

ICP Waters Report 137/2018

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



Photo: Carlos Escudero-Ojeda

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

Convention on Long-Range Transboundary Air Pollution



REPORT

Main Office

Gaustadalléen 21
NO-0349 Oslo, Norway
Phone (47) 22 18 51 00
Telefax (47) 22 18 52 00
Internet: www.niva.no

NIVA Region South

Jon Lilletuns vei 3
NO-4879 Grimstad, Norway
Phone (47) 22 18 51 00
Telefax (47) 37 04 45 13

NIVA Region East

Sandvikaveien 59
NO-2312 Ottestad, Norway
Phone (47) 22 18 51 00
Telefax (47) 62 57 66 53

NIVA Region West

Thormøhlensgate 53 D
NO-5006 Bergen Norway
Phone (47) 22 18 51 00
Telefax (47) 55 31 22 14

NIVA Denmark

Ørestads Boulevard 73
DK-2300 Copenhagen
Phone (45) 8896 9670

Title Intercomparison 1832: pH, Conductivity, Alkalinity, NO ₃ -N, Cl, SO ₄ , Ca, Mg, Na, K, TOC, Tot-P, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn	Serial number 7316-2018	Date 15.12.2018
Author(s) Dr. Carlos Escudero-Oñate	Topic group Environmental contaminants - freshwater	Distribution Open
	Geographical area Europe, North America, Asia	Pages 72

Client(s) Norwegian Environment Agency United Nations Economic Commission for Europe (UNECE)	Client's reference
Client's publication: ICP Waters report 137/2018	Printed NIVA Project number 10300

Summary

In the current edition, 32 laboratories from 19 countries were included in the 2019 ICP-Waters intercomparison. Similar to earlier intercomparisons, two sample sets were prepared: one for the determination of major ions and one for heavy metals. Based on the general target accuracy of $\pm 20\%$, or the special accuracy limit for pH and conductivity (± 0.2 pH units and $\pm 10\%$ respectively), 81% of the overall results were accepted. The best results were for the variables sulphate, calcium, iron, manganese, and zinc. For these variables the acceptance was higher than 90%. Good results were obtained this year also for pH, in contrast to with previous editions. 81% of the participants provided results within the acceptance criteria. The higher accuracy in the pH results in this year was due to the ease of its determination when compared earlier; instead of circumneutral or slightly acidic pH, the sample set AB had been adjusted to acidic pH; about 4.5. The analysis of Total-P has exhibited a remarkable increase in the quality of the results; 33% of the results provided by the participants met the acceptance criteria (in contrast with the 21% obtained in the former edition). Harmonization of the analytical methods used may be the most important way to improve the comparability for these parameters.

Four keywords	Fire emneord
1. Sammenligning	1. Intercomparison
2. Sur nedbør	2. Acid precipitation
3. Kvalitetskontroll	3. Quality Control
4. Overvåking	4. Monitoring

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

Carlos Escudero-Oñate
Project Manager

Cathrine B Gundersen
Quality assurance

Heleen de Wit
Research Manager

ISBN 978-82-577-7051-8
NIVA-report ISSN 1894-7948

CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR
POLLUTION

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

**Intercomparison 1832:
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 2018

Preface

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

Numerous assessments, workshops, reports and publications covering the effects of long-range transported air pollution have been published over the years.

The ICP Waters Programme Centre is hosted by the Norwegian Institute for Water Research (NIVA), while the Norwegian Environment Agency leads the programme. The Programme Centre's work is supported financially by the Norwegian Environment Agency.

The objective of the Programme is to establish an international network of surface water monitoring sites and promote international harmonization of monitoring practices. One of the aims is to detect long-term trends in effects of acidic deposition on surface water chemistry and aquatic biota, and to reveal the dose/response relationship between water chemistry and aquatic biota.

One of the tools in this work is inter-laboratory quality assurance tests. The bias between analyses carried out by the individual participants of the Programme has to be clearly identified and controlled.

We hereby report the results from the 32nd intercomparison of chemical analysis.



Carlos Escudero-Oñate

ICP Waters Programme Centre
Oslo, December 2018

Table of contents

Summary	5
1 Introduction	6
2 Accomplishment of the intercomparison	7
3 Discussion	8
4 Results	10
4.1 pH 10	
4.2 Conductivity	11
4.3 Alkalinity.....	11
4.4 Nitrate + nitrite-nitrogen.....	11
4.5 Chloride	11
4.6 Sulphate	12
4.7 Calcium.....	12
4.8 Magnesium.....	12
4.9 Sodium	12
4.10 Potassium	13
4.11 Total organic carbon	13
4.12 Total P.....	13
4.13 Aluminium	13
4.14 Iron	14
4.15 Manganese.....	14
4.16 Cadmium	14
4.17 Lead	14
4.18 Copper.....	15
4.19 Nickel.....	15
4.20 Zinc	15
5 Literature	38
Reports and publications from the ICP Waters programme.....	67

Summary

The Intercomparison was organized as part of the between-laboratory quality control programme, as stated in "Manual for Chemical and Biological Monitoring" (1), by the International Cooperative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes (ICP Waters).

The intercomparison was performed in the period April-November 2018, and included the determination of major ions and metals in natural water samples. The participants were invited to determine pH, conductivity, alkalinity, nitrate, chloride, sulphate, calcium, magnesium, sodium, potassium, total organic carbon, total phosphorous, aluminium, iron, manganese, cadmium, lead, copper, nickel and zinc.

Two sample sets were prepared for this intercomparison, one for the determination of the major ions (plus TOC and Total-P) and one for heavy metals. 33 laboratories from 19 countries accepted the invitation to join the ICP-Waters intercomparison. 32 of them received the samples and reported their analytical results successfully into NIVA's database. 19 countries are represented in the current intercomparison program.

The median value of the results received from the participants for each variable was selected as "true" value. On average, 81% of the results from analysed sample pairs were considered acceptable. The target limit was the median value $\pm 20\%$, except for pH and conductivity where special acceptance limits were set to ± 0.2 pH units and $\pm 10\%$, respectively.

For pH, the accuracy limit was, as in earlier intercomparisons, extended from the target acceptance limit of ± 0.1 units to ± 0.2 units, and 81% of the result pairs were acceptable when using this extended limit. A total error of ± 0.2 units for pH measurements, therefore, seems to be a more reasonable basis for the assessment of the accuracy between laboratories than the target limit of ± 0.1 units. The alkalinity results have been omitted for calculations due to the low pH of the sample set AB.

The best results in terms of acceptance were obtained for sulphate, calcium, iron, manganese and zinc, with 90% or more of the results accepted. The worst performance has been observed for the variable Total-P, with only 33% of acceptable results. However, there has been a remarkable improvement on the determination of this variable compared to the previous intercomparison.

1 Introduction

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

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

As stated in the "ICP Waters Programme Manual" (1), between-laboratory quality control is necessary in a multilaboratory programme to assure clear identification and control of the bias between analyses carried out by individual participants of the Programme. Such biases may arise by use of different analytical methods, errors in the laboratory calibration solutions or through inadequate within-laboratory control.

The between-laboratory control carried out by the Programme Centre is based on the "round robin" concept and the procedure of Youden (2, 3), which is briefly described in Appendix C. This thirty-first intercomparison test, called 1832, included the determination of the major ionic components and metal ions in natural water samples: pH, conductivity, alkalinity, nitrate, chloride, sulphate, calcium, magnesium, sodium, potassium, total organic carbon, total phosphorous, aluminium, iron, manganese, cadmium, lead, copper, nickel and zinc.

2 Accomplishment of the intercomparison

The preparation of the sample solutions that were delivered to the different participating laboratories is presented in Appendix B. At the Task Force meeting in Burlington, Canada (October 2009), it was decided that, as earlier, two sample sets should be included in this intercomparison; one sample pair for the determination of the major ions and one for heavy metals. It was also decided that total organic carbon and aluminium should be included. Recently it was also decided to include Total-P as additional variable.

The samples were shipped from the Programme Centre during week 26 of 2018. With some exceptions, the participants received the samples within one week. Despite samples were sent with a declaration of absence of commercial value and description of only testing samples, in some cases, delays in the reception of the samples were reported by the laboratories. One of the participants did not manage to get the samples due to issues with the custom authorities.

To ensure the integrity and minimal degradation of the samples, participants were encouraged to analyse them as soon as possible and to save their analytical results in the Organization's database as soon as possible.

3 Discussion

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

In Table 1 an evaluation of the results of intercomparison 1832 is presented with the number and percentage of acceptable results based on the target accuracy (except for pH and conductivity), in addition to some historical data for comparison. In Appendix D, Table 4, the individual results of each laboratory are presented. Some laboratories use far more digits than are statistically significant. This is unnecessary, and each laboratory should determine how many digits are significant for each of their analytical methods. It is however acceptable to report results with one digit more than is statistically significant as this will reduce the round-off error in the statistical calculations.

In this edition 32 laboratories submitted results to the intercomparison. If results for the different variables are averaged, 81% of them were located within the general target accuracy of $\pm 20\%$, or the special accuracy limit for pH and conductivity (± 0.2 pH units and $\pm 10\%$ respectively). This result is in line with previous editions. As previously stated, the best acceptance ($\geq 90\%$) was observed in the determination of sulphate, calcium, iron, manganese and zinc.

The determination of pH has provided a large number of acceptable results, 81%. In the current edition, the pH was lowered on purpose to reach a target value about 4.5 using nitric, sulphuric and chlorhydric acids.

The lowest acceptable results were reported for Total-P (33%), but the Organization has gladly observed a general improvement on the quality of the results compared to the previous edition. Alkalinity has not been included in the report of the intercomparison because the low pH of the samples A and B provokes it to be extremely low.

Due to the high precision of the reported results for conductivity in earlier intercomparisons, from the 2012 edition the Organization decided to reduce the acceptance limit for this analytical variable from the target value of $\pm 20\%$ to $\pm 10\%$ and this criterion was still used in the current one. It has been observed a general decay in the accuracy of the results reported for heavy metals probably due to the lower concentration of them in the sample set AC. In the current intercomparison, the samples were spiked with the different heavy metals, but to a lower level. The concentration for some of the heavy metals remains still higher than these expected in natural waters.

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

The low fraction of acceptable results in the determination of some of the variables may in some cases be explained by either rather low concentration, compared to the methods that have been used, or that the samples were not sufficiently stable. When the concentrations are close to the detection limits of the methods used by the participants, it is expected that the spread of the results will be greater than $\pm 20\%$. The laboratories which reported results outside this limit should improve their methods to obtain a better accuracy and then be able to get a better score in the intercomparison assay. In

general terms the use of some analytical methods seems to be less suited for the water samples analysed in this programme, as the detection limits of some methods applied by participants are too high. This is especially true for some manual methods, and some of the methods used for the determination of metals, especially when the concentration is very low. It is important that methods with detection limits low enough are used by the participating laboratories.

It should be further discussed which concentration levels for the heavy metals would be most useful for ICP Waters in the coming intercomparisons as well as whether *absolute* acceptance limits should be used instead of the *relative* one ($\pm 20\%$), which is used in this intercomparison, in cases where the results are close to the detection limit. In such cases, it is important that the steering committee decides the target detection limit that should be achieved by the participating laboratories.

Table 1. Evaluation of the results from intercomparison 1832.

Variable	Sample pair	Sample 1	Sample 2	Acceptable Limit	Number of pairs		Acceptable results for intercalibration (%)				
				%	Total	Accept.	1832	1731	1630	1529	
pH	AB	4.56	4.6	4.3	27	22	81	53	56	64	
Conductivity		6.32	5.87	10	27	23	85	77	77	89	
Alkalinity		--	--	20	17	0	--	17	46	75	
NO ₃ +NO ₂ -N		897	838	20	27	23	85	35	71	88	
Chloride		7.61	7.04	20	27	22	81	82	87	97	
Sulphate		6.7	6.2	20	27	26	96	90	90	97	
Calcium		3.6	3.4	20	28	27	93	83	93	97	
Magnesium		0.85	0.79	20	27	23	82	93	89	100	
Sodium		3.23	3.0	20	28	25	86	86	96	97	
Potassium		0.68	0.62	20	27	23	82	69	86	97	
TOC		2.9	2.7	20	19	14	74	81	81	70	
Total P		16	15	20	21	7	33	21	-	-	
Aluminium		CD	16.4	14.5	20	20	12	57	82	75	89
Iron			129.2	115.2	20	20	20	95	74	87	81
Manganese	22.00		20.26	20	21	21	91	100	84	84	
Cadmium	1.30		1.15	20	24	22	88	92	90	100	
Lead	1.46		1.35	20	22	15	65	88	86	77	
Copper	17.9		16.6	20	24	21	84	95	86	93	
Nickel	6.24		5.48	20	22	20	87	100	90	97	
Zinc	12.3		13.4	20	21	20	91	96	77	83	
Total					476	386	81	(76)	(81)	(88)	

Units: Conductivity: mS/m
 Alkalinity: mmol HCO₃/l
 Nitrate+nitrite-N: µg N/l
 Total P: µg P/l
 Chloride, Sulphate, Calcium, Magnesium, Sodium, Potassium, TOC: mg/l
 Aluminium, Iron, Manganese, Cadmium, Lead, Copper, Nickel and Zinc: µg/l

4 Results

In the current edition of the ICP-Waters intercomparison, 32 laboratories from 19 different countries accepted the invitation and signed up to NIVA's database. When signing up, the participants were invited to fill the required information about their institution and to order the sample sets they wanted to analyse. After that, the samples were prepared and shipped to them. At the end of the program, almost all the laboratories that agreed to participate had submitted results to the Programme Centre. The participants and the numerical identity employed along the report are listed in Appendix A. In the same appendix, a table summarizing the number of laboratories that participated in the 2018 intercomparison and the represented countries can be also found.

The analytical results received from the laboratories were treated by the Youden method (2, 3). A short description of this method and the statistical treatment of the analytical data are presented in Appendix C. The purpose of this test is to evaluate the comparability of the analytical results produced by the laboratories participating in the International Cooperative Programme. The real "true value" is not known exactly for the natural water samples used in this intercomparison. Therefore, the median value -determined from the analytical results submitted by the participating laboratories after excluding outliers- was selected as the "true value" for each analytical variable. The median value is considered to be an acceptable estimate of the true value for this purpose, as long as most of the participants are using essentially the same analytical method. For certain variables, for instance pH, this may represent a problem as the different methods used may produce systematically different results (e.g. stirring, non-stirring, and equilibration of the test solution), and we cannot argue that one method is more correct than the others. Table 3 in Appendix C provides an estimate for the uncertainty of the assigned true values. This calculation is performed according to ISO 13528 (2005), "Statistical methods for use in proficiency testing by interlaboratory comparisons".

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

A summary of the results of intercomparison 1832 is presented in Tables 1 and 2. The individual results of the participants are presented in Table 4 in Appendix D, sorted by increasing identification number. More extensive statistical information is presented in the Tables 5.1 - 5.19 in the same appendix.

4.1 pH

The reported results for pH are graphically presented by a Youden graph (Figure 1), where the radius of the circle illustrates 0.2 pH units and shows the degree of comparability between the pH results from the participating laboratories. The values reported by the laboratories and the statistical calculations are presented in Table 2 and Table 5.1.

A total of 27 participants determined pH in the test samples A and B. Of these, 22 laboratories used a method based upon electrometry. As stated in previous intercomparisons, stirring has been observed to have a significant influence on the results, especially in samples with lower total ion strength than the samples used in this intercomparison (4, 5). As a result of this, the practice of establishing a "true value" based on the median value for all the reported results for pH is questionable. Whether an

individual “true value” for each method would be more appropriate should therefore be discussed. In this intercomparison the median value of all the reported results was chosen after excluding outliers. Based upon this, 81% of the results were acceptable, that is within the median value ± 0.2 pH units. The acceptance is larger than usual (Table 1), most likely because of the much lower pH of the samples when compared to previous editions.

The participants have reported data with high accuracy. The dataset is just affected by a slight random error.

4.2 Conductivity

The Youden chart for conductivity results is presented in Figure 2, where the large circle represents an accuracy limit of $\pm 10\%$, which is only half of the target accuracy limit given in the Manual (1). The values reported by the laboratories are presented in Table 2 and Table 5.2.

A total of 27 laboratories have reported results for conductivity in the current edition and all of them have indicated the use of electrometric methods on the determination of conductivity. Most laboratories achieved rather good agreement between the results for this variable, 85% of the results were within the acceptance limit of $\pm 10\%$.

Conductivity is affected mainly by systematic errors, as it can be observed in the distribution of the results in Figure 2. It has to be pointed out that an accurate temperature control or proper temperature correction is necessary when determining this variable, as the conductivity is changing by about two percent per $^{\circ}\text{C}$ at room temperature.

4.3 Alkalinity

The results of alkalinity have been omitted this year due to the relatively low pH of the sample set AB.

4.4 Nitrate + nitrite-nitrogen

A total of 27 laboratories reported results for nitrate + nitrite-nitrogen and the results are presented in Tables 2 and 5.3. Ion chromatography is the preferred technique for the determination of this variable in the samples, as it was used by 16 participants. A large improvement on the quality of the overall dataset has been observed, since just 85% of the results were considered as acceptable. The Youden plot (Figure 3) demonstrates that the dataset is just affected by a slight systematic error.

4.5 Chloride

27 laboratories reported results for chloride and, from them, 22 were accepted. 81% of the participants provided results that fulfilled the acceptance criteria. The results are presented in Figure 4, Table 2 and Table 5.4. The target accuracy of $\pm 20\%$ is represented by the circle in Figure 4.

Ion chromatography appears as the most widely employed technique, with 19 of the participants reporting its use. Other techniques such as photometry, capillary electrophoresis and others were employed in much lower extension. The participants have reported with a high degree of accuracy, as it might be observed in characteristic Youden plot. Just slight systematic error has affected the dataset.

4.6 Sulphate

A total of 27 laboratories reported results for sulphate. From them 96% fulfilled the target accuracy. The results obtained for the analysis of sulphate are presented in Figure 5, Table 2 and Table 5.5.

The circle in Figure 5 represents the target accuracy of $\pm 20\%$. As in the case of chloride, most of the laboratories (20 participants) used ion chromatography as the analytical technique in their determinations of sulphate. 3 participants reported the use of ICP-AES for the determination of this variable, 3 made use of photometry and 1 capillary electrophoresis.

Due to the small number of methods other than ion chromatography, it is not possible to discuss much about differences between them, but it can be concluded that both, IC and ICP-AES provided accurate results. As in the case of chloride, the Youden chart demonstrates excellent accuracy of the results provided by the participants. Just slight systematic error affects the results.

4.7 Calcium

A total of 28 laboratories reported results for calcium from which 93% fulfilled the target accuracy. This percentage is in line with those obtained in recent editions. The results are presented in Figure 6, Table 2 and Table 5.6. The circle in Figure 6 represents the target accuracy of $\pm 20\%$.

10 laboratories used ICP-AES and 9 ion chromatography. Flame atomic absorption spectrometry was used by 4 participants in their determination of calcium. 3 laboratories used ICP-MS. 1 participant made use of an electrophoretic technique and another determined the variable using other method different than the aforementioned. According to the characteristic Youden test, the results provided in the determination of calcium are mainly affected by random error.

4.8 Magnesium

A total of 27 laboratories reported results for magnesium and 82% of the results were considered as acceptable according to the criteria of the intercomparison.

The characteristic Youden chart obtained in the current edition is presented in Figure 7. Statistical results can be found in Tables 2 and 5.7. The circle in Figure 7 represents the target accuracy of $\pm 20\%$. 9 of the laboratories reported the use of ICP-AES, 4 employed ICP-MS and 9 ion chromatography. Flame atomic absorption spectrometry was used by 3 of the participants in their determination of this variable. 1 participant reported the use of capillary electrophoresis and 1 indicated the use of other method different than the aforementioned. The participants have contributed to generating a very accurate dataset, just affected by only minor systematic error.

4.9 Sodium

A total of 28 laboratories reported results for sodium. 86% of the results fulfilled the target accuracy established in the intercomparison. This is in agreement with the percentage of acceptance of previous editions.

The characteristics Youden chart is presented in Figure 8. Tables 2 and 5.8 summarize the statistical treatment of the data. The circle in Figure 8 represents the target accuracy of $\pm 20\%$. In this round of the intercomparison, 7 participants analysed sodium by ICP-AES and 5 by ICP-MS. Ion chromatography techniques are nearly as extended as plasma techniques, as 10 of the participants reported the use of

ion chromatography in this analytical determination. Among the flame techniques, atomic absorption is the preferred, as it was used by 3 laboratories. 1 participant reported the use of emission in flame. Just 1 laboratory reported the use of capillary electrophoresis and 1 indicated the use of other method different than the aforementioned. As in previous editions, the determination of sodium keeps a very good quality and there were no strong differences in the results obtained by the different analytical techniques. According to the distribution of the results in the Youden chart obtained in the determination of sodium, this analysis is affected by a small systematic error.

4.10 Potassium

A total of 27 laboratories reported results for potassium. From these results, 82% were acceptable. Regarding the analytical techniques used by the participants, a similar distribution to that observed in the case of the analysis of sodium is evidenced. The Youden chart obtained for the determination of potassium in this round is presented in Figure 9. Statistics results for this variable are presented in Tables 2 and 5.9. The circle in Figure 9 represents the target accuracy of $\pm 20\%$. The Youden chart points out that the deviating results are affected by both, random and systematic error with a larger dispersion than in the case of the determination of sodium.

4.11 Total organic carbon

A total of 19 laboratories reported results for total organic carbon. From them, 74% of the results were within the target accuracy of $\pm 20\%$. The results of the Youden test are presented in Figure 10, while the statistics can be found in Tables 2 and 5.10. The circle in Figure 10 represents the target accuracy of $\pm 20\%$. Combustion methods are preferred by most of the laboratories (10) whilst 4 reported the use of UV/peroxodisulfate oxidation method for this determination. 5 laboratories reported the use of other methods different from the aforementioned. Not significant differences have been detected between the results provided by the combustion and the UV/peroxodisulfate methods. The distribution of the results in the Youden's chart demonstrates that the deviating results are mainly affected by both, random and systematic error.

4.12 Total P

A total of 21 laboratories reported results for Total P, and from these 7 were accepted (33% of total). The results of the Youden test are presented in Figure 11, where the circle represents the target accuracy of $\pm 20\%$. The statistics of the analytics are presented in Tables 2 and 5.11. In the current edition, 12 laboratories employed photometry, 5 ICP-AES and 4 indicated the use of other methods. According to the distribution of the results in the Youden chart it can be stated that the deviating results are mainly affected by a large contribution of random error.

4.13 Aluminium

A total of 20 laboratories reported results for aluminium. From these 12 were accepted according to the target accuracy criteria (57% of total). The results of the Youden test are presented in Figure 12, where the circle represents the target accuracy of $\pm 20\%$. The statistics of the analytics are presented in Tables 2 and 5.12. In the current edition, 10 laboratories used ICP-MS and 5, ICP-AES. 4 participants reported the use of graphite furnace.

According to the distribution of the results in the Youden chart it can be stated that the deviating results are mainly by random error.

4.14 Iron

A total of 20 laboratories provided results for iron and 95% fulfilled the target accuracy criteria. This is a remarkable improvement when compared with previous recent editions of the intercomparison. The results of the Youden test are presented in Figure 13. The statistics calculations are presented in Table 2 and Table 8.13. The circle in Figure 13 represents the target accuracy of $\pm 20\%$. 8 of the laboratories have reported the use of ICP-AES and 8 to use ICP-MS. In this edition, 4 participants have indicated the use of atomic absorption-based techniques: 2 employed GFAAS and 2 FAAS.

The results have exhibited a large degree of accuracy and the distribution seems to be just slightly affected by random error.

4.15 Manganese

A total of 21 participants reported results in the analysis of manganese, and from them 91% fulfilled the acceptance criteria. The Youden chart is presented in Figure 14 and the statistical results in Tables 2 and 5.14. The circle in the figure represents the target accuracy of $\pm 20\%$.

All the participants reported the use of atomic techniques. From them, 10 and 7 participants have indicated the use of ICP-MS and ICP-AES, respectively, whilst 2 and 2 used graphite furnace atomic absorption and flame atomic absorption respectively. No relevant differences were detected in between the different techniques, but ICP-MS provided the most accurate results. According to the characteristic Youden test obtained in the current intercomparison for Mn, the analysis is affected by a small systematic error.

4.16 Cadmium

A total of 24 laboratories have reported results for cadmium in the set of samples C and D. 92% of the results were acceptable, according to the target accuracy.

The Youden graph for cadmium is presented in Figure 15 while the statistical calculations for this variable are presented in Tables 2 and 5.15. The circle in Figure 15 represents the target accuracy of $\pm 20\%$. Plasma techniques have been the most widely employed, as 17 participants reported its use. From them, 12 detected mass (ICP-MS) and 5 measured emitted radiation (ICP-AES). The preferred method employed by the participants that used atomic absorption techniques was the graphite furnace (GFAAS). The use of this technique was reported by 5 of the participants. In the current edition, 1 participant has reported the use of polarography. The Youden test obtained in the current intercomparison for Cd indicates that the results are affected by systematic error.

4.17 Lead

A total of 22 laboratories reported results for lead in samples C and D. From these, 65% were acceptable. This percentage is much lower than that observed in recent previous editions. The reason of this can be found in the lower concentration in the sample set CD, since the samples were as usually spiked, but to a much lower level than usual.

The characteristic Youden chart is presented in Figure 16 and statistical results in the determination of this variable in Tables 2 and 5.16. The circle in Figure 16 represents the target accuracy of $\pm 20\%$. In this case, almost all the laboratories have reported the use of atomic techniques. Plasma techniques have been the most employed, as 15 participants have communicated the use of ICP. From them, 12 used mass detection (ICP-MS) and 3, emitted radiation (ICP-AES). The preferred method employed by the participants that used atomic absorption techniques was graphite furnace (GFAAS). As it can be

observed in the characteristic Youden chart, the results are affected by both, systematic and random error.

4.18 Copper

A total of 24 laboratories reported results for copper in sample set C and D. From them, 84% were acceptable. Youden chart is presented in Figure 17 and statistical results in the determination of this variable in Tables 2 and 5.17. The circle in the figure represents the target accuracy of $\pm 20\%$. As it can be seen in the figure, almost all the results lied in the target accuracy established and the deviation in the results can be assigned mainly to systematic error.

By analysis, almost all the participants employed atomic based techniques, being plasma the most widely used with 12 of the participants using mass detectors and 5 using emitted light. Relevant is also the contribution of atomic absorption techniques to the characterization of Cu in the samples, as 5 of the participants employed graphite furnace (GFAAS) and 1 flame atomic absorption spectroscopy (FAAS). 1 of the participants reported the use of polarography in the determination of copper.

4.19 Nickel

A total of 22 laboratories reported results for nickel in samples C and D. Among these, 87% were classified as acceptable according to the target accuracy of the assay. Nickel's Youden chart is presented in Figure 18 and statistical results in Tables 2 and 5.18. The circle in the figure represents the target accuracy of $\pm 20\%$. By analysis type, it is remarkable the use of atomic based techniques. From them, plasma is the most widely used, with 17 participants. 12 employed ICP-MS while only 5 reported the use of ICP-AES. From the 5 laboratories that reported the use of atomic absorption based techniques, 4 employed graphite furnace and 1 flame atomic absorption spectroscopy. The distribution of the results in the Youden chart puts into evidence that the analysis is affected by slight random and systematic errors.

4.20 Zinc

A total of 21 laboratories reported results in the determination of zinc in sample set C and D. From these results, 91% fulfilled the acceptance criteria.

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

Plasma techniques are, by far, the most widely employed by the laboratories. From them, ICP-MS demonstrated to be the most widely used, with 12 participants, followed by emission in plasma (ICP-AES) that was used by 5 of the laboratories. From the techniques based on atomic absorption spectroscopy 2 laboratories made use of the graphite furnace (GFAAS) while just 2 participants reported the use of flame atomic absorption spectroscopy (FAAS). None of the participants reported results using non-atomic techniques.

Table 2. Statistical summary for intercomparison 1832

Analytical variable and method	Sample pair	TRUE Value		No. lab.		Median		Avg/Std.av.		Avg/Std.av.		Rel.std.av. %		Relative error %	
		S. 1	S. 2	Total	Om	S. 1	S. 2	Sample 1	Sample 2	S. 1	S. 2	S. 1	S. 2		
pH	AB	4.56	4.60	27	3	4.56	4.60	4.57	0.06	4.59	0.08	1.3	1.8	0.2	-0.2
Electrometry				22	2	4.56	4.60	4.57	0.04	4.58	0.06	1.0	1.4	0.2	-0.4
Electrometry (Stirring)				4	1	4.55	4.58	4.52	0.09	4.61	0.18	2.1	3.9	-0.8	0.1
Other method				1	0			4.70		4.70				3.1	2.2
Conductivity	AB	6.32	5.87	27	2	6.30	5.86	6.29	0.27	5.85	0.20	4.3	3.5	-0.5	-0.3
Electrometry				27	2	6.30	5.86	6.29	0.27	5.85	0.20	4.3	3.5	-0.5	-0.3
Nitrate+ nitrite; N	AB	897	838	27	2	897	838	911	62	834	52	6.8	6.2	1.5	-0.5
Ion chromatography				16	2	897	838	896	59	826	55	6.6	6.7	-0.1	-1.4
Autoanalyzer				4	0	925	850	936	50	850	41	5.3	4.8	4.3	1.5
Photometry				2	0			935		846				4.2	0.9
Photometry				2	0			881		811				-1.8	-3.2
Cap. electrophoresis				1	0			1080		950				20.4	13.4
Flow injection anal.				1	0			879		798				-2.0	-4.7
Hydrazine				1	0			883		812				-1.6	-3.1
Chloride	AB	7.6	7.0	27	1	7.6	7.0	7.6	0.6	7.0	0.6	8.2	8.5	0.1	-0.4
Ion chromatography				19	0	7.6	7.0	7.7	0.5	7.1	0.5	6.5	6.5	0.7	0.5
Other method				2	0			7.9		7.3				4.3	4.2
Photometry				2	0			7.1		6.4				-6.8	-8.5
^a				1	0			6.5		6.0				-14.5	-15.1
Cap. electrophoresis				1	0			8.1		7.4				6.5	5.1
Electrometry				1	0			7.8		6.9				2.0	-1.4
Potentiometry				1	1			10.6		8.9				39.8	25.9
Sulphate	AB	6.67	6.20	27	1	6.67	6.20	6.65	0.33	6.19	0.34	5.0	5.5	-0.3	-0.2
Ion chromatography				20	0	6.70	6.22	6.69	0.31	6.24	0.30	4.6	4.8	0.3	0.7
ICP-AES				3	0	6.85	6.34	6.65	0.53	6.15	0.49	8.0	7.9	-0.3	-0.8
Photometry				3	1			6.24		5.66				-6.5	-8.6
Cap. electrophoresis				1	0			6.60		6.20				-1.0	0.0
Calcium	AB	3.60	3.36	28	1	3.60	3.36	3.60	0.16	3.33	0.15	4.4	4.5	-0.1	-0.9
ICP-AES				10	1	3.60	3.33	3.60	0.17	3.34	0.14	4.6	4.3	-0.1	-0.8
Ion chromatography				9	0	3.61	3.37	3.58	0.13	3.34	0.15	3.5	4.6	-0.6	-0.5
FAAS				4	0	3.56	3.27	3.50	0.14	3.25	0.11	3.9	3.5	-2.7	-3.3
ICP-MS				3	0	3.69	3.25	3.64	0.14	3.25	0.16	3.8	4.9	1.0	-3.3
Cap. Electrophoresis				1	0			3.62		3.47				0.6	3.2
Other method				1	0			4.01		3.61				11.4	7.4
Magnesium	AB	0.85	0.79	27	2	0.85	0.79	0.84	0.05	0.78	0.04	6.5	5.7	-1.0	-1.0
Ion chromatography				9	0	0.85	0.78	0.83	0.05	0.77	0.04	6.2	5.3	-2.6	-1.8
ICP-AES				9	0	0.85	0.79	0.86	0.03	0.78	0.02	3.9	2.4	0.6	-0.3
ICP-MS				4	1	0.86	0.81	0.83	0.13	0.77	0.12	16.2	15.4	-2.2	-1.5
FAAS				3	0	0.86	0.79	0.86	0.01	0.79	0.02	1.7	2.2	0.7	0.6
Other method				1	0			0.83		0.76				-2.9	-3.8
Cap. Electrophoresis				1	1			0.97		0.96				14.1	22.1

Analytical variable and method	Sample pair	TRUE Value		No. lab.		Median		Avg/Std.av.		Avg/Std.av.		Rel.std.av. %		Relative error %	
		S. 1	S. 2	Total	Om	S. 1	S. 2	Sample 1		Sample 2		S. 1	S. 2	S. 1	S. 2
Sodium	AB	3.25	3.00	28	2	3.25	3.00	3.24	0.20	3.01	0.16	6.2	5.5	-0.3	0.3
Ion chromatography				10	0	3.21	3.00	3.20	0.25	2.97	0.19	7.8	6.3	-1.2	-0.9
ICP-AES				7	0	3.24	3.05	3.18	0.16	2.98	0.18	5.1	6.2	-2.1	-0.6
ICP-MS				5	1	3.28	3.00	3.28	0.05	3.02	0.07	1.5	2.2	1.2	0.7
FAAS				3	0	3.54	3.22	3.46	0.19	3.21	0.01	5.4	0.3	6.7	7.1
AES				1	0			3.23		2.95				-0.5	-1.7
Cap. Electrophoresis				1	0			3.10		2.97				-4.5	-1.0
Other method				1	1			2.40		2.22				-26.0	-26.0
Potassium	AB	0.68	0.62	27	1	0.68	0.62	0.68	0.06	0.63	0.05	8.6	8.3	0.5	0.5
Ion chromatography				10	0	0.68	0.62	0.67	0.07	0.61	0.06	11.0	10.6	-2.1	-1.7
ICP-AES				8	0	0.70	0.65	0.70	0.05	0.65	0.05	7.8	7.7	2.6	4.0
ICP-MS				4	0	0.67	0.61	0.67	0.01	0.61	0.02	1.8	3.0	-2.1	-2.4
FAAS				2	0			0.74		0.66				9.0	6.8
AES				1	0			0.73		0.62				6.8	-1.1
Cap. Electrophoresis				1	0			0.66		0.60				-3.7	-3.4
Other method				1	1			0.29		0.28				-57.4	-55.0
Total Organic Carbon	AB	2.90	2.67	19	0	2.90	2.67	2.87	0.41	2.65	0.41	14.4	15.5	-0.9	-0.7
Combustion				10	0	3.03	2.77	2.98	0.37	2.72	0.31	12.3	11.4	2.6	1.9
Other method				5	0	2.75	2.51	2.62	0.56	2.45	0.63	21.5	25.6	-9.8	-8.1
UV/peroxodisulphate				4	0	2.88	2.66	2.93	0.23	2.72	0.33	7.7	12.2	1.1	2.0
Total Phosphorous	AB	16.00	15.00	21	0	16.00	15.00	16.29	5.79	15.25	6.09	35.6	39.9	1.8	1.7
Photometry				12	0	18.29	17.00	17.36	6.63	16.80	7.17	38.2	42.7	8.5	12.0
ICP-AES				5	0	15.43	13.71	16.32	4.25	13.93	3.80	26.0	27.3	2.0	-7.1
Other method				4	0	12.83	12.43	13.04	4.48	12.26	3.90	34.3	31.8	-18.5	-18.3
Aluminium	CD	16	15	20	2	16	15	16	2	14	2	14.4	14.0	-1.2	-1.1
ICP-MS				11	0	17	14	17	2	14	1	14.4	10.6	1.0	-3.1
ICP-AES				5	0	15	16	15	2	15	3	14.9	19.4	-6.2	5.1
GFAAS				4	2			16		14				-0.4	-5.7
Iron	CD	129.2	115.2	20	0	129.2	115.2	130.7	5.6	115.5	4.3	4.3	3.7	1.2	0.2
ICP-AES				8	0	129.6	116.4	131.9	5.2	117.6	4.9	3.9	4.2	2.1	2.1
ICP-MS				8	0	128.0	112.5	129.5	6.6	113.0	2.8	5.1	2.5	0.2	-1.9
FAAS				2	0			134.1		118.3				3.8	2.6
GFAAS				2	0			127.2		113.9				-1.5	-1.1

Analytical variable and method	Sample pair	TRUE Value		No. lab.		Median		Avg/Std.av.		Avg/Std.av.		Rel.std.av. %		Relative error %	
		S. 1	S. 2	Total	Om	S. 1	S. 2	Sample 1		Sample 2		S. 1	S. 2	S. 1	S. 2
Cadmium	CD	1.30	1.15	24	0	1.30	1.15	1.29	0.10	1.13	0.10	7.9	9.1	-0.6	-1.6
ICP-MS				12	0	1.32	1.16	1.32	0.06	1.16	0.06	4.9	5.0	1.2	1.1
GFAAS				5	0	1.24	1.06	1.27	0.14	1.09	0.14	11.2	12.6	-2.2	-5.6
ICP-AES				5	0	1.37	1.18	1.33	0.09	1.17	0.09	6.5	8.0	1.9	1.8
FAAS				1	0			1.20		0.98				-7.8	-15.0
Polarography				1	0			1.05		0.93				-19.2	-19.1
Manganese	CD	22.00	20.26	21	0	22.00	20.26	22.21	1.03	20.25	0.82	4.6	4.1	1.0	0.0
ICP-MS				10	0	21.90	20.00	21.75	0.63	20.03	0.45	2.9	2.2	-1.1	-1.1
ICP-AES				7	0	22.42	20.50	22.46	1.13	20.43	1.17	5.0	5.7	2.1	0.8
FAAS				2	0			22.94		19.90				4.2	-1.8
GFAAS				2	0			22.90		21.10				4.1	4.1
Lead	CD	1.46	1.35	22	2	1.46	1.35	1.41	0.22	1.30	0.10	15.3	7.8	-3.2	-3.6
ICP-MS				12	0	1.48	1.35	1.50	0.10	1.34	0.03	6.6	2.2	2.9	-0.8
GFAAS				6	2	1.25	1.17	1.30	0.16	1.19	0.15	12.1	13.0	-10.6	-12.1
ICP-AES				3	0	1.30	1.35	1.24	0.48	1.33	0.13	38.9	9.4	-15.1	-1.2
Polarography				1	0			1.30		1.20				-11.0	-11.1
Copper	CD	17.90	16.60	24	0	17.90	16.60	17.50	2.60	16.35	2.15	14.9	13.2	-2.2	-1.5
ICP-MS				12	0	17.75	16.85	17.66	0.72	16.69	0.70	4.1	4.2	-1.4	0.6
GFAAS				5	0	17.90	16.60	16.23	3.86	15.54	2.71	23.8	17.4	-9.3	-6.4
ICP-AES				5	0	18.43	16.16	19.46	2.96	17.49	2.87	15.2	16.4	8.7	5.4
FAAS				1	0			12.22		11.15				-31.7	-32.8
Polarography				1	0			17.40		15.70				-2.8	-5.4
Nickel	CD	6.24	5.48	22	0	6.24	5.48	6.38	0.75	5.54	0.39	11.8	7.0	2.3	1.2
ICP-MS				12	0	6.28	5.48	6.28	0.14	5.47	0.11	2.2	2.0	0.7	-0.1
ICP-AES				5	0	6.22	5.58	6.64	1.05	5.73	0.50	15.8	8.7	6.5	4.7
GFAAS				4	0	5.82	5.15	5.79	0.46	5.47	0.76	7.9	13.9	-7.2	-0.1
FAAS				1	0			8.56		5.64				37.3	3.0
Zinc	CD	12.30	13.40	21	0	12.30	13.40	12.37	0.86	13.59	0.98	7.0	7.2	0.6	1.4
ICP-MS				12	0	12.78	13.75	12.69	0.90	14.04	0.94	7.1	6.7	3.2	4.8
ICP-AES				5	0	12.00	13.00	11.98	0.48	12.83	0.48	4.0	3.7	-2.6	-4.2
FAAS				2	0			11.76		13.27				-4.4	-1.0
GFAAS				2	0			12.05		13.15				-2.0	-1.9

*Om.: Sample pair omitted from the calculations

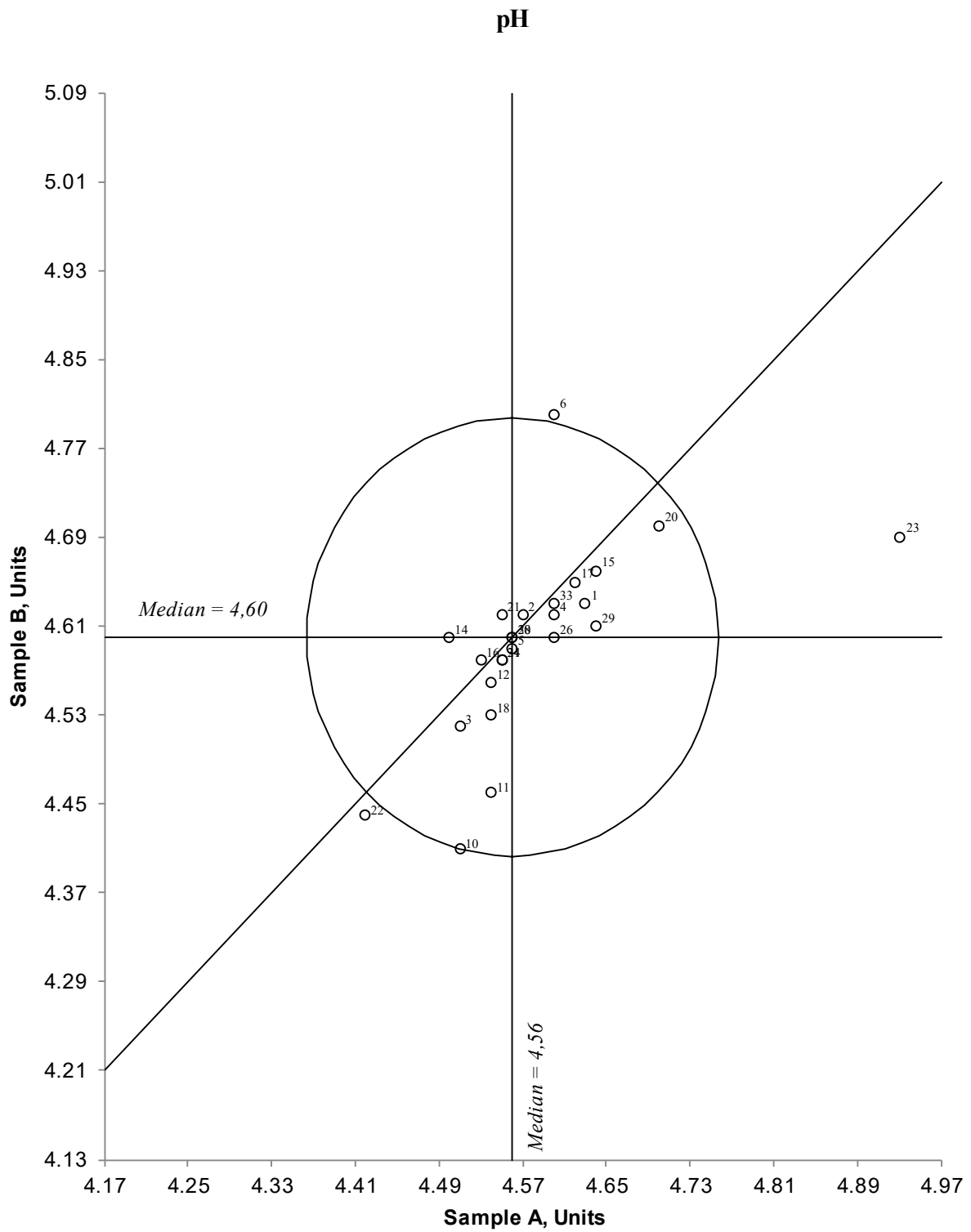


Figure 1. Youden diagram for pH. Sample pair AB. Acceptable limit, given by circle, is 4.3%.

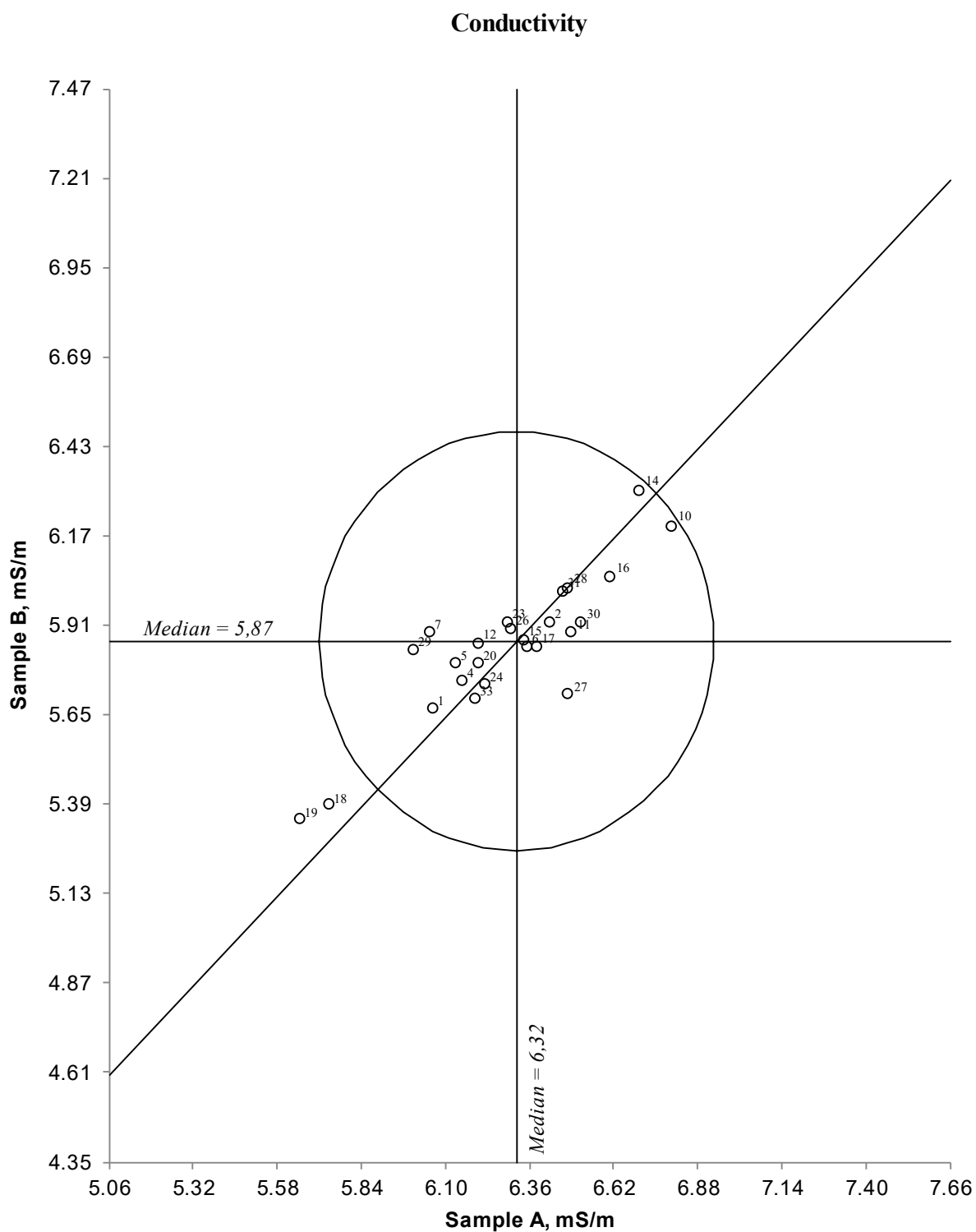


Figure 2. Youden diagram for conductivity. Sample pair AB. Acceptable limit, given by circle, is 10%.

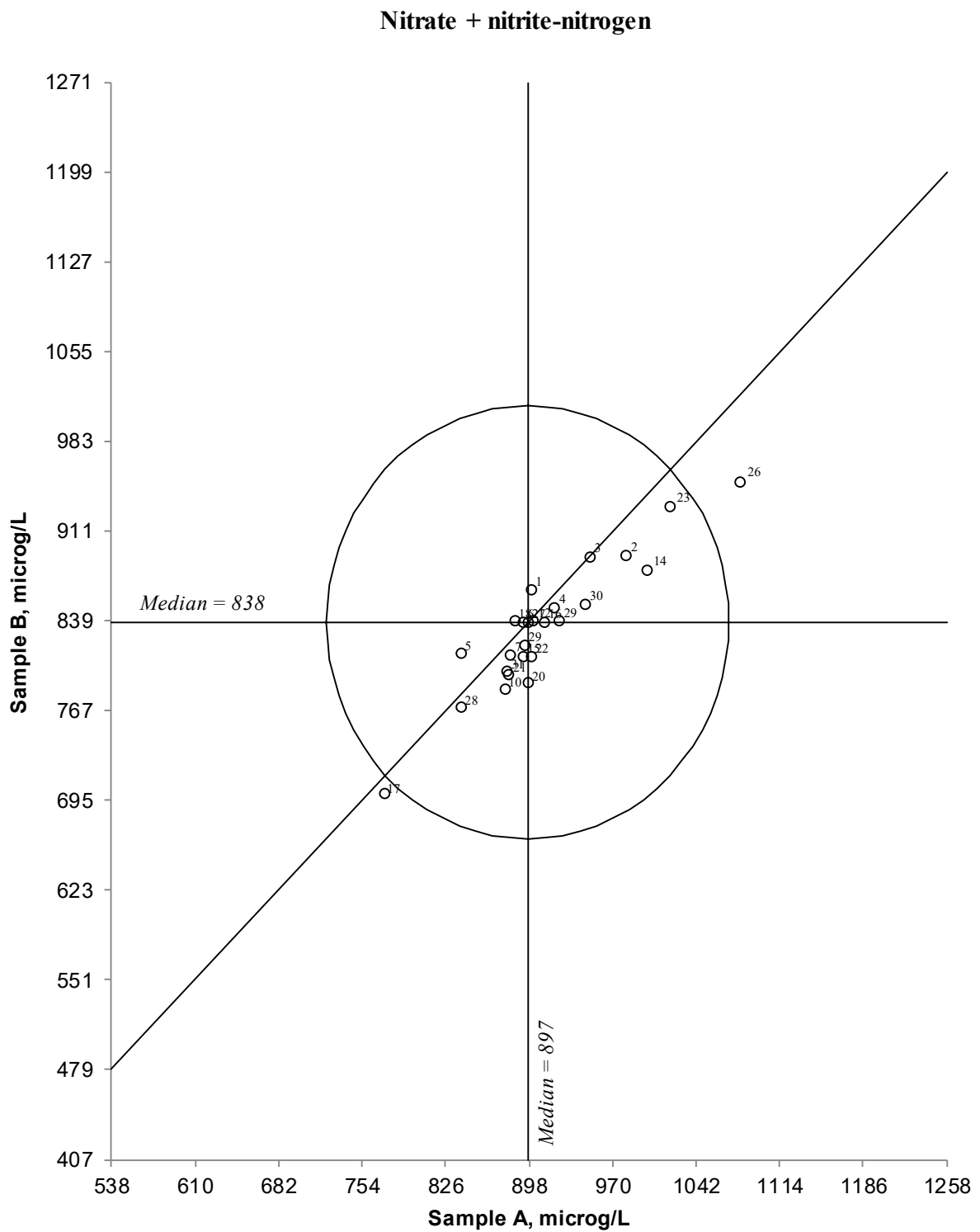


Figure 3. Youden diagram for NO₃ + NO₂-N. Sample pair AB. Acceptable limit, given by circle, is 20%.

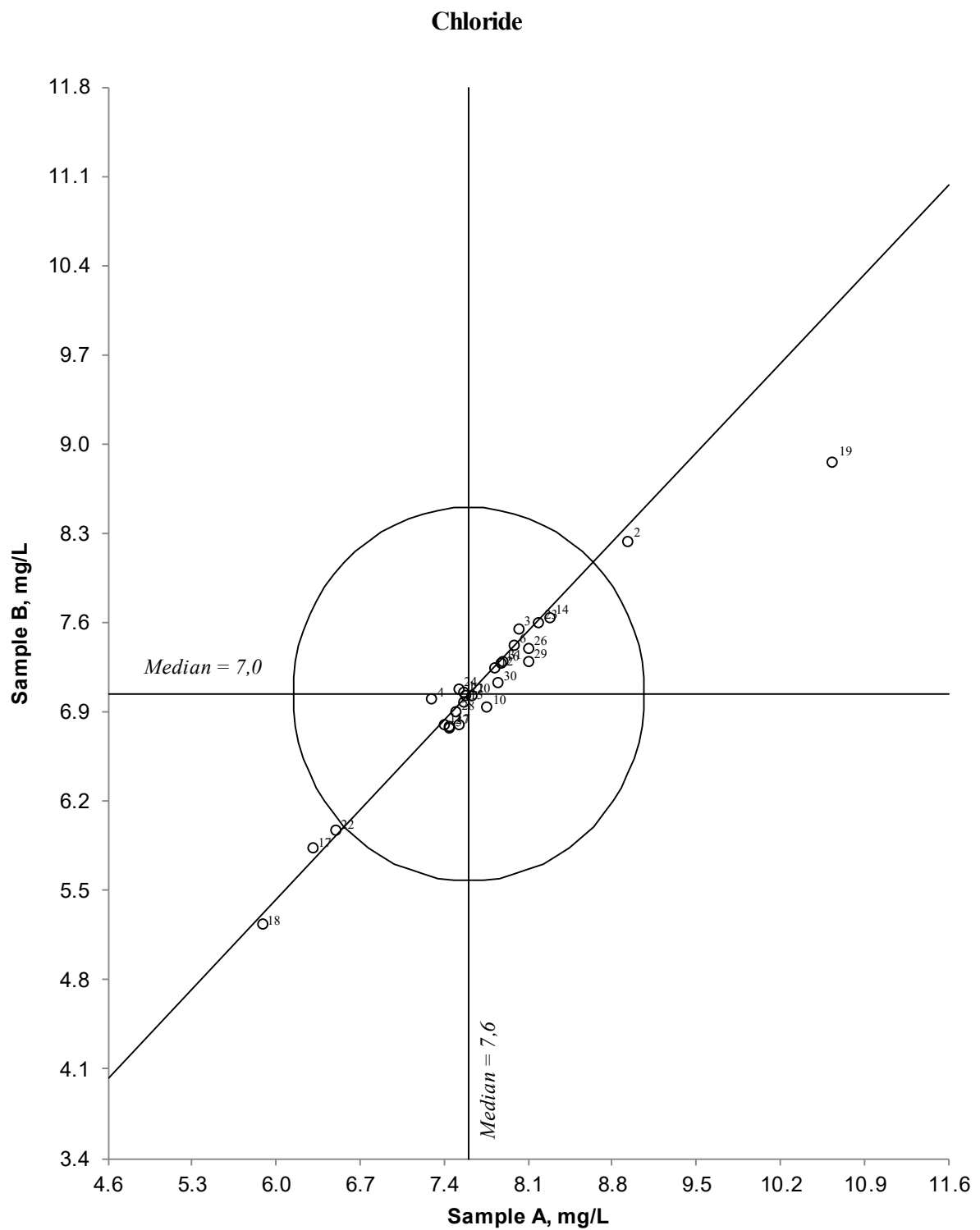


Figure 4. Youden diagram for Chloride. Sample pair AB. Acceptable limit, given by circle, is 20%.

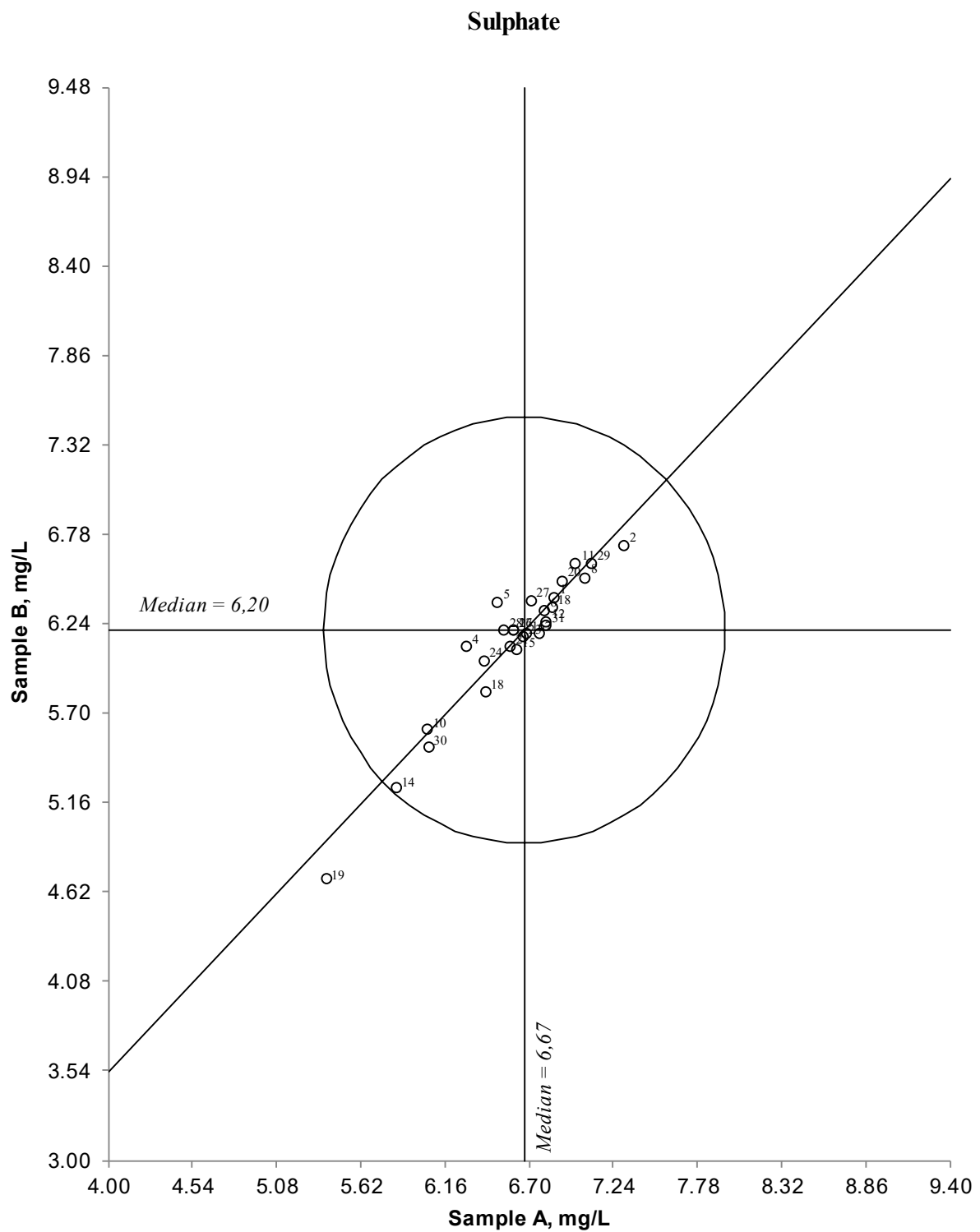


Figure 5. Youden diagram for Sulphate. Sample pair AB. Acceptable limit, given by circle, is 20%.

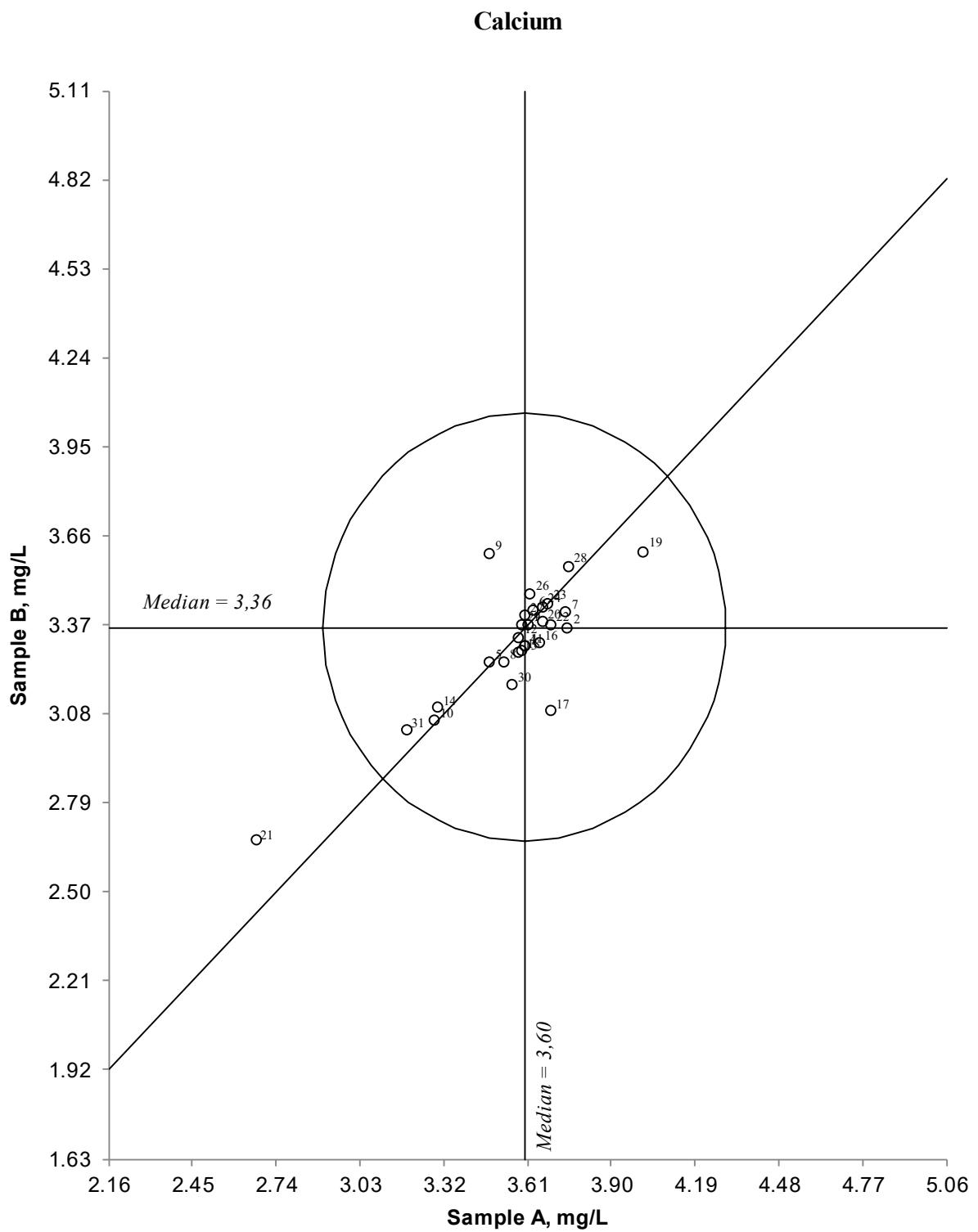


Figure 6. Youden diagram for Calcium. Sample pair AB. Acceptable limit, given by circle, is 20%.

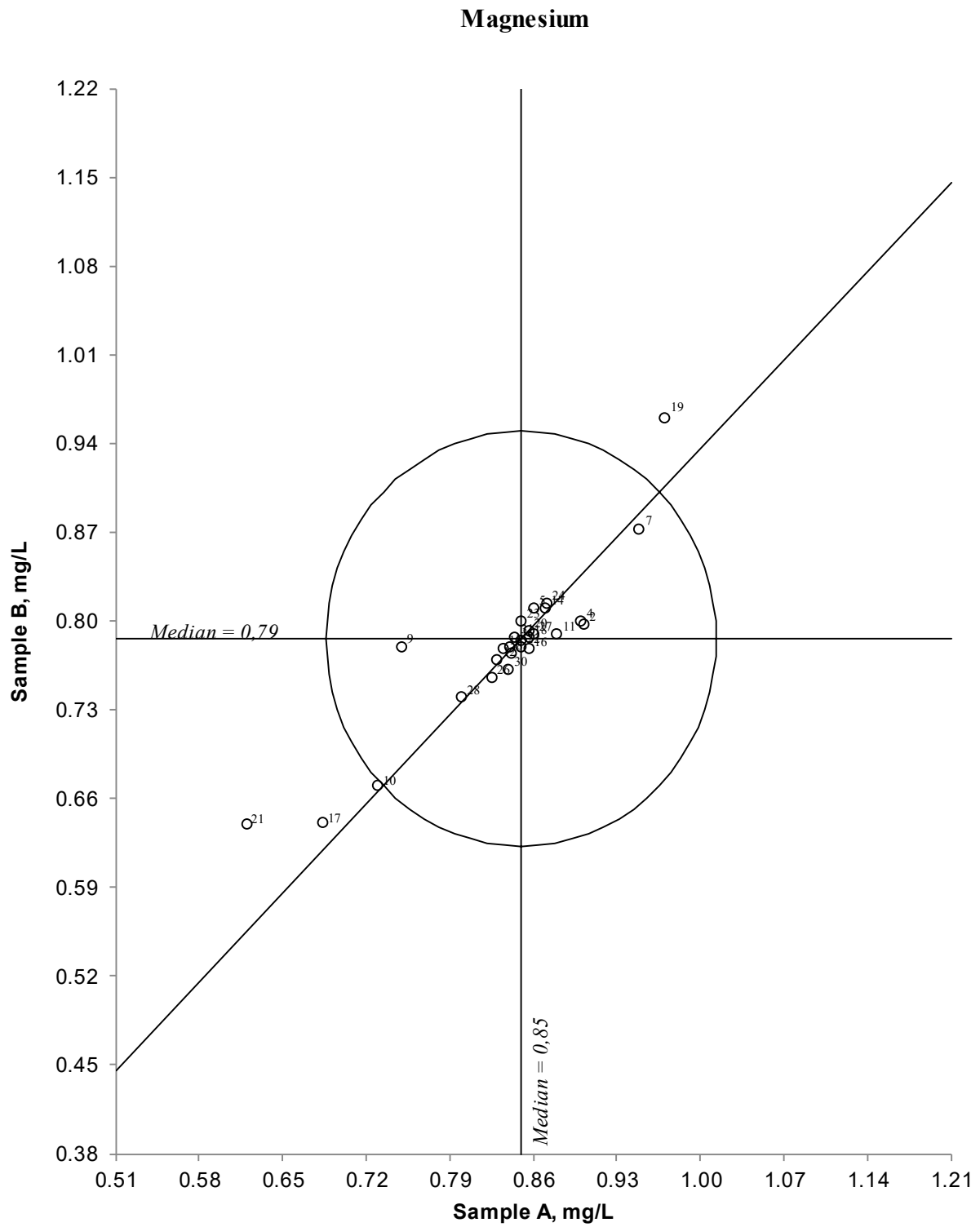


Figure 7. Youden diagram for Magnesium. Sample pair AB. Acceptable limit, given by circle, is 20%.

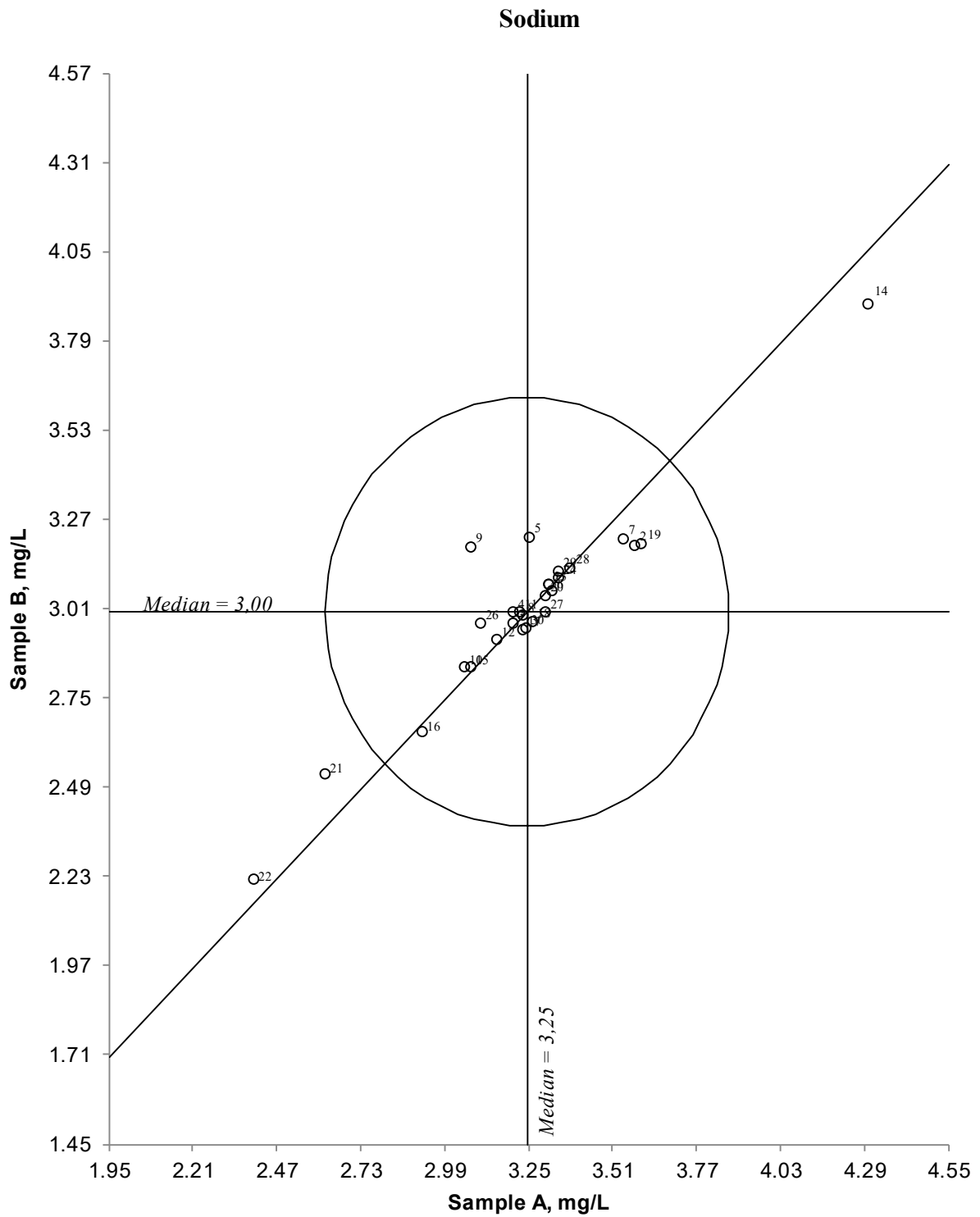


Figure 8. Youden diagram for Sodium. Sample pair AB. Acceptable limit, given by circle, is 20%.

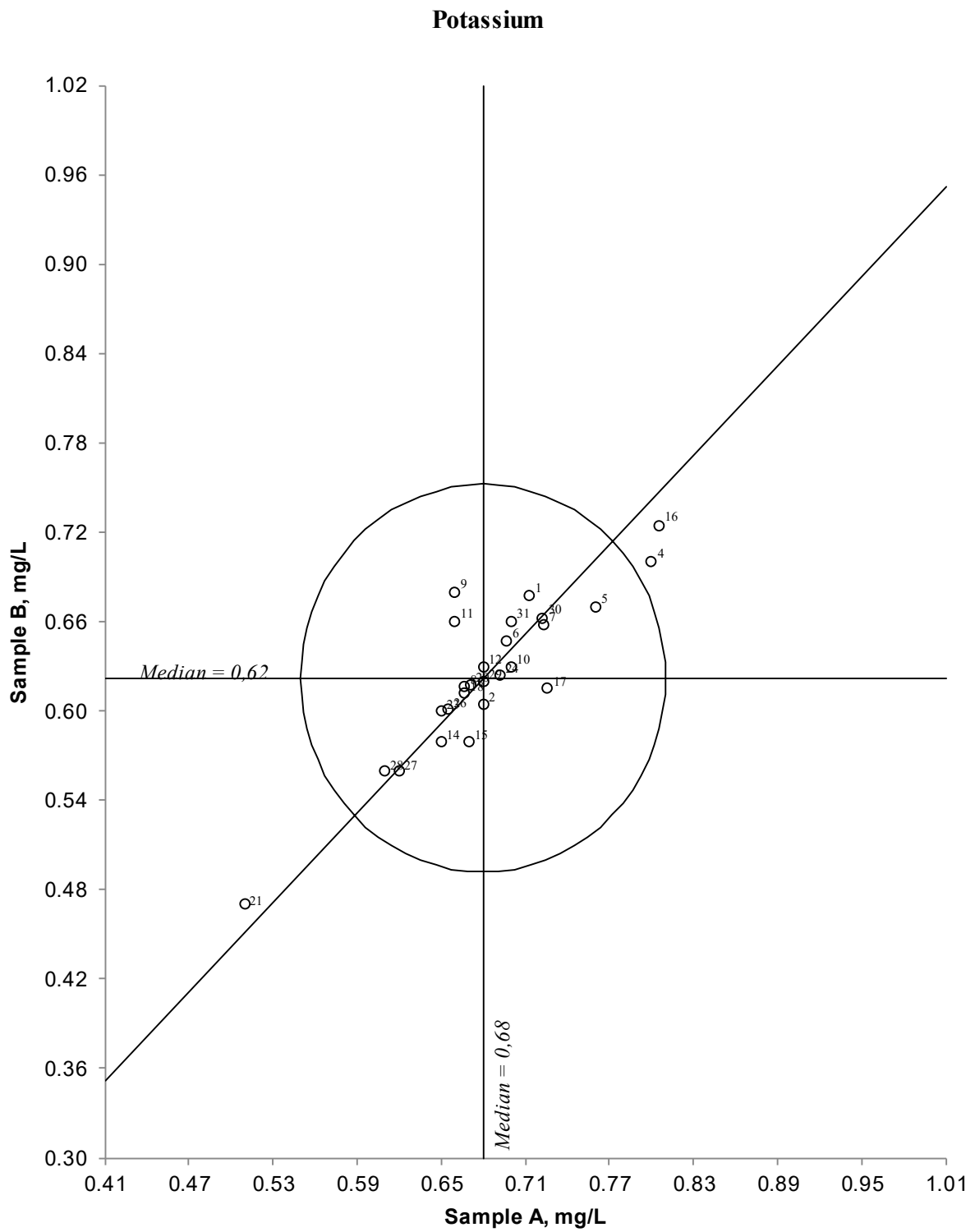


Figure 9. Youden diagram for Potassium. Sample pair AB. Acceptable limit, given by circle, is 20%.

Total organic carbon

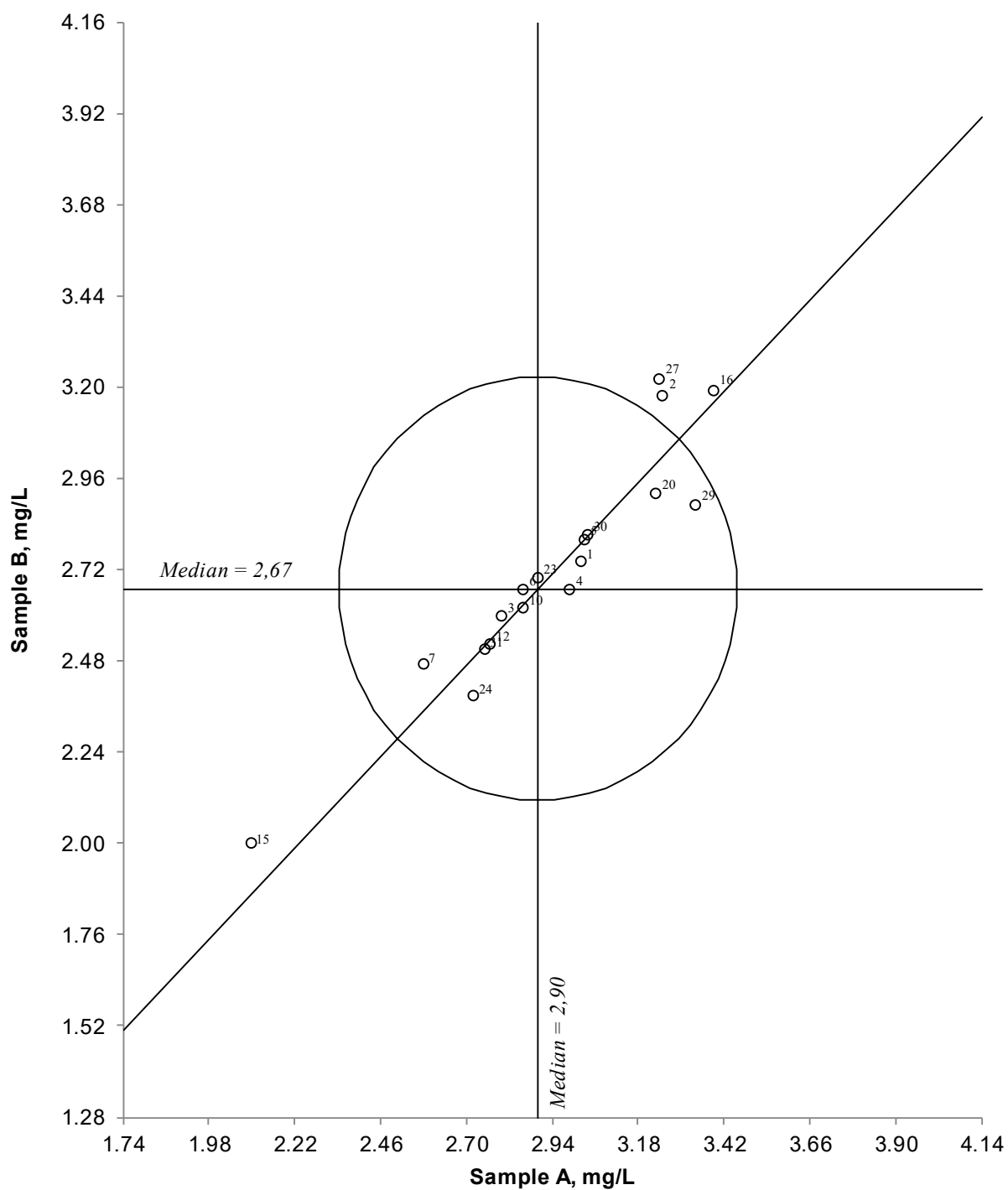


Figure 10. Youden diagram for TOC. Sample pair AB. Acceptable limit, given by circle, is 20%.

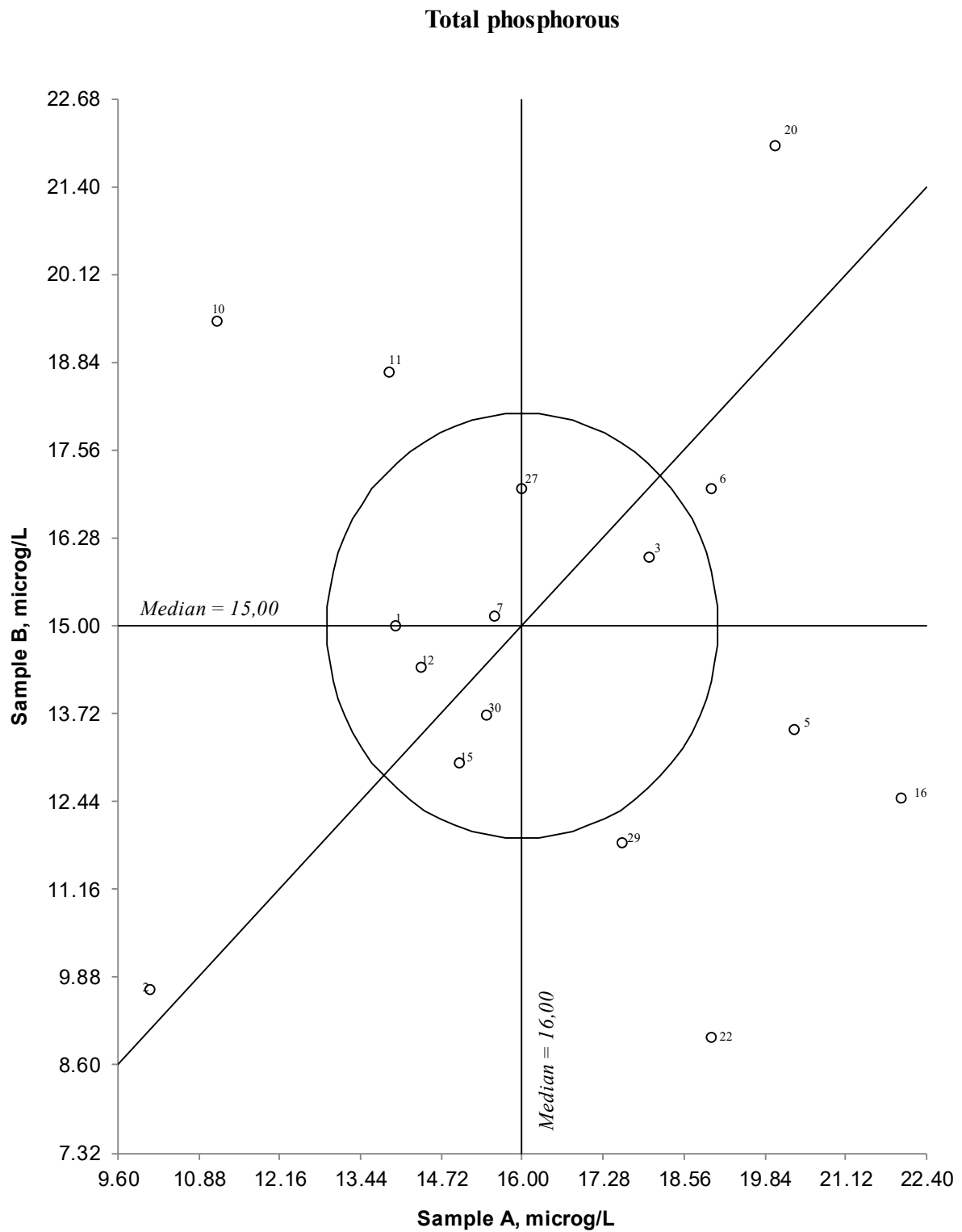


Figure 11. Youden diagram for Total-P. Sample pair AB. Acceptable limit, given by circle, is 20%.

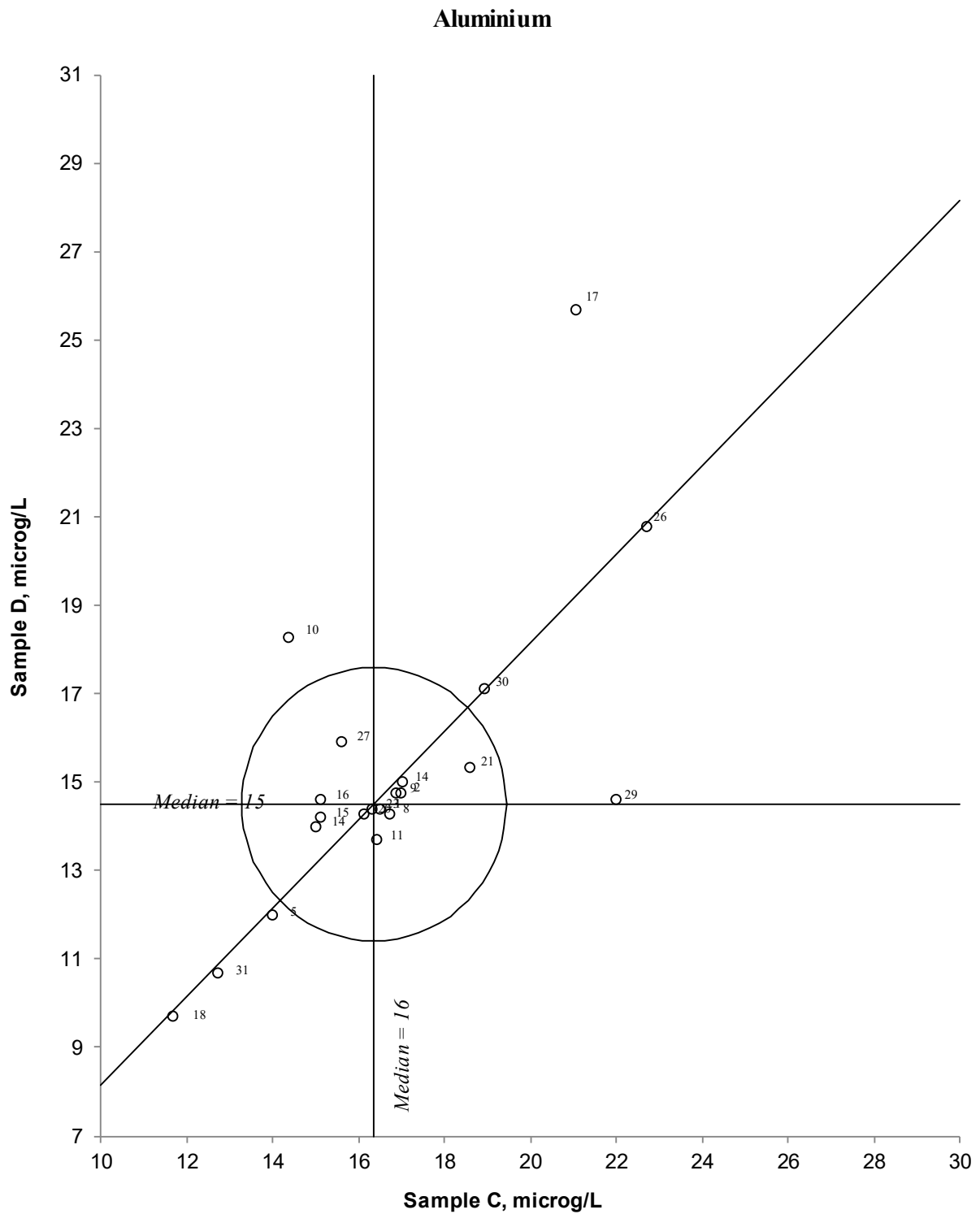


Figure 12. Youden diagram for Aluminium. Sample pair CD. Acceptable limit, given by circle, is 20%.

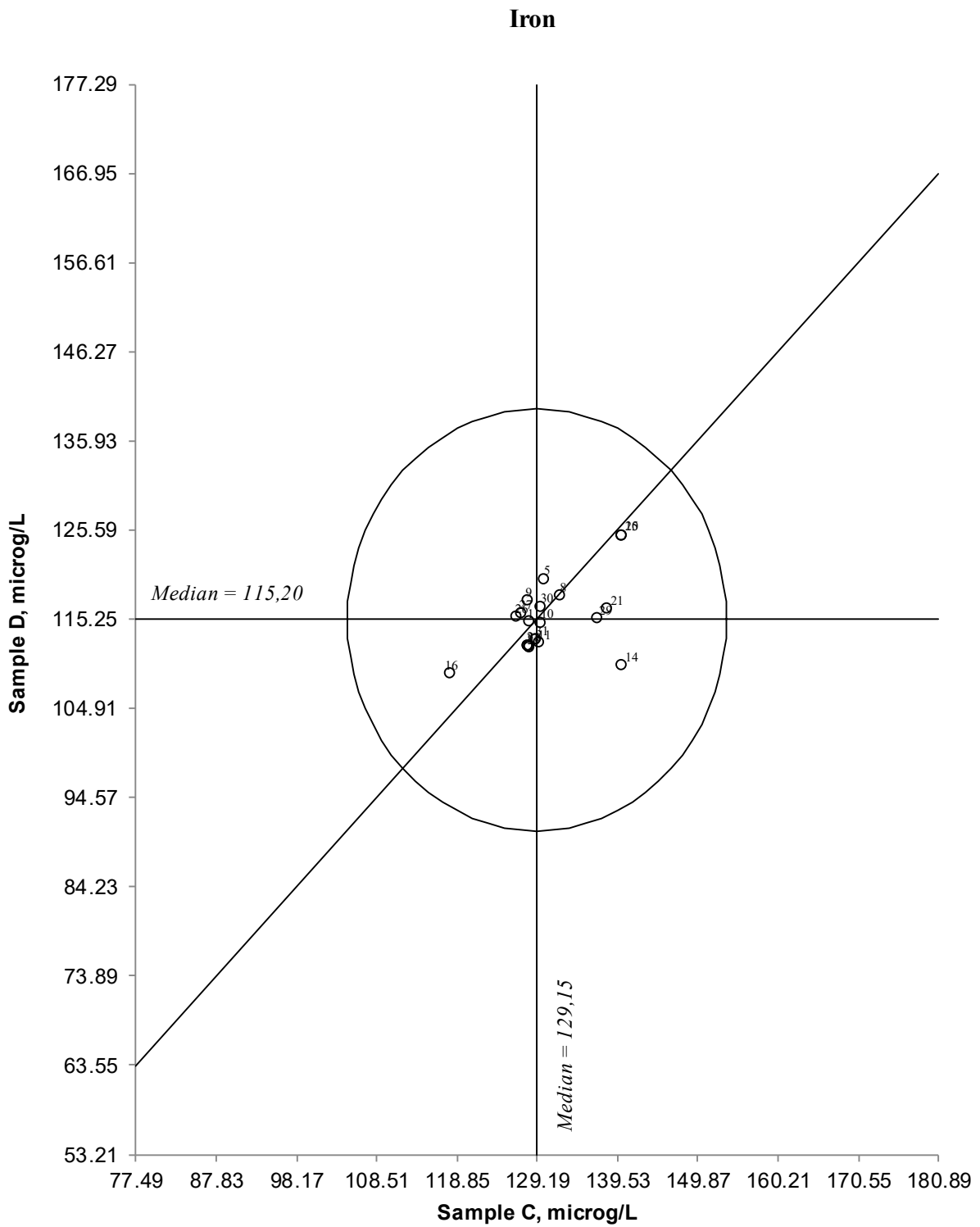


Figure 13. Youden diagram for Iron. Sample pair CD. Acceptable limit, given by circle, is 20%.

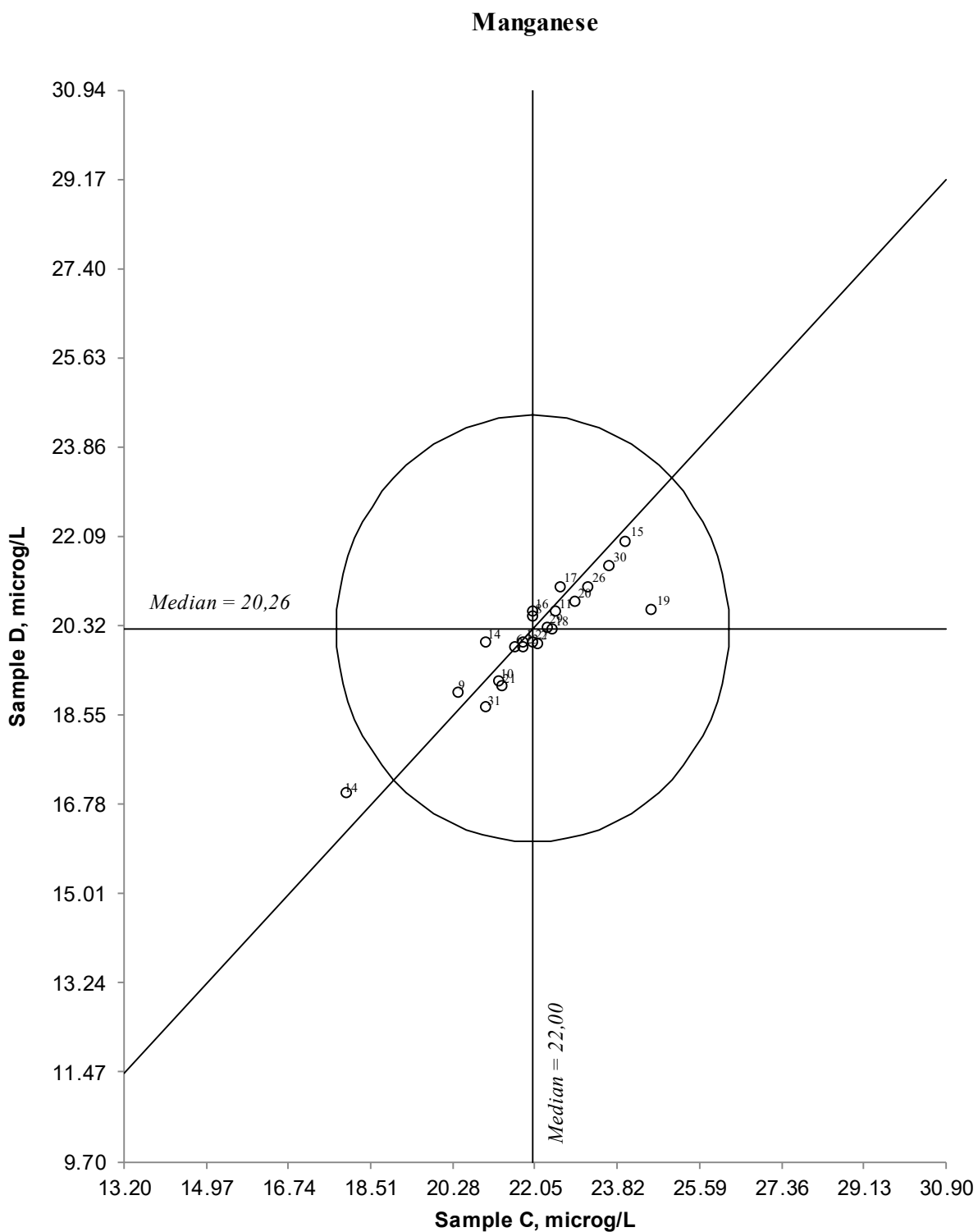


Figure 14. Youden diagram for Manganese. Sample pair CD. Acceptable limit, given by circle, is 20%.

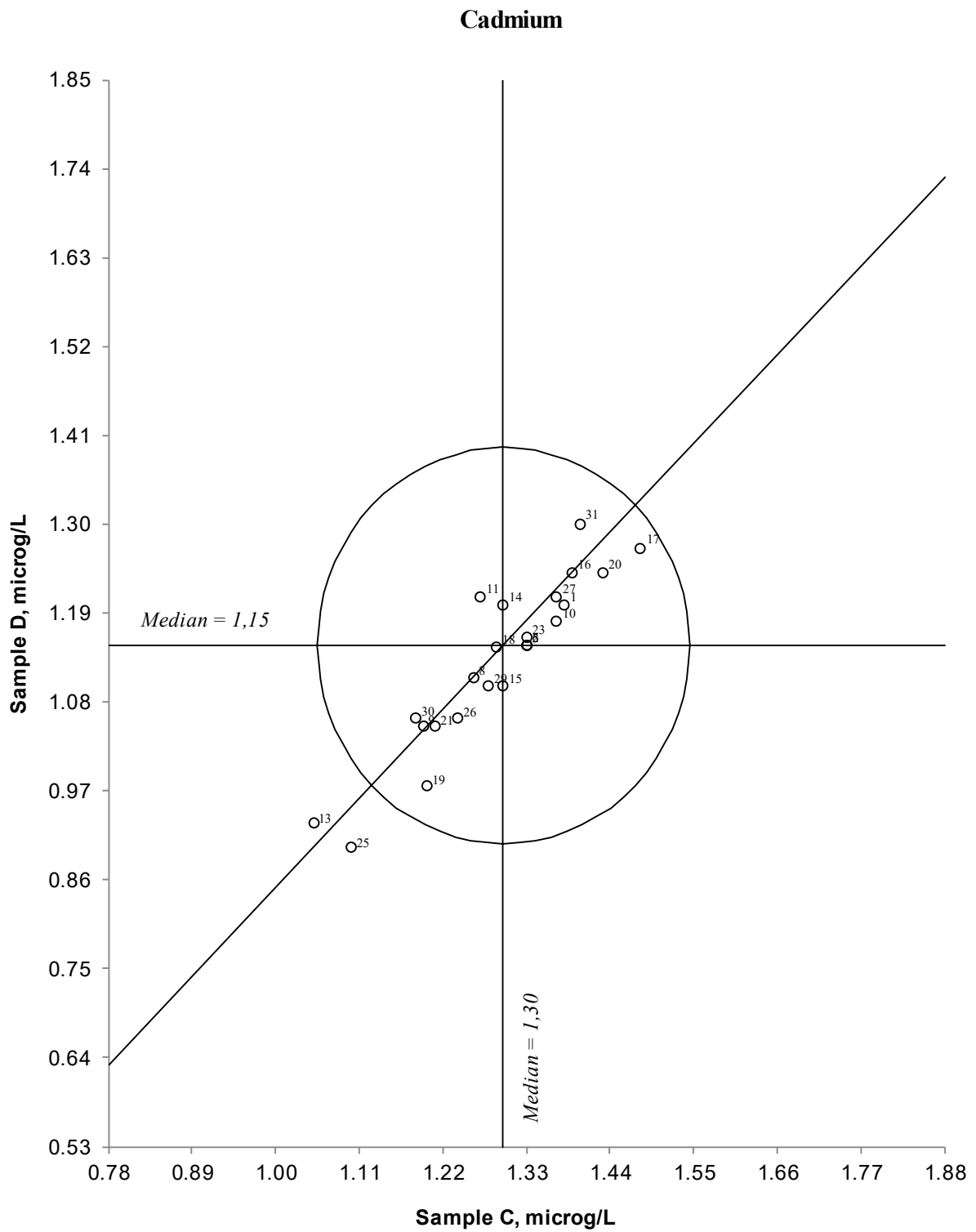


Figure 15. Youden diagram for Cadmium. Sample pair CD. Acceptable limit, given by circle, is 20%.

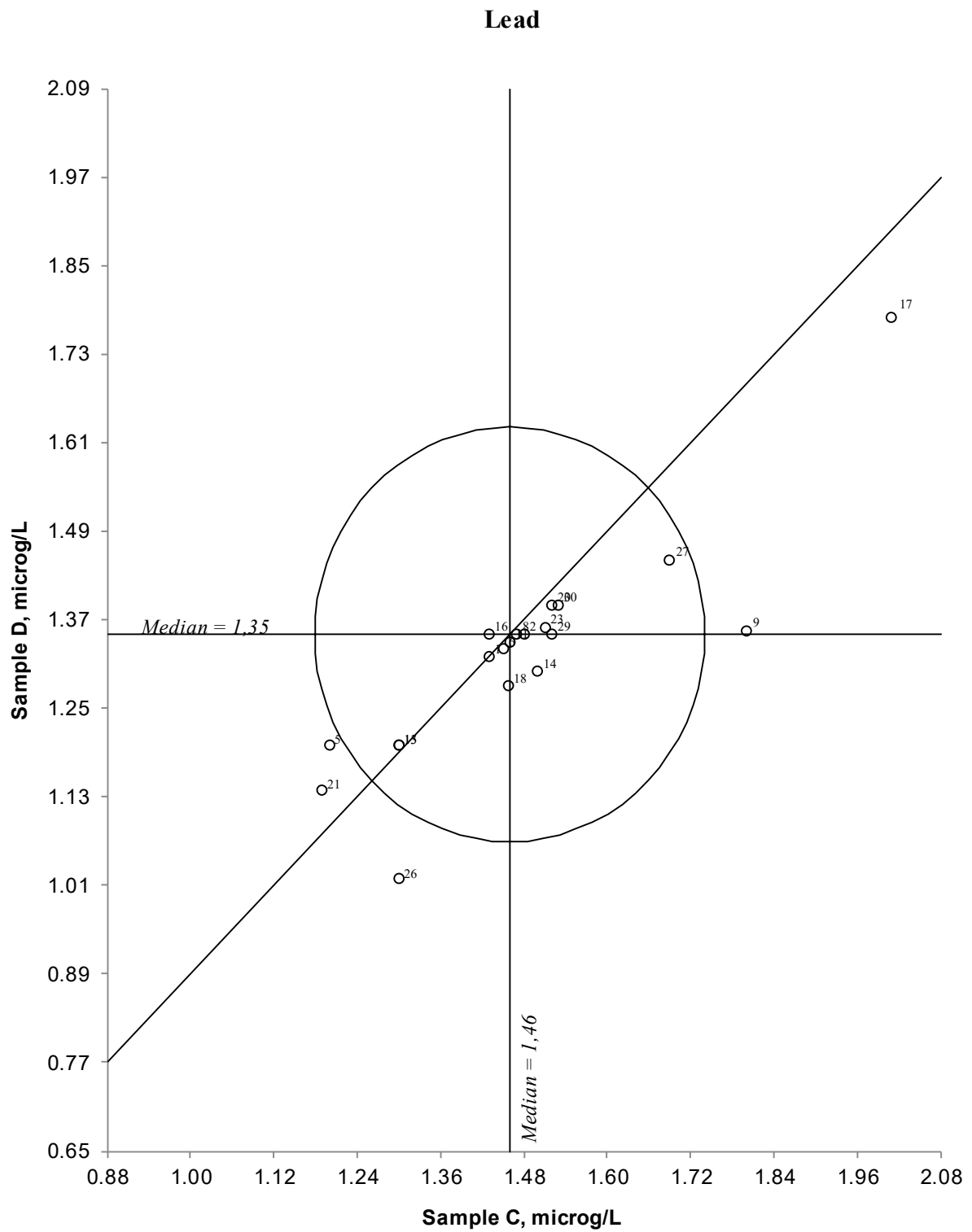


Figure 16. Youden diagram for Lead. Sample pair CD. Acceptable limit, given by circle, is 20%.

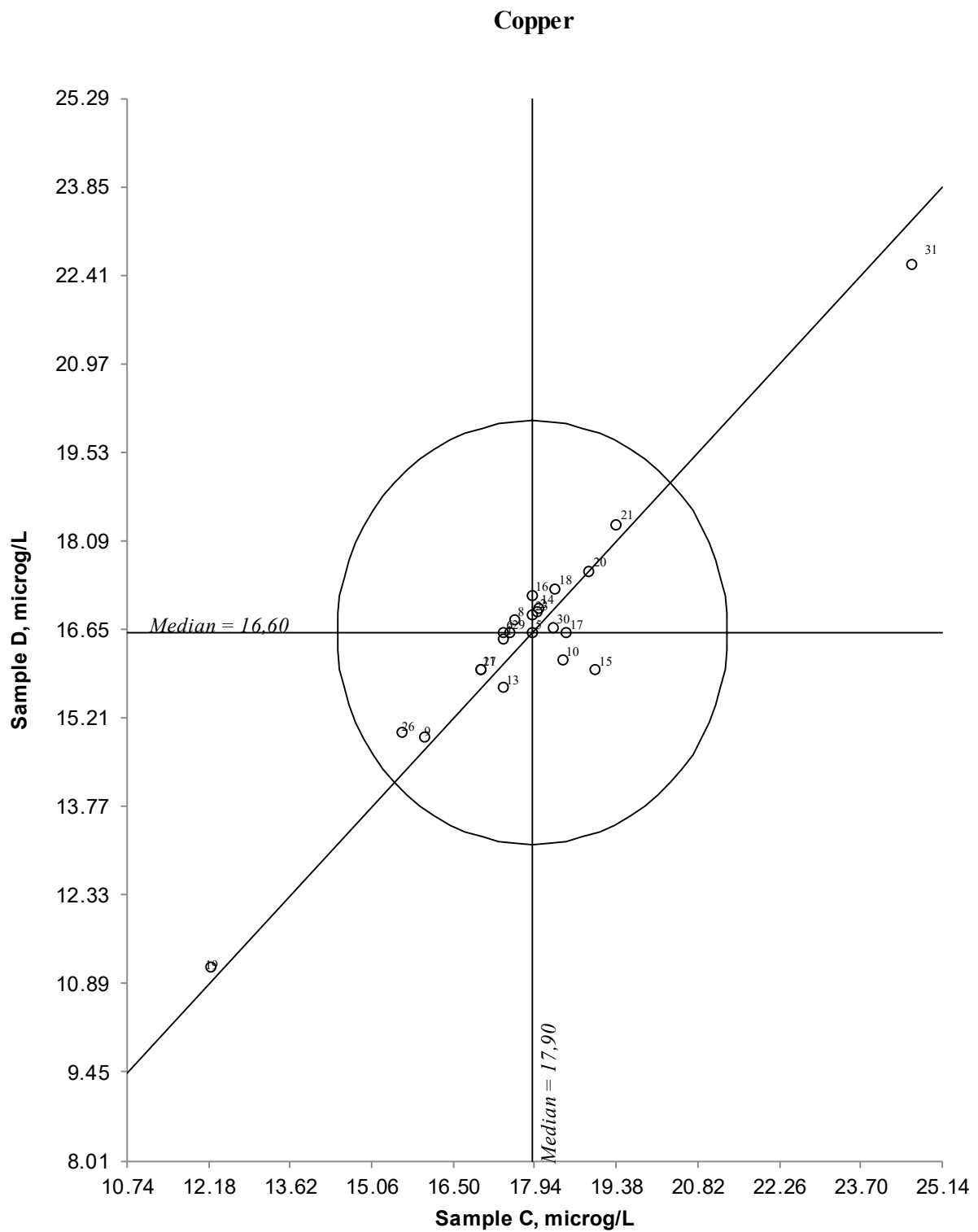


Figure 17. Youden diagram for Copper. Sample pair CD. Acceptable limit, given by circle, is 20%.

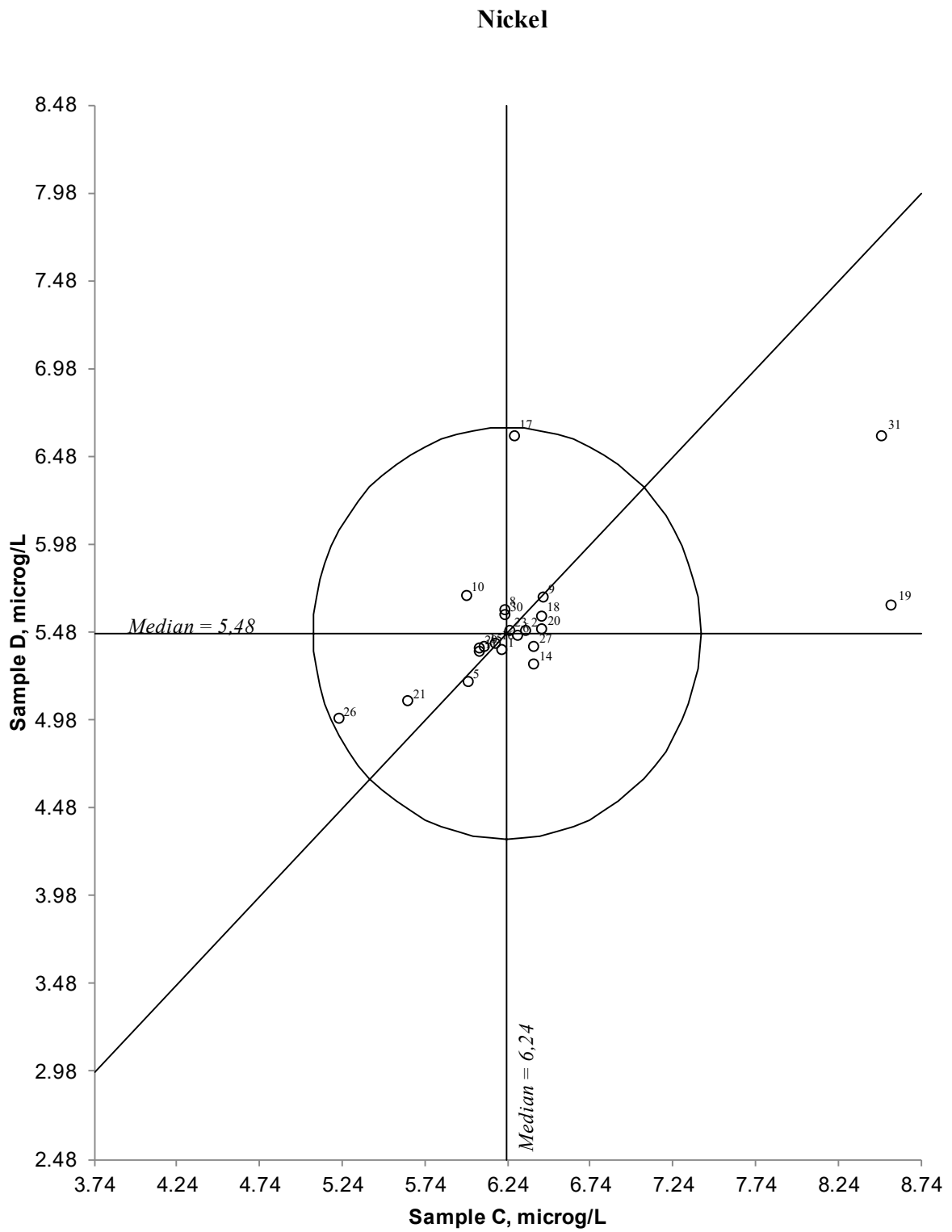


Figure 18. Youden diagram for Nickel. Sample pair CD. Acceptable limit, given by circle, is 20%.

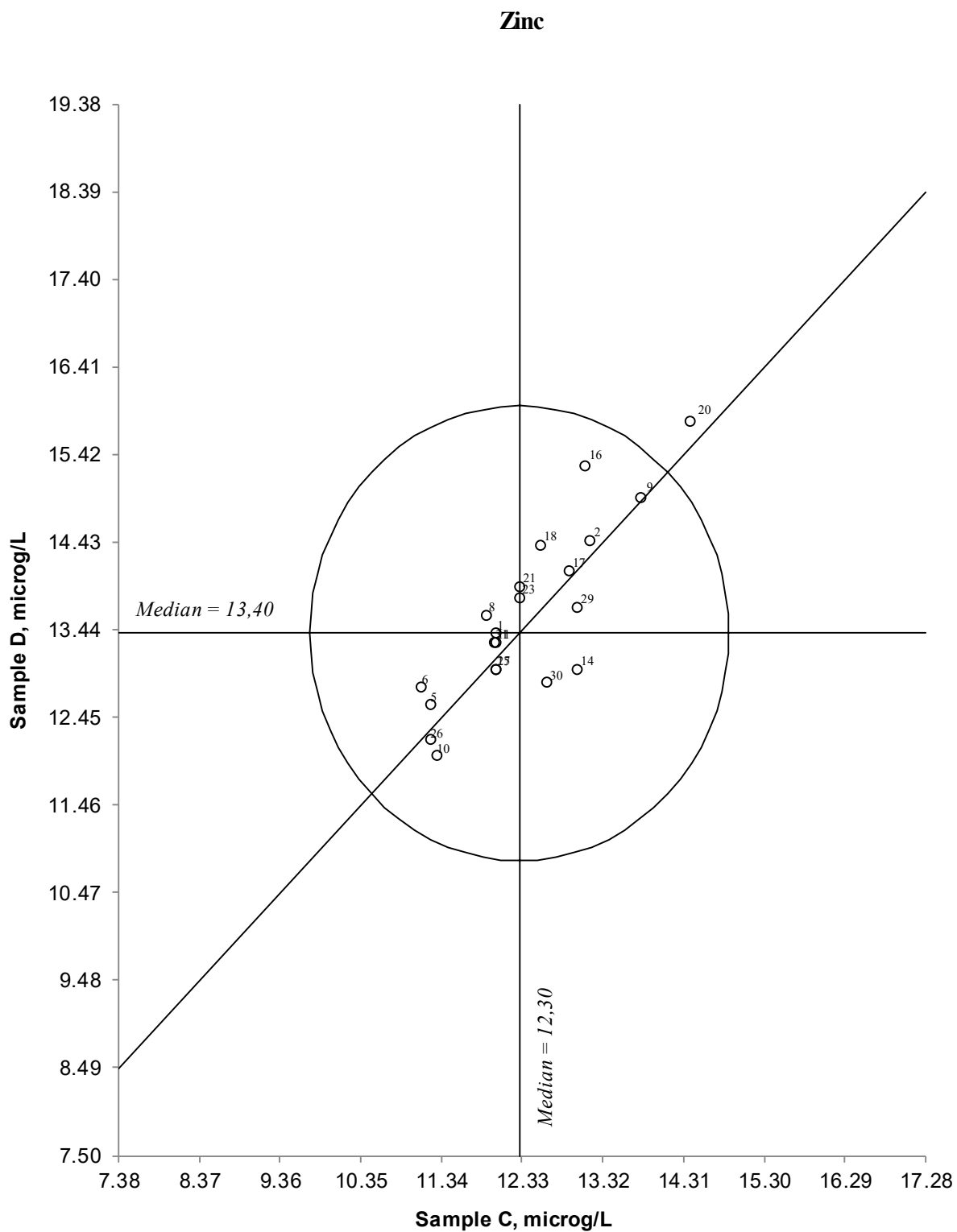


Figure 19. Youden diagram for Zinc. Sample pair CD. Acceptable limit, given by circle, is 20%.

5 Literature

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

No	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	Ufficio del Monitoraggio Ambientale - Laboratorio	Via Mirasole 22 6500 Bellinzona	Switzerland
3	EPA Regional Inspectorate Castlebar OEA	John Moore Road, Castlebar, Ireland.	Ireland
4	Staatliche Betriebsgesellschaft für Umwelt und Landwirtschaft (BfUL)	Dresdner Straße 183 D-09131 Chemnitz	Germany
5	Chemical Laboratory, Czech Geological Survey	Geologická 6, 152 00 Prague	Czech Republic
6	Estonian Environment Research Centre	Marja 4 D 10617 Tallinn Estonia	Estonia
7	MOEECC, DORSET Laboratory	P.O. Box 39 Dorset, Ontario Canada POA 1E0	Canada
8	NLS Starcross laboratory Staplake Mount	Starcross, Exeter, Devon, EX6 8FD	United Kingdom
9	Servei d'Anàlisi Química i Estructural	STR-UdG Pic de Peguera, 15 17003-Girona	Spain
10	Büsgen-Institute - Soil Science of Temperate Ecosystems	D-37077 Goettingen Buesgenweg 2	Germany
11	University of Helsinki Lab. of Geology and Geography	P.O.Box 64 00014 University of Helsinki	Finland
12	Institut für Ökologie	Technikerstrasse 25 6020 Innsbruck Austria	Austria
13	Institute for Public Health Pancevo	6 Oktobar No 9 26000 Pancevo	Serbia
14	EPA, Dublin Inspectorate McCumiskey Hs,	Richview, Clonskeagh Rd, Dublin, D14YR62, Ireland	Ireland
15	CNR Istituto Studio degli Ecosistemi	Largo Tonolli 50 I-28922 VERBANIA Pallanza	Italy
16	IVL Svenska miljöinstitutet AB	P.O. Box 53021 SE-400 14 Gothenburg	Sweden
17	Polish Academy of Sciences Institute of Botany	PAN Instytut Botaniki 31-512 Kraków ul. Lubicz 46	Poland
18	Natural Resources Wales Analytical Services (NRWAS)	Faraday Building, 2nd floor Swansea University Singleton Campus Swansea SA2 8PP	United Kingdom
19	State Hydrometeorological Service EQMD/SWQMC	134 Grenoble Str, Chisinau Moldova Republic MD-2072	Moldova, Republic Of
20	Bayerisches Landesamt fuer Umwelt	Ref 71 Bürgerm-Ulrich-Str. 160 D-86179 Augsburg	Germany
21	Environmental Pollution Monitoring Center Laboratory of surface and sea	Verkhne-Rostinskoe sh,51,MUGMS,Murmansk,183034	Russian Federation

No	Laboratory	Address	Country
22	Radbouduniversiteit afd. Ecologie t.a.v. G. Verheggen	Postbus 9010 6500 GL Nijmegen The Netherlands	Netherlands
23	Norsk institutt for vannforskning	Gaustadalléen 21 0439 OSLO	Norway
24	Marine Scotland Science Freshwater Laboratory	Faskally, Pitlochry, Perthshire, PH16 5BB, Scotland.	United Kingdom
25	Institute of Global Climate and Ecology (IGCE) Roshydromet and RAS Russian Academy of Sciences	20-B, Glebovskaya St., Moscow, 107258	Russian Federation
26	Hydrochemical Laboratory by Federal State Enterprise on Water Industry	10 A Stahanovskaya str., Pskov, 180004	Russian Federation
27	FGU «Baltvodhoz»	199004, Saint-Petersburg, V.O. Sredny pr. 26	Russian Federation
28	Staatliche Betriebgesellschaft für Umwelt und Landwirtschaft (BfUL)	Haus5, FB53 Waldheimer Str. 219 D-01683 Nossen	Germany
29	Swedish University for Agricultural Sciences Aquatic Sciences and Assessment	Box 7050 750 07 Uppsala	Sweden
30	Institute of Biology Komi SC UB RAS	Kommunisticheskaya st., 28 Syktyvkar, 167982, Russia	Russian Federation
31	Laboratoire d'Ecologie Fonctionnelle et Environnement (ECOLAB)	Avenue Agrobiopole 31326 Castanet Tolosan	France
32	Center for Environmental Monitoring, Primorsky Dept. for Hydrometeorology & Environmental Monitoring Primorsky CEM	Mordovtseva str. 3, Vladivostok 690091, Russia	Russian Federation
33	Institute of Environmental Protection-Puszcza Borecka station	Kolektorska 4, 01-692, Warszawa, Poland	Poland

Number of participating laboratories from the different countries represented in the intercomparison 1832

Country	No. of labs.	Country	No. of labs.
Austria	1	Netherlands	1
Canada	1	Norway	1
Czech Republic	1	Poland	2
Estonia	1	Russia	6
Finland	1	Serbia	1
France	1	Spain	1
Germany	5	Sweden	2
Ireland	2	Switzerland	1
Italy	1	United Kingdom	3
Moldova	1		

Total: 19 countries

Appendix B. Preparation of the samples

The sample solutions were prepared from water collected at lake Sagtjernet, located in Elverum, a small city and municipality in Hedmark county. The lake is a popular recreational area for the residents of Elverum during the summer. The water was collected in 25-liter plastic containers and immediately brought to the laboratory. The water was stored for about two weeks to allow it to equilibrate. The water was then filtrated through 0.45 μm cellulose acetate membrane and the filtrate was collected in polyethylene containers. After this process, the filtrate was stored at room temperature one more week to equilibrate. Small aliquots were taken from the filtrate to determine the background concentrations of the analytical variables of interest.

In the current edition the sample set AB was obtained lowering the natural pH of the effluent by addition of HCl, HNO₃ and H₂SO₄ diluted solutions. The TOC content was slightly increased by adding a few drops of a concentrated solution of humic acid. Phosphorous was added in organic form using a standard solution of inositol hexaphosphate (phytic acid).

The samples for the set CD were prepared by spiking the filtered water with stock solutions of stoichiometric compounds containing heavy metals and preserved by the addition of 5 mL concentrated nitric acid pr. liter sample to yield a 0.5% v/v concentration. In the current edition, the spiking was lower than usual, leading to a much lower concentration of heavy metals.

A few days before shipping, the samples were transferred to 500 mL (sample set AB) or 250 mL acid-washed (sample set CD) high density polyethylene bottles with screw cap. These samples were stored at room temperature until they were delivered to the participating laboratories.

Appendix C. Treatment of analytical data

The intercomparison was carried out by the method of Youden. This procedure requires two samples to be analyzed, and each laboratory shall report only one result per sample and analytical variable. In a coordinate system, the result of sample B is plotted against the result of sample A (see Figures 1 - 19).

The Youden's chart allows the possibility to distinguish between random and systematic errors affecting the results. The two straight lines drawn in the diagram represent the true values of the samples; or - as in this case, when the true value is not known - the median value of the results from the participating laboratories. The results being omitted in the statistical calculations are not used in the determination of the median value and thus, the true value. The diagram is thus divided into four quadrants. In a hypothetical case, when the analysis is affected by random errors only, the results will spread randomly over the four quadrants.

However, the results are usually located in the lower left and the upper right quadrant, constituting a characteristic elliptical pattern along the 45° line. This is reflecting the fact that many laboratories - due to systematic deviations - have attained too low or too high values for both samples.

The acceptance limit of the results may be represented by a circle with its center at the intersection of the two straight lines in the diagram (true or median values). The distance between the center of the circle and the mark representing the laboratory is a measure of the total error of the results. The distance along the 45° line gives the magnitude of the systematic error, while the distance perpendicular to the 45° line indicates the magnitude of the random error. The location of the laboratory in the Youden's diagram provides then important information about the size and type of analytical error, making it easier to ascertain which the source of error is.

The statistical treatment of the analytical results was accomplished in this way: Pairs of results where one or both of the values lie outside the true value $\pm 50\%$ are omitted from the statistical calculations. The remaining results are used for the calculation of the mean value (\bar{x}) and the standard deviation (s). Now the pairs of results where one or both of the values are lying outside $\bar{x} \pm 3s$, are omitted. The remaining results are used for a final calculation, the results of which are presented in the tables 5.1 - 5.20. Results being omitted from the calculations are marked with the letter "O".

Estimation of uncertainty of the true values

The median value of the reported results, after exclusion of strongly deviating results, is used as the true value for this intercomparison. Thus, the true value is based upon consensus value from the participants and therefore, the estimation of the uncertainty of the true value could be based on the method given in ISO 13528 (2005), Annex C (algorithm A).

For each parameter the median value is determined and an initial value for the robust standard deviation is calculated from the absolute differences between the median value and the result of each participating laboratory according to:

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

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

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

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

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

$$U = 2 \times u_x$$

It is important to know that there are some limitations in this approach for the estimation of the uncertainty of the true value:

- There may be no real consensus among the participants
- The consensus may be biased by the general use of faulty methodology and this bias will not be reflected in the standard uncertainty of the assigned value using this calculation.

Table 3. Estimation of uncertainty of the assigned true values

Parameter and unit	Sample	True value	Total no.	Robust std.dev.	Uncertainty	Expanded uncertainty
pH	A	4.56	26	0.061	0.015	0.030
	B	4.60	26	0.062	0.015	0.031
Conductivity (mS/m)	A	6.32	25	0.249	0.062	0.124
	B	5.87	26	0.164	0.040	0.080
Alkalinity (mmol/l)	A	--	--	--	--	--
	B	--	--	--	--	--
Nitrate + nitrite-nitrogen ($\mu\text{g N/l}$)	A	897	25	47.6	11.9	23.8
	B	838	25	44.4	11.1	22.2
Chloride (mg/l)	A	7.6	26	0.41	0.10	0.20
	B	7.0	26	0.39	0.10	0.19
Sulphate (mg/l)	A	6.67	27	0.341	0.082	0.164
	B	6.20	26	0.278	0.068	0.136
Calcium (mg/l)	A	3.60	27	0.107	0.026	0.051
	B	3.36	27	0.156	0.037	0.075
Magnesium (mg/l)	A	0.85	26	0.037	0.009	0.018
	B	0.79	27	0.027	0.006	0.013
Sodium (mg/l)	A	3.25	27	0.165	0.040	0.080
	B	3.00	27	0.151	0.036	0.073
Potassium (mg/l)	A	0.68	26	0.044	0.011	0.021
	B	0.62	26	0.047	0.012	0.023
Total organic carbon (mg/l)	A	2.90	19	0.317	0.091	0.182
	B	2.67	19	0.335	0.096	0.192
Total P ($\mu\text{g/l}$)	A	16.00	18	4.333	1.277	2.553
	B	15.00	17	3.970	1.204	2.407
Aluminium ($\mu\text{g/l}$)	C	16	20	2.7	0.8	1.5
	D	15	17	1.7	0.5	1.0
Iron ($\mu\text{g/l}$)	C	129.15	20	5.624	1.572	3.144
	D	115.20	20	3.759	1.051	2.101
Manganese ($\mu\text{g/l}$)	C	22.00	21	1.015	0.277	0.554
	D	20.26	21	0.857	0.234	0.468
Cadmium ($\mu\text{g/l}$)	C	1.30	24	0.097	0.025	0.050
	D	1.15	24	0.101	0.026	0.052
Lead ($\mu\text{g/l}$)	C	1.46	20	0.160	0.045	0.089
	D	1.35	20	0.089	0.025	0.050
Copper ($\mu\text{g/l}$)	C	17.90	24	1.173	0.299	0.599
	D	16.60	24	1.032	0.263	0.527
Nickel ($\mu\text{g/l}$)	C	6.24	22	0.235	0.063	0.125
	D	5.48	19	0.175	0.050	0.100
Zinc ($\mu\text{g/l}$)	C	12.30	21	0.880	0.240	0.480
	D	13.40	21	1.000	0.273	0.545

Appendix D. Results of participating laboratories

Table 4. The results of the participating laboratories.

Lab. nr.	pH		Conductivity, mS/m		Nitrate + nitrite-nitrogen, µg N/L		Chloride, mg/L		Sulphate, mg/L	
	A	B	A	B	A	B	A	B	A	B
1	4.63	4.63	6.06	5.67	900	864	7.6	7.1	6.86	6.40
2	4.57	4.62	6.42	5.92	981	891	8.9	8.2	7.31	6.71
3	4.51	4.52	8.70	6.50	950	890	8.0	7.6		
4	4.60	4.62	6.15	5.75	920	850	7.3	7.0	6.30	6.10
5	4.56	4.59	6.13	5.80	840	813	7.5	6.8	6.50	6.37
6	4.60	4.80	6.35	5.85	893	838	8.0	7.4	6.80	6.32
7	5.04	4.62	6.05	5.89	883	812	7.5	6.8	6.76	6.18
8									7.06	6.52
9										
10	4.51	4.41	6.80	6.20	877	784	7.8	6.9	6.05	5.60
11	4.54	4.46	6.49	5.89	3551	3459	7.4	6.8	7.00	6.60
12	4.54	4.56	6.20	5.86	902	839	7.8	7.2	6.81	6.25
13										
14	4.50	4.60	6.70	6.30	1000	880	8.3	7.6	5.85	5.25
15	4.64	4.66	6.34	5.87	893	811	7.6	7.0	6.62	6.08
16	4.53	4.58	6.61	6.05	911	838	7.9	7.3	6.68	6.18
17	4.62	4.65	6.38	5.85	774	700	6.3	5.8	6.60	6.20
18	4.54	4.53	5.74	5.39	886	839	5.9	5.2	6.85	6.34
19			5.65	5.35			10.6	8.9	5.40	4.70
20	4.70	4.70	6.20	5.80	897	789	7.6	7.0	6.91	6.50
21	4.55	4.62	62.65	58.30	881	796	7.6	7.0	6.58	6.10
22	4.42	4.44			900	811	6.5	6.0		
23	4.93	4.69	6.29	5.92	1020	930	8.2	7.6	6.66	6.16
24	4.55	4.58	6.22	5.74	3840	3672	7.5	7.1	6.41	6.02
25										
26	4.60	4.60	6.30	5.90	1080	950	8.1	7.4	6.60	6.20
27	4.68	5.17	6.48	5.71	897	838	7.5	6.8	6.71	6.38
28	4.56	4.60	6.48	6.02	840	770	7.5	6.9	6.54	6.20
29	4.64	4.61	6.00	5.84	924	839	8.1	7.3	7.10	6.60
30	4.56	4.60	6.52	5.92	946	853	7.9	7.1	6.05	5.50
31	4.55	4.58	6.46	6.01	879	798	7.9	7.3	6.81	6.23
33	4.60	4.63	6.19	5.70						

Lab. nr.	Sodium mg/l		Potassium mg/l		TOC mg/l		Total P µg/l		Aluminium µg/l		Iron µg/l	
	A	B	A	B	A	B	A	B	A	B	A	B
1	3.31	3.08	0.71	0.68	3.02	2.74	14.00	15.00	17	14	128.00	115.00
2	3.58	3.20	0.68	0.61	3.25	3.18	10.10	9.70	17	15	127.95	112.34
3					2.80	2.60	18.00	16.00				
4	3.20	3.00	0.80	0.70	2.99	2.67	23.00	23.00				
5	3.25	3.22	0.76	0.67	3.03	2.80	20.30	13.50	14	12	130.00	120.00
6	3.32	3.06	0.70	0.65	2.86	2.67	19.00	17.00				
7	3.54	3.22	0.72	0.66	2.58	2.47	15.56	15.15				
8	3.23	2.99	0.67	0.62					17	14	132.00	118.00
9	3.07	3.19	0.66	0.68					17	15	127.79	117.43
10	3.05	2.84	0.70	0.63	2.86	2.62	11.17	19.43	14	18	129.63	114.97
11	3.22	3.00	0.66	0.66			13.90	18.70	16	14	129.30	112.60
12	3.15	2.92	0.68	0.63	2.77	2.53	14.40	14.40				
13												
14	4.30	3.90	0.65	0.58					17	15	140.00	110.00
15	3.07	2.84	0.67	0.58	2.10	2.00	15.00	13.00	15	14	140.00	125.00
16	2.92	2.65	0.81	0.72	3.39	3.19	22.00	12.50	15	15	117.90	109.10
17	3.23	2.95	0.73	0.62					21	26	127.80	112.20
18	3.26	2.97	0.67	0.61			24.10	27.10	12	10	128.10	112.30
19	3.60	3.20										
20	3.30	3.05	0.67	0.62	3.23	2.92	20.00	22.00	16	14	140.00	125.00
21	2.62	2.53	0.51	0.47	1.71	1.47			19	15	138.20	116.50
22	2.40	2.22	0.29	0.28			19.00	9.00				
23	3.31	3.08	0.65	0.60	2.90	2.70	25.00	24.00	16	14	128.00	112.00
24	3.34	3.10	0.69	0.62	2.72	2.39	8.51	8.18				
25												
26	3.10	2.97	0.66	0.60			0.00	0.00	23	21	126.50	115.60
27	3.30	3.00	0.62	0.56	3.24	3.22	16.00	17.00	16	16	127.00	116.00
28	3.38	3.13	0.61	0.56								
29	3.34	3.12	0.68	0.62	3.34	2.89	17.58	11.85	22	15	136.80	115.40
30	3.24	2.96	0.72	0.66	3.04	2.81	15.43	13.71	19	17	129.60	116.80
31	3.20	2.97	0.70	0.66	2.75	2.51			13	11	129.00	113.00
33												

Lab. nr.	Manganese µg/l		Cadmium µg/l		Lead µg/l		Copper µg/l		Nickel µg/l		Zinc µg/l	
	A	B	A	B	A	B	A	B	C	D	C	D
1	21.80	20.00	1.38	1.20	1.43	1.32	17.40	16.50	6.21	5.38	12.00	13.40
2	22.11	19.98	1.33	1.15	1.48	1.35	17.98	16.93	6.35	5.49	13.16	14.44
3												
4												
5			1.33	1.15	1.20	1.20	17.90	16.60	6.00	5.20	11.20	12.60
6	21.60	19.90	1.33	1.15	1.45	1.33	17.40	16.60	6.30	5.46	11.10	12.80
7												
8	22.00	20.50	1.26	1.11	1.47	1.35	17.60	16.80	6.22	5.61	11.90	13.60
9	20.39	19.01	1.19	1.05	1.80	1.36	15.99	14.89	6.45	5.68	13.79	14.94
10	21.27	19.23	1.37	1.18	0.73	1.35	18.43	16.16	5.99	5.69	11.28	12.03
11	22.50	20.60	1.27	1.21	1.46	1.34	17.00	16.00	6.07	5.37	12.00	13.30
12												
13			1.05	0.93	1.30	1.20	17.40	15.70				
14	21.00	20.00	1.30	1.20	1.50	1.30	18.00	17.00	6.40	5.30	13.00	13.00
15	24.00	22.00	1.30	1.10	1.30	1.20	19.00	16.00	6.10	5.40	12.00	13.00
16	22.00	20.60	1.39	1.24	1.43	1.35	17.90	17.20	6.17	5.42	13.10	15.30
17	22.60	21.10	1.48	1.27	2.01	1.78	18.50	16.60	6.28	6.60	12.90	14.10
18	22.42	20.26	1.29	1.15	1.46	1.28	18.31	17.31	6.45	5.58	12.56	14.39
19	24.55	20.66	1.20	0.98			12.22	11.15	8.56	5.64		
20	22.90	20.80	1.43	1.24	1.52	1.39	18.90	17.60	6.45	5.50	14.40	15.80
21	21.32	19.14	1.21	1.05	1.19	1.14	19.37	18.35	5.64	5.09	12.31	13.93
22												
23	21.80	19.90	1.33	1.16	1.51	1.36	17.90	16.90	6.25	5.49	12.30	13.80
24												
25			1.10	0.90	2.80	6.30	9.80	11.20				
26	23.20	21.10	1.24	1.06	1.30	1.02	15.60	14.97	5.22	4.99	11.20	12.20
27	22.00	20.00	1.37	1.21	1.69	1.45	17.00	16.00	6.40	5.40	12.00	13.00
28												
29	22.30	20.30	1.28	1.10	1.52	1.35	17.50	16.60	6.07	5.39	13.00	13.70
30	23.64	21.51	1.19	1.06	1.53	1.39	18.27	16.69	6.22	5.58	12.63	12.84
31	21.00	18.70	1.40	1.30			24.60	22.60	8.50	6.60	11.98	13.30
33												

Table 5.1. Statistics. pH**Sample A**

Analytical method: All

Unit: Units

Number of participants	27	Range	0.28
Number of omitted results	3	Variance	0.00
True value	4.56	Standard deviation	0.06
Mean value	4.57	Relative standard deviation	1.3%
Median value	4.56	Relative error	0.2%

Analytical results in ascending order:

22	4.42	21	4.55	4	4.60
14	4.50	31	4.55	17	4.62
10	4.51	5	4.56	1	4.63
3	4.51	30	4.56	15	4.64
16	4.53	28	4.56	29	4.64
18	4.54	2	4.57	27	4.68 O
11	4.54	26	4.60	20	4.70
12	4.54	6	4.60	23	4.93 O
24	4.55	33	4.60	7	5.04 O

O = Omitted result

Sample B

Analytical method: All

Unit: Units

Number of participants	27	Range	0.39
Number of omitted results	3	Variance	0.01
True value	4.60	Standard deviation	0.08
Mean value	4.59	Relative standard deviation	1.8%
Median value	4.60	Relative error	-0.2%

Analytical results in ascending order:

10	4.41	5	4.59	4	4.62
22	4.44	26	4.60	1	4.63
11	4.46	30	4.60	33	4.63
3	4.52	28	4.60	17	4.65
18	4.53	14	4.60	15	4.66
12	4.56	29	4.61	23	4.69 O
31	4.58	7	4.62 O	20	4.70
24	4.58	21	4.62	6	4.80
16	4.58	2	4.62	27	5.17 O

O = Omitted result

Table 5.2. Statistics. Conductivity**Sample A**

Analytical method: All

Unit: mS/m

Number of participants	27	Range	1.15
Number of omitted results	2	Variance	0.07
True value	6.32	Standard deviation	0.27
Mean value	6.29	Relative standard deviation	4.3%
Median value	6.30	Relative error	-0.5%

Analytical results in ascending order:

19	5.65	12	6.20	28	6.48
18	5.74	24	6.22	27	6.48
29	6.00	23	6.29	11	6.49
7	6.05	26	6.30	30	6.52
1	6.06	15	6.34	16	6.61
5	6.13	6	6.35	14	6.70
4	6.15	17	6.38	10	6.80
33	6.19	2	6.42	3	8.70 O
20	6.20	31	6.46	21	62.65 O

O = Omitted result

Sample B

Analytical method: All

Unit: mS/m

Number of participants	27	Range	0.95
Number of omitted results	2	Variance	0.04
True value	5.87	Standard deviation	0.20
Mean value	5.85	Relative standard deviation	3.5%
Median value	5.86	Relative error	-0.3%

Analytical results in ascending order:

19	5.35	29	5.84	30	5.92
18	5.39	6	5.85	2	5.92
1	5.67	17	5.85	31	6.01
33	5.70	12	5.86	28	6.02
27	5.71	15	5.87	16	6.05
24	5.74	7	5.89	10	6.20
4	5.75	11	5.89	14	6.30
20	5.80	26	5.90	3	6.50 O
5	5.80	23	5.92	21	58.30 O

O = Omitted result

Table 5.3. Statistics. Nitrate + nitrite-nitrogen**Sample A**

Analytical method: All

Unit: microg/L

Number of participants	27	Range	306
Number of omitted results	2	Variance	3804
True value	897	Standard deviation	62
Mean value	911	Relative standard deviation	6.8%
Median value	897	Relative error	1.5%

Analytical results in ascending order:

17	774	6	893	29	924
5	840	29	894	30	946
28	840	20	897	3	950
10	877	27	897	2	981
31	879	22	900	14	1000
21	881	1	900	23	1020
7	883	12	902	26	1080
18	886	16	911	11	3551 O
15	893	4	920	24	3840 O

O = Omitted result

Sample B

Analytical method: All

Unit: microg/L

Number of participants	27	Range	250
Number of omitted results	2	Variance	2678
True value	838	Standard deviation	52
Mean value	834	Relative standard deviation	6.2%
Median value	838	Relative error	-0.5%

Analytical results in ascending order:

17	700	5	813	30	853
28	770	29	820	1	864
10	784	27	838	14	880
20	789	6	838	3	890
21	796	16	838	2	891
31	798	18	839	23	930
22	811	12	839	26	950
15	811	29	839	11	3459 O
7	812	4	850	24	3672 O

O = Omitted result

Table 5.4. Statistics. Chloride**Sample A**

Analytical method: All

Unit: mg/L

Number of participants	27	Range	3.0
Number of omitted results	1	Variance	0.4
True value	7.6	Standard deviation	0.6
Mean value	7.6	Relative standard deviation	8.2%
Median value	7.6	Relative error	0.1%

Analytical results in ascending order:

18	5.9	24	7.5	31	7.9
17	6.3	1	7.6	6	8.0
22	6.5	15	7.6	3	8.0
4	7.3	21	7.6	26	8.1
11	7.4	20	7.6	29	8.1
27	7.5	10	7.8	23	8.2
5	7.5	12	7.8	14	8.3
28	7.5	30	7.9	2	8.9
7	7.5	16	7.9	19	10.6 O

O = Omitted result

Sample B

Analytical method: All

Unit: mg/L

Number of participants	27	Range	3.0
Number of omitted results	1	Variance	0.4
True value	7.0	Standard deviation	0.6
Mean value	7.0	Relative standard deviation	8.5%
Median value	7.0	Relative error	-0.4%

Analytical results in ascending order:

18	5.2	15	7.0	31	7.3
17	5.8	4	7.0	29	7.3
22	6.0	20	7.0	26	7.4
5	6.8	21	7.0	6	7.4
27	6.8	1	7.1	3	7.6
7	6.8	24	7.1	23	7.6
11	6.8	30	7.1	14	7.6
28	6.9	12	7.2	2	8.2
10	6.9	16	7.3	19	8.9 O

O = Omitted result

Table 5.5. Statistics. Sulphate**Sample A**

Analytical method: All

Unit: mg/L

Number of participants	27	Range	1.46
Number of omitted results	1	Variance	0.11
True value	6.67	Standard deviation	0.33
Mean value	6.65	Relative standard deviation	5.0%
Median value	6.67	Relative error	-0.3%

Analytical results in ascending order:

19	5.40	O	21	6.58	12	6.81
14	5.85		17	6.60	31	6.81
10	6.05		26	6.60	18	6.85
30	6.05		15	6.62	1	6.86
4	6.30		23	6.66	20	6.91
24	6.41		16	6.68	11	7.00
18	6.42		27	6.71	8	7.06
5	6.50		7	6.76	29	7.10
28	6.54		6	6.80	2	7.31

O = Omitted result

Sample B

Analytical method: All

Unit: mg/L

Number of participants	27	Range	1.46
Number of omitted results	1	Variance	0.11
True value	6.20	Standard deviation	0.34
Mean value	6.19	Relative standard deviation	5.5%
Median value	6.20	Relative error	-0.2%

Analytical results in ascending order:

19	4.70	O	23	6.16	18	6.34
14	5.25		7	6.18	5	6.37
30	5.50		16	6.18	27	6.38
10	5.60		26	6.20	1	6.40
18	5.83		28	6.20	20	6.50
24	6.02		17	6.20	8	6.52
15	6.08		31	6.23	11	6.60
21	6.10		12	6.25	29	6.60
4	6.10		6	6.32	2	6.71

O = Omitted result

Table 5.6. Statistics. Calcium**Sample A**

Analytical method: All

Unit: mg/L

Number of participants	28	Range	0.82
Number of omitted results	1	Variance	0.03
True value	3.60	Standard deviation	0.16
Mean value	3.60	Relative standard deviation	4.4%
Median value	3.60	Relative error	-0.1%

Analytical results in ascending order:

21	2.67	O	18	3.59	24	3.66
31	3.19		29	3.59	23	3.68
10	3.29		4	3.60	22	3.69
14	3.30		27	3.60	17	3.69
5	3.48		11	3.60	7	3.74
9	3.48		1	3.61	2	3.75
8	3.53		26	3.62	28	3.75
30	3.56		6	3.63	19	4.01
12	3.58		16	3.65		
15	3.58		20	3.66		

O = Omitted result

Sample B

Analytical method: All

Unit: mg/L

Number of participants	28	Range	0.58
Number of omitted results	1	Variance	0.02
True value	3.36	Standard deviation	0.15
Mean value	3.33	Relative standard deviation	4.5%
Median value	3.36	Relative error	-0.9%

Analytical results in ascending order:

21	2.67	O	11	3.30	7	3.41
31	3.03		4	3.30	6	3.42
10	3.06		16	3.31	24	3.43
17	3.09		12	3.33	23	3.44
14	3.10		2	3.36	26	3.47
30	3.18		22	3.37	28	3.56
5	3.25		29	3.37	9	3.60
8	3.25		1	3.37	19	3.61
15	3.28		20	3.38		
18	3.29		27	3.40		

O = Omitted result

Table 5.7. Statistics. Magnesium**Sample A**

Analytical method: All

Unit: mg/L

Number of participants	27	Range	0.27
Number of omitted results	2	Variance	0.00
True value	0.85	Standard deviation	0.05
Mean value	0.84	Relative standard deviation	6.5%
Median value	0.85	Relative error	-1.0%

Analytical results in ascending order:

21	0.62	O	15	0.84	5	0.86
17	0.68		8	0.84	27	0.86
10	0.73		31	0.85	14	0.87
9	0.75		22	0.85	24	0.87
28	0.80		6	0.85	11	0.88
26	0.83		23	0.85	4	0.90
12	0.83		16	0.86	2	0.90
1	0.84		20	0.86	7	0.95
30	0.84		18	0.86	19	0.97 O

O = Omitted result

Table 5.8. Statistics - Magnesium

Sample B

Analytical method: All

Unit: mg/L

Number of participants	27	Range	0.23
Number of omitted results	2	Variance	0.00
True value	0.79	Standard deviation	0.04
Mean value	0.78	Relative standard deviation	5.7%
Median value	0.79	Relative error	-1.0%

Analytical results in ascending order:

21	0.64	O	1	0.78	20	0.79
17	0.64		22	0.78	2	0.80
10	0.67		15	0.78	4	0.80
28	0.74		9	0.78	23	0.80
26	0.76		6	0.79	5	0.81
30	0.76		18	0.79	14	0.81
12	0.77		31	0.79	24	0.81
8	0.78		27	0.79	7	0.87
16	0.78		11	0.79	19	0.96 O

O = Omitted result

Table 5.8. Statistics. Sodium**Sample A**

Analytical method: All

Unit: mg/L

Number of participants	28	Range	0.98
Number of omitted results	2	Variance	0.04
True value	3.25	Standard deviation	0.20
Mean value	3.24	Relative standard deviation	6.2%
Median value	3.25	Relative error	-0.3%

Analytical results in ascending order:

22	2.40	O	11	3.22	6	3.32
21	2.62		8	3.23	29	3.34
16	2.92		17	3.23	24	3.34
10	3.05		30	3.24	28	3.38
9	3.07		5	3.25	7	3.54
15	3.07		18	3.26	2	3.58
26	3.10		20	3.30	19	3.60
12	3.15		27	3.30	14	4.30
4	3.20		23	3.31		
31	3.20		1	3.31		

O = Omitted result

Sample B

Analytical method: All

Unit: mg/L

Number of participants	28	Range	0.69
Number of omitted results	2	Variance	0.03
True value	3.00	Standard deviation	0.16
Mean value	3.01	Relative standard deviation	5.5%
Median value	3.00	Relative error	0.3%

Analytical results in ascending order:

22	2.22	O	18	2.97	29	3.12
21	2.53		8	2.99	28	3.13
16	2.65		27	3.00	9	3.19
15	2.84		4	3.00	2	3.20
10	2.84		11	3.00	19	3.20
12	2.92		20	3.05	7	3.22
17	2.95		6	3.06	5	3.22
30	2.96		1	3.08	14	3.90
26	2.97		23	3.08		
31	2.97		24	3.10		

O = Omitted result

Table 5.9. Statistics. Potassium**Sample A**

Analytical method: All

Unit: mg/L

Number of participants	27	Range	0.30
Number of omitted results	1	Variance	0.00
True value	0.68	Standard deviation	0.06
Mean value	0.68	Relative standard deviation	8.6%
Median value	0.68	Relative error	0.5%

Analytical results in ascending order:

22	0.29	O	8	0.67	10	0.70
21	0.51		18	0.67	31	0.70
28	0.61		15	0.67	1	0.71
27	0.62		20	0.67	30	0.72
14	0.65		12	0.68	7	0.72
23	0.65		29	0.68	17	0.73
26	0.66		2	0.68	5	0.76
9	0.66		24	0.69	4	0.80
11	0.66		6	0.70	16	0.81

O = Omitted result

Sample B

Analytical method: All

Unit: mg/L

Number of participants	27	Range	0.25
Number of omitted results	1	Variance	0.00
True value	0.62	Standard deviation	0.05
Mean value	0.63	Relative standard deviation	8.3%
Median value	0.62	Relative error	0.5%

Analytical results in ascending order:

22	0.28	O	18	0.61	7	0.66
21	0.47		17	0.62	31	0.66
28	0.56		8	0.62	11	0.66
27	0.56		20	0.62	30	0.66
14	0.58		29	0.62	5	0.67
15	0.58		24	0.62	1	0.68
23	0.60		10	0.63	9	0.68
26	0.60		12	0.63	4	0.70
2	0.61		6	0.65	16	0.72

O = Omitted result

Table 5.10. Statistics. Total organic carbon**Sample A**

Analytical method: All

Unit: mg/L

Number of participants	19	Range	1.68
Number of omitted results	0	Variance	0.17
True value	2.90	Standard deviation	0.41
Mean value	2.87	Relative standard deviation	14.4%
Median value	2.90	Relative error	-0.9%

Analytical results in ascending order:

21	1.71	6	2.86	20	3.23
15	2.10	10	2.86	27	3.24
7	2.58	23	2.90	2	3.25
24	2.72	4	2.99	29	3.34
31	2.75	1	3.02	16	3.39
12	2.77	5	3.03		
3	2.80	30	3.04		

O = Omitted result

Sample B

Analytical method: All

Unit: mg/L

Number of participants	19	Range	1.75
Number of omitted results	0	Variance	0.17
True value	2.67	Standard deviation	0.41
Mean value	2.65	Relative standard deviation	15.5%
Median value	2.67	Relative error	-0.7%

Analytical results in ascending order:

21	1.47	10	2.62	29	2.89
15	2.00	4	2.67	20	2.92
24	2.39	6	2.67	2	3.18
7	2.47	23	2.70	16	3.19
31	2.51	1	2.74	27	3.22
12	2.53	5	2.80		
3	2.60	30	2.81		

O = Omitted result

Table 5.11. Statistics. Total P**Sample A**

Analytical method: All

Unit: microg/L

Number of participants	21	Range	25.00
Number of omitted results	0	Variance	33.58
True value	16.00	Standard deviation	5.79
Mean value	16.29	Relative standard deviation	35.6%
Median value	16.00	Relative error	1.8%

Analytical results in ascending order:

26	0.00	15	15.00	22	19.00
24	8.51	30	15.43	20	20.00
2	10.10	7	15.56	5	20.30
10	11.17	27	16.00	16	22.00
11	13.90	29	17.58	4	23.00
1	14.00	3	18.00	18	24.10
12	14.40	6	19.00	23	25.00

O = Omitted result

Sample B

Analytical method: All

Unit: microg/L

Number of participants	21	Range	27.10
Number of omitted results	0	Variance	37.07
True value	15.00	Standard deviation	6.09
Mean value	15.25	Relative standard deviation	39.9%
Median value	15.00	Relative error	1.7%

Analytical results in ascending order:

26	0.00	5	13.50	6	17.00
24	8.18	30	13.71	11	18.70
22	9.00	12	14.40	10	19.43
2	9.70	1	15.00	20	22.00
29	11.85	7	15.15	4	23.00
16	12.50	3	16.00	23	24.00
15	13.00	27	17.00	18	27.10

O = Omitted result

Table 5.12. Statistics. Aluminium**Sample C**

Analytical method: All

Unit: microg/L

Number of participants	20	Range	10
Number of omitted results	2	Variance	5
True value	16	Standard deviation	2
Mean value	16	Relative standard deviation	14.4%
Median value	16	Relative error	-1.2%

Analytical results in ascending order:

18	12	20	16	14	17
31	13	23	16	21	19
5	14	11	16	30	19
10	14	1	17	17	21 O
16	15	8	17	29	22
15	15	9	17	26	23 O
27	16	2	17		

O = Omitted result

Sample D

Analytical method: All

Unit: microg/L

Number of participants	20	Range	9
Number of omitted results	2	Variance	4
True value	15	Standard deviation	2
Mean value	14	Relative standard deviation	14.0%
Median value	15	Relative error	-1.1%

Analytical results in ascending order:

18	10	1	14	21	15
31	11	23	14	27	16
5	12	29	15	30	17
11	14	16	15	10	18
15	14	9	15	26	21 O
20	14	2	15	17	26 O
8	14	14	15		

O = Omitted result

Table 5.13. Statistics. Iron**Sample C**

Analytical method: All

Unit: microg/L

Number of participants	20	Range	22.10
Number of omitted results	0	Variance	31.75
True value	129.15	Standard deviation	5.63
Mean value	130.68	Relative standard deviation	4.3%
Median value	129.15	Relative error	1.2%

Analytical results in ascending order:

16	117.90	1	128.00	8	132.00
26	126.50	18	128.10	29	136.80
27	127.00	31	129.00	21	138.20
9	127.79	11	129.30	15	140.00
17	127.80	30	129.60	14	140.00
2	127.95	10	129.63	20	140.00
23	128.00	5	130.00		

O = Omitted result

Sample D

Analytical method: All

Unit: microg/L

Number of participants	20	Range	15.90
Number of omitted results	0	Variance	18.08
True value	115.20	Standard deviation	4.25
Mean value	115.46	Relative standard deviation	3.7%
Median value	115.20	Relative error	0.2%

Analytical results in ascending order:

16	109.10	31	113.00	30	116.80
14	110.00	10	114.97	9	117.43
23	112.00	1	115.00	8	118.00
17	112.20	29	115.40	5	120.00
18	112.30	26	115.60	20	125.00
2	112.34	27	116.00	15	125.00
11	112.60	21	116.50		

O = Omitted result

Table 5.14. Statistics. Manganese**Sample C**

Analytical method: All

Unit: microg/L

Number of participants	21	Range	4.16
Number of omitted results	0	Variance	1.06
True value	22.00	Standard deviation	1.03
Mean value	22.21	Relative standard deviation	4.6%
Median value	22.00	Relative error	1.0%

Analytical results in ascending order:

9	20.39	23	21.80	11	22.50
14	21.00	8	22.00	17	22.60
31	21.00	16	22.00	20	22.90
10	21.27	27	22.00	26	23.20
21	21.32	2	22.11	30	23.64
6	21.60	29	22.30	15	24.00
1	21.80	18	22.42	19	24.55

O = Omitted result

Sample D

Analytical method: All

Unit: microg/L

Number of participants	21	Range	3.30
Number of omitted results	0	Variance	0.68
True value	20.26	Standard deviation	0.82
Mean value	20.25	Relative standard deviation	4.1%
Median value	20.26	Relative error	0.0%

Analytical results in ascending order:

31	18.70	1	20.00	11	20.60
9	19.01	14	20.00	19	20.66
21	19.14	27	20.00	20	20.80
10	19.23	18	20.26	17	21.10
6	19.90	29	20.30	26	21.10
23	19.90	8	20.50	30	21.51
2	19.98	16	20.60	15	22.00

O = Omitted result

Table 5.15. Statistics. Cadmium**Sample C**

Analytical method: All

Unit: microg/L

Number of participants	24	Range	0.43
Number of omitted results	0	Variance	0.01
True value	1.30	Standard deviation	0.10
Mean value	1.29	Relative standard deviation	7.9%
Median value	1.30	Relative error	-0.6%

Analytical results in ascending order:

13	1.05	11	1.27	2	1.33
25	1.10	29	1.28	10	1.37
30	1.19	18	1.29	27	1.37
9	1.19	15	1.30	1	1.38
19	1.20	14	1.30	16	1.39
21	1.21	5	1.33	31	1.40
26	1.24	6	1.33	20	1.43
8	1.26	23	1.33	17	1.48

O = Omitted result

Sample D

Analytical method: All

Unit: microg/L

Number of participants	24	Range	0.40
Number of omitted results	0	Variance	0.01
True value	1.15	Standard deviation	0.10
Mean value	1.13	Relative standard deviation	9.1%
Median value	1.15	Relative error	-1.6%

Analytical results in ascending order:

25	0.90	15	1.10	14	1.20
13	0.93	8	1.11	1	1.20
19	0.98	18	1.15	11	1.21
21	1.05	2	1.15	27	1.21
9	1.05	5	1.15	16	1.24
26	1.06	6	1.15	20	1.24
30	1.06	23	1.16	17	1.27
29	1.10	10	1.18	31	1.30

O = Omitted result

Table 5.16. Statistics. Lead**Sample C**

Analytical method: All

Unit: microg/L

Number of participants	22	Range	1.07
Number of omitted results	2	Variance	0.05
True value	1.46	Standard deviation	0.22
Mean value	1.41	Relative standard deviation	15.3%
Median value	1.46	Relative error	-3.2%

Analytical results in ascending order:

10	0.73	6	1.45	20	1.52
21	1.19	18	1.46	30	1.53
5	1.20	11	1.46	27	1.69
26	1.30	8	1.47	9	1.80
13	1.30	2	1.48	17	2.01 O
15	1.30	14	1.50	25	2.80 O
1	1.43	23	1.51		
16	1.43	29	1.52		

O = Omitted result

Sample D

Analytical method: All

Unit: microg/L

Number of participants	22	Range	0.43
Number of omitted results	2	Variance	0.01
True value	1.35	Standard deviation	0.10
Mean value	1.30	Relative standard deviation	7.8%
Median value	1.35	Relative error	-3.6%

Analytical results in ascending order:

26	1.02	6	1.33	23	1.36
21	1.14	11	1.34	30	1.39
13	1.20	16	1.35	20	1.39
15	1.20	29	1.35	27	1.45
5	1.20	8	1.35	17	1.78 O
18	1.28	10	1.35	25	6.30 O
14	1.30	2	1.35		
1	1.32	9	1.36		

O = Omitted result

Table 5.17. Statistics. Copper**Sample C**

Analytical method: All

Unit: microg/L

Number of participants	24	Range	14.80
Number of omitted results	0	Variance	6.77
True value	17.90	Standard deviation	2.60
Mean value	17.50	Relative standard deviation	14.9%
Median value	17.90	Relative error	-2.2%

Analytical results in ascending order:

25	9.80	13	17.40	30	18.27
19	12.22	29	17.50	18	18.31
26	15.60	8	17.60	10	18.43
9	15.99	5	17.90	17	18.50
11	17.00	23	17.90	20	18.90
27	17.00	16	17.90	15	19.00
1	17.40	2	17.98	21	19.37
6	17.40	14	18.00	31	24.60

O = Omitted result

Sample D

Analytical method: All

Unit: microg/L

Number of participants	24	Range	11.45
Number of omitted results	0	Variance	4.62
True value	16.60	Standard deviation	2.15
Mean value	16.35	Relative standard deviation	13.2%
Median value	16.60	Relative error	-1.5%

Analytical results in ascending order:

19	11.15	10	16.16	23	16.90
25	11.20	1	16.50	2	16.93
9	14.89	17	16.60	14	17.00
26	14.97	5	16.60	16	17.20
13	15.70	6	16.60	18	17.31
11	16.00	29	16.60	20	17.60
27	16.00	30	16.69	21	18.35
15	16.00	8	16.80	31	22.60

O = Omitted result

Table 5.18. Statistics. Nickel**Sample C**

Analytical method: All

Unit: microg/L

Number of participants	22	Range	3.34
Number of omitted results	0	Variance	0.57
True value	6.24	Standard deviation	0.75
Mean value	6.38	Relative standard deviation	11.8%
Median value	6.24	Relative error	2.3%

Analytical results in ascending order:

26	5.22	1	6.21	27	6.40
21	5.64	8	6.22	18	6.45
10	5.99	30	6.22	20	6.45
5	6.00	23	6.25	9	6.45
11	6.07	17	6.28	31	8.50
29	6.07	6	6.30	19	8.56
15	6.10	2	6.35		
16	6.17	14	6.40		

O = Omitted result

Sample D

Analytical method: All

Unit: microg/L

Number of participants	22	Range	1.61
Number of omitted results	0	Variance	0.15
True value	5.48	Standard deviation	0.39
Mean value	5.54	Relative standard deviation	7.0%
Median value	5.48	Relative error	1.2%

Analytical results in ascending order:

26	4.99	15	5.40	8	5.61
21	5.09	16	5.42	19	5.64
5	5.20	6	5.46	9	5.68
14	5.30	23	5.49	10	5.69
11	5.37	2	5.49	31	6.60
1	5.38	20	5.50	17	6.60
29	5.39	18	5.58		
27	5.40	30	5.58		

O = Omitted result

Table 5.19. Statistics. Zn**Sample C**

Analytical method: All

Unit: microg/L

Number of participants	21	Range	3.30
Number of omitted results	0	Variance	0.75
True value	12.30	Standard deviation	0.86
Mean value	12.37	Relative standard deviation	7.0%
Median value	12.30	Relative error	0.6%

Analytical results in ascending order:

6	11.10	27	12.00	17	12.90
5	11.20	1	12.00	29	13.00
26	11.20	11	12.00	14	13.00
10	11.28	23	12.30	16	13.10
8	11.90	21	12.31	2	13.16
31	11.98	18	12.56	9	13.79
15	12.00	30	12.63	20	14.40

O = Omitted result

Sample D

Analytical method: All

Unit: microg/L

Number of participants	21	Range	3.77
Number of omitted results	0	Variance	0.96
True value	13.40	Standard deviation	0.98
Mean value	13.59	Relative standard deviation	7.2%
Median value	13.40	Relative error	1.4%

Analytical results in ascending order:

10	12.03	15	13.00	21	13.93
26	12.20	11	13.30	17	14.10
5	12.60	31	13.30	18	14.39
6	12.80	1	13.40	2	14.44
30	12.84	8	13.60	9	14.94
14	13.00	29	13.70	16	15.30
27	13.00	23	13.80	20	15.80

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/>

- Velle, G., Johannessen, A. and Landås, T.S. 2018. Biological intercalibration: Invertebrates 2018. NIVA 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 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.**
- Escudero-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. 2014. 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 Hruška, 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.**
- Escudero-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., Indrikson 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 113/2013.**
- 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, HCO₃, NO₃-N, Cl, SO₄, 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, HCO₃, NO₃-N, Cl, SO₄, 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, HCO₃, NO₃-N, Cl, SO₄, 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, 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 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 Wright, 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, 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 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. 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 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 SNO4384-2001. **ICP Waters report 62/2001.**
- Raddum, G.G. and Skjelkvåle 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, K₂₅, NO₃ + NO₂, Cl, SO₄, 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, 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 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.



Norwegian Institute for Water Research

Gaustadalléen 21 • NO-0349 Oslo, Norway
Telephone: +47 22 18 51 00 • Fax: 22 18 52 00
www.niva.no • post@niva.no