Convention on Long-range Transboundary Air Pollution

International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes

ICP-WATERS REPORT

NIVA Norwegian Institute for Water Research

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Intercomparison 9913:

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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Abstract

57 laboratories in 24 countries participated in intercomparison 9913. Two sample sets were used, one for the determination of major ions and one for organic matter and aluminium fractions. Based on the general target accuracy of ± 20 %, 78 % of the results were acceptable. More than 80 % of the result pairs were acceptable for conductivity, chloride, sulfate, magnesium, sodium, and dissolved organic carbon. For pH only 57 % of the result pairs were acceptable in relation to the extended target accuracy of ± 0.2 units. For three analytical variables it was decided **not** to evaluate the reported results, reactive and non-labile aluminium because of the great spread between the results from the few participants, and nitrate + nitrite because of the instability of sample A. Normalization of the methods is necessary to improve the comparability for pH and aluminium fractions. Manual methods are generally less sensitive compared to instrumental methods, and are not always suitable for acid rain monitoring.

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CONVENTION ON LONG-RANGE
TRANSBOUNDARY AIR POLLUTION

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

Intercomparison 9913

*p*H, K25, HCO_3^-, $NO_3^-+NO_2^-$, Cl^-, SO_4^{--}
Ca^{++}, Mg^{++}, Na^+, K^+,
Al, Al-R, Al-I, DOC and Cod-Mn

Prepared by the Programme Centre
Norwegian Institute for Water Research
Oslo, September 1999

Preface

The International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters) was established under the Executive Body of the Convention on Long Range Transboundary Air Pollution at its third session in Helsinki in July 1985. The Executive Body has also accepted Norway's offer to provide facilities for the Programme Centre, which has been established at the Norwegian Institute for Water Research, NIVA. A programme subcentre is established at the Laboratory of Freshwater Ecology and Inland Fisheries at University of Bergen. The ICP Waters programme has been lead by Berit Kvæven, Norwegian Pollution Control Authority.

The Programme objective is to establish an international network of surface water monitoring sites and promote international harmonization of monitoring practices. One of the tools in this work is inter-laboratory quality assurance tests. The bias between analyses carried out by the individual participants of the Programme has to be clearly identified and controlled.

We here report the results from the 13th intercomparison of chemical analysis.

Oslo, September 1999

Håvard Hovind

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Summary

Intercomparison 9913 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 May-June 1999, 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 were prepared for this intercomparison, one for the determination of the major ions, and the other for aluminium fractions and unspecific organic matter. 57 laboratories determined all, or some of the analytical variables in the samples.

87 laboratories were invited to participate in this intercomparison, and the samples were sent to 65 laboratories who accepted to participate. 57 laboratories submitted results to the Programme Centre before the final statistical treatment of the data. 24 countries were represented in this laboratory group.

The median value of the results received from the participants was selected as "true" value for each variable. For two analytical variables - reactive and non-labile aluminium - this definition of the "true value" is not acceptable, because of the great spread between the results from the few laboratories determining this variable. It was therefore decided not to evaluate the reported results for these varibles. The content of nitrate + nitrite proved to be unstable in sample A, therefore this varible was excluded from the evaluation too. Excluding these varibles from the evalution, 78 % of the result pairs were regarded as acceptable, the target limit being the median value ± 20 %, except for pH and conductivity where the acceptance limits were ± 0,02 units and ± 10 %, respectively.

For pH the accuracy limit was extended to ± 0.2 units, and only 57 % 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 median value for all the reported results for pH, when the methods are different, is questionable, and on the next meeting it should be discussed wether a certain "true value" for **each method** would be more informative.

The best results were reported for conductivity, chloride, sulfate, magnesium, sodium, and dissolved organic carbon, as more than 80 % of the result pairs were acceptable. Rather poor comparability was observed for pH and aluminium species. To improve the comparability of the results for these variables, it is necessary to normalize the analytical method and the 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 by use of different analytical methods, errors in the laboratory calibration solutions, or through inadequate within-laboratory control.

The between laboratory control carried out by the Programme Centre is based on the "round robin" concept and the procedure of Youden (2, 3), which is briefly described in Appendix 3. This thirteenth intercomparison test, called 9913, 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 1998 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 May 20, 1999. Most of the participating laboratories received the samples within one week, with very 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 one month after the samples arrived at the laboratory. Most results were received within the end of June.

3. Results

87 laboratories were invited to participate in the intercomparison, and 65 laboratories accepted and received samples. The 57 laboratories who submitted results to the Programme Centre, are representing 24 countries. It was a problem that some of the laboratories submitted the results several weeks after the deadline, 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. For certain varibles, like pH, this may represent a problem as the methods used are producing systematically different results.

The results are illustrated in Figure 1 - 15, where each laboratory is represented by a small circle and an identification number. Some laboratories with strongly deviating results may be located outside the plot. The 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 9913 is presented in Table 1. The individual results of the participants are presented in Table 4 in the Appendix, 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 circle is 0.2 pH units, and visualizes the degree of comparability between the pH results from the participating laboratories. The values reported by the laboratories are given in Table 5.1.

The participating laboratories determined pH in the test solutions using their own routine method. An electrometric method was used by all laboratories. 54 laboratories reported results for pH, of this group 19 indicated that they read the pH value during stirring the solution. The stirring are normally lowering the observed pH result, however, as shown in Table 1, there is no significant difference between the results determined in a quiescent solution, and when determined during stirring the solution in this intercomparison.

Figure 1 shows that the reported results are spread out along the 45 ° line, indicating that the results are influenced by systematic effects. Two laboratories 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. These results should not be evaluated by comparing them to the mean value of all the reported results, because this method is giving systematically different results. The information given by the pH measured after equilibrating the solution, is quite different from the two other methods where pH is read directly or after stirring.

The CO_2 concentration of samples in the circumneutral range may be above the atmospheric equilibrium. This may lead to systematic errors, the magnitude will vary between the

(The text continues on page 26)

Table 1. Statistical summary of intercomparison 9913

Analytical variable and method	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	Rel.st.dev. % 2	Rel. error % 1	Rel. error % 2
pH	AB	6.48	6.95	54	1	6.48	6.95	6.47	0.18	6.93	0.19	2.9	2.7	-0.1	-0.2
Electrometry				33	1	6.44	6.92	6.45	0.17	6.90	0.19	2.6	2.7	-0.5	-0.8
Stirring				19	0	6.50	6.98	6.47	0.16	6.96	0.15	2.4	2.1	-0.2	0.1
Equilibration				2	0			6.92		7.33				6.8	5.5
Conductivity	AB	3.00	4.80	53	4	3.00	4.80	2.99	0.13	4.76	0.21	4.3	4.4	-0.2	-0.8
Alkalinity	AB	0.085	0.170	48	12	0.085	0.170	0.088	0.014	0.171	0.016	16.4	9.4	3.0	0.5
Gran plot titration				17	3	0.085	0.170	0.087	0.008	0.167	0.008	9.1	4.6	2.8	-1.7
End point titration				9	2	0.090	0.165	0.086	0.016	0.171	0.019	18.6	11.4	0.9	0.5
End point 5.6				1	0			0.072		0.161				-15.3	-5.3
End point 5.4				2	0			0.076		0.175				-11.2	2.9
End point 4.5				13	4	0.100	0.180	0.098	0.018	0.185	0.017	18.9	9.4	15.0	8.8
Not documented				6	3	0.074	0.158	0.075	0.007	0.152	0.013	9.4	8.4	-11.3	-10.6
Nitrate + nitrite-nitrogen	AB	120	182	52	17	115	182	119	35	179	18	29.4	10.3	-0.7	-1.7
Autoanalyzer				17	4	125	185	126	29	182	13	22.8	7.1	5.1	-0.2
Photometry				9	5	132	183	128	56	185	14	43.7	7.6	6.9	1.4
Ion chromatography				24	7	130	180	113	35	178	21	31.2	11.9	-5.5	-2.3
Hydrazine				1	1			203		213				69.2	17.0
Cap. electrophoresis				1	0			90		138				-25.0	-24.2
Chloride	AB	2.03	3.58	54	2	2.03	3.58	2.05	0.19	3.55	0.22	9.1	6.3	0.8	-0.7
Ion chromatography				41	1	2.01	3.56	2.02	0.15	3.52	0.19	7.3	5.4	-0.5	-1.7
Autoanalyzer				3	0	2.18	3.69	2.17	0.18	3.73	0.12	8.3	3.2	6.7	4.3
Argentometry				3	0	2.20	3.95	2.29	0.19	3.92	0.20	8.1	5.2	12.6	9.4
Manual, Hg				5	1	2.19	3.77	2.16	0.29	3.63	0.36	13.2	10.0	6.4	1.3
Cap. electrophoresis				1	0			1.56		3.27				-23.1	-8.6
Potentiometry				1	0			2.04		3.43				0.5	-4.2

Analytical variable and method	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	Rel.st.dev. % 2	Rel. error % 1	Rel. error % 2
Sulfate	AB	4.00	5.33	52	3	4.00	5.33	3.95	0.30	5.24	0.40	7.6	7.7	-1.3	-1.7
Ion chromatography				41	1	4.01	5.34	3.95	0.21	5.26	0.26	5.2	5.0	-1.9	-1.3
Photometry				4	2			3.73		4.93				-6.9	-7.6
Nephelometry				5	0	4.20	5.60	3.97	0.73	5.22	1.07	18.5	20.5	-0.7	-2.1
ICP				1	0			4.20		5.23				5.0	-1.9
Cap. electrophoresis				1	0			3.56		5.02				-11.0	-5.8
Calcium	AB	2.75	3.55	55	4	2.75	3.55	2.77	0.26	3.60	0.37	9.5	10.2	0.6	1.4
FAAS				25	3	2.68	3.49	2.67	0.26	3.45	0.31	9.7	9.0	-3.0	-2.8
ICP				12	0	2.83	3.75	2.87	0.14	3.74	0.21	4.9	5.6	4.2	5.4
EDTA				4	1	2.81	4.01	2.85	0.18	3.66	0.75	6.3	20.5	3.6	3.2
Ion chromatography				13	0	2.77	3.57	2.80	0.33	3.70	0.43	11.8	11.5	1.8	4.4
ICP-MS				3	0			3.00		3.60				9.1	1.4
Magnesium	AB	0.47	0.86	55	5	0.47	0.86	0.47	0.05	0.87	0.08	10.7	9.2	0.9	1.5
FAAS				25	1	0.46	0.85	0.46	0.05	0.85	0.05	10.9	5.9	-2.3	-0.8
ICP				12	0	0.48	0.90	0.49	0.05	0.91	0.06	10.5	7.0	5.2	6.1
EDTA				4	3			0.61		0.61				29.8	-29.1
Ion chromatography				13	0	0.48	0.87	0.47	0.04	0.89	0.09	8.2	10.3	0.7	3.8
ICP-MS				1	1			1.00		1.00				112.8	16.3
Sodium	AB	1.73	2.84	53	2	1.73	2.84	1.74	0.12	2.85	0.20	7.1	7.1	0.5	0.3
FAAS				18	2	1.72	2.86	1.71	0.05	2.84	0.12	3.2	4.2	-1.2	-0.1
ICP				10	0	1.70	2.78	1.70	0.14	2.78	0.26	8.5	9.4	-2.0	-2.3
AES				10	0	1.78	2.98	1.80	0.16	2.94	0.27	9.1	9.2	4.1	3.5
Ion chromatography				14	0	1.75	2.83	1.76	0.13	2.86	0.19	7.4	6.5	1.4	0.5
ICP-MS				1	0			1.80		2.80				4.0	-1.4
Potassium	AB	0.36	0.37	53	6	0.36	0.37	0.36	0.03	0.37	0.03	8.9	9.4	-0.2	-0.6
FAAS				19	0	0.37	0.37	0.37	0.02	0.36	0.02	5.2	5.9	1.4	-1.6
ICP				9	2	0.36	0.37	0.35	0.05	0.35	0.05	13.7	14.7	-1.9	-4.5
AES				10	2	0.35	0.36	0.34	0.02	0.35	0.03	6.1	7.4	-4.7	-4.7
Ion chromatography				14	2	0.36	0.38	0.36	0.04	0.39	0.04	11.3	9.8	-0.3	5.2
ICP-MS				1	0			0.40		0.40				11.1	8.1

Analytical variable and method	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	Rel.st.dev. % 2	Rel. error % 1	Rel. error % 2
Aluminium	CD	87	148	22	1	87	145	86	17	145	22	19.8	15.1	-0.8	-1.9
GFAAS				7	0	89	146	88	20	143	27	23.1	18.6	1.0	-3.3
ICP				6	0	88	140	88	21	144	28	23.4	19.3	1.5	-3.0
ICP-MS				3	0	83	149	85	4	149	1	5.0	0.7	-2.1	0.7
Photometry				6	1	89	156	82	16	148	18	19.6	12.5	-5.3	-0.3
Aluminium, reactive	CD	31	44	12	3	31	44	30	5	45	10	16.9	23.3	-4.4	1.5
Aluminium, nonlabile	CD	49	95	10	4	49	95	51	7	96	9	14.2	9.0	4.1	1.2
Dissolved organic carbon	CD	3.79	3.69	23	1	3.79	3.69	3.79	0.39	3.76	0.42	10.4	11.2	-0.1	1.8
Combustion				14	0	3.71	3.61	3.77	0.43	3.75	0.43	11.3	11.4	-0.5	1.5
UV S_2O_8				4	0	3.62	3.62	3.64	0.18	3.58	0.20	4.9	5.6	-3.9	-3.0
Phenolphthalein				5	1	3.99	3.94	4.00	0.43	3.97	0.55	10.7	13.7	5.4	7.6
Chemical oxygen demand	CD	4.39	4.30	13	0	4.39	4.30	4.31	0.73	4.12	0.63	17.0	15.3	-1.8	-4.2

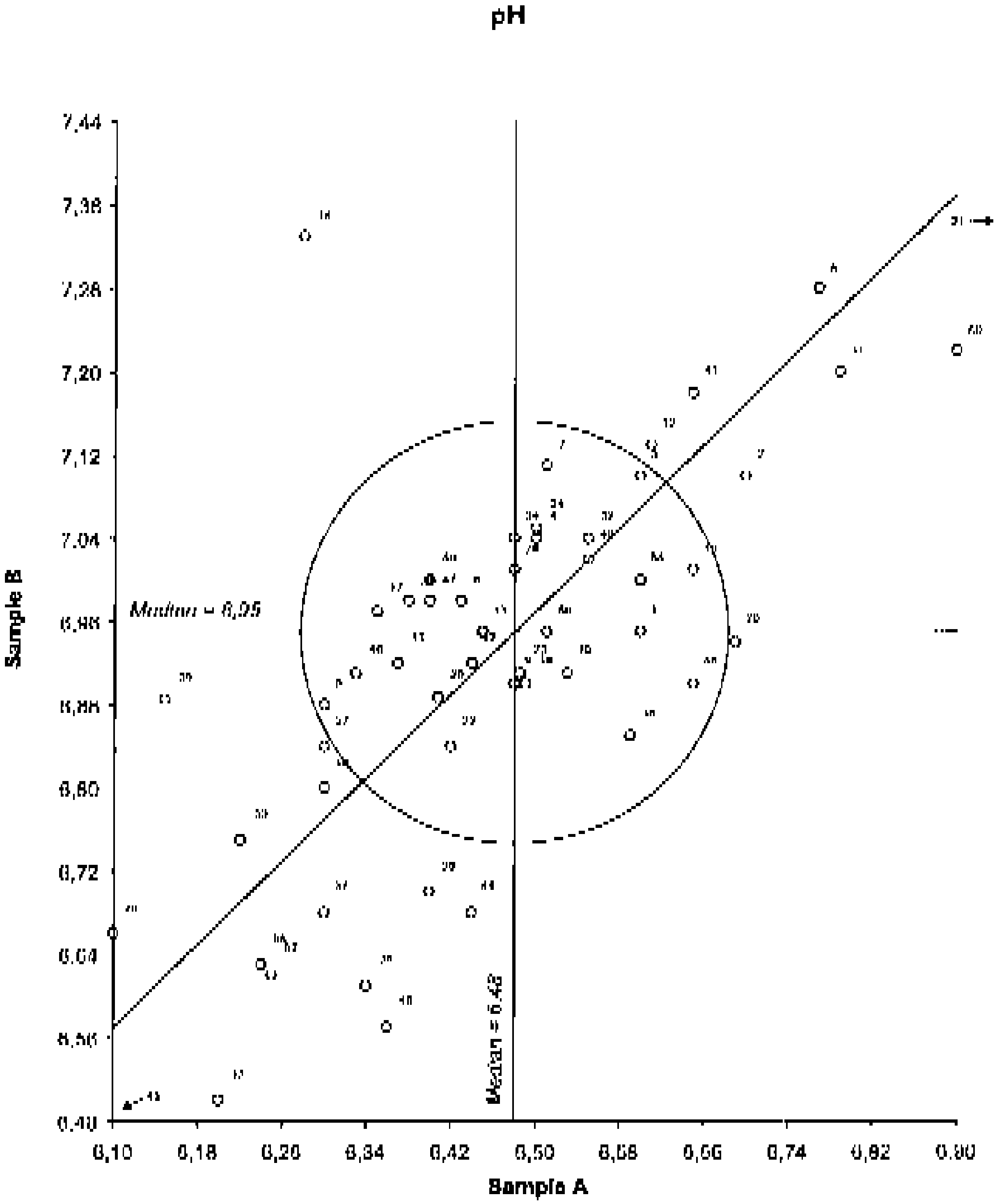

Figure 1. Youden diagramme for pH, Sample pair AB
Acceptance limit is 0,2 pH units

Conductivity

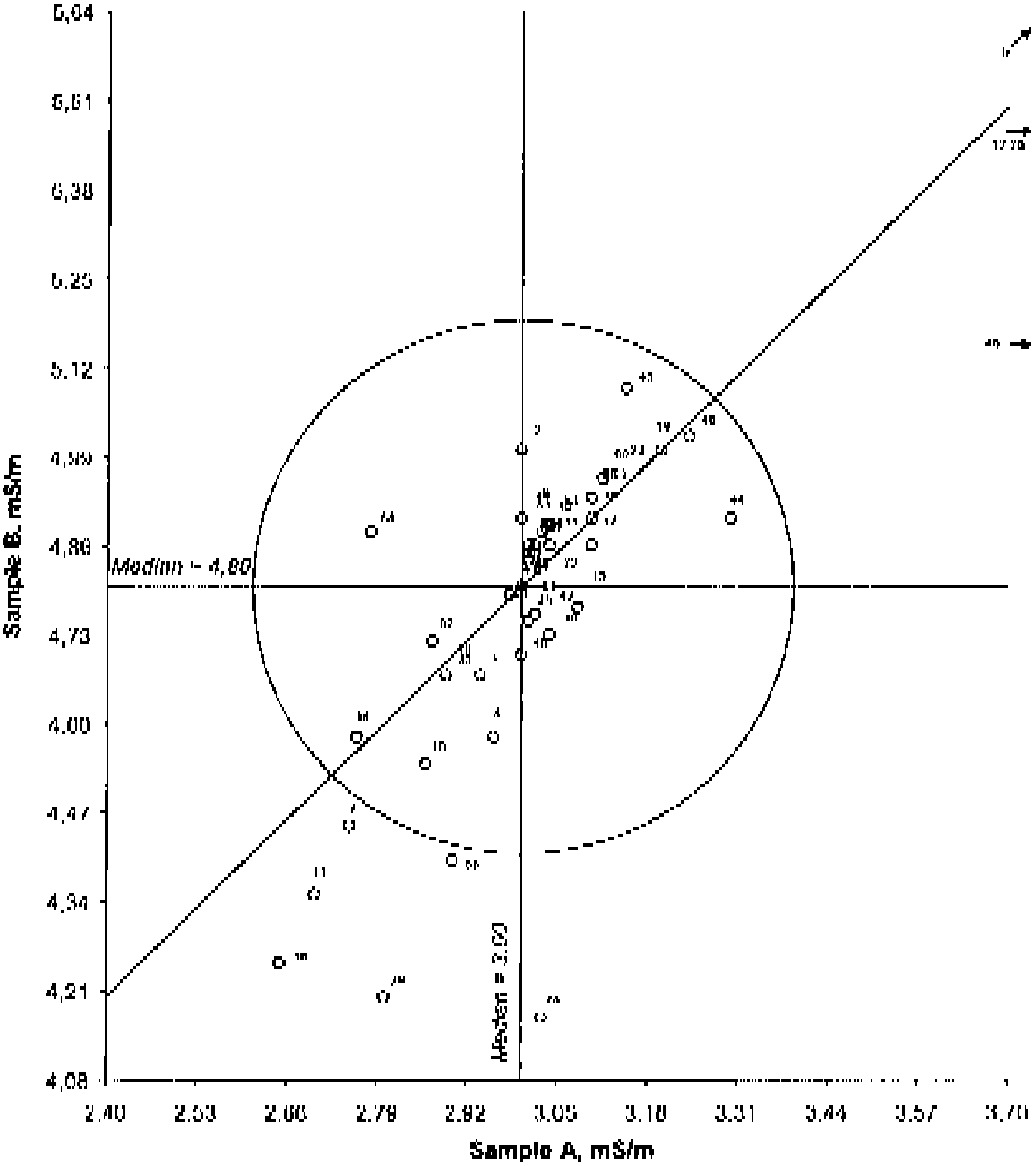

Figure 2. Youden diagram for conductivity, Sample pair AB Acceptance limit is 10 %

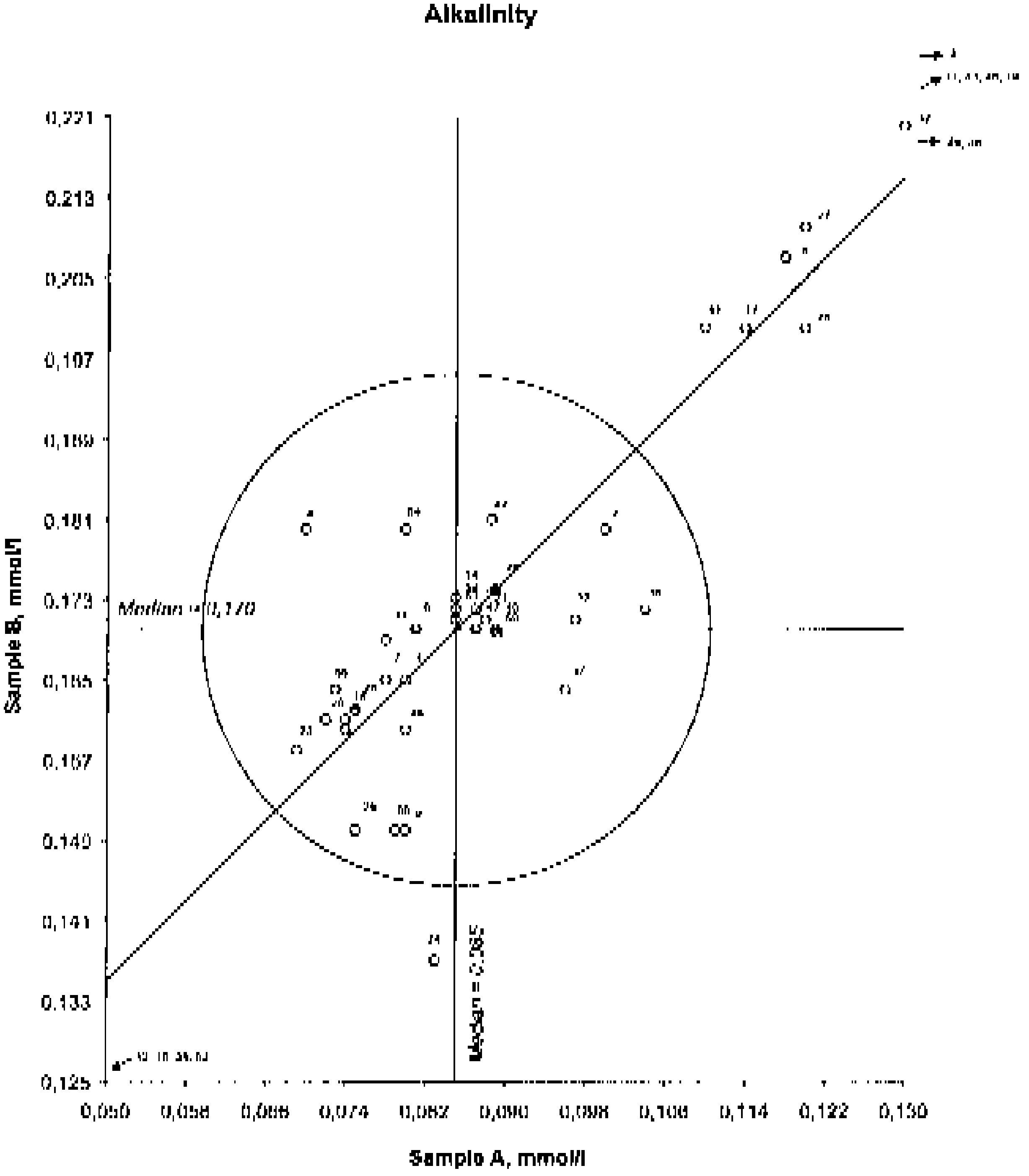

Figure 3. Youden diagram for alkalinity. Sample pair AB
Acceptance limit is 20 %

Nitrate + nitrite-nitrogen

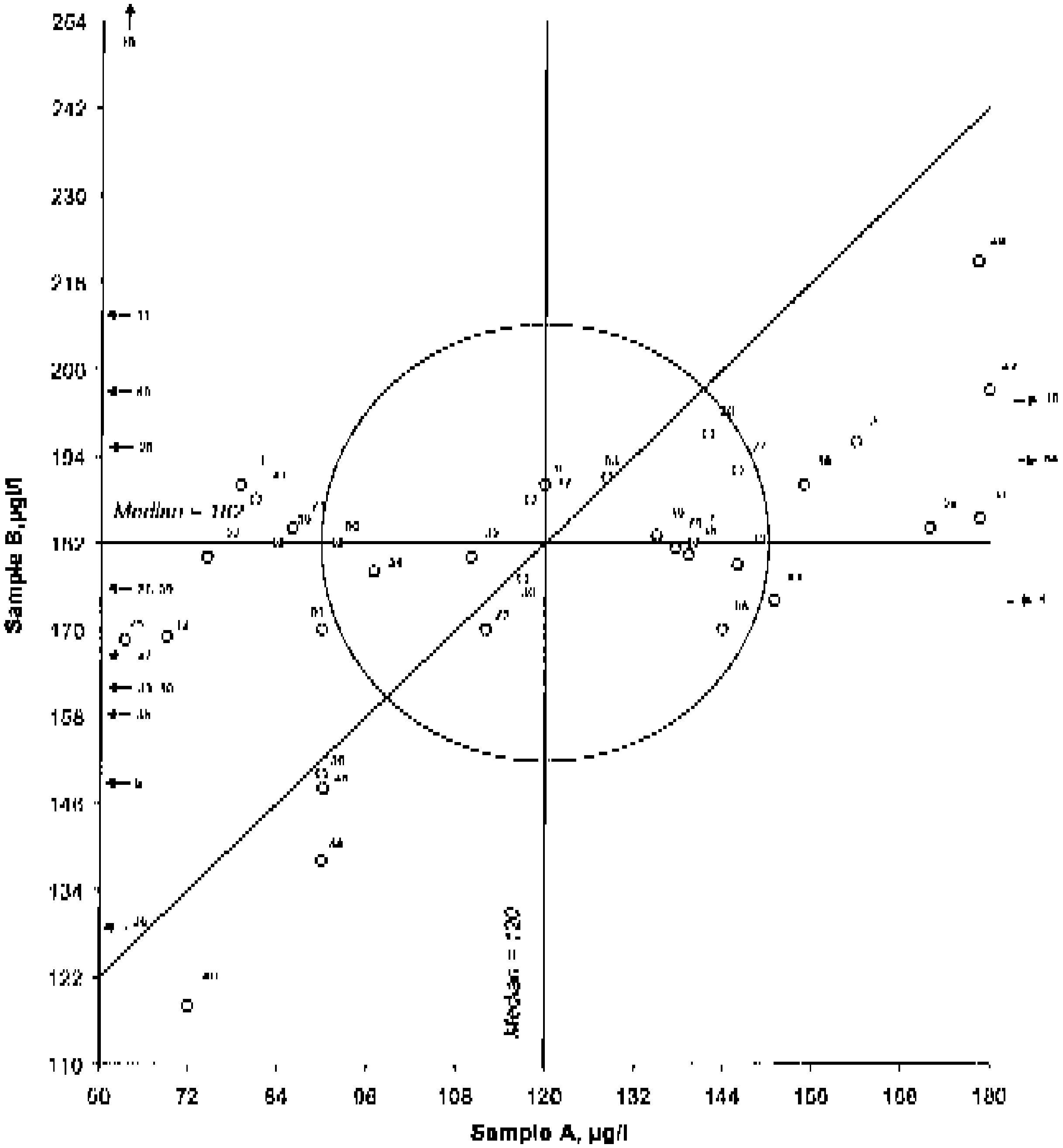

Figure 4. Youden diagramme for nitrate + nitrite-nitrogen, Sample pair AB
Acceptance limit is 20 %

Chloride

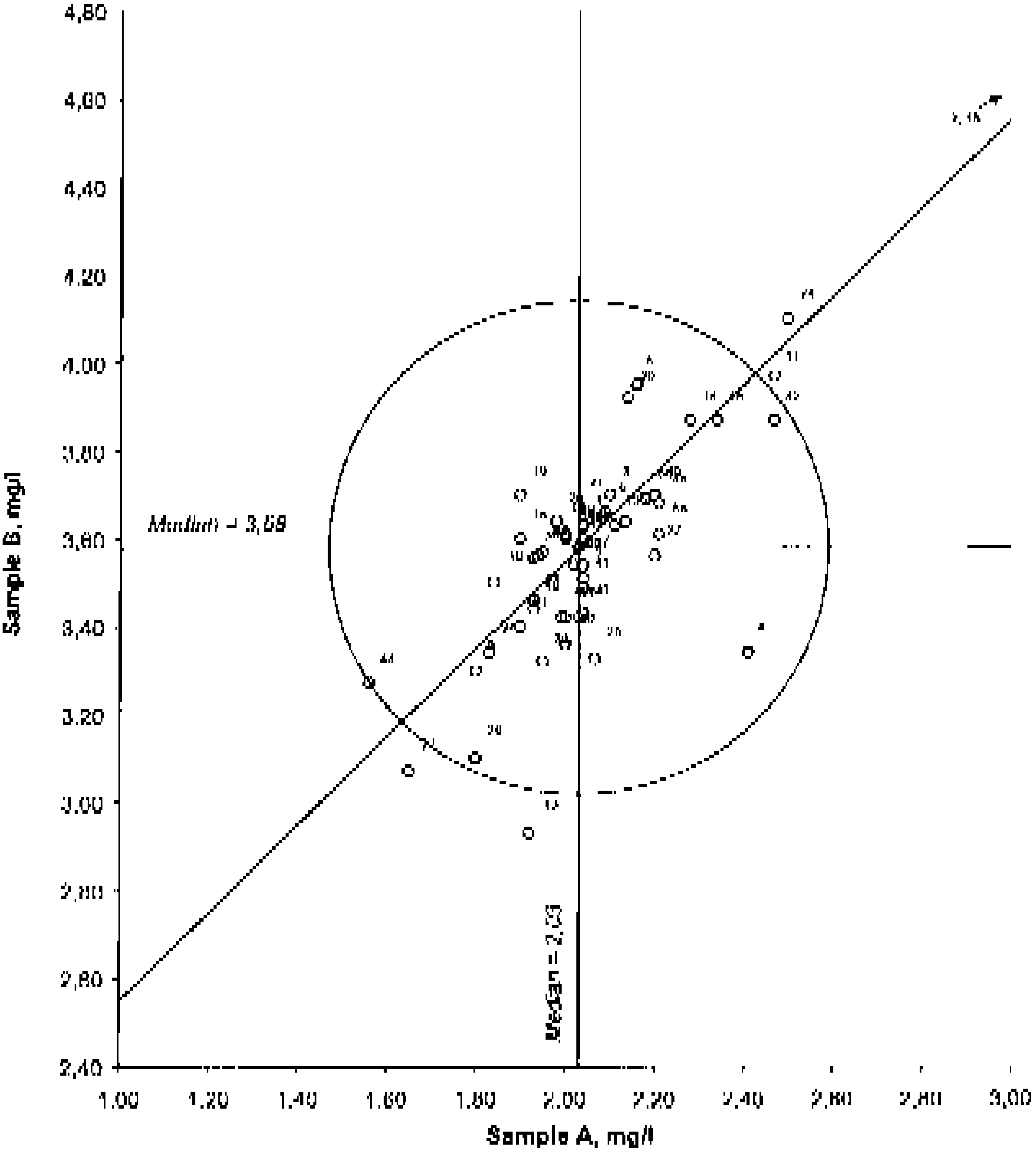

Figure 5. Youden diagramme for chloride, Sample pair AB
Acceptance limit is 20 %

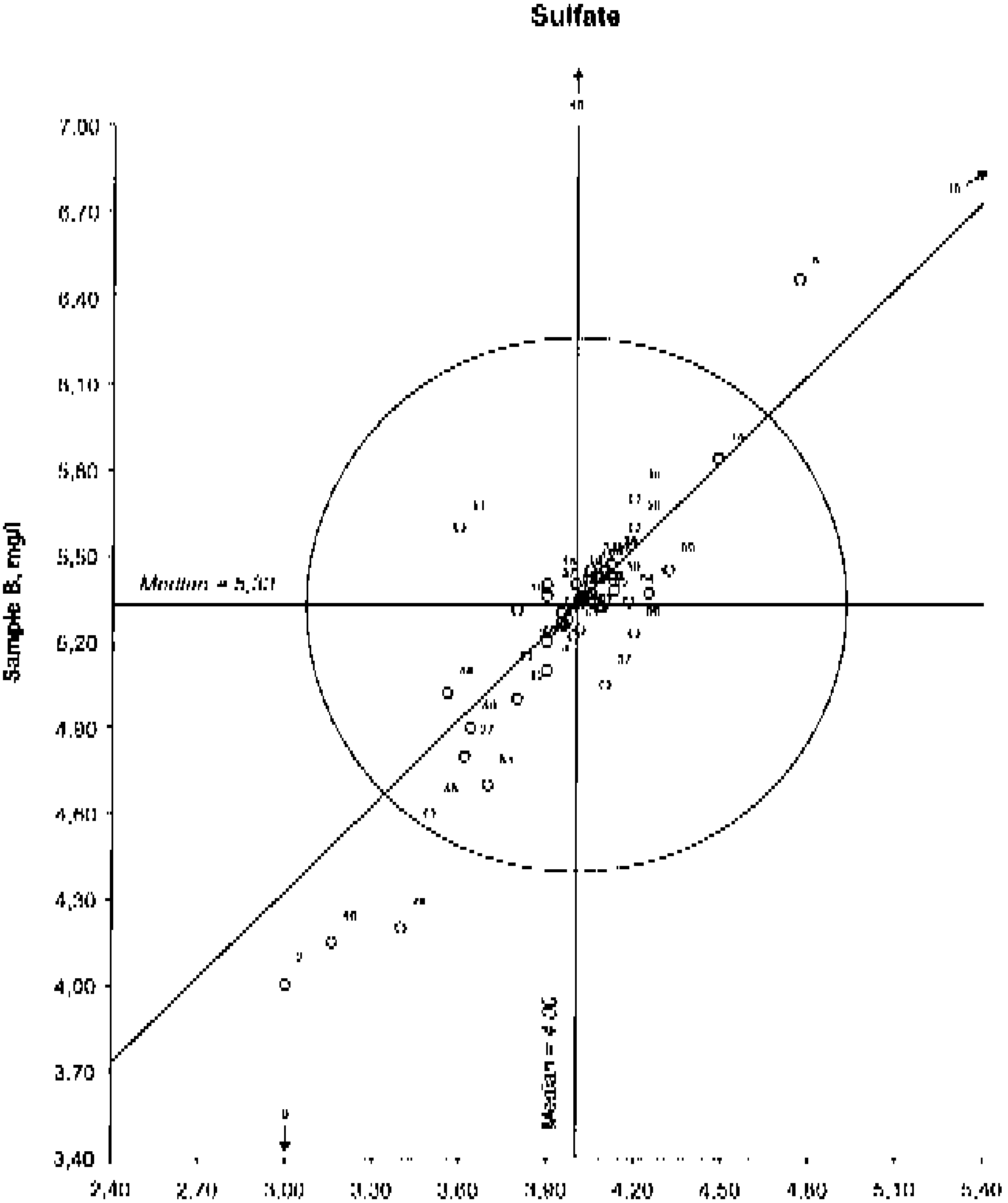

Figure 6. Youden diagramme for sulfate, Sample pair AB
Acceptance limit is 20 %

Calcium

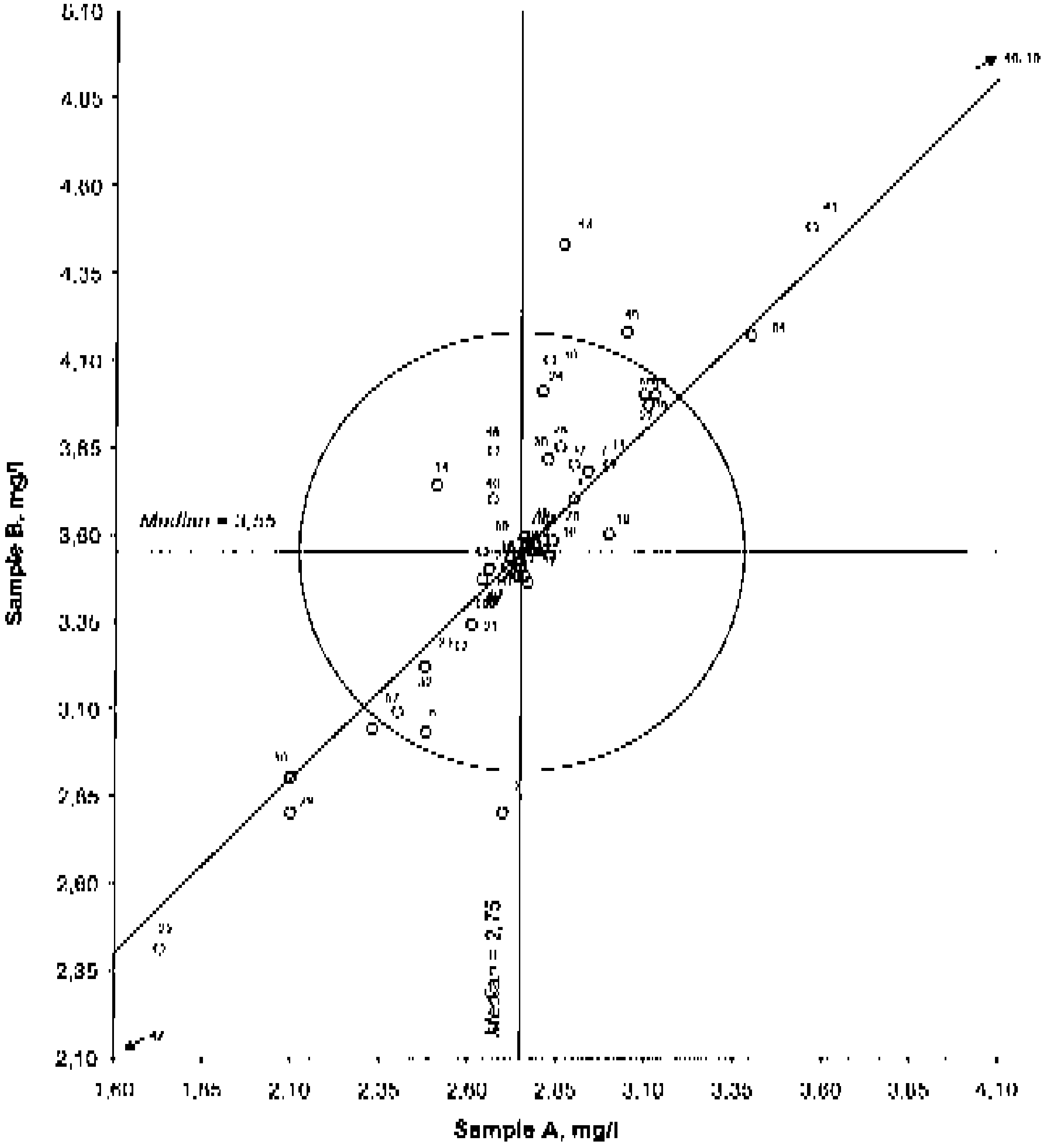

**Figure 7. Youden diagramme for calcium, Sample pair AB
Acceptance limit is 20 %**

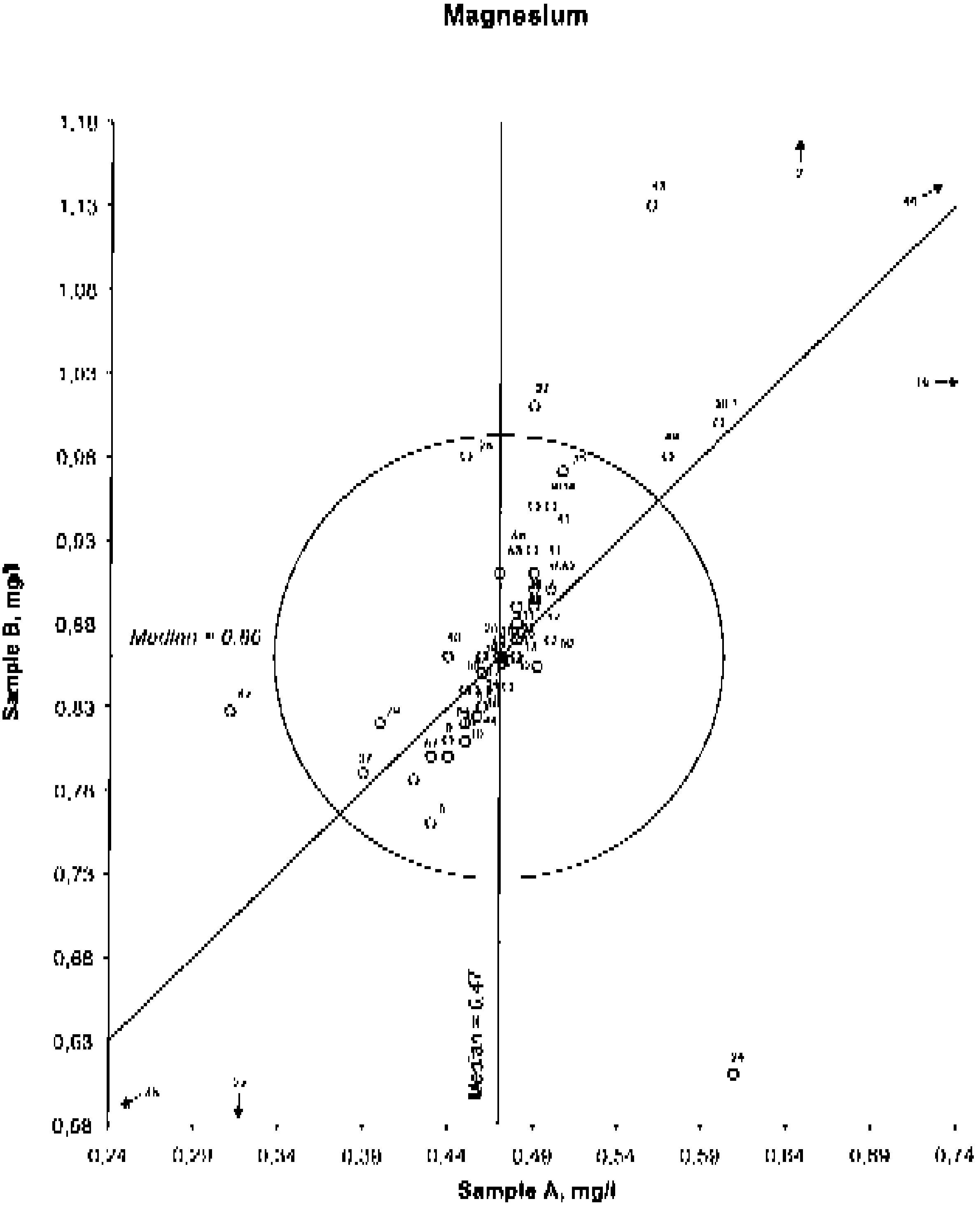

Figure 6. Youden diagramme for magnesium, Sample pair AB
Acceptance limit is 20 %

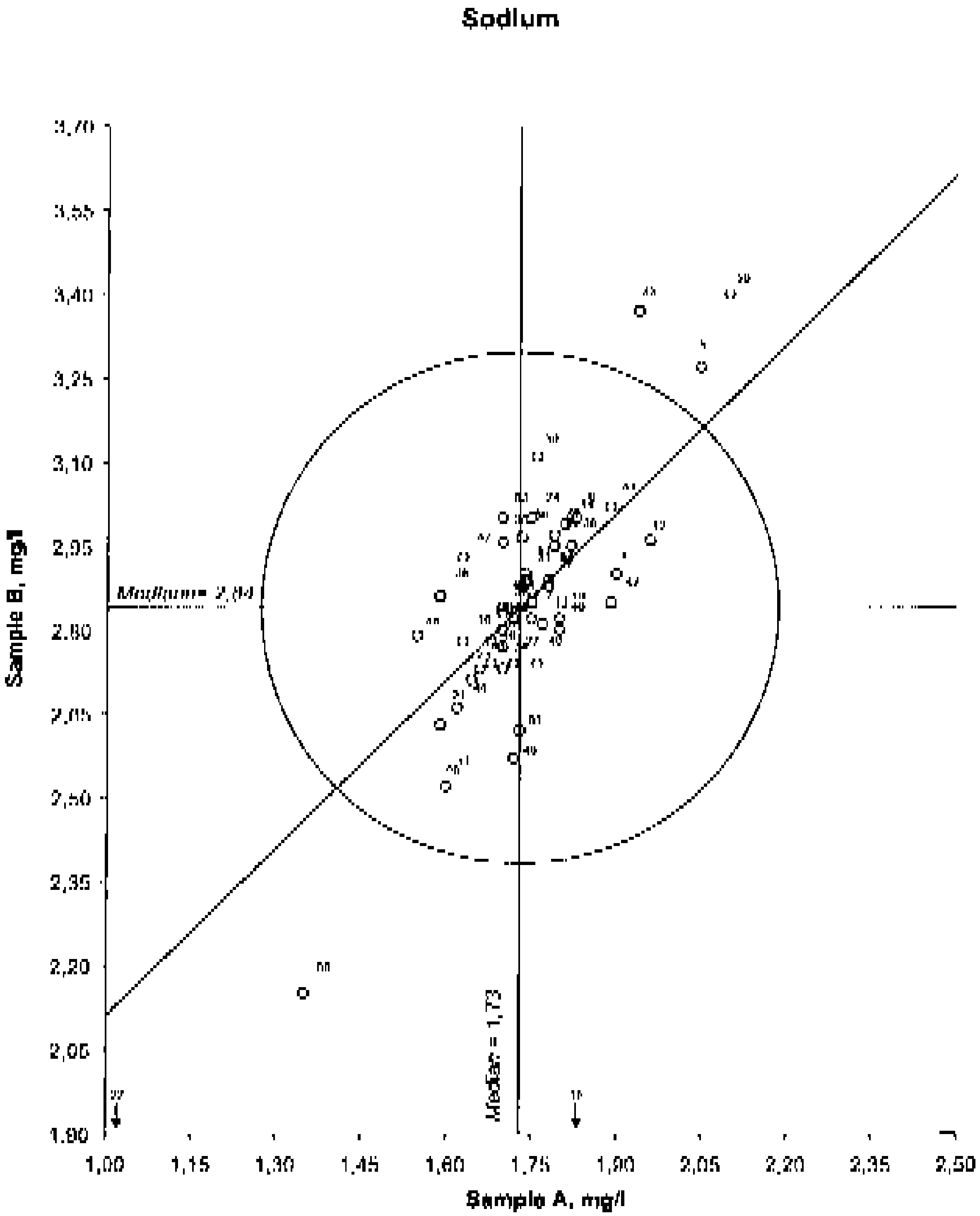

Figure 9. Youden diagramme for sodium, Sample pair AB
Acceptance limit is 20 %

Potassium

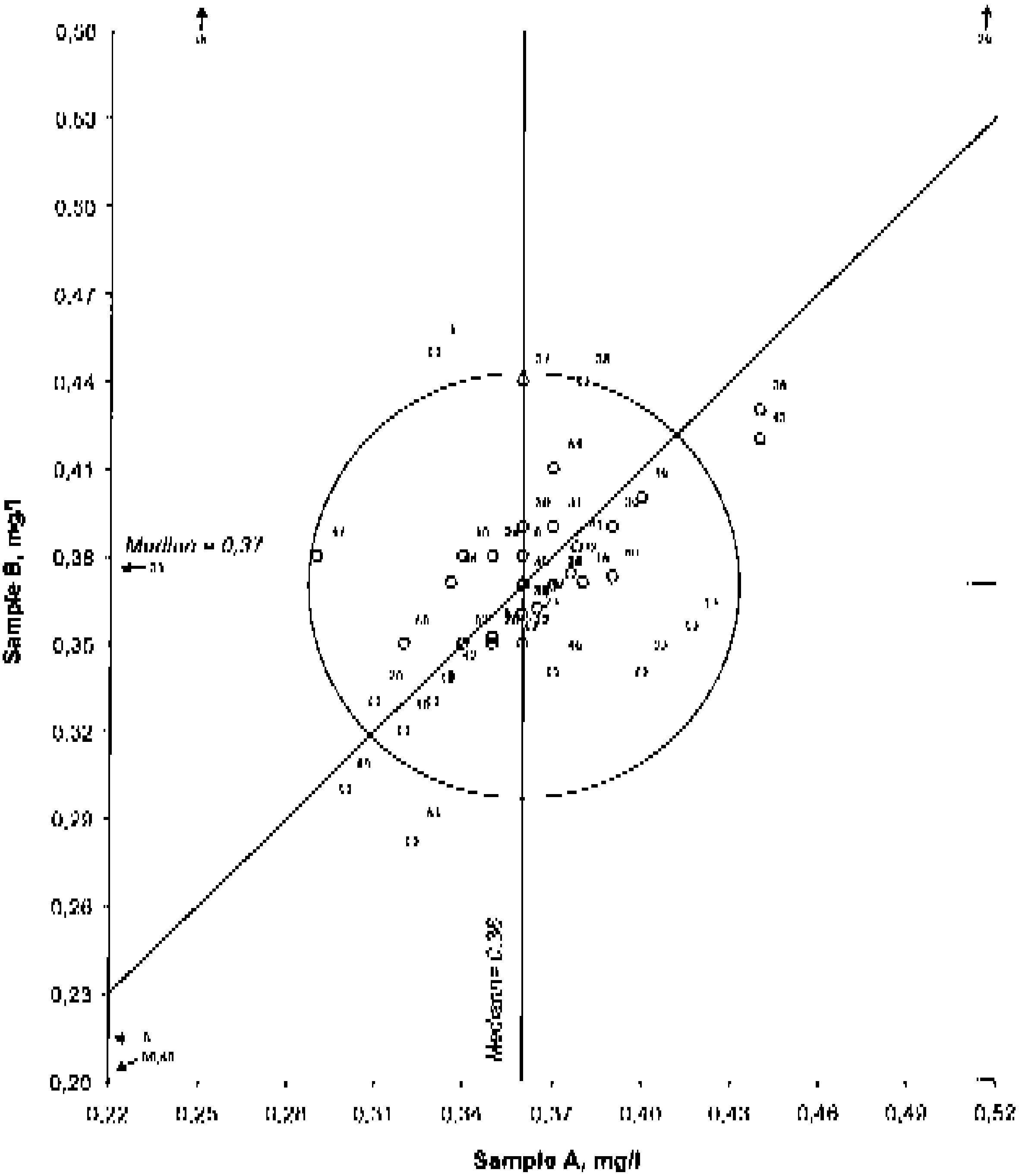

Figure 10. Youden diagramme for potassium, Sample pair AB Acceptance limit is 20 %

Aluminium

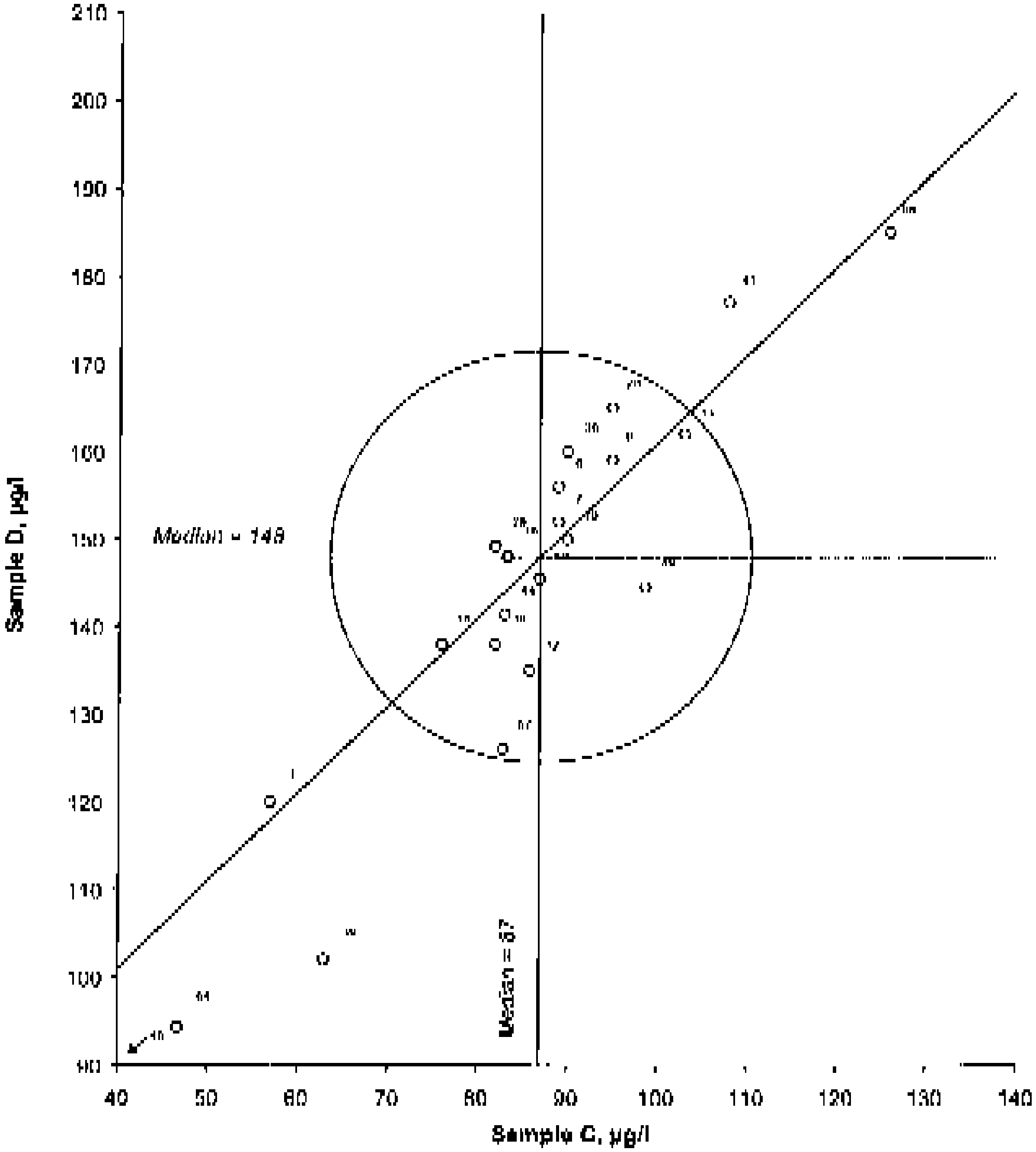

**Figure 11. Youdendiagram for aluminium, Sample pair CD
Acceptance limit is 20 %**

Aluminium, reactive

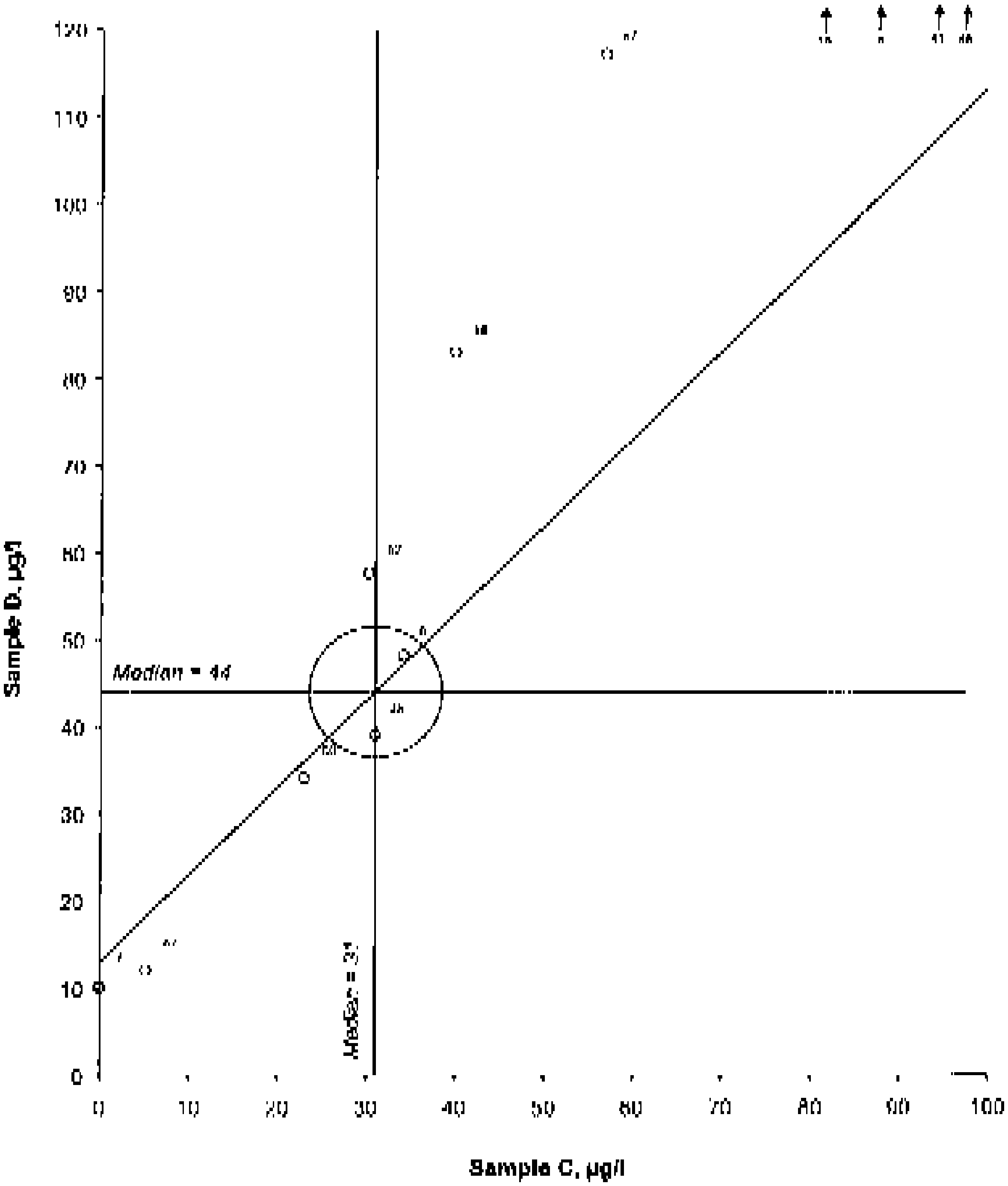

Figure 12. Youdendiagram for aluminium, reactive, Sample pair CD
Acceptance limit is 20 %

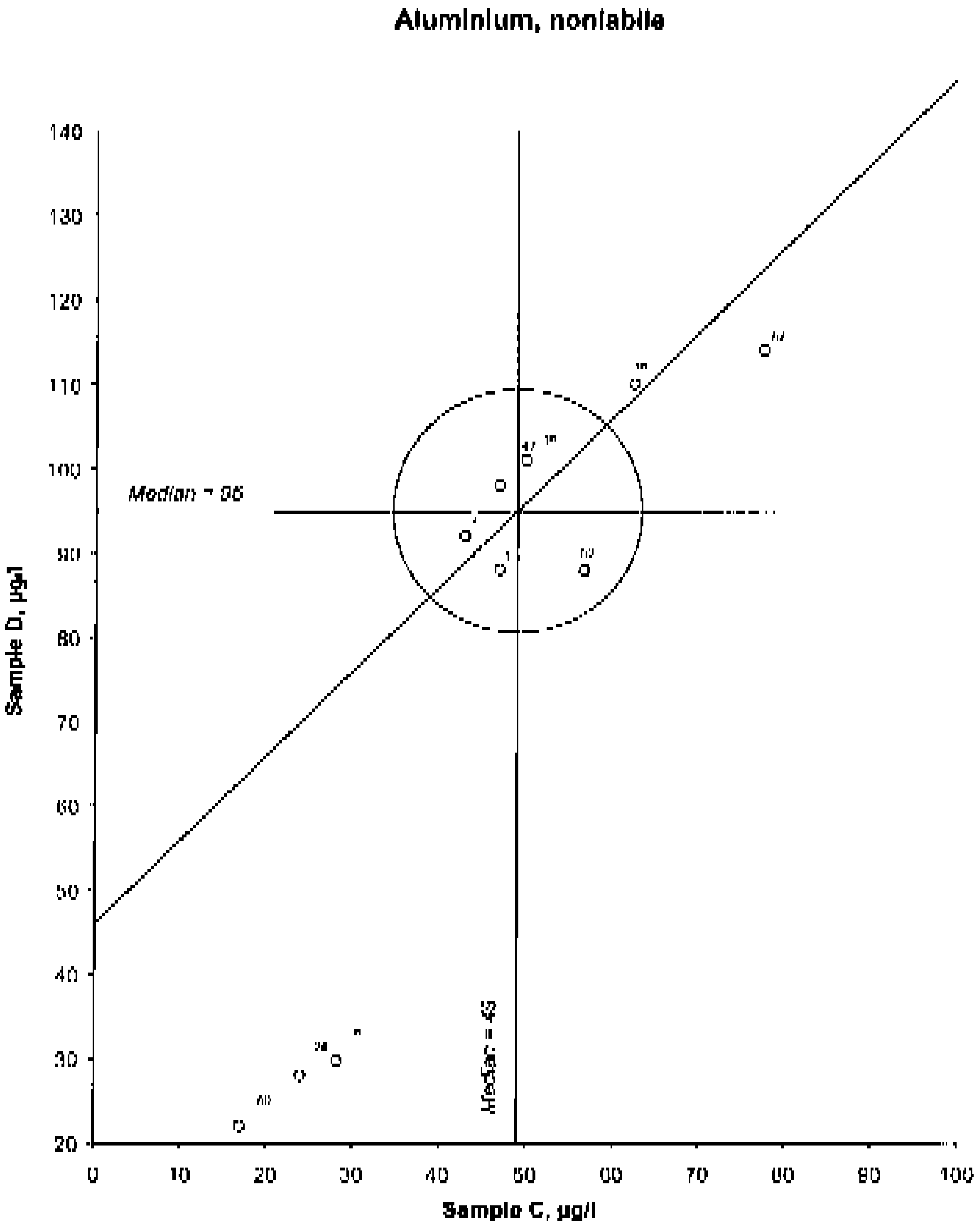

Figure 13. Youdendiagram for aluminium, nonlabile, Sample pair CD
Acceptance limit is 20 %

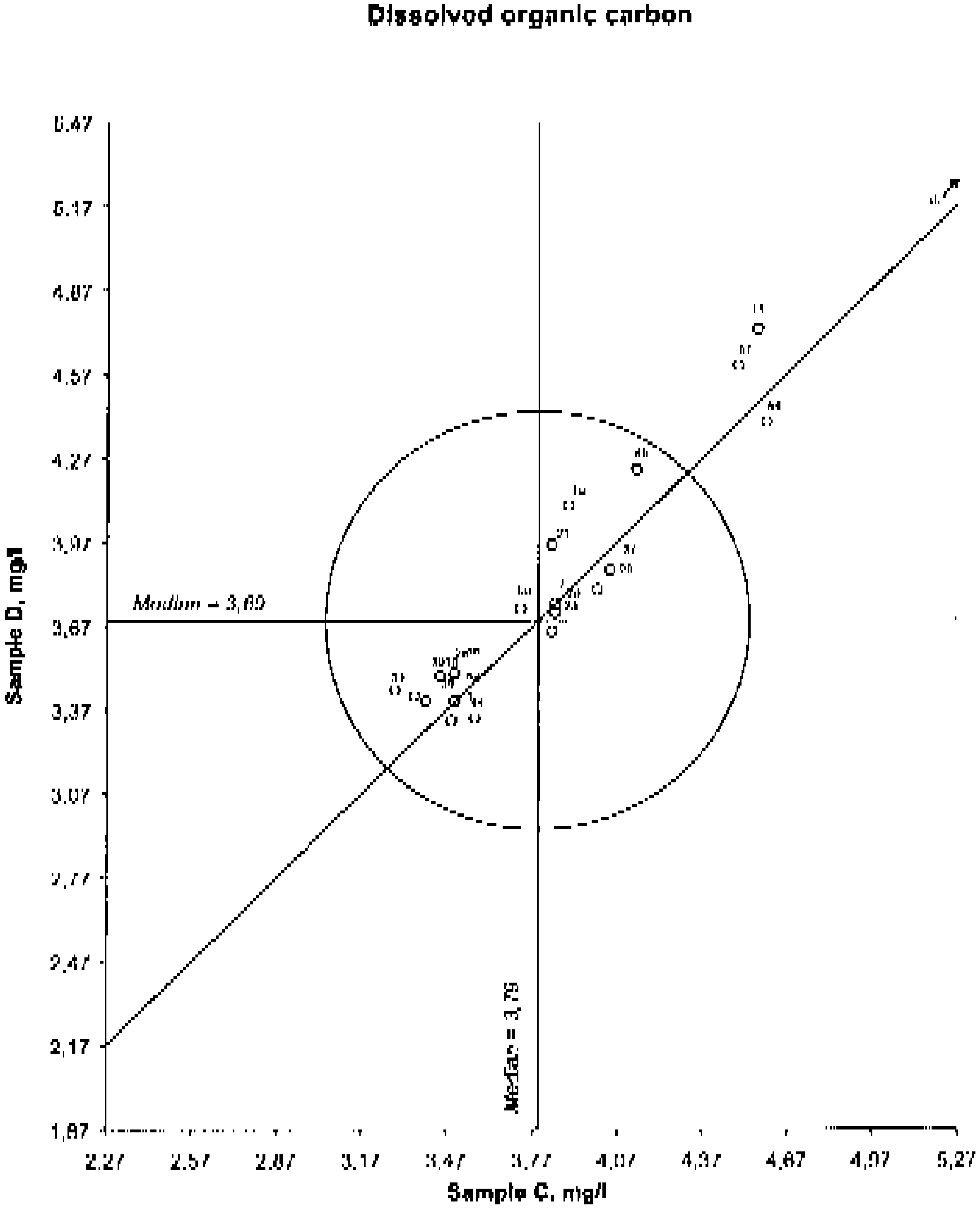

Figure 14. Youdendiagram for dissolved organic carbon, Sample pair CD
Acceptance limit is 20 %

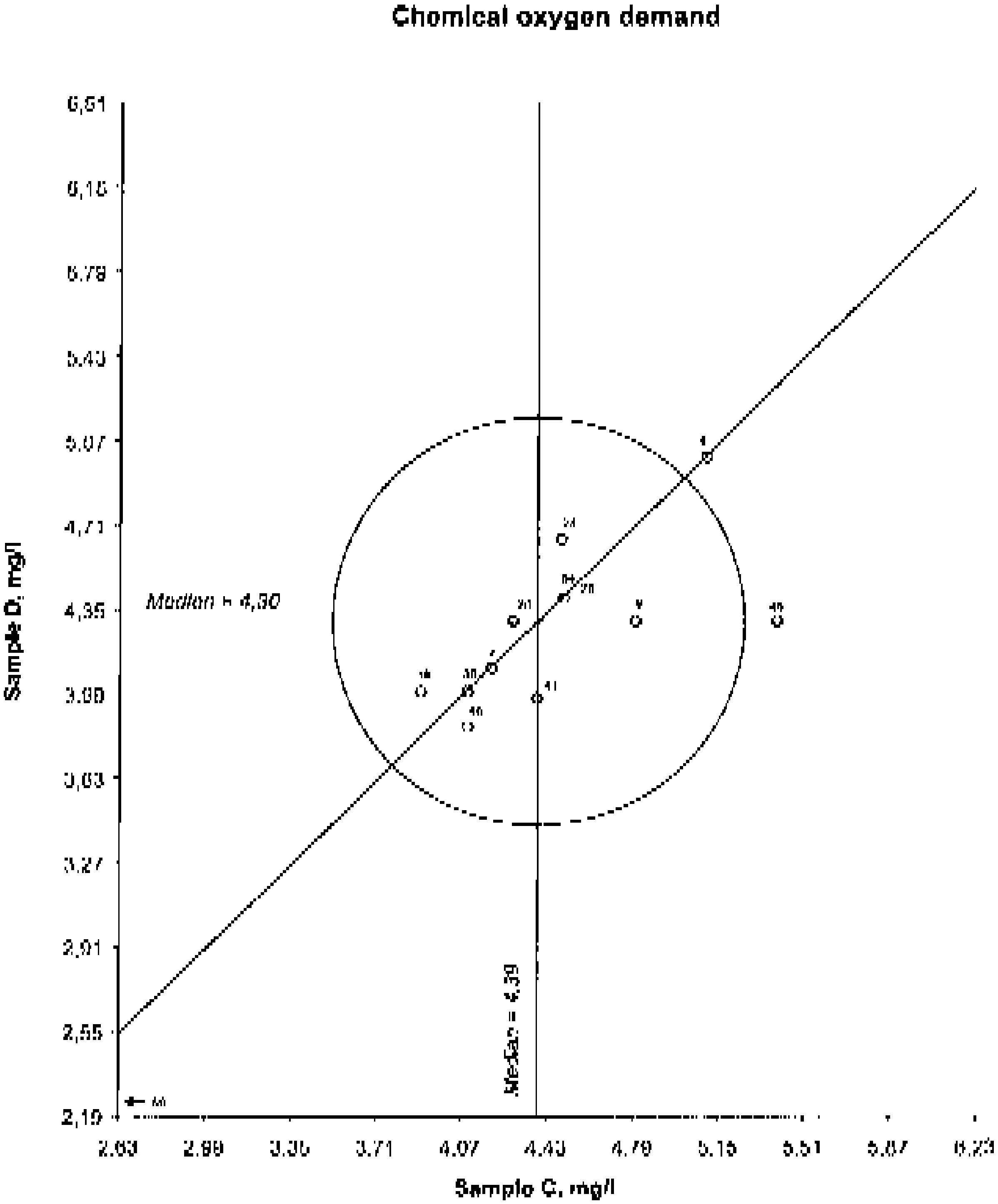

Figure 15. Youdendiagram for chemical oxygen demand, Sample pair CD Acceptance limit is 20 %

laboratories due to the different levels of partial pressure of CO_2 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 samples were stable when stored at our 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 the electrodes, as different electrodes may give rise to different results (4, 5). The main reason for the differences in the reported results, however, is obviously connected to the small differences in the measurement techniques 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 ± 10 %. The reported results are given in Table 5.2. Six 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. These results were recalculated to mS/cm by the Programme Center. For one laboratory the result had to be multiplied by the factor 100 to obtain values comparable to the other laboratories.

All participants used an electrometric method for the determination of conductivity. Most laboratories achieved very good agreement between the results for this variable. Four laboratories reported results being systematically too high for both samples, and six laboratories reported results being systematically too low. If the accuracy limit is extended to ± 20 %, the lower results would be located within the circle. A proper temperature correction is necessary when determining this 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. 48 laboratories reported results for alkalinity, and about one third of the participants 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 certain pH value only (4.2, 4,5, 5.4, or 5.6).

The results for alkalinity are spread out along the 45 ° line in Figure 3, indicating systematic differences between the results. This is obviously 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 normally located close to the centrum of the circle. With one exception all the results determined by the end point titration to pH 4.2 or 4.5 alone, are located in the upper right part of Figure 3, beeing systematically too high. The end point titration to pH 5.6 or 5.4 gave results mainly located within the acceptance circle.

Two laboratories reported values being about half of the median value, they have probably calculated the result as mmol/l CO_3^{--} instead of HCO_3^-. Division of the results from four laboratories by a factor of 1000, gave values comparable to the other laboratories. For one laboratory the results had to be dievided by a factor of 100. These laboratories have reported the results in another unit the the requested mmol/l, with no indication of what unit they use.

The alkalinity value 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 more than one third 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 a small difference between the results determined by the different methods, the photometric methods are producing higher results than ion chromatography. Most of the very low results reported have been determined by ion chromatography.

The results reported for sample A and B are quite different, the results for sample A are much more spread out than for sample B. Thus the relative standard deviation for sample A is several times greater than for sample B. This is strange, because the two samples are prepared from the same water, the only difference is that sample B is spiked to increase the concentration for some of the analytical variables. As the control analyses at the laboratory of the Programme Centre disclosed that the content of nitrate and nitrite in sample A was decreasing during the weeks after the samples were mailed to the participants, this variable is excluded from the evaluation of this intercomparison.

3.5 Chloride

The chloride results are presented in Figure 5, and the reported results from the participants are given in Table 5. The target accuracy of ± 20 % is represented by the circle. 41 out of 54 laboratories determined chloride by ion chromatography. The greatest deviations are observed for the manual photometric methods, and the argentometric method which have too high detection limit, the latter method is not sensitive enough for most of the acid rain samples. The results produced by ion chromatography are lower than for the other methods. One laboratory determined chloride with capillary electrophoresis, the result being somewhat lower than results determined with ion chromatography

3.6 Sulfate

The sulfate results are illustrated in Figure 6, and the reported values are given in Table 5.6. The circle is representing the target accuracy of ± 20 %. Ion chromatography is used by 41 of 52 laboratories for the determination of this analytical variable. Four laboratories used a photometric method based on the dissociation of the barium-thorin complex, and five laboratories used a nephelometric method. The results produced by these methods are higher than with ion chromatography, and the relative standard deviation is much greater too. One laboratory used capillary electrophoresis with acceptable results.

3.7 Calcium

The calcium results are illustrated in Figure 7, and the reported values are given in Table 5.7. The target accuracy is ± 20 %, and is represented by the circle in Figure 7. 25 of the participants used flame atomic absorption spectrometry for the determination of calcium. ICP techniques and ion chromatography are used by 12 and 13 laboratories, respectively. The atomic absorption results are slightly lower than the median value, and the ICP results slightly higher than the median value. The complexometric titration method, used by four laboratories, is not sensitive enough for most of this kind of samples. The result pairs being not acceptable are dominated by systematic errors.

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 and ion chromatography was used by 12 and 13 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. The most used methods give comparable results,

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 10 participants used ICP, and 10 used flame photometry. The relative standard deviation was smalles for the results produced with flame atomic absorption. 89 % of the result pairs are located within the general target accuracy of ± 20.

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, many laboratories used flame atomic absorption spectrometry for the determination of this element, however, emission spectrometry is used by the same number of laboratories. The greatest deviations observed in the Figure 10 are mainly of systematic nature. Only one laboratory reported results as less than the detection limit.

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 %. Nine laboratories used emission techniques, and six of the participants used photometry for the determination of aluminium. Graphite furnace atomic absorption was used by seven laboratories. 73 % of the result pairs are located within the target accuracy.

3.12 Reactive aluminium

The results for reactive aluminium are illustrated in Figure 12, and the reported values are given in Table 5.12. Twelve laboratories reported results for reactive aluminium, however, the results are very different. The results are strongly affected by systematic effects caused by the analytical method used. The statistical treatment according to Youden is not applicable for this situation, therefore none of the results are located within the acceptance circle. 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. The situation is very much alike what we observe for reactive aluminium. Most laboratories have indicated that they determined non-labile aluminium according to the automated method of Rogeberg 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 32). 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 strongly.

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. 23 laboratories determined this analytical variable in the sample pair CD. 14 laboratories used a combustion technique, and a wet oxidation technique with UV and peroxodisulfate was used by four laboratories only. There is no evidence for any significant differences between the reported results determined with these two methods for the samples used in this intercomparison. Five laboratories used the photometric method based on the use of phenolphthalein, and on average their results are slightly higher than the others.

The great circle in Figure 14 and 15 is representing a general target accuracy of ± 20 %. Only four 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 13 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. Ten of the result pairs are located within the circle representing the target accuracy of ± 20 %.

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 9913 is presented, based on the target accuracy (except for pH and conductivity), 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, one laboratory out of four is located outside the acceptance limit. By some improvement of the routine analytical method, these laboratories should be able to obtain results more comparable to the other participants.

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 with this limit only 57 % of the result pairs are evaluated as acceptable.

Table 2. Evaluation of the results of intercomparison 9913. *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 icluded in the evaluation.

Variable	Sample pair	N	Limit	n	%
pH	AB	54	0.2 *	31	57
Conductivity	AB	53	10 % ◊	43	81
Alkalinity	AB	48	20 %	30	63
Nitrate + nitrite-nitrogen	AB	(52)	20 %	(16)	(31)
Chloride	AB	54	20 %	48	89
Sulfate	AB	52	20 %	45	87
Calcium	AB	55	20 %	43	78
Magnesium	AB	55	20 %	44	80
Sodium	AB	53	20 %	48	91
Potassium	AB	53	20 %	41	77
Aluminium, total	AB	22	20 %	16	73
Aluminium, reactive	CD	(12)	20 %	(7)	-
Aluminium, non-labile	CD	(10)	20 %	(5)	-
Dissolved organic carbon	CD	23	20 %	19	83
Chemical oxygen demand	CD	13	20 %	10	77
Sum		535		418	78

* The acceptance limit is extended from the target value 0.1 to 0.2 pH units.
◊ The acceptance limit is reduced from the target value 20 to 10 %.

The problem with poor comparability between the reported results for pH is probably due to the fact that the pH values in a nearly neutral solution are much more spread out than in more acid solutions. Additionally, 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 by the participating laboratories. Therefore it should be discussed wether a more "correct" approach should be used, for instance using different "true values" for pH, one for each method?

For alkalinity, as we have observed earlier, the reported results for solutions with low alkalinity values are more widely spread than in solutions with higher concentrations of bicarbonate. In this intercomparison, the results are slightly better than in some earlier intercomparisons, probably because of the somewhat higher bicarbonate concentrations in the samples this time.

Because of the high precision of the reported results for conductivity, we have decided to reduce the acceptance limit for this analytical variable. If we increase the acceptance limit to the target value, the six lower result pairs being outside the circle in Figure 2, would be inside the circle.

For nitrate + nitrite a very strange picture is observed, as only 31 % of the result pairs are acceptable. This is caused by the fact that the results for sample A is very widely spread out, especially many laboratories have reported very low results for nitrate in this sample. The samples A and B have been prepared from the same water, the only difference is that sample B have been spiked to increase the concentrations of the analytical variables. In sample A no additions were made. The control analyses performed at the laboratory of the Programme Centre disclosed that the content of nitrate and nitrite in sample A was not stable, therfore this variable is excluded from the evaluation of this intercomparison. So far we have not found any explanation for the instability of this solution.

We have decided to exclude two more variables, reactive and non labile aluminium, from the evaluation of the intercomparison, because of the very great differences between the few reported values. 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

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

variables printed in bold in the scheme presented in Figure 16. 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 fact 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 between the results for the aluminium fractions.

For the major constituents the results are fairly well in this intercomparison, as 70 - 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. Some of the manual methods are not sensitive enough for samples typically analyzed for acid rain monitoring.

5. Conclusion

57 laboratories submitted results for this intercomparison. The best results were reported for the variables conductivity, chloride, sulfate, magnesium, sodium, and dissolved organic carbon. More than 80 % of the results were evaluated as acceptable for these analytical variables.

Rather poor comparability was observed for the results of aluminium species and nitrate + nitrite. The differences between the methods used for the determination of aluminium species, are probably the reason for the poor comparability for these variables. For nitrate + nitrite the poor results are due to the wide spread of the results reported for sample A, however, so far no explanation has been found to why this solution has proved to be instable.

Overall, 78 % of the evaluated 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 several 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 the 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. On the next meeting, it should be discussed whether we are continuing to use only one "true value" for all the pH results, or to have different "true value" for each method, because there are obviously systematic differences between the methods used by the participating laboratories.

6. Literature

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Appendix A. The participating laboratories

Identity	Name	Town	Country
1	Institute of Hydrobiology	Budejovice	Czech Republic
2	Virumaa Environmental Research	Joehvi	Estonia
3	Staatliche Umweltbetriebgesellschaft im UBG	Chemnitz	Germany
4	Institute for Ecology of Industrial Areas	Katowice	Poland
5	Food and Environment Agency	Torshavn	Faeroe Islands
6	ITM Stockholm University	Stockholm	Sweden
7	DAFS Freshwater Laboratory	Pitlochry	Scotland
8	Länsstyrelsen i Kalmar Län	Kalmar	Sweden
9	Northern Water Problems Institute	Petrozavodsk	Russia
10	Laboratorio Biologico Provinciale	Laives	Italy
11	T.G.Masaryk Water Research Institute	Prague	Czech Republic
12	Environmental Research Unit	Dublin	Ireland
13	NILU, Dept. Inorganic Analysis	Kjeller	Norway
14	University of Helsinki	Helsinki	Finland
15	University of Bern	Bern	Switzerland
16	National Rivers Authority	Llanelli	United Kingdom
17	MOEE, Dorset Research Centre	Dorset	Canada
18	Norwegian Institute for Water Research	Oslo	Norway
19	Kärntner Institut für Seewasser Forschung	Klagenfurt	Austria
20	Swedish University for Agricultural Sciences	Uppsala	Sweden
21	Aquatic Chemistry Project	Winnipeg	Canada
22	Polish Academy of Sciences	Krakow	Poland
23	Great Lakes Forest Centre	Sault Ste. Marie	Canada
24	Environmental Protection Ministry	Vilnius	Lithuania
25	Adirondack Lakes Survey Corporation	New York	USA
26	Werkgroep Milieubiologie	Nijmegen	Netherlands
27	Federal Environmental agency	Salzburg	Austria
28	National Board of Waters and the	Helsinki	Finland
29	Institute of Biology	Syktyvkar	Russia
30	Swiss Federal Institute for Forest, Snow and	Birmensdorf	Switzerland
31	Lapland Water and Environment District	Rovaniemi	Finland
32	MOEE, Toronto Laboratory	Etobicoke	Canada
33	CNR Istituto Italiano di Idrobiologia	Pallanza	Italy
34	Czech Geologic Survey Prague	Prague	Czech Republic
35	Forest Ecosystem Research Group	Dublin	Ireland
36	Bayerische Landesamt für Wasserwirtschaft	Munchen	Germany
37	Institut für Zologie, Universitat Innsbruck	Innsbruck	Austria
38	University of Innsbruck	Innsbruck	Austria
39	Centre National de la Recherche Scientifique	Toulouse	France
40	Karelian Research Centre	Petrozavodsk	Russia
41	South Estonian Environm. Protection Agency	Tartu	Estonia
42	Water Pollution Observation Laboratory	Riga	Latvia
43	Bayerisches Landesamt für Wasserwirtschaft	Wielenbach	Germany
44	Institute of Environmental Protection	Warszaw	Poland
45	Institute for Ecological Toxicology	Baikalsk	Russia

46	Hiiumaa Environmental Laboratory	Kärdla	Estonia
47	Charles University	Prague	Czech Republic
48	Center for Marine Analytical Ref. and Stds.	Trivandrum	India
49	D.R. Ambiente Alentejo	Santo Andre	Portugal
50	METI, US Environmental Protection Agency	Corvallis	USA
51	Landesumweltamt Nordrhein Westfalen	Essen	Germany
52	University of Maine	Orono	USA
53	Kymen Water and Environment District	Kouvola	Finland
54	Estonian Environment Research Laboratory	Tallinn	Estonia
55	University of Barcelona	Barcelona	Spain
56	Center for Chemical Analysis Keldnaholt	Reykjavik	Iceland
57	Swedish Environmental Research Institute	Stockholm	Sweden

Appendix B. Preparation of samples

The sample solutions were prepared from natural water collected from the lake Maridalsvannet, located outside Oslo, Norway. Raw water was collected in polyethylene containers and brought to the laboratory for storage. These containers 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 analytical variables of interest.

Sample B was prepared by spiking the filtrated water with stock solutions of stoichiometric compounds containing the major ions. No additions were made to prepare sample A.

A few days before mailing the samples 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	6,45	0,07	6,78	0,10				
Conductivity mS/m	2,89	0,02	4,58	0,12				
Alkalinity mmol/l	0,083	0,005	0,162	0,009				
Nitrate/nitrite µg/l	125	74	184	13				
Chloride mg/l	2,05	0,07	3,60	0,06				
Sulfate mg/l	4,02	0,08	5,40	0,02				
Calcium mg/l	2,74	0,06	3,58	0,09				
Magnesium mg/l	0,45	0,01	0,85	0,02				
Sodium mg/l	1,64	0,04	2,79	0,08				
Potassium mg/l	0,35	0,02	0,45	0,02				
Aluminium total, µg/l					74	4,0	142	4,8
Reactive aluminium µg/l					47	6,0	97	9,0
Non labile alumin. µg/l					40	5,3	81	10,9
Diss.org. C mg/l					3,52	0,08	3,46	0,09
COD-Mn, mg/l					3,90	0,06	3,90	0,10

Sample control analyses

During the intercomparison 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 in the beginning of May 1999, a couple of weeks before mailing the samples to the participants. The last sample was analyzed in the middle of July 1999. 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 for nitrate + nitrite in sample A.

Appendix C. Treatment of analytical data

The intercomparison was carried out by the method of Youden. This procedure requires two samples to be analyzed, and 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 - 18).

The graphical presentation creates a possibility to distinguish between random and systematic errors affecting the results. The two straight 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.

Lab. no.	pH A	pH B	Cond. mS/m A	Cond. mS/m B	Alkalin. mmol/l A	Alkalin. mmol/l B	NO3+NO2 µg/l A	NO3+NO2 µg/l B
1	6,60	6,95	3,01	4,84	0,080	0,165	79	190
2	6,70	7,10	3,00	5,00	0,100	0,180		
3	6,60	7,10	2,94	4,67	0,140	0,230	162	196
4	6,50	7,04	2,96	4,58	0,074	0,160	268	170
5	6,77	7,28	3,01	4,86	0,118	0,207	169	259
6	6,43	6,98	3,01	4,85	0,081	0,170	120	190
7	6,51	7,11	2,75	4,45	0,078	0,165	140	182
8	6,30	6,88	3,00	4,80	0,070	0,180		
9	6,48	6,90	3,27	5,81	0,080	0,150	15	150
10	6,51	6,95	3,03	4,88	0,089	0,170	40	160
11	6,57	6,92	2,70	4,35	0,150	0,250	18	215
12	6,61	7,13	4,10	5,50	0,005	0,009	146	179
13	6,45	6,95	3,08	4,77				
14	6,28	7,33	2,76	4,58	0,085	0,173	69	169
15	6,53	6,91	2,86	4,54			0	1400
16	6,65	7,01	2,65	4,25	0,038	0,084	203	213
17	6,35	6,97	3,10	4,86	0,114	0,200	118	188
18	6,49	6,90	2,89	4,67	0,074	0,161	155	190
19	6,30	6,80	3,20	5,00	0,350	0,490	135	183
20	6,69	6,94	3,10	4,93	0,072	0,161	142	197
21	7,07	7,38	3,00	4,80	0,088	0,171	86	184
22	6,42	6,84	3,04	4,80			75	180
23	6,49	6,91	3,14	4,97	0,069	0,158	112	170
24	6,50	7,05	3,03	4,17	0,083	0,137	172	184
25	6,41	6,89	3,01	4,75	0,089	0,174	63	169
26	6,10	6,66	4,00	5,50	0,120	0,200	48	195
27	6,30	6,84	3,00	4,90	0,120	0,210	146	192
28	6,48	7,01	3,00	4,90	0,075	0,162	138	181
29	6,40	6,70	2,80	4,20	0,075	0,150	2	130
30							112	177
31	6,79	7,20	3,04	4,86	0,078	0,169	179	185
32	6,55	7,04	3,10	4,90	0,130	0,220	110	180
33	6,20	6,50	2,89	4,67	0,097	0,171	0	160
34	6,48	7,04	3,02	4,86	0,085	0,172	97	178
35	6,15	6,89	3,00	4,90	0,015	0,050	139	180
36	6,59	6,85	3,10	4,90	0,150	0,220	90	150
37	6,30	6,68	3,00	4,79	0,096	0,164	0	173
38	6,34	6,61	3,00	4,80	0,104	0,172	14	158
39	6,38	6,98	3,04	4,73	0,087	0,172	84	182
40	6,40	7,00					72	118
41	6,65	7,18	2,98	4,79	0,110	0,200	81	188
42	6,44	6,92	3,02	4,76	0,089	0,181	180	203
43	5,70	5,80	3,15	5,09	0,200	0,300	151	174
44	6,44	6,68	3,30	4,90			96	138
45	6,65	6,90					34	202

Lab. no.	pH A	pH B	Cond. mS/m A	Cond. mS/m B	Alkalin. mmol/l A	Alkalin. mmol/l B	NO3+NO2 µg/l A	NO3+NO2 µg/l B
46	6,33	6,91	4,12	5,15	0,260	0,340	90	148
47	6,40	6,98	3,02	4,85	0,087	0,170	77	168
48	6,36	6,57	3,00	4,70	0,080	0,160	84	863
49	6,55	7,02	3,24	5,02	0,136	0,220	179	221
50	6,90	7,22	3,12	4,96	0,089	0,170	92	182
51			3,00	4,90			90	170
52	6,25	6,62	2,87	4,72	0,045	0,088		
53	6,22	6,75	3,04	4,89	0,085	0,171	128	191
54	6,60	7,00	2,78	4,88	0,080	0,180	191	196
55	6,74	6,63	2,90	4,40	0,079	0,150	12	174
56	6,51	6,95	3,00	4,80	0,073	0,164	144	170
57								

Lab. no.	Cl mg/l A	Cl mg/l B	SO4 mg/l A	SO4 mg/l B	Ca mg/l A	Ca mg/l B	Mg mg/l A	Mg mg/l B
1	2.04	3,63	4,05	5,37	2,74	3,52	0,48	0,87
2	5.50	7.50	3,00	4,00	2,70	2,80	0,65	1,30
3	3,10	3,70	3,90	5.10	2.90	3.70	0,60	1,00
4	2,41	3,34	4,35	5,47	2,78	3,55	0,47	0,86
5	2.16	3,95	4,77	6,46	2,48	3,03	0,43	0,76
6	1,80	3,30	3,90	5.20	2,76	3,48	0,43	0,80
7	2,04	3,51	4,10	5,35	2.94	3,78	0,49	0,89
8								
9	2.09	3.66	3,00	3,30	2,77	3,53	0,48	0,86
10	1,84	3,50	3.80	5,31	2.10	2,90	0,44	0,80
11	2,47	3,97	3,60	5,60	3,00	3,80	0,49	0,91
12	1,92	2,93	3,80	5,00	2,77	3,46	0,50	0,87
13	2.11	3.63	4,01	5,33	2,74	3,48	0,48	0,86
14	2,28	3,87	4,49	5,84	2,51	3,74	0,50	0,95
15	5,13	9,72	7,08	8,39	5.16	5,47	0,49	0,90
16	2.34	3,87			2,83	3,54	0,45	0,82
17	2,04	3,54	3,95	5,30	2,64	3,40	0,46	0,84
18	1,90	3,60	3,90	5,40	2.66	3.50	0,46	0.86
19	1,90	3,70	4,00	5,40	3,00	3,60	1,00	1,00
20	2.14	3,92	3,96	5,26	2,74	3,57	0,46	0,86
21	2,03	3,67	4,08	5,35	2.58	3.28	0,46	0,85
22	2,20	3,56	4,09	5,42	1,73	2,41	0,32	0,56
23	2.13	3.64	4,01	5,35	2,48	3,22	0,46	0,82
24	2,50	4,10	3,40	4.20	2,81	4,01	0,61	0,61
25	2,07	3,33	4,07	5,15				
26	1.98	3.64			2,86	3,85	0,45	0,98
27	1,65	3,07	3.62	4,80	3,13	4,00	0,49	1,01
28	1,83	3,34	3,91	5.24	2.84	3.58	0,47	0.86
29	1,80	3,10	4,20	5,60	2,10	2,80	0,40	0,82
30	1.95	3.32	4,07	5,43	2,83	4,10	0,49	0,95
31	2,04	3,43	3.95	5.25	2.68	3.43	0,48	0,88
32	1,94	3,56	4,10	5,05	2,40	3,09	0,48	0,84
33	2.04	3,59	4,05	5,45	2,64	3,47	0,47	0,87
34	1,93	3.46	3.83	5,15	2,75	3,50	0,46	0,83
35	1,93	3.56	4.01	5.24	2.83	3,82	0,51	0,97
36	2,00	3,60	4,20	5,70	3.10	4,00	0,60	1.00
37	1.95	3,57	3,90	5,36	2,90	3,80	0,39	0,79
38	2.04	3.60	4,12	5,47	2,77	3,57	0,48	0,89
39	2,07	3,54	4,13	5.38	2.72	3.53	0,46	0,85
40	2,00	3,36	3,64	4,90	2,67	3,70	0,44	0,86
41	2,01	3,49	4,04	5,42	3,57	4,48	0,49	0,92
42	2.47	3.87			0,18	0,64	0,33	0,83
43	1,99	3,42	3,98	5,34	2,87	4,43	0,56	1,13
44	1,56	3,27	3,56	5,02	2.67	3,41	0,45	0.81
45	2,20	3,70	3,50	4,60	3,05	4,18	0,23	0,23

Lab. no.	Cl mg/l A	Cl mg/l B	SO4 mg/l A	SO4 mg/l B	Ca mg/l A	Ca mg/l B	Mg mg/l A	Mg mg/l B
46			4,00	49,10	4,19	5,28	1,10	1,38
47	2,03	3,58	4,06	5,34	2,66	3,40	0,45	0,82
48	2,21	3,68	3,16	4,15	2,67	3,84	0,47	0,91
49	1,93	3,44	3,95	5,27	2,76	3,59	0,57	0,98
50	2,00	3,61	3,97	5,28	2,71	3,51	0,49	0,85
51	2,00	3,42	3,99	5,22	2,75	3,52	0,47	0,86
52	2,00	3,60	4,10	5,45	2,61	3,34	0,50	0,90
53	1,90	3,40	3,70	4,70	3,10	4,00	0,47	0,91
54	2,03	3,42	4,18	5,34	3,40	4,17	0,44	0,81
55	2,21	3,61	4,32	5,45	2,64	3,55	0,45	0,84
56	2,18	3,69	4,20	5,23	3,11	3,97	0,48	0,88
57					2,33	3,04	0,42	0,79

Lab. no.	Na mg/l A	Na mg/l B	K mg/l A	K mg/l B	Al µg/l C	Al µg/l D	Al-R µg/l C	Al-R µg/l D
1	1,75	2,85	0,33	0,45	57	120		
2								
3	1,90	2,90	0,30	0,30				
4	1,70	2,77	0,36	0,37				
5	2,05	3,27	0,16	0,22				
6	1,70	2,84	0,36	0,38	95	159	34	48
7	1,75	2,82	0,35	0,35	89	152	0	10
8					89	156	87	147
9	1,83	3,00	0,33	0,33				
10	1,80	2,82	0,34	0,38				
11	1,60	2,52	0,36	0,36	103	162		
12	1,96	2,96	0,36	0,35				
13	1,77	2,81	0,42	0,36				
14	1,81	2,99	0,36	0,36				
15	1,71	1,83	0,32	0,32				
16	1,68	2,74	0,38	0,37	83	148	81	133
17	1,72	2,82	0,37	0,36				
18	1,63	2,78	0,37	0,37	76	138	40	83
19	1,80	2,80	0,40	0,40	90	150		
20	1,68	2,78	0,31	0,33	95	165		
21	1,59	2,63	0,37	0,37				
22	1,01	1,74	0,40	0,34				
23	1,65	2,71	0,36	0,36				
24	1,75	3,00	0,35	0,38				
25								
26	1,79	2,97	0,35	0,35				
27	1,72	2,74	0,37	0,37				
28	1,71	2,84	0,37	0,37	82	149	31	39
29	2,10	3,40	0,52	0,59				
30	1,76	3,11	0,36	0,39	82	138		
31	1,74	2,89	0,37	0,39				
32	1,78	2,88	0,38	0,37	86	135		
33	1,66	2,73	0,11	0,38				
34	1,70	2,73	0,37	0,37				
35	1,70	2,96	0,29	0,60				
36	1,82	2,95	0,44	0,43	90	160		
37	1,70	2,83	0,36	0,44				
38	1,59	2,86	0,38	0,44				
39	1,70	2,83	0,39	0,39	63	102		
40	1,76	2,74	0,36	0,37				
41	1,89	3,02	0,38	0,38	108	177	93	164
42	1,64	2,93	0,34	0,34				
43	1,94	3,37	0,44	0,42				
44	1,62	2,66	0,34	0,37	83	141		
45	1,70	2,80	0,30	0,30	41	42		

Lab. no.	**Na mg/l A**	**Na mg/l B**	**K mg/l A**	**K mg/l B**	**Al µg/l C**	**Al µg/l D**	**Al-R µg/l C**	**Al-R µg/l D**
46							96	132
47	1,89	2,85	0,29	0,38			57	117
48	1,55	2,79	0,20	0,17				
49	1,72	2,57	0,37	0,34	99	145		
50	1,73	2,97	0,39	0,37			23	34
51	1,73	2,62	0,32	0,28				
52	1,79	2,95	0,34	0,35	87	146	30	58
53	1,70	3,00	0,36	0,36				
54	1,78	2,89	0,37	0,41	47	94		
55	1,60	2,52	0,32	0,35				
56	1,35	2,15	0,10	0,10	126	185		
57	1,74	2,90	0,35	0,35	83	126	5	13

Lab. no.	Al-I µg/l C	Al-I µg/l D	DOC mg/l C	DOC mg/l D	COD-Mn mg/l C	COD-Mn mg/l D
1	47	88	3,49	3,33		
2					4,20	4,10
3						
4					5,10	5,00
5						
6	28	30				
7	43	92	3,85	3,25		
8						
9					4,80	4,30
10						
11			4,57	4,23		
12						
13						
14						
15						
16	63	110	3,50	3,50		
17						
18	50	101	3,40	3,40	3,90	4,00
19			3,90	4,10		
20			3,85	3,72	4,29	4,30
21			3,84	3,96		
22						
23			3,84	3,65		
24					4,49	4,65
25						
26						
27						
28	24	28	3,45	3,49	4,50	4,40
29						
30						
31						
32			3,50	3,40		
33			3,29	3,44		
34						
35			27,27	27,10		
36			3,40	3,40	4,10	4,00
37			4,04	3,87		
38						
39			3,36	3,42		
40						
41					4,39	3,97
42						
43						
44			3,57	3,34		
45			4,14	4,23	5,40	4,30

Lab. no.	Al-I µg/l C	Al-I µg/l D	DOC mg/l C	DOC mg/l D	COD-Mn mg/l C	COD-Mn mg/l D
46					4,10	3,85
47	47	98				
48						
49						
50	17	22	3,73	3,73		
51						
52	57	88	3,50	3,40		
53						
54			4,60	4,40	4,50	4,40
55			4.00	3,80		
56					2.30	2.30
57	78	114	4,50	4,60		

Table 5.1. Statistics - pH

Sample A

Number of participants	54	Range	0,97
Number of omitted results	1	Variance	0,03
True value	6,48	Standard deviation	0,18
Mean value	6,47	Relative standard deviation	2,9%
Median value	6,48	Relative error	-0,1%

Analytical results in ascending order:

43	5,70 U	29	6,40	7	6,51
26	6,10	47	6,40	15	6,53
35	6,15	40	6,40	49	6,55
33	6,20	25	6,41	32	6,55
53	6,22	22	6,42	36	6,59
55	6,24	6	6,43	1	6,60
52	6,25	42	6,44	3	6,60
14	6,28	44	6,44	54	6,60
37	6,30	13	6,45	12	6,61
19	6,30	9	6,48	41	6,65
27	6,30	28	6,48	45	6,65
8	6,30	34	6,48	16	6,65
46	6,33	23	6,49	20	6,69
38	6,34	18	6,49	2	6,70
17	6,35	24	6,50	5	6,77
48	6,36	4	6,50	31	6,79
11	6,37	56	6,51	50	6,90
39	6,38	10	6,51	21	7,07

Sample B

Number of participants	54	Range	0,88
Number of omitted results	1	Variance	0,04
True value	6,95	Standard deviation	0,19
Mean value	6,93	Relative standard deviation	2,7%
Median value	6,95	Relative error	-0,2%

Analytical results in ascending order:

43	5,80 U	18	6,90	40	7,00
33	6,50	45	6,90	28	7,01
48	6,57	9	6,90	16	7,01
38	6,61	23	6,91	49	7,02
52	6,62	15	6,91	34	7,04
55	6,63	46	6,91	4	7,04
26	6,66	42	6,92	32	7,04
37	6,68	11	6,92	24	7,05
44	6,68	20	6,94	2	7,10
29	6,70	1	6,95	3	7,10
53	6,75	13	6,95	7	7,11
19	6,80	56	6,95	12	7,13
22	6,84	10	6,95	41	7,18
27	6,84	17	6,97	31	7,20
36	6,85	39	6,98	50	7,22
8	6,88	6	6,98	5	7,28
35	6,89	47	6,98	14	7,33
25	6,89	54	7,00	21	7,38

U Omitted result

Table 5.2, Statistics - Conductivity, mS/m

Sample A

Number of participants	53	Range	0,65
Number of omitted results	4	Variance	0,02
True value	3,00	Standard deviation	0,13
Mean value	2,99	Relative standard deviation	4,3%
Median value	3,00	Relative error	-0,2%

Analytical results in ascending order:

16	2,65	56	3,00	22	3,04
11	2,70	27	3,00	39	3,04
7	2,75	8	3,00	13	3,08
14	2,76	28	3,00	32	3,10
54	2,78	37	3,00	17	3,10
29	2,80	48	3,00	36	3,10
15	2,86	21	3,00	20	3,10
52	2,87	1	3,01	50	3,12
18	2,89	5	3,01	23	3,14
33	2,89	6	3,01	43	3,15
55	2,90	25	3,01	19	3,20
3	2,94	34	3,02	49	3,24
4	2,96	42	3,02	44	3,30
41	2,98	47	3,02	9	3,77 U
2	3,00	10	3,03	26	4,00 U
51	3,00	24	3,03	12	4,10 U
38	3,00	31	3,04	46	4,12 U
35	3,00	53	3,04		

Sample B

Number of participants	53	Range	0,92
Number of omitted results	4	Variance	0,04
True value	4,80	Standard deviation	0,21
Mean value	4,76	Relative standard deviation	4,4%
Median value	4,80	Relative error	0,8%

Analytical results in ascending order:

24	4,17	41	4,79	36	4,90
29	4,20	37	4,79	44	4,90
16	4,25	38	4,80	35	4,90
11	4,35	8	4,80	32	4,90
55	4,40	22	4,80	27	4,90
7	4,45	56	4,80	28	4,90
15	4,54	21	4,80	20	4,93
14	4,58	1	4,84	50	4,96
4	4,58	6	4,85	23	4,97
18	4,67	47	4,85	19	5,00
3	4,67	31	4,86	2	5,00
33	4,67	34	4,86	49	5,02
48	4,70	17	4,86	43	5,09
52	4,72	5	4,86	46	5,15 U
39	4,73	54	4,88	26	5,50 U
25	4,75	10	4,88	12	5,50 U
42	4,76	53	4,89	9	5,81 U
13	4,77	51	4,90		

U - Omitted result

Table 5.3. Statistics - Alkalinity, mmol/l

Sample A

Number of participants	48	Range	0,051
Number of omitted results	12	Variance	0,000
True value	0,085	Standard deviation	0,014
Mean value	0,088	Relative standard deviation	16,4%
Median value	0,085	Relative error	3,0%

Analytical results in ascending order:

12	0,005 U	48	0,080	33	0,097
35	0,015 U	1	0,080	2	0,100
16	0,038 U	54	0,080	38	0,104
52	0,045 U	6	0,081	41	0,110
23	0,069	24	0,083	17	0,114
8	0,070	14	0,085	5	0,118
20	0,072	34	0,085	27	0,120
56	0,073	53	0,085	26	0,120
18	0,074	39	0,087	32	0,130 U
4	0,074	47	0,087	49	0,136 U
28	0,075	21	0,088	3	0,140 U
29	0,075	42	0,089	36	0,150 U
31	0,078	25	0,089	11	0,150 U
7	0,078	10	0,089	43	0,200 U
55	0,079	50	0,089	46	0,260 U
9	0,080	57	0,096	19	0,350 U

Sample B

Number of participants	48	Range	0,073
Number of omitted results	12	Variance	0,000
True value	0,170	Standard deviation	0,016
Mean value	0,171	Relative standard deviation	9,4%
Median value	0,170	Relative error	0,8%

Analytical results in ascending order:

12	0,009 U	7	0,165	54	0,180
35	0,050 U	1	0,165	2	0,180
16	0,084 U	31	0,169	42	0,181
52	0,088 U	50	0,170	17	0,200
24	0,137	47	0,170	26	0,200
55	0,150	10	0,170	41	0,200
29	0,150	6	0,170	5	0,207
9	0,150	33	0,171	27	0,210
23	0,158	53	0,171	32	0,220 U
48	0,160	21	0,171	36	0,220 U
4	0,160	34	0,172	49	0,220 U
20	0,161	39	0,172	3	0,230 U
18	0,161	38	0,172	11	0,250 U
28	0,162	14	0,173	43	0,300 U
56	0,164	25	0,174	46	0,340 U
57	0,164	8	0,180	19	0,490 U

U = Omitted result

Table 5.4. Statistics - Nitrate + nitrite-nitrogen, µg/l

Sample A

Number of participants	52	Range	117
Number of omitted results	17	Variance	1230
True value	120	Standard deviation	35
Mean value	119	Relative standard deviation	29,4%
Median value	118	Relative error	-0,7%

Analytical results in ascending order.

37	0 U	48	84 U	7	140
33	0 U	39	84	20	142
15	0 U	21	86	56	144
29	2 U	36	90	27	146
55	12 U	44	90	12	146
38	14 U	51	90	43	151
9	15 U	46	90	18	155
11	18 U	50	92	3	162
47	22 U	34	97	5	169 U
45	34 U	32	110	24	172
10	40 U	23	112	49	179
26	48 U	30	117	31	179
25	63	17	118	42	180
14	69	6	120	54	191 U
40	72	53	128	16	203 U
22	75	19	135	4	268 U
1	79	28	138		
41	81	35	139		

Sample B

Number of participants	52	Range	103
Number of omitted results	17	Variance	341
True value	182	Standard deviation	18
Mean value	179	Relative standard deviation	10,3%
Median value	182	Relative error	-1,7%

Analytical results in ascending order.

40	118	43	174	1	190
29	130 U	30	177	18	190
44	138	34	178	53	191
46	148	12	179	27	192
36	150	22	180	26	195 U
9	150 U	32	180	54	196 U
38	158 U	35	180	3	196
33	160 U	28	181	20	197
10	160 U	50	182	45	202 U
47	168 U	39	182	42	203
25	169	7	182	16	213 U
14	169	19	183	11	215 U
4	170 U	24	184	49	221
56	170	21	184	5	259 U
51	170	31	185	48	863 U
23	170	41	188	15	1400 U
37	173 U	17	188		
55	174 U	6	190		

U - Omitted result

Table 5.5. Statistics - Chloride, mg/l

Sample A

Number of participants	54	Range	0,94
Number of omitted results	2	Variance	0,03
True value	2,03	Standard deviation	0,19
Mean value	2,05	Relative standard deviation	9,1%
Median value	2,03	Relative error	0,8%

Analytical results in ascending order:

44	1,56	40	2,00	3	2,10
27	1,65	52	2,00	13	2,11
6	1,80	50	2,00	23	2,13
29	1,80	36	2,00	20	2,14
28	1,83	51	2,00	5	2,16
10	1,84	39	2,02	56	2,18
19	1,90	54	2,03	45	2,20
53	1,90	21	2,03	22	2,20
18	1,90	47	2,03	48	2,21
12	1,92	33	2,04	55	2,21
49	1,93	17	2,04	14	2,28
35	1,93	31	2,04	16	2,34
34	1,93	41	2,04	4	2,41
32	1,94	38	2,04	11	2,47
37	1,95	1	2,04	42	2,47
30	1,95	7	2,04	24	2,50
26	1,98	25	2,07	15	8,13 U
43	1,99	9	2,09	2	5,50 U

Sample B

Number of participants	54	Range	1,17
Number of omitted results	2	Variance	0,05
True value	3,58	Standard deviation	0,22
Mean value	3,55	Relative standard deviation	6,3%
Median value	3,58	Relative error	0,7%

Analytical results in ascending order:

12	2,93	10	3,50	23	3,64
27	3,07	7	3,51	26	3,64
29	3,10	17	3,54	9	3,66
44	3,27	39	3,54	21	3,67
6	3,30	35	3,56	48	3,68
30	3,32	22	3,56	56	3,69
25	3,33	32	3,56	19	3,70
4	3,34	37	3,57	45	3,70
28	3,34	47	3,58	3	3,70
40	3,36	33	3,59	14	3,87
53	3,40	36	3,60	16	3,87
51	3,42	38	3,60	42	3,87
54	3,42	52	3,60	20	3,92
43	3,42	18	3,60	5	3,95
31	3,43	55	3,61	11	3,97
49	3,44	50	3,61	24	4,10
34	3,46	1	3,63	2	7,50 U
41	3,49	13	3,63	15	9,72 U

U = Omitted result

Table 5.6. Statistics - Sulfate, mg/l

Sample A

Number of participants	52	Range	1,77
Number of omitted results	3	Variance	0,09
True value	4,00	Standard deviation	0,30
Mean value	3,95	Relative standard deviation	7,6%
Median value	4,00	Relative error	1,3%

Analytical results in ascending order.

2	3,00	31	3,95	21	4,08
9	3,00 U	17	3,95	22	4,09
48	3,16	49	3,95	52	4,10
24	3,40	20	3,96	32	4,10
45	3,50	50	3,97	7	4,10
44	3,56	43	3,98	38	4,12
11	3,60	51	3,99	39	4,13
27	3,62	46	4,00 U	54	4,18
40	3,64	19	4,00	56	4,20
53	3,70	13	4,01	29	4,20
10	3,80	35	4,01	36	4,20
12	3,80	23	4,01	4	4,25
34	3,83	25	4,02	55	4,32
18	3,90	41	4,04	14	4,49
3	3,90	33	4,05	5	4,77
6	3,90	1	4,05	15	7,08 U
37	3,90	47	4,06		
28	3,91	30	4,07		

Sample B

Number of participants	52	Range	2,46
Number of omitted results	3	Variance	0,16
True value	5,33	Standard deviation	0,40
Mean value	5,24	Relative standard deviation	7,7%
Median value	5,33	Relative error	1,7%

Analytical results in ascending order.

9	3,30 U	31	5,25	39	5,38
2	4,00	20	5,26	18	5,40
48	4,15	49	5,27	19	5,40
24	4,20	50	5,28	41	5,42
45	4,60	17	5,30	30	5,43
53	4,70	10	5,31	33	5,45
27	4,80	22	5,32	52	5,45
40	4,90	13	5,33	55	5,45
12	5,00	54	5,34	38	5,47
44	5,02	47	5,34	11	5,60
32	5,05	43	5,34	29	5,60
3	5,10	25	5,35	36	5,70
34	5,15	7	5,35	14	5,84
6	5,20	21	5,35	5	6,46
51	5,22	23	5,35	15	8,92 U
56	5,23	37	5,36	46	49,10 U
28	5,24	4	5,37		
35	5,24	1	5,37		

U Omitted result

Table 5.7. Statistics - Calcium, mg/l

Sample A

Number of participants			
Number of omitted results	55	Range	1,47
True value	4	Variance	0.07
Mean value	2.75	Standard deviation	0.26
Median value	2,77	Relative standard deviation	9,5%
	2,78	Relative error	0,6%

Analytical results in ascending order:

42	0,18 U	31	2,68	28	2,84
22	1,73 U	2	2,70	26	2,86
10	2,10	50	2,71	43	2,87
29	2.10	39	2,72	3	2.90
57	2,33	13	2,74	37	2.90
32	2,40	20	2,74	7	2,94
23	2,48	1	2.74	11	3,00
5	2.48	34	2.75	19	3,00
14	2,51	51	2,75	45	3,05
21	2,58	49	2,76	36	3,10
52	2.61	6	2.76	53	3,10
17	2.64	9	2,77	56	3.11
55	2,64	38	2,77	27	3,13
33	2,64	12	2.77	54	3,40
47	2.66	4	2,78	41	3,57
18	2,66	24	2,81	46	4,19 U
48	2,67	35	2.83	15	5,16 U
40	2,67	30	2.83		
44	2.67	16	2,83		

Sample B

Number of participants			
Number of omitted results	55	Range	1,68
True value	4	Variance	0.13
Mean value	3,55	Standard deviation	0,37
Median value	3,60	Relative standard deviation	10,2%
	3.55	Relative error	1,4%

Analytical results in ascending order:

42	0,64 U	34	3,50	11	3,80
22	2,41 U	18	3.50	37	3,80
2	2.80	50	3,51	35	3.82
29	2.80	51	3,52	48	3,84
10	2,90	1	3,52	26	3,85
5	3,03	9	3,53	56	3,97
57	3,04	39	3,53	27	4,00
32	3.09	16	3,54	53	4.00
23	3,27	4	3,55	36	4,00
21	3,28	55	3,55	24	4,01
52	3,34	20	3,57	30	4,10
47	3.40	38	3,57	54	4,17
17	3.40	28	3,58	45	4,18
44	3,41	49	3,59	43	4,43
31	3,43	19	3,60	41	4,48
12	3,46	40	3,70	46	5,28 U
33	3,47	3	3,70	15	5,47 U
6	3,48	14	3.74		
13	3.48	7	3,78		

U Omitted result

Table 5.8. Statistics - Magnesium, mg/l

Sample A

Number of participants			
Number of omitted results	55	Range	0,30
True value	5	Variance	0,00
Mean value	0,47	Standard deviation	0,05
Median value	0,47	Relative standard deviation	10,7%
	0,47	Relative error	0,9%

Analytical results in ascending order:

45	0,25 U	20	0,46	7	0,49
42	0,31	21	0,46	15	0,49
22	0,32 U	34	0,46	27	0,49
37	0,39	39	0,46	30	0,49
29	0,40	33	0,47	50	0,49
57	0,42	4	0,47	12	0,50
6	0,43	48	0,47	52	0,50
5	0,43	53	0,47	14	0,50
40	0,44	51	0,47	35	0,51
54	0,44	28	0,47	43	0,56
10	0,44	13	0,48	49	0,57
26	0,45	32	0,48	36	0,60
47	0,45	38	0,48	3	0,60
44	0,45	1	0,48	24	0,61
55	0,45	31	0,48	2	0,65 U
16	0,45	56	0,48	19	1,00 U
17	0,46	9	0,48	46	1,10 U
23	0,46	41	0,49		
18	0,46	11	0,49		

Sample B

Number of participants			
Number of omitted results	55	Range	0,52
True value	5	Variance	0,01
Mean value	0,86	Standard deviation	0,08
Median value	0,87	Relative standard deviation	9,1%
	0,86	Relative error	1,5%

Analytical results in ascending order:

45	0,23 U	39	0,85	15	0,90
22	0,56 U	21	0,85	48	0,91
24	0,61	50	0,85	11	0,91
5	0,76	28	0,86	53	0,91
57	0,79	13	0,86	41	0,92
37	0,79	51	0,86	30	0,95
6	0,80	9	0,86	14	0,95
10	0,80	4	0,86	35	0,97
44	0,81	20	0,86	49	0,98
54	0,81	18	0,86	26	0,98
47	0,82	40	0,86	3	1,00
29	0,82	33	0,87	19	1,00 U
16	0,82	12	0,87	36	1,00
23	0,82	1	0,87	27	1,01
42	0,83	31	0,88	43	1,13
34	0,83	56	0,88	2	1,30 U
55	0,84	7	0,89	46	1,38 U
17	0,84	38	0,89		
32	0,84	52	0,90		

U - Omitted result

Table 5.9. Statistics - Sodium, mg/l

Sample A

Number of participants			
Number of omitted results	53	Range	0,75
True value	2	Variance	0,02
Mean value	1,73	Standard deviation	0,12
Median value	1,74	Relative standard deviation	7,1%
	1,73	Relative error	0,5%

Analytical results in ascending order:

22	1,01 U	37	1,70	13	1,77
56	1,35	6	1,70	54	1,78
48	1,55	39	1,70	32	1,78
38	1,59	35	1,70	26	1,79
21	1,59	15	1,71 U	52	1,79
55	1,60	28	1,71	19	1,80
11	1,60	17	1,72	10	1,80
44	1,62	27	1,72	14	1,81
18	1,63	49	1,72	36	1,82
42	1,63	51	1,73	9	1,83
23	1,65	50	1,73	47	1,89
33	1,66	57	1,74	41	1,89
20	1,68	31	1,74	3	1,90
16	1,68	1	1,75	43	1,94
45	1,70	7	1,75	12	1,96
34	1,70	24	1,75	5	2,05
53	1,70	30	1,76	29	2,10
4	1,70	40	1,76		

Sample B

Number of participants			
Number of omitted results	53	Range	1,25
True value	2	Variance	0,04
Mean value	2,84	Standard deviation	0,20
Median value	2,85	Relative standard deviation	7,1%
	2,84	Relative error	0,3%

Analytical results in ascending order:

22	1,74 U	48	2,79	3	2,90
15	1,83 U	45	2,80	42	2,93
56	2,15	19	2,80	36	2,95
11	2,52	13	2,81	52	2,95
55	2,52	10	2,82	35	2,96
49	2,57	7	2,82	12	2,96
51	2,62	17	2,82	50	2,97
21	2,63	37	2,83	26	2,97
44	2,66	39	2,83	14	2,99
23	2,71	6	2,84	24	3,00
34	2,73	28	2,84	53	3,00
33	2,73	47	2,85	9	3,00
16	2,74	1	2,85	41	3,02
27	2,74	38	2,86	30	3,11
40	2,74	32	2,88	5	3,27
4	2,77	54	2,89	43	3,37
18	2,78	31	2,89	29	3,40
20	2,78	57	2,90		

U Omitted result

Table 5.10. Statistics - Potassium, mg/l

Sample A

Number of participants			
Number of omitted results	53	Range	0,15
True value	6	Variance	0,00
Mean value	0,36	Standard deviation	0,03
Median value	0,36	Relative standard deviation	8,9%
	0,36	Relative error	-0,2%

Analytical results in ascending order:

56	0,10 U	7	0,35	18	0,37
33	0,11 U	57	0,35	31	0,37
5	0,16 U	26	0,35	49	0,37
48	0,20 U	24	0,35	28	0,37
47	0,29	14	0,36	27	0,37
35	0,29 U	12	0,36	32	0,38
3	0,30	11	0,36	41	0,38
45	0,30	40	0,36	38	0,38
20	0,31	30	0,36	16	0,38
15	0,32	4	0,36	39	0,39
55	0,32	6	0,36	50	0,39
51	0,32	37	0,36	19	0,40
1	0,33	53	0,36	22	0,40
9	0,33	23	0,36	13	0,42
42	0,34	17	0,37	43	0,44
44	0,34	34	0,37	36	0,44
10	0,34	54	0,37	29	0,52 U
52	0,34	21	0,37		

Sample B

Number of participants			
Number of omitted results	53	Range	0,17
True value	6	Variance	0,00
Mean value	0,37	Standard deviation	0,03
Median value	0,37	Relative standard deviation	9,4%
	0,37	Relative error	-0,6%

Analytical results in ascending order:

56	0,10 U	13	0,36	24	0,38
48	0,17 U	23	0,36	10	0,38
5	0,22 U	53	0,36	47	0,38
51	0,28	11	0,36	33	0,38 U
3	0,30	14	0,36	41	0,38
45	0,30	17	0,36	39	0,39
15	0,32	40	0,37	30	0,39
20	0,33	34	0,37	31	0,39
9	0,33	4	0,37	19	0,40
42	0,34	28	0,37	54	0,41
22	0,34	21	0,37	43	0,42
49	0,34	18	0,37	36	0,43
55	0,35	27	0,37	37	0,44
7	0,35	44	0,37	38	0,44
52	0,35	16	0,37	1	0,45
12	0,35	50	0,37	29	0,59 U
26	0,35	32	0,37	35	0,60 U
57	0,35	6	0,38		

U - Omitted result

Table 5.11. Statistics - Aluminium, µg/l

Sample C

Number of participants			
Number of omitted results	22	Range	79
True value	1	Variance	291
Mean value	87	Standard deviation	17
Median value	86	Relative standard deviation	19,8%
	87	Relative error	-0,8%

Analytical results in ascending order:

45	41 U	44	83	6	95
54	47	16	83	20	95
1	57	32	86	49	99
39	63	52	87	11	103
18	76	7	89	41	108
30	82	8	89	56	126
28	82	36	90		
57	83	19	90		

Sample D

Number of participants			
Number of omitted results	22	Range	91
True value	1	Variance	479
Mean value	148	Standard deviation	22
Median value	145	Relative standard deviation	15,1%
	148	Relative error	-1,9%

Analytical results in ascending order:

45	42 U	44	141	6	159
54	94	49	145	36	160
39	102	52	146	11	162
1	120	16	148	20	165
57	126	28	149	41	177
32	135	19	150	56	185
30	138	7	152		
18	138	8	156		

U - Omitted result

Table 5.12. Statistics - Aluminium, reactive, µg/l

Sample C

Number of participants			
Number of omitted results	12	Range	11
True value	8	Variance	22
Mean value	31	Standard deviation	5
Median value	30	Relative standard deviation	16,0%
	31	Relative error	4,4%

Analytical results in ascending order:

7	0 U	28	31	16	81 U
57	5 U	6	34	8	87 U
50	23	18	40 U	41	93 U
52	30	47	57 U	46	96 U

Sample D

Number of participants			
Number of omitted results	12	Range	24
True value	8	Variance	108
Mean value	44	Standard deviation	10
Median value	45	Relative standard deviation	23,5%
	44	Relative error	1,5%

Analytical results in ascending order:

7	10 U	6	48	46	132 U
57	12 U	52	58	16	135 U
50	34	18	83 U	8	147 U
28	39	47	117 U	41	164 U

U Omitted result

Table 5.13. Statistics - Aluminium, nonlabile, µg/l

Sample C

Number of participants			
Number of omitted results	10	Range	20
True value	4	Variance	52
Mean value	49	Standard deviation	7
Median value	51	Relative standard deviation	14,2%
	49	Relative error	-4,1%

Analytical results in ascending order:

50	17	U	1	47		16	63	
28	24	U	47	47		57	78	U
6	28	U	18	50				
7	43		52	57				

Sample D

Number of participants			
Number of omitted results	10	Range	22
True value	4	Variance	74
Mean value	95	Standard deviation	9
Median value	96	Relative standard deviation	9,0%
	95	Relative error	1,2%

Analytical results in ascending order:

50	22	U	1	88		16	110	
28	28	U	7	92		57	114	U
6	30	U	47	98				
52	88		18	101				

U Omitted result

Table 5.14. Statistics - Dissolved organic carbon, mg/l

Sample C

Number of participants			
Number of omitted results	23	Range	1,31
True value	1	Variance	0,16
Mean value	3,79	Standard deviation	0,39
Median value	3,79	Relative standard deviation	10,4%
	3,79	Relative error	-0,1%

Analytical results in ascending order:

33	3,29	32	3,50	55	4,00
39	3,36	44	3,57	37	4,04
18	3,40	50	3,73	45	4,14
36	3,40	21	3,84	57	4,50
28	3,45	23	3,84	11	4,57
1	3,49	20	3,85	54	4,60
52	3,50	7	3,85	35	27,27 U
16	3,50	19	3,90		

Sample D

Number of participants			
Number of omitted results	23	Range	1,40
True value	1	Variance	0,18
Mean value	3,69	Standard deviation	0,42
Median value	3,76	Relative standard deviation	11,2%
	3,69	Relative error	1,8%

Analytical results in ascending order:

1	3,33	28	3,49	21	3,96
44	3,34	16	3,50	19	4,10
18	3,40	23	3,65	45	4,23
52	3,40	20	3,72	54	4,40
32	3,40	50	3,73	57	4,60
36	3,40	7	3,75	11	4,73
39	3,42	55	3,80	35	27,10 U
33	3,44	37	3,87		

U Omitted result

Table 5.15. Statistics - Chemical oxygen demand, mg/l

Sample C

Number of participants			
Number of omitted results	13	Range	3,10
True value	0	Variance	0,54
Mean value	4,39	Standard deviation	0,73
Median value	4,31	Relative standard deviation	17,0%
	4,39	Relative error	-1,8%

Analytical results in ascending order:

56	2,30	20	4,29	9	4,80
18	3,90	41	4,39	4	5,10
46	4,10	24	4,49	45	5,40
36	4,10	28	4,50		
2	4,20	54	4,50		

Sample D

Number of participants			
Number of omitted results	13	Range	2,70
True value	0	Variance	0,40
Mean value	4,30	Standard deviation	0,63
Median value	4,12	Relative standard deviation	15,3%
	4,30	Relative error	-4,2%

Analytical results in ascending order:

56	2,30	2	4,10	54	4,40
46	3,85	9	4,30	24	4,65
41	3,97	20	4,30	4	5,00
18	4,00	45	4,30		
36	4,00	28	4,30		

U Omitted result

Appendix E. Reports and publications from the ICP-Waters Programme

1. Manual for Chemical and Biological Monitoring. Programme Manual. Prepared by the Programme Centre, Norwegian Institute for Water Research. NIVA, Oslo 1987.

2. Norwegian Institute for Water Research, 1987. Intercalibration 8701. pH, Ks, SO_4, Ca. Programme Centre, NIVA, Oslo.

3. Norwegian Institute for Water Research, 1988. Data Report 1987 and available Data from Previous Years. Programme Centre, NIVA, Oslo.

4. Norwegian Institute for Water Research, 1988. Intercalibration 8802: pH, K_{25}, HCO_3, NO_3, SO_4, Cl, Ca, Mg, Na, K. NIVA, Oslo.

5. Proceedings of the Workshop on Assessment and Monitoring of Acidification in Rivers and Lakes, Espoo, Finland, 3rd to 5th October 1988. Prepared by the Finnish Acidification Research Project, HAPRO, Ministry of Environment, October 1988.

6. Norwegian Institute for Water Research, 1989. Intercalibration 8903: Dissolved organic carbon and aluminium fractions. Programme Centre, NIVA, Oslo. NIVA Rep. 2238-89, ISBN 82-577-1534-6.

7. Note: Some reflections about the determination of pH and alkalinity. Prepared by the Programme Centre, Norwegian Institute for Water Research. Håvard Hovind, NIVA, Oslo October 1989.

8. Hovind, H. 1990. Intercalibration 9004: pH and alkalinity. Programme Centre, NIVA, Oslo. NIVA Rep. 2465-90. ISBN 82-577-1776-2.

- Skjelkvale, B.L., and Wright, R.F. 1990. Overview of areas sensitive to acidification: Europe. Programme Centre, NIVA, Oslo. Acid Rain Research Report 20/1990. NIVA report 2405-90, ISBN 82-577-1706-1.

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