CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

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

Intercomparison 9711

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

Norwegian Institute for Water Research

REPORT

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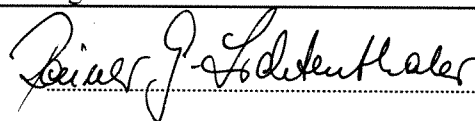| Client(s)	Client ref.
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Abstract

47 laboratories in 22 countries participated in intercomparison 9711. One sample set for the determination of major ions, organic matter and aluminium fractions, were used. Based on the general target accuracy of ± 20 %, 78 % of the results were acceptable. More than 80 % of the result pairs were acceptable for chloride, sulfate, calcium, magnesium, sodium, dissolved organic carbon and chemical oxygen demand. For pH only 43 % of the result pairs were acceptable in relation to the extended target accuracy of ± 0.2 units. For three analytical variables, nitrate + nitrite, 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. Normalization of the methods is necessary to improve the comparability for these variables. Manual methods are generally less sensitive compared to instrumental methods, and are not always suitable for acid rain monitoring.

4 keywords, Norwegian	4 keywords, English
1. Prøvningssammenligning	1. Intercomparison
2. Sur nedbør	2. Acid precipitation
3. Kvalitetskontroll	3. Quality Control
4. Overvåking	4. Monitoring

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

INTERCOMPARISON 9711

$$\text{PH}, \kappa_{25}, \text{HCO}_3{}^-, \text{NO}_3{}^- + \text{NO}_2{}^-, \text{CL}^-, \text{SO}_4{}^-$$
$$\text{CA}^{++}, \text{MG}^{++}, \text{NA}^+, \text{K}^+, \text{AL}, \text{AL-R}, \text{AL-I}, \text{DOC AND COD-MN}$$

Oslo, September 1997
Håvard Hovind

Contents

Summary

Intercomparison 9711 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 April - May 1997, 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 was prepared for this intercomparison, one for the determination of the major ions, and the other for aluminium fractions and unspecific organic matter. 47 laboratories determined all, or some of the analytical variables in the samples.

The samples were sent to 50 laboratories, and 47 submitted results to the Programme Centre before the final statistical treatment of the data. 22 countries were represented in this laboratory group.

As "true" value for each variable was selected the median value of the results received from the participants. For three analytical variables - nitrate + nitrite, reactive and non-labile aluminium - this definition of the "true value" is not acceptable, because of the extreme spread between the results from the different participants. It was therefore decided not to evaluate the reported results for these variables. Excluding these three variables from the evaluation, 78 % of the result pairs were regarded as acceptable, the target limit being the median value ± 20 %.

For pH the accuracy limit was extended to ± 0.2 units, and only 43 % of the result pairs were included by this special limit. A total error of ± 0.2 units for pH measurements seems to be a more reasonable assessment of the accuracy between laboratories, than the target limit of ± 0.1 units. The reason for the great spread of pH results is mainly due to the fact that different measurement routines are used by the participants, leading to systematically different results. To establish a "true value" based on the mean value for **all** the reported results for pH, when the methods are different, is questionable.

The best results were reported for chloride, sulfate, calcium, magnesium, sodium and both analytical variables for organic compounds. Rather poor comparability was observed for pH, nitrate + nitrite and aluminium species. To improve the comparability of the results for pH and aluminium species, it is necessary to normalize the analytical method and determination technique used.

1. Introduction

As stated in "Manual for Chemical and Biological Monitoring" (1), between-laboratory quality control is necessary in a multilaboratory programme to assure clear identification and control of the bias between analyses carried out by individual participants of the Programme. Such biases may arise 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 eleventh intercomparison test, called 9711, included the determination of the major 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).

2. 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 1996 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 compounds.

The samples were mailed from the Programme Centre on April 9, 1997. Most of the participating laboratories received the samples within one week, with some few exceptions. 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 six weeks after the samples arrived at the laboratory. Most results were received within the middle of June. The results from one laboratory were received too late to be included in this report, the results arrived after the statistical treatment of the data was finalized.

3. Results

The samples were sent to 50 laboratories. The 47 boratories who submitted results to the Programme Centre, are representing 22 countries. It was a problem that some of the laboratories submitted the results several weeks after the deadline (which was June 1), and a reminder letter had to be mailed to some of the 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 most of the participants are using essentially the same analytical method.

The results are illustrated in Figure 1 - 15, 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 9711 is presented in Table 1. The individual results of the participants are presented in Table 4, sorted in order of increasing identification number. More extensive statistical informations are presented in the Tables 5.1 - 5.15.

3.1 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.

Figure 1 shows that the reported results are localized mainly in two groups, most of the results determined during stirring the solution are lowered compared to the nonstirred readings, and most of the results determined without stirring the solution are located in the upper right part of the diagramme. Especially for sample A this effect is pronounced. One laboratory that equilibrated the solutions by bubbling with air containing 350 ppm CO_2 before reading the pH value, reported far higher results than the other laboratories.

The participating laboratories determined pH in the test solutions by their own routine method. An electrometric method was used by all laboratories. 44 laboratories reported results for pH, of this group 21 indicated that they read the pH value during stirring the solution. As shown in Table 1, there is a small, but systematic difference between the results determined in a quiescent solution, and when determined during stirring the solution. The stirring are lowering the reported pH results. One laboratory reported that it was very difficult to determine pH, because the value was drifting up to 0.5 pH units during reading.

As the CO_2 concentration of samples in the circumneutral range may be far above the atmospheric equilibrium, the relatively high pCO_2 levels will lead to large systematic errors,

Table 1. Statistical summary of intercomparison 9711

Analytical variables	Sample pair	True value 1	True value 2	Total number	Number excluded	Median 1	Median 2	Mean Sample 1	St.dev 1	Mean Sample 2	St.dev 2	Rel. st.dev. % 1.0	Rel. st.dev. % 2.0	Rel. error % 1.0	Rel. error % 2.0
pH	AB	7.10	6.80												
No stirring				44	1	7.10	6.80	7.02	0.32	6.76	0.21	4.6	3.1	-1.2	-0.5
Stirring				21	0	7.12	6.82	7.02	0.34	6.77	0.17	4.8	2.4	-1.1	-0.5
Equilibration				22	1	6.96	6.76	6.97	0.26	6.73	0.22	3.7	3.2	-1.9	-1.0
				1	0			7.89		7.30				11.1	7.4
Conductivity	AB	8.60	5.45	43	3	8.60	5.44	8.62	0.51	5.45	0.37	5.9	6.9	0.2	-0.1
Alkalinity	AB	0.332	0.093												
Gran plot titration				37	10	0.332	0.093	0.336	0.021	0.100	0.018	6.4	19.3	1.2	7.6
End point titration				11	1	0.335	0.093	0.337	0.014	0.096	0.012	4.2	12.7	2.1	2.9
End point 5.6				8	2	0.346	0.097	0.346	0.013	0.104	0.017	3.7	16.7	4.7	12.1
End point 5.4				1				0.323		0.087				-2.1	-6.5
End point 4.5				5	1	0.318	0.083	0.316	0.014	0.081	0.008	4.4	10.0	-4.2	-12.9
				7	3	0.342	0.114	0.346	0.018	0.112	0.017	5.3	15.4	4.8	20.4
Colorimetry				1	1			0.320		0.140				-3.0	50.5
Not documented				4	2			0.305		0.108				-7.6	16.1
Nitrate + nitrite-nitrogen	AB	105	278												
Autoanalyzer				40	15	105	278	108	51	280	58	22.0	11.0	3.0	3.0
Photometry				17	6	105	275	107	24	282	60	22.7	21.2	6.9	2.2
				1	1			<20		251				-	-9.7
Ion chromatography				18	6	95	278	103	23	278	9	22.4	3.2	3.2	0.6
Hydrazine				2	1			280		310				167.0	11.5
Cap. electrophoresis				1	1			24		251				-77.0	-9.7
Photometry				1	1			47		56				-55.0	-80.0
Chloride	AB	8.30	6.89												
Ion chromatography				42	3	8.30	6.89	8.33	0.45	6.89	0.42	5.4	6.1	0.4	-0.1
AA				33	1	8.30	6.88	8.28	0.39	6.88	0.37	4.7	5.4	-0.2	-0.1
Argententometry				5	0	8.30	6.95	8.65	0.79	6.89	0.78	9.2	11.3	4.3	0.0
Manual, Hg				1	1			0.97		0.66				-88.3	-90.4
Cap. electrophoresis				1	1			10.30		8.50				24.1	23.4
Potentiometry				1	0			8.33		7.03				0.4	2.0
				1	0			8.30		6.80				0.0	-1.3

Analytical variables	Sample pair	True value 1	True value 2	Total number	Number excluded	Median 1	Median 2	Mean Sample 1	St.dev. Sample 1	Mean Sample 2	St.dev. Sample 2	Rel. st.dev. % 1.0	Rel. st.dev. % 2.0	Rel. error % 1.0	Rel. error % 2.0
Sulfate	AB	7.52	5.33	41	3	7.52	5.33	7.52	0.29	5.31	0.18	3.8	3.4	0.0	-0.3
Ion chromatography				33	1	7.54	5.34	7.52	0.25	5.31	0.19	3.4	3.5	-0.3	-0.4
Photometry				6	2	7.71	5.34	7.68	0.60	5.37	0.19	7.8	3.5	1.8	0.8
Nephelometry				1	0			7.60		5.20				0.8	-2.4
Cap. electrophoresis				1	0			7.42		5.32				-1.6	-0.2
Calcium	AB	4.74	3.80	43	4	4.74	3.80	4.75	0.34	3.79	0.25	7.2	6.7	0.1	-0.2
FAAS				23	3	4.73	3.80	4.68	0.39	3.76	0.25	8.4	6.6	-1.2	-1.0
ICP				10	0	4.74	3.80	4.74	0.19	3.81	0.14	4.0	3.6	0.0	0.3
EDTA				2	1			5.30		3.14				11.8	-17.4
Ion chromatography				7	0	4.96	4.00	4.87	0.35	3.96	0.28	7.1	7.1	2.7	4.2
ICP-MS				1	0			4.60		3.70				-3.0	-2.6
Magnesium	AB	1.07	0.61	43	3	1.07	0.61	1.07	0.08	0.61	0.04	7.5	6.4	0.3	-0.2
FAAS				23	1	1.06	0.60	1.05	0.07	0.60	0.04	6.8	6.2	-1.8	-2.2
ICP				9	0	1.10	0.61	1.09	0.08	0.62	0.04	7.5	7.0	2.3	2.2
EDTA				2	2			1.51		1.03				41.1	68.9
Ion chromatography				7	0	1.10	0.62	1.12	0.10	0.63	0.03	8.9	5.5	4.5	3.0
ICP-MS				2	0			1.07		0.61				-0.4	-0.3
Sodium	AB	10.00	2.10	42	3	10.00	2.10	9.91	0.70	2.12	0.10	7.0	4.8	-0.9	0.8
FAAS				18	3	10.10	2.13	9.91	0.78	2.12	0.11	7.9	5.1	-0.9	1.0
ICP				7	0	10.38	2.14	10.21	0.75	2.16	0.13	7.3	5.9	2.1	2.8
AES				8	0	10.00	2.09	9.83	0.30	2.10	0.09	3.1	4.1	-1.7	0.2
Ion chromatography				7	0	9.88	2.11	9.80	0.88	2.11	0.04	9.0	1.7	-2.0	0.4
ICP-MS				2	0			9.63		2.00				-3.8	-4.8
Potassium	AB	1.41	0.44	42	2	1.41	0.44	1.42	0.12	0.44	0.04	8.8	8.4	0.9	0.6
FAAS				19	1	1.41	0.43	1.43	0.10	0.44	0.03	7.3	7.7	1.3	-0.6
ICP				6	0	1.49	0.44	1.51	0.14	0.45	0.06	9.4	12.8	6.9	2.9
AES				8	0	1.44	0.46	1.47	0.08	0.46	0.03	5.4	6.5	3.9	4.2
Ion chromatography				7	1	1.31	0.44	1.30	0.15	0.44	0.03	11.4	7.7	-8.0	-0.4
ICP-MS				2	0			1.34		0.41				-5.3	-6.5

Analytical variables	Sample pair	True value 1	True value 2	Total number	Number excluded	Median 1	Median 2	Mean Sample 1	St.dev. Sample 1	Mean Sample 2	St.dev. Sample 2	Rel. st.dev. % 1.0	Rel. st.dev. % 2.0	Rel. error % 1.0	Rel. error % 2.0
Aluminium	CD	149	122	22	1	149	122	148	16	125	16	10.9	12.9	-0.4	2.2
FAAS				1	0			146		131				-2.0	7.4
GFAAS				9	0	155	122	153	16	124	11	10.2	8.8	2.5	2.0
ICP				4	0	146	114	143	24	114	18	17.0	15.9	-3.9	-6.5
ICP-MS				3	0	140	116	144	8	118	4	5.8	3.7	-3.1	-3.3
Photometry				5	1	153	138	148	19	139	22	12.9	16.0	-0.8	14.1
Aluminium, reactive	CD	80	80	9	5	80	80	77	22	80	12	27.8	15.1	-3.2	0.3
Aluminium, nonlabile	CD	79	67	9	5	79	67	78	12	67	5	15.1	8.0	-1.9	0.0
Dissolved organic carbon	CD	7.77	2.91	16	1	7.77	2.91	7.69	0.67	2.99	0.24	8.6	8.4	-1.0	2.7
Combustion				7	1	7.57	2.91	7.44	0.86	2.93	0.09	11.6	3.0	-3.9	0.6
UV/S2O8				7	0	7.90	3.12	8.00	0.45	3.11	0.30	5.6	9.8	3.3	6.9
Phenolphthalein				1	0			7.20		2.70				-7.0	-7.2
				1	0			7.60		2.80				-1.8	-3.8
Chemical oxygen demand	CD	8.51	2.75	11	2	8.51	2.75	8.37	0.29	2.71	0.31	3.5	11.2	-1.6	-1.6

pH
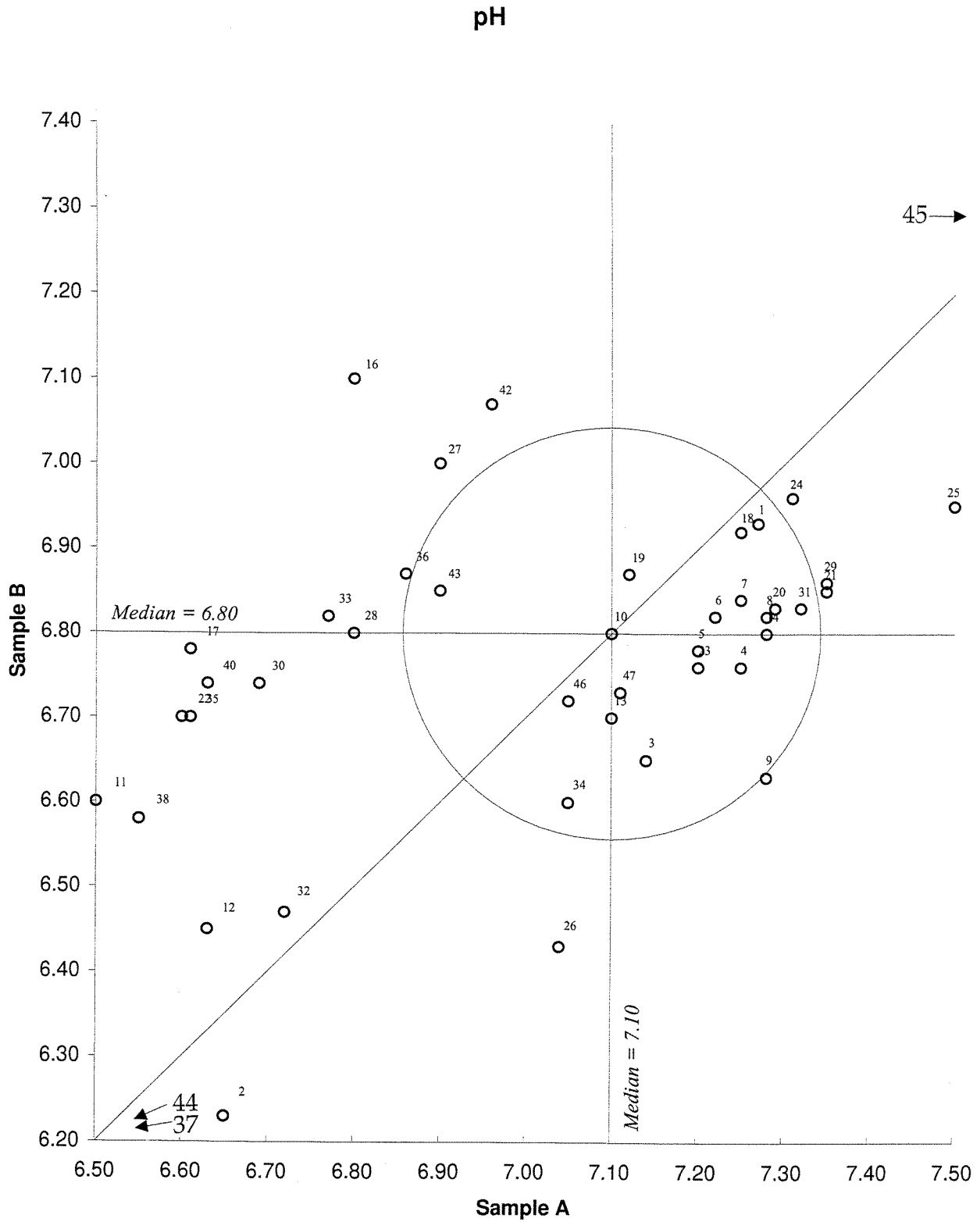
Figure 1. Youden-diagramme for pH, Pair AB
Acceptance criterium, given by the circel, is 3.5%
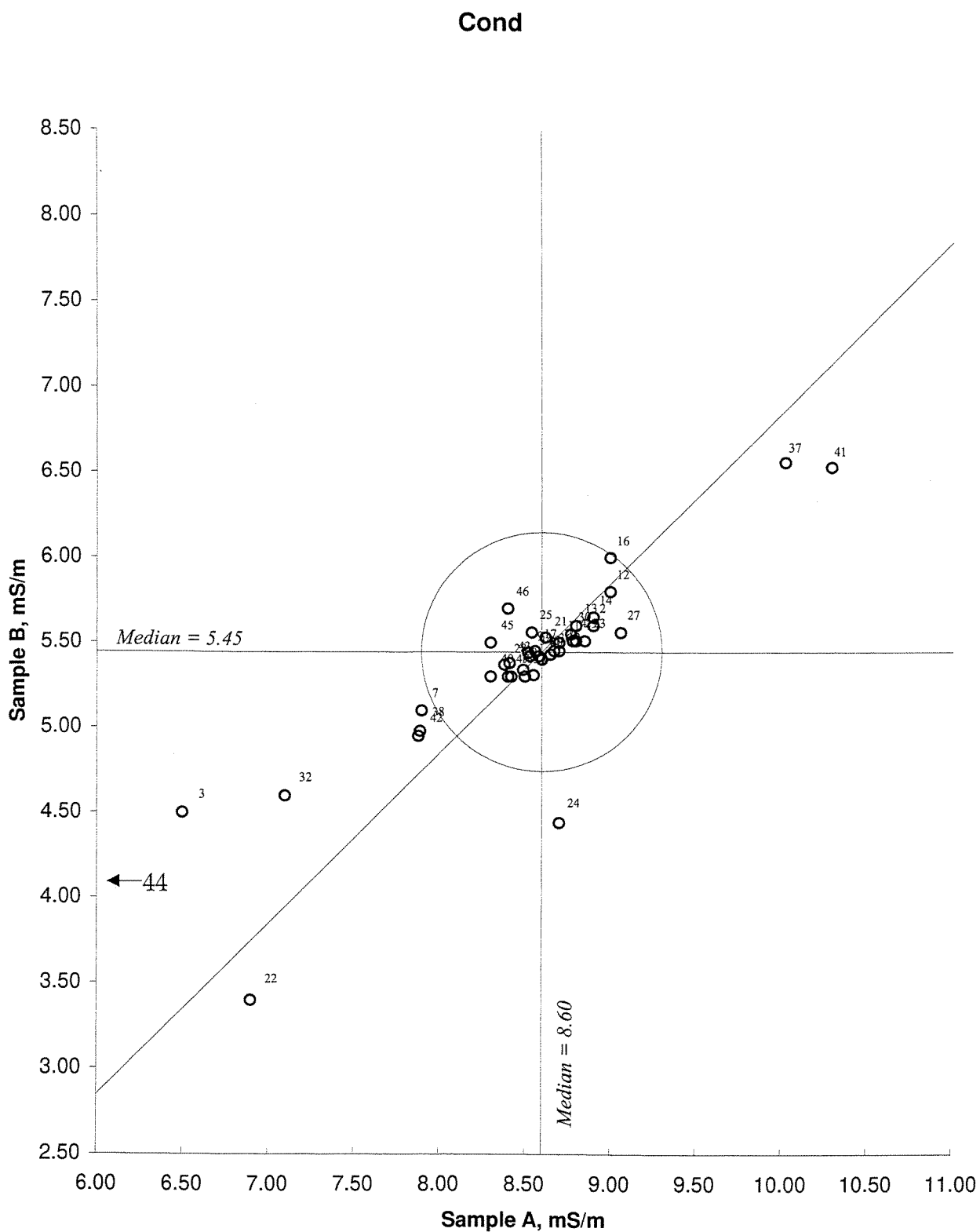
Cond

Figure 2.   Youden-diagramme for conductivity, Pair AB
Acceptance criterium, given by the circel, is 10%

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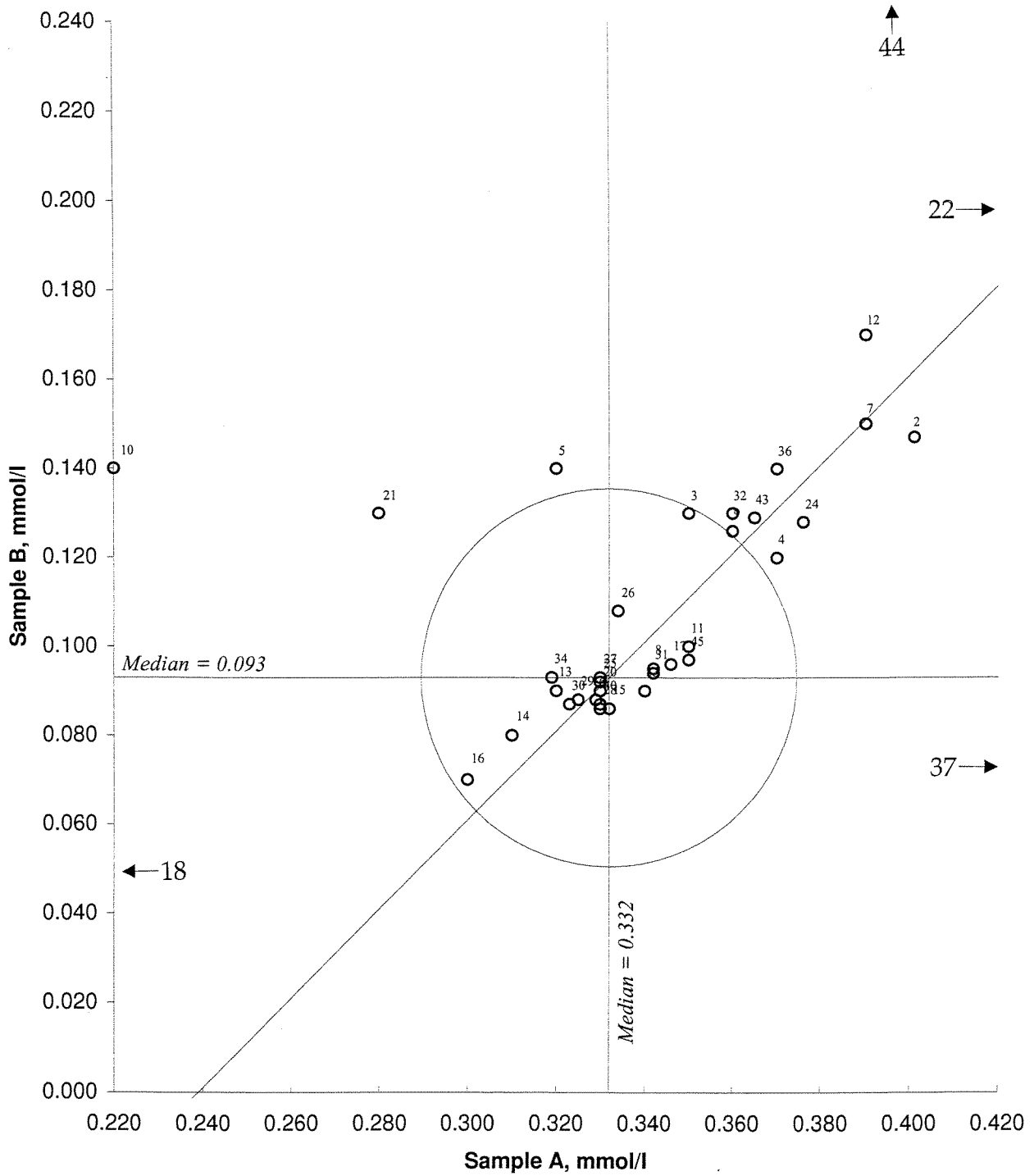
Figure 3. Youden-diagramme for alkalinity, Pair AB
Acceptance criterium, given by the circel, is 20%

NO3+NO2
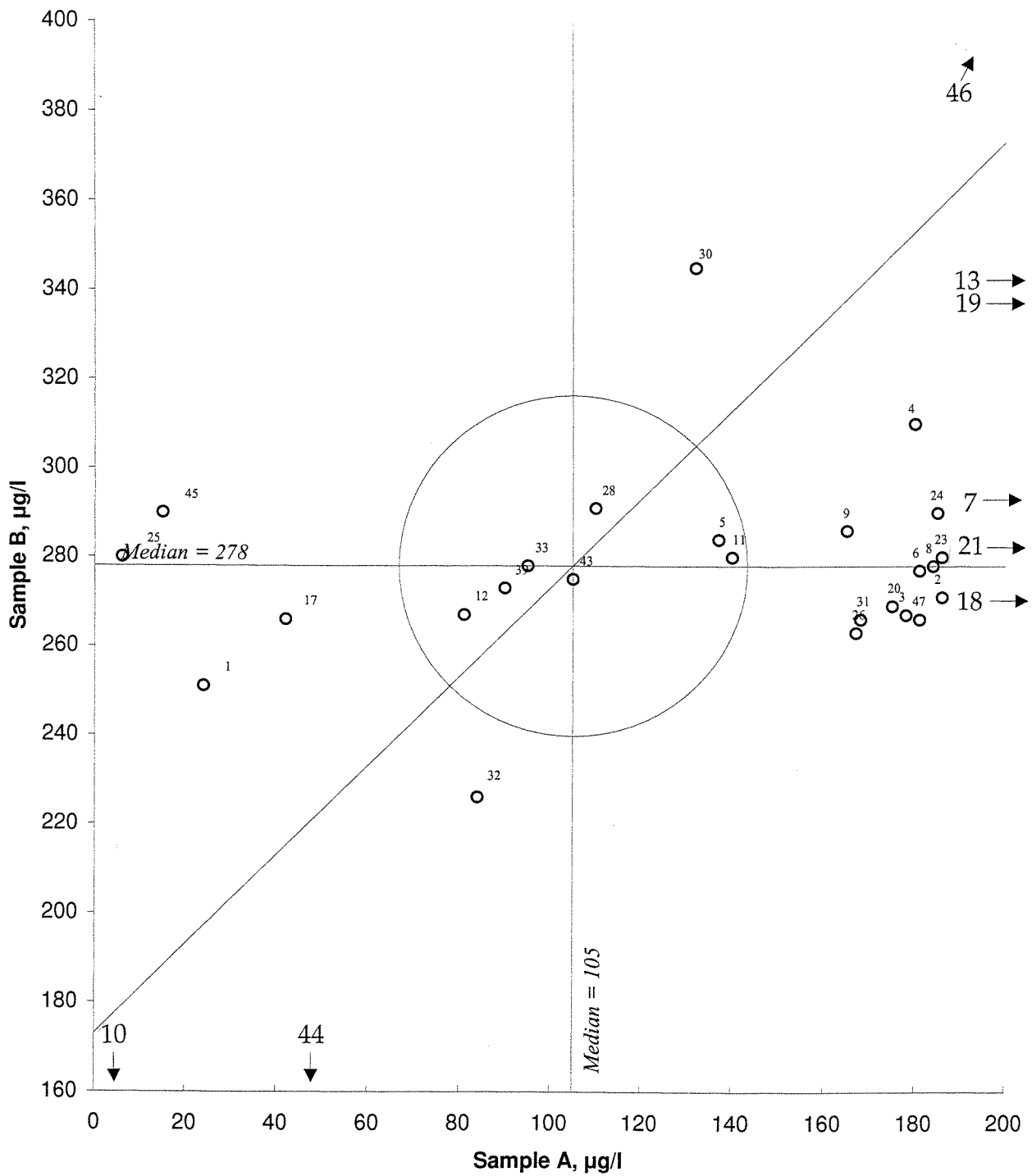
Figure 4. Youden-diagramme for nitrate + nitrite-nitrogen, Pair AB
Acceptance criterium, given by the circel, is 20%

Cl
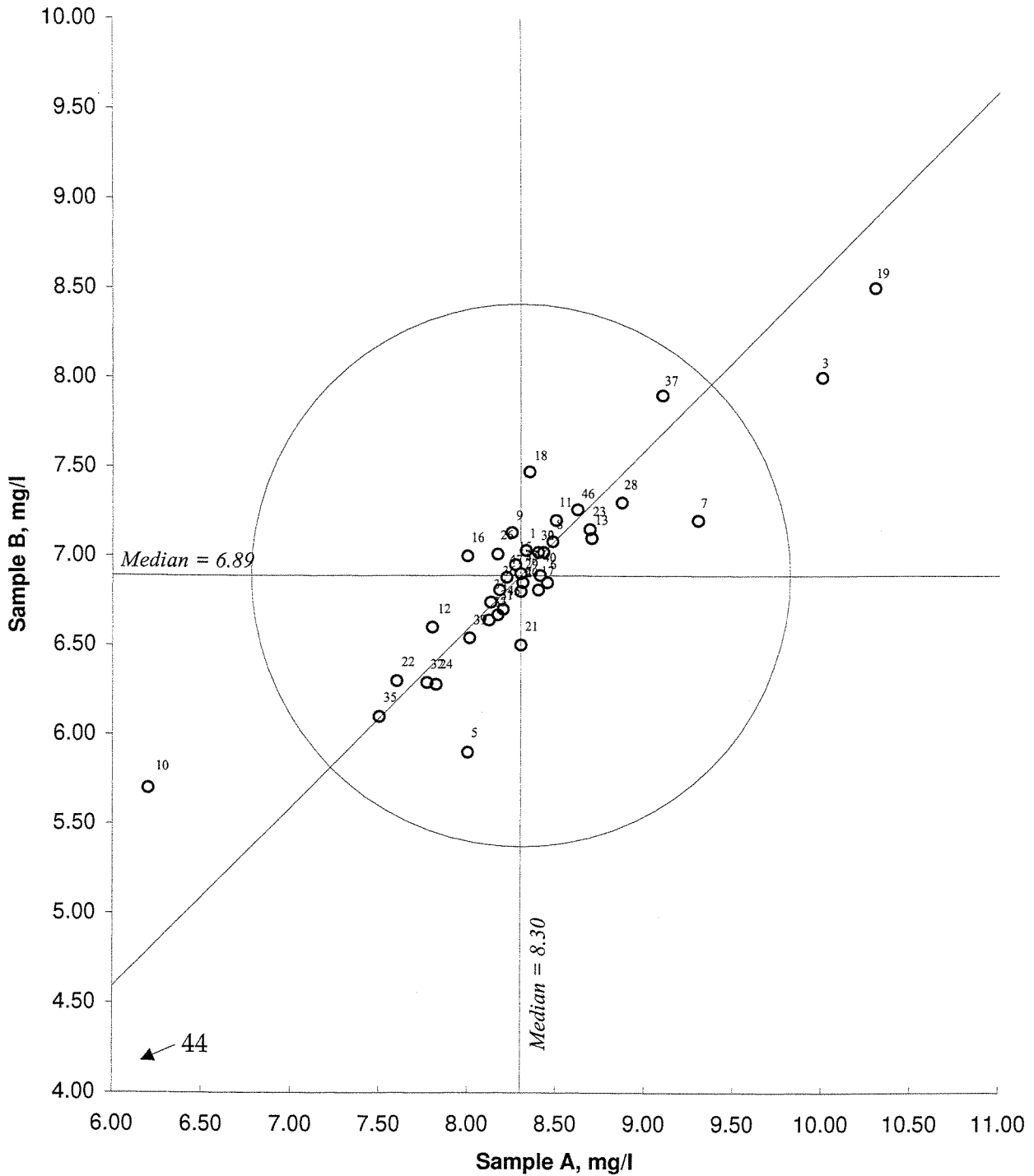
Figure 5. Youden-diagramme for chloride, Pair AB
Acceptance criterium, given by the circel, is 20%

SO4
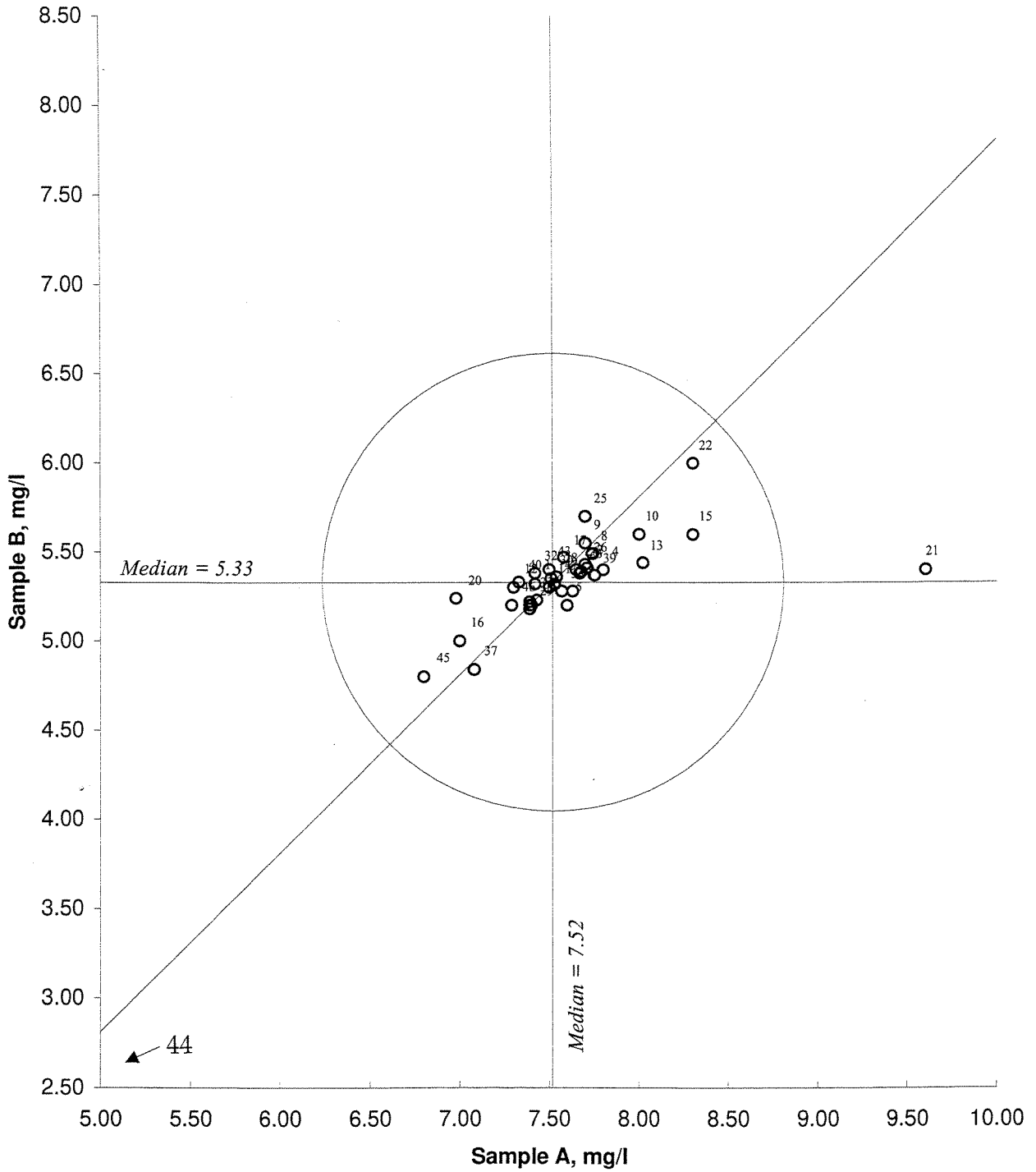
Figure 6.   Youden-diagramme for sulfate, Pair AB
Acceptance criterium, given by the circel, is 20%

Ca
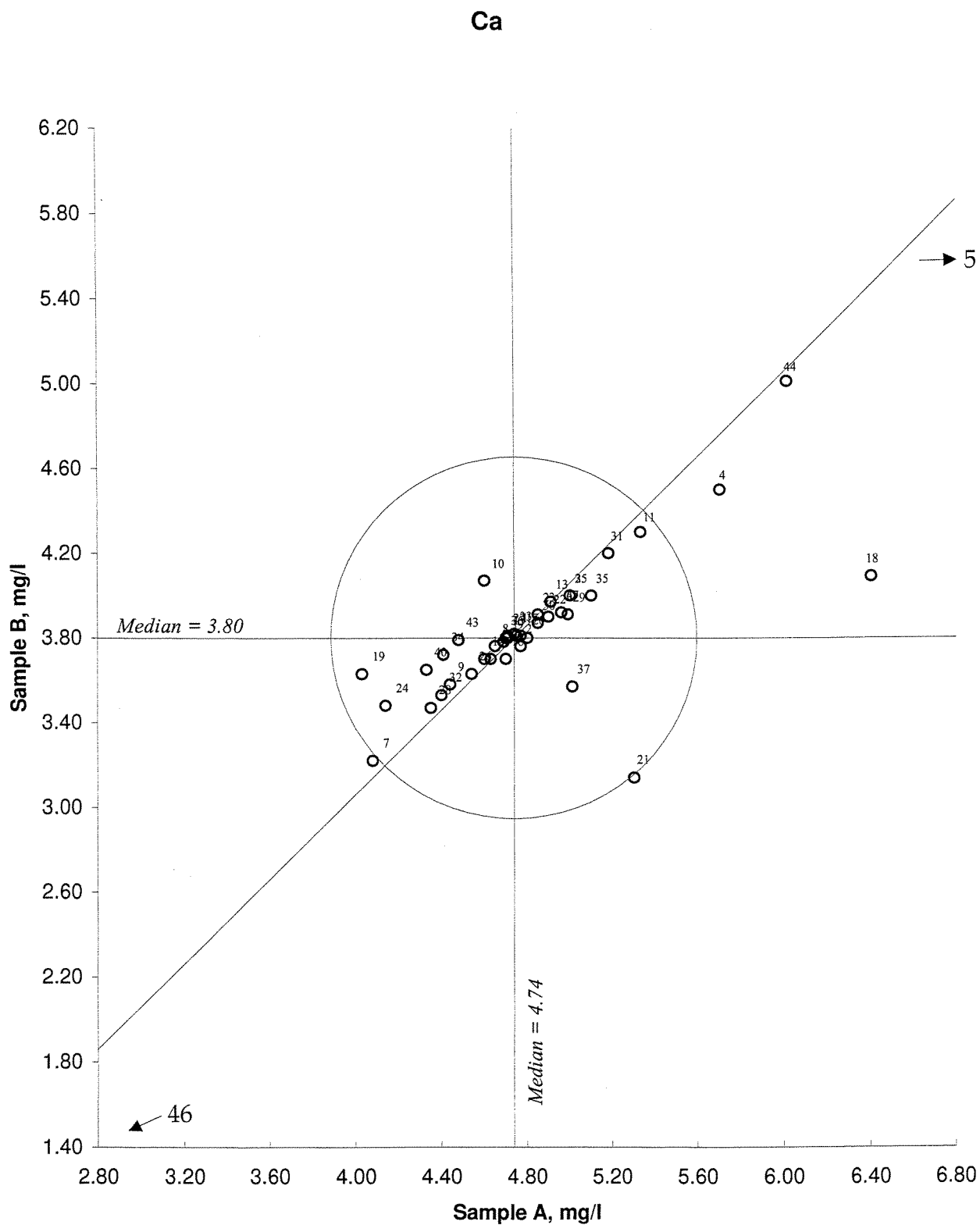
Figure 7.   Youden-diagramme for calcium, Pair AB
            Acceptance criterium, given by the circel, is 20%

Mg
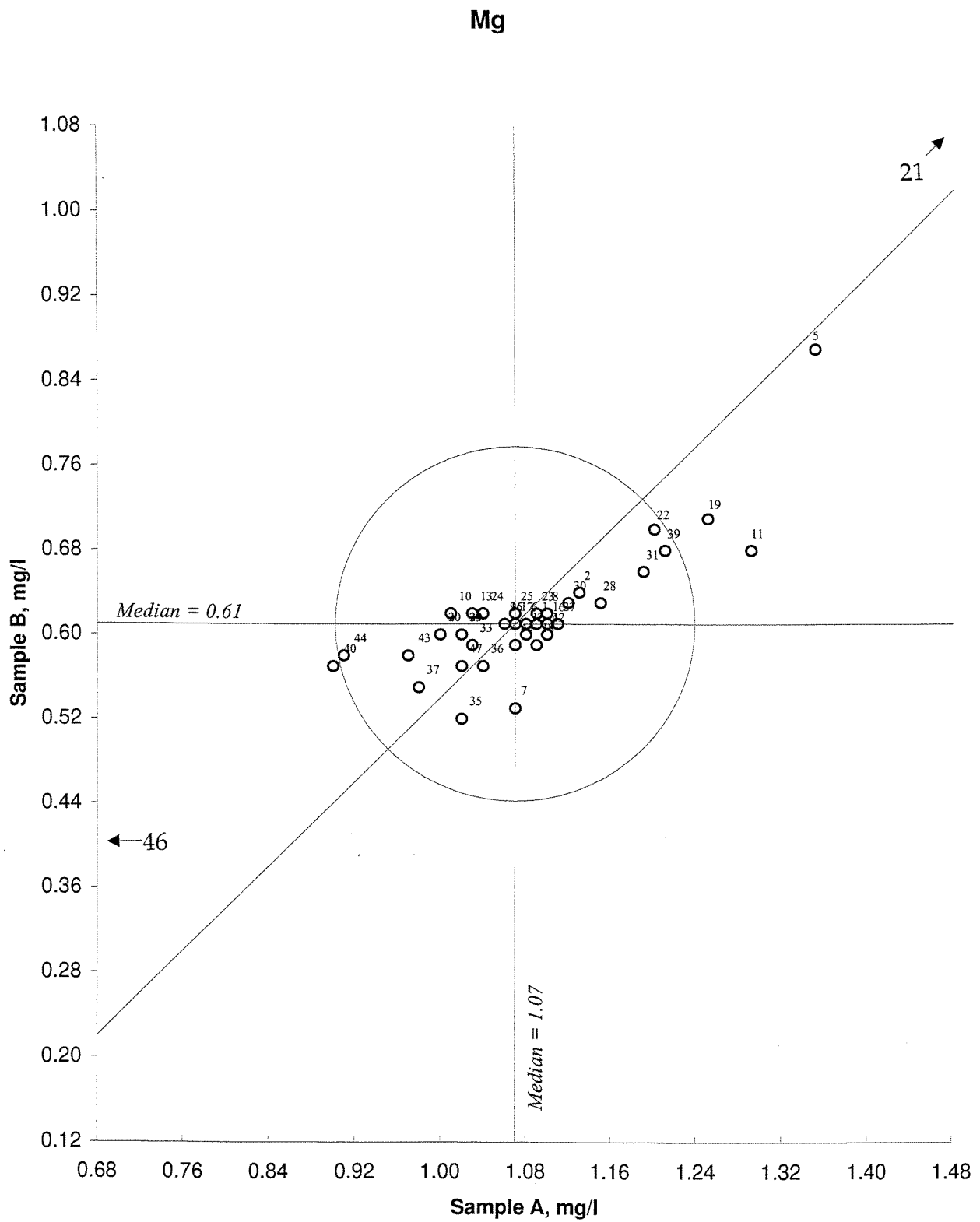
Figure 8.   Youden-diagramme for magnesium, Pair AB
Acceptance criterium, given by the circel, is 20%

Na
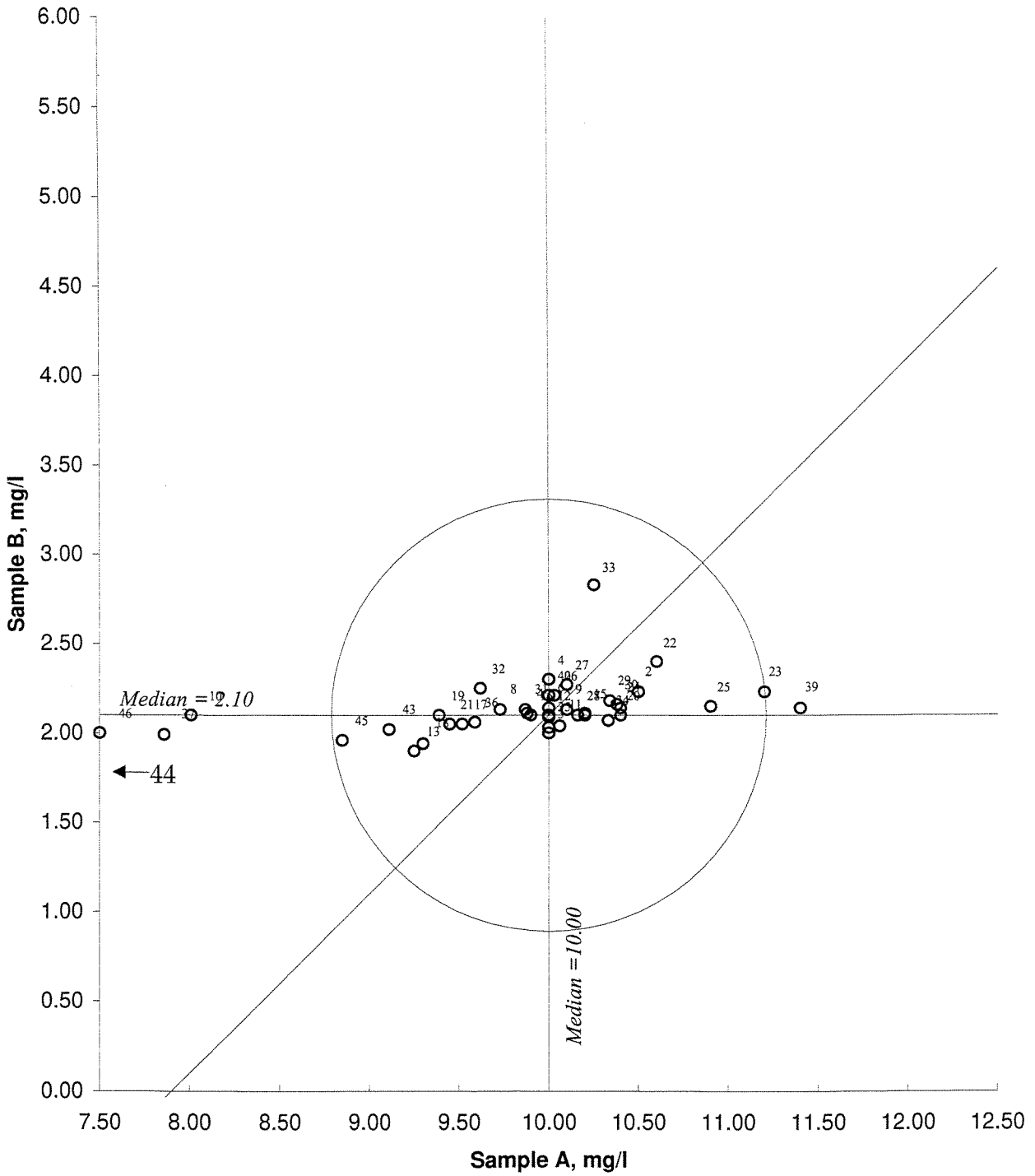
Figure 9. Youden-diagramme for sodium, Pair AB
Acceptance criterium, given by the circel, is 20%

K
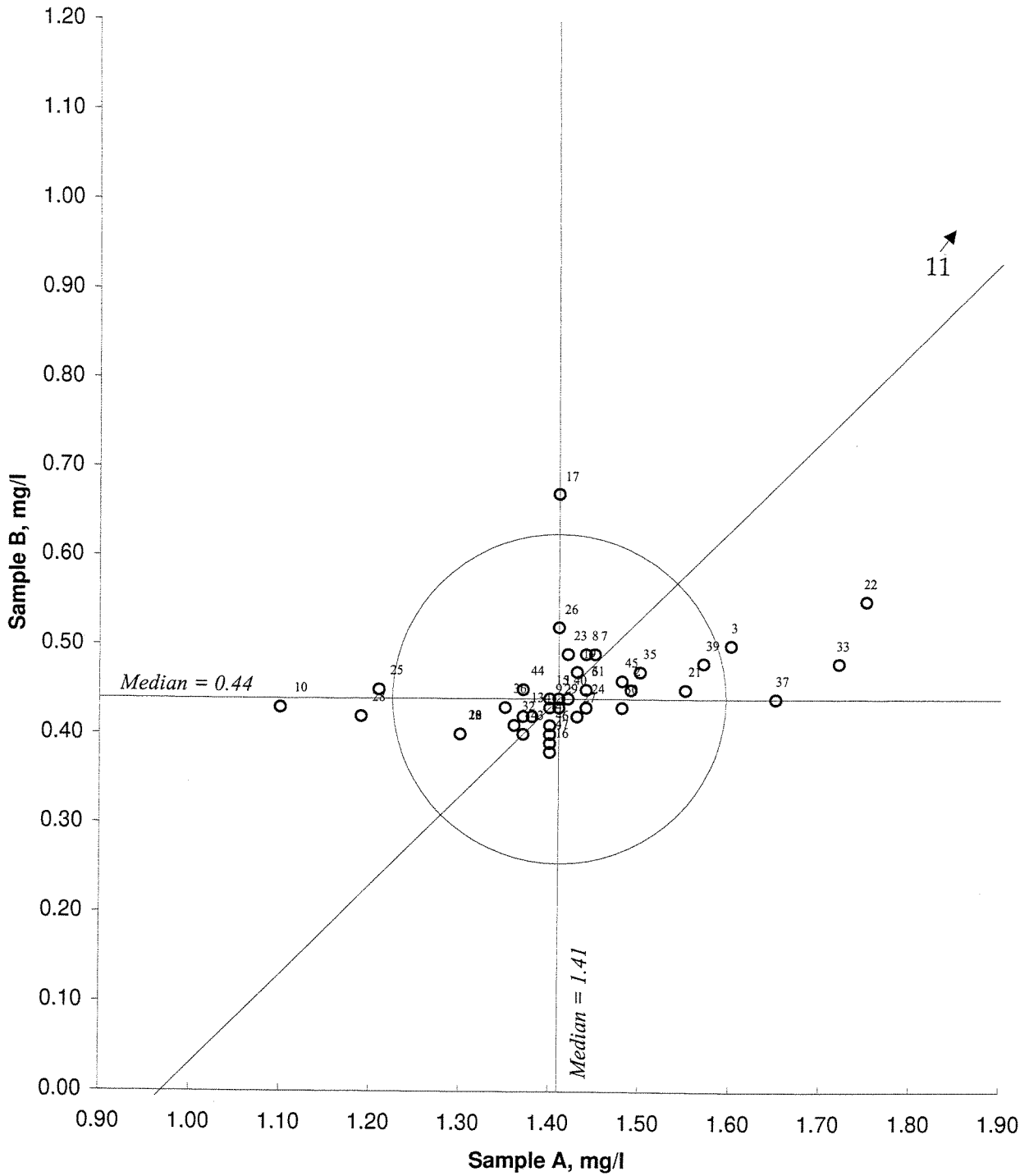
Figure 10. Youden-diagramme for potassium, Pair AB
Acceptance criterium, given by the circel, is 20%

Al

Figure 11. Youden-diagramme for aluminium, Pair CD
Acceptance criterium, given by the circel, is 20%

Al-R
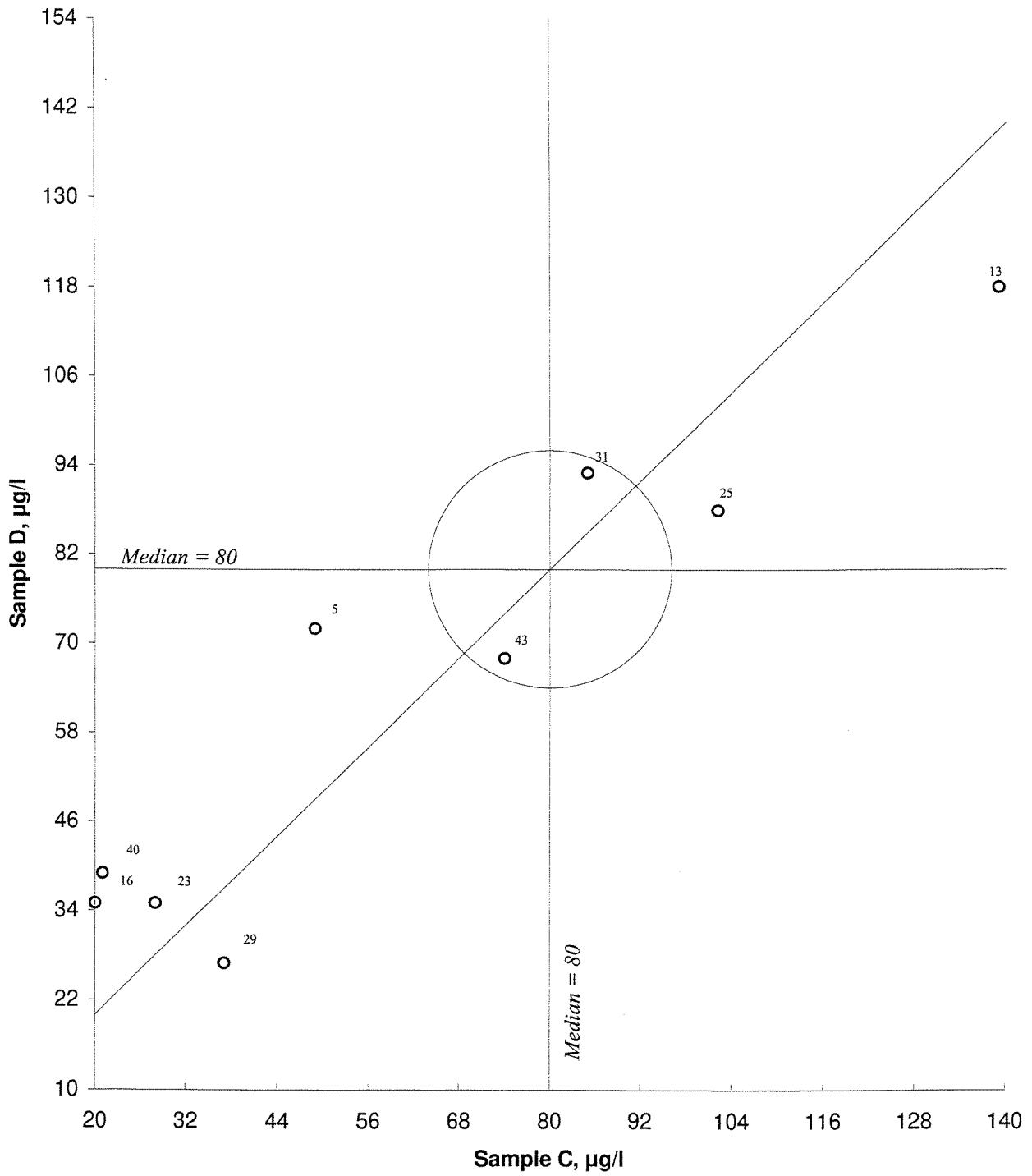
Figure 12. Youden-diagramme for aluminium, reactive, Pair CD
Acceptance criterium, given by the circel, is 20%

Al-I
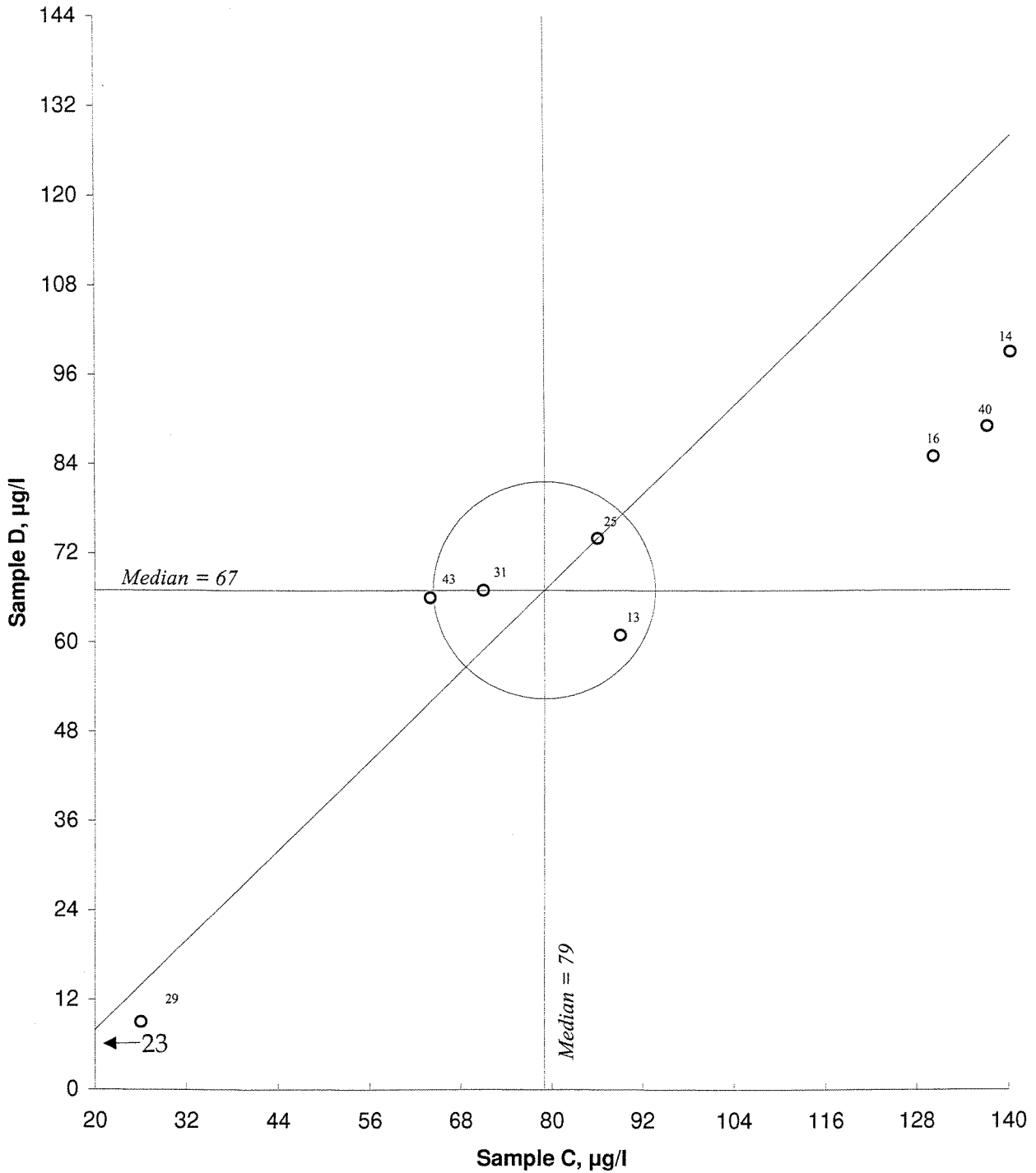
Figure 13. Youden-diagramme for aluminium, nonlabile, Pair CD
Acceptance criterium, given by the circel, is 20%

DOC
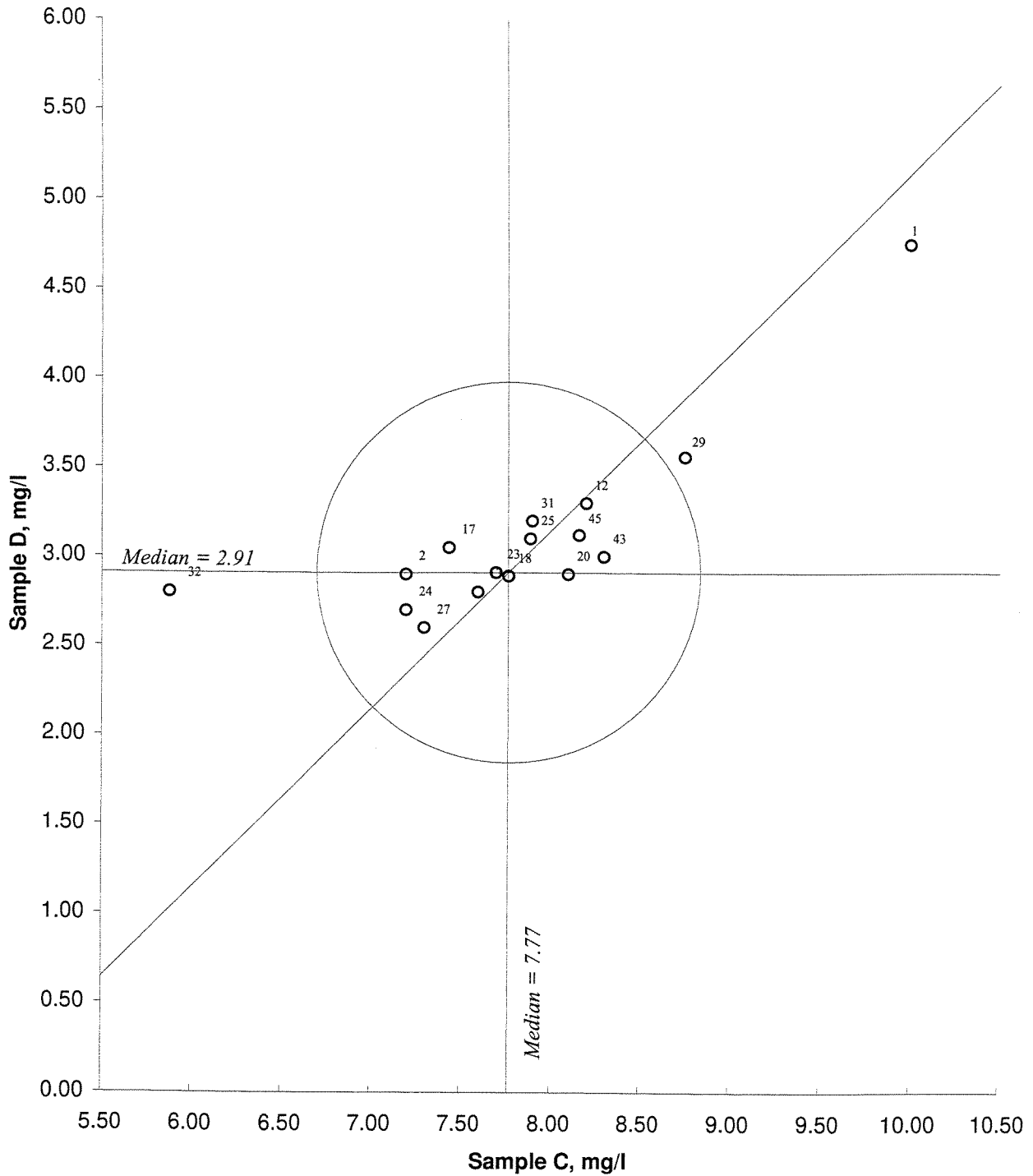
Figure 14. Youden-diagramme for dissolved organic carbon, Pair CD
Acceptance criterium, given by the circel, is 20%

COD-Mn
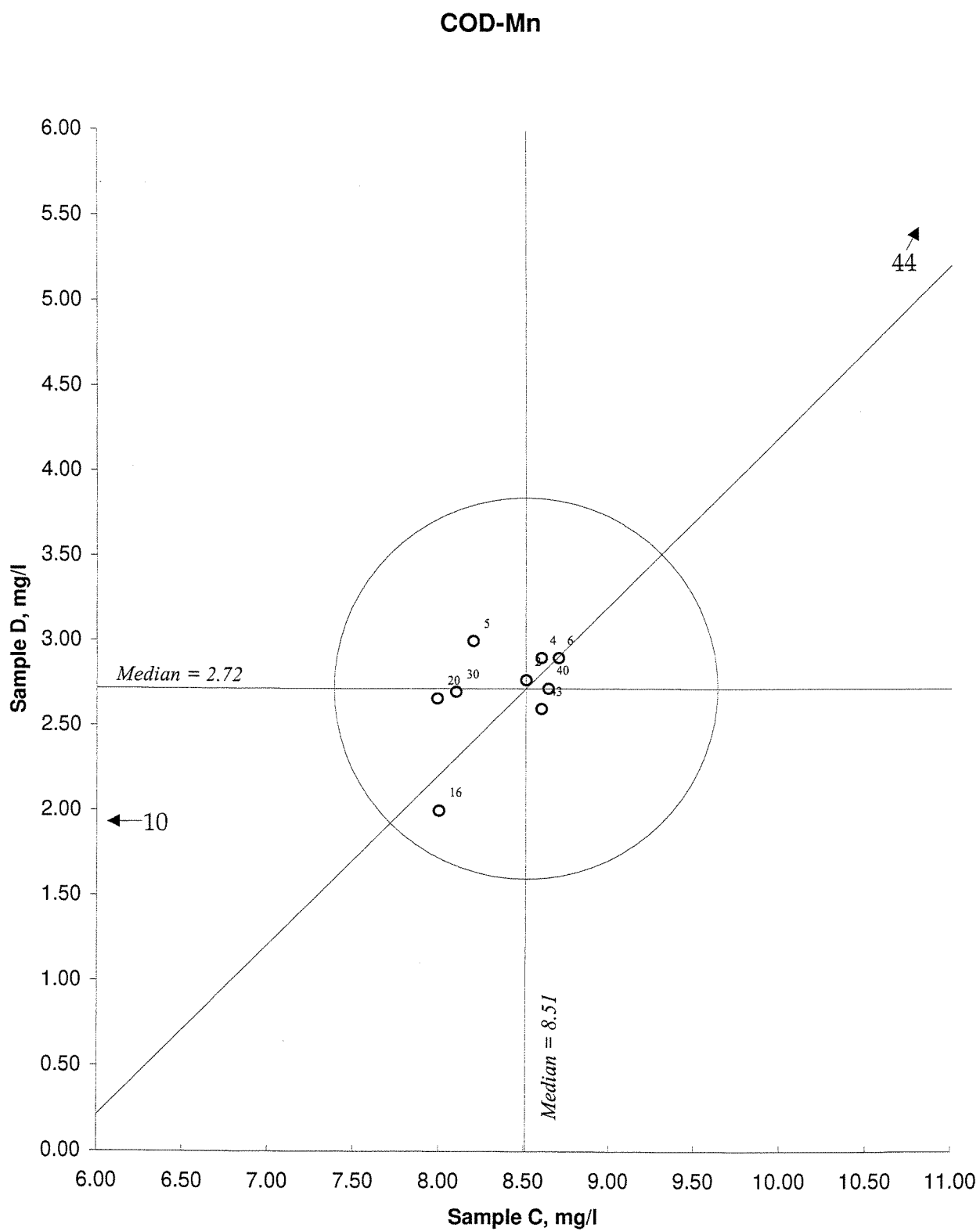
Figure 15. Youden-diagramme for chemical oxygen demand, Pair CD
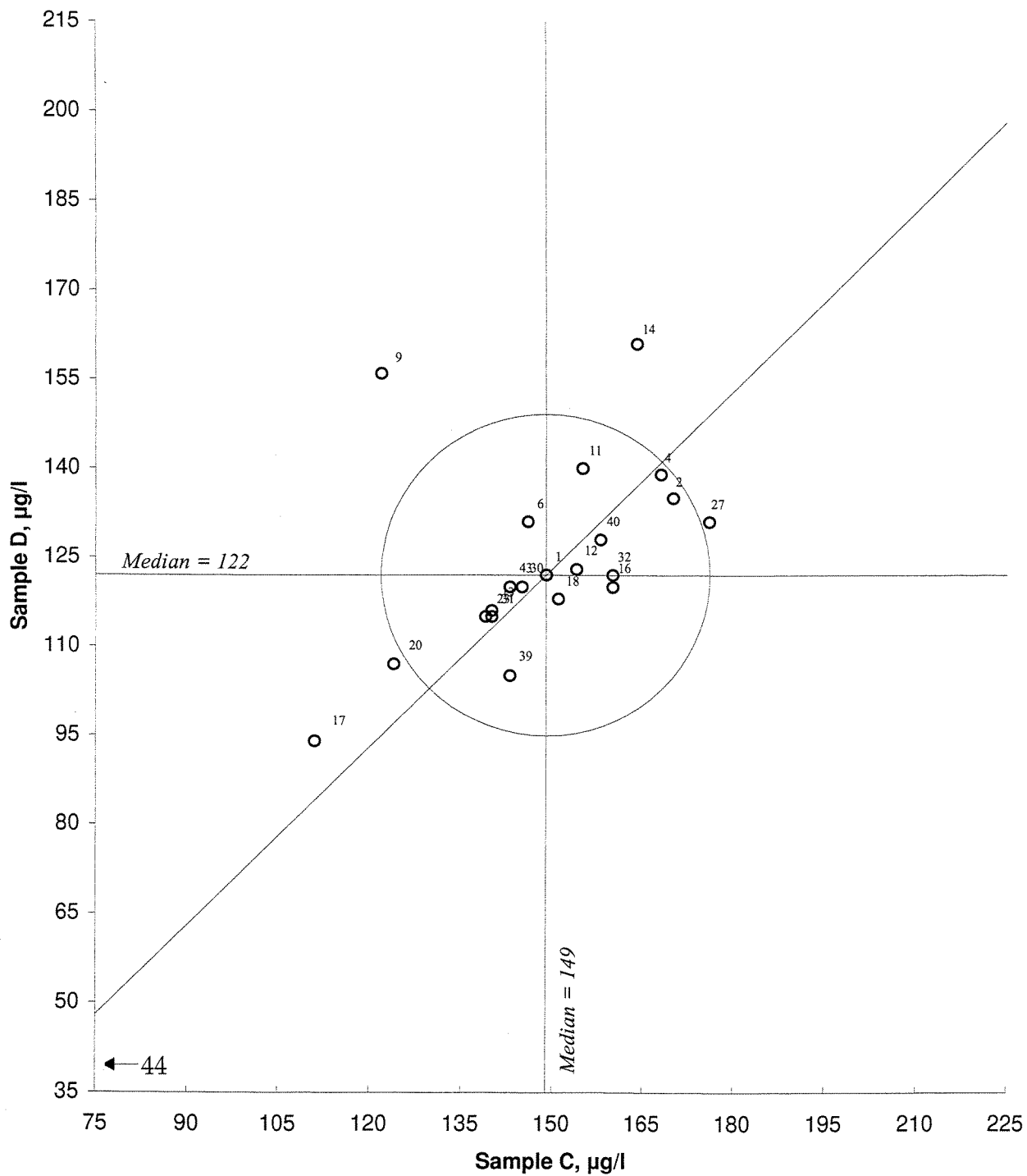Acceptance criterium, given by the circel, is 20%

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 control analyses carried out at the Program Centre proved that the sample B was stable when stored within one laboratory, while sample A proved to be unstable for nitrate + nitrite. 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, 5). The main reason for the differences in the reported results, however, must be connected to the different measurement methods used by the participants.

3.2 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. Some laboratories reported the conductivity results in the unit µS/cm, which is the unit they use routinely, instead of the requested mS/m at 25 °C. Therefore, some correspondance with these laboratories was necessary to clarify the results, which were recalculated to mS/cm. For two of the participants the results were recalculated without any response from the laboratory. All participants used an electrometric method for the determination of conductivity.

Most laboratories achieved very good agreement between the results for this variable. Two laboratories reported results being systematically too high for both the samples, and three laboratories reported results being systematically too low. Only four more result would be located outside the acceptance limit, if the general target accuracy is reduced from ± 20 % to ± 10 %.

A proper temperature correction is necessary when determining this analytical variable, as the conductivity is changing by about two percents pr degree at room temperature.

3.3 Alkalinity

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 5.3. About one third of the participating laboratories used the Gran plot titration method suggested in the Manual (1). The others used end point titration, either to pH 4.5 and 4.2, or to one given pH value only (4.2, 4,5, 5.4, or 5.6).

There is a systematically spread of the results for alkalinity at this intercomparison, and this is mainly due to the different methods used by the laboratories. By a closer examination of the results, a clear connection between the method used and the location in Figure 3 was observed. The laboratories using the Gran plot titration reported results located7 close to the centrum of the circle. The results determined by the end point titration to pH 4.2 or 4.5 alone,

are mainly located in the upper right part of Figure 3. The end point titration to pH 5.6 or 5.4 gave results mainly located within the acceptance circle.

Three laboratories have reported values being about half of the median value, they have obviously calculated the result as mmol/ as CO_3^{--} instead of HCO_3^-. The strongly devating results have been produced mainly by not documented methods.

The alkalinity value may vary significantly with the end-point pH used for the titration. In waters containing high concentrations of total inorganic carbon, the equivalence point is close to pH = 5.4. 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.

3.4 Nitrate + nitrite

The results reported for this parameter are presented in Figure 4, and the reported results are given in Table 5.4. The circle in Figure 4 is representing a general target accuracy of ± 20 %. Ion chromatography is used by an increasing number of laboratories, and is now used by nearly 50 % of the participants. The others are determining this analytical variable by photometric methods, most of these laboratories are using an automated version of the cadmium reduction method. There is no significant difference between the results determined by the principally different methods. However, some few strongly deviating results are determined by manual methods. One laboratory used a method with too high detection limit.

Obviously a large number of laboratories had great problems with the determination of nitrate + nitrite in sample A. Figure 4 shows that most of the results for sample B are within the acceptance limits, while only a few results are acceptable for sample A, which has the lowest concentration. This sample was collected in a creek from a pond in a marsh area in the winter time, the water probably being anoxic at this time of the year, which is probably the reason for the high concentration of ammonia in this sample. The special composition of this sample may introduce interferences problems for some laboratories. The control analyses at the Programme center indicated that sample A was not stable enough with respect to this analytical variable.

3.5 Chloride

The chloride results are presented in Figure 5, and the reported results from the participants are given in Table 5. 33 out of 42 laboratories determined chloride by ion chromatography. In addition, five 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 methods, and the argentomertic method which have too high detection limit, the latter method is not sensitive enough for most of this kind of samples.

3.6 Sulfate

The sulfate results are illustrated in Figure 6, and the reported values are given in Table 5.6. Ion chromatography is used by 33 of 41 laboratories for the determination of this analytical variable. Six laboratories used a photometric method based on the dissociation of the barium-thorin complex, and one laboratory used a nephelometric method. One laboratory used capillary chromatography with acceptable results.

An accuracy limit of ± 20 % is represented by the circle in Figure 6, and 95 % of the result pairs are located within this general target accuracy. The strongly deviating results are mainly determined by manual photometric or turbidimetric methods.

3.7 Calcium

The calcium results are illustrated in Figure 7, and the reported values are given in Table 5.7. 23 of the participants used flame atomic absorption spectrometry for the determination of calcium. ICP and ICP-MS techniques, and ion chromatography, are used by ten, two and seven laboratories, respectively. The complexometric titration method, used by two laboratories, is not sensitive enough for most of this kind of samples.

3.8 Magnesium

The magnesium results are presented in Figure 8, and the reported values are given in Table 5.8. Most of the participants are still using flame atomic absorption spectrometry for the determination of magnesium. ICP emission spectrometry, ICP-MS, and ion chromatography was used by nine, two and six 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 rather low for this technique.

3.9 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. 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, thus seven participants used ICP, two ICP-MS and eight flame photometry.

82 % of the result pairs are located within the general target accuracy of ± 20 %. Five laboratories reported results which are systematically high, and one where the deviations are

of random nature. The sodium concentrations in the two samples are very different, illustrated by the "flat" spread of the results in Figure 9, this may cause a problem when the results are evaluated by the Youden technique.

3.10 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. As for sodium, most laboratories used flame atomic absorption spectrometry for the determination of this element, however, emission spectrometry is used by 14 of the laboratories. The deviations are mainly of systematic nature. However, for some laboratories the deviations are quite random. As for sodium, the potassium concentrations in the two samples are relatively different.

3.11 Total aluminium

The results for total aluminium are illustrated in Figure 11, and the reported values are given in Table 5.11. The great circle is representing the general accuracy target of ± 20 %. Seven laboratories are using emission techniques, and five of the participants used photometry for the determination of aluminium. 79 % of the result pairs are located within the target accuracy. One of the deviating results are probably affected by random errors.

3.12 Reactive aluminium

The results for reactive aluminium are illustrated in Figure 12, and the reported values are given in Table 5.12. Only nine laboratories reported results for reactive aluminium. The statistical treatment according to Youden, leads to the exclusion of five laboratories, indicating that the results are rather different. 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 will lead to dissolution of complexes and even dissolution of some particulate matter containing aluminium. The results are expected to increase towards an upper limit when the pretreatment time is prolonged.

3.13 Non-labile aluminium

The results for non-labile aluminium are illustrated in Figure 13, and the reported values are given in Table 5.13. Five of the nine 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 16, page 30). 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 therefore will affect the results.

It is not possible to evaluate the analytical results properly when the result pairs are very spread out. Therefore, the "true" values and the 20 % circle in Figure 13 are indicative only. 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, affecting the analytical results.

3.14 Dissolved organic carbon

The results for this variable are presented in Figure 14, and the reported values are given in Table 5.14. Only 16 laboratories determined this analytical variable in the sample pair CD. A wet oxidation technique with UV and peroxodisulfate is used by seven laboratories, and seven laboratories used a combustion technique. There is no evidence for any differences in the reported results determined with these two methods for the samples used in this intercomparison. However, it is rather strange that the median value of the reported results determined by the UV/peroxodisulfate method is higher than the corresponding combustion results. Two laboratories used a photometric methods.

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

3.15 Chemical oxygen demand, COD-Mn

The results for this parameter are presented in Figure 15, and the reported values are given in Table 5.15. Only eleven 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. Nine of the result pairs were acceptable.

4. 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 being the greater.

In table 2 an evaluation of the results of intercomparison 9711 is presented, based on the target accuracy (except for pH), where the number and percentage of acceptable results are given. 78 % of the results are acceptable when compared to the acceptance limits given above. For the reported results in this intercomparison, on average, nearly one laboratory out of four is located outside the acceptance limit. By some improvement of the routine analytical method, these laboratories should obtain results more comparable to the other laboratories.

For pH the general target accuracy is ± 0.1 pH units, and far less than 50 % of the result pairs are found 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 two samples which are nearly neutral, and therefore are supposed not to be completely in CO_2-equilibrium. Even then only 43 % of the result pairs are evaluated as acceptable.

Table 2. Evaluation of the results of intercalibration 9711. N is the number of result pairs reported, and n is the number of acceptable results within the given target accuracy. Numbers in brackets are not evaluated.

Variable	Sample pair	N	Limit	n	%
pH	AB	44	0.2*	19	43
Conductivity	AB	43	20 %	33	77
Alkalinity	AB	37	20 %	21	57
Nitrate + nitrite-nitrogen	AB	(40)	20 %	(7)	-
Chloride	AB	42	20 %	38	90
Sulfate	AB	41	20 %	39	95
Calcium	AB	43	20 %	36	84
Magnesium	AB	43	20 %	37	86
Sodium	AB	42	20 %	37	88
Potassium	AB	42	20 %	33	79
Aluminium, total	AB	22	20 %	16	73
Aluminium, reactive	CD	(9)	20 %	(2)	-
Aluminium, non-labile	CD	(9)	20 %	(3)	-
Dissolved organic carbon	CD	16	20 %	13	81
Chemical oxygen demand	CD	11	20 %	9	82
Sum		426		331	78

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

For pH the problem of comparability between the reported results is dominated by the fact that the pH values in nearly neutral solutions are much more spread out than in more acid solutions. The difference between pH values measured in stirred solutions are systematically lower than in quiescent solutions. This problem has been demonstrated through several intercomparisons, and will remain as a problem as long as different methods for pH determination are used at the participating laboratories. Therefore it should be discussed wether a more "correct" approach should be used, with different "true values", one for each method?

For alkalinity, as we also have observed earlier, the reported results for solutions with low alkalinity values are spread out much more than in solutions with higher concentrations of bicarbonate. In this intercomparison the results are far better than in the two last intercomparisons, probably because of the somewhat higher bicarbonate concentrations in these samples.

For three variables, nitrate + nitrite, reactive and non-labile aluminium, we have decided to exclude these from the evaluation, because of the very great spread of the reported values. Obviously many participants had problems with the determination of nitrate + nitrite, maybe because the sample A was rather atypical for acid rain problems, and this sample proved to be unstable during the control analyses.

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 are some confusions 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 16. There have obviously been reported some results

Figure 16. 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

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 the results for the aluminium fractions.

For the major constituents the results are fairly well in this intercomparison, as 80 - 90 % of the results are acceptable. Some of the laboratories that reported results outside the acceptance limits used methods being different from the major group of participants. Many of the manual methods are not sensitive enough for samples typically analyzed for acid rain monitoring.

5. Conclusion

47 laboratories submitted results for this intercomparison. Good results were reported for chloride, sulfate, calcium, magnesium, sodium and the unspecific organic compounds, dissolved organic carbon and chemical oxygen demand, more than 80 % being evaluated as acceptable for these analytical variables.

Rather poor comparability was observed for the results of nitrate + nitrite and aluminium species. The differences between the methods used for the determination of aluminium species, are probably the reason for the poor comparability for these variables. Obviously some laboratories had special problems for determining nitrate and nitrite in sample A, which was prepared from water collected in a creek from an anoxic marsh area, and thus containing high concentration of ammonium and organic anions. As this sample also proved to be unstable with respect to nitrate + nitrite, it was decided not to evaluate the reported results for these three analytical variables in this intercomparison.

Overall, 78 % of the reported results were located 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 water samples which are analyzed in this programme, as the detection limit of many manual methods may be too high. If these laboratories are going to analyze the low concentration samples in the future, it is important that they lower the detection 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 16.

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.

6. Literature

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Appendix A. The participating laboratories

Identity   Laboratory

1	Institute of Environ. Protection, Warsawa, Poland
2	Bayerische Landesamt fur Wasserwirtschaft, München, Germany
3	Werkgroep Milieubiologie, Katholieke Universitet, Nijmegen, Netherlands
4	South Estonian Env. Protection Laboratory, Tartu, Estonia
5	Hiiumaä Environmental Laboratory, Kärdla, Estonia
6	Uusimaa Regional Environmental Centre, Helsinki, Finland
7	Estonian Environm. Research Laboratory, Tallinn, Estonia
8	CNR Istituto Italiano di Idrobiologia, Pallanza, Italy
9	MOEE, Dorset Research Centre, Dorset, Canada
10	Centre for Marine Analytical Reference and Standards, Trivandrum, India
11	Bayerische Landesamt für Wasserwirtschaft, Wielenbach, Germany
12	Amt der Kärntner Landesregierung, Klagenfurt, Austria
13	The Environment Agency, NLS Laboratory, Llanelli, United Kingdom
14	Länsstyrelsen i Kalmar Län, Kalmar, Sweden
15	National Laboratory for Environmental Testing, Burlington, Canada
16	SWELAB, Kalmar, Sweden
17	Centre de Geochimie de la Surface, Laboratoire de Chimie des Eaux, Strasbourg, France
18	University of Maine, Water Research Institute, Orono, USA
19	Water Pollution Observation Laboratory, Riga, Latvia
20	Lapland Regional Environment Centre, Rovaniemi, Finland
21	Environmental Protection Ministry, Joint Research Centre, Vilnius, Lithuania
22	Gewässergütelabor Chemnitz, UBG, Chemnitz, Germany
23	Finland Environment Agency Research Laboratory, Helsinki, Finland
24	Ministry of Environment and Ecology, Etobicoke, Canada
25	Academy of Sciences Hydrobiological Institute, Budejovice, Czech Republic
26	University of Alberta, Limnology Laboratory, Edmonton, Canada
27	Swedish Environment Research Institute (IVL), Stockholm, Sweden
28	Swedish Environment Research Institute (IVL), Gothenburg, Sweden
29	Stocholm University, ITM Solna, Stockholm, Sweden
30	Swedish University of Agricultural Sciences, Uppsala, Sweden
31	Freshwater Fisheries Laboratory, Pitlochry, Scotland
32	T.G.Masaryk Water Research Institute, Prague, Czech Republic
33	Adirondac Lake Survey Corporation, Ray Brook, USA
34	Czech Geological Survey, Prague, Czech Republic
35	Forest Research Institute, Karelian Research Centre, Petrozavodsk, Russia
36	Geological Survey of Finland Chemical Laboratory, Espoo, Finland
37	Institute for Ecology of Industrial Areas, Katowice, Poland
38	Swiss Federal Institute, LWF Laboratory, Birmensdorf, Switzerland
39	Swiss Federal Institute, WSL Central Laboratory, Birmensdorf, Switzerland
40	Kola Science Centre, Apatity, Russia
41	Swiss Federal Institute, Stoffbilanz Laboratory, Birmensdorf, Switzerland
42	Swiss Federal Institute, Nitrex Laboratory, Birmensdorf, Switzerland
43	Norwegian Institute for Water Research, Oslo, Norway
44	Research and Engineering Institute for Environment, Buchuresti, Romania
45	Freshwater Institute, Winnipeg, Canada
46	Polish Academy of Sciences Institute of Botany, Krakow, Poland
47	Environmental Protection Agency, Dublin, Ireland

Appendix B. Preparation of samples

The sample solutions were prepared from natural water collected at two locations, a creek from a pond in a marsh area (Svartkulp), and from the Lake Maridalsvatn, both locations outside Oslo, Norway. Raw water was collected in polyethylene containers and brought to the laboratory for storage. Sample A was prepared from the water from the pond called Svartkulp. Sample B was prepared from water sampled in the lake Maridalsvatn. 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 Mean	Std. dev.	Sample B Mean	Std. dev.	Sample C Mean	Std. dev.	Sample D Mean	Std. dev.
pH	7.28	0.13	6.88	0.07				
Conductivity mS/m	8.45	0.11	5.41	0.04				
Alkalinity mmol/l	0.369	0.007	0.128	0.003				
Nitrate/nitrite µg/l	143	53	280	4				
Chloride mg/l	8.35	0.10	6.98	0.15				
Sulfate mg/l	7.58	0.05	5.38	0.05				
Calcium mg/l	4.72	0.20	3.80	0.08				
Magnesium mg/l	1.05	0.07	0.59	0.02				
Sodium mg/l	9.56	0.36	2.05	0.04				
Potassium mg/l	1.35	0.02	0.42	0.02				
Aluminium total, µg/l					150	5	123	4
Reactive aluminium µg/l					79	4	78	7
Non-labile alumin. µg/l					69	4	71	4
Diss.org. C mg/l					8.28	0.25	3.00	0.24
COD.Mn, mg/l					8.18	0.31	2.55	0.13

Sample control analyses

During the intercalibration period, four 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 end of June 1997. 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 for all analytical variables except nitrate + nitrite, which was decreasing during the control periode.

Appendix C. 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 analytical variable. In a coordinate system the result of sample B is plotted against the result of sample A (see Figures 1 - 15).

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 ± 3s, are omitted. The remaining results are used for a final calculation, the results of which are presented in the tables 5.1 - 5.15. Results being omitted from the calculations, are marked with the letter "U".

Appendix D.   Table 4. The results of the participating laboratories.

Identity	pH A	pH B	Cond A	Cond B	Alk A	Alk B	NO3+NO2 A	NO3+NO2 B
1	7.27	6.93	8.55	5.31			24	250.7
2	6.65	6.23	8.90	5.60	0.401	0.147	186	271
3	7.14	6.65.	6.50	4.50	0.35	0.13	178	267
4	7.25	6.76	8.78	5.51	0.37	0.12	180	310
5	7.20	6.78	8.60	5.40	0.32	0.14	0.137	0.284
6	7.22	6.82	8.6	5.4	0.329	0.088	181	277
7	7.25	6.84	7.9	5.1	0.39	0.15	210	290
8	7.28	6.82	8.49	5.34	0.342	0.095	184	278
9	7.28	6.63	8.52	5.44	0.360	0.126	165	286
10	7.1	6.8			0.22	0.14	0.23	1.10
11	6.5	6.6	8.70	5.50	0.35	0.1	140	280
12	6.63	6.45	9.0	5.8	0.39	0.17	81	267
13	7.1	6.7	8.8	5.6	0.32	0.09	280	340
14	7.28	6.80	8.9	5.65	0.31	0.08		
15					0.332	0.0859	< 10	270
16	6.8	7.1	9.0	6.0	0.30	0.07	-	290
17	6.61	6.78	8.56	5.45	0.346	0.096	42	266
18	7.25	6.92	8.42	5.30	0.163	0.0468	314	271
19	7.12	6.87	8.67	5.45			260	330
20	7.29	6.83	8.6	5.4	0.33	0.09	175	269
21	7.35	6.85	8.62	5.53	0.28	0.13	215	279
22	6.6	6.7	6.9	3.4	0.44	0.2	< 500	< 500
23	7.20	6.76	8.85	5.51			186	280
24	7.31	6.96	8.70	4.44	0.376	0.128	185	290
25	7.5	6.95	8.54	5.56	0.33	0.092	6	280
26	7.04	6.43	8.70	5.45	0.334	0.108	167.19	262.45
27	6.9	7.0	9.06	5.56	0.33	0.093		
28	6.8	6.8	8.38	5.37	0.33	0.086	110	291
29	7.35	6.86	8.80	5.51	0.325	0.088		
30	6.69	6.74	8.77	5.55	0.323	0.087	132	345
31	7.32	6.83	8.5	5.3	0.342	0.094	168	266
32	6.72	6.47	7.1	4.6	0.36	0.13	83.6	226
33	6.768	6.819	8.58	5.42	0.34	0.090	94.877	277.85
34	7.05	6.60	8.53	5.42	0.319	0.093		
35	6.61	6.70					< 20	271
36	6.86	6.87	8.65	5.43	0.37	0.14	< 20	290
37	6.29	6.18	10.02	6.56	0.60	0.09	< 20	251
38	6.55	6.58	7.89	4.98				
39							90.1	273
40	6.63	6.74	8.3	5.3	0.33	0.087	< 1	297
41			10.29	6.53				
42	6.96	7.07	7.88	4.95				
43	6.90	6.85	8.41	5.38	0.365	0.129	105	275
44	5.45	4.87	2.9	4.6	0.4	0.3	46.92	56.32
45	7.89	7.30	8.3	5.5	0.35	0.097	15	290
46	7.05	6.72	8.40	5.70			290	1230
47	7.11	6.73	8.4	5.3			181	266

Identity	Cl A	Cl B	SO4 A	SO4 B	Ca A	Ca B	Mg A	Mg B
1	8.33	7.03	7.42	5.32	4.75	3.81	1.089	0.607
2	8.43	7.02	7.71	5.41	4.77	3.76	1.13	0.64
3	10	8			5	4	1.0	0.6
4	8.3	6.8	7.8	5.4	5.7	4.5	1.1	0.60
5	8.0	5.9	7.6	5.2	9.49	5.58	1.35	0.87
6	8.45	6.85	7.67	5.38	4.96	3.92	1.08	0.61
7	9.3	7.2	7.4	5.2	4.08	3.22	1.07	0.53
8	8.48	7.08	7.74	5.49	4.65	3.76	1.10	0.62
9	8.25	7.13	7.70	5.55	4.44	3.58	1.06	0.605
10	6.20	5.70	8.00	5.60	4.60	4.07	1.01	0.62
11	8.5	7.2	7.5	5.3	5.33	4.30	1.29	0.68
12	7.8	6.6	7.3	5.3	4.6	3.7	1.1	0.6
13	8.7	7.1	8.02	5.44	4.91	3.97	1.031	0.616
14								
15	8.27	6.95	8.3	5.6	4.71	3.80	1.06	0.61
16	8.0	7.0	7.0	5.0	4.7	3.7	1.1	0.61
17	8.40	6.81	7.58	5.47	4.77	3.81	1.07	0.61
18	8.35	7.47	7.39	5.20	6.4	4.09	1.09	0.59
19	10.3	8.5	7.4	5.2	4.03	3.63	1.25	0.71
20	8.3	6.8	6.98	5.24	4.8	3.8	1.0	0.6
21	8.3	6.5	9.6	5.4	5.30	3.14	1.67	1.19
22	7.6	6.3	8.3	6.0	4.9	3.9	1.2	0.7
23	8.69	7.15	7.68	5.39	4.85	3.91	1.09	0.62
24	7.82	6.28	7.65	5.40	4.14	3.48	1.04	0.618
25	8.3	6.9	7.7	5.7	5.0	4.0	1.07	0.62
26	8.17	7.01	7.70	5.43	4.54	3.63	1.06	0.61
27					4.71	3.81	1.11	0.608
28	8.87	7.30	7.54	5.36	4.35	3.47	1.15	0.63
29	8.31	6.85	7.39	5.18	4.99	3.91	1.02	0.60
30	8.40	7.02	7.51	5.35	4.85	3.87	1.12	0.63
31	8.17	6.67	7.63	5.28	5.18	4.20	1.19	0.66
32	7.77	6.29	7.42	5.38	4.40	3.53	1.08	0.60
33	8.12	6.64	7.57	5.28	4.74	3.82	1.03	0.59
34	8.13	6.74	7.39	5.22	4.41	3.72	1.02	0.60
35	7.5	6.1	7.4	5.2	5.1	4.0	1.02	0.52
36	8.18	6.81	7.43	5.23	4.70	3.80	1.04	0.57
37	9.10	7.90	7.08	4.84	5.01	3.57	0.98	0.55
38								
39	8.01	6.54	7.75	5.37	4.69	3.78	1.21	0.68
40	8.41	6.89	7.33	5.33	4.33	3.65	0.90	0.57
41								
42								
43	8.3	6.9	7.5	5.4	4.48	3.79	0.97	0.58
44	0.97	0.66	1.89	0.99	6.01	5.01	0.91	0.58
45	8.20	6.70	6.80	4.80	4.63	3.70	1.07	0.59
46	8.62	7.26	7.29	5.20	1.0	1.2	0.6	0.4
47	8.22	6.88	7.53	5.32	4.96	3.92	1.02	0.57

Identity	Na A	Na B	K A	K B	Al C	Al D	Al-R C	Al-R D
1	10.00	2.088	1.412	0.439	148.6	122.1		
2	10.5	2.23	1.49	0.45	170	135		
3	10	2	1.6	0.5				
4	10	2.3	1.4	0.41	168	139		
5							48.9	72.15
6	10.0	2.1	1.44	0.45	146	131		
7	10.2	2.1	1.45	0.49				
8	9.73	2.1	1.44	0.49				
9	10.1	2.1	1.40	0.43	122	156		
10	8.01	2.1	1.10	0.43				
11	10.06	2.0	12.30	4.05	155	140		
12	10	2.1	1.3	0.4	154	123		
13	9.25	1.9	1.37	0.423	140	116	139	118
14					164	161		
15	10.2	2.11	1.40	0.44				
16	9.9	2.1	1.4	0.38	160	120	20	35
17	9.52	2.05	1.41	0.67	111	94		
18	9.3	1.94	1.30	0.40	151	118		
19	9.39	2.10	1.43	0.47				
20	10.4	2.1	1.3	0.4	124	107		
21	9.45	2.05	1.55	0.45				
22	10.6	2.4	1.75	0.55				
23	11.2	2.23	1.42	0.49	139	115	28	35
24	10.4	2.14	1.44	0.432				
25	10.9	2.15	1.21	0.45			102	88
26	10.03	2.21	1.41	0.52				
27	10.1	2.27	1.43	0.422	176	131		
28	10.16	2.10	1.19	0.42				
29	10.34	2.18	1.41	0.43			37.0	26.9
30	10.38	2.16	1.48	0.43	145	120		
31	9.87	2.13	1.44	0.45	140	115	85	93
32	9.62	2.25	1.36	0.41	160	122		
33	10.25	2.83	1.72	0.48				
34	10.33	2.07	1.38	0.42				
35	10.00	2.03	1.50	0.47				
36	9.59	2.06	1.35	0.427				
37	7.86	1.99	1.65	0.44				
38								
39	11.4	2.14	1.57	0.48	143	105		
40	10.0	2.21	1.42	0.44	158	128	21	39
41								
42								
43	9.11	2.02	1.37	0.40	143	120	74	68
44	2.60	1.81	1.37	0.45	44	39		
45	8.85	1.96	1.48	0.46				
46	7.5	2.0	1.4	0.4				
47	9.88	2.11	1.40	0.39				

Identity	Al-I C	Al-I D	DOC C	DOC D	COD-Mn C	COD-Mn D
1			10	4.75		
2			7.20	2.90	8.51	2.77
3						
4					8.6	2.9
5					8.2	3.0
6					8.7	2.9
7						
8						
9						
10					2.96	1.94
11						
12			8.2	3.3		
13	89	61	7.6	2.8		
14	140	99				
15						
16	130	85			8	2
17			7.44	3.05		
18			7.77	2.89		
19						
20			8.1	2.9	7.99	2.66
21						
22						
23	16	7	7.70	2.91		
24			7.2	2.7		
25	86	74	7.89	3.10		
26						
27			7.3	2.6		
28						
29	26.0	8.7	8.75	3.56		
30					8.1	2.7
31	71	67	7.9	3.2		
32			5.88	2.80		
33						
34						
35						
36						
37						
38						
39						
40	137	89			8.64	2.72
41						
42						
43	64	66	8.3	3.0	8.6	2.6
44					38.55	12.96
45			8.16	3.12		
46						
47						

Table 5. 1. Statistics - pH

Analytical method: All
Unit: -

Sample A

Number of participants	44	Range	1.60
Number of omitted results	1	Variance	0.11
True value	7.10	Standard deviation	0.32
Mean value -	7.02	Relative Standard deviation	4.60 %
Median value	7.10	Relative error	-1.20 %

Analytical results in ascending order:

44	5.45 U	36	6.86	7	7.25
37	6.29	27	6.90	18	7.25
11	6.50	43	6.90	4	7.25
38	6.55	42	6.96	1	7.27
22	6.60	26	7.04	9	7.28
17	6.61	46	7.05	8	7.28
35	6.61	34	7.05	14	7.28
40	6.63	10	7.10	20	7.29
12	6.63	13	7.10	24	7.31
2	6.65	47	7.11	31	7.32
30	6.69	19	7.12	21	7.35
32	6.72	3	7.14	29	7.35
33	6.77	23	7.20	25	7.50
28	6.80	5	7.20	45	7.89
16	6.80	6	7.22		

Sample B

Number of participants	44	Range	1.12
Number of omitted results	1	Variance	0.04
True value	6.80	Standard deviation	0.21
Mean value	6.76	Relative Standard deviation	3.10 %
Median value	6.80	Relative error	-0.50 %

Analytical results in ascending order:

44	4.87 U	47	6.73	7	6.84
37	6.18	40	6.74	21	6.85
2	6.23	30	6.74	43	6.85
26	6.43	23	6.76	29	6.86
12	6.45	4	6.76	36	6.87
32	6.47	17	6.78	19	6.87
38	6.58	5	6.78	18	6.92
34	6.60	10	6.80	1	6.93
11	6.60	28	6.80	25	6.95
9	6.63	14	6.80	24	6.96
3	6.65	33	6.82	27	7.00
22	6.70	8	6.82	42	7.07
13	6.70	6	6.82	16	7.10
35	6.70	31	6.83	45	7.30
46	6.72	20	6.83		

U = Omitted results

Table 5. 2. Statistics - Conductivity

Analytical method: All
Unit: mS/m

Sample A

Number of participants	43	Range	3.19
Number of omitted results	3	Variance	0.26
True value	8.60	Standard deviation	0.51
Mean value	8.62	Relative Standard deviation	5.90 %
Median value	8.60	Relative error	0.20 %

Analytical results in ascending order:

44	2.90 U	31	8.50	11	8.70
3	6.50 U	9	8.52	30	8.77
22	6.90 U	34	8.53	4	8.78
32	7.10	25	8.54	13	8.80
42	7.88	1	8.55	29	8.80
38	7.89	17	8.56	23	8.85
7	7.90	33	8.58	14	8.90
40	8.30	5	8.60	2	8.90
45	8.30	20	8.60	12	9.00
28	8.38	6	8.60	16	9.00
47	8.40	21	8.62	27	9.06
46	8.40	36	8.65	37	10.02
43	8.41	19	8.67	41	10.29
18	8.42	26	8.70		
8	8.49	24	8.70		

Sample B

Number of participants	43	Range	2.12
Number of omitted results	3	Variance	0.14
True value	5.45	Standard deviation	0.37
Mean value	5.45	Relative Standard deviation	6.90 %
Median value	5.45	Relative error	-0.10 %

Analytical results in ascending order:

22	3.40 U	43	5.38	4	5.51
24	4.44	5	5.40	21	5.53
3	4.50 U	20	5.40	30	5.55
32	4.60	6	5.40	27	5.56
44	4.60 U	34	5.42	25	5.56
42	4.95	33	5.42	13	5.60
38	4.98	36	5.43	2	5.60
7	5.10	9	5.44	14	5.65
40	5.30	26	5.45	46	5.70
47	5.30	17	5.45	12	5.80
18	5.30	19	5.45	16	6.00
31	5.30	11	5.50	41	6.53
1	5.31	45	5.50	37	6.56
8	5.34	23	5.51		
28	5.37	29	5.51		

U = Omitted results

Table 5. 3. Statistics - Alkalinity

Analytical method: All
Unit: mmol/l

Sample A

Number of participants	37	Range	0.100
Number of omitted results	10	Variance	0.000
True value	0.332	Standard deviation	0.021
Mean value	0.336	Relative Standard deviation	6.40 %
Median value	0.332	Relative error	1.20 %

Analytical results in ascending order:

18	0.163 U	28	0.330	9	0.360		
10	0.220 U	27	0.330	43	0.365		
21	0.280	20	0.330	36	0.370 U		
16	0.300	15	0.332	4	0.370		
14	0.310	26	0.334	24	0.376		
34	0.319	33	0.340	7	0.390 U		
5	0.320 U	8	0.342	12	0.390 U		
13	0.320	31	0.342	44	0.400 U		
30	0.323	17	0.346	2	0.401 U		
29	0.325	3	0.350	22	0.440 U		
6	0.329	11	0.350	37	0.600 U		
40	0.330	45	0.350				
25	0.330	32	0.360				

Sample B

Number of participants	37	Range	0.060
Number of omitted results	10	Variance	0.000
True value	0.093	Standard deviation	0.018
Mean value	0.100	Relative Standard deviation	19.30 %
Median value	0.093	Relative error	7.60 %

Analytical results in ascending order:

18	0.047 U	25	0.092	21	0.130		
16	0.070	27	0.093	32	0.130		
14	0.080	34	0.093	3	0.130		
15	0.086	31	0.094	36	0.140 U		
28	0.086	8	0.095	10	0.140 U		
40	0.087	17	0.096	5	0.140 U		
30	0.087	45	0.097	2	0.147 U		
29	0.088	11	0.100	7	0.150 U		
6	0.088	26	0.108	12	0.170 U		
37	0.090 U	4	0.120	22	0.200 U		
13	0.090	9	0.126	44	0.300 U		
33	0.090	24	0.128				
20	0.090	43	0.129				

U = Omitted results

Table 5. 4. Statistics - Nitrate + nitrite-nitrogen

Analytical method: All
Unit: µg/l

Sample A

Number of participants	40	Range		199
Number of omitted results	15	Variance		2608
True value	105	Standard deviation		51.1
Mean value	108	Relative Standard deviation		22.00 %
Median value	105	Relative error		3.00 %

Analytical results in ascending order:

16	- U	32	84	47	181
22	< 500 U	39	90	6	181
36	< 50 U	33	95	8	184
37	< 20 U	43	105	24	185
35	< 20 U	28	110	23	186
15	< 10 U	30	132	2	186
40	< 1 U	5	137	7	210
10	0 U	11	140	21	215
25	6 U	9	165	19	260
45	15 U	26	167	13	280
1	24 U	31	168	46	290 U
17	42 U	20	175	18	314 U
44	47 U	3	178		
12	81	4	180		

Sample B

Number of participants	40	Range		119
Number of omitted results	15	Variance		3438
True value	278	Standard deviation		58.6
Mean value	280	Relative Standard deviation		11.00 %
Median value	278	Relative error		3.00 %

Analytical results in ascending order:

22	< 500 U	2	271	36	290 U
10	1 U	18	271 U	7	290
44	56 U	35	271 U	24	290
32	226	39	273	16	290 U
1	251 U	43	275	45	290 U
37	251 U	6	277	28	291
26	263	33	278	40	297 U
17	266 U	8	278	4	310
47	266	21	279	19	330
31	266	25	280 U	13	340
12	267	23	280	30	345
3	267	11	280	46	1230 U
20	269	5	284		
15	270 U	9	286		

U = Omitted results

Table 5. 5. Statistics - Chloride

Analytical method: All
Unit: mg/l

Sample A

Number of participants	42	Range	2.50
Number of omitted results	3	Variance	0.21
True value	8.30	Standard deviation	0.45
Mean value	8.33	Relative Standard deviation	5.40 %
Median value	8.30	Relative error	0.40 %

Analytical results in ascending order:

44	0.97 U	36	8.18	30	8.40
10	6.20 U	45	8.20	40	8.41
35	7.50	47	8.22	2	8.43
22	7.60	9	8.25	6	8.45
32	7.77	15	8.27	8	8.48
12	7.80	25	8.30	11	8.50
24	7.82	21	8.30	46	8.62
5	8.00	43	8.30	23	8.69
16	8.00	20	8.30	13	8.70
39	8.01	4	8.30	28	8.87
33	8.12	29	8.31	37	9.10
34	8.13	1	8.33	7	9.30
26	8.17	18	8.35	3	10.00
31	8.17	17	8.40	19	10.30 U

Sample B

Number of participants	42	Range	2.10
Number of omitted results	3	Variance	0.17
True value	6.89	Standard deviation	0.42
Mean value	6.89	Relative Standard deviation	6.10 %
Median value	6.89	Relative error	-0.10 %

Analytical results in ascending order:

44	0.66 U	20	6.80	2	7.02
10	5.70 U	4	6.80	1	7.03
5	5.90	36	6.81	8	7.08
35	6.10	17	6.81	13	7.10
24	6.28	29	6.85	9	7.13
32	6.29	6	6.85	23	7.15
22	6.30	47	6.88	7	7.20
21	6.50	40	6.89	11	7.20
39	6.54	25	6.90	46	7.26
12	6.60	43	6.90	28	7.30
33	6.64	15	6.95	18	7.47
31	6.67	16	7.00	37	7.90
45	6.70	26	7.01	3	8.00
34	6.74	30	7.02	19	8.50 U

U = Omitted results

Table 5. 6. Statistics - Sulfate

Analytical method: All
Unit: mg/l

Sample A

Number of participants	41	Range	1.50
Number of omitted results	3	Variance	0.08
True value	7.52	Standard deviation	0.29
Mean value	7.52	Relative Standard deviation	3.80 %
Median value	7.52	Relative error	0.00 %

Analytical results in ascending order:

44	1.89 U	32	7.42	23	7.68
45	6.80	1	7.42	25	7.70
20	6.98	36	7.43	9	7.70
16	7.00	43	7.50	26	7.70
37	7.08	11	7.50	2	7.71
46	7.29	30	7.51	8	7.74
12	7.30	47	7.53	39	7.75
40	7.33	28	7.54	4	7.80
18	7.39	33	7.57	10	8.00
34	7.39	17	7.58	13	8.02
29	7.39	5	7.60	15	8.30
7	7.40	31	7.63	22	8.30 U
19	7.40	24	7.65	21	9.60 U
35	7.40	6	7.67		

Sample B

Number of participants	41	Range	0.90
Number of omitted results	3	Variance	0.03
True value	5.33	Standard deviation	0.18
Mean value	5.31	Relative Standard deviation	3.40 %
Median value	5.33	Relative error	-0.30 %

Analytical results in ascending order:

44	0.99 U	31	5.28	21	5.40 U
45	4.80	33	5.28	43	5.40
37	4.84	12	5.30	4	5.40
16	5.00	11	5.30	2	5.41
29	5.18	47	5.32	26	5.43
7	5.20	1	5.32	13	5.44
5	5.20	40	5.33	17	5.47
46	5.20	30	5.35	8	5.49
19	5.20	28	5.36	9	5.55
18	5.20	39	5.37	15	5.60
35	5.20	32	5.38	10	5.60
34	5.22	6	5.38	25	5.70
36	5.23	23	5.39	22	6.00 U
20	5.24	24	5.40		

U = Omitted results

Table 5. 7. Statistics - Calcium

Analytical method: All
Unit: mg/l

Sample A

Number of participants	43	Range		1.67
Number of omitted results	4	Variance		0.12
True value	4.74	Standard deviation		0.34
Mean value	4.75	Relative Standard deviation		7.20 %
Median value	4.74	Relative error		0.10 %

Analytical results in ascending order:

46	1.00 U	39	4.69	6	4.96
19	4.03	36	4.70	29	4.99
7	4.08	16	4.70	25	5.00
24	4.14	15	4.71	3	5.00
40	4.33	27	4.71	37	5.01
28	4.35	33	4.74	35	5.10
32	4.40	1	4.75	31	5.18
34	4.41	17	4.77	21	5.30
9	4.44	2	4.77	11	5.33
43	4.48	20	4.80	4	5.70
26	4.54	23	4.85	44	6.01 U
10	4.60	30	4.85	18	6.40 U
12	4.60	22	4.90	5	9.49 U
45	4.63	13	4.91		
8	4.65	47	4.96		

Sample B

Number of participants	43	Range		1.36
Number of omitted results	4	Variance		0.06
True value	3.80	Standard deviation		0.25
Mean value	3.79	Relative Standard deviation		6.70 %
Median value	3.80	Relative error		-0.20 %

Analytical results in ascending order:

46	1.20 U	8	3.76	47	3.92
21	3.14	2	3.76	6	3.92
7	3.22	39	3.78	13	3.97
28	3.47	43	3.79	25	4.00
24	3.48	15	3.80	3	4.00
32	3.53	36	3.80	35	4.00
37	3.57	20	3.80	10	4.07
9	3.58	17	3.81	18	4.09 U
26	3.63	27	3.81	31	4.20
19	3.63	1	3.81	11	4.30
40	3.65	33	3.82	4	4.50
12	3.70	30	3.87	44	5.01 U
16	3.70	22	3.90	5	5.58 U
45	3.70	23	3.91		
34	3.72	29	3.91		

U = Omitted results

Table 5. 8. Statistics - Magnesium

Analytical method: All
Unit: mg/l

Sample A

Number of participants	43	Range	0.39
Number of omitted results	3	Variance	0.01
True value	1.07	Standard deviation	0.08
Mean value	1.07	Relative Standard deviation	7.50 %
Median value	1.07	Relative error	0.30 %

Analytical results in ascending order:

46	0.60 U	24	1.04	16	1.10
40	0.90	15	1.06	4	1.10
44	0.91	9	1.06	27	1.11
43	0.97	26	1.06	30	1.12
37	0.98	25	1.07	2	1.13
3	1.00	7	1.07	28	1.15
20	1.00	17	1.07	31	1.19
10	1.01	45	1.07	22	1.20
47	1.02	32	1.08	39	1.21
35	1.02	6	1.08	19	1.25
34	1.02	1	1.09	11	1.29
29	1.02	23	1.09	5	1.35 U
33	1.03	18	1.09	21	1.67 U
13	1.03	8	1.10		
36	1.04	12	1.10		

Sample B

Number of participants	43	Range	0.19
Number of omitted results	3	Variance	0.00
True value	0.61	Standard deviation	0.04
Mean value	0.61	Relative Standard deviation	6.40 %
Median value	0.61	Relative error	-0.20 %

Analytical results in ascending order:

46	0.40 U	34	0.60	23	0.62
35	0.52	20	0.60	10	0.62
7	0.53	29	0.60	8	0.62
37	0.55	4	0.60	28	0.63
40	0.57	9	0.61	30	0.63
36	0.57	1	0.61	2	0.64
47	0.57	27	0.61	31	0.66
43	0.58	15	0.61	39	0.68
44	0.58	26	0.61	11	0.68
18	0.59	17	0.61	22	0.70
33	0.59	16	0.61	19	0.71
45	0.59	6	0.61	5	0.87 U
12	0.60	13	0.62	21	1.19 U
32	0.60	24	0.62		
3	0.60	25	0.62		

U = Omitted results

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Table 5. 9. Statistics - Sodium

Analytical method: All
Unit: mg/l

Sample A

Number of participants	42	Range	3.54
Number of omitted results	3	Variance	0.48
True value	10.00	Standard deviation	0.70
Mean value	9.91	Relative Standard deviation	7.00 %
Median value	10.00	Relative error	-0.90 %

Analytical results in ascending order:

44	2.60 U	31	9.87	28	10.16		
46	7.50 U	47	9.88	15	10.20		
37	7.86	16	9.90	7	10.20		
10	8.01	40	10.00	33	10.25 U		
45	8.85	12	10.00	34	10.33		
43	9.11	3	10.00	29	10.34		
13	9.25	35	10.00	30	10.38		
18	9.30	1	10.00	24	10.40		
19	9.39	4	10.00	20	10.40		
21	9.45	6	10.00	2	10.50		
17	9.52	26	10.03	22	10.60		
36	9.59	11	10.06	25	10.90		
32	9.62	9	10.10	23	11.20		
8	9.73	27	10.10	39	11.40		

Sample B

Number of participants	42	Range	0.50
Number of omitted results	3	Variance	0.01
True value	2.10	Standard deviation	0.10
Mean value	2.12	Relative Standard deviation	4.80 %
Median value	2.10	Relative error	0.80 %

Analytical results in ascending order:

44	1.81 U	1	2.09	39	2.14		
13	1.90	7	2.10	6	2.14		
18	1.94	10	2.10	25	2.15		
45	1.96	28	2.10	30	2.16		
37	1.99	12	2.10	29	2.18		
46	2.00 U	19	2.10	40	2.21		
3	2.00	20	2.10	26	2.21		
43	2.02	16	2.10	23	2.23		
35	2.03	15	2.11	2	2.23		
11	2.04	47	2.11	32	2.25		
17	2.05	9	2.13	27	2.27		
21	2.05	8	2.13	4	2.30		
36	2.06	31	2.13	22	2.40		
34	2.07	24	2.14	33	2.83 U		

U = Omitted results

Table 5. 10. Statistics - Potassium

Analytical method: All
Unit: mg/l

Sample A

Number of participants	42	Range			0.65
Number of omitted results	2	Variance			0.02
True value	1.41	Standard deviation			0.12
Mean value	1.42	Relative Standard deviation			8.80 %
Median value	1.41	Relative error			0.90 %

Analytical results in ascending order:

10	1.10	47	1.40	31	1.44
28	1.19	46	1.40	6	1.44
25	1.21	16	1.40	7	1.45
12	1.30	4	1.40	30	1.48
18	1.30	26	1.41	45	1.48
20	1.30	17	1.41 U	2	1.49
36	1.35	29	1.41	35	1.50
32	1.36	1	1.41	21	1.55
13	1.37	40	1.42	39	1.57
43	1.37	23	1.42	3	1.60
44	1.37	27	1.43	37	1.65
34	1.38	19	1.43	33	1.72
15	1.40	24	1.44	22	1.75
9	1.40	8	1.44	11	12.3 U

Sample B

Number of participants	42	Range			0.17
Number of omitted results	2	Variance			0.00
True value	0.44	Standard deviation			0.04
Mean value	0.44	Relative Standard deviation			8.40 %
Median value	0.44	Relative error			0.60 %

Analytical results in ascending order:

16	0.38	9	0.43	6	0.45
47	0.39	10	0.43	45	0.46
12	0.40	29	0.43	19	0.47
46	0.40	30	0.43	35	0.47
43	0.40	24	0.43	33	0.48
18	0.40	1	0.44	39	0.48
20	0.40	40	0.44	7	0.49
32	0.41	15	0.44	23	0.49
4	0.41	37	0.44	8	0.49
28	0.42	25	0.45	3	0.50
34	0.42	21	0.45	26	0.52
27	0.42	2	0.45	22	0.55
13	0.42	31	0.45	17	0.67 U
36	0.43	44	0.45	11	4.05 U

U = Omitted results

Table 5. 11. Statistics - Aluminium

Analytical method: All
Unit: mg/l

Sample C

Number of participants	22	Range	65
Number of omitted results	1	Variance	265
True value	149	Standard deviation	16
Mean value	148	Relative Standard deviation	10.9 %
Median value	149	Relative error	-0.4 %

Analytical results in ascending order:

44	44 U	39	143	32	160
17	111	30	145	16	160
9	122	6	146	14	164
20	124	1	149	4	168
23	139	18	151	2	170
13	140	12	154	27	176
31	140	11	155		
43	143	40	158		

Sample D

Number of participants	22	Range	67
Number of omitted results	1	Variance	248
True value	122	Standard deviation	16
Mean value	125	Relative Standard deviation	12.9 %
Median value	122	Relative error	2.2 %

Analytical results in ascending order:

44	39 U	43	120	6	131
17	94	30	120	2	135
39	105	16	120	4	139
20	107	32	122	11	140
23	115	1	122	9	156
31	115	12	123	14	161
13	116	40	128		
18	118	27	131		

U = Omitted results

Table 5. 12. Statistics - Aluminium, reactive

Analytical method: All
Unit: mg/l

Sample C

Number of participants	9	Range		53
Number of omitted results	5	Variance		496
True value	80	Standard deviation		22
Mean value	77	Relative Standard deviation		27.8 %
Median value	80	Relative error		-3.2 %

Analytical results in ascending order:

16	20 U	29	37 U	31	85
40	21 U	5	49	25	102
23	28 U	43	74	13	139 U

Sample D

Number of participants	9	Range		25
Number of omitted results	5	Variance		146
True value	80	Standard deviation		12
Mean value	80	Relative Standard deviation		15.1 %
Median value	80	Relative error		0.3 %

Analytical results in ascending order:

29	27 U	40	39 U	25	88
23	35 U	43	68	31	93
16	35 U	5	72	13	118 U

U = Omitted results

Table 5. 13. Statistics - Aluminium, nonlabile

Analytical method: All
Unit: mg/l

Sample C

Number of participants	9	Range	25
Number of omitted results	5	Variance	143
True value	79	Standard deviation	12
Mean value	78	Relative Standard deviation	15.1 %
Median value	79	Relative error	-1.9 %

Analytical results in ascending order:

23	16 U	31	71	16	130 U
29	26 U	25	86	40	137 U
43	64	13	89	14	140 U

Sample D

Number of participants	9	Range	13
Number of omitted results	5	Variance	29
True value	67	Standard deviation	5
Mean value	67	Relative Standard deviation	8.0 %
Median value	67	Relative error	0.0 %

Analytical results in ascending order:

23	7 U	43	66	16	85 U
29	9 U	31	67	40	89 U
13	61	25	74	14	99 U

U = Omitted results

Table 5. 14. Statistics - Dissolved organic carbon

Analytical method: All
Unit: mg/l

Sample C

Number of participants	16	Range		2.87
Number of omitted results	1	Variance		0.44
True value	7.77	Standard deviation		0.67
Mean value	7.69	Relative Standard deviation		8.60 %
Median value	7.77	Relative error		-1.00 %

Analytical results in ascending order:

32	5.88	23	7.70	12	8.20
24	7.20	18	7.77	43	8.30
2	7.20	25	7.89	29	8.75
27	7.30	31	7.90	1	10.00 U
17	7.44	20	8.10		
13	7.60	45	8.16		

Sample D

Number of participants	16	Range		0.96
Number of omitted results	1	Variance		0.06
True value	2.91	Standard deviation		0.24
Mean value	2.99	Relative Standard deviation		8.40 %
Median value	2.91	Relative error		2.70 %

Analytical results in ascending order:

27	2.60	20	2.90	31	3.20
24	2.70	23	2.91	12	3.30
13	2.80	43	3.00	29	3.56
32	2.80	17	3.05	1	4.75 U
18	2.89	25	3.10		
2	2.90	45	3.12		

U = Omitted results

Table 5. 15. Statistics - Chemical oxygen demand

Analytical method: All
Unit: mg/l

Sample C

Number of participants	11	Range	0.71
Number of omitted results	2	Variance	0.09
True value	8.51	Standard deviation	0.29
Mean value	8.37	Relative Standard deviation	3.50 %
Median value	8.51	Relative error	-1.60 %

Analytical results in ascending order:

10	2.96 U	5	8.20	40	8.64
20	7.99	2	8.51	6	8.70
16	8.00	4	8.60	44	38.6 U
30	8.10	43	8.60		

Sample D

Number of participants	10	Range	1.00
Number of omitted results	2	Variance	0.10
True value	2.75	Standard deviation	0.31
Mean value	2.71	Relative Standard deviation	11.20 %
Median value	2.75	Relative error	-1.60 %

Analytical results in ascending order:

10	1.94 U	30	2.70	6	2.90
16	2.00	40	2.72	5	3.00
43	2.60	2	2.77	44	12.96 U
20	2.66	4	2.90		

U = Omitted results