Norwegian Institute for Water Research

REPORT

Main Office
P.O. Box 173, Kjelsås
N-0411 Oslo
Norway
Phone (47) 22 18 51 00
Telefax (47) 22 18 52 00
Internet: www.niva.no

Regional Office, Sørlandet
Televeien 3
N-4879 Grimstad
Norway
Phone (47) 37 29 50 55
Telefax (47) 37 04 45 13

Regional Office, Østlandet
Sandvikaveien 41
N-2312 Ottestad
Norway
Phone (47) 62 57 64 00
Telefax (47) 62 57 66 53

Regional Office, Vestlandet
Nordnesboder 5
N-5008 Bergen
Norway
Phone (47) 55 30 22 50
Telefax (47) 55 30 22 51

Akvaplan-NIVA A/S
N-9005 Tromsø
Norway
Phone (47) 77 68 52 80
Telefax (47) 77 68 05 09

Title	Serial No.	Date
International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes. Intercomparison 0317: pH, Cond, HCO_3, NO_3+NO_2, Cl, SO_4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni, and Zn	4715-2003	September 2003
	Report No. Sub-No. O-23300 B	Pages Price 69
Author(s) Håvard Hovind	Topic group Analysis	Distribution
	Geographical area	Printed NIVA

Client(s)	Client ref.
Norwegian Pollution Control Authority	

Abstract

75 laboratories received samples for the intercomparison 0317, and 69 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 %, 71 % of the overall results were considered acceptable. The best results were reported for the analytical variables sodium, sulfate and copper, with a percentage of acceptable results of 92, 83 and 83 %, respectively. Lowest percentage of acceptable results were observed for manganese, lead, and iron. Common for these analytical variables is their low concentrations being rather close to their detection limits. For pH and alkalinity only 57 % and 58 % of the result pairs, respectively, were acceptable based on a target accuracy of ± 0.2 units. Harmonization of the analytical methods used is necessary to improve the comparability for pH.

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

Håvard Hovind

Project manager
Håvard Hovind

Øyvind Skaugrud

Head of chemistry department
Øyvind Skaugrud

ISBN 82-577-4385-2

CONVENTION ON LONG-RANGE
TRANSBOUNDARY AIR POLLUTION

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

Intercomparison 0317

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, September 2003

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 17th intercomparison of chemical analysis.

Oslo, September 2003

Håvard Hovind

Contents

1. Summary

Intercomparison 0317 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 2003, 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. 115 laboratories were invited to participate in this intercomparison, and the samples were sent to the 75 laboratories who accepted to participate. 69 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 40).

The median value of the results received from the participants was selected as "true" value for each variable. 71 % of the result pairs were considered as acceptable, the target limit being the median value ± 20 %, except for pH and conductivity where the special acceptance limits were selected, being ± 0,2 units and ± 10 %, respectively.

For pH, the accuracy limit was extended from 0,1 to ± 0,2 units, but still only 57 % of the result pairs were acceptable using this special limit. A total error of ± 0,2 units for pH measurements is a more reasonable basis for theassessment 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.

The best results were reported for the analytical variables sodium, sulfate and copper, where 92, 83 and 83 %, respectively, of the results were acceptable. The worst results were observed for manganese, lead and iron, with 36, 49 and 51 % acceptable results. A common feature for these last analytical variables is that the concentrations are quite low in the samples used in this intercomparison. To improve the comparability of the results for these variables, it is necessary to use analytical methods being sensitive enough.

For the fourth time in this intercomparison programme, the heavy metals iron, manganese, cadmium, lead, copper, nickel, and zinc were included. The best results were obtained for copper and zinc where 83 % of the results were acceptable. For these elements the concentrations are quite higher than their detection limits, while some of the others are quite close to their detection limits of the 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 sevententh intercomparison test, called 0317, 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 2002 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 samples were mailed from the Programme Centre on June 4, 2003, and the following days. Most of the participating laboratories received the samples within one week, with some very few exceptions. Some laboratories commented that they received the sample sets with some leakage from the bottles, this time we obviously have received a second-hand set of sample bottles. Hopefully this problem has not affected the concentrations in the sample solutions. Before the next round we will try to find bottles of better quality.

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 before 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. Six laboratories who received samples did not return analytical results.

4. Results

115 laboratories were invited to participate in this intercomparison, and 75 laboratories accepted and therefore received samples. The 69 laboratories which submitted results to the

Programme Centre, are representing 27 countries. Some laboratories submitted 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, which also includes a table illustrating how many laboratories are participating from each country (see page 40). 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.

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 water 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, and 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. The great circle in the Figures are representing a selected accuracy limit, either the general target limit of ± 20 % of the mean true values for the sample pair, or a special accuracy limit defined in the sections below. A survey of the results of intercomparison 0317 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. 69 laboratories reported results for pH, of this group 35 indicated that they read the pH value i quiescent solution, and 33 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 0,01 and 0,03 pH units, respectively, in sample A and B. The differences between the mean values are a little greater, 0,08 and 0,07 pH units, respectively.

(The text continues on page 29

Table 1. Statistical summary of intercomparison 0317

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.dev % 1	Rel. std.dev % 2	Relative error % 1	Relative error % 2
pH	AB	6,76	7,06	69	1	6,76	7,06	6,71	0,27	6,98	0,27	4,0	3,9	-0,8	-1,1
No stirring				35	1	6,77	7,06	6,74	0,20	7,01	0,17	2,9	2,4	-0,3	-0,6
Stirring				33	0	6,76	7,03	6,66	0,31	6,94	0,34	4,7	4,9	-1,4	-1,7
Equilibration				1	0			7,13		7,43				5,5	5,2
Conductivity	AB	3,80	3,21	66	4	3,80	3,21	3,80	0,22	3,20	0,16	5,8	5,1	-0,1	-0,3
Alkalinity	AB	0,106	0,151	55	4	0,106	0,151	0,106	0,021	0,148	0,027	19,8	18,2	0,0	-1,9
Gran plot titration				23	1	0,107	0,150	0,101	0,019	0,140	0,027	19,0	19,5	-4,9	-7,6
End point titration				14	0	0,106	0,150	0,111	0,016	0,156	0,017	14,3	11,0	5,1	3,5
End point 5.6				2	0			0,102		0,152				-3,8	0,7
End point 4.5				14	3	0,125	0,173	0,111	0,031	0,154	0,036	27,6	23,2	4,5	1,7
Colorimetry				1	0			0,115		0,180				8,5	19,2
Not documented				1	0			0,092		0,125				-13,2	-17,2
Nitrate + nitrite-nitrogen	AB	295	188	65	7	295	188	296	21	189	14	7,0	7,3	0,4	0,4
Autoanalyzer				20	1	296	185	297	19	186	14	6,5	7,6	0,5	-1,1
Photometry				9	3	308	202	308	21	198	8	7,0	4,2	4,4	5,4
Ion chromatography				30	2	294	187	293	22	189	15	7,6	7,9	-0,6	0,6
Flow injection anal.				1	0			310		193				5,1	2,7
Hydrazine				3	0	299	182	297	17	183	9	5,6	4,7	0,8	-2,7
Cap. electrophoresis				2	1			287		187				-2,7	-0,5
Chloride	AB	3,58	1,99	62	8	3,58	1,99	3,61	0,26	2,00	0,16	7,1	8,0	0,8	0,6
Ion chromatography				46	3	3,57	1,99	3,57	0,22	1,98	0,11	6,0	5,4	-0,2	-0,5
AA				5	1	3,53	2,12	3,73	0,47	2,16	0,19	12,7	8,7	4,1	8,5
Argentometry				3	3			4,59		3,91				28,2	96,5
Manual, Hg				5	1	3,75	2,05	3,90	0,32	2,07	0,45	8,3	21,6	8,8	4,0
Cap. electrophoresis				1	0			3,63		2,03				1,4	2,0
Potentiometry				2	0			3,59		2,02				0,3	1,5

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.dev. % 1	Rel. std.dev. % 2	Relative error % 1	Relative error % 2
Sulfate	AB	3,51	2,58	60	7	3,51	2,58	3,49	0,19	2,54	0,18	5,4	7,2	-0,5	-1,4
Ion chromatography				46	2	3,54	2,60	3,54	0,15	2,56	0,15	4,2	5,7	0,7	-0,9
Photometry				6	1	3,13	2,55	3,19	0,26	2,57	0,34	8,2	13,4	-9,1	-0,5
Nephelometry				4	3			3,40		2,00				-3,1	-22,5
ICP				1	0			3,40		2,39				-3,1	-7,4
Cap. electrophoresis				1	0			3,60		2,64				2,6	2,3
Gravimetry				2	1			3,25		2,47				-7,4	-4,2
Calcium	AB	3,60	3,24	66	5	3,60	3,24	3,60	0,39	3,24	0,37	10,9	11,5	0,0	0,1
FAAS				22	2	3,57	3,18	3,59	0,30	3,17	0,30	8,4	9,5	-0,2	-2,1
ICP				16	0	3,61	3,19	3,56	0,19	3,16	0,18	5,4	5,8	-1,2	-2,5
EDTA				4	0	3,25	2,99	3,29	0,69	2,98	0,44	20,9	14,6	-8,7	-8,2
Ion chromatography				20	3	3,72	3,46	3,76	0,52	3,48	0,51	13,9	14,5	4,6	7,4
ICP-MS				2	0			3,60		3,17				-0,1	-2,3
Photometry				1	0			3,08		3,26				-14,4	0,6
Cap. Electrophoresis				1	0			3,41		3,13				-5,3	-3,4
Magnesium	AB	0,54	0,60	66	7	0,54	0,60	0,54	0,04	0,60	0,05	8,3	8,7	0,2	0,2
FAAS				21	2	0,55	0,60	0,55	0,05	0,60	0,06	9,5	9,5	1,2	-0,1
ICP				17	0	0,54	0,60	0,55	0,03	0,60	0,03	5,3	5,8	1,1	-0,1
EDTA				4	3			0,56		0,63				3,7	5,0
Ion chromatography				20	2	0,54	0,62	0,53	0,05	0,60	0,07	9,8	11,2	-1,1	0,8
ICP-MS				2	0			0,54		0,59				0,0	-2,5
Photometry				1	0			0,46		0,56				-14,8	-6,7
Cap. Electrophoresis				1	0			0,54		0,63				0,0	5,0
Sodium	AB	2,10	1,55	64	2	2,10	1,55	2,10	0,14	1,54	0,12	6,5	7,8	0,0	-0,4
FAAS				20	1	2,08	1,52	2,04	0,11	1,48	0,09	5,3	6,0	-2,8	-4,4
ICP				16	0	2,13	1,58	2,11	0,11	1,56	0,09	5,1	6,0	0,4	0,7
AES				5	0	2,12	1,57	2,12	0,13	1,57	0,18	6,0	11,3	1,1	1,1
Ion chromatography				21	1	2,10	1,56	2,14	0,17	1,57	0,14	8,1	8,9	1,8	1,3
ICP-MS				1	0			2,20		1,70				4,8	9,7
Cap. Electrophoresis				1	0			2,12		1,63				1,0	5,2

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.dev. % 1	Rel. std.dev. % 2	Relative error % 1	Relative error % 2
Potassium	AB	0,37	0,50	64	5	0,37	0,50	0,37	0,05	0,49	0,06	13,9	11,3	0,1	-1,1
FAAS				20	2	0,37	0,50	0,35	0,05	0,48	0,06	13,9	13,1	-4,8	-3,6
ICP				16	1	0,37	0,50	0,38	0,05	0,51	0,03	12,4	6,5	2,5	1,4
AES				5	0	0,38	0,53	0,43	0,07	0,54	0,05	16,4	9,1	15,8	8,9
Ion chromatography				21	2	0,38	0,50	0,37	0,04	0,49	0,06	11,6	11,9	-0,1	-2,4
ICP-MS				1	0			0,37		0,50				0,0	0,0
Cap. Electrophoresis				1	0			0,29		0,41				-21,6	-18,0
Iron	CD	23	48	39	7	23	48	23	5	46	6	22,3	13,8	-1,4	-3,5
FAAS				7	3	28	52	27	4	51	6	15,2	11,7	15,7	6,9
GFAAS				5	1	21	40	21	4	42	10	20,2	23,0	-8,9	-12,3
ICP				18	0	23	48	23	4	47	5	18,1	11,6	-0,8	-1,8
ICP-MS				7	3	16	41	16	4	41	5	27,6	12,5	-29,1	-13,9
Photometry				2	0			30		48				29,6	-1,0
Manganese	CD	1,14	0,77	42	25	1,14	0,77	1,15	0,11	0,77	0,08	9,6	10,1	0,5	0,0
FAAS				3	3										
GFAAS				12	9	1,17	0,76	1,17	0,03	0,79	0,05	2,7	6,0	2,6	2,1
ICP				18	9	1,10	0,77	1,11	0,12	0,75	0,09	10,8	12,2	-2,5	-2,5
ICP-MS				8	3	1,20	0,82	1,19	0,12	0,80	0,07	9,7	8,4	4,6	3,4
Photometry				1	1			38,60		27,20					
Cadmium	CD	0,53	1,21	42	9	0,53	1,21	0,53	0,09	1,18	0,13	16,3	11,3	-0,2	-2,8
GFAAS				20	2	0,54	1,23	0,54	0,09	1,18	0,16	17,5	13,4	2,1	-2,7
ICP				13	7	0,49	1,15	0,46	0,09	1,12	0,10	19,1	8,8	-12,4	-7,2
ICP-MS				8	0	0,55	1,22	0,55	0,04	1,23	0,08	8,1	6,4	3,9	1,8
Polarography				1	0			0,52		1,05				-1,9	-13,2
Lead	CD	3,27	4,81	43	14	3,27	4,81	3,26	0,48	4,81	0,46	14,7	9,6	-0,3	-0,1
GFAAS				22	5	3,30	4,90	3,28	0,62	4,81	0,60	18,9	12,4	0,4	0,0
ICP				12	8	3,19	4,76	3,14	0,18	4,77	0,11	5,8	2,2	-4,0	-0,8
ICP-MS				8	1	3,31	4,82	3,30	0,10	4,86	0,14	3,0	2,9	1,0	1,1
Polarography				1	0			3,07		4,54				-6,1	-5,6

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.dev. % 1	Rel. std.dev. % 2	Relative error % 1	Relative error % 2
Copper	CD	132,2	82,2	42	4	132,2	82,2	133,8	10,6	82,7	6,5	7,9	7,9	1,2	0,6
FAAS				6	0	130,4	82,2	131,6	7,7	80,5	9,0	5,9	11,2	-0,4	-2,1
GFAAS				14	3	131,0	81,4	130,9	11,4	83,1	6,3	8,7	7,6	-1,0	1,1
ICP				13	0	133,0	82,1	136,9	12,7	83,4	7,1	9,3	8,5	3,6	1,4
ICP-MS				8	0	134,4	82,9	134,2	7,2	82,6	4,2	5,4	5,0	1,5	0,5
Polarography				1	1			25,0		18,0				-81,1	-78,1
Nickel	CD	5,64	9,80	41	6	5,64	9,80	5,71	0,76	9,70	1,05	13,3	10,9	1,2	-1,0
FAAS				1	1			<100		<100					
GFAAS				18	2	5,75	9,69	5,84	1,00	9,82	1,39	17,1	14,1	3,6	0,2
ICP				13	3	5,56	9,65	5,47	0,53	9,45	0,83	9,8	8,8	-3,1	-3,6
ICP-MS				9	0	5,78	9,91	5,73	0,35	9,76	0,47	6,2	4,9	1,6	-0,4
Zinc	CD	39,7	26,0	42	4	39,7	26,0	38,7	4,0	25,2	3,3	10,4	12,9	-2,5	-3,2
FAAS				11	1	38,0	26,1	39,2	4,6	26,5	3,2	11,8	12,0	-1,3	1,9
GFAAS				6	2	37,1	23,9	36,5	6,8	22,9	5,3	18,7	23,3	-8,2	-12,1
ICP				16	0	39,7	25,2	38,0	3,2	24,2	3,0	8,5	12,3	-4,2	-7,0
ICP-MS				8	0	41,1	26,4	40,7	2,6	26,6	1,3	6,4	4,9	2,4	2,3
Polarography				1	1			65,3		39,6				64,5	52,3

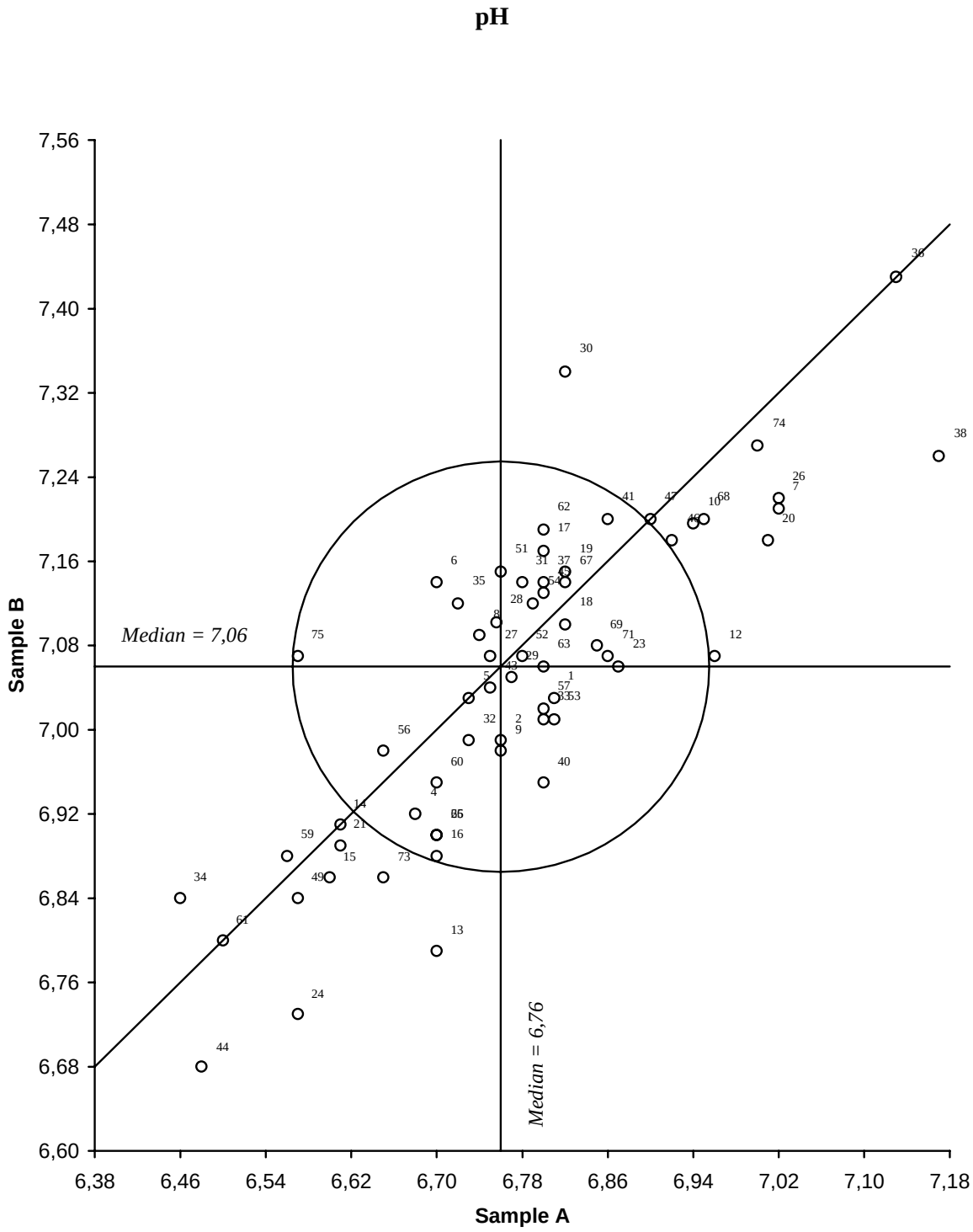

Figure 1. Youdendiagramme for pH, sample pair AB
Acceptable limit, given by the circle, is 0,2 pH units

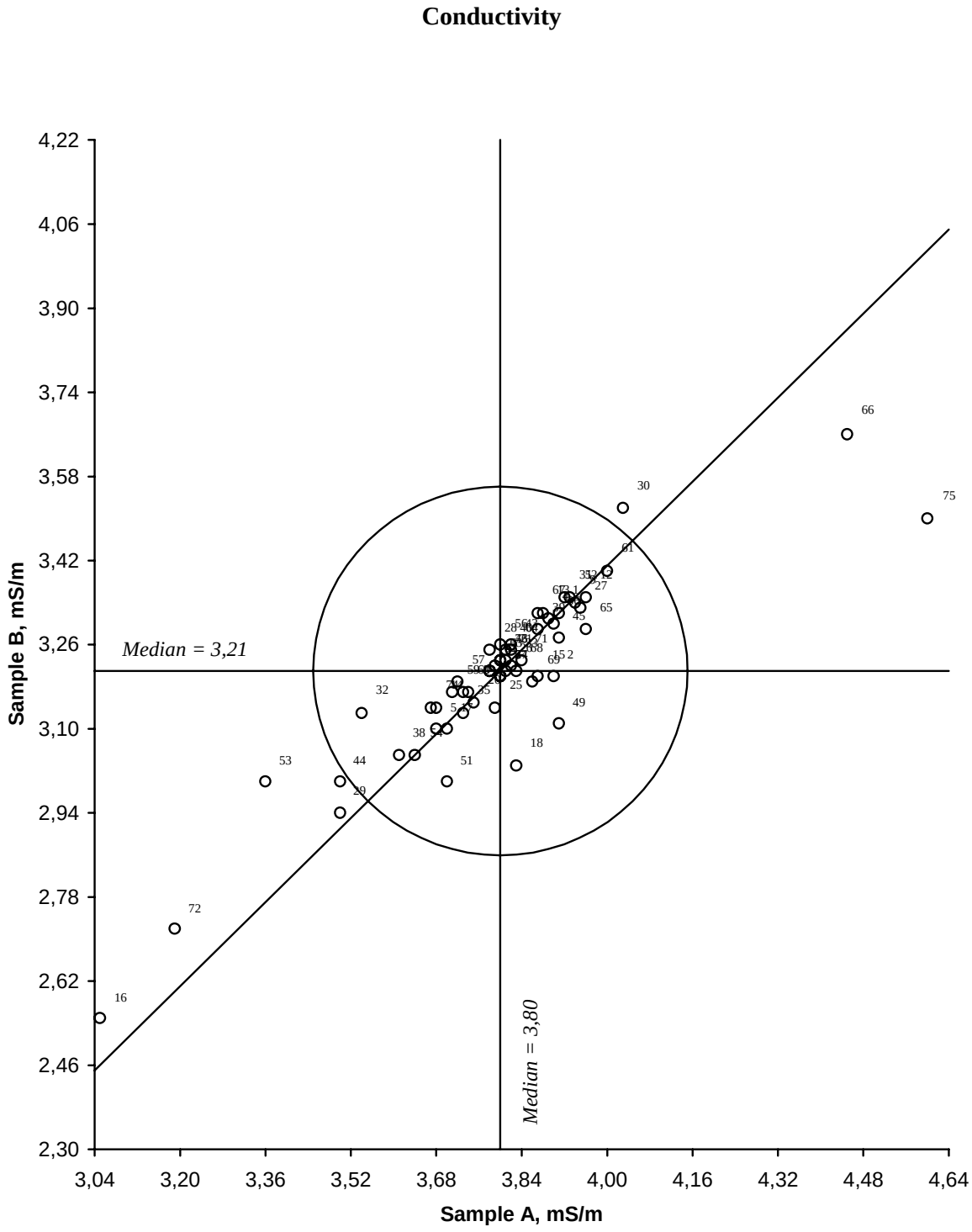

Figure 2. Youdendiagramme for conductivity, sample pair AB
Acceptable limit, given by the circle, is 10 %

Alkalinity

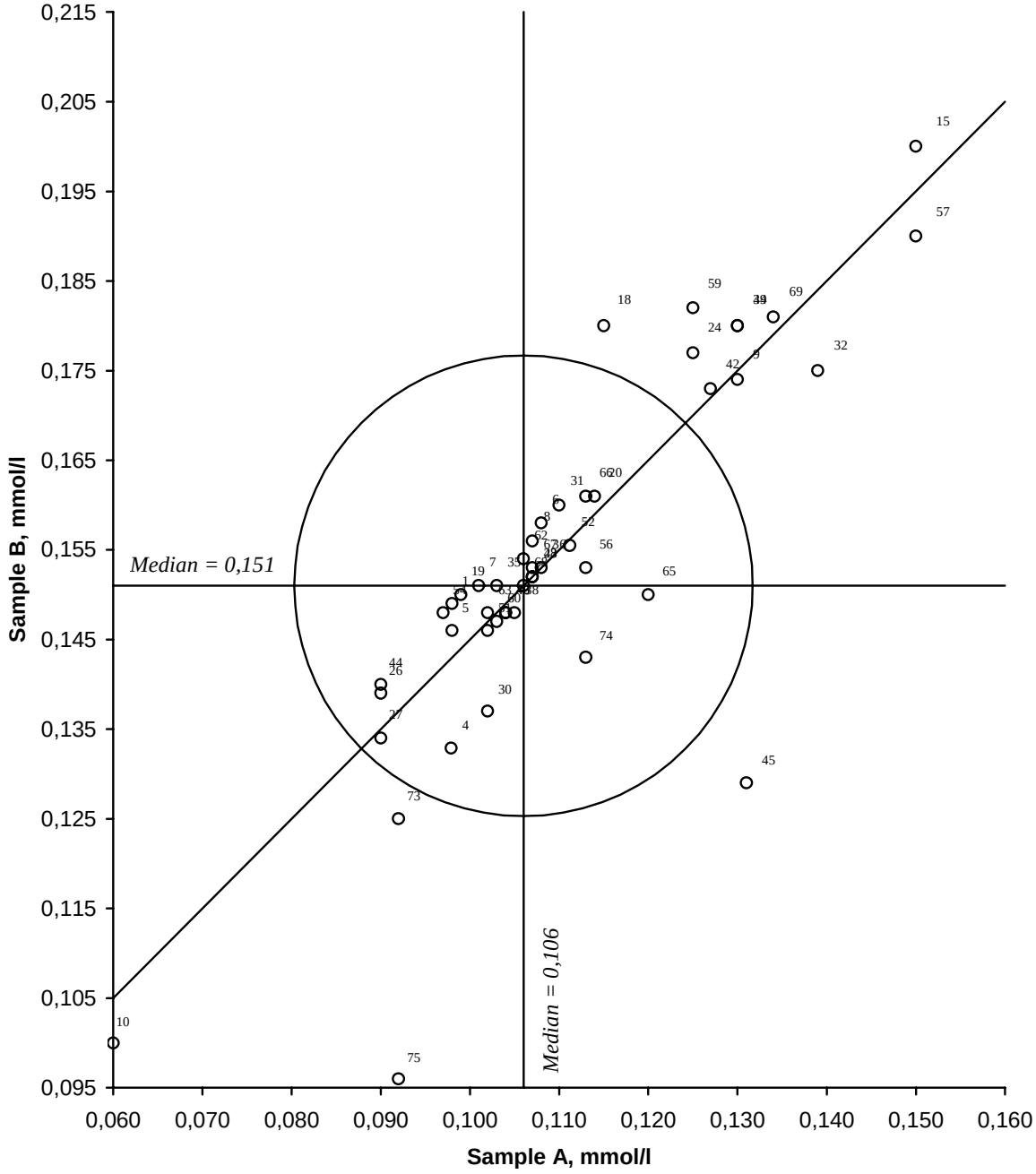

Figure 3. Youdendiagramme for alkalinity, sample pair AB
Acceptable limit, given by the circle, is 20 %

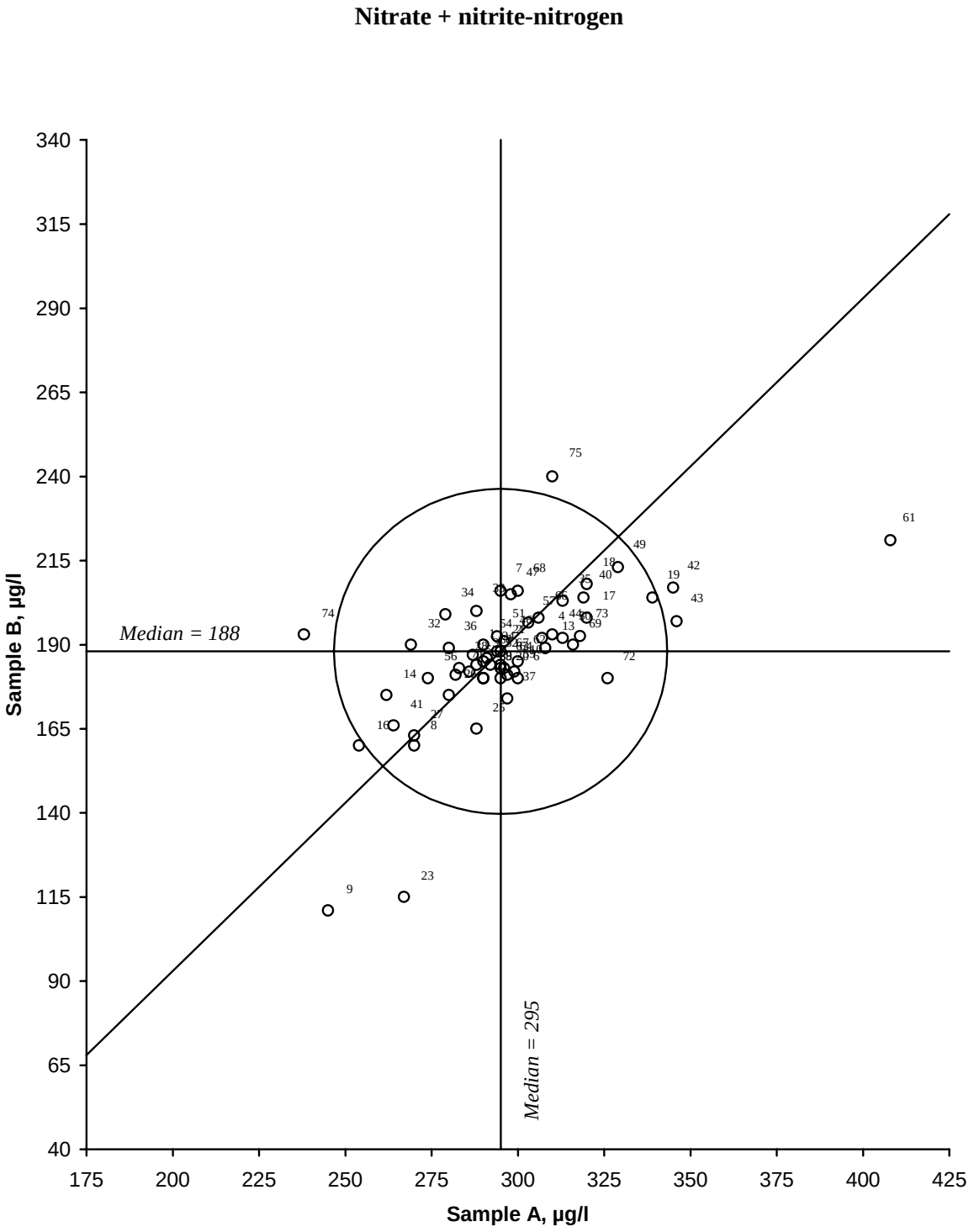

Figure 4. Youdendiagramme for nitrate + nitrite-nitrogen, sample pair AB
Acceptable limit, given by the circle, is 20 %

Chloride

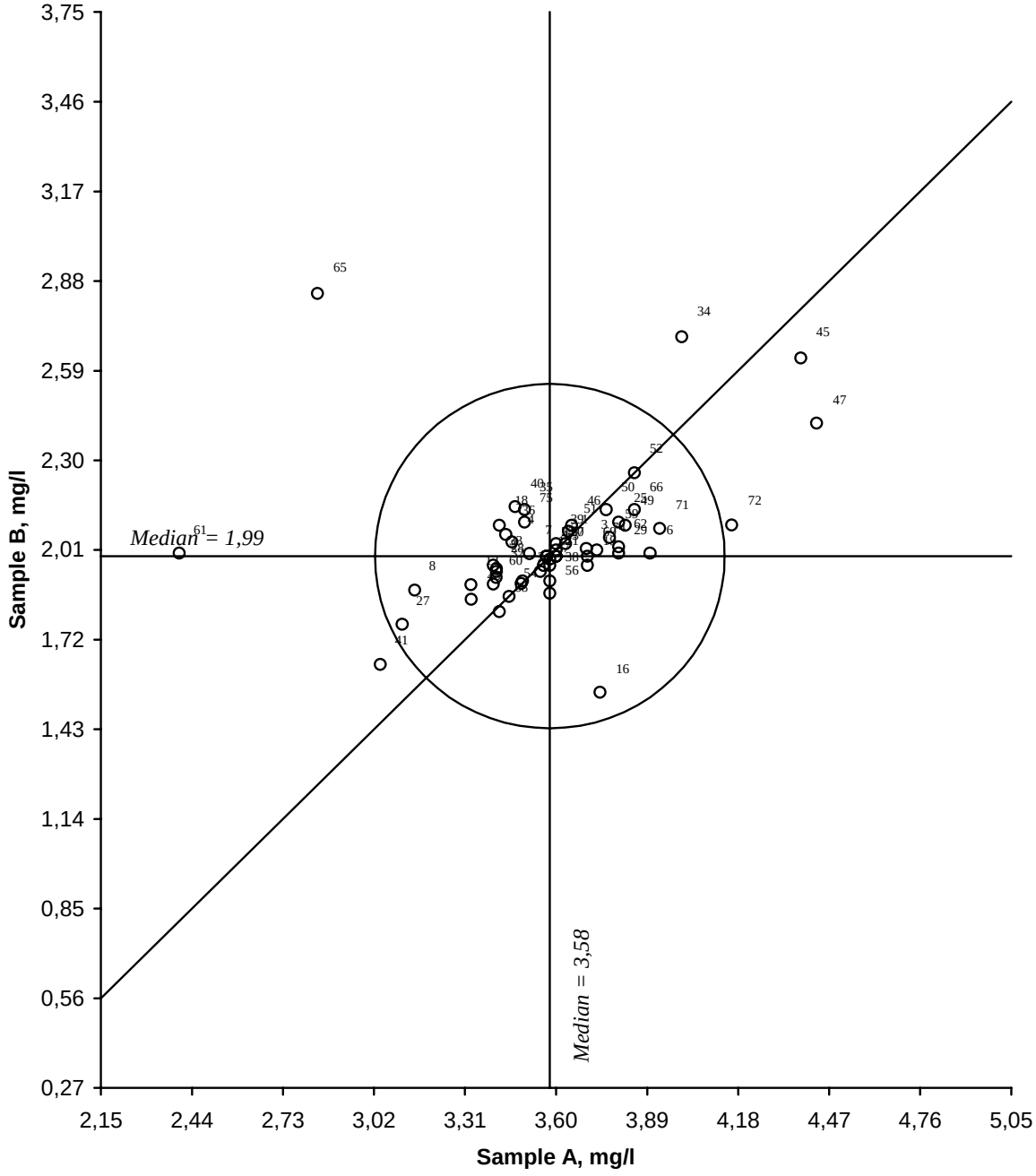

Figure 5. Youdendiagramme for chloride, sample pair AB
Acceptable limit, given by the circle, is 20 %

Sulfate

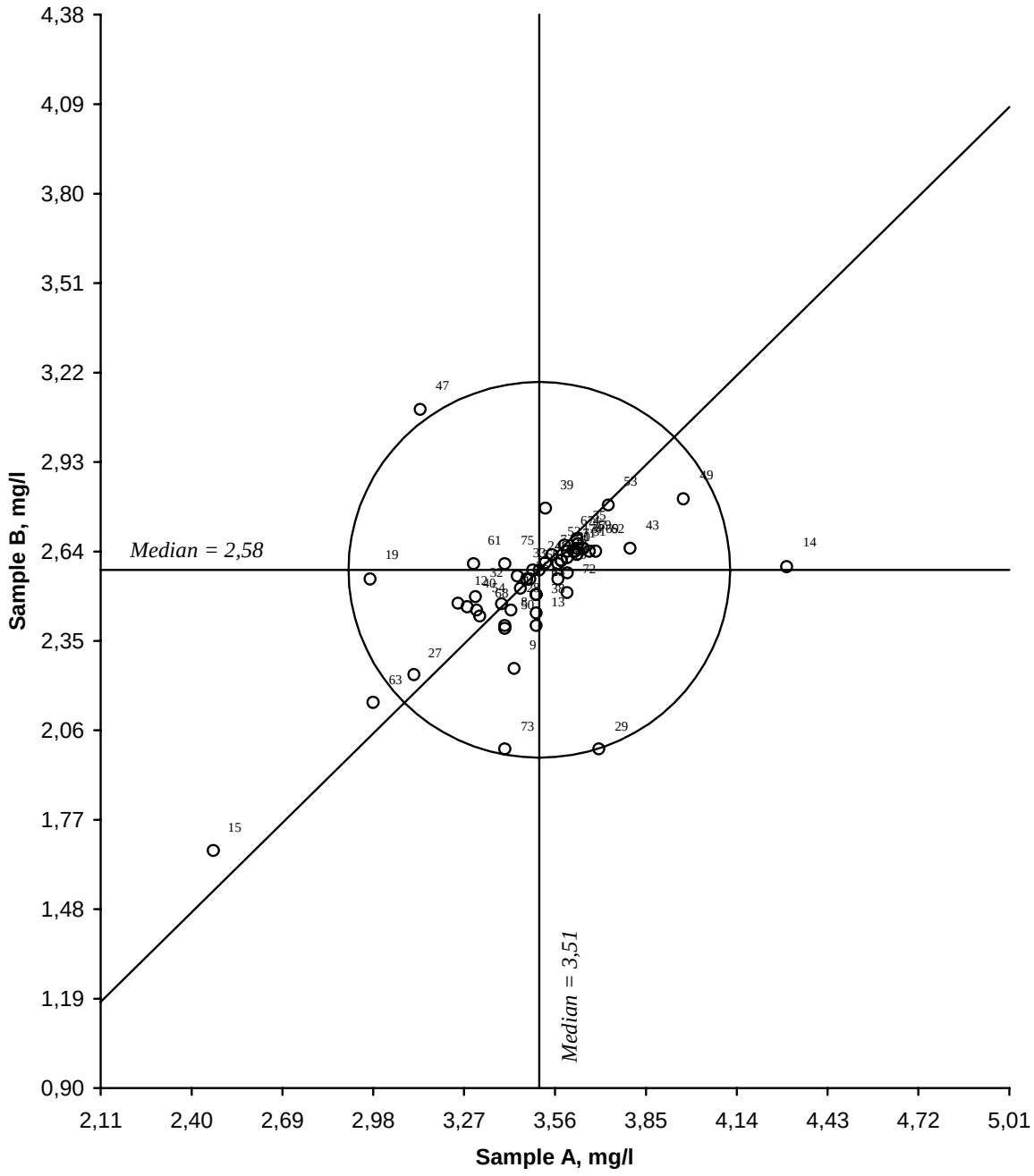

Figure 6. Youdendiagramme for sulfate, sample pair AB
Acceptable limit, given by the circle, is 20 %

Calcium

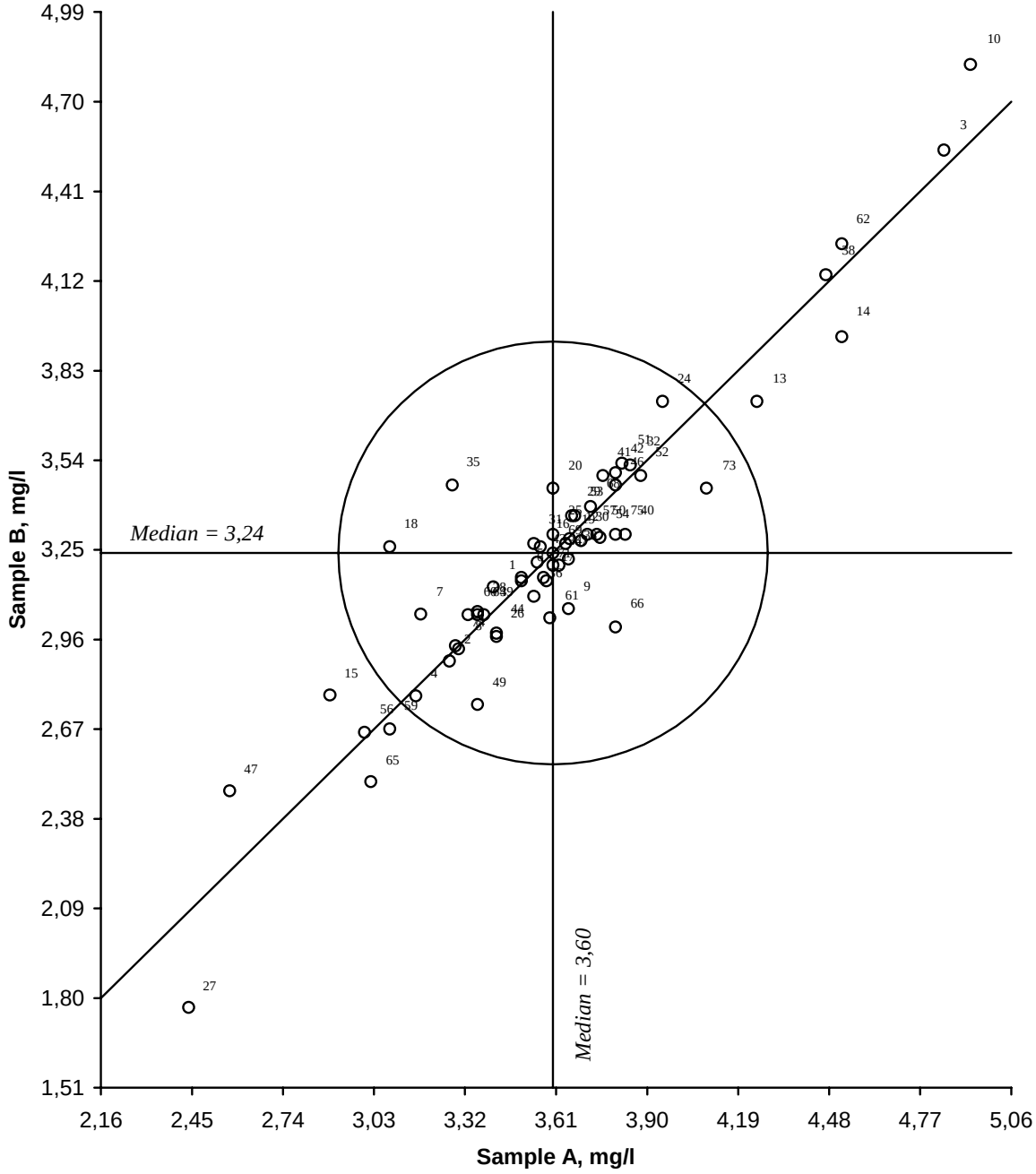

Figure 7. Youdendiagramme for calcium, sample pair AB
Acceptable limit, given by the circle, is 20 %

Magnesium

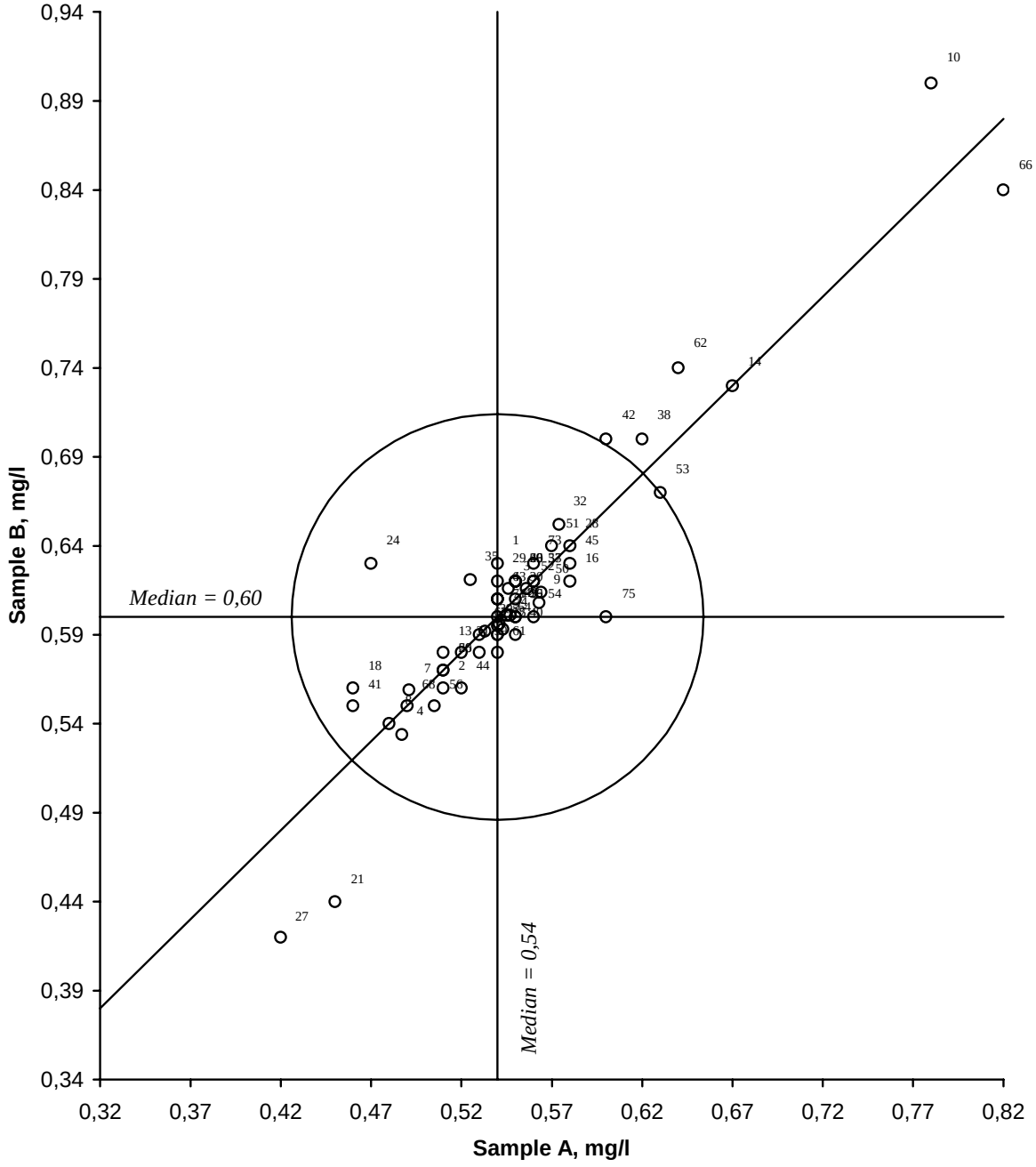

Figure 8. Youdendiagramme for magnesium, sample pair AB
Acceptable limit, given by the circle, is 20 %

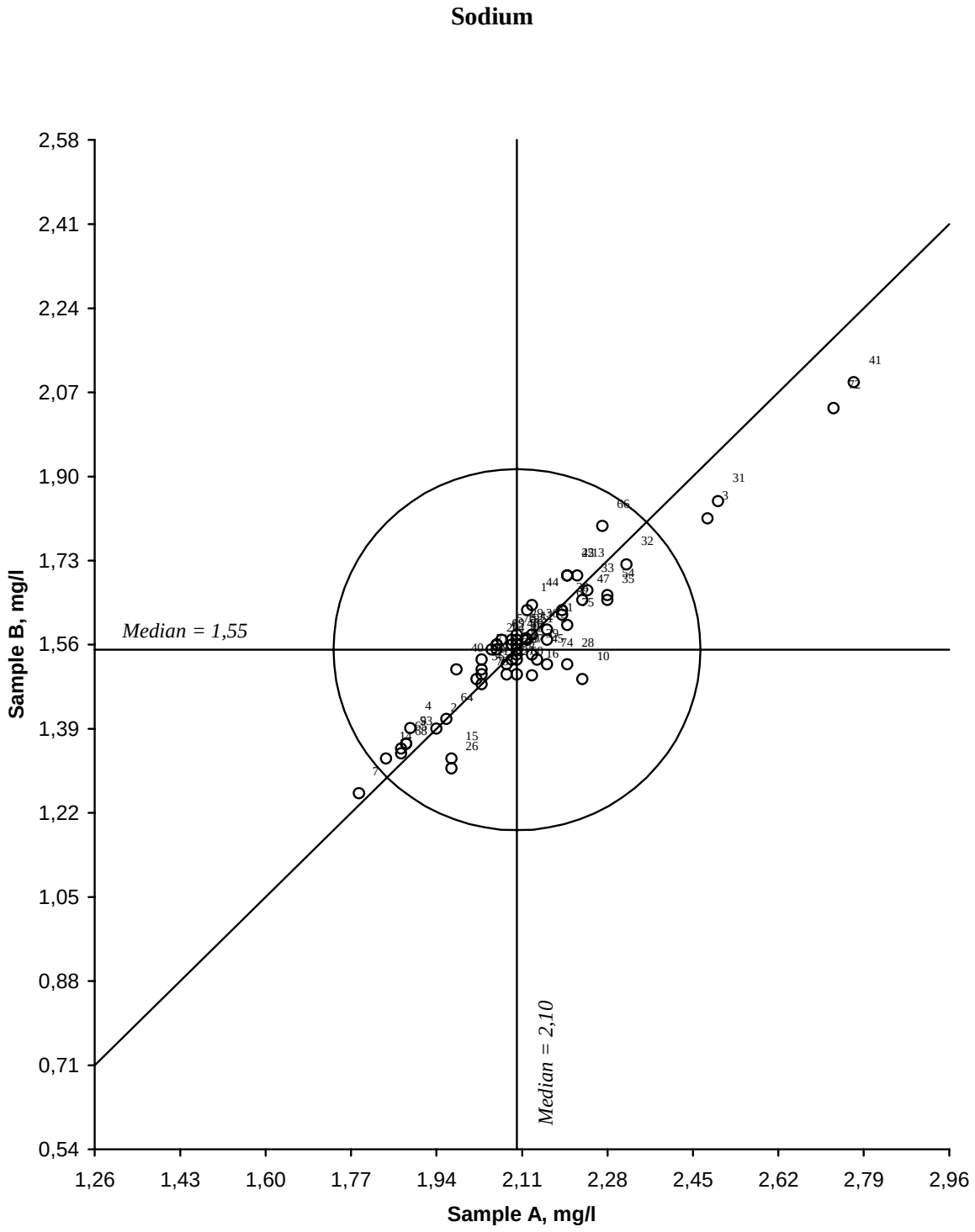

Figure 9. Youdendiagramme for sodium, sample pair AB
Acceptable limit, given by the circle, is 20 %

Potassium

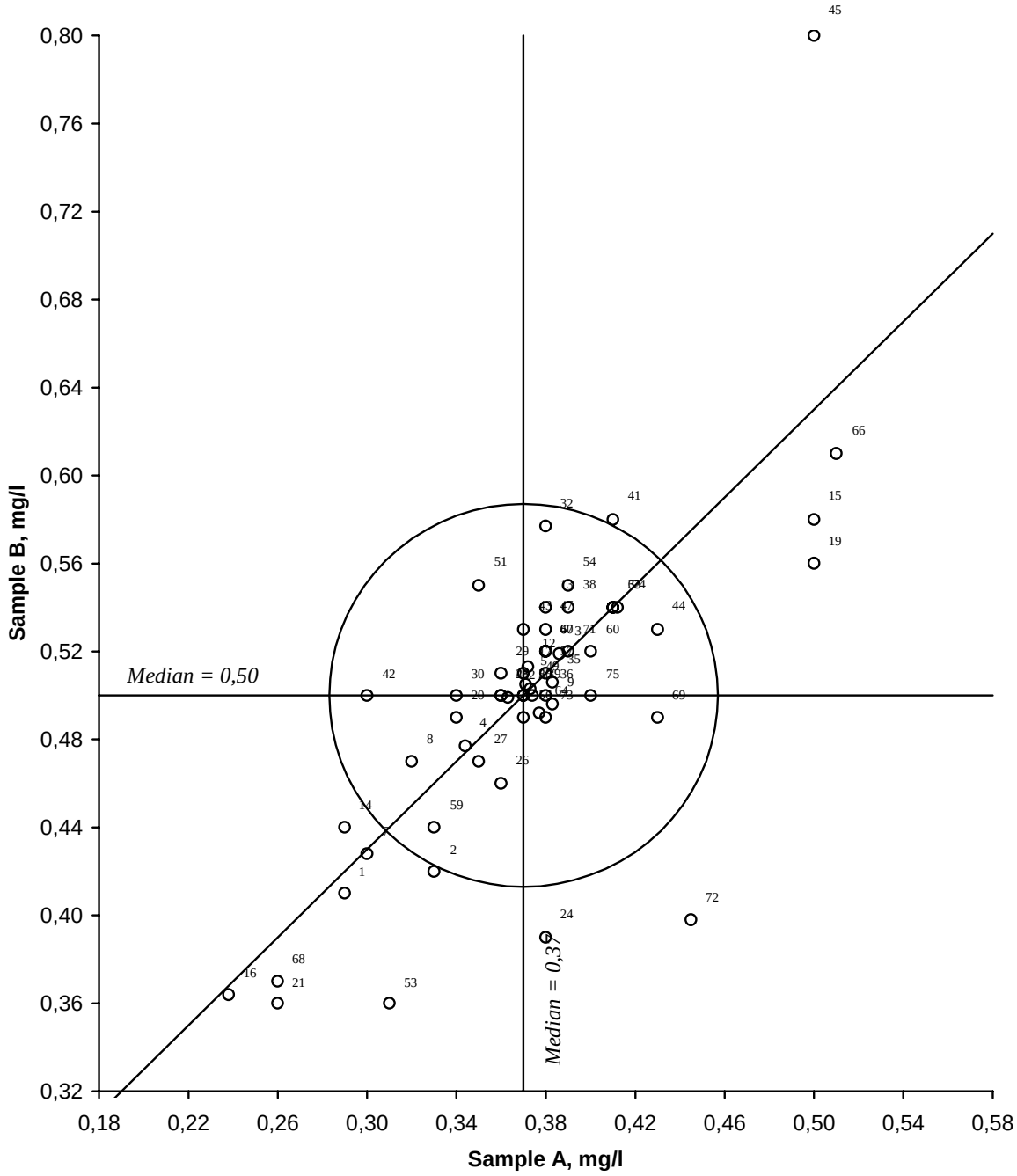

Figure 10. Youdendiagramme for potassium, sample pair AB
Acceptable limit, given by the circle, is 20 %

Iron

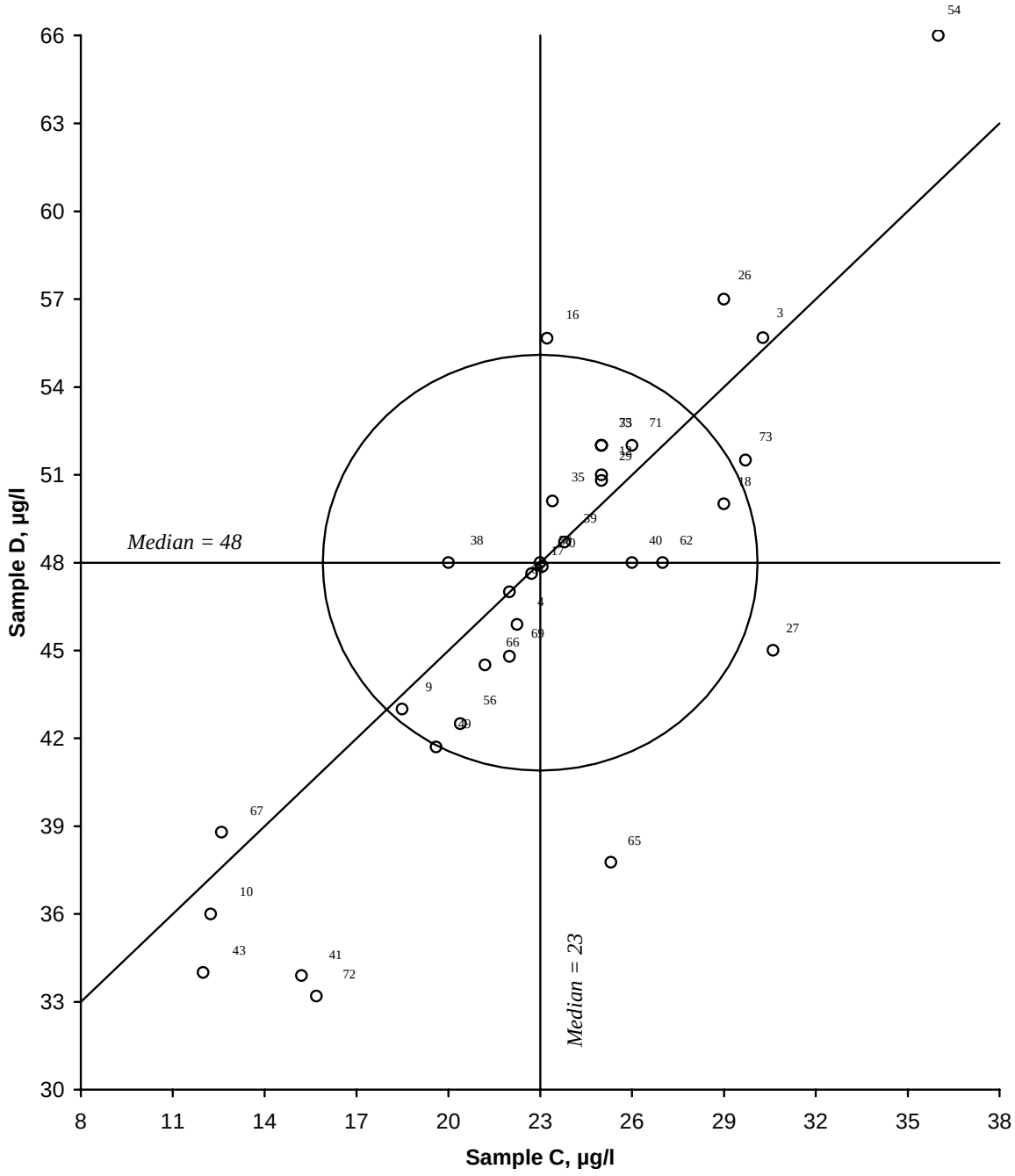

Figure 11. Youdendiagramme for iron, sample pair CD
Acceptable limit, given by the circle, is 20 %

Manganese

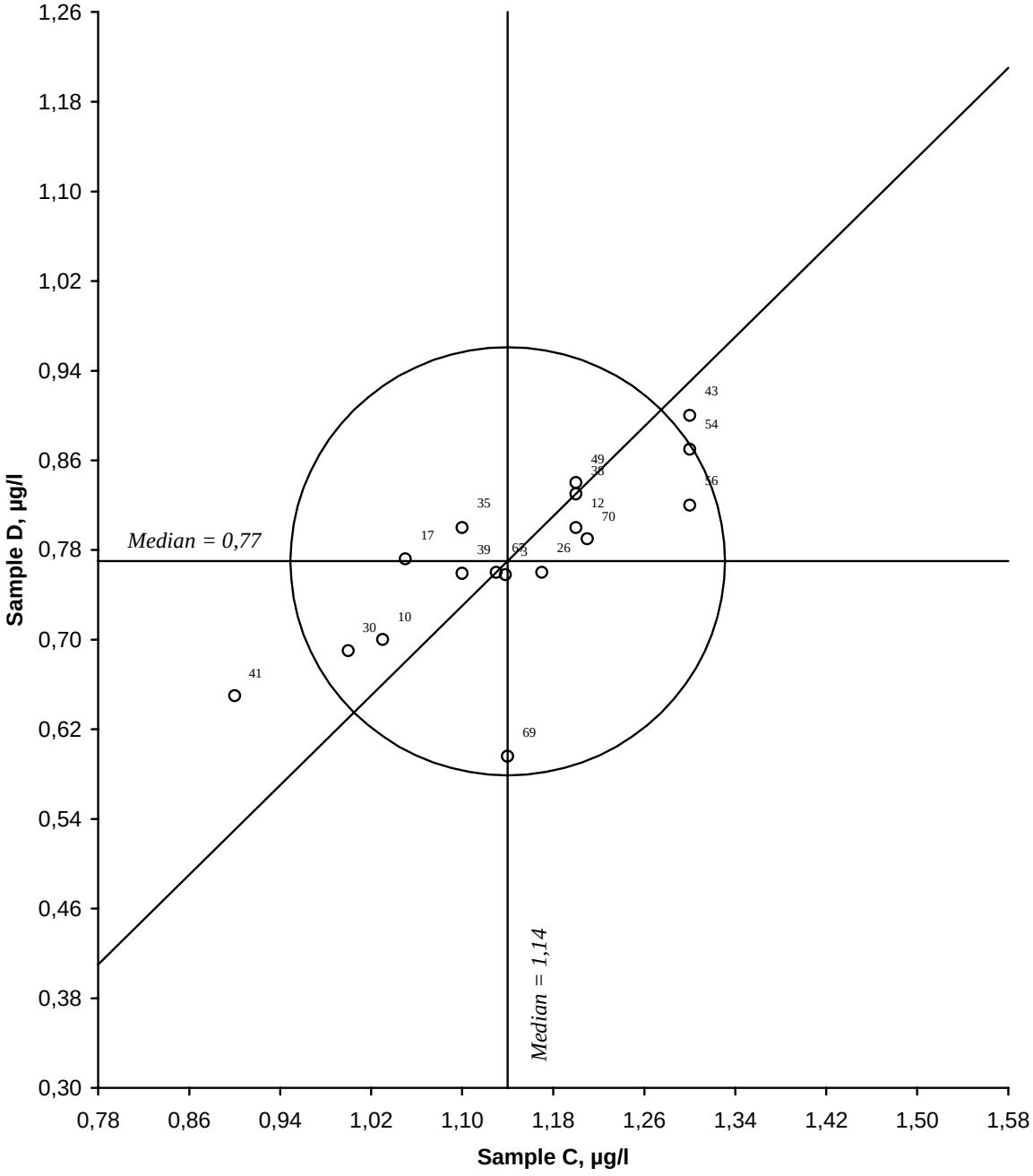

Figure 12. Youdendiagramme for manganese, sample pair CD
Acceptable limit, given by the circle, is 20 %

Cadmium

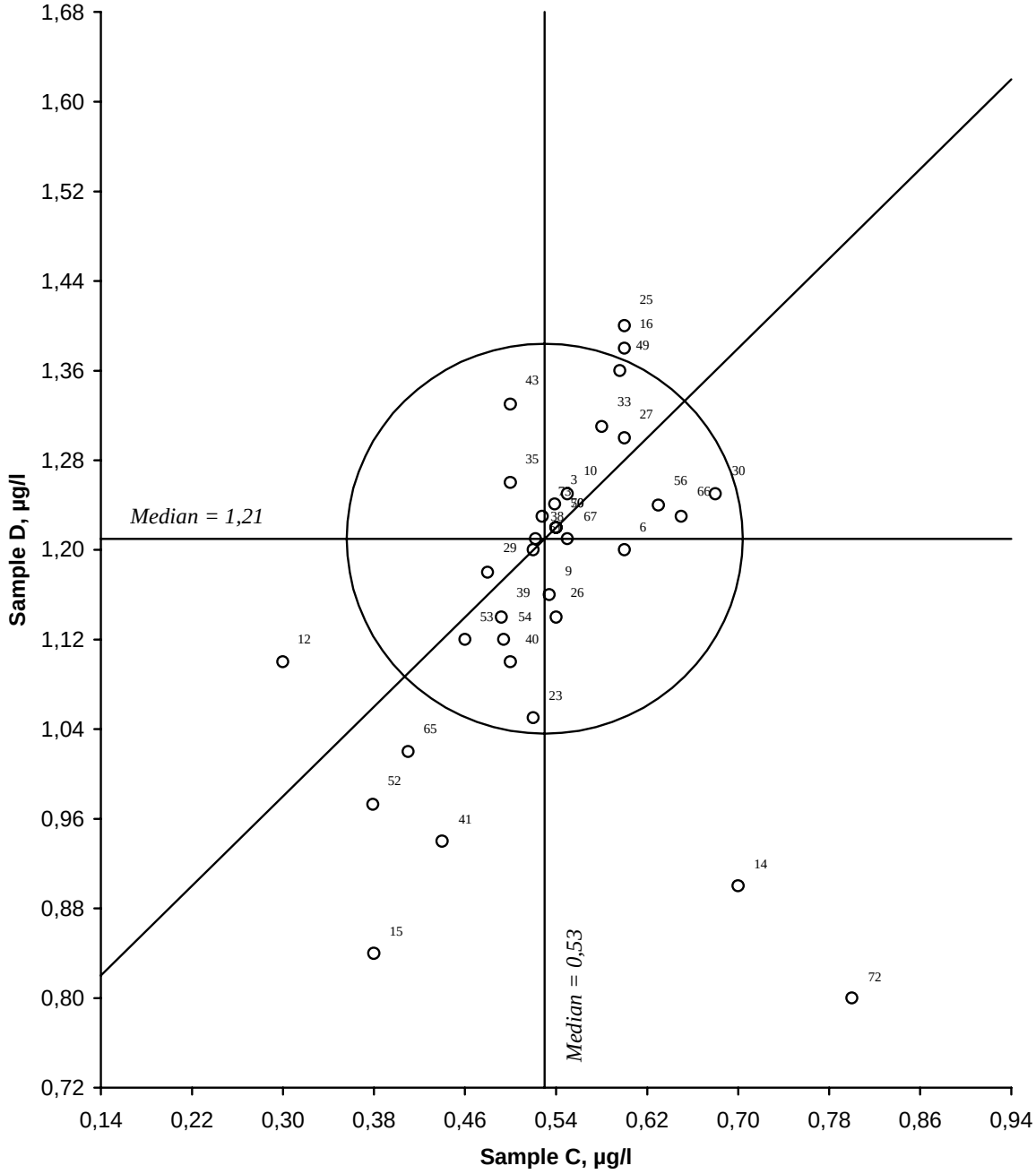

Figure 13. Youdendiagramme for cadmium, sample pair CD
Acceptable limit, given by the circle, is 20 %

Lead

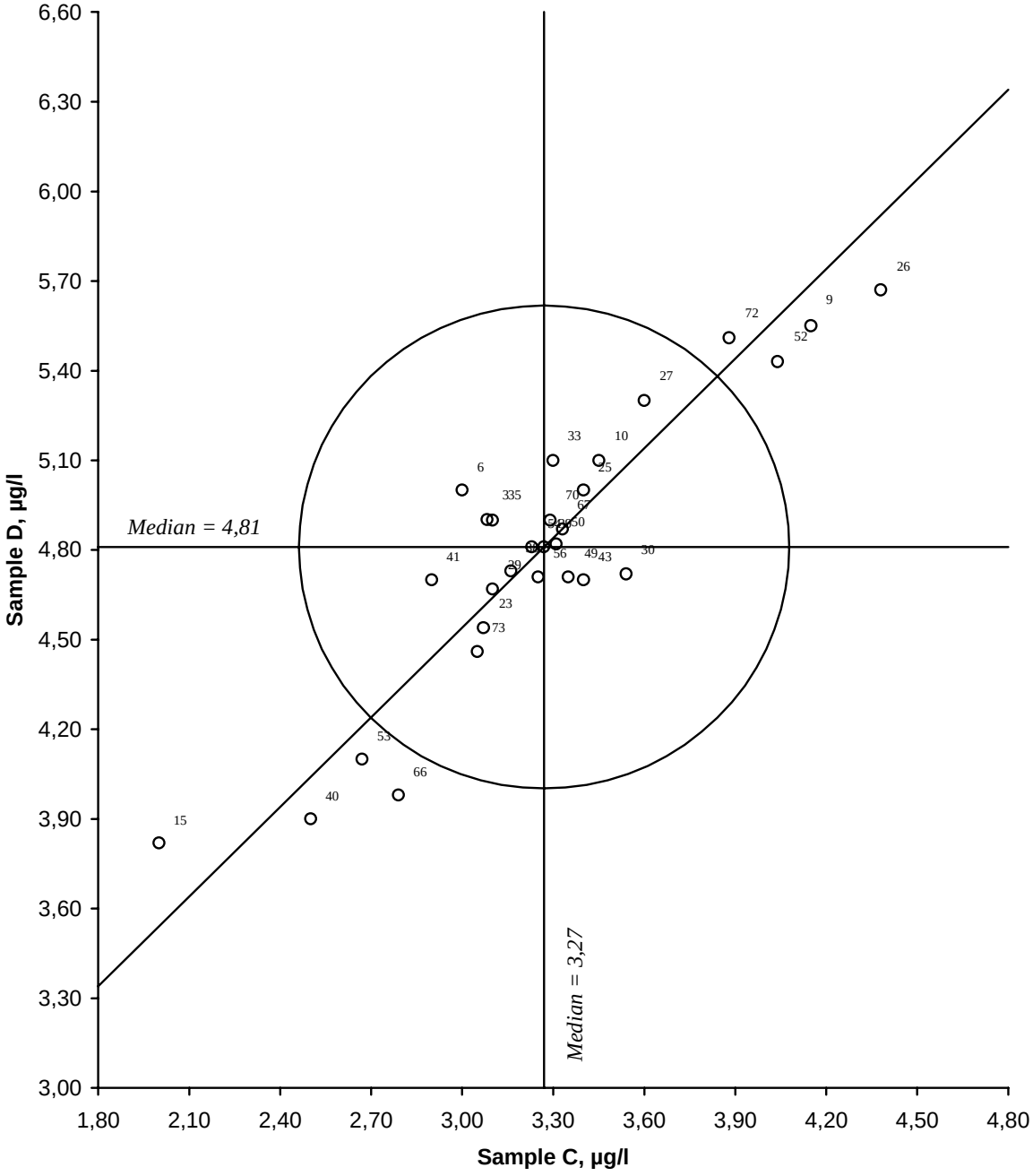

Figure 14. Youdendiagramme for lead, sample pair CD
Acceptable limit, given by the circle, is 20 %

Copper

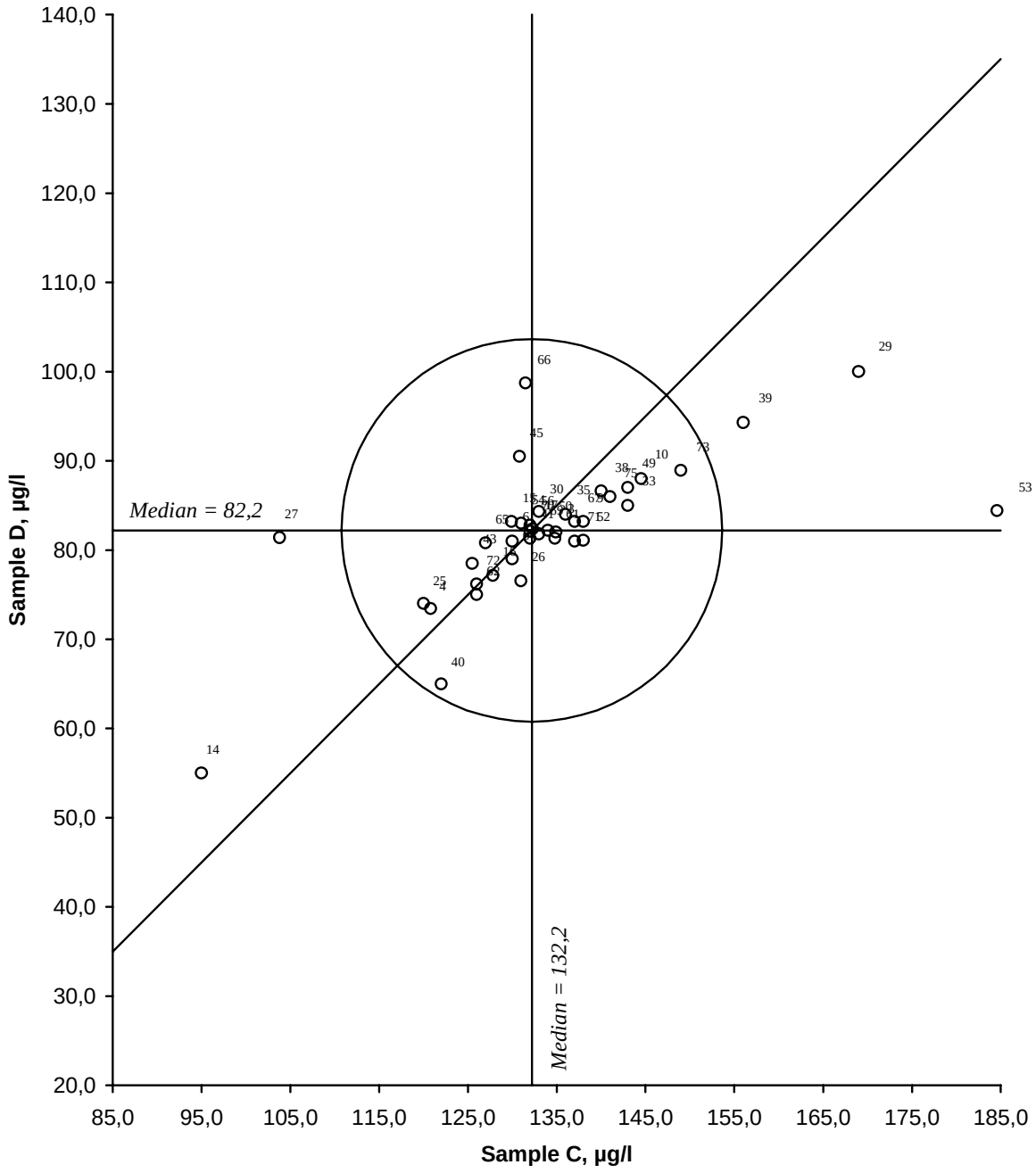

Figure 15. Youdendiagramme for copper, sample pair CD
Acceptable limit, given by the circle, is 20 %

Nickel

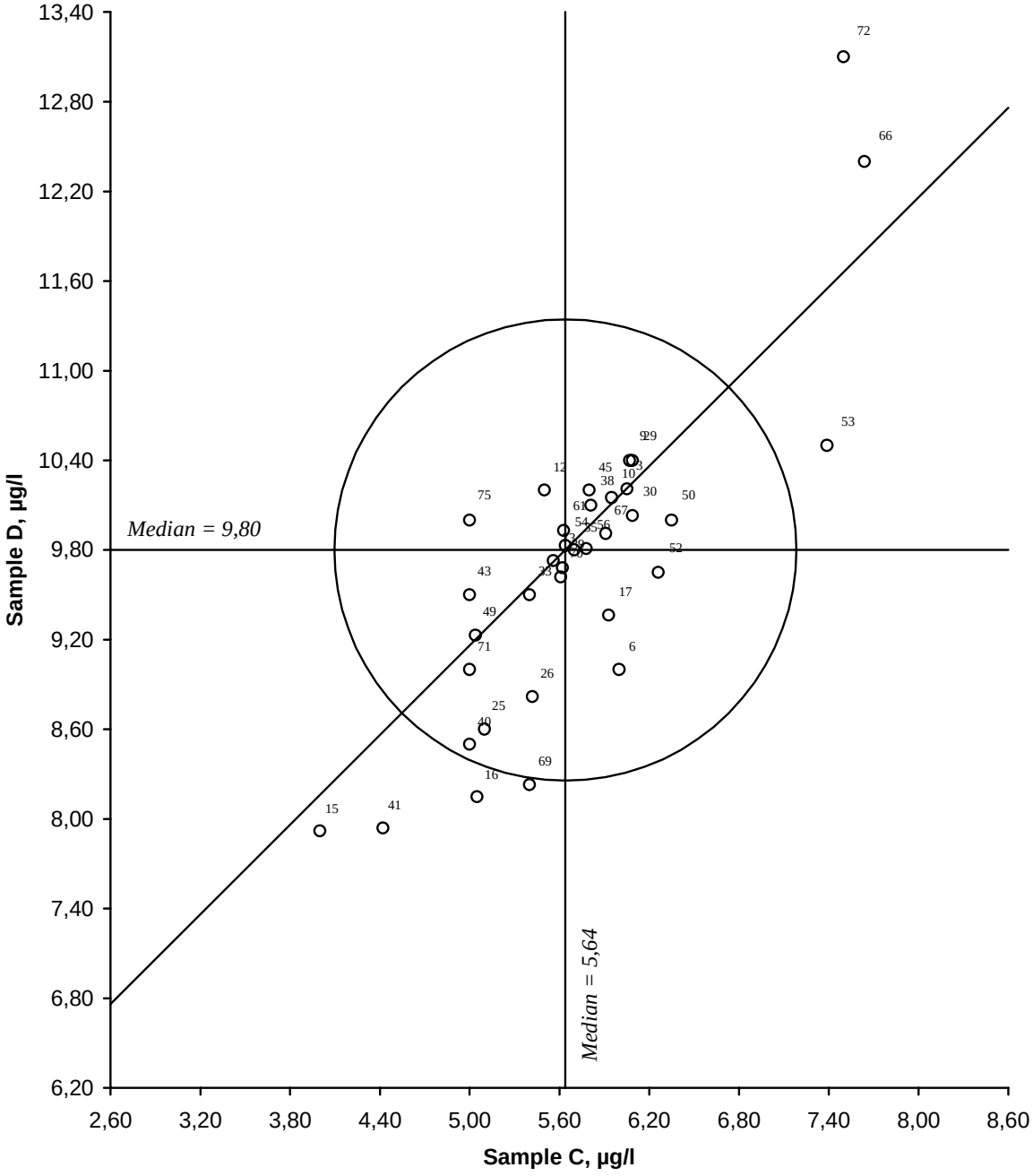

Figure 16. Youdendiagramme for nickel, sample pair CD
Acceptable limit, given by the circle, is 20 %

Zinc

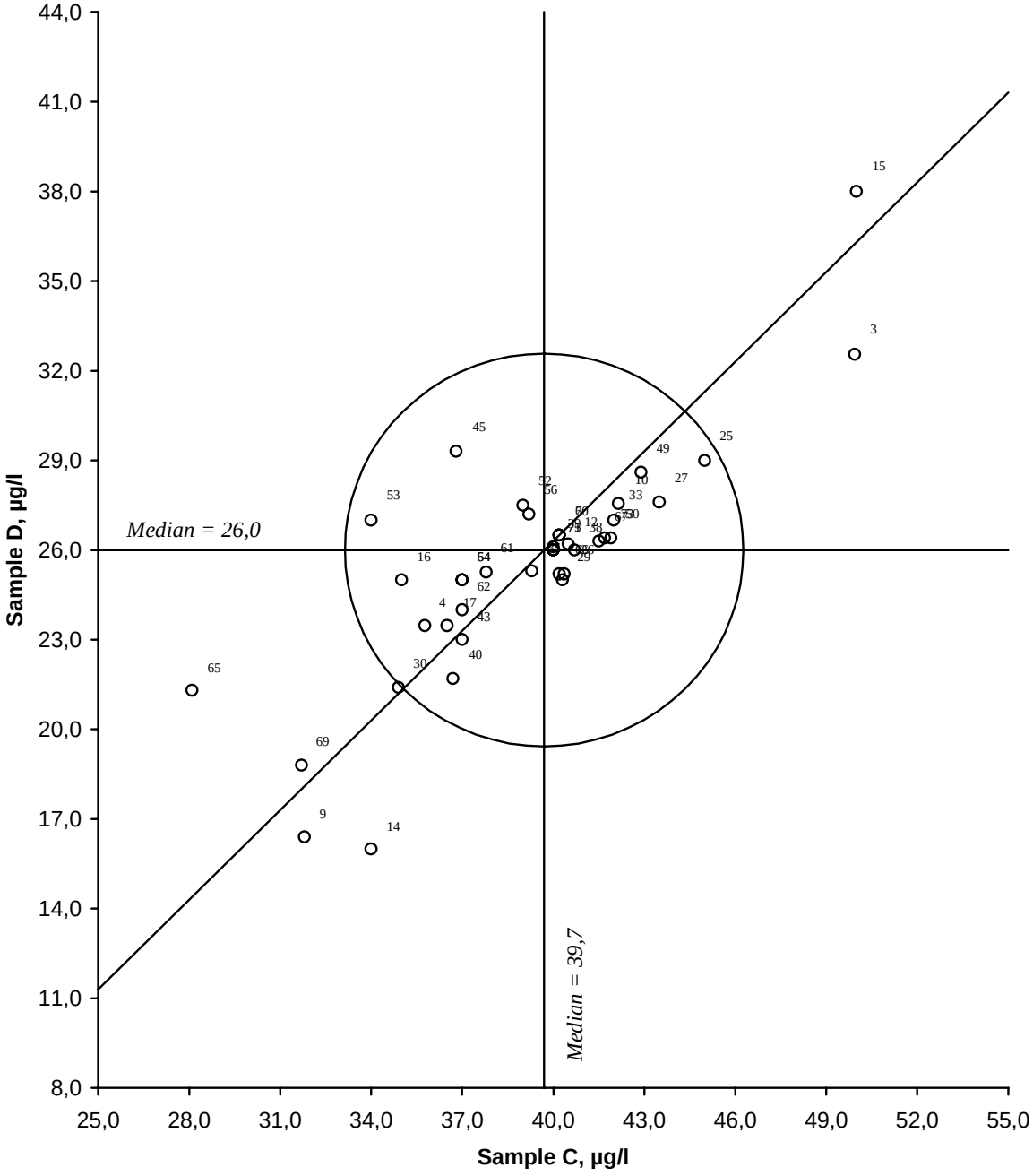

Figure 17. Youdendiagramme for zinc, sample pair CD
Acceptable limit, given by the circle, is 20 %

Just one laboratory equilibrated the solutions by bubbling with air containing 350 ppm CO_2 before reading the pH value, reported only somewhat higher results than the other laboratories. In the sample solutions used in this 17th intercomparison, the pH of the equilibrated solutions are about 0,4 units 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 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 for many laboratories.

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 misunderstanding, and the results from the responding laboratories 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 had been extended to the target value of ± 20 %, defined in the Manual (1), only three more results located just outside the 10 % acceptance circle, would be located within the circle and thus be defined as acceptable. An acceptance limit of ± 10 % seems to be a reasonable request.

4.3 Alkalinity

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 5.3. 55 laboratories reported results for alkalinity, and nearly 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). The results reported for the method using titration to both pH = 4,5 and 4,2 were very close to the results produced with the Gran plot method. One laboratory used a colorimetric method with methyl orange as indicator, and one laboratory used a method 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 or titration to both pH 4,5 and 4,2 reported, with few exceptions, results 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 in most cases beeing systematically too high. The end point titration to pH 5,6 gave results mainly located within the acceptance circle.

The overall result for alkalinity in this intercomparison is somewhat better than in the last intercomparison, even though only a little more than half of the results are acceptable. A possible reason for this is the fact that samples with low 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 values 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 these two methods. The hydrazine method used by three laboratories gave acceptable 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 good results in one laboratory, while the results from the other laboratory were extremely too high.

This time 82 % of the results are evaluated as acceptable, which is much better than in the last intercomparison. One probable reason for this may be that the concentrations of nitrate-nitrogen were higher 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. 46 out of 62 laboratories determined chloride by ion chromatography. The greatest deviations are observed for the manual photometric methods. The results determined with the argentometric method were too high, while somewhat varying results were reported for the mercurimetric method. One laboratory determined chloride with capillary electrophoresis, for chloride this method works well and the results being acceptable. The method using potentiometric titration gave acceptable results.

81 % acceptable results is the highest score for the last four intercomparisons, even when the concentrations for this analytical variable were not much higher than usual.

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 46 of 60 laboratories for the determination of the sulfate content. Six laboratories used a photometric method based on the dissociation of the barium-thorin complex. Three out of four result pairs were acceptable for the nephelometric method. One laboratory used capillary electrophoresis, the result pair being acceptable.

83 % acceptable result pairs is somewhat better than 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. 66 laboratories reported results for calcium, and 21 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 four 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.

77 % acceptable result pairs is higher than the last years intercomparison.

4.8 Magnesium

The magnesium results are presented in Figure 8, and the reported values are given in Table 5.8. One third of the participants is 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, 79 % 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 technique becomes increasingly more popular routine determinations of the alkaline metals, thus 21 participants used this technique in this intercomparison. ICP was used by 16 laboratories, and 5 used flame photometry. 92 % of the result pairs are located within the general target accuracy of ± 20 %, which is considered as a very 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. One laboratory using ICP-AES reported the 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 only 51 % of the result pairs are located inside this circle. 39 laboratories submitted results for iron, of which 18 and 7 used ICP and ICP-MS, respectively, while 7 and 5 used flame and graphite furnace atomic absorption, respectively. Only two laboratories used a photometric method, one laboratory using a manual determination with TPTZ, the other one used an automated method, both laboratories had acceptable results.

Some laboratories using ICP-AES have rather high detection limits, and thus reported their results as "less than" the value of the detection limit. 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. As little as 36 % of the result pairs are located inside this circle, which is extremely low compared to the former intercomparisons, however, the concentrations used this time are much lower than earlier. 42 laboratories submitted results for manganese, of which 18 and 8 used ICP and ICP-MS, respectively, while 3 and 12 used flame and graphite furnace atomic absorption, respectively. The flame atomic absorption spectrometry is not

sensitive enough for these sample concentrations. 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, 60 % of the result pairs are located inside this circle. 42 laboratories submitted results for cadmium, of which 13 and 8 used ICP-AES and ICP-MS, respectively, while 20 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-AES - 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 dominating some 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, only 49 % of the result pairs are located inside this circle. 43 laboratories submitted results for lead, of which 12 and 8 used ICP-AES and ICP-MS, respectively, while 22 used graphite furnace atomic absorption. There are only small differences between the results determined by the different methods for lead, however, the ICP-AES method is probably too little 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 ten laboratories have reported their results below the detection limit. The results from determination with polarography are acceptable.

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, 83 % of the result pairs are located inside this circle, which is very good. Very high concentrations used for copper this time are surely a reason for the good results. 42 laboratories submitted results for copper, of which 13 used ICP-AES and 8 used ICP-MS, while 14 and 6 used graphite furnace and flame atomic absorption, respectively. The deviating results are affected mainly by systematic errors. The results determined with polarography are extremely too low for this metal.

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. 41 laboratories submitted results for nickel, of which 13 and 9 used ICP-AES and ICP-MS,

respectively, while 18 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, 76 % of the result pairs are located inside this circle. 42 laboratories submitted results for zinc, of which 16 and 8 used ICP-AES and ICP-MS, respectively, while 11 and 6 used flame and graphite furnace atomic absorption, respectively. The results determined with polarography are systematically too low. Generally, 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, i.e. fixed or relative acceptance limits.

In Table 2 an evaluation of the results of intercomparison 0317 is presented, based on the target accuracy (except for pH and conductivity), where the number and percentage of acceptable results are given. 71 % of the results submitted by the participants are acceptable when compared to the acceptance limits given above, i.e. on average, about 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 accurate and 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 spreading 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 wider acceptance limit only 57 % 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 strongly 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. This is especially important for the equilibration method, which normally gives results quite higher than the other methods. This time the differences between the results produced during stirring the solution, or no stirring, were only minor.

Because of the high precision of the reported results for conductivity in earlier intercomparisons, we have reduced the acceptance limit for this analytical variable from ± 20 % to ± 10 %. The number of acceptable results for conductivity, 82 %, is better than the last intercomparison (Table 2). If we increase the acceptance limit to the target value, only a few more result pairs would be inside the circle, and the number of acceptable results would increase a little. It is a problem that many laboratories report their results in the units they normally use at their laboratory. They very often do not write the unit used, nor do they use the unit asked for in this intercomparison, mS/m. Some correspondence with the laboratories was therefore necessary to clarify the right results.

Table 2. Evaluation of the results of intercomparison 0317. 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 included in the evaluation.

Analyte and unit	Sample pair	True value 1	True value 2	Accept. limit, %	N	n	% accepatble res. for intecalibration 0317	0216	0115	14
pH	AB	6,76	7,06	0,2 *	69	39	57	66	58	57
Conductivity, mS/m	AB	3,8	3,21	10 ¤	66	54	82	75	82	64
Alkalinity, mmol/l	AB	0,106	0,151	20	55	32	58	53	76	46
Nitrate + nitrite-nitrogen, µg/l	AB	295	188	20	65	53	82	59	77	51
Chloride, mg/l	AB	3,58	1,99	20	62	50	81	66	79	73
Sulfate, mg/l	AB	3,51	2,58	20	60	50	83	76	82	72
Calcium, mg/l	AB	3,6	3,24	20	66	51	77	62	82	55
Magnesium, mg/l	AB	0,54	0,6	20	66	52	79	67	75	58
Sodium, mg/l	AB	2,1	1,55	20	64	59	92	88	93	91
Potassium, mg/l	AB	0,37	0,5	20	64	45	70	73	85	76
Iron, µg/l	CD	23	48	20	39	20	51	71	41	74
Manganese, µg/l	CD	1,14	0,77	20	42	15	36	76	64	75
Cadmium, µg/l	CD	0,53	1,21	20	42	25	60	63	66	65
Lead, µg/l	CD	3,27	4,81	20	43	21	49	59	51	47
Copper, µgl	CD	132,2	82,2	20	42	35	83	73	75	67
Nickel, µg/L	CD	5,64	9,8	20	41	28	68	68	68	42
Zinc, µg/l	CD	39,7	26	20	42	32	76	64	53	47
Total					928	661	71	(68)	(71)	(63)

* 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 better than in the last intercomparison, probably because the concentrations of bicarbonate in the samples used this time is a little higher than earlier. Also for this parameter there is some confusion about the unit.

For nitrate + nitrite 82 % of the result pairs are acceptable, this is much better compared to last year. The main reason for this is probably that the concentrations are higher 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 a little higher than usual. 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. The best results were obtained for copper and zinc, where 83 and 76 % of the results, respectively, are acceptable. For these elements the concentrations were well above the detection limits 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 limits for the methods used, and even below the detection limits 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

75 laboratories submitted results for this intercomparison. The best results were reported for the analytical variables sodium, sulfate and copper, where 92, 83 and 83 % of the results, respectively, were acceptable. The worst results were observed for lead, iron and manganese. Common for these analytical variables is that their concentrations are rather low and close to the detection limits of the methods used.

Overall, 71 % of the evaluated results were located within the general target accuracy of ± 20 %, or the special accuracy limit for pH and conductivity. Thus, about two third of the reported results are acceptable, which in part is explained by the rather low concentrations used for several analytical variables this time. When the concentrations are close to the detection limits 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 accuracy and comparability. Generally, the application of some analytical methods seems to be less suited for the water samples analyzed in this programme, as the detection limits of some methods applied by participants are too high, this is especially true for some manual methods. It is important that methods with sufficiently low detection limits 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

1. Convention on Long-range Transboundary Air Pollution. International Cooperative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes. Manual for Chemical and Biological Monitoring. March 1987, revised september 1996.

2. Youden, W.J.: Graphical Diagnosis of Interlaboratory Test Results. Industrial Quality Control. 1959, pp 15 - 24.

3. Youden, W.J., Steiner, E.H.: Statistical Manual of the Association of Official Analytical Chemists. Statistical Techniques for Collaborative Tests. Arlington, 1975.

4. Hindar, A.: The Effect of Stirring on pH Readings in Solutions of Low and High Ionic Strength Measured with Electrodes of Different Condition. Vatten 1984, 40, pp 312 - 19 (in norwegian).

5. Galloway, J.N., Cosby, B.T., Likens, G.E.: Acid Precipitation: Measurement of pH and Alkalinity. Limnol. Oceanogr. 1979, 24, 1161.

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	University of Barcelona	Vielha	Spain
2	Forest Ecosystem Research Group	Dublin	Ireland
3	Vlaamse Milieumaatschappij	Antwerpen	Belgium
4	Great Lakes Forest Centre	Sault St. Marie	Canada
5	MOEE, Dorseth Research Facility	Dorseth	Canada
6	North Ostrobothnia Regional Env. Centre	Oulu	Finland
7	Universita degli Studi di Siena	Siena	Italy
8	Laboratorio Biologico Provinciale	Laives	Italy
9	T.G.Masaryk Water Research Institute	Prague	Czech Republic
10	Environmental Research Unit	Dublin	Ireland
12	Institute of Environmental Protection	Warsaw	Poland
13	EAWAG Limnological Research Center	Kastanienbaum	Switzerland
14	Polish Academy of Sciences	Krakow	Poland
15	Geological Survey of Estonia	Tallinn	Estonia
16	Heilongjang Environmental Monitoring	Harbin	China
17	MOEE, Toronto Laboratory	Etobicoke	Canada
18	Huumaa Environmental Laboratory	Kardla	Estonia
19	Center for Chemical Analysis Keldnaholt	Reykjavik	Iceland
20	CNR Istituto Italiano di Idrobiologia	Pallanza	Italy
21	IVL	Gothenburg	Sweden
23	Yantai Environmental Monitoring Centre	Yantai	China
24	National Institute of Biology, LFTER	Ljubljana	Slovenia
25	Staatliche Umweltbetriebgesellschaft, UBG	Chemnitz	Germany
26	Water Pollution Observation Laboratory	Riga	Latvia
27	Laboratorio Studi Ambientali	Paradiso	Switzerland
28	Adirondac Lakes Survey Corporation	Raybrook	USA
29	University of Maine	Orono	USA
30	Institute for Ecology of Industrial Areas	Katowice	Poland
31	Charles University	Prague	Czech Republic
32	Hunan Research Institute of Env. Prot.	Changsha	China
34	Laboratory of Hydrochemistry at the	Tartu	Estonia
35	South Estonian Environm. Protection Agency	Tartu	Estonia
36	Aquatic Chemistry Project	Winnipeg	Canada
37	Freshwater Institute	Winnipeg	Canada
38	Norsk institutt for vannforskning	Oslo	Norway
39	Landesumweltamt Nordrhein Westfalen	Essen	Germany
40	Karelian Research Centre	Petrozavodsk	Russia
41	ISSeP Colfontaine	Colfontaine	Belgium
42	Werkgroep Milieubiologie	Nijmegen	Netherlands
43	Chemical Laboratory of CGU	Praha 5	Czech Republic
44	SLU, Skoglig Marklæra	Uppsala	Sweden
45	Water Pollution Observation Laboratory	Minsk	Belarussia

46	Institut fur Zologie, Universitat Innsbruck	Innsbruck	Austria
47	Institute for Ecological Toxicology	Baikalsk	Russia
49	Estonian Environment Research Laboratory	Tallinn	Estonia
50	National Rivers Authority	Furnace	United Kingdom
51	DAFS Freshwater Laboratory	Pitlochry	United Kingdom
52	Kymen Water and Environment District	Kouvola	Finland
53	D.R. Ambiente Alentejo	Santo Andre	Portugal
54	Swedish University for Agricultural Sciences	Uppsal	Sweden
56	Istituto Agrario di S. Michele	Michele	Italy
57	Guizhou Research Instiute of Environmental	Guiyang	China
59	Acid Deposition and Oxidant Research	Niigata-shi	Japan
60	Institute of Hydrobiology	Budejovice	Czech Republic
61	Karntner Institut fur Seewasser Forschung	Klagenfurt	Austria
62	Finnish Forest Research Institute	Rovaniemi	Finland
63	Lapland Water and Environment District	Rovaniemi	Finland
64	Finnish Forest Research Institute	Vantaa	Finland
65	S.C. Abnalist Service S.R.L.	Bucharest	Romania
66	Instuitute of Biology	Syktyvkar	Russia
67	National Board of Waters and the	Helsinki	Finland
68	CNR-IRSA Water Research Institute	Milano	Italy
69	Chongqing Inst. Of Environmental Science	Chongqing	China
70	Umweltbundesamt, II 6.6	Langen	Germany
71	Umweltbundesamt, II 6.5	Langen	Germany
72	Guangzhou Research Institute of	Guangzhou	China
73	Environmental Protection Ministry	Vilnius	Lithuania
74	METI, US Environmental Protection Agency	Corvallis	USA
75	Centre for Ecology & Hydrology	Wallingford	United Kingdom

Number of participating laboratories (N) from the different countries being represented in intercomparison 031.

Country	N	Country	N
Austria	2	Lithuania	1
Belarussia	1	Netherlands	1
Belgium	2	Norway	1
Canada	5	Poland	3
China	6	Portugal	1
Czech Republic	4	Romania	1
Estonia	5	Russia	3
Finland	6	Slovenia	1
Germany	4	Spain	1
Iceland	1	Sweden	3
Ireland	2	Switzerland	2
Italy	5	United Kingdom	3
Japan	1	USA	3
Latvia	1		

Appendix B.

Preparation of samples

The sample solutions were prepared from natural water collected from the river Ula, located in Rondane, and the lake Maridalsvannet, located outside Oslo, Norway. Raw water was collected in polyethylene containers and brought to the laboratory for storage. These containers were stored at room temperature for several weeks at the laboratory. During this stabilization period suspended matter settled. The solutions were filtrated through 0,45 µm membrane filter, and small aliquots were removed from the filtrate to determine the background 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 2003, a few weeks before mailing the samples to the participants. The last sample was analyzed at the end of July 2003. 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	6,93	0,11	7,15	0,07
Conductivity mS/m	3,65	0,04	3,06	0,02
Alkalinity mmol/l	0,104	0,002	0,146	0,003
Nitrate/nitrite µg/l	287	10	192	12
Chloride mg/l	3,54	0,11	1,95	0,05
Sulfate mg/l	3,48	0,10	2,54	0,09
Calcium mg/l	3,60	0,04	3,20	0,04
Magnesium mg/l	0,534	0,002	0,589	0,009
Sodium mg/l	2,18	0,01	1,62	0,01
Potassium mg/l	0,383	0,006	0,533	0,006
	Sample C		**Sample D**	
Iron, µg/l	20,0	0,0	47,3	0,6
Manganese, µg/l	1,1	0,1	0,79	0,03
Cadmium, µg/l	0,539	0,020	1,23	0,02
Lead, µg/l	3,20	0,05	4,72	0,01
Copper, µg/l	139	1,2	84,9	1,6
Nickel, µg/l	5,71	0,09	9,94	0,19
Zinc, µg/l	40,5	0,2	25,8	0,2

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	6,81	7,03	3,91	3,32	0,098	0,149	287	187
2	6,76	6,99	3,90	3,20	0,069	0,093	295	188
3	6,16	6,54	3,8	3,2			288	184
4	6,68	6,92	3,89	3,31	0,0979	0,1329	307	192
5	6,73	7,03	3,68	3,10	0,098	0,146	286	182
6	6,70	7,14	3,80	3,20	0,108	0,158	300	180
7	7,02	7,21	3,8	3,2	0,101	0,151	295	206
8	6,74	7,09	3,74	3,17	0,107	0,156	270	160
9	6,76	6,98	3,94	3,34	0,130	0,174	245	111
10	6,940	7,196	4,83	3,99	0,060	0,100	299	182
12	6,96	7,07	3,96	3,35			1177	802
13	6,70	6,79	3,88	3,32	0,172	0,210	308	189
14	6,61	6,91	3,68	3,14			262	175
15	6,60	6,86	3,87	3,20	0,15	0,20		
16	6,70	6,88	3,05	2,55	4,43	6,89	254	160
17	6,80	7,17	3,70	3,10			320	198
18	6,82	7,10	3,83	3,03	0,115	0,180	320	208
19	6,82	7,15	37,50	31,80	0,099	0,150	339	204
20	7,01	7,18	3,75	3,15	0,114	0,161	295	180
21	6,61	6,89	3,81	3,23			294	188
23	6,87	7,06					267	115
24	6,57	6,73	3,8	3,2	0,125	0,177	291	186
25	6,7	6,9	3,79	3,14	0,17	0,22	288	165
26	7,02	7,22	3,81	3,21	0,090	0,139	280	175
27	6,75	7,07	3,95	3,33	0,090	0,134	270	163
28	6,756	7,102	3,78	3,25	0,107	0,152	283	183
29	6,77	7,05	3,50	2,94	0,056	0,079		
30	6,82	7,34	4,03	3,52	0,102	0,137		
31	6,78	7,14	3,92	3,35	0,11	0,16		
32	6,73	6,99	3,54	3,13	0,139	0,175	269	190
33	6,80	7,01	3,82	3,22			288	200
34	6,46	6,84	4,12	4,38	0,13	0,18	279	199
35	6,72	7,12	3,73	3,13	0,103	0,151	313	203
36	7,13	7,43	3,9	3,3	0,108	0,153	280	189
37	6,80	7,14	3,8	3,2			297	174
38	7,17	7,26	3,61	3,05	0,105	0,148	290	180
39	6,17	6,69	3,87	3,29			290	180
40	6,80	6,95	3,81	3,25	0,104	0,148	319	204
41	6,86	7,20	3,78	3,21			264	166
42	5,92	5,98			0,127	0,173	345	207
43	6,75	7,04	3,82	3,26	0,107	0,152	346	197
44	6,48	6,68	3,5	3,0	0,09	0,14	310	193
45	6,80	7,13	3,910	3,273	0,131	0,129	131	144

Lab.	pH		Cond, mS/m		Alk, mmol/l		NO3+NO2, µg/l	
	A	B	A	B	A	B	A	B
46	6,92	7,18	3,80	3,23	0,104	0,148	296	191
47	6,90	7,20					298	205
49	6,57	6,84	3,91	3,11	0,13	0,18	329	213
50	6,08	6,17	2,98	2,38	0,0545	0,080	313	192
51	6,76	7,15	3,7	3,0	0,102	0,146	294	192,5
52	6,78	7,07	3,93	3,35	0,1112	0,1555	292	184
53	6,81	7,01	3,36	3,00	0,062	0,085	461,18	357,70
54	6,79	7,12	3,64	3,05	0,097	0,148	290	190
56	6,65	6,98	3,80	3,26	0,113	0,153	274	180
57	6,80	7,02	3,72	3,19	0,15	0,19	303,00	196,50
59	6,56	6,88	3,71	3,17	0,125	0,182	297	181
60	6,70	6,95	3,73	3,17	0,103	0,147	290	185
61	6,5	6,8	4,0	3,4	0,22	0,25	408	221
62	6,80	7,19	3,78	3,21	0,106	0,154	300	185
63	6,80	7,06	3,79	3,22	0,102	0,148	295	183
64	6,35	6,72	3,82	3,25			296	183
65	5,50	5,83	3,96	3,29	0,12	0,15	15,39	4,47
66	6,70	6,90	4,45	3,66	0,113	0,161	306	198
67	6,82	7,14	3,87	3,32	0,107	0,153	295	184
68	6,95	7,20	3,83	3,21	0,106	0,151	300	206
69	6,85	7,08	3,86	3,19	0,134	0,181	316	190
70								
71	6,86	7,07	3,84	3,23			282	181
72	4,26	4,18	3,19	2,72			326	180
73	6,65	6,86	3,80	3,23	0,092	0,125	318,0	192,6
74	7,00	7,27	3,67	3,14	0,113	0,143	238	193
75	6,57	7,07	4,6	3,5	0,092	0,096	310	240

Lab.	Cl, mg/l		SO4, mg/l		Ca, mg/l		Mg, mg/l	
	A	B	A	B	A	B	A	B
1	3,63	2,03	3,60	2,64	3,41	3,13	0,54	0,63
2	3,494	1,910	3,47	2,55	3,27	2,89	0,51	0,56
3	3,697	2,015	3,625	2,641	4,846	4,543	0,546	0,616
4	3,46	2,04	3,63	2,66	3,164	2,778	0,487	0,534
5	3,60	2,01	3,65	2,65	3,50	3,16	0,54	0,60
6	3,9	2,0	3,5	2,5	3,50	3,15	0,54	0,61
7	3,515	1,998	3,530	2,603	3,179	3,042	0,491	0,559
8	3,15	1,88	3,40	2,40	3,30	2,93	0,48	0,54
9	3,41	1,95	3,43	2,26	3,65	3,06	0,56	0,61
10	6,39	1,87	3,57	2,55	4,93	4,82	0,78	0,90
12	3,329	1,898	3,251	2,472	3,653	3,286	0,545	0,601
13	1,95	0,98	3,50	2,40	4,25	3,73	0,51	0,58
14	3,56	1,96	4,30	2,59	4,52	3,94	0,67	0,73
15	6,01	4,78	2,47	1,67	2,89	2,78	1,60	1,41
16	3,74	1,55	5,05	6,83	3,56	3,26	0,58	0,62
17					3,58	3,15	0,54	0,59
18	3,42	2,09	3,60	2,57	3,08	3,26	0,46	0,56
19	3,70	1,96	2,97	2,55	3,64	3,27	0,55	0,60
20	3,60	1,99	3,58	2,61	3,60	3,45	0,55	0,62
21	3,58	1,96	3,58	2,61	2,09	1,35	0,45	0,44
23	4,92	4,11						
24	3,57	1,99	3,49	2,58	3,95	3,73	0,47	0,63
25	3,8	2,1	3,5	2,5	3,6	3,3	0,54	0,59
26	3,489	1,901	10,791	8,094	3,42	2,97	0,51	0,57
27	3,11	1,77	3,11	2,24	2,44	1,77	0,42	0,42
28	3,41	1,94	3,42	2,45	3,36	3,05	0,58	0,64
29	3,8	2,0	3,7	2,0	3,66	3,36	0,54	0,62
30					3,69	3,28	0,55	0,61
31					3,54	3,27	0,52	0,58
32	3,409	1,921	3,306	2,493	3,847	3,525	0,574	0,652
33	3,40	1,96	3,44	2,56	3,65	3,22	0,56	0,62
34	4,0	2,7			3,6	3,2	1,3	0,66
35	3,50	2,14	3,63	2,68	3,28	3,46	0,525	0,621
36	3,44	2,06	3,45	2,52	3,54	3,10	0,55	0,60
37								
38	3,58	1,91	3,50	2,44	4,47	4,14	0,62	0,70
39	3,60	2,03	3,53	2,78	3,38	3,04	0,533	0,592
40	3,47	2,15	3,28	2,46	3,83	3,30	0,55	0,59
41	3,04	1,64	3,39	2,47	3,76	3,49	0,46	0,55
42	6,7	2,5			3,8	3,5	0,6	0,7
43	3,33	1,85	3,80	2,65	3,55	3,21	0,54	0,61
44					3,42	2,98	0,52	0,56
45	4,38	2,63	5,65	3,87	1,52	1,10	0,58	0,63

Lab.	Cl, mg/l		SO4, mg/l		Ca, mg/l		Mg, mg/l	
	A	B	A	B	A	B	A	B
46	3,65	2,09	3,51	2,58	3,80	3,46	0,55	0,62
47	4,43	2,42	3,13	3,10	2,57	2,47	1,39	2,04
49	3,82	2,09	3,97	2,81	3,36	2,75	0,547	0,601
50	3,76	2,14	3,40	2,39	3,74	3,30	0,564	0,614
51	3,64	2,07	3,63	2,63	3,82	3,53	0,57	0,64
52	3,85	2,26	3,55	2,63	3,88	3,49	0,556	0,616
53	3,57	1,99	3,73	2,79	3,67	3,36	0,63	0,67
54	3,45	1,86	3,31	2,45	3,75	3,29	0,56	0,60
56	3,58	1,87	3,57	2,60	3,00	2,66	0,505	0,550
57	3,60	1,99	3,63	2,65	3,71	3,30	0,56	0,62
59	3,77	2,05	3,65	2,65	3,08	2,67	0,53	0,58
60	3,4	1,9	3,48	2,55	3,33	3,04	0,51	0,57
61	2,4	2,0	3,3	2,6	3,59	3,03	0,54	0,58
62	3,80	2,02	3,69	2,64	4,52	4,24	0,64	0,74
63	3,58	1,98	2,98	2,15				
64					3,36	3,04	0,543	0,593
65	2,84	2,84	0,79	0,64	3,02	2,50	0,20	0,27
66	3,85	2,14	5,96	4,74	3,8	3,0	0,82	0,84
67	3,55	1,94	3,59	2,66	3,62	3,20	0,53	0,59
68	3,42	1,81	3,32	2,43	3,72	3,39	0,49	0,55
69	3,70	1,99	3,67	2,64	3,60	3,24	0,55	0,62
70								
71	3,93	2,08	3,60	2,62	3,57	3,16	0,54	0,60
72	4,160	2,091	3,599	2,506	1,894	2,105	0,347	0,318
73			3,4	2,0	4,09	3,45	0,56	0,63
74	3,73	2,01	3,62	2,64	3,29	2,94	0,54	0,60
75	3,5	2,1	3,4	2,6	3,8	3,3	0,6	0,6

Lab.	Na, mg/l		K, mg/l		Fe, µg/l		Mn, µg/l	
	A	B	A	B	C	D	C	D
1	2,12	1,63	0,29	0,41				
2	1,94	1,39	0,33	0,42				
3	2,479	1,815	0,386	0,519	30,28	55,68	1,138	0,758
4	1,888	1,391	0,34	0,48	22,25	45,89	<2	<2
5	2,16	1,57	0,371	0,505				
6	2,06	1,56	0,38	0,52			2	1
7	1,786	1,260	0,300	0,428				
8	2,10	1,54	0,32	0,47				
9	1,88	1,36	0,383	0,496	18,5	43	<5	<5
10	2,23	1,49	3,25	0,46	12	36	1,03	0,70
12	2,118	1,573	0,372	0,513	25,0	51,0	1,2	0,8
13	2,22	1,70	0,38	0,54				
14	1,84	1,33	0,29	0,44	11	19	0,2	0,1
15	1,97	1,33	0,50	0,58			<5	<5
16	2,13	1,498	0,238	0,364	23,23	55,66	2,26	1,48
17	2,10	1,55	0,37	0,51	22,73	47,63	1,050	0,772
18					29,0	50,0		
19	2,09	1,57	0,50	0,56				
20	2,05	1,55	0,34	0,49				
21	2,03	1,50	0,26	0,36				
23								
24	2,06	1,55	0,38	0,39				
25	2,2	1,7	0,37	0,50	<30	<30	<1	<1
26	1,97	1,31	0,36	0,46	29,00	57,00	1,17	0,76
27	2,08	1,50	0,35	0,47	30,6	45,0	38,6	27,2
28	2,20	1,52	0,36	0,50				
29	2,10	1,58	0,36	0,51	25,0	50,8	1,06	<1
30	2,13	1,58	0,34	0,50	23,1	47,9	1,00	0,69
31	2,50	1,85	0,23	0,28				
32	2,318	1,722	0,380	0,577				
33	2,24	1,67	0,41	0,54	25	52	<1	<1
34								
35	2,28	1,65	0,383	0,506	23,4	50,1	1,1	0,8
36	2,08	1,52	0,38	0,50				
37								
38	2,19	1,63	0,39	0,54	20	48	1,20	0,83
39	2,13	1,54	0,374	0,500	23,8	48,7	1,10	0,759
40	1,98	1,51	0,38	0,52	26,0	48,0	2,1	1,1
41	2,77	2,09	0,41	0,58	15,21	33,9	0,90	0,65
42	2,2	1,7	0,3	0,5				
43	2,10	1,55	0,37	0,53	12	34	1,3	0,9
44	2,13	1,64	0,43	0,53				
45	2,14	1,53	0,50	0,80			2,2	1,9

Lab.	Na, mg/l		K, mg/l		Fe, µg/l		Mn, µg/l	
	A	B	A	B	C	D	C	D
46	2,09	1,56	0,36	0,50				
47	2,23	1,65	0,38	0,53				
49	2,06	1,56	0,373	0,503	19,60	41,7	1,20	0,84
50	2,10	1,56	0,37	0,50	23	48	<2	<2
51	2,12	1,57	0,35	0,55	50	20	0	0
52	2,10	1,57	0,363	0,499	100	<100	<50	<50
53	1,88	1,36	0,31	0,36	<5	15	<2,15	<2,15
54	2,28	1,66	0,39	0,55	36	66	1,3	0,87
56	2,02	1,49	0,370	0,490	20,4	42,5	1,30	0,82
57	2,07	1,57	0,38	0,51				
59	2,09	1,53	0,33	0,44				
60	2,1	1,5	0,40	0,52				
61	2,16	1,59	<0,01	<0,01	<10	26	<0,04	<0,04
62	2,19	1,62	0,41	0,54	27	48	<0,5	<0,5
63								
64	1,96	1,41	0,377	0,492	22	47	1,1	<1
65	1,87	1,35	0,78	0,79	25,31	37,77	1,97	0,86
66	2,27	1,80	0,51	0,61	21,2	44,5	1,37	1,55
67	2,10	1,53	0,38	0,52	12,6	38,8	1,13	0,76
68	1,87	1,34	0,26	0,37				
69	2,03	1,51	0,43	0,49	22,0	44,8	1,14	0,596
70							1,21	0,79
71	2,03	1,53	0,39	0,52	26	52	<3	<3
72	2,730	2,038	0,445	0,398	15,7	33,2	0,50	0,08
73	2,03	1,48	0,38	0,49	29,7	51,5	1,86	0,83
74	2,16	1,52	0,412	0,540				
75	2,2	1,6	0,4	0,5	25	52	1,10	<1

Lab.	Cd, µg/l		Pb, µg/l		Cu, µg/l		Ni, µg/l	
	C	D	C	D	C	D	C	D
1								
2								
3	0,539	1,241	3,082	4,902	134,9	82,03	6,051	10,21
4	<1	<1	<2	<2	120,8	73,45	8,68	12,46
5								
6	0,6	1,2	3	5	130	81	6	9
7								
8								
9	0,534	1,16	4,15	5,55	138	83,2	6,07	10,4
10	0,55	1,25	3,45	5,10	144,5	88,0	5,95	10,15
12	0,3	1,1	<10	<10			5,5	10,2
13								
14	0,7	0,9	2,1	2,4	95	55	8,0	5,6
15	0,38	0,84	2,00	3,82	129,9	83,2	4,00	7,92
16	0,60	1,38	<10	<10	127,84	77,14	5,05	8,15
17	<1	1,23	<10	<10	132,3	82,37	5,930	9,363
18								
19								
20								
21								
23	0,52	1,05	3,07	4,54	25,0	18,0	<100	<100
24								
25	0,60	1,40	3,4	5,0	120	74	5,1	8,6
26	0,54	1,14	4,38	5,67	130,98	76,56	5,42	8,82
27	0,6	1,3	3,6	5,3	103,8	81,4		
28								
29	0,48	1,18	3,10	4,67	169	100	6,09	10,4
30	0,68	1,25	3,54	4,72	133	84,3	6,09	10,03
31								
32								
33	0,58	1,31	3,3	5,1	143	85	5,4	9,5
34								
35	0,50	1,26	3,1	4,9	136	84	5,7	9,8
36								
37								
38	0,522	1,21	3,16	4,73	140	86,6	5,81	10,1
39	0,492	1,14	3,27	4,81	156	94,3	5,62	9,68
40	0,5	1,1	2,5	3,9	122	65	5,0	8,5
41	0,44	0,94	2,9	4,7	132	81,3	4,42	7,94
42								
43	0,50	1,33	3,4	4,7	125,5	78,5	5,0	9,5
44								
45	1,1	1,7	<7,5	<7,5	130,8	90,5	5,8	10,2

Lab.	Cd, µg/l		Pb, µg/l		Cu, µg/l		Ni, µg/l	
	C	D	C	D	C	D	C	D
46								
47								
49	0,596	1,36	3,35	4,71	143	87	5,04	9,23
50	0,54	1,22	3,31	4,82	134	82,2	6,35	10,0
51			2	1	71	125		
52	0,379	0,973	4,04	5,43	138	81,1	6,26	9,65
53	0,46	1,12	2,67	4,10	184,57	84,39	7,39	10,50
54	0,494	1,12	3,23	4,81	131	83	5,64	9,83
56	0,63	1,24	3,25	4,71	132	82,8	5,78	9,81
57								
59								
60								
61	0,52	1,2	3,31	1,53	134,8	81,3	5,63	9,93
62	<0,1	<0,1	<0,5	<0,5	126	75,0	<0,5	<0,5
63								
64	<1	1	<15	<15	130	79	<8	8,40
65	0,41	1,02	15	2,49	127	80,8	7,89	4,37
66	0,65	1,23	2,79	3,98	131,5	98,7	7,64	12,40
67	0,55	1,21	3,33	4,87	137	83,2	5,91	9,91
68								
69	2,38	2,50	<0,8	<0,8	133	81,8	5,40	8,23
70	0,54	1,22	3,29	4,90	132	82,1	5,61	9,62
71	<4	<4	<15	<15	137	81	5	9
72	0,80	0,80	3,88	5,51	126	76,2	7,5	13,1
73	0,528	1,23	3,05	4,46	149	88,9	5,56	9,73
74								
75	1,1	1,10	<10	<10	141	86	5	10

Lab.	Zn, µg/l	
	C	D
1		
2		
3	49,94	32,54
4	35,77	23,47
5		
6	40,2	26,5
7		
8		
9	31,8	16,4
10	42,2	27,6
12	40,5	26,2
13		
14	34	16
15	50,0	38,0
16	35	25
17	36,50	23,47
18		
19		
20		
21		
23	65,3	39,6
24		
25	45	29
26	40,37	25,20
27	43,5	27,6
28		
29	40,3	25,0
30	34,9	21,4
31		
32		
33	42	27
34		
35	39,3	25,3
36		
37		
38	40,7	26,0
39	40,0	26,1
40	36,7	21,7
41		
42		
43	37,0	23,0
44		
45	36,8	29,3

Lab.	Zn, µg/l	
	C	D
46		
47		
49	42,9	28,6
50	41,9	26,4
51	21	31
52	39,0	27,5
53	34,00	27,00
54	37	25
56	39,2	27,2
57		
59		
60		
61	37,79	25,26
62	37,0	24,0
63		
64	37	25
65	28,1	21,3
66	40,2	25,2
67	41,5	26,3
68		
69	31,7	18,8
70	40,2	26,5
71	40	26
72	13,9	13,1
73	41,7	26,4
74		
75	40	26

Table 5.1. Statistics - pH

Sample A

Number of participants	69	Range	1,67
Number of omitted results	1	Variance	0,07
True value	6,76	Standard deviation	0,27
Mean value	6,71	Relative standard deviation	4,0%
Median value	6,76	Relative error	-0,8%

Analytical results in ascending order:

72	4,26 U	25	6,70	17	6,80
65	5,50	60	6,70	40	6,80
42	5,92	13	6,70	1	6,81
50	6,08	35	6,72	53	6,81
3	6,16	5	6,73	19	6,82
39	6,17	32	6,73	18	6,82
64	6,35	8	6,74	67	6,82
34	6,46	27	6,75	30	6,82
44	6,48	43	6,75	69	6,85
61	6,50	28	6,76	41	6,86
59	6,56	9	6,76	71	6,86
24	6,57	2	6,76	23	6,87
75	6,57	51	6,76	47	6,90
49	6,57	29	6,77	46	6,92
15	6,60	31	6,78	10	6,94
14	6,61	52	6,78	68	6,95
21	6,61	54	6,79	12	6,96
73	6,65	62	6,80	74	7,00
56	6,65	63	6,80	20	7,01
4	6,68	33	6,80	7	7,02
16	6,70	57	6,80	26	7,02
66	6,70	37	6,80	36	7,13
6	6,70	45	6,80	38	7,17

Sample B

Number of participants	69	Range	1,60
Number of omitted results	1	Variance	0,07
True value	7,06	Standard deviation	0,27
Mean value	6,98	Relative standard deviation	3,9%
Median value	7,06	Relative error	-1,1%

Analytical results in ascending order:

72	4,18 U	60	6,95	35	7,12
65	5,83	56	6,98	54	7,12
42	5,98	9	6,98	45	7,13
50	6,17	32	6,99	67	7,14
3	6,54	2	6,99	31	7,14
44	6,68	53	7,01	6	7,14
39	6,69	33	7,01	37	7,14
64	6,72	57	7,02	19	7,15
24	6,73	5	7,03	51	7,15
13	6,79	1	7,03	17	7,17
61	6,80	43	7,04	46	7,18
34	6,84	29	7,05	20	7,18
49	6,84	23	7,06	62	7,19
15	6,86	63	7,06	10	7,20
73	6,86	12	7,07	68	7,20
59	6,88	52	7,07	41	7,20
16	6,88	27	7,07	47	7,20
21	6,89	75	7,07	7	7,21
66	6,90	71	7,07	26	7,22
25	6,90	69	7,08	38	7,26
14	6,91	8	7,09	74	7,27
4	6,92	18	7,10	30	7,34
40	6,95	28	7,10	36	7,43

U = Omitted result

Table 5.2. Statistics - Conductivity, mS/m

Sample A

Number of participants	66	Range	1,55
Number of omitted results	4	Variance	0,05
True value	3,80	Standard deviation	0,22
Mean value	3,80	Relative standard deviation	5,8%
Median value	3,80	Relative error	-0,1%

Analytical results in ascending order:

50	2,98 U	62	3,78	15	3,87
16	3,05	63	3,79	67	3,87
72	3,19	25	3,79	13	3,88
53	3,36	46	3,80	4	3,89
44	3,50	6	3,80	2	3,90
29	3,50	3	3,80	36	3,90
32	3,54	37	3,80	1	3,91
38	3,61	7	3,80	49	3,91
54	3,64	56	3,80	45	3,91
74	3,67	73	3,80	31	3,92
5	3,68	24	3,80	52	3,93
14	3,68	21	3,81	9	3,94
17	3,70	40	3,81	27	3,95
51	3,70	26	3,81	65	3,96
59	3,71	64	3,82	12	3,96
57	3,72	33	3,82	61	4,00
60	3,73	43	3,82	30	4,03
35	3,73	68	3,83	34	4,12 U
8	3,74	18	3,83	66	4,45
20	3,75	71	3,84	75	4,60
28	3,78	69	3,86	10	4,83 U
41	3,78	39	3,87	19	37,50 U

Sample B

Number of participants	66	Range	1,11
Number of omitted results	4	Variance	0,03
True value	3,21	Standard deviation	0,16
Mean value	3,20	Relative standard deviation	5,1%
Median value	3,21	Relative error	-0,3%

Analytical results in ascending order:

50	2,38 U	69	3,19	43	3,26
16	2,55	57	3,19	56	3,26
72	2,72	15	3,20	45	3,27
29	2,94	3	3,20	39	3,29
44	3,00	6	3,20	65	3,29
53	3,00	24	3,20	36	3,30
51	3,00	2	3,20	4	3,31
18	3,03	37	3,20	13	3,32
38	3,05	7	3,20	67	3,32
54	3,05	62	3,21	1	3,32
17	3,10	68	3,21	27	3,33
5	3,10	26	3,21	9	3,34
49	3,11	41	3,21	52	3,35
32	3,13	63	3,22	12	3,35
35	3,13	33	3,22	31	3,35
14	3,14	73	3,23	61	3,40
25	3,14	21	3,23	75	3,50
74	3,14	46	3,23	30	3,52
20	3,15	71	3,23	66	3,66
59	3,17	28	3,25	10	3,99 U
60	3,17	64	3,25	34	4,38 U
8	3,17	40	3,25	19	31,80 U

U = Omitted result

Table 5.3. Statistics - Alkalinity, mmol/l

Sample A

Number of participants	55	Range	0,096
Number of omitted results	4	Variance	0,000
True value	0,106	Standard deviation	0,021
Mean value	0,106	Relative standard deviation	19,8%
Median value	0,106	Relative error	0,0%

Analytical results in ascending order:

50	0,055	60	0,103	18	0,115
29	0,056	35	0,103	65	0,120
10	0,060	40	0,104	24	0,125
53	0,062	46	0,104	59	0,125
2	0,069	38	0,105	42	0,127
26	0,090	62	0,106	49	0,130
27	0,090	68	0,106	34	0,130
44	0,090	28	0,107	9	0,130
73	0,092	43	0,107	45	0,131
75	0,092	8	0,107	69	0,134
54	0,097	67	0,107	32	0,139
4	0,098	6	0,108	15	0,150
5	0,098	36	0,108	57	0,150
1	0,098	31	0,110	25	0,170 U
19	0,099	52	0,111	13	0,172 U
7	0,101	56	0,113	61	0,220 U
51	0,102	74	0,113	16	4,430 U
63	0,102	66	0,113		
30	0,102	20	0,114		

Sample B

Number of participants	55	Range	0,121
Number of omitted results	4	Variance	0,001
True value	0,151	Standard deviation	0,027
Mean value	0,148	Relative standard deviation	18,2%
Median value	0,151	Relative error	-1,9%

Analytical results in ascending order:

29	0,079	38	0,148	66	0,161
50	0,080	63	0,148	20	0,161
53	0,085	54	0,148	42	0,173
2	0,093	1	0,149	9	0,174
75	0,096	65	0,150	32	0,175
10	0,100	19	0,150	24	0,177
73	0,125	35	0,151	18	0,180
45	0,129	68	0,151	34	0,180
4	0,133	7	0,151	49	0,180
27	0,134	43	0,152	69	0,181
30	0,137	28	0,152	59	0,182
26	0,139	56	0,153	57	0,190
44	0,140	67	0,153	15	0,200
74	0,143	36	0,153	13	0,210 U
5	0,146	62	0,154	25	0,220 U
51	0,146	52	0,156	61	0,250 U
60	0,147	8	0,156	16	6,890 U
46	0,148	6	0,158		
40	0,148	31	0,160		

U = Omitted result

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

Sample A

Number of participants	65	Range	108
Number of omitted results	7	Variance	427
True value	295	Standard deviation	21
Mean value	296	Relative standard deviation	7,0%
Median value	295	Relative error	0,4%

Analytical results in ascending order:

65	15 U	39	290	57	303
45	131 U	54	290	66	306
74	238	38	290	4	307
9	245 U	60	290	13	308
16	254	24	291	44	310
14	262	52	292	75	310
41	264	51	294	50	313
23	267 U	21	294	35	313
32	269	20	295	69	316
27	270	63	295	73	318
8	270	2	295	40	319
56	274	67	295	17	320
34	279	7	295	18	320
36	280	64	296	72	326
26	280	46	296	49	329
71	282	59	297	19	339
28	283	37	297	42	345
5	286	47	298	43	346
1	287	10	299	61	408 U
33	288	68	300	53	461 U
25	288	6	300	12	1177 U
3	288	62	300		

Sample B

Number of participants	65	Range	80
Number of omitted results	7	Variance	192
True value	188	Standard deviation	14
Mean value	189	Relative standard deviation	7,3%
Median value	188	Relative error	0,4%

Analytical results in ascending order:

65	4 U	28	183	74	193
9	111 U	64	183	44	193
23	115 U	63	183	57	197
45	144 U	67	184	43	197
16	160	52	184	17	198
8	160	3	184	66	198
27	163	62	185	34	199
25	165	60	185	33	200
41	166	24	186	35	203
37	174	1	187	19	204
14	175	21	188	40	204
26	175	2	188	47	205
39	180	36	189	68	206
38	180	13	189	7	206
6	180	32	190	42	207
56	180	69	190	18	208
72	180	54	190	49	213
20	180	46	191	61	221 U
71	181	4	192	75	240
59	181	50	192	53	358 U
10	182	51	193	12	802 U
5	182	73	193		

U = Omitted result

Table 5.5. Statistics - Chloride, mg/l

Sample A

Number of participants	62	Range	1,39
Number of omitted results	8	Variance	0,07
True value	3,58	Standard deviation	0,26
Mean value	3,61	Relative standard deviation	7,1%
Median value	3,58	Relative error	0,8%

Analytical results in ascending order:

13	1,95 U	75	3,50	74	3,73
61	2,40 U	35	3,50	16	3,74
65	2,84 U	7	3,52	50	3,76
41	3,04	67	3,55	59	3,77
27	3,11	14	3,56	25	3,80
8	3,15	53	3,57	62	3,80
12	3,33	24	3,57	29	3,80
43	3,33	63	3,58	49	3,82
33	3,40	56	3,58	66	3,85
60	3,40	21	3,58	52	3,85
32	3,41	38	3,58	6	3,90
9	3,41	5	3,60	71	3,93
28	3,41	57	3,60	34	4,00 U
68	3,42	20	3,60	72	4,16
18	3,42	39	3,60	45	4,38
36	3,44	1	3,63	47	4,43
54	3,45	51	3,64	23	4,92 U
4	3,46	46	3,65	15	6,01 U
40	3,47	3	3,70	10	6,39 U
26	3,49	69	3,70	42	6,70 U
2	3,49	19	3,70		

Sample B

Number of participants	62	Range	1,08
Number of omitted results	8	Variance	0,03
True value	1,99	Standard deviation	0,16
Mean value	2,00	Relative standard deviation	8,0%
Median value	1,99	Relative error	0,6%

Analytical results in ascending order:

13	0,98 U	33	1,96	51	2,07
16	1,55	19	1,96	71	2,08
41	1,64	63	1,98	18	2,09
27	1,77	69	1,99	49	2,09
68	1,81	57	1,99	46	2,09
43	1,85	24	1,99	72	2,09
54	1,86	53	1,99	25	2,10
56	1,87	20	1,99	75	2,10
10	1,87 U	7	2,00	35	2,14
8	1,88	6	2,00	66	2,14
12	1,90	29	2,00	50	2,14
60	1,90	61	2,00 U	40	2,15
26	1,90	5	2,01	52	2,26
2	1,91	74	2,01	47	2,42
38	1,91	3	2,02	42	2,50 U
32	1,92	62	2,02	45	2,63
28	1,94	39	2,03	34	2,70 U
67	1,94	1	2,03	65	2,84 U
9	1,95	4	2,04	23	4,11 U
21	1,96	59	2,05	15	4,78 U
14	1,96	36	2,06		

U = Omitted result

Table 5.6. Statistics - Sulfate, mg/l

Sample A

Number of participants	60	Range	1,00
Number of omitted results	7	Variance	0,04
True value	3,51	Standard deviation	0,19
Mean value	3,49	Relative standard deviation	5,4%
Median value	3,51	Relative error	-0,5%

Analytical results in ascending order:

65	0,79 U	36	3,45	18	3,60
15	2,47 U	2	3,47	74	3,62
19	2,97	60	3,48	3	3,63
63	2,98	24	3,49	57	3,63
27	3,11	25	3,50	51	3,63
47	3,13	38	3,50	35	3,63
12	3,25	13	3,50	4	3,63
40	3,28	6	3,50	5	3,65
61	3,30	46	3,51	59	3,65
32	3,31	7	3,53	69	3,67
54	3,31	39	3,53	62	3,69
68	3,32	52	3,55	29	3,70
41	3,39	56	3,57	53	3,73
8	3,40	10	3,57	43	3,80
75	3,40	21	3,58	49	3,97
73	3,40	20	3,58	14	4,30 U
50	3,40	67	3,59	16	5,05 U
28	3,42	72	3,60	45	5,65 U
9	3,43	71	3,60	66	5,96 U
33	3,44	1	3,60	26	10,79 U

Sample B

Number of participants	60	Range	1,10
Number of omitted results	7	Variance	0,03
True value	2,58	Standard deviation	0,18
Mean value	2,54	Relative standard deviation	7,2%
Median value	2,58	Relative error	-1,4%

Analytical results in ascending order:

65	0,64 U	72	2,51	74	2,64
15	1,67 U	36	2,52	1	2,64
73	2,00	2	2,55	69	2,64
29	2,00	10	2,55	62	2,64
63	2,15	60	2,55	3	2,64
27	2,24	19	2,55	57	2,65
9	2,26	33	2,56	43	2,65
50	2,39	18	2,57	5	2,65
8	2,40	46	2,58	59	2,65
13	2,40	24	2,58	67	2,66
68	2,43	14	2,59 U	4	2,66
38	2,44	61	2,60	35	2,68
54	2,45	56	2,60	39	2,78
28	2,45	75	2,60	53	2,79
40	2,46	7	2,60	49	2,81
41	2,47	20	2,61	47	3,10
12	2,47	21	2,61	45	3,87 U
32	2,49	71	2,62	66	4,74 U
6	2,50	52	2,63	16	6,83 U
25	2,50	51	2,63	26	8,09 U

U = Omitted result

Table 5.7. Statistics - Calcium, mg/l

Sample A

Number of participants	66	Range	2,28
Number of omitted results	5	Variance	0,16
True value	3,60	Standard deviation	0,39
Mean value	3,60	Relative standard deviation	10,9%
Median value	3,60	Relative error	0,0%

Analytical results in ascending order:

45	1,52 U	26	3,42	30	3,69
72	1,89 U	44	3,42	57	3,71
21	2,09 U	5	3,50	68	3,72
27	2,44 U	6	3,50	50	3,74
47	2,57	31	3,54	54	3,75
15	2,89	36	3,54	41	3,76
56	3,00	43	3,55	75	3,80
65	3,02	16	3,56	46	3,80
59	3,08	71	3,57	66	3,80
18	3,08	17	3,58	42	3,80
4	3,16	61	3,59	51	3,82
7	3,18	25	3,60	40	3,83
2	3,27	34	3,60	32	3,85
35	3,28	20	3,60	52	3,88
74	3,29	69	3,60	24	3,95
8	3,30	67	3,62	73	4,09
60	3,33	19	3,64	13	4,25
28	3,36	33	3,65	38	4,47
49	3,36	9	3,65	62	4,52
64	3,36	12	3,65	14	4,52
39	3,38	29	3,66	3	4,85
1	3,41	53	3,67	10	4,93 U

Sample B

Number of participants	66	Range	2,07
Number of omitted results	5	Variance	0,14
True value	3,24	Standard deviation	0,37
Mean value	3,24	Relative standard deviation	11,5%
Median value	3,24	Relative error	0,1%

Analytical results in ascending order:

45	1,10 U	28	3,05	75	3,30
21	1,35 U	9	3,06	25	3,30
27	1,77 U	36	3,10	40	3,30
72	2,11 U	1	3,13	53	3,36
47	2,47	6	3,15	29	3,36
65	2,50	17	3,15	68	3,39
56	2,66	71	3,16	20	3,45
59	2,67	5	3,16	73	3,45
49	2,75	67	3,20	35	3,46
4	2,78	34	3,20	46	3,46
15	2,78	43	3,21	41	3,49
2	2,89	33	3,22	52	3,49
8	2,93	69	3,24	42	3,50
74	2,94	16	3,26	32	3,53
26	2,97	18	3,26	51	3,53
44	2,98	31	3,27	24	3,73
66	3,00	19	3,27	13	3,73
61	3,03	30	3,28	14	3,94
64	3,04	12	3,29	38	4,14
39	3,04	54	3,29	62	4,24
60	3,04	57	3,30	3	4,54
7	3,04	50	3,30	10	4,82 U

U = Omitted result

Table 5.8. Statistics - Magnesium, mg/l

Sample A

Number of participants	66	Range	0,25
Number of omitted results	7	Variance	0,00
True value	0,54	Standard deviation	0,04
Mean value	0,54	Relative standard deviation	8,3%
Median value	0,54	Relative error	0,2%

Analytical results in ascending order:

65	0,20 U	5	0,54	33	0,56
72	0,35 U	71	0,54	54	0,56
27	0,42	61	0,54	57	0,56
21	0,45	29	0,54	73	0,56
41	0,46	17	0,54	9	0,56
18	0,46	6	0,54	50	0,56
24	0,47	1	0,54	51	0,57
8	0,48	43	0,54	32	0,57
4	0,49	25	0,54	28	0,58
68	0,49	74	0,54	16	0,58
7	0,49	64	0,54	45	0,58
56	0,51	12	0,55	75	0,60
2	0,51	3	0,55	42	0,60
13	0,51	49	0,55	38	0,62
26	0,51	46	0,55	53	0,63
60	0,51	20	0,55	62	0,64
31	0,52	19	0,55	14	0,67
44	0,52	69	0,55	10	0,78 U
35	0,53	30	0,55	66	0,82 U
59	0,53	36	0,55	34	1,30 U
67	0,53	40	0,55	47	1,39 U
39	0,53	52	0,56	15	1,60 U

Sample B

Number of participants	66	Range	0,32
Number of omitted results	7	Variance	0,00
True value	0,60	Standard deviation	0,05
Mean value	0,60	Relative standard deviation	8,7%
Median value	0,60	Relative error	0,2%

Analytical results in ascending order:

65	0,27 U	25	0,59	29	0,62
72	0,32 U	39	0,59	69	0,62
27	0,42	64	0,59	57	0,62
21	0,44	5	0,60	20	0,62
4	0,53	74	0,60	35	0,62
8	0,54	19	0,60	45	0,63
68	0,55	36	0,60	1	0,63
56	0,55	71	0,60	73	0,63
41	0,55	54	0,60	24	0,63
7	0,56	75	0,60	51	0,64
18	0,56	49	0,60	28	0,64
44	0,56	12	0,60	32	0,65
2	0,56	9	0,61	34	0,66 U
60	0,57	30	0,61	53	0,67
26	0,57	6	0,61	42	0,70
13	0,58	43	0,61	38	0,70
59	0,58	50	0,61	14	0,73
61	0,58	3	0,62	62	0,74
31	0,58	52	0,62	66	0,84 U
40	0,59	16	0,62	10	0,90 U
67	0,59	33	0,62	15	1,41 U
17	0,59	46	0,62	47	2,04 U

U = Omitted result

Table 5.9. Statistics - Sodium, mg/l

Sample A

Number of participants	64	Range	0,71
Number of omitted results	2	Variance	0,02
True value	2,10	Standard deviation	0,14
Mean value	2,10	Relative standard deviation	6,5%
Median value	2,10	Relative error	0,0%

Analytical results in ascending order:

7	1,79	36	2,08	61	2,16
14	1,84	27	2,08	5	2,16
65	1,87	59	2,09	38	2,19
68	1,87	46	2,09	62	2,19
9	1,88	19	2,09	75	2,20
53	1,88	52	2,10	42	2,20
4	1,89	60	2,10	28	2,20
2	1,94	29	2,10	25	2,20
64	1,96	67	2,10	13	2,22
15	1,97	8	2,10	47	2,23
26	1,97	50	2,10	10	2,23
40	1,98	43	2,10	33	2,24
56	2,02	17	2,10	66	2,27
73	2,03	12	2,12	35	2,28
21	2,03	51	2,12	54	2,28
71	2,03	1	2,12	32	2,32
69	2,03	44	2,13	3	2,48
20	2,05	39	2,13	31	2,50
49	2,06	16	2,13	72	2,73 U
24	2,06	30	2,13	41	2,77 U
6	2,06	45	2,14		
57	2,07	74	2,16		

Sample B

Number of participants	64	Range	0,59
Number of omitted results	2	Variance	0,01
True value	1,55	Standard deviation	0,12
Mean value	1,54	Relative standard deviation	7,8%
Median value	1,55	Relative error	-0,4%

Analytical results in ascending order:

7	1,26	36	1,52	30	1,58
26	1,31	71	1,53	61	1,59
14	1,33	59	1,53	75	1,60
15	1,33	67	1,53	62	1,62
68	1,34	45	1,53	38	1,63
65	1,35	39	1,54	1	1,63
53	1,36	8	1,54	44	1,64
9	1,36	43	1,55	35	1,65
2	1,39	17	1,55	47	1,65
4	1,39	24	1,55	54	1,66
64	1,41	20	1,55	33	1,67
73	1,48	6	1,56	13	1,70
56	1,49	49	1,56	25	1,70
10	1,49	50	1,56	42	1,70
16	1,50	46	1,56	32	1,72
21	1,50	57	1,57	66	1,80
60	1,50	52	1,57	3	1,82
27	1,50	5	1,57	31	1,85
69	1,51	19	1,57	72	2,04 U
40	1,51	51	1,57	41	2,09 U
74	1,52	12	1,57		
28	1,52	29	1,58		

U = Omitted result

Table 5.10. Statistics - Potassium, mg/l

Sample A

Number of participants	64	Range	0,27
Number of omitted results	5	Variance	0,00
True value	0,37	Standard deviation	0,05
Mean value	0,37	Relative standard deviation	13,9%
Median value	0,37	Relative error	0,1%

Analytical results in ascending order:

61	<0,01 U	52	0,36	35	0,38
31	0,23 U	25	0,37	3	0,39
16	0,24	56	0,37	71	0,39
68	0,26	17	0,37	54	0,39
21	0,26	50	0,37	38	0,39
14	0,29	43	0,37	75	0,40
1	0,29	5	0,37	60	0,40
7	0,30	12	0,37	41	0,41
42	0,30	49	0,37	33	0,41
53	0,31	39	0,37	62	0,41
8	0,32	64	0,38	74	0,41
59	0,33	57	0,38	44	0,43
2	0,33	6	0,38	69	0,43
30	0,34	40	0,38	72	0,45
20	0,34	24	0,38	45	0,50 U
4	0,34	36	0,38	19	0,50
51	0,35	67	0,38	15	0,50
27	0,35	13	0,38	66	0,51
26	0,36	47	0,38	65	0,78 U
46	0,36	73	0,38	10	3,25 U
29	0,36	32	0,38		
28	0,36	9	0,38		

Sample B

Number of participants	64	Range	0,25
Number of omitted results	5	Variance	0,00
True value	0,50	Standard deviation	0,06
Mean value	0,49	Relative standard deviation	11,3%
Median value	0,50	Relative error	-1,1%

Analytical results in ascending order:

61	<0,01 U	64	0,49	67	0,52
31	0,28 U	9	0,50	40	0,52
53	0,36	52	0,50	60	0,52
21	0,36	30	0,50	43	0,53
16	0,36	46	0,50	47	0,53
68	0,37	75	0,50	44	0,53
24	0,39	39	0,50	13	0,54
72	0,40	42	0,50	38	0,54
1	0,41	50	0,50	62	0,54
2	0,42	36	0,50	33	0,54
7	0,43	25	0,50	74	0,54
14	0,44	28	0,50	51	0,55
59	0,44	49	0,50	54	0,55
26	0,46	5	0,51	19	0,56
10	0,46 U	35	0,51	32	0,58
27	0,47	57	0,51	15	0,58
8	0,47	17	0,51	41	0,58
4	0,48	29	0,51	66	0,61
56	0,49	12	0,51	65	0,79 U
73	0,49	3	0,52	45	0,80 U
69	0,49	71	0,52		
20	0,49	6	0,52		

U = Omitted result

Table 5.11. Statistics - Iron, µg/l

Sample C

Number of participants	39	Range	19
Number of omitted results	7	Variance	26
True value	23	Standard deviation	5
Mean value	23	Relative standard deviation	22,3%
Median value	23	Relative error	-1,4%

Analytical results in ascending order:

52	<100 U	56	20	33	25
25	<30 U	66	21	75	25
61	<10 U	64	22	65	25
53	<5 U	69	22	71	26
14	11 U	4	22	40	26
43	12	17	23	62	27
10	12	50	23	26	29
67	13	30	23	18	29
41	15	16	23	73	30
72	16	35	23	3	30
9	19	39	24	27	31
49	20	29	25	54	36 U
38	20	12	25	51	50 U

Sample D

Number of participants	39	Range	24
Number of omitted results	7	Variance	41
True value	48	Standard deviation	6
Mean value	46	Relative standard deviation	13,8%
Median value	48	Relative error	-3,5%

Analytical results in ascending order:

52	<100 U	56	43	39	49
25	<30 U	9	43	18	50
53	15 U	66	45	35	50
14	19 U	69	45	29	51
51	20 U	27	45	12	51
61	26 U	4	46	73	52
72	33	64	47	71	52
41	34	17	48	75	52
43	34	30	48	33	52
10	36	62	48	16	56
65	38	38	48	3	56
67	39	40	48	26	57
49	42	50	48	54	66 U

U = Omitted result

Table 5.12. Statistics - Manganese, µg/l

Sample C

Number of participants	42	Range	0,40
Number of omitted results	25	Variance	0,01
True value	1,14	Standard deviation	0,11
Mean value	1,15	Relative standard deviation	9,6%
Median value	1,14	Relative error	0,5%

Analytical results in ascending order:

52	<50 U	41	0,90	49	1,20
15	<5 U	30	1,00	12	1,20
9	<5 U	10	1,03	70	1,21
71	<3 U	17	1,05	54	1,30
53	<2,15 U	29	1,06 U	43	1,30
4	<2 U	39	1,10	56	1,30
50	<2 U	64	1,10 U	66	1,37 U
25	<1 U	75	1,10 U	73	1,86 U
33	<1 U	35	1,10	65	1,97 U
62	<1 U	67	1,13	6	2,00 U
61	<0,04 U	3	1,14	40	2,10 U
51	0,00 U	69	1,14	45	2,20 U
14	0,20 U	26	1,17	16	2,26 U
72	0,50 U	38	1,20	27	38,60 U

Sample D

Number of participants	42	Range	0,30
Number of omitted results	25	Variance	0,01
True value	0,77	Standard deviation	0,08
Mean value	0,77	Relative standard deviation	10,1%
Median value	0,77	Relative error	0,0%

Analytical results in ascending order:

52	<50 U	51	0,00 U	35	0,80
15	<5 U	72	0,08 U	56	0,82
9	<5 U	14	0,10 U	38	0,83
71	<3 U	69	0,60	73	0,83 U
53	<2,15 U	41	0,65	49	0,84
50	<2 U	30	0,69	65	0,86 U
4	<2 U	10	0,70	54	0,87
33	<1 U	3	0,76	43	0,90
25	<1 U	39	0,76	6	1,00 U
64	<1 U	67	0,76	40	1,10 U
75	<1 U	26	0,76	16	1,48 U
29	<1 U	17	0,77	66	1,55 U
62	<1 U	70	0,79	45	1,90 U
61	<0,04 U	12	0,80	27	27,20 U

U = Omitted result

Table 5.13. Statistics - Cadmium, µg/l

Sample C

Number of participants	42	Range	0,40
Number of omitted results	9	Variance	0,01
True value	0,53	Standard deviation	0,09
Mean value	0,53	Relative standard deviation	16,3%
Median value	0,53	Relative error	-0,2%

Analytical results in ascending order:

71	<4 U	35	0,50	33	0,58
64	<1 U	43	0,50	49	0,60
4	<1 U	40	0,50	25	0,60
17	<1 U	61	0,52	16	0,60
62	<0,1 U	23	0,52	27	0,60
12	0,30	38	0,52	6	0,60
52	0,38	73	0,53	56	0,63
15	0,38	9	0,53	66	0,65
65	0,41	3	0,54	30	0,68
41	0,44	50	0,54	14	0,70
53	0,46	26	0,54	72	0,80 U
29	0,48	70	0,54	75	1,10 U
39	0,49	67	0,55	45	1,10 U
54	0,49	10	0,55	69	2,38 U

Sample D

Number of participants	42	Range	0,56
Number of omitted results	9	Variance	0,02
True value	1,21	Standard deviation	0,13
Mean value	1,18	Relative standard deviation	11,3%
Median value	1,21	Relative error	-2,8%

Analytical results in ascending order:

71	<4 U	53	1,12	17	1,23 U
4	<1 U	54	1,12	56	1,24
62	<0,1 U	39	1,14	3	1,24
72	0,80 U	26	1,14	10	1,25
15	0,84	9	1,16	30	1,25
14	0,90	29	1,18	35	1,26
41	0,94	61	1,20	27	1,30
52	0,97	6	1,20	33	1,31
64	1,00 U	38	1,21	43	1,33
65	1,02	67	1,21	49	1,36
23	1,05	50	1,22	16	1,38
12	1,10	70	1,22	25	1,40
75	1,10 U	73	1,23	45	1,70 U
40	1,10	66	1,23	69	2,50 U

U = Omitted result

Table 5.14. Statistics - Lead, µg/l

Sample C

Number of participants	43	Range	2,38
Number of omitted results	14	Variance	0,23
True value	3,27	Standard deviation	0,48
Mean value	3,26	Relative standard deviation	14,7%
Median value	3,27	Relative error	-0,3%

Analytical results in ascending order:

71	<15 U	66	2,79	50	3,31
64	<15 U	41	2,90	67	3,33
17	<10 U	6	3,00	49	3,35
16	<10 U	73	3,05	25	3,40
12	<10 U	23	3,07	43	3,40
75	<10 U	3	3,08	10	3,45
45	<7,5 U	35	3,10	30	3,54
4	<2 U	29	3,10	27	3,60
69	<0,8 U	38	3,16	72	3,88
62	<0,5 U	54	3,23	52	4,04
51	2,00 U	56	3,25	9	4,15
15	2,00	39	3,27	26	4,38
14	2,10 U	70	3,29	65	15,00 U
40	2,50	33	3,30		
53	2,67	61	3,31 U		

Sample D

Number of participants	43	Range	1,85
Number of omitted results	14	Variance	0,21
True value	4,81	Standard deviation	0,46
Mean value	4,81	Relative standard deviation	9,6%
Median value	4,81	Relative error	-0,1%

Analytical results in ascending order:

71	<15 U	40	3,90	67	4,87
64	<15 U	66	3,98	70	4,90
12	<10 U	53	4,10	35	4,90
75	<10 U	73	4,46	3	4,90
17	<10 U	23	4,54	6	5,00
16	<10 U	29	4,67	25	5,00
45	<7,5 U	41	4,70	10	5,10
4	<2 U	43	4,70	33	5,10
69	<0,8 U	49	4,71	27	5,30
62	<0,5 U	56	4,71	52	5,43
51	1,00 U	30	4,72	72	5,51
61	1,53 U	38	4,73	9	5,55
14	2,40 U	39	4,81	26	5,67
65	2,49 U	54	4,81		
15	3,82	50	4,82		

U = Omitted result

Table 5.15. Statistics - Copper, µg/l

Sample C

Number of participants	42	Range	65,2
Number of omitted results	4	Variance	112,4
True value	132,2	Standard deviation	10,6
Mean value	133,8	Relative standard deviation	7,9%
Median value	132,2	Relative error	1,2%

Analytical results in ascending order:

23	25,0 U	64	130,0	35	136,0
51	71,0 U	45	130,8	71	137,0
14	95,0 U	26	131,0	67	137,0
27	103,8	54	131,0	9	138,0
25	120,0	66	131,5	52	138,0
4	120,8	70	132,0	38	140,0
40	122,0	41	132,0	75	141,0
43	125,5	56	132,0	33	143,0
72	126,0	17	132,3	49	143,0
62	126,0	69	133,0	10	144,5
65	127,0	30	133,0	73	149,0
16	127,8	50	134,0	39	156,0
15	129,9	61	134,8	29	169,0
6	130,0	3	134,9	53	184,6 U

Sample D

Number of participants	42	Range	35,0
Number of omitted results	4	Variance	42,4
True value	82,2	Standard deviation	6,5
Mean value	82,7	Relative standard deviation	7,9%
Median value	82,2	Relative error	0,6%

Analytical results in ascending order:

23	18,0 U	52	81,1	35	84,0
14	55,0 U	61	81,3	30	84,3
40	65,0	41	81,3	53	84,4 U
4	73,5	27	81,4	33	85,0
25	74,0	69	81,8	75	86,0
62	75,0	3	82,0	38	86,6
72	76,2	70	82,1	49	87,0
26	76,6	50	82,2	10	88,0
16	77,1	17	82,4	73	88,9
43	78,5	56	82,8	45	90,5
64	79,0	54	83,0	39	94,3
65	80,8	15	83,2	66	98,7
6	81,0	67	83,2	29	100,0
71	81,0	9	83,2	51	125,0 U

U = Omitted result

Table 5.16. Statistics - Nickel, µg/l

Sample C

Number of participants	41	Range	3,64
Number of omitted results	6	Variance	0,57
True value	5,64	Standard deviation	0,76
Mean value	5,71	Relative standard deviation	13,3%
Median value	5,64	Relative error	1,2%

Analytical results in ascending order:

23	<100 U	26	5,42	6	6,00
64	<8 U	12	5,50	3	6,05
62	<0,5 U	73	5,56	9	6,07
15	4,00	70	5,61	30	6,09
41	4,42	39	5,62	29	6,09
40	5,00	61	5,63	52	6,26
71	5,00	54	5,64	50	6,35
75	5,00	35	5,70	53	7,39
43	5,00	56	5,78	72	7,50
49	5,04	45	5,80	66	7,64
16	5,05	38	5,81	65	7,89 U
25	5,10	67	5,91	14	8,00 U
33	5,40	17	5,93	4	8,68 U
69	5,40	10	5,95		

Sample D

Number of participants	41	Range	5,18
Number of omitted results	6	Variance	1,11
True value	9,80	Standard deviation	1,05
Mean value	9,70	Relative standard deviation	10,9%
Median value	9,80	Relative error	-1,0%

Analytical results in ascending order:

23	<100 U	49	9,23	50	10,00
62	<0,5 U	17	9,36	30	10,03
65	4,37 U	33	9,50	38	10,10
14	5,60 U	43	9,50	10	10,15
15	7,92	70	9,62	45	10,20
41	7,94	52	9,65	12	10,20
16	8,15	39	9,68	3	10,21
69	8,23	73	9,73	9	10,40
64	8,40 U	35	9,80	29	10,40
40	8,50	56	9,81	53	10,50
25	8,60	54	9,83	66	12,40
26	8,82	67	9,91	4	12,46 U
6	9,00	61	9,93	72	13,10
71	9,00	75	10,00		

U = Omitted result

Table 5.17. Statistics - Zinc, µg/l

Sample C

Number of participants	42	Range	21,8
Number of omitted results	4	Variance	16,1
True value	39,7	Standard deviation	4,0
Mean value	38,7	Relative standard deviation	10,4%
Median value	39,7	Relative error	-2,5%

Analytical results in ascending order:

72	13,9 U	64	37,0	26	40,4
51	21,0 U	54	37,0	12	40,5
65	28,1	62	37,0	38	40,7
69	31,7	61	37,8	67	41,5
9	31,8	52	39,0	73	41,7
53	34,0	56	39,2	50	41,9
14	34,0	35	39,3	33	42,0
30	34,9	39	40,0	10	42,2
16	35,0	71	40,0	49	42,9
4	35,8	75	40,0	27	43,5
17	36,5	66	40,2	25	45,0
40	36,7	6	40,2	3	49,9
45	36,8	70	40,2	15	50,0 U
43	37,0	29	40,3	23	65,3 U

Sample D

Number of participants	42	Range	16,5
Number of omitted results	4	Variance	10,6
True value	26,0	Standard deviation	3,3
Mean value	25,2	Relative standard deviation	12,9%
Median value	26,0	Relative error	-3,2%

Analytical results in ascending order:

72	13,1 U	16	25,0	70	26,5
14	16,0	26	25,2	53	27,0
9	16,4	66	25,2	33	27,0
69	18,8	61	25,3	56	27,2
65	21,3	35	25,3	52	27,5
30	21,4	38	26,0	10	27,6
40	21,7	75	26,0	27	27,6
43	23,0	71	26,0	49	28,6
17	23,5	39	26,1	25	29,0
4	23,5	12	26,2	45	29,3
62	24,0	67	26,3	51	31,0 U
64	25,0	50	26,4	3	32,5
29	25,0	73	26,4	15	38,0 U
54	25,0	6	26,5	23	39,6 U

U = Omitted result