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Intercomparison 0216:

pH, K_{25}, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni and Zn

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REPORT

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Abstract

79 laboratories received samples for the intercomparison 0216, and 75 laboratories in 27 countries submitted results. Two sample sets were used, one for the determination of major ions, and one for heavy metals. Based on the general target accuracy of ± 20 %, 68 % of the results were considered acceptable. The best results were reported for the analytical variables sodium, sulfate and manganese, where 88, 76 and 76 % of the results were acceptable. The worst results were observed for alkalinity, nitrate + nitrite, and lead, common for these analytical variables is that the concentrations are rather low. For pH only 58 % of the result pairs were acceptable in relation to the extended target accuracy of ± 0.2 units. Normalization of the analytical methods used is necessary to improve the comparability for pH. Determination of heavy metals was included in the intercomparison for the third time, with fairly good results for most of them. The lowest acceptance was obtained for lead, 59 %, and this may be due to the low concentrations used for the metal.

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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 0216

pH, Cond, HCO_3, NO_3+NO_2,
Cl, SO_4, Ca, Mg, Na, K, Fe, Mn,
Cd, Pb, Cu, Ni, and Zn

Prepared by the Programme Centre
Norwegian Institute for Water Research
Oslo, August 2002

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 the 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 16th intercomparison of chemical analysis.

Oslo, August 2002

Håvard Hovind

Contents

1. Summary

Intercomparison 0216 was organized as a part of the between-laboratory quality control programme, as stated in "Manual for Chemical and Biological Monitoring" (1), by the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes.

The intercomparison was performed in June - July 2002, and included the determination of major ions and metals in natural water samples. The participants were asked to determine pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, iron, manganese, cadmium, lead, copper, nickel and zinc.

Two sample sets were prepared for this intercomparison, one for the determination of the major ions, and one for the heavy metals. 114 laboratories were invited to participate in this intercomparison, and the samples were sent to 79 laboratories who accepted to participate. 75 laboratories submitted results to the Programme Centre before the final statistical treatment of the data. 27 countries were represented in this laboratory group (see Appendix A, page 48).

The median value of the results received from the participants was selected as "true" value for each variable. 68 % of the result pairs were considered as acceptable, the target limit being the median value ± 20 %, except for pH and conductivity where the acceptance limits were ± 0,2 units and ± 10 %, respectively.

For pH, the accuracy limit was extended from 0,1 to ± 0,2 units, but still only 66 % of the result pairs were acceptable using 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 spreading of pH results is mainly due to the fact that different routines are used for the determination of pH by the participants, leading to small systematical differences in the results. In this intercomparison the differences between the methods are rather small, and therefore a slightly greater fraction of pH results are acceptable compared to earlier intercomparisons.

The best results were reported for the analytical variables sodium, sulfate and manganese, where 88, 76 and 76 % of the results were acceptable. The worst results were observed for alkalinity, nitrate + nitrite, and lead with 58, 59 and 59 % acceptable results. Common for these last analytical variables is that the concentrations are rather low in the samples used in this intercomparison. To improve the comparability of the results for these variables, it is necessary to normalize the analytical methods used.

For the third time in this intercomparison programme, the heavy metals iron, manganese, cadmium, lead, copper, nickel, and zinc were included. The best results were obtained for manganese where 76 % of the results were acceptable. For this element, and copper and iron with 73 and 71 % acceptable results, the concentrations are quite higher than the detection limit of the most sensitive methods used.

2. 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 sixteenth intercomparison test, called 0216, 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, iron, manganese, cadmium, lead, copper, nickel and zinc.

3. Accomplishment of the intercomparison

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 2001 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 for the heavy metals. The previous years there has also been included one sample set for the determination of aluminium fractions and unspecific organic compounds, but this time it was decided to exclude these parameters from the intercomparison test.

The samples were mailed from the Programme Centre on May 29 and the following days, 2002. Most of the participating laboratories received the samples within one week, with some very few exceptions. One laboratory received the sample set with some damage on the bottles, and had to be supplied with an extra set. 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. By different reasons a few laboratories asked for some delay for reporting the results to the Programme centre, which they were permitted to do, however, the results had to be reported in due time beffore the statistical calculations. Most results were received within the end of June, the last results included in the report were received in the beginning of August. Two of the laboratories who reported corrections of their first results were too late to be incorporated in this report, as the statistical treatment of the reported data was terminated.

4. Results

114 laboratories were invited to participate in this intercomparison, and 79 laboratories accepted and therefore received samples. The 75 laboratories who submitted results to the Programme Centre, are representing 27 countries. It was a problem that some laboratories

submitted the results several weeks after the deadline, and a reminder letter was mailed to some few participants. A survey of the participants and their code numbers are listed in Appendix 1. Here are also included a table illustrating how many laboratories are participating from each country (see page 41). One participant reported a double set of results, produced at differently located laboratories of the institute, these result sets are included as different laboratories in the report. One laboratory reported results determined with different methods in the same laboratory, here we selected the first set of results as representative for the laboratory. It is preferred that the participants are reporting results determined with the method normally used for the analysis of acid rain samples in the laboratory.

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 the laboratories participting in the International Cooperative Programme. 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 variables, like pH, this may represent a problem as the methods used may produce systematically different results (stirring, non-stirring, equilibration), and we cannot argue that one method is more correct than the others.

The results are illustrated in Figure 1 - 17, 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. One laboratory which reported results for sample B only, and not for sample A, is not found in the plots either. 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 0216 is presented in Table 1. The individual results of the participants are presented in Table 4 in Appendix D, sorted in order of increasing identification number. More extensive statistical informations are presented in the Tables 5.1 - 5.17 in Appendix D.

4.1 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. 72 laboratories reported results for pH, of this group 38 indicated that they read the pH value during stirring the solution. The stirring are normally lowering the observed pH result. In this intercomparison the median values are only slightly lowered in the stirred samples compared to the non-stirred samples (see Table 1), the differences are 0,08 pH units, however, this difference is statistically significant.

(The text continues on page 29

Table 1. Statistical summary of intercomparison 0216

Analytical variable and method	Sample pair	True value 1	True value 2	Total no.	Labs excl.	Median 1	Median 2	Mean Sample 1	St.dev. Sample 1	Mean Sample 2	St.dev. Sample 2	Rel.std. % 1	Rel.std. % 2	Relative error 1	Relative error 2
pH	AB	6,72	6,58	72	2	6,72	6,58	6,70	0,16	6,57	0,16	2,4	2,4	-0,4	-0,2
Electrometry				31	0	6,75	6,61	6,73	0,14	6,60	0,15	2,0	2,3	0,1	0,2
Stirring				38	2	6,67	6,53	6,66	0,16	6,53	0,15	2,4	2,4	-0,9	-0,8
Equilibration				3	0	6,78	6,67	6,84	0,28	6,69	0,24	4,1	3,5	1,8	1,6
Conductivity	AB	2,84	2,57	72	4	2,84	2,57	2,83	0,21	2,60	0,20	7,4	7,7	-0,2	1,1
Alkalinity	AB	0,134	0,103	61	13	0,134	0,103	0,132	0,021	0,102	0,016	16,2	15,7	-1,5	-1,3
Gran plot titration				29	5	0,135	0,103	0,133	0,018	0,101	0,013	13,3	12,7	-1,0	-2,0
End point 4,5 and 4,2				10	1	0,135	0,104	0,136	0,013	0,102	0,008	9,3	7,7	1,4	-0,5
End point 5,6				1	0			0,110		0,083				-17,9	-19,4
End point 5,4				2	0			0,136		0,097				1,5	-6,3
End point 4,5				13	3	0,142	0,112	0,136	0,030	0,110	0,023	22,1	21,3	1,2	6,8
Colorimetry				2	2			0,070		0,165				-47,8	60,2
Not documented				4	2			0,098		0,080				-26,9	-22,8
Nitrate + nitrite-nitrogen	AB	85	118	67	17	85	118	84	8	117	12	10,1	10,2	-1,1	-0,6
Autoanalyzer				29	4	84	119	83	10	118	12	11,6	10,0	-2,0	-0,4
Ion chromatography				31	8	85	119	85	7	117	13	8,8	11,0	-0,3	-0,7
Hydrazine				2	0			86		115				1,2	-2,5
Cap. electrophoresis				2	2										
Photometry				3	3										
Chloride	AB	1,05	1,39	69	13	1,05	1,39	1,07	0,11	1,42	0,14	10,1	10,1	1,5	2,0
Ion chromatography				51	4	1,05	1,39	1,06	0,10	1,41	0,14	9,2	9,6	1,2	1,7
Autoanalyzer				1	1			1,60		2,00				52,4	43,9
Argentometry				3	2			1,10		1,50				4,8	7,9
Manual, Hg				8	5	1,04	1,49	1,14	0,22	1,48	0,13	19,6	8,8	8,9	6,2
Cap. electrophoresis				2	0			1,06		1,51				1,4	8,6
Potentiometry				3	1			0,93		1,22				-11,4	-12,6
Not specified				1	0			1,23		1,56				17,1	12,2

Analytical variable and method	Sample pair	True value 1	True value 2	Total no.	Labs excl.	Median 1	Median 2	Mean Sample 1	St.dev. Sample 1	Mean Sample 2	St.dev. Sample 2	Rel.std. % 1	Rel.std. % 2	Relative error 1	Relative error 2
Sulfate	AB	2,71	2,11	67	11	2,71	2,11	2,72	0,20	2,14	0,14	7,5	6,5	0,4	1,2
Ion chromatography				51	4	2,71	2,11	2,74	0,14	2,14	0,14	5,3	6,6	1,1	1,5
Photometry				9	6	2,02	2,00	2,21	0,35	2,04	0,10	15,9	5,0	-18,3	-3,2
Nephelometry				4	1	3,06	2,10	2,92	0,27	2,14	0,24	9,4	11,1	7,6	1,6
ICP				1	0			2,72		2,11				0,4	0,0
Cap. electrophoresis				2	0			2,73		2,15				0,6	1,8
Calcium	AB	0,97	1,20	68	7	0,97	1,20	0,99	0,15	1,21	0,16	15,5	13,5	2,3	0,7
FAAS				24	2	0,95	1,15	0,96	0,13	1,18	0,15	13,3	12,6	-0,6	-1,8
ICP				17	0	0,97	1,18	0,95	0,13	1,18	0,13	13,4	11,4	-2,4	-1,7
EDTA				5	1	1,04	1,14	1,07	0,28	1,11	0,11	26,5	10,4	10,1	-7,5
Ion chromatography				20	4	1,05	1,30	1,06	0,17	1,29	0,20	15,9	15,1	9,4	7,8
Photometry				1	0			1,02		1,19				5,2	-0,8
Cap. Electrophoresis				1	0			0,95		1,40				-2,1	16,7
Magnesium	AB	0,539	0,380	69	8	0,539	0,380	0,526	0,065	0,383	0,040	12,3	10,5	-2,4	0,9
FAAS				25	2	0,530	0,380	0,523	0,053	0,382	0,038	10,2	9,9	-3,0	0,6
ICP				17	0	0,533	0,380	0,524	0,059	0,378	0,037	11,3	9,7	-2,7	-0,4
EDTA				5	3			0,480		0,405				-10,9	6,6
Ion chromatography				20	3	0,550	0,400	0,537	0,078	0,387	0,049	14,5	12,7	-0,3	1,8
Photometry				1	0			0,520		0,390				-3,5	2,6
Cap. Electrophoresis				1	0			0,530		0,390				-1,7	2,6
Sodium	AB	3,89	3,08	66	2	3,89	3,08	3,86	0,28	3,09	0,25	7,4	8,2	-0,8	0,2
FAAS				20	0	3,87	3,06	3,82	0,26	3,02	0,19	6,8	6,5	-1,9	-1,9
ICP				15	0	3,82	3,04	3,73	0,32	2,97	0,26	8,6	8,7	-4,1	-3,7
AES				9	0	3,87	3,08	3,82	0,26	3,04	0,24	6,9	7,9	-1,9	-1,3
Ion chromatography				21	2	3,97	3,18	4,01	0,24	3,25	0,22	6,0	6,9	3,1	5,6
Cap. Electrophoresis				1	0			4,03		3,48				3,6	13,0

Analytical variable and method	Sample pair	True value 1	True value 2	Total no.	Labs excl.	Median 1	Median 2	Mean Sample 1	St.dev. Sample 1	Mean Sample 2	St.dev. Sample 2	Rel.std. % 1	Rel.std. % 2	Relative error 1	Relative error 2
Potassium	AB	0,370	0,473	63	6	0,370	0,473	0,372	0,054	0,468	0,054	14,5	11,5	0,6	-1,1
FAAS				18	2	0,370	0,475	0,375	0,053	0,469	0,048	14,1	10,3	1,5	-0,9
ICP				15	1	0,380	0,475	0,369	0,053	0,468	0,055	14,4	11,8	-0,4	-1,0
AES				9	1	0,373	0,477	0,380	0,070	0,450	0,072	18,4	15,9	2,6	-5,0
Ion chromatography				20	2	0,365	0,469	0,369	0,053	0,474	0,053	14,5	11,1	-0,4	0,3
Cap. Electrophoresis				1	0			0,370		0,470				0,0	-0,6
Iron	CD	168	220	38	5	168	220	169	23	213	29	13,4	13,4	0,5	-3,0
FAAS				9	2	182	225	187	28	225	39	14,9	17,5	11,3	2,2
GFAAS				4	0	140	191	142	21	189	43	14,6	22,8	-15,8	-14,3
ICP				15	1	174	222	175	13	222	15	7,3	6,8	4,1	0,8
ICP-MS				9	1	157	202	156	13	201	19	8,5	9,6	-7,1	-8,6
Photometry				1	1			30		26				-82,4	-88,4
Manganese	CD	29,0	35,4	45	4	29,0	35,4	29,4	3,3	35,5	3,5	11,1	9,7	1,3	0,4
FAAS				10	1	27,0	34,0	28,0	3,2	32,9	3,2	11,5	9,7	-3,6	-7,2
GFAAS				9	0	32,1	38,2	32,2	3,7	38,3	4,2	11,5	10,9	10,9	8,3
ICP				15	2	28,1	35,4	28,0	2,5	35,0	1,8	8,8	5,2	-3,4	-1,2
ICP-MS				11	1	29,2	35,6	29,9	2,2	36,2	2,9	7,3	8,0	3,2	2,2
Cadmium	CD	1,34	1,80	41	4	1,34	1,80	1,32	0,21	1,72	0,25	16,3	14,7	-1,7	-4,5
FAAS				4	1	1,30	1,80	1,35	0,09	1,74	0,22	6,8	12,6	1,0	-3,1
GFAAS				18	1	1,35	1,78	1,28	0,25	1,70	0,31	19,2	18,0	-4,4	-5,6
ICP				8	2	1,25	1,77	1,21	0,18	1,68	0,28	15,0	16,5	-9,4	-6,7
ICP-MS				11	0	1,38	1,81	1,42	0,17	1,76	0,17	12,1	9,5	5,9	-2,0
Lead	CD	2,33	3,21	41	9	2,33	3,21	2,40	0,32	3,28	0,44	13,3	13,6	2,8	2,0
FAAS				4	3			2,40		3,40				3,0	5,9
GFAAS				18	2	2,27	3,33	2,34	0,33	3,42	0,41	14,2	12,0	0,4	6,4
ICP				8	4	2,43	3,18	2,36	0,27	2,98	0,68	11,3	22,9	1,2	-7,1
ICP-MS				11	0	2,35	3,20	2,49	0,34	3,17	0,37	13,5	11,7	6,9	-1,4

Analytical variable and method	Sample pair	True value 1	True value 2	Total no.	Labs excl.	Median 1	Median 2	Mean Sample 1	St.dev. Sample 1	Mean Sample 2	St.dev. Sample 2	Rel.std. % 1	Rel.std. % 2	Relative error 1	Relative error 2
Copper	CD	19,5	20,5	44	5	19,5	20,5	19,1	2,0	20,1	2,6	10,4	13,0	-1,9	-2,1
FAAS				4	0	17,0	18,6	17,0	3,1	17,8	3,8	18,2	21,4	-12,9	-13,3
GFAAS				18	3	19,7	20,8	19,2	2,0	20,6	2,6	10,3	12,7	-1,5	0,7
ICP				11	2	19,4	20,1	19,7	1,3	20,6	1,8	6,5	8,9	1,0	0,7
ICP-MS				11	0	19,8	20,3	19,4	1,8	19,7	2,5	9,2	12,8	-0,7	-4,1
Nickel	CD	10,00	14,60	40	5	10,00	14,60	10,03	1,53	14,49	1,30	15,2	9,0	0,3	-0,7
FAAS				4	1	10,00	14,00	8,72	2,22	13,71	1,46	25,4	10,7	-12,8	-6,1
GFAAS				15	2	10,00	14,80	10,72	1,64	14,62	1,55	15,3	10,6	7,2	0,2
ICP				10	1	9,91	14,60	9,66	1,71	14,49	1,58	17,6	10,9	-3,4	-0,8
ICP-MS				11	1	10,03	14,59	9,87	0,38	14,57	0,54	3,9	3,7	-1,3	-0,2
Zinc	CD	35,8	24,8	41	5	35,8	24,8	35,9	4,7	24,9	2,9	13,0	11,7	0,2	0,3
FAAS				11	3	34,5	23,5	34,1	3,9	22,9	3,0	11,4	13,1	-4,7	-7,5
GFAAS				6	2	40,3	27,7	40,4	3,4	27,8	2,5	8,5	9,0	12,8	12,1
ICP				14	0	34,5	24,1	35,2	3,4	24,0	1,9	9,8	7,9	-1,8	-3,1
ICP-MS				10	0	36,6	26,2	36,5	6,3	26,4	2,8	17,2	10,7	1,9	6,5

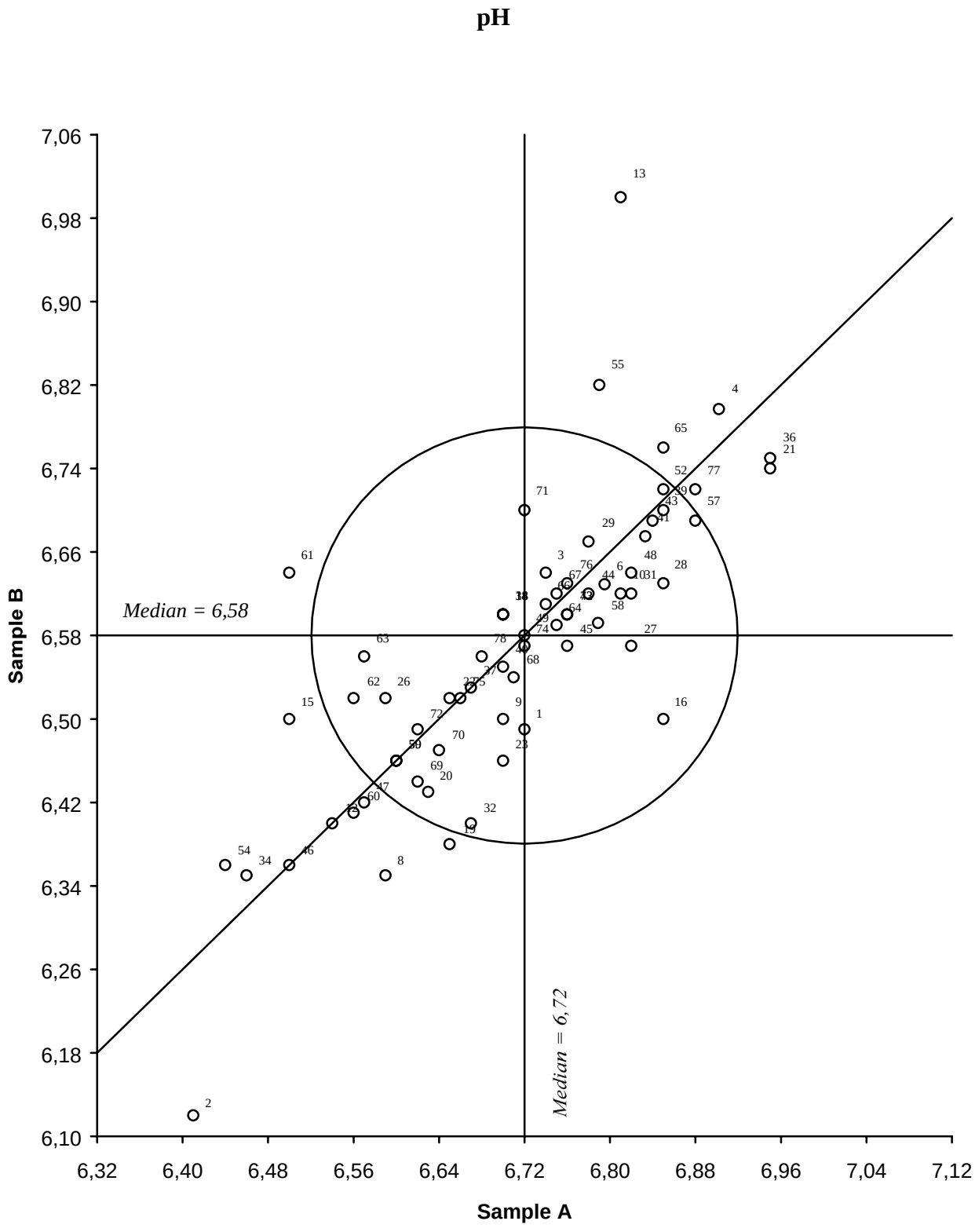

Figure 1. Youden diagramme for pH, sample pair AB
Acceptance limit, given by the circle, is 0,2 pH units

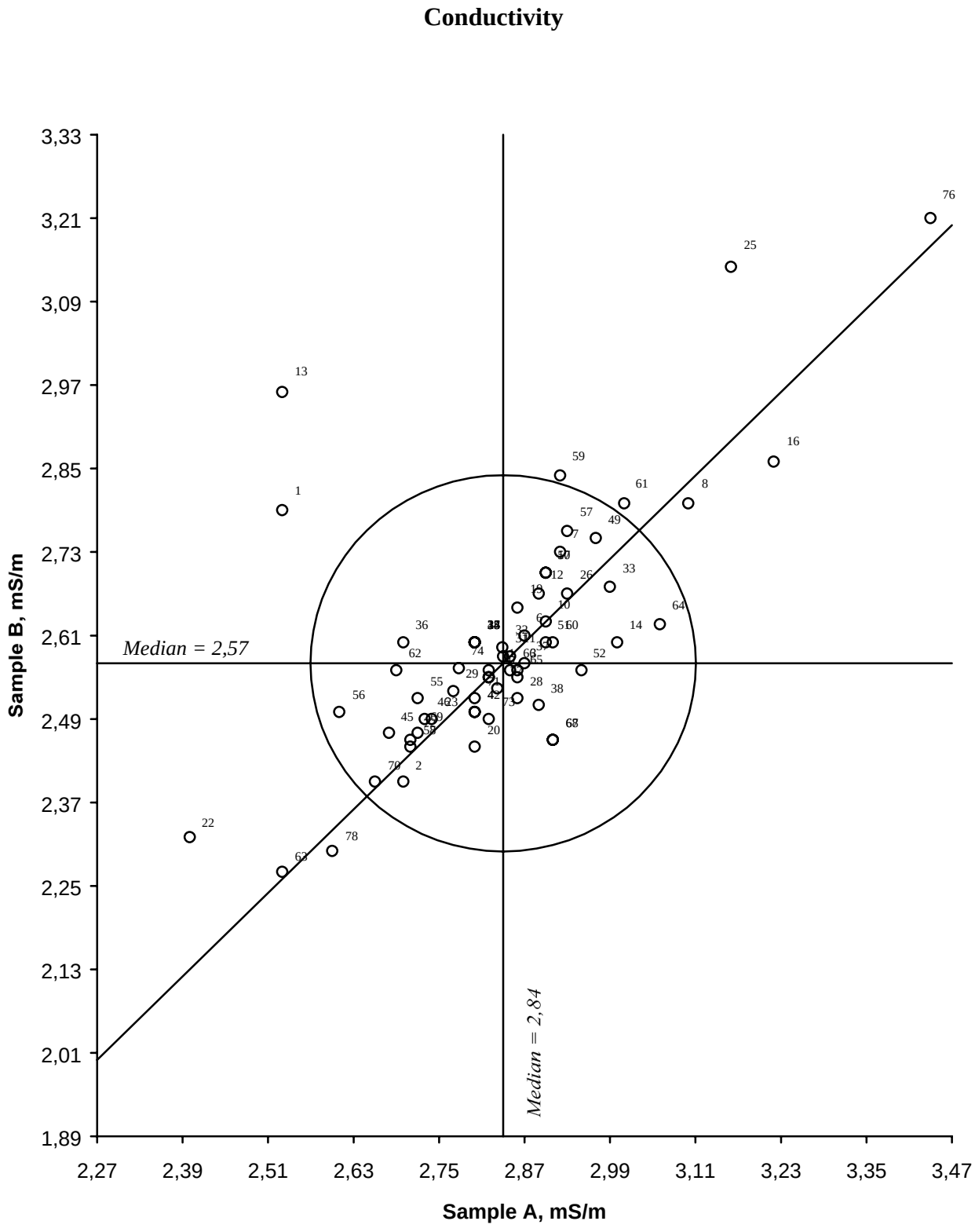

Figure 2. Youden diagramme for conductivity, sample pair AB
Acceptance limit, given by the circle, is 10 %

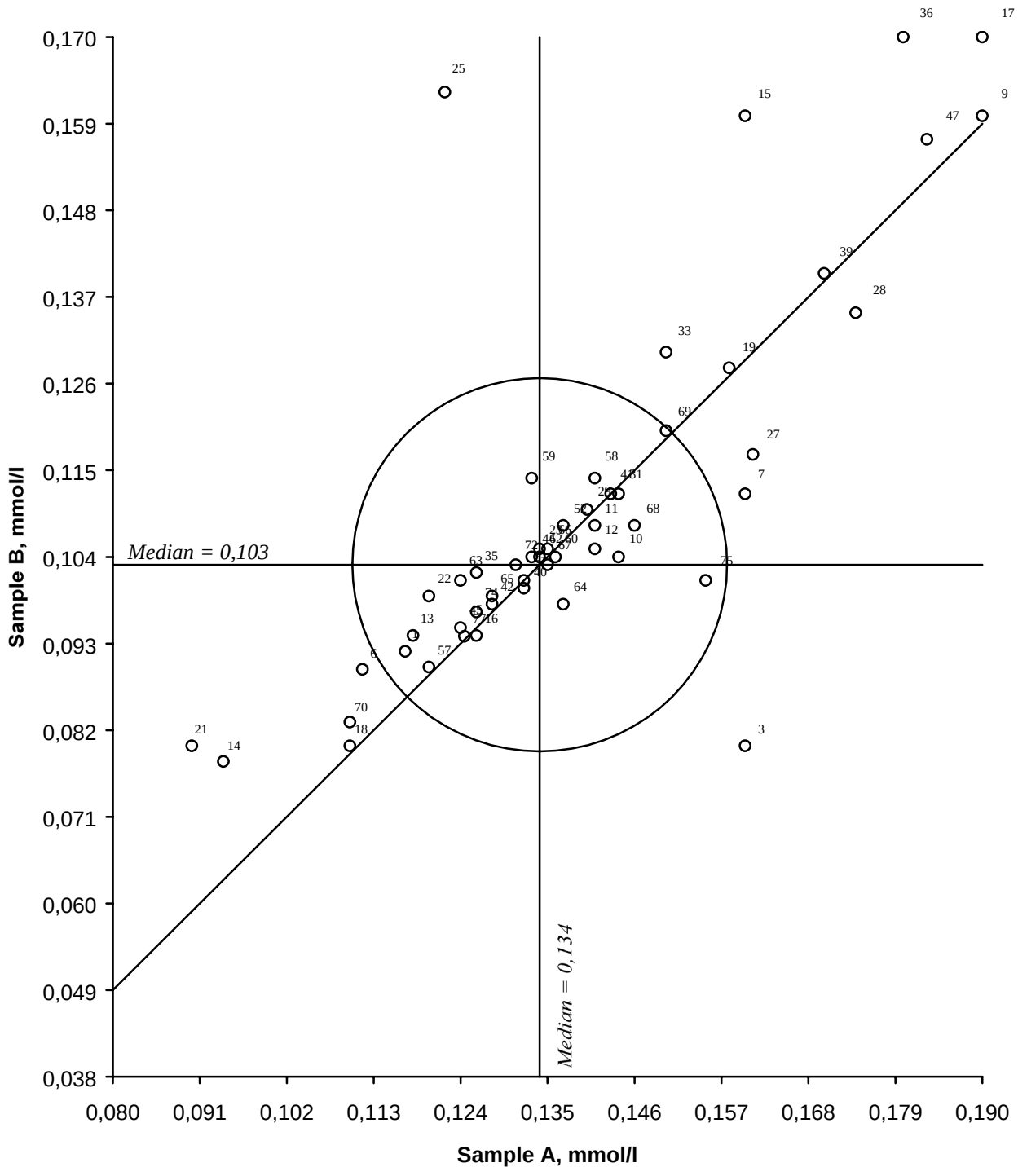

Figure 3. Youden diagramme for alkalinity, sample pair AB
Acceptance limit, given by the circle, is 20 %

Nitrate + nitrite-nitrogen

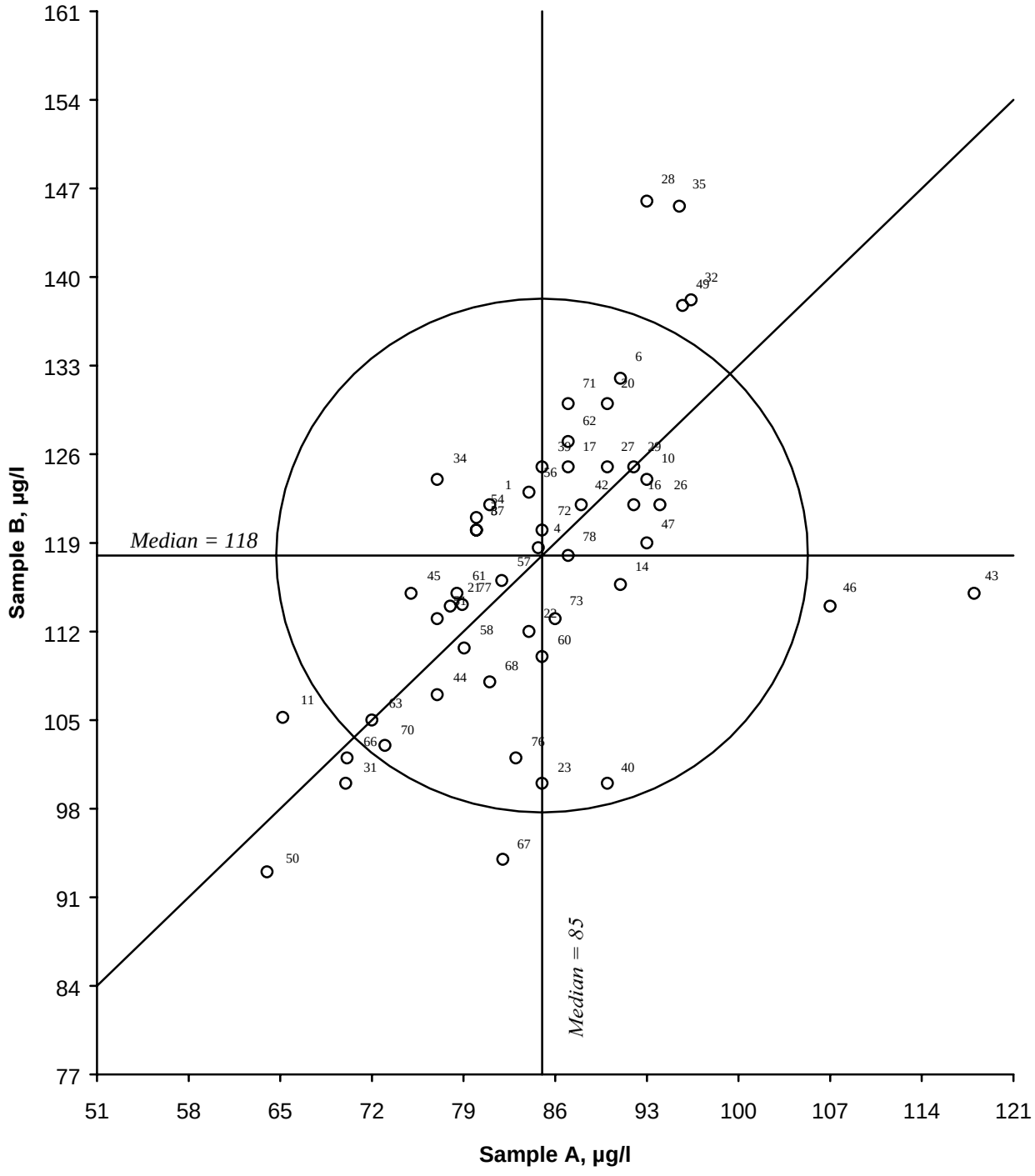

Figure 4. Youden diagramme for nitrate + nitrite-nitrogen, sample pair AB
Acceptance limit, given by the circle, is 20 %

Chloride

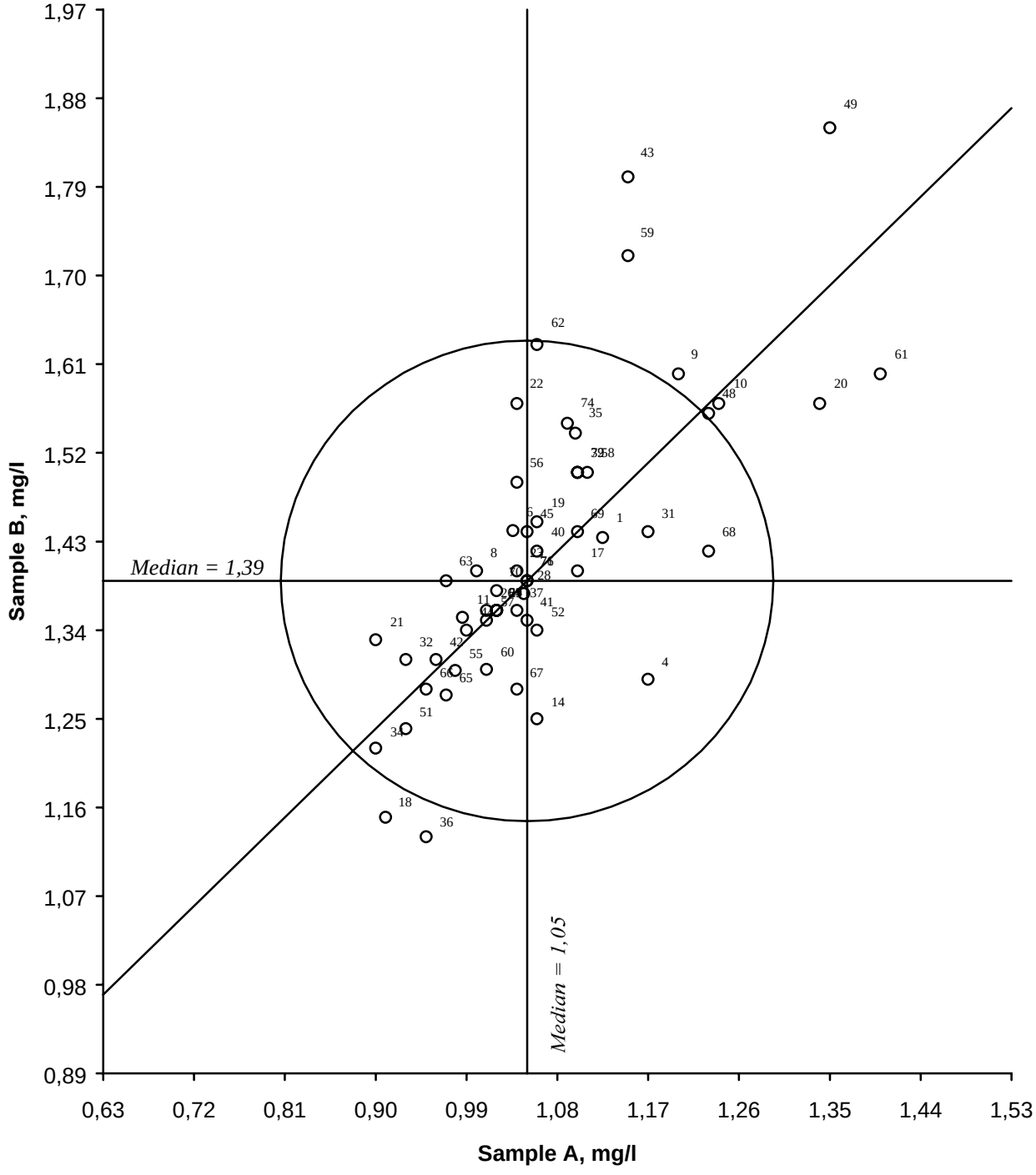

Figure 5. Youden diagramme for chloride, sample pair AB
Acceptance limit, given by the circle, is 20 %

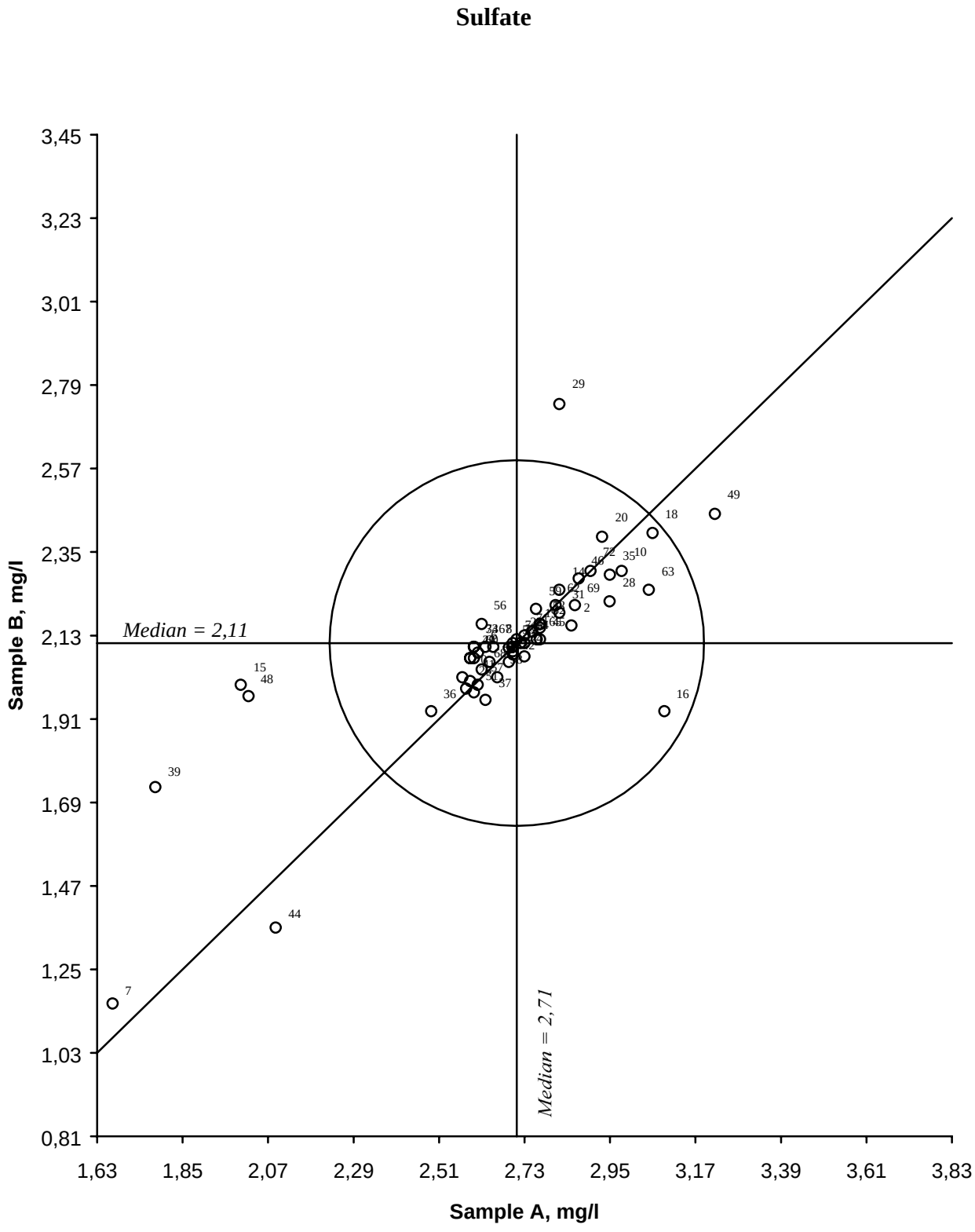

Figure 6. Youden diagramme for sulfate, sample pair AB
Acceptance limit, given by the circle, is 20 %

Calcium

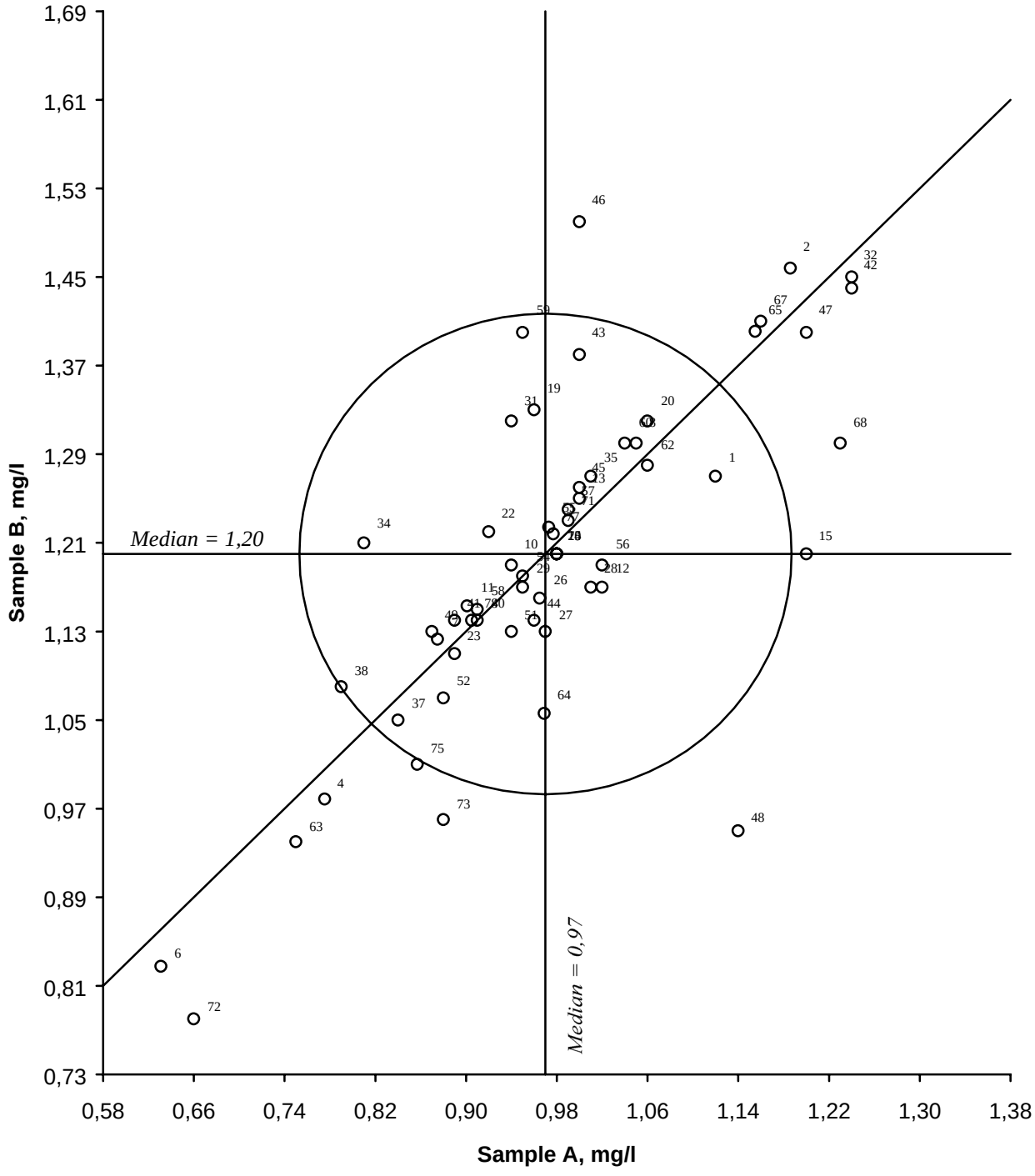

Figure 7. Youden diagramme for calcium, sample pair AB
Acceptance limit, given by the circle, is 20 %

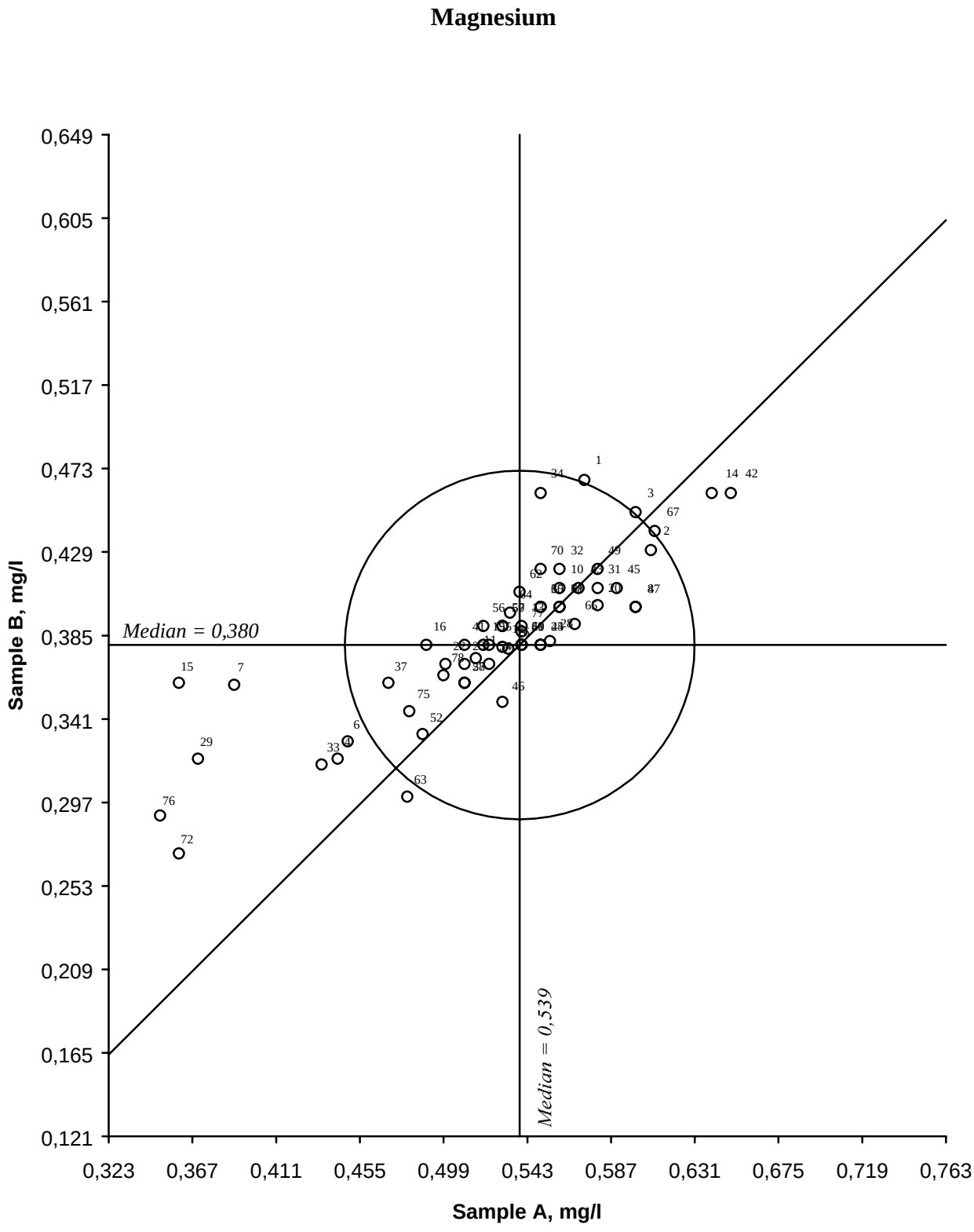

Figure 8. Youden diagramme for magnesium, sample pair AB
Acceptance limit, given by the circle, is 20 %

Sodium

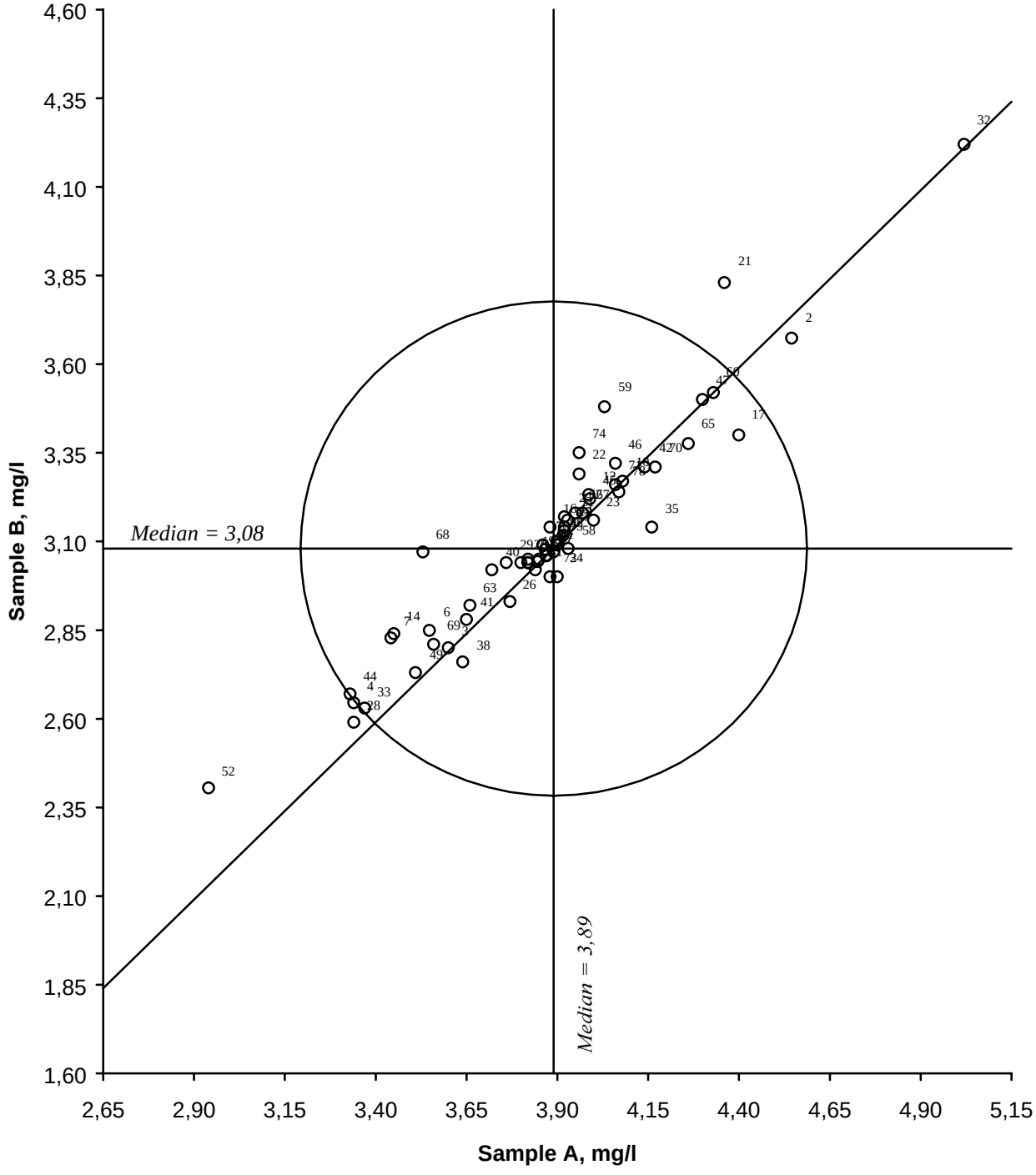

Figure 9. Youden diagramme for sodium, sample pair AB
Acceptance limit, given by the circle, is 20 %

Potassium

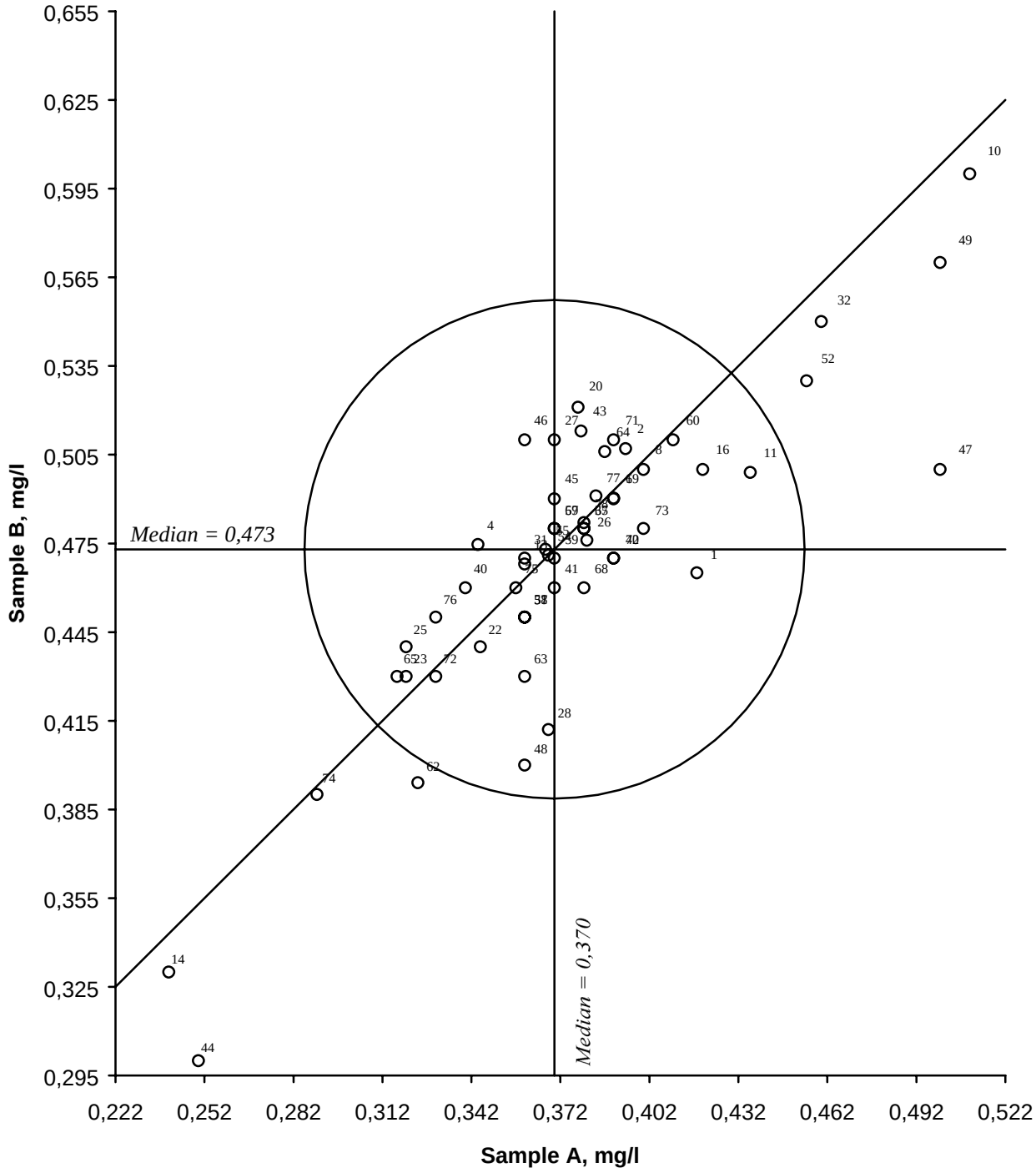

Figure 10. Youden diagramme for potassium, sample pair AB
Acceptance limit, given by the circle, is 20 %

Iron

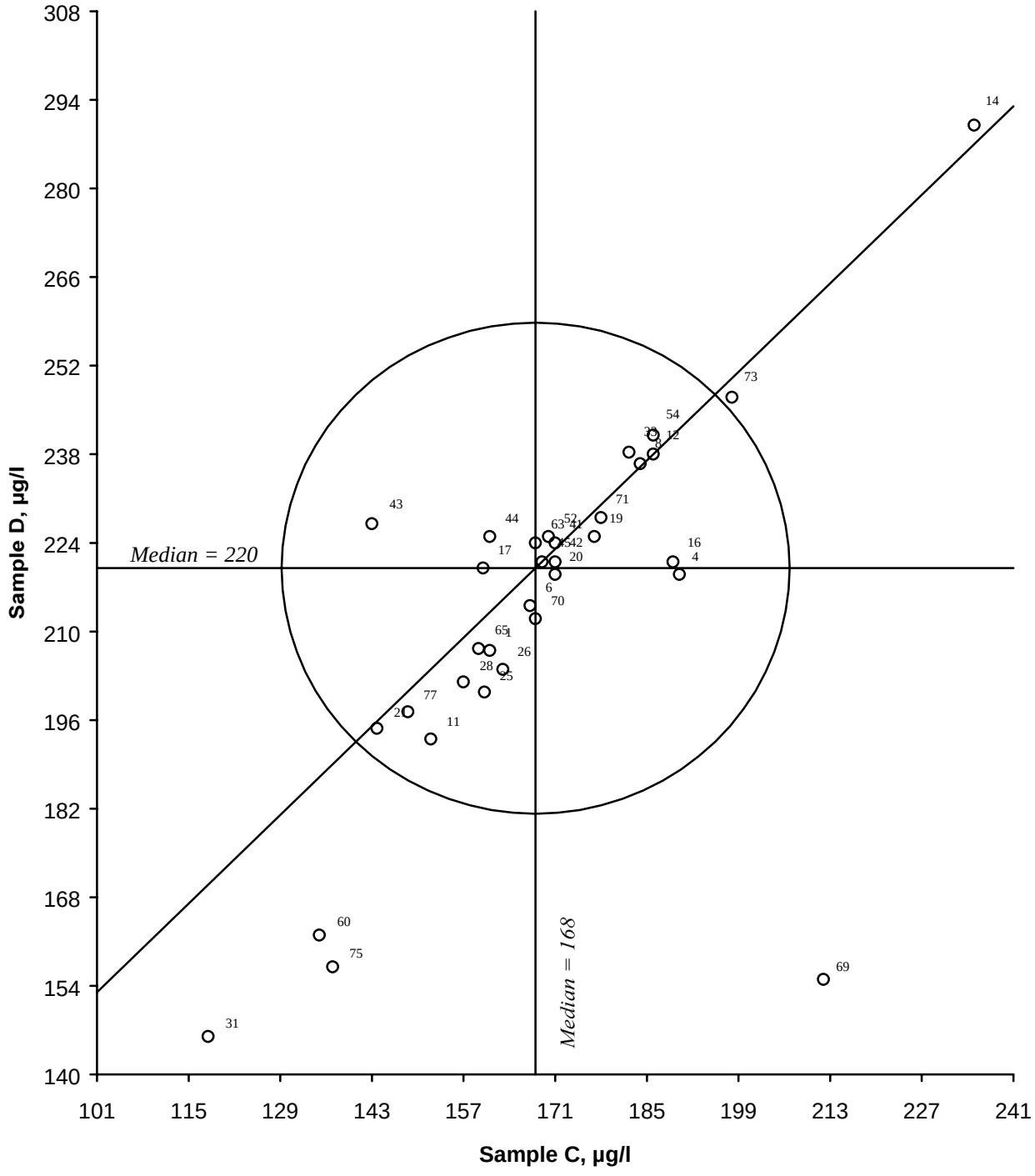

Figure 11. Youden diagramme for iron, sample pair CD
Acceptance limit, given by the circle, is 20 %

Manganese

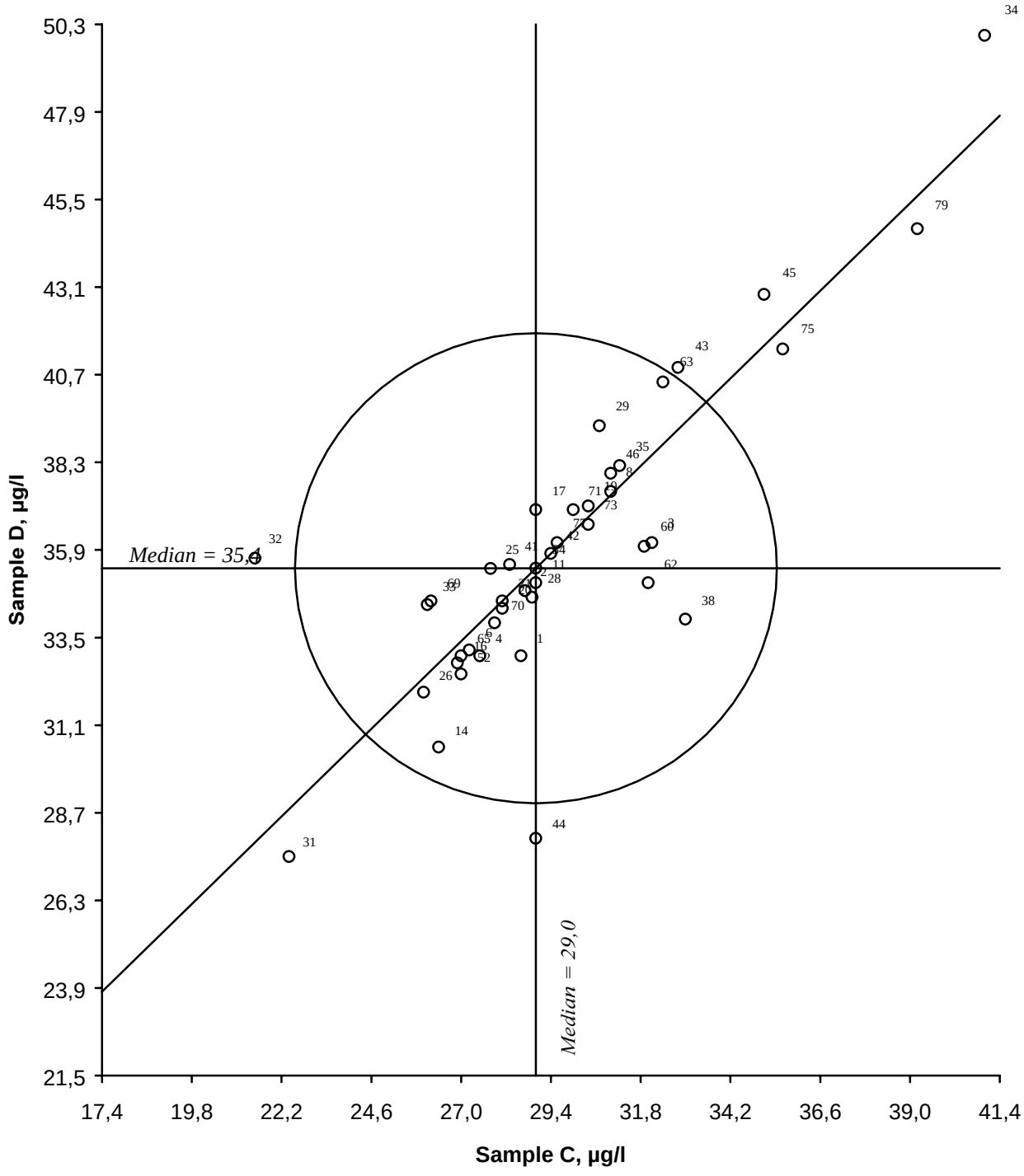

Figure 12. Youden diagramme for manganese, sample pair CD
Acceptance limit, given by the circle, is 20 %

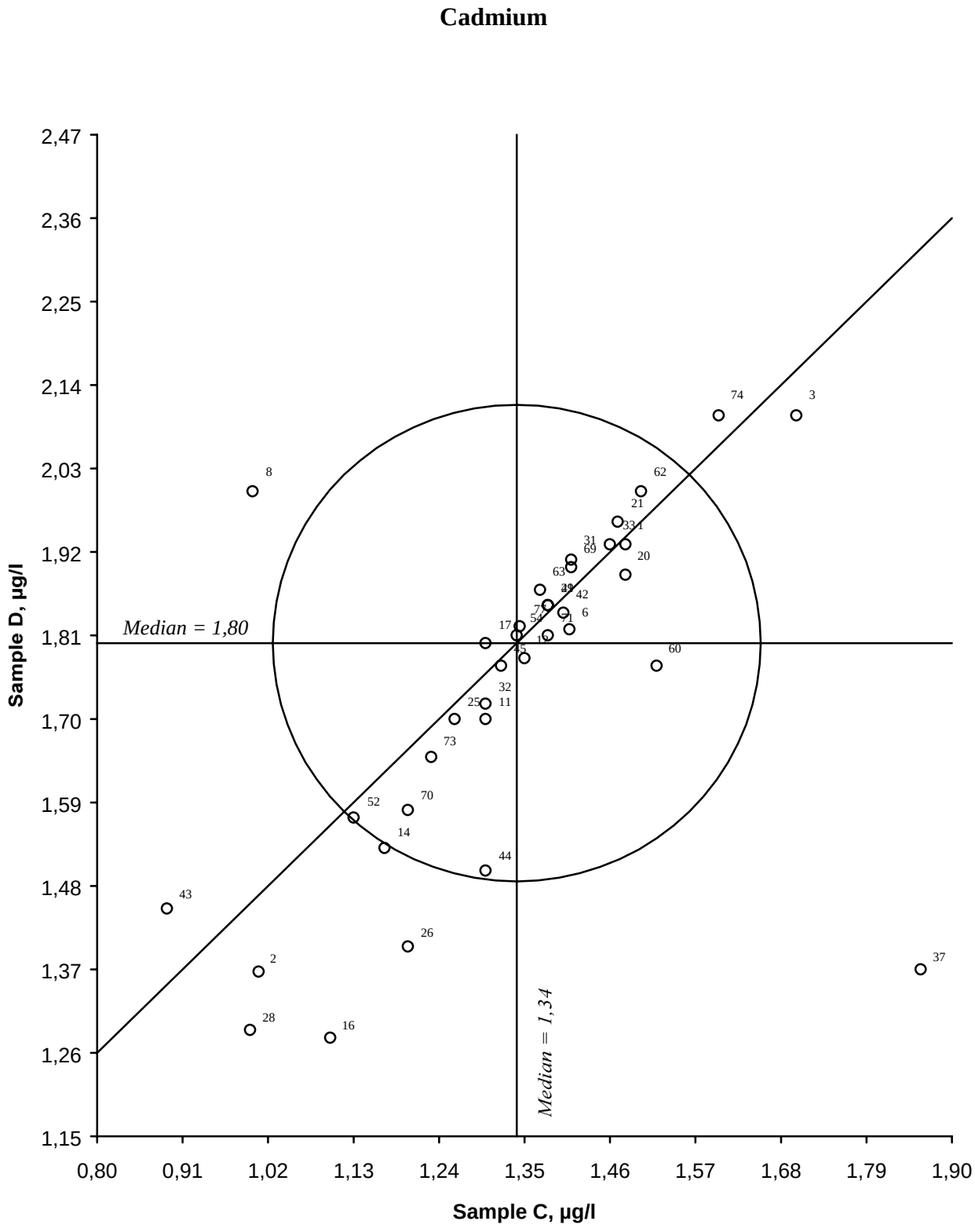

Figure 13. Youden diagramme for cadmium, sample pair CD
Acceptance limit, given by the circle, is 20 %

Lead

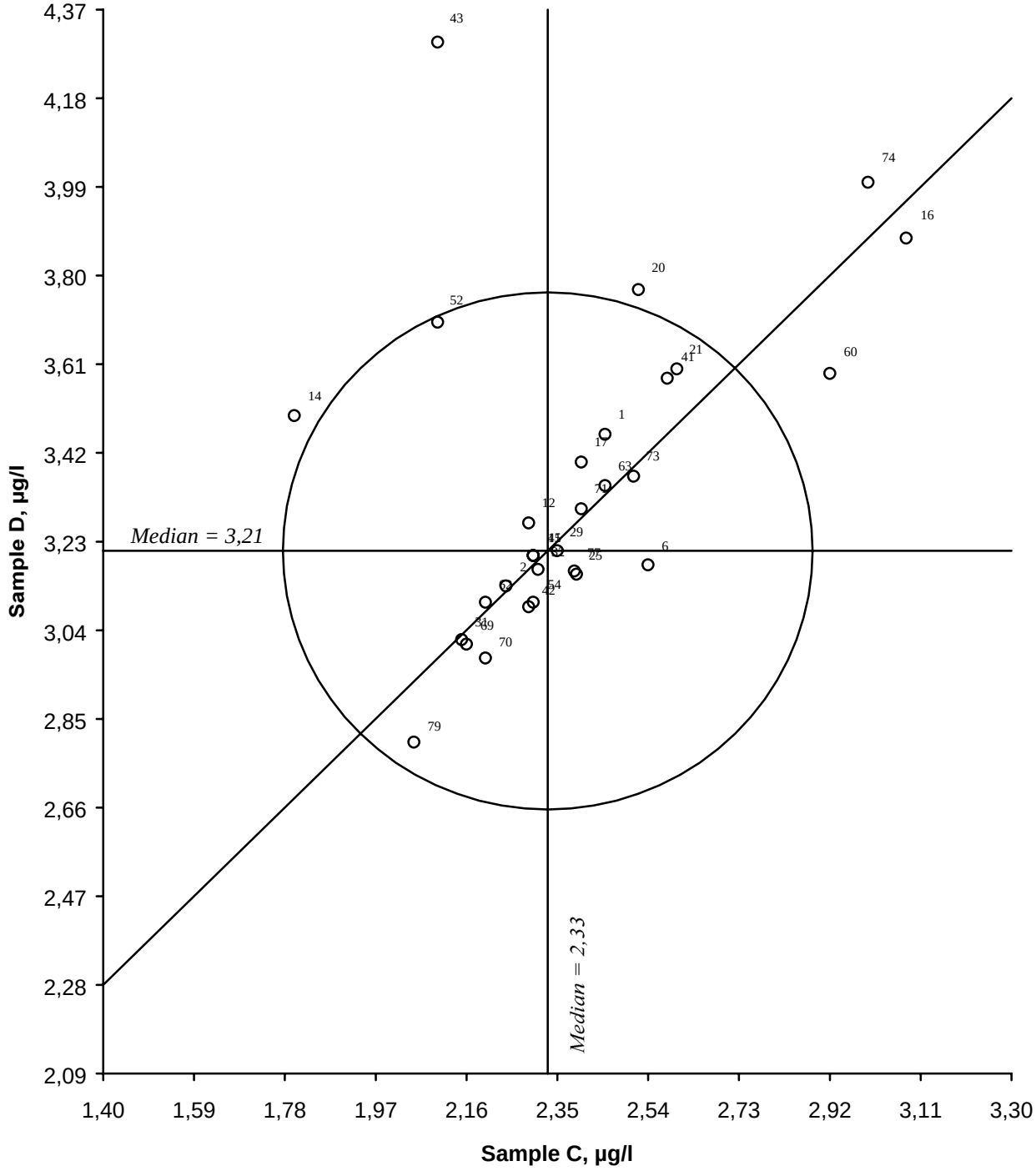

Figure 14. Youden diagramme for lead, sample pair CD
Acceptance limit, given by the circle, is 20 %

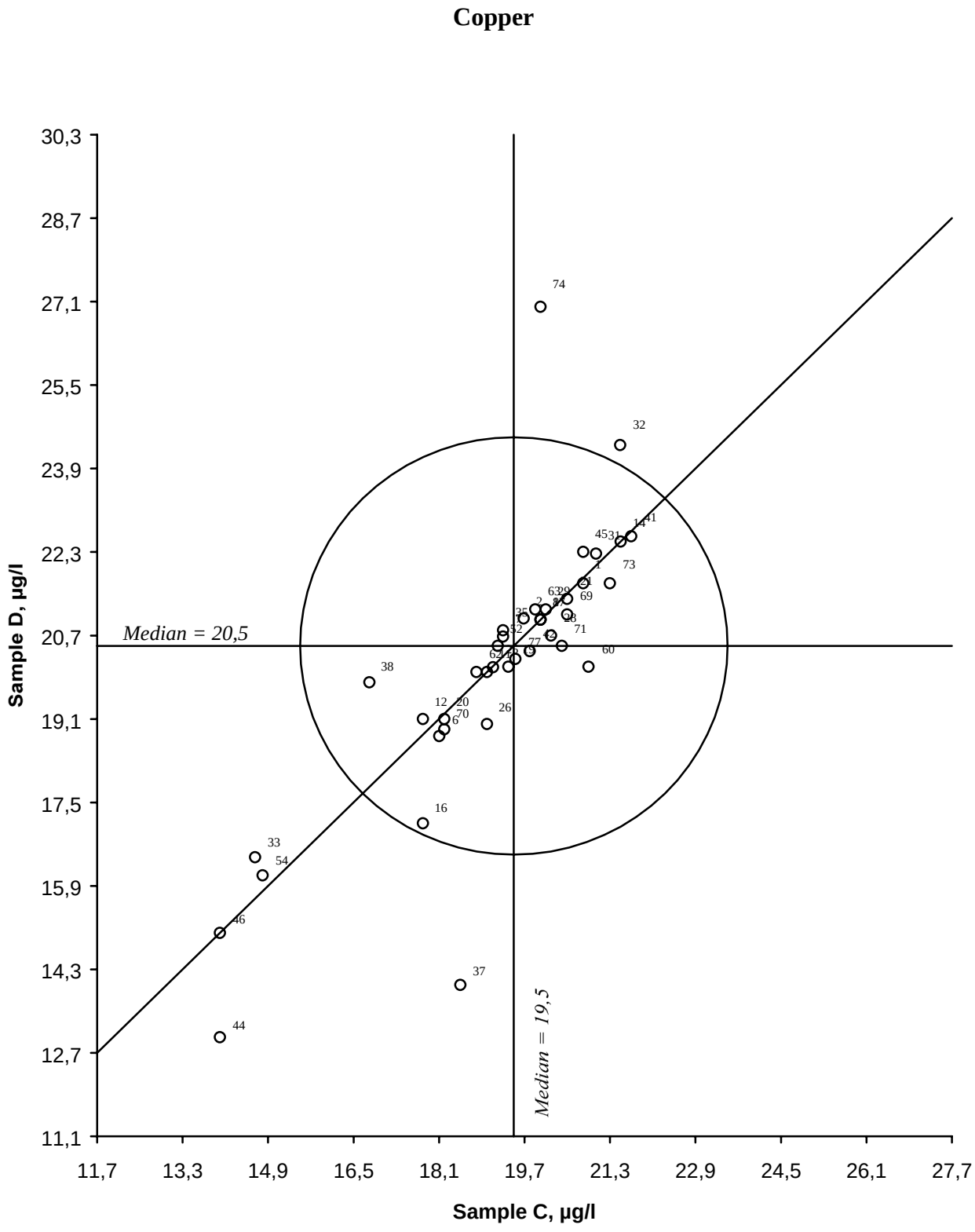

Figure 15. Youden diagramme for copper, sample pair CD
Acceptance limit, given by the circle, is 20 %

Nickel

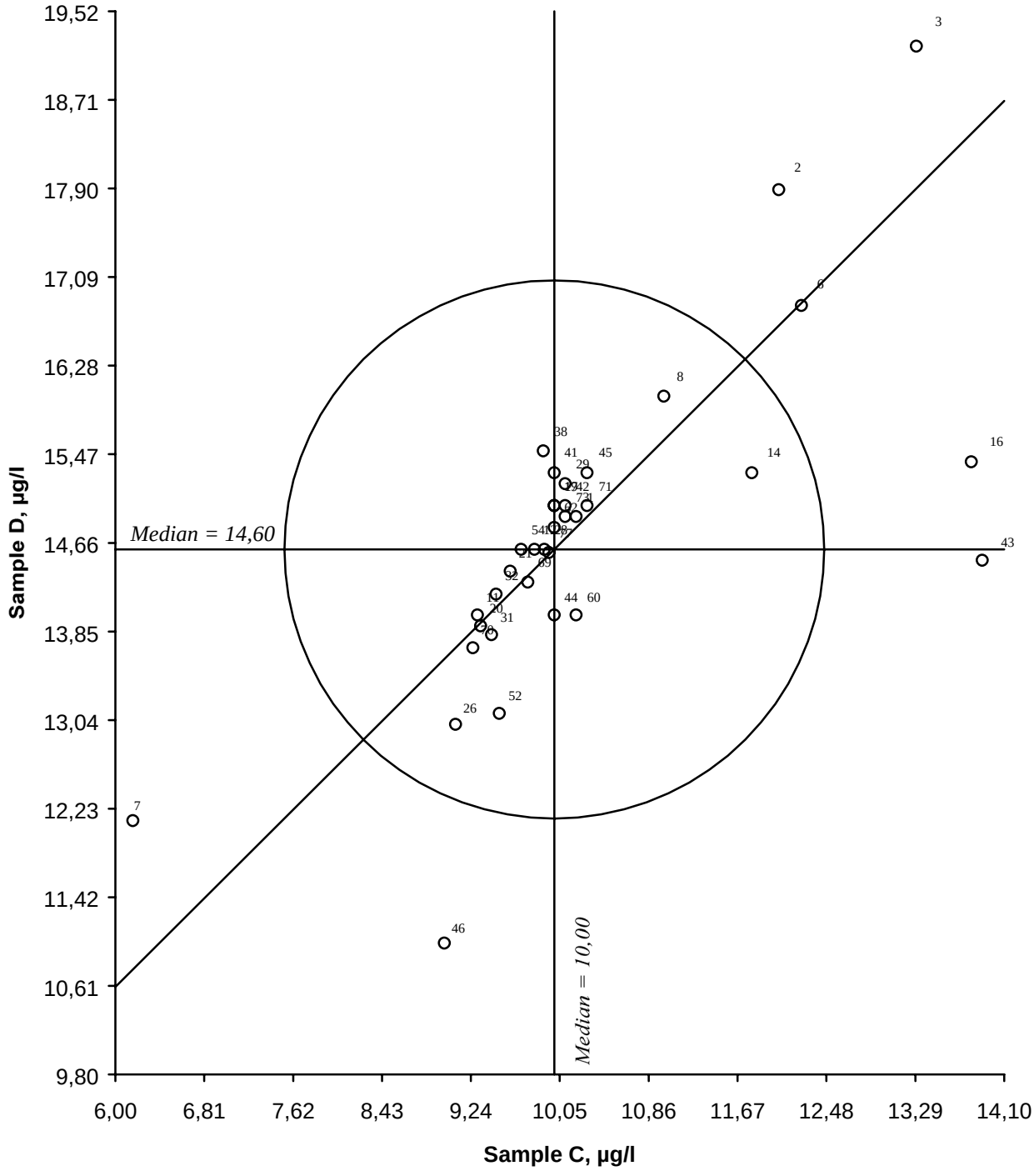

Figure 16. Youden diagramme for nickel, sample pair CD
Acceptance limit, given by the circle, is 20 %

Zinc

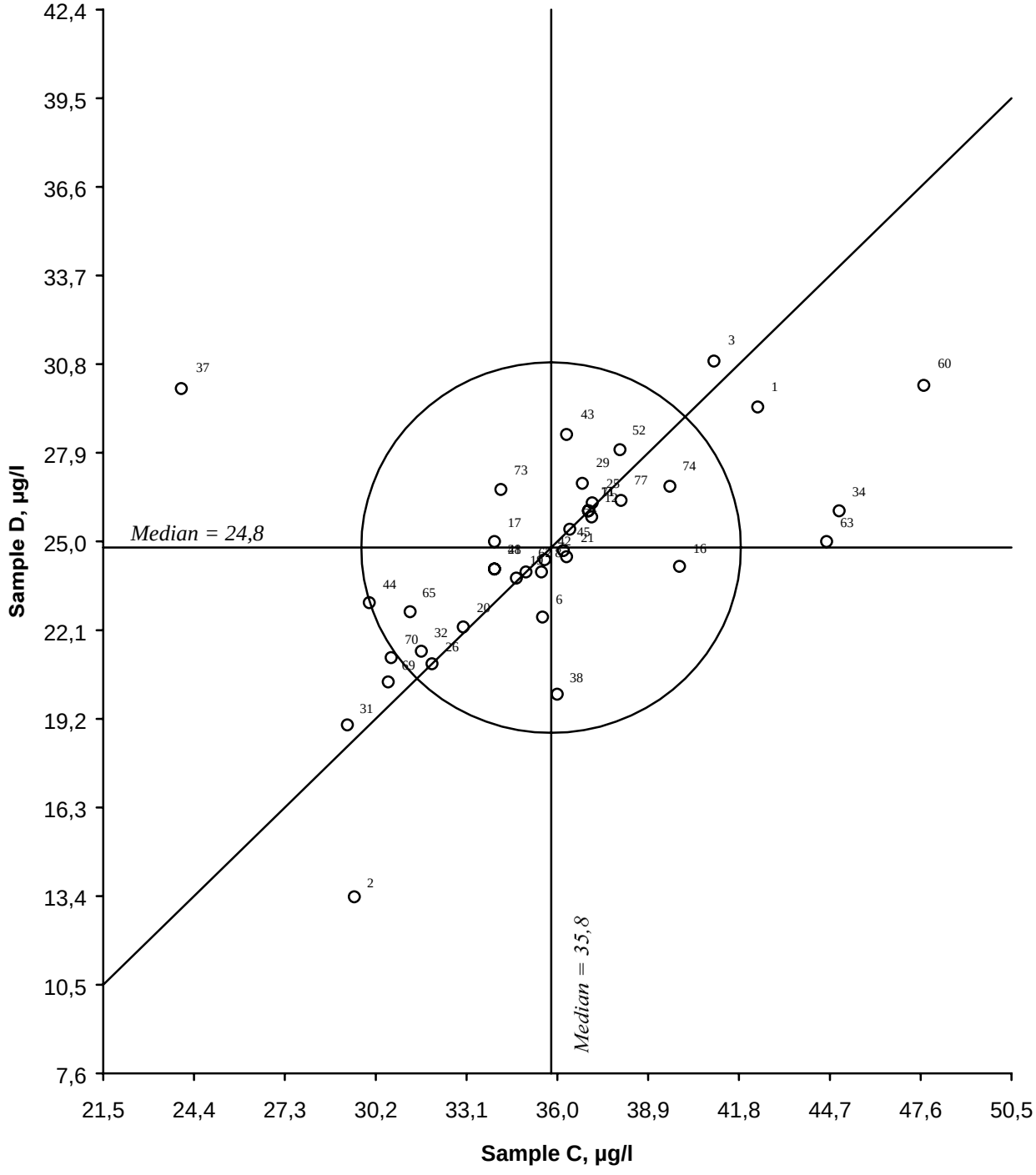

Figure 17. Youden diagramme for zinc, sample pair CD
Acceptance limit, given by the circle, is 20 %

Three laboratories that equilibrated the solutions by bubbling with air containing 350 ppm CO_2 before reading the pH value, reported only a little higher results than the other laboratories. In the sample solutions used in this 16th intercomparison, the pH of the equilibrated solutions are only slightly higher than in the non-stirred solutions. The information obtained by pH measurement after equilibrating the solution, is different from pH-values read directly, or during stirring the sample. Especialy in cases where the difference between the results of the methods are greater than here, it is questionable to establish a "true value" based on the median value for all the reported results for pH, and it should be discussed whether an individual "true value" for each method would be more appropriate.

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.

Figure 1 shows that the reported results are spread out along the 45 ° line, indicating that the influence by systematic effects on the results are dominating. 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 probably connected to the small differences in the analytical methods used by the participants. Random errors are affecting the results to a greater degree for pH than many other variables, illustrated in Figure 1 by the spread of the small circles away from the 45° line.

4.2 Conductivity

The conductivity results are presented in Figure 2, where the great circle is representing an accuracy limit of ± 10 %, which is only half of the target accuracy limit given in the Manual (1). The reported results are given in Table 5.2. Several laboratories have obviously reported the conductivity results in another unit than the requested one which was mS/m at 25°C, the reported results being at least one decade too high. These laboratories were contacted to clarify the mistake, and the results were recalculated to mS/m.

All participants used an electrometric method for the determination of conductivity. Most laboratories achieved very good agreement between the results for this variable. After correcting the wrong unit used, only a few laboratories reported results being systematically too high for both samples, or systematically too low. A proper temperature correction is necessary when determining this variable, as the conductivity is changing by about two percents pr. degree at room temperature. If the accuracy limit is extended to the target value of ± 20 %, defined in the Manual (1), nine more results located just outside the 10 % acceptance circle, would be located within the circle and thus be defined as acceptable.

4.3 Alkalinity

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 5.3. 61 laboratories reported results for alkalinity, and about one half 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 (4,5, 4,2, 5,4, or 5,6). Two laboratories used colorimetric methods, with either methyl red or methyl orange as indicator.

These results were mainly systematically low, one result being too high. Four laboratories used methods not being specified.

The results for alkalinity are spread out along the 45 ° line, most result pairs being quite close to this line, as illustrated in Figure 3, indicating that systematic effects are the dominating reason for the differences observed between many results. This is most likely due to the different methods used by the laboratories. By a closer examination of the results, a certain connection between the method used and the location in Figure 3 was observed. The laboratories using the Gran plot titration reported, with few exceptions, results normally located close to the centrum of the circle. With very few exceptions the results determined by the end point titration to pH 4,5 alone, are located in the upper right part of Figure 3, the results beeing systematically too high. The end point titration to pH 5,4 gave results mainly located within the acceptance circle, while titration to pH 4,2 or 5,6 gave too low results.

The overall result for alkalinity in this intercomparison is worse than in the last intercomparison, as only a little more than half of the results are acceptable. A possible reason for this is the fact that samples with lower alkalinity have been used for this intercomparison. The alkalinity value varies 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” may overestimate the true alkalinity or the “equivalence” alkalinity.

4.4 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 represents a general target accuracy of ± 20 %. Ion chromatography is used by an increasing number of laboratories, and is now used by nearly half 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 mostly used methods. The hydrazine method used by two laboratories gave acceptable results, while the salicylate method gave systematically too high results. One laboratory using photometric method may have reported the results in wrong unit, the results beeing very low. The capillary electrophoresis method used by two laboratories gave too low results.

This time 59 % of the results are evaluated as acceptable, which is less than in the last intercomparison. One probable reason for this observation may be that the concentrations of nitrate-nitrogen were much lower this time. The control analyses at the Programme Centre demonstrated that these samples were stable with respect to the content of nitrate and nitrite, throughout the whole periode of the intercomparison.

4.5 Chloride

The chloride results are presented in Figure 5, and the reported results from the participants are given in Table 5.5. The target accuracy of ± 20 % is represented by the great circle in figure 5. 51 out of 69 laboratories determined chloride by ion chromatography. The greatest

deviations are observed for the manual photometric methods. Most of the results determined with the mercurimetric method were too high. One high and one acceptable result pair was reported for the argentometric method. Two laboratories determined chloride with capillary electrophoresis, for chloride this method works well and the results being acceptable. The method using potentiometric tiration gave one acceptable result pair, one much too high and one a little too low.

66 % acceptable results is the lowest score for the last four intercomparisons, and the reason may probably be connected to the fact that we used rather low concentrations for this analytical variable this time.

4.6 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 51 of 67 laboratories for the determination of the sulfate content. Eight laboratories used a photometric method based on the dissociation of the barium-thorin complex, five of these result pairs deviated too much from the true value. Three out of four result pairs were acceptable for the nephelometric method. Two laboratories used capillary electrophoresis, both result pairs being acceptable.

76 % acceptable result pairs is about the same as in earlier acid rain intercomparisons.

4.7 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 great circle in Figure 7. 68 laboratories reported results for calcium, and 24 of them used flame atomic absorption spectrometry for the determination. The ICP technique is used by 17 laboratories, and an increasing number of laboratories, this time 20, used ion chromatography. The complexometric titration method, used by five laboratories, is usually not sensitive enough for this kind of samples, and some of the laboratories using this method reported results clearly affected by random errors.

61 % acceptable result pairs is lower than the last years intercomparison, and the rather low concentration used this time is probably contributing to a greater number of deviating results.

4.8 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 was used by 17 laboratories, and 20 laboratories used ion chromatography. Systematic errors are dominating the results being outside the acceptance limit, 67 % of the results are located inside the target accuracy of ± 20 %. The great deviations observed for manual titrations indicate that the concentrations of the samples used in this intercomparison are rather low for this technique. The most used methods give comparable results.

4.9 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. 20 laboratories used flame atomic absorption spectrometry for this determination. However, in many laboratories the ion chromatographic techniques are taking over the routine determinations of the alkaline metals, thus 21 participants used this technique in this intercomparison. ICP was used by 17 laboratories, and 9 used flame photometry. 88 % of the result pairs are located within the general target accuracy of ± 20 %, which is considered as a good result.

4.10 Potassium

The potassium results are presented in Figure 10. The great circle is representing the target 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, and emission spectrometry is used by the same number of laboratories. The deviations observed in Figure 10 are both of systematic and random nature. Two laboratories reported results as less than the detection limit.

4.11 Iron

The results for iron are illustrated in Figure 11, and the values reported by the participants are given in Table 5.11. The target accuracy is ± 20 %, and is represented by the great circle in Figure 11, this time as much as 71 % of the result pairs are located inside this circle. 38 laboratories submitted results for iron, of which 15 and 9 used ICP and ICP-MS, respectively, while 9 and 4 used flame and graphite furnace atomic absorption, respectively. Only one laboratory used a photometric method, the result being far too low. The deviating results are mainly affected by systematic errors. There is observed a significant difference between the results determined by the different methods for iron, thus the flame atomic absorption gives systematically higher results than the graphite furnace. In between these average values we find the ICP and the ICP-MS results, the ICP results being higher than the ICP-MS.

4.12 Manganese

The manganese results are illustrated in Figure 12, and the values reported by the participants are given in Table 5.12. The target accuracy is ± 20 %, and is represented by the great circle in Figure 12. 76 % of the result pairs are located inside this circle, this is better than the former intercomparisons, however, the concentrations used this time are quite higher than earlier. 45 laboratories submitted results for manganese, of which 15 and 11 used ICP and ICP-MS, respectively, while 10 and 9 used flame and graphite furnace atomic absorption, respectively. There small differences between the results determined by the different methods for manganese, thus the flame atomic absorption results are systematically lower than the graphite furnace results. ICP and ICP-MS give more comparable results. The deviating results are mainly affected by systematic errors.

4.13 Cadmium

The results for cadmium are illustrated in Figure 13, and the values reported by the participants are given in Table 5.13. The target accuracy is ± 20 % and is represented by the great circle in Figure 13, 63 % of the result pairs are located inside this circle. 41 laboratories submitted results for cadmium, of which 8 and 11 used ICP and ICP-MS, respectively, while 18 used graphite furnace atomic absorption. There are some small differences between the results determined by the different methods for cadmium, thus the results produced with ICP - on average - is clearly lower than those produced with ICP-MS. The deviating results are affected mainly by systematic errors, even if random errors are affecting som few result pairs.

4.14 Lead

The results for lead are illustrated in Figure 14, and the values reported by the participants are given in Table 5.14. The target accuracy is ± 20 %, and is represented by the great circle in Figure 14, 59 % of the result pairs are located inside this circle. 41 laboratories submitted results for lead, of which 8 and 11 used ICP and ICP-MS, respectively, while 18 used graphite furnace atomic absorption and 4 flame atomic absorption. There are only small differences between the results determined by the different methods for lead, however, the flame atomic absorption and the ICP methods are probably too less sensitive for the low concentrations used in these samples. The deviating results are affected by both systematic and random errors. The concentrations are quite close to the detection limit of the method used at some of the laboratories, and as much as six laboratories have reported their results below their detection limit.

4.15 Copper

The copper results are illustrated in Figure 15, and the values reported by the participants are given in Table 5.15. The target accuracy is ± 20 %, and is represented by the great circle in Figure 15, 73 % of the result pairs are located inside this circle. 44 laboratories submitted results for copper, of which 11 used ICP and 11 used ICP-MS, while 18 and 4 used graphite furnace and flame atomic absorption, respectively. The results from the flame atomic absorption method is clearly lower than the results from the other methods. The deviating results are affected mainly by systematic errors.

4.16 Nickel

The results for nickel are illustrated in Figure 16, and the values reported by the participants are given in Table 5.16. The target accuracy is ± 20 %, and is represented by the great circle in Figure 16, This time as much as 68 % of the result pairs are located inside this circle. 40 laboratories submitted results for nickel, of which 10 and 11 used ICP and ICP-MS, respectively, while 15 used graphite furnace atomic absorption. There is no significant difference between the results determined by the different methods for nickel. The deviating results are affected mainly by systematic errors.

4.17 Zinc

The results for zinc are illustrated in Figure 17, and the values reported by the participants are given in Table 5.17. The target accuracy is ± 20 %, and is represented by the great circle in Figure 17, 62 % of the result pairs are located inside this circle. 41 laboratories submitted results for zinc, of which 14 and 10 used ICP and ICP-MS, respectively, while 11 and 6 used flame and graphite furnace atomic absorption, respectively. The deviating results are affected by both systematic and random errors, some too high values indicate that contamination may be a problem for some laboratories when determining the zinc concentration.

5. 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 0216 is presented, based on the target accuracy (except for pH and conductivity), where the number and percentage of acceptable results are given. 68 % of the results submitted by the participants are acceptable when compared to the acceptance limits given above, i.e. on average, nearly one out of three result pairs is located outside the acceptance limit. By improvement of the routine analytical method, the laboratories should be able to obtain more comparable results.

For pH, the general target accuracy is ± 0,1 pH units (1), 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 close to neutrality, and therefore are supposed not to be completely in CO_2-equilibrium. Even with this acceptance limit only 66 % of the result pairs are evaluated as acceptable.

Problems with poor comparability between the reported results for pH probably arise from the fact that the pH results are much more affected by the method used, when measuring in nearly neutral solutions. This problem has been demonstrated through several earlier 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 whether a different approach should be used for the comparison of the results, for instance different “true values” for pH, one for each method? This is especially important for the equilibration method, which very often gives results different from the other methods in a lot of samples.

Because of the high precision of the reported results for conductivity in earlier intercomparisons, we reduced the acceptance limit for this analytical variable from ± 20 to ± 10 %. The number of acceptable results for conductivity, 75 %, is a little less than the last intercomparison (Table 2). If we increase the acceptance limit to the target value, nine more result pairs would be inside the circle, and the number of acceptable results would increase to 88 %. It is a problem that many laboratories report their results in the units they normally use

at their laboratory, and not in the unit asked for in this intercomparison, mS/m. Some correspondence with the laboratories was therefore necessari to clarify the right results.

Table 2. Evaluation of the results of intercomparison 0216. 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.

Table 2. Evaluation

Analyte and unit	Sample pair	True value 1	True value 2	Accept. limit, %	N	n	% acceptable res. for intercalibration 0216	0115	0014	9913
pH	AB	6,72	6,58	0,1 *	73	48	66	58	57	57
Conductivity, mS/m	AB	2,84	2,57	10 ¤	73	55	75	82	64	81
Alkalinity, mmol/l	AB	0,134	0,103	20	62	33	53	76	46	63
Nitrate + nitrite-nitrogen, µg/l	AB	85	118	20	68	40	59	77	51	31
Chloride, mg/l	AB	1,05	1,39	20	70	46	66	79	73	87
Sulfate, mg/l	AB	2,71	2,11	20	68	52	76	82	72	87
Calcium, mg/l	AB	0,97	1,2	20	69	42	61	82	55	78
Magnesium, mg/l	AB	0,539	0,38	20	70	47	67	75	58	78
Sodium, mg/l	AB	3,89	3,08	20	67	59	88	93	91	89
Potassium, mg/l	AB	0,37	0,473	20	64	47	73	85	76	77
Iron, µg/l	CD	168	220	20	38	27	71	41	74	-
Manganese, µg/l	CD	29	35,4	20	45	34	76	64	75	-
Cadmium, µg/l	CD	1,34	1,8	20	41	26	63	66	65	-
Lead, µg/l	CD	2,33	3,21	20	41	24	59	51	47	-
Copper, µg/l	CD	19,5	20,5	20	44	32	73	75	67	-
Nickel, µg/l	CD	10	14,6	20	40	28	68	68	42	-
Zinc, µg/l	CD	35,8	24,8	20	42	26	62	53	47	-
Total					976	666	68	(71)	(63)	(72)

* The acceptance limit is extended from the target value of ± 0,1 to ± 0,2 pH units
¤ The acceptance limit is reduced from the target value of ± 20 % to ± 10 %

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 less good than in the last intercomparison, probably because of the lower concentrations of bicarbonate in the samples used this time.

For nitrate + nitrite 59 % of the result pairs are acceptable, this is worse than the last year, probably because that the concentrations are rather low compared to earlier intercomparisons. In some earlier intercomparisons this analytical variable proved to be unstable, however, this time the control analyses at the Programme Centre demonstrated that the samples were stable with respect to the content of nitrate and nitrite, throughout the whole periode of the intercomparison.

For calcium and magnesium a greater fraction of the result pairs are acceptable in this intercomparison, and the % acceptance is comparable to some earlier intercomparisons. One possible explanation for this observation may be that the concentrations of the analytical variables are somewhat lower than usual. In addition to this, some of the laboratories that

reported results outside the acceptance limits used methods being different from the major group of participants, some of the methods used may not be sensitive enough for samples typically analyzed for acid rain monitoring.

The heavy metals iron, manganese, cadmium, lead, copper, nickel, and zinc were included in this intercomparison Programme for the third time. The best results were obtained for manganese, copper, and iron, where 76, 73 and 71 % of the results are acceptable. For these elements the concentrations were well above the detection limit of the most sensitive methods used. For the rest of the heavy metals, a little less results were acceptable. However, the concentrations of these elements are closer to the detection limit for the methods used, and even below the detection limit of the method used by some of the laboratories. Therefore, it should be discussed whether absolute acceptance limits should be used instead of the relative one (20 %) used in this intercomparison, when the results are close to the detection limit. If so, it is important that it is decided what target detection limit should be obtained by the laboratories.

6. Conclusion

79 laboratories submitted results for this intercomparison. The best results were reported for the analytical variables sodium, sulfate and manganese, where 88, 76 and 76 % of the results were acceptable. The worst results were observed for alkalinity, nitrate + nitrite, and lead, common for these analytical variables is that the concentrations are rather low.

Overall, 68 % of the evaluated results were located within the general target accuracy of ± 20 %, or the special accuracy limit for pH and conductivity. The reason for the overall worse results this time compared to som earlier intercomparisons, is in part explained by the somewhat lower concentrations used for several analytical variables this time. When the concentrations are close to the detection limit of some of the methods used by the participants, it must be expected that the spread of the results will be more than ± 20 % for many of the participants.

The laboratories which reported results outside this limit should improve their methods to obtain a better comparability. Generally, the application of some analytical methods seems to be less suited for the water samples analyzed in this programme, as the detection limit of some methods applied by participants are too high. It is important that methods with sufficiently detection limit are used by the participating laboratories.

A total error of ± 0,2 pH units seems to be a reasonable assessment of the accuracy for pH measurements when near neutral water samples - which are not in CO_2 equilibrium - are analyzed. There are obviously systematic differences between the methods used by the participating laboratories, therefore it is necessary to use some wider acceptance limit for pH.

7. Literature

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Appendices

A The participating laboratories

B Preparation of samples

C Treatment of analytical data

D The results of the participating laboratories

Appendix A.

The participating laboratories

Identity	Laboratory	City	Country
1	Stocholm University, ITM	Stockholm	Sweden
2	Vlaamse Milieumaatschappij	Antwerpen	Belgium
3	Water Pollution Observation Laboratory	Minsk	Belarus
4	Forest Ecosystem Research Group	Belfield	Ireland
6	Natural resources Canada, Forestry Services	Sault Ste Marie	Canada
7	Analis service S.R.L.	Bucurest	Romania
8	Centre for Ecology & Hydrology	Wallington	United Kingdom
9	Staatliche Umweltbetriebs-gesellschaft	Chemnitz	Germany
10	Universita degli Studi di Siena	Siena	Italy
11	CNRS /Universite Paul Sabatier	Toulouse	France
12	T.G.Masaryk Water Research Inst., Analytical Lab.	Praha	Czech Republic
13	University of Helsinki, Lab. of Physical Geography	Helsinki	Finland
14	D.R. Ambiente do Alentejo	Evora	Portugal
15	Virumaa Environmental Research Ltd	J'ohvi	Estonia
16	Ecoanalytical Laboratory "ECOANALYT"	Syktyvkar	Russia
17	Amt der Kärntner Landesreg. Abt. 15 Umweltschutz	Klagenfurt	Austria
18	Food and Environmental Agency	Torshavn	Faroe Islands
19	Umweltbundesamt - Dienst-gebaude Langen, Abt. II 6.5	Langen	Germany
20	Landesumweltamt NRW	Essen	Germany
21	Environmental Protection Agency	Dublin	Ireland
22	Dorset Research Facility, MOEE	Dorset	Canada
23	CNR Istituto Studio degli Ecosistemi	Pallanza	Italy
25	Institute for Ecology of Industrial Areas	Katowice	Poland
26	Finnish Forest Research Institute, Central Laboratory	Vantaa	Finland
27	National Institute of Biology	Ljublana	Slovenia
28	Chongqing Inst. of Environm. Science and Monitoring	Chongqing	China
29	Charles University, Department of Hydrobiology	Blatna	Czech Republic
31	Latvian Laboratory Department	Riga	Latvia
32	ISSeP Colfontaine	Paturages	Belgium
33	Water and Environment Protection Ministry Research	Buchuresti	Romania
34	SLU, Skoglig marklära	Uppsala	Sweden
35	North Ostrobothnian Regional Environmental Centre	Oulu	Finland
36	EAWAG, Limnological Research Center	Kastanienbaum	Switzerland
37	Norwegian Institute for Air Research	Kjeller	Norway
38	Geological Survey of Estonia	Tallinn	Estonia
39	Tallinn Technical University, Inst. of Environm. Eng.	Tallinn	Estonia
40	Laboratorio Biologico Provinciale APPA-BZ	Laives	Italy
41	University of Maine, Environmental Chemistry Lab.	Orono	USA
42	Freshwater Fisheries Laboratory	Perthshire	Scotland
43	Forest Research Institute, Karelian Res. Centre	Petrozavodsk	Russia
44	Northern Water Problems Institute	Petrozavodsk	Russia
45	Norwegian Institute for Water Reseearc	Oslo	Norway
46	Universidad de Granada, Instituto del Agua	Granada	Spain
47	Aquatische Oecologie en Milieubiologie	Nijmegen	Netherlands

48	Laboratory of Ecological Chemistry, ABIET	Baikalsk	Russia
49	Polish Academy of Sciences Institute of Botany	Krakow	Poland
50	Freshwater Institute	Winnipeg	Canada
51	ELA Satellite Laboratory	Winnipeg	Canada
52	Chemical Laboratory of CGS	Praha	Czech Republic
54	The Environment Agency, NLS Laboratory	Llanelli	United Kingdom
55	Institute of Environmental Protection, Monitoring Lab.	Warsawa	Poland
56	Hiiumaä Environmental Laboratory	Kärdla	Estonia
57	University of Alberta, Biological Science Centre	Edmonton	Canada
58	Adirondac Lake Survey Corporation	Ray Brook	USA
59	University of Barcelona, Center for High Mountain Res.	Vielha	Spain
60	Istituto Agrario di S. Michele all'Adige	S.Michele	Italy
61	Lab. of Hydrochemistry at the Vortsjarv Limn. Station	Rannu	Estonia
62	Tartu Environmental Research	Tartu	Estonia
63	Kola Science Centre, INEP	Apatity	Russia
64	US Environmental Protection Agency	Corvallis	USA
65	Finnish Forest Research Inst., Rovaniemi Res. Station	Rovaniemi	Finland
66	Lapland Regional Environment Centre	Rovaniemi	Finland
67	Universität Innsbruck, Inst für Zoologie und Limnologie	Innsbruck	Austria
68	Univ.of Innsbruck, Inst. of Meterology and Geophysics	Innsbruck	Austria
69	Estonian Environment Research Centre	Tallinn	Estonia
70	Swedish University of Agricultural Sciences	Uppsala	Sweden
71	Bayerische Landesamt fur Wasserwirtschaft	München	Germany
72	ASCR, Hydrobiological Institute	Budejovice	Czech Republic
73	Environ. Protection Ministry, Joint Research Centre	Vilnius	Lithuania
74	Laboratorio Studi Ambientali SPAA	Lugano	Switzerland
75	Swedish Environment Research Institute (IVL)	Stockholm	Sweden
76	Swedish Environment Research Institute (IVL)	Göteborg	Sweden
77	Finnish Environment Institute Research Laboratory	Helsinki	Finland
78	Ontario Ministry of Environment	Etobicoke	Canada
79	Guangzhou Research Inst. of Environmental Protection	Guangzhou	China

Number of participating laboratories (N) from the different countries being represented in intercomparison 0216.

Country	N	Country	N
Austria	3	Lithuania	1
Belgium	2	Netherlands	1
Belarus	1	Norway	2
Canada	6	Poland	3
China	2	Portugal	1
Czech republic	4	Romania	2
Estonia	7	Russia	5
Faroe Islands	1	Slovenia	1
Finland	6	Spain	2
France	1	Sweden	5
Germany	4	Switzerland	2
Ireland	2	United Kingdom	3
Italy	4	USA	3
Latvia	1		

Appendix B.

Preparation of samples

The sample solutions were prepared from natural water collected from a creek Langtjernelva, 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 aliquots were removed from the filtrate to determine the concentrations of the analytical variables of interest.

The samples were prepared by spiking the filtrated water with stock solutions of stoichiometric compounds containing the major ions, or heavy metals. The samples C and D were prepared for the determination of metals, and preserved by addition of 5 ml concentrated nitric acid pr. liter sample. A few days before mailing the samples to the participants, the solutions were transferred to 1/2 liter high density polyethylene bottles with screw cap. These samples were stored at room temperature until mailing to the participating laboratories.

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 at the beginning of May 2002, a few weeks before mailing the samples to the participants. The last sample was analyzed at the end of July 2002. 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.

Table 3. Summary of the control analyses.

Analytical variable	Sample A		Sample B	
	Mean	Std. dev.	Mean	Std. dev.
pH	6,78	0,06	6,58	0,04
Conductivity mS/m	2,69	0,07	2,46	0,02
Alkalinity mmol/l	0,130	0,007	0,101	0,006
Nitrate/nitrite µg/l	76	2,3	115	0,0
Chloride mg/l	1,07	0,03	1,44	0,05
Sulfate mg/l	2,73	0,04	2,13	0,05
Calcium mg/l	0,98	0,15	1,26	0,17
Magnesium mg/l	0,60	0,04	0,42	0,02
Sodium mg/l	4,04	0,04	3,24	0,02
Potassium mg/l	0,38	0,01	0,49	0,01
	Sample C		**Sample D**	
Iron, µg/l	168,3	10,0	218,3	9,3
Manganese, µg/l	32,3	3,7	39,7	4,7
Cadmium, µg/l	1,35	0,04	1,77	0,01
Lead, µg/l	2,35	0,07	3,22	0,11
Copper, µg/l	20,4	1,2	21,3	0,96
Nickel, µg/l	9,96	0,32	14,7	0,60
Zinc, µg/l	36,1	2,8	24,7	1,45

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 - 17).

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

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

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

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

Appendix D.

Table 4. The results of the participating laboratories.

Lab.	pH		Cond, mS/m		Alk, mmol/l		NO3+NO2, µg/l	
	A	B	A	B	A	B	A	B
1	6,72	6,49	2,53	2,79	0,117	0,092	81	122
2	6,41	6,12	2,70	2,40			267	296
3	6,74	6,64	2,86	2,56	0,16	0,08	70	50
4	6,90	6,80	2,80	2,50	0,069	0,059	85	119
5								
6	6,80	6,63	2,87	2,61	0,112	0,090	91	132
7	6,17	5,96	2,92	2,73	0,160	0,112	18	187
8	6,59	6,35	3,10	2,80	0,088	-0,055	80	120
9	6,70	6,50	2,82	2,55	0,190	0,160	122	168
10	6,81	6,62	2,90	2,63	0,144	0,104	93	124
11	6,20	6,91	2,85	2,58	0,141	0,108	65	105
12	6,54	6,40	2,89	2,67	0,141	0,105	545	520
13	6,81	7,00	7,37	14,91	0,118	0,094	165	220
14	6,70	6,60	3,00	2,60	0,094	0,078	91	116
15	6,50	6,50	2,00	2,00	0,160	0,160		
16	6,85	6,50	3,22	2,86	0,126	0,094	92	122
17	6,30	6,20	2,90	2,70	0,190	0,170	87	125
18	6,70	6,60	2,80	2,60	0,110	0,080		
19	6,65	6,38	2,86	2,65	0,158	0,128	81	282
20	6,63	6,43	2,80	2,45			90	130
21	6,95	6,74	0,04	0,04	0,090	0,080	78	114
22	6,65	6,52	2,40	2,32	0,120	0,099	84	112
23	6,70	6,46	2,74	2,49	0,134	0,105	85	100
24								
25	7,36	7,04	3,16	3,14	0,122	0,163		
26	6,59	6,52	2,93	2,67			94	122
27	6,82	6,57	2,80	2,60	0,161	0,117	90	125
28	6,85	6,63	2,86	2,52	0,174	0,135	93	146
29	6,78	6,67	2,77	2,53	0,140	0,110	92	125
30								
31	6,82	6,62	2,84	2,58	0,144	0,112	70	100
32	6,67	6,40	2,84	2,59			96	138
33	6,31	6,18	2,99	2,68	0,150	0,130	3	5
34	6,46	6,35	2,80	2,60	3,260	2,710	77	124
35			2,80	2,60	0,126	0,102	96	146
36	6,95	6,75	2,70	2,60	0,180	0,170	211	231
37	6,67	6,53	2,87	2,57			80	120
38	6,70	6,60	2,89	2,51	0,230	0,180		
39	6,85	6,70	4,40	3,00	0,170	0,140	85	125
40	6,70	6,55	2,82	2,55	0,132	0,100	90	100
41	6,83	6,68	2,82	2,56	0,143	0,112		
42	6,76	6,60	2,80	2,50	0,128	0,098	88	122
43	6,84	6,69					118	115
44	6,78	6,62	2,80	2,60	0,133	0,104	77	107

Lab.	pH		Cond, mS/m		Alk, mmol/l		NO3+NO2, µg/l	
	A	B	A	B	A	B	A	B
45	6,76	6,57	2,68	2,47	0,124	0,095	75	115
46	6,50	6,36	2,73	2,49	0,380	0,220	107	114
47	6,57	6,42	3,57	3,37	0,183	0,157	93	119
48	6,82	6,64					380	450
49	6,72	6,58	2,97	2,75			96	138
50	6,60	6,46	2,90	2,70			64	93
51	7,15	6,93	2,90	2,60	0,132	0,101	77	113
52	6,85	6,72	2,95	2,56	0,137	0,108	138	124
53								
54	6,44	6,36	1,60	1,40	0,063	0,048	80	121
55	6,79	6,82	2,72	2,52			<80	110
56			2,61	2,50	0,090	0,280	84	123
57	6,88	6,69	2,93	2,76	0,120	0,090	82	116
58	6,79	6,59	2,71	2,45	0,141	0,114	79	111
59	6,60	6,46	2,92	2,84	0,133	0,114	54	54
60	6,56	6,41	2,91	2,60	0,136	0,104	85	110
61	6,50	6,64	3,01	2,80	0,050	0,050	79	115
62	6,56	6,52	2,69	2,56	0,134	0,104	87	127
63	6,57	6,56	2,53	2,27	0,124	0,101	72	105
64	6,75	6,59	3,06	2,63	0,137	0,098	189	140
65	6,85	6,76	2,86	2,55	0,128	0,099		
66	6,74	6,61	2,85	2,56	0,135	0,105	70	102
67	6,75	6,62	2,91	2,46	0,135	0,103	82	94
68	6,71	6,54	2,91	2,46	0,146	0,108	81	108
69	6,62	6,44	2,72	2,47	0,150	0,120	149	170
70	6,64	6,47	2,66	2,40	0,110	0,083	73	103
71	6,72	6,70	2,80	2,52			87	130
72	6,62	6,49	2,71	2,46	0,131	0,103	85	120
73	6,76	6,60	2,82	2,49	0,078	0,065	86	113
74	6,72	6,57	2,778	2,563	0,126	0,097	90	164
75	6,66	6,52	6,34	5,36	0,155	0,101		
76	6,76	6,63	3,44	3,21			83	102
77	6,88	6,72	2,83	2,53	0,125	0,094	79	114
78	6,68	6,56	2,60	2,30			87	118
79		6,57		2,53		0,142		110

Lab.	Cl, mg/l		SO4, mg/l		Ca, mg/l		Mg, mg/l	
	A	B	A	B	A	B	A	B
1	1,13	1,43	2,77	2,16	1,12	1,27	0,573	0,467
2	1,61	1,79	2,85	2,16	1,19	1,46	0,608	0,430
3	1,64	1,72	10,80	10,11	0,34	0,43	0,600	0,450
4	1,17	1,29	2,73	2,08	0,78	0,98	0,443	0,320
5								
6	1,04	1,44	2,61	2,08	0,63	0,83	0,449	0,329
7	3,19	2,69	1,67	1,16	0,88	1,12	0,389	0,359
8	1,00	1,40	2,65	2,10	1,05	1,30	0,600	0,400
9	1,20	1,60	5,60	2,60				
10	1,24	1,57	2,98	2,30	0,94	1,19	0,560	0,410
11	0,99	1,35	2,70	2,09	0,90	1,15	0,516	0,373
12	2,16	2,53	4,08	2,50	1,02	1,17	0,530	0,379
13	2,00	2,70	5,44	4,25	1,00	1,25	0,540	0,390
14	1,06	1,25	2,82	2,25	0,98	1,20	0,640	0,460
15	<2	<2	2,00	2,00	1,20	1,20	0,360	0,360
16	1,65	1,62	3,09	1,93	0,37	0,56	0,490	0,380
17	1,10	1,40	2,70	2,10	<2	<2	0,500	<0,5
18	0,91	1,15	3,06	2,40				
19	1,06	1,45	2,75	2,14	0,96	1,33	0,520	0,380
20	1,34	1,57	2,93	2,39	1,06	1,32	0,580	0,401
21	0,90	1,33	2,59	2,07	1,58	2,15	0,650	0,740
22	1,04	1,57	2,71	2,12	0,92	1,22	0,500	0,370
23	1,04	1,40	2,70	2,10	0,89	1,11	0,510	0,370
24								
25					0,98	1,20	0,550	0,380
26	1,01	1,36	2,58	1,99	0,97	1,16	0,533	0,378
27	1,02	1,36	2,70	2,08	0,97	1,13	0,510	0,360
28	1,05	1,38	2,95	2,22	1,01	1,17	0,555	0,382
29	1,02	1,36	2,82	2,74	0,95	1,17	0,370	0,320
30								
31	1,17	1,44	2,82	2,19	0,94	1,32	0,580	0,410
32	0,93	1,31	2,77	2,15	1,24	1,45	0,560	0,420
33	2,55	2,27	4,10	3,70			0,435	0,317
34	0,90	1,22	2,60	2,10	0,81	1,21	0,550	0,460
35	1,10	1,54	2,95	2,29	1,01	1,27	0,550	0,400
36	0,95	1,13	2,49	1,93	<0,4	<0,4	<0,3	<0,3
37	1,04	1,36	2,63	1,96	0,84	1,05	0,470	0,360
38	0,38	0,38	<2	<2	0,79	1,08	0,940	0,770
39	1,10	1,50	1,78	1,73	1,40	1,20	1,200	1,000
40	1,06	1,42	2,59	2,07	0,91	1,14	0,540	0,380
41	1,05	1,35	2,59	2,01	0,89	1,14	0,510	0,380
42	0,96	1,31	2,69	2,06	1,24	1,44	0,650	0,460
43	1,15	1,80	2,64	2,06	1,00	1,38	0,570	0,410
44	0,99	1,34	2,09	1,36	0,96	1,14	0,550	0,380
45	1,05	1,44	2,77	2,12	1,00	1,26	0,590	0,410
46	0,72	0,88	2,87	2,28	1,00	1,50	0,530	0,350
47	1,60	2,00			1,20	1,40	0,600	0,400
48	1,23	1,56	2,02	1,97	1,14	0,95	0,820	0,570

Lab.	Cl, mg/l		SO4, mg/l		Ca, mg/l		Mg, mg/l	
	A	B	A	B	A	B	A	B
49	1,35	1,85	3,22	2,45	0,87	1,13	0,580	0,420
50								
51	0,93	1,24	2,60	1,98	0,94	1,13	0,540	0,380
52	1,06	1,34	2,77	2,16	0,88	1,07	0,488	0,333
53								
54	1,60	2,09	2,72	2,11	0,95	1,18	0,523	0,370
55	0,98	1,30	2,69	2,10	0,97	1,22	0,523	0,380
56	1,04	1,49	2,62	2,16	1,02	1,19	0,520	0,390
57	1,01	1,35	2,61	2,00	0,99	1,24	0,530	0,390
58	1,11	1,50	2,66	2,02	0,91	1,15	0,510	0,360
59	1,15	1,72	2,76	2,20	0,95	1,40	0,530	0,390
60	1,01	1,30	2,60	2,07	1,04	1,30	0,550	0,400
61	1,40	1,60	2,00	<2				
62	1,06	1,63	2,81	2,21	1,06	1,28	0,539	0,408
63	0,97	1,39	3,05	2,25	0,75	0,94	0,480	0,300
64	1,02	1,36	2,73	2,11	0,97	1,06	0,534	0,397
65	0,97	1,27	2,76	2,12	1,16	1,40	0,568	0,391
66	0,95	1,28						
67	1,04	1,28	2,63	2,1	1,16	1,41	0,61	0,44
68	1,23	1,42	2,62	2,04	1,23	1,3	0,56	0,40
69	1,10	1,44	2,86	2,21	1,39	1,62	0,540	0,380
70	1,02	1,38	2,57	2,02	0,98	1,20	0,550	0,420
71	1,05	1,39	2,73	2,13	0,99	1,23	0,560	0,400
72	1,10	1,50	2,90	2,30	0,66	0,78	0,360	0,270
73	1,71	1,96	2,60	2,10	0,88	0,96	1,410	1,560
74	1,09	1,55	2,70	2,11	0,47	0,55	0,240	0,180
75					0,86	1,01	0,481	0,345
76	1,05	1,39	2,71	4,17	0,50	0,67	0,350	0,290
77					0,98	1,22	0,540	0,387
78					0,91	1,14	0,499	0,364
79		1,82		0,466	2,335		0,789	

Lab.	Na, mg/l		K, mg/l		Fe, µg/l		Mn, µg/l	
	A	B	A	B	C	D	C	D
1	3,89	3,07	0,418	0,465	161	207	28,6	33,0
2	4,55	3,67	0,394	0,507			28,7	34,8
3	3,60	2,80	0,550	0,660			32,1	36,1
4	3,34	2,65	0,344	0,475	190	219	27,5	33,0
5								
6	3,55	2,85	0,390	0,490	167	214	27,2	33,2
7	3,44	2,83			308	354	185,8	230,5
8	3,90	3,10	0,400	0,500	184	237	31,0	37,5
9								
10	4,08	3,27	0,510	0,600				
11	3,93	3,16	0,436	0,499	152	193	29,0	35,0
12	3,99	3,23	0,216	0,310	186	238	0,2	0,3
13	3,92	3,13	0,360	0,468				
14	3,45	2,84	0,240	0,330	235	290	26,4	30,5
15								
16	3,88	3,14	0,420	0,500	189	221	26,9	32,8
17	4,40	3,40	<0,6	<0,6	160	220	29,0	37,0
18								
19	3,82	3,05	0,390	0,490	177	225	30,4	37,1
20	3,80	3,04	0,378	0,521	171	219	28,1	34,3
21	4,36	3,83	0,160	0,460	144	195	28,1	34,5
22	3,96	3,29	0,345	0,440				
23	4,00	3,16	0,320	0,430				
24								
25	3,92	3,17	0,320	0,440	160,2	200,4	27,79	35,39
26	3,77	2,93	0,381	0,476	163	204	26,0	32,0
27	3,87	3,06	0,370	0,510				
28	3,34	2,59	0,368	0,412	157	202	28,9	34,6
29	3,76	3,04					30,7	39,3
30								
31	3,84	3,02	0,360	0,470	118	146	22,4	27,5
32	5,02	4,22	0,460	0,550			21,5	35,7
33	3,37	2,63			182	238	26,1	34,4
34	3,90	3,00	1,200	1,200	280	330	41,0	50,0
35	4,16	3,14	0,380	0,480			31,2	38,2
36	1,10	0,40	-0,100	-0,100				
37	3,87	3,06	0,360	0,450	202	108	33,3	21,2
38	3,64	2,76	0,260	0,270	30	26	33,0	34,0
39								
40	3,72	3,02	0,340	0,460				
41	3,65	2,88	0,370	0,460	171	224	28,3	35,5
42	4,14	3,31	0,390	0,470				
43	3,92	3,14	0,100	0,150	143	227	32,8	40,9
44	3,33	2,67	0,250	0,300	161	225	29,0	28,0
45	3,99	3,22	0,370	0,490	169	221	35,1	42,9
46	4,06	3,32	0,360	0,510			31	38
47	4,30	3,50	0,500	0,500				
48	3,90	3,10	0,360	0,400				

Lab.	Na, mg/l		K, mg/l		Fe, µg/l		Mn, µg/l	
	A	B	A	B	C	D	C	D
49	3,51	2,73	0,500	0,570				
50								
51	3,82	3,04	0,360	0,450				
52	2,94	2,41	0,455	0,530	170	225	27,0	32,5
53								
54	3,82	3,04	0,368	0,471	186	241	29,0	35,4
55	3,87	3,08	0,367	0,473				
56								
57	3,87	3,06	0,370	0,480				
58	3,93	3,08	0,360	0,450				
59	4,03	3,48	0,370	0,470				
60	4,33	3,52	0,410	0,510	135	162	31,9	36,0
61								
62	3,95	3,18	0,324	0,394			32,0	35,0
63	3,66	2,92	0,360	0,430	168	224	32,4	40,5
64	3,85	3,04	0,387	0,506				
65	4,26	3,38	0,317	0,430	159	207	27,0	33,0
66								
67	3,97	3,18	0,38	0,48				
68	3,53	3,07	0,38	0,46				
69	3,56	2,81	0,370	0,480	212	155	26,2	34,5
70	4,17	3,31	0,390	0,470	168	212	27,9	33,9
71	4,06	3,26	0,390	0,510	178	228	30,0	37,0
72	3,88	3,00	0,330	0,430				
73	3,85	3,05	0,400	0,480	198	247	30,4	36,6
74	3,96	3,35	0,290	0,390				
75	3,90	3,09	0,357	0,460	137	157	35,6	41,4
76	3,86	3,09	0,330	0,450				
77	3,92	3,12	0,384	0,491	149	197	29,6	36,1
78	4,07	3,24	0,380	0,482				
79	3,487		0,395		260	280	39,2	44,7

Lab.	Cd, µg/l		Pb, µg/l		Cu, µg/l		Ni, µg/l	
	C	D	C	D	C	D	C	D
1	1,48	1,93	2,45	3,46	20,8	21,7	10,20	14,90
2	1,01	1,37	2,24	3,14	19,7	21,0	12,05	17,89
3	1,70	2,10	21,50	21,30	8,5	8,9	13,30	19,20
4								
5								
6	1,41	1,82	2,54	3,18	18,1	18,8	12,25	16,83
7	<5	<5	-8,00	-8,00	19,3	20,7	6,16	12,12
8	1,00	2,00	<10	<10	20,0	21,0	11,00	16,00
9								
10								
11	1,30	1,70	2,30	3,20	19,0	20,0	9,30	14,00
12	1,35	1,78	2,29	3,27	17,8	19,1	9,82	14,60
13								
14	1,17	1,53	1,80	3,50	21,5	22,5	11,80	15,30
15								
16	1,10	1,28	3,08	3,88	17,8	17,1	13,80	15,40
17	1,30	1,80	2,40	3,40	20,0	21,0	10,00	15,00
18								
19	<4	<4	<10	<10	19,4	20,1	10,00	15,00
20	1,48	1,89	2,52	3,77	18,2	19,1	9,33	13,90
21	1,47	1,96	2,60	3,60	20,5	21,4	9,60	14,40
22								
23								
24								
25	1,26	1,7	2,39	3,16	19,11	20,09	5,92	11,57
26	1,20	1,40	<15	<15	19,0	19,0	9,10	13,00
27								
28	1,00	1,29	2,00	2,00	20,2	20,7	1,88	1,44
29	1,38	1,85	2,35	3,21	20,1	21,2	10,10	15,20
30								
31	1,41	1,91	2,15	3,02	21,0	22,3	9,43	13,82
32	1,30	1,72	2,31	3,17	21,5	24,4	9,47	14,19
33	1,46	1,93	8,60	7,70	14,7	16,5	9,91	14,60
34					67,0	70,0		
35					19,3	20,8		
36								
37	1,86	1,37	3,31	2,23	18,5	14,0	12,80	6,85
38	0,78	0,98	<2	<2	16,8	19,8	9,90	15,50
39								
40								
41	1,38	1,85	2,58	3,58	21,7	22,6	10,00	15,30
42								
43	0,89	1,45	2,10	4,30	6,8	7,1	13,90	14,50
44	1,30	1,50	8,00	9,00	14,0	13,0	10,00	14,00
45	1,32	1,77	2,30	3,20	20,8	22,3	10,3	15,3
46					15	15	9	11
47								
48								

Lab.	Cd, µg/l		Pb, µg/l		Cu, µg/l		Ni, µg/l	
	C	D	C	D	C	D	C	D
49								
50								
51								
52	1,13	1,57	2,10	3,70	19,2	20,5	9,50	13,10
53								
54	1,34	1,81	2,30	3,10	14,8	16,1	9,70	14,60
55								
56								
57								
58								
59								
60	1,52	1,77	2,92	3,59	20,9	20,1	10,20	14,00
61								
62	1,50	2,00	2,20	3,10	18,8	20,0	10,00	14,80
63	1,37	1,87	2,45	3,35	19,9	21,2		
64								
65	<24	<24	<319	<319	<32	<32	<58	<58
66								
67								
68								
69	1,41	1,90	2,16	3,01	20,5	21,1	9,76	14,30
70	1,20	1,58	2,20	2,98	18,2	18,9	9,26	13,70
71	1,38	1,81	2,40	3,30	20,4	20,5	10,30	15,00
72								
73	1,23	1,65	2,51	3,37	21,3	21,7	10,10	14,90
74	1,60	2,10	3,00	4,00	20,0	27,0		
75								
76								
77	1,34	1,82	2,39	3,17	19,5	20,3	9,95	14,57
78								
79	3,56	4,16	2,05	2,80	10,6	17,5	12,60	22,40

Lab.	Zn, µg/l	
	C	D
1	42,4	29,4
2	29,5	13,4
3	41,0	30,9
4		
5		
6	35,5	22,5
7	76,8	49,8
8	35,5	24,0
9		
10		
11	37,0	26,0
12	37,1	25,8
13		
14	15,0	50,0
15		
16	39,9	24,2
17	34,0	25,0
18		
19	34,7	23,8
20	33,0	22,2
21	36,3	24,5
22		
23		
24		
25	37,12	26,26
26	32,0	21,0
27		
28	34,0	24,1
29	36,8	26,9
30		
31	29,3	19,0
32	31,7	21,4
33	60,1	28,3
34	45,0	26,0
35		
36		
37	24,0	30,0
38	36,0	20,0
39		
40		
41	34,0	24,1
42		
43	36,3	28,5
44	30,0	23,0
45	36,2	24,7
46		
47		

Lab.	Zn, µg/l	
	C	D
48		
50		
51		
49		
52	38,0	28,0
53		
54	36,4	25,4
55		
56		
57		
58		
59		
60	47,7	30,1
61		
62	35,0	24,0
63	44,6	25,0
64		
65	31,3	22,7
66		
67		
68		
69	30,6	20,4
70	30,7	21,2
71	37,0	26,0
72		
73	34,2	26,7
74	39,6	26,8
75		
76		
77	38,0	26,3
78		
79	62,4	59,3

Table 5.1. Statistics - pH

Sample A

Number of participants	72	Range	0,95
Number of omitted results	2	Variance	0,03
True value	6,72	Standard deviation	0,16
Mean value	6,70	Relative standard deviation	2,4%
Median value	6,72	Relative error	-0,4%

Analytical results in ascending order:

79		U	19	6,65		44	6,78	
7	6,17	U	75	6,66		58	6,79	
11	6,20		32	6,67		55	6,79	
17	6,30		37	6,67		6	6,80	
33	6,31		78	6,68		13	6,81	
2	6,41		14	6,70		10	6,81	
54	6,44		23	6,70		31	6,82	
34	6,46		18	6,70		27	6,82	
15	6,50		9	6,70		48	6,82	
46	6,50		40	6,70		41	6,83	
61	6,50		38	6,70		43	6,84	
12	6,54		68	6,71		16	6,85	
62	6,56		71	6,72		28	6,85	
60	6,56		1	6,72		65	6,85	
47	6,57		74	6,72		39	6,85	
63	6,57		49	6,72		52	6,85	
8	6,59		3	6,74		57	6,88	
26	6,59		66	6,74		77	6,88	
59	6,60		64	6,75		4	6,90	
50	6,60		67	6,75		36	6,95	
72	6,62		73	6,76		21	6,95	
69	6,62		45	6,76		51	7,15	
20	6,63		42	6,76		25	7,36	U
70	6,64		76	6,76				
22	6,65		29	6,78				

Sample B

Number of participants	72	Range	0,88
Number of omitted results	2	Variance	0,03
True value	6,58	Standard deviation	0,16
Mean value	6,57	Relative standard deviation	2,4%
Median value	6,58	Relative error	-0,2%

Analytical results in ascending order:

7	5,96	U	26	6,52		6	6,63	
2	6,12		75	6,52		76	6,63	
33	6,18		62	6,52		28	6,63	
17	6,20		37	6,53		48	6,64	
8	6,35		68	6,54		3	6,64	
34	6,35		40	6,55		61	6,64	
46	6,36		78	6,56		29	6,67	
54	6,36		63	6,56		41	6,68	
19	6,38		45	6,57		57	6,69	
12	6,40		27	6,57		43	6,69	
32	6,40		79	6,57	U	39	6,70	
60	6,41		74	6,57		71	6,70	
47	6,42		49	6,58		77	6,72	
20	6,43		64	6,59		52	6,72	
69	6,44		58	6,59		21	6,74	
23	6,46		38	6,60		36	6,75	
59	6,46		18	6,60		65	6,76	
50	6,46		14	6,60		4	6,80	
70	6,47		42	6,60		55	6,82	
1	6,49		73	6,60		11	6,91	
72	6,49		66	6,61		51	6,93	
9	6,50		31	6,62		13	7,00	
15	6,50		44	6,62		25	7,04	U
16	6,50		10	6,62				
22	6,52		67	6,62				

U = Omitted result

Table 5.2. Statistics - Conductivity, mS/m

Sample A

Number of participants	72	Range	1,57
Number of omitted results	4	Variance	0,04
True value	2,84	Standard deviation	0,21
Mean value	2,83	Relative standard deviation	7,4%
Median value	2,84	Relative error	-0,2%

Analytical results in ascending order:

79		U	18	2,80	10	2,90		
54	1,60	U	44	2,80	17	2,90		
15	2,00		4	2,80	60	2,91		
22	2,40		42	2,80	68	2,91		
13	2,53		71	2,80	67	2,91		
1	2,53		34	2,80	7	2,92		
63	2,53		9	2,82	59	2,92		
78	2,60		41	2,82	26	2,93		
56	2,61		73	2,82	57	2,93		
70	2,66		40	2,82	52	2,95		
45	2,68		77	2,83	49	2,97		
62	2,69		32	2,84	33	2,99		
36	2,70		31	2,84	14	3,00		
2	2,70		66	2,85	61	3,01		
58	2,71		11	2,85	64	3,06		
72	2,71		28	2,86	8	3,10		
55	2,72		19	2,86	25	3,16		
69	2,72		3	2,86	16	3,22		
46	2,73		65	2,86	76	3,44		
23	2,74		6	2,87	47	3,57		
29	2,77		37	2,87	21	4,02	U	
74	2,78		12	2,89	39	4,40	U	
20	2,80		38	2,89	75	6,34	U	
35	2,80		50	2,90				
27	2,80		51	2,90				

Sample B

Number of participants	72	Range	1,37
Number of omitted results	4	Variance	0,04
True value	2,57	Standard deviation	0,20
Mean value	2,60	Relative standard deviation	7,7%
Median value	2,57	Relative error	1,1%

Analytical results in ascending order:

54	1,40	U	29	2,53	64	2,63		
15	2,00		77	2,53	10	2,63		
63	2,27		65	2,55	19	2,65		
78	2,30		9	2,55	26	2,67		
22	2,32		40	2,55	12	2,67		
2	2,40		41	2,56	33	2,68		
70	2,40		3	2,56	50	2,70		
58	2,45		66	2,56	17	2,70		
20	2,45		52	2,56	7	2,73		
68	2,46		62	2,56	49	2,75		
67	2,46		74	2,56	57	2,76		
72	2,46		37	2,57	1	2,79		
69	2,47		11	2,58	8	2,80		
45	2,47		31	2,58	61	2,80		
73	2,49		32	2,59	59	2,84		
23	2,49		18	2,60	16	2,86		
46	2,49		35	2,60	13	2,96		
4	2,50		44	2,60	39	3,00	U	
42	2,50		27	2,60	25	3,14		
56	2,50		34	2,60	76	3,21		
38	2,51		36	2,60	47	3,37		
55	2,52		14	2,60	21	3,50	U	
28	2,52		60	2,60	75	5,36	U	
71	2,52		51	2,60				
79	2,53	U	6	2,61				

U = Omitted result

Table 5.3. Statistics - Alkalinity, mmol/l

Sample A

Number of participants	61	Range	0,105
Number of omitted results	13	Variance	0,000
True value	0,134	Standard deviation	0,021
Mean value	0,132	Relative standard deviation	16,2%
Median value	0,134	Relative error	-1,5%

Analytical results in ascending order:

79		U	35	0,126		31	0,144	
61	0,050	U	16	0,126		10	0,144	
54	0,063	U	42	0,128		68	0,146	
4	0,069		65	0,128		33	0,150	
73	0,078		72	0,131		69	0,150	
8	0,088	U	40	0,132		75	0,155	
21	0,090		51	0,132		19	0,158	
56	0,090	U	44	0,133		7	0,160	
14	0,094		59	0,133		3	0,160	
70	0,110		23	0,134		15	0,160	U
18	0,110		62	0,134		27	0,161	
6	0,112		67	0,135		39	0,170	
1	0,117		66	0,135		28	0,174	
13	0,118		60	0,136		36	0,180	U
57	0,120		64	0,137		47	0,183	U
22	0,120		52	0,137		17	0,190	U
25	0,122	U	29	0,140		9	0,190	U
63	0,124		11	0,141		38	0,230	U
45	0,124		12	0,141		46	0,380	U
77	0,125		58	0,141		34	3,260	U
74	0,126		41	0,143				

Sample B

Number of participants	61	Range	0,081
Number of omitted results	13	Variance	0,000
True value	0,103	Standard deviation	0,016
Mean value	0,102	Relative standard deviation	15,7%
Median value	0,103	Relative error	-1,3%

Analytical results in ascending order:

8	<0,055	U	65	0,099		7	0,112	
54	0,048	U	40	0,100		59	0,114	
61	0,050	U	75	0,101		58	0,114	
4	0,059		63	0,101		27	0,117	
73	0,065		51	0,101		69	0,120	
14	0,078		35	0,102		19	0,128	
21	0,080		72	0,103		33	0,130	
3	0,080		67	0,103		28	0,135	
18	0,080		10	0,104		39	0,140	
70	0,083		62	0,104		79	0,142	U
6	0,090		60	0,104		47	0,157	U
57	0,090		44	0,104		9	0,160	U
1	0,092		66	0,105		15	0,160	U
77	0,094		12	0,105		25	0,163	U
13	0,094		23	0,105		17	0,170	U
16	0,094		52	0,108		36	0,170	U
45	0,095		11	0,108		38	0,180	U
74	0,097		68	0,108		46	0,220	U
42	0,098		29	0,110		56	0,280	U
64	0,098		41	0,112		34	2,710	U
22	0,099		31	0,112				

U = Omitted result

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

Sample A

Number of participants	67	Range	43
Number of omitted results	17	Variance	72
True value	85	Standard deviation	8
Mean value	84	Relative standard deviation	10,1%
Median value	85	Relative error	-1,1%

Analytical results in ascending order:

79		U	1	81		14	91	
55	<80	U	19	81	U	6	91	
33	3	U	68	81		29	92	
7	18	U	57	82		16	92	
59	54	U	67	82		28	93	
50	64		76	83		47	93	
11	65		56	84		10	93	
3	70	U	22	84		26	94	
31	70		4	85		35	96	
66	70		23	85		49	96	
63	72		72	85		32	96	
70	73		60	85		46	107	
45	75		39	85		43	118	U
44	77		73	86		9	122	U
51	77		62	87		52	138	U
34	77		17	87		69	149	U
21	78		71	87		13	165	U
61	79		78	87		64	189	U
77	79		42	88		36	211	U
58	79		74	90	U	2	267	U
37	80		27	90		48	380	U
54	80		20	90		12	545	U
8	80		40	90				

Sample B

Number of participants	67	Range	53
Number of omitted results	17	Variance	143
True value	118	Standard deviation	12
Mean value	117	Relative standard deviation	10,2%
Median value	118	Relative error	-0,6%

Analytical results in ascending order:

33	5	U	46	114		17	125	
3	50	U	77	114		29	125	
59	54	U	43	115	U	27	125	
50	93		45	115		62	127	
67	94		61	115		71	130	
40	100		14	116		20	130	
31	100		57	116		6	132	
23	100		78	118		49	138	
76	102		4	119		32	138	
66	102		47	119		64	140	U
70	103		37	120		35	146	
63	105		72	120		28	146	
11	105		8	120		74	164	U
44	107		54	121		9	168	U
68	108		42	122		69	170	U
79	110	U	26	122		7	187	U
60	110		1	122		13	220	U
55	110	U	16	122		36	231	U
58	111		56	123		19	282	U
22	112		52	124	U	2	296	U
51	113		10	124		48	450	U
73	113		34	124		12	520	U
21	114		39	125				

U = Omitted result

Table 5.5. Statistics - Chloride, mg/l

Sample A

Number of participants	69	Range	0,50
Number of omitted results	13	Variance	0,01
True value	1,05	Standard deviation	0,11
Mean value	1,07	Relative standard deviation	10,1%
Median value	1,05	Relative error	1,5%

Analytical results in ascending order:

79		U	70	1,02		1	1,13	
15	<2	U	6	1,04		59	1,15	
38	0,38	U	56	1,04		43	1,15	
46	0,72	U	23	1,04		31	1,17	
21	0,90		37	1,04		4	1,17	
34	0,90		22	1,04		9	1,20	
18	0,91		67	1,04		48	1,23	
51	0,93		28	1,05		68	1,23	
32	0,93		76	1,05		10	1,24	
66	0,95		45	1,05		20	1,34	
36	0,95		41	1,05		49	1,35	
42	0,96		71	1,05		61	1,40	
63	0,97		62	1,06		54	1,60	U
65	0,97		14	1,06		47	1,60	U
55	0,98		40	1,06		2	1,61	U
11	0,99		52	1,06		3	1,64	U
44	0,99		19	1,06		16	1,65	U
8	1,00		74	1,09		73	1,71	U
57	1,01		35	1,10		13	2,00	U
26	1,01		69	1,10		12	2,16	U
60	1,01		17	1,10		33	2,55	U
64	1,02		72	1,10		7	3,19	U
27	1,02		39	1,10				
29	1,02		58	1,11				

Sample B

Number of participants	69	Range	0,72
Number of omitted results	13	Variance	0,02
True value	1,39	Standard deviation	0,14
Mean value	1,42	Relative standard deviation	10,1%
Median value	1,39	Relative error	2,0%

Analytical results in ascending order:

15	<2	U	27	1,36		74	1,55	
38	0,38	U	64	1,36		48	1,56	
46	0,88	U	37	1,36		22	1,57	
36	1,13		28	1,38		10	1,57	
18	1,15		70	1,38		20	1,57	
34	1,22		63	1,39		9	1,60	
51	1,24		71	1,39		61	1,60	
14	1,25		76	1,39		16	1,62	U
65	1,27		8	1,40		62	1,63	
66	1,28		17	1,40		3	1,72	U
67	1,28		23	1,40		59	1,72	
4	1,29		68	1,42		2	1,79	U
55	1,30		40	1,42		43	1,80	
60	1,30		1	1,43		79	1,82	U
32	1,31		45	1,44		49	1,85	
42	1,31		69	1,44		73	1,96	U
21	1,33		31	1,44		47	2,00	U
52	1,34		6	1,44		54	2,09	U
44	1,34		19	1,45		33	2,27	U
57	1,35		56	1,49		12	2,53	U
41	1,35		58	1,50		7	2,69	U
11	1,35		39	1,50		13	2,70	U
26	1,36		72	1,50				
29	1,36		35	1,54				

U = Omitted result

Table 5.6. Statistics - Sulfate, mg/l

Sample A

Number of participants	67	Range	1,22
Number of omitted results	11	Variance	0,04
True value	2,71	Standard deviation	0,20
Mean value	2,72	Relative standard deviation	7,5%
Median value	2,71	Relative error	0,4%

Analytical results in ascending order:

79		U	37	2,63		52	2,77	
38	<2	U	43	2,64		62	2,81	
7	1,67	U	8	2,65		29	2,82	
39	1,78	U	58	2,66		14	2,82	
61	2,00	U	55	2,69		31	2,82	
15	2,00		42	2,69		2	2,85	
48	2,02		11	2,70		69	2,86	
44	2,09	U	27	2,70		46	2,87	
36	2,49		74	2,70		72	2,90	
70	2,57		17	2,70		20	2,93	
26	2,58		23	2,70		28	2,95	
21	2,59		76	2,71	U	35	2,95	
40	2,59		22	2,71		10	2,98	
41	2,59		54	2,72		63	3,05	
34	2,60		71	2,73		18	3,06	
51	2,60		4	2,73		16	3,09	
60	2,60		64	2,73		49	3,22	
73	2,60		19	2,75		12	4,08	U
57	2,61		59	2,76		33	4,10	U
6	2,61		65	2,76		13	5,44	U
68	2,62		45	2,77		9	5,60	U
56	2,62		32	2,77		3	10,80	U
67	2,63		1	2,77				

Sample B

Number of participants	67	Range	0,81
Number of omitted results	11	Variance	0,02
True value	2,11	Standard deviation	0,14
Mean value	2,14	Relative standard deviation	6,5%
Median value	2,11	Relative error	1,2%

Analytical results in ascending order:

38	<2	U	4	2,08		52	2,16	
61	<2	U	27	2,08		31	2,19	
79	0,47	U	6	2,08		59	2,20	
7	1,16	U	11	2,09		62	2,21	
44	1,36	U	55	2,10		69	2,21	
39	1,73	U	73	2,10		28	2,22	
16	1,93		67	2,10		63	2,25	
36	1,93		23	2,10		14	2,25	
37	1,96		17	2,10		46	2,28	
48	1,97		34	2,10		35	2,29	
51	1,98		8	2,10		10	2,30	
26	1,99		64	2,11		72	2,30	
57	2,00		54	2,11		20	2,39	
15	2,00		74	2,11		18	2,40	
41	2,01		22	2,12		49	2,45	
58	2,02		65	2,12		12	2,50	U
70	2,02		45	2,12		9	2,60	U
68	2,04		71	2,13		29	2,74	
42	2,06		19	2,14		33	3,70	U
43	2,06		32	2,15		76	4,17	U
40	2,07		2	2,16		13	4,25	U
60	2,07		56	2,16		3	10,11	U
21	2,07		1	2,16				

U = Omitted result

Table 5.7. Statistics - Calcium, mg/l

Sample A

Number of participants	68	Range	0,77
Number of omitted results	7	Variance	0,02
True value	0,97	Standard deviation	0,15
Mean value	0,99	Relative standard deviation	15,5%
Median value	0,97	Relative error	2,3%

Analytical results in ascending order:

79		U	58	0,91		13	1,00	
17	<2	U	40	0,91		45	1,00	
36	<0,4	U	22	0,92		35	1,01	
3	0,34	U	10	0,94		28	1,01	
16	0,37	U	51	0,94		56	1,02	
74	0,47	U	31	0,94		12	1,02	
76	0,50	U	54	0,95		60	1,04	
6	0,63		59	0,95		8	1,05	
72	0,66		29	0,95		20	1,06	
63	0,75		19	0,96		62	1,06	
4	0,78		44	0,96		1	1,12	
38	0,79		26	0,97		48	1,14	
34	0,81		64	0,97		65	1,16	
37	0,84		27	0,97		67	1,16	
75	0,86		55	0,97		2	1,19	
49	0,87		77	0,98		15	1,20	
7	0,88		70	0,98		47	1,20	
52	0,88		25	0,98		68	1,23	
73	0,88		14	0,98		42	1,24	
41	0,89		71	0,99		32	1,24	
23	0,89		57	0,99		69	1,39	
11	0,90		43	1,00		39	1,40	
78	0,91		46	1,00		21	1,58	U

Sample B

Number of participants	68	Range	0,84
Number of omitted results	7	Variance	0,03
True value	1,20	Standard deviation	0,16
Mean value	1,21	Relative standard deviation	13,5%
Median value	1,20	Relative error	0,7%

Analytical results in ascending order:

17	<2	U	41	1,14		13	1,25	
36	<0,4	U	44	1,14		45	1,26	
3	0,43	U	40	1,14		1	1,27	
74	0,55	U	58	1,15		35	1,27	
16	0,56	U	11	1,15		62	1,28	
76	0,67	U	26	1,16		68	1,30	
72	0,78		28	1,17		8	1,30	
6	0,83		29	1,17		60	1,30	
63	0,94		12	1,17		20	1,32	
48	0,95		54	1,18		31	1,32	
73	0,96		10	1,19		19	1,33	
4	0,98		56	1,19		43	1,38	
75	1,01		14	1,20		59	1,40	
37	1,05		39	1,20		47	1,40	
64	1,06		25	1,20		65	1,40	
52	1,07		70	1,20		67	1,41	
38	1,08		15	1,20		42	1,44	
23	1,11		34	1,21		32	1,45	
7	1,12		77	1,22		2	1,46	
51	1,13		22	1,22		46	1,50	
27	1,13		55	1,22		69	1,62	
49	1,13		71	1,23		21	2,15	U
78	1,14		57	1,24		79	2,34	U

U = Omitted result

Table 5.8. Statistics - Magnesium, mg/l

Sample A

Number of participants	69	Range	0,300
Number of omitted results	8	Variance	0,004
True value	0,539	Standard deviation	0,065
Mean value	0,526	Relative standard deviation	12,3%
Median value	0,539	Relative error	-2,4%

Analytical results in ascending order:

79		U	19	0,520		71	0,560	
36	<0,3	U	56	0,520		10	0,560	
74	0,240	U	54	0,523		68	0,560	
76	0,350		55	0,523		65	0,568	
72	0,360		46	0,530		43	0,570	
15	0,360		59	0,530		1	0,573	
29	0,370		12	0,530		20	0,580	
7	0,389		57	0,530		31	0,580	
33	0,435		26	0,533		49	0,580	
4	0,443		64	0,534		45	0,590	
6	0,449		62	0,539		3	0,600	
37	0,470		13	0,540		8	0,600	
63	0,480		77	0,540		47	0,600	
75	0,481		69	0,540		2	0,608	
52	0,488		40	0,540		67	0,610	
16	0,490		51	0,540		14	0,640	
78	0,499		35	0,550		21	0,650	U
22	0,500		44	0,550		42	0,650	
17	0,500	U	70	0,550		48	0,820	U
41	0,510		60	0,550		38	0,940	U
58	0,510		25	0,550		39	1,200	U
27	0,510		34	0,550		73	1,410	U
23	0,510		28	0,555				
11	0,516		32	0,560				

Sample B

Number of participants	69	Range	0,197
Number of omitted results	8	Variance	0,002
True value	0,380	Standard deviation	0,040
Mean value	0,383	Relative standard deviation	10,5%
Median value	0,380	Relative error	0,9%

Analytical results in ascending order:

17	<0,5	U	12	0,379		20	0,401	
36	<0,3	U	55	0,380		62	0,408	
74	0,180	U	40	0,380		10	0,410	
72	0,270		25	0,380		43	0,410	
76	0,290		19	0,380		45	0,410	
63	0,300		69	0,380		31	0,410	
33	0,317		41	0,380		70	0,420	
4	0,320		51	0,380		49	0,420	
29	0,320		44	0,380		32	0,420	
6	0,329		16	0,380		2	0,430	
52	0,333		28	0,382		67	0,440	
75	0,345		77	0,387		3	0,450	
46	0,350		59	0,390		42	0,460	
7	0,359		57	0,390		34	0,460	
27	0,360		13	0,390		14	0,460	
15	0,360		56	0,390		1	0,467	
58	0,360		65	0,391		48	0,570	U
37	0,360		64	0,397		21	0,740	U
78	0,364		35	0,400		38	0,770	U
22	0,370		47	0,400		79	0,789	U
54	0,370		71	0,400		39	1,000	U
23	0,370		8	0,400		73	1,560	U
11	0,373		60	0,400				
26	0,378		68	0,400				

U = Omitted result

Table 5.9. Statistics - Sodium, mg/l

Sample A

Number of participants	66	Range	1,61
Number of omitted results	2	Variance	0,08
True value	3,89	Standard deviation	0,28
Mean value	3,86	Relative standard deviation	7,4%
Median value	3,89	Relative error	-0,8%

Analytical results in ascending order:

79		U	51	3,82		22	3,96	
36	1,10	U	31	3,84		74	3,96	
52	2,94		64	3,85		67	3,97	
44	3,33		73	3,85		12	3,99	
28	3,34		76	3,86		45	3,99	
4	3,34		55	3,87		23	4,00	
33	3,37		57	3,87		59	4,03	
7	3,44		27	3,87		46	4,06	
14	3,45		37	3,87		71	4,06	
49	3,51		16	3,88		78	4,07	
68	3,53		72	3,88		10	4,08	
6	3,55		1	3,89		42	4,14	
69	3,56		34	3,90		35	4,16	
3	3,60		48	3,90		70	4,17	
38	3,64		75	3,90		65	4,26	
41	3,65		8	3,90		47	4,30	
63	3,66		77	3,92		60	4,33	
40	3,72		43	3,92		21	4,36	
29	3,76		13	3,92		17	4,40	
26	3,77		25	3,92		2	4,55	
20	3,80		11	3,93		32	5,02	U
19	3,82		58	3,93				
54	3,82		62	3,95				

Sample B

Number of participants	66	Range	1,43
Number of omitted results	2	Variance	0,06
True value	3,08	Standard deviation	0,25
Mean value	3,09	Relative standard deviation	8,2%
Median value	3,08	Relative error	0,2%

Analytical results in ascending order:

36	0,40	U	29	3,04		62	3,18	
52	2,41		64	3,04		67	3,18	
28	2,59		19	3,05		45	3,22	
33	2,63		73	3,05		12	3,23	
4	2,65		57	3,06		78	3,24	
44	2,67		27	3,06		71	3,26	
49	2,73		37	3,06		10	3,27	
38	2,76		1	3,07		22	3,29	
3	2,80		68	3,07		42	3,31	
69	2,81		55	3,08		70	3,31	
7	2,83		58	3,08		46	3,32	
14	2,84		75	3,09		74	3,35	
6	2,85		76	3,09		65	3,38	
41	2,88		48	3,10		17	3,40	
63	2,92		8	3,10		59	3,48	
26	2,93		77	3,12		79	3,49	U
72	3,00		13	3,13		47	3,50	
34	3,00		43	3,14		60	3,52	
31	3,02		35	3,14		2	3,67	
40	3,02		16	3,14		21	3,83	
54	3,04		23	3,16		32	4,22	U
51	3,04		11	3,16				
20	3,04		25	3,17				

U = Omitted result

Table 5.10. Statistics - Potassium, mg/l

Sample A

Number of participants	63	Range	0,294
Number of omitted results	6	Variance	0,003
True value	0,370	Standard deviation	0,054
Mean value	0,372	Relative standard deviation	14,5%
Median value	0,370	Relative error	0,6%

Analytical results in ascending order:

79		U	37	0,360		64	0,387	
17	<0,6	U	63	0,360		6	0,390	
36	<0,1	U	31	0,360		70	0,390	
21	0,160	U	46	0,360		19	0,390	
12	0,216		48	0,360		71	0,390	
14	0,240		55	0,367		42	0,390	
44	0,250		28	0,368		2	0,394	
38	0,260	U	54	0,368		8	0,400	
74	0,290		69	0,370		73	0,400	
65	0,317		41	0,370		60	0,410	
25	0,320		27	0,370		1	0,418	
23	0,320		57	0,370		16	0,420	
62	0,324		45	0,370		11	0,436	
76	0,330		59	0,370		52	0,455	
72	0,330		20	0,378		32	0,460	
40	0,340		43	0,379		49	0,500	
4	0,344		67	0,380		47	0,500	
22	0,345		35	0,380		10	0,510	
75	0,357		78	0,380		3	0,550	U
51	0,360		68	0,380		34	1,200	U
58	0,360		26	0,381				
13	0,360		77	0,384				

Sample B

Number of participants	63	Range	0,300
Number of omitted results	6	Variance	0,003
True value	0,473	Standard deviation	0,054
Mean value	0,468	Relative standard deviation	11,5%
Median value	0,473	Relative error	-1,1%

Analytical results in ascending order:

17	<0,6	U	75	0,460		6	0,490	
36	<0,1	U	68	0,460		77	0,491	
38	0,270	U	41	0,460		11	0,499	
44	0,300		40	0,460		16	0,500	
12	0,310		1	0,465		8	0,500	
14	0,330		13	0,468		47	0,500	
74	0,390		70	0,470		64	0,506	
62	0,394		59	0,470		2	0,507	
79	0,395	U	42	0,470		60	0,510	
48	0,400		31	0,470		46	0,510	
28	0,412		54	0,471		27	0,510	
23	0,430		55	0,473		71	0,510	
65	0,430		4	0,475		43	0,513	
72	0,430		26	0,476		20	0,521	
63	0,430		35	0,480		52	0,530	
25	0,440		69	0,480		32	0,550	
22	0,440		67	0,480		49	0,570	
76	0,450		73	0,480		10	0,600	
37	0,450		57	0,480		3	0,660	U
51	0,450		78	0,482		34	1,200	U
58	0,450		19	0,490				
21	0,460	U	45	0,490				

U = Omitted result

Table 5.11. Statistics - Iron, µg/l

Sample C

Number of participants	38	Range	117
Number of omitted results	5	Variance	512
True value	168	Standard deviation	23
Mean value	169	Relative standard deviation	13,4%
Median value	168	Relative error	0,5%

Analytical results in ascending order:

38	30	U	44	161		8	184	
31	118		26	163		54	186	
60	135		6	167		12	186	
75	137		70	168		16	189	
43	143		63	168		4	190	
21	144		45	169		73	198	
77	149		52	170		37	202	U
11	152		42	171		69	212	
28	157		41	171		14	235	
65	159		20	171		79	260	U
17	160		19	177		34	280	U
25	160		71	178		7	308	U
1	161		33	182				

Sample D

Number of participants	38	Range	144
Number of omitted results	5	Variance	815
True value	220	Standard deviation	29
Mean value	213	Relative standard deviation	13,4%
Median value	220	Relative error	-3,0%

Analytical results in ascending order:

38	26	U	65	207		52	225	
37	108	U	70	212		43	227	
31	146		6	214		71	228	
69	155		4	219		8	237	
75	157		20	219		12	238	
60	162		17	220		33	238	
11	193		16	221		54	241	
21	195		45	221		73	247	
77	197		42	221		79	280	U
25	200		41	224		14	290	
28	202		63	224		34	330	U
26	204		44	225		7	354	U
1	207		19	225				

U = Omitted result

Table 5.12. Statistics - Manganese,µg/l

Sample C

Number of participants	45	Range	17,7
Number of omitted results	4	Variance	10,6
True value	29,0	Standard deviation	3,3
Mean value	29,4	Relative standard deviation	11,1%
Median value	29,0	Relative error	1,3%

Analytical results in ascending order:

12	0,2	U	21	28,1		46	31,0	
32	21,5		41	28,3		8	31,0	
31	22,4		1	28,6		35	31,2	
26	26,0		2	28,7		60	31,9	
33	26,1		28	28,9		62	32,0	
69	26,2		54	29,0		3	32,1	
14	26,4		44	29,0		63	32,4	
16	26,9		17	29,0		43	32,8	
52	27,0		11	29,0		38	33,0	
65	27,0		42	29,4		37	33,3	U
6	27,2		77	29,6		45	35,1	
4	27,5		71	30,0		75	35,6	
25	27,8		73	30,4		79	39,2	
70	27,9		19	30,4		34	41,0	U
20	28,1		29	30,7		7	185,8	U

Sample D

Number of participants	45	Range	17,2
Number of omitted results	4	Variance	12,0
True value	35,4	Standard deviation	3,5
Mean value	35,5	Relative standard deviation	9,7%
Median value	35,4	Relative error	0,4%

Analytical results in ascending order:

12	0,3	U	33	34,4		73	36,6	
37	21,2	U	69	34,5		71	37,0	
31	27,5		21	34,5		17	37,0	
44	28,0		28	34,6		19	37,1	
14	30,5		2	34,8		8	37,5	
26	32,0		11	35,0		46	38,0	
52	32,5		62	35,0		35	38,2	
16	32,8		25	35,4		29	39,3	
1	33,0		54	35,4		63	40,5	
4	33,0		41	35,5		43	40,9	
65	33,0		32	35,7		75	41,4	
6	33,2		42	35,8		45	42,9	
70	33,9		60	36,0		79	44,7	
38	34,0		3	36,1		34	50,0	U
20	34,3		77	36,1		7	230,5	U

U = Omitted result

Table 5.13. Statistics - Cadmium, µg/l

Sample C

Number of participants	41	Range	1,08
Number of omitted results	4	Variance	0,05
True value	1,34	Standard deviation	0,21
Mean value	1,32	Relative standard deviation	16,3%
Median value	1,34	Relative error	-1,7%

Analytical results in ascending order:

65	<24	U	25	1,26		6	1,41	
7	<5	U	32	1,30		69	1,41	
19	<4	U	11	1,30		31	1,41	
38	0,78		17	1,30		33	1,46	
43	0,89		44	1,30		21	1,47	
28	1,00		45	1,32		20	1,48	
8	1,00		54	1,34		1	1,48	
2	1,01		77	1,34		62	1,50	
16	1,10		12	1,35		60	1,52	
52	1,13		63	1,37		74	1,60	
14	1,17		29	1,38		3	1,70	
70	1,20		71	1,38		37	1,86	
26	1,20		41	1,38		79	3,56	U
73	1,23		42	1,40				

Sample D

Number of participants	41	Range	1,12
Number of omitted results	4	Variance	0,06
True value	1,80	Standard deviation	0,25
Mean value	1,72	Relative standard deviation	14,7%
Median value	1,80	Relative error	-4,5%

Analytical results in ascending order:

65	<24	U	73	1,65		29	1,85	
7	<5	U	25	1,70		63	1,87	
19	<4	U	11	1,70		20	1,89	
38	0,98		32	1,72		69	1,90	
16	1,28		60	1,77		31	1,91	
28	1,29		45	1,77		33	1,93	
2	1,37		12	1,78		1	1,93	
37	1,37		17	1,80		21	1,96	
26	1,40		71	1,81		62	2,00	
43	1,45		54	1,81		8	2,00	
44	1,50		6	1,82		74	2,10	
14	1,53		77	1,82		3	2,10	
52	1,57		42	1,84		79	4,16	U
70	1,58		41	1,85				

U = Omitted result

Table 5.14. Statistics - Lead, µg/l

Sample C

Number of participants	41	Range	1,51
Number of omitted results	9	Variance	0,10
True value	2,33	Standard deviation	0,32
Mean value	2,40	Relative standard deviation	13,3%
Median value	2,33	Relative error	2,8%

Analytical results in ascending order:

65	<315	U	62	2,20		63	2,45	
26	<15	U	2	2,24		73	2,51	
8	<10	U	42	2,29		20	2,52	
19	<10	U	12	2,29		6	2,54	
7	<8	U	11	2,30		41	2,58	
38	<2	U	45	2,30		21	2,60	
14	1,80		54	2,30		60	2,92	
28	2,00		32	2,31		74	3,00	
79	2,05		29	2,35		16	3,08	
43	2,10		77	2,39		37	3,31	
52	2,10		25	2,39		44	8,00	U
31	2,15		71	2,40		33	8,60	U
69	2,16		17	2,40		3	21,50	U
70	2,20		1	2,45				

Sample D

Number of participants	41	Range	2,30
Number of omitted results	9	Variance	0,20
True value	3,21	Standard deviation	0,44
Mean value	3,28	Relative standard deviation	13,6%
Median value	3,21	Relative error	2,0%

Analytical results in ascending order:

65	<319	U	54	3,10		1	3,46	
26	<15	U	2	3,14		14	3,50	
19	<10	U	25	3,16		41	3,58	
8	<10	U	77	3,17		60	3,59	
7	<8	U	32	3,17		21	3,60	
38	<2	U	6	3,18		52	3,70	
28	2,00		11	3,20		20	3,77	
37	2,23		45	3,20		16	3,88	
79	2,80		29	3,21		74	4,00	
70	2,98		12	3,27		43	4,30	
69	3,01		71	3,30		33	7,70	U
31	3,02		63	3,35		44	9,00	U
42	3,09		73	3,37		3	21,30	U
62	3,10		17	3,40				

U = Omitted result

Table 5.15. Statistics - Copper, µg/l

Sample C

Number of participants	44	Range	7,7
Number of omitted results	5	Variance	3,9
True value	19,5	Standard deviation	2,0
Mean value	19,1	Relative standard deviation	10,4%
Median value	19,5	Relative error	-1,9%

Analytical results in ascending order:

65	<32	U	62	18,8		29	20,1	
43	6,8	U	26	19,0		28	20,2	
3	8,5	U	11	19,0		71	20,4	
79	10,6	U	25	19,1		69	20,5	
46	14,0		52	19,2		21	20,5	
44	14,0		35	19,3		45	20,8	
33	14,7		7	19,3		1	20,8	
54	14,8		19	19,4		60	20,9	
38	16,8		77	19,5		31	21,0	
12	17,8		2	19,7		73	21,3	
16	17,8		42	19,8		32	21,5	
6	18,1		63	19,9		14	21,5	
70	18,2		8	20,0		41	21,7	
20	18,2		74	20,0		34	67,0	U
37	18,5		17	20,0				

Sample D

Number of participants	44	Range	14,0
Number of omitted results	5	Variance	6,8
True value	20,5	Standard deviation	2,6
Mean value	20,1	Relative standard deviation	13,0%
Median value	20,5	Relative error	-2,1%

Analytical results in ascending order:

65	<32	U	38	19,8		2	21,0	
43	7,1	U	11	20,0		69	21,1	
3	8,9	U	62	20,0		29	21,2	
44	13,0		25	20,1		63	21,2	
37	14,0		19	20,1		21	21,4	
46	15,0		60	20,1		73	21,7	
54	16,1		77	20,3		1	21,7	
33	16,5		42	20,4		31	22,3	
16	17,1		52	20,5		45	22,3	
79	17,5	U	71	20,5		14	22,5	
6	18,8		7	20,7		41	22,6	
70	18,9		28	20,7		32	24,4	
26	19,0		35	20,8		74	27,0	
12	19,1		8	21,0		34	70,0	U
20	19,1		17	21,0				

U = Omitted result

Table 5.16. Statistics - Nickel, µg/l

Sample C

Number of participants	40	Range	7,98
Number of omitted results	5	Variance	2,33
True value	10,00	Standard deviation	1,53
Mean value	10,03	Relative standard deviation	15,2%
Median value	10,00	Relative error	0,3%

Analytical results in ascending order:

65	<58	U	69	9,76		60	10,20	
33	4,18	U	12	9,82		45	10,30	
25	5,92		38	9,90		71	10,30	
7	6,16		28	9,91		8	11,00	
46	9,00		77	9,95		14	11,80	
26	9,10		62	10,00		2	12,05	
70	9,26		44	10,00		6	12,25	
11	9,30		41	10,00		79	12,60	U
20	9,33		19	10,00		37	12,80	U
31	9,43		17	10,00		3	13,30	U
32	9,47		73	10,10		16	13,80	
52	9,50		29	10,10		43	13,90	
21	9,60		42	10,10				
54	9,70		1	10,20				

Sample D

Number of participants	40	Range	6,89
Number of omitted results	5	Variance	1,70
True value	14,60	Standard deviation	1,30
Mean value	14,49	Relative standard deviation	9,0%
Median value	14,60	Relative error	-0,7%

Analytical results in ascending order:

65	<58	U	32	14,19		42	15,00	
33	6,48	U	69	14,30		29	15,20	
37	6,85	U	21	14,40		45	15,30	
46	11,00		43	14,50		41	15,30	
25	11,57		77	14,57		14	15,30	
7	12,12		12	14,60		16	15,40	
26	13,00		28	14,60		38	15,50	
52	13,10		54	14,60		8	16,00	
70	13,70		62	14,80		6	16,83	
31	13,82		73	14,90		2	17,89	
20	13,90		1	14,90		3	19,20	U
11	14,00		71	15,00		79	22,40	U
60	14,00		19	15,00				
44	14,00		17	15,00				

U = Omitted result

Table 5.17. Statistics - Zinc, µg/l

Sample C

Number of participants	42	Range	23,7
Number of omitted results	5	Variance	21,9
True value	35,8	Standard deviation	4,7
Mean value	35,9	Relative standard deviation	13,0%
Median value	35,8	Relative error	0,2%

Analytical results in ascending order:

37	24,0		19	34,7		25	37,1	
31	29,3		62	35,0		52	38,0	
2	29,5	U	8	35,5		77	38,0	
44	30,0		6	35,5		74	39,6	
69	30,6		42	35,6		16	39,9	
70	30,7		38	36,0		3	41,0	
65	31,3		45	36,2		1	42,4	
32	31,7		43	36,3		63	44,6	
26	32,0		21	36,3		34	45,0	
20	33,0		54	36,4		14	45,0	U
17	34,0		29	36,8		60	47,7	
41	34,0		71	37,0		33	60,1	U
28	34,0		11	37,0		79	62,4	U
73	34,2		12	37,1		7	76,8	U

Sample D

Number of participants	42	Range	11,9
Number of omitted results	5	Variance	8,5
True value	24,8	Standard deviation	2,9
Mean value	24,9	Relative standard deviation	11,7%
Median value	24,8	Relative error	0,3%

Analytical results in ascending order:

2	13,4	U	28	24,1		77	26,3	
31	19,0		41	24,1		73	26,7	
38	20,0		16	24,2		74	26,8	
69	20,4		42	24,4		29	26,9	
26	21,0		21	24,5		52	28,0	
70	21,2		45	24,7		33	28,3	U
32	21,4		17	25,0		43	28,5	
20	22,2		63	25,0		1	29,4	
6	22,5		54	25,4		37	30,0	
65	22,7		12	25,8		60	30,1	
44	23,0		11	26,0		3	30,9	
19	23,8		34	26,0		7	49,8	U
62	24,0		71	26,0		14	50,0	U
8	24,0		25	26,3		79	59,3	U

U = Omitted result