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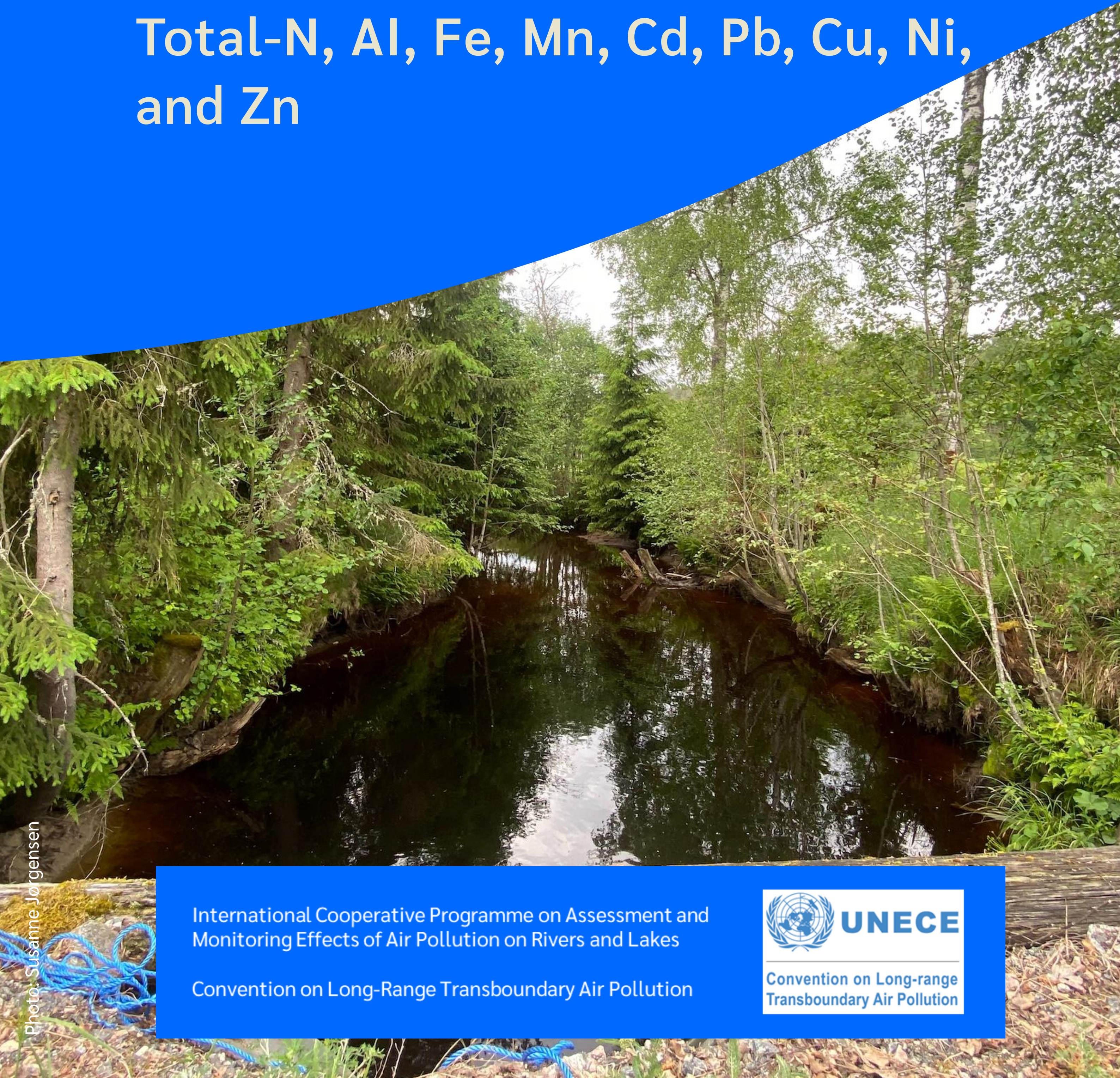
ICP Waters Report 157/2024

Intercomparison 2438: 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



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

Convention on Long-Range Transboundary Air Pollution

UNECE

Convention on Long-range Transboundary Air Pollution

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Abstract
Twenty-one 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: Laboratoriesammenlikning, 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 2438
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 2024

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

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

One 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. Inter-laboratory quality assurance tests are a tool in this work. Here any biases between analyses carried out by the individual participants in the programme are identified and controlled.

Here we report the results from the 38th intercomparison of chemical analyses.

Oslo, 9th of December 2024

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, samples of the same water are distributed to all the participating laboratories which analyse the samples for a set repertoire of parameters with their method of choice. Two different sets of samples are prepared and distributed, one for the determination of ions and the other for metals. 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.

The 2438 edition of the test was conducted in the period from June to October 2024. A total of 21 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 unstable and could not be determined.

The acceptance criteria used was the same as last year. Together with the consensus value, a standard deviation for proficiency assessment (SDPA) is calculated from the participants’ results, and Z’-scores are calculated. Participants reporting values with a Z’ score < ±2 are said to have acceptable results. The circle in the Youden charts is set at 2xSDPA, which means that points inside the circle have Z’ score < ±2 for both samples represented by the point. As such, the Youden charts can be used as a visual representation of the participants’ Z’ score results.

The relative SDPA values show the conformity of the reported results for each analysis parameter and sample. Low relative SDPA means that the results have high conformity and the parameters with the lowest rel. SDPA was chloride (2-3%), iron and zinc (3%). Parameters with low conformity and high rel. SPDA this year was alkalinity (23-26%), Tot-P (18-23%), Tot-N (13-16%) and nickel (11-15%). In addition, TOC had one sample with rel. SDPA of 14%.

For several of the parameters, different analytical techniques was used by the various laboratories. The use of different techniques can challenge the unity of the results, with the effect typically being more severe for low analyte concentrations. For total phosphorous, as much as seven different methods was 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 confirm the trends observed 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 overvåking av overflatevann hos de ulike programdeltakerne. Testen utføres årlig, og er basert på ringtest-prinsippet. Dette foregår ved at en prøve av det samme vannet distribueres til alle deltakende laboratorier, som deretter analyserer prøven for gitte parametere, med den metoden de ønsker. To ulike prøvesett prepareres og distribueres, ett for bestemmelse av ioner, og et for bestemmelse av metaller. Resultatene blir sammenstilt og analysert, ved hjelp av statistiske metoder. En konsensverdi («tildelt verdi») beregnes for hver prøve, ved å bruke deltakernes rapporterte verdier.

Denne 2438-utgaven av testen ble utført i perioden juni til oktober 2024. Totalt 21 laboratorier deltok, og disse representerte 15 ulike land. Deltakerne ble invitert til å determinere 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 var nitrat ustabil og kunne ikke benyttes.

Akseptansekriteriene som ble benyttet var de samme som i fjor. Sammen med konsensverdi, ble det utregnet «standard deviation for proficiency assessment» (SDPA) fra deltakernes resultater. Z'-score utregnes for resultatene og resultater med Z'-score < ±2 ble behandlet som akseptable resultater. Sirkelen i Youdendiagrammene er satt til 2xSDPA, som betyr at punkter innenfor sirkelen har Z' score < ±2 for begge prøvene representert av det aktuelle punktet. Youdendiagrammene kan derfor benyttes som en visuell representering av deltakernes Z' score-resultater.

De relative SDPA-verdiene viser hvor mye samsvar det i de innrapporterte resultatene for hver analyseparameter og prøve. Lav relative SDPA betyr at resultatene har stort samsvar og parameterne med lavest relativ SDPA var klorid (2-3%), jern og sink (3%). Parametere med lite samsvar og høy relative SDPA var i år alkalinitet (23-26%), Tot-P (18-23%), Tot-N (13-16%) og nikkel (11-15%). I tillegg hadde TOC én prøve med relativ SDPA på 14%.

For mange av parameterne ble det benyttet flere ulike analytiske teknikker. Variasjon i teknikkene som benyttes til analyse kan utfordre konsensusen i resultatene, og effekten er typisk større for analytter med lav konsentrasjon. For totalfosfor, ble hele syv ulike metoder benyttet. 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 sensitive ICP-MS den mest foretrukne teknikken. Dette bekrefter trendene som er observert de siste årene, at plasmateknikker tar over for de mer tradisjonelle atomabsorpsjon-teknikkene. I tillegg erstatter den mer sensitive massedetektoren (ICP-MS) mer og mer den optiske omisjons 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 contributes with data from their national monitoring programmes.

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

The acceptance criteria were changed in 2023 and is now based on the Z'-scores obtained for each result. 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 systematic effect will be evident in the distribution of the results in the Youden chart, by the points residing along the 45° angled line. One other cause of poor acceptance ratio is when the concentration in the sample is low, and close to the limit of quantification of the method used. This will most often appear in the Youden chart as a distribution of the results perpendicular to the 45° angled line.

This thirty-eight chemical intercomparison test, called 2438, 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, total organic carbon and aluminium was 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 24th of June 2024. 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 can lead to strong systematic biases in the results. Since not one method can be argued to be better than another, this issue has persisted in the interlaboratory harmonisation.

As for the previous year's intercomparison test, new statistical software was used. The switch of statistical software 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. The Youden charts are still used as a visual evaluation of the results. The circle is set to 2xSDPA (standard deviation for proficiency assessment), 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. With the new software, results from each sample in the sample sets is evaluated individually and each is assigned a Z'-score. More information on the statistics used can be found in Appendix C.

Individual results, including Z'-scores and the relative deviation (%D) from the assigned values can be found in Table 6 to Table 26 in the Appendix 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

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

Sample	Measurand description	Assigned value	Unit	SDPA	Rel. SDPA	# values[1]
ICPW38-A	pH	6.06	PH-units	0.34	5.60 %	19
ICPW38-B	pH	6.09	PH-units	0.32	5.30 %	18
ICPW38-A	Conductivity	3.72	mS/m	0.18	4.76 %	18
ICPW38-B	Conductivity	3.86	mS/m	0.18	4.64 %	17
ICPW38-A	Alkalinity	0.133	mmol/l	0.035	26.01 %	14
ICPW38-B	Alkalinity	0.142	mmol/l	0.032	22.60 %	13
ICPW38-A	Cl - Chloride	3.29	mg/l	0.06	1.91 %	17
ICPW38-B	Cl - Chloride	3.47	mg/l	0.09	2.68 %	17
ICPW38-A	SO4 - Sulphate	1.75	mg/l	0.07	4.28 %	18
ICPW38-B	SO4 - Sulphate	1.78	mg/l	0.08	4.48 %	17
ICPW38-A	Ca - Calcium	2.43	mg/l	0.21	8.47 %	20
ICPW38-B	Ca - Calcium	2.45	mg/l	0.19	7.71 %	19
ICPW38-A	Mg - Magnesium	0.634	mg/l	0.043	6.78 %	20
ICPW38-B	Mg - Magnesium	0.646	mg/l	0.038	5.82 %	19
ICPW38-A	Na - Sodium	2.59	mg/l	0.10	3.96 %	20
ICPW38-B	Na - Sodium	2.70	mg/l	0.15	5.52 %	19
ICPW38-A	K - Potassium	1.80	mg/l	0.08	4.29 %	20
ICPW38-B	K - Potassium	1.89	mg/l	0.10	5.16 %	19
ICPW38-A	TOC - Total organic carbon	14.3	mg/l	1.0	6.95 %	15
ICPW38-B	TOC - Total organic carbon	14.5	mg/l	2.0	13.79 %	14
ICPW38-A	TOT-P - Total phosphorus	113	µg/l P	21	18.27 %	16
ICPW38-B	TOT-P - Total phosphorus	118	µg/l P	27	23.14 %	15
ICPW38-A	TOT-N - Total nitrogen	768	µg/l N	119	15.50 %	13
ICPW38-B	TOT-N - Total nitrogen	875	µg/l N	116	13.24 %	12
ICPW38-C	Al - Aluminium	146	µg/l	11	7.40 %	13
ICPW38-D	Al - Aluminium	153	µg/l	8.0	5.10 %	13
ICPW38-C	Fe - Iron	239	µg/l	8.0	3.37 %	15
ICPW38-D	Fe - Iron	240	µg/l	7.0	2.96 %	15
ICPW38-C	Mn - Manganese	1.68	µg/l	0.09	5.53 %	13
ICPW38-D	Mn - Manganese	1.56	µg/l	0.09	5.56 %	13
ICPW38-C	Cd - Cadmium	1.11	µg/l	0.08	7.35 %	14
ICPW38-D	Cd - Cadmium	0.986	µg/l	0.08	8.11 %	14
ICPW38-C	Pb - Lead	1.20	µg/l	0.10	8.48 %	13
ICPW38-D	Pb - Lead	1.13	µg/l	0.11	9.32 %	13
ICPW38-C	Cu - Copper	14.5	µg/l	1.5	10.34 %	13
ICPW38-D	Cu - Copper	16.6	µg/l	1.5	8.99 %	13
ICPW38-C	Ni - Nickel	1.69	µg/l	0.26	15.07 %	14
ICPW38-D	Ni - Nickel	1.84	µg/l	0.20	10.98 %	14
ICPW38-C	Zn - Zinc	25.9	µg/l	0.80	3.23 %	14
ICPW38-D	Zn - Zinc	20.3	µg/l	0.60	2.78 %	14

[1] *Number of values used for the statistics calculations. This may differ from the number of reported results, since values lower than the quantification limit are not used for the statistic calculations.*

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	37	35	2	0	95
Conductivity (mS/m)	35	32	2	1	91
Alkalinity (mmol/L)	27	25	0	2	93
Cl - Chloride (mg/L)	35	28	2	5	80
SO4 - Sulphate (mg/L)	37	33	1	3	89
Ca - Calcium (mg/L)	39	34	5	0	87
Mg - Magnesium (mg/L)	39	35	2	2	90
Na - Sodium (mg/L)	39	36	2	1	92
K - Potassium (mg/L)	39	37	0	2	95
TOC - Total organic carbon (mg/L)	29	25	2	2	86
TOT-P - Total phosphorus (µg P/L)	31	29	1	1	94
TOT-N - Total nitrogen (µg N/L)	25	25	0	0	100
Al - Aluminium (µg/L)	26	24	0	2	92
Fe - Iron (µg/L)	30	27	1	2	90
Mn - Manganese (µg/L)	28	25	3	0	89
Cd - Cadmium (µg/L)	28	25	2	1	89
Pb - Lead (µg/L)	28	26	1	1	93
Cu - Copper (µg/L)	26	24	1	1	92
Ni - Nickel (µg/L)	28	26	2	0	93
Zn - Zinc (µg/L)	28	25	2	1	89
Total	661	603	31	27	91

3.1 pH

Values of pH were reported by 19 laboratories, among which 18 results were marked as satisfactory (|Z'| < 2). The calculated SDPA is quite large, at over Δ0.3 pH units, meaning that results within approximately Δ0.6 pH units from the assigned value is marked as satisfactory. It seems that samples analysed within the first month are more correlated than results measured on samples being stored for a longer time. This can be seen in Figure 1 where the reported results for pH are sorted by the analysis date.

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.

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 1 participant used equilibration. The final participant did not give any information about the method used. The Youden chart showed that most errors were systematic in the data set for pH (Figure 2)

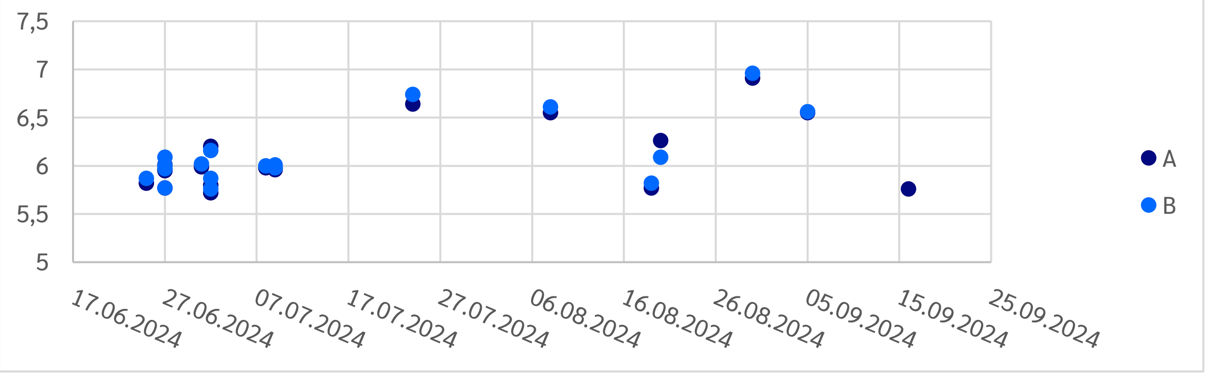

Figure 1. Diagram showing reported results for pH, sorted by analysis date.

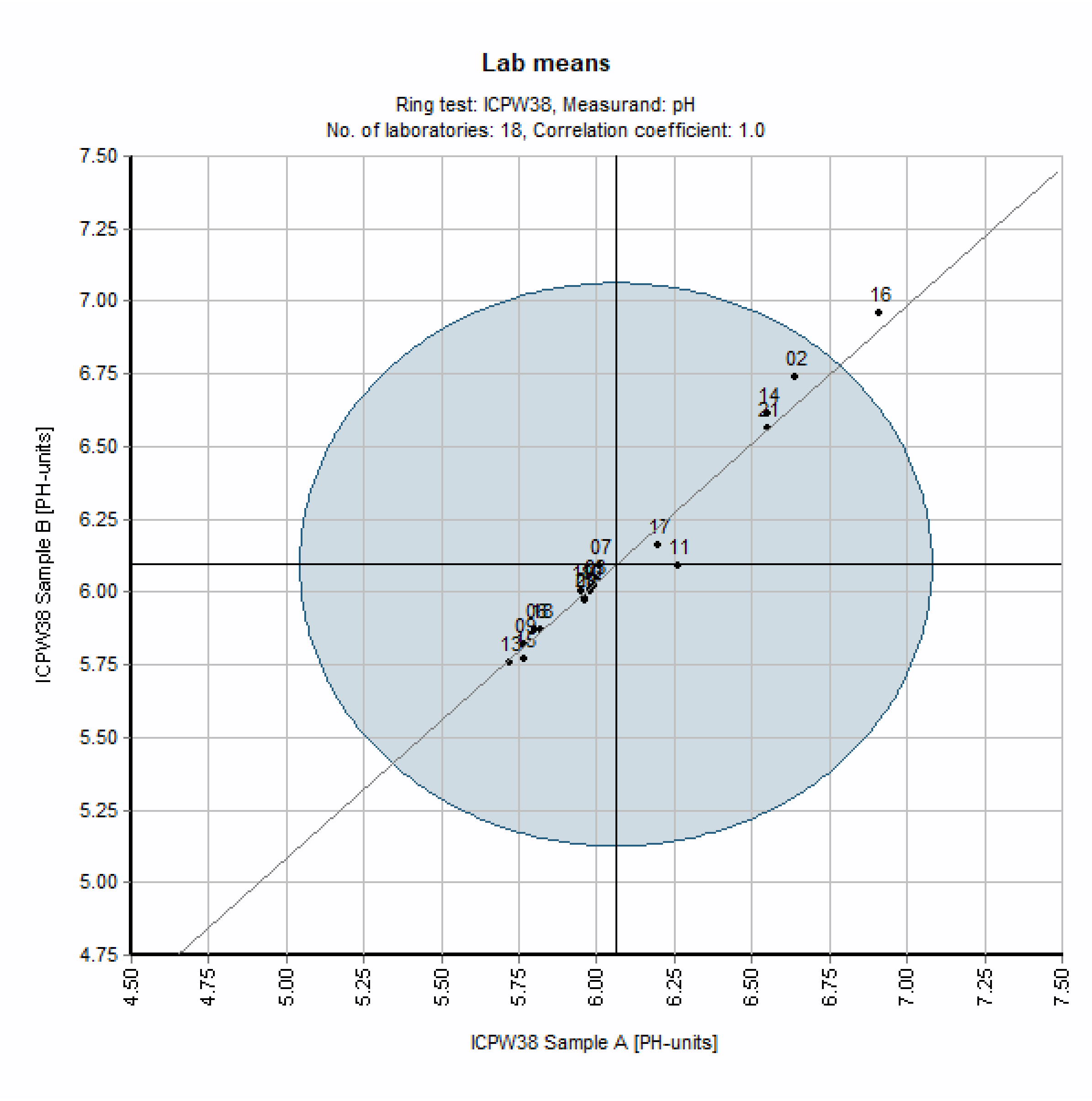

Figure 2. Youden diagram for pH. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA.

3.2 Conductivity

Conductivity was measured by 18 laboratories, and 92% of the results were marked as satisfactory (|Z'| < 2). Most of the reported results had relatively high conformity, with the SDPA being at around 5% for both samples. The satisfactory results were all within ±10% of the assigned value.

All but one of the 18 participants reported to have used electrometry for the determination of conductivity, and of these, 5 reported to have followed ISO 7888. The final participant did not specify the method used. The Youden chart (Figure 3) 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.

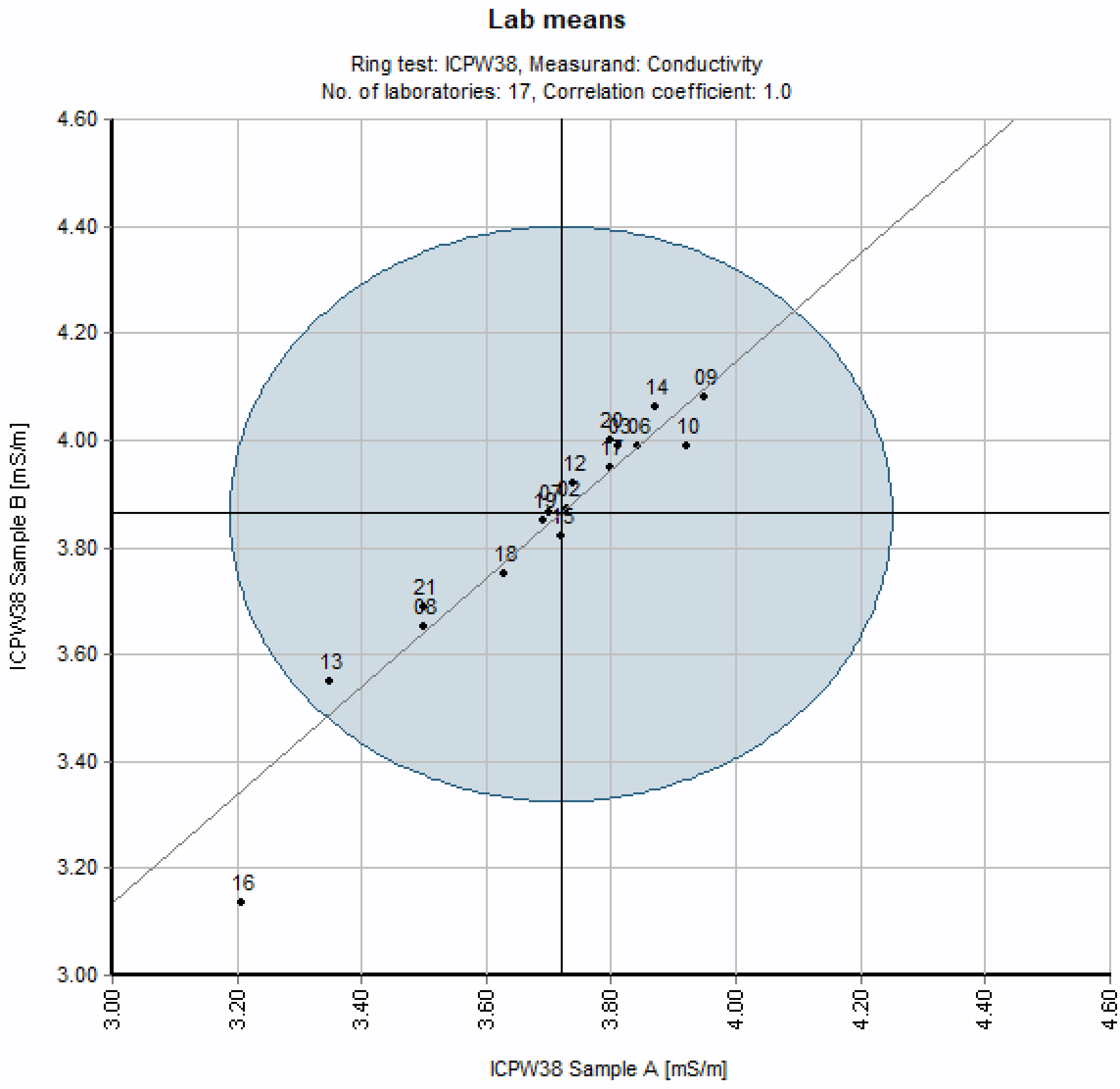

Figure 3. Youden diagram for Conductivity. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA

3.3 Alkalinity

Alkalinity was reported by 14 of the laboratories. One laboratory reported using the wrong units, but all other results were marked as satisfactory (|Z'| < 2). The SDPA of alkalinity was high, which meant results having a deviation of almost 50% from the assigned value could still have a satisfactory Z' score. 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.

Titration to endpoint pH 4.5 was used by 8 of the laboratories, while 2 laboratories titrated to pH 4.5+4.2. Of the rest, 1 reported to have titrated to another endpoint, 1 reported to have used colorimetry, and the final 2 reported to have used an unspecified method. The Youden chart (Figure 4) shows that systematic errors dominate the data set, while random errors seem very small. Results that fall outside the chart area, are marked with an arrow.

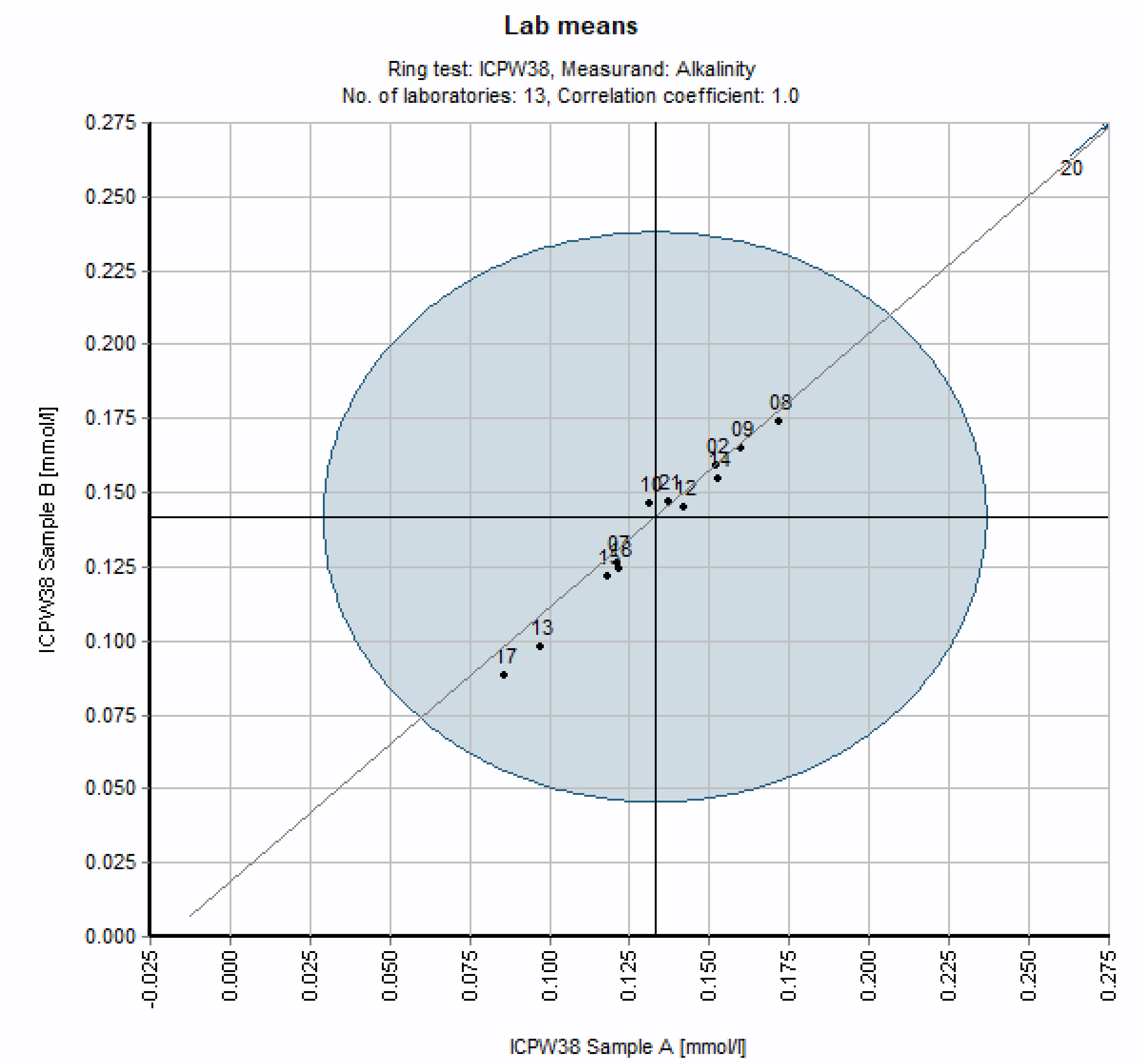

Figure 4. Youden diagram for Alkalinity. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA

3.4 Nitrate-nitrogen

Same as last year, the levels of nitrate in the samples were found to be unstable. Results were reported by 14 of the laboratories, but the results were highly variable. During the preparation of the samples, NIVA's initial analysis of the water (before spiking) showed a nitrate concentration of around 35 µg N/L. Samples were then spiked with an additional 500 µg N/L of KNO_3. It seems, however, that most of the nitrate was likely changed to ammonium. Control samples analyzed at NIVA in July and August, showed increased amounts of ammonium while nitrate had mostly disappeared.

Participants' results, and the calculated statistical parameters of nitrate-nitrogen can be found Table 9.

3.5 Chloride

Chloride was reported by 18 laboratories. Of all the reported values, 79% were marked as satisfactory (|Z'| < 2). Most of the results had high conformity, with the relative SDPA being only 2-3 % of the assigned value. Participants having unsatisfactory Z' scores should evaluate if their relative deviation (D%) is within their own measurement uncertainty.

The most used technique was ion chromatography, which was used by 17 participants. The final participant used photometry for the determination. The distribution of the results in the Youden diagram (Figure 5) shows that both random and systematic errors are present in the dataset.

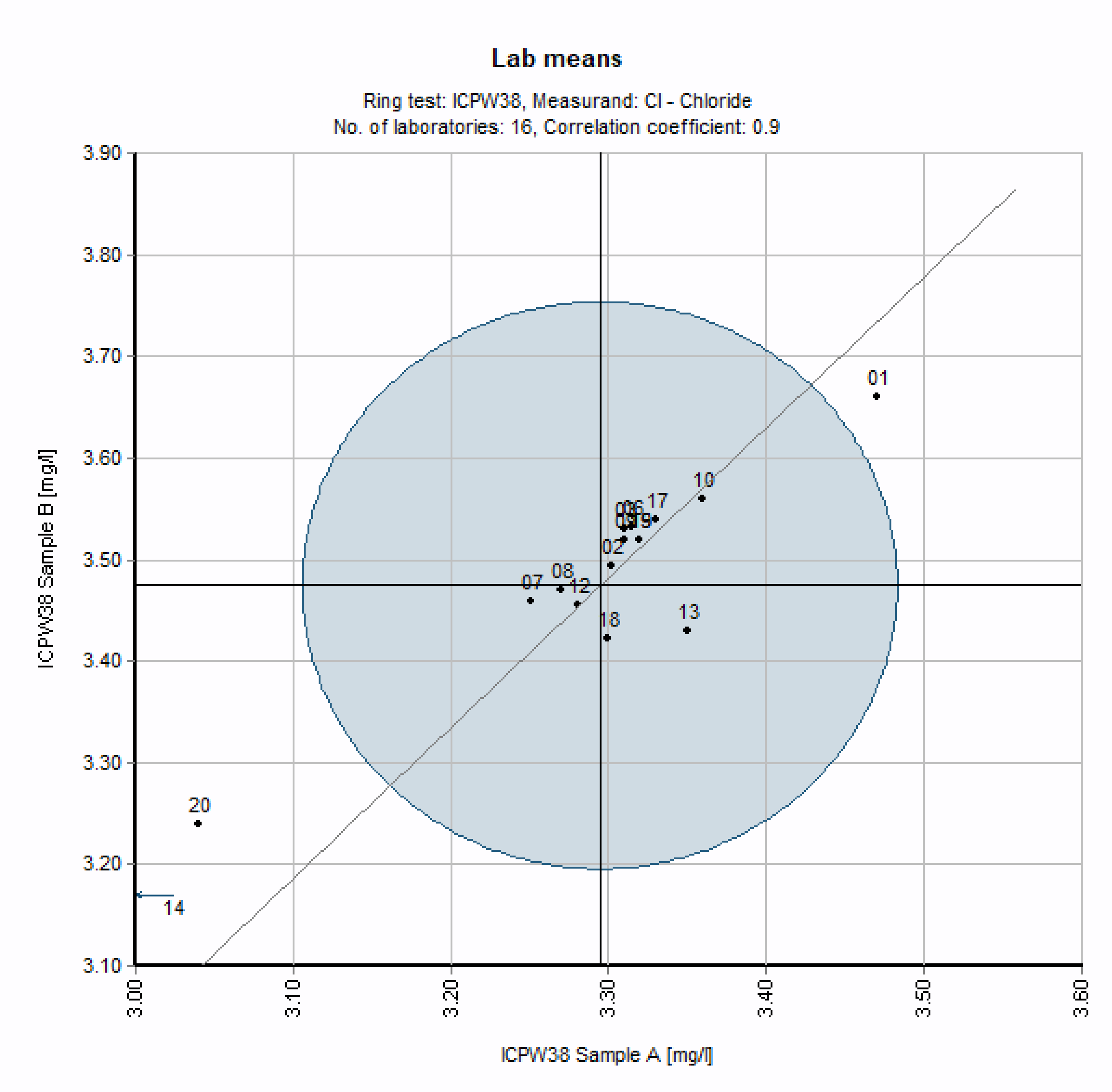

Figure 5. Youden diagram for Chloride. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA

3.6 Sulphate

Sulphate was reported by 19 laboratories, and all except for 2 had used ion chromatography for the determination. The final participants used ICP-AES and photometry. 89% of the results were marked as satisfactory (|Z'| < 2). There was a general high conformity of the reported results, with the SDPA being under 5% for both samples, causing the satisfactory cutoff to be approximately ±9% of the assigned value. The Youden chart in Figure 6 shows that most errors are small and systematic.

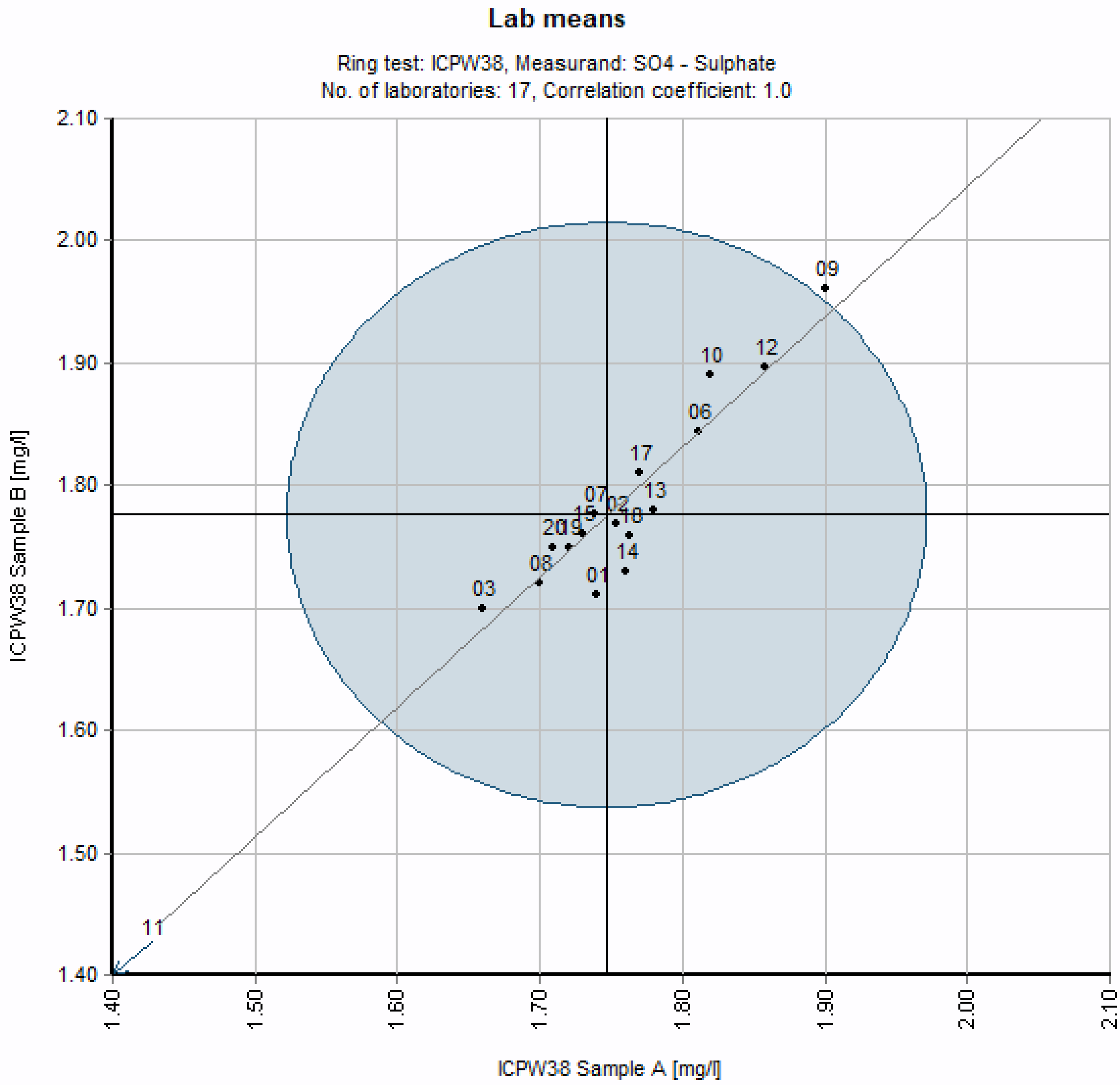

Figure 6. Youden diagram for Sulphate. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA

3.7 Calcium

Calcium was reported by 20 laboratories. The most used technique was ion chromatography (9 laboratories), followed by ICP-AES and ICP-MS (4 laboratories each). The last 3 participants reported to have used Flame AAS, MP-AES and an unspecified method. Satisfactory results (|Z'| < 2) were obtained by 87% of the results.

The SDPA of the results was around 8-9%, indicating some spread of the reported results. The Youden diagram in Figure 7 shows both systematic and random errors in the dataset.

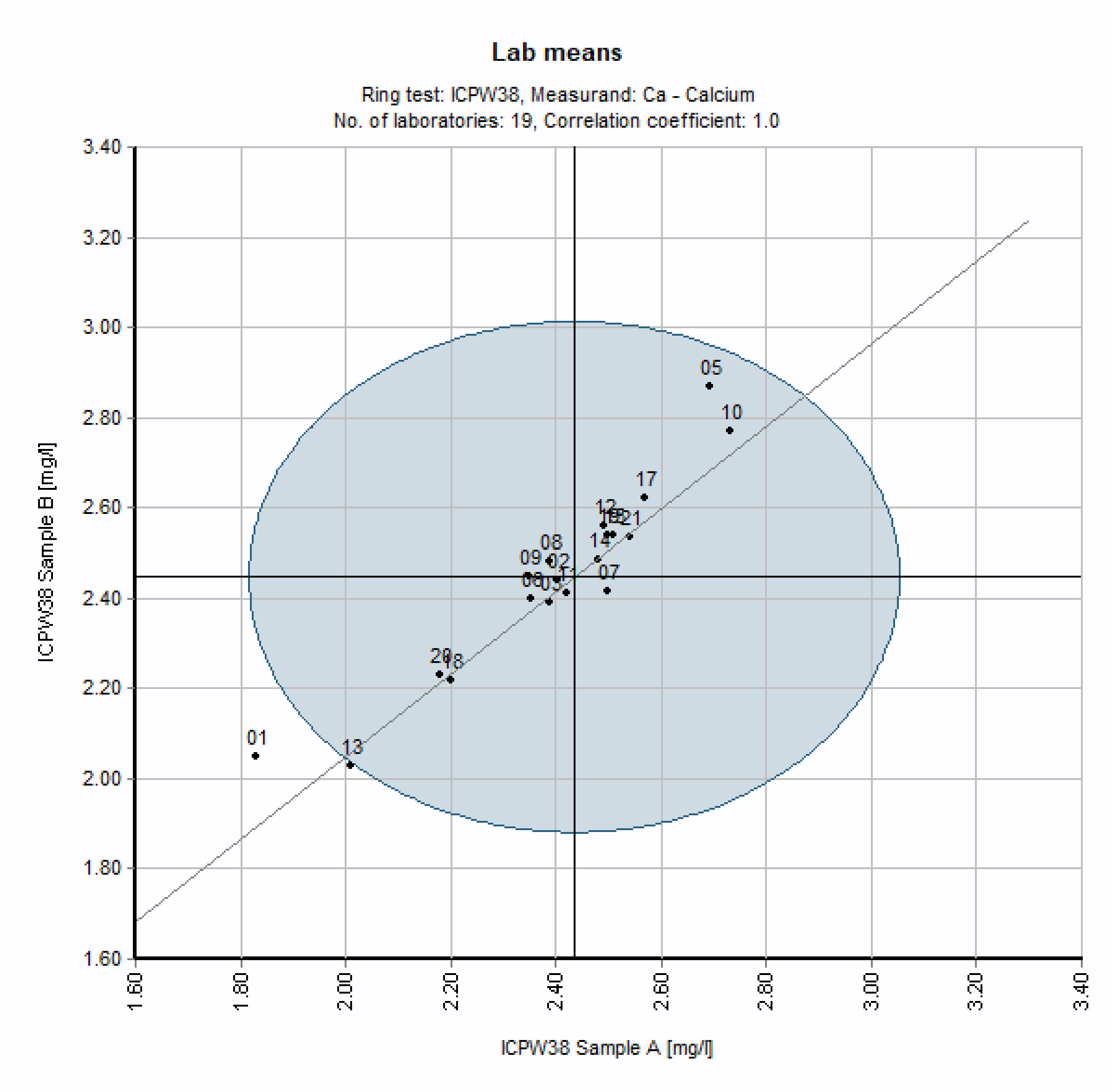

Figure 7. Youden diagram for Calcium. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA

3.8 Magnesium

Magnesium was reported by 20 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 (9 laboratories), ICP-AES and ICP-MS (4 laboratories each), and the last 3 participants used Flame AAS, MP-AES and an unspecified method.

Satisfactory score (|Z'| < 2) were obtained for 90% of the results. The results have a good conformity, with the SDPA being around 6-7% for both samples. Most laboratories report results within ±10% deviation of the assigned value. The Youden diagram (Figure 8) shows that systematic errors dominate the dataset.

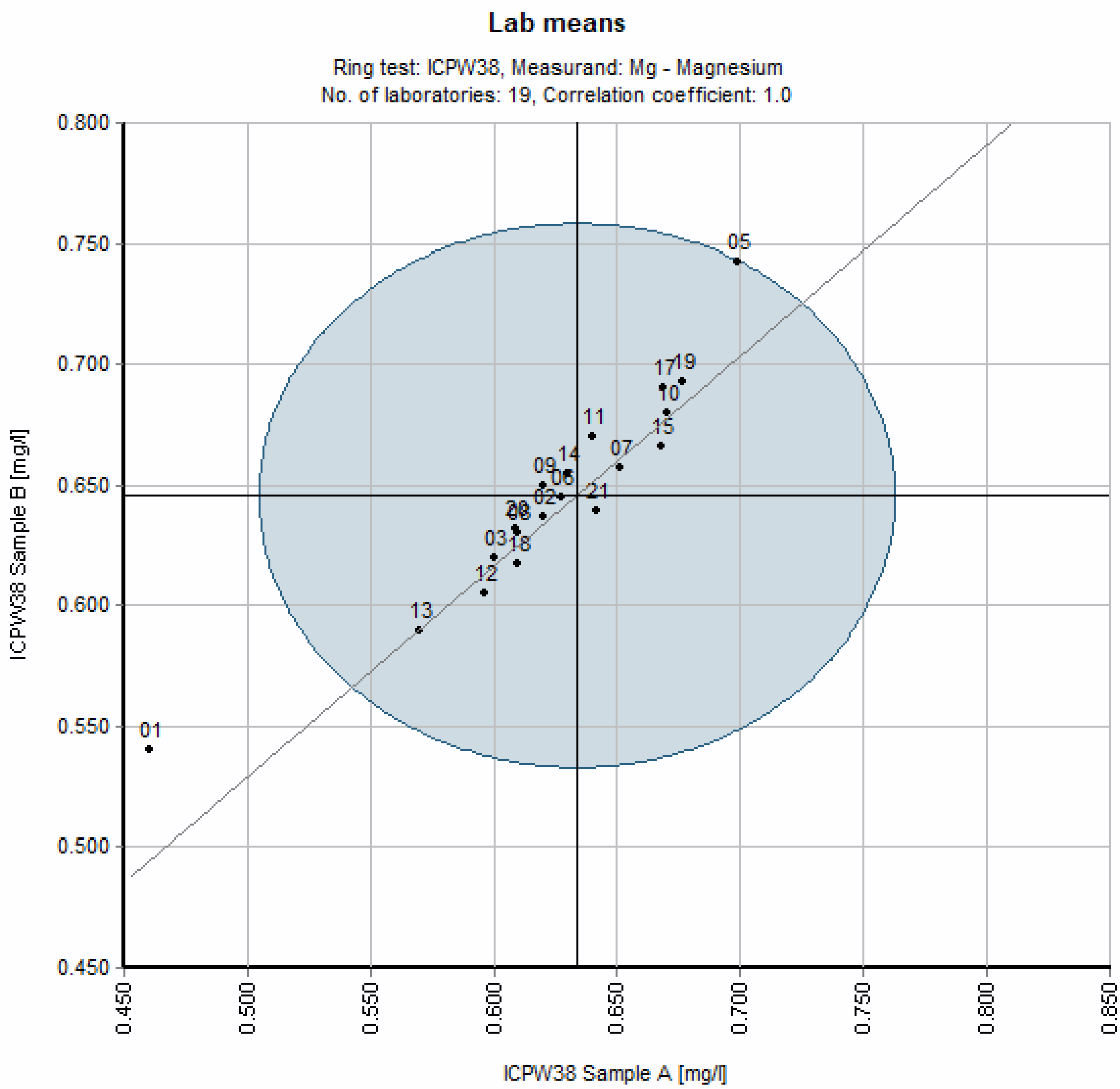

Figure 8. Youden diagram for Magnesium. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA

3.9 Sodium

Sodium was also measured by 20 laboratories, and the techniques used were the same as for calcium and magnesium. Of the reported results, 92% were deemed satisfactory (|Z'| < 2). The results have a high conformity, with the SDPA being around 4-5% for the two samples. All reported results are within ±20% deviation from the assigned value, so laboratories with Z'-scores higher than |2| should also consider their own measurement uncertainty when assessing if their result is ok or not.

The Youden diagram (Figure 9) shows that both random and systematic errors are present in the dataset.

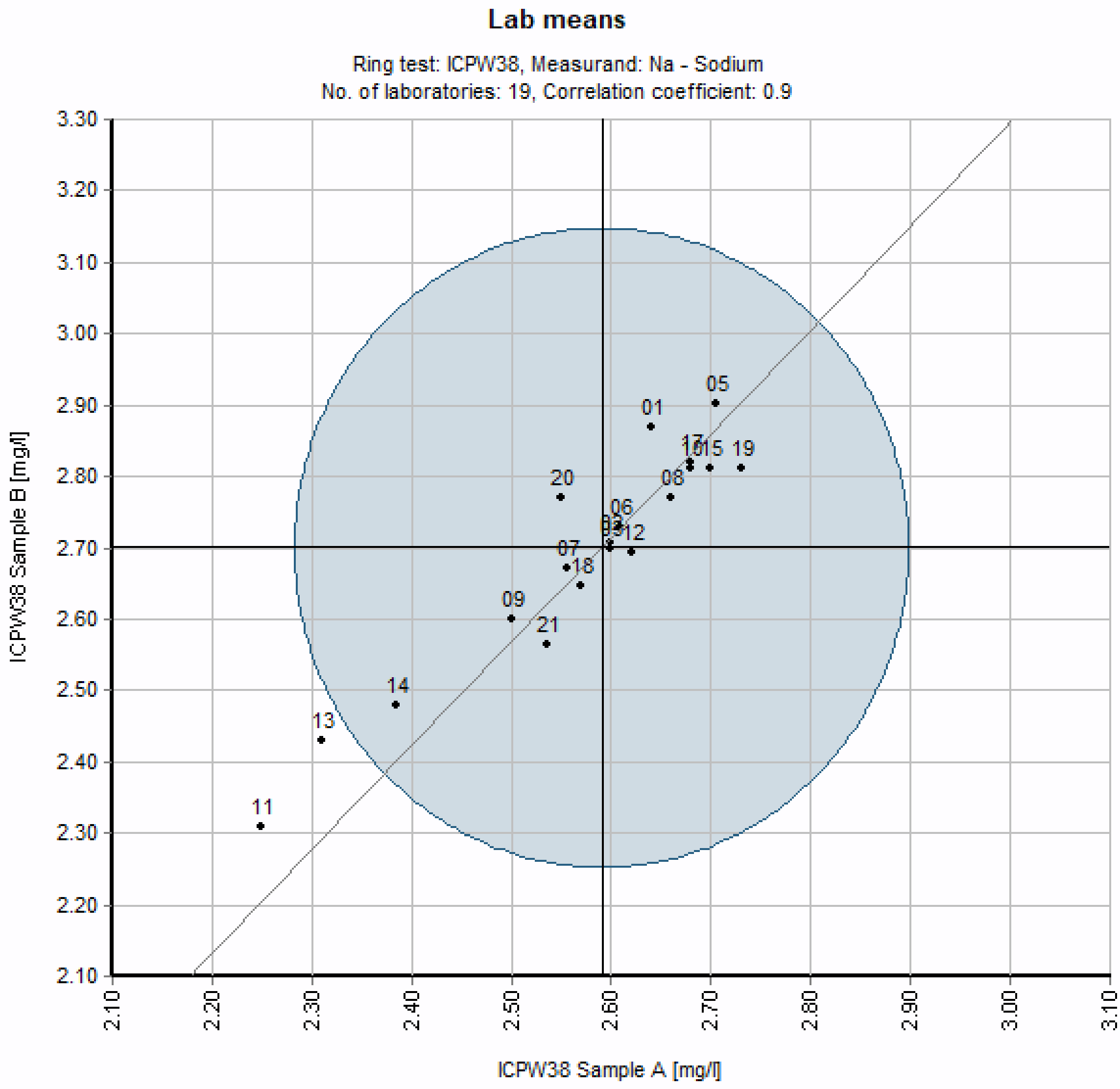

Figure 9. Youden diagram for Sodium. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA

3.10 Potassium

Potassium was also measured by 20 laboratories, and the techniques used were the same as for calcium, magnesium, and sodium.

The samples had a 95% satisfactory rate (|Z'| < 2). The results have a relatively high conformity, with the SDPA being around 4-5% for both samples. All satisfactory results were within ±10% of the assigned. The Youden diagram in Figure 10 shows that the spread of the results is mostly systematic, with some small random errors.

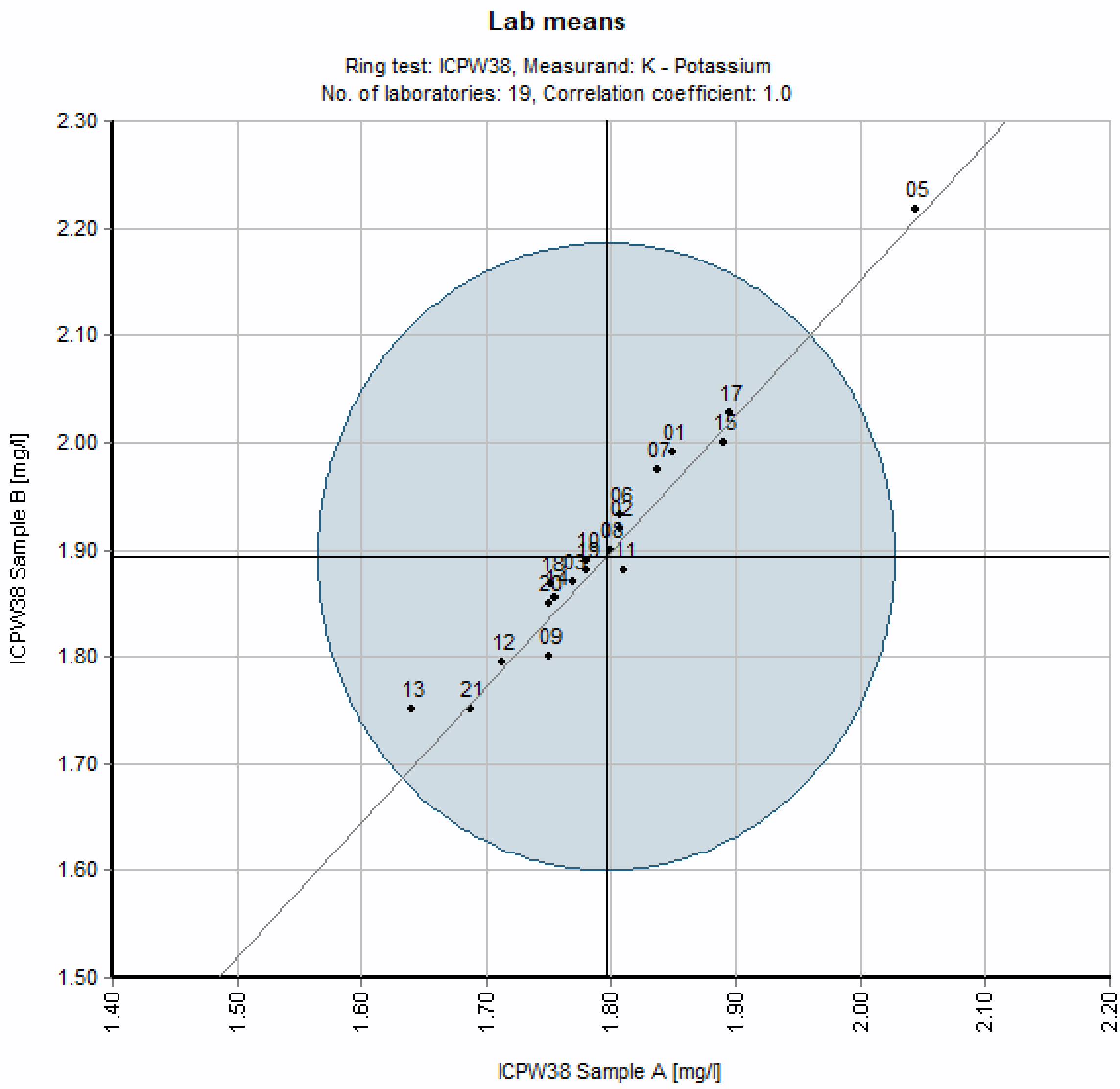

Figure 10. Youden diagram for Potassium. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA

3.11 Total organic carbon

Total organic carbon was reported by 15 laboratories. The most used technique was catalytic combustion. Of these, 7 laboratories reported that they followed EN 1484 and 4 reported to be following EN ISO 20236. In addition, 1 laboratory reported to follow EN 1484 but use UV-light and peroxodisulphate for oxidizing the samples. The last 3 laboratories reported to have used an unspecified method.

Satisfactory score (|Z'| < 2) was obtained by 86% of the results. Sample A had an SDPA of 7% while sample B had an SDPA of almost 14%. Some participants reported to see particles / growth in the bottles when they were stored for a while before analysis, and instability in the samples seem to affect this analysis parameter. The Youden chart for total organic carbon in Figure 11 shows both random and systematic errors.

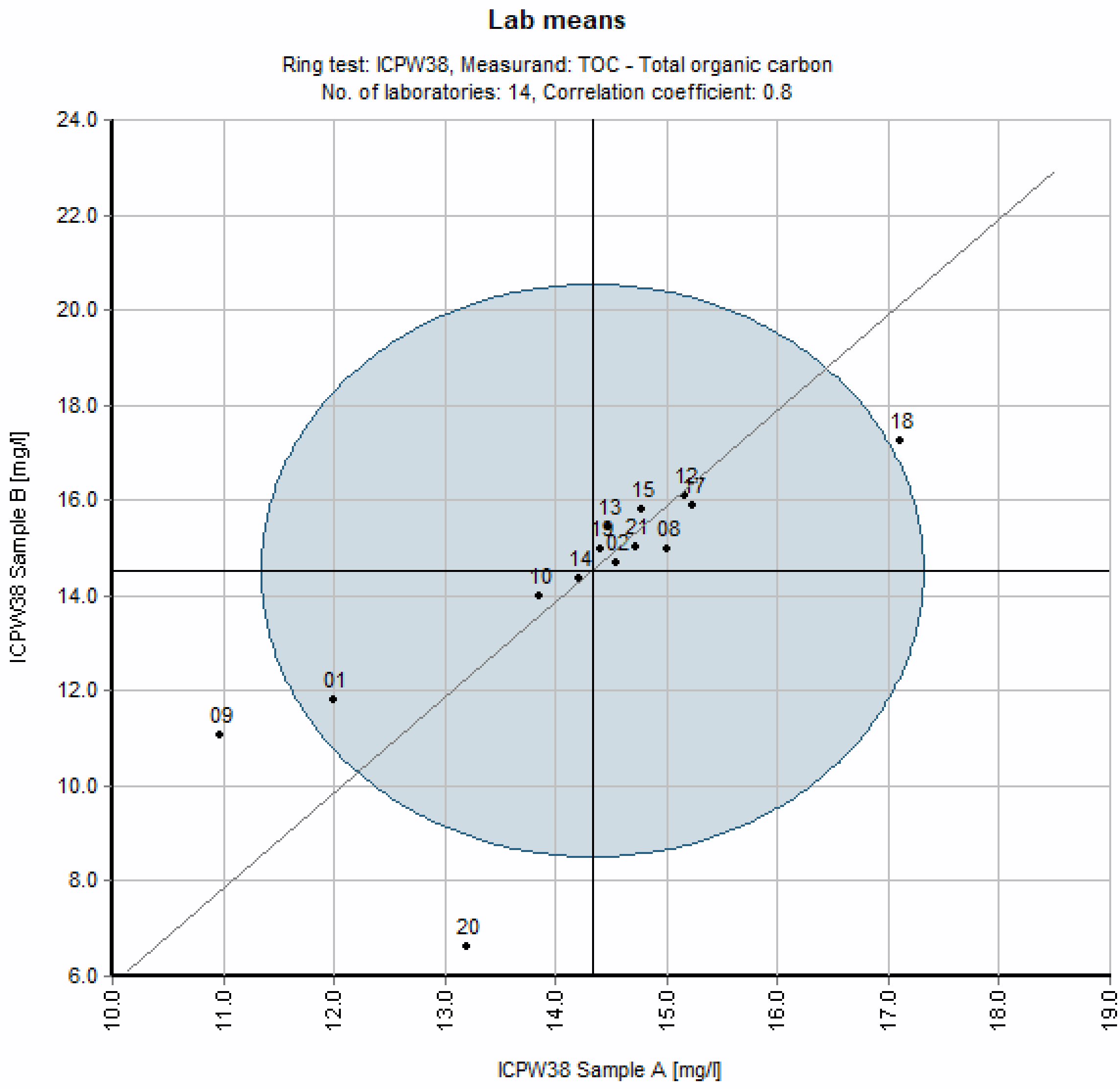

Figure 11. Youden diagram for TOC. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA

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 (4 laboratories), EN-ISO 15681-2 (3 laboratories), simplified photometry (3 laboratories), and ICP-MS (2 laboratories). Lastly, one laboratory each reported to have used either ICP-AES, ion chromatography, NS 4725 or an unspecified method.

The reported results had quite a high spread, which again causes the SDPA to be quite high, at 18-23%. It is lower than last year, but still causes results to be marked as satisfactory (|Z'| < 2), even with quite a high deviation from the assigned results. A total of 94% of the results were marked as satisfactory. The Youden chart (Figure 12) shows the large spread, with the circle set at 2xSDPA. Most of the errors are still systematic in nature

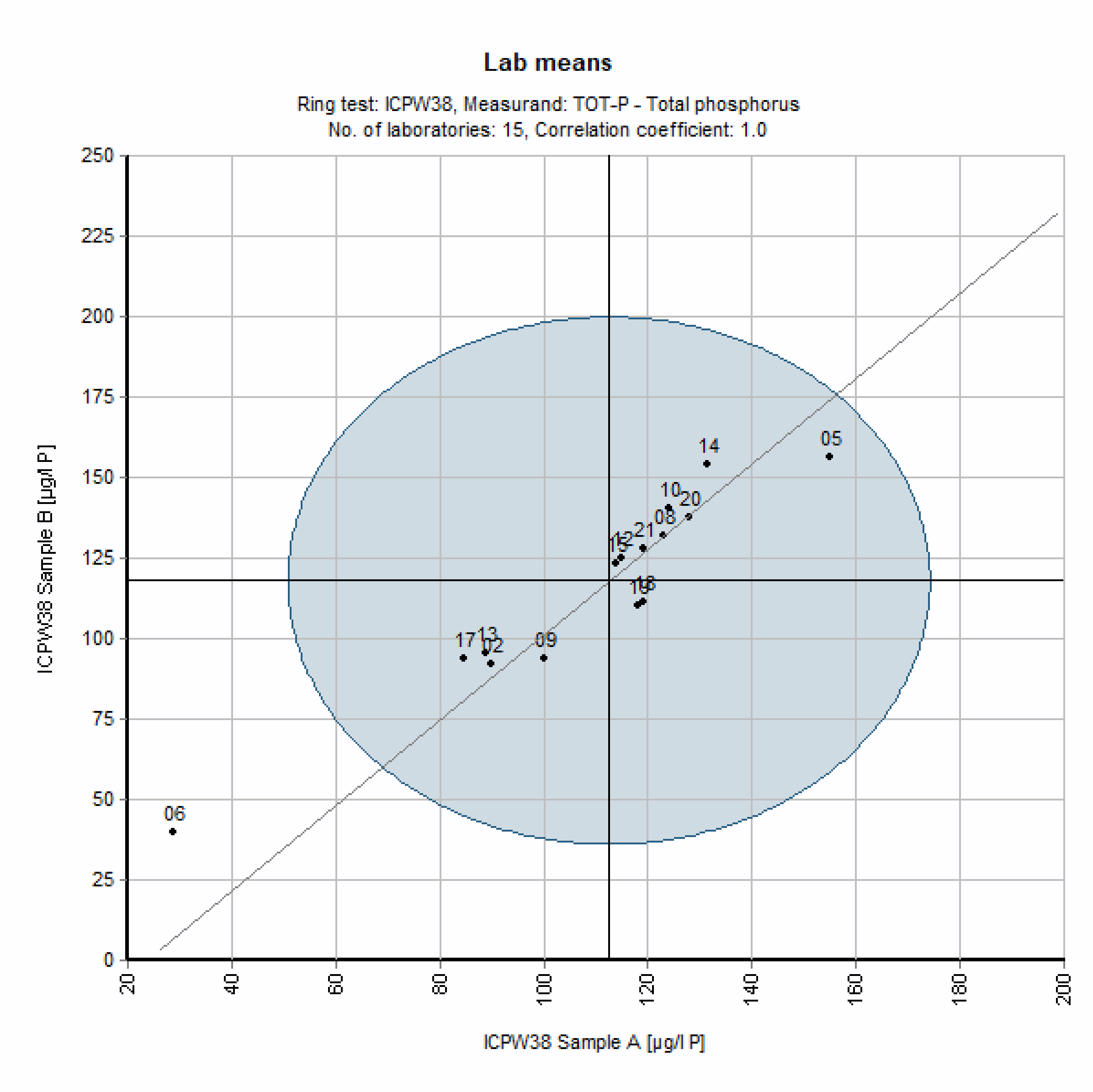

Figure 12. Youden diagram for TOT-P. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA

3.13 Total nitrogen

Total nitrogen was determined by 13 laboratories and all results were deemed satisfactory (|Z'| < 2). The most used technique was catalytic combustion, which was used by 7 of the participants. Of these, 4 referred to EN 12260 (withdrawn), while 3 referred to EN ISO 20236 (current). Persulfate oxidation in combination with spectrophotometric determination was used by 5 participants, where 3 reported to have used unbuffered oxidation solution and 2 used a buffered solution (EN ISO 19905-1). The final participant used an unspecified method.

Although all results were satisfactory, some participants have deviations of up to 25% of the assigned value. The reason for this is the spread of the reported results, causing an SDPA of 13-16%, and a relatively high uncertainty in the assigned value. The Youden chart (Figure 13) shows that random errors dominate the dataset.

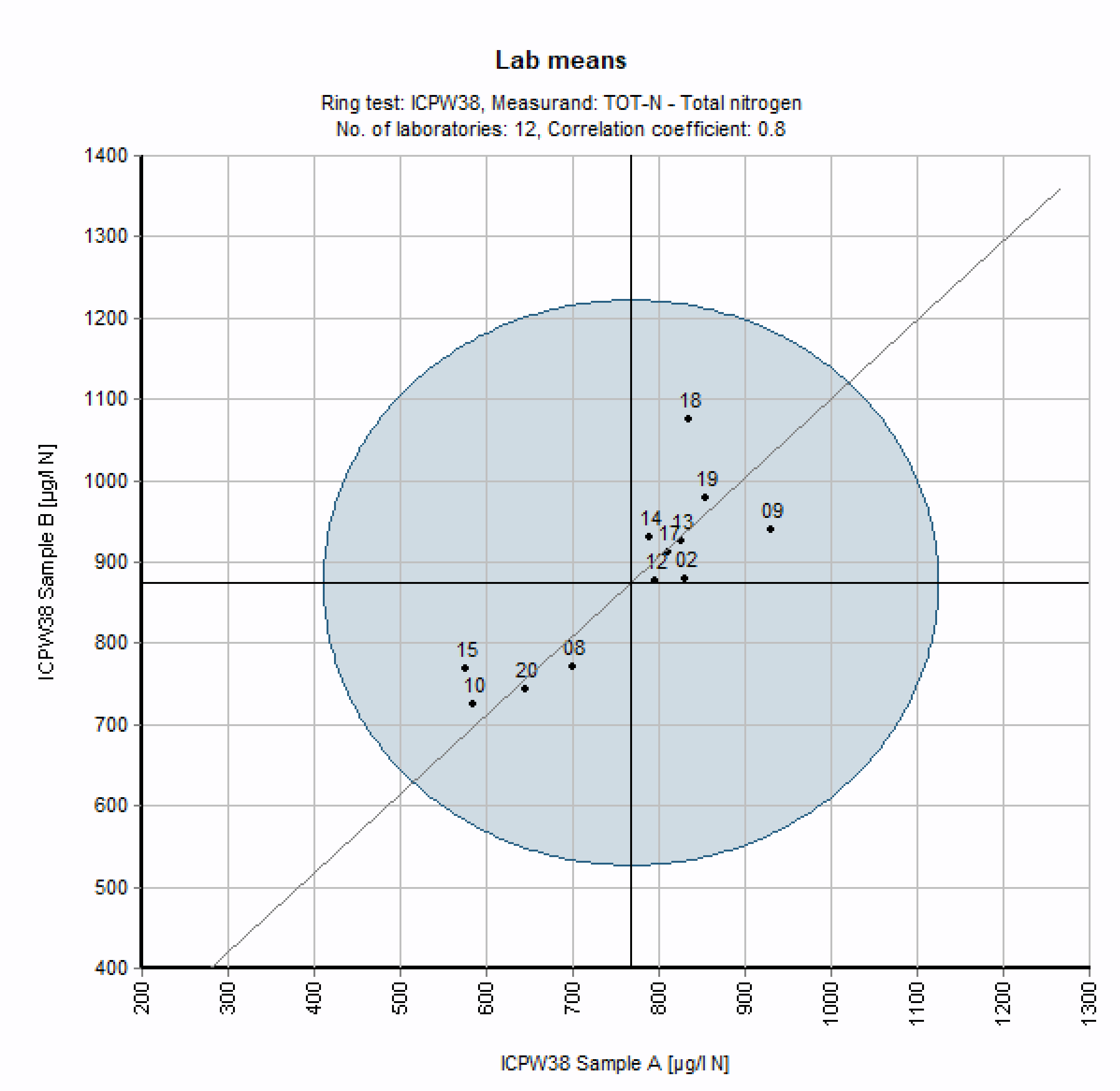

Figure 13. Youden diagram for TOT-N. Sample pair AB. Acceptable limit, given by circle, is 2xSDPA

3.14 Aluminium

Aluminium was reported by 13 participants. Most results were deemed satisfactory (|Z'| < 2). The spread of the results is not too high and gives an SDPA of around 5-7%. All satisfactory results are within ±12% deviation from the assigned value.

The most used technique for determination was ICP-MS, which was used by 9 laboratories. Furthermore, 3 laboratories used ICP-AES, and the last used GF-AAS. The Youden chart for aluminium (Figure 14) shows that most of the errors were small and systematic.

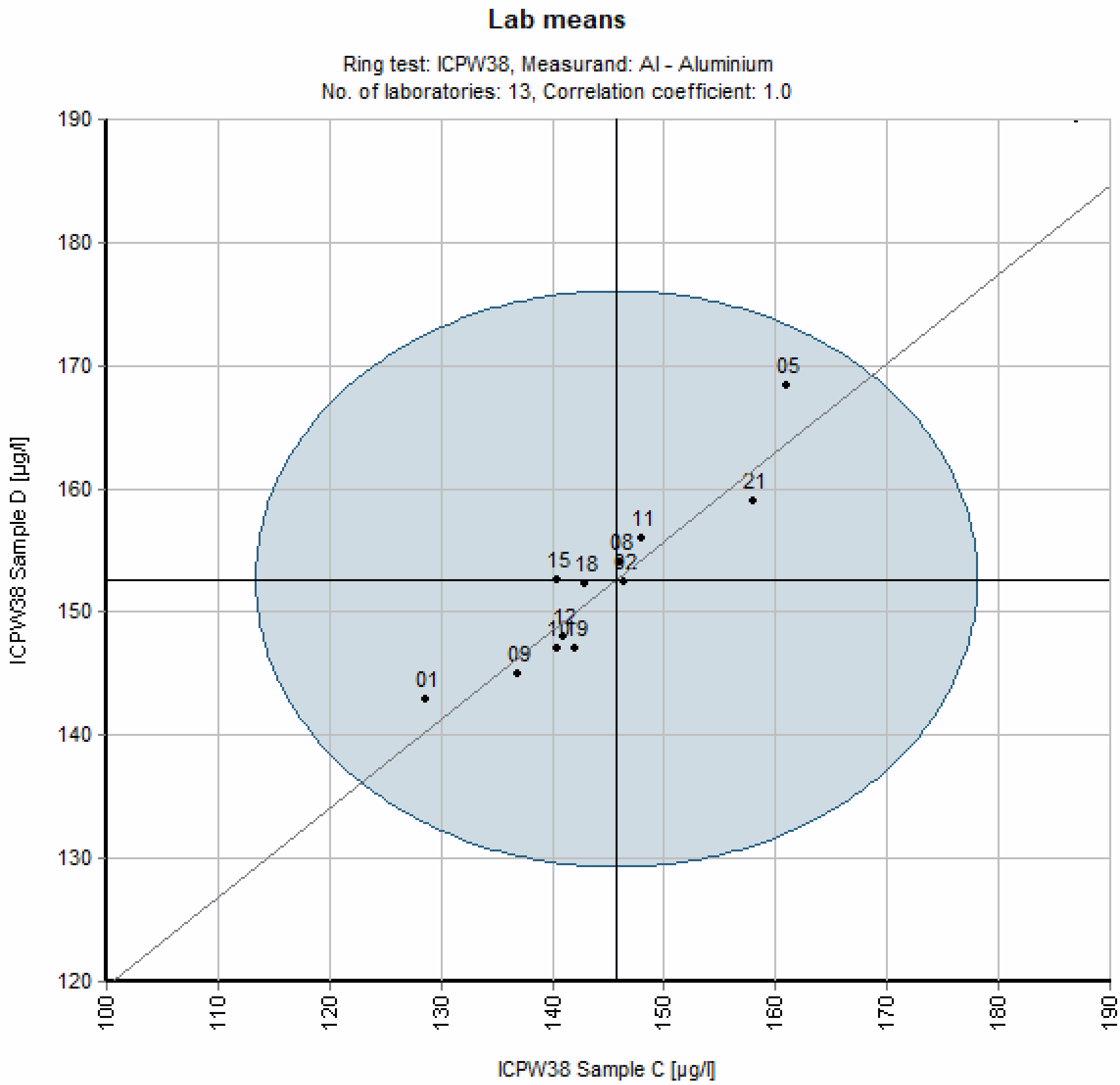

Figure 14. Youden diagram for Al. Sample pair CD. Acceptable limit, given by circle, is 2xSDPA

3.15 Iron

Iron was determined by 15 laboratories. ICP-MS was the most used technique, with 10 laboratories reported to have used the technique to determine iron. ICP-AES was used by 4 laboratories, while the last laboratory reported to have used flame AAS.

The percentage of results with satisfactory score was 90%. The SDPA was as low as around 3%, which means that most laboratories reported quite similar results. The result with the highest Z' score is still only 12% from the assigned value, so participants with Z'scores > |2| should also use the deviation to assess their own performance. The Youden chart (Figure 15) shows that the spread of the results is mostly small and systematic

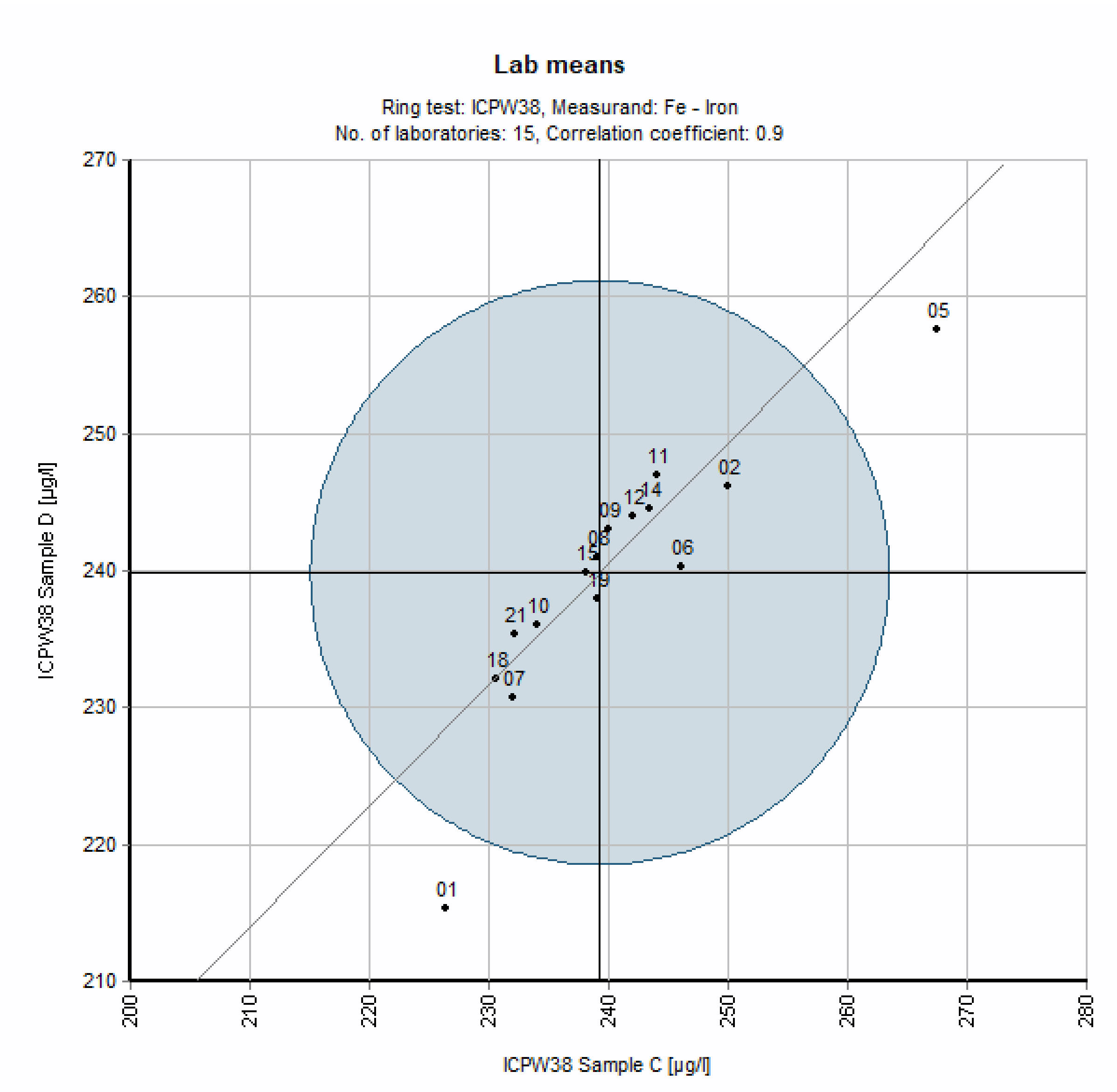

Figure 15. Youden diagram for Fe. Sample pair CD. Acceptable limit, given by circle, is 2xSDPA

3.16 Manganese

Manganese was determined by 14 laboratories. but one participant reported that the result was below their LOQ. ICP-MS was the most used technique (11 laboratories), while the last 3 used ICP-AES. A total of 88% of the results were deemed satisfactory (|Z'| < 2). The SDPA is around 5-6% for both samples. The Youden chart (Figure 16) shows mostly small random errors with a few laboratories systematically over- or underestimating the concentration.

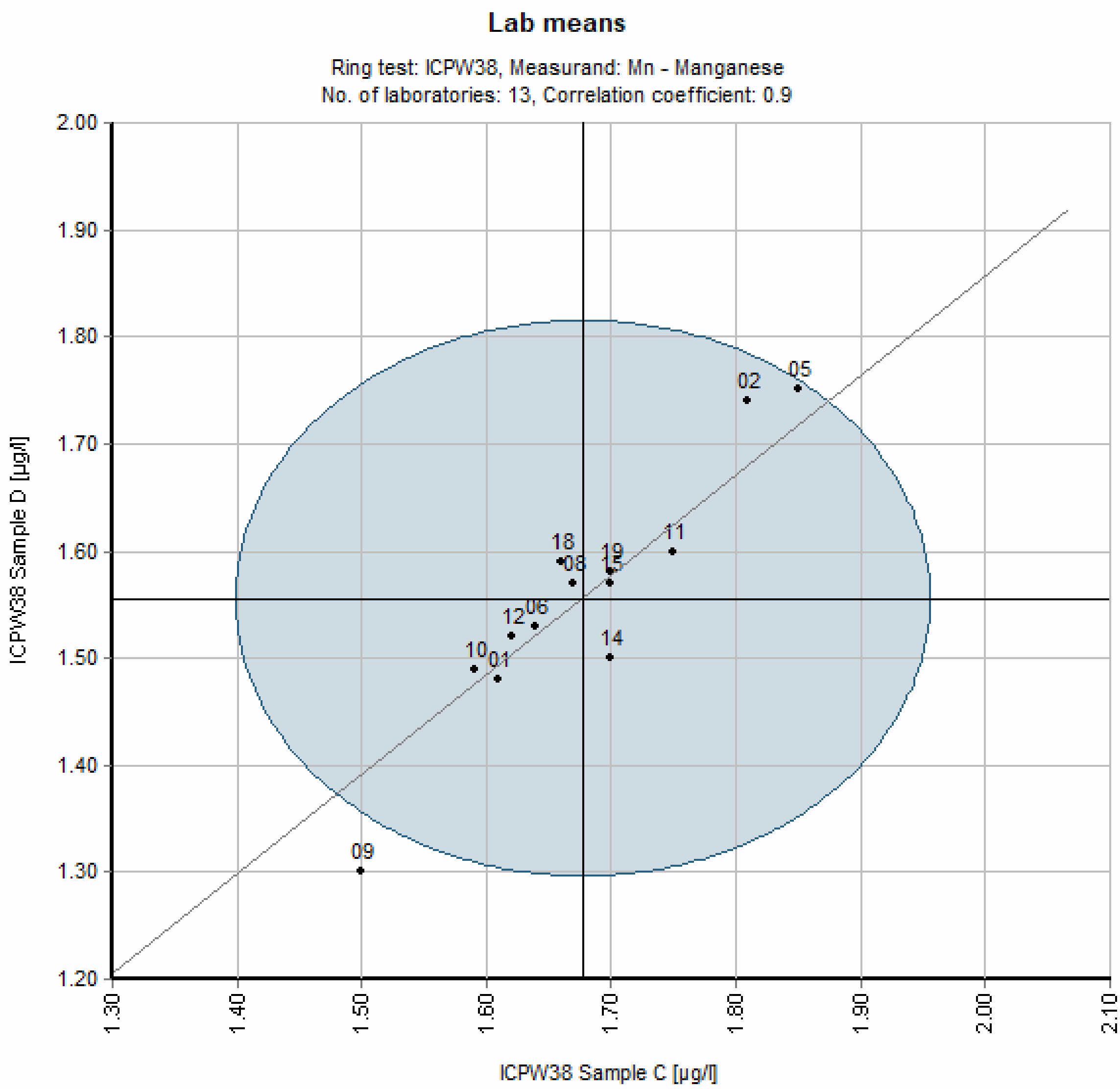

Figure 16. Youden diagram for Mn. Sample pair CD. Acceptable limit, given by circle, is 2xSDPA

3.17 Cadmium

Cadmium was determined by 14 laboratories. ICP-MS was used by 11 participants, ICP-AES was used by 2 participants and the last participant used GF-AAS. The percentage of satisfactory results (|Z'| < 2) was 89%. The reported results were a bit spread, creating an SDPA of around 8%. All satisfactory results were within ±10% of the assigned results. The Youden chart (Figure 17) shows most errors are small and systematic.

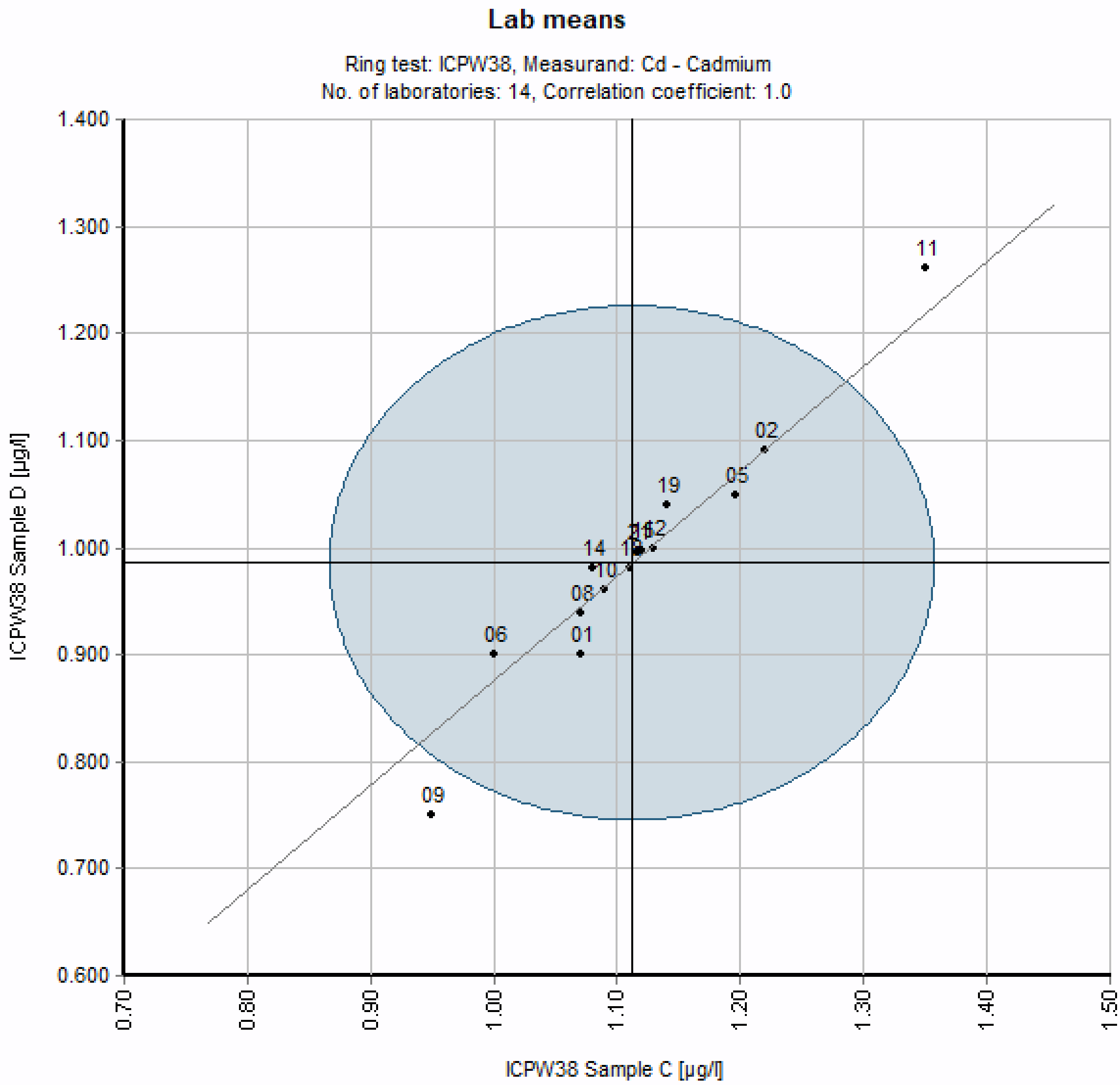

Figure 17. Youden diagram for Cd. Sample pair CD. Acceptable limit, given by circle, is 2xSDPA

3.18 Lead

Lead was determined by 14 laboratories. ICP-MS was used by 11 participants, ICP-AES was used by 2 participants and the final had uses GF-AAS. The percentage of satisfactory results (|Z'| < 2) was 92%. The spread of the reported results gave an SDPA of around 9%.

The Youden chart (Figure 18) shows that most errors are systematic.

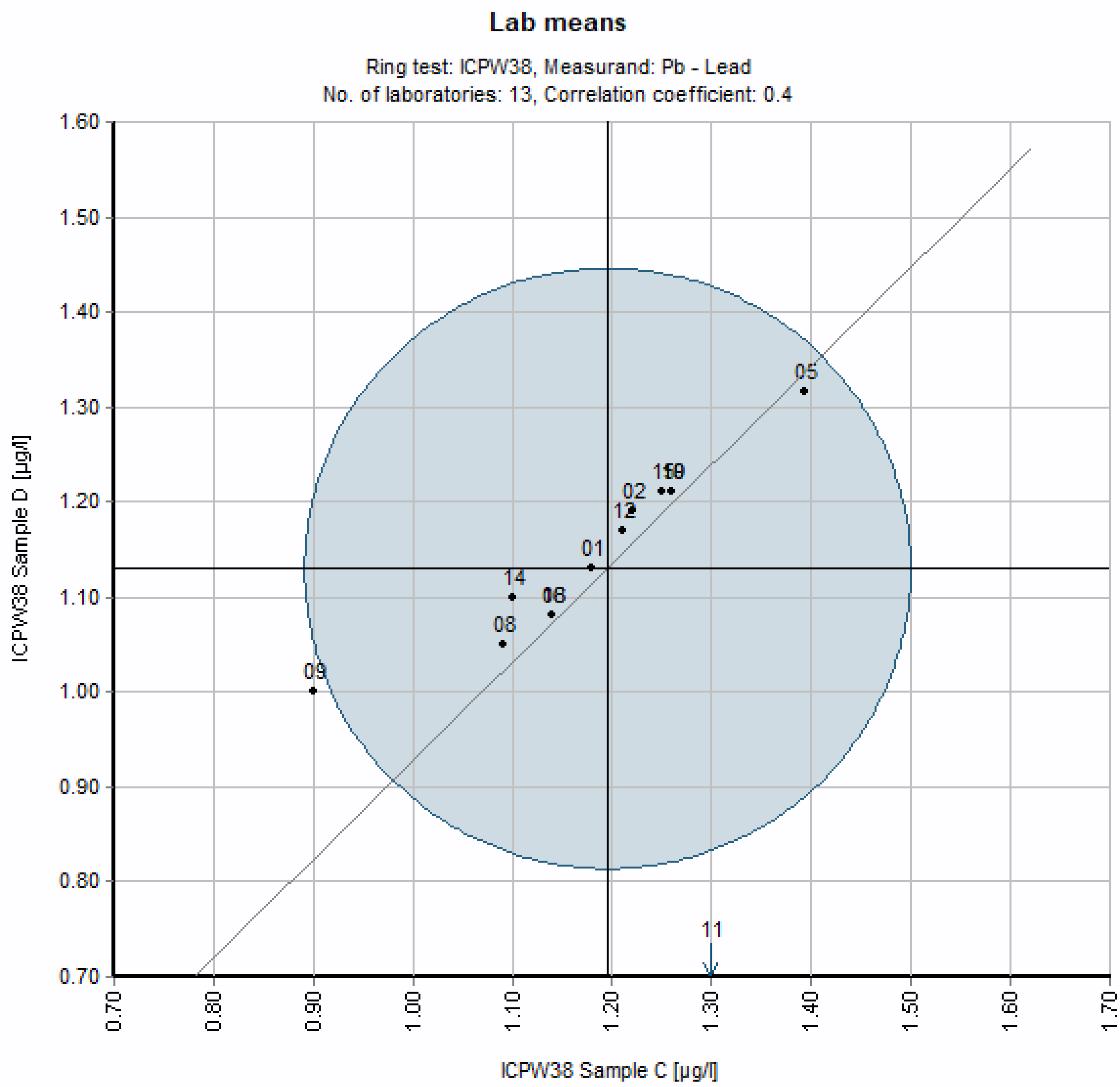

Figure 18. Youden diagram for Pb. Sample pair CD. Acceptable limit, given by circle, is 2xSDPA

3.19 Copper

Copper was determined by 13 laboratories. ICP-MS was used by 10 participants, 2 participants had used ICP-AES and the last participant used GF-AAS. The percentage of satisfactory results (|Z'| < 2) were 92%. The SDPA of the assigned value was approximately 10%, which is relatively high. Of the satisfactory results, all were within ±20% of the assigned value.

The distribution of the results in the Youden chart (Figure 19) shows that systematic errors dominate the results.

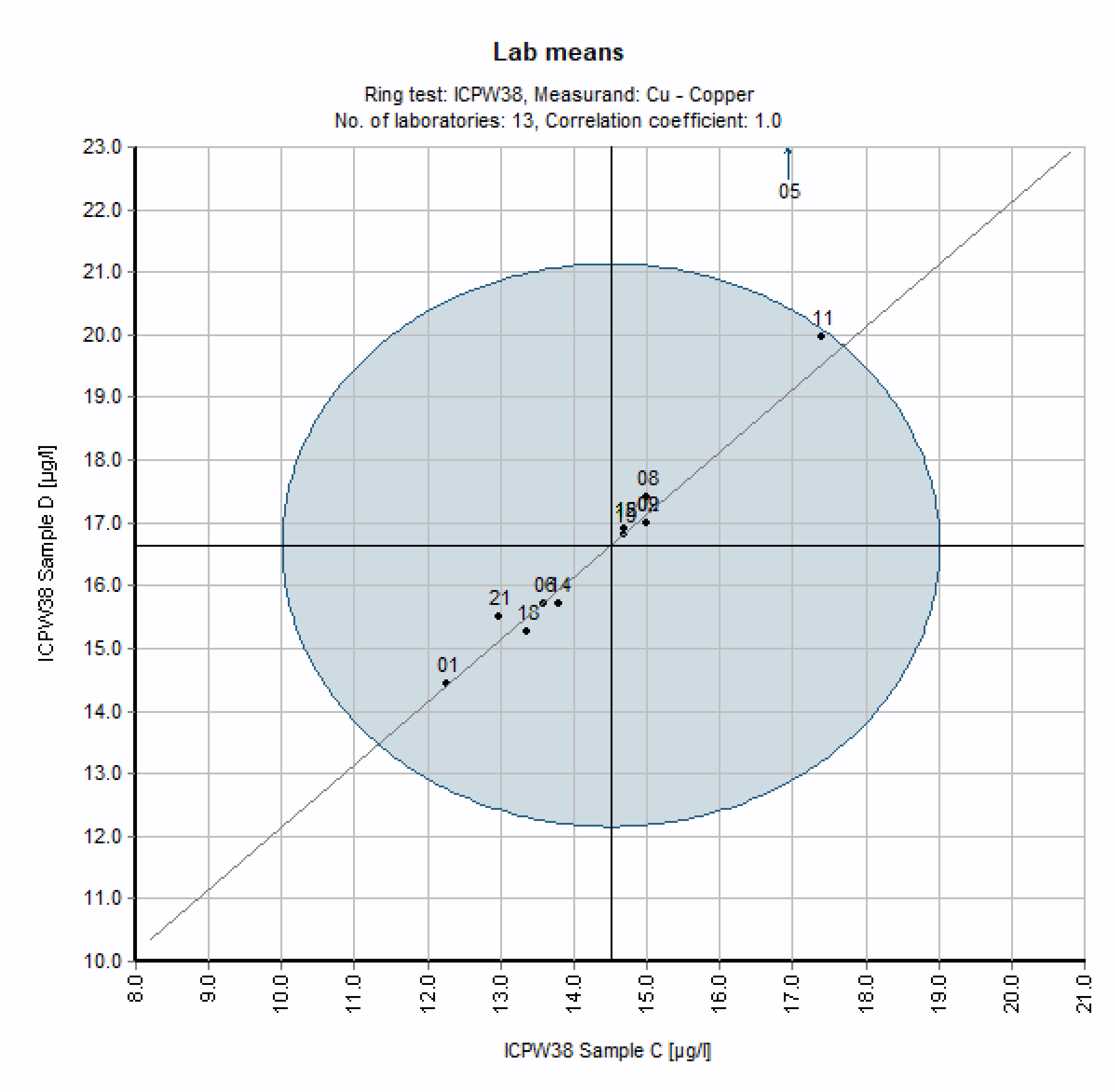

Figure 19. Youden diagram for Cu. Sample pair CD. Acceptable limit, given by circle, is 2xSDPA

3.20 Nickel

Nickel was determined by 14 laboratories. ICP-MS was the most used technique for determination, being used by 11 laboratories. Furthermore, 2 had used ICP-AES and the last participant used GF-AAS. Of the reported results, 93% were deemed satisfactory (|Z'| < 2).

The reported results were spread over a relatively large concentration area, creating more uncertainty in the assigned results and furthermore an SDPA of around 15% for sample C and 11% for sample D. This means that results having a relatively large deviation from the assigned value can still be deemed satisfactory. The Youden chart (Figure 20) shows that quite large systematic errors are dominating the spread of the results.

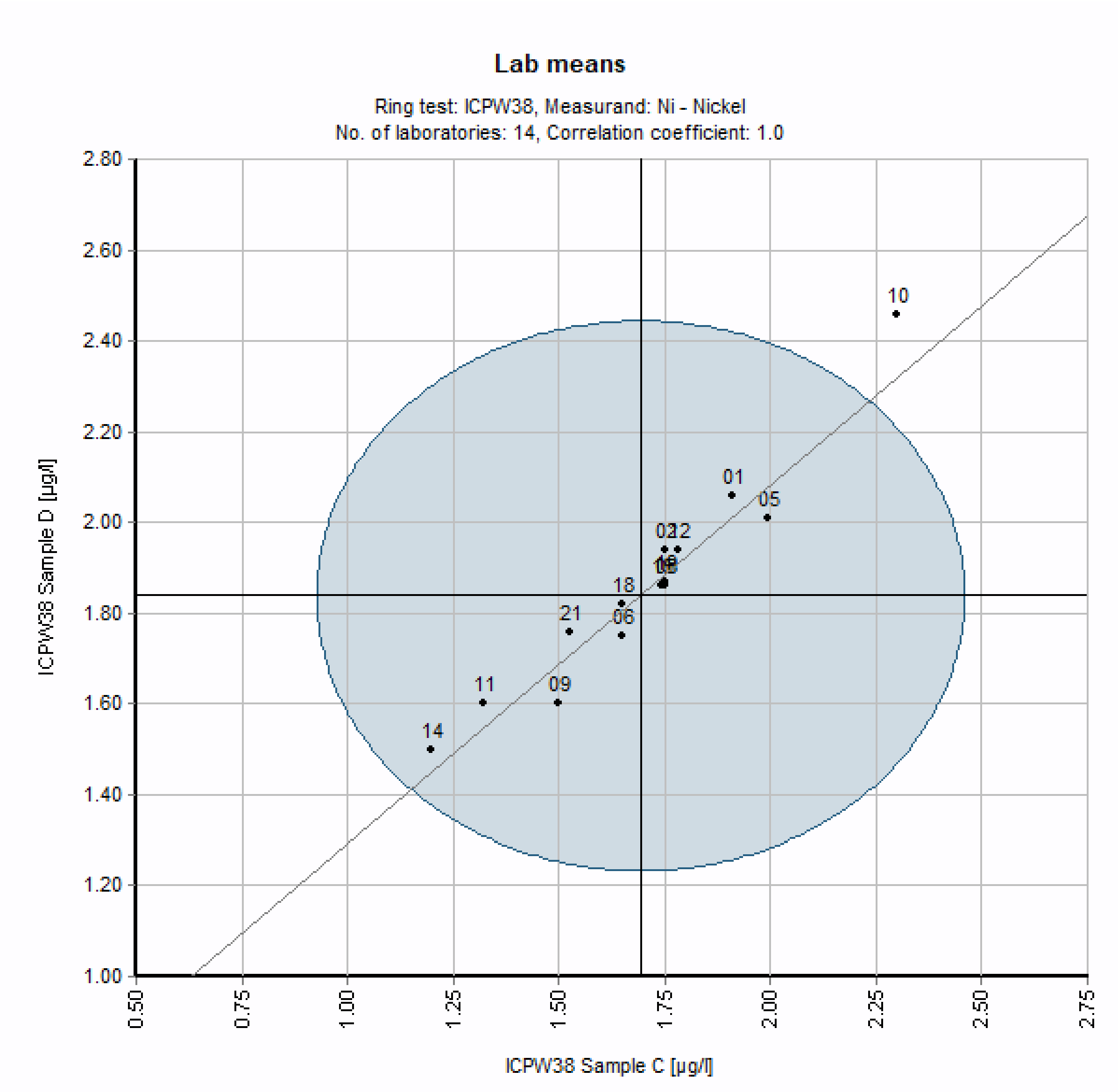

Figure 20. Youden diagram for Ni. Sample pair CD. Acceptable limit, given by circle, is 2xSDPA

3.21 Zinc

Nickel was determined by 14 laboratories, and all but two reported to have used ICP-MS for the determination. The last 2 laboratories reported to have used ICP-AES. Of the reported values, 89% were marked satisfactory (|Z'| < 2). Good precision in the reported results gives SDPA of only 3% for both samples, and all reported values were within 20% of the assigned value.

The Youden chart (Figure 21) shows both random and systematic errors in the dataset.

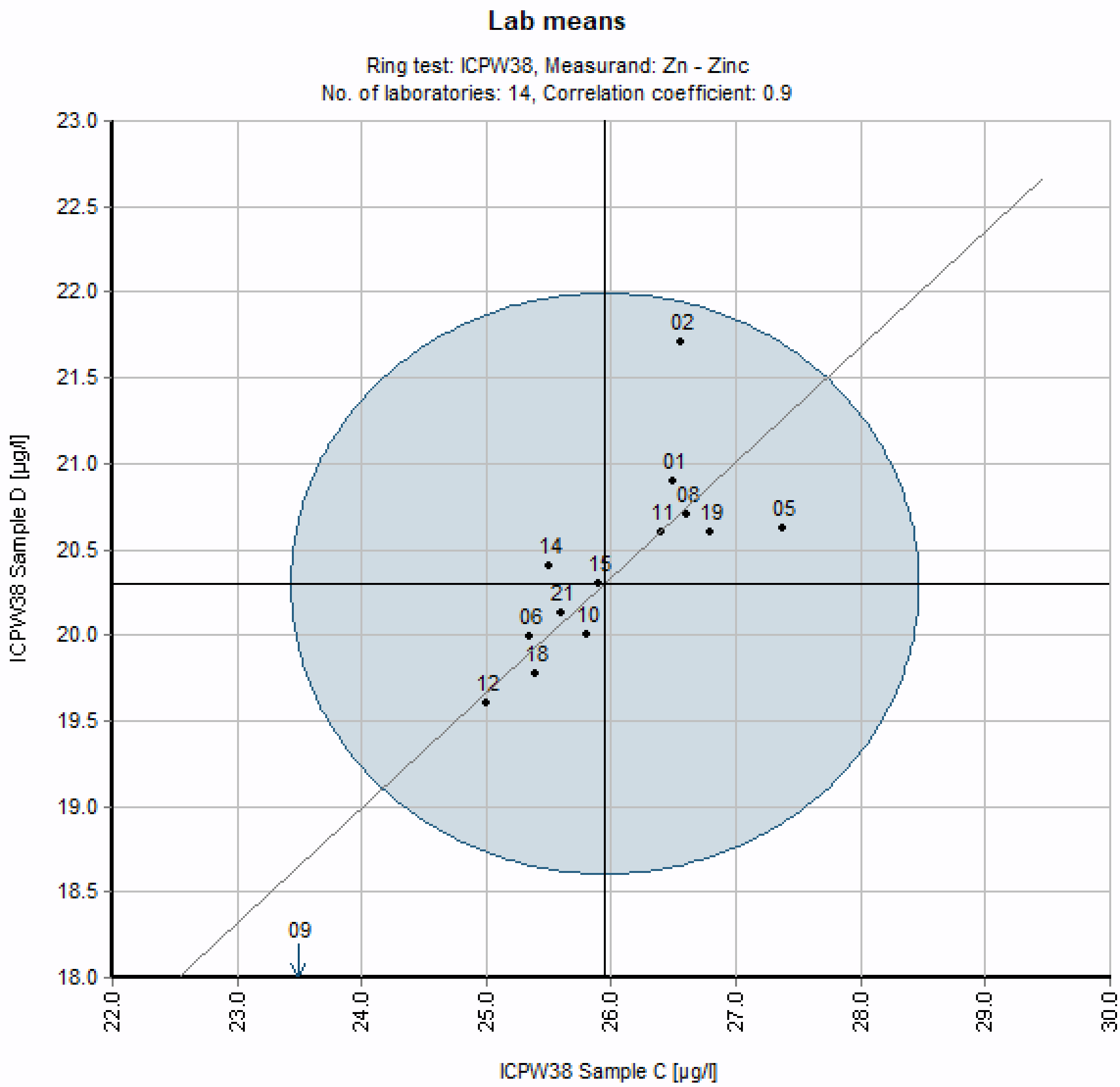

Figure 21. Youden diagram for Zn. Sample pair CD. Acceptable limit, given by circle, is 2xSDPA

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 3. Information of the participating laboratories, including participant ID, name and country.

Lab code	Lab	Country
1	Serveis Tècnics de Recerca-UdG	Spain
2	Bayerische Landesanstalt für Wald und Forstwirtschaft	Germany
3	Staatliche Betriebsgesellschaft für Umwelt und Landwirtschaft, Labor Nossen	Germany
4	Laboratoire d'écologie fonctionnelle et environnement	France
5	VMM	Belgium
6	ISSeP-CAN	Belgium
7	Freshwater Fisheries Laboratory	United Kingdom
8	Norsk institutt for vannforskning	Norway
9	CNR IRSA Verbania	Italy
10	Department of Ecology	Austria
11	Radboud Universiteit	Netherlands
12	Estonian Environmental Research Centre	Estonia
13	IISD Experimental Lakes Area Analytical Service Laboratory	Canada
14	Chemical Laboratory, Czech Geological Survey	Czech Republic
15	Swedish University of Agricultural Sciences, Aquatic Sciences and Assessment	Sweden
16	Puszcza Borecka Integrated Monitoring Station	Poland
17	Laboratorio de Calidad de las Aguas (CEDEX)	Spain
18	Ufficio del Monitoraggio Ambientale - Laboratorio	Switzerland
19	Bayerisches Landesamt für Umwelt	Germany
20	Dorset Environmental Science Centre	Canada
21	Natural Resources Wales	United Kingdom

Table 4. 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	2	Norway	1
Czech Republic	1	Poland	1
Estona	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 stream Kvisla in Aurskog-Høland municipality outside of Oslo, Norway. The stream is high in humic substances and has a higher conductivity than water used in the last few rounds.

The water was collected during the 27th of May 2024 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 of the parameters included in the intercomparison test, and the filtered water was stored for another 1-2 weeks before the results were available. 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, and some inorganic phosphorous was added in the form of potassium dihydrogen phosphate (KH_2PO_4). For nitrate, a relatively high concentration was set at 500 µg N/l using KNO_3, since, during the previous years the nitrate in the samples had been transformed to other forms. Unfortunately, this year it was still unsuccessful. As an effect of the mentioned spikes, potassium also increased from the original water, but other parameters were kept as they were. Finally, Sample A 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: cadmium and nickel. The rest of the parameters were already present in reasonable amounts. 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 in 500 mL bottles and the water for sample set CD in 250 mL bottles. The samples were shipped the 24th of June 2024 to the participating laboratories.

Appendix C. Statistical treatment of the results.

Initial treatment of the analytical results

The statistical software PROLab by QuoData was used to process the data. The results were collected via the web service PROLab_HUB (https://niva.quodata.de/). After the deadline had passed, the participants were given randomized participant ID's via the website. The data was then downloaded and imported into PROLab Plus where the statistical computations were performed.

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 $|x_i - x^*|$ $(i = 1, 2 \ldots . p)$

The new values for x* and S* are then calculated according to equations (C.7) – (C.10) in Annex C of ISO 13528 (2022). 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 formular determines the confidence limits, which are the minimum and maximum of the 95% probability range of possible mean values. A low relative value indicates a high likeliness that the true mean value is close to the assigned mean value. The calculated values of the standard uncertainty of the assigned values can be found in Table 5.

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 5. Standard uncertainty of the assigned values.

		absolute	relative	absolute	relative
		Sample A		Sample B	
pH		0.097	1.6 %	0.095	1.6 %
Conductivity	mS/m	0.052	1.4 %	0.054	1.4 %
Alkalinity	mmol/L	0.012	8.7 %	0.011	7.8 %
Chloride	mg/L	0.019	0.6 %	0.028	0.8 %
Sulphate	mg/L	0.022	1.3 %	0.024	1.4 %
Calcium	mg/L	0.058	2.4 %	0.054	2.2 %
Magnesium	mg/L	0.012	1.9 %	0.011	1.7 %
Sodium	mg/L	0.029	1.1 %	0.043	1.6 %
Potassium	mg/L	0.022	1.2 %	0.028	1.5 %
Total organic carbon	mg/L	0.321	2.2 %	0.669	4.6 %
Total phosphorous	µg/L	6.4	5.7 %	8.8	7.5 %
Total nitrogen	µg/L	41	5.4 %	42	4.8 %
		Sample C		Sample D	
Al - aluminium	µg/L	3.7	2.6 %	2.7	1.8 %
Fe - iron	µg/L	2.6	1.1 %	2.3	1.0 %
Mn - manganese	µg/L	0.032	1.9 %	0.030	1.9 %
Cd - cadmium	µg/L	0.027	2.5 %	0.027	2.7 %
Pb - lead	µg/L	0.035	2.9 %	0.037	3.2 %
Cu - copper	µg/L	0.52	3.6 %	0.52	3.1 %
Ni - nickel	µg/L	0.085	5.0 %	0.067	3.7 %
Zn -zinc	µg/L	0.28	1.1 %	0.19	0.9 %

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 years before 2023, the tolerance limit has been fixed in relative terms. Most often, it used to be ±20% from the assigned "true" value. In many cases, this was 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-scores 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 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 is actionable. Figures of the Z'-score distribution for each parameter can be seen in Figure 22 to Figure 41.

Appendix D. Results reported by the participating laboratories

D.1. Survey of Z’ scores

Z’ scores between |2| and |3| are marked as yellow and Z’ scores >|3| are marked as red.

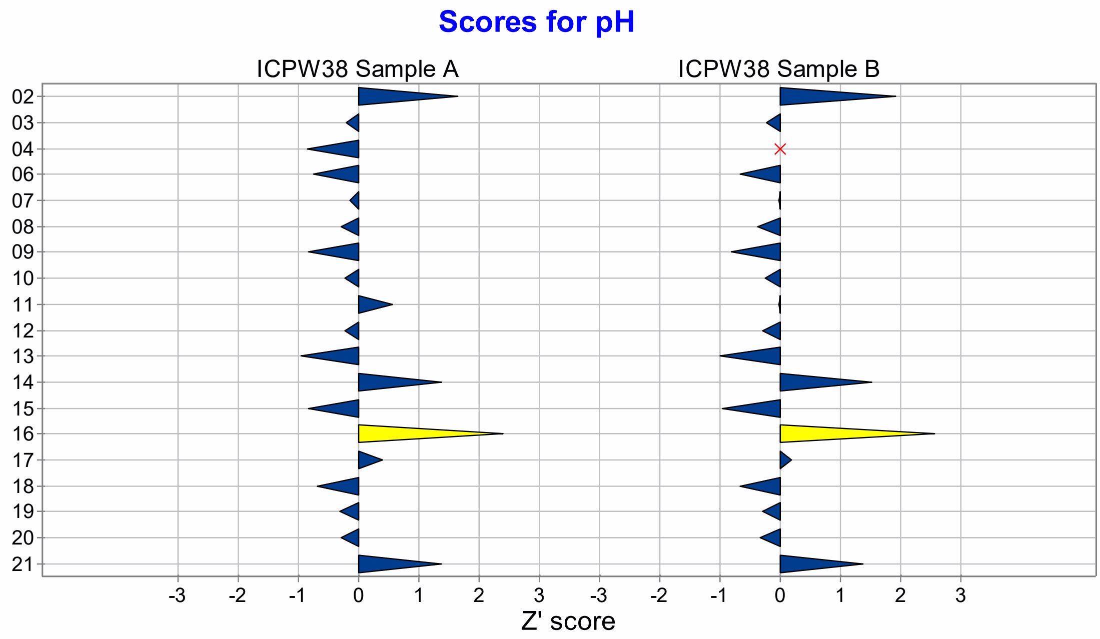

Figure 22. Z’-scores for pH.

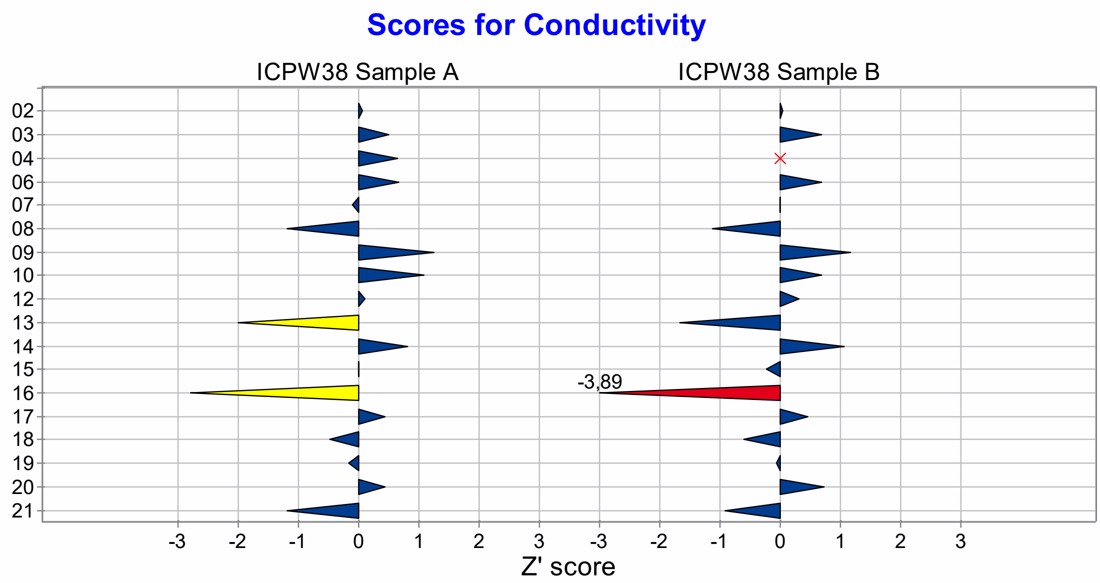

Figure 23. Z’-scores for Conductivity.

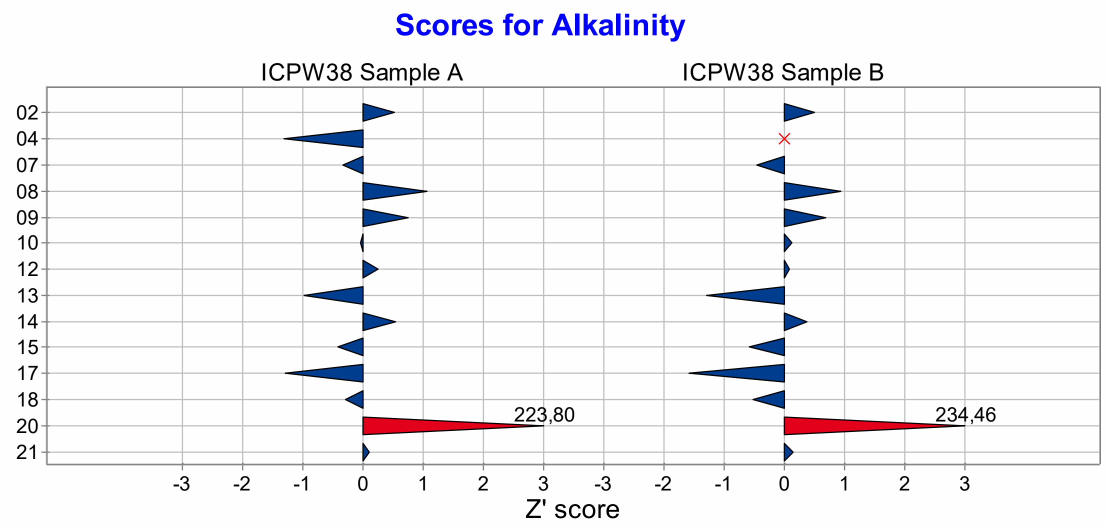

Figure 24. Z'-scores for Alkalinity.

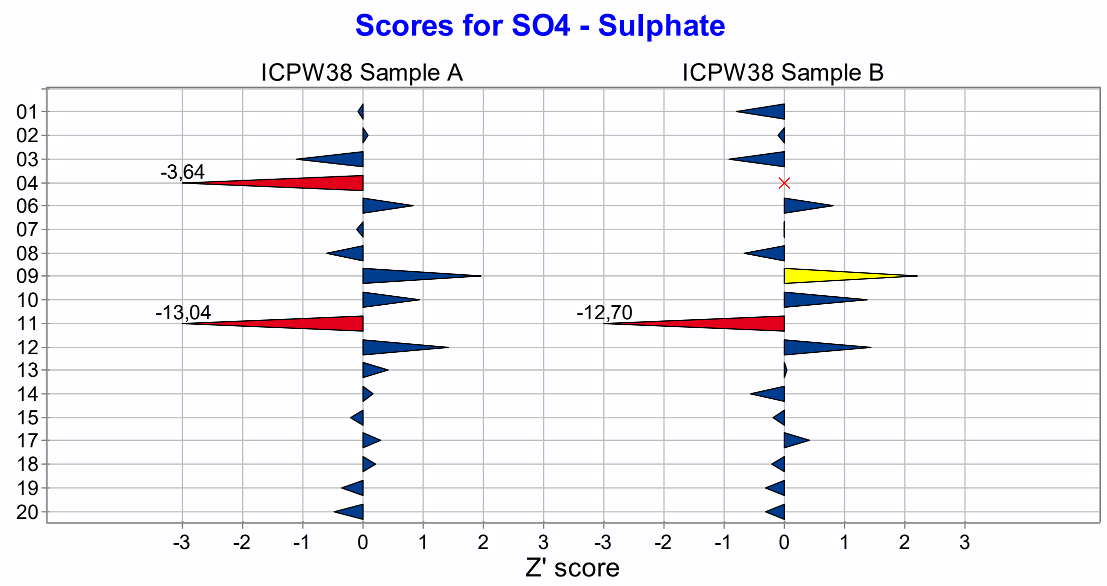

Figure 25. Z'-scores for Sulphate.

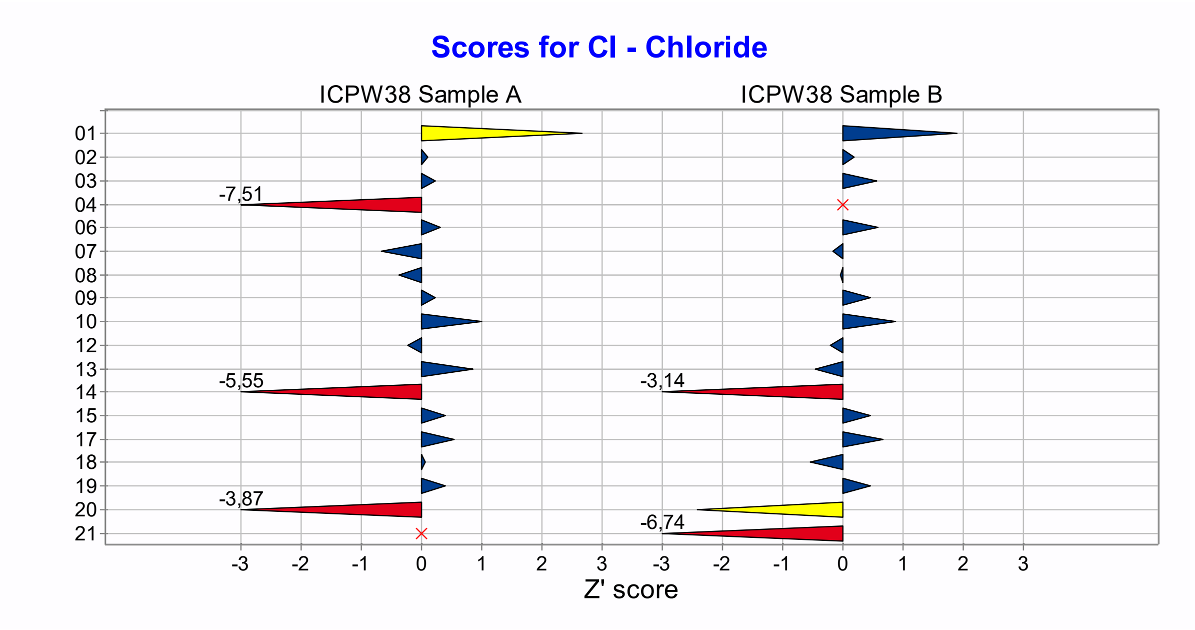

Figure 26. Z'-scores for Chloride.

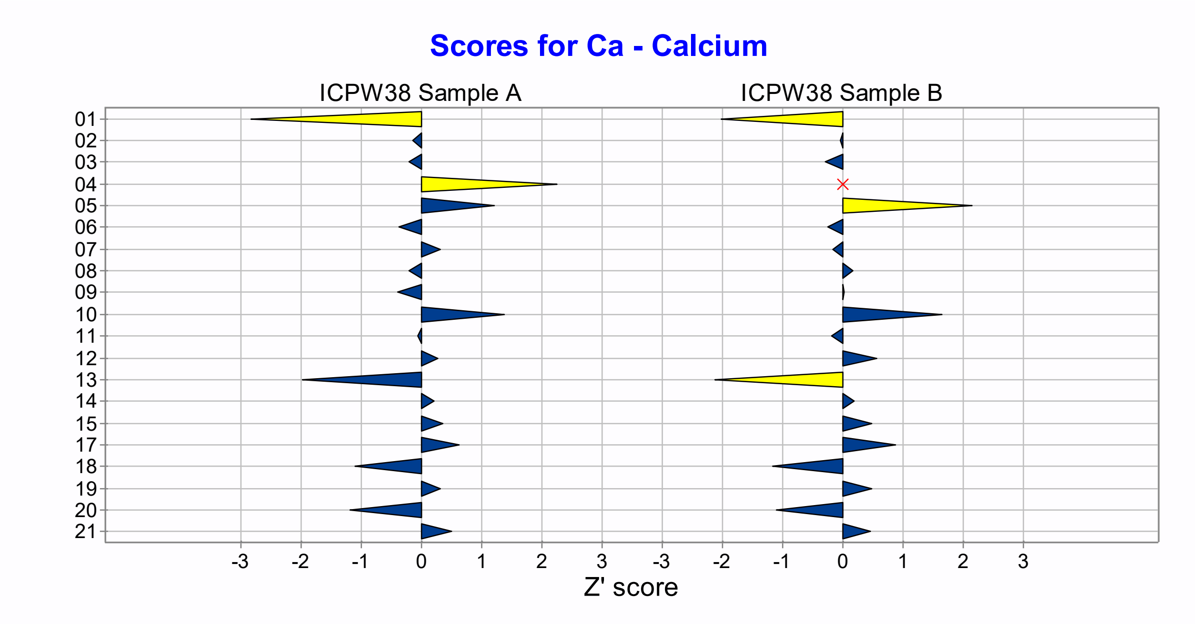

Figure 27. Z'-scores for Calcium.

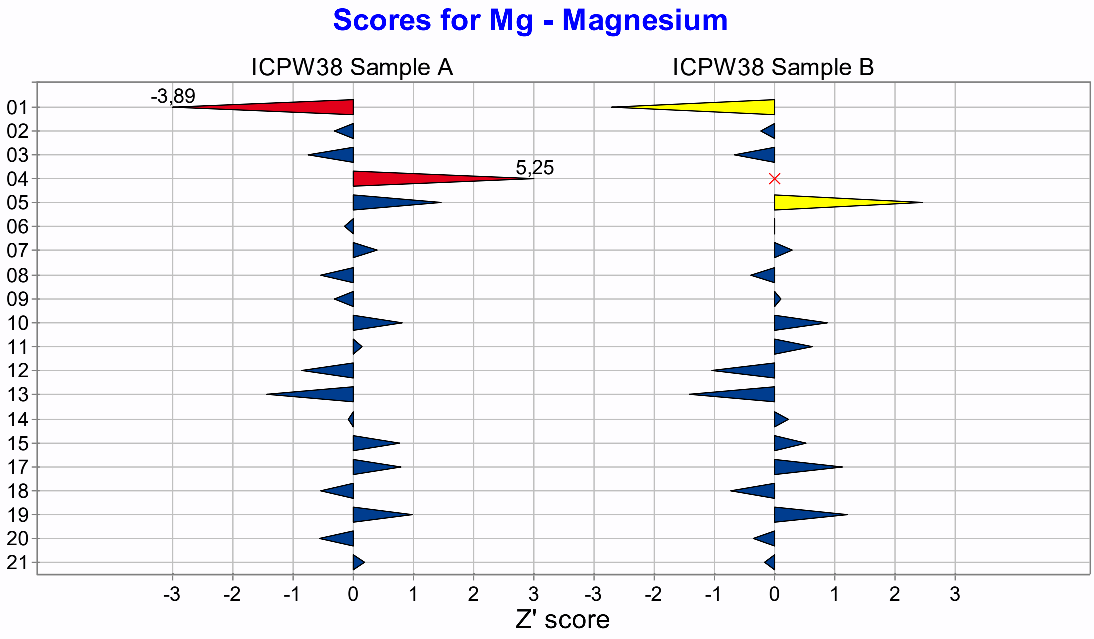

Figure 28. Z'-scores for Magnesium.

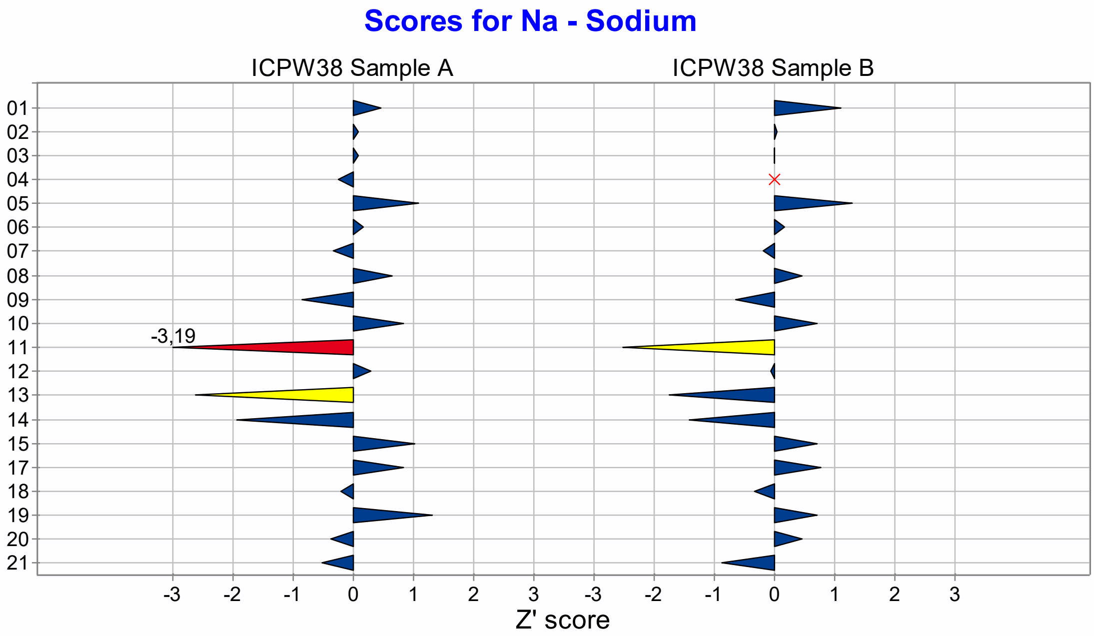

Figure 29. Z'-scores for Sodium.

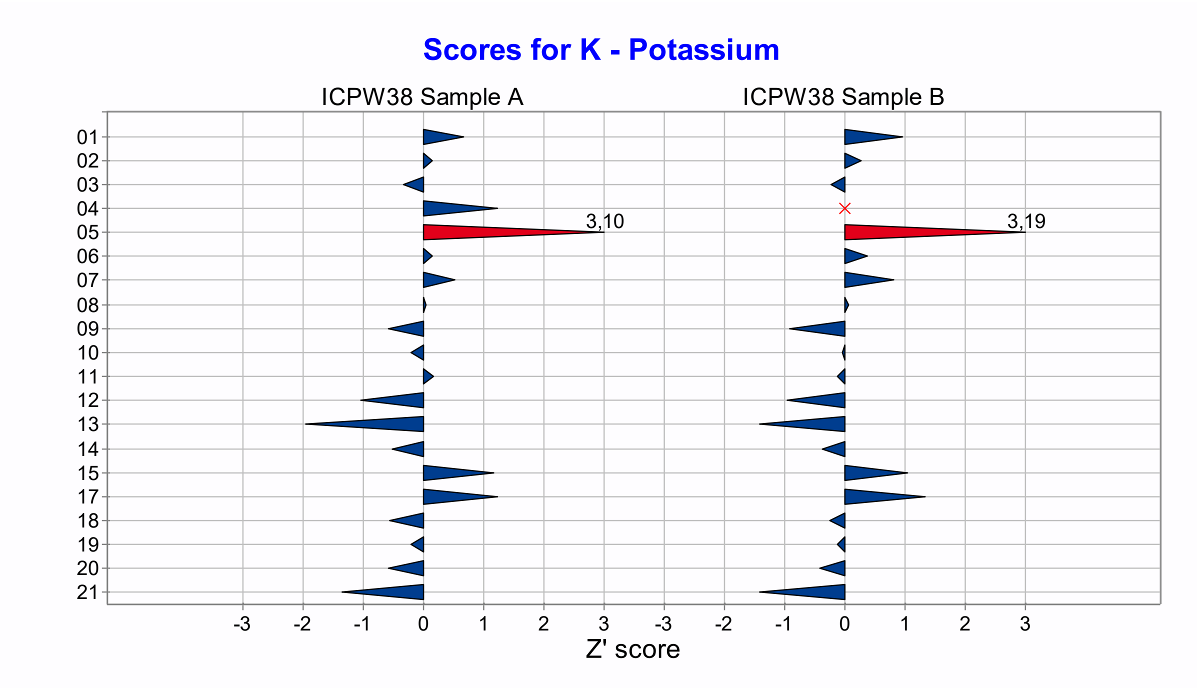

Figure 30. Z'-scores for Potassium.

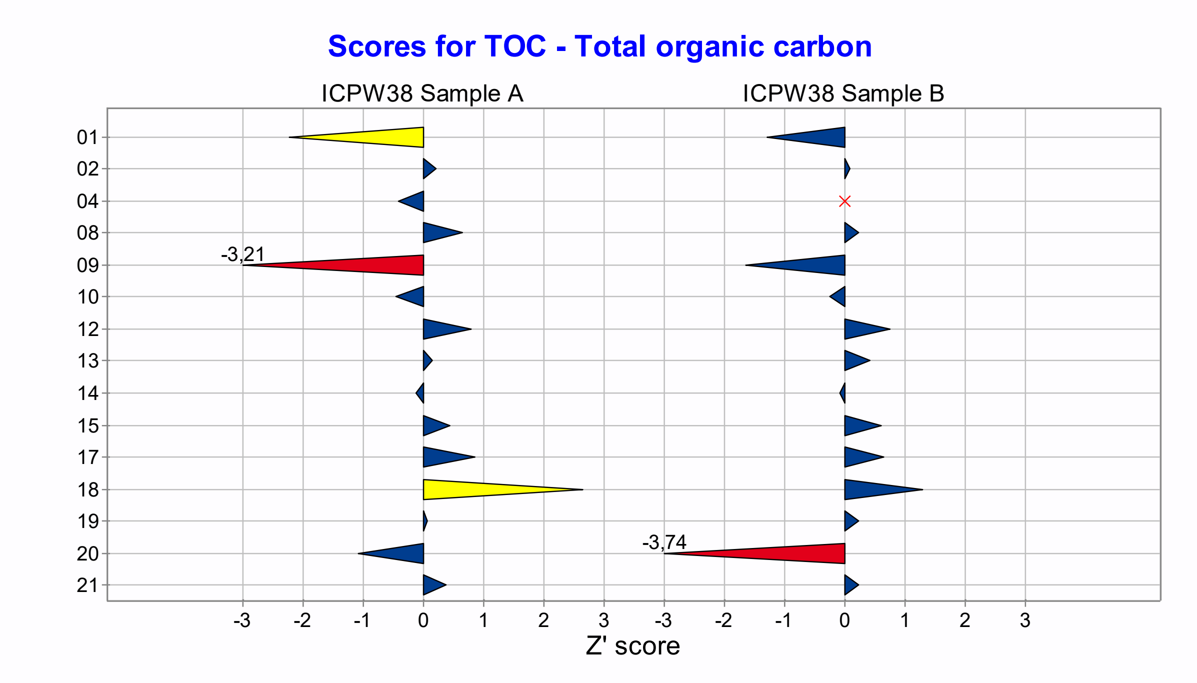

Figure 31. Z'-scores for Total organic carbon (TOC).

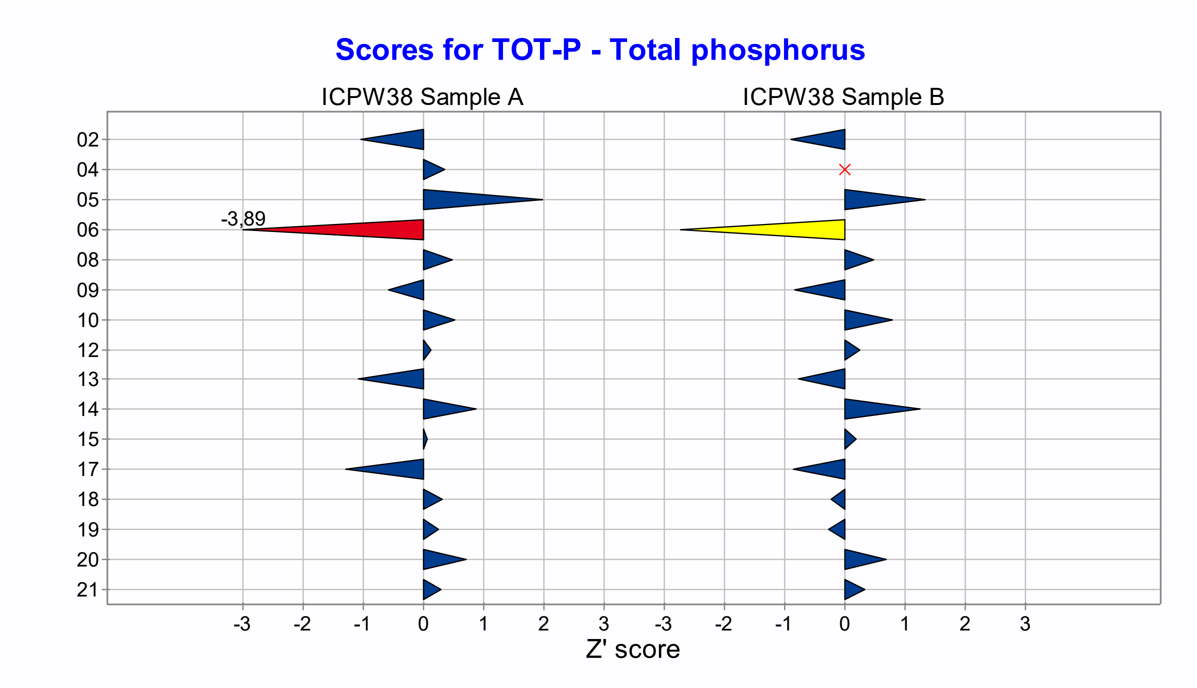

Figure 32. Z'-scores for Total phosphorous (TOT-P).

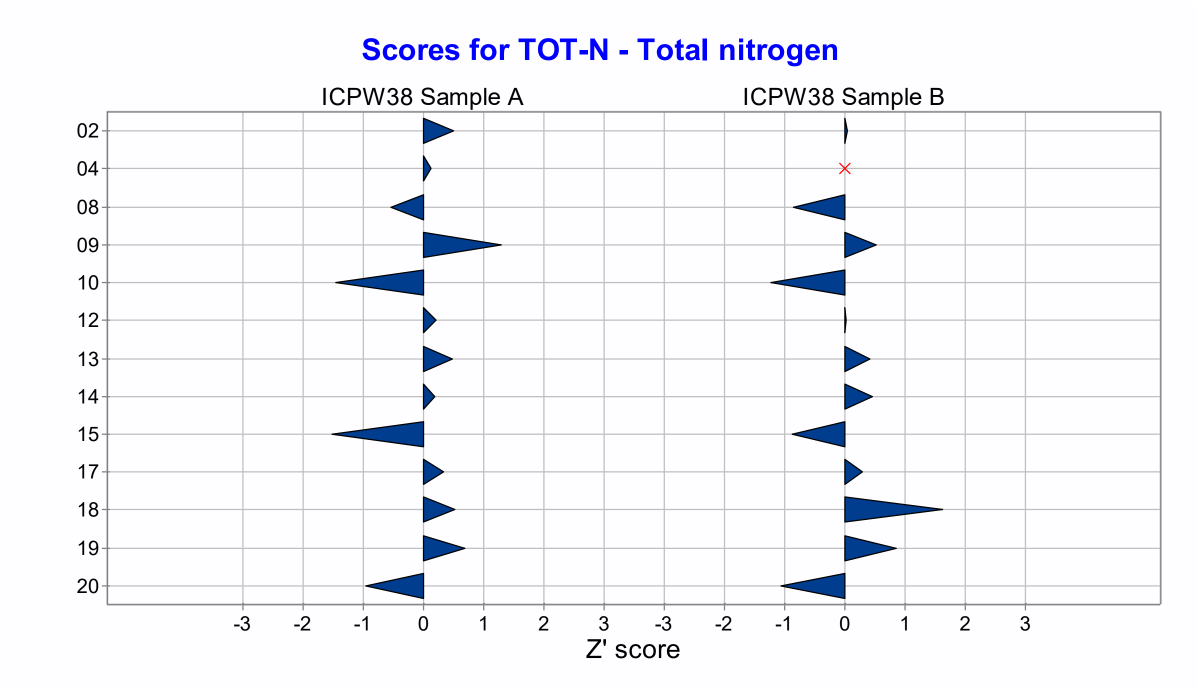

Figure 33. Z'-scores for Total nitrogen (TOT-N).

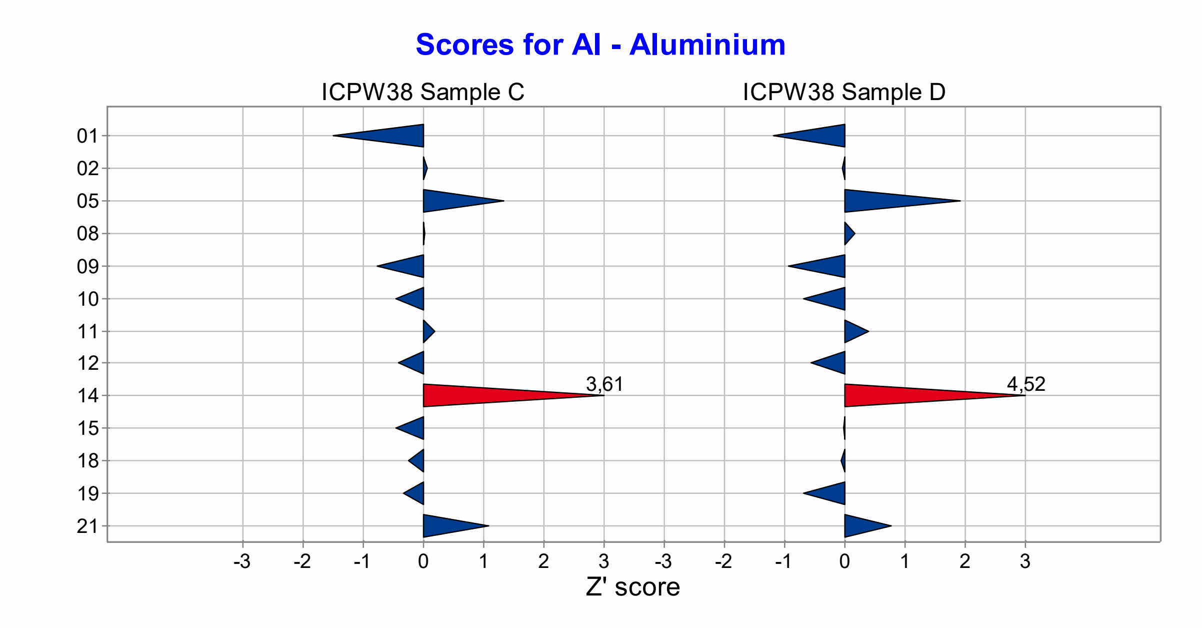

Figure 34. Z'-scores for Aluminium (Al).

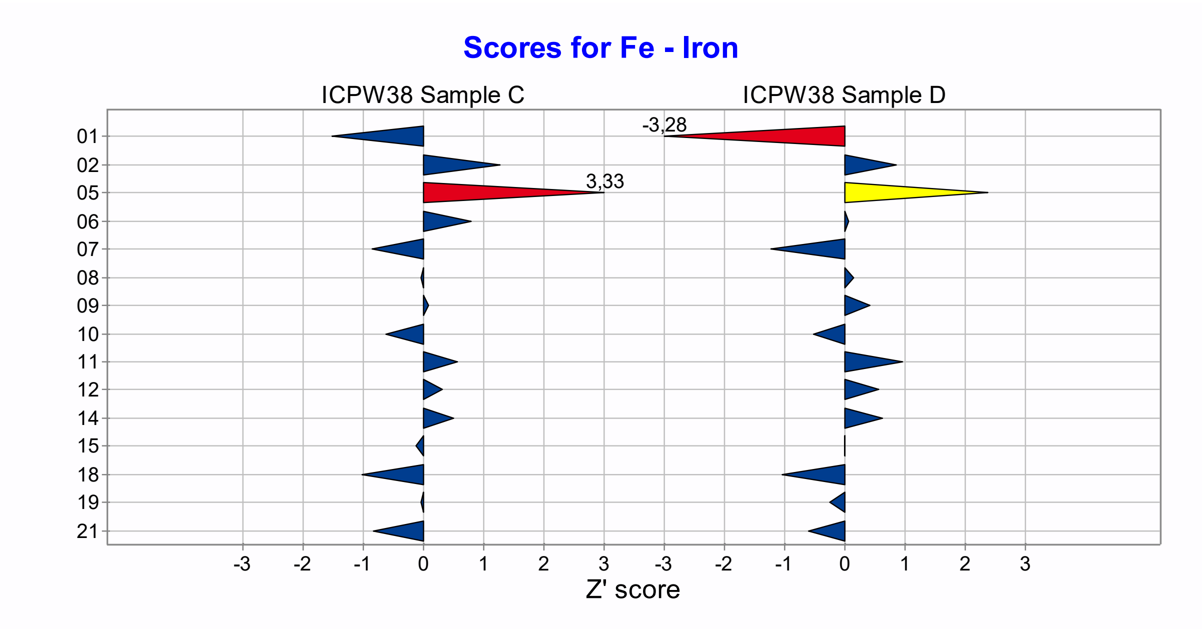

Figure 35. Z'-scores for Iron (Fe).

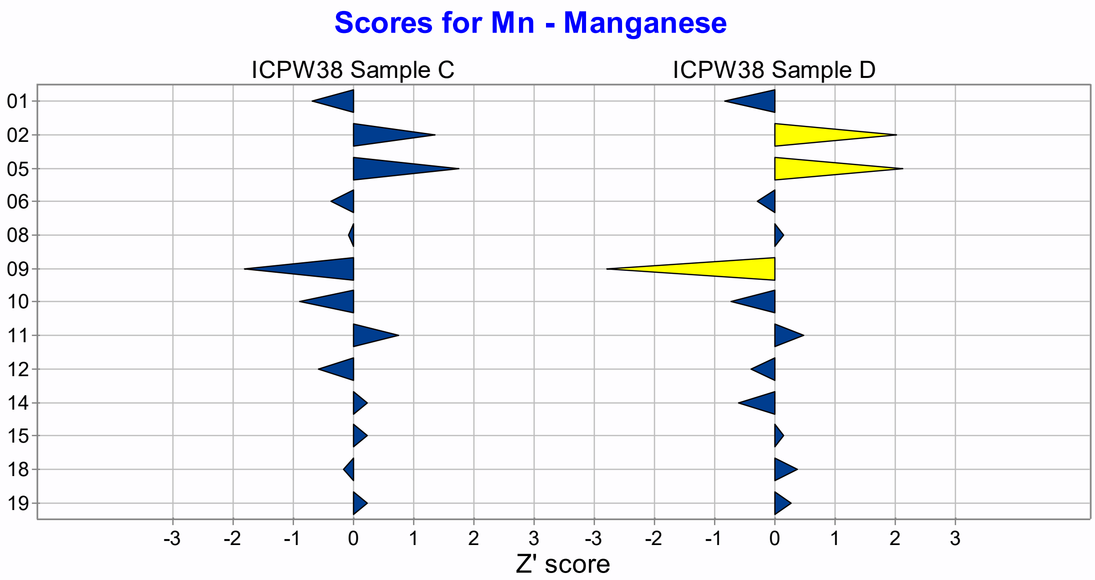

Figure 36. Z'-scores for Manganese (Mn).

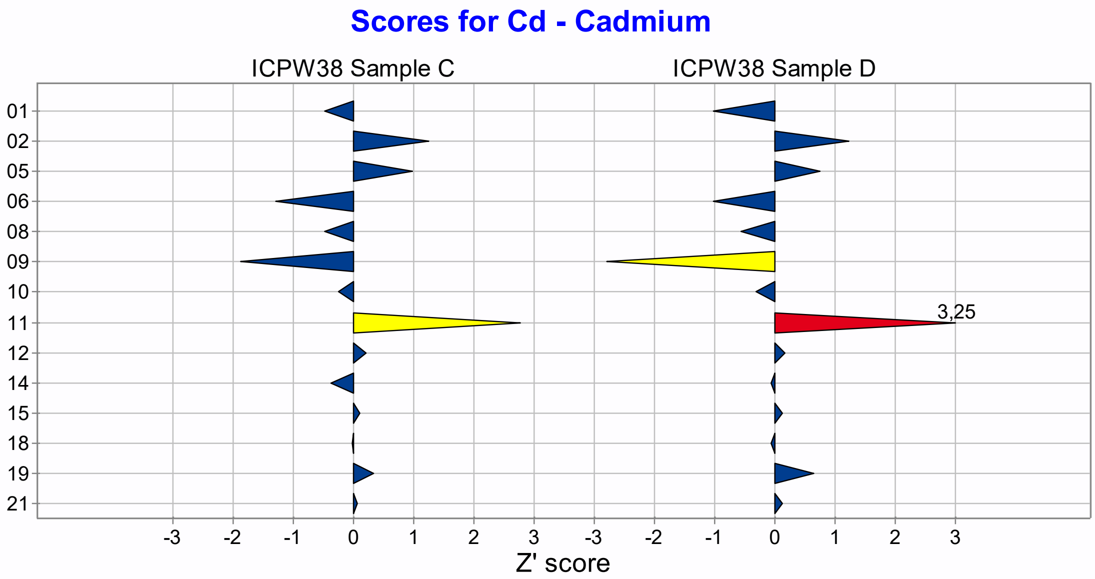

Figure 37. Z'-scores for Cadmium (Cd).

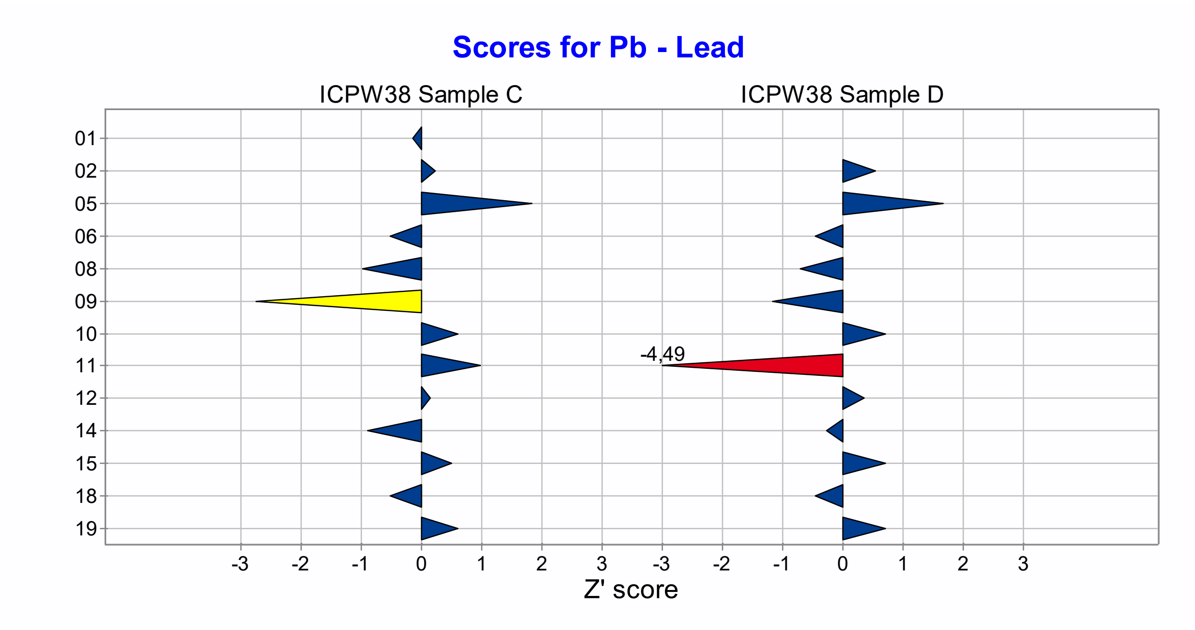

Figure 38. Z'-scores for Lead (Pb).

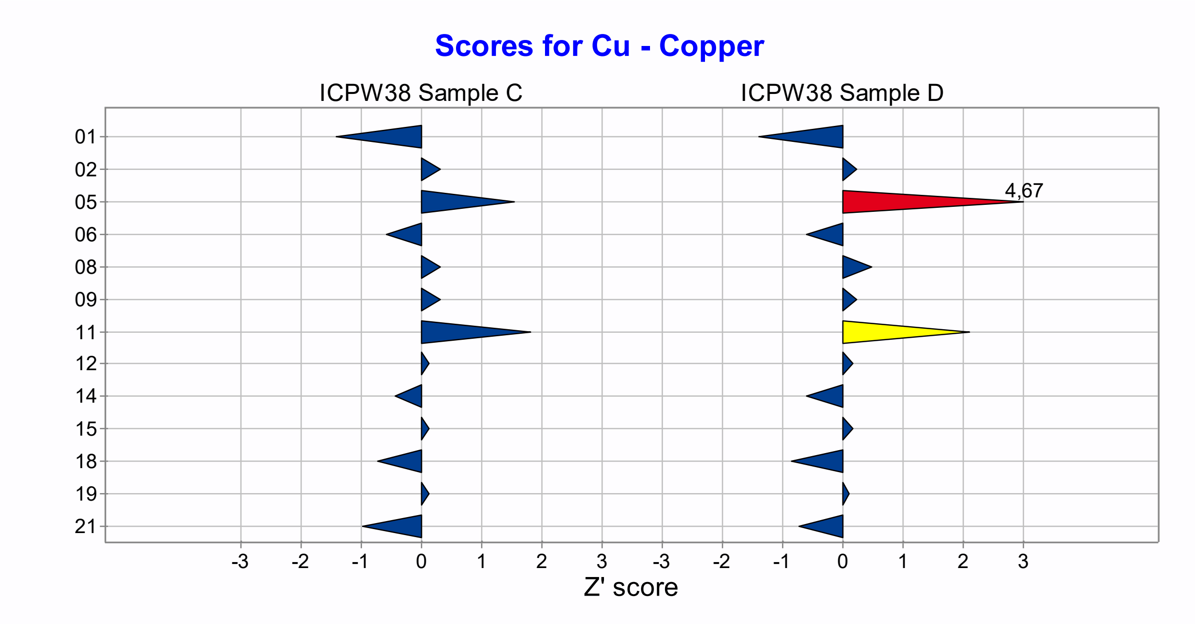

Figure 39. Z'-scores for Copper (Cu).

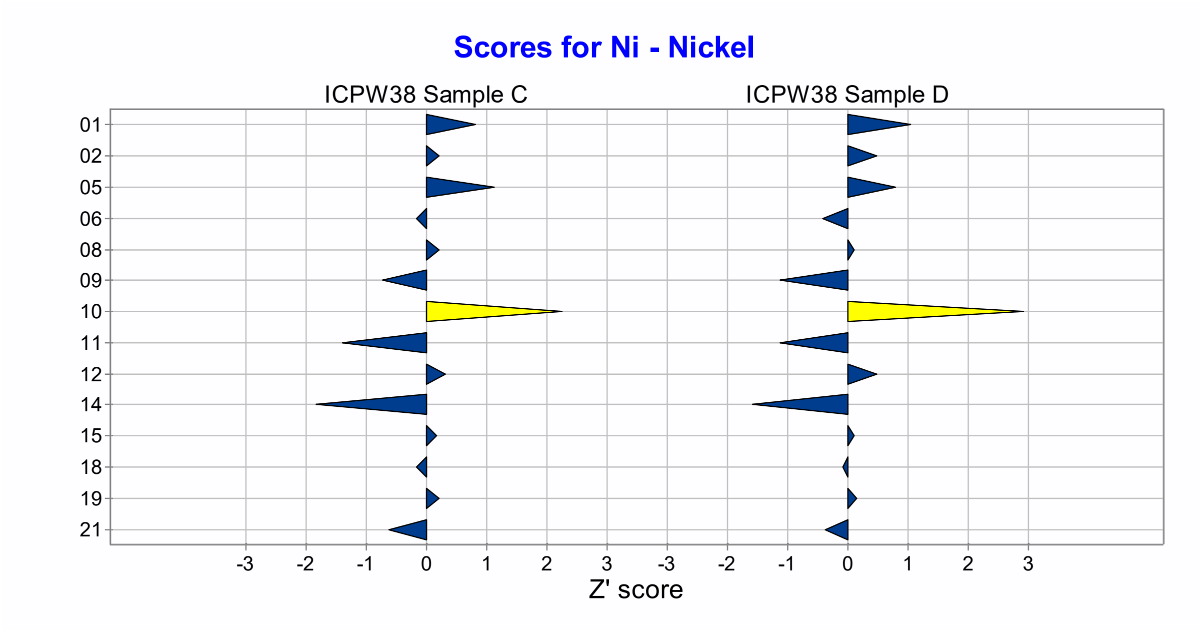

Figure 40. Z'-scores for Nickel (Ni).

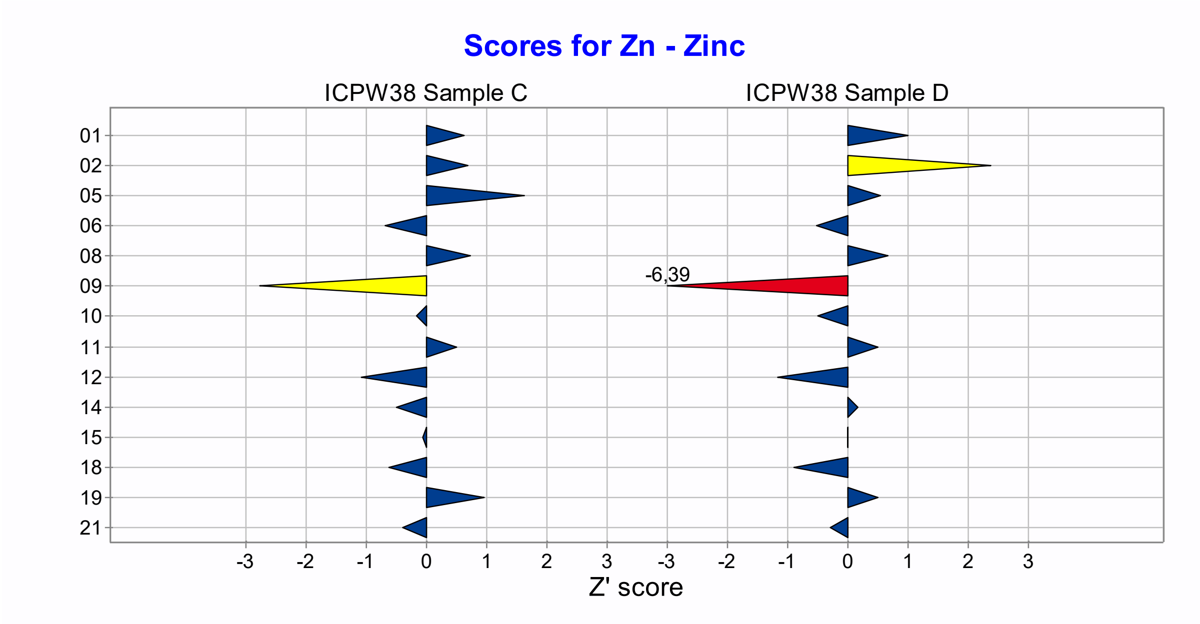

Figure 41. Z'-scores for Zinc (Zn).

D.2. Visual representation of reported values with the different techniques used

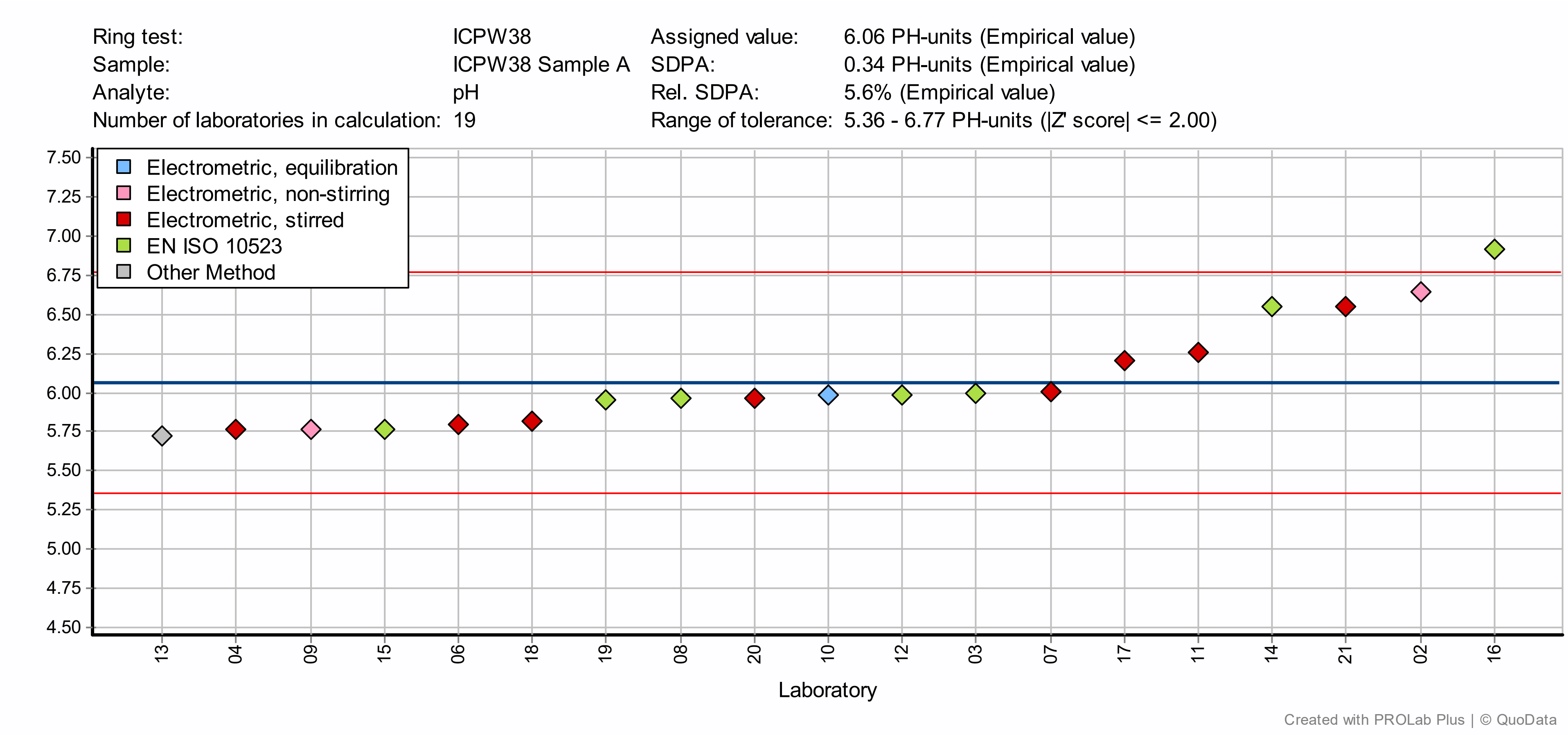

Figure 42. Reported values of pH in sample A, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

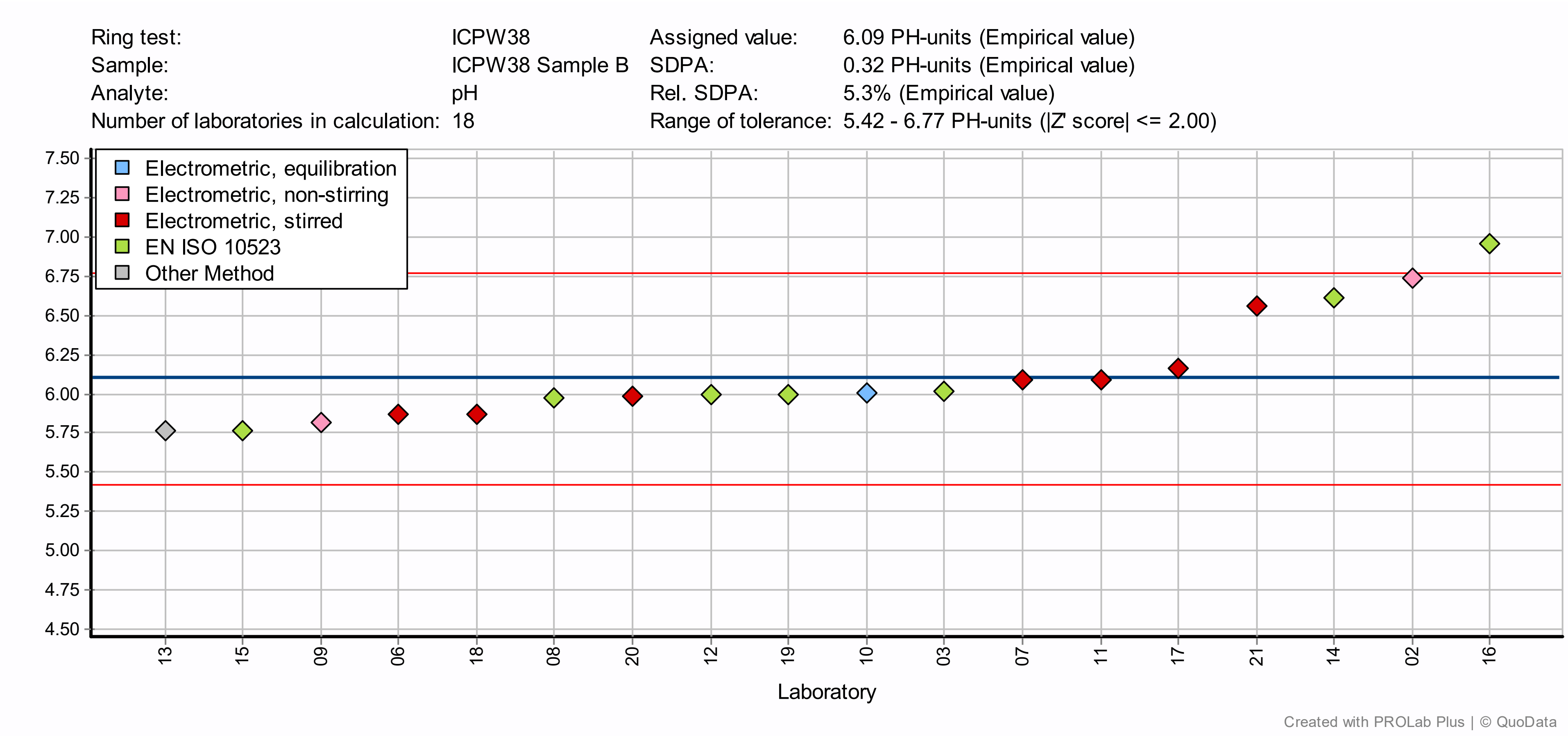

Figure 43. Reported values of pH in sample B, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

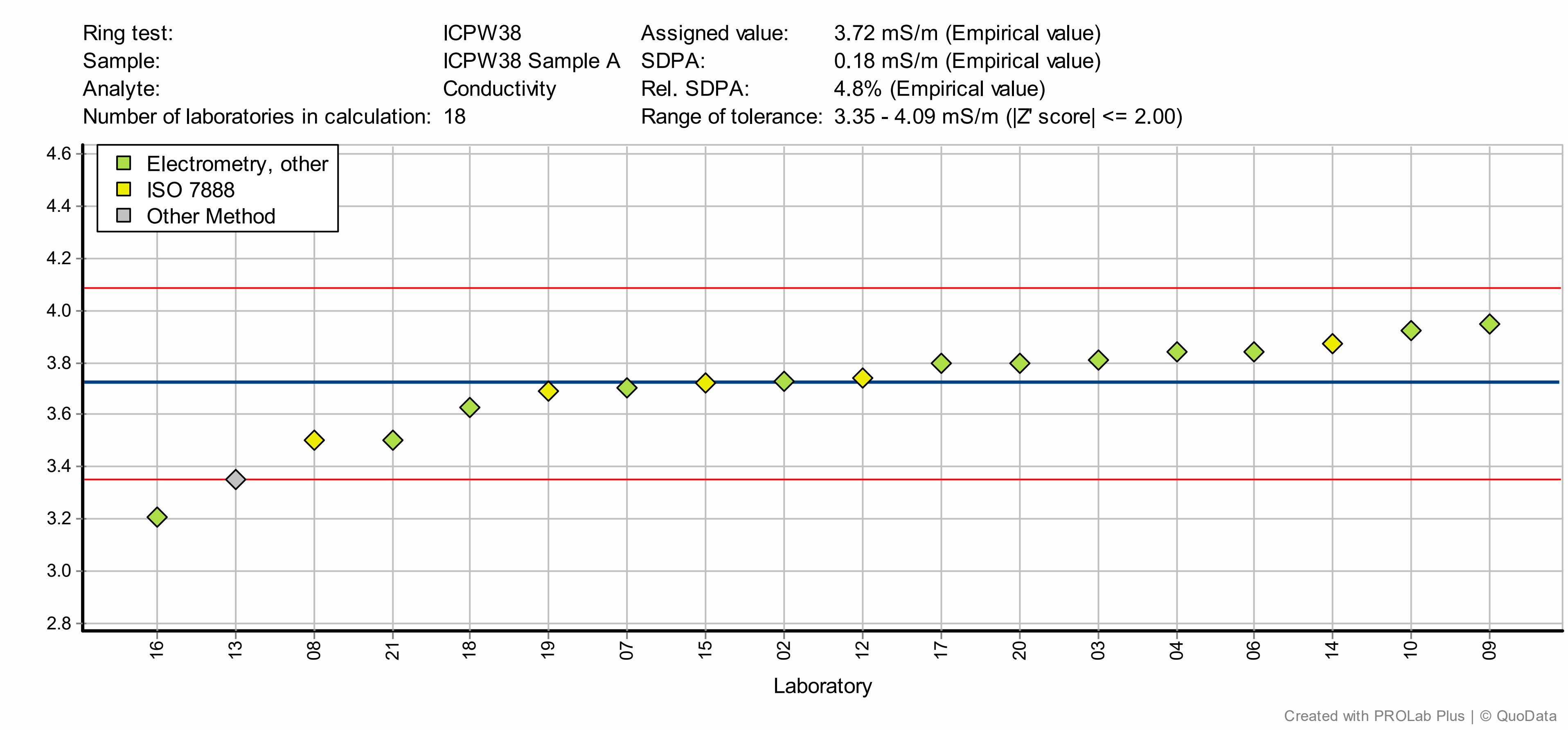

Figure 44. Reported values of Conductivity in sample A, sorted by concentration levels, and colour coded by method. Limit of tolerance lines indicates Z' score of ±2.

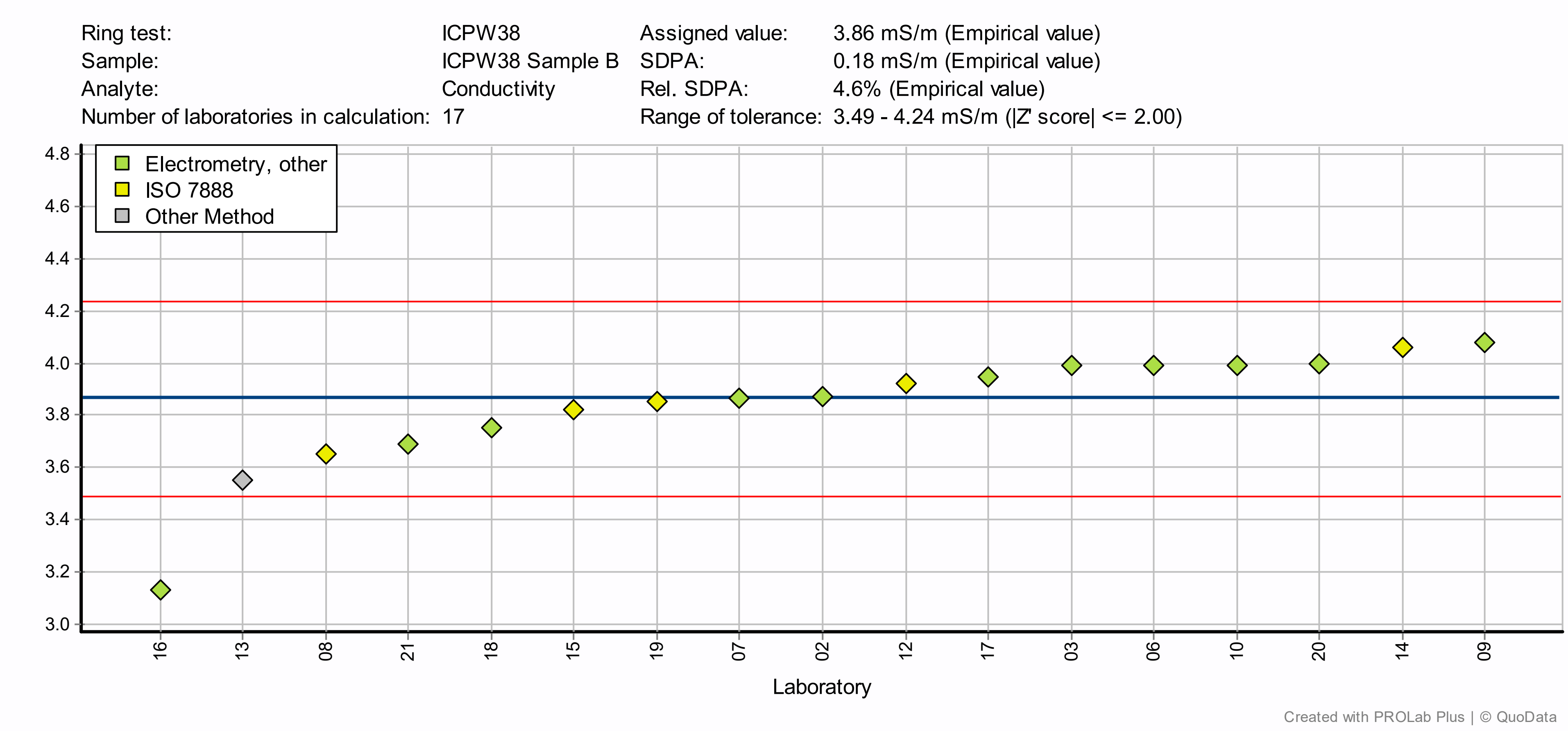

Figure 45. Reported values of Conductivity in sample B, sorted by concentration levels, and colour coded by method. Limit of tolerance lines indicates Z' score of ±2.

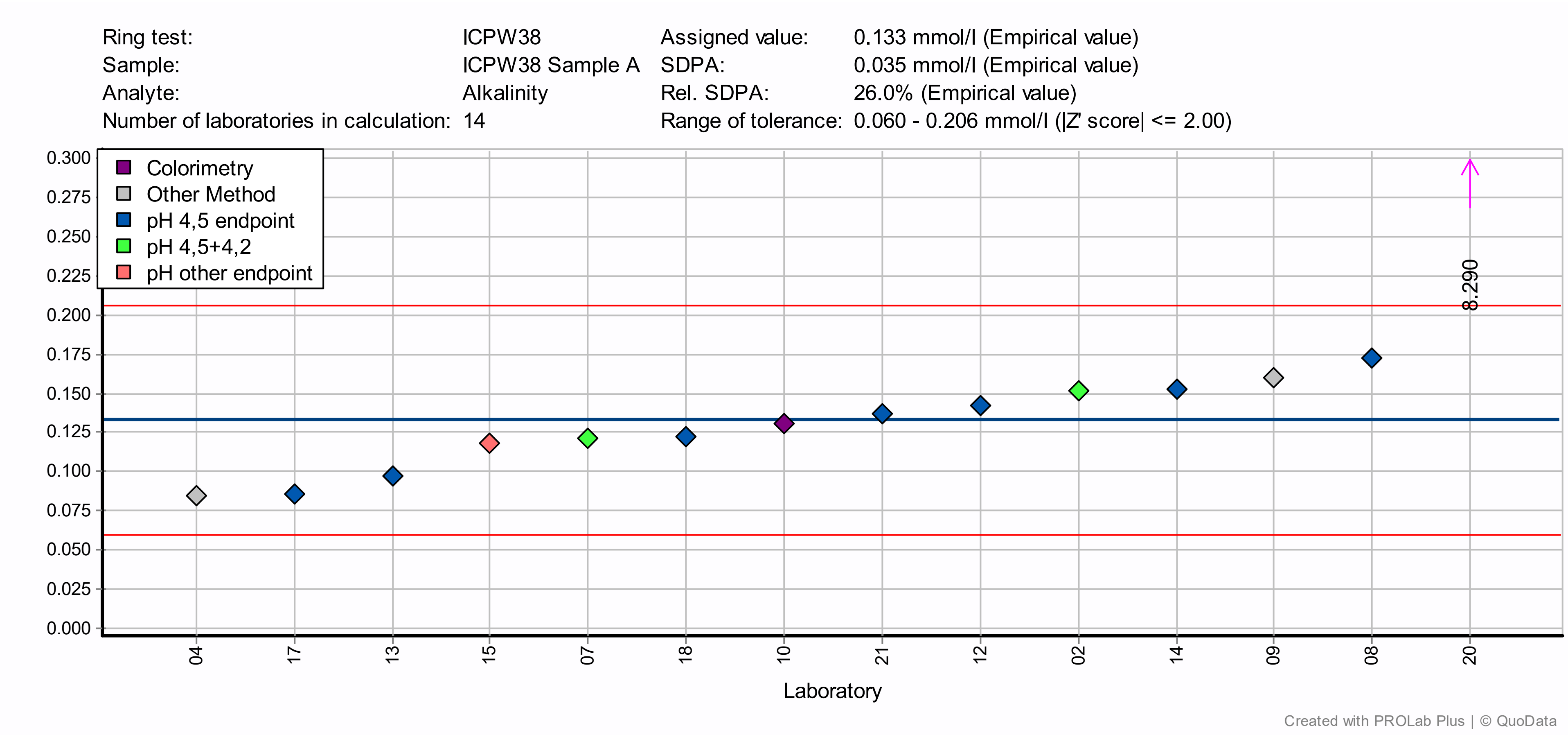

Figure 46. Reported values of Alkalinity in sample A, sorted by concentration levels, and colour coded by method. Limit of tolerance lines indicates Z' score of ±2.

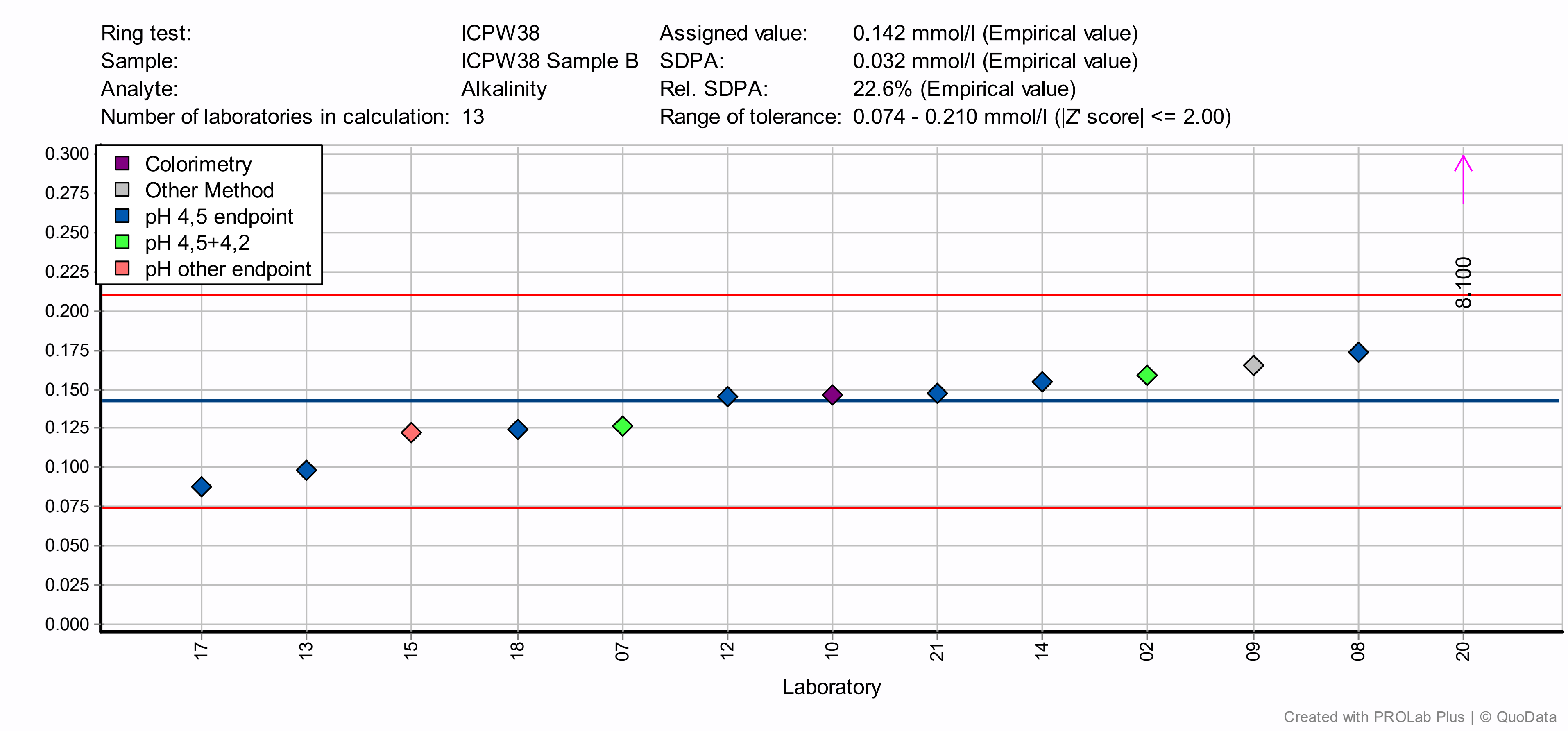

Figure 47. Reported values of Alkalinity in sample B, sorted by concentration levels, and colour coded by method. Limit of tolerance lines indicates Z' score of ±2.

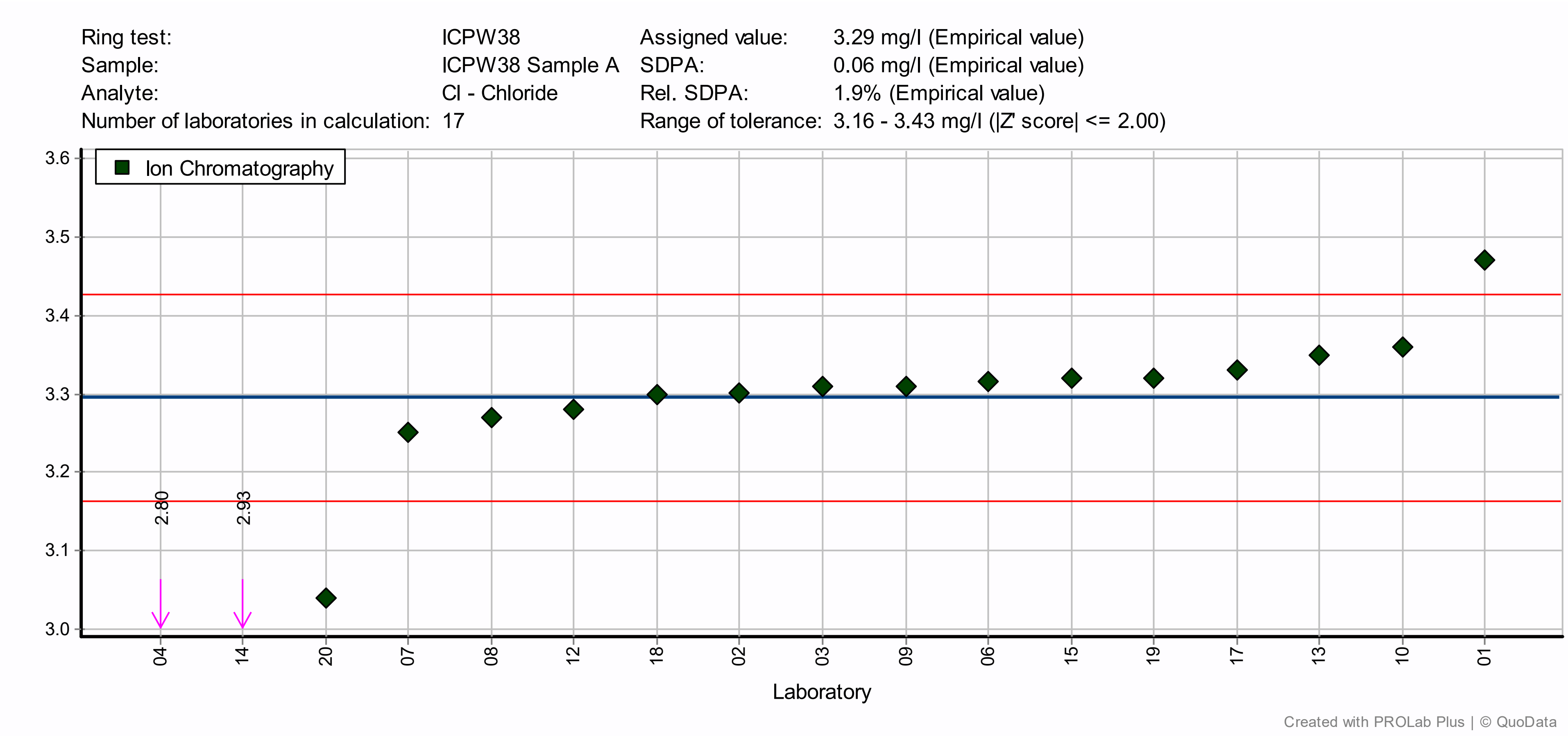

Figure 48. Reported values of Chloride in sample A, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2. Results below LOQ are not visualized in this figure.

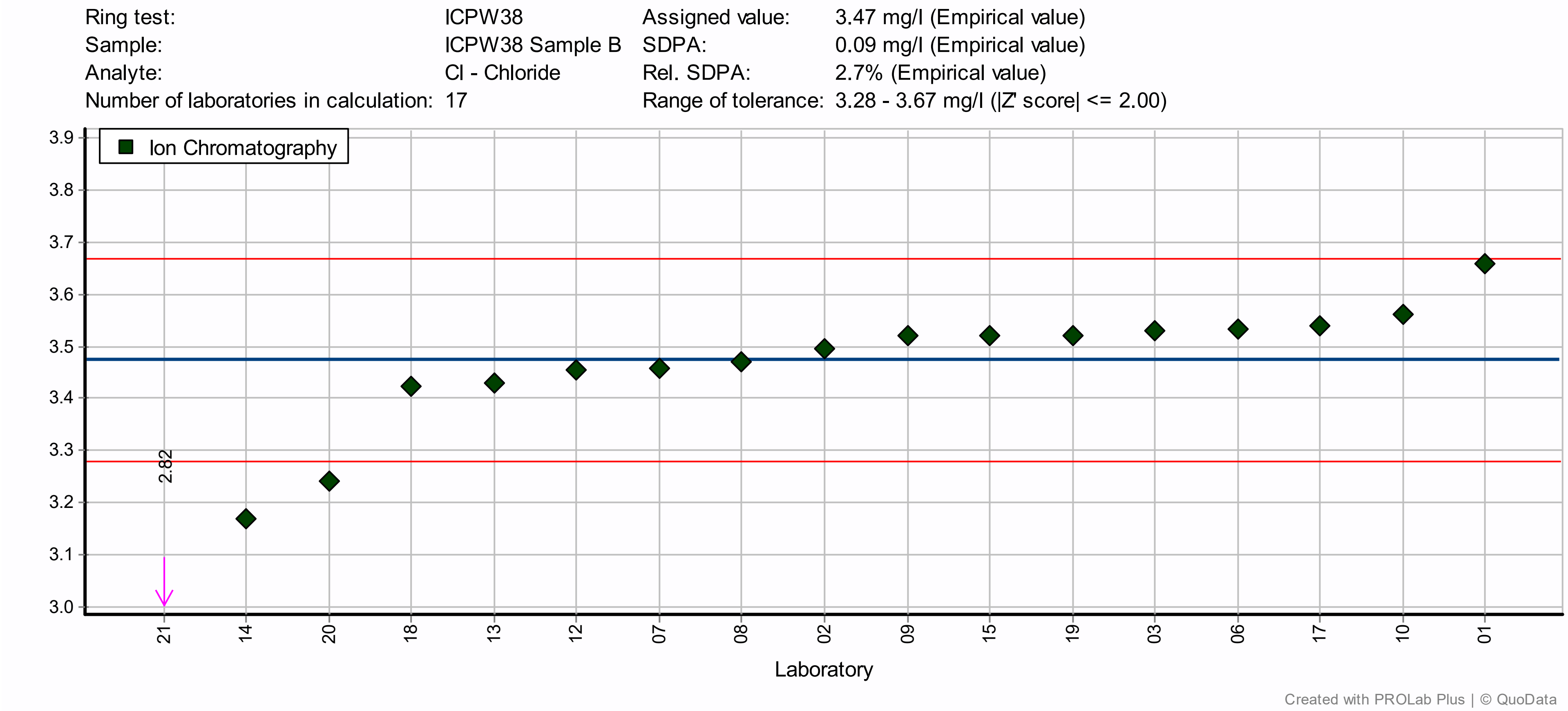

Figure 49. Reported values of Chloride in sample B, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

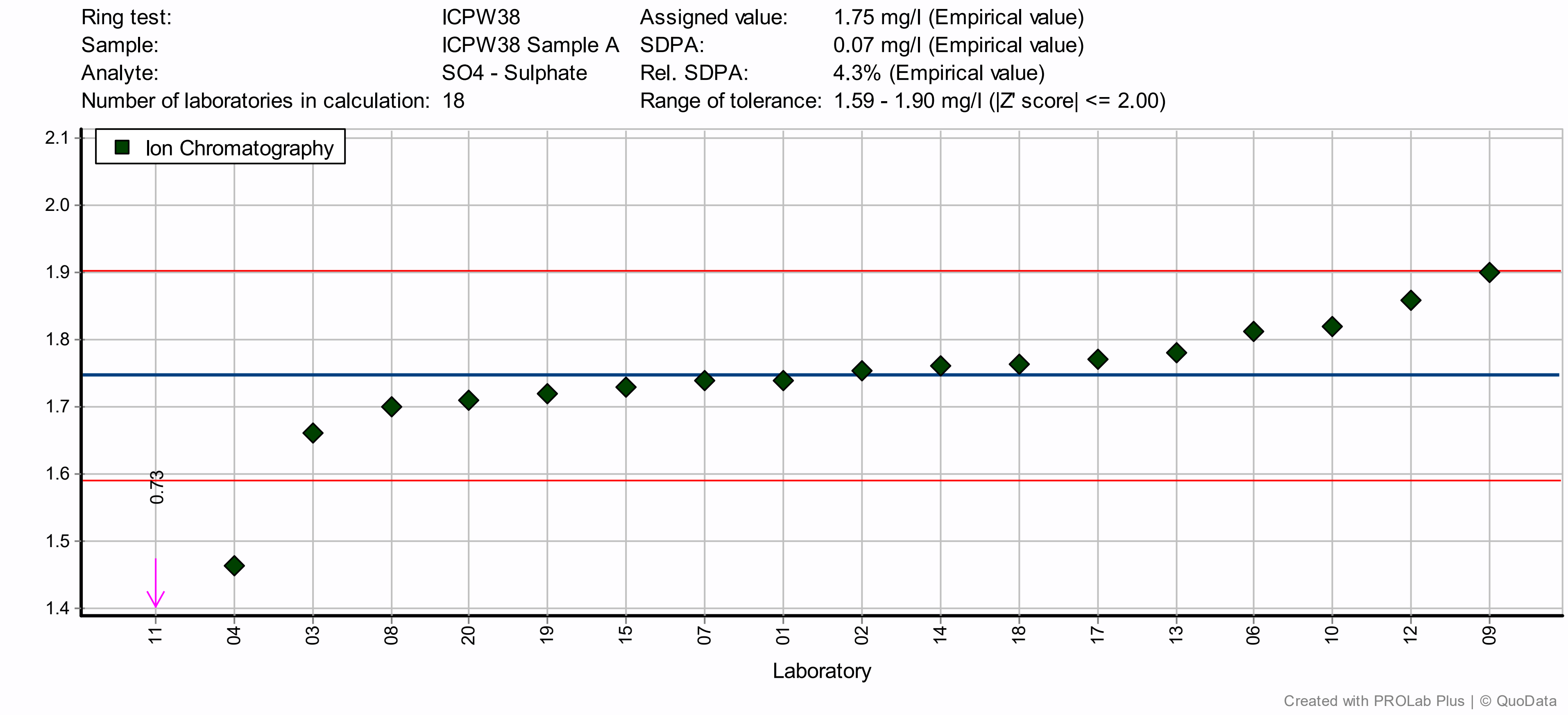

Figure 50. Reported values of Sulphate in sample A, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2. Results below LOQ are not visualized in this figure.

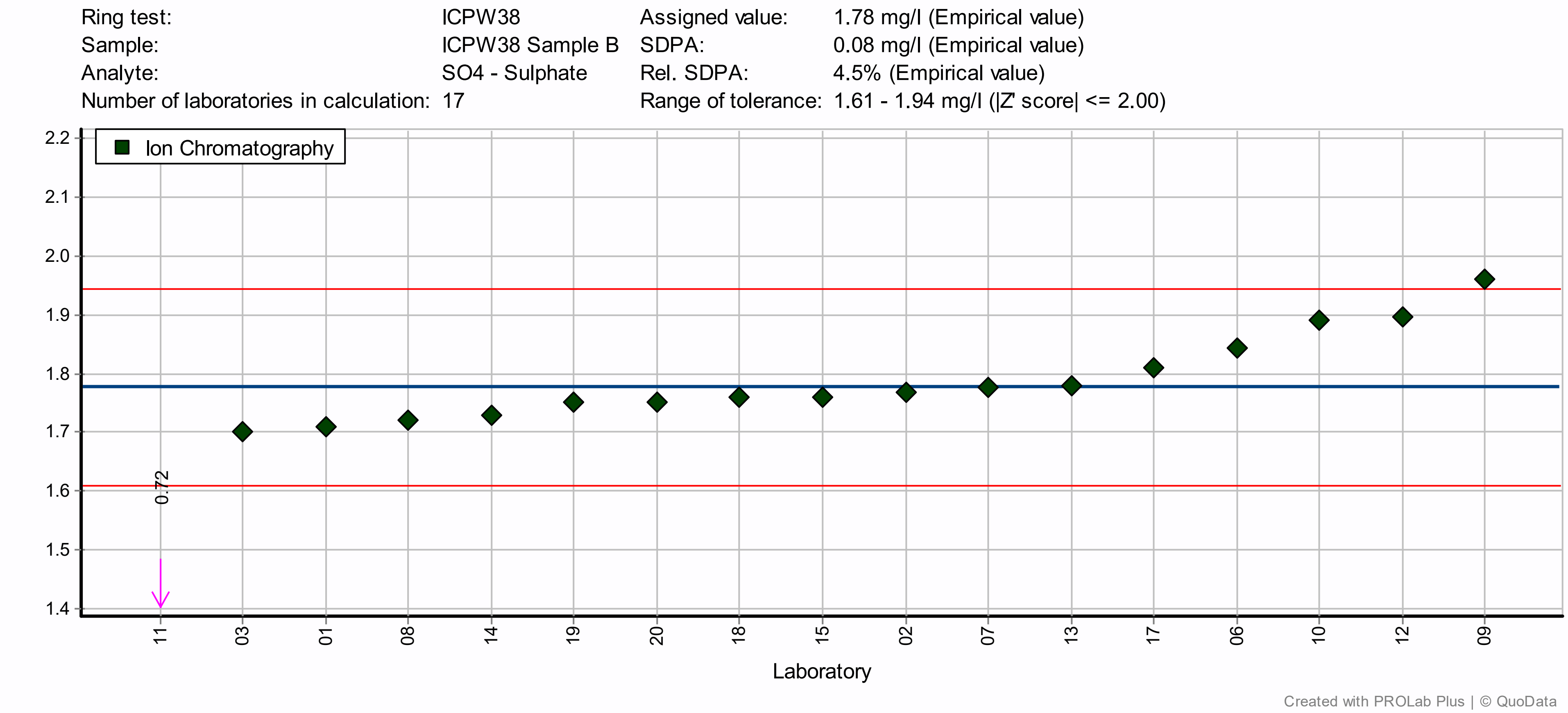

Figure 51. Reported values of Sulphate in sample B, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2. Results below LOQ are not visualized in this figure.

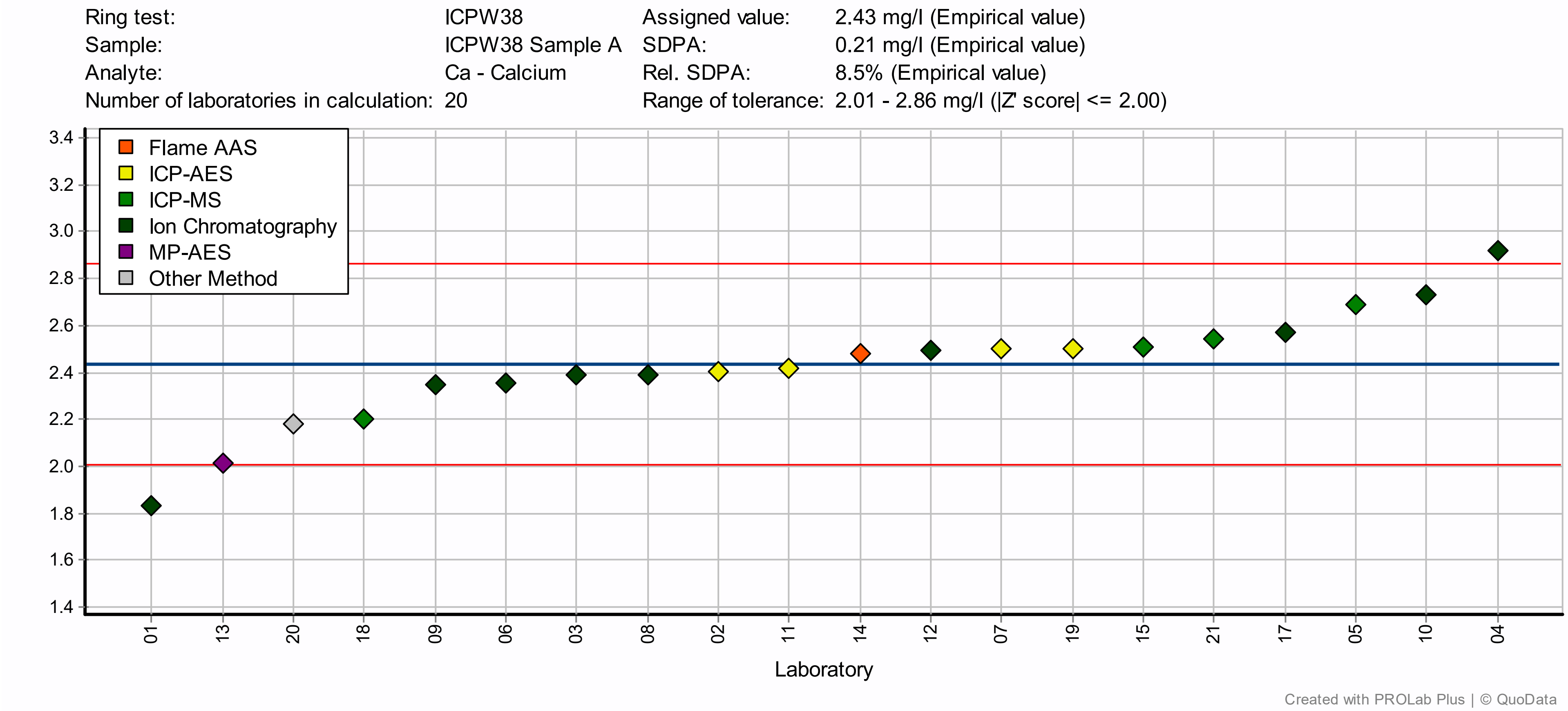

Figure 52. Reported values of Calcium in sample A, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

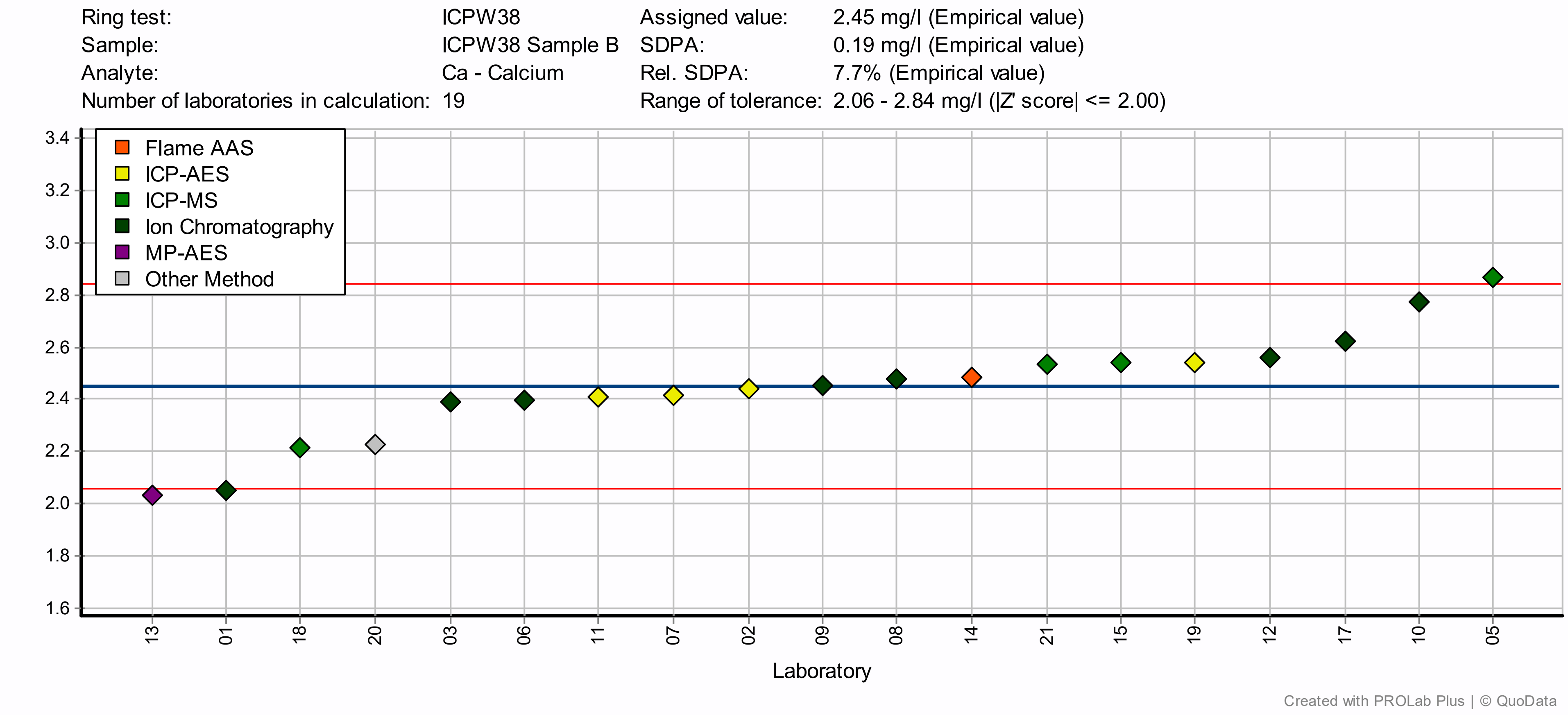

Figure 53. Reported values of Calcium in sample B, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

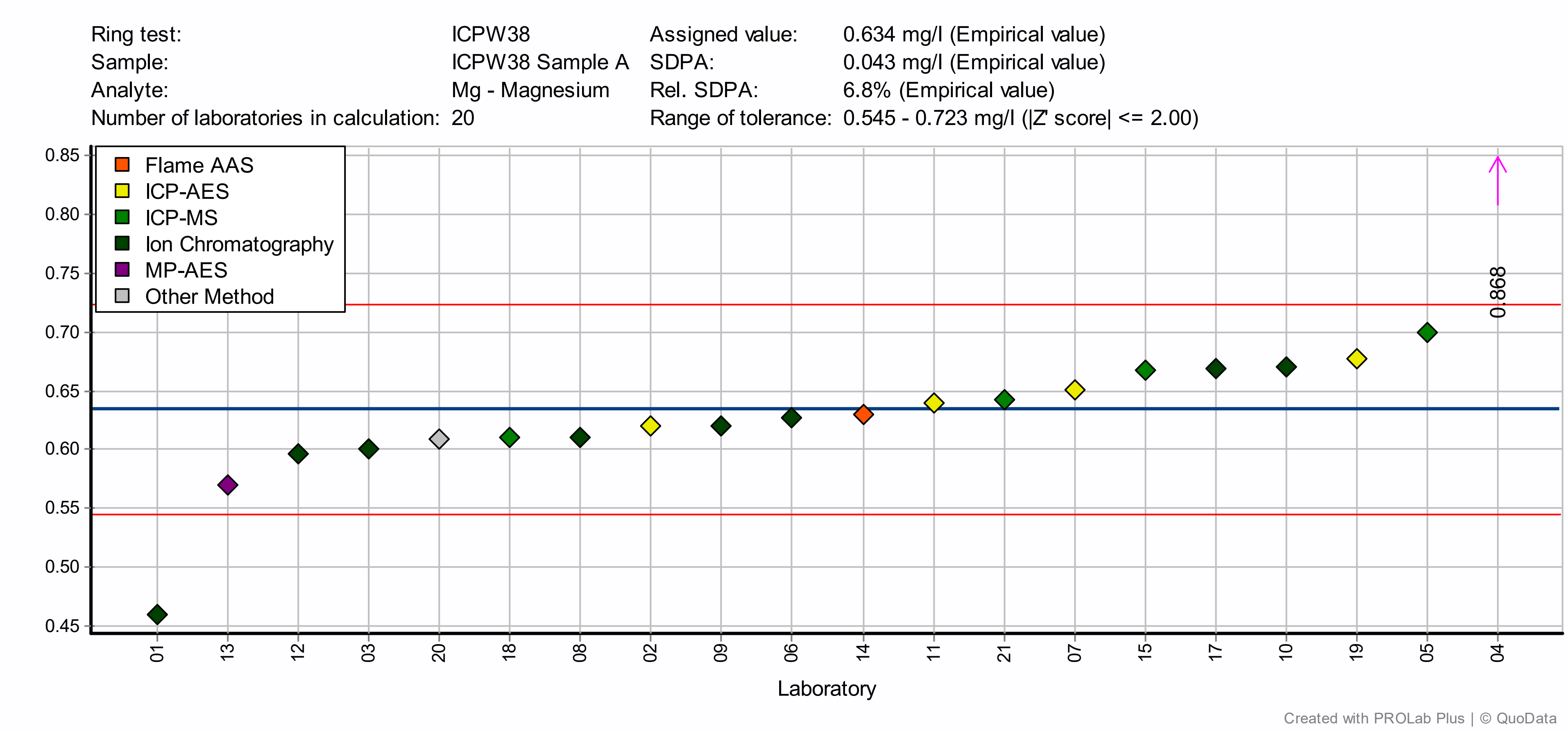

Figure 54. Reported values of Magnesium in sample A, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

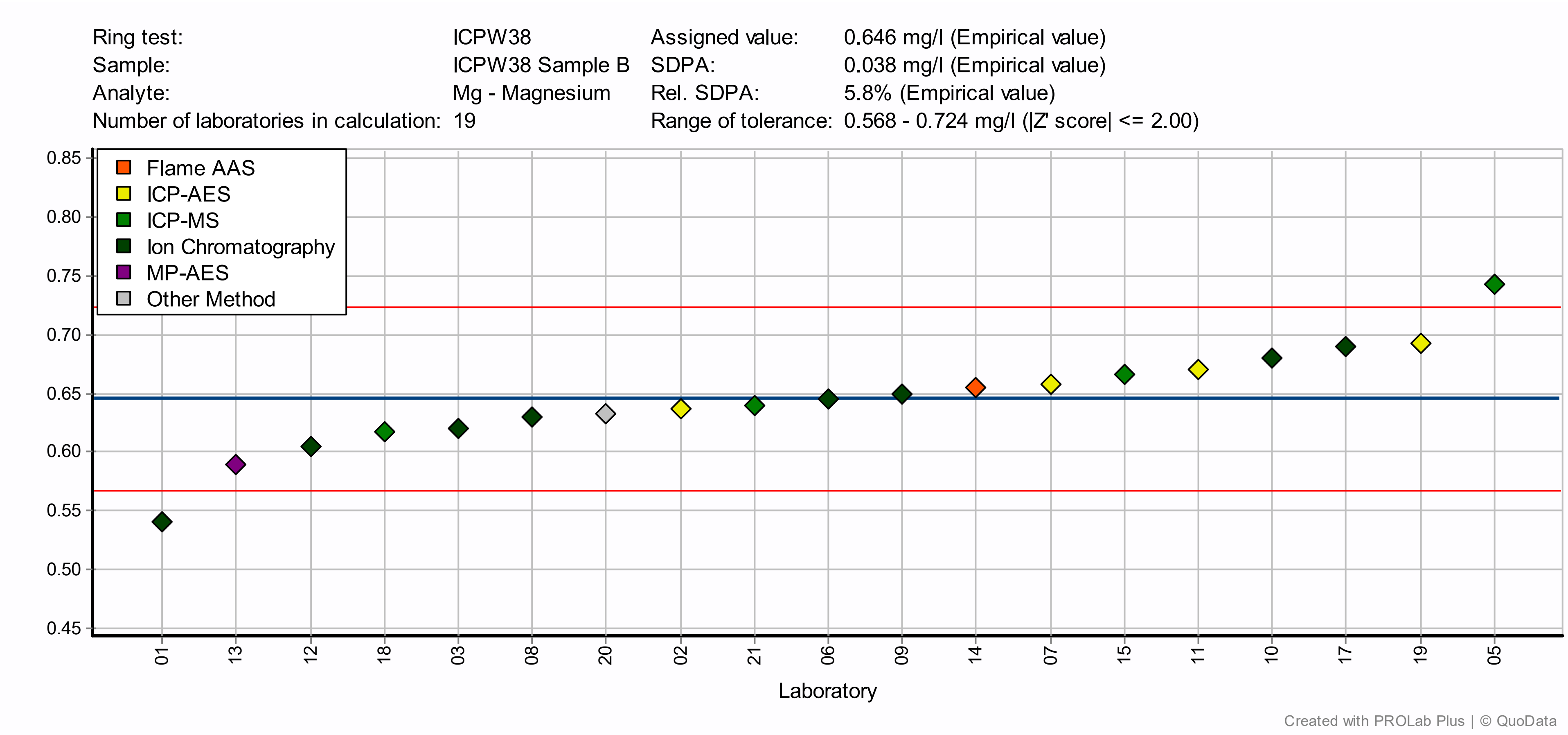

Figure 55. Reported values of Magnesium in sample B, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

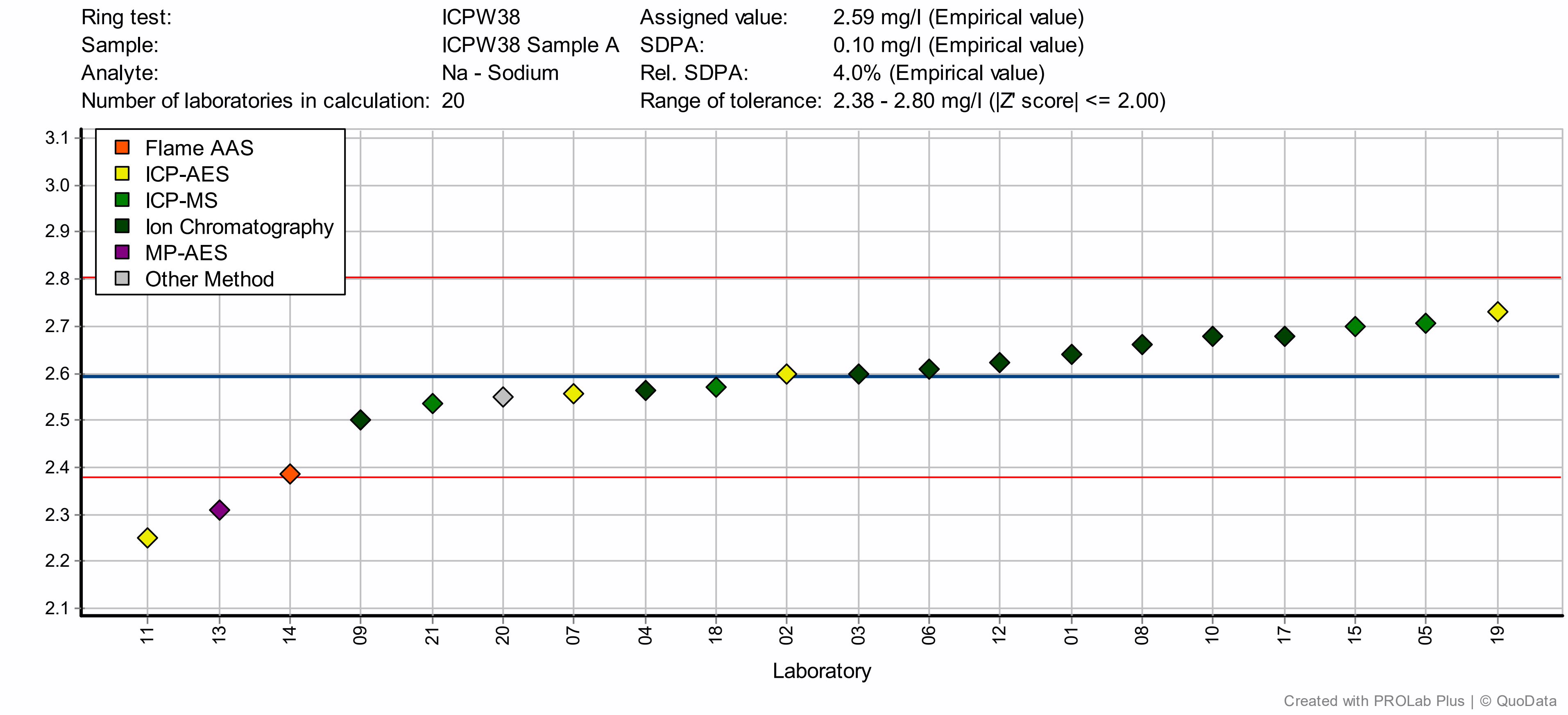

Figure 56. Reported values of Sodium in sample A, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

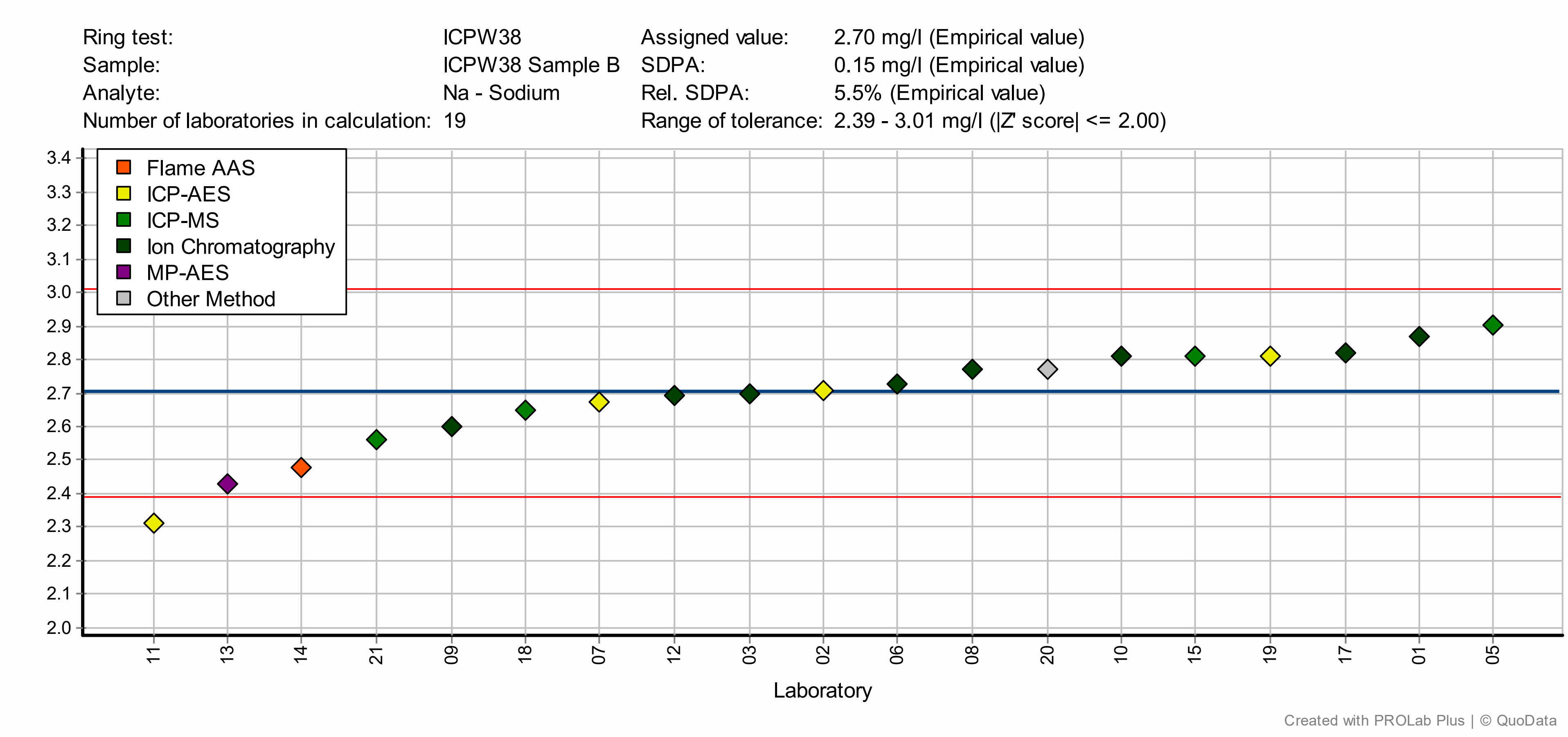

Figure 57. Reported values of Sodium in sample B, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

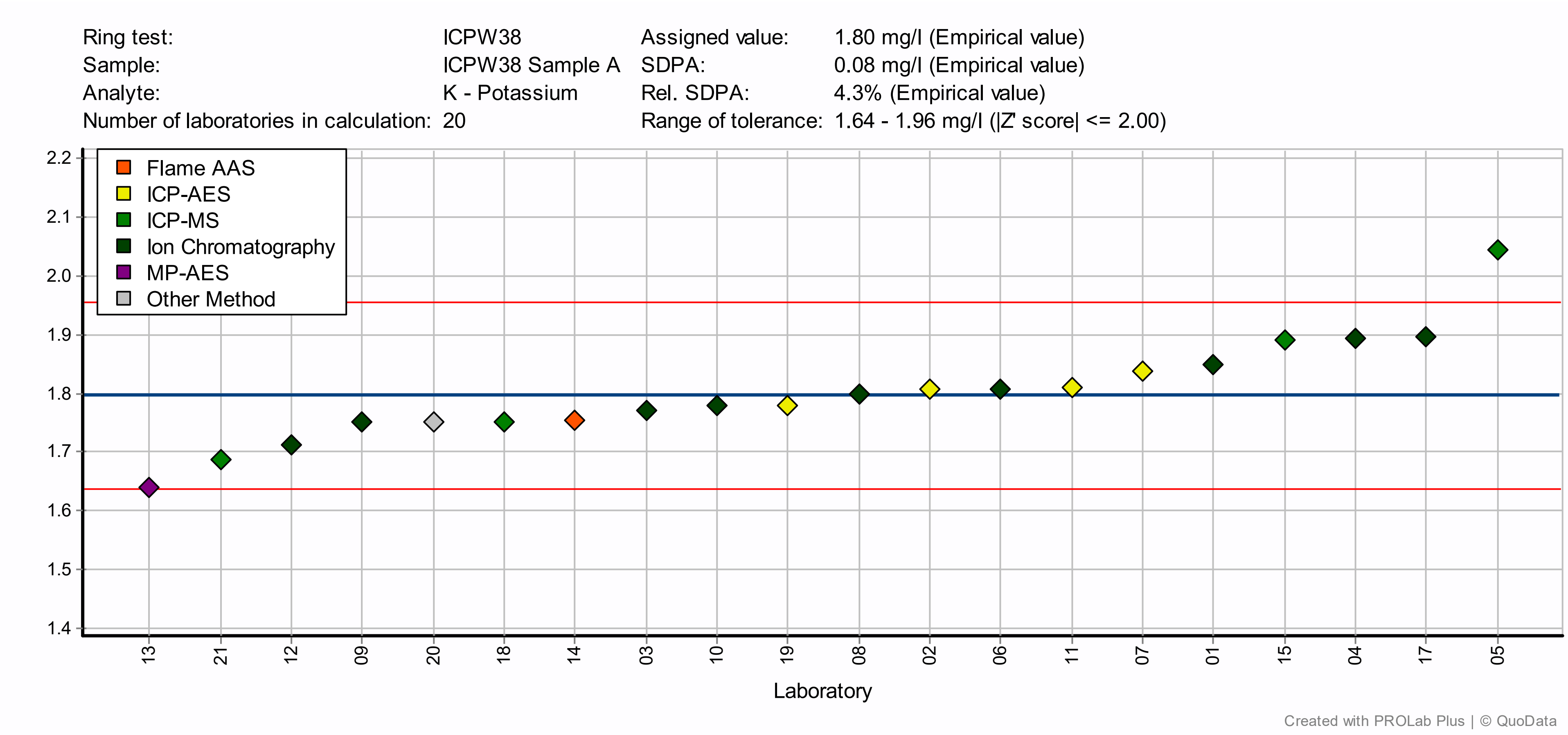

Figure 58. Reported values of Potassium in sample A, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

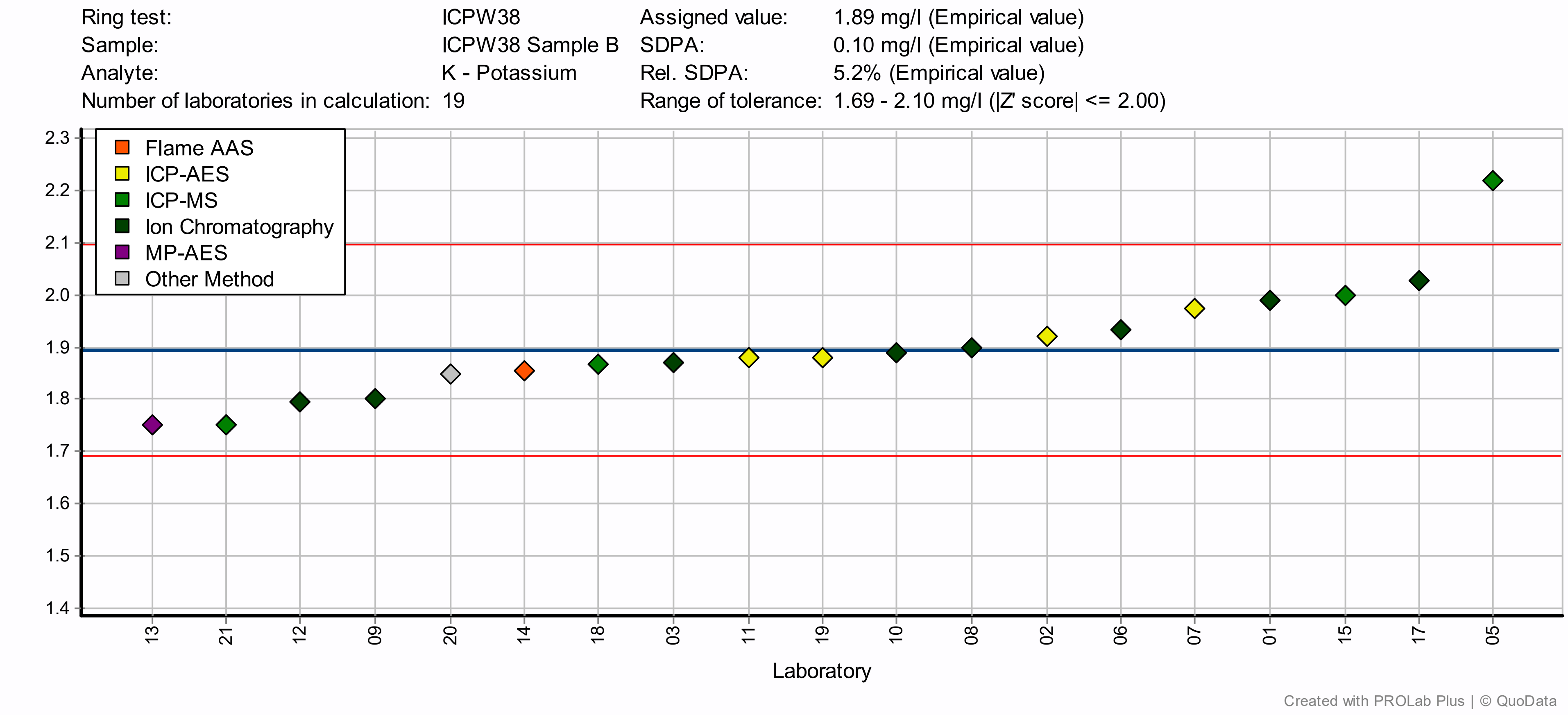

Figure 59. Reported values of Potassium in sample B, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

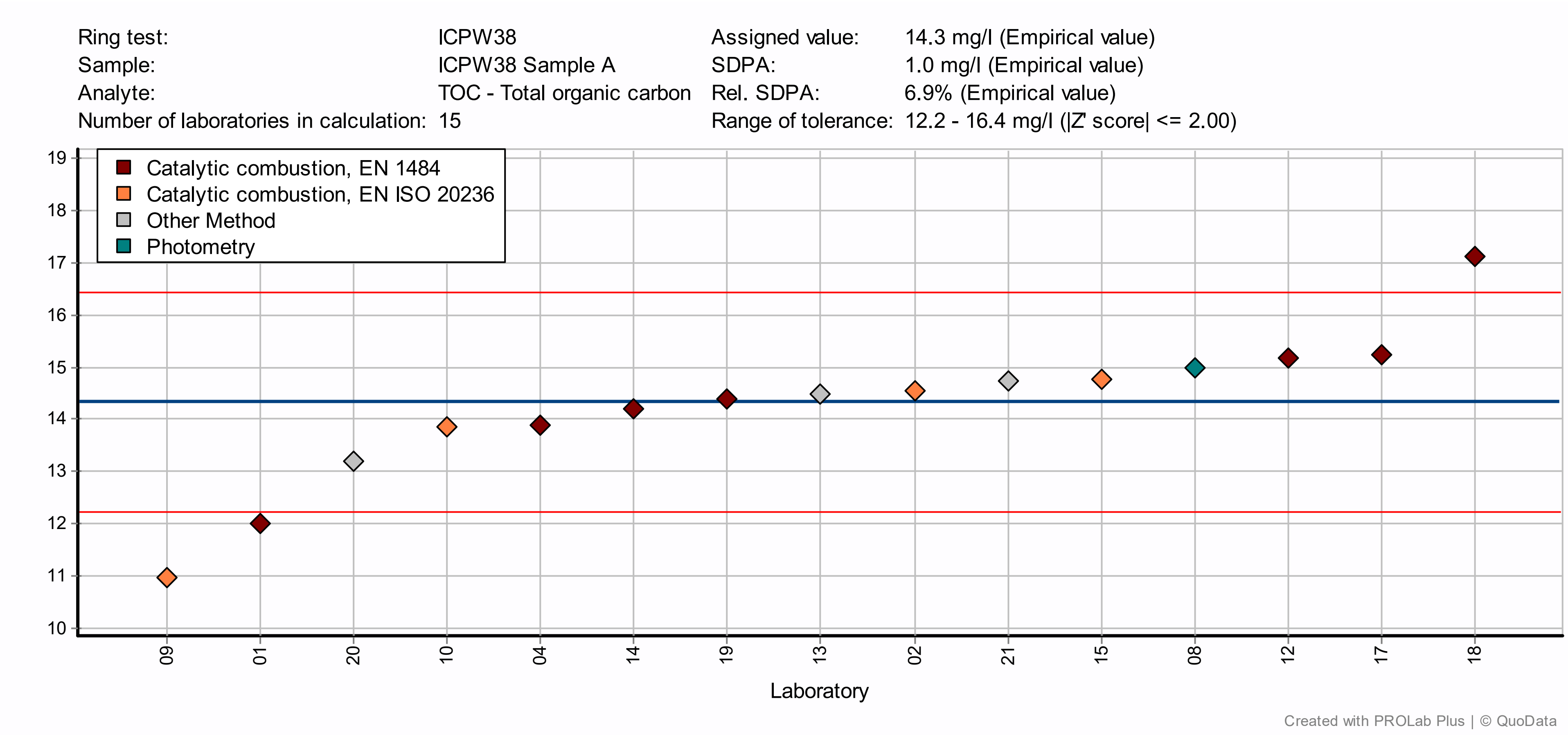

Figure 60. Reported values of TOC in sample A, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

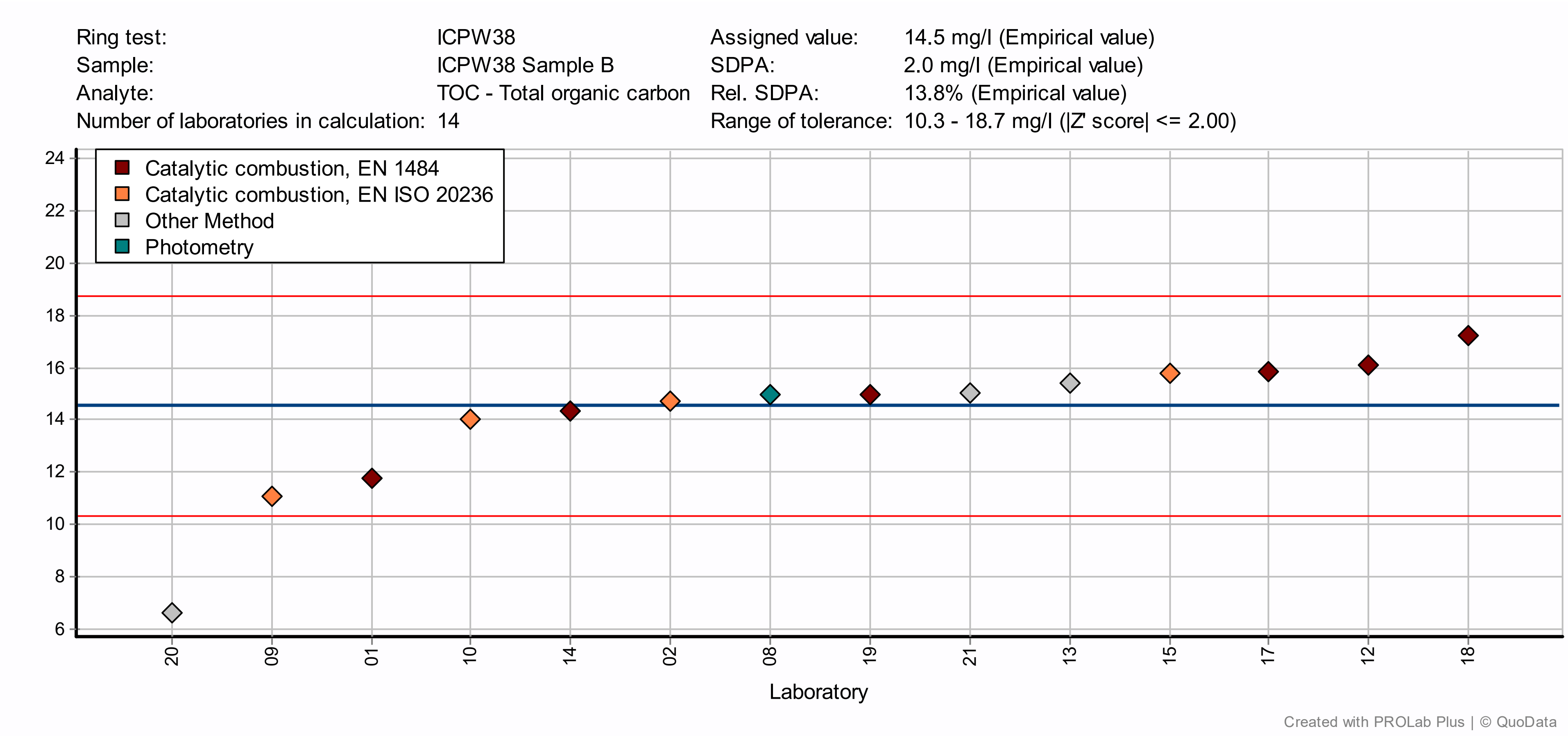

Figure 61. Reported values of TOC in sample B, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

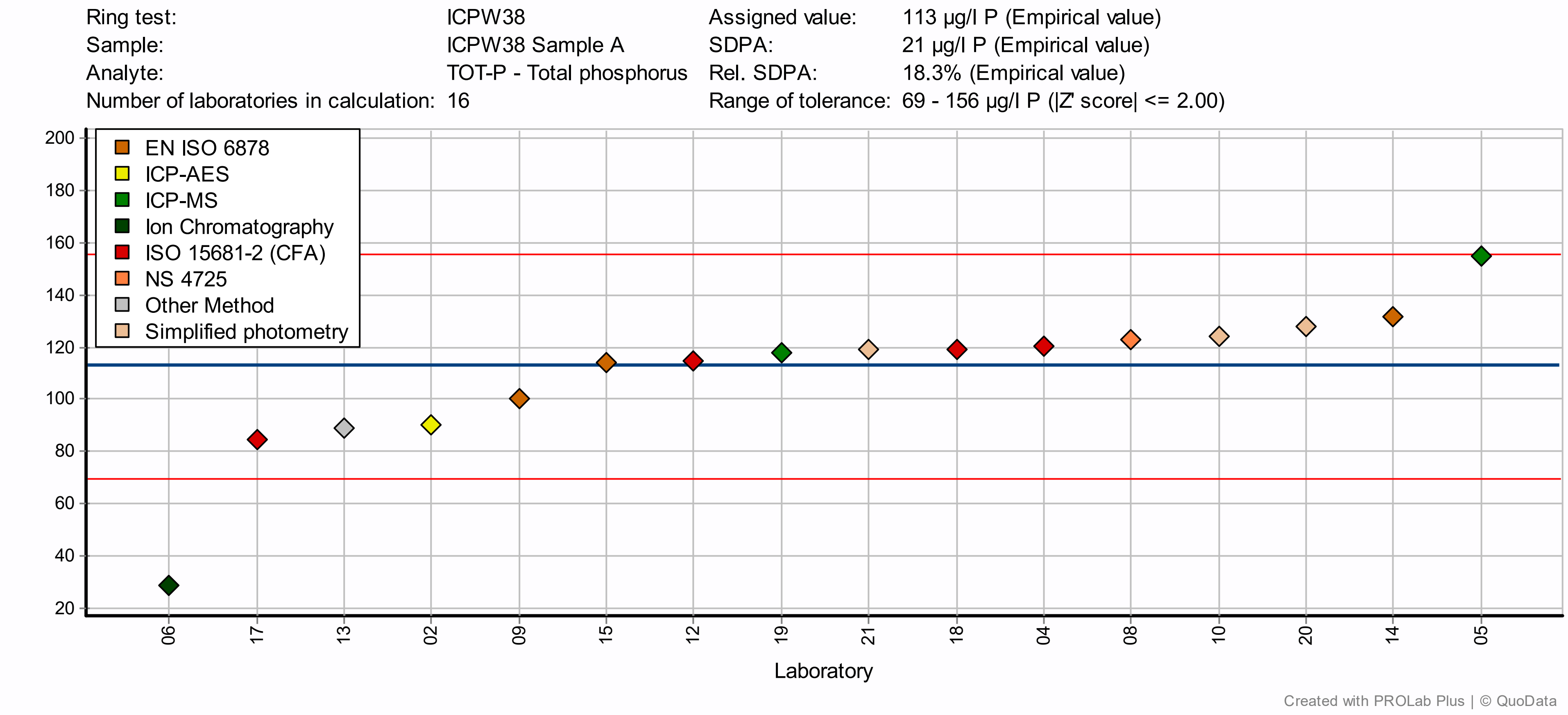

Figure 62. Reported values of TOT-P in sample A, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

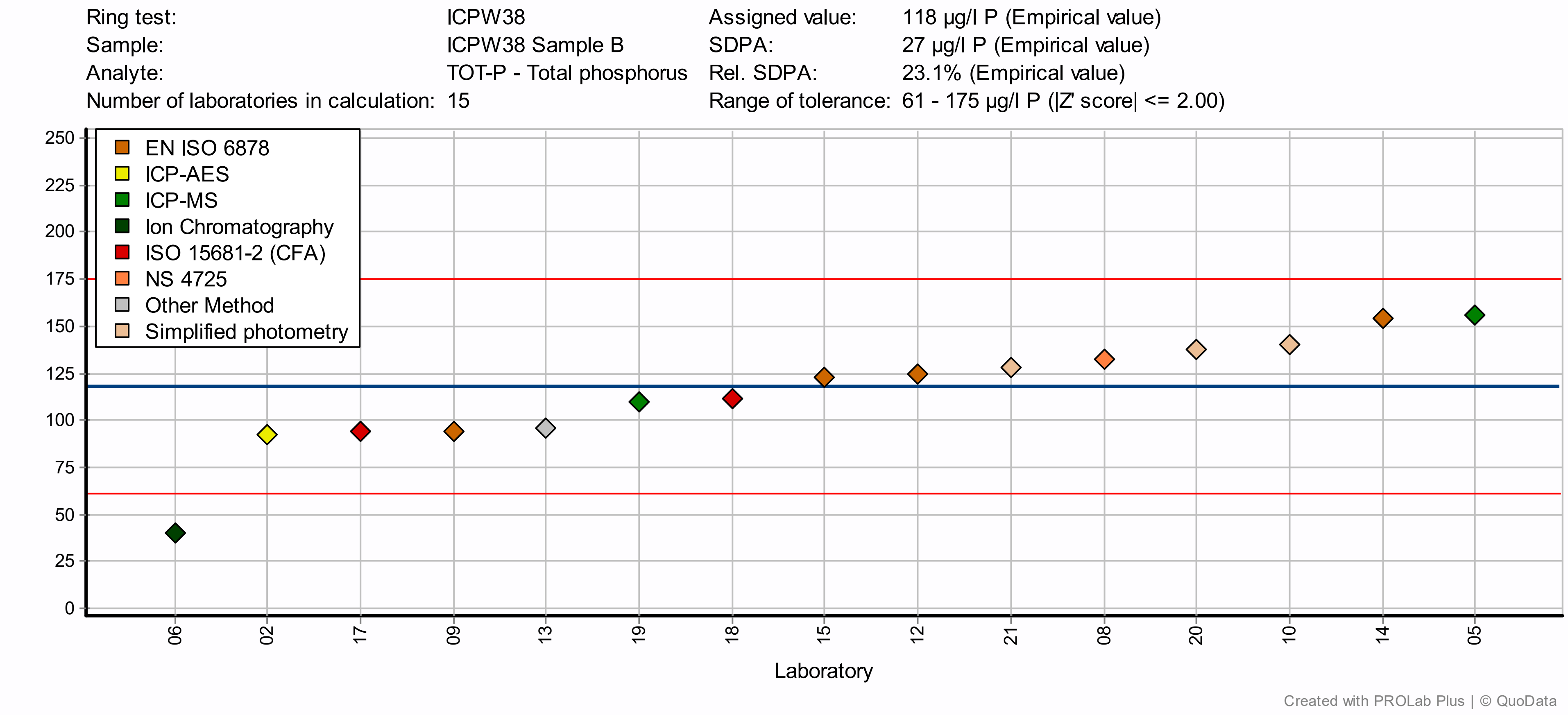

Figure 63. Reported values of TOT-P in sample B, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

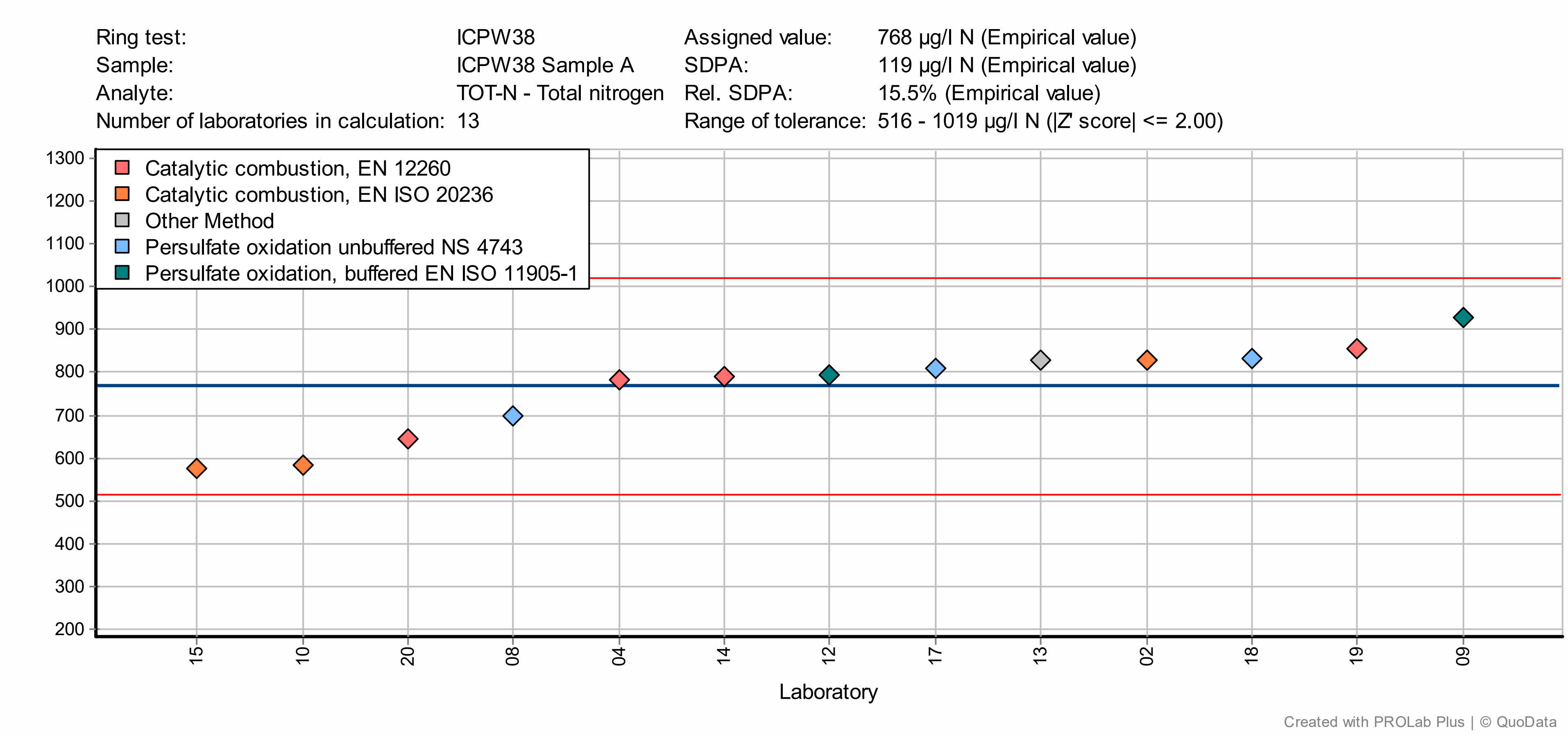

Figure 64. Reported values of TOT-N in sample A, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

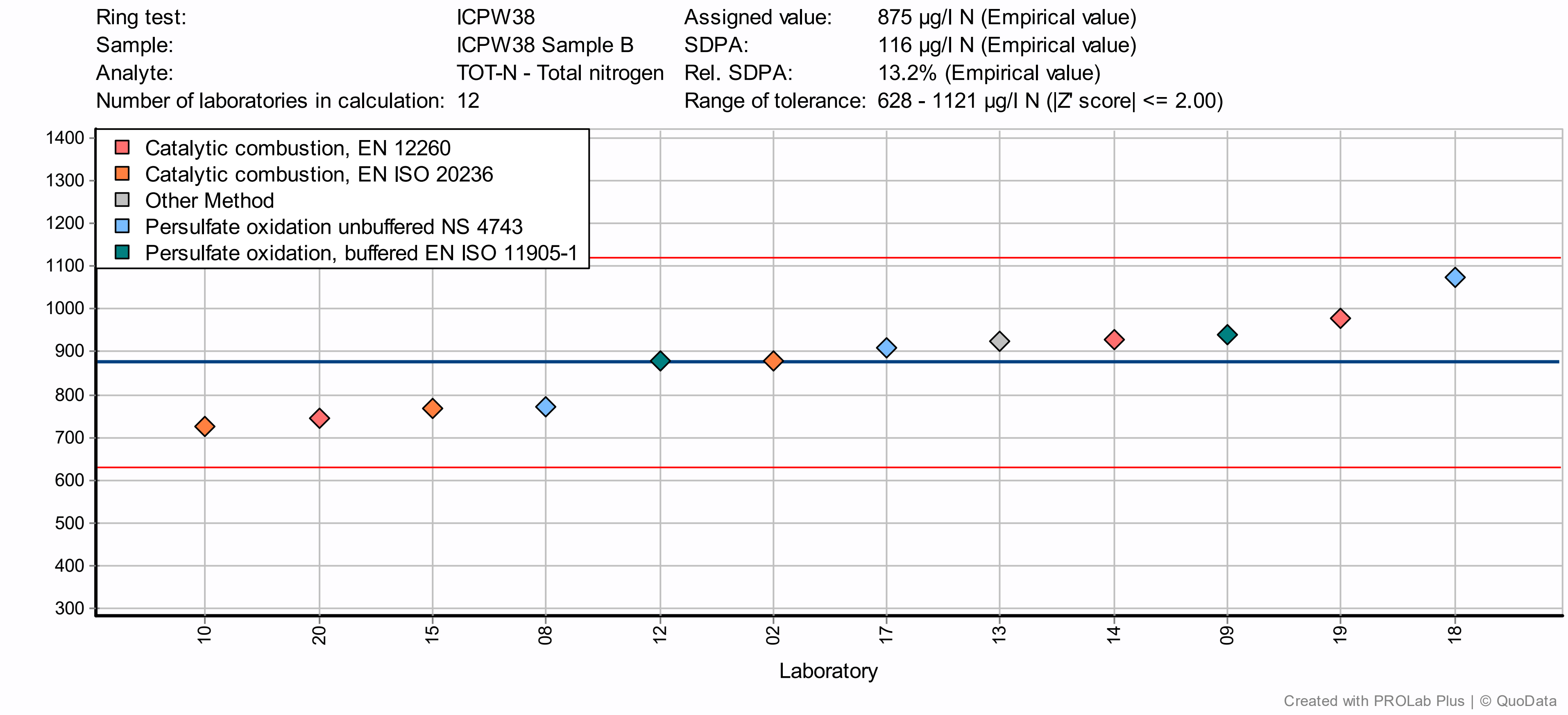

Figure 65. Reported values of TOT-N in sample B, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

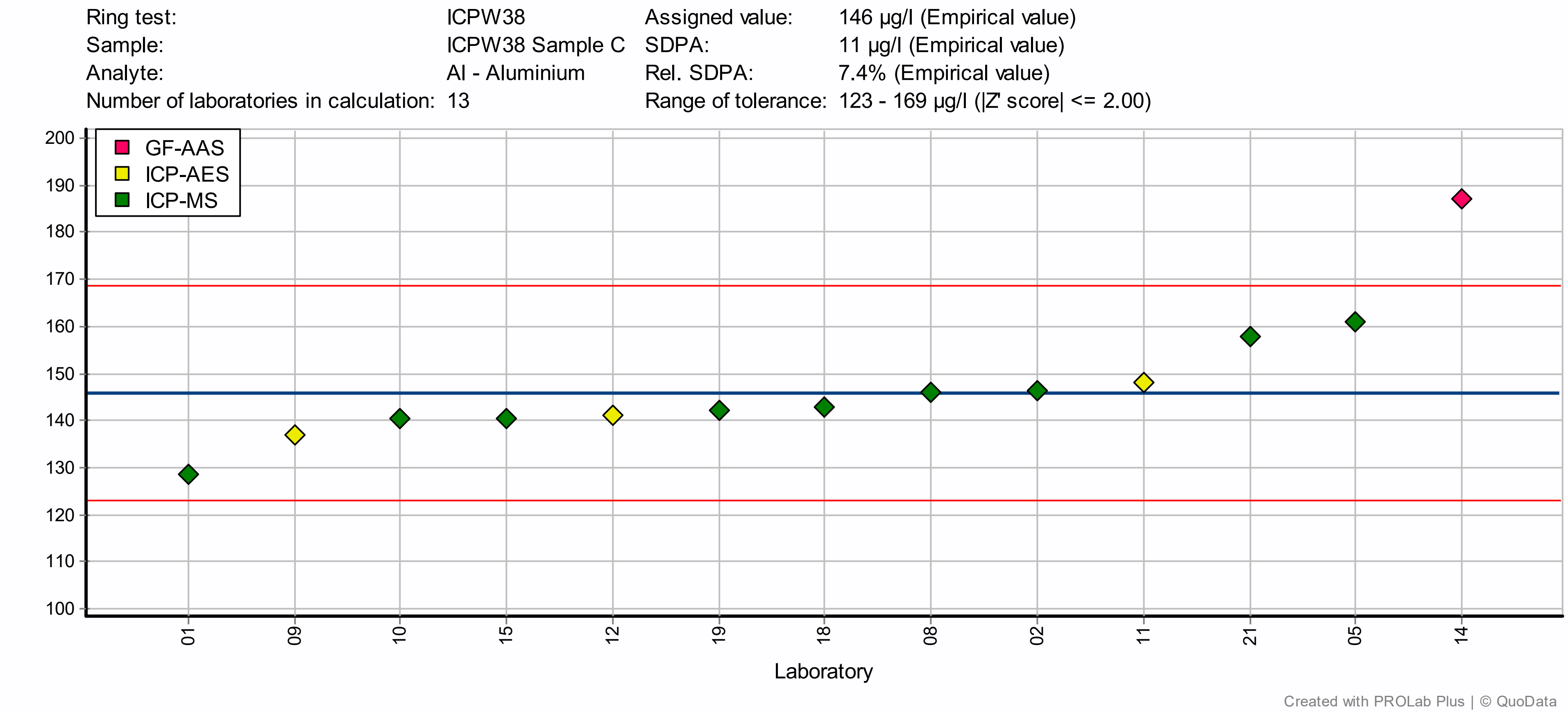

Figure 66. Reported values of Al in sample C, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

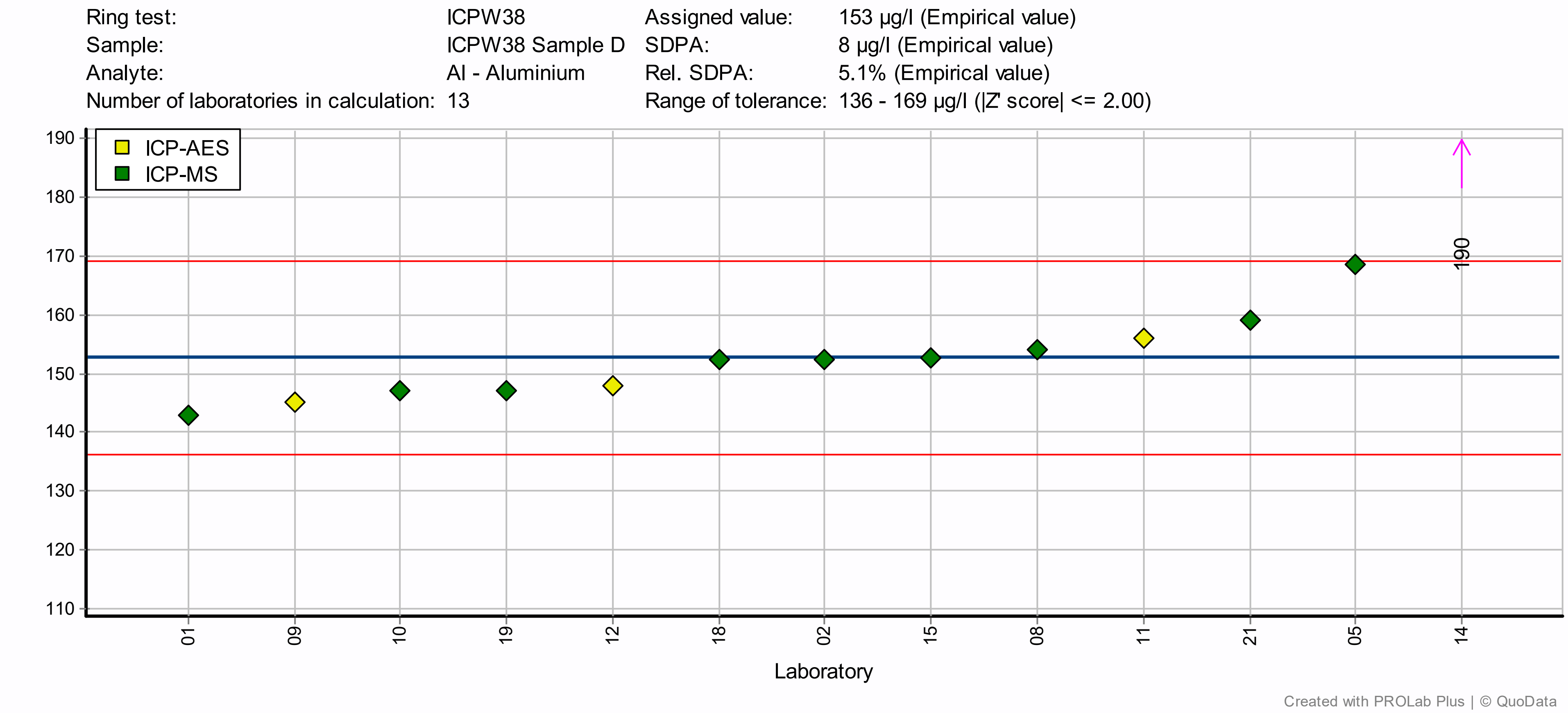

Figure 67. Reported values of Al in sample D, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

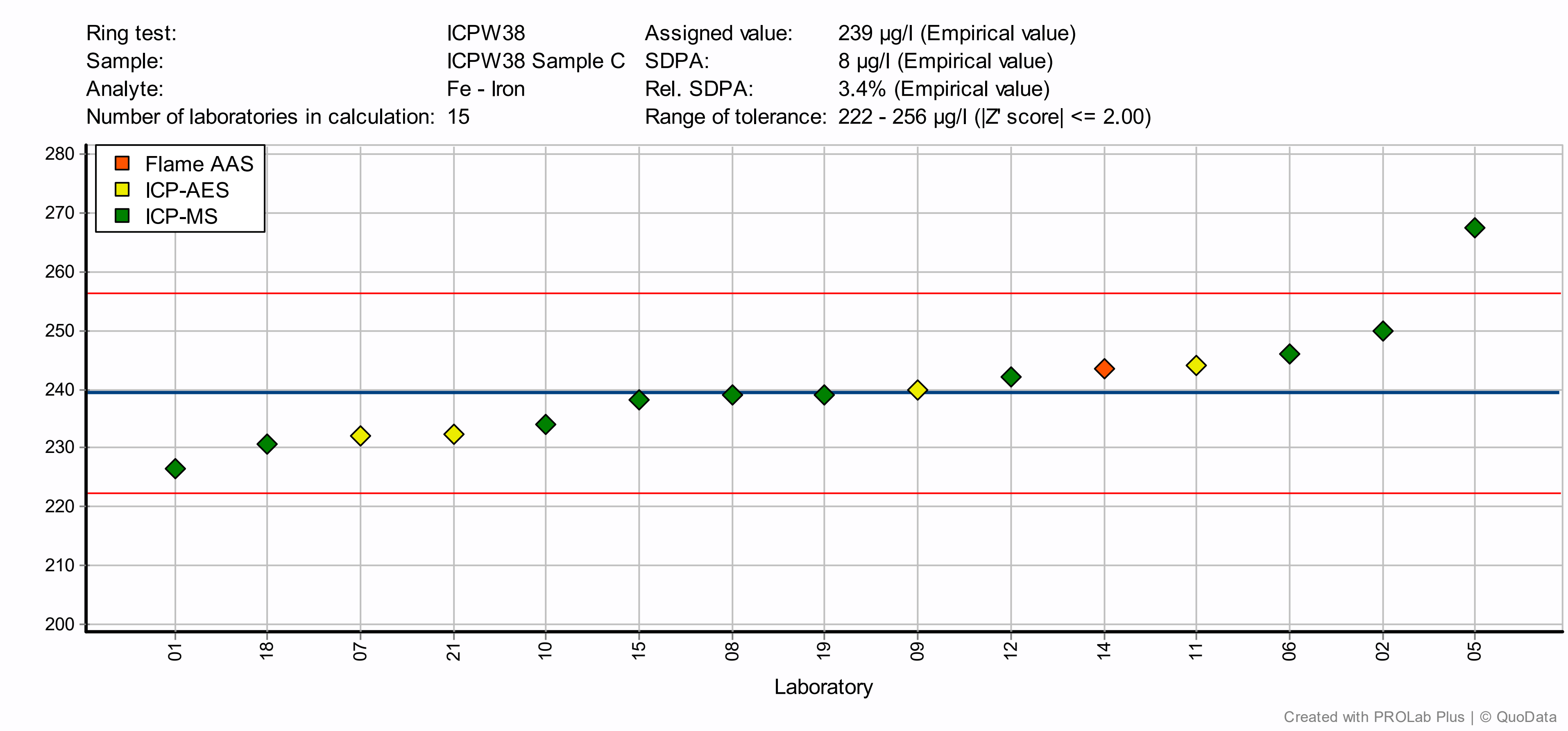

Figure 68. Reported values of Fe in sample C, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2.

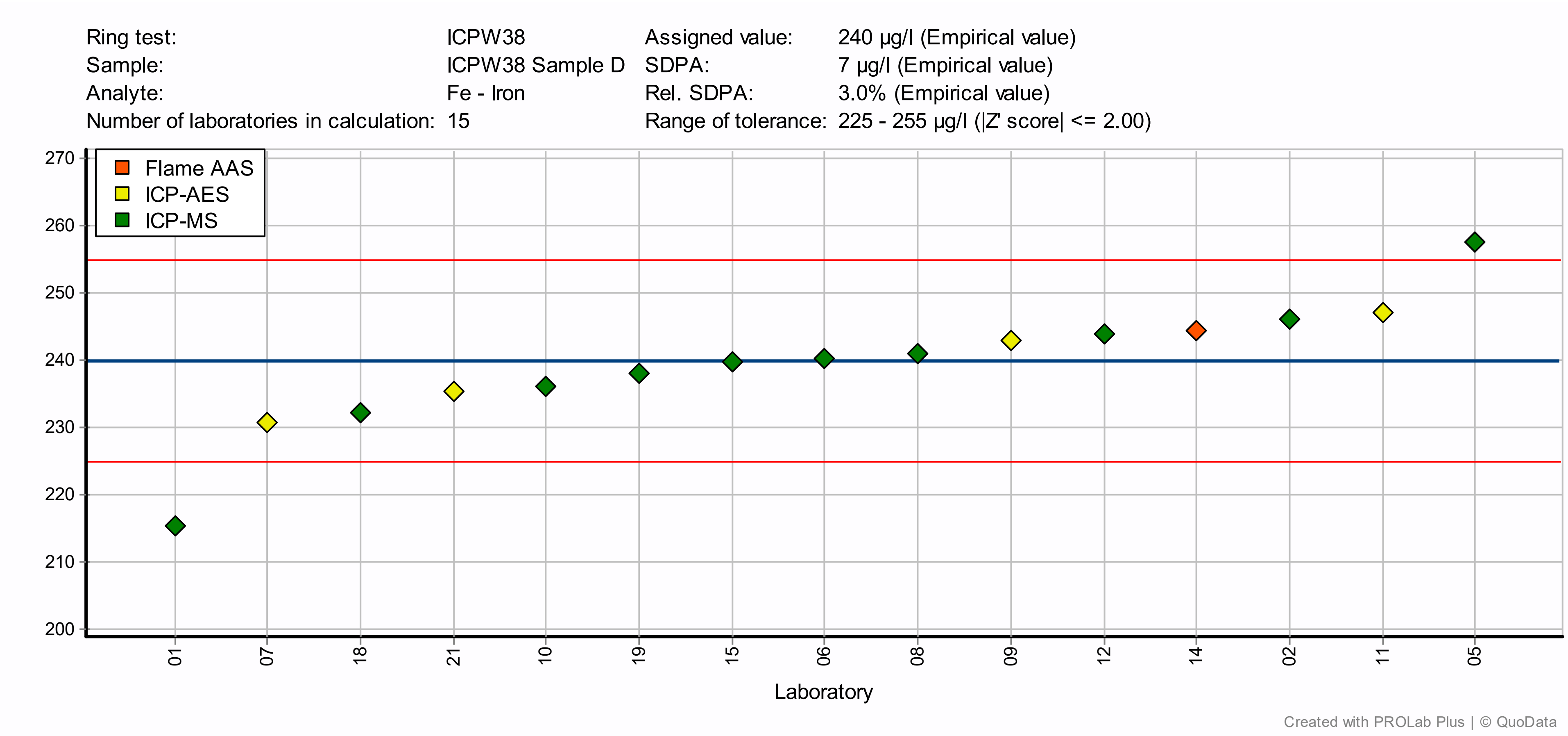

Figure 69. Reported values of Fe in sample D, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2

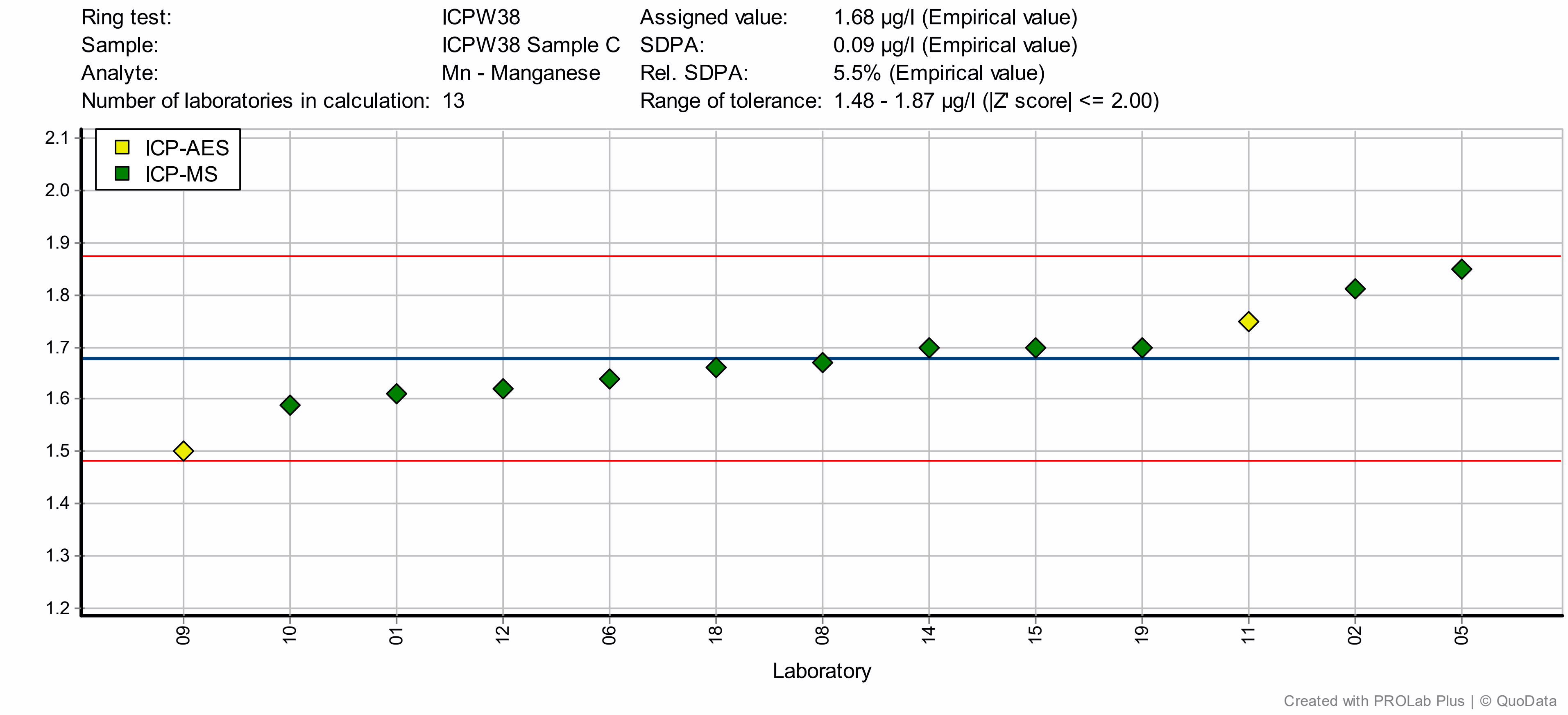

Figure 70. Reported values of Mn in sample C, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2. Results below LOQ are not visualized in this figure.

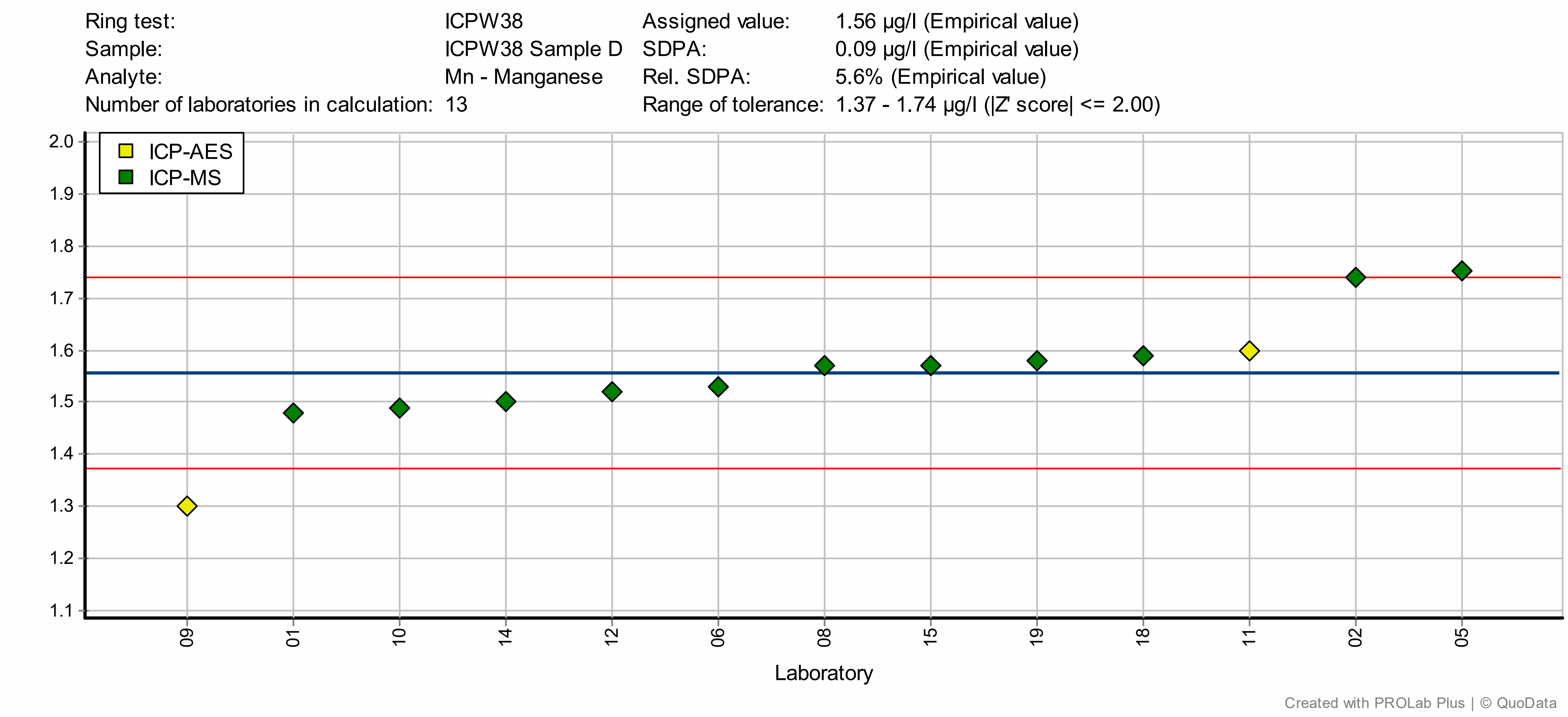

Figure 71. Reported values of Mn in sample D, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2. Results below LOQ are not visualized in this figure.

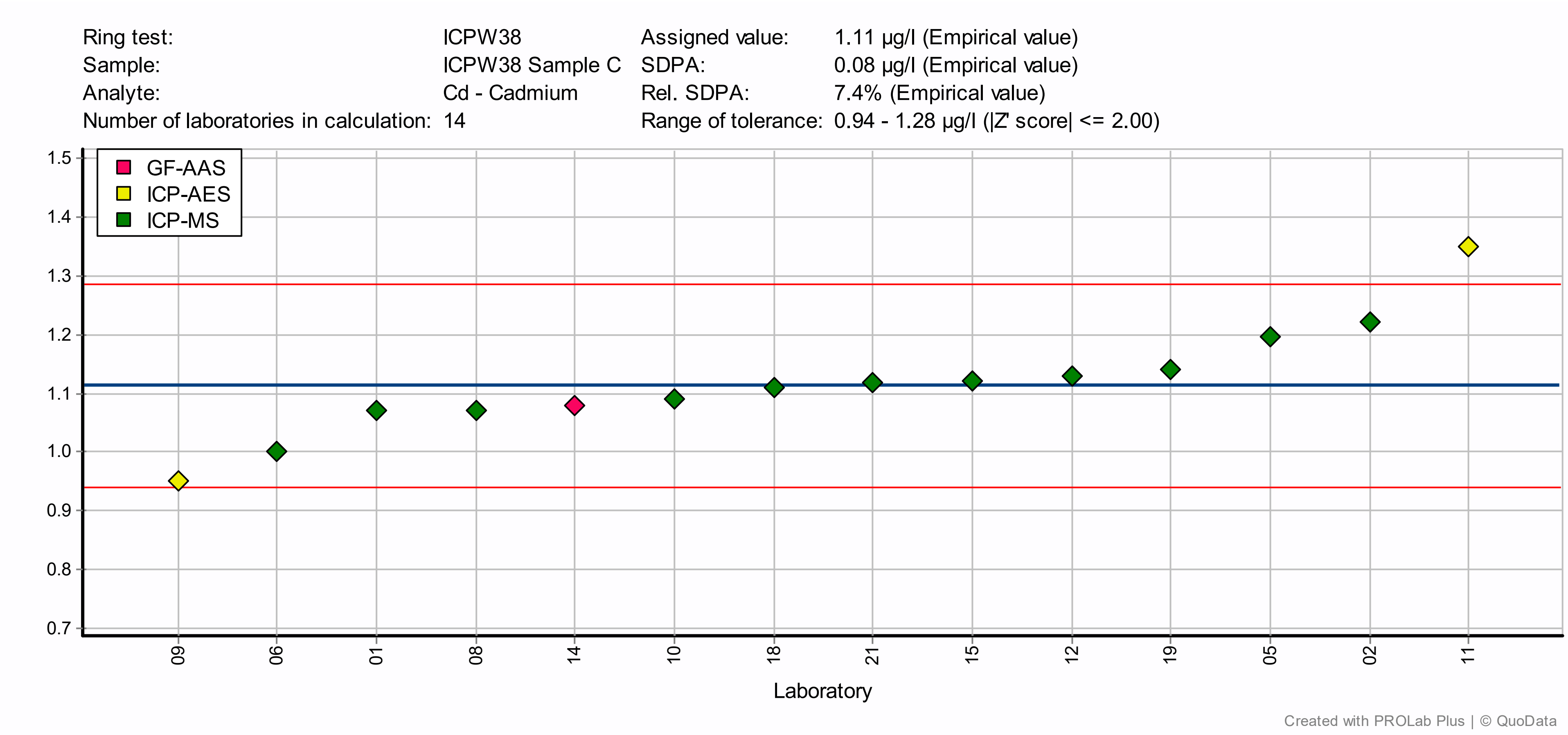

Figure 72. Reported values of Cd in sample C, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2

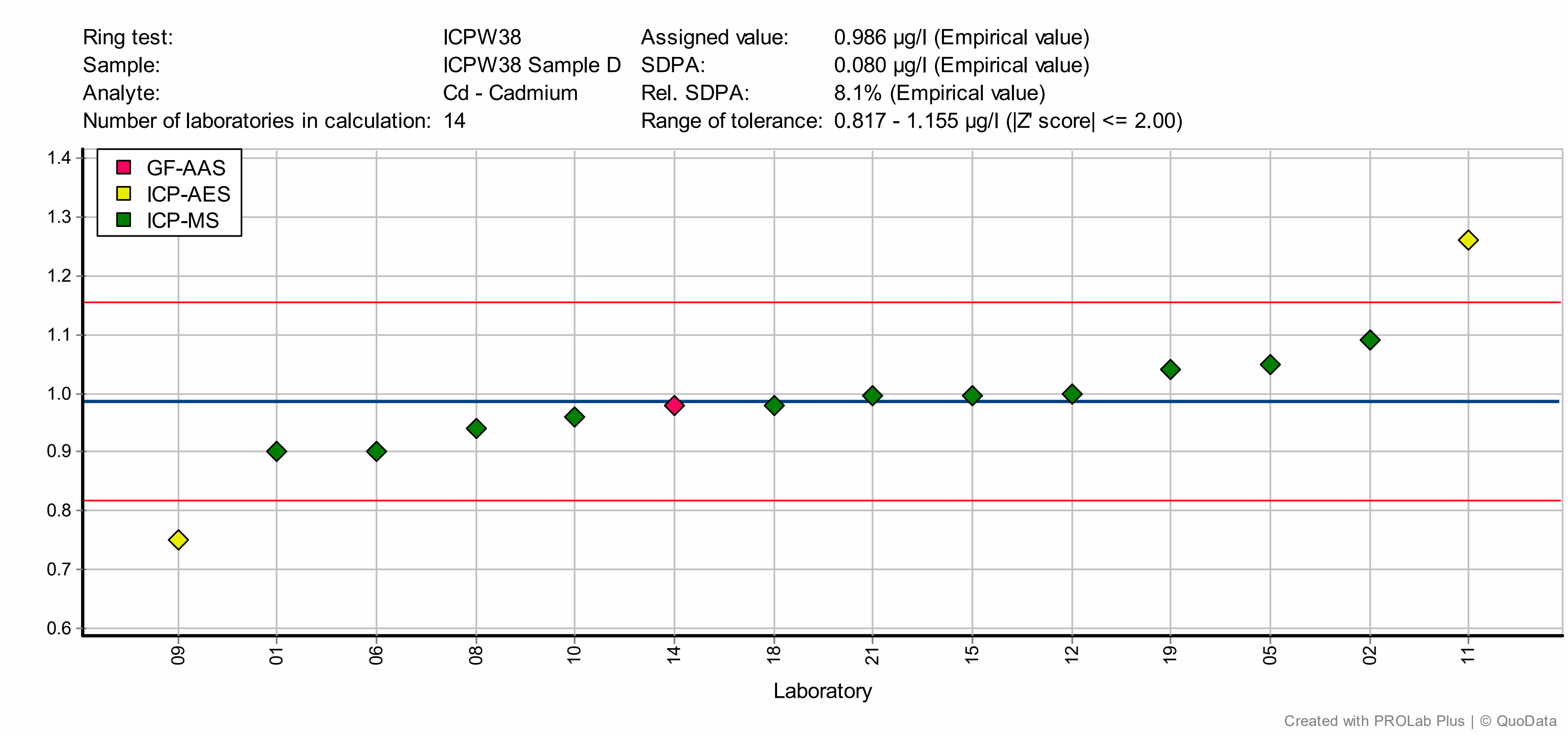

Figure 73. Reported values of Cd in sample D, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2

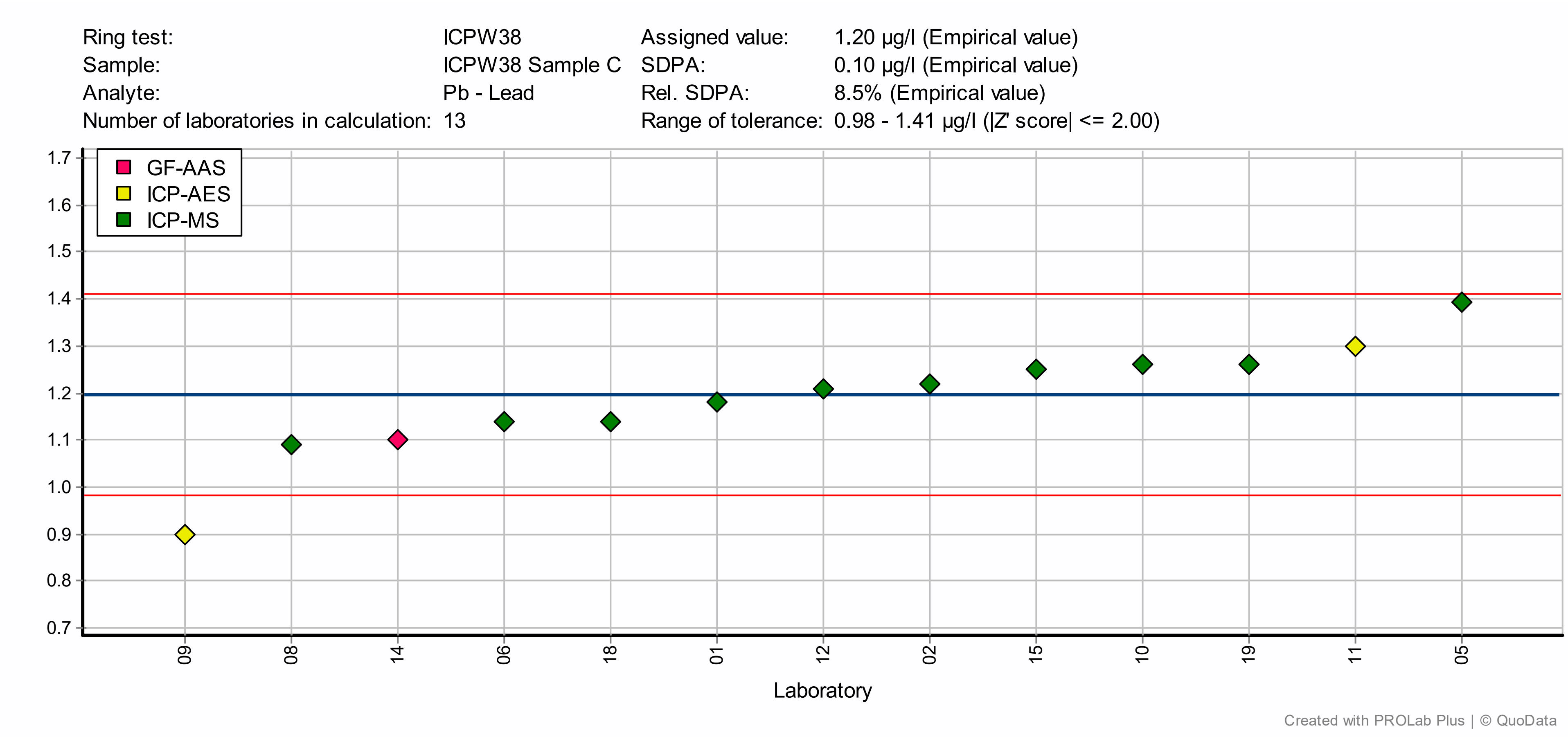

Figure 74. Reported values of Pb in sample C, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2. Results below LOQ are not visualized in this figure.

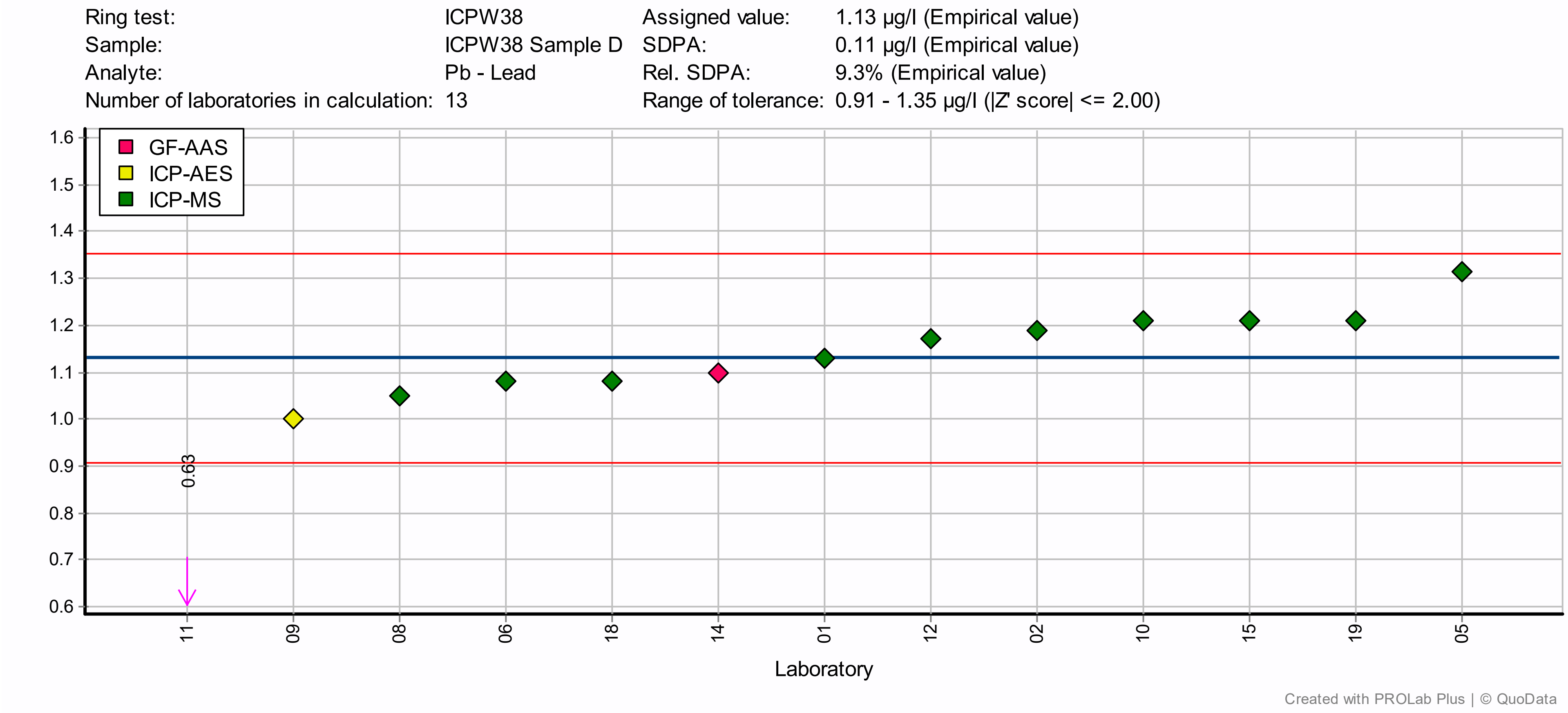

Figure 75. Reported values of Cd in sample D, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2. Results below LOQ are not visualized in this figure.

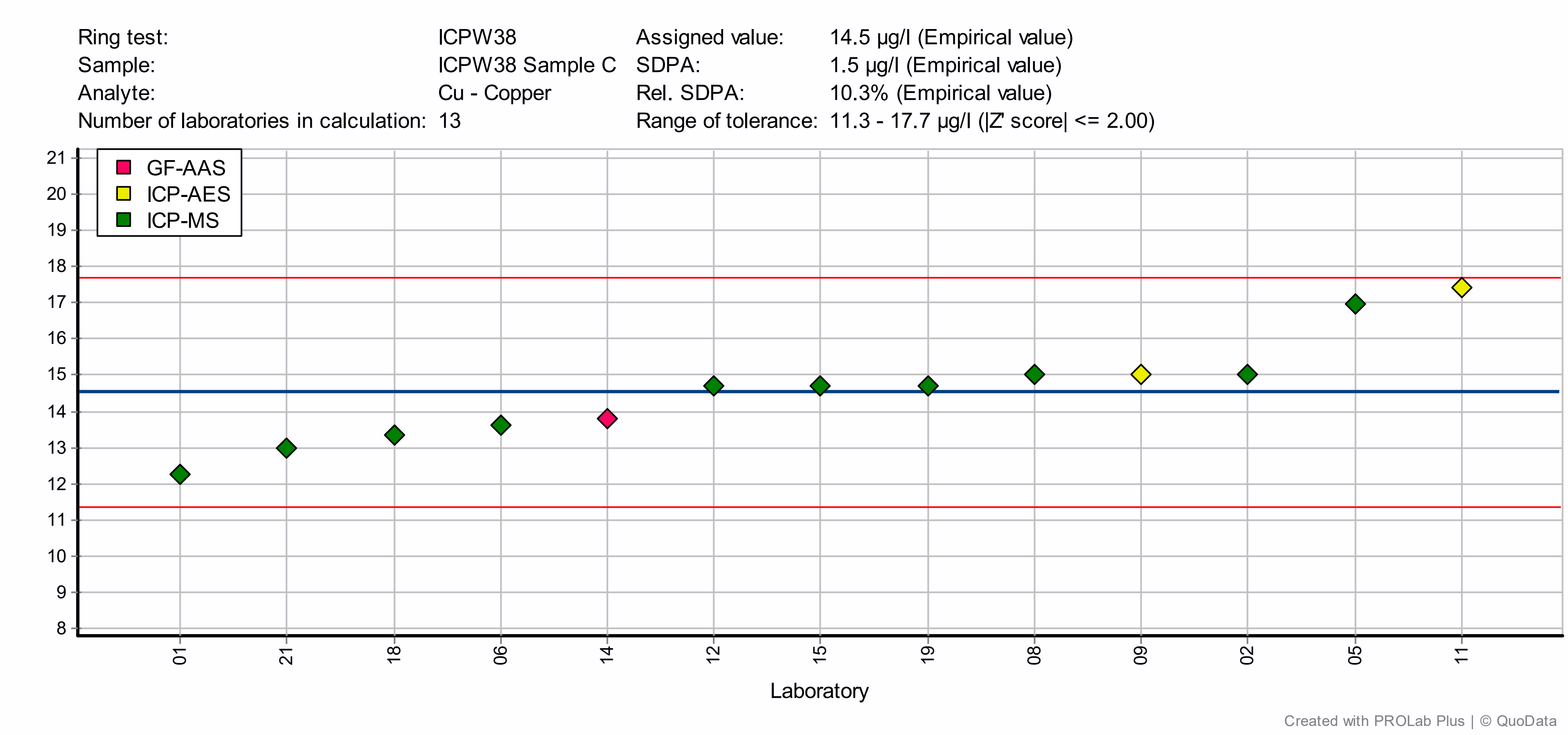

Figure 76. Reported values of Cu in sample C, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2

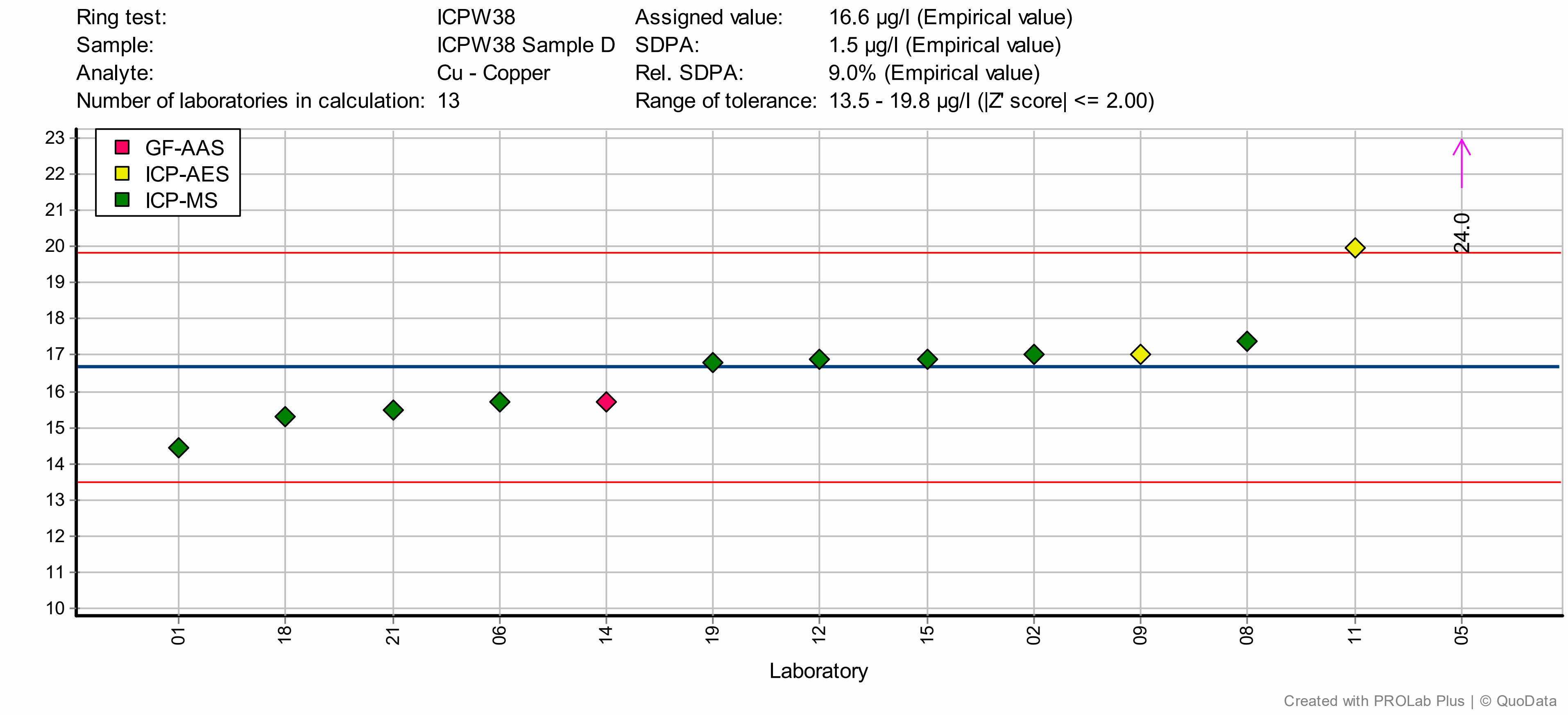

Figure 77. Reported values of Cu in sample D, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2

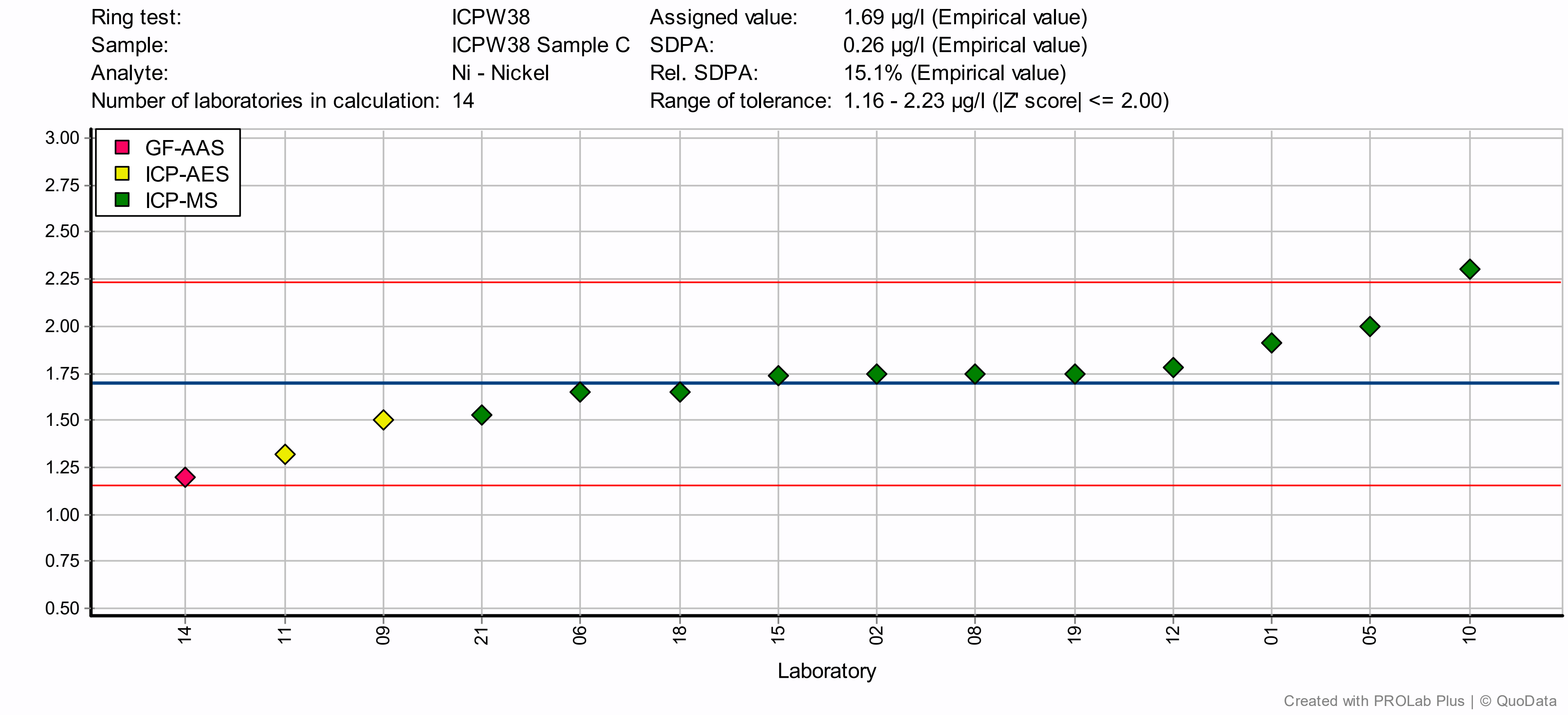

Figure 78. Reported values of Ni in sample C, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2

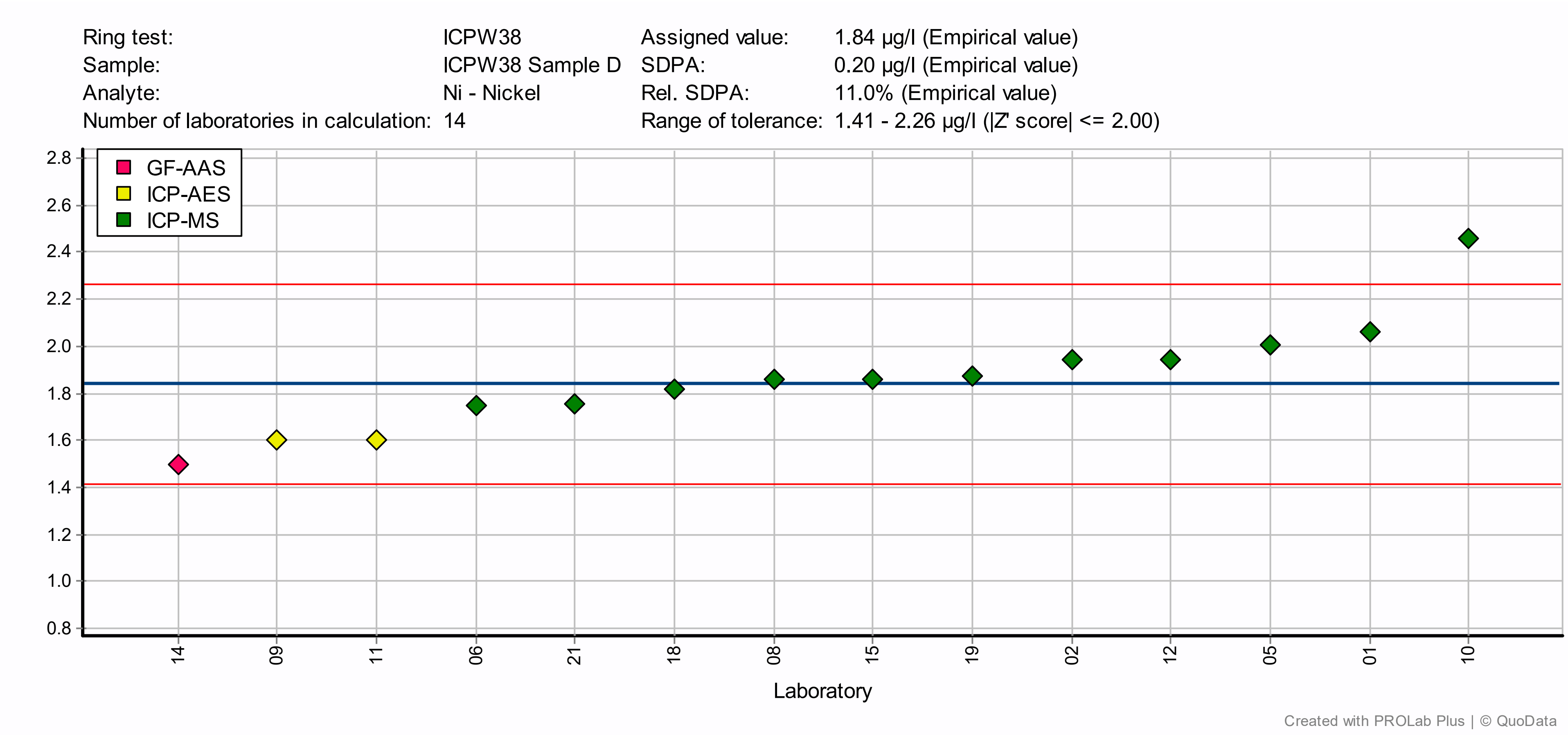

Figure 79. Reported values of Ni in sample D, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2

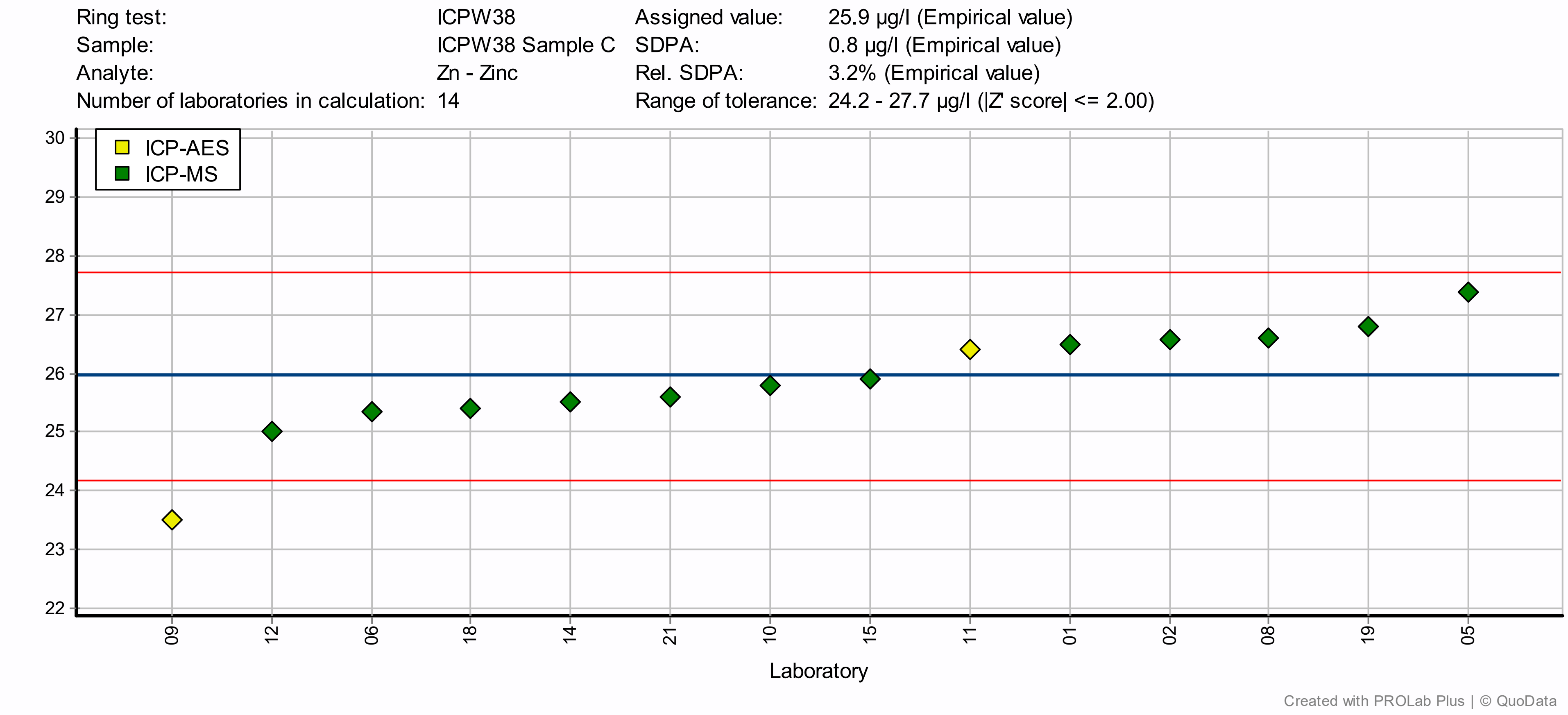

Figure 80. Reported values of Zn in sample C, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2

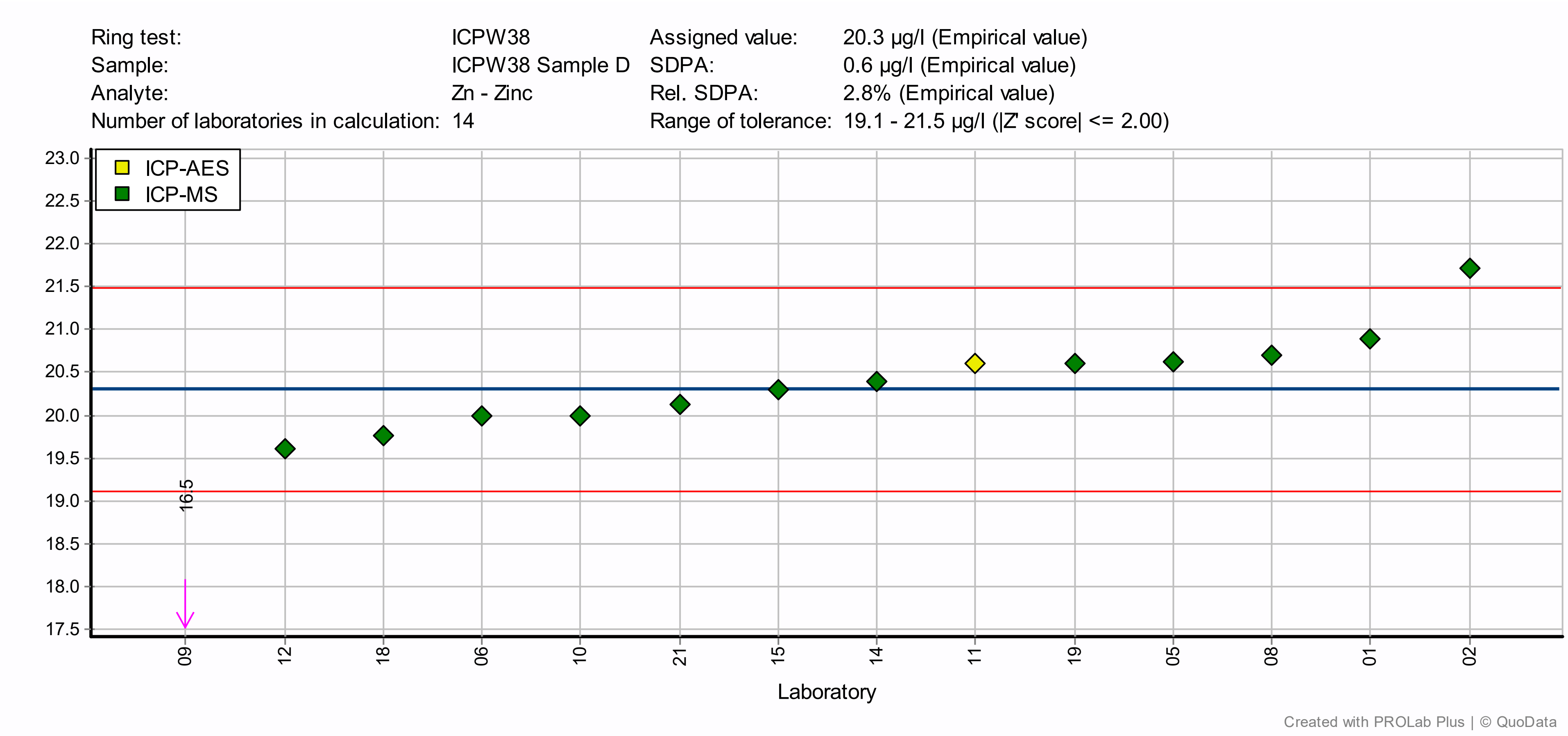

Figure 81. Reported values of Zn in sample D, sorted by concentration levels, and colour coded by analysis method. Limit of tolerance lines indicates Z' score of ±2

D.3. Statistics per analysis parameter

Table 6. Table of laboratory results and statistical parameters for pH.

pH	ICPW38 Sample A			ICPW38 Sample B			
Laboratory	PH-units	Z' score	D%	PH-units	Z' score	D%	Analytical method
2	6.64	1.64	9.5 %	6.74	1.92	10.6 %	Electrometric, non-stirring
3	5.99	-0.20	-1.2 %	6.02	-0.22	-1.2 %	EN ISO 10523
4	5.76	-0.85	-5.0 %	not tested			Electrometric, stirred
6	5.80	-0.74	-4.3 %	5.87	-0.67	-3.7 %	Electrometric, stirred
7	6.01	-0.15	-0.9 %	6.09	-0.01	-0.1 %	Electrometric, stirred
8	5.96	-0.29	-1.7 %	5.97	-0.37	-2.0 %	EN ISO 10523
9	5.77	-0.83	-4.8 %	5.82	-0.82	-4.5 %	Electrometric, non-stirring
10	5.98	-0.23	-1.3 %	6.01	-0.25	-1.4 %	Electrometric, equilibration
11	6.26	0.56	3.3 %	6.09	-0.01	-0.1 %	Electrometric, stirred
12	5.98	-0.23	-1.3 %	6.00	-0.28	-1.6 %	EN ISO 10523
13	5.72	-0.97	-5.6 %	5.76	-0.99	-5.5 %	Other Method
14	6.55	1.38	8.1 %	6.61	1.53	8.5 %	EN ISO 10523
15	5.77	-0.83	-4.8 %	5.77	-0.97	-5.3 %	EN ISO 10523
16	6.91	2.40	14.0 %	6.96	2.57	14.2 %	EN ISO 10523
17	6.20	0.39	2.3 %	6.16	0.19	1.1 %	Electrometric, stirred
18	5.82	-0.68	-4.0 %	5.87	-0.67	-3.7 %	Electrometric, stirred
19	5.95	-0.32	-1.8 %	6.00	-0.28	-1.6 %	EN ISO 10523
20	5.96	-0.29	-1.7 %	5.98	-0.34	-1.9 %	Electrometric, stirred
21	6.55	1.38	8.1 %	6.56	1.38	7.6 %	Electrometric, stirred
Assigned value	6.06			6.09			
SDPA	0.34			0.32			
Rel. SDPA	5.6 %			5.3 %			
No. of laboratories that submitted results	19			18			
Percentage of satisfactory scores	94.7 %			94.4 %			
Percentage of questionable scores	5.3 %			5.6 %			
Percentage of unsatisfactory scores	0.0 %			0.0 %			
Mean	6.06			6.09			
Median	5.98			6.00			

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

Conductivity	ICPW38 Sample A			ICPW38 Sample B			
Laboratory	mS/m	Z' score	D%	mS/m	Z' score	D%	Analytical method
2	3.73	0.06	0.3 %	3.87	0.04	0.2 %	Electrometry, other
3	3.81	0.49	2.4 %	3.99	0.68	3.3 %	Electrometry, other
4	3.84	0.65	3.2 %	not tested			Electrometry, other
6	3.84	0.67	3.3 %	3.99	0.68	3.3 %	Electrometry, other
7	3.70	-0.10	-0.5 %	3.86	0.00	0.0 %	Electrometry, other
8	3.50	-1.19	-5.9 %	3.65	-1.14	-5.5 %	ISO 7888
9	3.95	1.25	6.2 %	4.08	1.16	5.6 %	Electrometry, other
10	3.92	1.09	5.4 %	3.99	0.68	3.3 %	Electrometry, other
12	3.74	0.11	0.5 %	3.92	0.31	1.5 %	ISO 7888
13	3.35	-2.00	-9.9 %	3.55	-1.67	-8.1 %	Other Method
14	3.87	0.82	4.0 %	4.06	1.06	5.1 %	ISO 7888
15	3.72	0.00	0.0 %	3.82	-0.23	-1.1 %	ISO 7888
16	3.21	-2.78	-13.8 %	3.13	-3.89	-18.9 %	Electrometry, other
17	3.80	0.44	2.2 %	3.95	0.47	2.3 %	Electrometry, other
18	3.63	-0.49	-2.4 %	3.75	-0.60	-2.9 %	Electrometry, other
19	3.69	-0.16	-0.8 %	3.85	-0.07	-0.3 %	ISO 7888
20	3.80	0.44	2.2 %	4.00	0.74	3.6 %	Electrometry, other
21	3.50	-1.19	-5.9 %	3.69	-0.92	-4.5 %	Electrometry, other
–	–	–	–	–	–	–	–
Assigned value	3.72			3.86			
SDPA	0.18			0.18			
Rel. SDPA	4.8 %			4.6 %			
No. of laboratories that submitted results	18			17			
Percentage of satisfactory scores	88.9 %			94.1 %			
Percentage of questionable scores	11.1 %			0.0 %			
Percentage of unsatisfactory scores	0.0 %			5.9 %			
Mean	3.72			3.86			
Median	3.74			3.87			

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

Alkalinity	ICPW38 Sample A			ICPW38 Sample B			
Laboratory	mmol/l	Z' score	D%	mmol/l	Z' score	D%	Analytical method
2	0.152	0.52	14.4 %	0.159	0.50	12.1 %	pH 4,5+4,2
4	0.085	-1.31	-36.0 %	not tested			Other Method
7	0.121	-0.33	-9.0 %	0.126	-0.47	-11.2 %	pH 4,5+4,2
8	0.172	1.07	29.4 %	0.174	0.95	22.6 %	pH 4,5 endpoint
9	0.160	0.74	20.4 %	0.165	0.68	16.3 %	Other Method
10	0.131	-0.05	-1.4 %	0.146	0.12	2.9 %	Colorimetry
12	0.142	0.25	6.9 %	0.145	0.09	2.2 %	pH 4,5 endpoint
13	0.097	-0.98	-27.0 %	0.098	-1.29	-30.9 %	pH 4,5 endpoint
14	0.153	0.55	15.0 %	0.155	0.38	9.0 %	pH 4,5 endpoint
15	0.118	-0.41	-11.2 %	0.122	-0.59	-14.0 %	pH other endpoint
17	0.086	-1.29	-35.3 %	0.088	-1.59	-38.0 %	pH 4,5 endpoint
18	0.122	-0.30	-8.2 %	0.124	-0.53	-12.6 %	pH 4,5 endpoint
20	8.29	224	6137.9 %	8.10	234	5609.0 %	pH 4,5 endpoint
21	0.137	0.11	3.1 %	0.147	0.15	3.6 %	pH 4,5 endpoint
–	–	–	–	–	–	–	–
Assigned value	0.133			0.142			
SDPA	0.035			0.032			
Rel. SDPA	26.0 %			22.6 %			
No. of laboratories that submitted results	14			13			
Percentage of satisfactory scores	92.9 %			92.3 %			
Percentage of questionable scores	0.0 %			0.0 %			
Percentage of unsatisfactory scores	7.1 %			7.7 %			
Mean	0.133			0.142			
Median	0.134			0.146			

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

Nitrate	ICPW38 Sample A			ICPW38 Sample B			Analytical method
Laboratory	µg/l N	Z' score	D%	µg/l N	Z' score	D%	
2	18.9	0.74	62.8 %	18.8	0.58	54.2 %	Ion Chromatography
3	22	1.06	89.8 %	24	1.04	96.7 %	Ion Chromatography
4	2.9	-0.88	-74.7 %	not tested			Ion Chromatography
6	22.5	1.11	94.0 %	22.5	0.91	84.6 %	Ion Chromatography
7	16.1	0.46	38.9 %	20.3	0.71	66.3 %	Ion Chromatography
8	2	-0.98	-82.7 %	2	-0.9	-83.6 %	Ion Chromatography
9	10	-0.16	-13.7 %	not tested			Ion Chromatography
10	not tested			not tested			Ion Chromatography
12	< 20.0			< 20.0			Ion Chromatography
13	not tested			1	-0.99	-91.8 %	Automatic Cd-red. spectrophotometry
15	2.1	-0.97	-81.9 %	2.5	-0.85	-79.5 %	Automatic Cd-red. spectrophotometry
17	18	0.65	55.3 %	18	0.51	47.5 %	Ion Chromatography
18	8	-0.37	-31.0 %	7.7	-0.4	-36.9 %	Ion Chromatography
19	< 50.0			< 50.0			Ion Chromatography
20	5	-0.67	-56.9 %	5.2	-0.62	-57.4 %	Simplified photometry
21	< 200.0			< 200.0			Automatic Cd-red. spectrophotometry
–	–	–	–	–	–	–	–
Assigned value	11.6			12.2			
SDPA	9.2			10.6			
Rel. SDPA	79.3 %			86.6 %			
No. of values used for the statistics	11			10			
No. of laboratories that submitted results	14			13			
Percentage of satisfactory scores	100.0 %			100.0 %			
Percentage of questionable scores	0.0 %			0.0 %			
Percentage of unsatisfactory scores	0.0 %			0.0 %			
Mean	11.6			12.2			
Median	10.0			12.8			

NOTE: The highly variable reported results for nitrate means that the information in this table must be used with caution and a critical view, if used at all.

Table 10. Table of laboratory results and statistical parameters for Chloride.

Chloride	ICPW38 Sample A			ICPW38 Sample B			Analytical method
Laboratory	mg/l	Z' score	D%	mg/l	Z' score	D%	
1	3.47	2.67	5.3 %	3.66	1.90	5.3 %	Ion Chromatography
2	3.30	0.11	0.2 %	3.49	0.20	0.6 %	Ion Chromatography
3	3.31	0.24	0.5 %	3.53	0.57	1.6 %	Ion Chromatography
4	2.80	-7.51	-15.0 %	not tested			Ion Chromatography
6	3.31	0.31	0.6 %	3.53	0.59	1.7 %	Ion Chromatography
7	3.25	-0.66	-1.3 %	3.46	-0.16	-0.5 %	Ion Chromatography
8	3.27	-0.37	-0.7 %	3.47	-0.05	-0.1 %	Ion Chromatography
9	3.31	0.24	0.5 %	3.52	0.46	1.3 %	Ion Chromatography
10	3.36	1.00	2.0 %	3.56	0.88	2.5 %	Ion Chromatography
12	3.28	-0.22	-0.4 %	3.46	-0.20	-0.6 %	Ion Chromatography
13	3.35	0.84	1.7 %	3.43	-0.46	-1.3 %	Ion Chromatography
14	2.93	-5.55	-11.1 %	3.17	-3.14	-8.8 %	Ion Chromatography
15	3.32	0.39	0.8 %	3.52	0.46	1.3 %	Ion Chromatography
17	3.33	0.54	1.1 %	3.54	0.67	1.9 %	Ion Chromatography
18	3.30	0.07	0.1 %	3.42	-0.54	-1.5 %	Ion Chromatography
19	3.32	0.39	0.8 %	3.52	0.46	1.3 %	Ion Chromatography
20	3.04	-3.87	-7.7 %	3.24	-2.42	-6.8 %	Ion Chromatography
21	< 2.00			2.82	-6.74	-18.8 %	Photometry, autoanalyzer
–	–	–	–	–	–	–	–
Assigned value	3.29			3.47			
SDPA	0.06			0.09			
Rel. SDPA	1.9 %			2.7 %			
No. of values used for the statistics	17			17			
No. of laboratories that submitted results	18			17			
Percentage of satisfactory scores	76.5 %			82.4 %			
Percentage of questionable scores	5.9 %			5.9 %			
Percentage of unsatisfactory scores	17.6 %			11.8 %			
Mean	3.29			3.47			
Median	3.31			3.49			

Table 11. Table of laboratory results and statistical parameters for Sulphate.

Sulphate	ICPW38 Sample A			ICPW38 Sample B			Analytical method
Laboratory	mg/l	Z' score	D%	mg/l	Z' score	D%	
1	1.74	-0.09	-0.4 %	1.71	-0.79	-3.7 %	Ion Chromatography
2	1.75	0.09	0.4 %	1.77	-0.10	-0.5 %	Ion Chromatography
3	1.66	-1.11	-5.0 %	1.70	-0.91	-4.3 %	Ion Chromatography
4	1.46	-3.64	-16.2 %	not tested			Ion Chromatography
6	1.81	0.83	3.7 %	1.84	0.81	3.8 %	Ion Chromatography
7	1.74	-0.11	-0.5 %	1.78	0.00	0.0 %	Ion Chromatography
8	1.70	-0.60	-2.7 %	1.72	-0.67	-3.2 %	Ion Chromatography
9	1.90	1.96	8.8 %	1.96	2.21	10.4 %	Ion Chromatography
10	1.82	0.94	4.2 %	1.89	1.37	6.4 %	Ion Chromatography
11	0.73	-13.04	-58.2 %	0.72	-12.70	-59.5 %	ICP-AES
12	1.86	1.43	6.4 %	1.90	1.44	6.8 %	Ion Chromatography
13	1.78	0.43	1.9 %	1.78	0.05	0.2 %	Ion Chromatography
14	1.76	0.17	0.8 %	1.73	-0.55	-2.6 %	Ion Chromatography
15	1.73	-0.22	-1.0 %	1.76	-0.19	-0.9 %	Ion Chromatography
17	1.77	0.30	1.3 %	1.81	0.41	1.9 %	Ion Chromatography
18	1.76	0.21	0.9 %	1.76	-0.21	-1.0 %	Ion Chromatography
19	1.72	-0.34	-1.5 %	1.75	-0.31	-1.5 %	Ion Chromatography
20	1.71	-0.47	-2.1 %	1.75	-0.31	-1.5 %	Ion Chromatography
21	< 5.00			< 5.00			Photometry
–	–	–	–	–	–	–	–
Assigned value	1.75			1.78			
SDPA	0.07			0.08			
Rel. SDPA	4.3 %			4.5 %			
No. of values used for the statistics	18			17			
No. of laboratories that submitted results	19			18			
Percentage of satisfactory scores	88.9 %			88.2 %			
Percentage of questionable scores	0.0 %			5.9 %			
Percentage of unsatisfactory scores	11.1 %			5.9 %			
Mean	1.75			1.78			
Median	1.75			1.76			

Table 12. Table of laboratory results and statistical parameters for Calcium.

Calcium	ICPW38 Sample A			ICPW38 Sample B			Analytical method
Laboratory	mg/l	Z' score	D%	mg/l	Z' score	D%	
1	1.83	-2.82	-24.8 %	2.05	-2.03	-16.2 %	Ion Chromatography
2	2.40	-0.15	-1.3 %	2.44	-0.03	-0.3 %	ICP-AES
3	2.39	-0.21	-1.8 %	2.39	-0.29	-2.3 %	Ion Chromatography
4	2.92	2.25	19.8 %	not tested			Ion Chromatography
5	2.69	1.20	10.6 %	2.87	2.14	17.2 %	ICP-MS
6	2.35	-0.38	-3.3 %	2.40	-0.25	-2.0 %	Ion Chromatography
7	2.50	0.30	2.7 %	2.42	-0.17	-1.3 %	ICP-AES
8	2.39	-0.21	-1.8 %	2.48	0.17	1.3 %	Ion Chromatography
9	2.35	-0.40	-3.5 %	2.45	0.01	0.1 %	Ion Chromatography
10	2.73	1.38	12.1 %	2.77	1.64	13.2 %	Ion Chromatography
11	2.42	-0.07	-0.6 %	2.41	-0.19	-1.5 %	ICP-AES
12	2.49	0.27	2.3 %	2.56	0.56	4.5 %	Ion Chromatography
13	2.01	-1.98	-17.4 %	2.03	-2.13	-17.1 %	MP-AES
14	2.48	0.21	1.9 %	2.48	0.19	1.5 %	Flame AAS
15	2.51	0.35	3.1 %	2.54	0.47	3.8 %	ICP-MS
17	2.57	0.63	5.6 %	2.62	0.88	7.1 %	Ion Chromatography
18	2.20	-1.10	-9.7 %	2.22	-1.17	-9.4 %	ICP-MS
19	2.50	0.30	2.7 %	2.54	0.47	3.8 %	ICP-AES
20	2.18	-1.19	-10.5 %	2.23	-1.11	-8.9 %	Other Method
21	2.54	0.50	4.4 %	2.54	0.45	3.6 %	ICP-MS
–	–	–	–	–	–	–	–
Assigned value	2.43			2.45			
SDPA	0.21			0.19			
Rel. SDPA	8.5 %			7.7 %			
No. of laboratories that submitted results	20			19			
Percentage of satisfactory scores	90.0 %			84.2 %			
Percentage of questionable scores	10.0 %			15.8 %			
Percentage of unsatisfactory scores	0.0 %			0.0 %			
Mean	2.43			2.45			
Median	2.45			2.45			

Table 13. Table of laboratory results and statistical parameters for Magnesium.

Magnesium	ICPW38 Sample A			ICPW38 Sample B			Analytical method
Laboratory	mg/l	Z' score	D%	mg/l	Z' score	D%	
1	0.460	-3.89	-27.4 %	0.540	-2.71	-16.4 %	Ion Chromatography
2	0.620	-0.31	-2.2 %	0.637	-0.22	-1.3 %	ICP-AES
3	0.600	-0.76	-5.3 %	0.620	-0.66	-4.0 %	Ion Chromatography
4	0.868	5.25	37.0 %	not tested			Ion Chromatography
5	0.699	1.46	10.3 %	0.742	2.47	14.9 %	ICP-MS
6	0.627	-0.14	-1.0 %	0.645	-0.01	-0.1 %	Ion Chromatography
7	0.651	0.39	2.7 %	0.657	0.29	1.8 %	ICP-AES
8	0.610	-0.53	-3.7 %	0.630	-0.40	-2.4 %	Ion Chromatography
9	0.620	-0.31	-2.2 %	0.650	0.11	0.7 %	Ion Chromatography
10	0.670	0.81	5.7 %	0.680	0.88	5.3 %	Ion Chromatography
11	0.640	0.14	1.0 %	0.670	0.62	3.8 %	ICP-AES
12	0.596	-0.85	-6.0 %	0.605	-1.04	-6.3 %	Ion Chromatography
13	0.570	-1.43	-10.1 %	0.590	-1.43	-8.6 %	MP-AES
14	0.630	-0.08	-0.6 %	0.655	0.24	1.4 %	Flame AAS
15	0.668	0.77	5.4 %	0.666	0.52	3.1 %	ICP-MS
17	0.669	0.79	5.6 %	0.690	1.13	6.9 %	Ion Chromatography
18	0.610	-0.54	-3.8 %	0.617	-0.73	-4.4 %	ICP-MS
19	0.677	0.97	6.8 %	0.693	1.21	7.3 %	ICP-AES
20	0.609	-0.55	-3.9 %	0.632	-0.35	-2.1 %	Other Method
21	0.642	0.19	1.3 %	0.639	-0.17	-1.0 %	ICP-MS
–	–	–	–	–	–	–	–
Assigned value	0.634			0.646			
SDPA	0.043			0.038			
Rel. SDPA	6.8 %			5.8 %			
No. of laboratories that submitted results	20			19			
Percentage of satisfactory scores	90.0 %			89.5 %			
Percentage of questionable scores	0.0 %			10.5 %			
Percentage of unsatisfactory scores	10.0 %			0.0 %			
Mean	0.634			0.646			
Median	0.629			0.645			

Table 14. Table of laboratory results and statistical parameters for Sodium.

Sodium	ICPW38 Sample A			ICPW38 Sample B			Analytical method
Laboratory	mg/l	Z' score	D%	mg/l	Z' score	D%	
1	2.64	0.47	1.9 %	2.87	1.09	6.3 %	Ion Chromatography
2	2.60	0.08	0.3 %	2.71	0.05	0.3 %	ICP-AES
3	2.60	0.09	0.4 %	2.70	0.00	0.0 %	Ion Chromatography
4	2.56	-0.25	-1.0 %	not tested			Ion Chromatography
5	2.71	1.08	4.4 %	2.90	1.29	7.4 %	ICP-MS
6	2.61	0.17	0.7 %	2.73	0.18	1.0 %	Ion Chromatography
7	2.56	-0.32	-1.3 %	2.67	-0.18	-1.0 %	ICP-AES
8	2.66	0.65	2.7 %	2.77	0.45	2.6 %	Ion Chromatography
9	2.50	-0.85	-3.5 %	2.60	-0.65	-3.7 %	Ion Chromatography
10	2.68	0.84	3.5 %	2.81	0.71	4.1 %	Ion Chromatography
11	2.25	-3.19	-13.1 %	2.31	-2.51	-14.5 %	ICP-AES
12	2.62	0.29	1.2 %	2.69	-0.05	-0.3 %	Ion Chromatography
13	2.31	-2.63	-10.8 %	2.43	-1.74	-10.0 %	MP-AES
14	2.38	-1.93	-7.9 %	2.48	-1.42	-8.2 %	Flame AAS
15	2.70	1.03	4.2 %	2.81	0.71	4.1 %	ICP-MS
17	2.68	0.84	3.5 %	2.82	0.77	4.4 %	Ion Chromatography
18	2.57	-0.20	-0.8 %	2.65	-0.34	-2.0 %	ICP-MS
19	2.73	1.31	5.4 %	2.81	0.71	4.1 %	ICP-AES
20	2.55	-0.38	-1.6 %	2.77	0.45	2.6 %	Other Method
21	2.54	-0.51	-2.1 %	2.56	-0.88	-5.1 %	ICP-MS
–	–	–	–	–	–	–	–
Assigned value	2.59			2.70			
SDPA	0.1			0.15			
Rel. SDPA	4.0 %			5.5 %			
No. of laboratories that submitted results	20			19			
Percentage of satisfactory scores	90.0 %			94.7 %			
Percentage of questionable scores	5.0 %			5.3 %			
Percentage of unsatisfactory scores	5.0 %			0.0 %			
Mean	2.59			2.70			
Median	2.60			2.71			

Table 15. Table of laboratory results and statistical parameters for Potassium.

Potassium	ICPW38 Sample A			ICPW38 Sample B			Analytical method
Laboratory	mg/l	Z' score	D%	mg/l	Z' score	D%	
1	1.85	0.68	3.0 %	1.99	0.95	5.1 %	Ion Chromatography
2	1.81	0.14	0.6 %	1.92	0.26	1.4 %	ICP-AES
3	1.77	-0.33	-1.4 %	1.87	-0.23	-1.2 %	Ion Chromatography
4	1.89	1.23	5.5 %	not tested			Ion Chromatography
5	2.04	3.10	13.8 %	2.22	3.19	17.1 %	ICP-MS
6	1.81	0.15	0.7 %	1.93	0.38	2.0 %	Ion Chromatography
7	1.84	0.51	2.3 %	1.98	0.80	4.3 %	ICP-AES
8	1.80	0.05	0.2 %	1.90	0.07	0.4 %	Ion Chromatography
9	1.75	-0.58	-2.6 %	1.80	-0.92	-4.9 %	Ion Chromatography
10	1.78	-0.20	-0.9 %	1.89	-0.03	-0.2 %	Ion Chromatography
11	1.81	0.17	0.8 %	1.88	-0.13	-0.7 %	ICP-AES
12	1.71	-1.04	-4.6 %	1.79	-0.97	-5.2 %	Ion Chromatography
13	1.64	-1.95	-8.7 %	1.75	-1.41	-7.6 %	MP-AES
14	1.75	-0.51	-2.3 %	1.85	-0.38	-2.0 %	Flame AAS
15	1.89	1.18	5.2 %	2.00	1.05	5.6 %	ICP-MS
17	1.90	1.24	5.5 %	2.03	1.33	7.1 %	Ion Chromatography
18	1.75	-0.56	-2.5 %	1.87	-0.24	-1.3 %	ICP-MS
19	1.78	-0.20	-0.9 %	1.88	-0.13	-0.7 %	ICP-AES
20	1.75	-0.58	-2.6 %	1.85	-0.43	-2.3 %	Other Method
21	1.69	-1.35	-6.0 %	1.75	-1.41	-7.6 %	ICP-MS
–	–	–	–	–	–	–	–
Assigned value	1.80			1.89			
SDPA	0.08			0.10			
Rel. SDPA	4.3 %			5.2 %			
No. of laboratories that submitted results	20			19			
Percentage of satisfactory scores	95.0 %			94.7 %			
Percentage of questionable scores	0.0 %			0.0 %			
Percentage of unsatisfactory scores	5.0 %			5.3 %			
Mean	1.80			1.89			
Median	1.79			1.88			

Table 16. Table of laboratory results and statistical parameters for TOC.

Total organic carbon (TOC)	ICPW38 Sample A			ICPW38 Sample B			Analytical method
Laboratory	mg/l	Z' score	D%	mg/l	Z' score	D%	
1	12.0	-2.23	-16.3 %	11.8	-1.29	-18.8 %	Catalytic combustion, EN 1484
2	14.5	0.20	1.5 %	14.7	0.08	1.2 %	Catalytic combustion, EN ISO 20236
4	13.9	-0.42	-3.1 %	not tested			Catalytic combustion, EN 1484
8	15.0	0.64	4.7 %	15.0	0.22	3.3 %	UV/peroxodisulphate oxidation EN 1484
9	11.0	-3.21	-23.5 %	11.1	-1.64	-23.8 %	Catalytic combustion, EN ISO 20236
10	13.8	-0.46	-3.4 %	14.0	-0.25	-3.6 %	Catalytic combustion, EN ISO 20236
12	15.2	0.80	5.9 %	16.1	0.74	10.8 %	Catalytic combustion, EN 1484
13	14.5	0.14	1.0 %	15.4	0.42	6.2 %	Other Method
14	14.2	-0.12	-0.8 %	14.4	-0.07	-1.1 %	Catalytic combustion, EN 1484
15	14.8	0.43	3.1 %	15.8	0.60	8.8 %	Catalytic combustion, EN ISO 20236
17	15.2	0.86	6.3 %	15.9	0.64	9.2 %	Catalytic combustion, EN 1484
18	17.1	2.66	19.4 %	17.2	1.28	18.7 %	Catalytic combustion, EN 1484
19	14.4	0.07	0.5 %	15.0	0.22	3.3 %	Catalytic combustion, EN 1484
20	13.2	-1.08	-7.9 %	6.60	-3.74	-54.4 %	Other Method
21	14.7	0.37	2.7 %	15.0	0.24	3.5 %	Other Method
–	–	–	–	–	–	–	–
Assigned value	14.3			14.5			
SDPA	1			2			
Rel. SDPA	6.9 %			13.8 %			
No. of laboratories that submitted results	15			14			
Percentage of satisfactory scores	80.0 %			92.9 %			
Percentage of questionable scores	13.3 %			0.0 %			
Percentage of unsatisfactory scores	6.7 %			7.1 %			
Mean	14.3			14.5			
Median	14.5			15.0			

Table 17. Table of laboratory results and statistical parameters for TOT-P.

Total phosphorous (TOT-P)	ICPW38 Sample A			ICPW38 Sample B			Analytical method
Laboratory	µg/l P	Z' score	D%	µg/l P	Z' score	D%	
2	90	-1.05	-20.0 %	92	-0.91	-22.0 %	ICP-AES
4	120	0.36	6.8 %	not tested			ISO 15681-2 (CFA)
5	155	1.97	37.7 %	156	1.33	32.2 %	ICP-MS
6	29	-3.89	-74.4 %	40	-2.73	-66.3 %	Ion Chromatography
8	123	0.49	9.3 %	132	0.49	11.9 %	NS 4725
9	100	-0.58	-11.1 %	94	-0.84	-20.3 %	EN ISO 6878
10	124	0.53	10.2 %	141	0.79	19.2 %	Simplified photometry
12	115	0.11	2.2 %	125	0.25	6.0 %	EN ISO 6878, ISO 15681-2 (CFA)
13	89	-1.09	-20.9 %	96	-0.78	-18.9 %	Other Method
14	132	0.89	16.9 %	154	1.25	30.4 %	EN ISO 6878
15	114	0.07	1.3 %	123	0.18	4.4 %	EN ISO 6878
17	85	-1.30	-24.9 %	94	-0.85	-20.5 %	ISO 15681-2 (CFA)
18	119	0.31	5.9 %	111	-0.24	-5.7 %	ISO 15681-2 (CFA)
19	118	0.25	4.9 %	110	-0.28	-6.8 %	ICP-MS
20	128	0.72	13.7 %	138	0.68	16.6 %	Simplified photometry
21	119	0.30	5.8 %	128	0.34	8.3 %	Simplified photometry
–	–	–	–	–	–	–	–
Assigned value	113			118			
SDPA	21			27			
Rel. SDPA	18.3 %			23.1 %			
No. of laboratories that submitted results	16			15			
Percentage of satisfactory scores	93.8 %			93.3 %			
Percentage of questionable scores	0.0 %			6.7 %			
Percentage of unsatisfactory scores	6.3 %			0.0 %			
Mean	113			118			
Median	118			123			

Table 18. Table of laboratory results and statistical parameters for TOT-N.

Total nitrogen (Tot-N)	ICPW38 Sample A			ICPW38 Sample B			Analytical method
Laboratory	µg/l N	Z' score	D%	µg/l N	Z' score	D%	
2	830	0.5	8.1 %	880	0.04	0.6 %	Catalytic combustion, EN ISO 20236
4	784	0.13	2.1 %	not tested			Catalytic combustion, EN 12260
8	700	-0.54	-8.8 %	770	-0.85	-12.0 %	Persulfate oxidation unbuffered NS 4743
9	930	1.29	21.2 %	940	0.53	7.5 %	Persulfate oxidation, buffered EN ISO 11905-1
10	585	-1.45	-23.8 %	724	-1.22	-17.2 %	Catalytic combustion, EN ISO 20236
12	795	0.22	3.6 %	877	0.02	0.3 %	Persulfate oxidation, buffered EN ISO 11905-1
13	827	0.47	7.7 %	926	0.42	5.9 %	Other Method
14	790	0.18	2.9 %	930	0.45	6.3 %	Catalytic combustion, EN 12260
15	576	-1.52	-25.0 %	768	-0.87	-12.2 %	Catalytic combustion, EN ISO 20236
17	810	0.34	5.5 %	911	0.29	4.1 %	Persulfate oxidation unbuffered NS 4743
18	834	0.53	8.7 %	1074	1.62	22.8 %	Persulfate oxidation unbuffered NS 4743
19	854	0.69	11.3 %	979	0.85	11.9 %	Catalytic combustion, EN 12260
20	646	-0.97	-15.8 %	743	-1.07	-15.1 %	Catalytic combustion, EN 12260
–	–	–	–	–	–	–	–
Assigned value	768			875			
SDPA	119			116			
Rel. SDPA	15.5 %			13.2 %			
No. of laboratories that submitted results	13			12			
Percentage of satisfactory scores	100.0 %			100.0 %			
Percentage of questionable scores	0.0 %			0.0 %			
Percentage of unsatisfactory scores	0.0 %			0.0 %			
Mean	768			875			
Median	795			896			

Table 19. Table of laboratory results and statistical parameters for Al.

Aluminium (Al)	ICPW38 Sample C			ICPW38 Sample D			Analytical method
Laboratory	µg/l	Z' score	D%	µg/l	Z' score	D%	
1	129	-1.49	-11.7 %	143	-1.18	-6.4 %	ICP-MS
2	146	0.06	0.4 %	152	-0.03	-0.2 %	ICP-MS
5	161	1.33	10.4 %	168	1.91	10.3 %	ICP-MS
8	146	0.02	0.2 %	154	0.16	0.9 %	ICP-MS
9	137	-0.77	-6.0 %	145	-0.93	-5.0 %	ICP-AES
10	140	-0.46	-3.6 %	147	-0.69	-3.7 %	ICP-MS
11	148	0.20	1.5 %	156	0.40	2.2 %	ICP-AES
12	141	-0.42	-3.3 %	148	-0.57	-3.1 %	ICP-AES
14	187	3.61	28.3 %	190	4.52	24.4 %	GF-AAS
15	140	-0.46	-3.6 %	153	-0.01	-0.1 %	ICP-MS
18	143	-0.25	-1.9 %	152	-0.05	-0.3 %	ICP-MS
19	142	-0.33	-2.6 %	147	-0.69	-3.7 %	ICP-MS
21	158	1.07	8.4 %	159	0.77	4.1 %	ICP-MS
–	–	–	–	–	–	–	–
Assigned value	146			153			
SDPA	11			8			
Rel. SDPA	7.4 %			5.1 %			
No. of laboratories that submitted results	13			13			
Percentage of satisfactory scores	92.3 %			92.3 %			
Percentage of questionable scores	0.0 %			0.0 %			
Percentage of unsatisfactory scores	7.7 %			7.7 %			
Mean	146			153			
Median	143			152			

Table 20. Table of laboratory results and statistical parameters for Fe.

Iron (Fe) Laboratory	ICPW38 Sample C µg/l	Z' score	D%	ICPW38 Sample D µg/l	Z' score	D%	Analytical method
1	226	-1.52	-5.4 %	215	-3.28	-10.2 %	ICP-MS
2	250	1.26	4.5 %	246	0.84	2.6 %	ICP-MS
5	267	3.33	11.8 %	258	2.37	7.4 %	ICP-MS
6	246	0.80	2.8 %	240	0.06	0.2 %	ICP-MS
7	232	-0.86	-3.0 %	231	-1.22	-3.8 %	ICP-AES
8	239	-0.03	-0.1 %	241	0.15	0.5 %	ICP-MS
9	240	0.09	0.3 %	243	0.42	1.3 %	ICP-AES
10	234	-0.62	-2.2 %	236	-0.52	-1.6 %	ICP-MS
11	244	0.56	2.0 %	247	0.96	3.0 %	ICP-AES
12	242	0.32	1.1 %	244	0.56	1.7 %	ICP-MS
14	244	0.50	1.8 %	244	0.62	1.9 %	Flame AAS
15	238	-0.13	-0.4 %	240	-0.01	0.0 %	ICP-MS
18	231	-1.03	-3.6 %	232	-1.04	-3.2 %	ICP-MS
19	239	-0.03	-0.1 %	238	-0.25	-0.8 %	ICP-MS
21	232	-0.83	-3.0 %	235	-0.60	-1.9 %	ICP-AES
–	–	–	–	–	–	–	–
Assigned value	239			240			
SDPA	8			7			
Rel. SDPA	3.4 %			3.0 %			
No. of laboratories that submitted results	15			15			
Percentage of satisfactory scores	93.3 %			86.7 %			
Percentage of questionable scores	0.0 %			6.7 %			
Percentage of unsatisfactory scores	6.7 %			6.7 %			
Mean	239			240			
Median	239			240			

Table 21. Table of laboratory results and statistical parameters for Mn.

Manganese (Mn)	ICPW38 Sample C			ICPW38 Sample D			Analytical method
Laboratory	µg/l	Z' score	D%	µg/l	Z' score	D%	
1	1.61	-0.68	-4.0 %	1.48	-0.83	-4.9 %	ICP-MS
2	1.81	1.35	7.9 %	1.74	2.01	11.8 %	ICP-MS
5	1.85	1.76	10.3 %	1.75	2.13	12.5 %	ICP-MS
6	1.64	-0.38	-2.2 %	1.53	-0.28	-1.7 %	ICP-MS
8	1.67	-0.07	-0.4 %	1.57	0.15	0.9 %	ICP-MS
9	1.50	-1.80	-10.6 %	1.30	-2.80	-16.5 %	ICP-AES
10	1.59	-0.89	-5.2 %	1.49	-0.72	-4.2 %	ICP-MS
11	1.75	0.74	4.3 %	1.60	0.48	2.8 %	ICP-AES
12	1.62	-0.58	-3.4 %	1.52	-0.39	-2.3 %	ICP-MS
14	1.70	0.23	1.4 %	1.50	-0.61	-3.6 %	ICP-MS
15	1.70	0.23	1.4 %	1.57	0.15	0.9 %	ICP-MS
18	1.66	-0.18	-1.0 %	1.59	0.37	2.2 %	ICP-MS
19	1.70	0.23	1.4 %	1.58	0.26	1.5 %	ICP-MS
21	< 10.00			< 10.00			ICP-AES
–	–	–	–	–	–	–	–
Assigned value	1.68			1.56			
SDPA	0.09			0.09			
Rel. SDPA	5.5 %			5.6 %			
No. of values used for the statistics	13			13			
No. of laboratories that submitted results	14			14			
Percentage of satisfactory scores	100.0 %			76.9 %			
Percentage of questionable scores	0.0 %			23.1 %			
Percentage of unsatisfactory scores	0.0 %			0.0 %			
Mean	1.68			1.56			
Median	1.67			1.57			

Table 22. Table of laboratory results and statistical parameters for Cd.

Cadmium (Cd)	ICPW38 Sample C			ICPW38 Sample D			Analytical method
Laboratory	µg/l	Z' score	D%	µg/l	Z' score	D%	
1	1.07	-0.49	-3.8 %	0.900	-1.02	-8.7 %	ICP-MS
2	1.22	1.25	9.7 %	1.09	1.23	10.6 %	ICP-MS
5	1.20	0.98	7.6 %	1.05	0.75	6.4 %	ICP-MS
6	1.00	-1.30	-10.1 %	0.900	-1.02	-8.7 %	ICP-MS
8	1.07	-0.49	-3.8 %	0.939	-0.56	-4.8 %	ICP-MS
9	0.95	-1.88	-14.6 %	0.75	-2.80	-23.9 %	ICP-AES
10	1.09	-0.25	-2.0 %	0.960	-0.31	-2.6 %	ICP-MS
11	1.35	2.76	21.4 %	1.26	3.25	27.8 %	ICP-AES
12	1.13	0.21	1.6 %	1.00	0.17	1.4 %	ICP-MS
14	1.08	-0.37	-2.9 %	0.980	-0.07	-0.6 %	GF-AAS
15	1.12	0.09	0.7 %	0.997	0.13	1.1 %	ICP-MS
18	1.11	-0.02	-0.2 %	0.980	-0.07	-0.6 %	ICP-MS
19	1.14	0.33	2.5 %	1.04	0.64	5.5 %	ICP-MS
21	1.12	0.06	0.5 %	0.996	0.12	1.0 %	ICP-MS
–	–	–	–	–	–	–	–
Assigned value	1.11			0.986			
SDPA	0.08			0.08			
Rel. SDPA	7.4 %			8.1 %			
No. of laboratories that submitted results	14			14			
Percentage of satisfactory scores	92.9 %			85.7 %			
Percentage of questionable scores	7.1 %			7.1 %			
Percentage of unsatisfactory scores	0.0 %			7.1 %			
Mean	1.11			0.986			
Median	1.11			0.988			

Table 23. Table of laboratory results and statistical parameters for Pb.

Lead (Pb)	ICPW38 Sample C			ICPW38 Sample D			Analytical method
Laboratory	**µg/l**	**Z' score**	**D%**	**µg/l**	**Z' score**	**D%**	
1	1.18	-0.14	-1.3 %	1.13	0.00	0.0 %	ICP-MS
2	1.22	0.23	2.1 %	1.19	0.54	5.3 %	ICP-MS
5	1.39	1.84	16.5 %	1.31	1.66	16.4 %	ICP-MS
6	1.14	-0.52	-4.6 %	1.08	-0.45	-4.4 %	ICP-MS
8	1.09	-0.98	-8.8 %	1.05	-0.72	-7.1 %	ICP-MS
9	0.90	-2.75	-24.7 %	1.00	-1.17	-11.5 %	ICP-AES
10	1.26	0.60	5.4 %	1.21	0.72	7.1 %	ICP-MS
11	1.30	0.97	8.7 %	0.63	-4.49	-44.2 %	ICP-AES
12	1.21	0.14	1.2 %	1.17	0.36	3.5 %	ICP-MS
14	1.10	-0.89	-8.0 %	1.10	-0.27	-2.7 %	GF-AAS
15	1.25	0.51	4.6 %	1.21	0.72	7.1 %	ICP-MS
18	1.14	-0.52	-4.6 %	1.08	-0.45	-4.4 %	ICP-MS
19	1.26	0.60	5.4 %	1.21	0.72	7.1 %	ICP-MS
21	< 2.00			< 2.00			ICP-MS
–	–	–	–	–	–	–	–
Assigned value	1.20			1.13			
SDPA	0.10			0.11			
Rel. SDPA	8.5 %			9.3 %			
No. of values used for the statistics	13			13			
No. of laboratories that submitted results	14			14			
Percentage of satisfactory scores	92.3 %			92.3 %			
Percentage of questionable scores	7.7 %			0.0 %			
Percentage of unsatisfactory scores	0.0 %			7.7 %			
Mean	1.20			1.13			
Median	1.21			1.13			

Table 24. Table of laboratory results and statistical parameters for Cu.

Copper (Cu)	ICPW38 Sample C			ICPW38 Sample D			Analytical method
Laboratory	µg/l	Z' score	D%	µg/l	Z' score	D%	
1	12.3	-1.41	-15.4 %	14.4	-1.39	-13.2 %	ICP-MS
2	15.0	0.31	3.4 %	17.0	0.22	2.1 %	ICP-MS
5	16.9	1.53	16.8 %	24.0	4.67	44.5 %	ICP-MS
6	13.6	-0.57	-6.3 %	15.7	-0.60	-5.7 %	ICP-MS
8	15.0	0.31	3.4 %	17.4	0.48	4.5 %	ICP-MS
9	15.0	0.31	3.4 %	17.0	0.22	2.1 %	ICP-AES
11	17.4	1.82	19.9 %	20.0	2.10	20.0 %	ICP-AES
12	14.7	0.12	1.3 %	16.9	0.16	1.5 %	ICP-MS
14	13.8	-0.45	-4.9 %	15.7	-0.60	-5.7 %	GF-AAS
15	14.7	0.12	1.3 %	16.9	0.16	1.5 %	ICP-MS
18	13.4	-0.72	-7.9 %	15.3	-0.86	-8.2 %	ICP-MS
19	14.7	0.12	1.3 %	16.8	0.10	0.9 %	ICP-MS
21	13.0	-0.97	-10.6 %	15.5	-0.73	-6.9 %	ICP-MS
–	–	–	–	–	–	–	–
Assigned value	14.5			16.6			
SDPA	1.5			1.5			
Rel. SDPA	10.3 %			9.0 %			
No. of laboratories that submitted results	13			13			
Percentage of satisfactory scores	100.0 %			84.6 %			
Percentage of questionable scores	0.0 %			7.7 %			
Percentage of unsatisfactory scores	0.0 %			7.7 %			
Mean	14.5			16.6			
Median	14.7			16.9			

Table 25. Table of laboratory results and statistical parameters for Ni.

Nickel (Ni)	ICPW38 Sample C			ICPW38 Sample D			Analytical method
Laboratory	µg/l	Z' score	D%	µg/l	Z' score	D%	
1	1.91	0.80	12.8 %	2.06	1.04	12.0 %	ICP-MS
2	1.75	0.21	3.3 %	1.94	0.48	5.5 %	ICP-MS
5	2.00	1.12	17.8 %	2.01	0.79	9.2 %	ICP-MS
6	1.65	-0.16	-2.6 %	1.75	-0.42	-4.8 %	ICP-MS
8	1.75	0.21	3.3 %	1.86	0.10	1.2 %	ICP-MS
9	1.50	-0.72	-11.4 %	1.60	-1.12	-13.0 %	ICP-AES
10	2.30	2.25	35.8 %	2.46	2.92	33.8 %	ICP-MS
11	1.32	-1.39	-22.1 %	1.60	-1.12	-13.0 %	ICP-AES
12	1.78	0.32	5.1 %	1.94	0.48	5.5 %	ICP-MS
14	1.20	-1.83	-29.1 %	1.50	-1.59	-18.4 %	GF-AAS
15	1.74	0.17	2.7 %	1.86	0.10	1.2 %	ICP-MS
18	1.65	-0.16	-2.6 %	1.82	-0.09	-1.0 %	ICP-MS
19	1.75	0.21	3.3 %	1.87	0.15	1.7 %	ICP-MS
21	1.53	-0.62	-9.8 %	1.76	-0.38	-4.4 %	ICP-MS
–	–	–	–	–	–	–	–
Assigned value	1.69			1.84			
SDPA	0.26			0.2			
Rel. SDPA	15.1 %			11.0 %			
No. of laboratories that submitted results	14			14			
Percentage of satisfactory scores	92.9 %			92.9 %			
Percentage of questionable scores	7.1 %			7.1 %			
Percentage of unsatisfactory scores	0.0 %			0.0 %			
Mean	1.69			1.84			
Median	1.75			1.86			

Table 26. Table of laboratory results and statistical parameters for Zn.

Zinc (Zn)	ICPW38 Sample C			ICPW38 Sample D			Analytical method
Laboratory	µg/l	Z' score	D%	µg/l	Z' score	D%	
1	26.5	0.62	2.1 %	20.9	0.99	2.9 %	ICP-MS
2	26.6	0.69	2.4 %	21.7	2.37	6.9 %	ICP-MS
5	27.4	1.62	5.5 %	20.6	0.54	1.6 %	ICP-MS
6	25.4	-0.68	-2.3 %	20.0	-0.52	-1.5 %	ICP-MS
8	26.6	0.73	2.5 %	20.7	0.67	2.0 %	ICP-MS
9	23.5	-2.77	-9.4 %	16.5	-6.39	-18.7 %	ICP-AES
10	25.8	-0.17	-0.6 %	20.0	-0.50	-1.5 %	ICP-MS
11	26.4	0.51	1.7 %	20.6	0.50	1.5 %	ICP-AES
12	25.0	-1.07	-3.7 %	19.6	-1.18	-3.4 %	ICP-MS
14	25.5	-0.51	-1.7 %	20.4	0.17	0.5 %	ICP-MS
15	25.9	-0.06	-0.2 %	20.3	0.00	0.0 %	ICP-MS
18	25.4	-0.63	-2.2 %	19.8	-0.89	-2.6 %	ICP-MS
19	26.8	0.96	3.3 %	20.6	0.50	1.5 %	ICP-MS
21	25.6	-0.40	-1.3 %	20.1	-0.29	-0.8 %	ICP-MS
–	–	–	–	–	–	–	–
Assigned value	25.9			20.3			
SDPA	0.8			0.6			
Rel. SDPA	3.2 %			2.8 %			
No. of laboratories that submitted results	14			14			
Percentage of satisfactory scores	92.9 %			85.7 %			
Percentage of questionable scores	7.1 %			7.1 %			
Percentage of unsatisfactory scores	0.0 %			7.1 %			
Mean	25.9			20.3			
Median	25.9			20.4			

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.

Vogt, R.D., Aurle, J., Austnes, K., van Dam, H., Futter, M., Fölster, J., Brecke Gundersen., Higgins, S., Houle, D., Hruška, J., Kolada, A., Monteith, D., Rogora, M., Sample, J., Stoddard, J., Steingruber, S., Ulańczyk, R., Vuorenmaa, J. & de Wit, H. NIVA SNO 7931-2024. **ICP Waters report 156/2024.**

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**.