NIVA REPORT 7918-2023

Norsk institutt for vannforskning

ICP Waters Report 154/2023

Intercomparison 2337: pH, Conductivity, Alkalinity, NO_3-N, Cl, SO_4, Ca, Mg, Na, K, TOC, Tot-P, Tot-N, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn.

Foto: Anne Luise Ribeiro

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

Convention on Long-Range Transboundary Air Pollution

UNECE

Convention on Long-range Transboundary Air Pollution

Report

Serial no: 7918-2023

ICP Waters Report 154/2023

ISBN 978-82-577-7654-1
NIVA report
ISSN 1894-7948

This report has been quality assured according to NIVA's quality system and has been approved by:

Tina Bryntesen
Main Author

Cathrine Brecke Gundersen
Quality Assurer

Hans Fredrik V Braaten
Research Manager

www.niva.no

Norwegian Institute for Water Research

Title
Intercomparison 2337: pH, Conductivity, Alkalinity, NO_3-N, Cl, SO_4, Ca, Mg, Na, K, TOC, Tot-P, Tot-N, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn.

Pages
34 + appendix

Date
15.12.2023

Author(s)
Tina Bryntesen

Topic group
Monitoring

Distribution
Open

Client(s)
Norwegian Ministry of Climate and Environment
United Nations Economic Commission for Europe (UNECE)

Client's contact person
Eli Marie Åsen

Published by NIVA
10300

Abstract
Twenty laboratories from fifteen countries accepted the invitation to join the ICP Waters chemical intercomparison. Two sets of samples were prepared and distributed to the participants: one for the determination of ions and one for metals. This year, acceptance rates were based on the Z'-scores obtained by the participants. In general, acceptance rates were high for all parameters. General trends in the choice of techniques continue to shift towards plasma from atomic absorption, and to mass detection from ionic emission. This is especially promising for the determination of metals at low levels.

Keywords: Intercomparison, Acid precipitation, Quality control, ICP Waters
Emneord: Laboratoriesammenligning, Sur nedbør, Kvalitetskontroll, ICP Waters

CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

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

Intercomparison 2337
pH, Conductivity, Alkalinity, NO_3-N, Cl, SO_4, Ca, Mg, Na, K, TOC, Total-P, Total-N, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn

Prepared at the ICP Waters Programme Centre
Norwegian Institute for Water Research
Oslo, December 2023

Table of contents

Preface

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

ICP Waters and its Programme Centre is chaired and hosted by the Norwegian Institute for Water Research (NIVA). A programme subcentre has been established at NORCE, Bergen. ICP Waters is supported financially by the Norwegian Ministry of Climate and Environment and the Trust Fund of the UNECE LRTAP Convention.

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

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

Here we report the results from the 37th intercomparison of chemical analyses.

Oslo, 15th of December, 2023

Tina Bryntesen

ICP Waters Programme Centre

Summary

The chemical interlaboratory comparison is an important tool for the ICP Waters to ensure consistency and comparability of the surface water monitoring results among the programme participants. The test is conducted yearly and is based on the "round robin" principle. In short, bottles containing aliquots of the same water sample is distributed to all the participating laboratories which analyse the sample for a set repertoire of parameters with their method of choice. Then, the results are compiled and analysed, using statistical methods. A consensus value (assigned value) is calculated for each sample, using the reported results from the participants. Two different sets of samples are prepared and distributed, one for the determination of ions and another for metals.

The 2337 edition of the test was conducted in the period from June to October 2023. A total of 20 laboratories representing 15 different countries signed up. The participants were invited to determine pH, conductivity, alkalinity, nitrate-nitrogen, chloride, sulphate, calcium, magnesium, sodium, potassium, total organic carbon, total phosphorus, total nitrogen, aluminium, iron, manganese, cadmium, lead, copper, nickel, and zinc. Unfortunately, the nitrate was found to be unstable, and the results could not be used.

This year, the method for assigning the acceptance criteria has been updated along with the implementation of a new statistical software. Together with the consensus value, a standard deviation for proficiency assessment (SDPA) is calculated which is subsequently used to compute Z'-scores. Participants reporting values with a Z' score < ±2 are said to have acceptable results. Further, the variability in the reported results is assessed using the Youden charts and the SDPA values. The difference in assessment means that acceptance rates from this year cannot be directly related to previous years.

The highest acceptances were obtained for total organic carbon (100%), sulphate (97%), and copper (96%). Other parameters with acceptance rates above 90% were alkalinity, magnesium, potassium, total phosphorous, total nitrogen, aluminium, manganese, lead, and nickel. The poorest acceptance rate was obtained for zinc, with 76% acceptable results. It should be noted that total phosphorous and total nitrogen had relatively high SDPA's, which results in a wider range of acceptable results.

The use of different techniques and/or methods can challenge the unity of the results, as both detection principle and sample preparations or method specific details can influence the final result. This effect is typically more severe for low analyte concentrations. For several of the parameters, different techniques and/or methods were reported. For total phosphorous, as many as seven different methods were reported to have been used.

Some overall patterns in the preferred technique could be found. Ion chromatography was preferred for the determination of anions, and ion chromatography or some form of plasma technique (ICP-OES/ICP-MS) were most frequently employed for the cations. For all the metals, the sensitive ICP-MS was the preferred technique of choice. This confirms the trends observed in the last years, that plasma techniques are taking over for the more traditional atomic absorption techniques, and that the much more sensitive mass detector is replacing the optical emission spectroscopy detector.

Sammendrag

Den kjemiske interlaboratoriske sammenlikningen er et viktig verktøy for ICP Waters, for å sikre konsistens og sammenlignbarhet av resultatene fra overvåkning av overflatevann hos de ulike programdeltakerne. Testen utføres årlig, og er basert på ringtest-prinsippet. Dette foregår ved at flasker som inneholder delprøver fra den samme vannprøven blir distribuert til alle deltakende laboratorier. Deltakerne analyserer så prøven for gitte parametere, med de metodene de ønsker. Deretter blir resultatene sammenstilt og analysert, ved hjelp av statistiske metoder. En konsensverdi («sann verdi») beregnes for hver prøve, ved å bruke deltakernes rapporterte verdier. To ulike prøvesett prepareres og distribueres, ett for bestemmelse av ioner, og et for bestemmelse av metaller.

Denne 2337-utgaven av testen ble utført i perioden juni til oktober 2023. Totalt 20 laboratorier deltok, og disse representerte 15 ulike land. Deltakerne ble invitert til å bestemme pH, konduktivitet, alkalinitet, nitrat-nitrogen, klorid, sulfat, kalsium, magnesium, natrium, kalium, totalt organisk karbon, totalfosfor, totalnitrogen, aluminium, jern, mangan, kadmium, bly, kobber, nikkel og sink. Dessverre viste nitrat seg å være ustabil og resultatene kunne derfor ikke benyttes.

I denne runden ble metoden for å fastsette akseptkriteriene oppdatert samtidig som en ny programvare for statistikkbehandling ble tatt i bruk. Sammen med konsensverdi, ble det fra deltakernes resultater utregnet «standard deviation for proficiency assessment» (SDPA) som igjen ble benyttet til å beregne Z'-score. Resultater med Z'-score < ±2 ble akseptert. Variasjonen i resultatene beskrives ved Youdendiagrammer og SDPA verdier. Endringen av evalueringen betyr at antallet akseptable verdier fra i år ikke kan sammenliknes direkte med tidligere års andel av akseptable resultater.

Parameterne med høyest andel akseptable resultater var totalt organisk karbon (100 %), sulfat (97 %) og kobber (96 %). Andre parametere som hadde andel akseptable resultater over 90 % var alkalinitet, magnesium, kalium, totalfosfor, totalnitrogen, aluminium, mangan, bly og nikkel. Dårligst andel akseptable resultater hadde sink, med 76 %. Det bør nevnes at totalfosfor og totalnitrogen hadde begge relativt høy SDPA, noe som betyr at resultater med relativt høyt avvik fra konsensverdien fortsatt blir angitt som akseptable.

Bruken av ulike teknikker og/eller analysemetoder kan utfordre konsensusen i resultatene, siden både deteksjonsprinsipp og prøvepreparering eller metodespesifikke detaljer kan påvirke det endelige resultatet. Effekten er typisk større for analytter med lav konsentrasjon. For mange av parameterne ble det benyttet flere ulike teknikker og/eller metoder. For totalfosfor hadde hele syv ulike metoder blitt benyttet for analysen.

Det er mulig å se noen mønstre i de foretrukne teknikkene. Ionekromatografi var foretrukket for å bestemme anioner, og ionekromatografi eller en form for plasmateknikk (ICP-OES/ICP-MS) ble oftest brukt for kationer. For alle metaller er den følsomme ICP-MS den mest foretrukne teknikken. Dette bekrefter trenden som har blitt observert de siste årene, der plasmateknikker tar over for de mer tradisjonelle atomabsorpsjon-teknikkene. I tillegg erstatter den mer følsomme massedetektoren (ICP-MS) oftere og oftere den optiske emisjons spektroskopi-detektoren (ICP-OES).

1. Introduction

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

To ensure that the results across the entire ICP Waters are consistent and comparable, inter-laboratory quality controls are necessary, as stated in the "ICP Waters Programme Manual" (1). In a multi laboratory programme, typical causes of inconsistency include the use of different types of analytical techniques, errors in the calibration procedure, etc. The between-laboratory control carried out by the Programme Centre of ICP Waters is based on the "round robin" concept meaning that the same sample is analysed by the different participating laboratories using their analytical principle and method of choice. The levels of the variables should be set to be as close to the expected natural levels as possible, and that the range from year-to-year shall cover the variation among countries of the participating laboratories.

The method for assigning the acceptance criteria have been changed in 2023 and is now based on the Z'-score. The variability of the results is evaluated by the standard deviation for proficiency assessment (SDPA). The analytical results are moreover analysed using the Youden test statistics (2, 3) that assesses the consistency of the results between the laboratories and can indicate whether the results are affected by a systematic effect (e.g., different analytical techniques give slightly different results) or only by random errors (typically most pronounced at levels close to the method limit of quantification). Several factors can contribute to the acceptance ratio and the obtained score, and these should be considered when participants evaluate their results. For example, different methods used by different laboratories may give systematically different results (higher or lower). Based on the method used by most of the participating laboratories, the assigned value may be biased. Such a systematic effect will be evident in the distribution of the results in the Youden chart, by the points residing along the 45° angled line. One other cause of poor acceptance ratio is when the concentration in the sample is low, and close to the limit of quantification of the method used. This will most often appear in the Youden chart as a distribution of the results perpendicular to the 45° angled line. The Youden test is briefly described in Appendix C.

This thirty-seventh chemical intercomparison test, called 2337, covered the determination of the following constituents of natural surface waters: pH, conductivity, alkalinity, nitrate-nitrogen, chloride, sulphate, calcium, magnesium, sodium, potassium, total organic carbon, total phosphorus, total nitrogen, aluminium, iron, manganese, cadmium, lead, copper, nickel, and zinc. While most of these variables have been part of the test since it started some have been included later. Total organic carbon and aluminium were included in 2009, total phosphorus in 2017, and total nitrogen in 2022.

2. Procedures of the intercomparison

Two different sets of samples were prepared by the Programme Centre and distributed to the participating laboratories: one pair for the determination of major ions (A + B) and one pair for the determination of metals (C + D) (as agreed upon at the Task Force meeting in Burlington, Canada, 2009). The procedure for the preparation of the two sample sets is presented in Appendix B. The samples were shipped from the Programme Centre on the 26th of June 2023. Most shipments arrived in due time, but some experienced delays. Participants were encouraged to conduct the analyses as soon as possible after reception.

The analytical results were treated by the Youden method (2, 3) to evaluate the comparability of the analytical results produced by the laboratories participating, and to assess potential systematic and/or random error in the distribution of the results. For each variable, the assigned value was set as a consensus value from the participants' reported results. This way of assigning the value is considered acceptable if the participants mainly use the same analytical techniques. However, this is not always the case, and for parameters such as pH and alkalinity different techniques/methods are frequently used which leads to strong systematic bias in the results. Since not one method can be argued to be better than another, this issue has persisted in the interlaboratory harmonisation.

For the 2337 edition of the chemical intercomparison test, a new statistical software was used. The reason for this was that the previously used MS Access based self-developed database was too old and outdated. The switch of statistical software also means a change towards using Z'-scores for evaluating the results. A Z'-score lower than ±2 is marked as acceptable, which is the same criteria used in most commercial intercomparison tests. For the Youden charts, the circle is set to 2xSDPA, which corresponds closely with a Z-score of ±2. This way of setting the acceptance criteria is opposed to previous years, where only the deviation from the assigned value was considered. If the assigned value is set from a low number of reported results or if the reported results are spread over a wider area, the uncertainty of the assigned value is higher. The previous way of only using relative deviation did not take this into account. Now, the circle in the Youden charts will become wider in response to e.g., a large spread in the reported results. As an example, the 2xSDPA circle for total phosphorous is set approximately 70% from the assigned values due to the high variability of the reported results. Also new this year is that the results from each sample in the sample sets is evaluated individually and each assigned a Z'-score.

Individual results, including Z'-scores and the relative deviation (%D) from the assigned values can be found in Table 7 to Table 27, and in the Appendix part D.3. In the Manual for Chemical and Biological Monitoring (1), a list of suggested target accuracies can be found, and participants are invited to use those criteria in addition to the Z'-scores when assessing their own results. This is especially helpful if the SDPA of a parameter is very low, in which case it is possible to get a not acceptable Z'-score even if the relative deviation is quite low.

3. Results and Discussion

In the 2337 edition of the chemical intercomparison test, a total of 20 laboratories (representing 15 different countries) registered to participate. Information about the participating laboratories is provided in Appendix A, both by the identity of the laboratories (Table 4) and by a summary of the different countries represented (Table 5).

In Table 1, the statistical parameters of the 2337 chemical intercomparison test is summarized, constituting for each parameter: the assigned value, the standard uncertainty of the assigned value, and the absolute and relative SDPA. In addition, the number of values reported is listed. Table 2 summarizes the performance of the participants, listing the percentage of satisfactory results for each parameter (Z'-score < ±2). If the Z'-score is outside ±2, it is deemed to be questionable, and a score outside of ±3 is said to be actionable. Lastly, Table 3 summarizes the results from previous years, where fixed acceptance ratios of sample pairs were used.

Throughout this chapter the results for each variable will be presented and discussed based on accuracy and variability, and on the presence of systematic and/or random errors. This is done using the Z'-scores (Figure 21 to Figure 40 in Appendix D) and the relative deviation from the assigned value (D% in Table 7 to Table 27 in Appendix D); the relative SDPA; and the visual distribution of the results in the Youden chart (Figure 1 to Figure 20), respectively. In the Youden chart, each laboratory is presented by one point, and the distribution of points can indicate the occurrence of random and/or systematic errors among the results from the laboratories. The circle in the Youden chart is set to 2xSDPA. A visual distribution of the results with information on the analytical techniques used for analysis can be found in Figure 41 to Figure 80. Factors that are typically found to influence the compliance among the results are low parameter values and the use of several different analytical methods for the determination of the same parameter. Both factors will lead to increased variability in the results.

For more detailed information on the uncertainty of the assigned values see Table 6 (Appendix C). The calculation has been performed according to ISO 13528 (2022), "Statistical methods for use in proficiency testing by interlaboratory comparisons" (5). The individual results reported by the laboratories, together with more detailed statistics for each parameter, are listed in Table 7 to Table 27 (Appendix D).

Table 1. Summary table of the statistical parameters of the intercomparison test.

Sample	Measurand description	Assigned value	Unit	SDPA	rel. SDPA	# values
A	pH	6.44	PH-units	0.17	2.6 %	18
B	pH	6.50	PH-units	0.13	2.0 %	18
A	Conductivity	2.14	mS/m	0.13	6.2 %	18
B	Conductivity	2.02	mS/m	0.11	5.3 %	18
A	Alkalinity	0.0955	mmol/L	0.010	11 %	14
B	Alkalinity	0.0969	mmol/L	0.023	23 %	14
A	Cl - Chloride	1.35	mg/L	0.070	4.9 %	17
B	Cl - Chloride	1.23	mg/L	0.070	6.1 %	17
A	SO4 - Sulphate	1.70	mg/L	0.11	6.3 %	16
B	SO4 - Sulphate	1.62	mg/L	0.11	6.7 %	16
A	Ca - Calcium	2.21	mg/L	0.19	8.6 %	19
B	Ca - Calcium	2.10	mg/L	0.19	9.2 %	19
A	Mg - Magnesium	0.349	mg/L	0.021	6.0 %	19
B	Mg - Magnesium	0.324	mg/L	0.022	6.6 %	19
A	Na - Sodium	1.06	mg/L	0.030	3.0 %	19
B	Na - Sodium	0.977	mg/L	0.042	4.3 %	19
A	K - Potassium	0.424	mg/L	0.025	5.9 %	19
B	K - Potassium	0.405	mg/L	0.027	6.6 %	19
A	TOC - Total organic carbon	4.43	mg/L	0.52	12 %	14
B	TOC - Total organic carbon	4.13	mg/L	0.41	9.9 %	14
A	TOT-P - Total phosphorus	16.2	µg/L P	5.2	32 %	16
B	TOT-P - Total phosphorus	14.8	µg/L P	5.4	36 %	16
A	TOT-N - Total nitrogen	204	µg/L N	47	23 %	11
B	TOT-N - Total nitrogen	192	µg/L N	47	25 %	11
C	Al - Aluminium	68.8	µg/L	6.6	9.5 %	12
D	Al - Aluminium	66.5	µg/L	8.3	13 %	12
C	Fe - Iron	21.8	µg/L	1.1	5.2 %	14
D	Fe - Iron	20.1	µg/L	1.3	6.3 %	14
C	Mn - Manganese	1.23	µg/L	0.11	9.3 %	12
D	Mn - Manganese	1.14	µg/L	0.10	9.1 %	12
C	Cd - Cadmium	1.97	µg/L	0.11	5.3 %	13
D	Cd - Cadmium	1.90	µg/L	0.12	6.5 %	13
C	Pb - Lead	2.07	µg/L	0.10	4.6 %	12
D	Pb - Lead	2.03	µg/L	0.08	3.8 %	12
C	Cu - Copper	2.38	µg/L	0.23	9.6 %	12
D	Cu - Copper	2.34	µg/L	0.32	14 %	11
C	Ni - Nickel	3.09	µg/L	0.14	4.5 %	11
D	Ni - Nickel	2.96	µg/L	0.12	4.0 %	11
C	Zn - Zinc	4.96	µg/L	0.52	10 %	13
D	Zn - Zinc	5.25	µg/L	0.52	9.8 %	12

Table 2. Overview of the performance of participants, using Z' scores for evaluation.

Parameter (unit)	Total	Satisfactory |Z'| < 2	Questionable 3 > |Z'| > 2	Unsatisfactory |Z'| > 3	% satisfactory
pH	36	32	2	2	89
Conductivity (mS/m)	36	31	0	5	86
Alkalinity (mmol/L)	28	26	0	2	93
Cl - Chloride (mg/L)	34	30	1	3	88
SO4 - Sulphate (mg/L)	32	31	1	0	97
Ca - Calcium (mg/L)	38	34	2	2	89
Mg - Magnesium (mg/L)	38	36	0	2	95
Na - Sodium (mg/L)	38	33	1	4	87
K - Potassium (mg/L)	38	36	2	0	95
TOC - Total organic carbon (mg/L)	28	28	0	0	100
TOT-P - Total phosphorus (µg P/L)	32	30	1	1	94
TOT-N - Total nitrogen (µg N/L)	22	21	1	0	95
Al - Aluminium (µg/L)	24	22	0	2	92
Fe - Iron (µg/L)	28	25	0	3	89
Mn - Manganese (µg/L)	24	22	0	2	92
Cd - Cadmium (µg/L)	26	23	1	2	88
Pb - Lead (µg/L)	24	22	2	0	92
Cu - Copper (µg/L)	23	22	0	1	96
Ni - Nickel (µg/L)	22	21	1	0	95
Zn - Zinc (µg/L)	25	19	0	6	76
Total	**596**	**544**	**15**	**37**	**91**

Table 3. Performance information of previous years' results, using fixed acceptable limits.

Parameter (unit)	Sample-pair	Acceptable limit, %	Acceptable results for intercalibration (%) 2236	2135	2034	1933
pH	AB	0.2 pH	50	65	75	60
Conductivity (mS/m)	AB	10	57	64	80	79
Alkalinity (mmol/L)	AB	20	57	42	44	62
Nitrate + nitrite-nitrogen (µg N/L)	AB	20	-	50	47	69
Chloride (mg/L)	AB	20	90	83	90	93
Sulphate (mg/L)	AB	20	76	91	76	75
Calcium (mg/L)	AB	20	79	69	89	90
Magnesium (mg/L)	AB	20	89	71	95	93
Sodium (mg/L)	AB	20	85	89	100	96
Potassium (mg/L)	AB	20	81	74	95	85
Total organic carbon (mg/L)	AB	20	81	71	73	80
Total phosphorous (µg P/L)	AB	20	33	29	41	35
Total nitrogen (µg N/L)	AB	20	33	-	-	-
Aluminium (µg/L)	CD	20	100	67	80	55
Iron (µg/L)	CD	20	100	56	94	76
Manganese (µg/L)	CD	20	81	65	93	71
Cadmium (µg/L)	CD	20	88	56	94	77
Lead (µg/L)	CD	20	82	24	88	73
Copper (µg/L)	CD	20	87	70	94	75
Nickel (µg/L)	CD	20	76	72	94	77
Zinc (µg/L)	CD	20	84	72	80	61
Total			**77**	**(65)**	**(81)**	**(75)**

3.1 pH

Values of pH were reported by 18 laboratories, among which 16 had results which were marked as satisfactory (|Z'| < 2). Of the satisfactory results, all were within Δ0.3 pH units from the assigned value. Electrometric determination was used by all participants. EN-ISO 10523 was reported to have been followed by 7 of the participants. The rest did not refer to a standard method. However, 8 reported to have stirred the samples, 2 reported to have not stirred the samples, and the last participant used equilibration.

The Youden chart showed that random errors are quite prominent in the data set for pH (Figure 1). It is important to remember that pH is a very sensitive parameter to determine, and that sample storage and handling, as well as the use of different analytical methods can affect the results (4). This parameter should be determined as soon as possible after the samples have arrived at the laboratory.

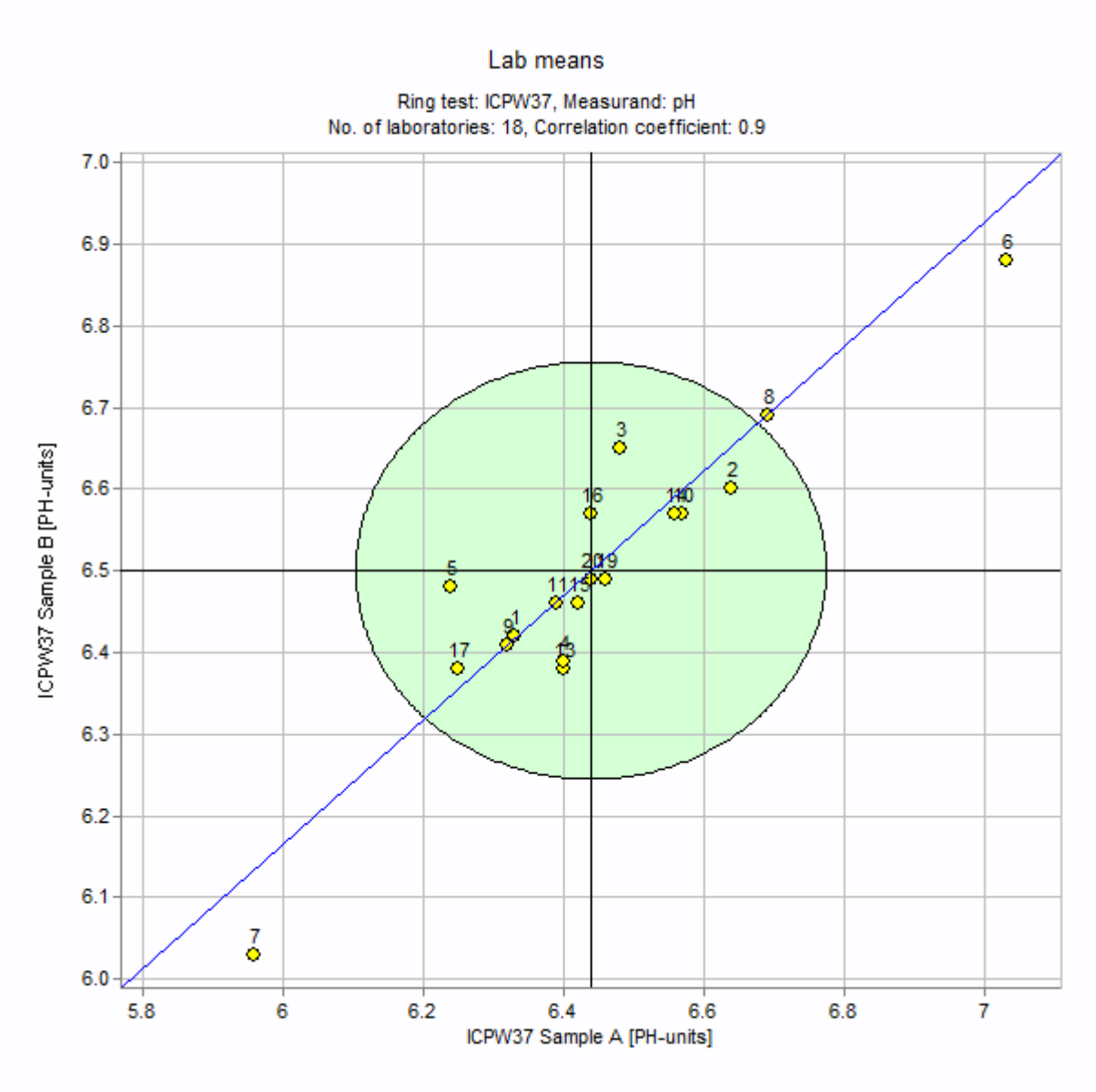

Figure 1. Youden diagram for pH. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.2 Conductivity

In this 2337 edition, conductivity was measured by 18 laboratories. Both sample A and B had 15 results marked as satisfactory (|Z'| < 2). Two of the participants have likely reported their results with the incorrect units so the results are far outside the accepted values. Most of the reported results had relatively high conformity, with the SDPA being at 6% and 5% for sample A and sample B, respectively. The satisfactory results were all within ±10% of the assigned value.

All the 18 participants reported to have used electrometry for the determination of conductivity, and of these, 5 reported to have followed ISO 7888. The Youden chart (Figure 2) shows that systematic errors dominate the distribution of the results. Conductivity is highly temperature dependent, and improper temperature correction may lead to deviating results. Conductivity will vary by 2% for each degree at the temperatures around room temperature.

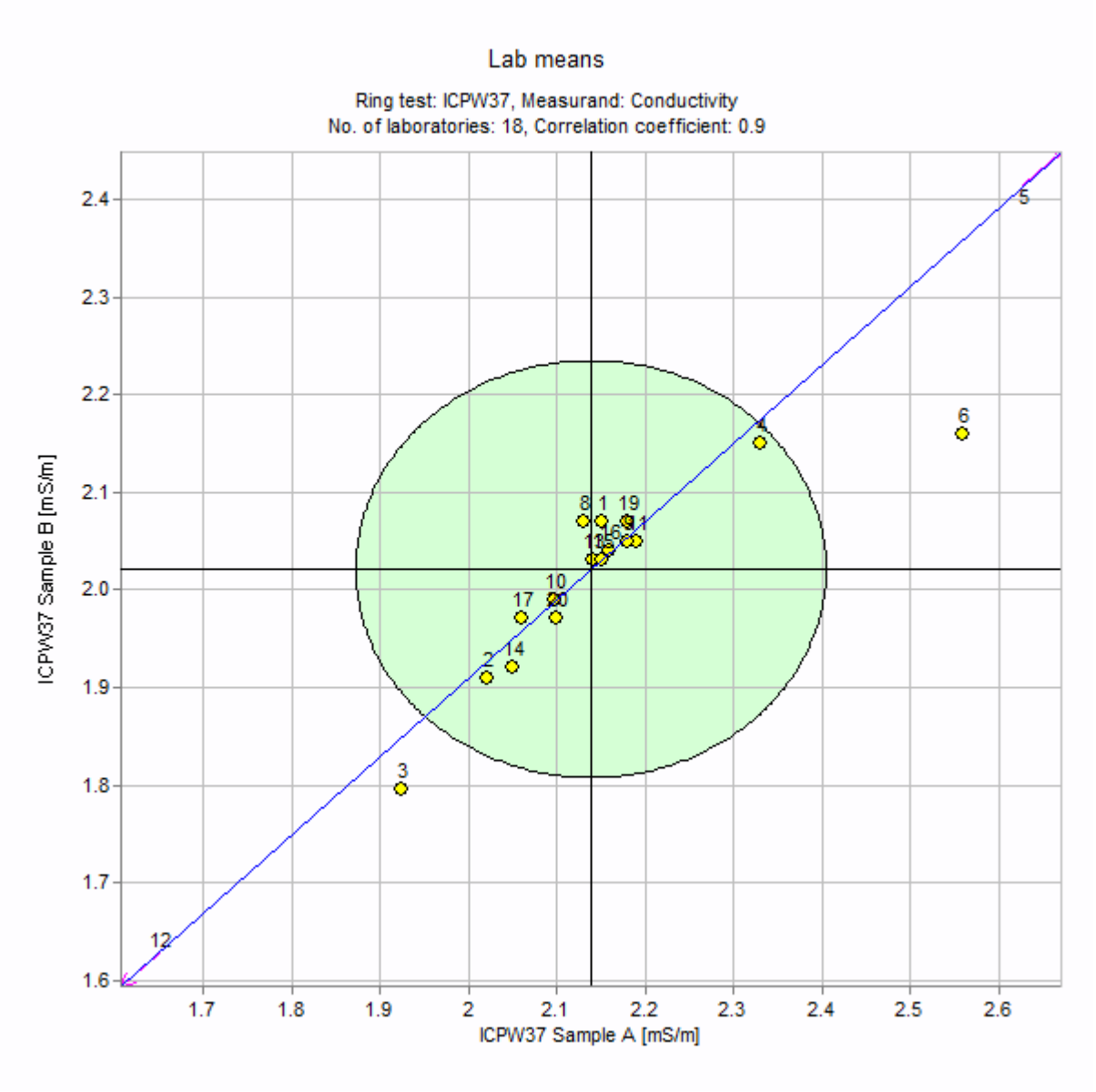

Figure 2. Youden diagram for conductivity. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.3 Alkalinity

Alkalinity was reported by 14 of the laboratories. The number of satisfactory results (|Z'| < 2) were 12 for sample A, while all results of sample B were deemed satisfactory. The SDPA of sample A was at 11% while sample B had an SDPA of 23%. The high SDPA of sample B means that results further away from the assigned value will be assessed as satisfactory. Titration to endpoint pH 4.5 was used by 7 of the laboratories, while 3 laboratories titrated to pH 4.5+4.2. Of the rest, 2 reported to have titrated to another endpoint, and the final 2 reported to have used an unspecified method. The Youden chart (Figure 3) shows that random errors dominate the data set. Note that results that fall outside the chart area, are marked with an arrow.

The alkalinity value may vary significantly with the end-point pH used for the titration. In waters containing high concentrations of total inorganic carbon, the equivalence point is close to pH = 4.5. In such a case, the relative error introduced by assuming affixed end-point pH of 4.5, is negligible. However, at lower alkalinities normally encountered in areas sensitive to acidification, the "total fixed end-point method" may overestimate the true alkalinity or the "equivalence" alkalinity.

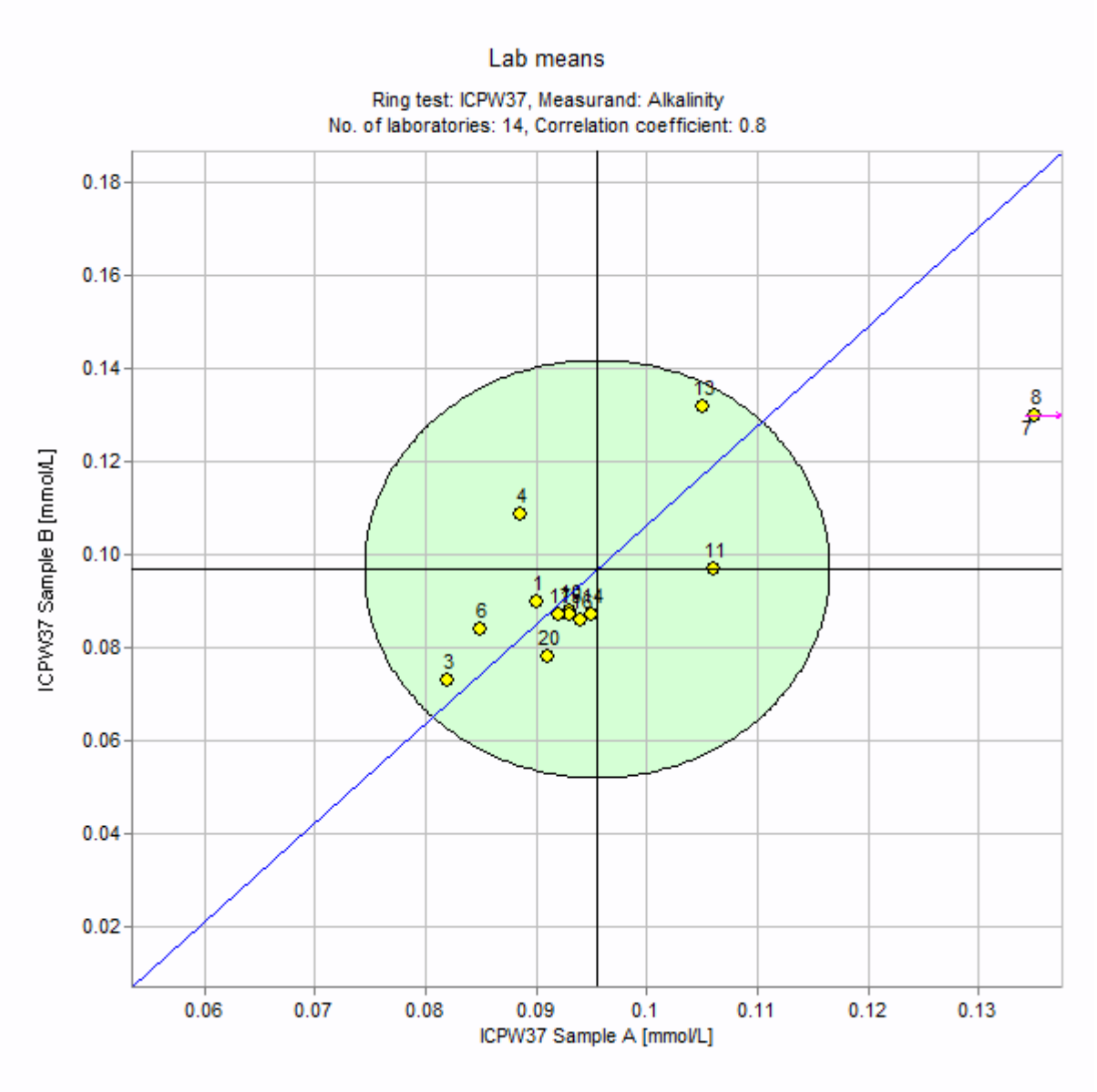

Figure 3. Youden diagram for alkalinity. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.4 Nitrate-nitrogen

Similar to the 2022 edition of the chemical intercomparison test, the samples were not stable for nitrate. Results for nitrate were reported by 18 of the laboratories, but most reported blank results or results under their LOQ. The quantitative results which were reported were spread over an area ranging from near zero to 30-40 µg N/L, while NIVAs initial analysis of the water after filtering was around 110 µg N/L. It seems clear that the nitrate was consumed or converted to other species during storage and handling.

Participants' results, and the calculated statistical parameters of nitrate-nitrogen can be found in Table 10.

3.5 Chloride

Chloride was reported by 18 laboratories. One participant reported that the results were below their LOQ and their results were excluded from the assessment. Sample A and B had 16 and 14 satisfactory results (|Z'| < 2), respectively. The conformity of the results was quite good, with the SDPA being 5% and 6% for sample A and B, respectively. The satisfactory results all had a deviation of less than ±10% from the assigned value.

The most used technique was ion chromatography, which was used by 15 participants. The final 3 used photometry for the determination. The distribution of the results in the Youden diagram (Figure 4) shows both random and systematic errors are present in the dataset.

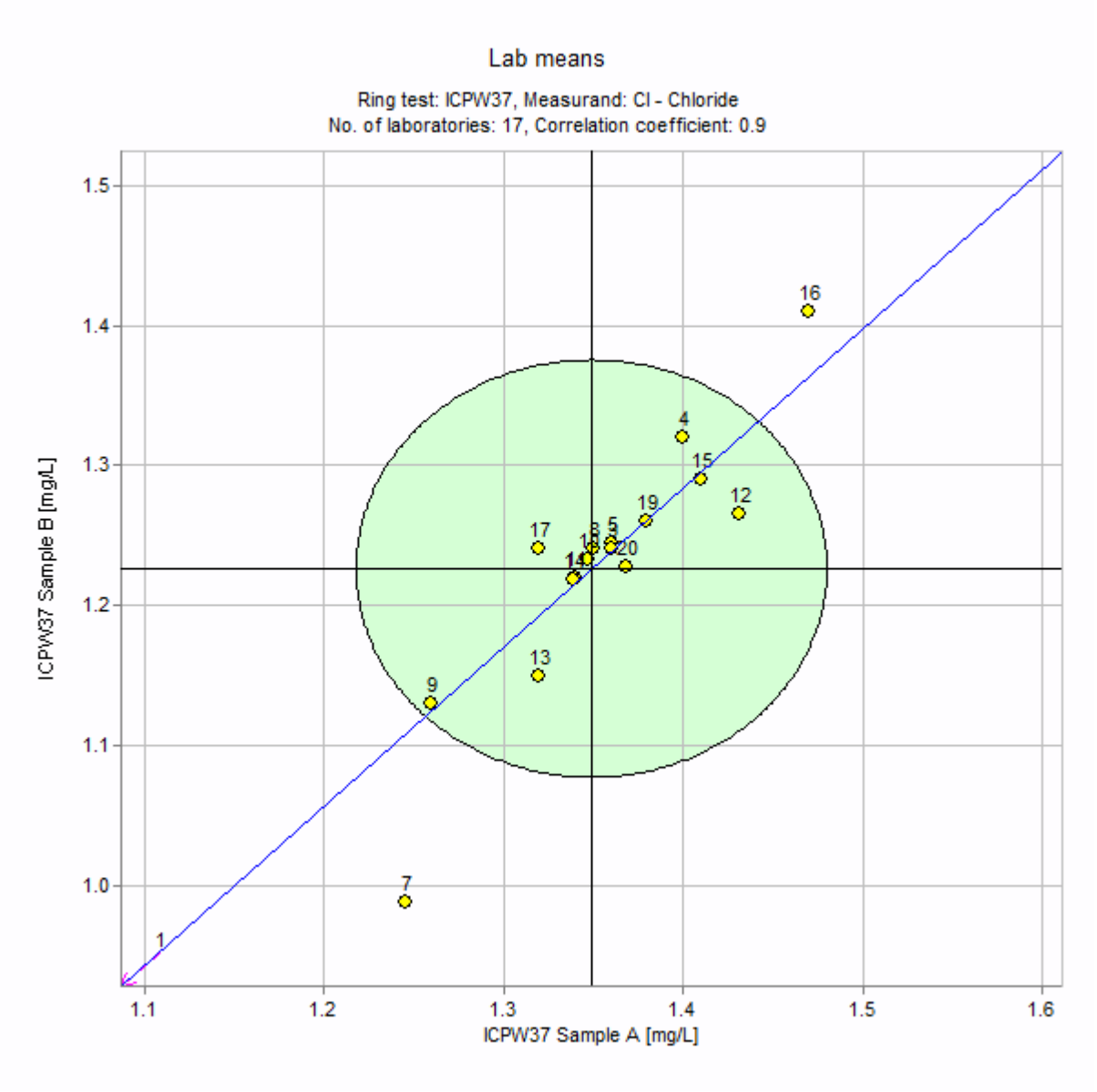

Figure 4. Youden diagram for chloride (Cl). Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.6 Sulphate

Sulphate was reported by 16 laboratories, and all except for one had used ion chromatography for the determination. The final participant used ICP-AES. All except one result were deemed satisfactory (|Z'| < 2). The highest deviation from the assigned value is reported by the participant using ICP-AES which indicates that there may be a method bias. There was a general high conformity of the reported results, with the SDPA being around 6-7% for both samples. For the results analysed by ion chromatography, all were within ±10% of the assigned value. The Youden chart in Figure 5 shows that most errors are small and systematic.

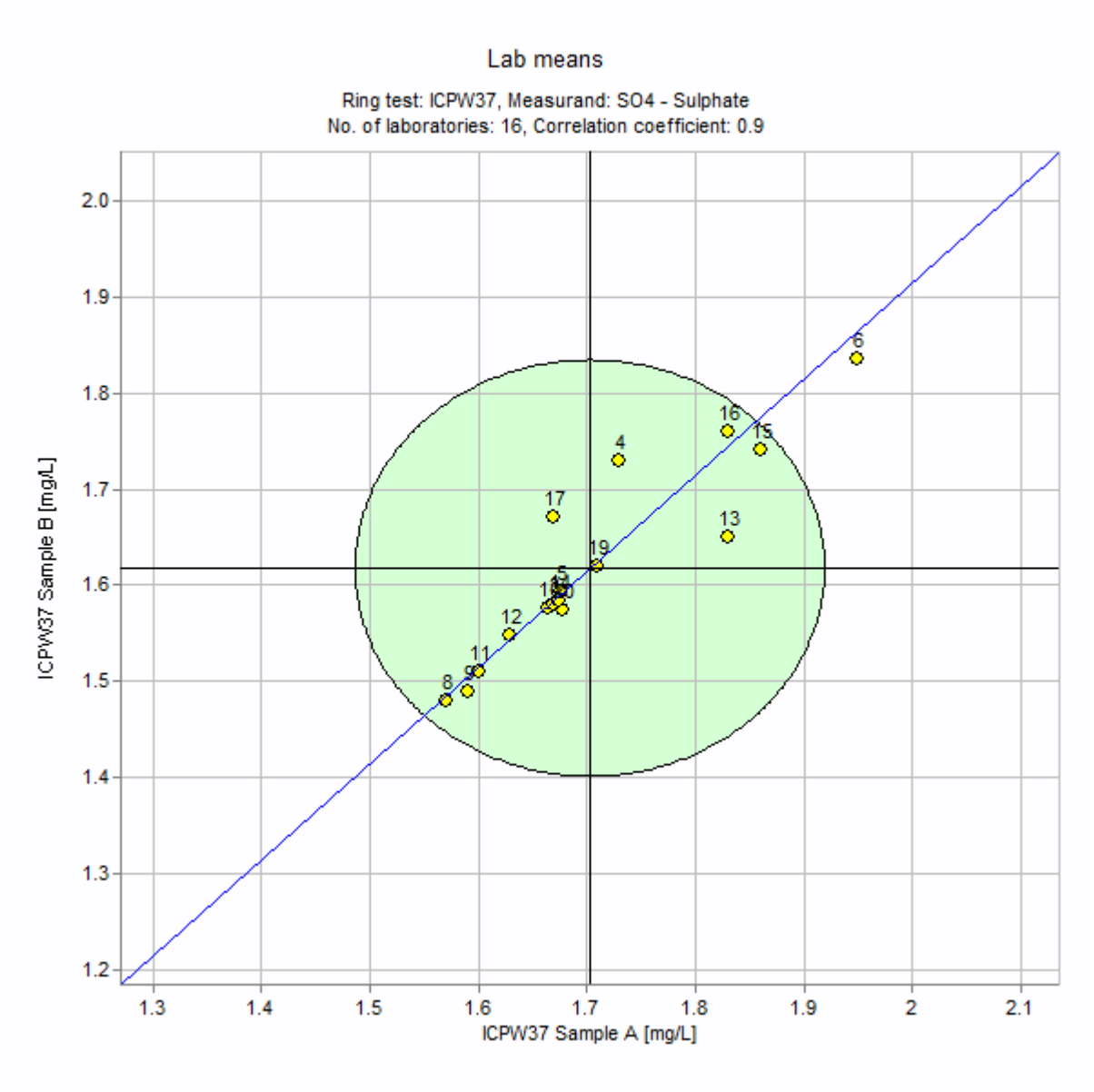

Figure 5. Youden diagram for sulphate (SO_4). Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.7 Calcium

Calcium was reported by 19 laboratories. The most used technique was ion chromatography (8 laboratories), followed by ICP-AES (5 laboratories), ICP-MS (4 laboratories), Flame AAS (1 laboratory) and an unspecified method (1 laboratory). Satisfactory results ($|Z'| < 2$) were obtained by 17 of the laboratories. The results not included as satisfactory seem to be systematically either over- or underestimated.

The SDPA of the results was around 9% for both samples, indicating some spread of the reported results. The results deemed satisfactory all had less than ±20 % deviation from the assigned value. The Youden diagram in Figure 6 shows that systematic errors dominate the dataset. It is also worth noting that the concentration of calcium was relatively low, and systematic errors may be more prominent if most of the results are from the lower calibration range of the participants.

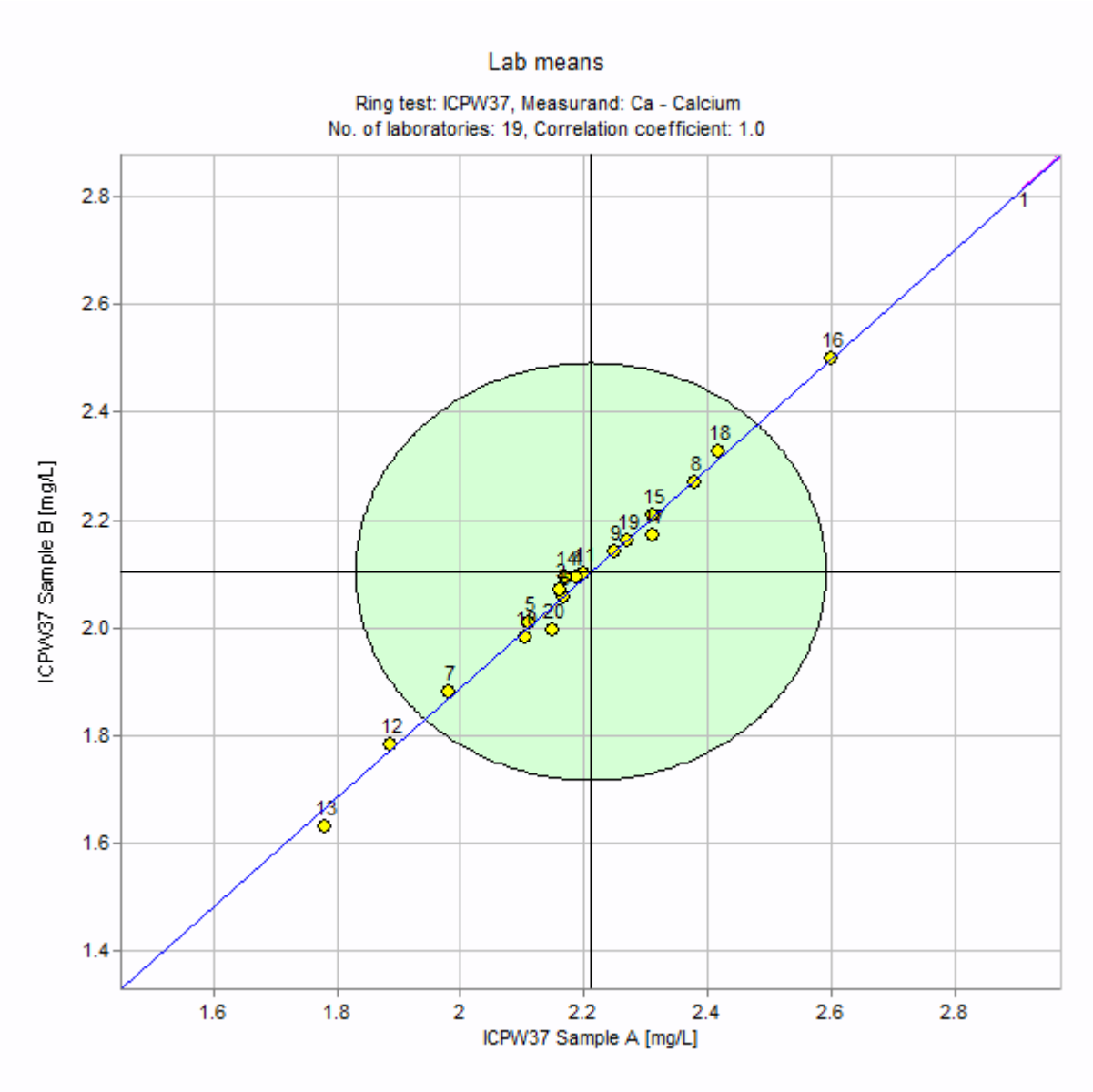

Figure 6. Youden diagram for calcium (Ca). Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.8 Magnesium

Magnesium was reported by 19 laboratories. All laboratories reported to have used the same technique for determining magnesium as they used for calcium. As such, the method distribution was ion chromatography (8 laboratories), ICP-AES (5 laboratories), ICP-MS (4 laboratories), flame AAS (1 laboratory), and an unspecified method (1 laboratory).

All but one laboratory reported satisfactory results ($|Z'| < 2$). The results have a high conformity, with the SDPA being around 6% for both sample A and B. Most laboratories report results within ±10% deviation of the assigned value, while one seems to be systematically overestimating magnesium. The Youden diagram (Figure 7) shows that systematic errors dominate the dataset.

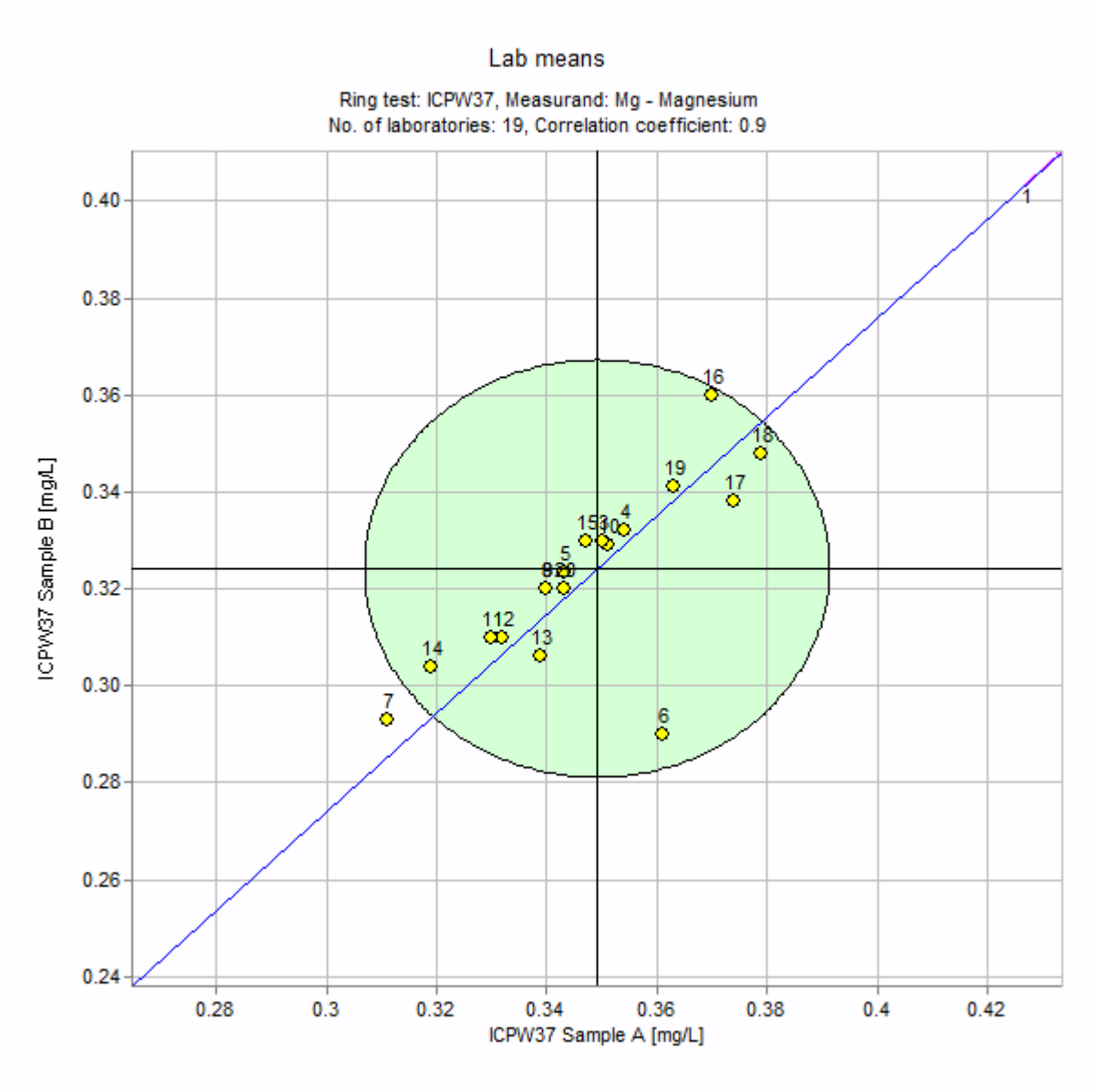

Figure 7. Youden diagram for magnesium (Mg). Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.9 Sodium

Sodium was also measured by 19 laboratories, and the techniques used were the same as for calcium and magnesium. Of the reported results, 87% were deemed satisfactory (|Z'| < 2), which corresponds to 16 satisfactory values for sample A and 17 for sample B. The results have a high conformity, with the SDPA being around 3 and 4% for sample A and B, respectively. This means that laboratories with a slightly higher deviation from the assigned value get marked as "questionable" or "non-satisfactory". All reported results are within ±20% deviation from the assigned value, so laboratories with Z'-scores higher than |2| must also consider their own measurement uncertainty when assessing if their result is ok or not.

The Youden diagram (Figure 8) shows that the dataset is dominated by small random errors. Since the circle in the Youden diagram is at 2x SDPA and the SDPA is small for these samples, the errors may seem larger than they really are.

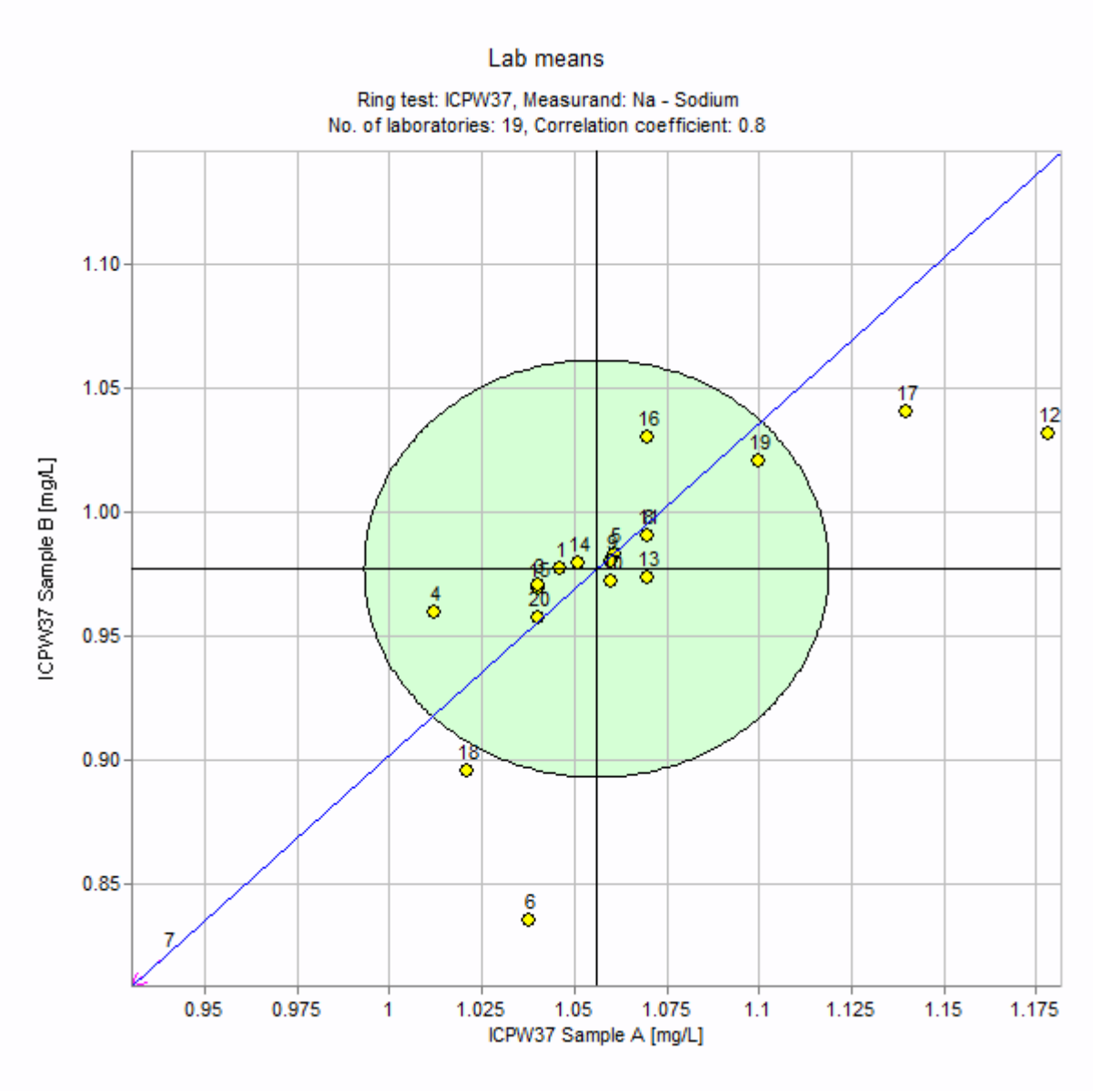

Figure 8. Youden diagram for sodium (Na). Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.10 Potassium

Sodium was also measured by 19 laboratories, and the techniques used were the same as for calcium, magnesium, and sodium.

For both sample A and sample B, 18 of the 19 results were deemed satisfactory (|Z'| < 2). The results have a relatively high conformity, with the SDPA being around 6-7% for both sample A and B. All satisfactory results were within ±10% of the assigned value. The Youden diagram in Figure 9 shows that the spread of the results is mostly systematic, with some small random errors.

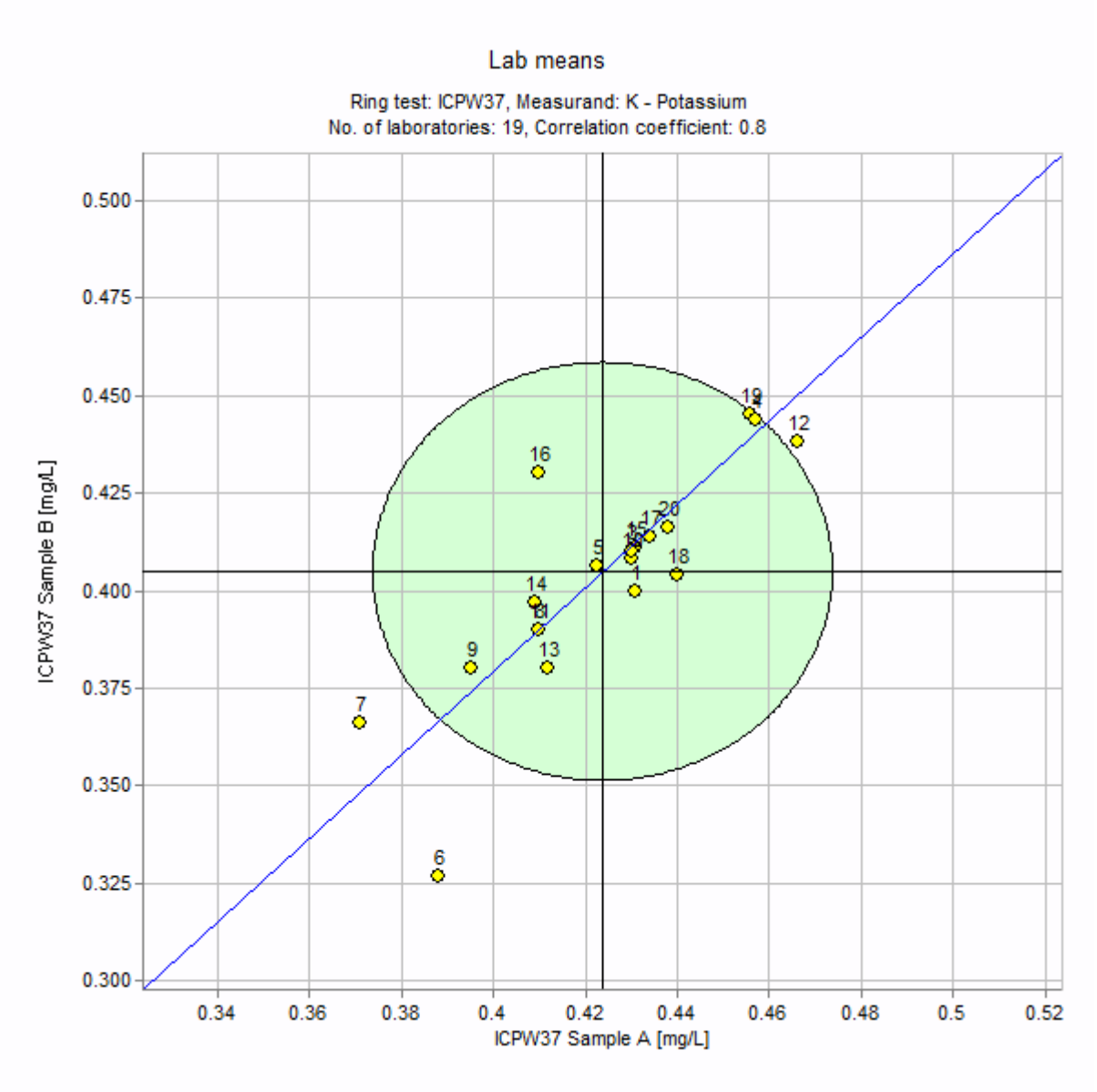

Figure 9. Youden diagram for potassium (K). Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.11 Total organic carbon

Total organic carbon was reported by 14 laboratories. The most used technique was catalytic combustion. Of these, 7 laboratories reported that they followed EN 1484 and 3 reported to be following EN ISO 20236. In addition, 2 laboratories reported to follow EN 1484 but use UV-light and peroxodisulphate for oxidizing the samples. The last 2 laboratories reported to have used an unspecified method.

All reported results were deemed satisfactory (|Z'| < 2), but the SDPA was approximately 12% and 10% for sample A and B, respectively. This means that the uncertainty of the assigned value is higher, and more results are deemed to be satisfactory even if their results deviate more from the assigned value. Still, all but one result is within ±20% of the assigned value. The Youden chart for total organic carbon in Figure 10 shows that most of the errors are systematic in nature.

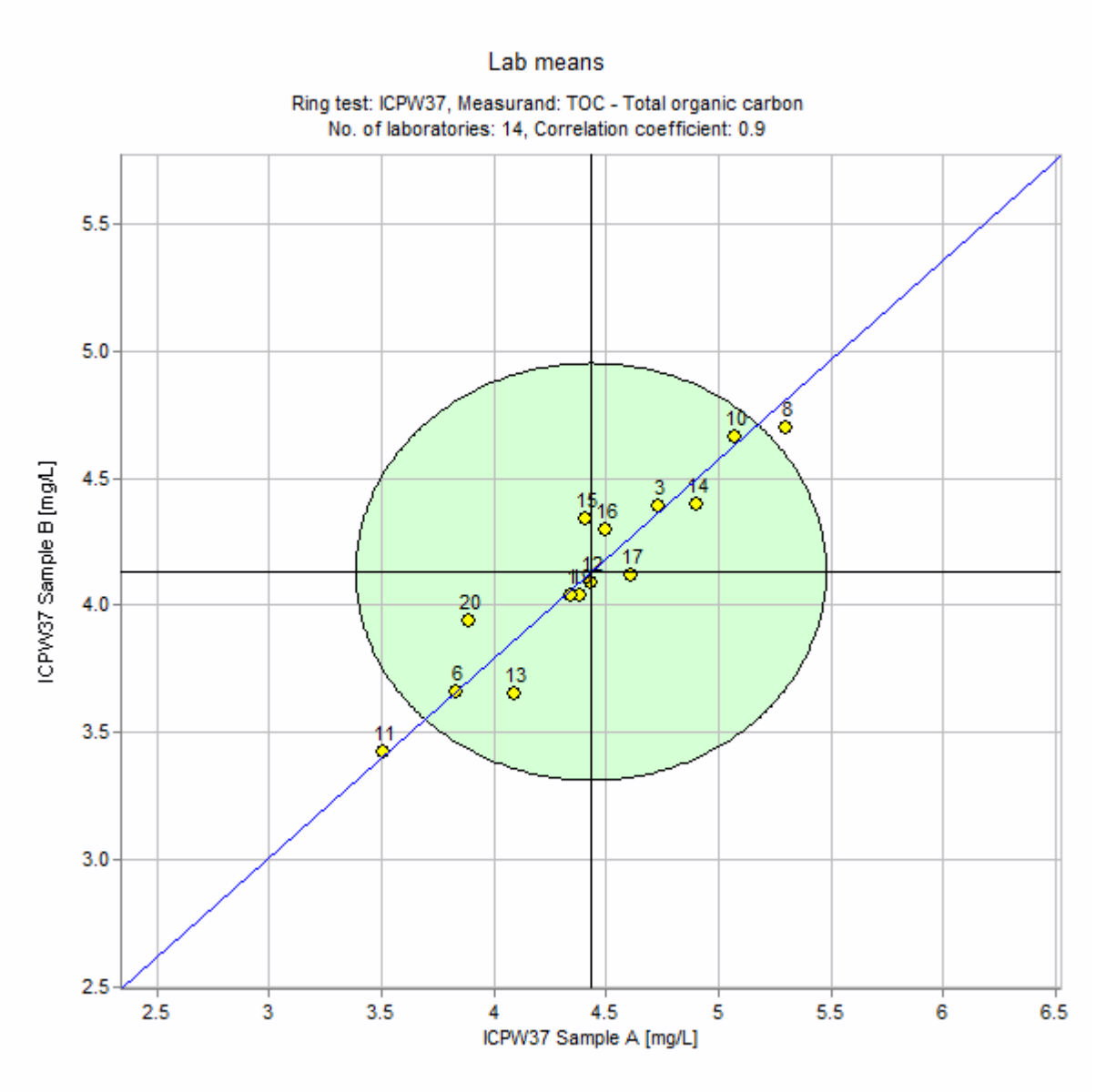

Figure 10. Youden diagram for TOC. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.12 Total phosphorus

Total phosphorus was determined by 16 laboratories. Several different methods were reported to have been used and covered EN-ISO 6878 (5 laboratories), EN-ISO 15681-2 (3 laboratories), simplified photometry (3 laboratories), and ICP-AES (2 laboratories). Lastly, one laboratory each reported to have used either ICP-MS, NS 4725 or an unspecified method.

Unfortunately, the reported results were spread over a relatively large range, causing the SDPA to be 32% and 36%, respectively. This causes most of the results to be deemed satisfactory (|Z'| < 2), even if most of the results have a high relative deviation from the assigned value. For instance, a deviation of around ±50% still results in a |Z'| score around 1.5. Previous years' tests show this same pattern, but the difference in assessment of the result means that this year sees a higher rate of acceptance than what has been seen previously. The Youden chart (Figure 11) shows the large spread, with the circle set at 2xSDPA. Most of the errors are still systematic in nature.

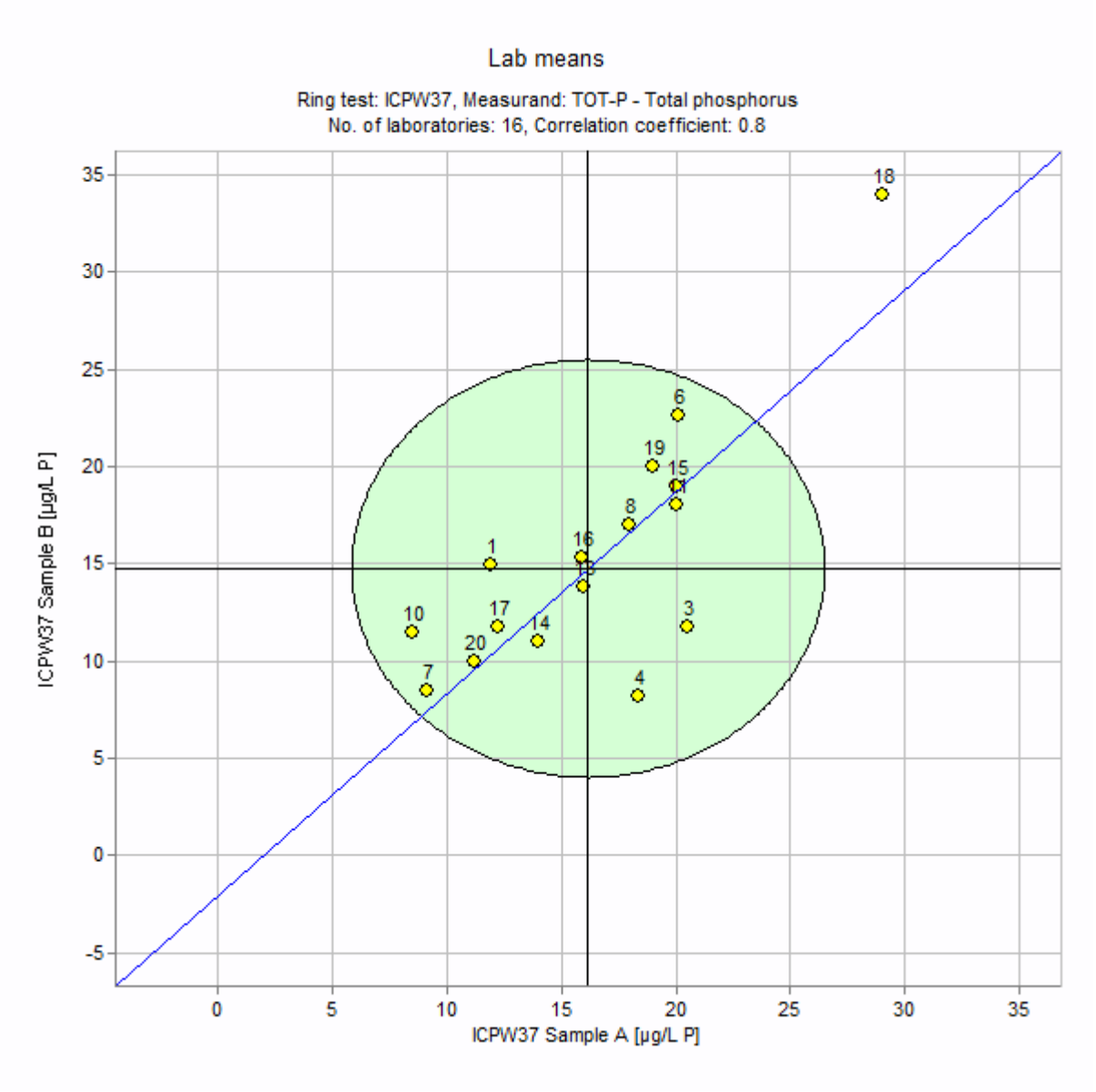

Figure 11. Youden diagram for Tot-P. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.13 Total nitrogen

Total nitrogen was determined by 11 laboratories, and all but one result was deemed satisfactory (|Z'| < 2). The most used technique was persulfate oxidation in combination with spectrophotometric determination, which was used by 6 laboratories. Of these, 3 reported to have used a buffered oxidation solution and referred to EN ISO 11905-1, while 3 reported to have used an unbuffered oxidation solution and referred to NS 4743. The last 5 participants used catalytic combustion for the determination. Of these, 3 laboratories referred to EN 12260 (withdrawn), while 2 referred to EN ISO 20236 (current).

The spread of the reported results was quite high, causing an SDPA of 23-25%. This causes some laboratories to have satisfactory Z' scores even if their results deviate around ±30% from the assigned values. The Youden chart (Figure 12) shows that systematic errors dominate the dataset.

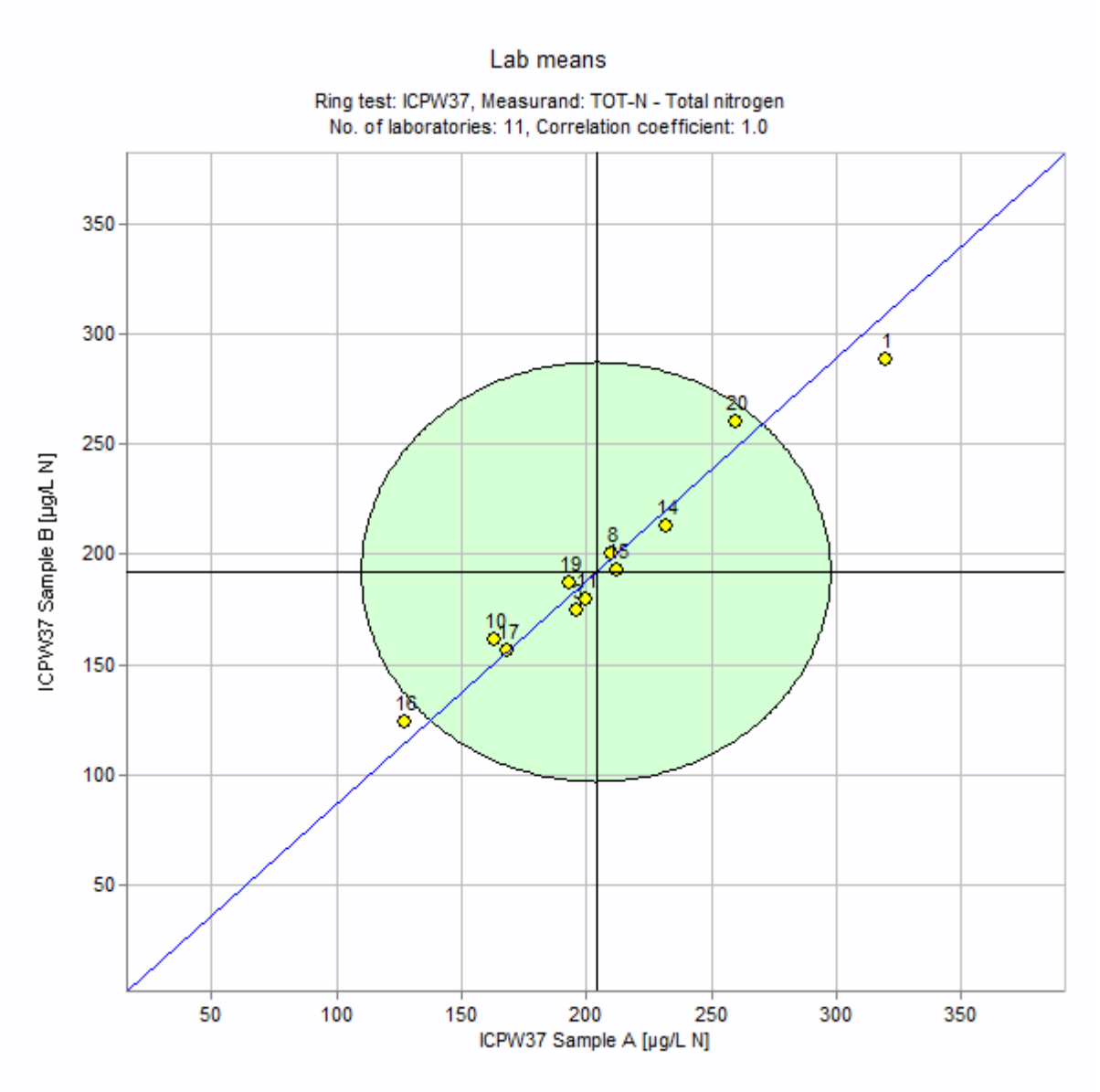

Figure 12. Youden diagram for Tot-N. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.14 Aluminium

Aluminium was reported by 12 participants. Most results were deemed satisfactory (|Z'| < 2). The spread of the results is a bit higher than what's preferred, and the SDPA is around 10-13%. Still, all satisfactory results are within ±20% deviation from the assigned value.

The most used technique for determination was ICP-MS, which was used by 9 laboratories. Furthermore, 2 laboratories used ICP-AES, and the last used GF-AAS. The Youden chart for aluminium (Figure 13) shows that most of the errors were small and systematic.

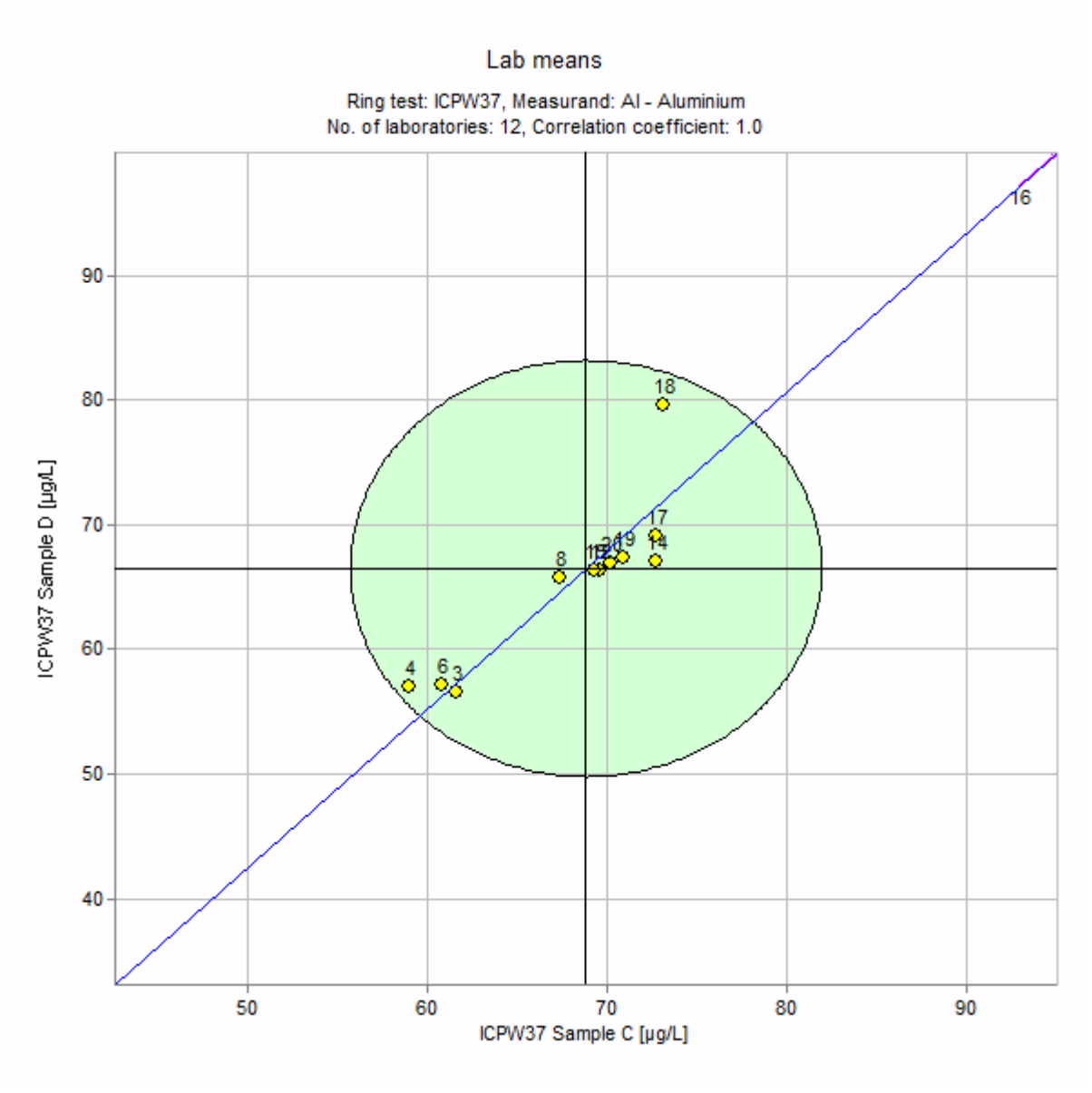

Figure 13. Youden diagram for aluminium (Al). Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.15 Iron

Iron was determined by 14 laboratories. ICP-MS was the most used technique, with 10 laboratories reported to have used ICP-MS to determine iron. ICP-AES was used by 3 laboratories, while the last laboratory reported to have used simplified photometry.

Of the 14 results reported for each sample, 13 were satisfactory for sample C, while 12 were satisfactory for sample D. The SDPA was around 5-6%, which means that most laboratories reported quite similar results. Of the satisfactory values, the deviation from the assigned values was within ±8%. The Youden chart (Figure 14) shows that the spread of the results is mostly small and systematic.

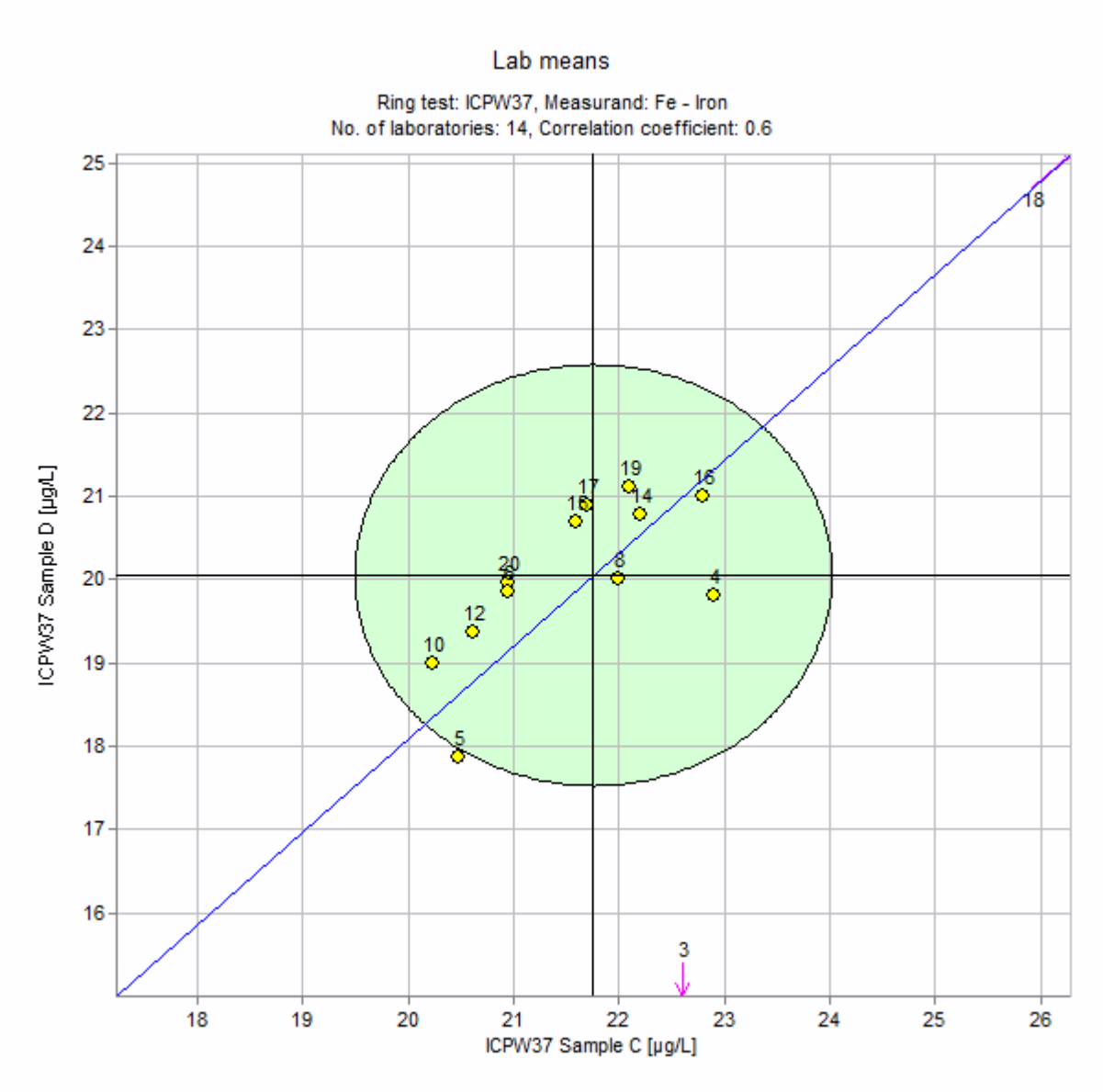

Figure 14. Youden diagram for iron (Fe). Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.16 Manganese

Manganese was determined by 13 laboratories, but one participant reported that the result was below their LOQ. ICP-MS was the most used technique (11 laboratories), while the last 2 used ICP-AES. One laboratory has reported results around twice the assigned value and thus not satisfactory, but the rest of the reported results are deemed satisfactory (|Z'| < 2). The SDPA is around 9% for both samples, and the participants with satisfactory results all have results with less than a ±15% deviation from the assigned value. The Youden chart in Figure 15 shows mostly small random errors.

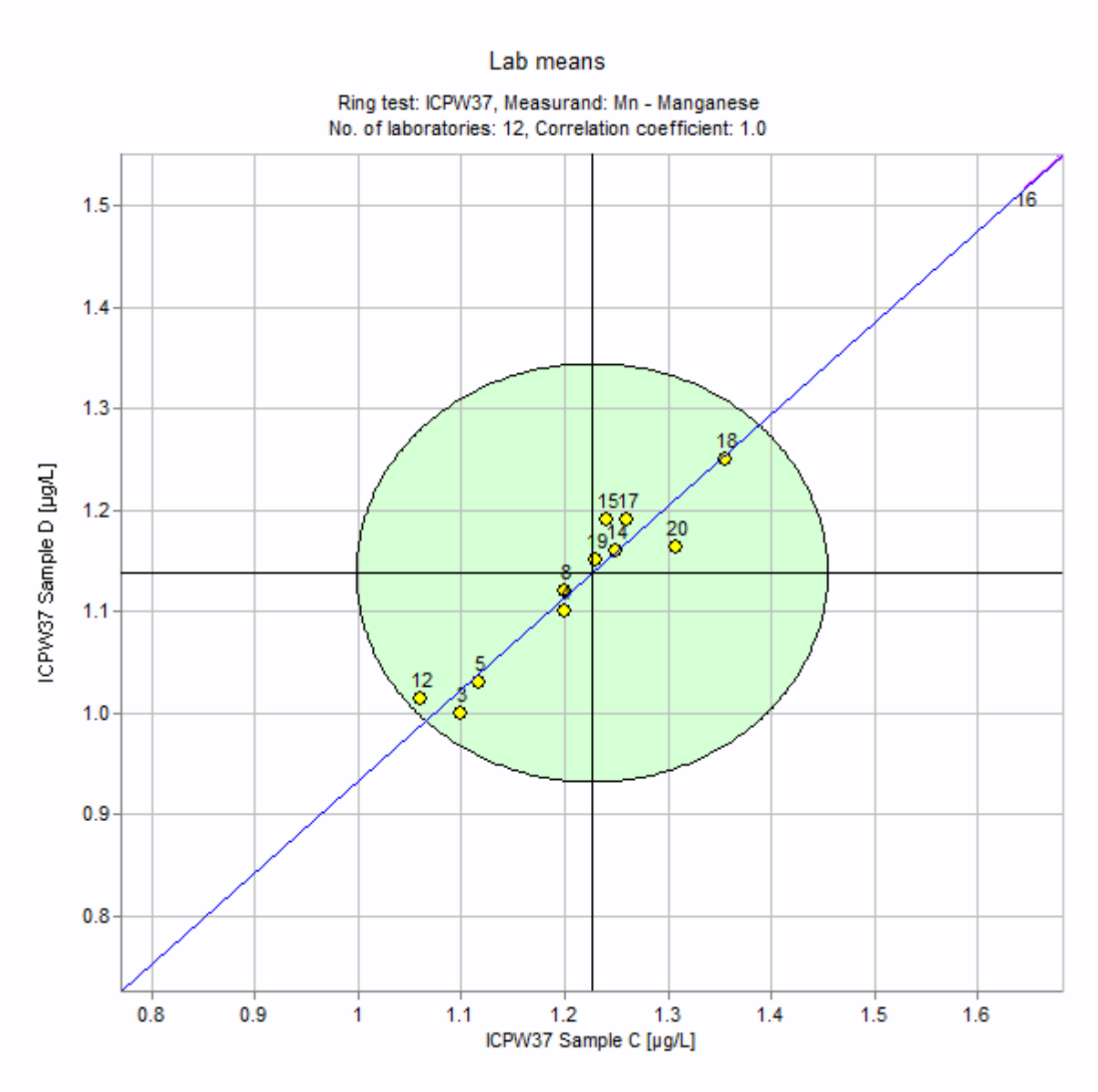

Figure 15. Youden diagram for manganese (Mn). Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.17 Cadmium

Cadmium was determined by 13 laboratories. ICP-MS was used by 11 participants, while either GF-AAS or ICP-AES was used by the last 2 participants. The number of results being deemed satisfactory (|Z'| < 2) was 11 for Sample C and 12 for Sample D. The reported results were quite close to each other, and the SDPA was at 5-6%. All satisfactory results were within ±13% of the assigned results. The Youden chart (Figure 16) shows both systematic and random errors.

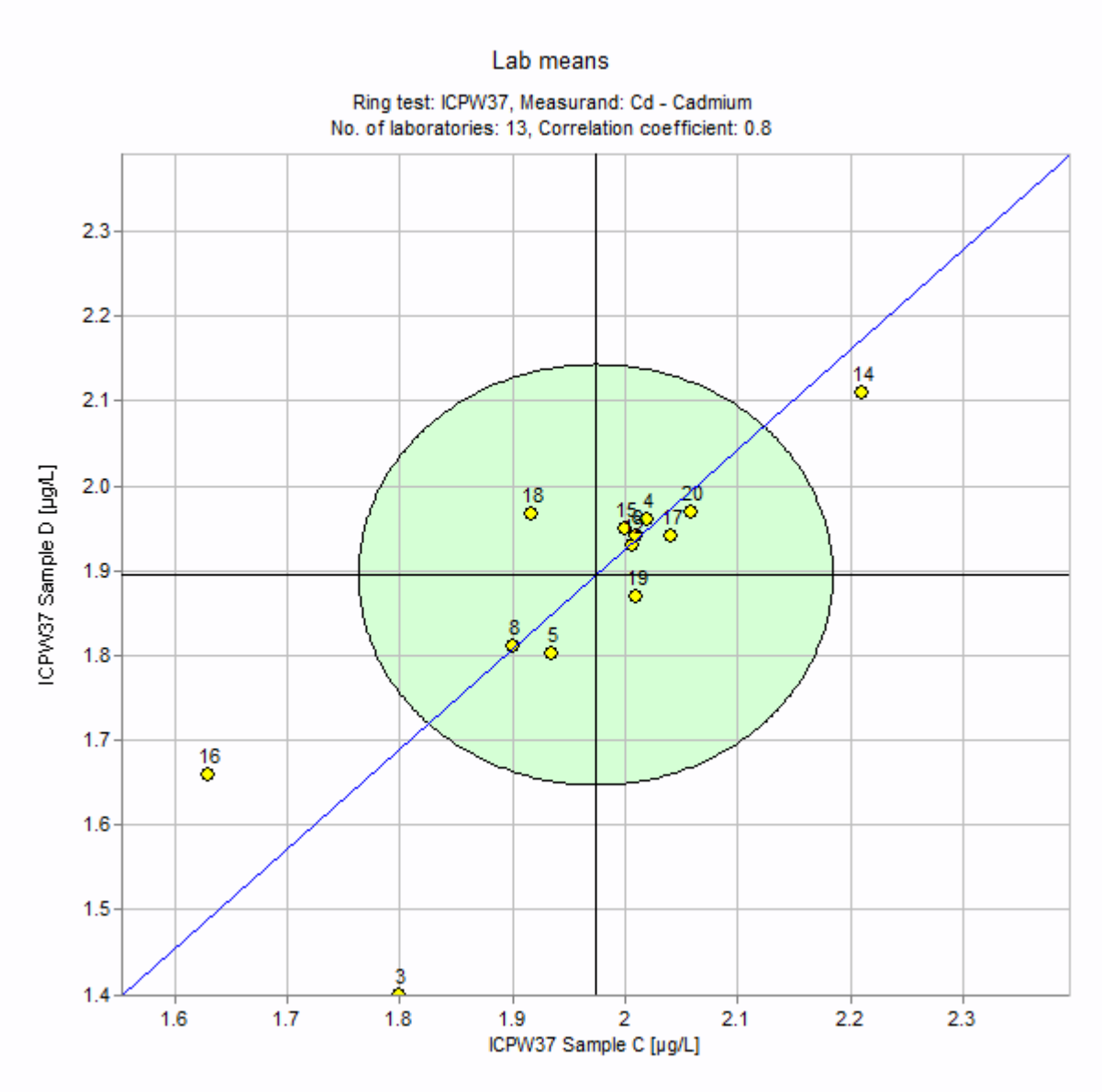

Figure 16. Youden diagram for cadmium (Cd). Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.18 Lead

Lead was determined by 13 laboratories. ICP-MS was used by 11 participants, while either GF-AAS or ICP-AES was used by the last 2 participants. All result for sample C was deemed satisfactory (|Z'| < 2), while 2 of the results from sample D was deemed questionable. The SDPA of the results was around 5% for sample C and 4% for sample D, which is quite good. All results for sample C were within ±9% of the assigned value. For sample D, the two questionable only deviated around ±10% from the assigned value, while all the satisfactory results were within ±5% of the assigned value.

The Youden chart (Figure 17) shows that most errors are small and systematic.

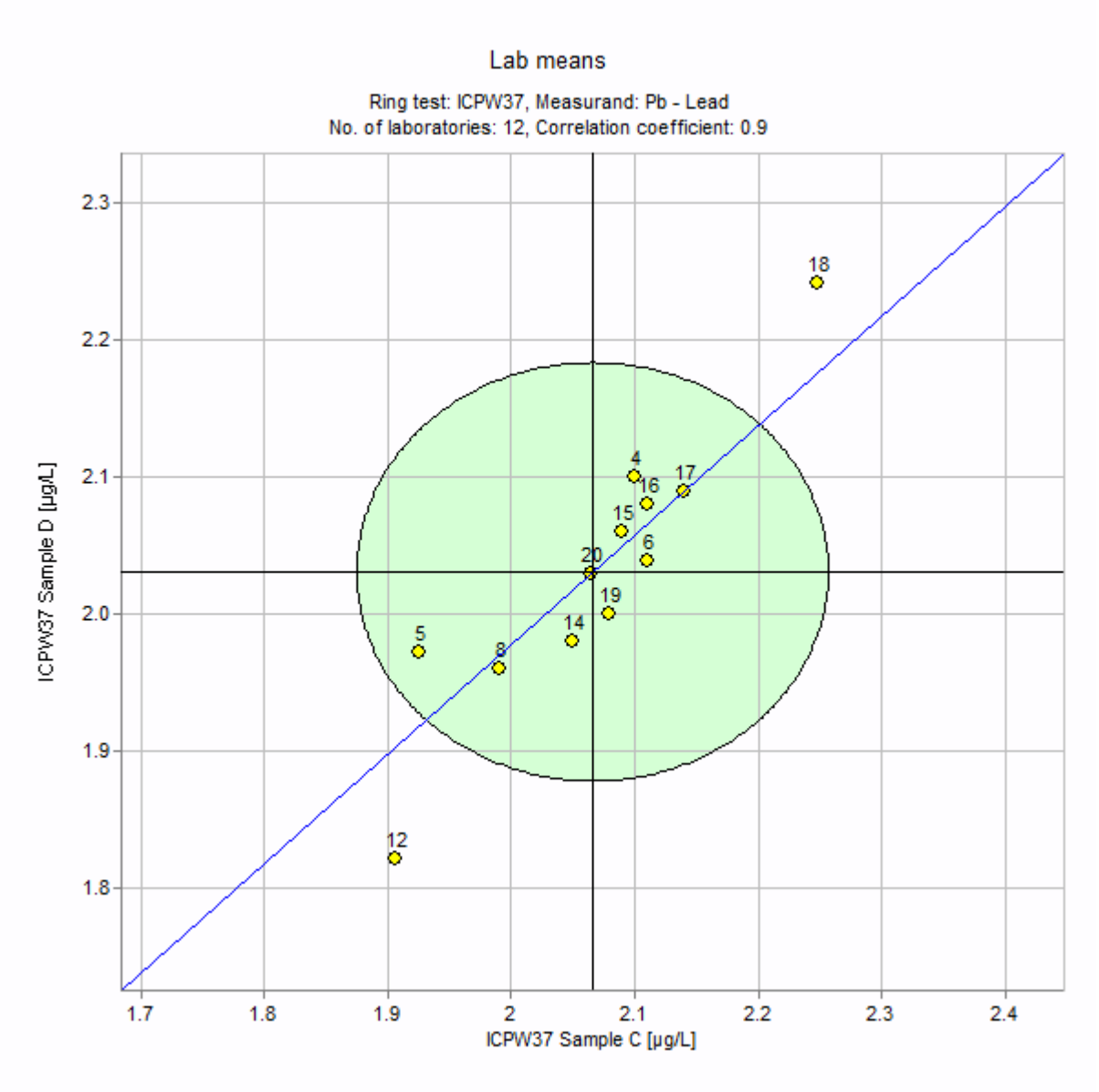

Figure 17. Youden diagram for lead (Pb). Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.19 Copper

Copper was determined by 12 laboratories. ICP-MS was used by 10 participants, while either GF-AAS or ICP-AES was used by the last 2 participants. All but one result was deemed satisfactory (|Z'| < 2). The SDPA of the assigned value was approximately 10% for sample C and 14% for sample D, which is relatively high. Of the satisfactory results, all were within ±25% of the assigned value.

The distribution of the results in the Youden chart in Figure 18 shows that systematic errors dominate the results.

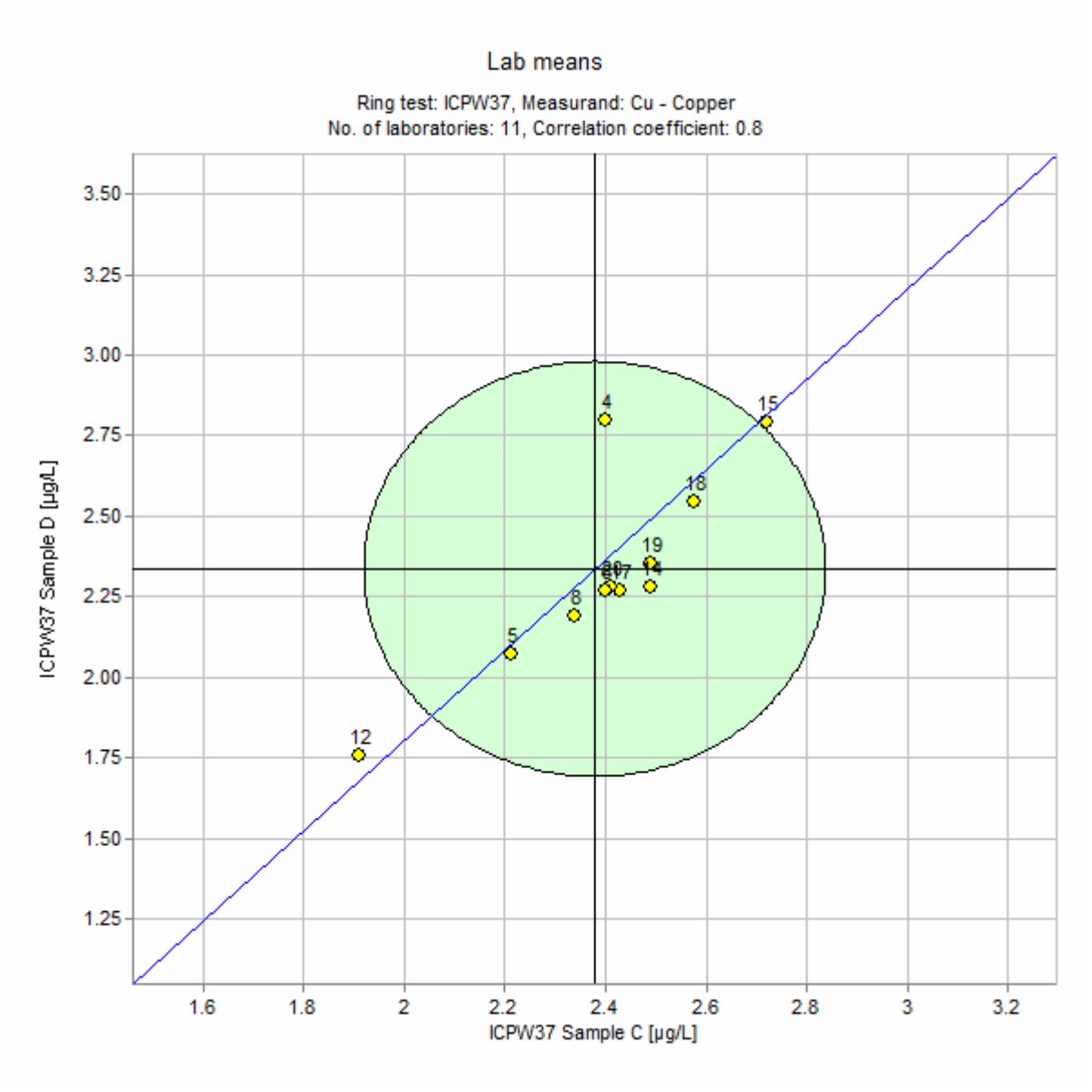

Figure 18. Youden diagram for copper (Cu). Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.20 Nickel

Nickel was determined by 12 laboratories. ICP-MS was the most used technique for determination, being used by 10 laboratories. Furthermore, either GF-AAS or ICP-AES was used by the last two. The laboratory having used ICP-AES reported that the results were below their quantification limit.

The SDPA were around 4% for both samples and all but one result was deemed satisfactory (|Z'| < 2). All reported results were still within ±11% of the assigned value. The Youden chart (Figure 19) shows that systematic errors are dominating the spread of the results.

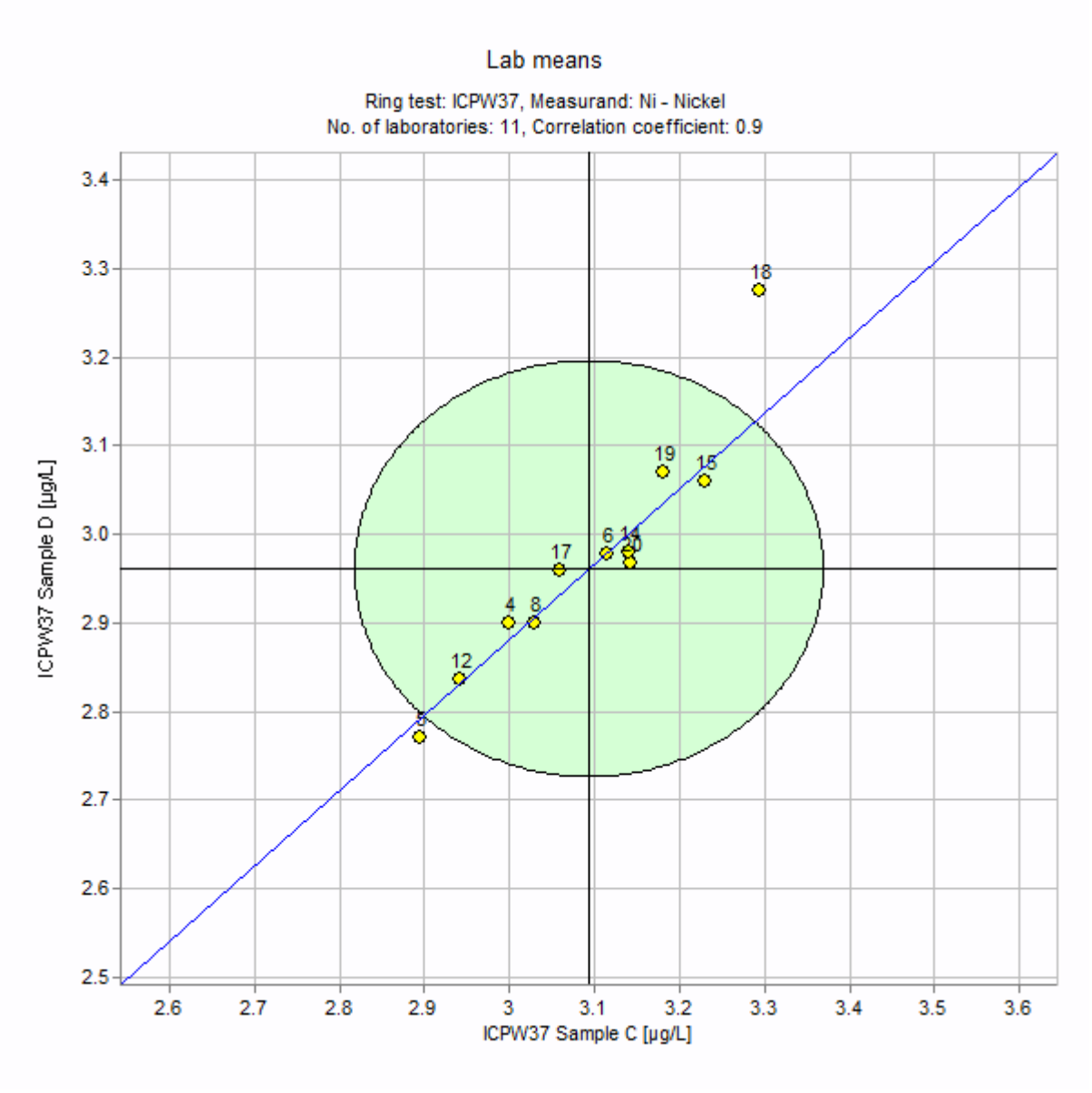

Figure 19. Youden diagram for nickel (Ni). Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.21 Zinc

Nickel was determined by 13 laboratories, and all but one reported to have used ICP-MS for the determination. The last laboratory reported to have used ICP-AES. Satisfactory results (|Z'| < 2) were obtained by 10 of the laboratories, while the last 3 had systematically high or low results. The satisfactory results were all within ±11% of the assigned values. The Youden chart Figure 20 shows that systematic errors dominate the results.

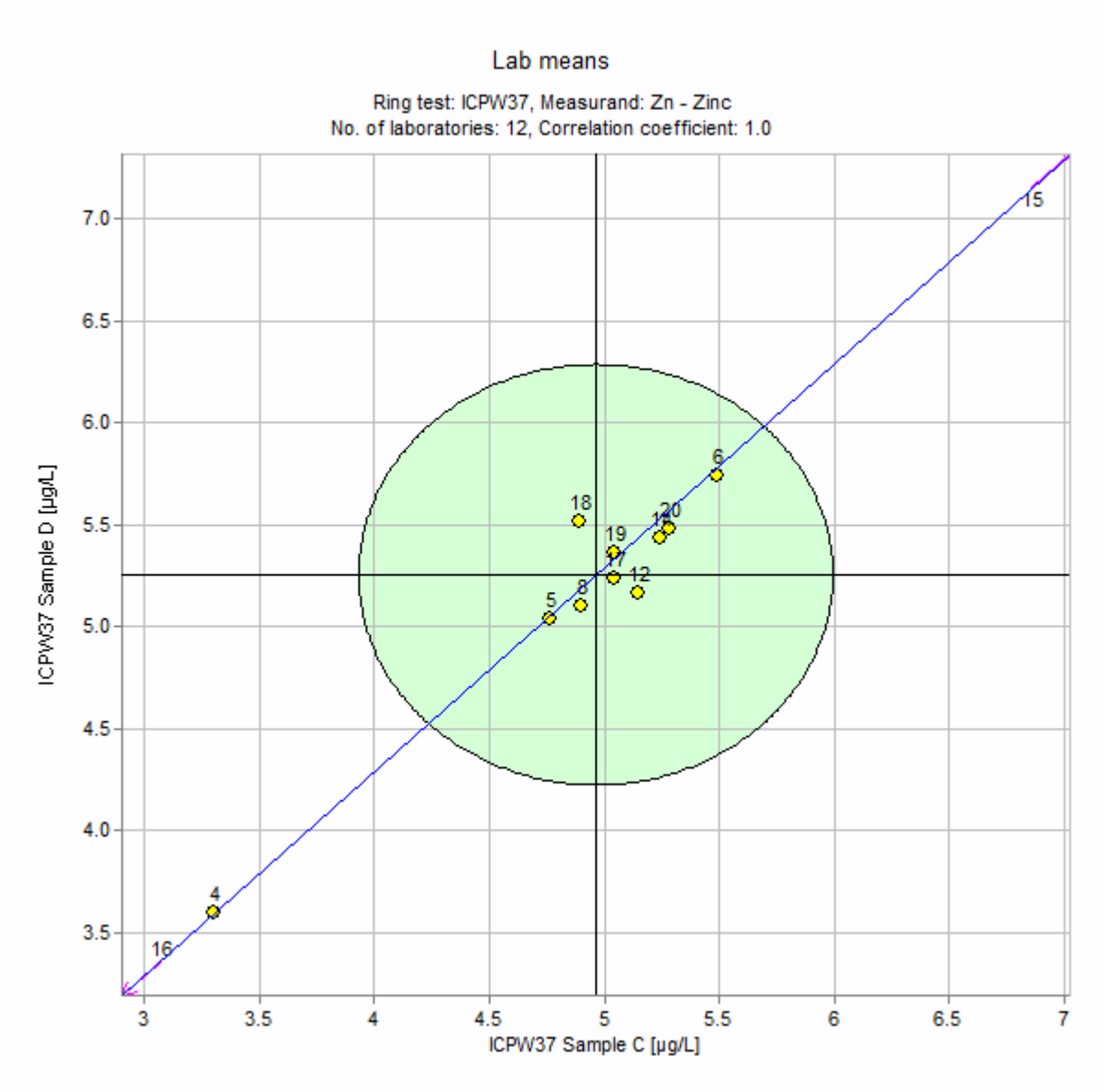

Figure 20. Youden diagram for zinc (Zn). Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

4 Litterature

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. ISO 13528 (2022): Statistical methods for use in proficiency testing by interlaboratory comparisons.

Appendix A. The participating laboratories

Table 4. Information of the participating laboratories including name, address, and country.

No.	Name of laboratory	Address	Country
1	Laboratoire d'écologie fonctionnelle et environnement	118 route de Narbonne - Bâtiment 4R1 31062 TOULOUSE	France
2	Puszcza Borecka Integrated Monitoring Station	ul. Kolektorska 4 01-692 Warszawa	Poland
3	Laboratorio de Calidad de las Aguas (CEDEX)	PASEO BAJO VIRGEN DEL PUERTO 3, (Centro de Estudios Hidrográficos) CEDEX 28005 Madrid	Spain
4	Chemical Laboratory, Czech Geological Survey	Geologicka 6 152 00 Praha 5	Czech Republic
5	ISSeP-CAN	rue de la Platinerie 7340 Colfontaine	Belgium
6	Natural Resources Wales	2nd Floor Faraday BuildingSwansea University (Singleton Campus) SA28PP Swansea	United Kingdom
7	Radboud Universiteit	Heijendaalseweg 135 6525 AJ Nijmegen	Netherlands
8	Norsk institutt for vannforskning	Økernveien 94 0579 Oslo	Norway
9	Staatliche Betriebsgesellschaft für Umwelt und Landwirtschaft, Labor Nossen	Waldheimer Straße 219 01683 Nossen	Germany
10	Freshwater Fisheries Laboratory	Faskally PH16 5LB Pitlochry	United Kingdom
11	CNR IRSA Verbania	L.go Tonolli 50 28922 Verbania	Italia
12	Serveis Tècnics de Recerca-UdG	Pic de Peguera, 15, Accés E 17003 Girona	Spain
13	Dorset Environmental Science Centre	1026 Bellwood Acres Road P0A1E0 Dorset	Canada
14	Bayerische Landesanstalt für Wald und Forstwirtschaft	Hans-Carl-von-Carlowitz-Platz 1 85354 Freising	Germany
15	Estonian Environmental Research Centre	Vaksali 17a 50410 Tartu	Estonia
16	Department of Ecology	Technikerstraße 25 6020 Department of Ecology	Austria
17	Swedish University of Agricultural Sciences, Aquatic Sciences and Assessment	Gerda Nilssons väg 5 756 51 Uppsala	Sweden
18	VMM	Raymonde de Larochelaan 1 9051 Sint-Denijs-Westrem	Belgium
19	Bayerisches Landesamt für Umwelt	Bürgermeister-Ulrich-Straße 160 86179 Augsburg	Germany
20	Ufficio del Monitoraggio Ambientale - Laboratorio	via Mirasole 22 6500 Bellinzona	Switzerland

Table 5. Overview of the different countries represented by the participating laboratories.

Country	No. of labs.	Country	No. of labs.
Austria	1	Italy	1
Belgium	2	Netherlands	1
Canada	1	Norway	1
Czech Republic	1	Poland	1
Estonia	1	Spain	2
France	1	Sweden	1
Germany	3	Switzerland	1
		United Kingdom	2
Total: 15 countries			

Appendix B. Preparation of the samples

Both sample sets, AB and CD, were prepared using water from the outlet of lake Krøderen, located a couple of hours drive outside of Oslo, Norway. The lake is low in lime and has a relatively low conductivity.

The water was collected during the 6th of June 2023 and transported to the laboratory using five 25 L plastic containers. The water was allowed to settle for approximately one week before it was filtered through 0.45 µm cellulose acetate membrane filters. The filtered water was distributed into four containers, one for each sample (A, B, C and D). Water was then collected for a preliminary analysis. Based on the results of the preliminary analysis, the below-mentioned additions were made to produce sample sets AB and CD.

To produce sample set AB, some amount of organic phosphorous was added in the form of phytic acid. The rest of the parameters (including nitrate) seemed to be present in reasonable amounts. Sample B was slightly diluted with Type 1 water, to create a small difference in parameter levels between sample A and sample B.

Sample set CD was created by spiking with standard solution of the metals: lead, cadmium, and nickel. The rest of the parameters were already present in reasonable amounts. Subsequently, sample D was slightly diluted to create a small difference in the concentration levels. Finally, the sample set CD was preserved by adding nitric acid to a concentration of 0.5% (v/v). The water prepared for sample set AB was distributed to 500 mL bottles and the water for sample set CD to 250 mL bottles. The samples were shipped a few days later to the participating laboratories.

Appendix C: Statistical treatment of the results

Initial treatment of the analytical results

This year, the statistical software PROLab by QuoData was used. The results were collected via the web service PROLab_HUB. After all participants had reported their results, the data was downloaded onto PROLab Plus where the statistical computations were performed. The main difference from previous years is that samples are now treated as individuals. In previous years, a sample pair was treated as a whole, meaning that one bad result meant that both results in the pair was omitted from the statistics.

Estimation the "true value" and uncertainty

First, the assigned value was determined from the reported results as a consensus mean value by using Algorithm A+S (ISO 13528/5725-5), which is the same algorithms used in previous years.

The algorithm yields robust estimates of the mean and the standard deviation of the data. An initial value for the robust estimate of the mean (x*) is first calculated from the median of the participants' results. The initial value for the robust standard deviation is calculated from the absolute differences between x* and the result of each participating laboratories according to:

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

The new values for x* and S* are then calculated according to equations (C.7) – (C.10) in Annex C of ISO 13528. The final values are derived by an iterative calculation by updating the values several times using the modified data, until the process converges. In PROLab Plus, the end of the iteration is when the values converge to 3 significant figures, but with at least 30 iterations.

The robust standard deviation S*, is named as the standard deviation for proficiency assessment (SDPA) and the robust estimate of the mean is used for the assigned value.

The standard uncertainty (k=1) u_X of the assigned value for the true value is calculated according to chapter 7.7 in ISO 13528 (2022):

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

The calculated values of the standard uncertainty of the assigned values can be found in Table 6.

It is important to note that there are some limitations to this approach for estimating the uncertainty of the true value:

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

Table 6. Standard uncertainty of the assigned values

		absolute	relative	absolute	relative
		Sample A		Sample B	
pH		0.05	0.8 %	0.04	0.6 %
conductivity	mS/m	0.04	1.8 %	0.03	1.6 %
alkalinity	mmol/L	0.004	3.7 %	0.008	7.7 %
chloride	mg/L	0.02	1.5 %	0.02	1.8 %
sulphate	mg/L	0.03	2 %	0.03	2.1 %
calcium	mg/L	0.06	2.5 %	0.06	2.6 %
magnesium	mg/L	0.006	1.7 %	0.006	1.9 %
sodium	mg/L	0.009	0.9 %	0.01	1.2 %
potassium	mg/L	0.007	1.7 %	0.008	1.9 %
total organic carbon	mg/L	0.18	3.9 %	0.14	3.3 %
total phosphorous	µg/L	1.6	10 %	1.7	11.4 %
total nitrogen	µg/L	18	8.7 %	18	9.3 %
		Sample C		Sample D	
Al - aluminium	µg/L	2.366	3.4 %	3.012	4.5 %
Fe - iron	µg/L	0.378	1.7 %	0.422	2.1 %
Mn - manganese	µg/L	0.041	3.4 %	0.037	3.3 %
Cd - cadmium	µg/L	0.036	1.8 %	0.043	2.3 %
Pb - lead	µg/L	0.034	1.7 %	0.028	1.4 %
Cu - copper	µg/L	0.083	3.5 %	0.121	5.2 %
Ni - nickel	µg/L	0.052	1.7 %	0.044	1.5 %
Zn -zinc	µg/L	0.179	3.6 %	0.186	3.5 %

The Youden statistical test

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

For example, if the results are affected by random errors only, the points will be spread randomly around the origo of the Youden chart. However, if systematic effects are influencing the results (e.g., from the use of different deviating analytical methods), the points in the chart will be distributed in a characteristic elliptical pattern along a 45° line in the chart. This reflects the fact that many laboratories - due to systematic deviations - have attained too low or too high values for both samples.

In the Youden charts, 2xSDPA is indicated by a circle around the origo. The distance from the center of the circle and the point of an individual laboratory is a measure of the absolute error of the result. The distance along the 45° line gives the magnitude of the systematic error, while the distance perpendicular to the 45° line indicates the magnitude of the random error. Thus, the location of the point of each laboratory in the Youden’s diagram provides important information of the size and type of analytical error (random or systematic) present in the dataset, making it possible to indicate what is the source of deviation from the consensus of the participating laboratories.

Computation of Z'-scores and tolerance limits

In previous years, the tolerance limit has been fixed in relative terms. Most often, it has been ±20% from the assigned "true" value. In many cases, this has been an ok way of assessment, but it does not consider the uncertainty of the assigned values. An assigned value with a high uncertainty connected to it may be wrong. Therefore, an acceptance limit fixed at 20% may be too strict for some parameters. By using Z'-scores and/or considering the SDPA, the acceptance limit is scaled according to the uncertainty of the assigned value.

Z-score is widely used in intercomparison tests and is a score which is calculated from the participants' result x, the assigned value x_{pt} and the σ_{pt} (SDPA). The formula used is $z = (x - x_{pt})/\sigma_{pt}$. If the score is outside ±2, it is often deemed to be questionable, and a score outside of ±3 is said to be actionable. The score is best used if the uncertainty of the assigned values is negligible compared to the uncertainty of the participants result.

Z'-score is a modified z-score, with the formula $z' = (x - x_{pt})/\sqrt{\sigma_{pt}^2 + u^2(x_{pt})}$. The modification is suggested to be used if the uncertainty of the assigned value is too high compared to the SDPA. Since this was the case for several of the parameters in this intercomparison test, Z'-scores were used for the assessment. Same as for Z-scores, results outside ±2 is deemed to be questionable and scores outside of ±3 are actionable. Figures of the Z'-score distribution for each parameter can be seen in Figure 21 to Figure 40 in Appendix D.

Appendix D: Results reported by the participating laboratories

D.1 Survey of Z' scores

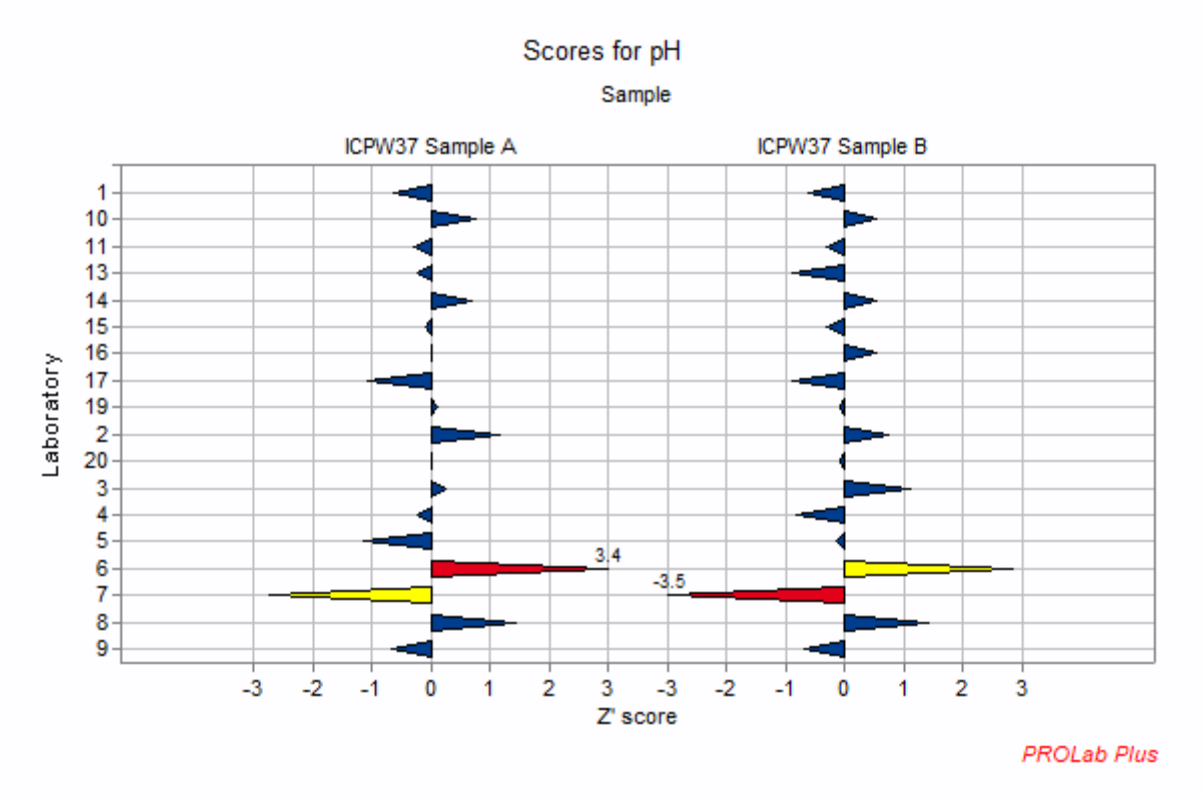

Figure 21. Z' scores for pH.

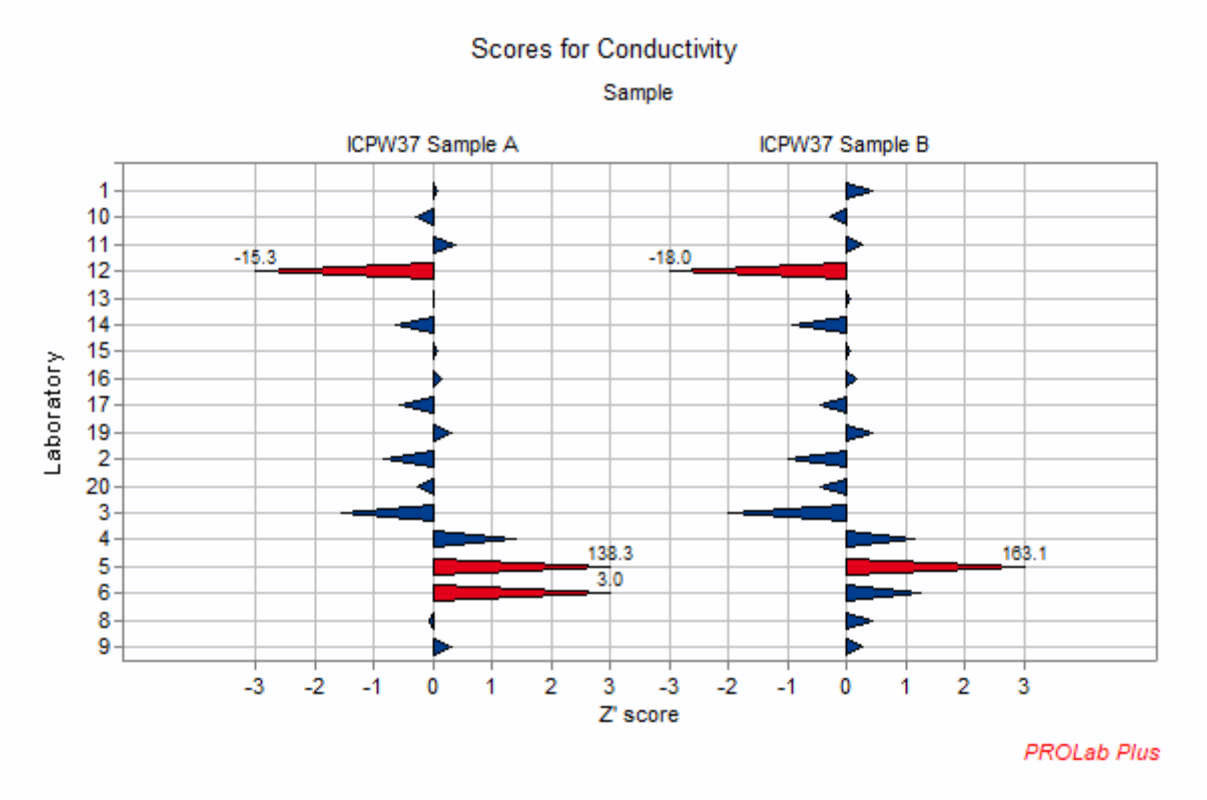

Figure 22. Z' scores for conductivity.

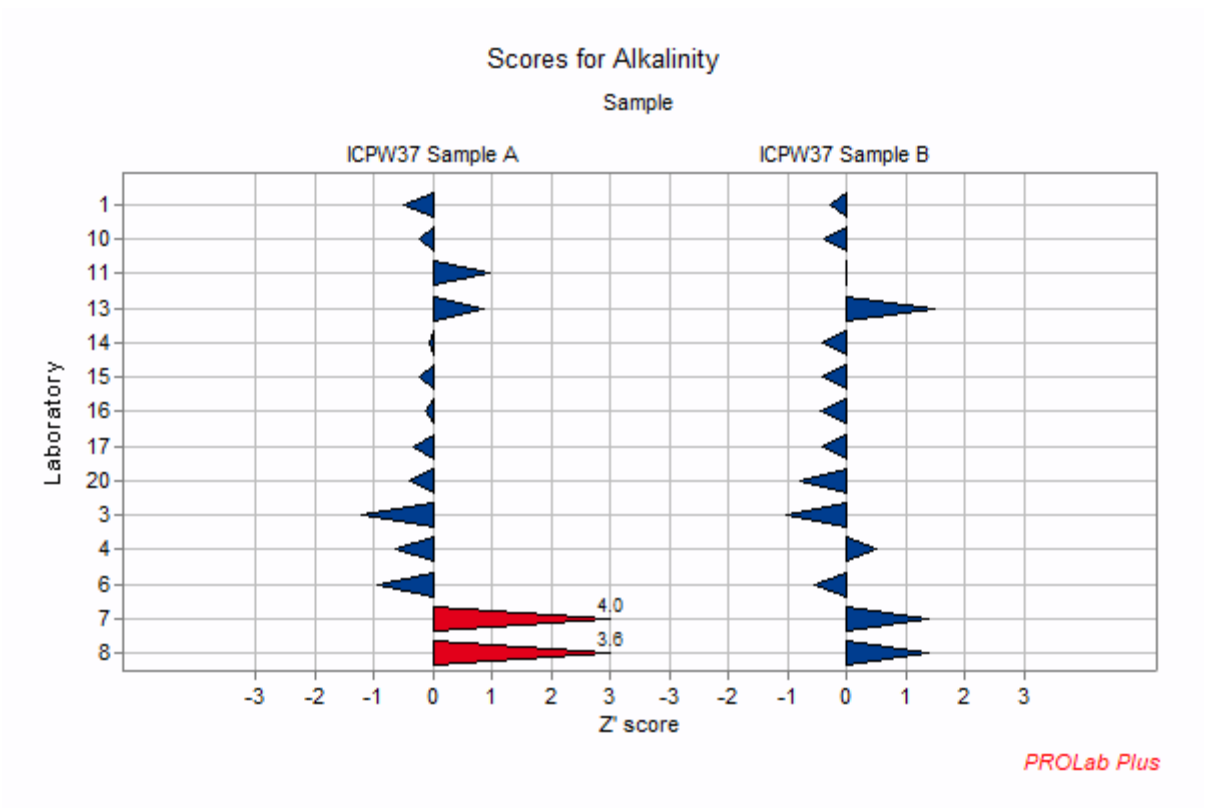

Figure 23. Z' scores for alkalinity.

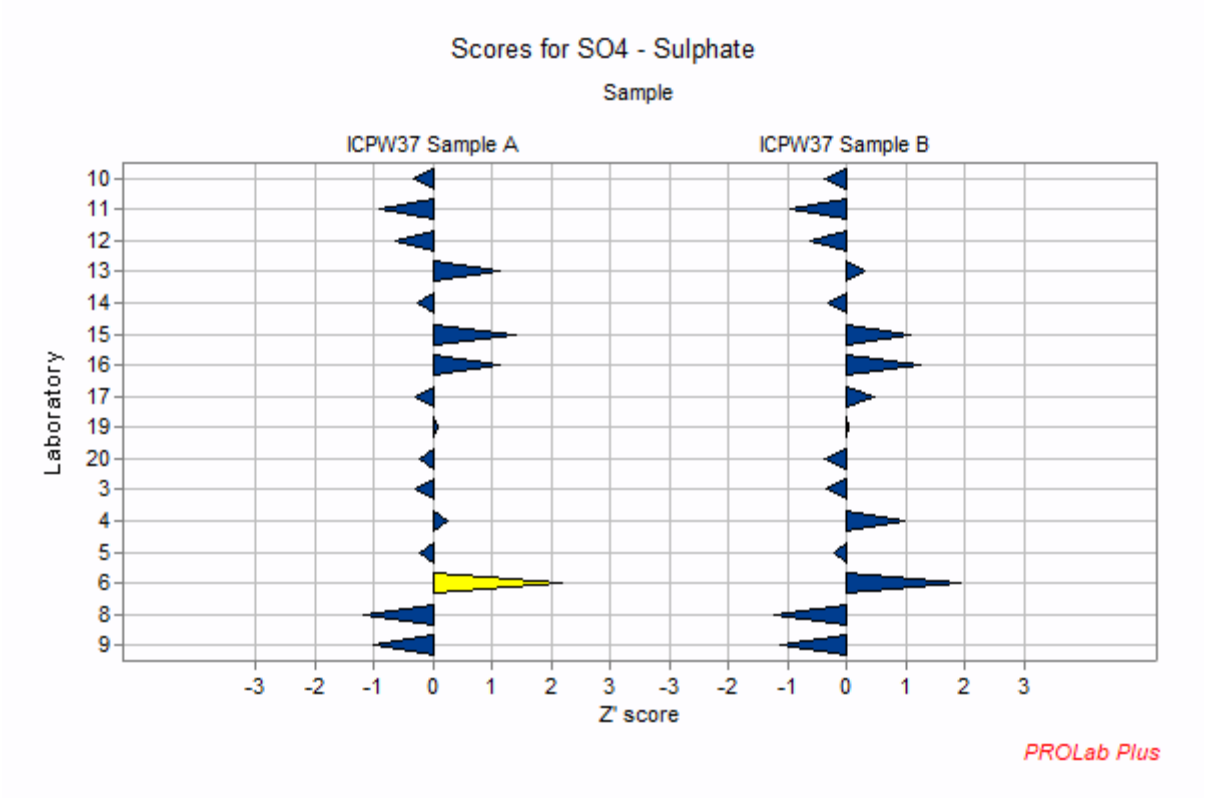

Figure 24. Z' scores for sulphate (SO_4).

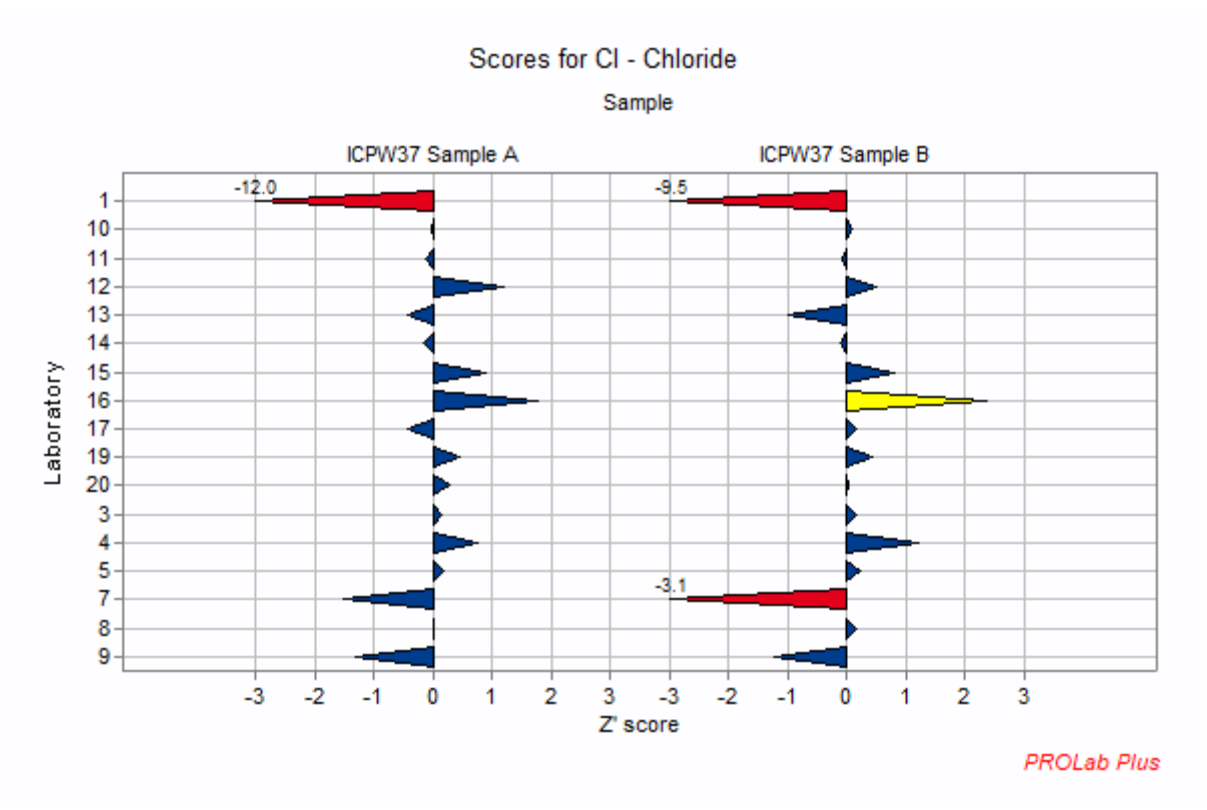

Figure 25. Z' scores for chloride (Cl).

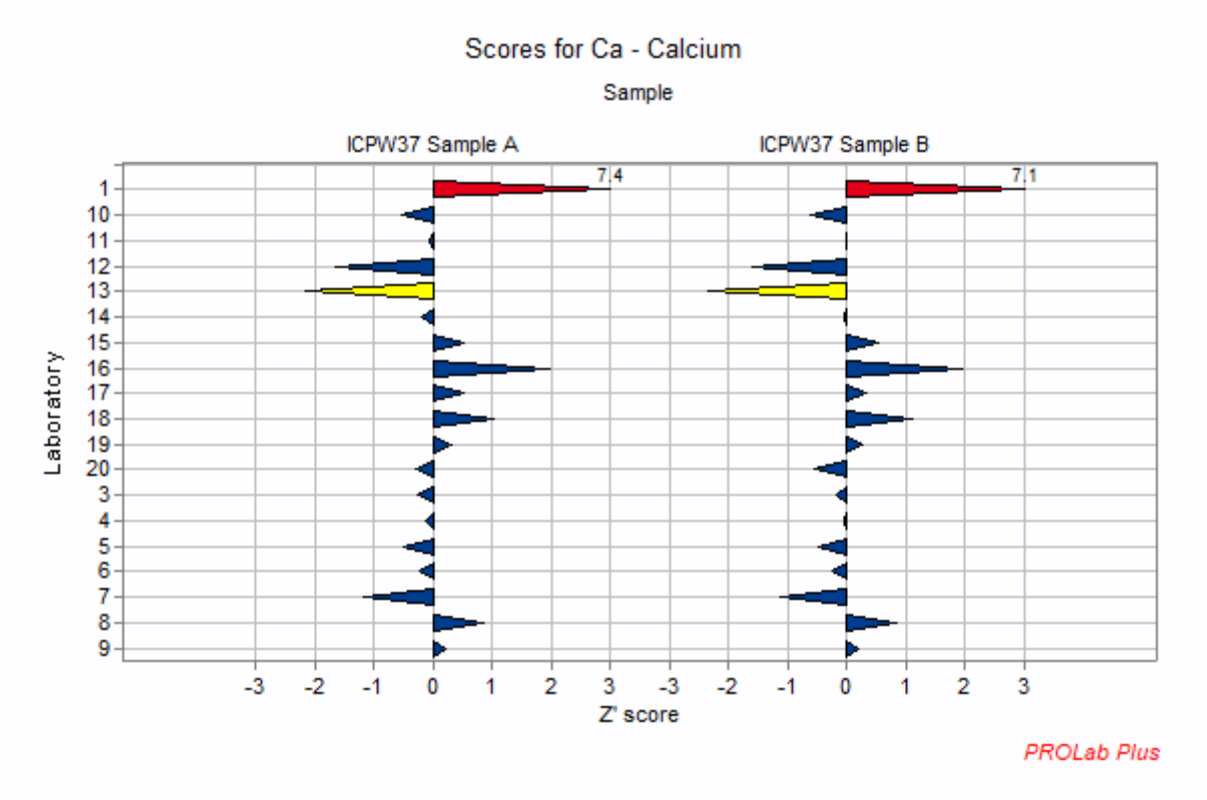

Figure 26. Z' scores for calcium (Ca).

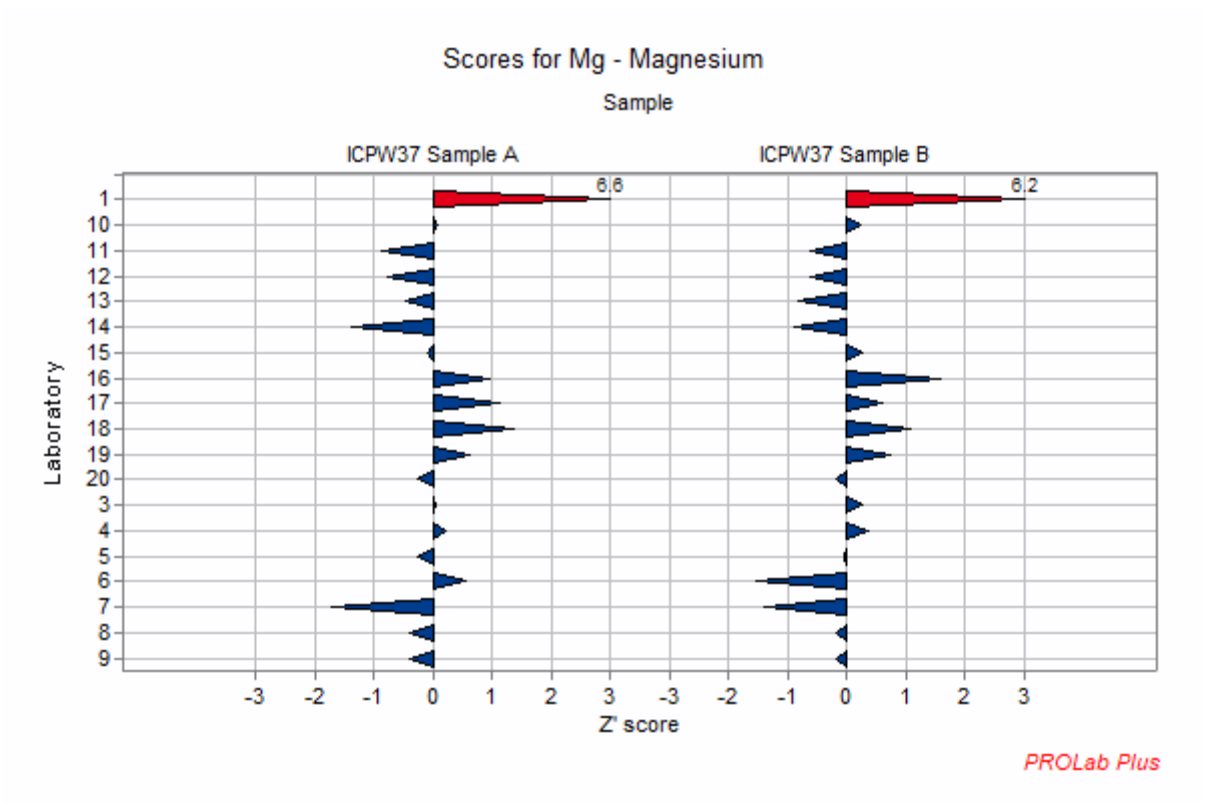

Figure 27. Z' scores for magnesium (Mg).

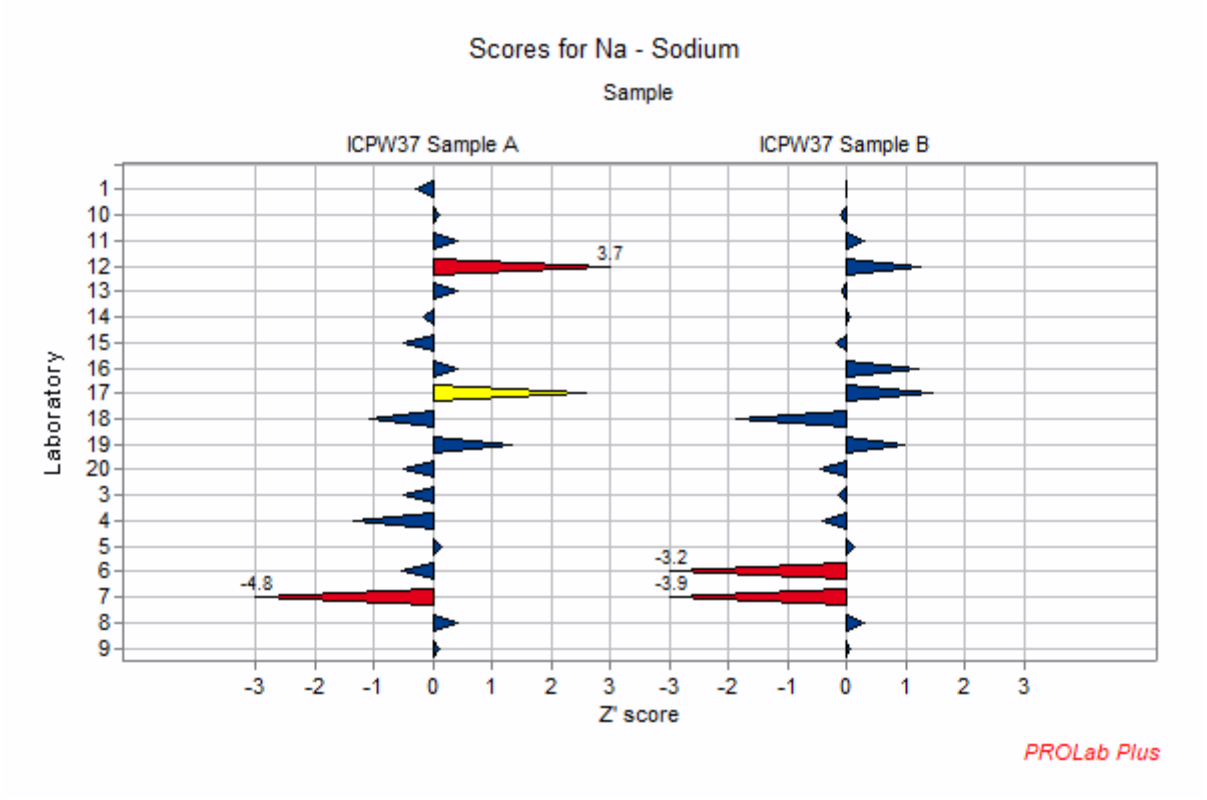

Figure 28. Z' scores for sodium (Na).

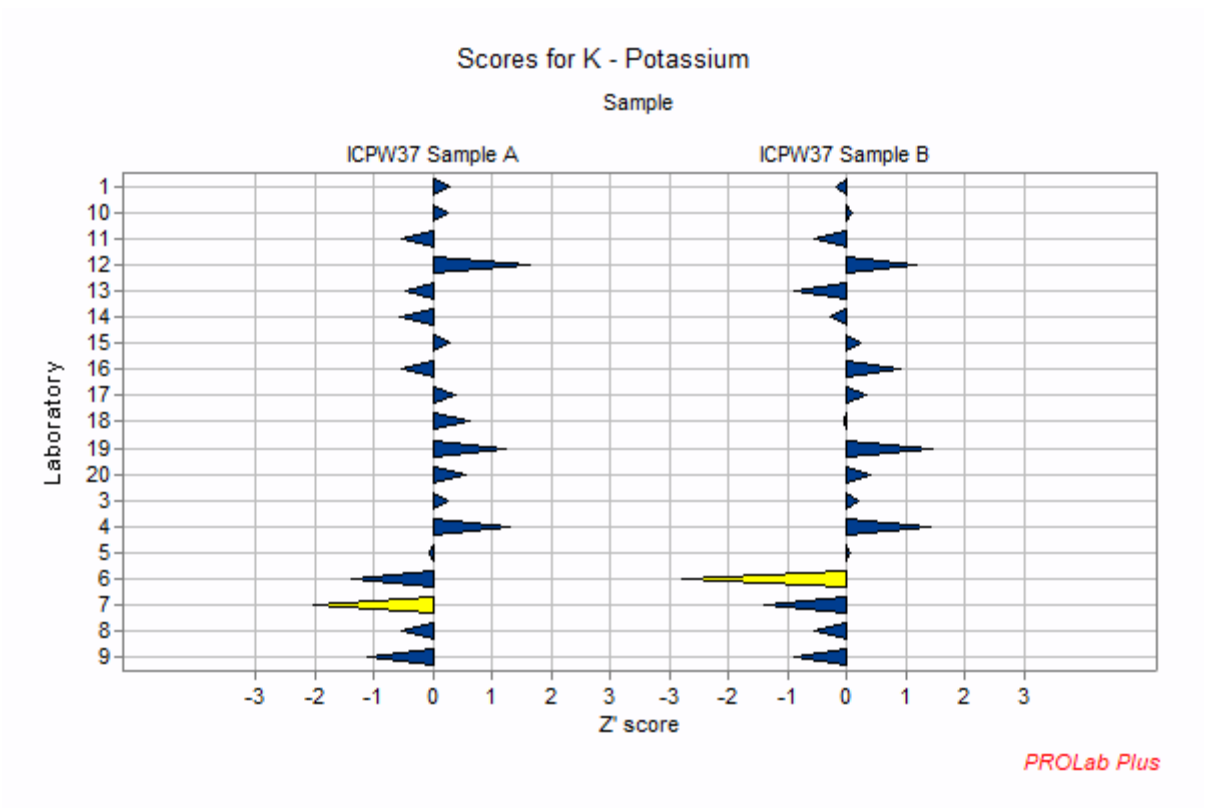

Figure 29. Z' scores for potassium (K).

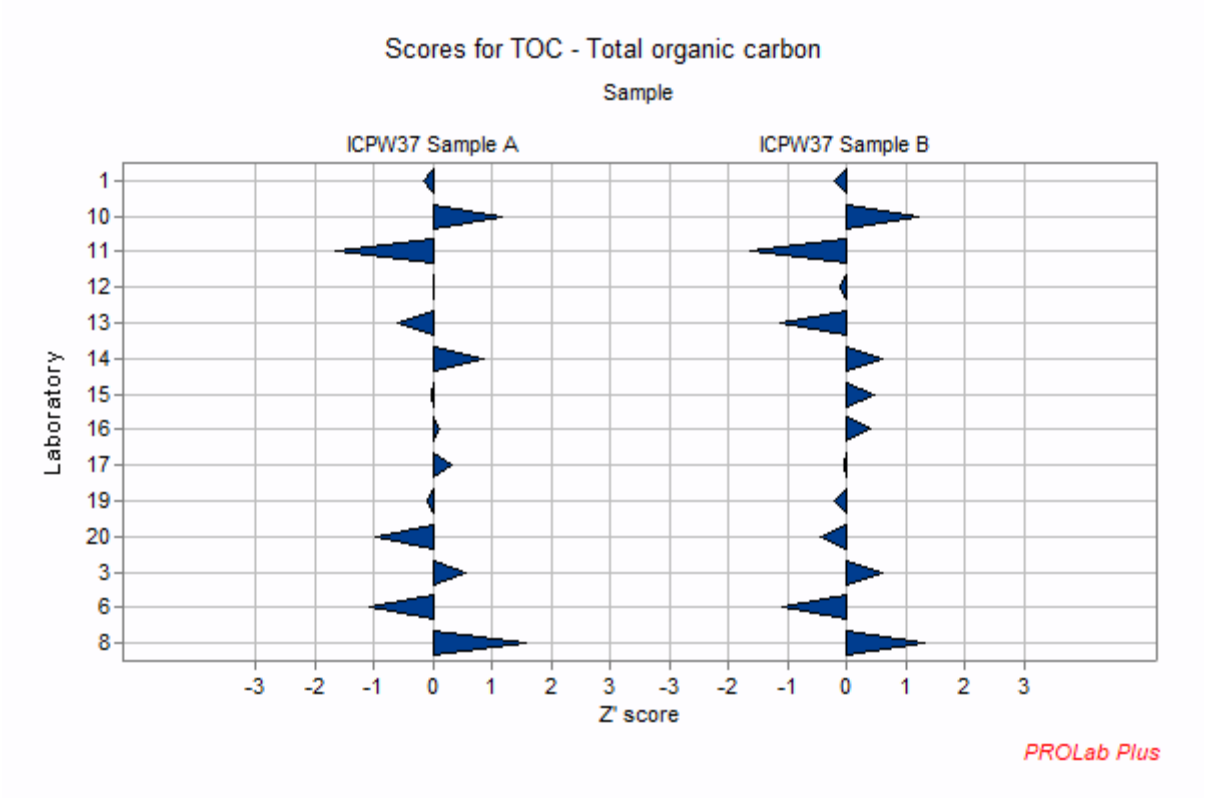

Figure 30. Z' scores for total organic carbon (TOC).

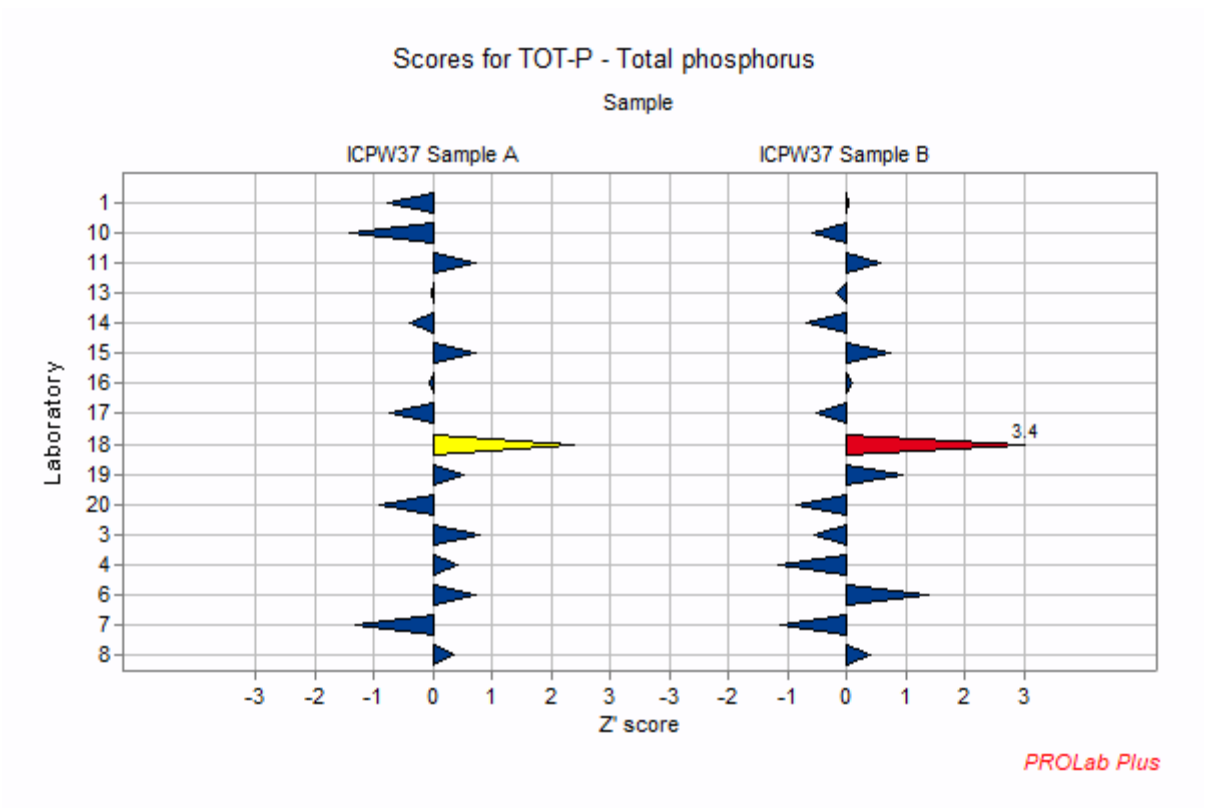

Figure 31. Z' scores for total phosphorus (TOT-P).

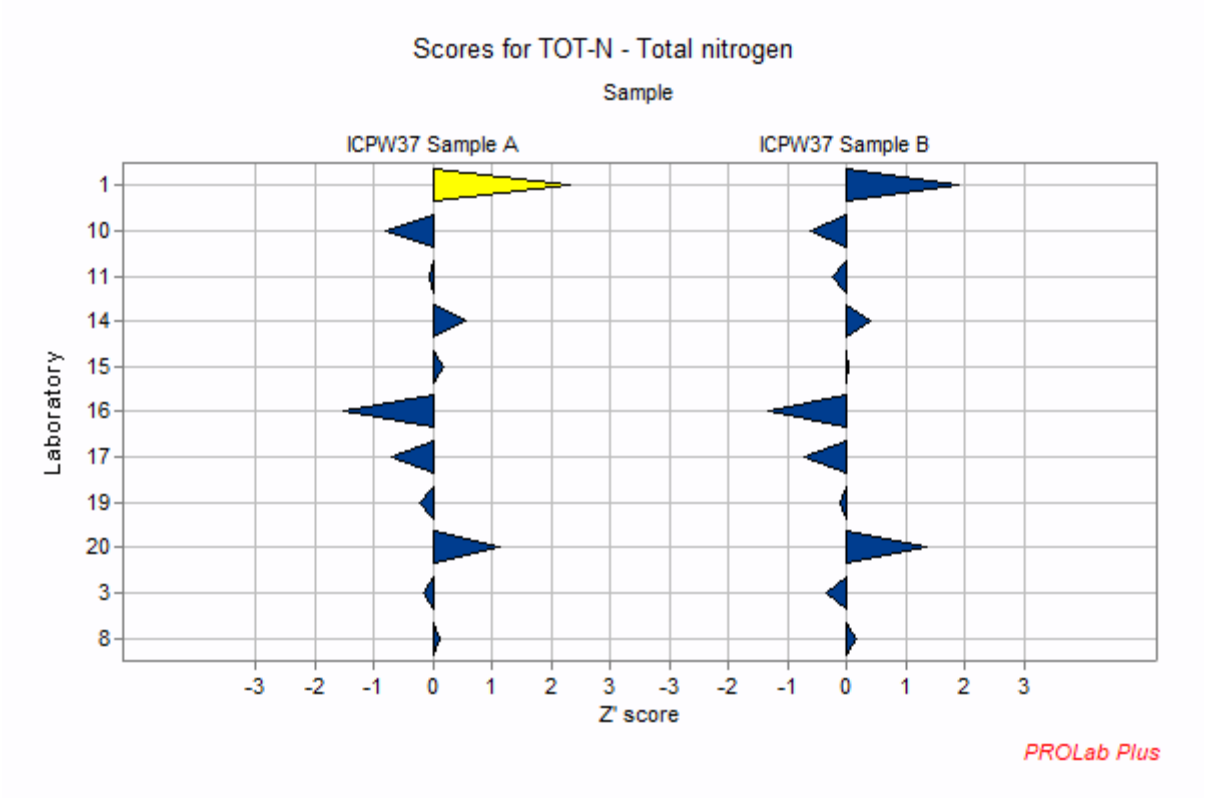

Figure 32. Z' scores for total nitrogen (Tot-N).

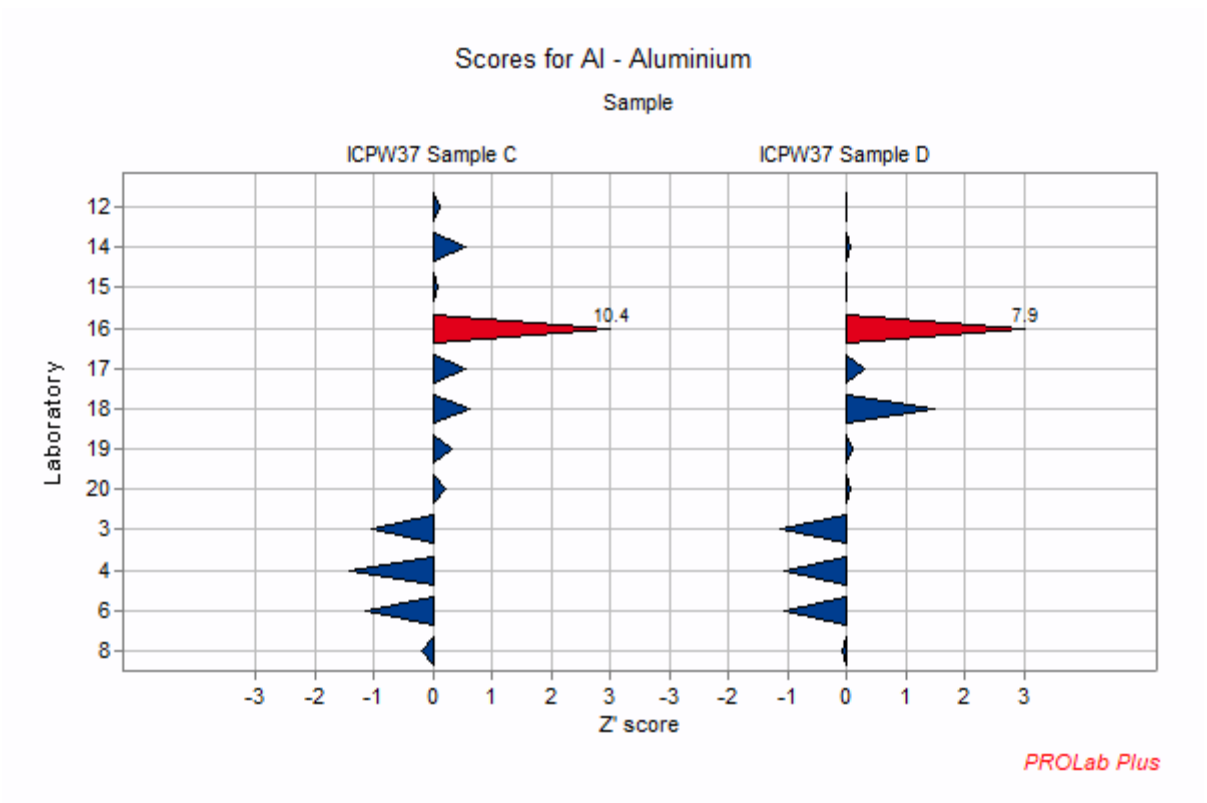

Figure 33. Z' scores for aluminum (Al).

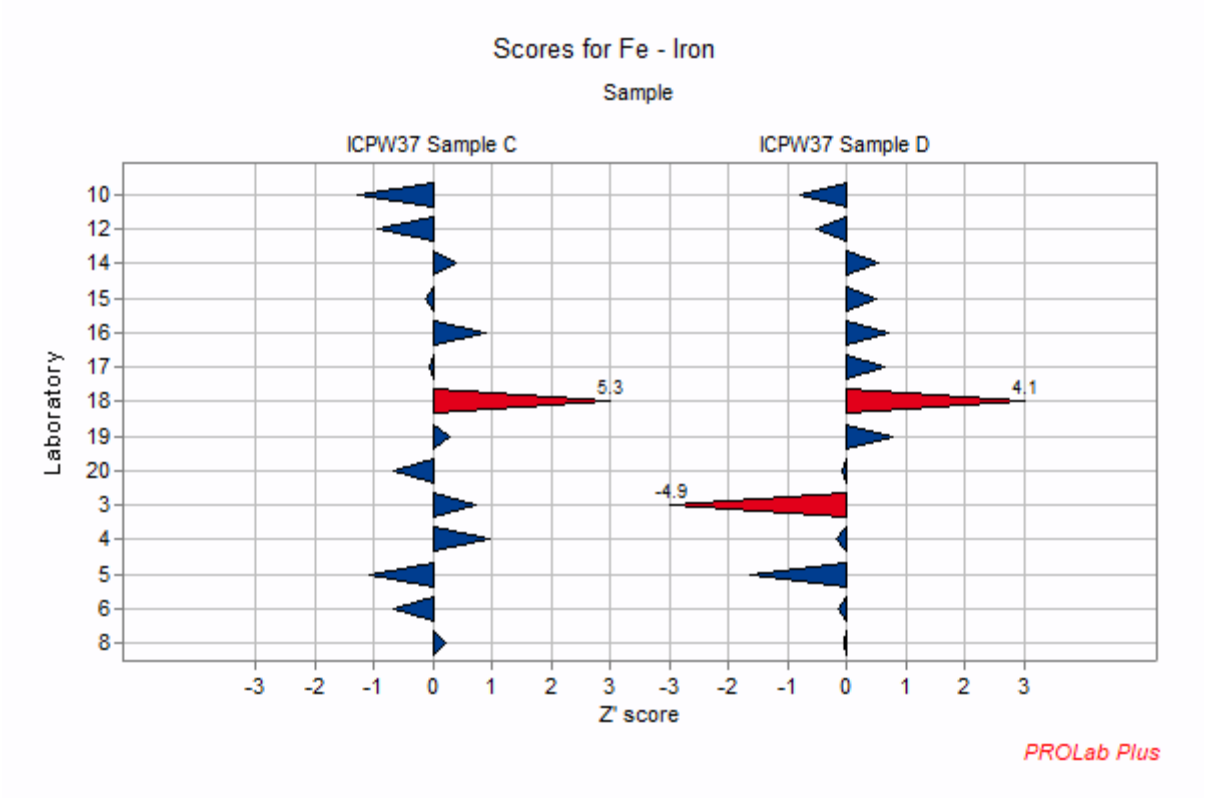

Figure 34. Z' scores for iron (Fe).

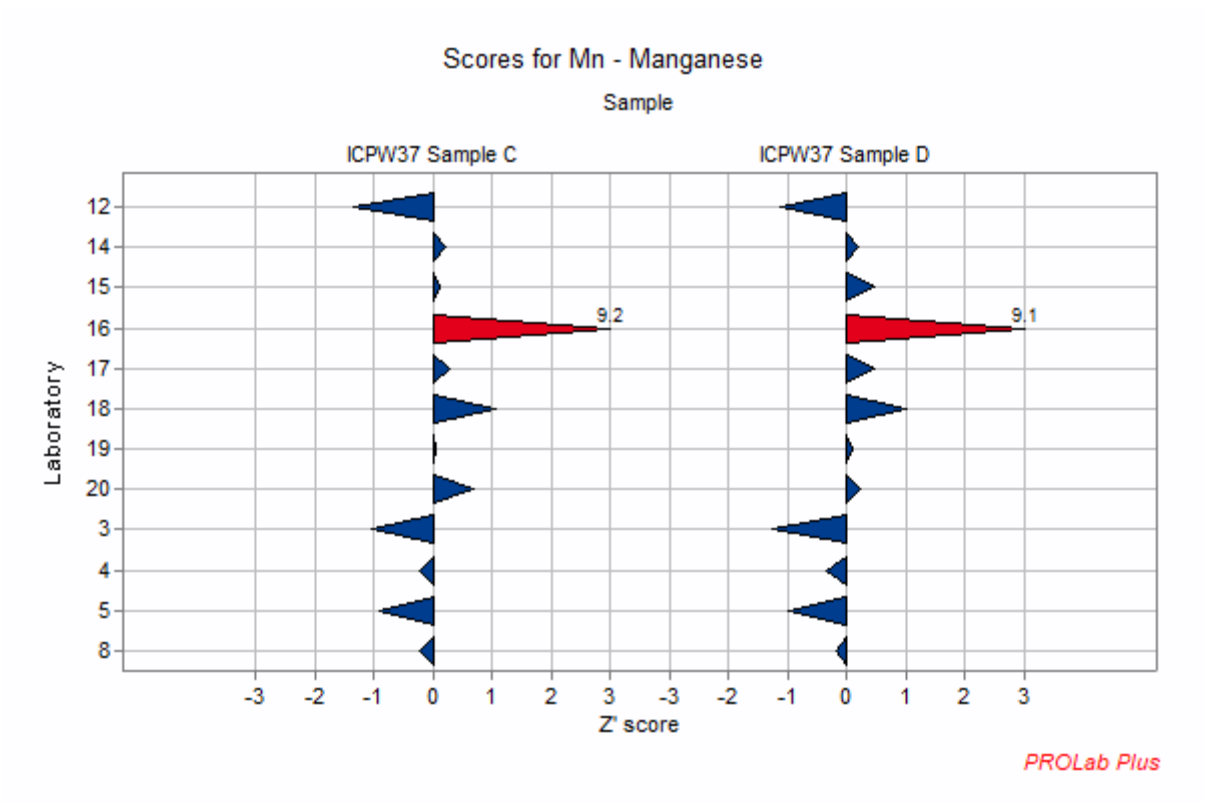

Figure 35. Z' scores for manganese (Mn).

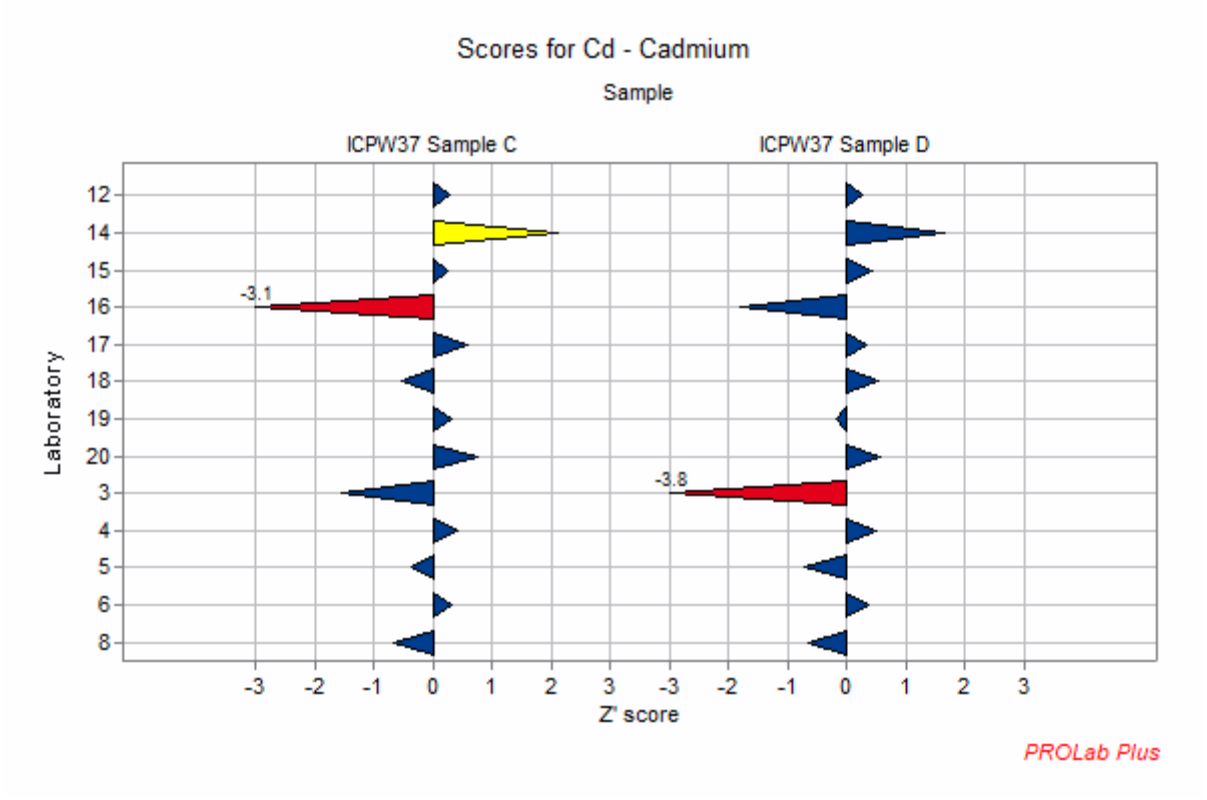

Figure 36. Z' scores for cadmium (Cd).

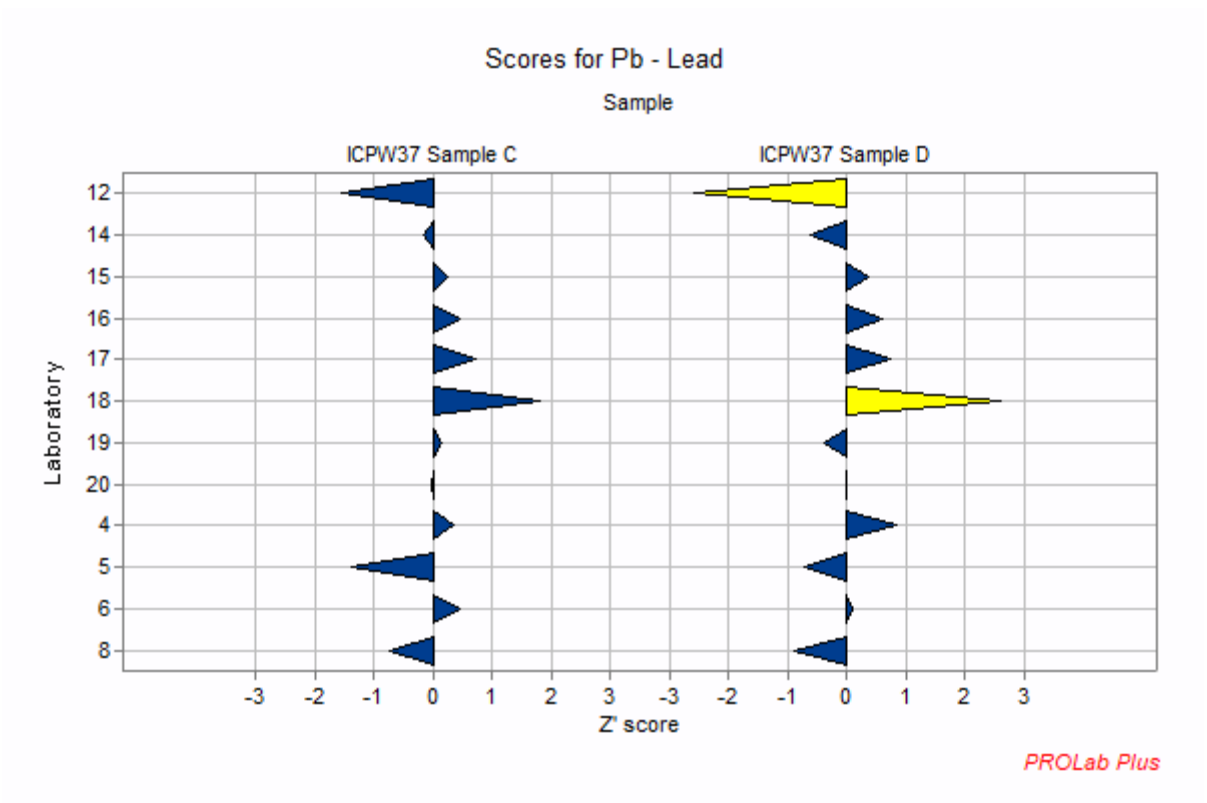

Figure 37. Z' scores for lead (Pb).

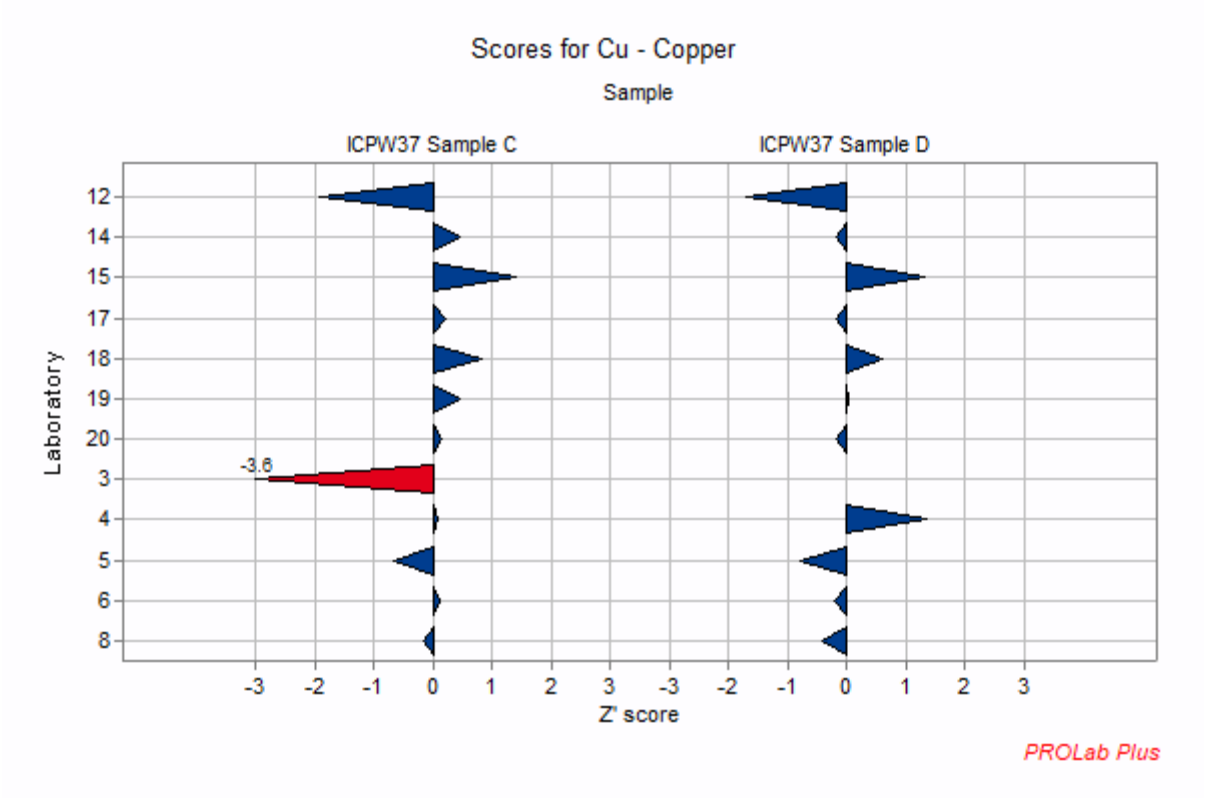

Figure 38. Z' scores for copper (Cu).

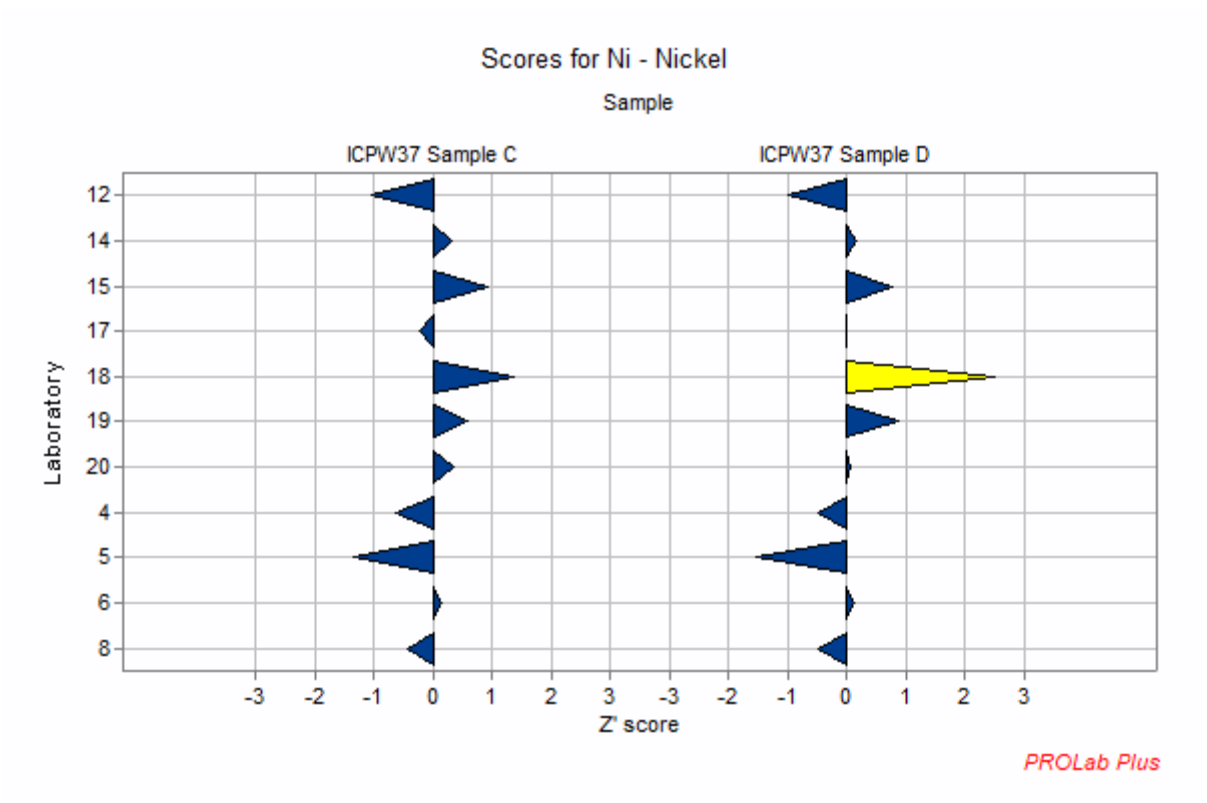

Figure 39. Z' scores for nickel (Ni).

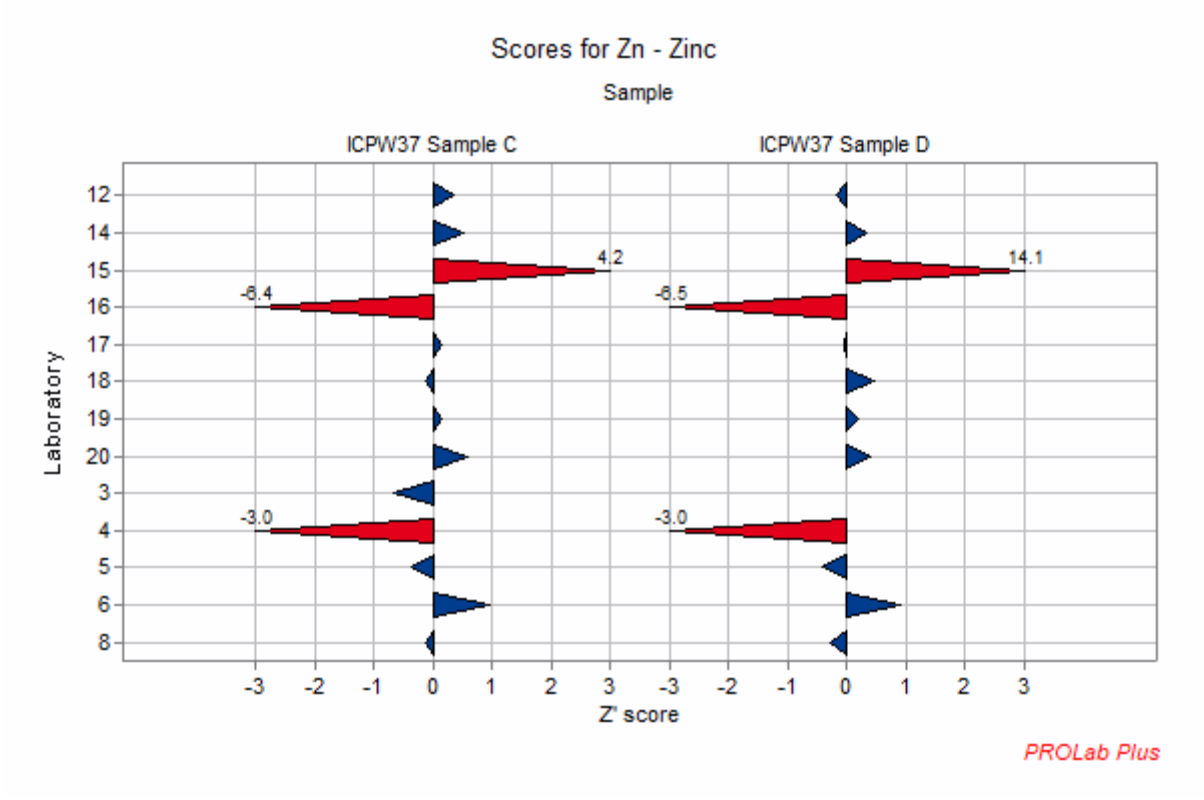

Figure 40. Z' scores for zinc (Zn).

D.2 Visual representation of reported values and the techniques used

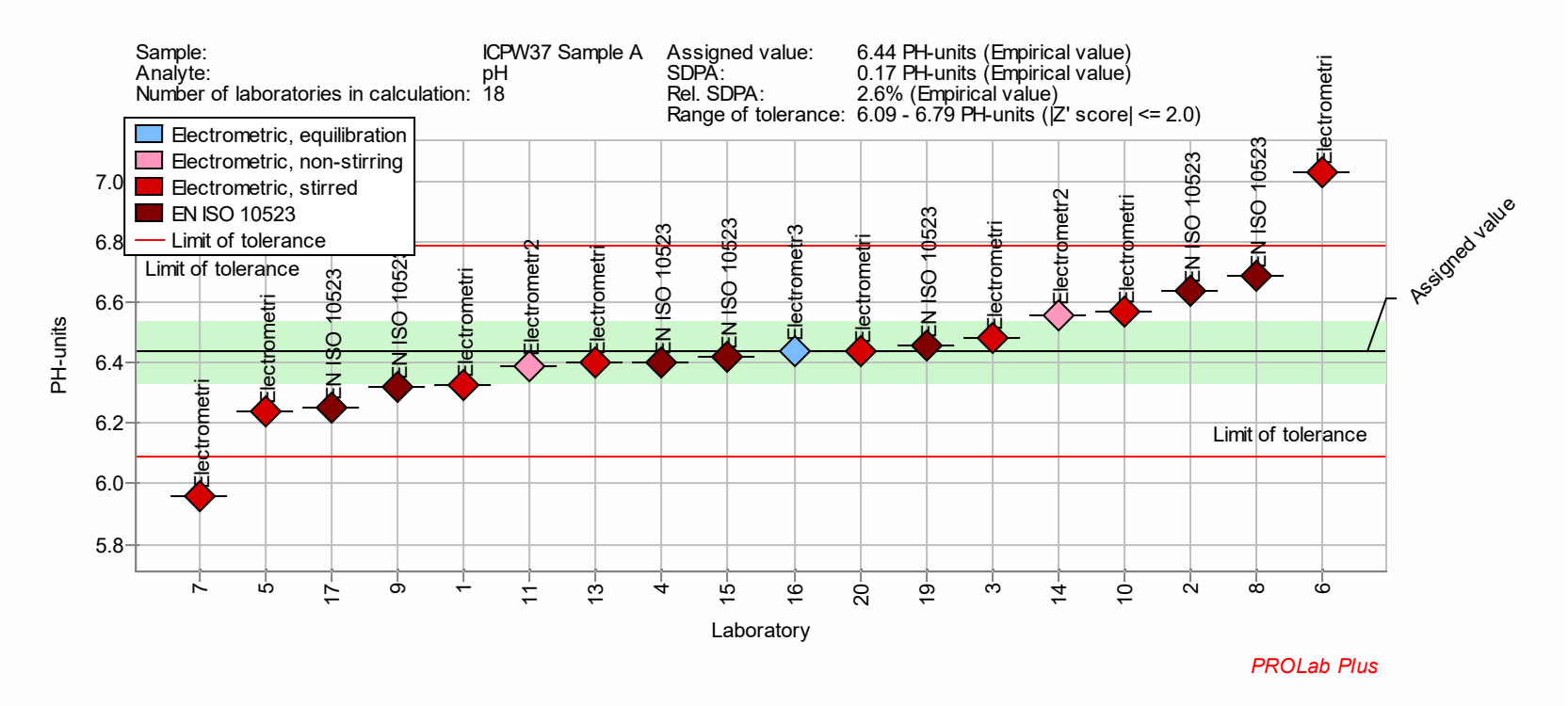

Figure 41. Reported values of pH in sample A, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

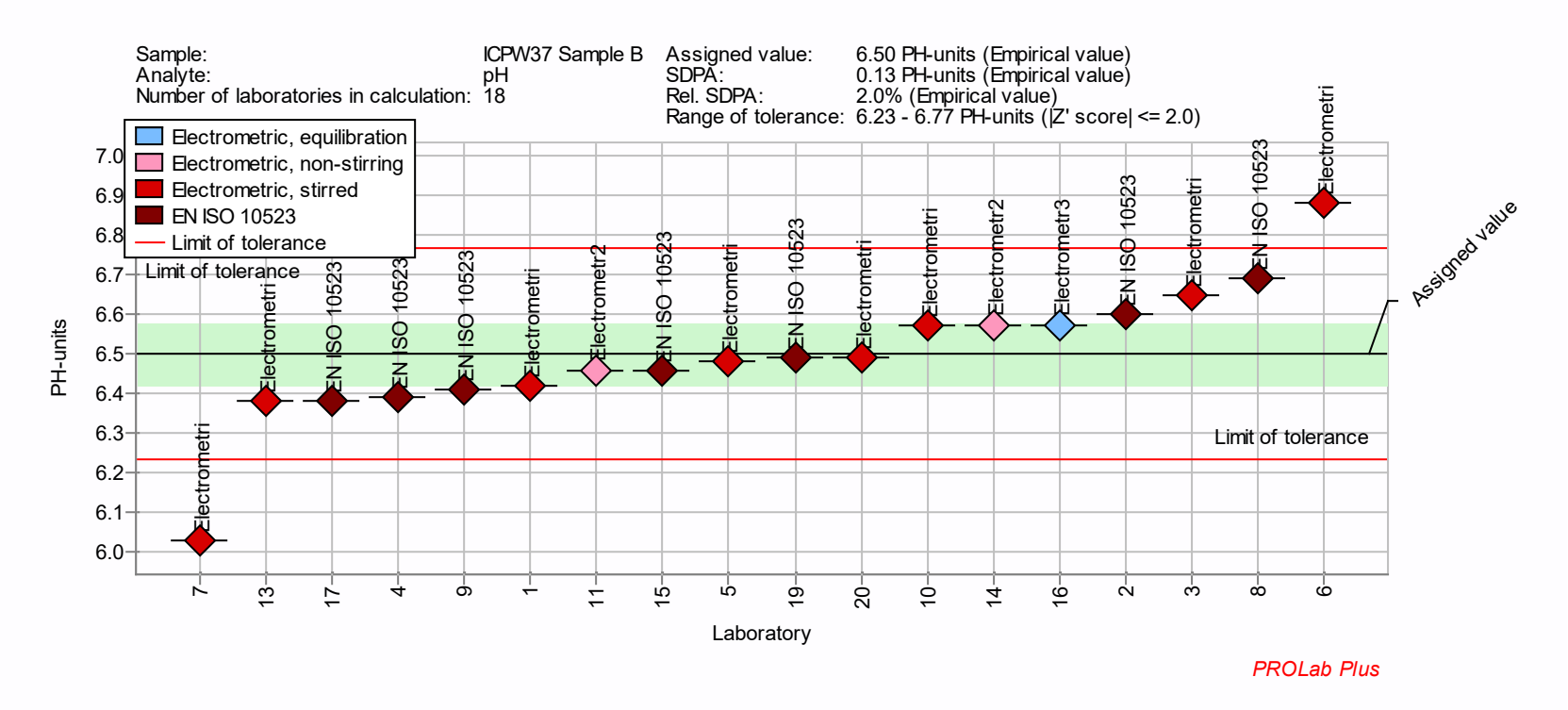

Figure 42. Reported values of pH in sample B, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

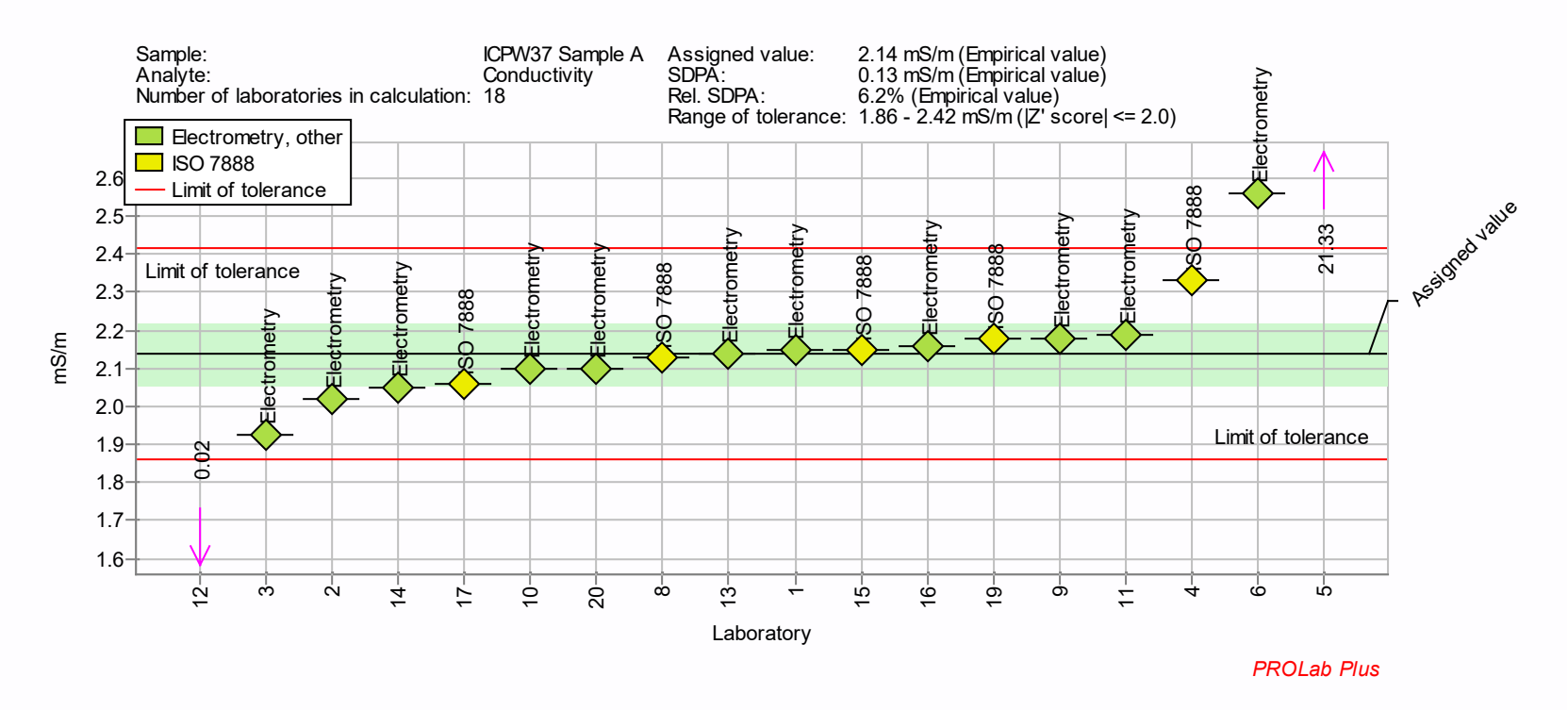

Figure 43. Reported values of conductivity in sample A, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

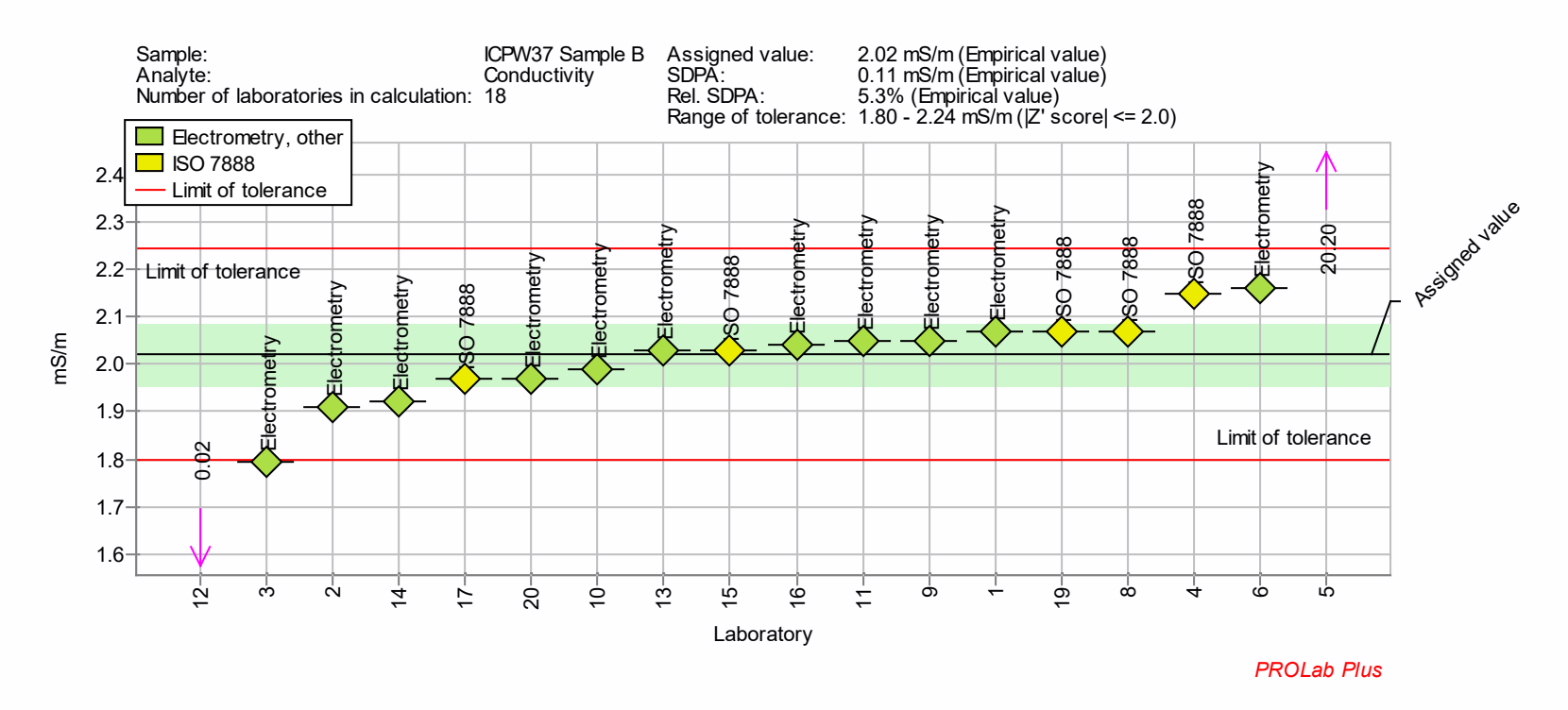

Figure 44. Reported values of conductivity in sample B, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

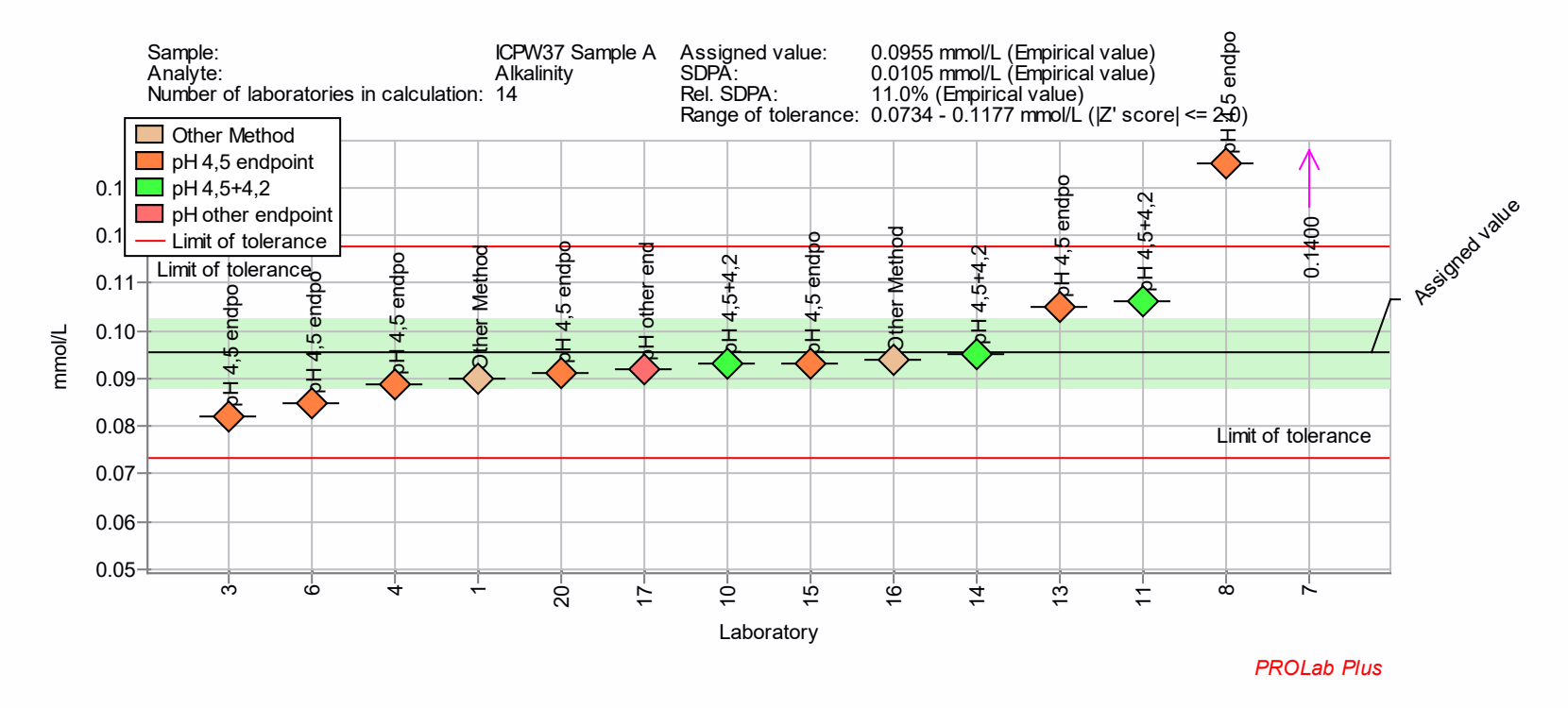

Figure 45. Reported values of alkalinity in sample A, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

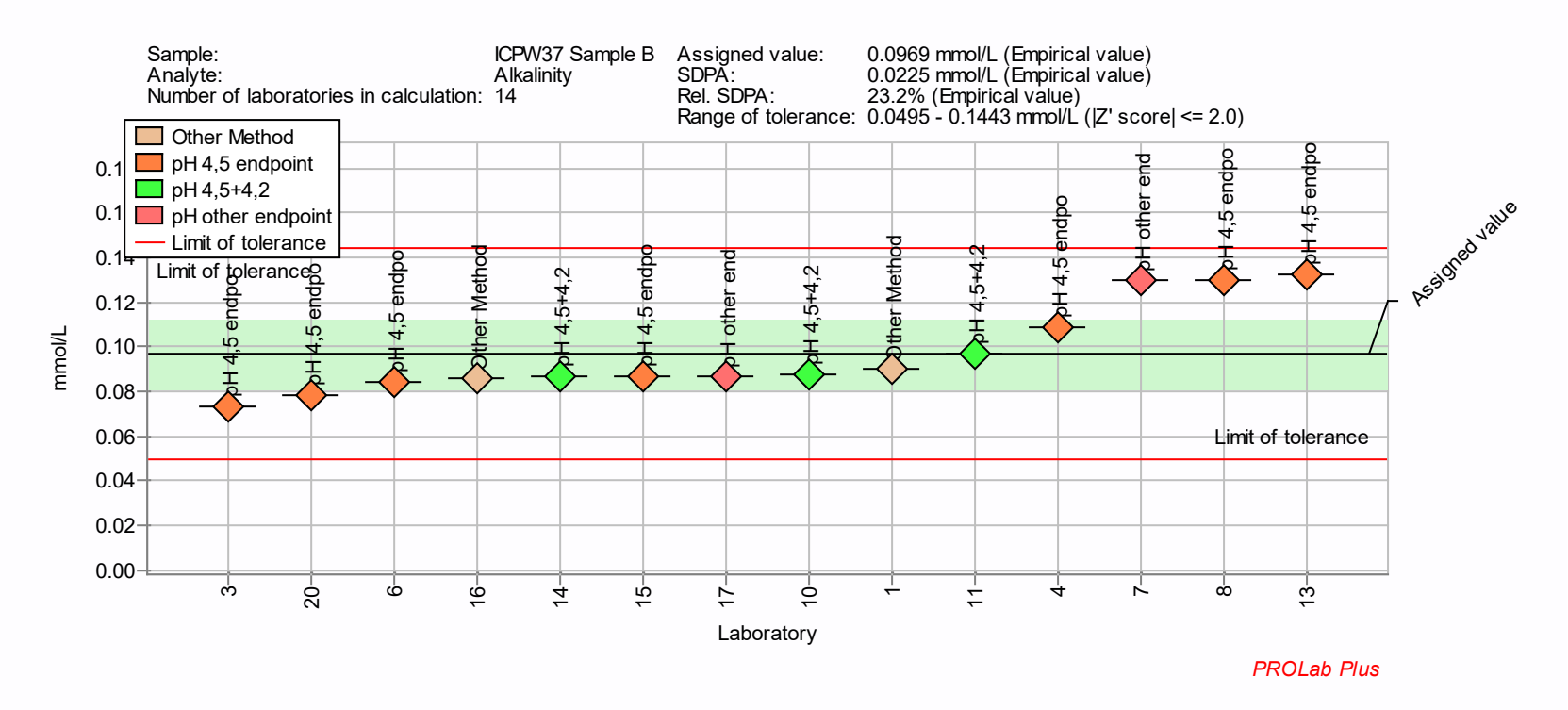

Figure 46. Reported values of alkalinity in sample B, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

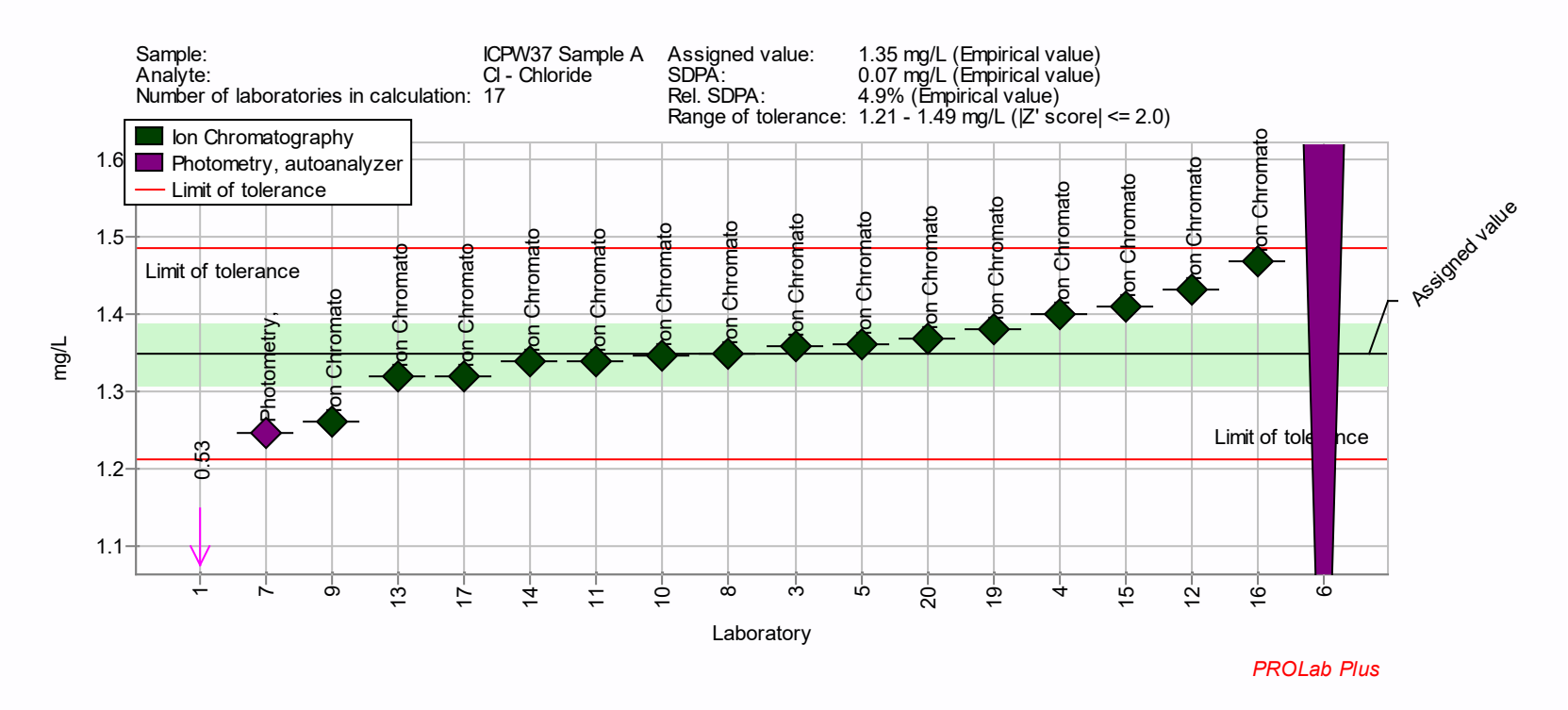

Figure 47. Reported values of chloride in sample A, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

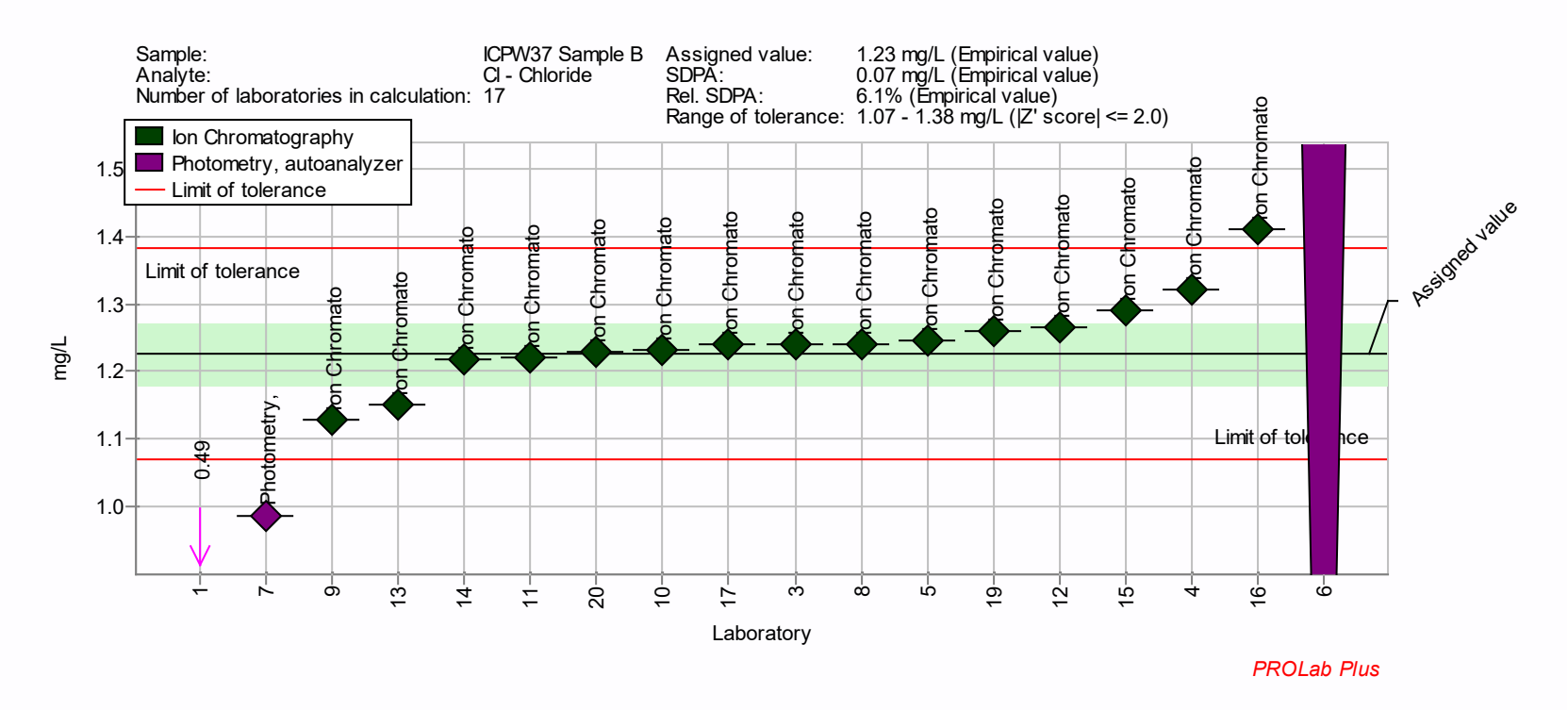

Figure 48. Reported values of chloride in sample B, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

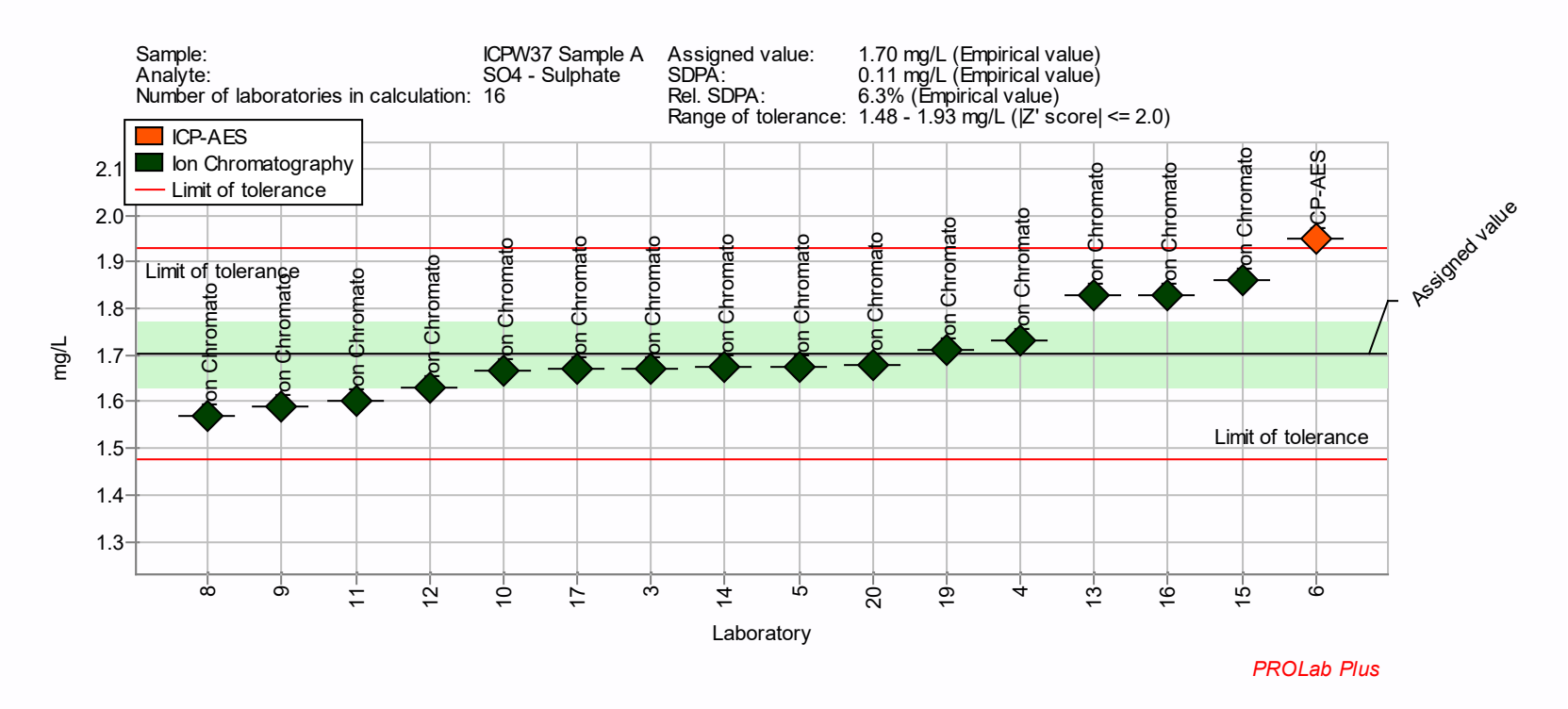

Figure 49. Reported values of sulphate in sample A, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

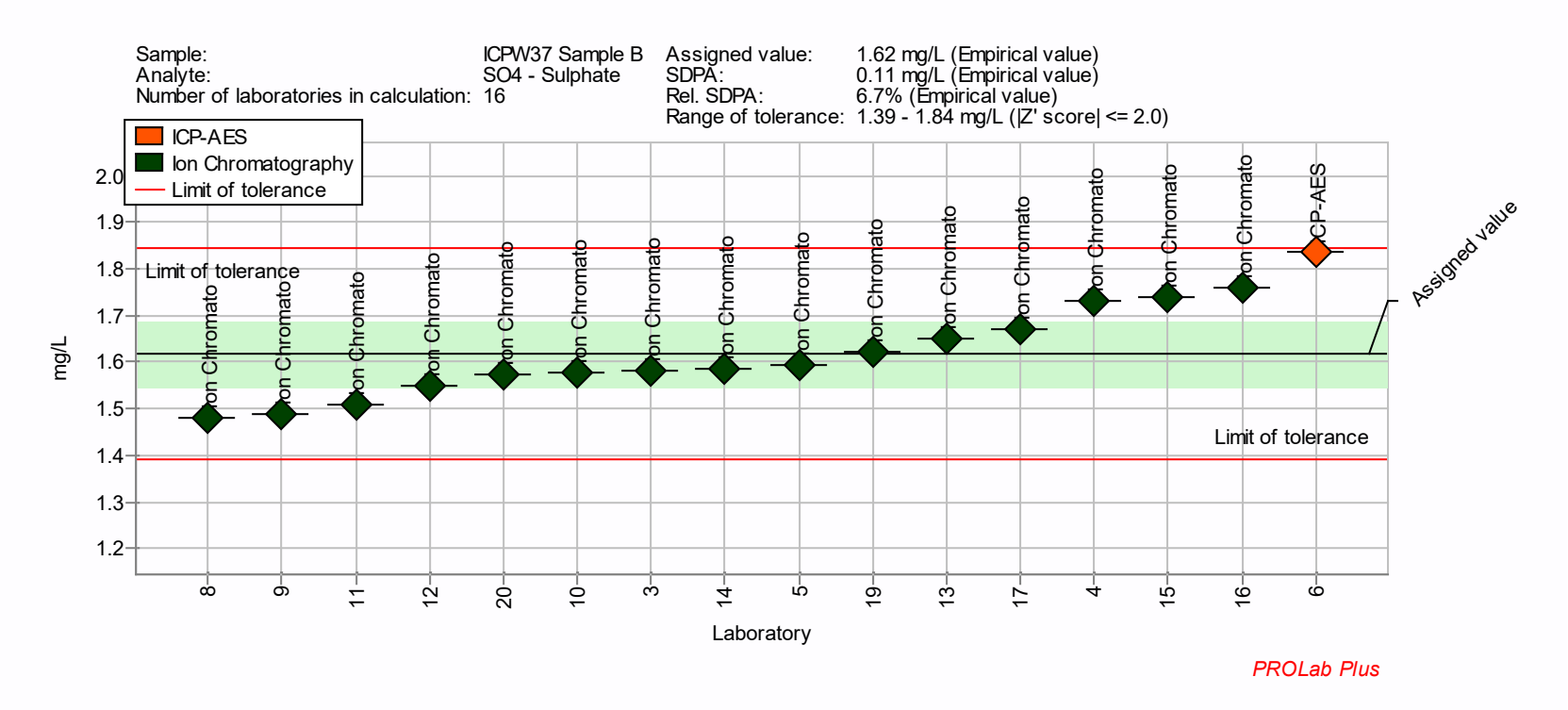

Figure 50. Reported values of sulphate in sample B, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

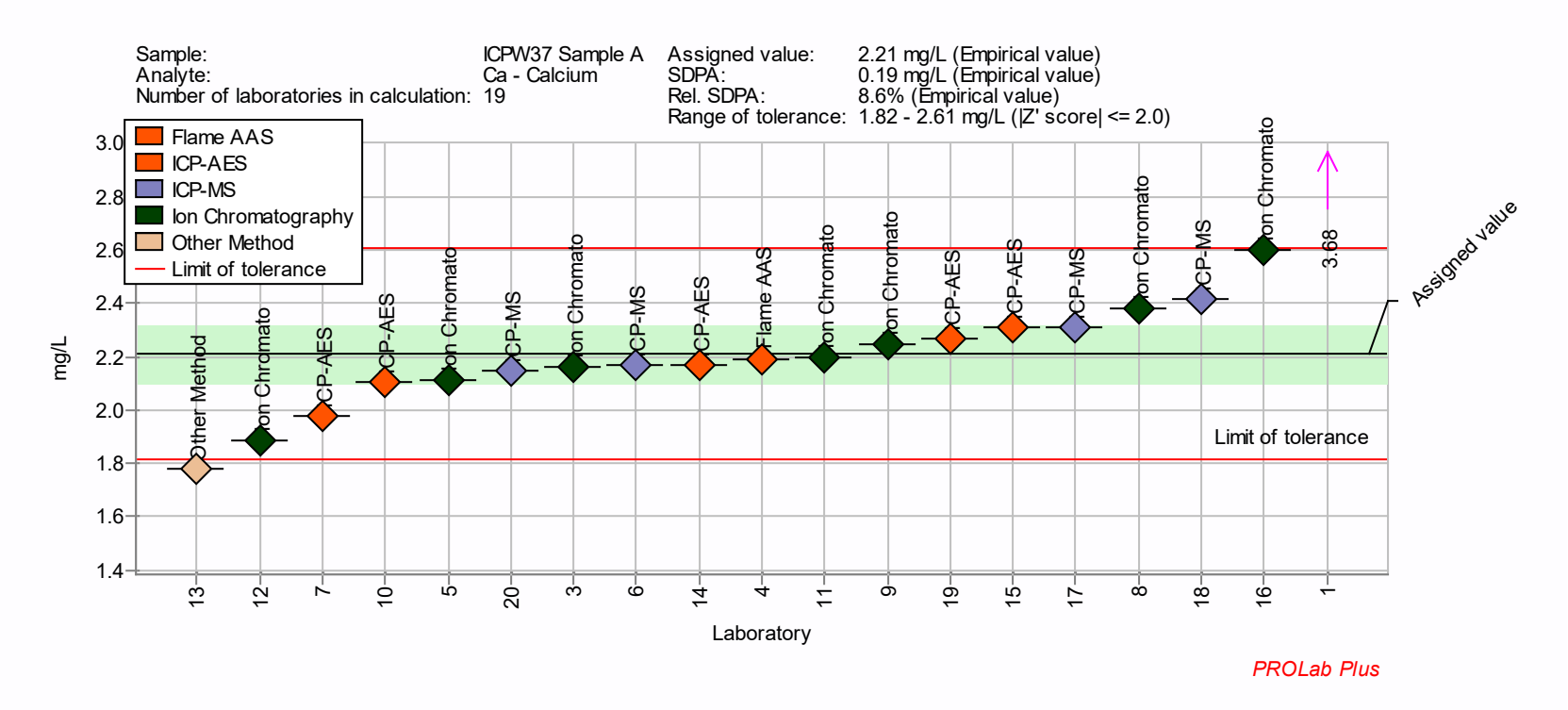

Figure 51. Reported values of calcium in sample A, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

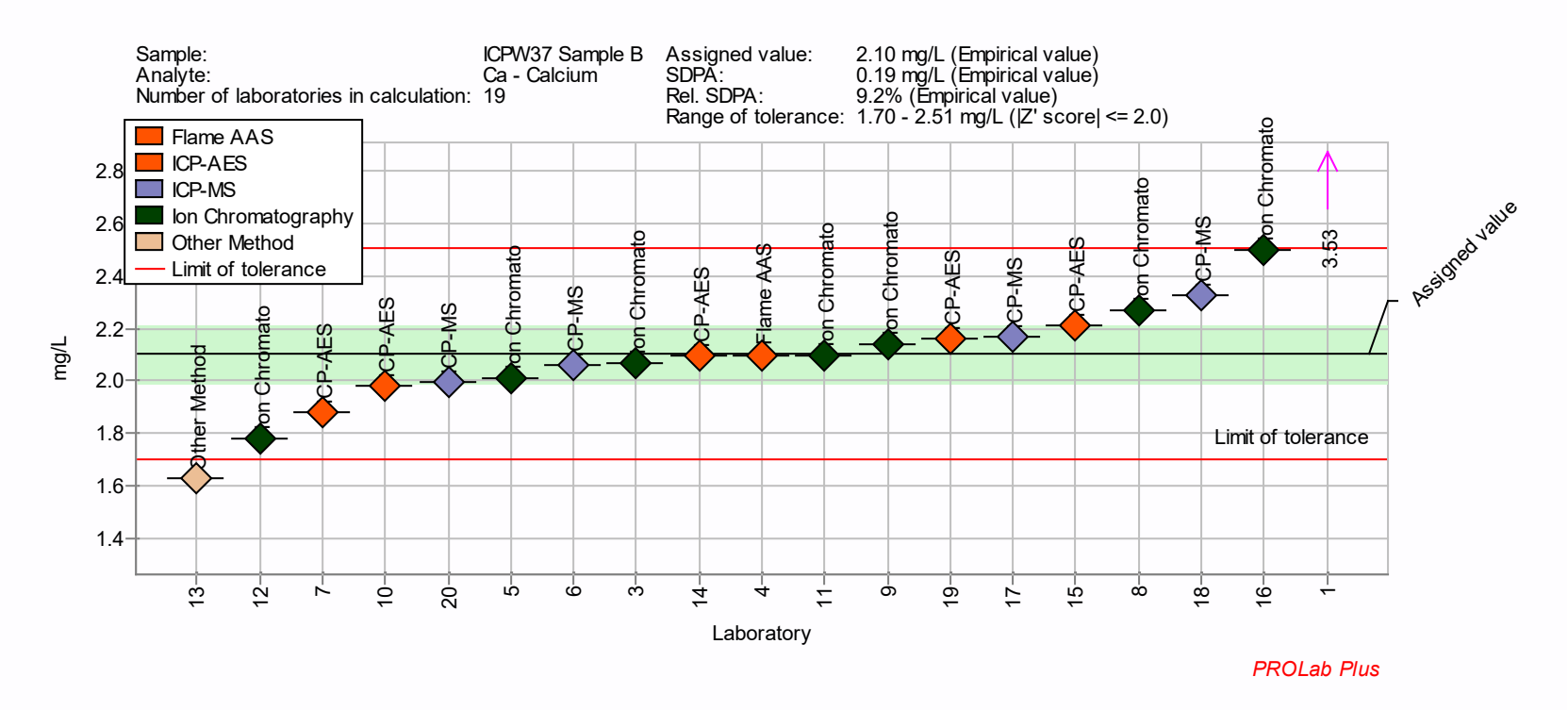

Figure 52. Reported values of calcium in sample B, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

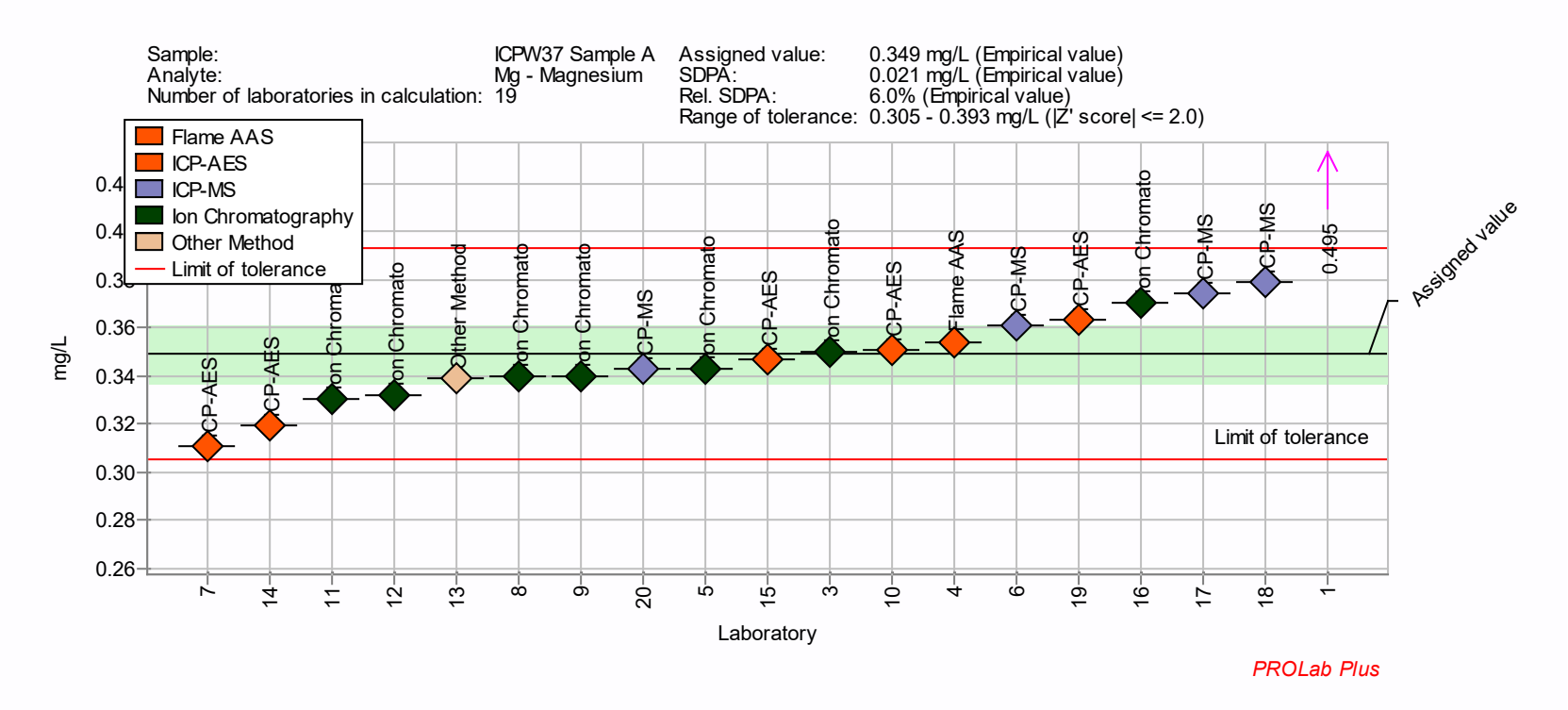

Figure 53. Reported values of magnesium in sample A, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

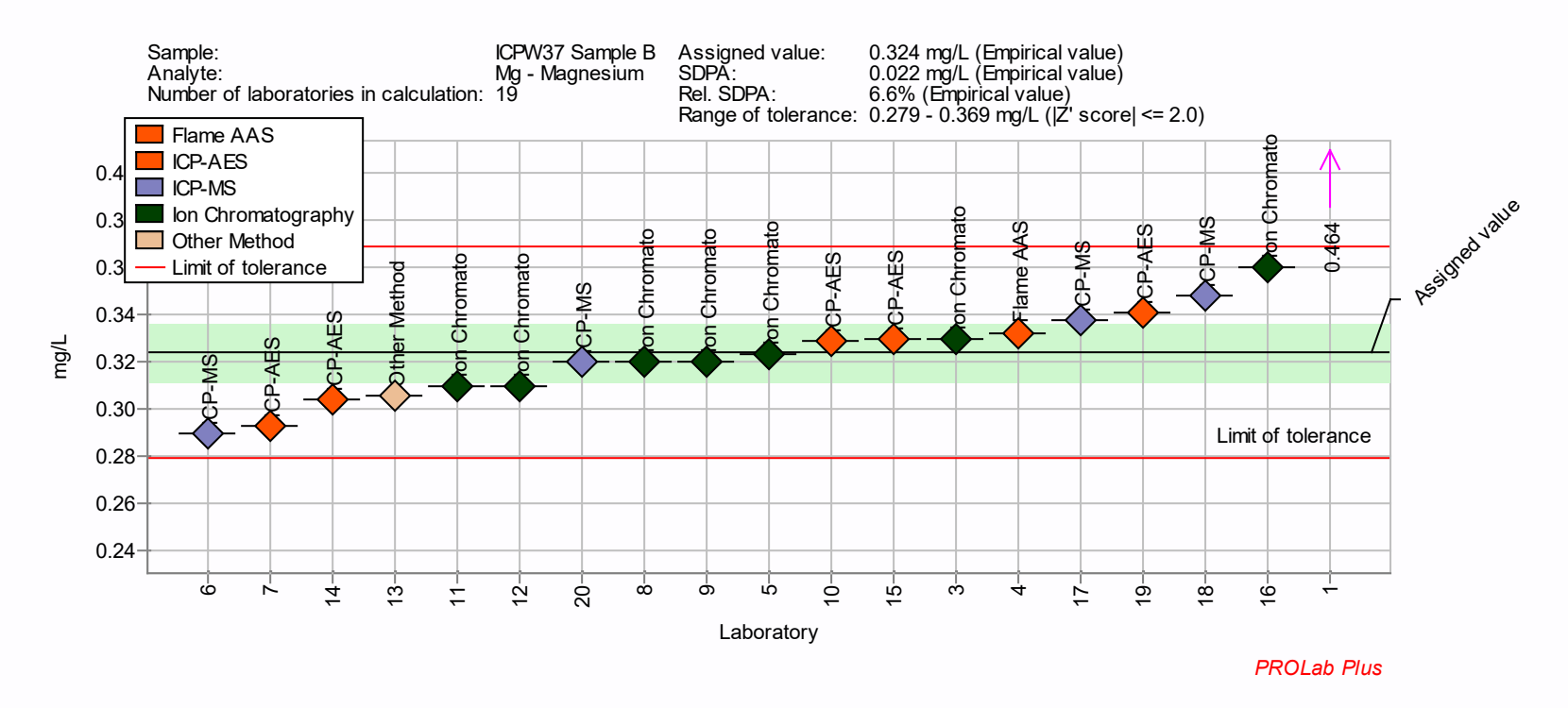

Figure 54. Reported values of magnesium in sample B, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

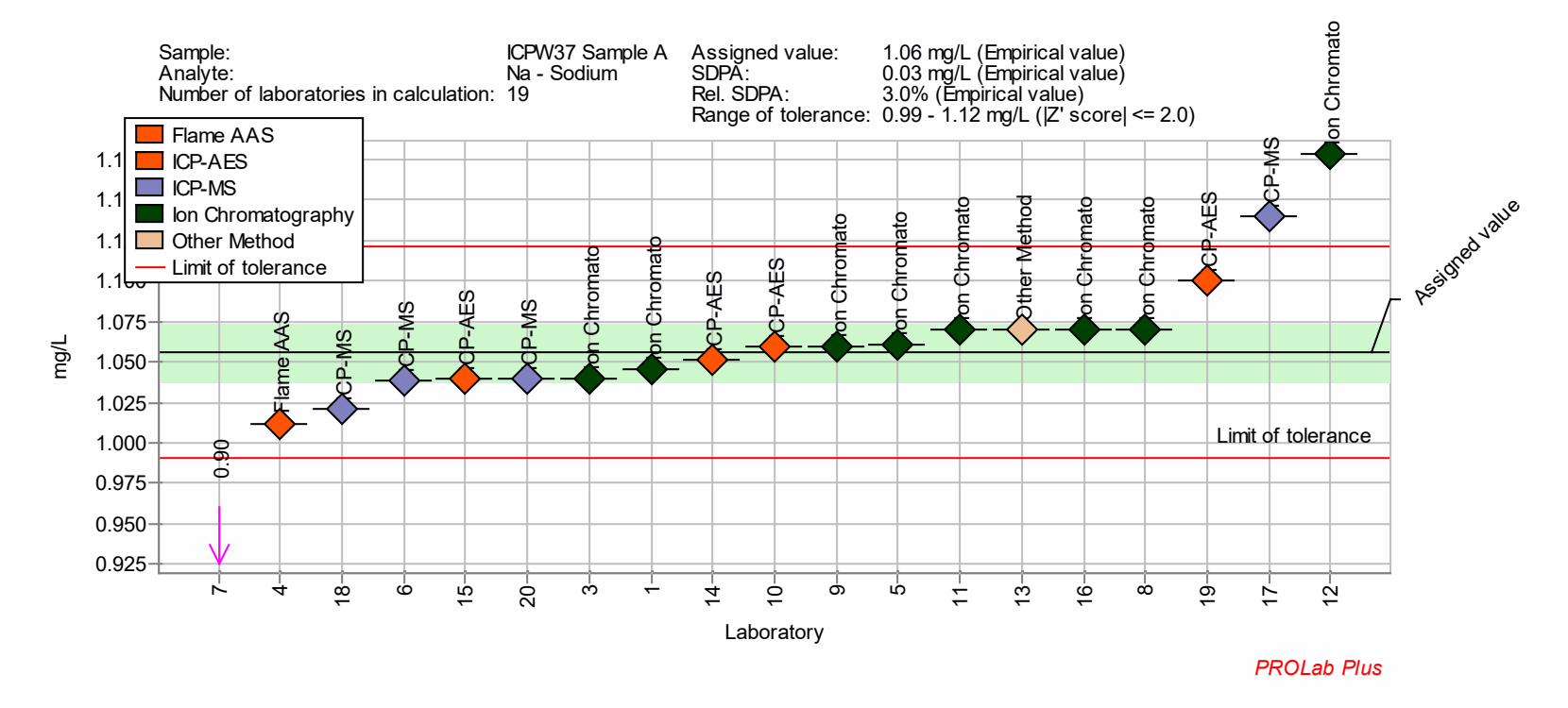

Figure 55. Reported values of sodium in sample A, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

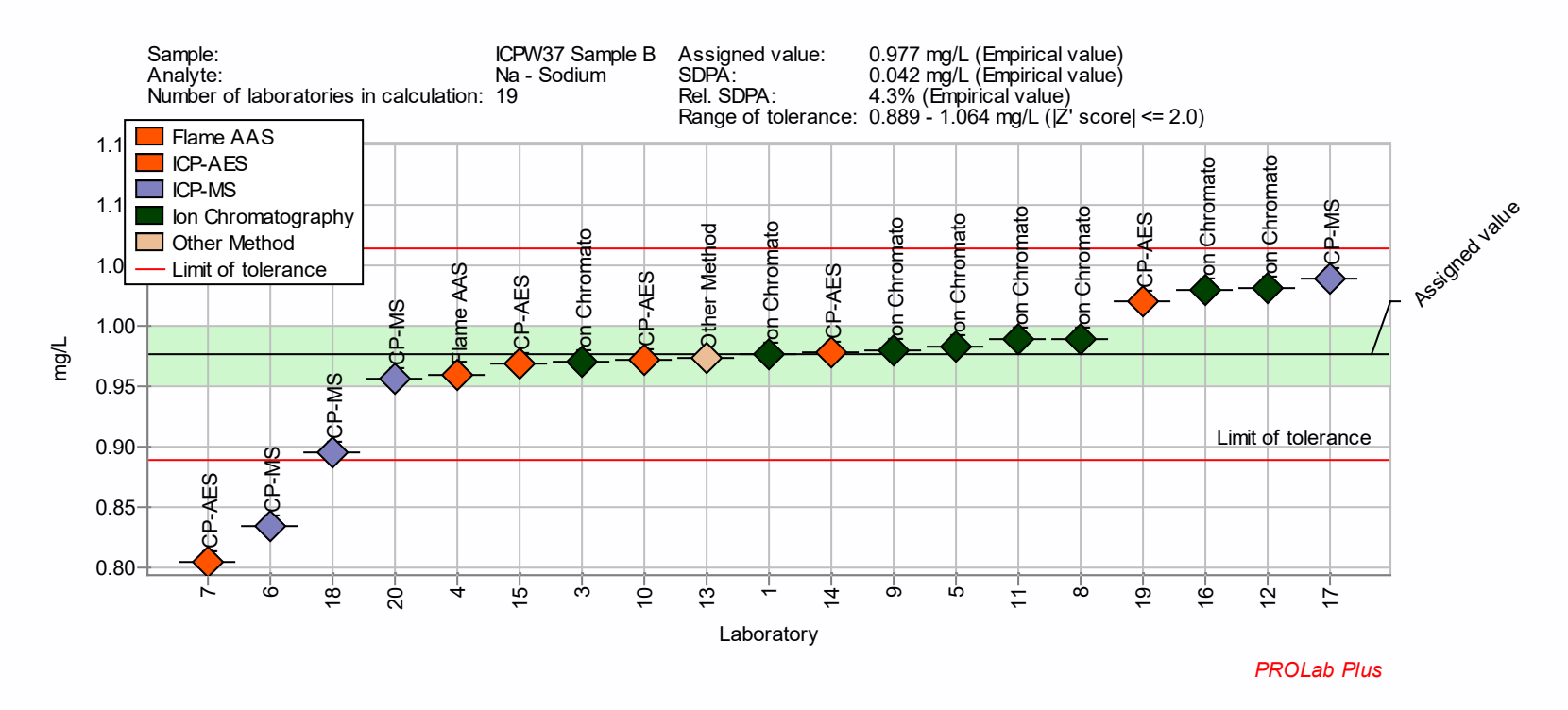

Figure 56. Reported values of sodium in sample B, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

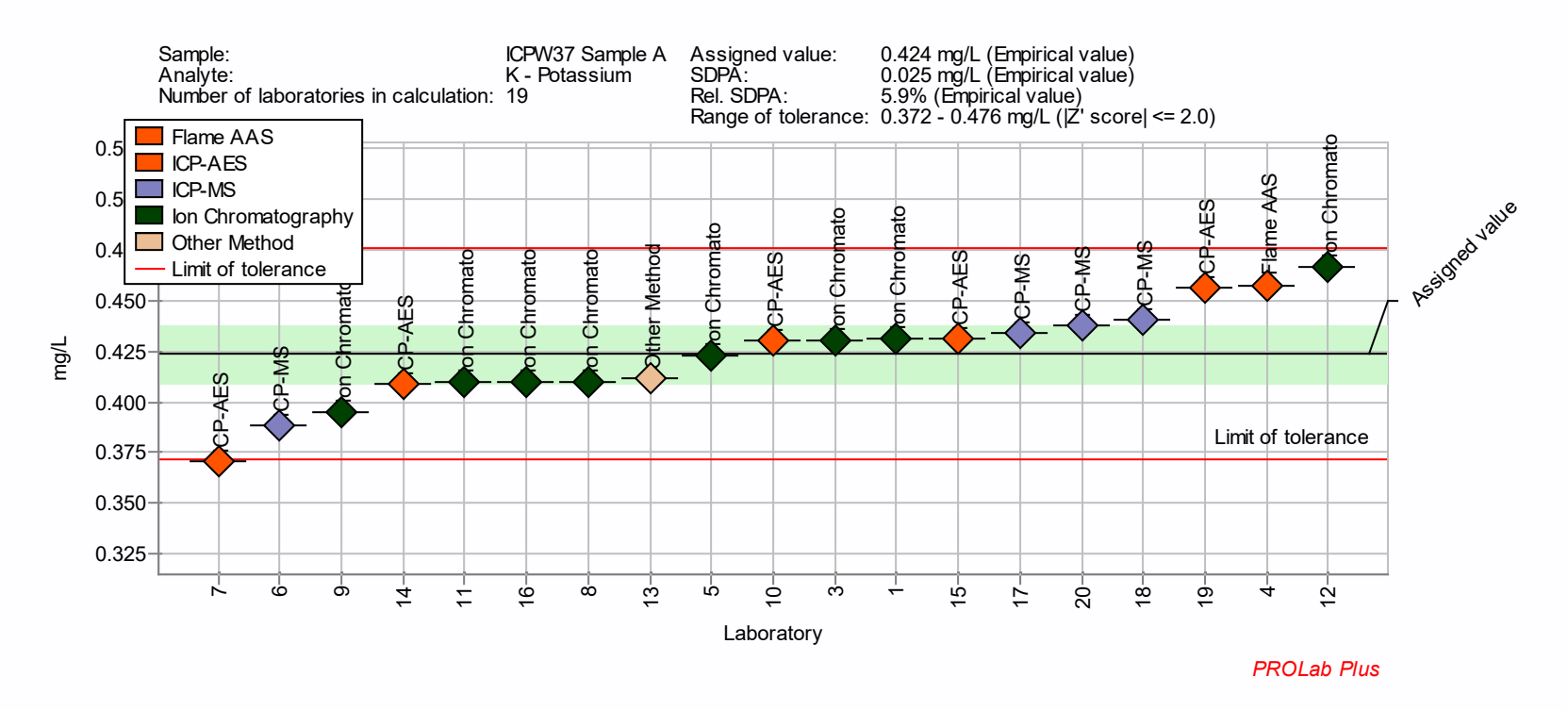

Figure 57. Reported values of potassium in sample A, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

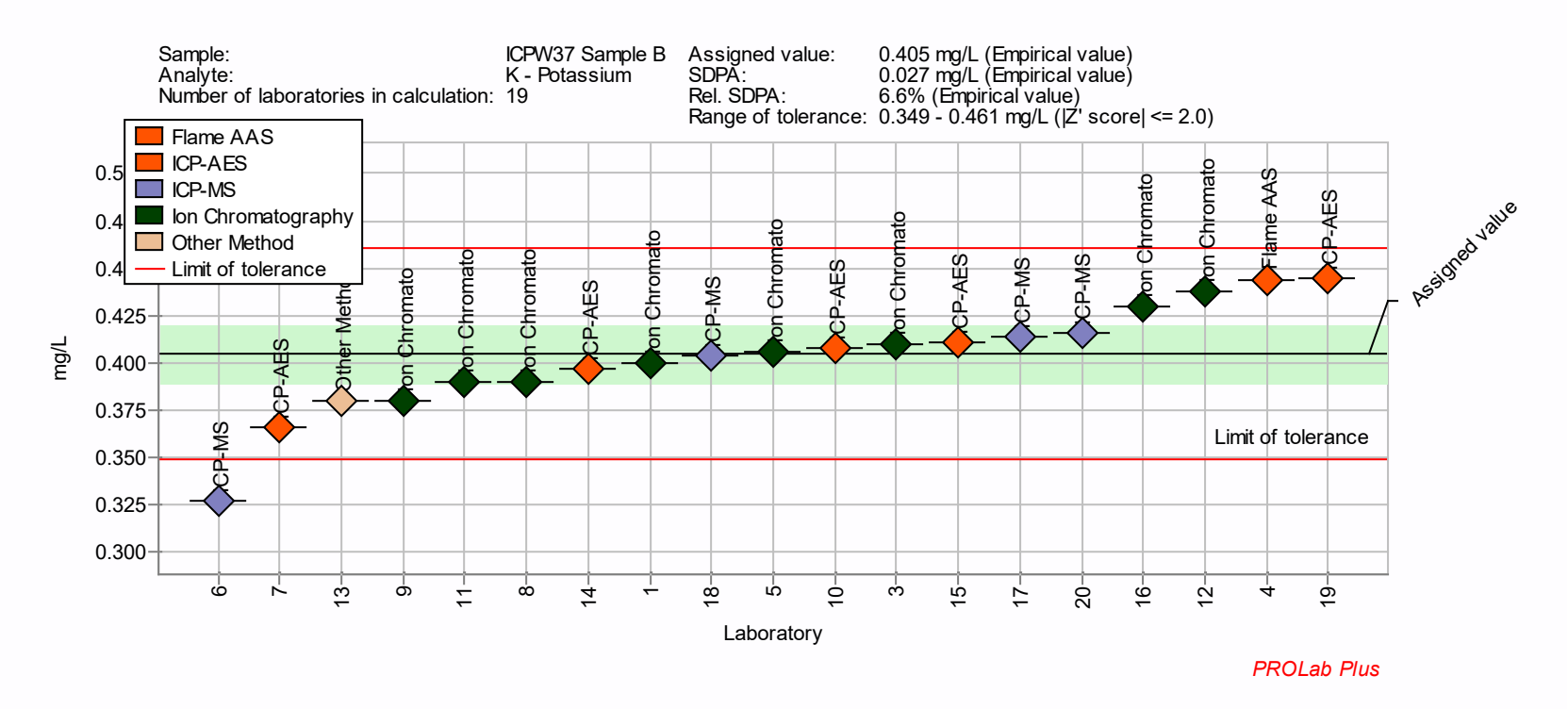

Figure 58. Reported values of potassium in sample B, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

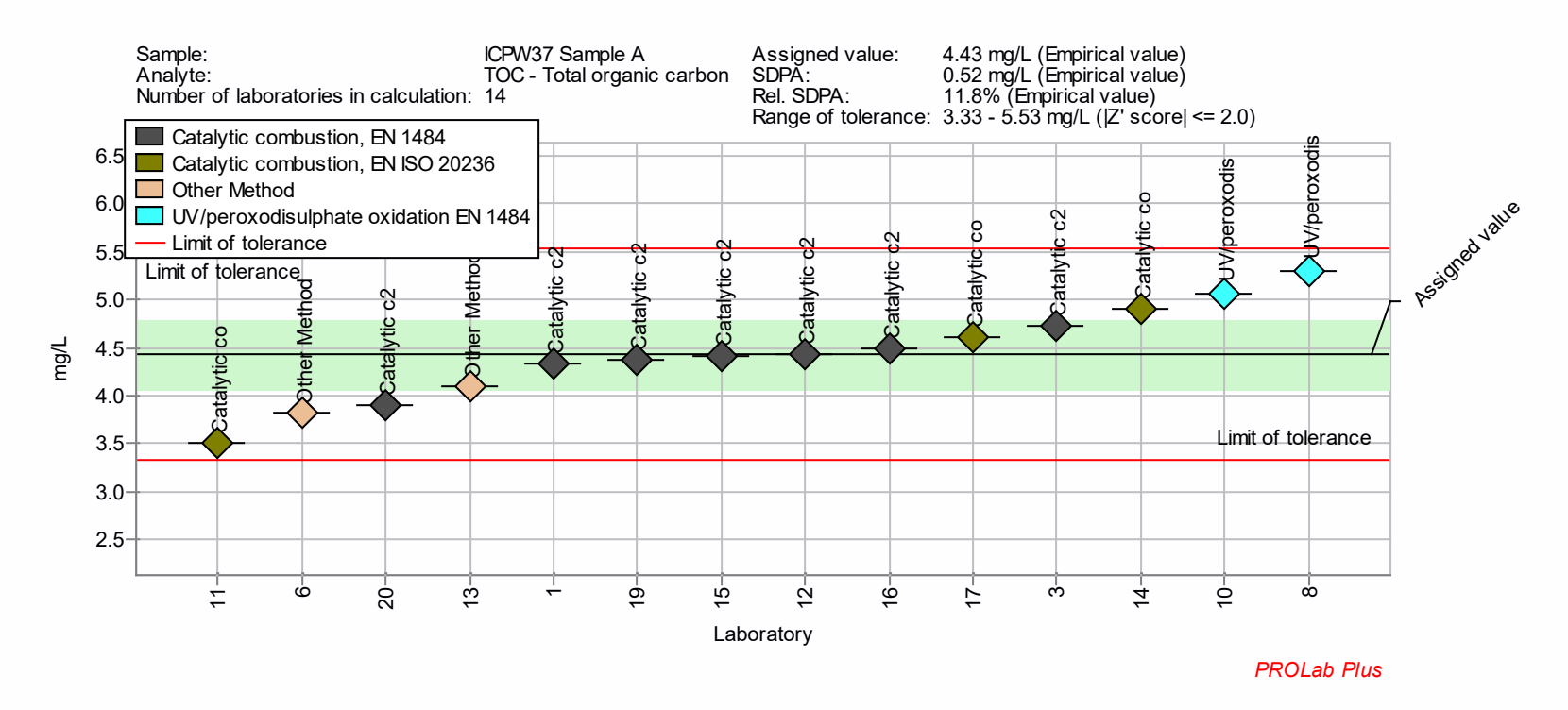

Figure 59. Reported values of total organic carbon in sample A, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

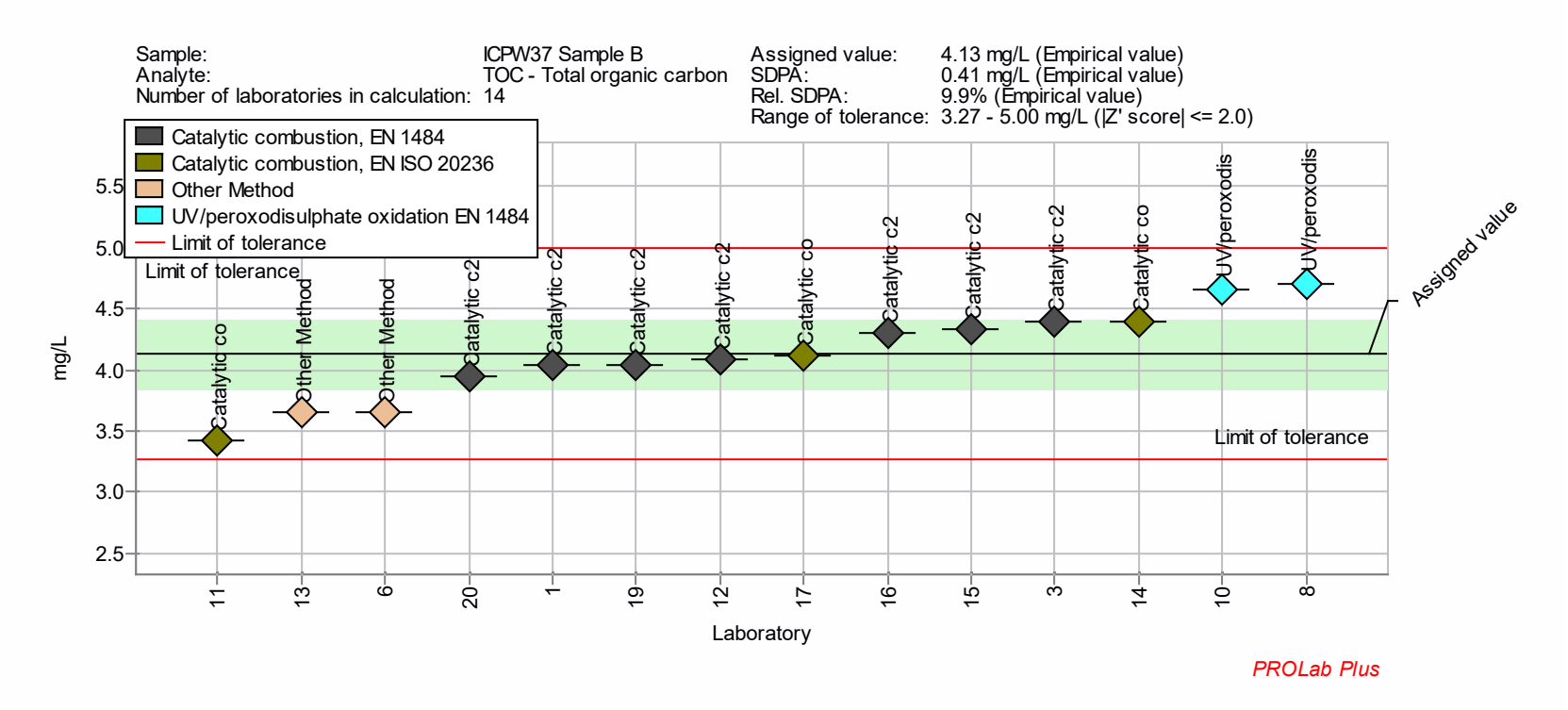

Figure 60. Reported values of total organic carbon in sample B, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

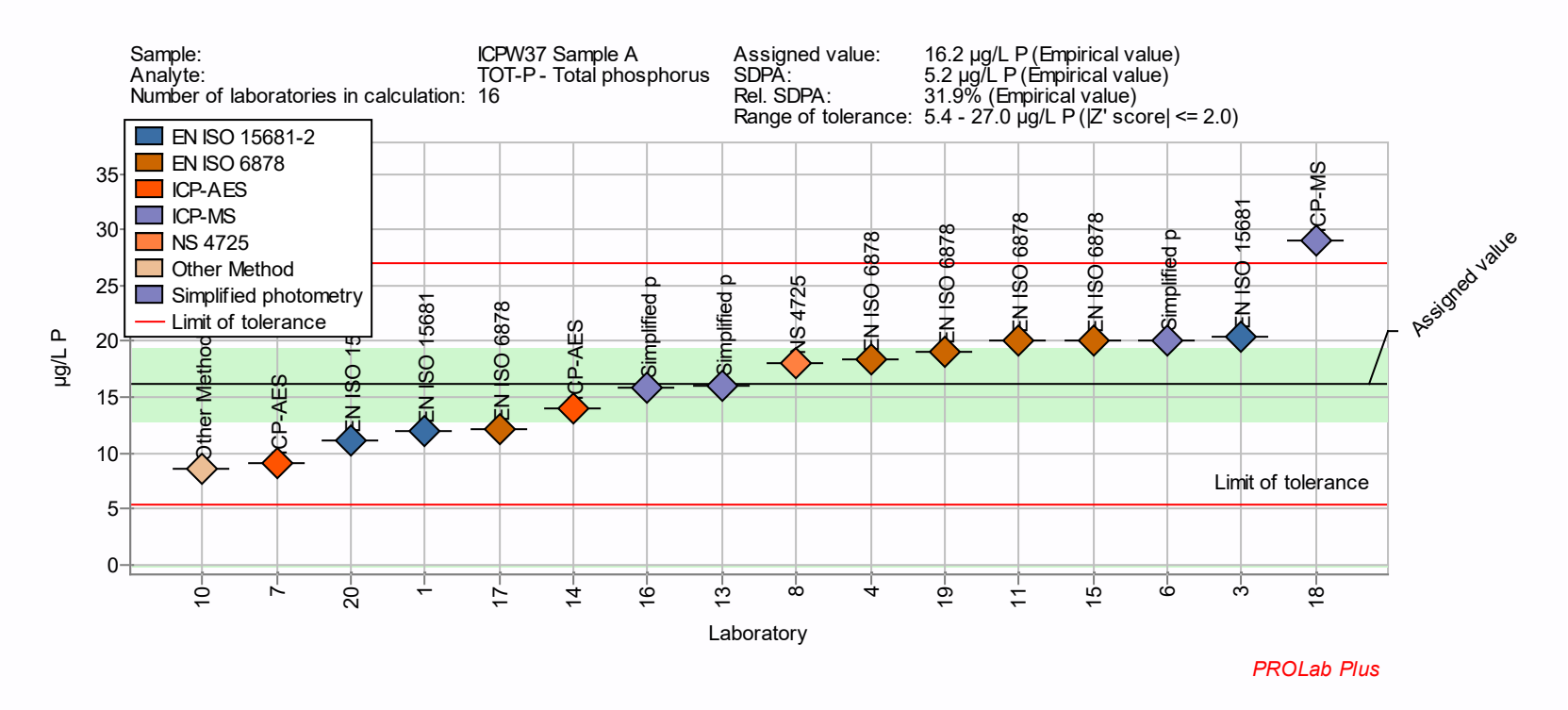

Figure 61. Reported values of total phosphorous in sample A, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

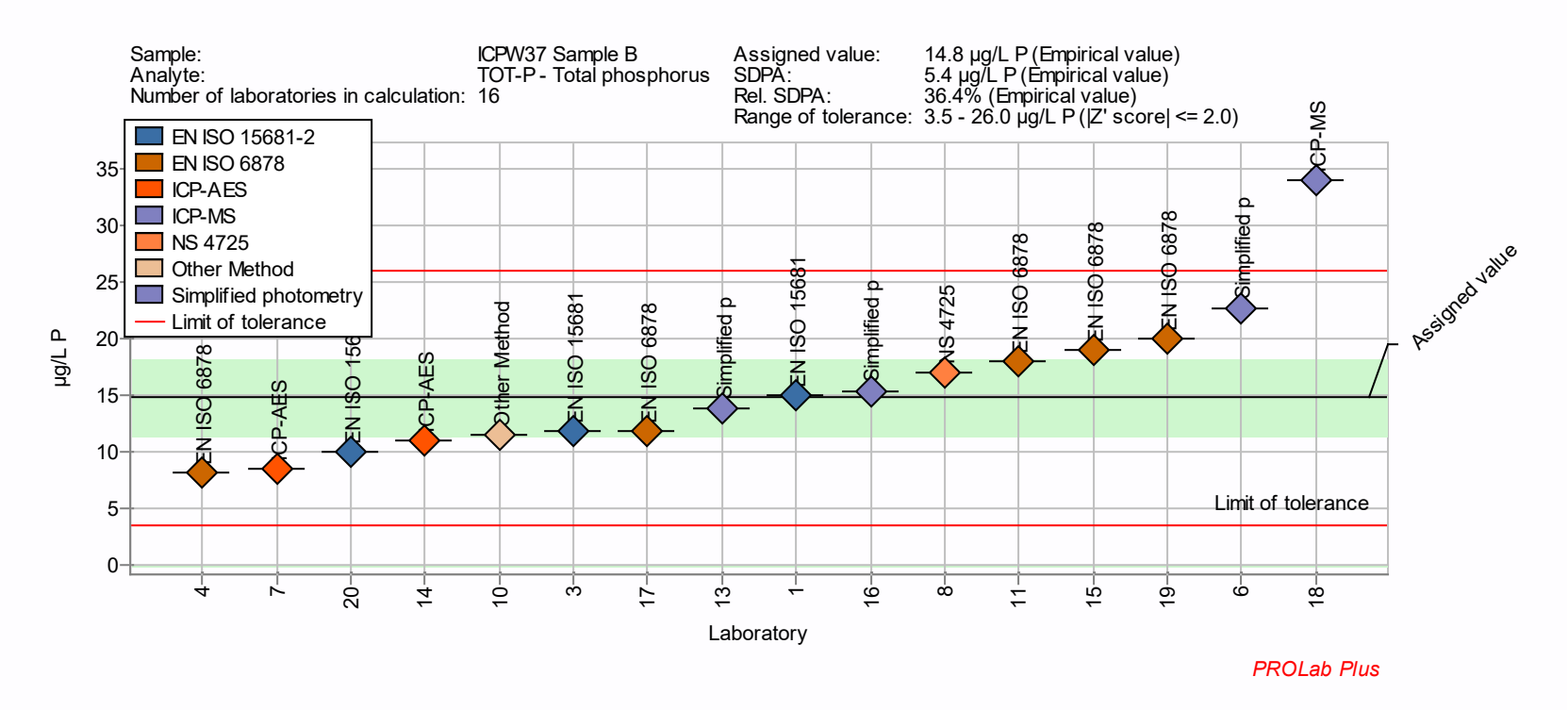

Figure 62. Reported values of total phosphorous in sample B, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

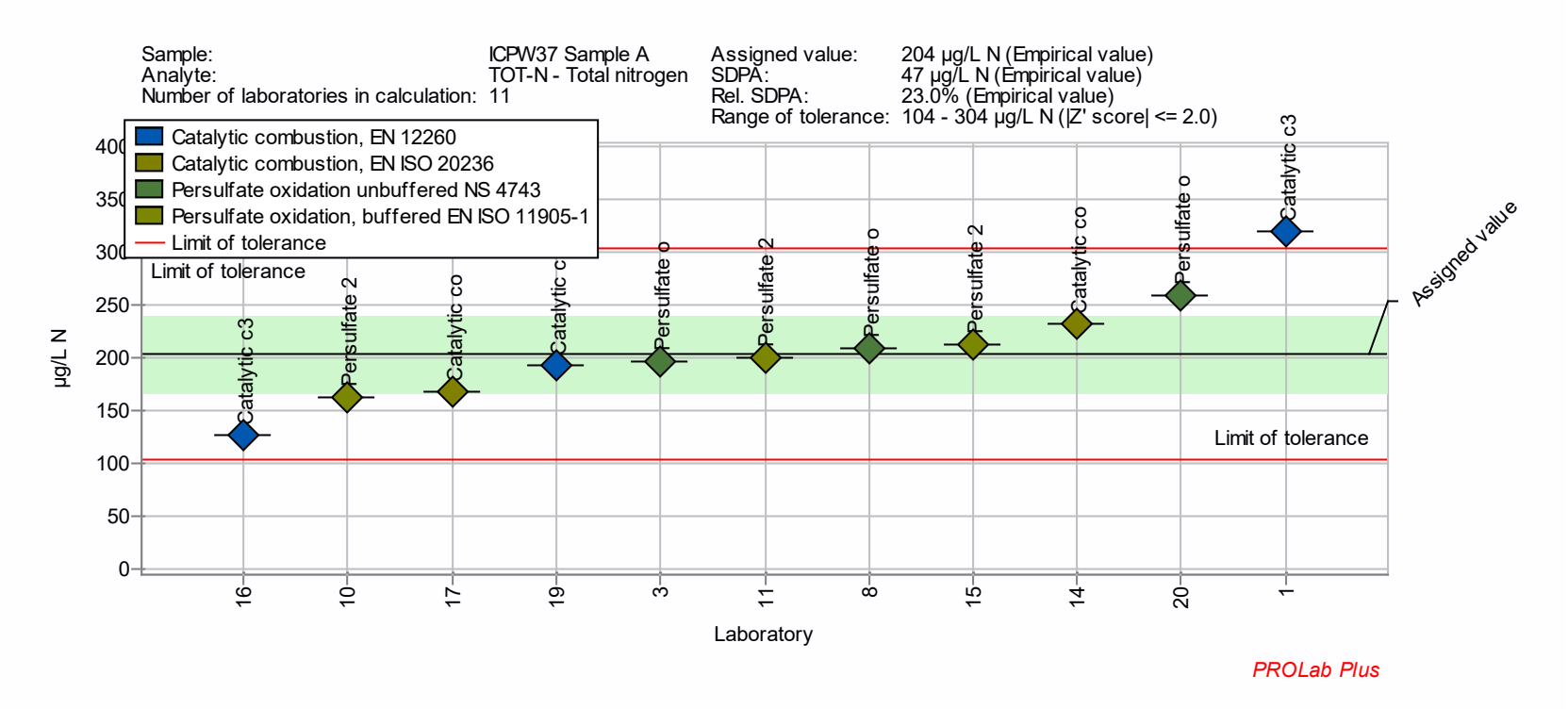

Figure 63. Reported values of total nitrogen in sample A, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

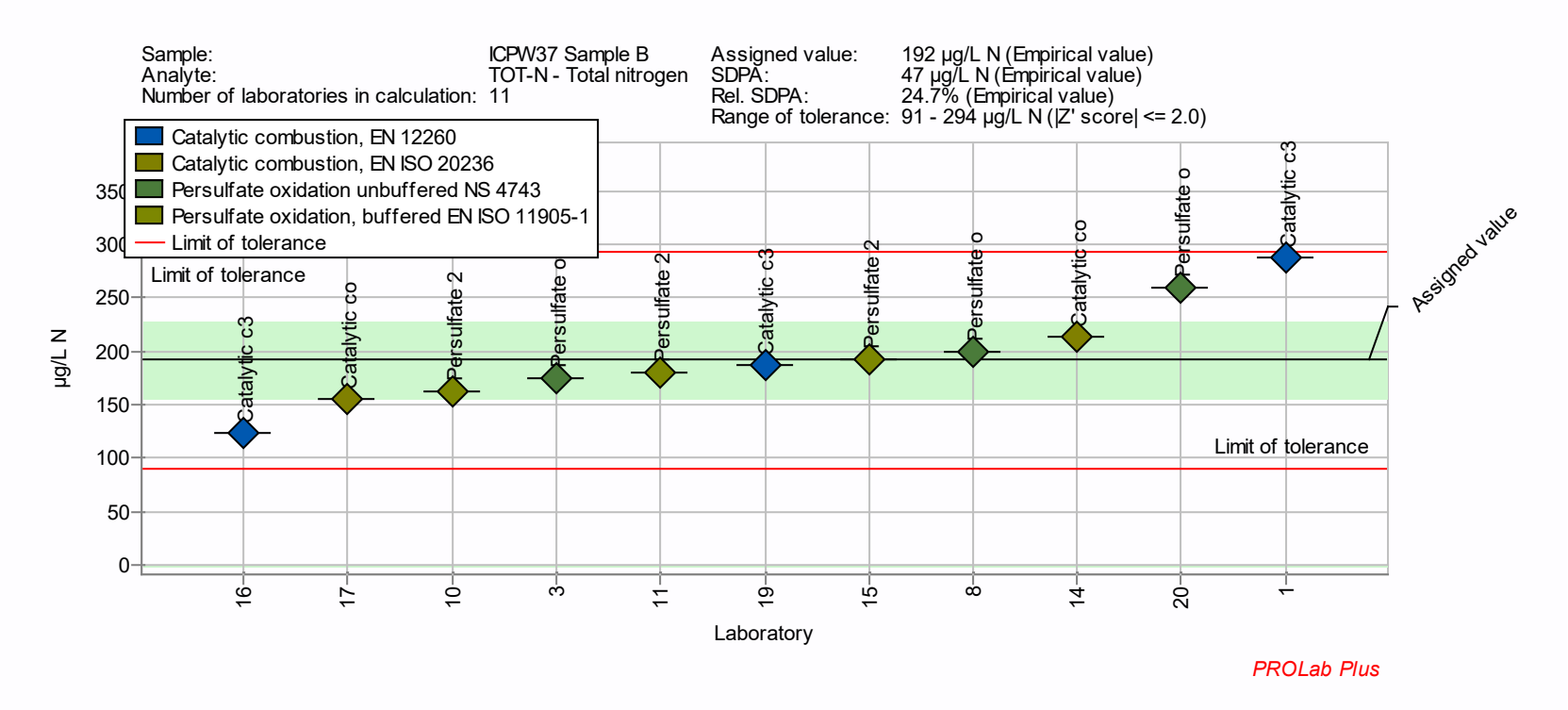

Figure 64. Reported values of total nitrogen in sample B, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

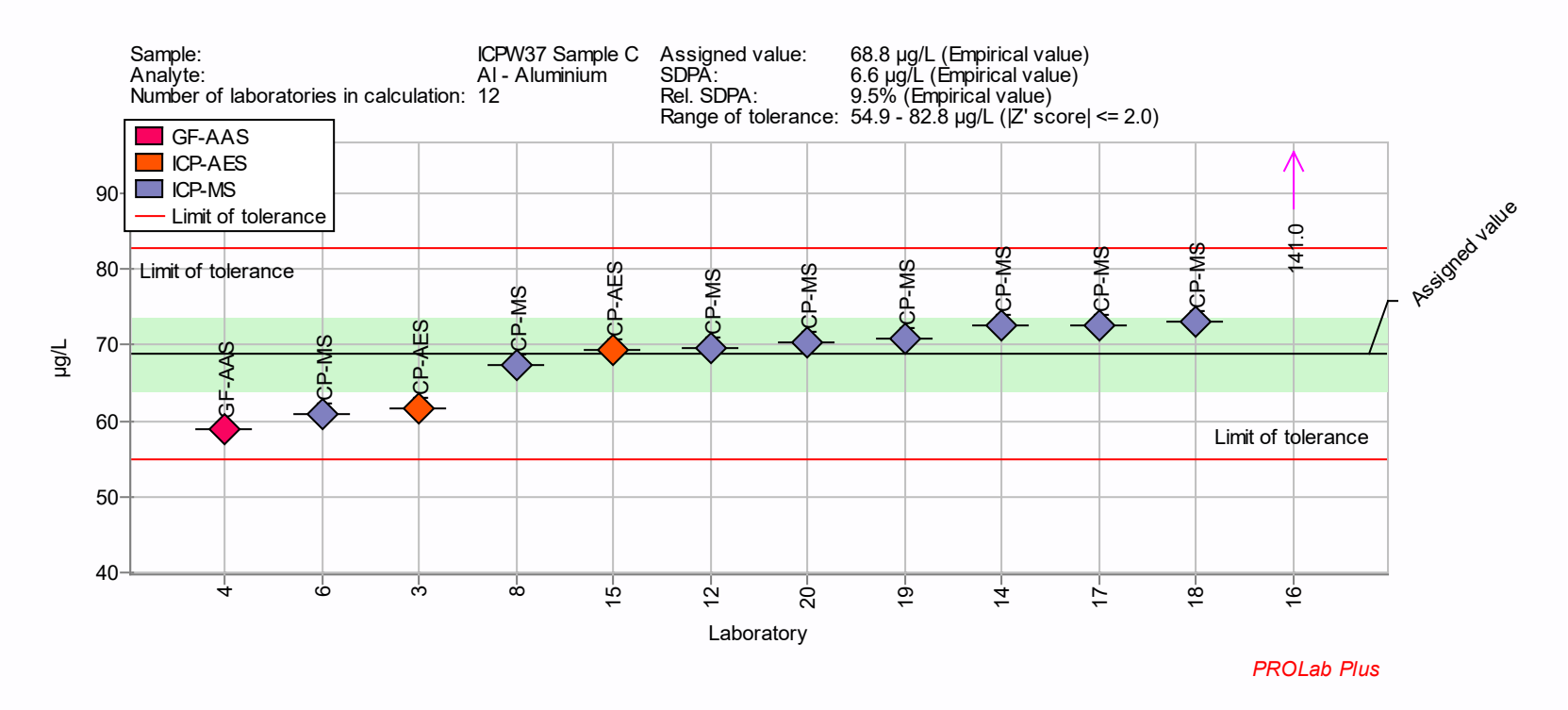

Figure 65. Reported values of aluminium in sample C, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

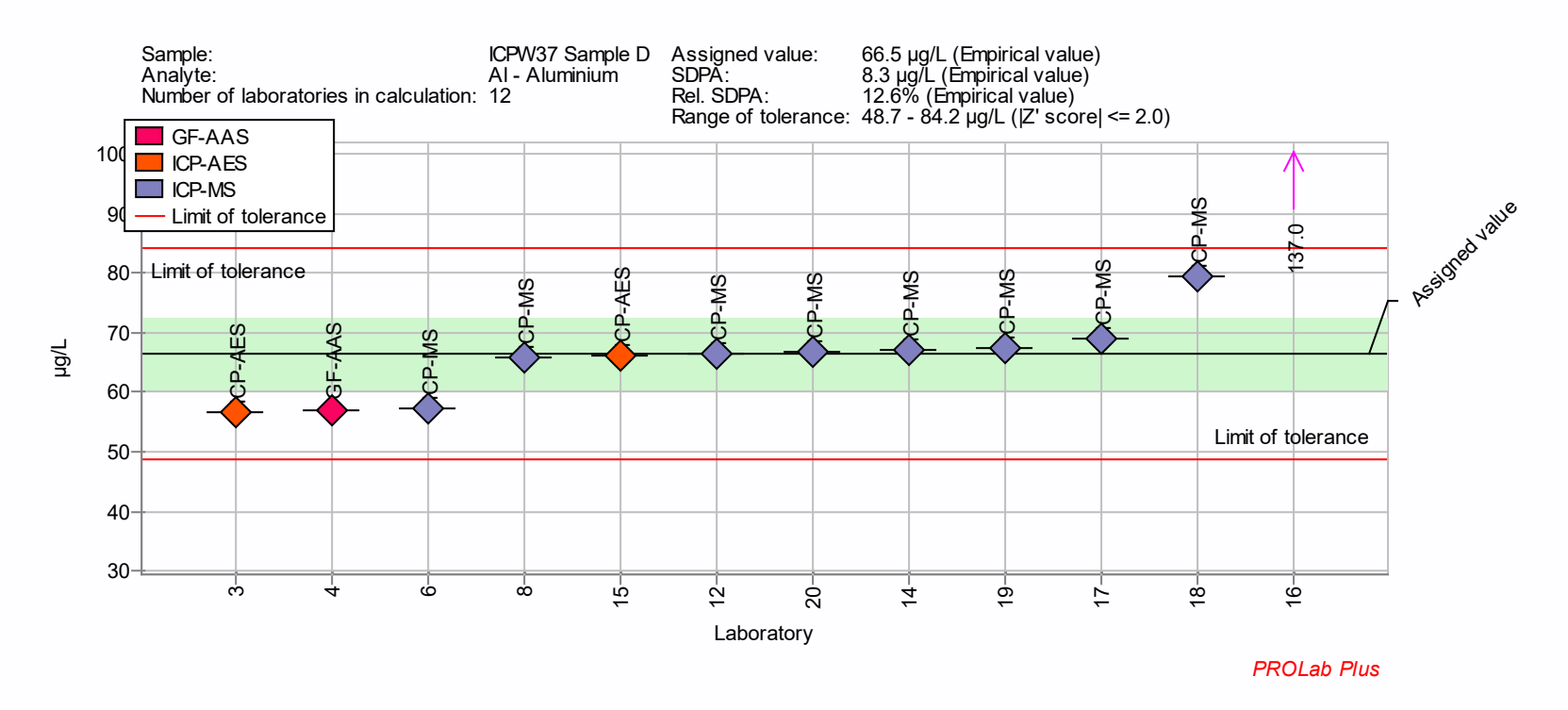

Figure 66. Reported values of aluminium in sample D, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

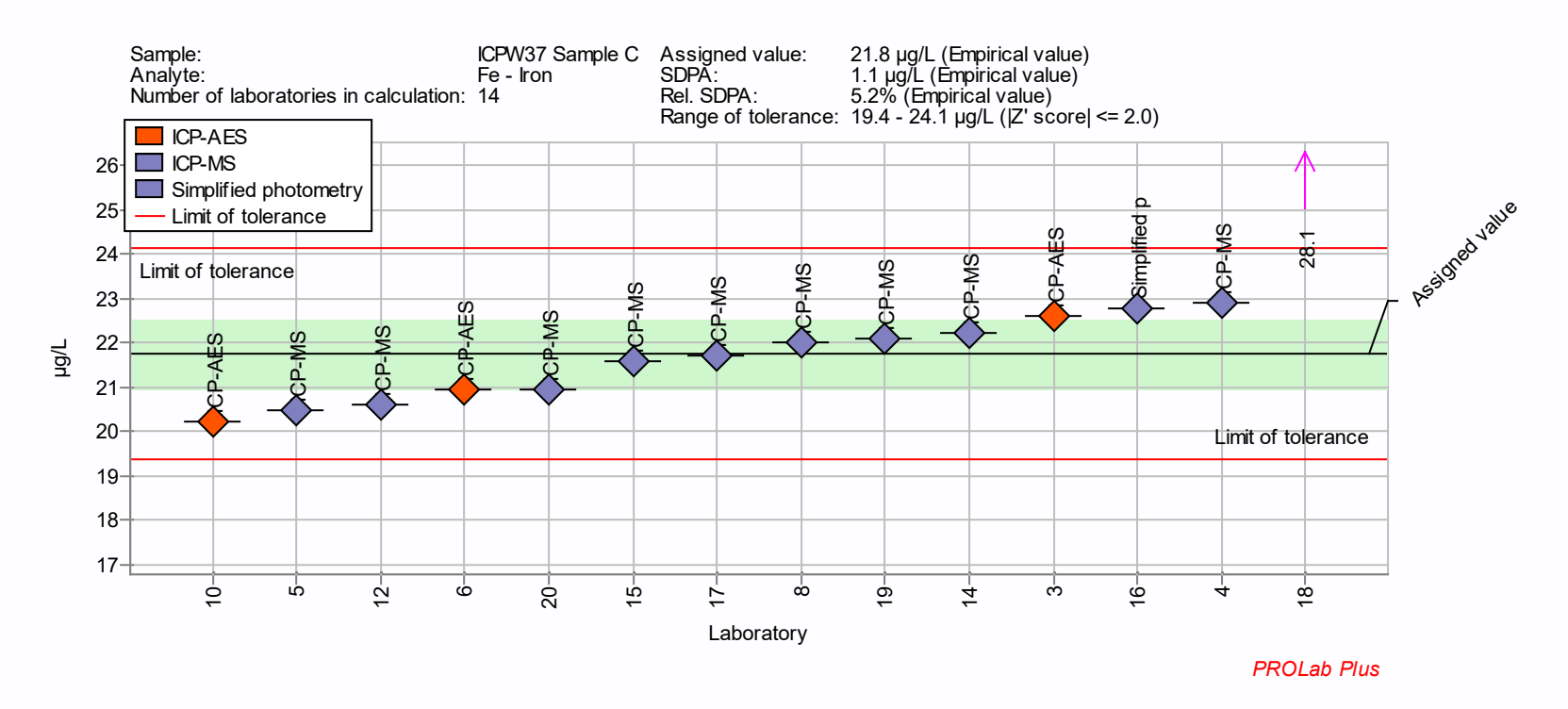

Figure 67. Reported values of iron in sample C, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

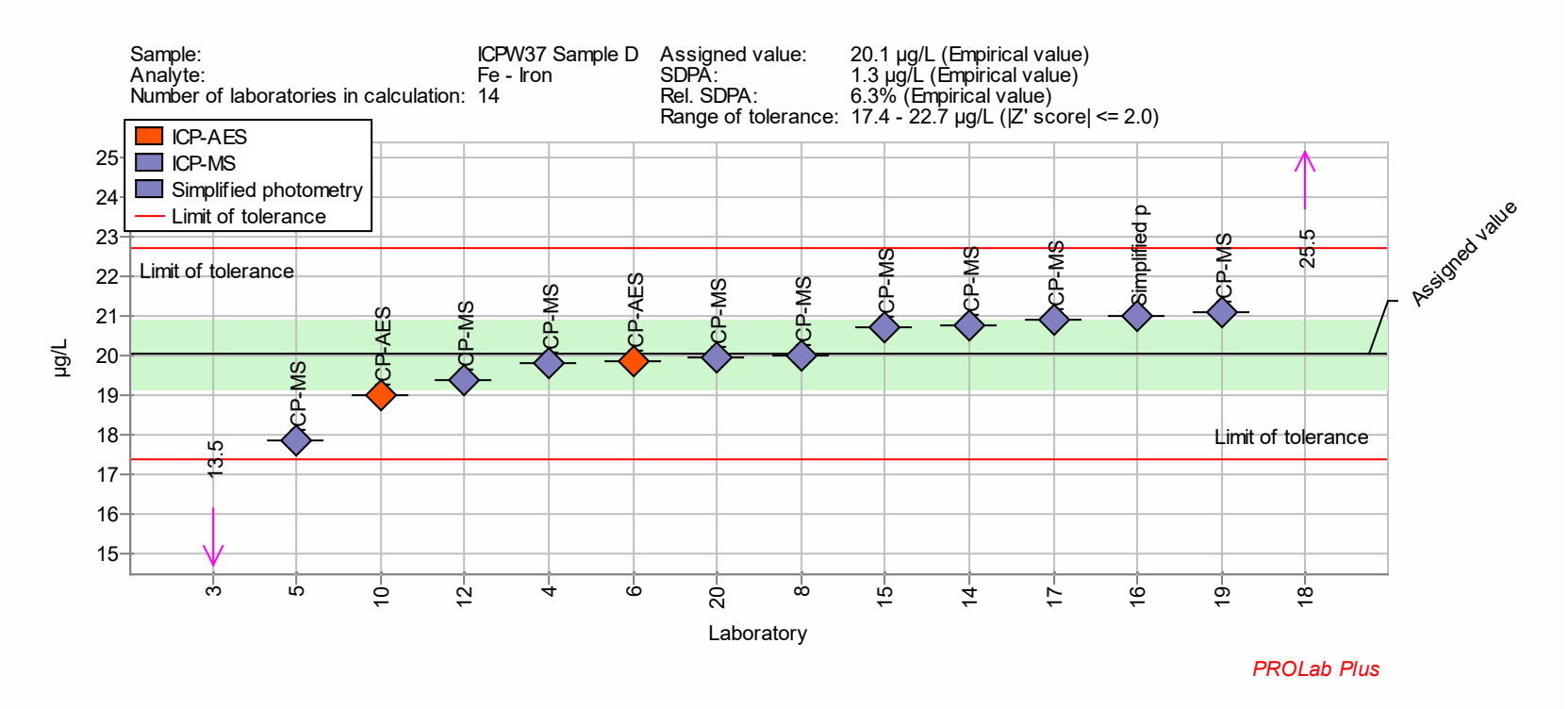

Figure 68. Reported values of iron in sample D, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

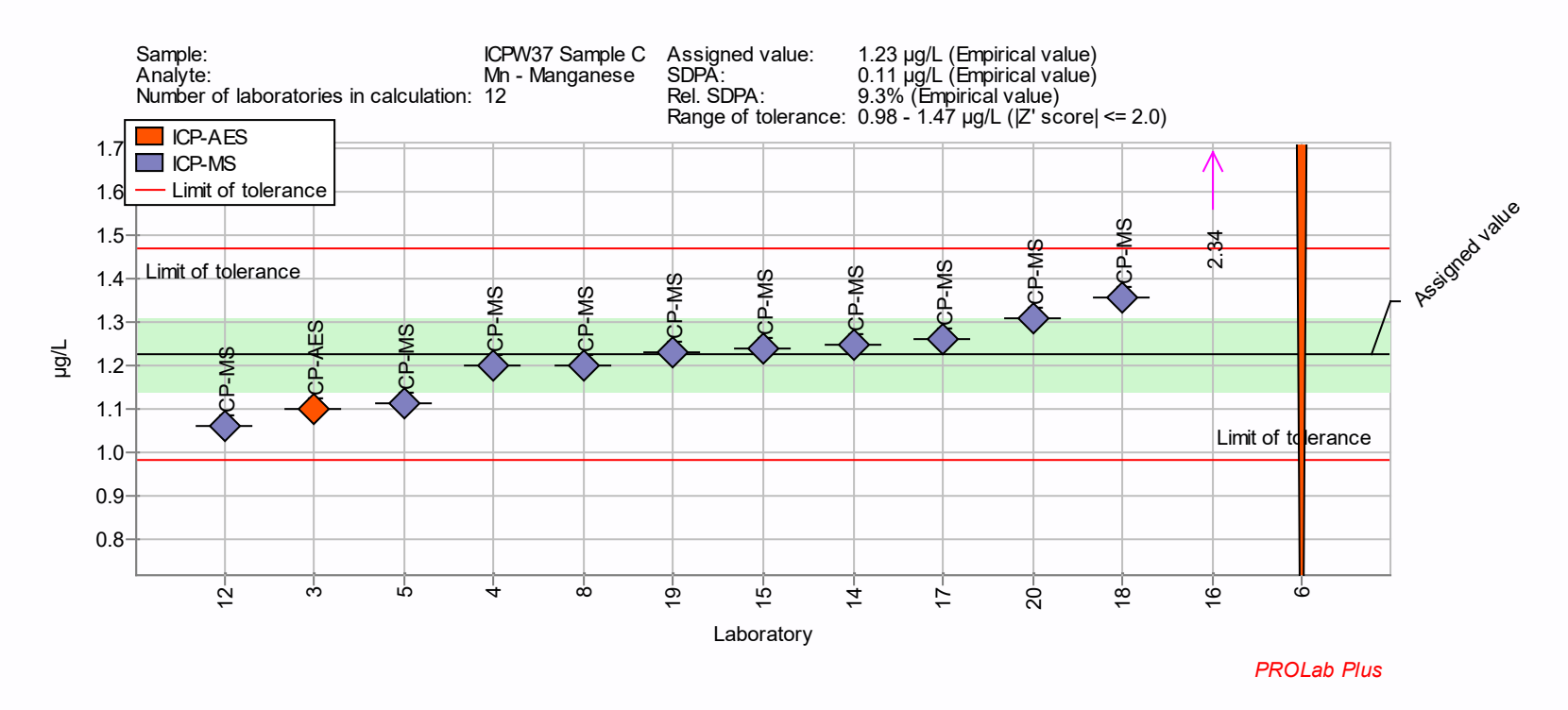

Figure 69. Reported values of manganese in sample C, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

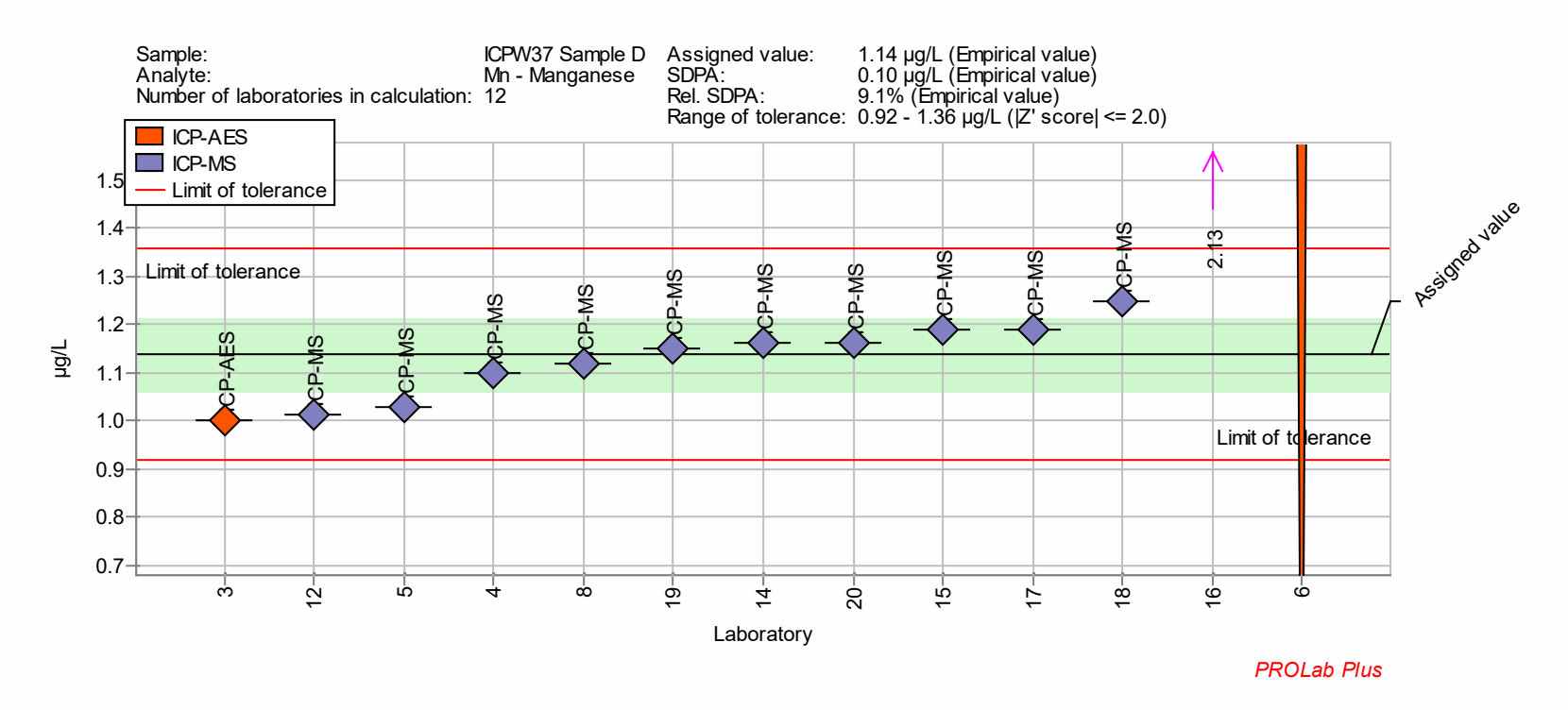

Figure 70. Reported values of manganese in sample D, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

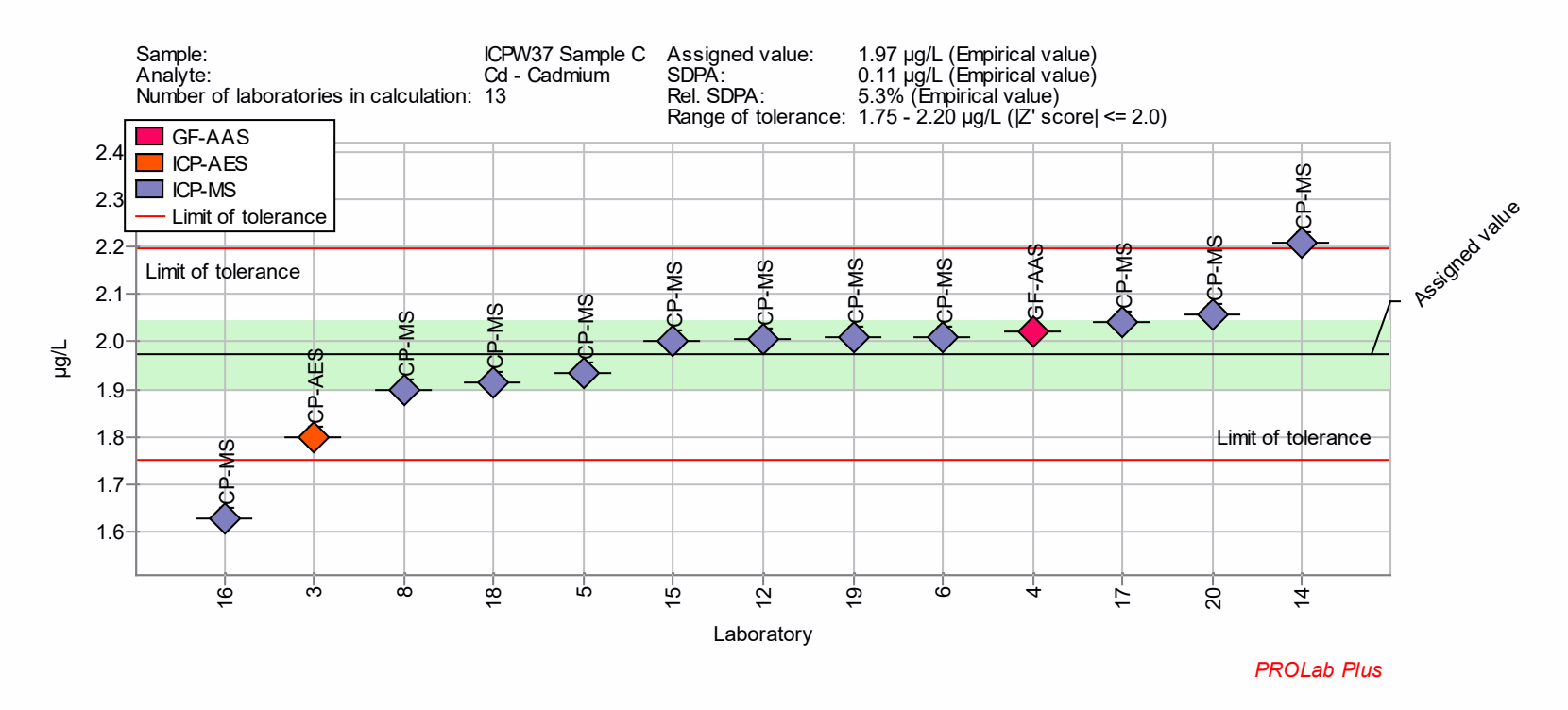

Figure 71. Reported values of cadmium in sample C, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

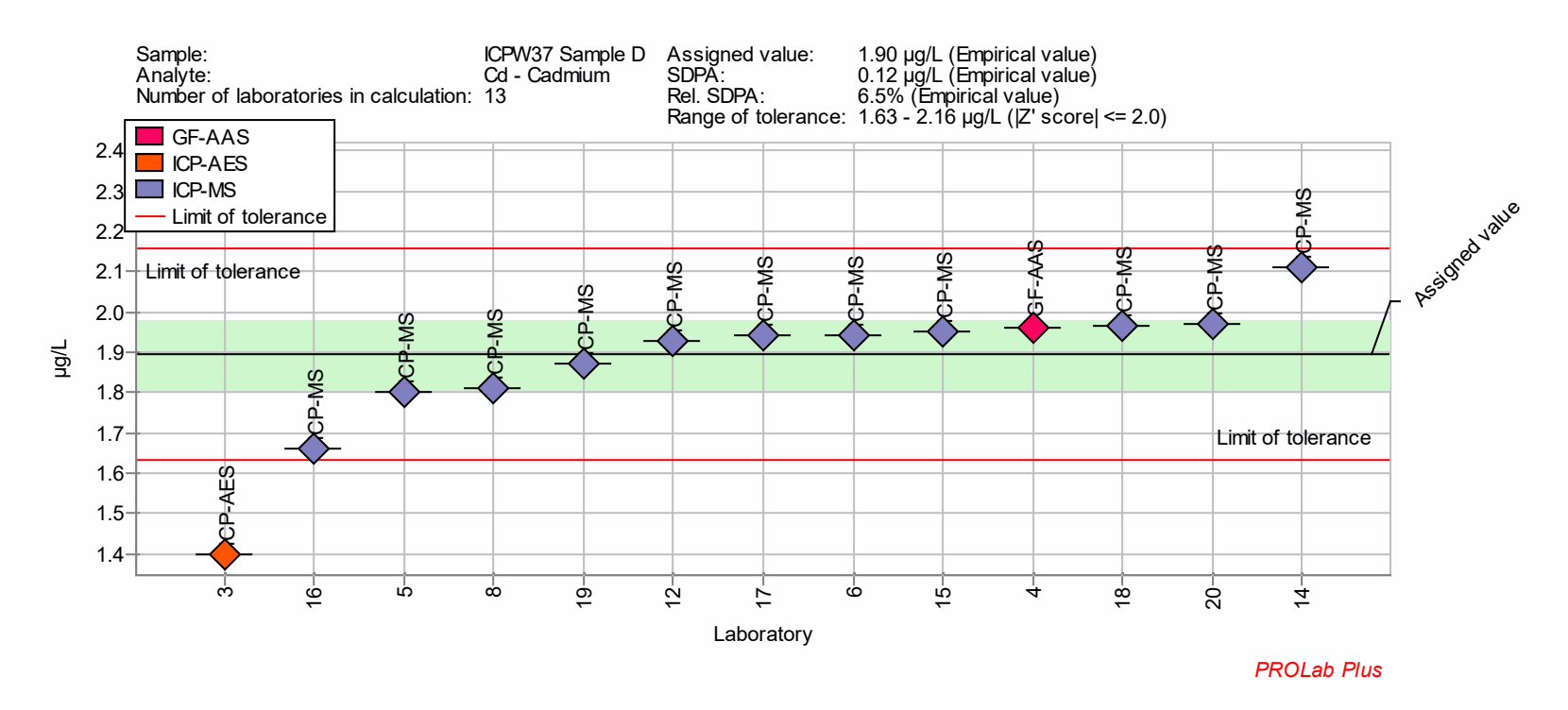

Figure 72. Reported values of cadmium in sample D, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

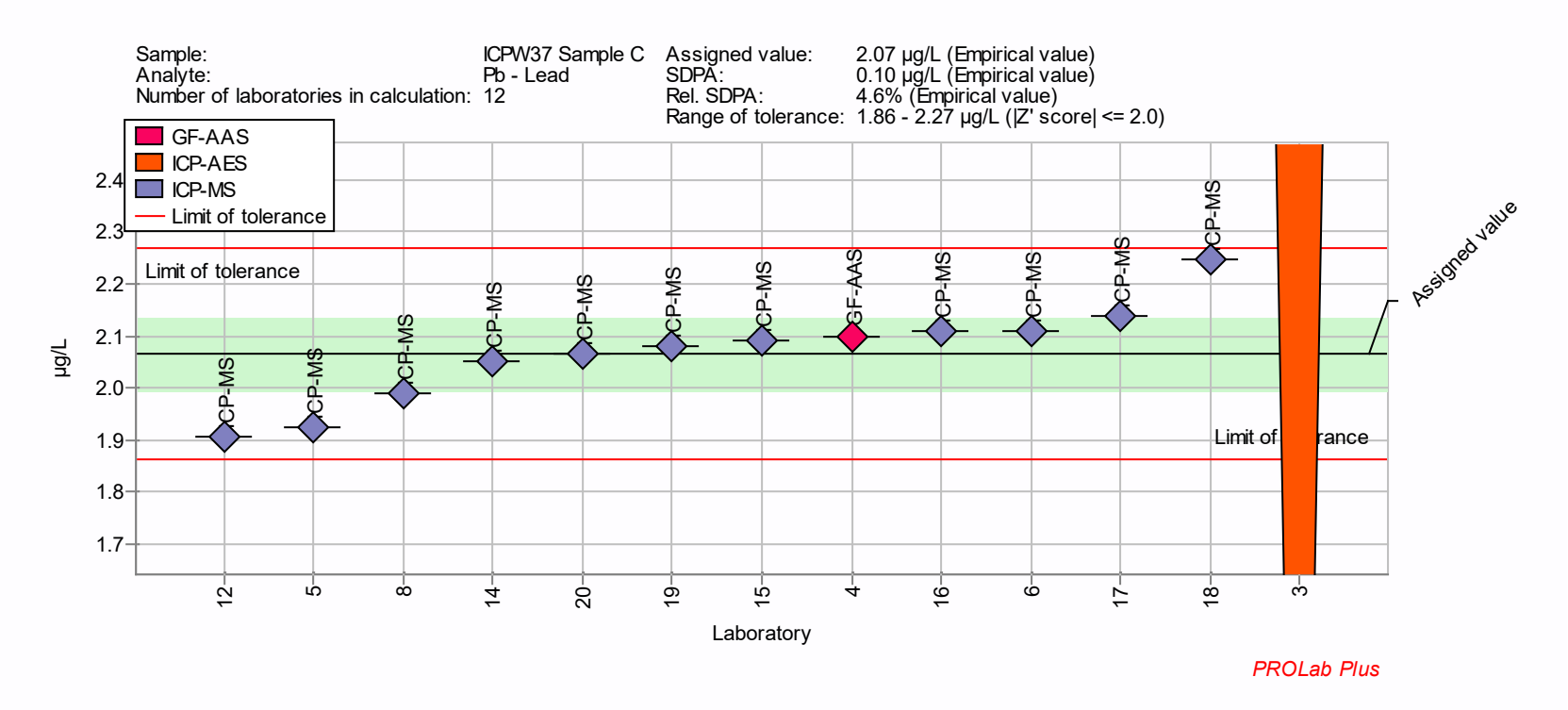

Figure 73. Reported values of lead in sample C, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

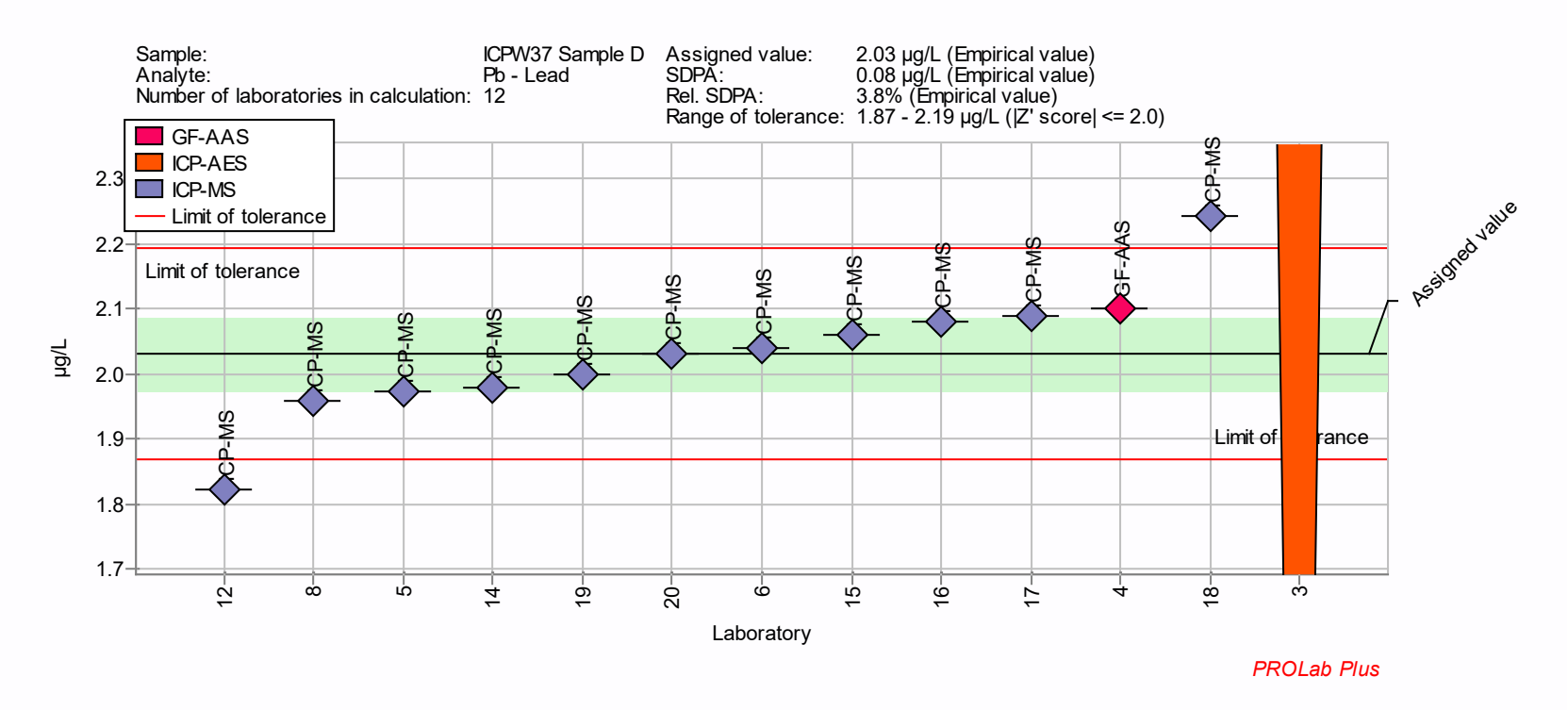

Figure 74. Reported values of lead in sample D, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

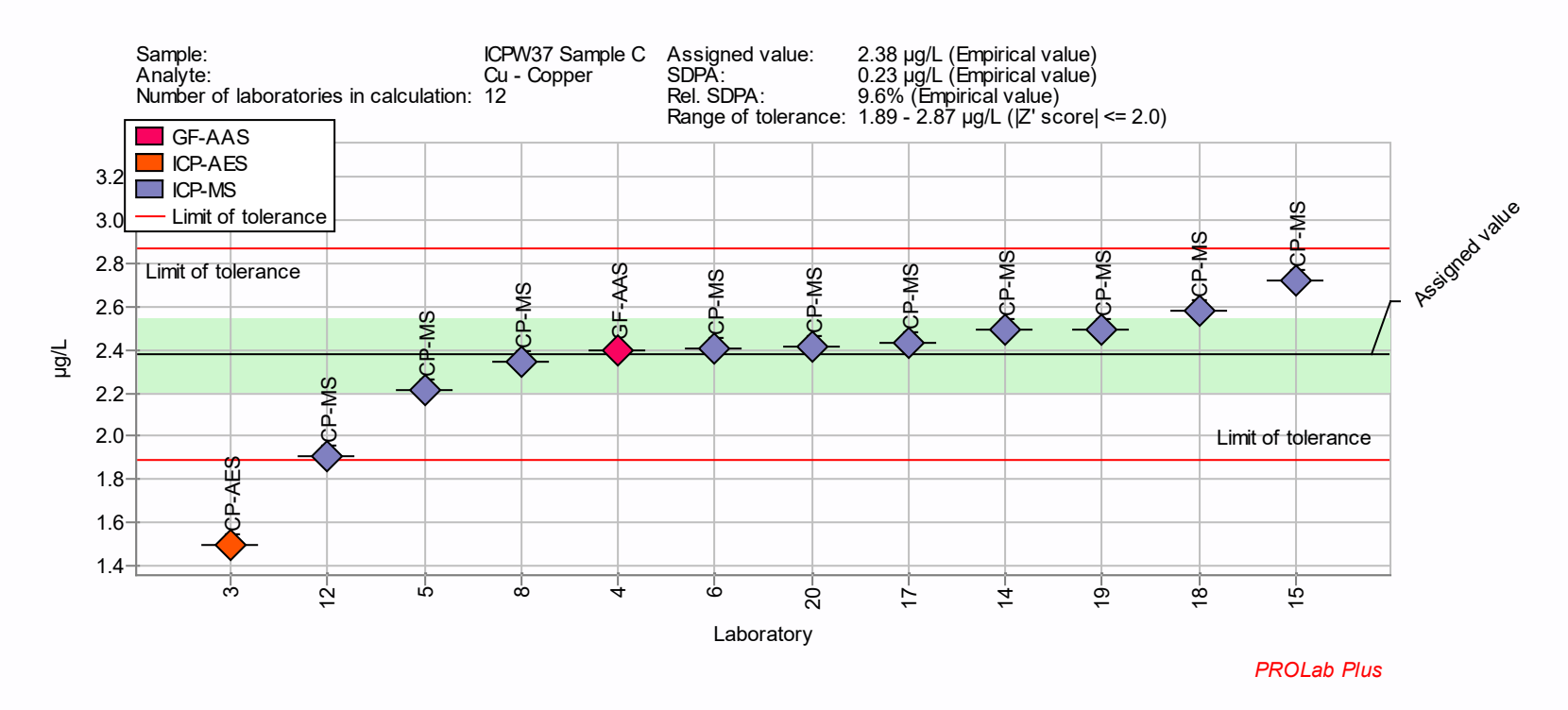

Figure 75. Reported values of copper in sample C, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

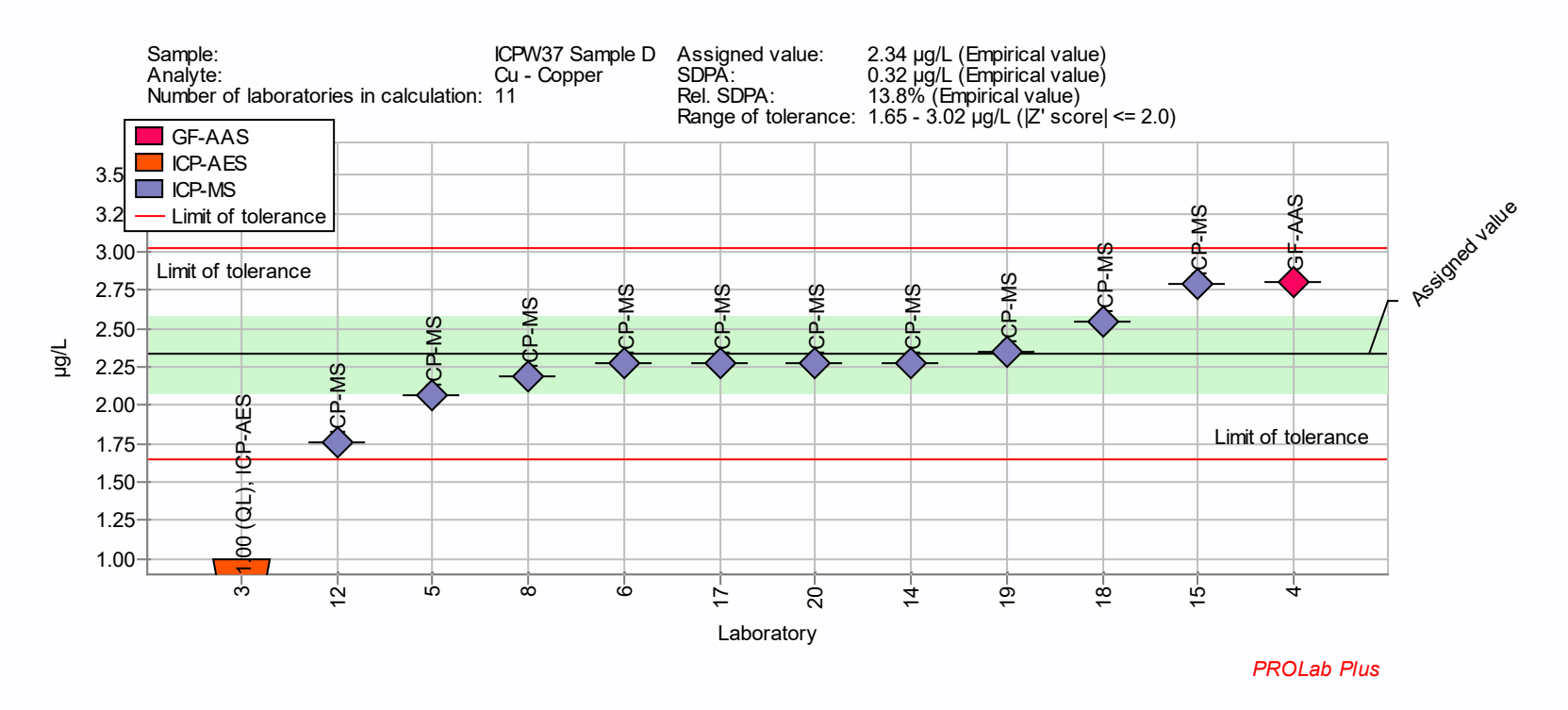

Figure 76. Reported values of copper in sample D, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

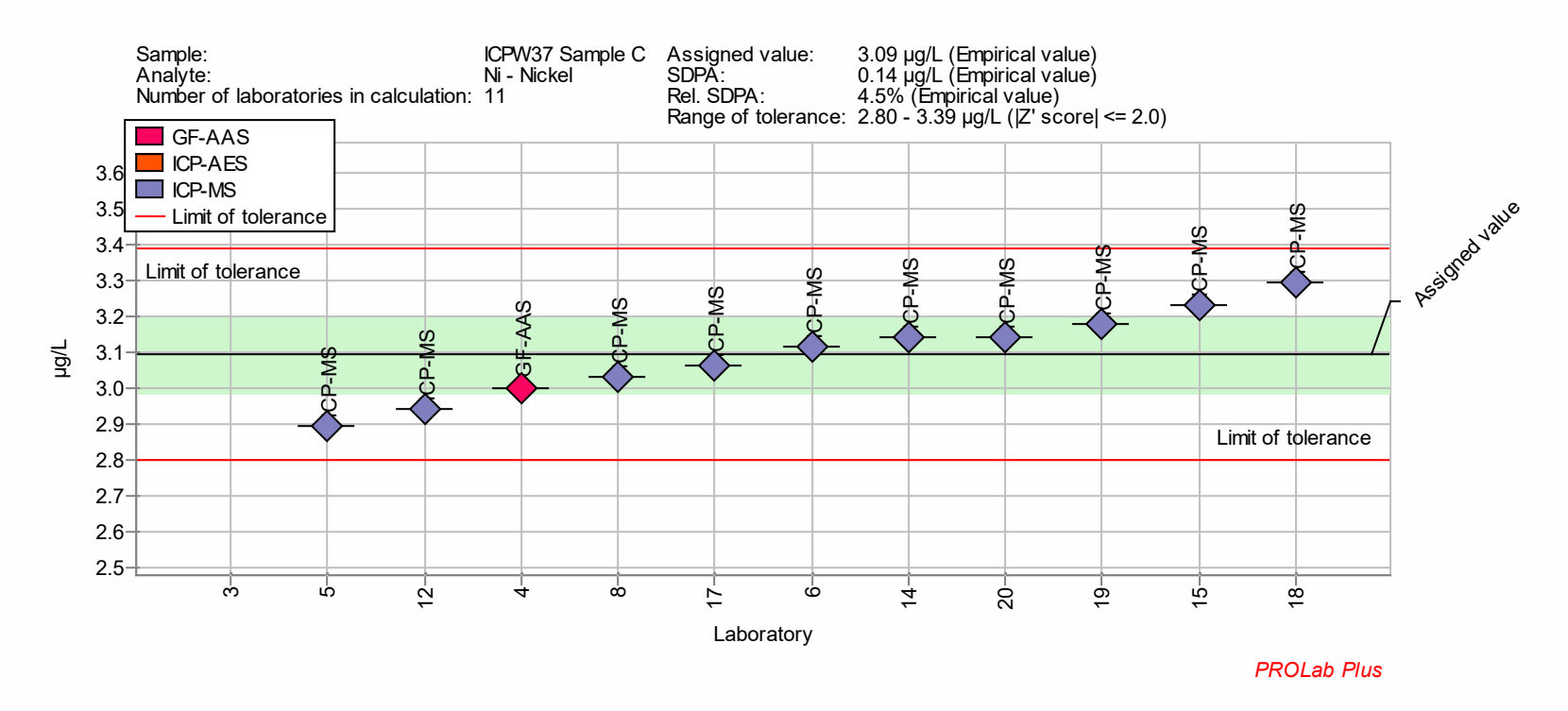

Figure 77. Reported values of nickel in sample C, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

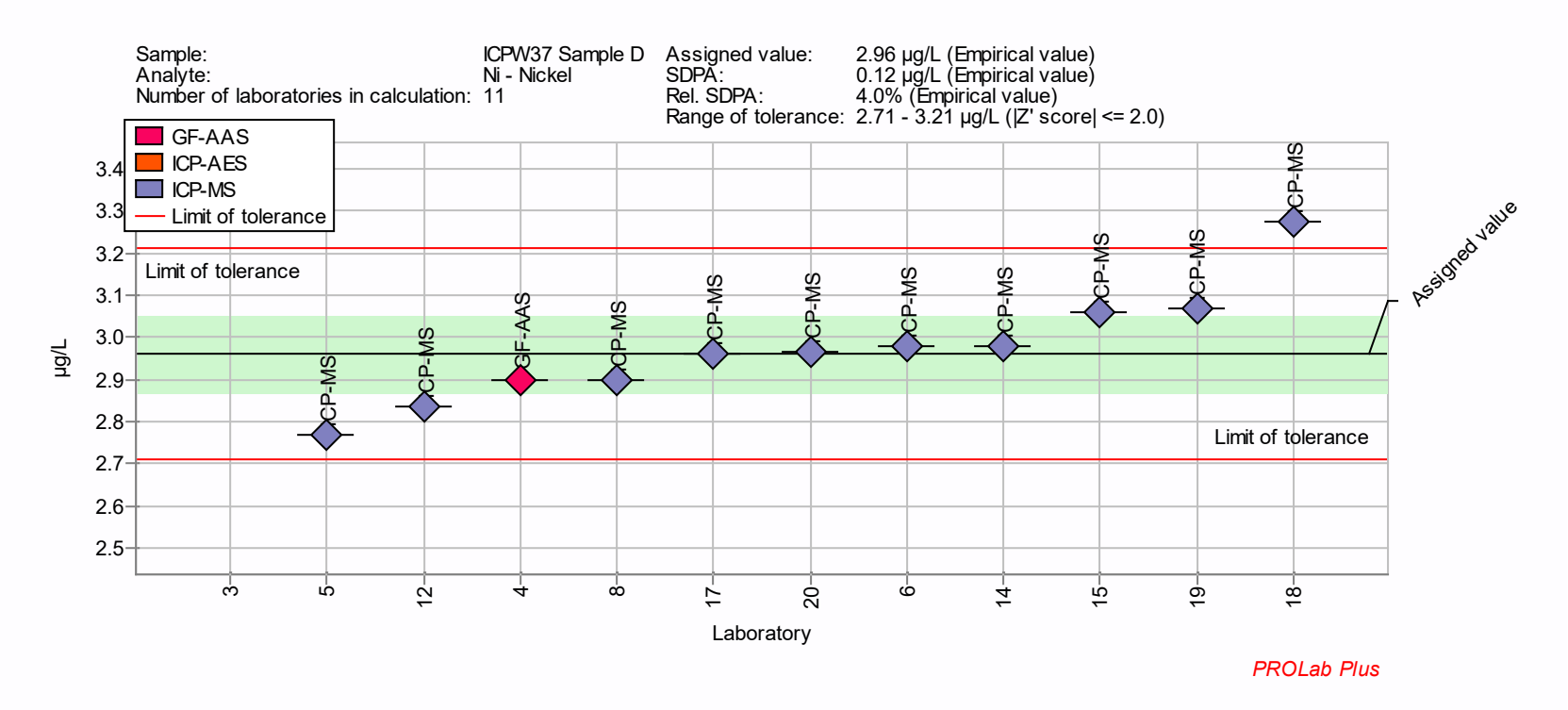

Figure 78. Reported values of nickel in sample D, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

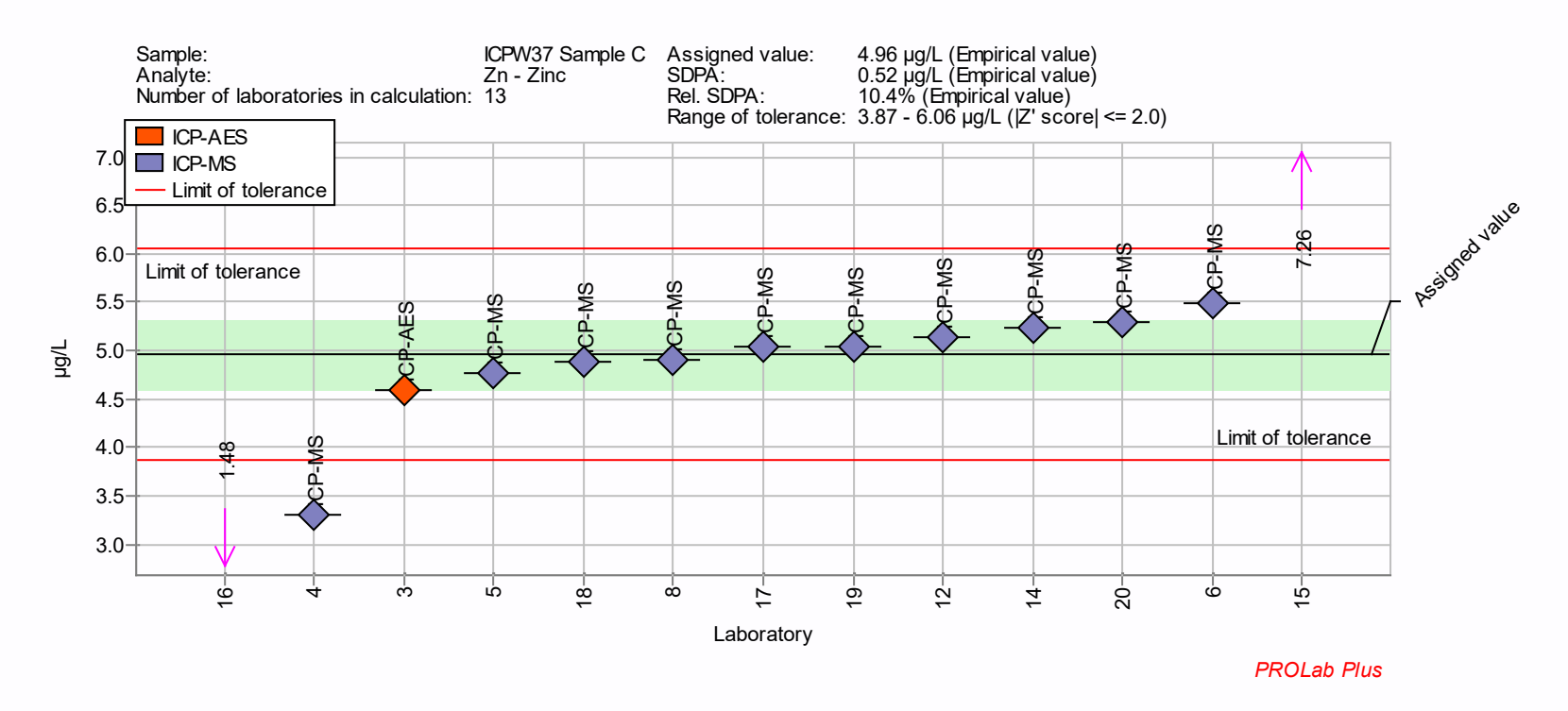

Figure 79. Reported values of zinc in sample C, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

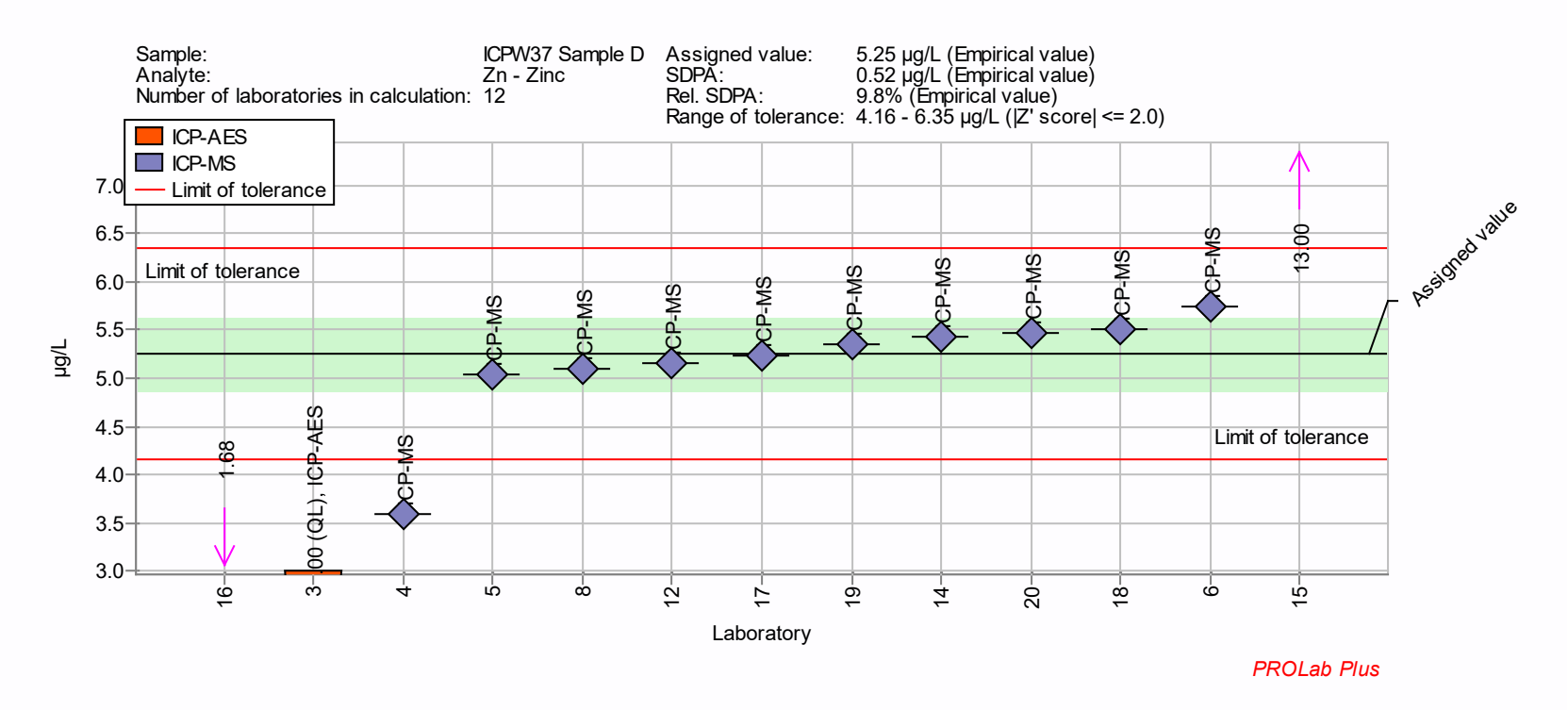

Figure 80. Reported values of zinc in sample D, sorted by concentration levels. Limit of tolerance lines indicates Z' score of ±2.

D.3. Statistics per analysis parameter

Table 7. Table of laboratory results and statistical parameters for pH.

pH	ICPW37-A				ICPW37-B				
Laboratory	Unit: PH-units	Z' score	Outlier type	D%	Unit: PH-units	Z' score	Outlier type	D%	Analytical method
1	6.33	-0.6		-1.7 %	6.42	-0.6		-1.2 %	Electrometric, stirred
2	6.64	1.1		3.1 %	6.60	0.7		1.5 %	EN ISO 10523
3	6.48	0.2		0.6 %	6.65	1.1		2.3 %	Electrometric, stirred
4	6.40	-0.2		-0.6 %	6.39	-0.8		-1.7 %	EN ISO 10523
5	6.24	-1.1		-3.1 %	6.48	-0.2		-0.3 %	Electrometric, stirred
6	7.03	3.4	E	9.2 %	6.88	2.8	E	5.8 %	Electrometric, stirred
7	5.96	-2.7	E	-7.4 %	6.03	-3.5	E	-7.2 %	Electrometric, stirred
8	6.69	1.4		3.9 %	6.69	1.4		2.9 %	EN ISO 10523
9	6.32	-0.7		-1.9 %	6.41	-0.7		-1.4 %	EN ISO 10523
10	6.57	0.7		2.0 %	6.57	0.5		1.1 %	Electrometric, stirred
11	6.39	-0.3		-0.8 %	6.46	-0.3		-0.6 %	Electrometric, non-stirring
13	6.40	-0.2		-0.6 %	6.38	-0.9		-1.9 %	Electrometric, stirred
14	6.56	0.7		1.9 %	6.57	0.5		1.1 %	Electrometric, non-stirring
15	6.42	-0.1		-0.3 %	6.46	-0.3		-0.6 %	EN ISO 10523
16	6.44	0.0		0.0 %	6.57	0.5		1.1 %	Electrometric, equilibration
17	6.25	-1.1		-2.9 %	6.38	-0.9		-1.9 %	EN ISO 10523
19	6.46	0.1		0.3 %	6.49	-0.1		-0.2 %	EN ISO 10523
20	6.44	0.0		0.0 %	6.49	-0.1		-0.2 %	Electrometric, stirred
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	18				18				
95% range of uncertainty of the mean (k=2)	±0.10				±0.08				
Median	6.43				6.49				
Assigned value	6.44				6.50				
Mean	6.44				6.50				
Reproducibility s.d. (SDPA)	0.17				0.13				
Rel. reproducibility s.d. (%SDPA)	2.6 %				2.0 %				
No. of meas. outside of tolerance limits	2				2				

Table 8. Table of laboratory results and statistical parameters for conductivity.

Conductivity	ICPW37-A				ICPW37-B				
Laboratory	mS/m	Z' score	Outlier type	D%	mS/m	Z' score	Outlier type	D%	Analytical method
1	2.15	0.1		0.5 %	2.07	0.4		2.4 %	Electrometry, other
2	2.02	-0.9		-5.5 %	1.91	-1.0		-5.5 %	Electrometry, other
3	1.92	-1.5		-10.0 %	1.80	-2.0	E	-11.1 %	Electrometry, other
4	2.33	1.4		9.0 %	2.15	1.2		6.4 %	ISO 7888
5	21.33	138.3	E	897.5 %	20.20	163.1	E	899.4 %	Electrometry, other
6	2.56	3.0	E	19.7 %	2.16	1.2		6.9 %	Electrometry, other
8	2.13	-0.1		-0.4 %	2.07	0.4		2.4 %	ISO 7888
9	2.18	0.3		1.9 %	2.05	0.3		1.4 %	Electrometry, other
10	2.10	-0.3		-1.9 %	1.99	-0.3		-1.5 %	Electrometry, other
11	2.19	0.4		2.4 %	2.05	0.3		1.4 %	Electrometry, other
12	0.02	-15.3	E	-99.0 %	0.02	-18.0	E	-99.0 %	Electrometry, other
13	2.14	0.0		0.1 %	2.03	0.1		0.4 %	Electrometry, other
14	2.05	-0.6		-4.1 %	1.92	-0.9		-5.0 %	Electrometry, other
15	2.15	0.1		0.5 %	2.03	0.1		0.4 %	ISO 7888
16	2.16	0.2		1.0 %	2.04	0.2		0.9 %	Electrometry, other
17	2.06	-0.6		-3.7 %	1.97	-0.5		-2.5 %	ISO 7888
19	2.18	0.3		1.9 %	2.07	0.4		2.4 %	ISO 7888
20	2.10	-0.3		-1.8 %	1.97	-0.5		-2.5 %	Electrometry, other
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	18				18				
95% range of uncertainty of the mean (k=2)	±0.08				±0.06				
Median	2.15				2.04				
Assigned value	2.14				2.02				
Mean	2.14				2.02				
Reproducibility s.d. (SDPA)	0.13				0.11				
Rel. reproducibility s.d. (%SDPA)	6.2 %				5.3 %				
No. of meas. outside of tolerance limits	3				3				

Table 9. Table of laboratory results and statistical parameters for alkalinity.

Alkalinity	ICPW37-A				ICPW37-B				
Laboratory	mmol/L	Z' score	Outlier type	D%	mmol/L	Z' score	Outlier type	D%	Analytical method
1	0.0900	-0.5		-5.8 %	0.0900	-0.3		-7.1 %	Other Method
3	0.0820	-1.2		-14.1 %	0.0730	-1.0		-24.7 %	pH 4,5 endpoint
4	0.0886	-0.6		-7.2 %	0.1088	0.5		12.3 %	pH 4,5 endpoint
6	0.0850	-0.9		-11.0 %	0.0840	-0.5		-13.3 %	pH 4,5 endpoint
7	0.1400	4.0	E	46.6 %	0.1300	1.4		34.2 %	pH other endpoint
8	0.1350	3.6	E	41.3 %	0.1300	1.4		34.2 %	pH 4,5 endpoint
10	0.0930	-0.2		-2.6 %	0.0880	-0.4		-9.2 %	pH 4,5+4,2
11	0.1060	0.9		11.0 %	0.0970	0.0		0.1 %	pH 4,5+4,2
13	0.1050	0.9		9.9 %	0.1320	1.5		36.2 %	pH 4,5 endpoint
14	0.0950	0.0		-0.5 %	0.0870	-0.4		-10.2 %	pH 4,5+4,2
15	0.0930	-0.2		-2.6 %	0.0870	-0.4		-10.2 %	pH 4,5 endpoint
16	0.0940	-0.1		-1.6 %	0.0860	-0.5		-11.2 %	Other Method
17	0.0920	-0.3		-3.7 %	0.0870	-0.4		-10.2 %	pH other endpoint
20	0.0910	-0.4		-4.7 %	0.0780	-0.8		-19.5 %	pH 4,5 endpoint
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	14				14				
95% range of uncertainty of the mean (k=2)	±0.0070				±0.0150				
Median	0.0930				0.0875				
Assigned value	0.0955				0.0969				
Mean	0.0955				0.0969				
Reproducibility s.d. (SDPA)	0.0105				0.0225				
Rel. reproducibility s.d. (%SDPA)	11.0 %				23.2 %				
No. of meas. outside of tolerance limits.	2								

Table 10. Table of laboratory results and statistical parameters for nitrate-nitrogen.

Nitrate-nitrogen - NO_3-N	ICPW37-A				ICPW37-B				
Laboratory	µg N/L	Z' score	Outlier type	D%	µg N/L	Z' score	Outlier type	D%	Analytical method
1	12.80	0.4		45.5 %	17.9	0.3		19.8 %	Automatic Cd-red. spectrophotometry
3	11.52	0.3		31.0 %	13.6	-0.1		-9.5 %	Ion Chromatography
4									Ion Chromatography
5	2.21	-0.7		-74.8 %	5.1	-0.9		-65.7 %	Ion Chromatography
6	< 200.00				< 200.0				Automatic Cd-red. spectrophotometry
7	0.10	-1.0		-98.9 %	2.7	-1.1		-82.0 %	Other Method
8	< 2.00				< 2.0				Ion Chromatography
9									Ion Chromatography
10					16.9	0.2		12.9 %	Ion Chromatography
11	14.00	0.6		59.1 %	15.0	0.0		0.1 %	Ion Chromatography
12	< 141.00				< 141.0				Ion Chromatography
13	6.20	-0.3		-29.5 %	13.9	-0.1		-7.2 %	Simplified photometry
14	23.27	1.6		164.5 %	27.5	1.2		83.7 %	Ion Chromatography
15	< 20.00				< 20.0				Ion Chromatography
16									Ion Chromatography
17	< 1.00				7.0	-0.7		-53.3 %	Automatic Cd-red. spectrophotometry
19	< 50.00				< 50.0				Ion Chromatography
20	2.37	-0.7		-73.1 %	36.4	2.0		143.0 %	Ion Chromatography
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	14				15				
95% range of uncertainty of the mean (k=2)	±7.30				±8.0				
Median	8.86				14.4				
Assigned value	8.80				15.0				
Mean	8.80				15.0				
Reproducibility s.d. (SDPA)	8.25				10.1				
Rel. reproducibility s.d. (%SDPA)	93.8 %				67.4 %				

Table 11. Table of laboratory results and statistical parameters for chloride (Cl).

Chloride - Cl	ICPW37-A				ICPW37-B				
Laboratory	mg/L	Z' score	Outlier type	D%	mg/L	Z' score	Outlier type	D%	Analytical method
1	0.53	-12.0	E	-60.7 %	0.49	-9.5	E	-60.3 %	Photometry, autoanalyzer
3	1.36	0.2		0.8 %	1.24	0.2		1.1 %	Ion Chromatography
4	1.40	0.7		3.8 %	1.32	1.2		7.6 %	Ion Chromatography
5	1.36	0.2		0.9 %	1.24	0.2		1.5 %	Ion Chromatography
6	< 2.00				< 2.00				Photometry, autoanalyzer
7	1.25	-1.5		-7.6 %	0.99	-3.1	E	-19.4 %	Photometry, autoanalyzer
8	1.35	0.0		0.1 %	1.24	0.2		1.1 %	Ion Chromatography
9	1.26	-1.3		-6.6 %	1.13	-1.2		-7.9 %	Ion Chromatography
10	1.35	0.0		-0.2 %	1.23	0.1		0.5 %	Ion Chromatography
11	1.34	-0.1		-0.7 %	1.22	-0.1		-0.5 %	Ion Chromatography
12	1.43	1.2		6.1 %	1.27	0.5		3.2 %	Ion Chromatography
13	1.32	-0.4		-2.2 %	1.15	-1.0		-6.2 %	Ion Chromatography
14	1.34	-0.1		-0.7 %	1.22	-0.1		-0.7 %	Ion Chromatography
15	1.41	0.9		4.5 %	1.29	0.8		5.2 %	Ion Chromatography
16	1.47	1.8		9.0 %	1.41	2.4	E	15.0 %	Ion Chromatography
17	1.32	-0.4		-2.2 %	1.24	0.2		1.1 %	Ion Chromatography
19	1.38	0.5		2.3 %	1.26	0.4		2.7 %	Ion Chromatography
20	1.37	0.3		1.4 %	1.23	0.0		0.1 %	Ion Chromatography
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	18				18				
95% range of uncertainty of the mean (k=2)	±0.04				±0.05				
Median	1.35				1.24				
Assigned value	1.35				1.23				
Mean	1.35				1.23				
Reproducibility s.d. (SDPA)	0.07				0.07				
Rel. reproducibility s.d. (%SDPA)	4.9 %				6.1 %				
No. of meas. outside of tolerance limits.	1				3				

Table 12. Table of laboratory results and statistical parameters for sulphate (SO_4).

Sulphate - SO_4	ICPW37-A				ICPW37-B				
Laboratory	mg/L	Z' score	Outlier type	D%	mg/L	Z' score	Outlier type	D%	Analytical method
3	1.67	-0.3		-1.9 %	1.58	-0.3		-2.3 %	Ion Chromatography
4	1.73	0.2		1.6 %	1.73	1.0		6.9 %	Ion Chromatography
5	1.68	-0.2		-1.5 %	1.59	-0.2		-1.5 %	Ion Chromatography
6	1.95	2.2	E	14.5 %	1.83	1.9		13.4 %	ICP-AES
8	1.57	-1.2		-7.8 %	1.48	-1.2		-8.5 %	Ion Chromatography
9	1.59	-1.0		-6.6 %	1.49	-1.1		-7.9 %	Ion Chromatography
10	1.67	-0.3		-2.2 %	1.58	-0.4		-2.6 %	Ion Chromatography
11	1.60	-0.9		-6.0 %	1.51	-1.0		-6.7 %	Ion Chromatography
12	1.63	-0.7		-4.3 %	1.55	-0.6		-4.3 %	Ion Chromatography
13	1.83	1.1		7.5 %	1.65	0.3		2.0 %	Ion Chromatography
14	1.67	-0.3		-1.7 %	1.58	-0.3		-2.1 %	Ion Chromatography
15	1.86	1.4		9.2 %	1.74	1.1		7.5 %	Ion Chromatography
16	1.83	1.1		7.5 %	1.76	1.3		8.8 %	Ion Chromatography
17	1.67	-0.3		-1.9 %	1.67	0.5		3.2 %	Ion Chromatography
19	1.71	0.1		0.4 %	1.62	0.0		0.1 %	Ion Chromatography
20	1.68	-0.2		-1.5 %	1.57	-0.4		-2.7 %	Ion Chromatography
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	16				16				
95% range of uncertainty of the mean (k=2)	±0.07				±0.07				
Median	1.68				1.59				
Assigned value	1.70				1.62				
Mean	1.70				1.62				
Reproducibility s.d. (SDPA)	0.11				0.11				
Rel. reproducibility s.d. (%SDPA)	6.3 %				6.7 %				
No. of meas. outside of tolerance limits.	1								

Table 13. Table of laboratory results and statistical parameters for calcium (Ca).

Calcium - Ca	ICPW37-A				ICPW37-B				
Laboratory	mg/L	Z' score	Outlier type	D%	mg/L	Z' score	Outlier type	D%	Analytical method
1	3.68	7.4	E	66.3 %	3.53	7.1	E	67.7 %	Ion Chromatography
3	2.16	-0.3		-2.3 %	2.07	-0.2		-1.6 %	Ion Chromatography
4	2.19	-0.1		-1.1 %	2.09	-0.1		-0.5 %	Flame AAS
5	2.11	-0.5		-4.5 %	2.01	-0.5		-4.5 %	Ion Chromatography
6	2.17	-0.2		-2.0 %	2.06	-0.2		-2.2 %	ICP-MS
7	1.98	-1.2		-10.5 %	1.88	-1.1		-10.6 %	ICP-AES
8	2.38	0.9		7.6 %	2.27	0.8		7.9 %	Ion Chromatography
9	2.25	0.2		1.8 %	2.14	0.2		1.7 %	Ion Chromatography
10	2.10	-0.5		-4.8 %	1.98	-0.6		-5.8 %	ICP-AES
11	2.20	-0.1		-0.5 %	2.10	0.0		-0.2 %	Ion Chromatography
12	1.89	-1.6		-14.7 %	1.78	-1.6		-15.3 %	Ion Chromatography
13	1.78	-2.2	E	-19.5 %	1.63	-2.3	E	-22.5 %	Other Method
14	2.17	-0.2		-1.8 %	2.09	-0.1		-0.5 %	ICP-AES
15	2.31	0.5		4.5 %	2.21	0.5		5.1 %	ICP-AES
16	2.60	2.0		17.6 %	2.50	2.0		18.8 %	Ion Chromatography
17	2.31	0.5		4.5 %	2.17	0.3		3.2 %	ICP-MS
18	2.42	1.0		9.3 %	2.33	1.1		10.7 %	ICP-MS
19	2.27	0.3		2.7 %	2.16	0.3		2.7 %	ICP-AES
20	2.15	-0.3		-2.8 %	2.00	-0.5		-5.2 %	ICP-MS
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	19				19				
95% range of uncertainty of the mean (k=2)	±0.11				±0.11				
Median	2.19				2.09				
Assigned value	2.21				2.10				
Mean	2.21				2.10				
Reproducibility s.d. (SDPA)	0.19				0.19				
Rel. reproducibility s.d. (%SDPA)	8.6 %				9.2 %				
No. of meas. outside of tolerance limits.	2				2				

Table 14. Table of laboratory results and statistical parameters for magnesium (Mg).

Magnesium - Mg	ICPW37-A				ICPW37-B				
Laboratory	mg/L	Z' score	Outlier type	D%	mg/L	Z' score	Outlier type	D%	Analytical method
1	0.495	6.6	E	41.8 %	0.464	6.2	E	43.1 %	Ion Chromatography
3	0.350	0.0		0.3 %	0.330	0.3		1.8 %	Ion Chromatography
4	0.354	0.2		1.4 %	0.332	0.3		2.4 %	Flame AAS
5	0.343	-0.3		-1.8 %	0.324	0.0		-0.2 %	Ion Chromatography
6	0.361	0.5		3.4 %	0.290	-1.5		-10.5 %	ICP-MS
7	0.311	-1.7		-10.9 %	0.293	-1.4		-9.6 %	ICP-AES
8	0.340	-0.4		-2.6 %	0.320	-0.2		-1.3 %	Ion Chromatography
9	0.340	-0.4		-2.6 %	0.320	-0.2		-1.3 %	Ion Chromatography
10	0.351	0.1		0.5 %	0.329	0.2		1.5 %	ICP-AES
11	0.330	-0.9		-5.5 %	0.310	-0.6		-4.4 %	Ion Chromatography
12	0.332	-0.8		-4.9 %	0.310	-0.6		-4.4 %	Ion Chromatography
13	0.339	-0.5		-2.9 %	0.306	-0.8		-5.6 %	Other Method
14	0.319	-1.4		-8.6 %	0.304	-0.9		-6.2 %	ICP-AES
15	0.347	-0.1		-0.6 %	0.330	0.3		1.8 %	ICP-AES
16	0.370	1.0		6.0 %	0.360	1.6		11.1 %	Ion Chromatography
17	0.374	1.1		7.1 %	0.338	0.6		4.3 %	ICP-MS
18	0.379	1.4		8.6 %	0.348	1.1		7.3 %	ICP-MS
19	0.363	0.6		4.0 %	0.341	0.8		5.2 %	ICP-AES
20	0.343	-0.3		-1.8 %	0.320	-0.2		-1.3 %	ICP-MS
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	19				19				
95% range of uncertainty of the mean (k=2)	±0.012				±0.012				
Median	0.347				0.324				
Assigned value	0.349				0.324				
Mean	0.349				0.324				
Reproducibility s.d. (SDPA)	0.021				0.022				
Rel. reproducibility s.d. (%SDPA)	6.0 %				6.6 %				
No. of meas. outside of tolerance limits.	1				1				

Table 15. Table of laboratory results and statistical parameters for sodium (Na).

Sodium - Na	ICPW37-A				ICPW37-B				
Laboratory	mg/L	Z' score	Outlier type	D%	mg/L	Z' score	Outlier type	D%	Analytical method
1	1.05	-0.3		-0.9 %	0.977	0.0		0.0 %	Ion Chromatography
3	1.04	-0.5		-1.5 %	0.970	-0.2		-0.7 %	Ion Chromatography
4	1.01	-1.3		-4.2 %	0.959	-0.4		-1.8 %	Flame AAS
5	1.06	0.1		0.5 %	0.983	0.1		0.6 %	Ion Chromatography
6	1.04	-0.6		-1.7 %	0.835	-3.2	E	-14.5 %	ICP-MS
7	0.90	-4.8	E	-15.0 %	0.805	-3.9	E	-17.6 %	ICP-AES
8	1.07	0.4		1.3 %	0.990	0.3		1.3 %	Ion Chromatography
9	1.06	0.1		0.4 %	0.980	0.1		0.3 %	Ion Chromatography
10	1.06	0.1		0.4 %	0.972	-0.1		-0.5 %	ICP-AES
11	1.07	0.4		1.3 %	0.990	0.3		1.3 %	Ion Chromatography
12	1.18	3.7	E	11.6 %	1.031	1.2		5.5 %	Ion Chromatography
13	1.07	0.4		1.3 %	0.973	-0.1		-0.4 %	Other Method
14	1.05	-0.2		-0.5 %	0.979	0.0		0.2 %	ICP-AES
15	1.04	-0.5		-1.5 %	0.969	-0.2		-0.8 %	ICP-AES
16	1.07	0.4		1.3 %	1.030	1.2		5.4 %	Ion Chromatography
17	1.14	2.6	E	8.0 %	1.040	1.4		6.5 %	ICP-MS
18	1.02	-1.1		-3.3 %	0.895	-1.9		-8.4 %	ICP-MS
19	1.10	1.3		4.2 %	1.020	1.0		4.4 %	ICP-AES
20	1.04	-0.5		-1.5 %	0.957	-0.5		-2.0 %	ICP-MS
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	19				19				
95% range of uncertainty of the mean (k=2)	±0.02				±0.024				
Median	1.06				0.977				
Assigned value	1.06				0.977				
Mean	1.06				0.977				
Reproducibility s.d. (SDPA)	0.03				0.042				
Rel. reproducibility s.d. (%SDPA)	3.0 %				4.3 %				
No. of meas. outside of tolerance limits.	3				2				

Table 16. Table of laboratory results and statistical parameters for potassium (K).

Potassium - K	ICPW37-A				ICPW37-B				
Laboratory	mg/L	Z' score	Outlier type	D%	mg/L	Z' score	Outlier type	D%	Analytical method
1	0.431	0.3		1.7 %	0.400	-0.2		-1.2 %	Ion Chromatography
3	0.430	0.2		1.5 %	0.410	0.2		1.2 %	Ion Chromatography
4	0.457	1.3		7.9 %	0.444	1.4		9.6 %	Flame AAS
5	0.422	0.0		-0.3 %	0.406	0.0		0.3 %	Ion Chromatography
6	0.388	-1.4		-8.4 %	0.327	-2.8	E	-19.2 %	ICP-MS
7	0.371	-2.0	E	-12.4 %	0.366	-1.4		-9.6 %	ICP-AES
8	0.410	-0.5		-3.2 %	0.390	-0.5		-3.7 %	Ion Chromatography
9	0.395	-1.1		-6.8 %	0.380	-0.9		-6.2 %	Ion Chromatography
10	0.430	0.2		1.5 %	0.408	0.1		0.8 %	ICP-AES
11	0.410	-0.5		-3.2 %	0.390	-0.5		-3.7 %	Ion Chromatography
12	0.466	1.6		10.0 %	0.438	1.2		8.2 %	Ion Chromatography
13	0.412	-0.5		-2.8 %	0.380	-0.9		-6.2 %	Other Method
14	0.409	-0.6		-3.5 %	0.397	-0.3		-2.0 %	ICP-AES
15	0.431	0.3		1.7 %	0.411	0.2		1.5 %	ICP-AES
16	0.410	-0.5		-3.2 %	0.430	0.9		6.2 %	Ion Chromatography
17	0.434	0.4		2.4 %	0.414	0.3		2.2 %	ICP-MS
18	0.440	0.6		3.8 %	0.404	0.0		-0.2 %	ICP-MS
19	0.456	1.2		7.6 %	0.445	1.4		9.9 %	ICP-AES
20	0.438	0.5		3.4 %	0.416	0.4		2.7 %	ICP-MS
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	19				19				
95% range of uncertainty of the mean (k=2)	±0.014				±0.015				
Median	0.430				0.406				
Assigned value	0.424				0.405				
Mean	0.424				0.405				
Reproducibility s.d. (SDPA)	0.025				0.027				
Rel. reproducibility s.d. (%SDPA)	5.9 %				6.6 %				
No. of meas. outside of tolerance limits.	1				1				

Table 17. Table of laboratory results and statistical parameters for total organic carbon (TOC).

Total organic carbon - TOC	ICPW37-A				ICPW37-B				
Laboratory	mg/L	Z' score	Outlier type	D%	mg/L	Z' score	Outlier type	D%	Analytical method
1	4.34	-0.2		-2.1 %	4.04	-0.2		-2.2 %	Catalytic combustion, EN 1484
3	4.73	0.5		6.7 %	4.39	0.6		6.2 %	Catalytic combustion, EN 1484
6	3.83	-1.1		-13.6 %	3.66	-1.1		-11.4 %	Other Method
8	5.30	1.6		19.6 %	4.70	1.3		13.8 %	UV/peroxodisulphate oxidation EN 1484
10	5.07	1.2		14.4 %	4.66	1.2		12.8 %	UV/peroxodisulphate oxidation EN 1484
11	3.51	-1.7		-20.8 %	3.42	-1.6		-17.2 %	Catalytic combustion, EN ISO 20236
12	4.43	0.0		0.0 %	4.09	-0.1		-1.0 %	Catalytic combustion, EN 1484
13	4.09	-0.6		-7.7 %	3.65	-1.1		-11.7 %	Other Method
14	4.90	0.8		10.5 %	4.40	0.6		6.4 %	Catalytic combustion, EN ISO 20236
15	4.41	0.0		-0.5 %	4.34	0.5		5.0 %	Catalytic combustion, EN 1484
16	4.50	0.1		1.5 %	4.30	0.4		4.1 %	Catalytic combustion, EN 1484
17	4.61	0.3		4.0 %	4.12	0.0		-0.3 %	Catalytic combustion, EN ISO 20236
19	4.38	-0.1		-1.2 %	4.04	-0.2		-2.2 %	Catalytic combustion, EN 1484
20	3.89	-1.0		-12.2 %	3.94	-0.4		-4.6 %	Catalytic combustion, EN 1484
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	14				14				
95% range of uncertainty of the mean (k=2)	±0.35				±0.27				
Median	4.42				4.11				
Assigned value	4.43				4.13				
Mean	4.43				4.13				
Reproducibility s.d. (SDPA)	0.52				0.41				
Rel. reproducibility s.d. (%SDPA)	11.8 %				9.9 %				

Table 18. Table of laboratory results and statistical parameters for total phosphorous (Tot-P).

Total phosphorous	ICPW37-A				ICPW37-B				
Laboratory	µg/L P	Z' score	Outlier type	D%	µg/L P	Z' score	Outlier type	D%	Analytical method
1	11.9	-0.8		-26.3 %	14.9	0.0		1.1 %	EN ISO 15681-2
3	20.5	0.8		26.7 %	11.8	-0.5		-20.3 %	EN ISO 15681-2
4	18.4	0.4		13.7 %	8.2	-1.2		-44.4 %	EN ISO 6878
6	20.1	0.7		24.3 %	22.6	1.4		53.1 %	Simplified photometry
7	9.2	-1.3		-43.4 %	8.5	-1.1		-42.4 %	ICP-AES
8	18.0	0.3		11.3 %	17.0	0.4		15.2 %	NS 4725
10	8.5	-1.4		-47.3 %	11.5	-0.6		-22.0 %	Other Method
11	20.0	0.7		23.6 %	18.0	0.6		21.9 %	EN ISO 6878
13	16.0	0.0		-1.1 %	13.8	-0.2		-6.5 %	Simplified photometry
14	14.0	-0.4		-13.5 %	11.0	-0.7		-25.5 %	ICP-AES
15	20.0	0.7		23.6 %	19.0	0.8		28.7 %	EN ISO 6878
16	15.9	-0.1		-1.7 %	15.3	0.1		3.6 %	Simplified photometry
17	12.2	-0.7		-24.6 %	11.8	-0.5		-20.1 %	EN ISO 6878
18	29.0	2.4	E	79.3 %	34.0	3.4	E	130.3 %	ICP-MS
19	19.0	0.5		17.5 %	20.0	0.9		35.5 %	EN ISO 6878
20	11.2	-0.9		-30.7 %	10.0	-0.9		-32.5 %	EN ISO 15681-2
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	16				16				
95% range of uncertainty of the mean (k=2)	±3.2				±3.4				
Median	17.0				14.4				
Assigned value	16.2				14.8				
Mean	16.2				14.8				
Reproducibility s.d. (SDPA)	5.2				5.4				
Rel. reproducibility s.d. (%SDPA)	31.9 %				36.4 %				
No. of meas. outside of tolerance limits.	1				1				

Table 19. Table of laboratory results and statistical parameters for total nitrogen (Tot-N).

Total nitrogen - Tot-N	ICPW37-A				ICPW37-B				
Laboratory	µg/L N	Z' score	Outlier type	D%	µg/L N	Z' score	Outlier type	D%	Analytical method
1	320	2.3	E	56.9 %	288	1.9		50.1 %	Catalytic combustion, EN 12260
3	196	-0.2		-3.8 %	175	-0.3		-8.9 %	Persulfate oxidation unbuffered NS 4743
8	210	0.1		3.1 %	200	0.2		4.1 %	Persulfate oxidation unbuffered NS 4743
10	163	-0.8		-20.0 %	161	-0.6		-16.0 %	Persulfate oxidation, buffered EN ISO 11905-1
11	200	-0.1		-1.8 %	180	-0.2		-6.3 %	Persulfate oxidation, buffered EN ISO 11905-1
14	232	0.6		13.9 %	213	0.4		10.9 %	Catalytic combustion, EN ISO 20236
15	212	0.2		4.0 %	193	0.0		0.5 %	Persulfate oxidation, buffered EN ISO 11905-1
16	127	-1.5		-37.7 %	124	-1.3		-35.4 %	Catalytic combustion, EN 12260
17	168	-0.7		-17.6 %	156	-0.7		-18.8 %	Catalytic combustion, EN ISO 20236
19	193	-0.2		-5.3 %	187	-0.1		-2.6 %	Catalytic combustion, EN 12260
20	260	1.1		27.6 %	260	1.3		35.4 %	Persulfate oxidation unbuffered NS 4743
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of labs that submitted results	11				11				
95% range of uncert. of the mean (k=2)	±35				±36				
Median	200				187				
Assigned value	204				192				
Mean	204				192				
Reproducibility s.d. (SDPA)	47				47				
Rel. reproducibility s.d. (%SDPA)	23.0 %				24.7 %				
No. of meas. outside of tol. limits.	1								

Table 20. Table of laboratory results and statistical parameters for aluminium (Al).

Aluminium - Al	ICPW37-C				ICPW37-D				
Laboratory	µg/L	Z' score	Outlier type	D%	µg/L	Z' score	Outlier type	D%	Analytical method
3	61.6	-1.0		-10.5 %	56.6	-1.1		-14.9 %	ICP-AES
4	59.0	-1.4		-14.3 %	57.0	-1.1		-14.3 %	GF-AAS
6	60.8	-1.1		-11.6 %	57.2	-1.0		-14.0 %	ICP-MS
8	67.4	-0.2		-2.1 %	65.7	-0.1		-1.2 %	ICP-MS
12	69.6	0.1		1.1 %	66.4	0.0		-0.1 %	ICP-MS
14	72.7	0.6		5.6 %	67.1	0.1		0.9 %	ICP-MS
15	69.3	0.1		0.7 %	66.3	0.0		-0.3 %	ICP-AES
16 (new instrument, not yet validated)	141.0	10.4	E	104.8 %	137.0	7.9	E	106.1 %	ICP-MS
17	72.7	0.6		5.6 %	69.1	0.3		4.0 %	ICP-MS
18	73.2	0.6		6.3 %	79.6	1.5		19.7 %	ICP-MS
19	70.9	0.3		3.0 %	67.4	0.1		1.4 %	ICP-MS
20	70.2	0.2		2.0 %	66.9	0.0		0.7 %	ICP-MS
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	12				12				
95% range of uncertainty of the mean (k=2)	±4.7				±6.0				
Median	69.9				66.7				
Assigned value	68.8				66.5				
Mean	68.8				66.5				
Reproducibility s.d. (SDPA)	6.6				8.3				
Rel. reproducibility s.d. (%SDPA)	9.5 %				12.6 %				
No. of meas. outside of tolerance limits.	1				1				

Table 21. Table of laboratory results and statistical parameters for iron (Fe).

Iron - Fe	ICPW37-C				ICPW37-D				
Laboratory	µg/L	Z' score	Outlier type	D%	µg/L	Z' score	Outlier type	D%	Analytical method
3	22.6	0.7		3.9 %	13.5	-4.9	E	-32.7 %	ICP-AES
4	22.9	1.0		5.3 %	19.8	-0.2		-1.3 %	ICP-MS
5	20.5	-1.1		-5.9 %	17.9	-1.6		-10.9 %	ICP-MS
6	20.9	-0.7		-3.7 %	19.9	-0.1		-1.0 %	ICP-AES
8	22.0	0.2		1.1 %	20.0	0.0		-0.3 %	ICP-MS
10	20.2	-1.3		-7.0 %	19.0	-0.8		-5.3 %	ICP-AES
12	20.6	-1.0		-5.2 %	19.4	-0.5		-3.4 %	ICP-MS
14	22.2	0.4		2.1 %	20.8	0.5		3.6 %	ICP-MS
15	21.6	-0.1		-0.7 %	20.7	0.5		3.2 %	ICP-MS
16	22.8	0.9		4.8 %	21.0	0.7		4.7 %	Simplified photometry
17	21.7	0.0		-0.3 %	20.9	0.6		4.2 %	ICP-MS
18	28.1	5.3	E	29.0 %	25.5	4.1	E	27.2 %	ICP-MS
19	22.1	0.3		1.6 %	21.1	0.8		5.2 %	ICP-MS
20	21.0	-0.7		-3.7 %	20.0	-0.1		-0.4 %	ICP-MS
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	14				14				
95% range of uncertainty of the mean (k=2)	±0.8				±0.8				
Median	21.9				20.0				
Assigned value	21.8				20.1				
Mean	21.8				20.1				
Reproducibility s.d. (SDPA)	1.1				1.3				
Rel. reproducibility s.d. (%SDPA)	5.2 %				6.3 %				
No. of meas. outside of tolerance limits.	1				2				

Table 22. Table of laboratory results and statistical parameters for manganese (Mn).

Manganese - Mn	ICPW37-C				ICPW37-D				
Laboratory	µg/L	Z' score	Outlier type	D%	µg/L	Z' score	Outlier type	D%	Analytical method
3	1.10	-1.0		-10.3 %	1.00	-1.3		-12.1 %	ICP-AES
4	1.20	-0.2		-2.2 %	1.10	-0.3		-3.4 %	ICP-MS
5	1.12	-0.9		-9.0 %	1.03	-1.0		-9.5 %	ICP-MS
6	< 10.00				< 10.00				ICP-AES
8	1.20	-0.2		-2.2 %	1.12	-0.2		-1.6 %	ICP-MS
12	1.06	-1.4		-13.5 %	1.01	-1.1		-10.9 %	ICP-MS
14	1.25	0.2		1.9 %	1.16	0.2		1.9 %	ICP-MS
15	1.24	0.1		1.1 %	1.19	0.5		4.5 %	ICP-MS
16 (new instrument, not yet validated)	2.34	9.2	E	90.8 %	2.13	9.1	E	87.1 %	ICP-MS
17	1.26	0.3		2.7 %	1.19	0.5		4.5 %	ICP-MS
18	1.35	1.1		10.5 %	1.25	1.0		9.7 %	ICP-MS
19	1.23	0.0		0.3 %	1.15	0.1		1.0 %	ICP-MS
20	1.31	0.7		6.6 %	1.16	0.2		2.2 %	ICP-MS
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	13				13				
95% range of uncertainty of the mean (k=2)	±0.08				±0.07				
Median	1.23				1.15				
Assigned value	1.23				1.14				
Mean	1.23				1.14				
Reproducibility s.d. (SDPA)	0.11				0.10				
Rel. reproducibility s.d. (%SDPA)	9.3 %				9.1 %				
No. of meas. outside of tolerance limits.	1				1				

Table 23. Table of laboratory results and statistical parameters for cadmium (Cd).

Cadmium - Cd	ICPW37-C				ICPW37-D				
Laboratory	µg/L	Z' score	Outlier type	D%	µg/L	Z' score	Outlier type	D%	Analytical method
3	1.80	-1.6		-8.8 %	1.40	-3.8	E	-26.1 %	ICP-AES
4	2.02	0.4		2.3 %	1.96	0.5		3.4 %	GF-AAS
5	1.93	-0.4		-2.0 %	1.80	-0.7		-5.0 %	ICP-MS
6	2.01	0.3		1.8 %	1.94	0.4		2.4 %	ICP-MS
8	1.90	-0.7		-3.7 %	1.81	-0.6		-4.5 %	ICP-MS
12	2.01	0.3		1.6 %	1.93	0.3		1.8 %	ICP-MS
14	2.21	2.1	E	12.0 %	2.11	1.6		11.3 %	ICP-MS
15	2.00	0.2		1.3 %	1.95	0.4		2.9 %	ICP-MS
16 (new instrument, not yet validated)	1.63	-3.1	E	-17.4 %	1.66	-1.8		-12.4 %	ICP-MS
17	2.04	0.6		3.4 %	1.94	0.3		2.4 %	ICP-MS
18	1.92	-0.5		-2.9 %	1.97	0.5		3.7 %	ICP-MS
19	2.01	0.3		1.8 %	1.87	-0.2		-1.3 %	ICP-MS
20	2.06	0.8		4.3 %	1.97	0.6		3.9 %	ICP-MS
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	13				13				
95% range of uncertainty of the mean (k=2)	±0.07				±0.09				
Median	2.01				1.94				
Assigned value	1.97				1.90				
Mean	1.97				1.90				
Reproducibility s.d. (SDPA)	0.11				0.12				
Rel. reproducibility s.d. (%SDPA)	5.3 %				6.5 %				
No. of meas. outside of tolerance limits.	2				1				

Table 24. Table of laboratory results and statistical parameters for lead (Pb).

Lead - Pb	ICPW37-C				ICPW37-D				
Laboratory	µg/L	Z' score	Outlier type	D%	µg/L	Z' score	Outlier type	D%	Analytical method
3	< 3.00				< 3.00				ICP-AES
4	2.10	0.3		1.6 %	2.10	0.8		3.4 %	GF-AAS
5	1.93	-1.4		-6.8 %	1.97	-0.7		-2.9 %	ICP-MS
6	2.11	0.4		2.1 %	2.04	0.1		0.4 %	ICP-MS
8	1.99	-0.8		-3.7 %	1.96	-0.9		-3.5 %	ICP-MS
12	1.91	-1.6		-7.7 %	1.82	-2.6	E	-10.3 %	ICP-MS
14	2.05	-0.2		-0.8 %	1.98	-0.6		-2.5 %	ICP-MS
15	2.09	0.2		1.2 %	2.06	0.4		1.4 %	ICP-MS
16 (new instrument, not yet validated)	2.11	0.4		2.1 %	2.08	0.6		2.4 %	ICP-MS
17	2.14	0.7		3.6 %	2.09	0.7		2.9 %	ICP-MS
18	2.25	1.8		8.8 %	2.24	2.6	E	10.4 %	ICP-MS
19	2.08	0.1		0.7 %	2.00	-0.4		-1.5 %	ICP-MS
20	2.06	0.0		-0.1 %	2.03	0.0		-0.1 %	ICP-MS
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	13				13				
95% range of uncertainty of the mean (k=2)	±0.07				±0.06				
Median	2.08				2.03				
Assigned value	2.07				2.03				
Mean	2.07				2.03				
Reproducibility s.d. (SDPA)	0.10				0.08				
Rel. reproducibility s.d. (%SDPA)	4.6 %				3.8 %				
No. of meas. outside of tolerance limits.					2				

Table 25. Table of laboratory results and statistical parameters for copper (Cu).

Copper - Cu	ICPW37-C				ICPW37-D				
Laboratory	µg/L	Z' score	Outlier type	D%	µg/L	Z' score	Outlier type	D%	Analytical method
3	1.50	-3.6	E	-36.9 %	< 1.00				ICP-AES
4	2.40	0.1		0.9 %	2.80	1.3		19.9 %	GF-AAS
5	2.21	-0.7		-6.9 %	2.07	-0.8		-11.4 %	ICP-MS
6	2.40	0.1		1.0 %	2.27	-0.2		-2.9 %	ICP-MS
8	2.34	-0.2		-1.6 %	2.19	-0.4		-6.2 %	ICP-MS
12	1.91	-1.9		-19.7 %	1.75	-1.7		-24.9 %	ICP-MS
14	2.49	0.5		4.7 %	2.28	-0.2		-2.4 %	ICP-MS
15	2.72	1.4		14.3 %	2.79	1.3		19.4 %	ICP-MS
17	2.43	0.2		2.2 %	2.27	-0.2		-2.8 %	ICP-MS
18	2.58	0.8		8.3 %	2.55	0.6		9.0 %	ICP-MS
19	2.49	0.5		4.7 %	2.35	0.0		0.6 %	ICP-MS
20	2.41	0.1		1.4 %	2.28	-0.2		-2.5 %	ICP-MS
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	12				12				
95% range of uncertainty of the mean (k=2)	±0.17				±0.24				
Median	2.41				2.28				
Assigned value	2.38				2.34				
Mean	2.38				2.34				
Reproducibility s.d. (SDPA)	0.23				0.32				
Rel. reproducibility s.d. (%SDPA)	9.6 %				13.8 %				
No. of meas. outside of tolerance limits.	1								

Table 26. Table of laboratory results and statistical parameters for nickel (Ni).

Nickel - Ni	ICPW37-C				ICPW37-D				
Laboratory	µg/L	Z' score	Outlier type	D%	µg/L	Z' score	Outlier type	D%	Analytical method
3	< 1.00				< 1.00				ICP-AES
4	3.00	-0.6		-3.0 %	2.90	-0.5		-2.1 %	GF-AAS
5	2.90	-1.3		-6.4 %	2.77	-1.5		-6.5 %	ICP-MS
6	3.11	0.1		0.7 %	2.98	0.1		0.6 %	ICP-MS
8	3.03	-0.4		-2.0 %	2.90	-0.5		-2.1 %	ICP-MS
12	2.94	-1.0		-4.9 %	2.84	-1.0		-4.2 %	ICP-MS
14	3.14	0.3		1.5 %	2.98	0.1		0.6 %	ICP-MS
15	3.23	0.9		4.4 %	3.06	0.8		3.3 %	ICP-MS
17	3.06	-0.2		-1.1 %	2.96	0.0		0.0 %	ICP-MS
18	3.29	1.4		6.5 %	3.28	2.5	E	10.6 %	ICP-MS
19	3.18	0.6		2.8 %	3.07	0.9		3.7 %	ICP-MS
20	3.14	0.3		1.6 %	2.97	0.0		0.2 %	ICP-MS
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	12				12				
95% range of uncertainty of the mean (k=2)	±0.10				±0.09				
Median	3.11				2.97				
Assigned value	3.09				2.96				
Mean	3.09				2.96				
Reproducibility s.d. (SDPA)	0.14				0.12				
Rel. reproducibility s.d. (%SDPA)	4.5 %				4.0 %				
No. of meas. outside of tolerance limits.					1				

Table 27. Table of laboratory results and statistical parameters for zinc (Zn).

Zinc - Zn	ICPW37-C				ICPW37-D				
Laboratory	µg/L	Z' score	Outlier type	D%	µg/L	Z' score	Outlier type	D%	Analytical method
3	4.60	-0.7		-7.3 %	< 3.00				ICP-AES
4	3.30	-3.0	E	-33.5 %	3.60	-3.0	E	-31.5 %	ICP-MS
5	4.77	-0.4		-4.0 %	5.03	-0.4		-4.2 %	ICP-MS
6	5.49	1.0		10.7 %	5.74	0.9		9.3 %	ICP-MS
8	4.90	-0.1		-1.3 %	5.10	-0.3		-2.9 %	ICP-MS
12	5.15	0.3		3.7 %	5.16	-0.2		-1.8 %	ICP-MS
14	5.24	0.5		5.6 %	5.43	0.3		3.4 %	ICP-MS
15	7.26	4.2	E	46.3 %	13.00	14.1	E	147.4 %	ICP-MS
16 (new instrument, not yet validated)	1.48	-6.4	E	-70.2 %	1.68	-6.5	E	-68.0 %	ICP-MS
17	5.04	0.1		1.5 %	5.24	0.0		-0.3 %	ICP-MS
18	4.89	-0.1		-1.4 %	5.51	0.5		4.9 %	ICP-MS
19	5.04	0.1		1.5 %	5.36	0.2		2.0 %	ICP-MS
20	5.29	0.6		6.5 %	5.48	0.4		4.3 %	ICP-MS
-	-	-	-	-	-	-	-	-	-
Statistical method	ISO 5725-5 (Alg. A+S)				ISO 5725-5 (Alg. A+S)				
Assessment	|Z'|<=2.0				|Z'|<=2.0				
No. of laboratories that submitted results	13				13				
95% range of uncertainty of the mean (k=2)	±0.36				±0.37				
Median	5.04				5.30				
Assigned value	4.96				5.25				
Mean	4.96				5.25				
Reproducibility s.d. (SDPA)	0.52				0.52				
Rel. reproducibility s.d. (%SDPA)	10.4 %				9.8 %				
No. of meas. outside of tolerance limits.	3				3				

Thematic reports from the ICP Waters programme

Since its establishment in 1985, the ICP Waters programme has prepared numerous assessments, reports and publications that address the effects of long-range transported air pollution, including thematic reports, chemical intercalibrations, biological intercalibrations, proceedings of Task Force meetings, and peer-reviewed articles. Reports and publications are available at the ICP Waters website; http://www.icp-waters.no/

Thematic reports from the ICP Waters programme from 2000 up to present are listed below.

Velle, G.; Bodin, C.L.; Arle, J.; Austnes, K.; Boggero, A.; Bojkova, J.; Fornaroli, R.; Fölster, J.; Goedkoop, W.; Jones, I.; Juggins, S.; Lau, D.C.P.; Monteith, D.; Murphy, J.; Musazzi, S.; Shilland, E.; Steingruber, S.; Wiklund, M.-L.; de Wit, H. 2023. Responses of benthic invertebrates to chemical recovery from acidification. NIVA SNO 7881-2023. **ICP Waters report 153/2023**.

Austnes, K., Hjermann, D.Ø., Sample, J., Wright, R. F., Kaste, Ø., and de Wit, H. 2022. Nitrogen in surface waters: time trends and geographical patterns explained by deposition levels and catchment characteristics. NIVA SNO 7728-2022. **ICP Waters report 149/2022**.

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

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

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**

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**.

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., 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**.

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

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

Velle, G., Telford, R.J., Curtis, C., Eriksson, L., Fjellheim, A., Frolova, M., Fölster J., Grudule N., Halvorsen G.A., Hildrew A., Hoffmann A., Indriksone I., Kamasová L., Kopáček J., Orton S., Krám P., Monteith D.T., Senoo T., Shilland E.M., Stuchlík E., Wiklund M.L., de Wit, H. and Skjelkvaale B.L. 2013. Biodiversity in

freshwaters. Temporal trends and response to water chemistry. NIVA report SNO 6580-2013. **ICP Waters Report 114/2013**.

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**.

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**.

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**.

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., 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**.

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**.

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**.

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**.

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.**

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.**

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

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

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

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

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

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.**

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**.

The Norwegian Institute for Water Research

We are Norway's premier research institute in the fields of water and the environment. We are experts on ecosystems in both freshwater and marine environments, from mountains, lakes and rivers, to fjords, coasts and oceans. We develop science-based knowledge and solutions to challenges related to the interaction between water and climate, the environment, nature, people, resources and society.