid professionalism, interdisciplinary working methods and holistic approach are key elements that make us an excellent advisor for government and society.

NIVA
Norwegian Institute for Water Research

Økernveien 94 • NO-0579 Oslo, Norway
Telephone: +47 22 18 51 00 • Fax: 22 18 52 00
www.niva.no • post@niva.no