CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

INTERNATIONAL COOPERATIVE PROGRAMME ON ASSESSMENT AND MONITORING OF ACIDIFICATION OF RIVERS AND LAKES

Intercomparison 9509

pH, k_{25}, HCO_3, NO_3+ NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC and COD-Mn

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P.O. Box 173 Kjelsås	Televeien 1	Rute 866	Thormøhlensgt 55	Søndre Tollbugate 3
N-0411 Oslo	N-4890 Grimstad	N-2312 Ottestad	N-5008 Bergen	N-9000 Tromsø
Norway	Norway	Norway	Norway	Norway
Phone (47) 22 18 51 00	Phone (47) 37 04 30 33	Phone (47) 62 57 64 00	Phone (47) 55 32 56 40	Phone (47) 77 68 52 80
Telefax (47) 22 18 52 00	Telefax (47) 37 04 45 13	Telefax (47) 62 57 66 53	Telefax (47) 55 32 88 33	Telefax (47) 77 68 05 09

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Abstract:

46 laboratories in 21 countries participated in intercomparison 9509. Two sample sets, one for the major ions and one for organic matter and aluminium fractions, were used. Based on the general target accuracy of ± 20 %, 72 % of the results were acceptable. For pH, less than 50 % of the result pairs were acceptable in relation to a target accuracy of ± 0.1 units, and 73 % in relation to the extended target accuracy of ± 0.2 units. For three analytical variables: alkalinity, reactive and non-labile aluminium, it was decided **not** to evaluate the reported results because of the extreme spread of the results between the participants. In the future a sample set with more suitable concentration for alkalinity has to be used. To improve the comparability for the determination of aluminium fractions, it is necessary to normalize the analytical method to be used. Manual methods are generally less sensitivecompared to instrumental methods, and may be less suited for typical acid precipitation samples.

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Project manager

Håvard Hovind

Håvard Hovind

For the Administration

Merete Johannessen

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INTERNATIONAL CO-OPERATIVE PROGRAMME FOR ASSESSMENT AND MONITORING OF ACIDIFICATION OF RIVERS AND LAKES

INTERCOMPARISON 9509

pH, κ_{25}, HCO_3^-, $NO_3^- + NO_2^-$, Cl^-, SO_4^{--}
Ca^{++}, Mg^{++}, Na^+, K^+, Al, Al-R, Al-I, DOC and COD-Mn

Oslo, October, 1995

Written at the Programme Centre, Norwegian Institute for Water Research

SUMMARY

Intercomparison 9509 was organized as a part of the between-laboratory quality control programme, as stated in "Manual for Chemical and Biological Monitoring" (1), by the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes.

The intercomparison was performed in June - July 1995, and included the determination of major ions in natural water samples. The participants were asked to determine pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, total aluminium, reactive and non-labile aluminium, dissolved organic carbon and chemical oxygen demand (COD-Mn).

Two sample sets with different concentrations were prepared for this intercomparison, one set for the determination of the major ions and one set for the determination of aluminium fractions and unspecific organic matter. 46 laboratories determined the analytical variables in one or both sample sets.

The samples were sent to 48 laboratories, and 46 submitted results to the Programme Centre before the final statistical treatment of the data submittet by the participants. 21 countries were represented in this laboratory group. From one laboratory we received the results too late to include them in this report.

As "true" value for each variable was selected the median value of the results received from the participants. On average 72 % of the result pairs were located within the general target accuracy of ± 20 %.

For pH the accuracy limit was extended to ± 0.2 units. 73 % of the result pairs were included by this special while less than 50 % of the results were located within the limits ± 0.1 pH units. A total error of ± 0.2 units for pH measurements seems to be a reasonable assessment of the accuracy between laboratories for samples which are weakly acid.

For three analytical variables: alkalinity, reactive and non-labile aluminium, it was decided not to evaluate the reported results because of the extreme spread between the results from the participants. A sample set with more suitable concentration for alkalinity has to be used in the future.

To improve the comparability of the determination of aluminium fractions, it is necessary to normalize the analytical method and determination technique used.

Generally, the application of manual analytical methods seem to be less suited for the water samples which are analyzed in this programme, as the detection limit of many manual methods are too high.

CONTENTS

INTRODUCTION

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

The between-laboratory control carried out by the Programme Centre is based on the "round robin" concept and the procedure of Youden (2,3), which is briefly described in Appendix 3. This ninth intercomparison test, called 9509, included the determination of the main components and some other ions in natural water samples: pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, total aluminium, reactive and non-labile aluminium, dissolved organic carbon and chemical oxygen demand (COD-Mn).

ACCOMPLISHMENT OF THE INTERCALIBRATION

The preparation of the sample solutions is described in Appendix 2. The results of the control analyses performed at the Programme Centre are also summarized in the same place. On the Task Force meeting in 1994 it was decided that two sample sets should be included in this intercomparison, one sample pair for the determination of the major ions, and one sample pair for aluminium fractions and unspecific organic matter. The idea that samples with higher concentrations should be available, was rejected.

The samples were mailed from the Programme Centre on May 31, 1995. Nearly all the participating laboratories received the samples within one week, except for some very few laboratories that received the samples up to six weeks after mailing from the Programme Center. To ensure that the effect of possible alterations in the solutions is minimized, the participants were asked to analyze the samples as soon as possible, and return the analytical results within four weeks after the samples arrived at the laboratory.

RESULTS

The samples were sent to 48 laboratories. The 46 laboratories who submitted results to the Programme Centre, are representing 21 countries. One laboratory returned the results too late to be included in this report. This time, too, it was a problem that many laboratories submitted the results several weeks after the deadline, and a reminder letter had to be mailed to several participants. A survey of the participants and their code numbers are listed in Appendix 1.

The analytical results received from the laboratories were treated by the method of Youden (2,3). A short description of this method, and the statistical treatment of the analytical data, are presented in Appendix 3.

The purpose of this test is to evaluate the comparability of the analytical results produced by different laboratories. The real "true value" is not known exactly for the natural samples used in this intercomparison. Therefore, we selected the median value, determined from the analytical results submitted by the participating laboratories, as the "true value" for each analytical variable. The median value is considered to be an acceptable estimate of the true value for this purpose, as long as the preponderate number of participants are using essentially the same analytical method.

The results are illustrated in Figure 1 - 17, where each laboratory is represented by a small circle and an identification number. The great circle in the figures are representing a selected accuracy limit, either the general target limit of ± 20 % of the mean true values of the sample pair, or a special accuracy limit defined in the sections below. A survey of the results of intercomparison 9509 is presented in Table 1. The individual results of the participants are presented in Table 4 in Appendix 4, sorted in order of increasing identification number. More extensive statistical informations are presented in the Tables 5.1 - 5.17.

pH

The reported results for pH are graphically presented in Figure 1, where the radius of the great circle is 0.2 pH units, and visualizes the degree of comparability between the pH results from the participating laboratories. The reported pH values are given in Table 5.1 in Appendix 4.

The participating laboratories determined pH in the test solutions by their own routine method. An electrometric method was used by all laboratories. One laboratory informed that they equilibrated the solutions before the measuring pH. The results from this laboratory was definitely higher than the median values. Five other result pairs deviating strongly from the median value are systematically low for both samples, which may be caused by the instrument, electrodes or the calibration. Two laboratories reported low results for sample B only, which indicates a random error.

As the CO_2 concentration of samples in the circumneutral range may be far above the atmospheric equilibrium, the relative high pCO_2 levels will lead to large systematic errors, the magnitude of which will vary between the laboratories due to different pCO_2 levels in the samples caused by different storage and handling conditions. This effect may also increase the random error as the samples may contain different amount of excess CO_2. The CO_2 effect is expected to be more pronounced in sample B (pH 6) than in sample A (pH 5). As we used water samples which were weakly acidic, this problem is dominating and is supposed to be the main reason for the scatter of the results in Figure 1.

The control analyses carried out at the Program Centre proved that the samples were stable when stored within one laboratory. However, the equilibrium of the samples may be influenced by variations in pressure and temperature when they are mailed to the participants. Some systematic deviations observed in Figure 1 may also be due to errors in the instrument, or more likely in the electrodes, as different electrodes may give rise to different results (4).

(The text continues on page 26)

Tabell 1. Statistical summary of intercomparison 9509

Analytical variable and methods	Sample pair	True value 1	True value 2	Number of labs. Total	Number of labs. Excl.	Median value 1	Median value 2	Mean Sample 1	Std.dev. Sample 1	Mean Sample 2	Std.dev. Sample 2	Rel. std.dev. % 1	Rel. std.dev. % 2	Relative error % 1	Relative error % 2
pH	AB	5.09	6.07	41	2	5.09	6.07	5.05	0.15	6.01	0.17	3.1	2.8	-0.7	-1.1
Electrometry				40	1	5.09	6.07	5.05	0.15	6.01	0.17	3.1	2.8	-0.7	-1.1
Equilibration				1	1			6.03		6.75				18.5	11.2
Conductivity, mS/m	AB	1.8	2.34	40	3	1.8	2.34	1.81	0.14	2.32	0.13	7.7	5.6	0.4	-0.8
Alkalinity	AB	0.29	1.22	31	22	0.29	1.22	0.38	0.11	1.27	0.26	28.3	20.5	29.7	4.3
Gran plot titration				14	8	0.3	1.28	0.37	0.12	1.27	0.31	33	24.2	27.6	4.1
End point titration				17	14	0.4	1.16	0.4	0	1.28	0	0	0	37.9	4.9
Nitrate + nitrite-nitroge	AB	57	158	39	8	57	158	57	6	157	9	9.7	6	0.5	-0.5
Autoanalyzer				18	2	57	159	58	6	159	8	10.6	4.7	1.8	0.8
Photometric				5	5			148		131				159.9	-17.1
Ion chromatography				13	1	56	155	56	6	152	9	9.9	5.9	-1.1	-3.5
Flow injection analysis				1	0			57		156				0	-1.1
Hydrazine				2	0			57		171				-0.7	8.3
Chloride	AB	0.83	0.67	41	9	0.83	0.67	0.86	0.14	0.67	0.11	16.7	16.8	3.3	-0.6
Ion chromatography				29	3	0.83	0.67	0.84	0.1	0.67	0.11	11.9	16.4	1.5	0.1
Autoanalyzer				9	3	0.95	0.64	0.92	0.27	0.65	0.13	29.1	19.6	11	-3.5
Argentometry				3	3			15.08		10.01					
Sulfate	AB	2.3	5.28	41	9	2.3	5.28	2.28	0.17	5.2	0.34	7.4	6.5	-1.1	-1.5
Ion chromatography				3	3	2.3	5.3	2.28	0.16	5.24	0.31	7.1	5.8	-0.8	-0.8
Photometry				30	2			2.32		5.14				0.7	-2.7
Nephelometry				5	4			2.04		4.55				-11.3	-13.8
ICP				2	0			2.27		5.06				-1.3	-4.2

Analytical variable and methods	Sample pair	True value 1	True value 2	Number of labs. Total	Number of labs. Excl.	Median value 1	Median value 2	Mean Sample 1	Std.dev. Sample 1	Mean Sample 2	Std.dev. Sample 2	Rel. std.dev. % 1	Rel. std.dev. % 2	Relative error % 1	Relative error % 2
Calcium	AB	0.88	1.59	39	4	0.88	1.59	0.88	0.12	1.57	0.2	14	12.8	-0.5	-1.4
FAAS				19	2	0.86	1.53	0.86	0.07	1.52	0.13	8.4	8.6	-2.8	-4.6
ICP				6	0	0.87	1.59	0.84	0.16	1.54	0.3	19	19.4	-4.6	-3.1
EDTA				5	2	0.95	1.61	1	0.22	1.66	0.24	21.9	14.7	13.6	4.2
Ion chromatography				6	0	0.94	1.71	0.9	0.17	1.68	0.27	18.8	16.3	1.9	5.5
ICP-MS				3	0	0.9	1.6	0.9	0.03	1.61	0.05	2.8	3.2	1.9	1.5
Magnesium	AB	0.19	0.83	40	9	0.19	0.83	0.19	0.02	0.83	0.1	9.5	11.7	2.5	-0.3
FAAS				19	3	0.19	0.83	0.19	0.02	0.81	0.08	8.1	10.1	2.3	-1.9
ICP				6	1	0.19	0.86	0.2	0.01	0.85	0.03	4.5	3.6	3.3	2.3
EDTA				5	5			1.29		0.51				580	-39
Ion chromatography				7	0	0.21	0.81	0.19	0.03	0.84	0.15	16.4	18.3	1.4	1.8
ICP-MS				3	0	0.2	0.84	0.2	0.01	0.82	0.11	5	13.6	5.3	-1.2
Sodium	AB	1.2	0.9	38	4	1.2	0.9	1.19	0.15	0.9	0.08	12.2	8.7	-0.5	0.2
FAAS				17	1	1.2	0.9	1.19	0.14	0.89	0.05	11.6	6	-1	-1.6
ICP				7	1	1.15	0.88	1.12	0.1	0.85	0.08	9	9.3	-6.8	-5.2
AES				5	1	1.36	0.99	1.35	0.14	0.99	0.09	10.1	8.8	12.3	10
Ion chromatography				6	1	1.22	0.9	1.24	0.1	0.93	0.11	7.9	12.3	3.5	3.4
ICP-MS				3	0	1.2	0.91	1.1	0.22	0.92	0.02	20.4	2.3	-8.6	1.9
Potassium	AB	0.52	0.2	38	4	0.52	0.2	0.52	0.05	0.2	0.03	9.5	16.7	-0.6	-1.4
FAAS				18	0	0.53	0.2	0.51	0.04	0.19	0.03	8	14.6	-1.9	-4.1
ICP				5	1	0.49	0.2	0.47	0.04	0.18	0.05	9.4	26.1	-9.3	-10
AES				5	1	0.55	0.22	0.55	0.05	0.24	0.05	9.5	20.1	5.8	17.5
Ion chromatography				6	2	0.52	0.19	0.54	0.06	0.2	0.02	11	11.6	3	-0.9
ICP-MS				4	0	0.54	0.2	0.54	0.06	0.2	0.01	10.7	4.1	3.7	0

Analytical variable and methods	Sample pair	True value 1	True value 2	Number of labs. Total	Number of labs. Excl.	Median value 1	Median value 2	Mean Sample 1	Std.dev. Sample 1	Mean Sample 2	Std.dev. Sample 2	Rel. std.dev. % 1	Rel. std.dev. % 2	Relative error % 1	Relative error % 2
Aluminium	CD	270	170	19	1	270	170	265	36	174	22	13.5	12.5	-1.7	2.3
FAAS				8	0	267	173	263	40	180	24	15.4	13.5	-2.6	5.9
GFAAS				2	0			272		177				0.6	4.1
ICP				4	0	263	169	269	17	175	14	6.5	8.3	-0.3	2.6
ICP-MS				3	1			294		176				8.7	3.2
Photometry				2	0			219		143				-19.1	-15.9
Aluminium, reactive	CD	214	140	13	6	214	140	228	33.1	135	32.7	14.5	24.2	6.5	3.6
Aluminium, nonlabile	CD	158	107	13	6	158	107	161	33.8	116	23.4	21.1	20.2	6.2	8.4
Dissolved org. carbon	AB	10	4.83	19	1	10	4.83	10.04	0.99	4.83	0.32	9.9	6.6	0.4	0.1
Combustion				7	1	9.98	4.65	9.8	0.65	4.69	0.29	6.6	6.1	-2	-3
UV/peroxodisulfate				10	0	10.15	4.95	10.37	1.13	4.99	0.28	10.9	5.7	3.7	3.3
Phenolphthalein				2	0			9.12		4.51				-8.8	-6.6
Dissolved org. carbon	CD	9.7	5.88	15	2	9.7	5.88	9.68	0.82	5.91	0.58	8.5	9.8	-0.2	0.5
Combustion				4	1	9.8	6	9.57	0.87	5.96	0.46	9.1	7.7	-1.4	1.4
UV/peroxodisulfate				10	1	9.7	5.88	9.83	0.82	6.01	0.56	8.4	9.3	1.3	2.2
Phenolphthalein				1	0			8.7		4.9				-10.3	-16.7
Chem. oxygen demand	AB	12.4	5.54	13	0	12.4	5.54	12.49	1.44	5.58	0.43	11.6	7.7	0.7	0.7
Volumetry				13	0	12.4	5.54	12.49	1.44	5.58	0.43	11.6	7.7	0.7	0.7
Chem. oxygen demand	CD	12.1	6.31	8	0	12.1	6.31	11.76	1.68	6.4	0.63	14.3	9.9	-2.8	1.4
Volumetry				8	0	12.1	6.31	11.76	1.68	6.4	0.63	14.3	9.9	-2.8	1.4

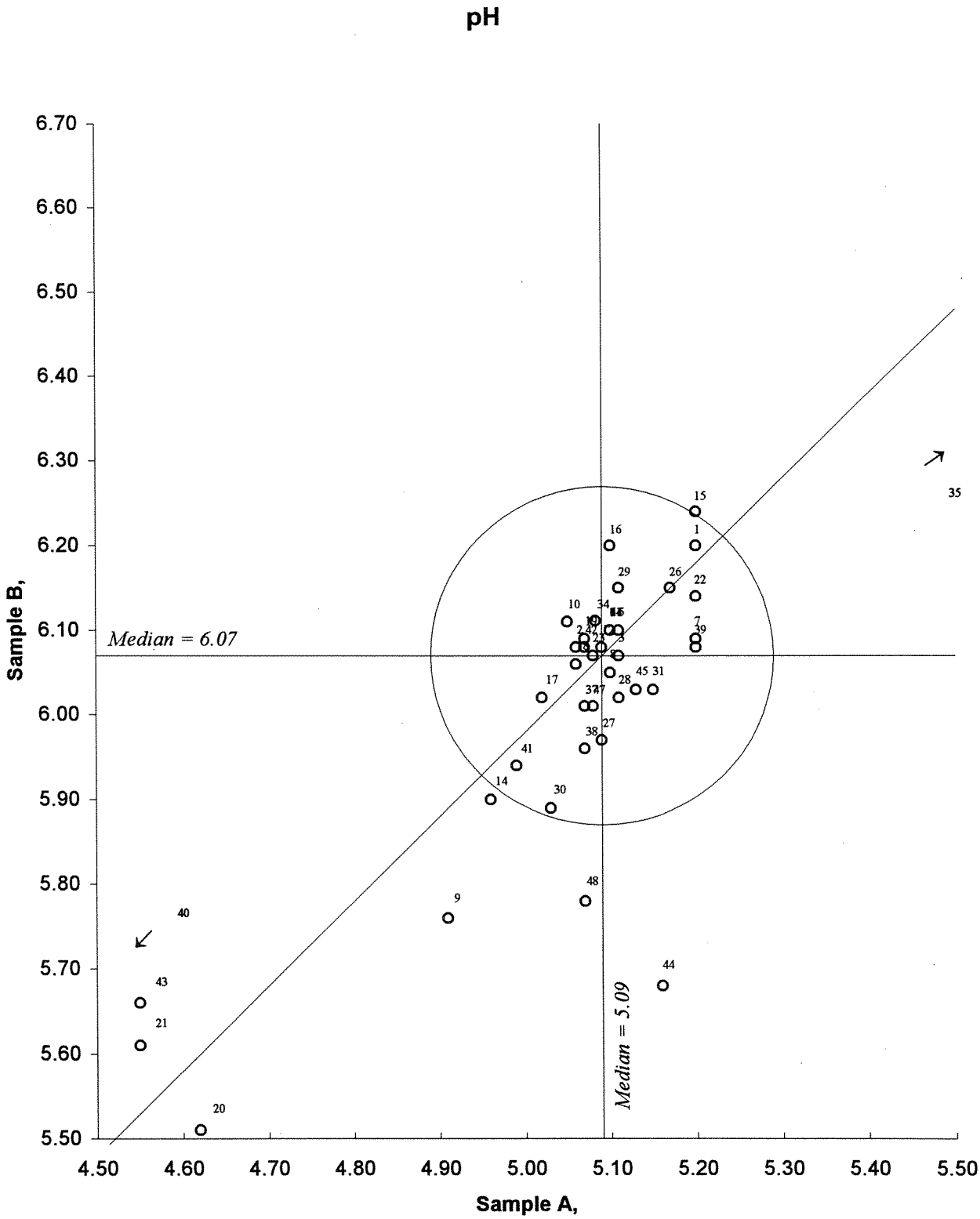

Figure 1. Youden-diagramme for pH, sample pair AB
Acceptance criteria, given by the circle, is 0.2 pH units (=3.58 %)

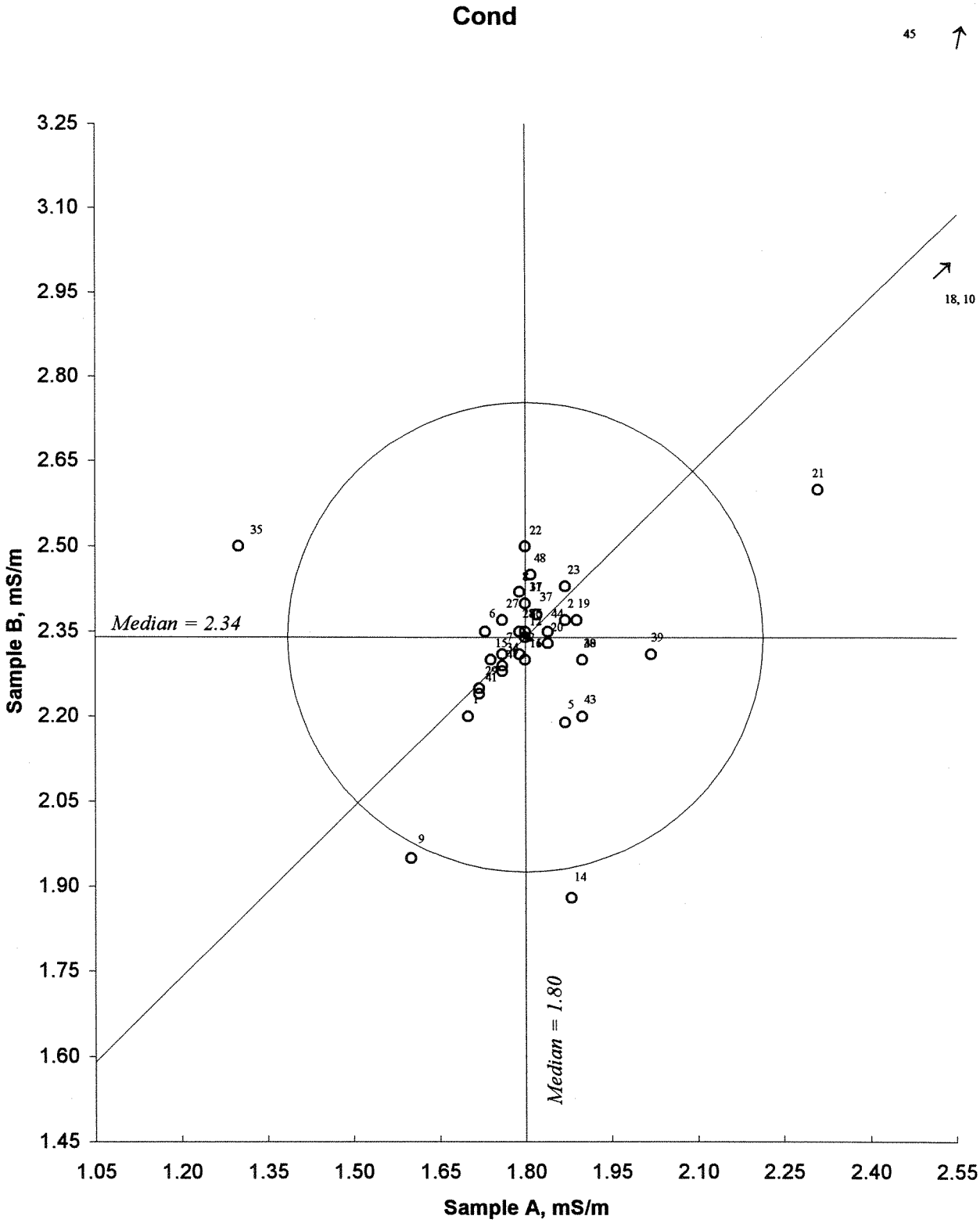

Figure 2. Youden-diagramme for conductivity, sample pair AB
Acceptance criteria, given by the circle, is 20 %

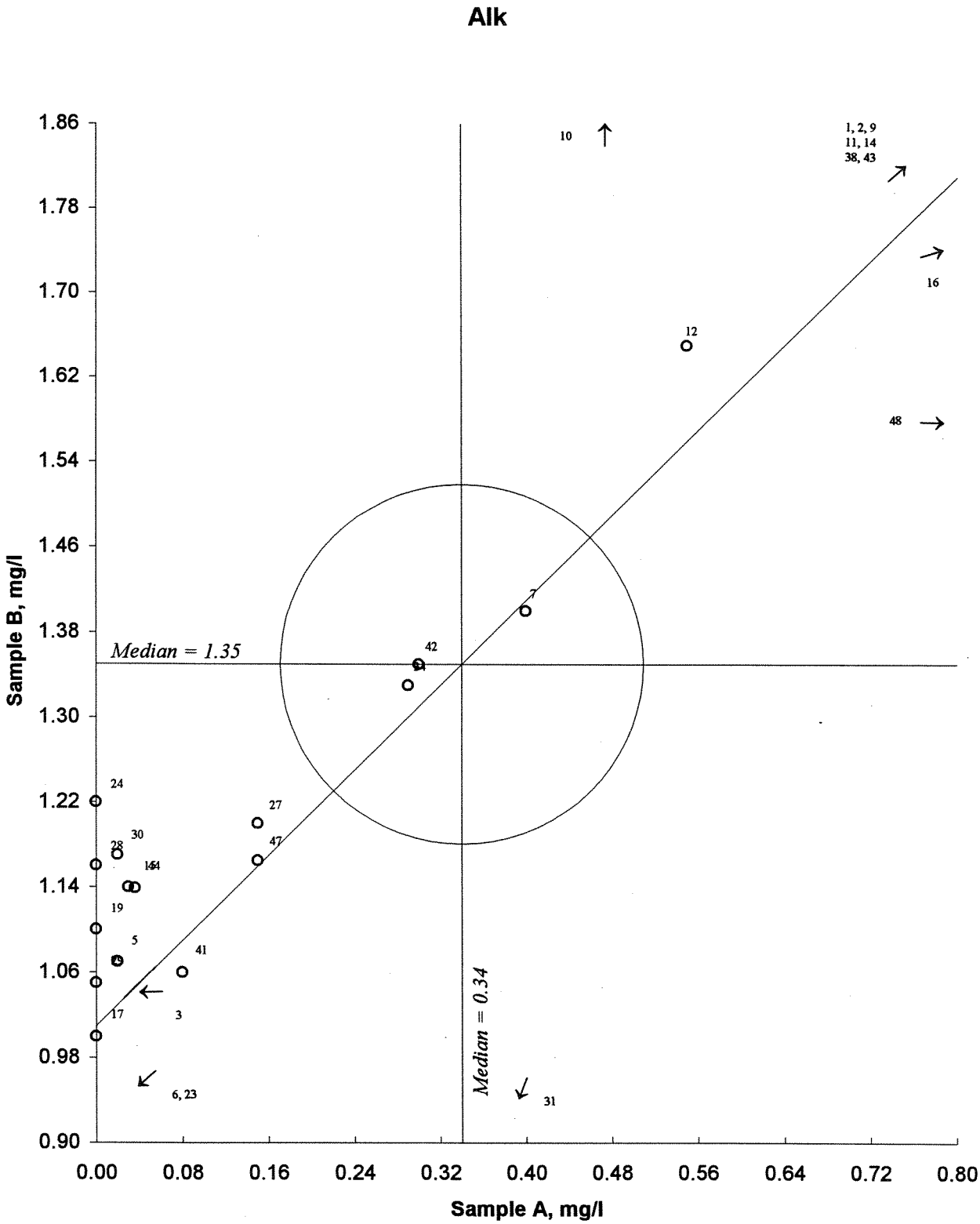

Figure 3. Youden-diagramme for alkalinity, Pair AB
Acceptance criterie, given by the circel, is 20%

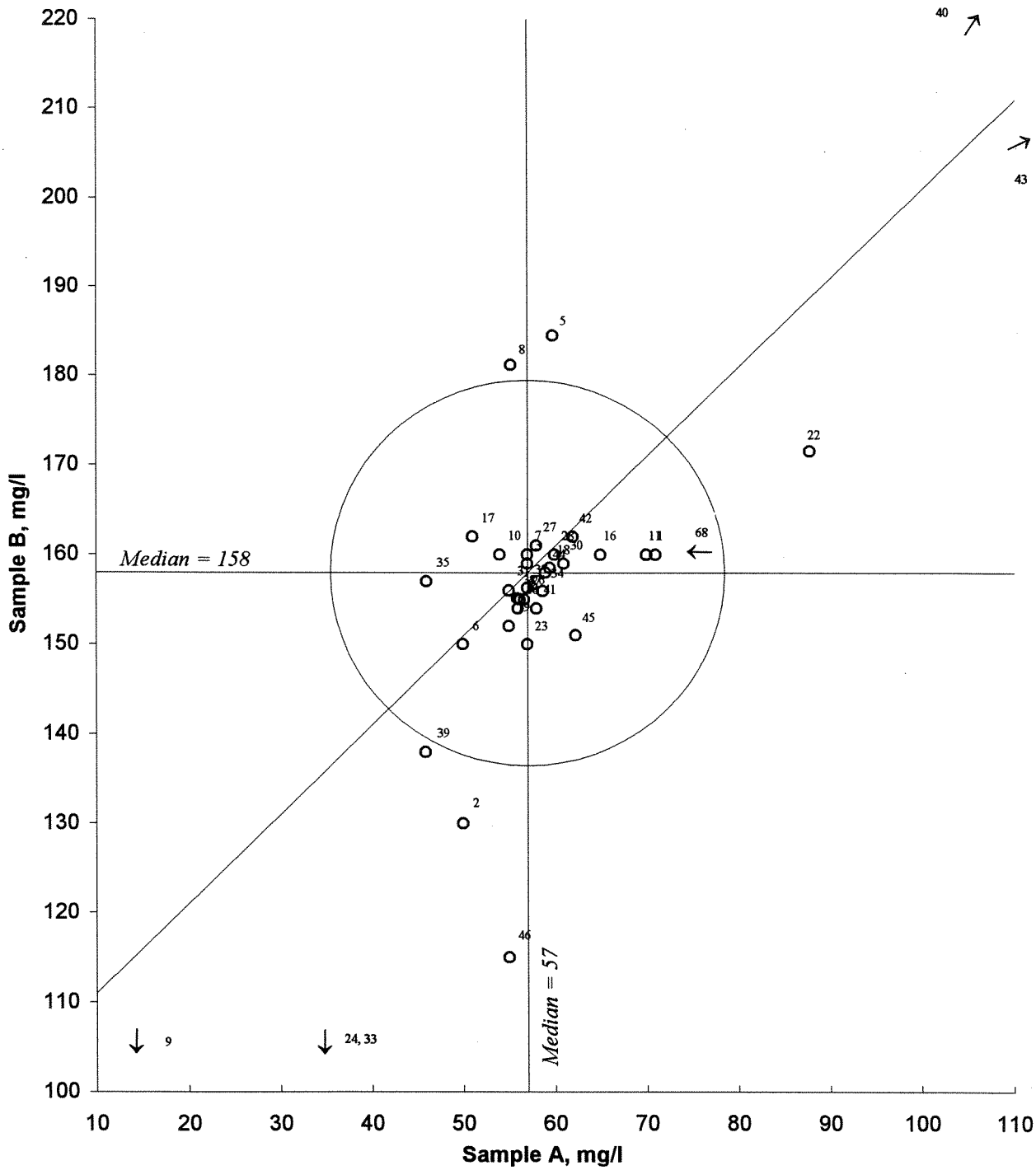

Figure 4. Youden-diagramme for nitrate + nitrite-nitrogen, sample pair AB
Acceptance criteria, given by the circle, is 20 %

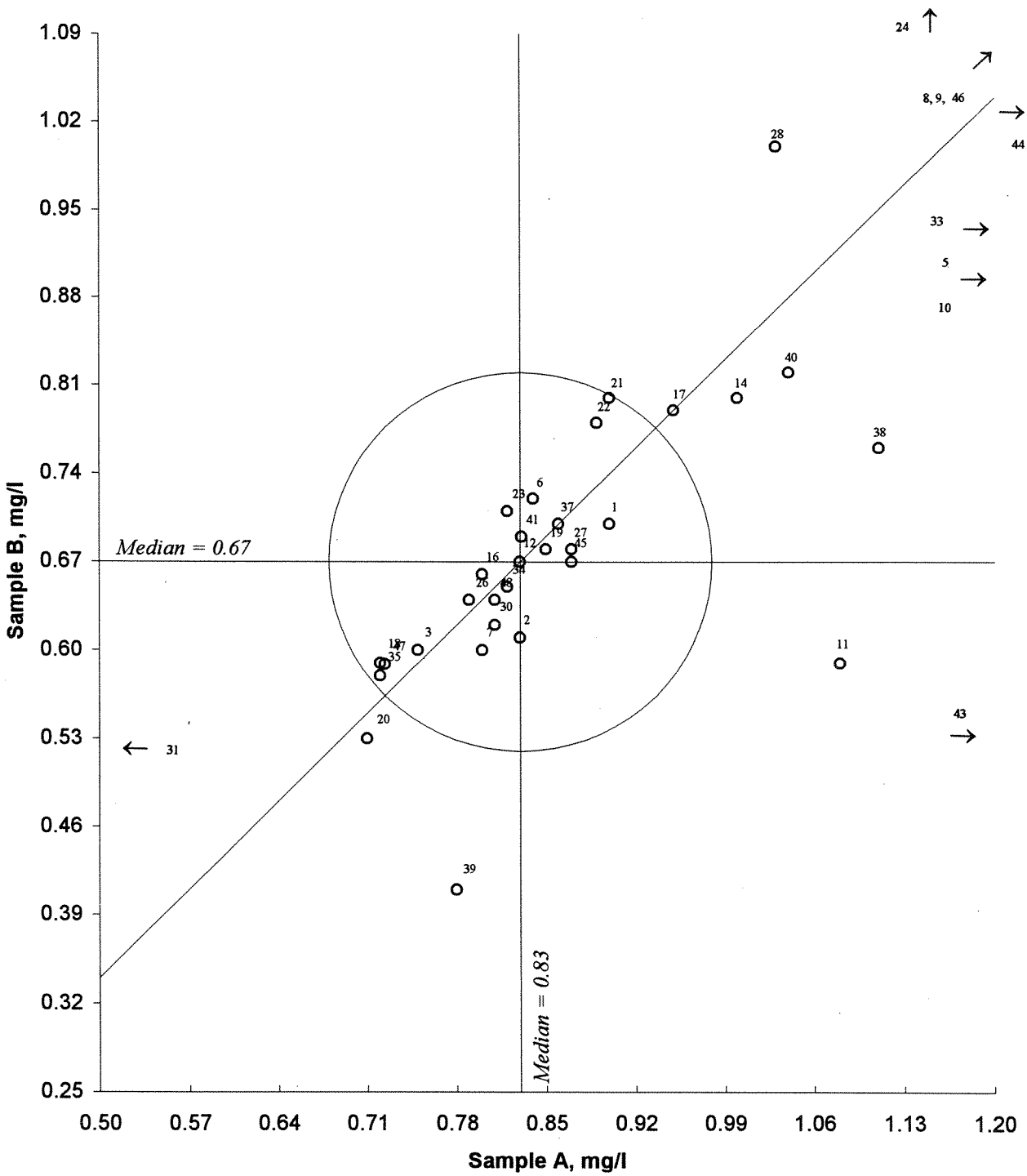

Figure 5. Youden-diagramme for chloride, sample pair AB
Acceptance criteria, given by the circle, is 20 %

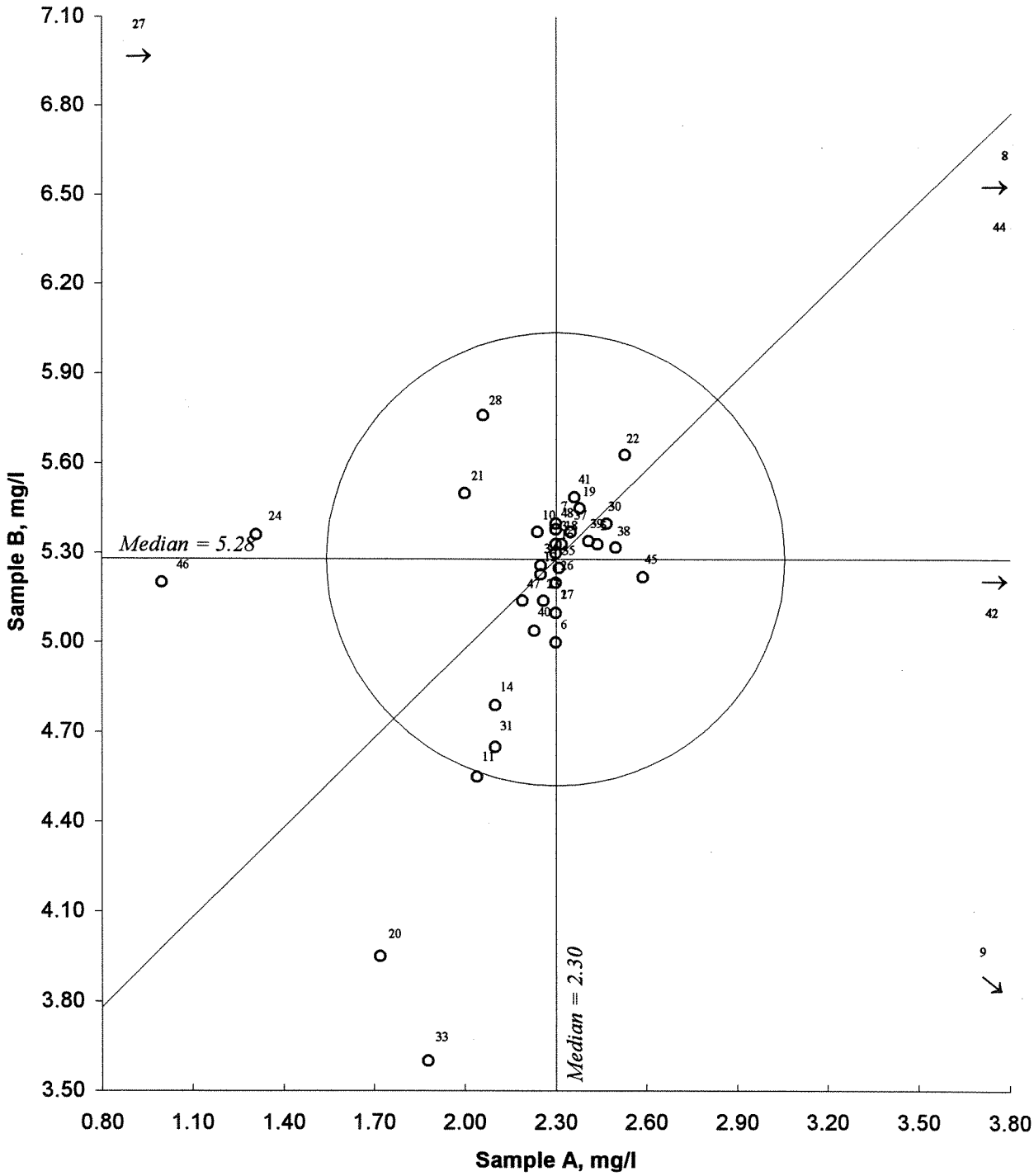

Figure 6. Youden-diagramme for sulfate, sample pair AB
Acceptance criteria, given by the circle, is 20 %

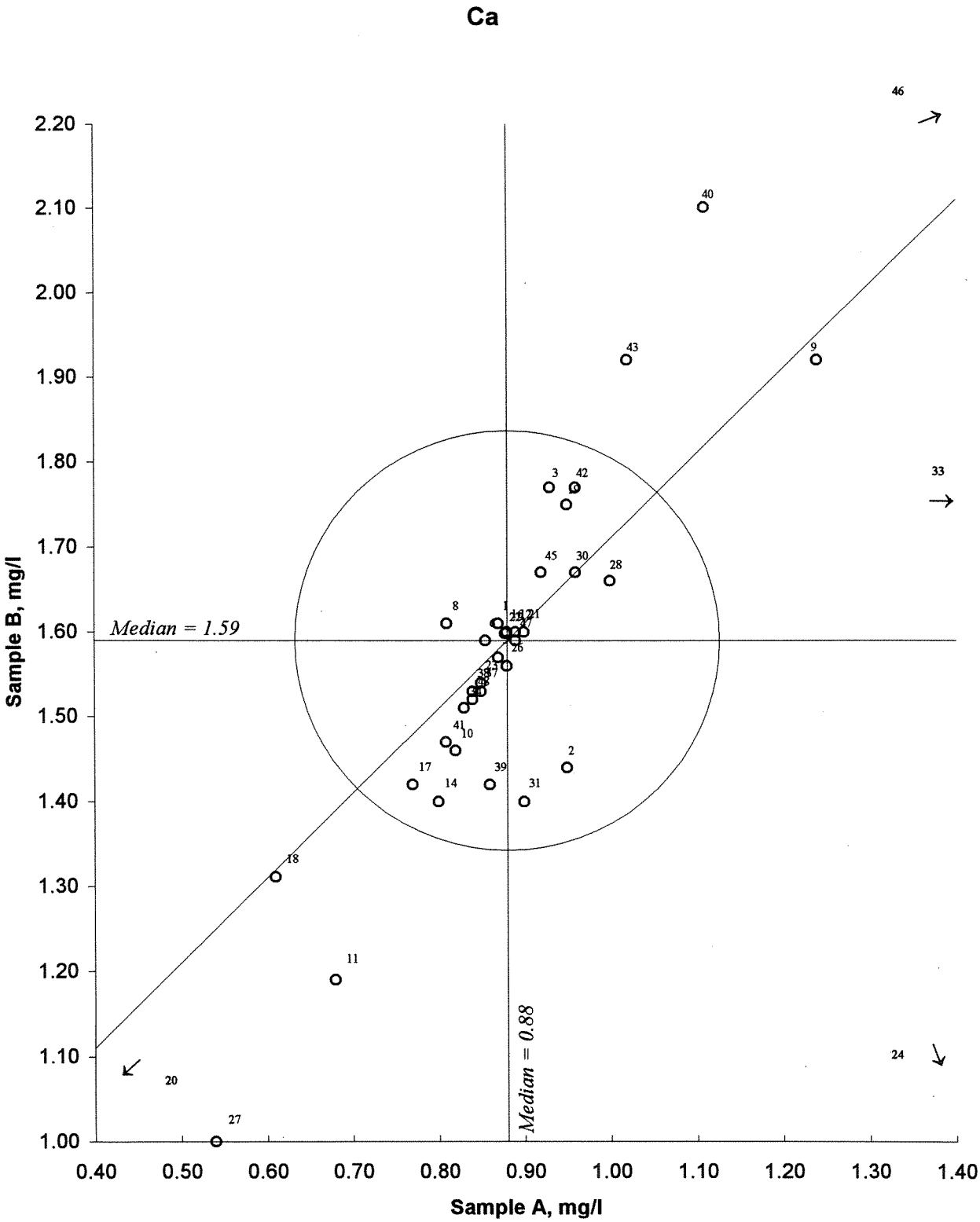

Figure 7. Youden-diagramme for calcium, sample pair AB
Acceptance criteria, given by the circle, is 20 %

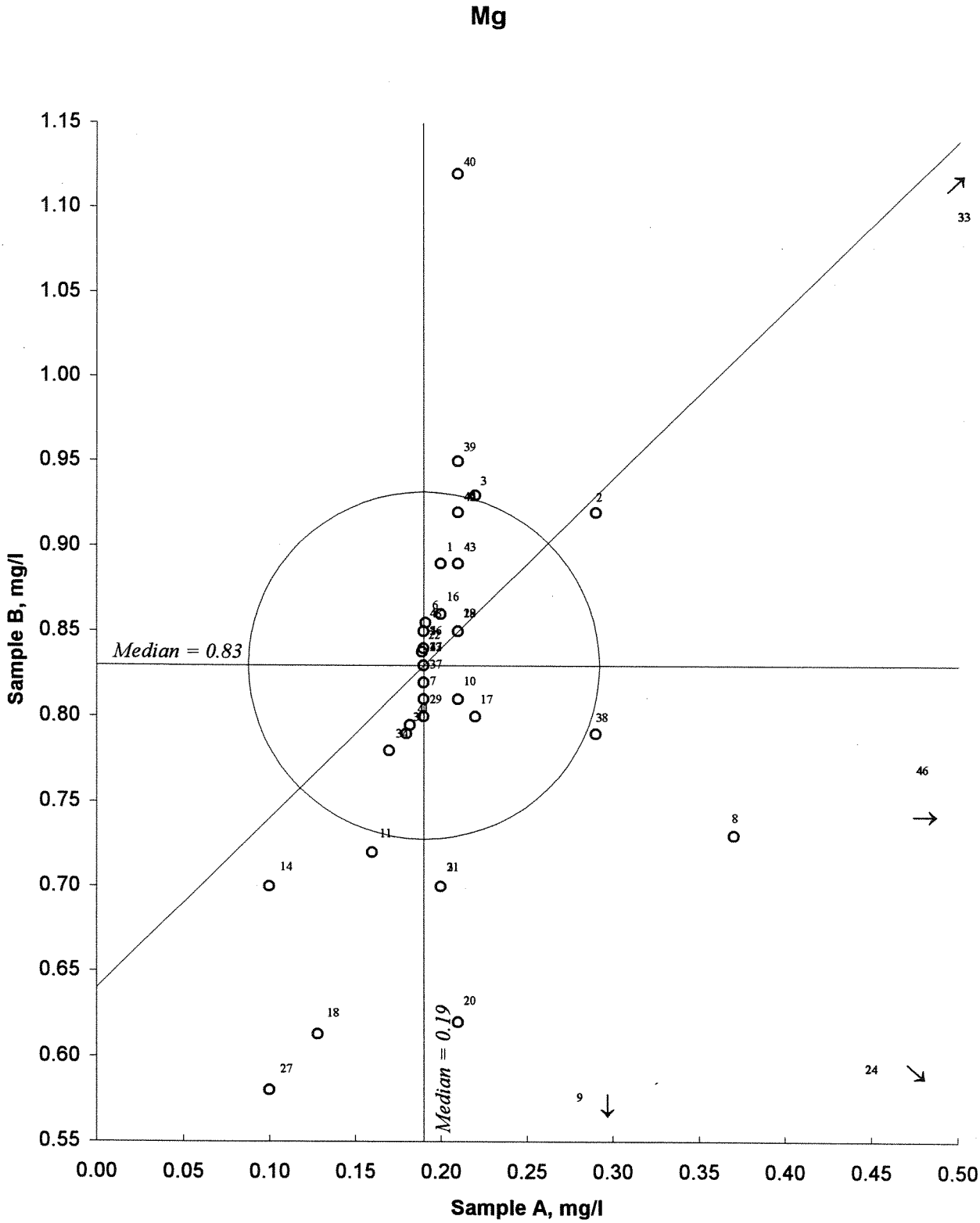

Figure 8. Youden-diagramme for magnesium, sample pair AB
Acceptance criteria, given by the circle, is 20 %

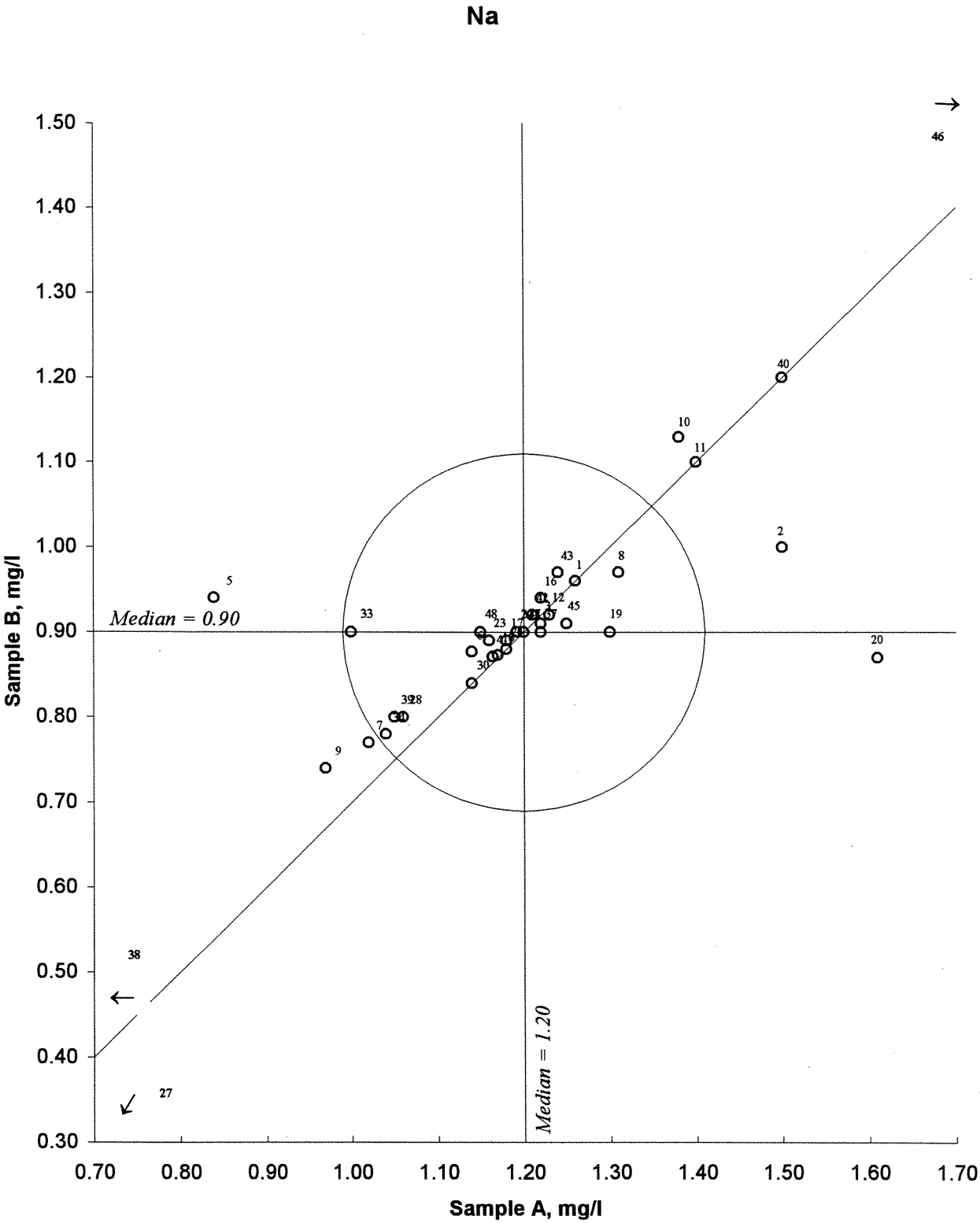

Figure 9. Youden-diagramme for sodium, sample pair AB
Acceptance criteria, given by the circle, is 20 %

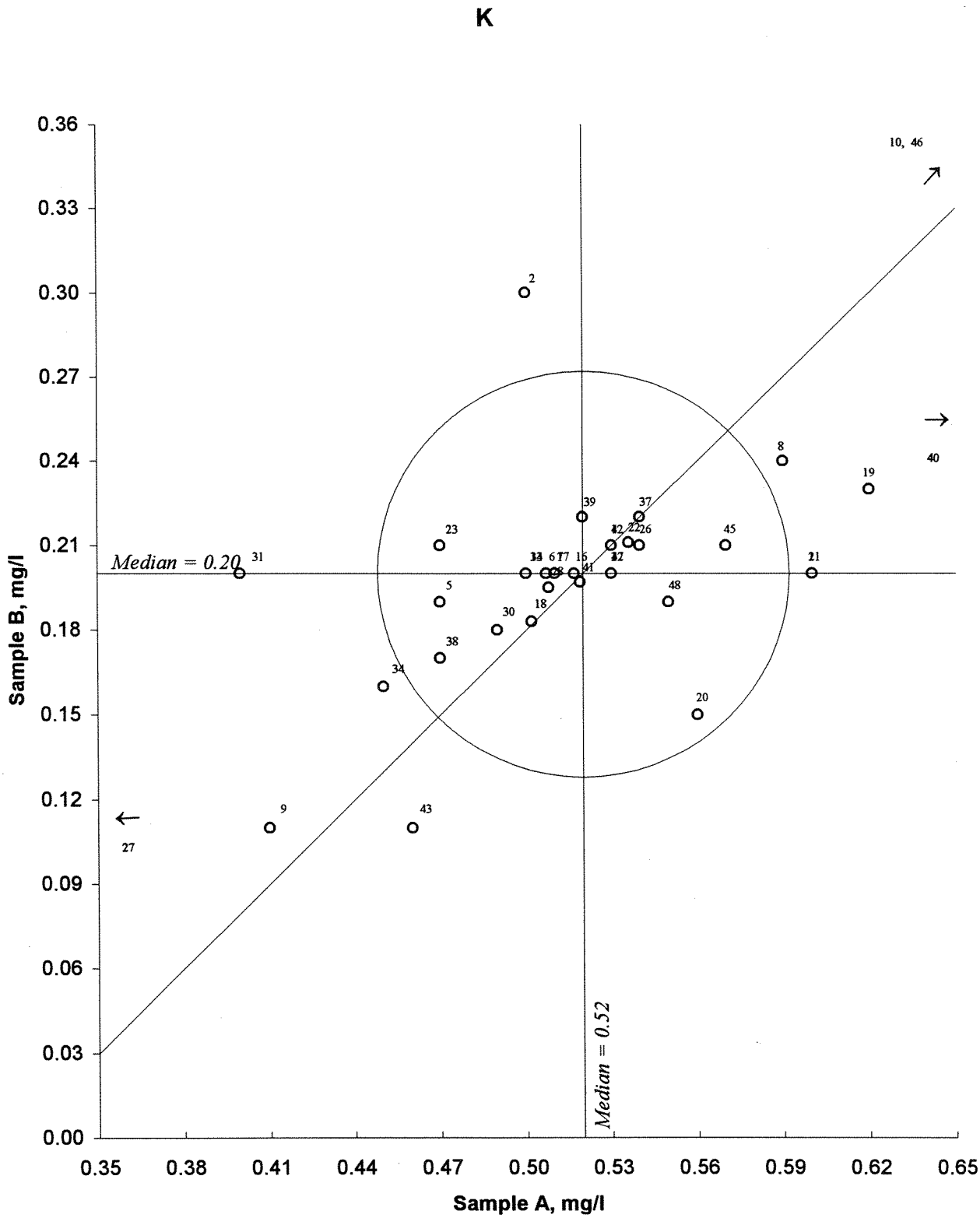

Figure 10. Youden-diagramme for potassium, sample pair AB
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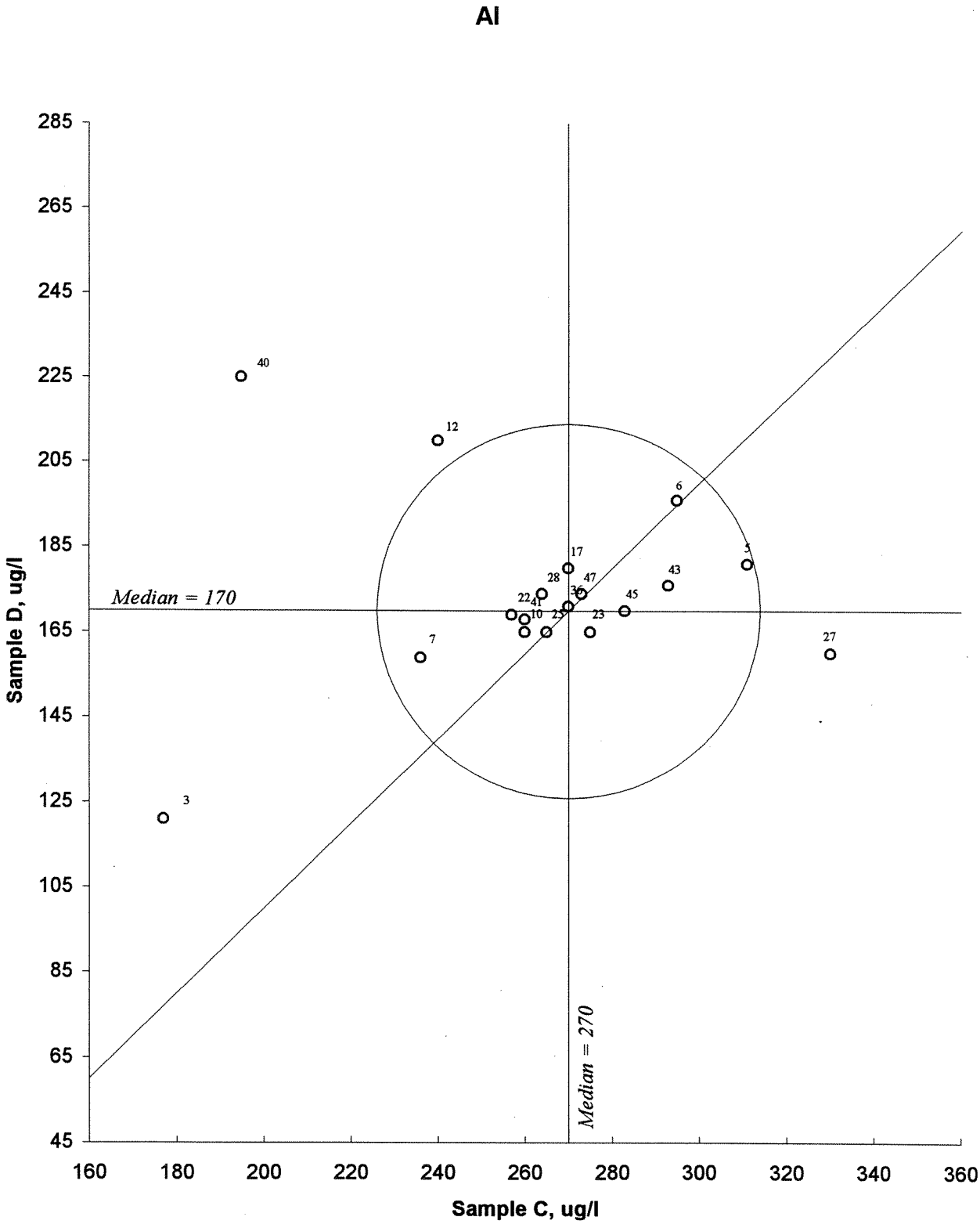

Figure 11. Youden-diagramme for aluminium, sample pair CD
Acceptance criteria, given by the circle, is 20 %

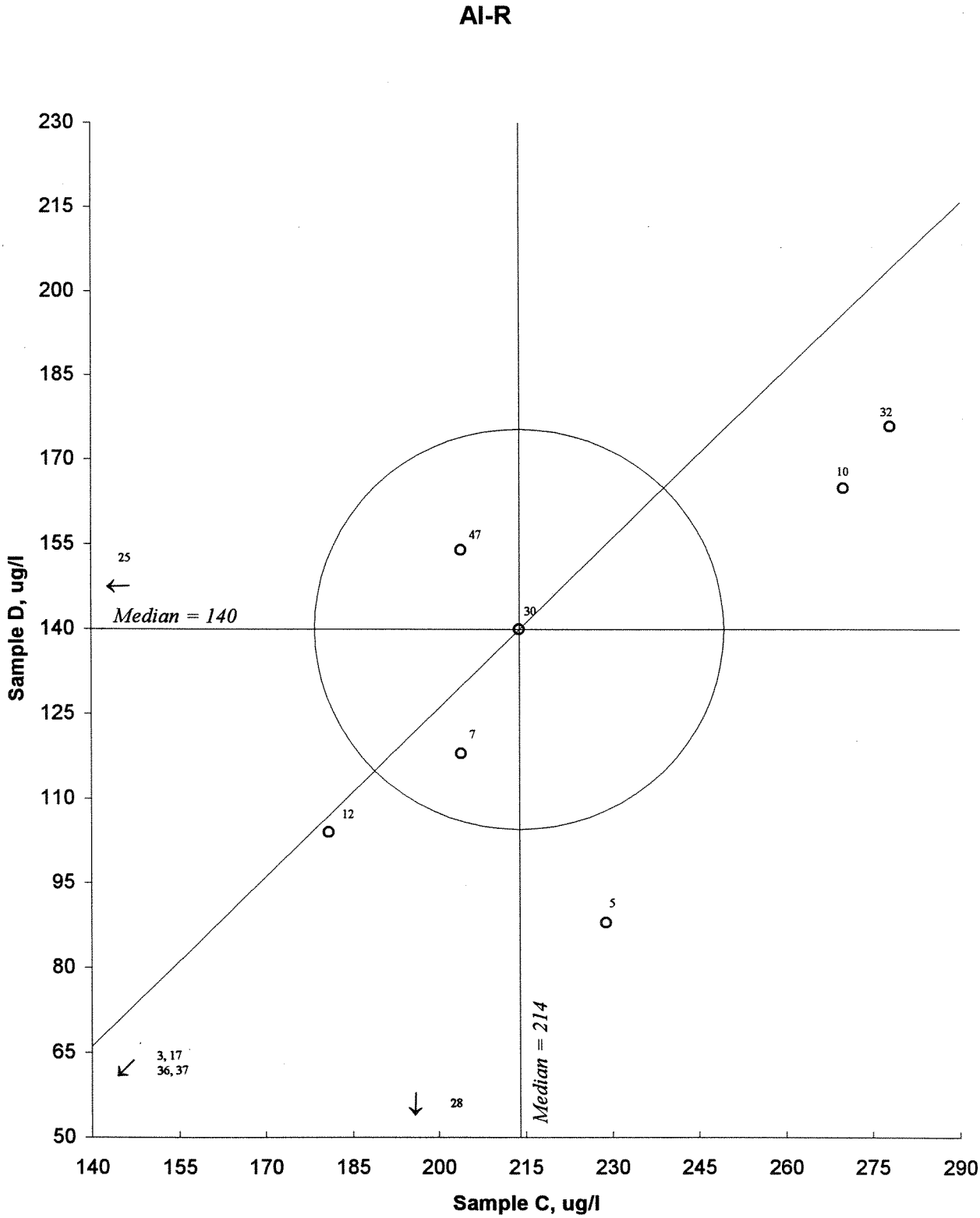

Figure 12. Youden-diagramme for aluminium, reactive, sample pair CD
Acceptance criteria, given by the circle, is 20%

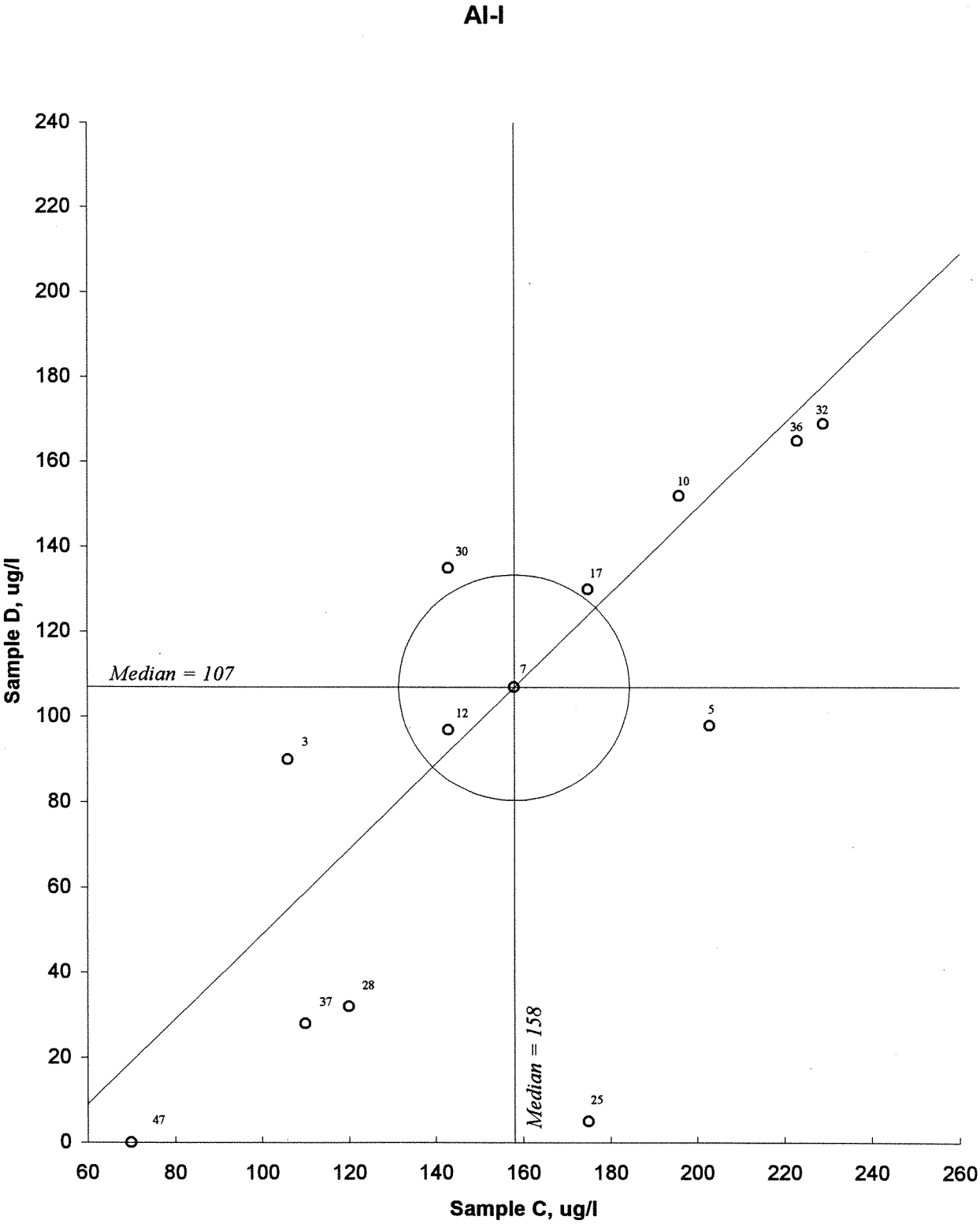

Figure 13. Youden-diagramme for aluminium, nonlabile, sample pair CD
Acceptance criteria, given by the circle, is 20%

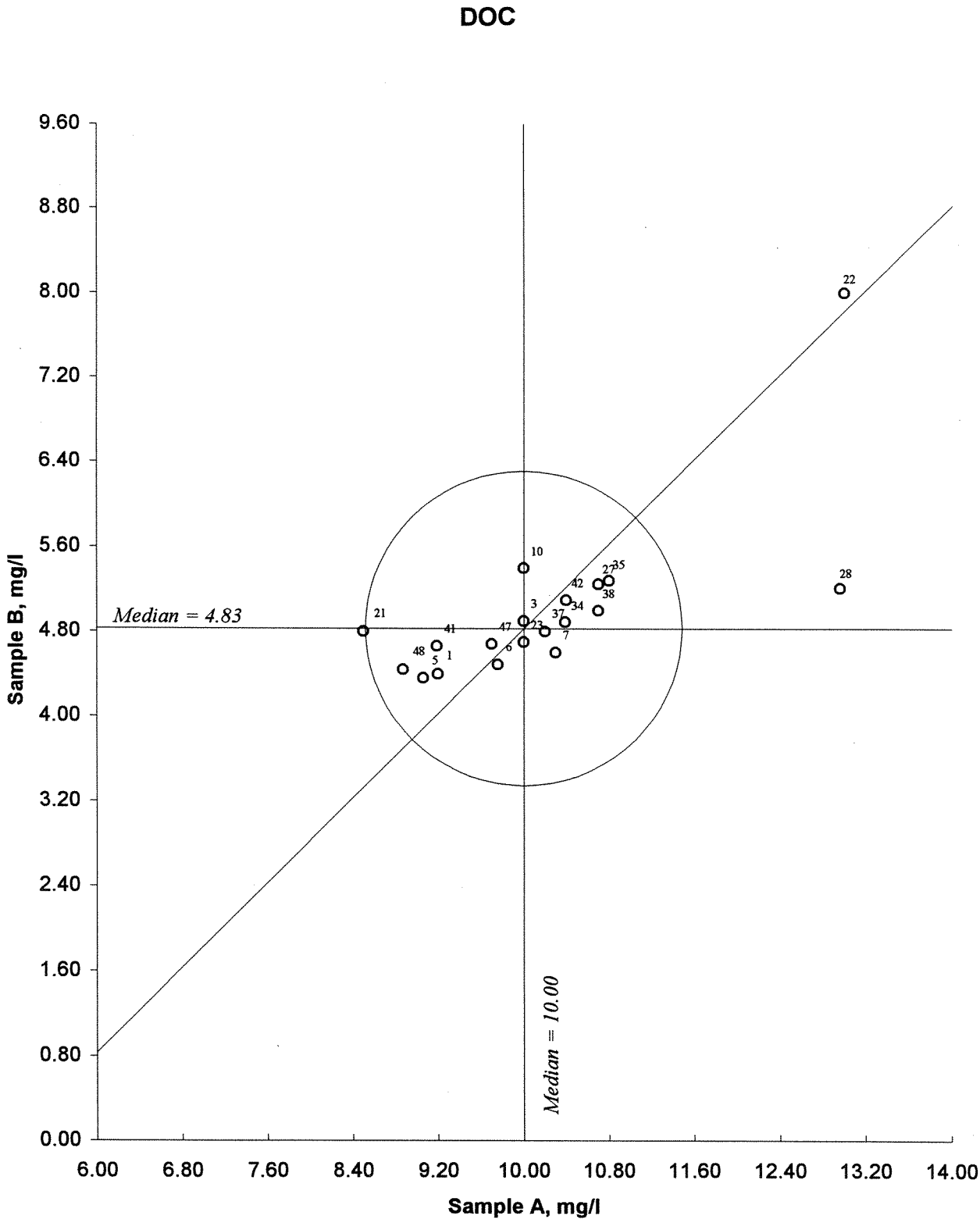

Figure 14. Youden-diagramme for dissolved organic carbon, sample pair AB
Acceptance criteria, given by the circle, is 20 %

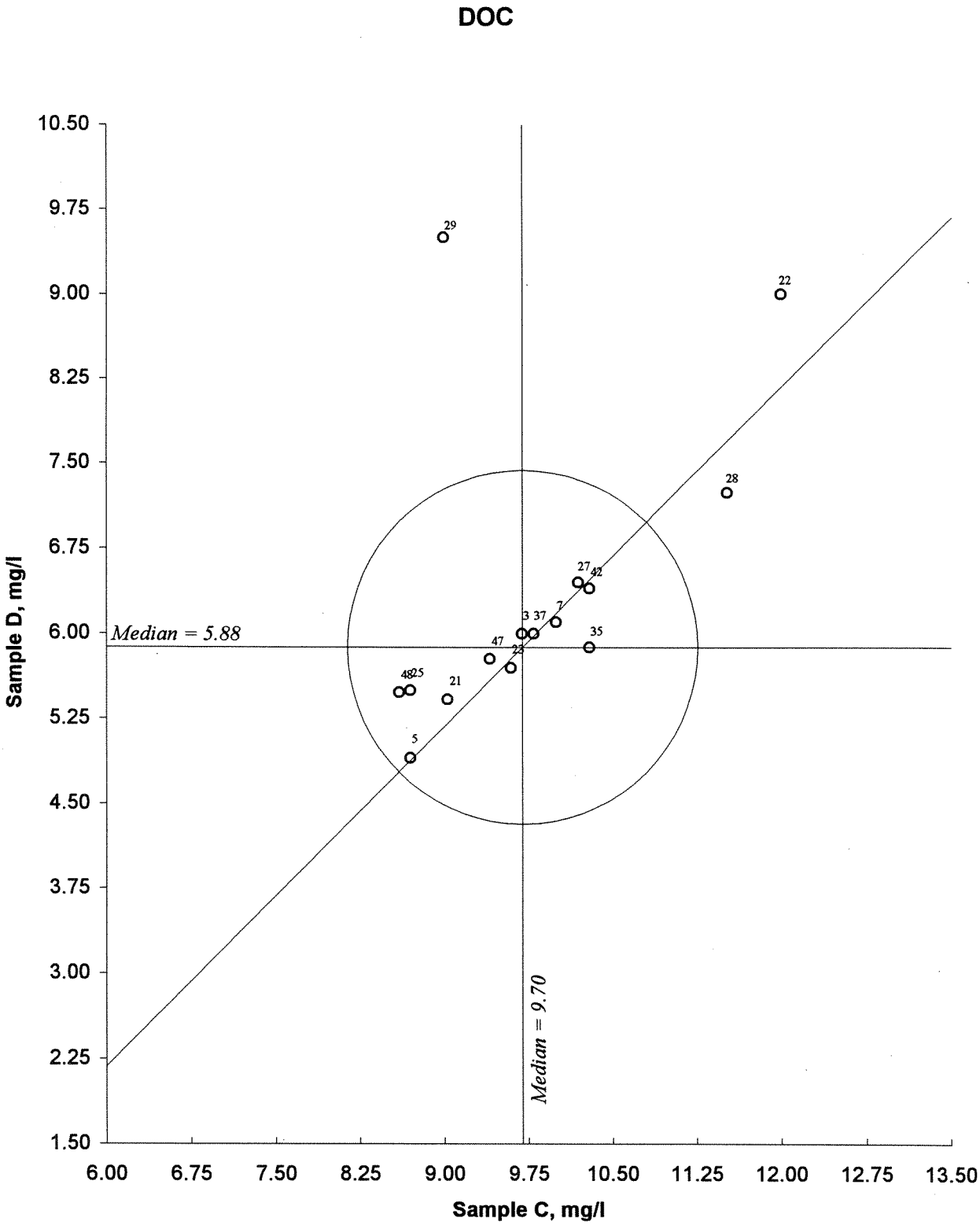

Figure 15. Youden-diagramme for dissolved organic carbon, sample pair CD
Acceptance criteria, given by the circle, is 20 %

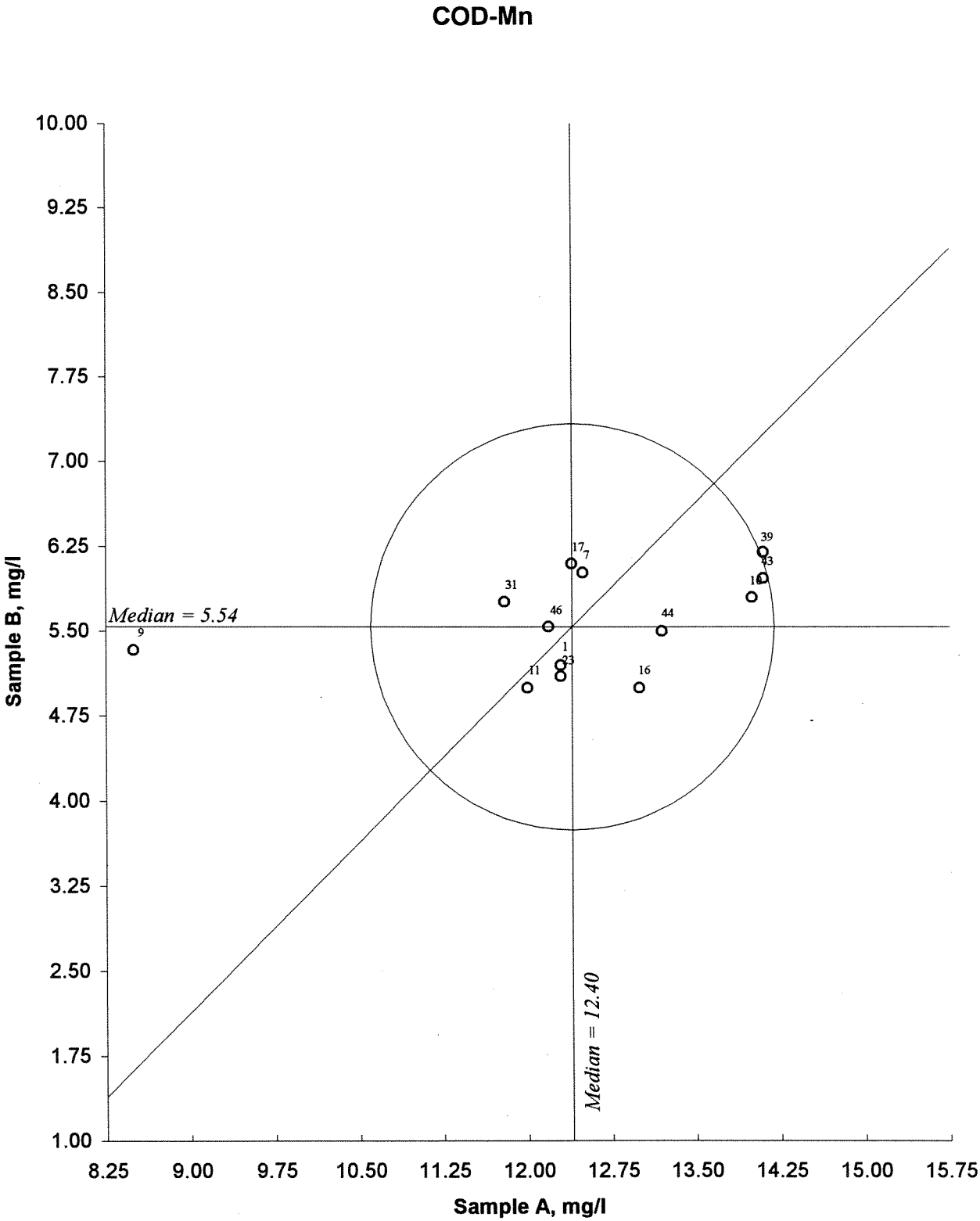

Figure 16. Youden-diagramme for chemical oxygen demand, sample pair AB
Acceptance criteria, given by the circle, is 20 %

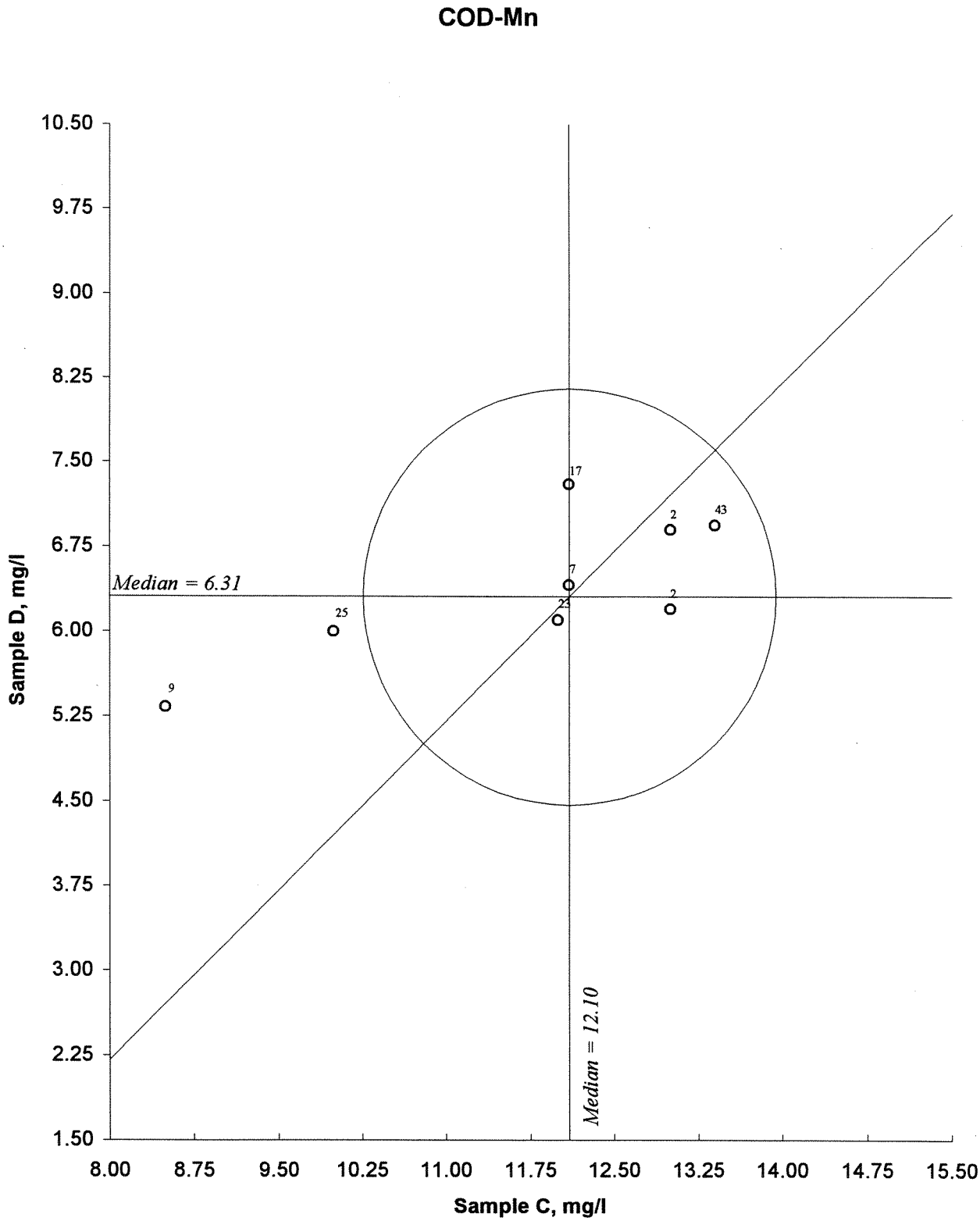

Figure 17. Youden-diagramme for chemical oxygen demand, sample pair CD
Acceptance criteria, given by the circle, is 20 %

Conductivity

The conductivity results are presented in Figure 2, where the great circle is representing an accuracy limit of ± 20 %. The reported results are given in Table 5.2 in Appendix 4. Some laboratories reported the conductivity results in the units they use routinely, instead of the requested mS/m at 25 °C. Therefore, correspondance with these participants was necessary to clarify the results. In addition, some few erratic calculations between different units were corrected. All participants used an electrometric method for the determination of conductivity.

Most laboratories achieved good agreement between the results for this variable. Four laboratories reported results being systematically too high for the sample pair AB, and three laboratories reported results being influenced by random error. Only one more result would be located outside the acceptance limit if the general target accuracy is reduced from ± 20 to ± 10 %.

Alkalinity

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 5.3 in Appendix 4. Roughly 50 % of the laboratories used the Gran plot titration method suggested in the Manual (1), and the others titrated to certain pH values. The extreme spread of alkalinity results documented by Figure 3, indicates that there must be a very wide range of methods used for determination of alkalinity, and we are not able to estimate a "correct" value for this variable. The "true" value in Figure 3 has therefore to be considered as an arbitrary value, even when it is calculated on a statistical basis.

Figure 3 demonstrates quite clearly that it is not possible to evaluate the results for alkalinity in this intercomparison, the alkalinity of the two samples being too different, and the alkalinity of sample A too close to zero. In the future, two samples with definite alkalinity different from zero have to be used, and the concentrations of the two samples should be more comparable than in this intercomparison.

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

Concerning the total fixed end-point titration to pH = 4.5, the most serious source of error is the determination of pH in dilute samples. It has been demonstrated that stirring of dilute samples may depress the pH reading (4,5). The magnitude of this effect depends both on the brand and the actual condition of the pH electrode. The error increases with time for each electrode because of the ageing of the glass membrane. Since this phenomenon is not mentioned in the description of the titration procedure, it may be assumed that most titrations are stopped at end points corresponding to readings of pH = 4.5 during stirring the solution. According to our experience, it is quite normal, even for electrodes of good quality, that pH

readings are depressed 0.1 to 0.3 units by stirring. This is corresponding to an undertitration between 0.35 and 1 mg/l as $CaCO_3$ for dilute bicarbonate solutions. For natural waters the underestimates may be even more serious because of the contribution from other buffer systems to the total fixed end-point alkalinity.

Nitrate + nitrite

The results reported for this parameter are presented in Figure 4, and the reported results are given in Table 5.4 in Appendix 4. The most common analytical method used for the determination of this parameter is photometric determination with autoanalyzer, and ion chromatography is used by an increasing number of laboratories There is no significant difference between the results determined by the two methods. However, many of the strongly deviating results are determined by manual methods.

The circle in Figure 4 is representing a general target accuracy of ± 20 %.

Chloride

The chloride results are presented in Figure 5, and the reported results are given in Table 5 (Appendix 4). A dominating number of laboratories determined chloride by ion chromatography. In addition, nine laboratories used photometric determination with the mercury thiocyanate method, and most of these laboratories used an automated version of the method. The greatest deviations are observed for the manual photometric and titrimetric methods. However, there are some ion chromatography data, too, outside the general target accuracy of ± 20 % shown in Figure 5.

Sulfate

The sulfate results are illustrated in Figure 6, and the reported values are given in Table 5.6 (Appendix 4). Most laboratories applied ion chromatography for the determination of this variable, while four laboratories used an automated photometric method based on the dissociation of the barium-thorin complex, and five laboratories used a nephelometric method. One lab determined total sulfur, and these data were recalculated to sulfate by the Programme Centre.

An accuracy limit of ± 20 % is represented by the circle in Figure 6, and 76 % of the result pairs are located within this general target accuracy. Most of the strongly deviating results are determined by manual photometric or turbidimetric methods.

Calcium

The calcium results are illustrated in Figure 7, and the reported values are given in Table 5.7 in Appendix 4. Nearly half of the participants used flame atomic absorption spectrometry for the

determination of calcium. ICP techniques and ion chromatography are used by nine and six laboratories, respectively.

A general target accuracy of ± 20 % is represented by the great circle in Figure 13 and 14. The systematic deviations are dominating all of the results being located outside the acceptance circle, indicating that the problem is attached to the method itself or the determination technique.

Magnesium

The magnesium results are presented in Figure 8, and the reported values are given in Table 5.8 in Appendix 4. Nearly half of the participants used flame atomic absorption spectrometry for the determination of magnesium. Different ICP emission spectrometry techniques and ion chromatography was used by nine and seven laboratories, respectively. Systematic deviations are dominating the results outside the target accuracy of ± 20 %, and the greatest deviations are observed for manual titrations, indicating that the concentrations of the samples used in this intercomparison are too low for this technique.

Sodium

The sodium results are presented in Figure 9, where the great circle is representing the general target accuracy of ± 20 %. The reported values are given in Table 5.9 (Appendix 4). Most laboratories used flame atomic absorption spectrometry for this determination, however, in many laboratories the emission spectrometric techniques are slowly taking over the routine determinations.

Only 71 % of the result pairs are lying within the general target accuracy of ± 20 %. Three laboratories reported results where the deviations are of random nature.

Potassium

The potassium results are presented in Figure 10. The great circle is representing a general acceptance limit of ± 20 %. The reported values are given in Table 5.10 in Appendix 4. As for sodium, most laboratories used flame atomic absorption spectrometry for the determination of this element, however, emission spectrometry is used by some of the laboratories. The deviations are mainly of systematic nature.

Total aluminium

The results for total aluminium are illustrated in Figure 11, and the reported values are given in Table 5.11 (Appendix 4). The great circle is representing the general accuracy target of ± 20 %. Most laboratories used atomic absorption spectrometry or ICP techniques for the determination of aluminium. One laboratory reported result for only one sample, however, the

results for both samples in a sample pair are necessary for the treatment of intercomparison data by the Youden technique.

79 % of the result pairs are located within the target accuracy. Three of the deviating results are probably affected by random errors. Only three of the laboratories reported results using photometric methods (autoanalyzer), the other laboratories used atomic absorption or ICP techniques.

Reactive aluminium

The results for reactive aluminium are illustrated in Figure 12, and the reported values are given in Table 5.12 (Appendix 4). Only 13 laboratories reported results for aluminium fractions, and the spread of the results are are dividing them into two main groups. The statistical treatment according to Youden, leads to the exclusion of six laboratories. All the excluded results are systematically very low. The median value used as a picture of the "true" value, therefore, has to be considered as indicative only.

The reported values for this aluminium fraction are strongly dependent on the chemical conditions in the reaction mixture. Most methods are based on the direct determination of aluminium in a non-acidified sample, preferably accomplished as soon as possible after sampling. By these methods acid is added as a part of the determination step. However, there are some methods based on acid pretreatment of the sample, then the results are dependent on how long time the acidified samples have been stored before the aluminium content is determined. Such acidification is no digestion, but it will lead to some dissolution of complexes and even of some particulate matter containing aluminium. The results are expected to increase towards an upper limit when the pretreatment time is prolonged.

Non-labile aluminium

The results for non-labile aluminium are illustrated in Figure 13, and the reported values are given in Table 5.13 (Appendix 4). Nearly half of the result pairs were excluded by the statistical treatment of the data, because of the great spread in the reported analytical values. Most laboratories have indicated that they determined non-labile aluminium according to the automated method of Røgeberg and Henriksen (6), which is based on the method of Driscoll (7). By this method non-labile aluminium is the fraction that passes through a cation exchange column, and consists of monomeric alumino-organic complexes (see Figure 18, page 42). Some of the informations given by the participants indicate that different resin forms have been used for this intercomparison, and it is well known that different resins have different exchange properties, and it is also known that the resin form will affect the results.

Therefore, for this variable too, it is difficult to evaluate the analytical results properly when the result pairs are very spread out. The main problem is the systematic deviations observed between the participating laboratories, indicating that the laboratories have applied different methods or slightly different modifications of a method.

Dissolved organic carbon

The results for this variable are presented in Figure 14 and 15, and the reported values are given in Table 5.14 and 5.15 (Appendix 4). Only 19 and 15 out of 46 laboratories determined this variable in the sample pairs AB and CD, respectively. A wet oxidation technique with UV and peroxodisulfate is used by most laboratories, however, seven and four laboratories used a combustion technique for the sample pairs AB and CD, respectively. There is no evidence for any differences in the reported results for these two methods for the samples used in this intercomparison. Two laboratories used a photometric method based on phenolphthalein.

The great circle in Figure 14 and 15 is representing a general target accuracy of ± 20 %. Only three laboratories reported results located outside this limit.

Chemical oxygen demand, COD-Mn

The results for this parameter are presented in Figure 16 and 17, and the reported values are given in Table 5.16 and 5.17 (Appendix 4). Only some few of the laboratories determined this parameter, which was included in the intercomparison because there are laboratories which do not have equipment for the determination of dissolved organic carbon. Random effects are dominating the few deviating results in Figure 16 and 17.

DISCUSSION

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

In table 2 an evaluation of the results of this intercomparison is presented, based on the target accuracy. For pH the general target accuracy is ± 0.1 pH units, and roughly 50 % of the result pairs are foud within these accuracy limits. However, we have chosen to extend the acceptance limit to ± 0.2 pH units, because of the great spread of the results for these samples which are weakly acid, and therefore are supposed not to be completely in CO_2-equilibrium. Compared to earlier intercomparisons, a larger part of the results in this intercomparison are lying inside the target accuracy of ± 0.1 pH units than last year.

In Table 2 is summarized an evaluation of the results of intercomparison 9509, where the number and percentage of acceptable results both for the general target acceptance and the selected special limits are given. 72 % of the results are acceptable when compared to the acceptance target. For these variables, on average, about one laboratory out of four is located outside the acceptance limit. By some improvement of the routine analytical method, these laboratories should obtain results with better comparablility to the others in this laboratory group.

Table 2. Evaluation of the results of intercalibration 9509. N is the number of result pairs reported, and n is the number of acceptable results within the given target accuracy.

Variable	Sample pair	N	Limit	n	%
pH	AB	41	0.2*	30	73
Conductivity	AB	40	20 %	33	83
Alkalinity	AB	(31)	20 %	(3)	-
Nitrate + nitrite-nitrogen	AB	38	20 %	27	71
Chloride	AB	41	20 %	23	56
Sulfate	AB	41	20 %	31	76
Calcium	AB	39	20 %	29	74
Magnesium	AB	40	20 %	24	60
Sodium	AB	38	20 %	27	71
Potassium	AB	38	20 %	25	66
Aluminium, total	AB	19	20 %	15	79
Aluminium, reactive	CD	(13)	20 %	(3)	-
Aluminium, non-labile	CD	(13)	20 %	(2)	-
Dissolved organic carbon	AB	19	20 %	16	84
	CD	15	20 %	12	80
Chemical oxygen demand	AB	13	20 %	11	85
	CD	8	20 %	6	75
Sum		430		309	72

* The accetance limit is extended from 0.1 to 0.2 pH units

For three variables: alkalinity, reactive and non-labile aluminium, we have decided not to evaluate the results reported by the participants, because of the very great differences between too many of the reported values. We have to use "better" samples to evaluate the results of the alkalinity determination in the future intercomparisons.

To evaluate the determination of aluminium fractions, it seems to be necessary that the laboratories normalize their analytical methods to improve the comparability for these variables. There is still existing some confusion about what aluminium fractions should be determined. The intention in this intercomparison was to compare the results for the variables printed in bold in the scheme presented in Figure 18. There have obviously been reported some results for other fractions than we asked for. This may be due to the fact that the Programme centre has chosen the definitions of aluminium species given by Driscoll (7), well aware of the possibility that other laboratories may use a slightly different definition system.

The non-exchangeable aluminium initially present in the samples of this intercomparison, is assumed to be associated with organic matter. The fact that the laboratories used different modifications and even different methods for the determination of aluminium species, may explain some of the great spread of these results.

Figure 18. Schematic representation of aluminium fractions according to Driscoll (7).

Aluminium measurement	**Total aluminium** acid digested		
	Reactive aluminium Total monomeric aluminium, no acid digestion		
	Monomeric aluminium, cation exchange treated		
Aluminium fraction	**Non-labile monomeric aluminium**	Labile monomeric aluminium	Acid soluble aluminium
Fraction composition	Monomeric alumino-organic complexes	Free aluminium, monomeric aluminiumsulfate, fluoride and hydroxide complexes	Colloidal polymeric aluminium, strong alumino-organic complexes

CONCLUSION

A total error of ± 0.2 pH units seems to be a reasonable assessment of the accuracy for pH measurements when weakly acid or neutral water samples - which is not in CO_2 equilibrium - are analyzed.

For the other analytical variables 72 % of the laboratories have reported results within the general target accuracy of ± 20 %. The laboratories which reported results outside this limit should improve their methods to obtain a better comparability. Generally, the application of manual analytical methods seem to be less suited for the kind of water samples which are analyzed in this programme, as the detection limit of many manual methods are too high. If these laboratories are going to analyze rather low concentration ICP-samples in the future, it is important that they lower the detectin limit of their methods.

To improve the comparability of the analytical results for aluminium fractions, it seems to be necessary to normalize the analytical methods and determination techniques used for these determinations, for instance to meet the definitions given in Figure 18.

When comparing the results of intercalibration 9509 with the previous one, it should be noted that the number of participating laboratories has been almost doubled from 26 to 46, and the number of participating countries increased frm 17 to 21. The overall result shows that the part of acceptable result pairs decreased from 81 to 72 %. It was expected that a marked increase in the number of participating laboratories would lead to a decrease of acceptable results, as it usually takes som time to evaluate the analytical methods in relation to this specific programme, and maybe, other standardized or normalized methods should be used for these samples.

LITERATURE

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APPENDIX I. Participants of intercomparison 9509

No.	Laboratory	Country
1	Bayerisches Landesamt für Wasserwirtschaft, München	Germany
2	South Estonian Environmental Protection Agency, Tartu	Estonia
3	DAFS Freshwater Laboratory, Pitlochry	Scotland
5	National Rivers Authority, Llanelli	Great Britain
6	Landesumweltamt Nordrhein Westfalen, Essen	Germany
7	Norwegian Institute for Water Research, Oslo	Norway
8	Water Pollution Observation Laboratory, Riga	Latvia
9	Research and Engineering Institute for Environment, Bucharest	Romania
10	KM-Lab, Halmstad	Sweden
11	Estonian Environment Research Laboratory, Tallinn	Estonia
12	Czech Geologic Survey Prague	Czech Republic
14	Werkgroep Milieubiologie, Nijmegen	Netherlands
15	US Environmental Protection Agency, Corvallis	USA
16	Geological Survey of Finland, Espoo	Finland
17	Kola Science Center, Apatity	Russia
18	Environmental Research Unit, Dublin	Ireland
19	CNR Istituto Italiano di Idrobiologia, Pallanza	Italy
20	Polish Academy of Sciences, Krakow	Poland
21	Kärntner Institut für Seewasser Forschung, Klagenfurt	Austria
22	Institute of Environmental Protection, Warsawa	Poland
23	Swedish University for Agricultural Sciences, Uppsala	Sweden
24	Institute of Global Climate and Ecology, Moscow	Russia
25	SWELAB Environmental Laboratories, Kalmar	Sweden
26	Uusima Regional Environmental Centre, Helsinki	Finland
27	Institute of Hydrobiology, Budejovice	Czech Republic
28	ITMm Stockholm University, Solna	Sweden
29	National Environmental Research Institute, Silkeborg	Denmark
30	Charles University, Prague	Czech Republic
31	Lapland Water and Environment District, Rovaniemi	Finland
32	Länsstyrelsen i Kalmar Län, Kalmar	Sweden
33	Institute for Ecological Toxicology, Baikal	Russia
34	Adirondac Lakes Survey Corporation, Raybrook	USA
35	Aquatic Chemistry Project, Winnipeg	Canada
36	Länsstyrelsen i Kronobergs Län, Vaxjö	Sweden
37	National Board of Waters and the Environment, Helsinki	Finland
38	University of Alberta, Edmonton	Canada
39	Institute for Ecology of Industrial Areas, Katowice	Poland
40	Bayerisches Landesamt für Wasserwirtschaft, Wielenbach	Germany
41	Great Lakes Forest Centre, Sault Ste. Marie	Canada
42	Institut für Zologie, Universität Innsbruck,	Austria
43	T.G.Masaryk Water Research Institute, Prague	Czech Republic
44	Kymen Water and Environment District, Kouvola	Finland
45	Swiss Federal Institute for Forest, Birmensdorf	Switzerland
46	Environmental Protection Ministry, Vilnius	Lithuania
47	University of Maine, Orono	USA
48	Centre National de la Recherche Scientifique, Strasbourg	France

APPENDIX 2

Preparation of samples

The sample solutions were prepared from natural water collected at two locations in the Langtjern area. Raw water was collected in polyethylene containers and brought to the laboratory for storage.

For sample A was used the water from a creek called Langtjernelva, and sample B was prepared from water from a lake called Buvatn. These solutions were stored at room temperature for several weeks at the laboratory. During this stabilization period suspended matter settled. The solutions were filtrated through 0.45 µm membrane filter, and small aliquouts were removed from the filtrate to determine the concentrations of the parameters of interest.

A few days before mailing to the participants, the solutions were transferred to 1/2 liter (and some few 1 liter) polyethylene bottles with screw cap. These samples were stored at room temperature until mailing to the participating laboratories.

Table 3. Summary of the control analyses.

Parameter	Sample A		Sample B		Sample C		Sample D	
	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.
pH	5.10	0.017	6.10	0.019				
Conductivity mS/m	1.77	0.015	2.24	0.025				
Alkalinity mmol/l	0.58	0.13	1.43	0.05				
Nitrate/nitrite µg/l	57.3	2.1	159	2.5				
Chloride mg/l	0.88	0.10	0.65	0.06				
Sulfate mg/l	2.33	0.05	5.35	0.06				
Calcium mg/l	0.88	0.02	1.57	0.06				
Magnesium mg/l	0.18	0.005	0.80	0.013				
Sodium mg/l	1.15	0.11	0.88	0.10				
Potassium mg/l	0.51	0.008	0.20	0.006				
Aluminium total, µg/l					280	22	170	9.7
Reactive aluminium µg/l					190	10	109	5.9
Non-labile alumin. µg/l					148	9.0	102	3.5
Diss.org. C mg/l	9.55	0.33	4.73	0.15	9.50	0.36	5.83	0.25
COD.Mn, mg/l	12.93	0.45	5.44	0.51	12.33	0.25	6.26	0.24

Sample control analyses

During the intercalibration period, three sets of samples were randomly selected from the batch for control analyses. The determinations were carried out by the laboratory at the Programme Centre, the first sample set being analyzed some days before mailing of the samples to the participants. The last sample was analyzed at the middle of July 1995. A summary of the control results is presented in Table 3. The control results confirmed that the stability of the sample solutions were acceptable during the intercalibration period.

APPENDIX 3

Treatment of analytical data

The intercalibration was carried out by the method of Youden. This procedure requires two samples to be analyzed, and every laboratory shall report only one result for each sample and parameter. In a coordinate system the result of sample 2 is plotted against the result of sample 1 (see Figures 1 - 17).

The graphical presentation creates a possibility to distinguish between random and systematic errors affecting the results. The two stright lines drawn in the diagram are representing the true values of the samples; or - as in this case, when the true value is not known - the median value of the results from all the participating laboratories. The diagram is thus divided into four quadrants. In a hypothetical case, when the analysis is affected by random errors only, the results will spread randomly over the four quadrants.

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

The acceptance limit of the results may be represented by a circle with its centrum at the intersection of the two straight lines in the diagram (true or median values). The distance between the centrum of the circle, and the mark representing the laboratory, is a measure of the total error of the results. The distance along the 45 ° line is giving the mangitude of the systematic error, while the distance perpendicular to the 45 ° line is indicating the magnitude of the random error. The location of the laboratory in the diagram is an important information about the size and type of analytical error, making it easier to disclose the cause of error.

The statistical treatment of the analytical results was accomplished in this way: Pairs of results where one or both of the values are lying outside the true value ± 50 %, are omitted from the statistical calculations. The remaining results are used for the calculation of the mean value (x) and the standard deviation (s). Now the pairs of results where both of the values are lying outside $x \pm 3s$, are omitted. The remaining results are used for a final calculation, the results of which are presented in the tables 5.1 - 5.17. Results being omitted from the calculations, are marked with the letter "U".

APPENDIX 4 **Table 4. The results reported by the participants.**

Identity	pH A	pH B	Cond A	Cond B	Alk A	Alk B	NO3+NO A	NO3+NO B
1	5.20	6.20	1.70	2.20	3.15	4.45	71	160
2	5.06	6.08	1.87	2.37	2.6	2.8	50	130
3	5.11	6.07	1.80	2.40	-0.05	1.05	57	159
5	5.11	6.10	1.87	2.19	0.02	1.07	59.8	184.5
6	5.10	6.10	1.73	2.35	< 10	< 10	50	150
7	5.20	6.09	1.76	2.31	0.4	1.4	57	160
8	5.10	6.05	1.79	2.42			55.2	181.2
9	4.91	5.76	1.60	1.95	6	6	13.65	4.98
10	5.05	6.11	5.80	6.90	< 1	2.79	54	160
11	5.10	6.10	1.80	2.30	2.0	3.4	70	160
12	5.09	6.08	1.80	2.34	0.55	1.65	< 68	160
14	4.96	5.90	1.88	1.88	2.8	3.7	56	154
15	5.20	6.24	1.74	2.30	0.03	1.14		
16	5.10	6.20	1.80	2.30	1.8	2.6	65	160
17	5.02	6.02	1.80	2.40	0	1	51	162
18	5.06	6.06	5.30	5.70			59.5	158.5
19	5.07	6.09	1.89	2.37	0.0	1.1	55	152
20	4.62	5.51	1.84	2.33				
21	4.55	5.61	2.31	2.60	2.05	8.5		
22	5.20	6.14	1.80	2.50			87.8	171.6
23	5.08	6.07	1.87	2.43	-0.65	0.85	57	150
24	5.10	6.10			< 0.1	1.22	36	70
25								
26	5.17	6.15	1.80	2.35			56.7	155
27	5.09	5.97	1.76	2.37	0.15	1.2	58	161
28	5.11	6.02	1.79	2.35	< 0.01	1.16	60	160
29	5.11	6.15	1.72	2.25	0	1.05		
30	5.03	5.89	1.80	2.35	0.02	1.17	61	159
31	5.15	6.03	1.80	2.40	0.34	0.8	55	156
32								
33					< 10	< 10	36	41
34	5.08	6.11	1.76	2.29	0.29	1.33	58.7	155.9
36								
37	5.07	6.01	1.82	2.38			57	156.3
38	5.07	5.96	1.90	2.30	2.38	3.25	55.9	155.1
39	5.20	6.08	2.02	2.31			45.9	138
40	3.80	5.00	1.90	2.30			310	640
41	4.99	5.94	1.72	2.24	0.08	1.06	58	154
43	4.55	5.66	1.90	2.20	3.0	8.0	488	334
44	5.16	5.68	1.84	2.35	0.036	1.139	59	158
45	5.13	6.03	2.58	3.42			62.3	151
46							55	115
47	5.08	6.01	1.76	2.28	0.15	1.165	56.2	155

Identity	Cl A	Cl B	SO4 A	SO4 B	Ca A	Ca B	Mg A	Mg B
1	0.90	0.70	2.3	5.1	0.87	1.61	0.20	0.89
2	0.83	0.61	2.3	5.1	0.95	1.44	0.29	0.92
3	0.75	0.60	2.3	5.33	0.93	1.77	0.22	0.93
5	1.376	0.885	2.44	5.33	0.87	1.57	0.19	0.84
6	0.84	0.72	2.3	5.0	0.855	1.59	0.191	0.855
7	0.8	0.6	2.3	5.4	0.89	1.59	0.19	0.81
8	1.80	1.40	6.2	6.6	0.81	1.61	0.37	0.73
9	42.60	27.70	4.8	1.84	1.24	1.92	0.3	0
10	1.75	0.88	2.24	5.37	0.82	1.46	0.21	0.81
11	1.08	0.59	2.04	4.55	0.68	1.19	0.16	0.72
12	0.83	0.67	2.25	5.23	0.89	1.60	0.19	0.83
14	1.0	0.8	2.1	4.79	0.8	1.4	0.10	0.70
15								
16	0.80	0.66	2.3	5.3	0.88	1.60	0.20	0.86
17	0.95	0.79	2.3	5.1	0.77	1.42	0.22	0.80
18	0.72	0.59	2.32	5.33	0.61	1.311	0.13	0.61
19	0.85	0.68	2.38	5.45	0.95	1.75	0.21	0.85
20	0.71	0.53	1.72	3.95	0.37	0.72	0.21	0.62
21	0.9	0.8	2.0	5.5	0.9	1.6	0.2	0.7
22	0.89	0.78	2.53	5.63	0.878	1.598	0.19	0.84
23	0.82	0.71	2.26	5.14	0.85	1.54	0.19	0.83
24	1.15	1.15	1.31	5.36	1.60	0.12	1.6	0.15
25								
26	0.79	0.64	2.3	5.2	0.88	1.56	0.19	0.84
27	0.87	0.68	< 5	6.9	0.54	1	0.1	0.58
28	1.03	1.00	2.06	5.76	1.00	1.66	0.21	0.85
29							0.19	0.80
30	0.81	0.62	2.47	5.4	0.96	1.67	0.18	0.79
31	0.45	0.50	2.10	4.65	0.90	1.40	0.20	0.70
32								
33	1.44	0.91	1.88	3.6	2.20	1.76	2.06	0.75
34	0.82	0.65	2.25	5.26	0.83	1.51	0.17	0.78
36								
37	0.86	0.70	2.35	5.37	0.85	1.53	0.19	0.82
38	1.11	0.76	2.50	5.32	0.84	1.53	0.29	0.79
39	0.78	0.41	2.41	5.34	0.86	1.42	0.21	0.95
40	1.04	0.82	2.23	5.04	1.11	2.10	0.21	1.12
41	0.831	0.690	2.362	5.488	0.809	1.47	0.182	0.795
43	1.24	0.53	2.5	2.5	1.02	1.92	0.21	0.89
44	1.32	1.03	4.88	6.5				
45	0.87	0.67	2.59	5.22	0.92	1.67	0.21	0.92
46	1.50	1.17	1.0	5.2	8.80	4.60	3.90	0.73
47	0.724	0.589	2.19	5.14	0.89	1.59	0.19	0.83

Identity	Na A	Na B	K A	K B	Al A	Al B	Al C	Al D
1	1.26	0.96	0.53	0.21				
2	1.5	1.0	0.5	0.3				
3	1.22	0.91	0.53	0.20			177	121
5	0.84	0.94	0.47	0.19			311	181
6	1.140	0.877	0.507	0.200			295	196
7	1.02	0.77	0.51	0.20			236	159
8	1.31	0.97	0.59	0.24				
9	0.97	0.74	0.41	0.11				
10	1.38	1.13	1.25	0.779			260	165
11	1.4	1.1	0.6	0.2				
12	1.23	0.92	0.53	0.20			240	210
14	1.2	0.9	0.5	0.2				
15								
16	1.22	0.94	0.517	0.200				
17	1.18	0.89	0.51	0.20			270	180
18	1.170	0.873	0.502	0.183				
19	1.30	0.90	0.62	0.23				
20	1.61	0.87	0.56	0.15				
21	1.2	0.9	0.6	0.2			286.6	
22	1.192	0.900	0.536	0.211			257	169
23	1.16	0.89	0.47	0.21			275	165
24								
25							265	165
26	1.18	0.88	0.54	0.21				
27	0.40	0.08	0.32	0.11			330	160
28	1.06	0.80	0.51	0.20			264	174
29								
30	1.14	0.84	0.49	0.18				
31	1.20	0.90	0.40	0.20				
32								
33	1.00	0.90	0.50	0.20				
34	1.04	0.78	0.45	0.16				
36							270	171
37	1.22	0.90	0.54	0.22				
38	0.54	0.45	0.47	0.17				
39	1.05	0.80	0.52	0.22				
40	1.5	1.2	0.8	0.3			195	225
41	1.16	0.87	0.52	0.20			260	168
43	1.24	0.97	0.46	0.11			293	176
44								
45	1.25	0.91	0.57	0.21			283	170
46	3.0	1.5	1.5	0.5				
47	1.20	0.90	0.53	0.20			273	174

Identity	Al-R C	Al-R D	Al-I C	Al-I D	DOC A	DOC B	DOC C	DOC D
1					9.2	4.4		
2								
3	71	31	106	90	10.0	4.9	9.7	6.0
5	229	88	203	98	9.06	4.36	8.7	4.9
6					9.76	4.49		
7	204	118	158	107	10.3	4.6	10.0	6.1
8								
9								
10	270	165	196	152	10	5.4		
11								
12	181	104	143	97				
14								
15								
16								
17	95	50	175	130				
18								
19								
20								
21					8.50	4.80	9.03	5.42
22					13	8	12	9
23					10.0	4.7	9.6	5.7
24								
25	90	145	175	5			8.7	5.5
26								
27					10.7	5.25	10.2	6.45
28	197	39	120	32	12.96	5.21	11.52	7.24
29							9.0	9.5
30	214	140	143	135				
31								
32	278	176	229	169				
33								
34					10.39	4.89		
36	47	6	223	165				
37	158	38	110	28	10.2	4.8	9.8	6.0
38					10.7	5.00		
39								
40								
41					9.187	4.661		
43								
44								
45								
46								
47	204	154	70	0	9.70	4.68	9.41	5.78

Identity	COD-Mn A	COD-Mn B	COD-Mn C	COD-Mn D
1	12.3	5.2		
2	1.3	6.2	13	6.9
3				
5				
6				
7	12.5	6.02	12.1	6.41
8				
9	8.5	5.33	8.5	5.33
10	14	5.8		
11	12.0	5.0		
12				
14				
15				
16	13	5		
17	12.4	6.1	12.1	7.3
18				
19				
20				
21				
22				
23	12.3	5.1	12.0	6.1
24				
25			10	6
26				
27				
28				
29				
30				
31	11.8	5.76		
32				
34				
36				
37				
38				
39	14.1	6.2		
40				
41				
43	14.1	5.97	13.4	6.94
44	13.2	5.50		
45				
46	12.19	5.54		
47				

Table 5.1. Statistics - pH

Analytical method: All
Unit:

Sample A

Number of participants	41	Range	0.65
Number of omitted results	2	Variance	0.02
True value	5.09	Standard deviation	0.15
Mean value	5.05	Relative Standard deviation	3.00 %
Median value	5.09	Relative error	-0.70 %

Analytical results in ascending order:

40	3.80 U	48	5.07	5	5.11
21	4.55	42	5.07	3	5.11
43	4.55	19	5.07	28	5.11
20	4.62	47	5.08	45	5.13
9	4.91	23	5.08	31	5.15
14	4.96	34	5.08	44	5.16
41	4.99	27	5.09	26	5.17
17	5.02	12	5.09	15	5.20
30	5.03	16	5.10	39	5.20
10	5.05	6	5.10	1	5.20
18	5.06	11	5.10	7	5.20
2	5.06	8	5.10	22	5.20
38	5.07	24	5.10	35	6.03 U
37	5.07	29	5.11		

Sample B

Number of participants	41	Range	0.73
Number of omitted results	2	Variance	0.03
True value	6.07	Standard deviation	0.17
Mean value	6.01	Relative Standard deviation	2.80 %
Median value	6.07	Relative error	-1.10 %

Analytical results in ascending order:

40	5.00 U	17	6.02	6	6.10
20	5.51	28	6.02	11	6.10
21	5.61	31	6.03	5	6.10
43	5.66	45	6.03	24	6.10
44	5.68	8	6.05	10	6.11
9	5.76	18	6.06	34	6.11
48	5.78	3	6.07	22	6.14
30	5.89	23	6.07	29	6.15
14	5.90	42	6.08	26	6.15
41	5.94	39	6.08	16	6.20
38	5.96	12	6.08	1	6.20
27	5.97	2	6.08	15	6.24
37	6.01	19	6.09	35	6.75 U
47	6.01	7	6.09		

U = Omitted results

Table 5.2. Statistics - Conductivity

Analytical method: All
Unit: mS/m

Sample A

Number of participants	40	Range	1.01
Number of omitted results	3	Variance	0.02
True value	1.80	Standard deviation	0.14
Mean value	1.81	Relative Standard deviation	7.70 %
Median value	1.80	Relative error	0.40 %

Analytical results in ascending order:

35	1.30	17	1.80	23	1.87
9	1.60	30	1.80	2	1.87
1	1.70	16	1.80	14	1.88
29	1.72	11	1.80	19	1.89
41	1.72	3	1.80	38	1.90
6	1.73	22	1.80	43	1.90
15	1.74	12	1.80	40	1.90
27	1.76	31	1.80	39	2.02
7	1.76	26	1.80	21	2.31
47	1.76	48	1.81	45	2.58 U
34	1.76	37	1.82	18	5.30 U
42	1.79	44	1.84	10	5.80 U
8	1.79	20	1.84		
28	1.79	5	1.87		

Sample B

Number of participants	40	Range	0.72
Number of omitted results	3	Variance	0.02
True value	2.34	Standard deviation	0.13
Mean value	2.32	Relative Standard deviation	5.60 %
Median value	2.34	Relative error	-0.80 %

Analytical results in ascending order:

14	1.88	42	2.31	17	2.40
9	1.95	39	2.31	3	2.40
5	2.19	7	2.31	31	2.40
43	2.20	20	2.33	8	2.42
1	2.20	12	2.34	23	2.43
41	2.24	30	2.35	48	2.45
29	2.25	6	2.35	22	2.50
47	2.28	44	2.35	35	2.50
34	2.29	28	2.35	21	2.60
15	2.30	26	2.35	45	3.42 U
38	2.30	27	2.37	18	5.70 U
16	2.30	19	2.37	10	6.90 U
11	2.30	2	2.37		
40	2.30	37	2.38		

U = Omitted results

Table 5.3. Statistics - Alkalinity

Analytical method: All
Unit: mg/l

Sample A

Number of participants	31	Range	0.26
Number of omitted results	26	Variance	0.01
True value	0.34	Standard deviation	0.11
Mean value	0.38	Relative Standard deviation	36.70 %
Median value	0.34	Relative error	10.52 %

Analytical results in ascending order:

6	< 10 U	5	0.02 U	48	0.95 U
10	< 1 U	15	0.03 U	16	1.8 U
24	< 0.1 U	44	0.04 U	11	2.0 U
28	< 0.01 U	41	0.08 U	21	2.05 U
23	-0.65 U	27	0.15 U	38	2.38 U
3	-0.05 U	47	0.15 U	2	2.6 U
17	0.00 U	34	0.29	14	2.8 U
29	0.00 U	42	0.30	43	3.0 U
19	0.00 U	31	0.34	1	3.15 U
30	0.02 U	7	0.40	9	6.0 U
		12	0.55		

Sample B

Number of participants	31	Range	0.85
Number of omitted results	26	Variance	0.07
True value	1.35	Standard deviation	0.31
Mean value	1.31	Relative Standard deviation	23.70 %
Median value	1.35	Relative error	3.05 %

Analytical results in ascending order:

6	< 10 U	15	1.14 U	16	2.6 U
31	0.80	28	1.16 U	10	2.79 U
23	0.85 U	47	1.17 U	2	2.8 U
17	1.00 U	30	1.17 U	38	3.25 U
29	1.05 U	27	1.20 U	11	3.4 U
3	1.05 U	24	1.22 U	14	3.7 U
41	1.06 U	34	1.33	1	4.45 U
5	1.07 U	42	1.35	9	6.0 U
19	1.10 U	7	1.40	43	8.0 U
44	1.14 U	48	1.50 U	21	8.5 U
		12	1.65		

U = Omitted results

Table 5.4. Statistics - Nitrate + nitrite-nitrogen

Analytical method: All
Unit: mg/l

Sample A

Number of participants	39	Range	25
Number of omitted results	8	Variance	31
True value	57	Standard deviation	6
Mean value	57	Relative Standard deviation	9.80 %
Median value	57	Relative error	0.50 %

Analytical results in ascending order:

12	< 68 U	8	55	44	59
9	14 U	38	56	18	60
33	36 U	48	56	5	60
24	36 U	14	56	28	60
39	46	47	56	30	61
35	46	26	57	42	62
6	50	37	57	45	62
2	50	7	57	16	65
17	51	3	57	11	70
10	54	23	57	1	71
19	55	27	58	22	88 U
46	55 U	41	58	40	310 U
31	55	34	59	43	488 U

Sample B

Number of participants	39	Range	55
Number of omitted results	8	Variance	89
True value	158	Standard deviation	9
Mean value	157	Relative Standard deviation	6.00 %
Median value	158	Relative error	-0.50 %

Analytical results in ascending order:

9	5 U	47	155	10	160
33	41 U	26	155	1	160
24	70 U	38	155	7	160
46	115 U	34	156	12	160 U
2	130	31	156	28	160
39	138	37	156	27	161
6	150	35	157	17	162
23	150	44	158	42	162
45	151	18	159	22	172 U
19	152	30	159	8	181
48	154	3	159	5	185
14	154	16	160	43	334 U
41	154	11	160	40	640 U

U = Omitted results

Table 5.5. Statistics - Chloride

Analytical method: All
Unit: mg/l

Sample A

Number of participants	41	Range	0.79
Number of omitted results	9	Variance	0.02
True value	0.83	Standard deviation	0.14
Mean value	0.86	Relative Standard deviation	17.30 %
Median value	0.83	Relative error	3.30 %

Analytical results in ascending order:

31	0.45	12	0.83	28	1.03
20	0.71	2	0.83	40	1.04
18	0.72	41	0.83	11	1.08
35	0.72	6	0.84	38	1.11
47	0.72	42	0.85 U	24	1.15 U
3	0.75	19	0.85	43	1.24
39	0.78	37	0.86	44	1.32 U
26	0.79	27	0.87	5	1.38 U
16	0.80	45	0.87	33	1.44 U
7	0.80	22	0.89	46	1.50 U
30	0.81	21	0.90	10	1.75 U
48	0.81	1	0.90	8	1.80 U
34	0.82	17	0.95	9	42.6 U
23	0.82	14	1.00		

Sample B

Number of participants	41	Range	0.59
Number of omitted results	9	Variance	0.01
True value	0.67	Standard deviation	0.11
Mean value	0.67	Relative Standard deviation	16.70 %
Median value	0.67	Relative error	-0.60 %

Analytical results in ascending order:

39	0.41	34	0.65	21	0.80
31	0.50	16	0.66	14	0.80
20	0.53	12	0.67	40	0.82
43	0.53	45	0.67	10	0.88 U
35	0.58	27	0.68	5	0.89 U
47	0.59	19	0.68	33	0.91 U
11	0.59	41	0.69	28	1.00
18	0.59	37	0.70	44	1.03 U
7	0.60	1	0.70	24	1.15 U
3	0.60	23	0.71	46	1.17 U
2	0.61	6	0.72	42	1.20 U
30	0.62	38	0.76	8	1.40 U
48	0.64	22	0.78	9	27.7 U
26	0.64	17	0.79		

U = Omitted results

Table 5.6. Statistics - Sulfate

Analytical method: All
Unit: mg/l

Sample A

Number of participants	41	Range	0.87
Number of omitted results	9	Variance	0.03
True value	2.30	Standard deviation	0.17
Mean value	2.28	Relative Standard deviation	7.40 %
Median value	2.30	Relative error	-1.10 %

Analytical results in ascending order:

27	< 5 U	34	2.25	41	2.36
46	1.00 U	23	2.26	19	2.38
24	1.31 U	17	2.30	39	2.41
20	1.72	16	2.30	5	2.44
33	1.88 U	6	2.30	30	2.47
21	2.00	48	2.30	38	2.50
11	2.04	1	2.30	43	2.50 U
28	2.06	7	2.30	22	2.53
14	2.10	3	2.30	45	2.59
31	2.10	2	2.30	42	4.30 U
47	2.19	26	2.30	9	4.80 U
40	2.23	35	2.31	44	4.88 U
10	2.24	18	2.32	8	6.20 U
12	2.25	37	2.35		

Sample B

Number of participants	41	Range	1.81
Number of omitted results	9	Variance	0.11
True value	5.28	Standard deviation	0.34
Mean value	5.20	Relative Standard deviation	6.40 %
Median value	5.28	Relative error	-1.50 %

Analytical results in ascending order:

9	1.84 U	42	5.20 U	37	5.37
43	2.50 U	46	5.20 U	10	5.37
33	3.60 U	26	5.20	48	5.38
20	3.95	45	5.22	30	5.40
11	4.55	12	5.23	7	5.40
31	4.65	35	5.25	19	5.45
14	4.79	34	5.26	41	5.49
6	5.00	16	5.30	21	5.50
40	5.04	38	5.32	22	5.63
17	5.10	18	5.33	28	5.76
1	5.10	5	5.33	44	6.50 U
2	5.10	3	5.33	8	6.60 U
47	5.14	39	5.34	27	6.90 U
23	5.14	24	5.36 U		

U = Omitted results

Table 5. 7 . Statistics - Calcium

Analytical method: Alle
Unit: mg/l

Sample A

Number of participants	39	Range	0.7
Number of omitted results	4	Variance	0.02
True value	0.88	Standard deviation	0.12
Mean value	0.88	Relative Standard deviation	14.00 %
Median value	0.88	Relative error	-0.50 %

Analytical results in ascending order:

20	0.37 U	23	0.85	45	0.92
27	0.54	6	0.86	3	0.93
18	0.61	39	0.86	19	0.95
11	0.68	5	0.87	2	0.95
17	0.77	1	0.87	30	0.96
14	0.80	22	0.88	42	0.96
41	0.81	16	0.88	28	1.00
8	0.81	26	0.88	43	1.02
10	0.82	7	0.89	40	1.11
34	0.83	47	0.89	9	1.24
38	0.84	12	0.89	24	1.60 U
48	0.84	21	0.90	33	2.20 U
37	0.85	31	0.90	46	8.80 U

Sample B

Number of participants	39	Range	1.1
Number of omitted results	4	Variance	0.04
True value	1.59	Standard deviation	0.2
Mean value	1.57	Relative Standard deviation	12.60 %
Median value	1.59	Relative error	-1.40 %

Analytical results in ascending order:

24	0.12 U	48	1.52	8	1.61
20	0.72 U	38	1.53	1	1.61
27	1.00	37	1.53	28	1.66
11	1.19	23	1.54	30	1.67
18	1.31	26	1.56	45	1.67
14	1.40	5	1.57	19	1.75
31	1.40	6	1.59	33	1.76 U
17	1.42	7	1.59	42	1.77
39	1.42	47	1.59	3	1.77
2	1.44	22	1.60	43	1.92
10	1.46	16	1.60	9	1.92
41	1.47	21	1.60	40	2.10
34	1.51	12	1.60	46	4.60 U

U = Omitted results

Table 5.8. Statistics - Magnesium

Analytical method: All
Unit: mg/l

Sample A

Number of participants	40	Range	0.09
Number of omitted results	9	Variance	0
True value	0.19	Standard deviation	0.02
Mean value	0.19	Relative Standard deviation	9.80 %
Median value	0.19	Relative error	2.50 %

Analytical results in ascending order:

27	0.10 U	12	0.19	28	0.21
14	0.10 U	23	0.19	45	0.21
18	0.13	26	0.19	40	0.21
11	0.16	6	0.19	17	0.22
34	0.17	16	0.20	3	0.22
30	0.18	21	0.20	38	0.29 U
41	0.18	1	0.20	2	0.29 U
22	0.19	31	0.20	9	0.30 U
29	0.19	10	0.21	8	0.37 U
37	0.19	42	0.21	24	1.60 U
48	0.19	19	0.21	33	2.06 U
5	0.19	39	0.21	46	3.90 U
7	0.19	20	0.21		
47	0.19	43	0.21		

Sample B

Number of participants	40	Range	0.51
Number of omitted results	9	Variance	0.01
True value	0.83	Standard deviation	0.1
Mean value	0.83	Relative Standard deviation	11.60 %
Median value	0.83	Relative error	-0.30 %

Analytical results in ascending order:

9	0 U	38	0.79 U	19	0.85
24	0.15 U	41	0.80	28	0.85
27	0.58 U	17	0.80	6	0.86
18	0.61	29	0.80	16	0.86
20	0.62	10	0.81	43	0.89
21	0.70	7	0.81	1	0.89
14	0.70 U	37	0.82	42	0.92
31	0.70	47	0.83	45	0.92
11	0.72	12	0.83	2	0.92 U
8	0.73 U	23	0.83	3	0.93
46	0.73 U	22	0.84	39	0.95
33	0.75 U	5	0.84	40	1.12
34	0.78	26	0.84		
30	0.79	48	0.85		

U = Omitted results

Table 5.9. Statistics - Sodium

Analytical method: All
Unit: mg/l

Sample A

Number of participants	38	Range	0.77
Number of omitted results	4	Variance	0.02
True value	1.20	Standard deviation	0.15
Mean value	1.19	Relative Standard deviation	12.10 %
Median value	1.20	Relative error	-0.50 %

Analytical results in ascending order:

27	0.40 U	41	1.16	12	1.23
38	0.54 U	18	1.17	43	1.24
5	0.84	17	1.18	45	1.25
9	0.97	26	1.18	1	1.26
33	1.00	22	1.19	19	1.30
7	1.02	21	1.20	8	1.31
34	1.04	14	1.20	10	1.38
39	1.05	47	1.20	11	1.40
28	1.06	31	1.20	2	1.50
30	1.14	42	1.21	40	1.50 U
6	1.14	16	1.22	20	1.61
48	1.15	37	1.22	46	3.00 U
23	1.16	3	1.22		

Sample B

Number of participants	38	Range	0.39
Number of omitted results	4	Variance	0.01
True value	0.90	Standard deviation	0.08
Mean value	0.90	Relative Standard deviation	8.70 %
Median value	0.90	Relative error	0.20 %

Analytical results in ascending order:

27	0.08 U	17	0.89	42	0.92
38	0.45 U	23	0.89	12	0.92
9	0.74	33	0.90	16	0.94
7	0.77	37	0.90	5	0.94
34	0.78	48	0.90	1	0.96
39	0.80	19	0.90	8	0.97
28	0.80	21	0.90	43	0.97
30	0.84	14	0.90	2	1.00
20	0.87	47	0.90	11	1.10
41	0.87	22	0.90	10	1.13
18	0.87	31	0.90	40	1.20 U
6	0.88	3	0.91	46	1.50 U
26	0.88	45	0.91		

U = Omitted results

Table 5.10. Statistics - Potassium

Analytical method: All
Unit: mg/l

Sample A

Number of participants	38	Range	0.22
Number of omitted results	4	Variance	0
True value	0.52	Standard deviation	0.05
Mean value	0.52	Relative Standard deviation	9.40 %
Median value	0.52	Relative error	-0.60 %

Analytical results in ascending order:

27	0.32 U	6	0.51	37	0.54
31	0.40	28	0.51	26	0.54
9	0.41	17	0.51	48	0.55
34	0.45	7	0.51	20	0.56
43	0.46	16	0.52	45	0.57
38	0.47	41	0.52	8	0.59
5	0.47	39	0.52	11	0.60
23	0.47	42	0.53	21	0.60
30	0.49	1	0.53	19	0.62
33	0.50	47	0.53	40	0.80 U
14	0.50	3	0.53	10	1.25 U
2	0.50	12	0.53	46	1.50 U
18	0.50	22	0.54		

Sample B

Number of participants	38	Range	0.19
Number of omitted results	4	Variance	0
True value	0.20	Standard deviation	0.03
Mean value	0.20	Relative Standard deviation	16.50 %
Median value	0.20	Relative error	-1.40 %

Analytical results in ascending order:

27	0.11 U	33	0.20	23	0.21
43	0.11	16	0.20	45	0.21
9	0.11	6	0.20	26	0.21
20	0.15	11	0.20	22	0.21
34	0.16	21	0.20	37	0.22
38	0.17	14	0.20	39	0.22
30	0.18	7	0.20	19	0.23
18	0.18	47	0.20	8	0.24
48	0.19	3	0.20	40	0.25 U
5	0.19	12	0.20	2	0.30
28	0.20	31	0.20	46	0.50 U
41	0.20	42	0.21	10	0.78 U
17	0.20	1	0.21		

U = Omitted results

Table 5. 11. Statistics - Aluminium

Analytical method: Alle
Unit: ug/l

Sample C

Number of participants	19	Range	153
Number of omitted results	1	Variance	1292
True value	270	Standard deviation	36
Mean value	265	Relative Standard deviation	13.30 %
Median value	270	Relative error	-1.70 %

Analytical results in ascending order:

3	177	28	264	45	283
40	195	25	265	21	287 U
7	236	17	270	43	293
12	240	36	270	6	295
22	257	47	273	5	311
10	260	23	275	27	330
41	260				

Sample D

Number of participants	19	Range	104
Number of omitted results	1	Variance	472
True value	170	Standard deviation	22
Mean value	174	Relative Standard deviation	12.80 %
Median value	170	Relative error	2.30 %

Analytical results in ascending order:

21	- U	41	168	43	176
3	121	22	169	17	180
7	159	45	170	5	181
27	160	36	171	6	196
10	165	47	174	12	210
23	165	28	174	40	225
25	165				

U = Omitted results

Table 5. 12. Statistics - Aluminium, reactive

Analytical method: All
Unit: ug/l

Sample C

Number of participants	13	Range	48
Number of omitted results	6	Variance	576
True value	214	Standard deviation	33.1
Mean value	228	Relative Standard deviation	14.52 %
Median value	214	Relative error	6.54 %

Analytical results in ascending order:

36	47 U	12	181	5	229
3	71 U	28	197 U	10	270
25	90 U	7	204	32	278
17	95 U	47	204		
37	158 U	30	214		

Sample D

Number of participants	13	Range	30
Number of omitted results	6	Variance	225
True value	140	Standard deviation	32.7
Mean value	135	Relative Standard deviation	24.24 %
Median value	140	Relative error	3.57 %

Analytical results in ascending order:

36	6 U	5	88	47	154
3	31 U	12	104	10	165
37	38 U	7	118	32	176
28	39 U	30	140		
17	50 U	25	145 U		

U = Omitted results

Table 5. 13. Statistics - Aluminium, nonlabile

Analytical method: Alle
Unit: ug/l

Sample C

Number of participant	13	Range	97
Number of omitted res	6	Variance	1080
True value	158	Standard deviation	33.8
Mean value	161	Relative Standard deviation	21.06 %
Median value	158	Relative error	6.21 %

Analytical results in ascending order:

47	70 U	12	143	5	203
3	106	7	158	36	223 U
37	110 U	17	175	32	229 U
28	120 U	25	175 U		
30	143	10	196		

Sample D

Number of participant	13	Range	45
Number of omitted res	6	Variance	349
True value	107	Standard deviation	23.4
Mean value	116	Relative Standard deviation	20.19 %
Median value	107	Relative error	11.21 %

Analytical results in ascending order:

47	0 U	12	97	10	152
25	5 U	5	98	36	165 U
37	28 U	7	107	32	169 U
28	32 U	17	130		
3	90	30	135		

U = Omitted results

Table 5.14. Statistics - Dissolved organic carbon

Analytical method: All
Unit: mg/l

Sample A

Number of participants	19	Range	4.46
Number of omitted results	1	Variance	0.98
True value	10.0	Standard deviation	0.99
Mean value	10.04	Relative Standard deviation	9.90 %
Median value	10.0	Relative error	0.40 %

Analytical results in ascending order:

21	8.5	10	10.0	27	10.7
48	8.87	3	10.0	38	10.7
5	9.06	23	10.0	35	10.8
41	9.19	37	10.2	28	12.96
1	9.2	7	10.3	22	13.0 U
47	9.7	34	10.39		
6	9.76	42	10.4		

Sample B

Number of participants	19	Range	1.04
Number of omitted results	1	Variance	0.1
True value	4.83	Standard deviation	0.32
Mean value	4.83	Relative Standard deviation	6.70 %
Median value	4.83	Relative error	0.10 %

Analytical results in ascending order:

5	4.36	23	4.7	28	5.21
1	4.4	37	4.8	27	5.25
48	4.44	21	4.8	35	5.28
6	4.49	34	4.89	10	5.4
7	4.6	3	4.9	22	8.0 U
41	4.66	38	5.0		
47	4.68	42	5.1		

U = Omitted results

Table 5.15. Statistics - Dissolved organic carbon

Analytical method: All
Unit: mg/l

Sample C

Number of participants	15	Range	2.92
Number of omitted results	2	Variance	0.68
True value	9.70	Standard deviation	0.82
Mean value	9.68	Relative Standard deviation	8.50 %
Median value	9.70	Relative error	-0.20 %

Analytical results in ascending order:

48	8.6	47	9.41	27	10.2
5	8.7	23	9.6	42	10.3
25	8.7	3	9.7	35	10.3
29	9.0 U	37	9.8	28	11.52
21	9.03	7	10.0	22	12.0 U

Sample D

Number of participants	15	Range	2.34
Number of omitted results	2	Variance	0.34
True value	5.88	Standard deviation	0.58
Mean value	5.91	Relative Standard deviation	9.90 %
Median value	5.88	Relative error	0.50 %

Analytical results in ascending order:

5	4.9	47	5.78	42	6.4
21	5.42	35	5.88	27	6.45
48	5.48	37	6.0	28	7.24
25	5.5	3	6.0	22	9.0 U
23	5.7	7	6.1	29	9.5 U

U = Omitted results

Table 5.16. Statistics - Chemical oxygen demand

Analytical method: All
Unit: mg/l

Sample A

Number of participants	13	Range	5.6
Number of omitted results	0	Variance	2.09
True value	12.4	Standard deviation	1.44
Mean value	12.49	Relative Standard deviation	11.60 %
Median value	12.4	Relative error	0.70 %

Analytical results in ascending order:

9	8.5	23	12.3	10	14.0
31	11.8	17	12.4	39	14.1
11	12.0	7	12.5	43	14.1
46	12.19	16	13.0		
1	12.3	44	13.2		

Sample B

Number of participants	13	Range	1.2
Number of omitted results	0	Variance	0.18
True value	5.54	Standard deviation	0.43
Mean value	5.58	Relative Standard deviation	7.70 %
Median value	5.54	Relative error	0.70 %

Analytical results in ascending order:

16	5.0	44	5.5	7	6.02
11	5.0	46	5.54	17	6.1
23	5.1	31	5.76	39	6.2
1	5.2	10	5.8		
9	5.33	43	5.97		

U = Omitted results

Table 5. 17. Statistics - Chemical oxygen demand

Analytical method: Alle
Unit: mg/l

Sample C

Number of participants	8	Range	4.9
Number of omitted results	0	Variance	2.83
True value	12.1	Standard deviation	1.68
Mean value	11.76	Relative Standard deviation	13.90 %
Median value	12.1	Relative error	-2.80 %

Analytical results in ascending order:

9	8.5	17	12.1	43	13.4
25	10	7	12.1		
23	12	2	13		

Sample D

Analytical method: Alle
Unit:mg/l

Number of participants	8	Range	1.97
Number of omitted results	0	Variance	0.4
True value	6.31	Standard deviation	0.63
Mean value	6.4	Relative Standard deviation	10.00 %
Median value	6.31	Relative error	1.40 %

Analytical results in ascending order:

9	5.33	7	6.41		
25	6	2	6.9	17	7.3
23	6.1	43	6.94		

U = Omitted results

Norwegian Institute for Water Research
P.O.Box 173, Kjelsås N-0411 Oslo, Norway
Phone: + 47 22 18 51 00 Fax: + 47 22 18 52 00

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