Convention on Long-range Transboundary Air Pollution

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

ICP-WATERS REPORT 78/2004

Intercomparison 0418:

pH, K_{25}, HCO_3, NO_3+NO_2, C1, SO_4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni and Zn

NIVA Norwegian Institute for Water Research

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 0418: pH, Cond, HCO_3, NO_3+NO_2, Cl, SO_4, Ca, Mg, Na, K, Fe, Mn, Cd, Pb, Cu, Ni, and Zn	4875-2004	September 2004
	Report No. Sub-No. O-23300 B	Pages Price 68
Author(s) Håvard Hovind	Topic group Analysis	Distribution
	Geographical area	Printed NIVA

Client(s)	Client ref.
Norwegian Pollution Control Authority	

Abstract

68 laboratories received samples for the intercomparison 0418, and 63 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 %, 77 % of the overall results were considered acceptable. The best results were reported for the analytical variables copper, sodium and sulphate, with a percentage of acceptable results of 95, 87 and 86 %, respectively. Lowest percentage of acceptable results were observed for alkalinity, pH and manganese, where only 52, 57 and 59 % of the result pairs, respectively, were acceptable. 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

Head of chemistry department
Øyvind Skaugrud

ISBN 82-577-4561-8

CONVENTION ON LONG-RANGE
TRANSBOUNDARY AIR POLLUTION

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

Intercomparison 0418

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 2004

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 18th intercomparison of chemical analysis.

Oslo, September 2004

Håvard Hovind

Contents

1. Summary

Intercomparison 0418 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 2004, 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, sulphate, 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. 116 laboratories were invited to participate in this intercomparison, and the samples were sent to the 68 laboratories who accepted to participate. 63 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. 77 % 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 the assessment of the accuracy between laboratories, than the target limit of ± 0,1 units. The reason for the great spread of pH results is mainly due to the fact that different routines are used for the determination of pH by the participants, leading to small systematic differences in the results.

The best results were reported for the analytical variables copper, sodium and sulphate where 95, 87 and 86 % of the results, respectively were acceptable. The concentration of copper was rather high in the samples used this time. The worst results were observed for alkalinity, pH and manganese, with 52, 57 and 59 % acceptable results. A harmonization of the analytical method used is necessary to improve the results for pH and alkalinity.

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 eighteenth intercomparison test, called 0418, included the determination of the major components and some other ions in natural water samples: pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulphate, 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 2003 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 21, 2004, and the following day. Most of the participating laboratories received the samples within one week, with some very few exceptions.

To ensure that the effect of possible alterations in the solutions is minimized, the participants were asked to analyze the samples as soon as possible, and return the analytical results within one month after the samples arrived at the laboratory. 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 before the statistical calculations. Most results were received within the end of July, the last results included in the report were received in the middle of August. Five laboratories who received samples did not return analytical results.

4. Results

116 laboratories were invited to participate in this intercomparison, and 68 laboratories accepted and therefore received samples. The 63 laboratories which submitted results to the Programme Centre, are representing 27 countries. Some laboratories submitted results a few 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 with different analytical methods, however, our computer system for statistical treatment does not allow us to have more than one set of results from one each participant. Therefore we selected one of the data sets from this laboratory.

The analytical results received from the laboratories were treated by the method of Youden (2, 3). A short description of this method, and the statistical treatment of the analytical data, are presented in Appendix 3. The purpose of this test is to evaluate the comparability of the analytical results produced by the laboratories participating 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 0418 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. 60 laboratories reported results for pH, of this group 29 indicated that they read the pH value i quiescent solution, and 30 during stirring the solution. The stirring are normally lowering the observed pH result. In this intercomparison the median values are not different in the stirred samples compared to the non-stirred samples (see Table 1). The differences between the mean values are not significantly different.

Just one laboratory equilibrated the solutions by bubbling with air containing 350 ppm CO_2 before reading the pH value, reported higher results than the other laboratories. In the sample solutions used in this eighteenth intercomparison, the pH of the equilibrated solutions are about 0,7 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

(The text continues on page 28

Table 1. Statistical summary of intercomparison 0418

Analytical variable and method	Sample pair	True value 1	True value 2	Total no.	Labs. excl.	Median 1	Median 2	Mean Std.dev. Sample 1		Mean Std.dev. Sample 2		Rel.std.dev. % 1	Rel.std.dev. % 2	Relative error 1	Relative error 2
pH	AB	6,63	6,86	60	3	6,63	6,86	6,62	0,24	6,86	0,21	3,6	3,0	-0,2	0,0
No stirring				29	1	6,65	6,85	6,64	0,23	6,84	0,20	3,4	2,8	0,1	-0,3
Stirring				30	2	6,63	6,86	6,57	0,22	6,86	0,19	3,4	2,7	-0,9	0,0
Equilibration				1	0			7,31		7,52				10,3	9,6
Conductivity	AB	3,40	4,36	60	3	3,40	4,36	3,41	0,18	4,32	0,18	5,3	4,1	0,4	-0,9
Alkalinity	AB	0,096	0,139	46	11	0,096	0,139	0,100	0,019	0,142	0,020	19,2	13,9	3,9	1,8
Gran plot titration				21	1	0,096	0,137	0,096	0,110	0,138	0,012	11,8	8,6	-0,5	-0,5
End point 4,5 and 4,2				6	4			0,094		0,142				-3,6	1,8
End point 5,6				1	0			0,088		0,135				-8,3	-2,9
End point 4,5				14	3	0,120	0,160	0,113	0,024	0,152	0,028	20,7	18,3	16,9	9,2
Not documented				4	3			0,057		0,103				-41,2	-25,9
Nitrate + nitrite-nitrogen	AB	283	340	54	3	283	340	281	33	335	23	11,9	6,9	-0,8	-1,6
Autoanalyzer				20	1	286	340	279	37	328	29	13,1	8,7	-1,6	-3,5
Photometry				7	0	289	332	293	24	341	22	8,3	6,4	2,8	0,3
Ion chromatography				23	1	273	344	277	33	338	19	12,0	5,6	-2,8	-0,6
Hydrazine				2	0			313		344				9,8	1,0
Unspesified				2	1			254		325				-10,9	-4,4
Chloride	AB	2,92	3,57	51	6	2,92	3,57	2,93	0,22	3,55	0,24	7,6	6,8	0,4	-0,7
Ion chromatography				40	1	2,92	3,57	2,90	0,17	3,52	0,21	5,8	5,9	-0,5	-1,3
Argentometry				3	2			2,70		3,38				-7,2	-5,3
Manual, Hg				6	2	3,10	3,75	3,27	0,42	3,86	0,38	12,9	9,8	12,0	8,0
Potentiometry				1	1			9,78		9,64				236,1	170,0
Photometry				1	0			2,84		3,34				-2,4	-6,4
Sulphate	AB	3,30	4,26	51	7	3,30	4,26	3,30	0,17	4,23	0,21	5,1	4,9	-0,1	-0,7
Ion chromatography				40	1	3,32	4,26	3,30	0,13	4,25	0,16	4,0	3,8	0,0	-0,2
Photometry				7	4	3,20	4,05	3,33	0,51	4,08	0,40	15,4	9,8	1,0	-4,1
Nephelometry				3	2			3,10		3,60				-6,1	-15,5
ICP-AES				1	0			3,21		4,41				-2,7	3,5

Analytical variable and method	Sample pair	True value 1	True value 2	Total no.	Labs. excl.	Median 1	Median 2	Mean Std.dev. Sample 1		Mean Std.dev. Sample 2		Rel.std.dev. % 1	Rel.std.dev. % 2	Relative error 1	Relative error 2
Calcium	AB	3,15	3,55	56	5	3,15	3,55	3,23	0,29	3,58	0,31	8,9	8,5	2,6	0,9
FAAS				14	1	3,10	3,48	3,17	0,32	3,55	0,41	10,0	11,4	0,8	0,0
ICP-AES				13	0	3,13	3,53	3,11	0,19	3,49	0,18	6,0	5,1	-1,2	-1,5
EDTA				7	1	3,35	3,55	3,35	0,34	3,53	0,19	10,2	5,5	6,3	-0,5
Ion chromatography				19	2	3,40	3,66	3,34	0,29	3,72	0,31	8,7	8,4	6,2	5,1
ICP-MS				2	0			3,09		3,37				-2,1	-4,9
Photometry				1	1			1,50		2,00				-52,4	-43,5
Magnesium	AB	0,490	0,736	56	7	0,490	0,736	0,496	0,038	0,745	0,054	7,7	7,3	1,2	1,2
FAAS				14	0	0,484	0,725	0,488	0,034	0,730	0,050	7,1	6,9	-0,5	-0,9
ICP-AES				12	0	0,484	0,730	0,487	0,022	0,731	0,026	4,4	3,6	-0,7	-0,7
EDTA				7	5			0,505		0,765				6,1	3,9
Ion chromatography				20	1	0,500	0,752	0,505	0,050	0,765	0,068	9,8	8,9	3,0	3,9
ICP-MS				2	0			0,505		0,725				3,1	-1,5
Photometry				1	1			0,300		0,480				-38,8	-34,8
Sodium	AB	1,88	2,96	53	1	1,88	2,96	1,87	0,16	2,93	0,24	8,4	8,3	-0,8	-1,1
FAAS				11	0	1,92	3,01	1,89	0,19	2,95	0,30	10,2	10,1	0,6	-0,5
ICP-AES				10	0	1,83	2,91	1,80	0,13	2,84	0,19	7,2	6,8	-4,3	-3,6
AES				10	1	1,85	2,90	1,82	0,17	2,87	0,29	9,4	10,1	-3,4	-3,2
Ion chromatography				20	1	1,88	2,97	1,90	0,14	2,99	0,21	7,4	7,2	1,3	1,3
ICP-MS				2	0			1,93		2,90				2,4	-1,7
Potassium	AB	0,330	0,480	53	9	0,330	0,480	0,333	0,021	0,487	0,043	6,4	8,9	0,8	1,5
FAAS				11	4	0,330	0,490	0,329	0,016	0,497	0,026	5,0	5,2	-0,3	3,6
ICP-AES				10	1	0,320	0,485	0,321	0,022	0,474	0,034	6,9	7,1	-2,6	-1,2
AES				10	3	0,350	0,480	0,341	0,026	0,506	0,093	7,6	18,3	3,5	5,4
Ion chromatography				20	0	0,330	0,480	0,336	0,020	0,483	0,024	6,1	5,0	1,7	0,6
ICP-MS				2	1			0,340		0,480				3,0	0,0
Iron	CD	18,0	202,0	36	13	18,0	202,0	17,9	2,0	204,5	11,0	11,3	5,4	-0,3	1,2
FAAS				6	4			18,8		215,1				3,6	6,5
GFAAS				3	1			17,6		203,7				-2,7	0,8
ICP-AES				15	3	17,8	202,0	18,0	1,4	203,9	9,6	7,9	4,7	-0,6	0,9
ICP-MS				11	4	18,7	2,0	17,7	3,0	202,7	13,4	16,6	6,6	-1,4	0,4
Photometry				1	1			140,0		220,0				678,0	8,9

Analytical variable and method	Sample pair	True value 1	True value 2	Total no.	Labs. excl.	Median 1	Median 2	Mean Std.dev. Sample 1		Mean Std.dev. Sample 2		Rel.std.dev. % 1	Rel.std.dev. % 2	Relative error 1	Relative error 2
Manganese	CD	1,20	5,93	37	8	1,20	5,93	1,23	0,15	6,03	0,73	12,4	12,2	2,7	1,7
FAAS				4	3			1,60		4,00				33,3	-32,3
GFAAS				6	1	1,34	6,72	1,32	0,08	6,70	0,65	6,3	9,6	10,1	13,3
ICP-AES				14	2	1,20	5,98	1,24	0,17	5,99	0,42	13,8	7,0	2,9	1,4
ICP-MS				13	2	1,15	5,89	1,15	0,08	5,95	0,71	7,0	11,9	-3,8	0,4
Cadmium	CD	1,98	3,96	38	7	1,98	3,96	1,96	0,12	3,96	0,28	6,0	7,0	-1,1	-0,1
FAAS				2	2			3,15		5,40				59,1	36,0
GFAAS				13	3	1,99	3,92	1,91	0,17	3,92	0,42	9,0	10,7	-3,5	-1,1
ICP-AES				9	2	1,95	3,90	1,99	0,11	3,99	0,21	5,4	5,2	0,4	0,4
ICP-MS				14	0	1,98	3,97	1,98	0,06	3,97	0,18	3,2	4,5	-0,1	0,1
Lead	CD	5,15	9,82	36	5	5,15	9,82	5,12	0,36	9,87	0,74	7,1	7,5	-0,6	0,5
FAAS				1	1			13,70		18,80				165,5	90,7
GFAAS				13	2	5,00	9,72	4,93	0,49	9,73	0,99	9,9	10,2	-4,4	-1,3
ICP-AES				8	2	5,30	10,11	5,32	0,31	10,14	0,81	5,9	8,0	3,1	2,8
ICP-MS				14	0	5,18	9,87	5,18	0,17	9,87	0,45	3,3	4,5	0,7	0,5
Copper	CD	175	128	37	2	175	128	175	10	127	9	5,7	6,9	0,0	-0,8
FAAS				5	0	163	129	169	12	126	14	6,9	10,8	-3,2	-1,9
GFAAS				7	1	177	130	177	7	128	5	4,0	3,9	1,0	-0,1
ICP-AES				11	1	175	129	177	11	127	9	6,0	7,4	1,0	-0,7
ICP-MS				14	0	175	128	175	10	127	8	5,8	6,6	0,0	-0,8
Nickel	CD	10,60	5,19	35	6	10,01	5,18	10,13	0,67	5,17	0,42	6,6	8,2	0,7	-0,5
FAAS				2	2			14,60		9,35				45,1	80,2
GFAAS				10	2	10,47	5,19	10,15	0,68	5,25	0,45	6,7	8,6	0,9	1,1
ICP-AES				10	2	10,05	5,04	10,07	0,88	5,19	0,52	8,8	10,0	0,1	-0,1
ICP-MS				13	0	10,00	5,26	10,16	0,56	5,10	0,37	5,6	7,2	0,9	-1,7
Zinc	CD	50,3	23,0	38	1	50,3	23,0	50,4	4,6	23,3	3,3	9,1	14,1	0,1	1,3
FAAS				9	1	48,5	22,6	46,6	6,1	22,2	4,9	13,1	22,3	-7,5	-3,4
GFAAS				2	0			54,4		29,1				7,9	26,5
ICP-AES				14	0	51,0	22,9	50,7	2,7	23,5	2,7	5,4	11,3	0,7	2,4
ICP-MS				13	0	50,3	22,7	51,6	4,3	22,8	1,9	8,3	8,3	2,6	-0,8

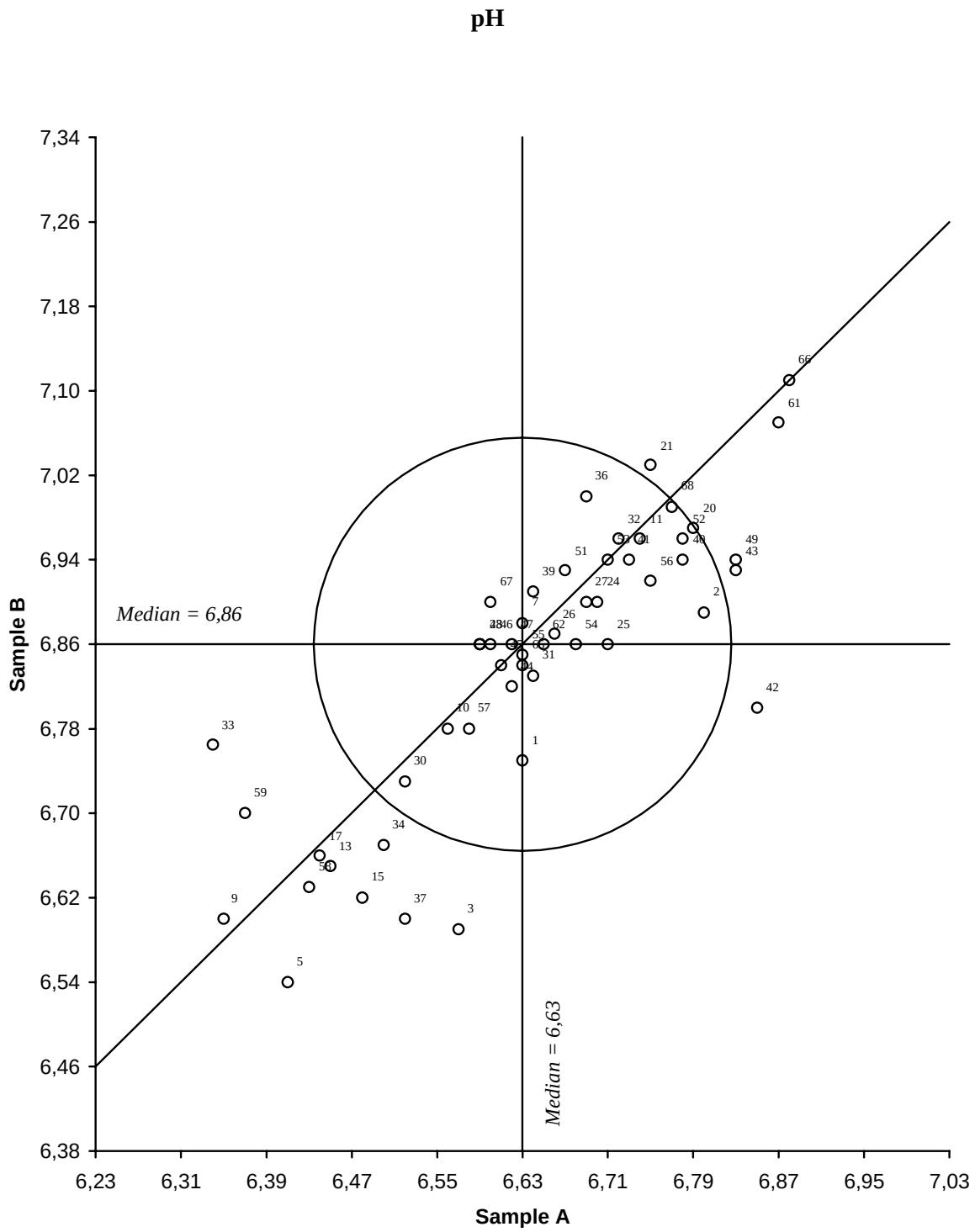

Figure 1. Youden diagramme for pH, sample pair AB
Acceptance limit, given by the circle, is 0,2 pH units

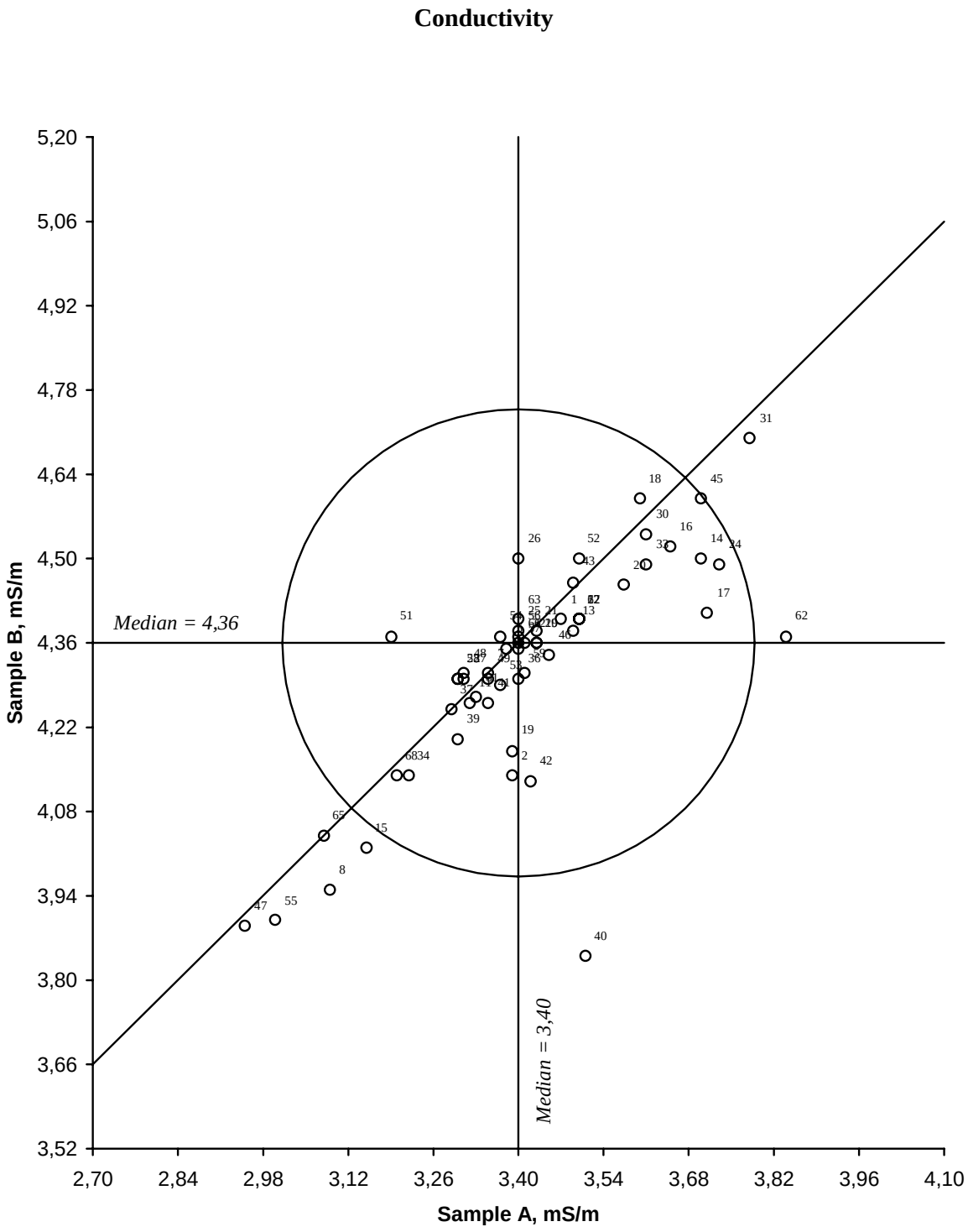

Figure 2. Youden diagramme for conductivity, sample pair AB
Acceptance limit, given by the circle, is 10 %

Alkalinity

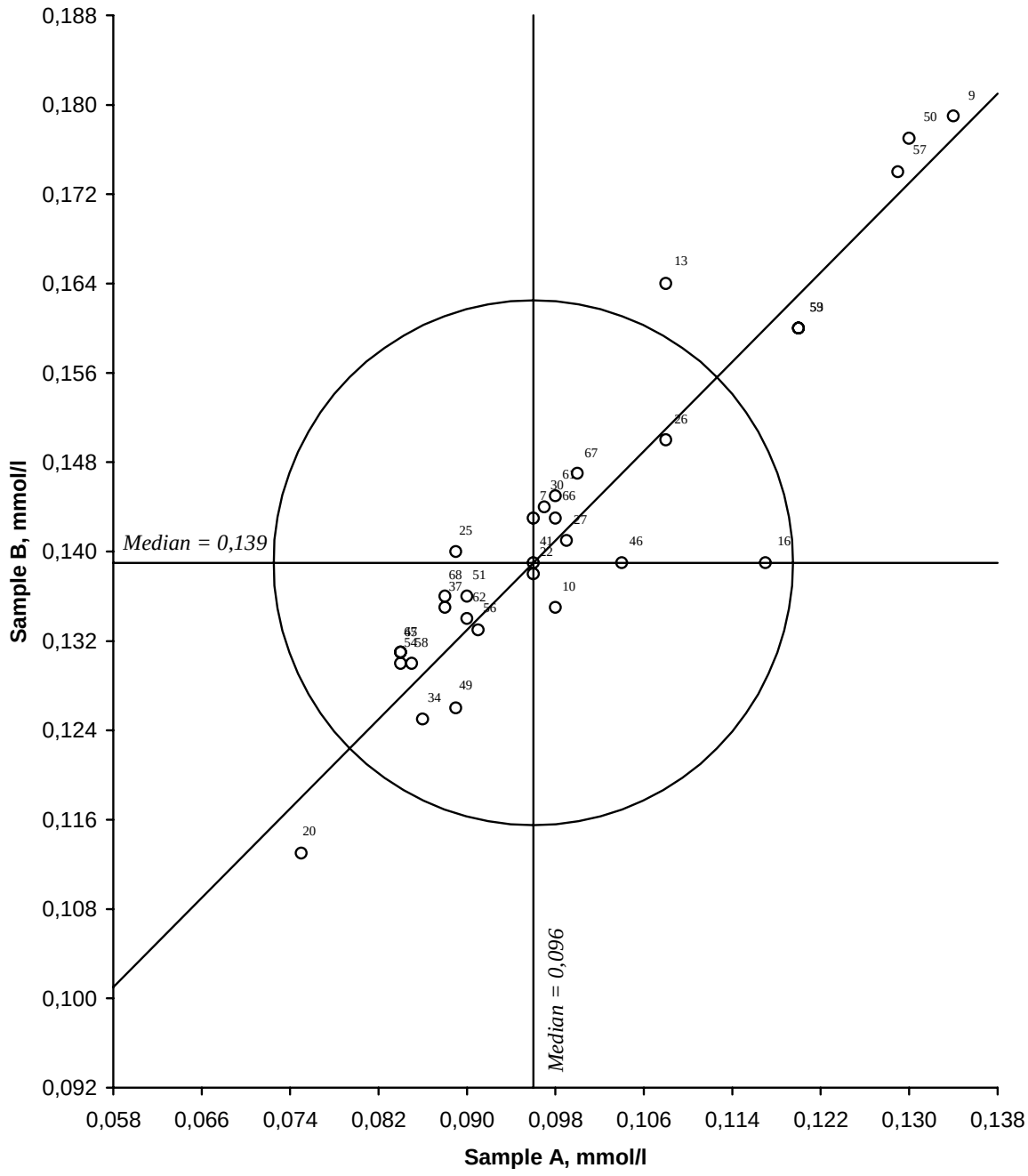

Figure 3. Youden diagramme for alkalinity, sample pair AB
Acceptance limit, given by the circle, is 20 %

Nitrate + nitrite-nitrogen

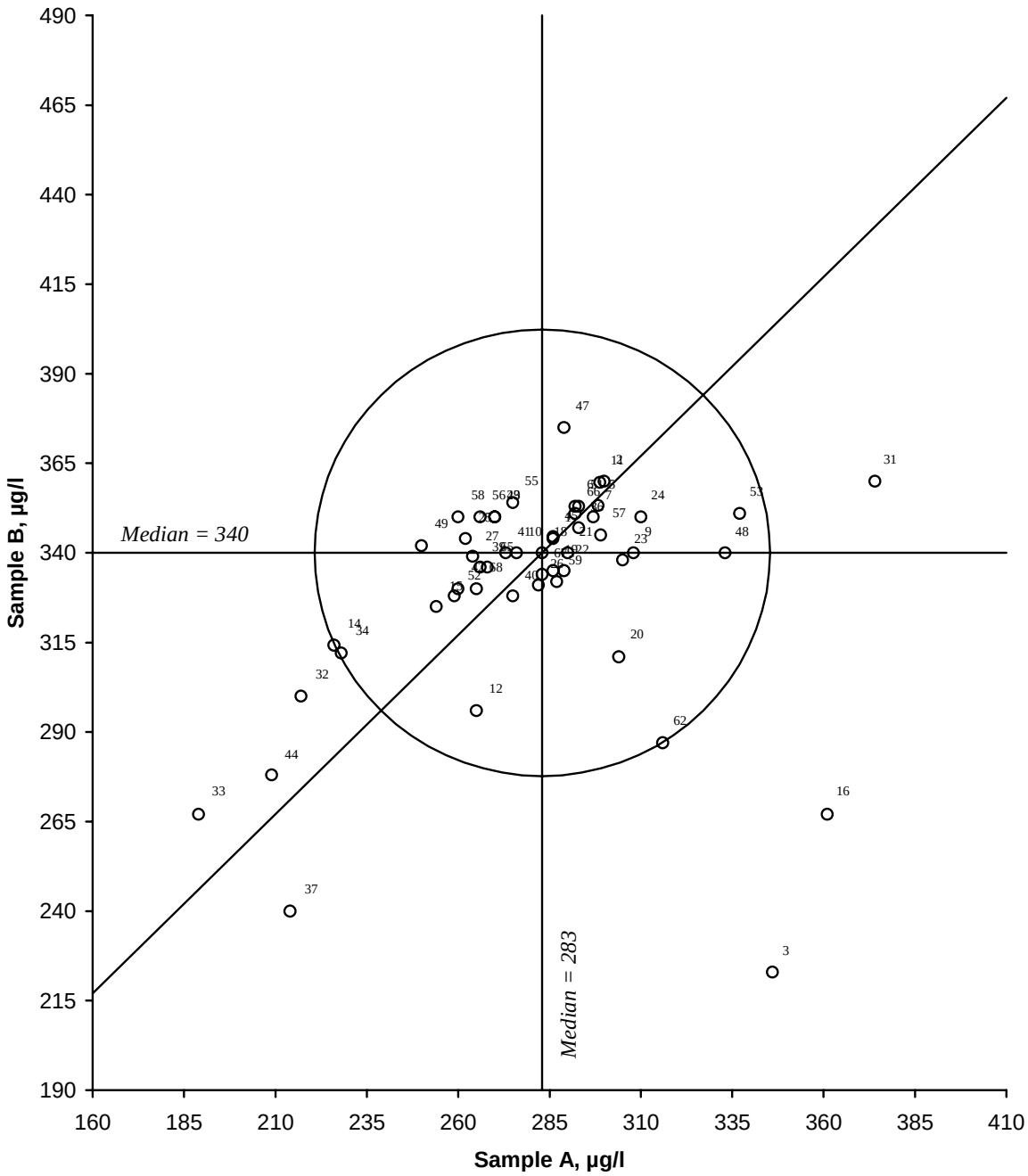

Figure 4. Youden diagramme for nitrate + nitrite-nitrogen, sample pair AB
Acceptance limit, given by the circle, is 20 %

Chloride

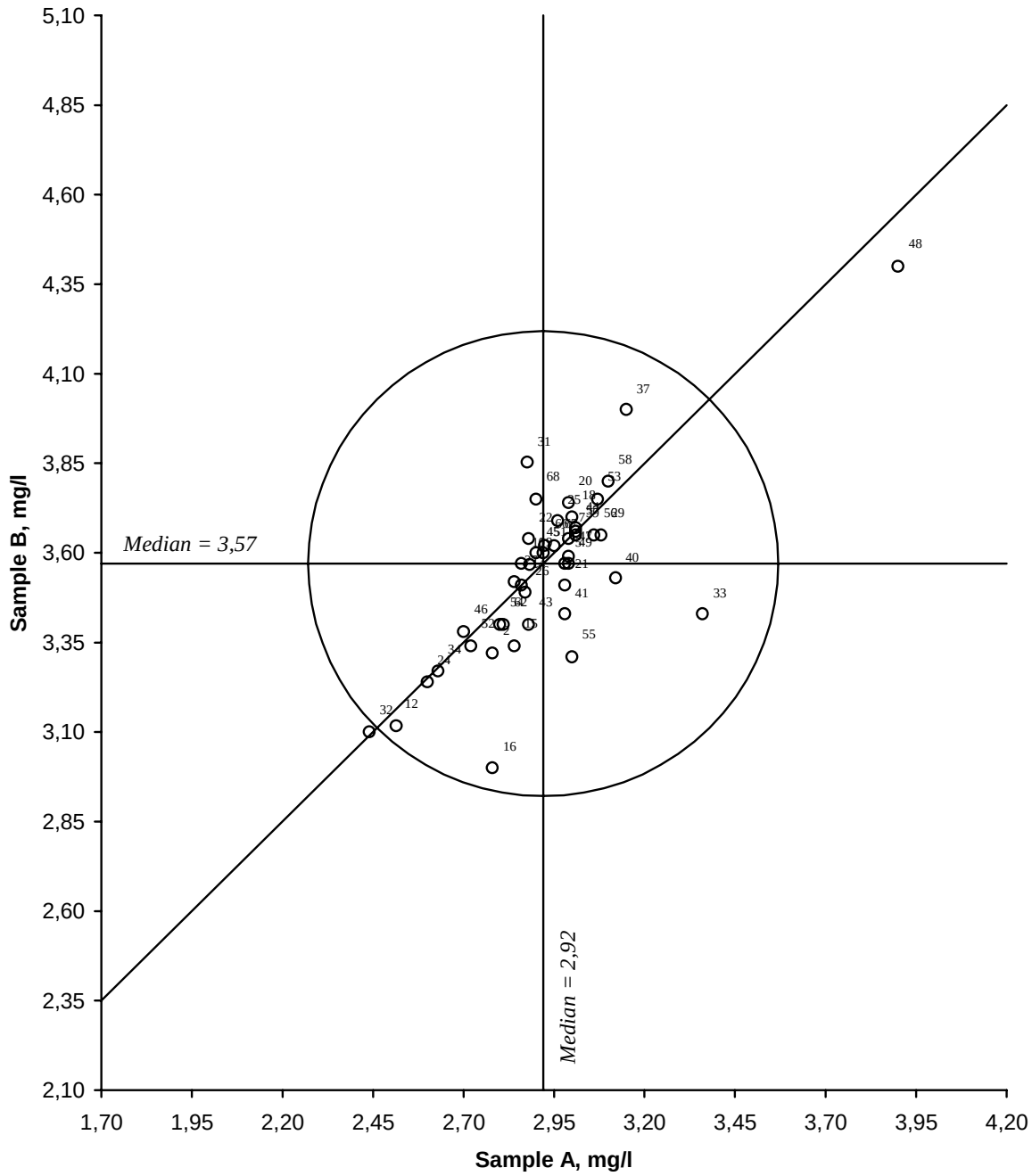

Figure 5. Youden diagramme for chloride, sample pair AB
Acceptance limit, given by the circle, is 20 %

Sulphate

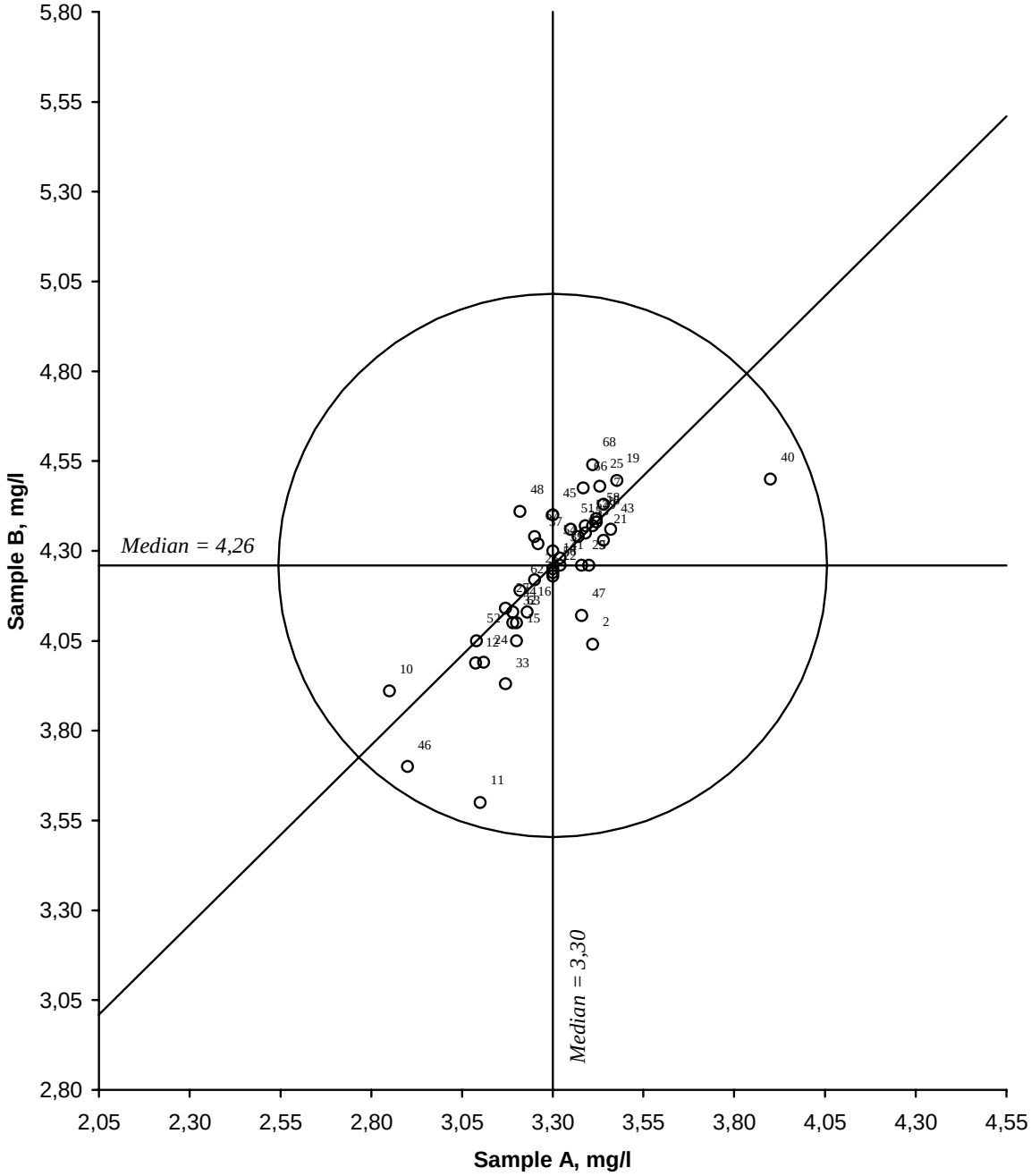

Figure 6. Youden diagramme for sulphate, sample pair AB
Acceptance limit, given by the circle, is 20 %

Calcium

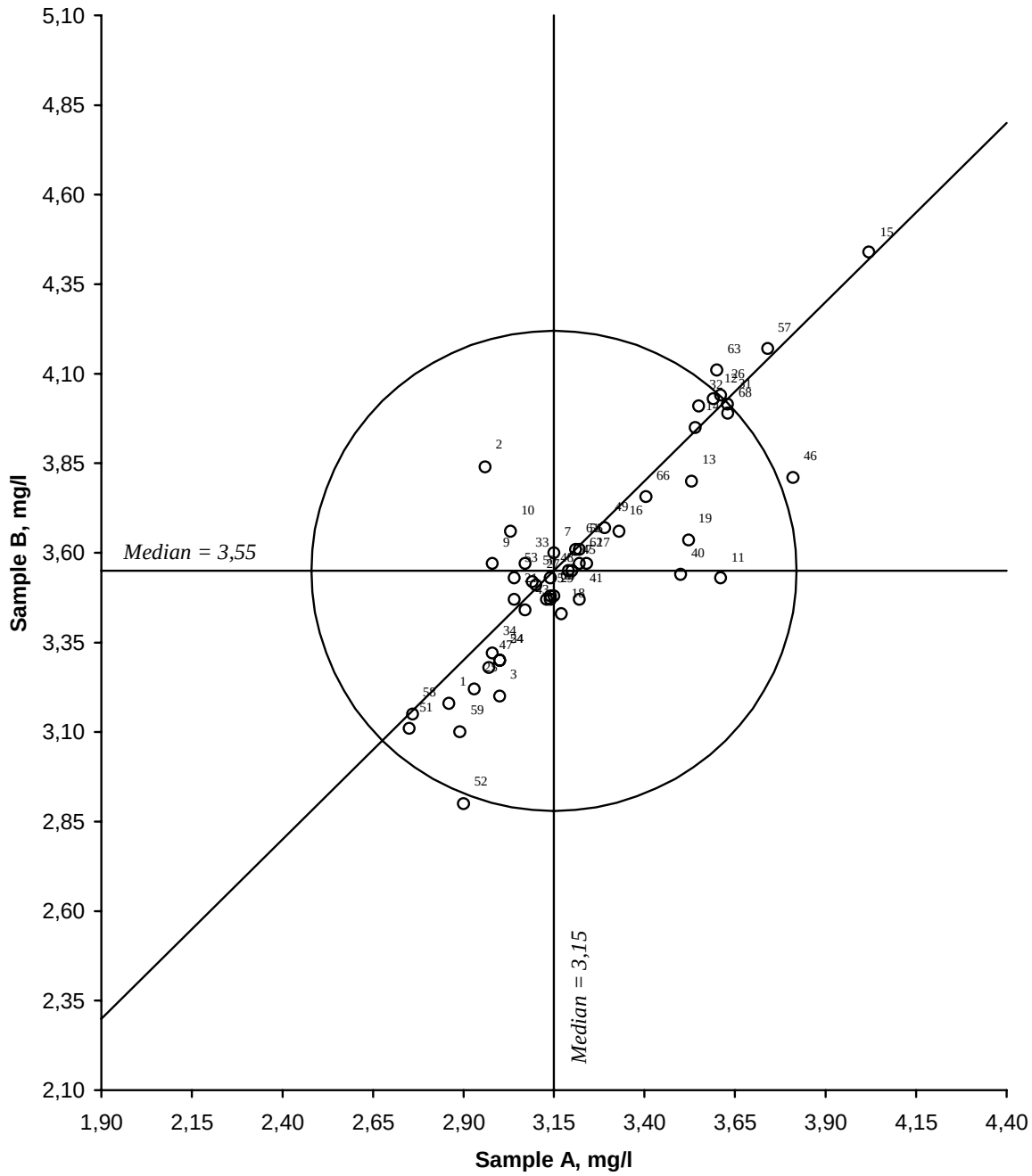

Figure 7. Youden diagramme for calcium, sample pair AB
Acceptance limit, given by the circle, is 20 %

Magnesium

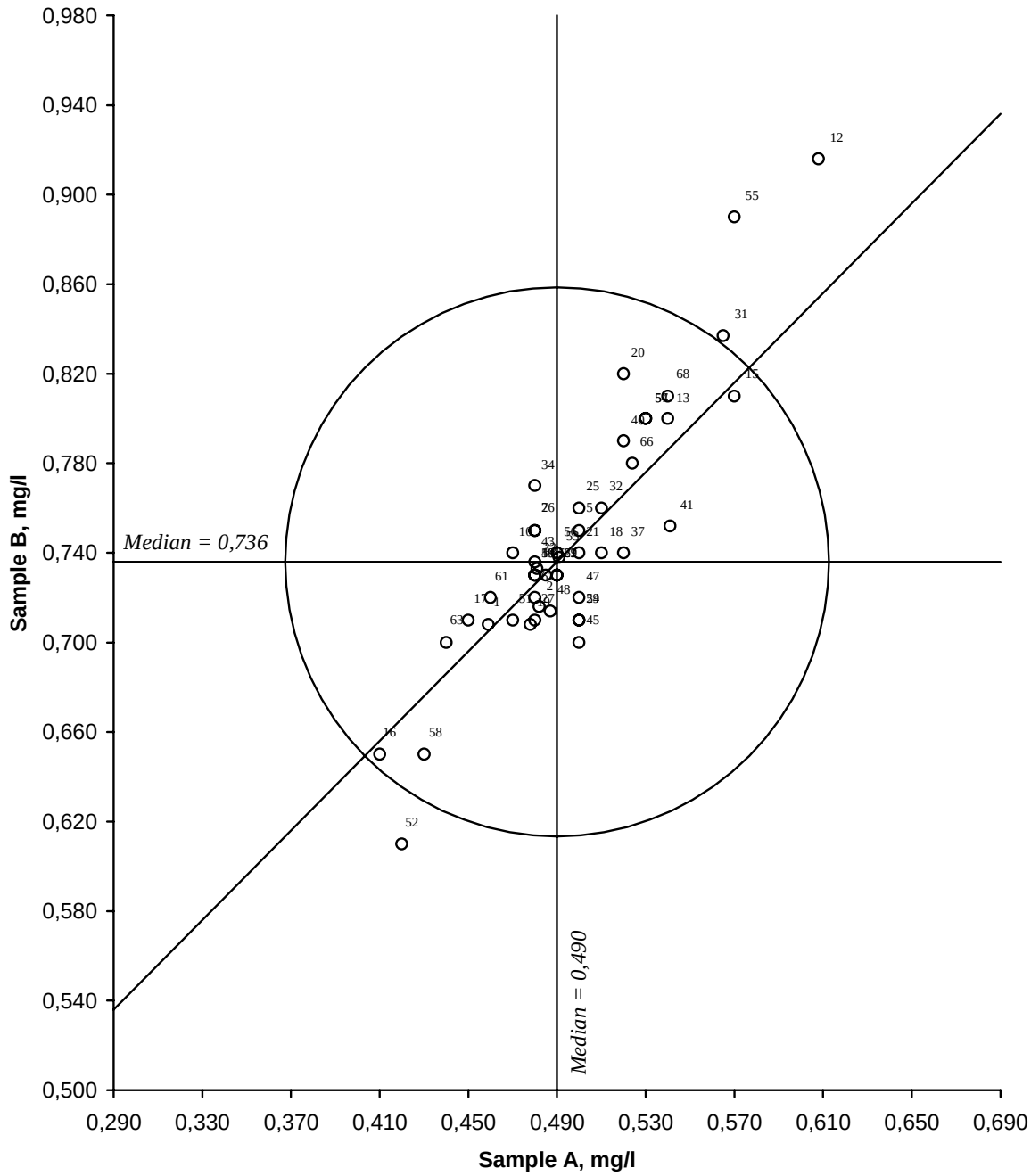

Figure 8. Youden diagramme for magnesium, sample pair AB
Acceptance limit, given by the circle, is 20 %

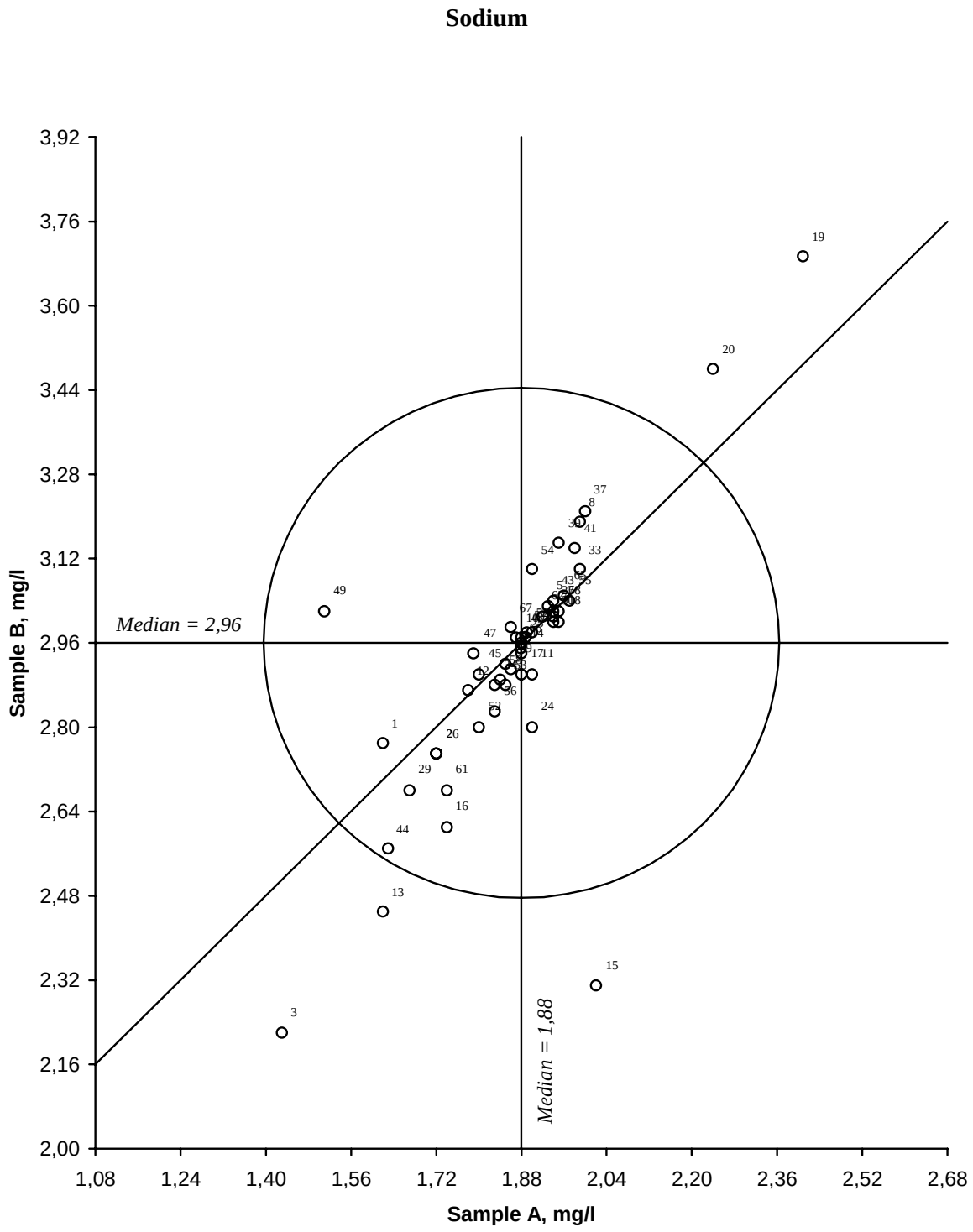

Figure 9. Youden diagramme for sodium, sample pair AB
Acceptance limit, given by the circle, is 20 %

Potassium

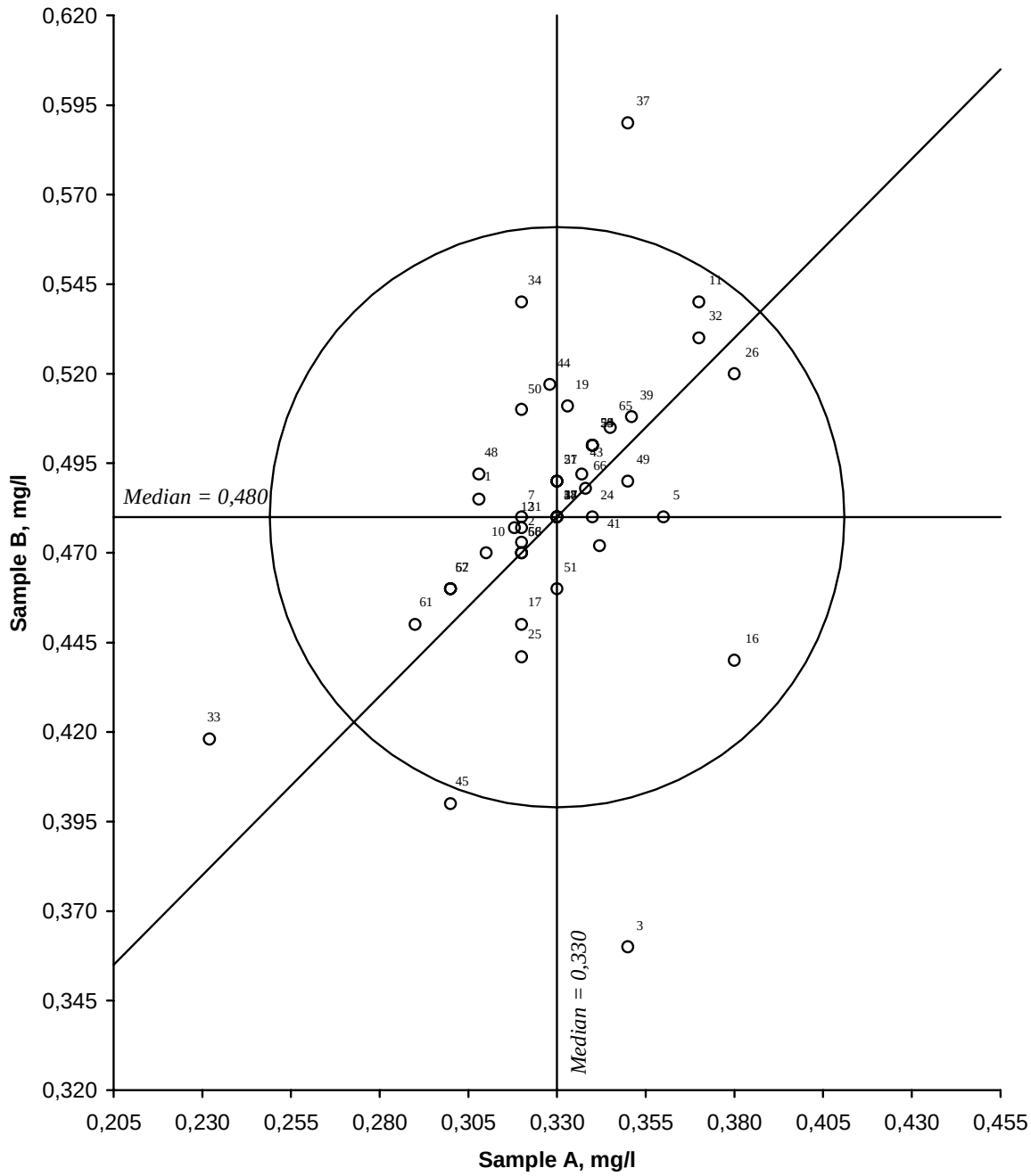

Figure 10. Youden diagramme for potassium, sample pair AB
Acceptance limit, given by the circle, is 20 %

Iron

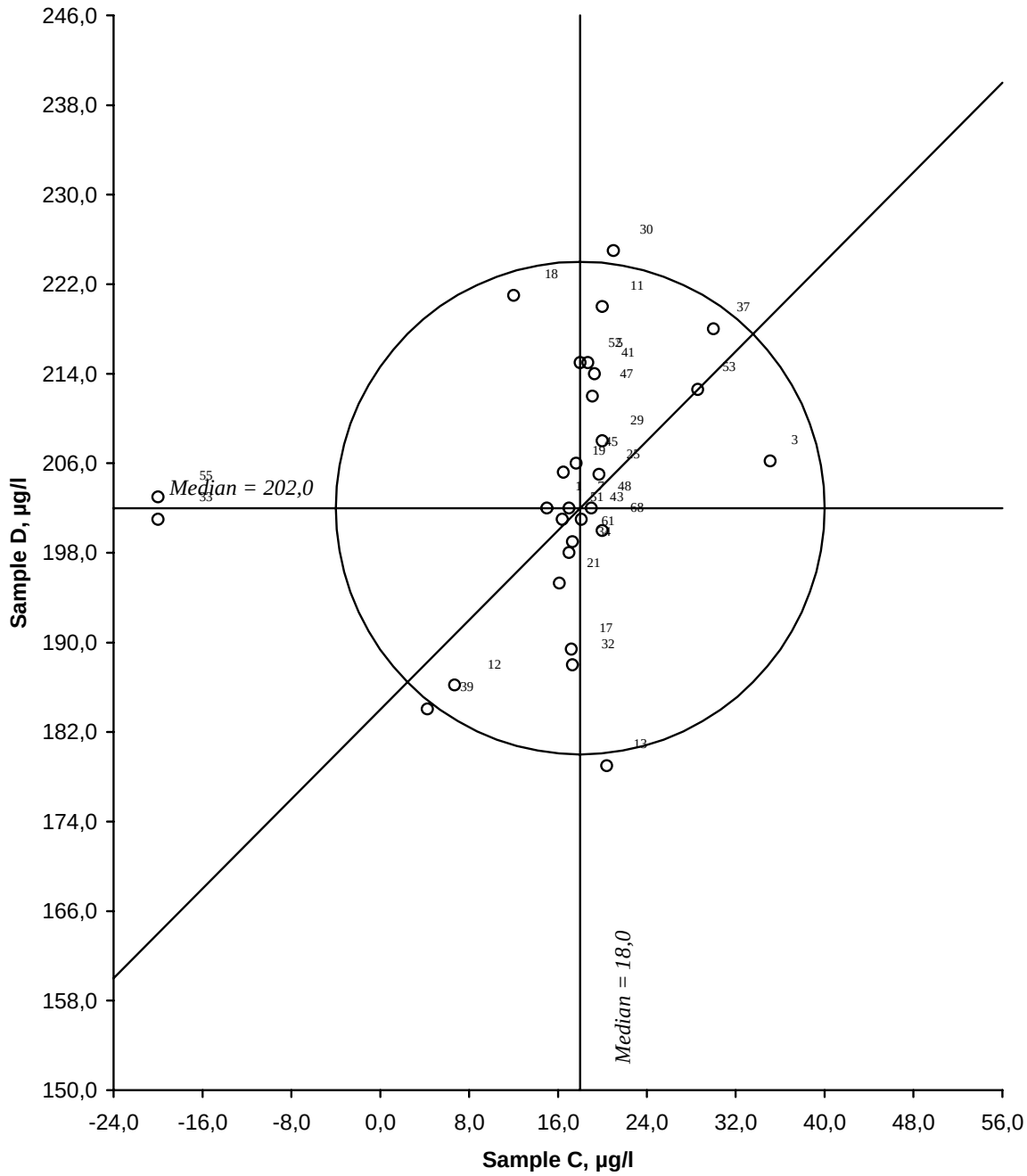

Figure 11. Youden diagramme for iron, sample pair CD
Acceptance limit, given by the circle, is 20 %

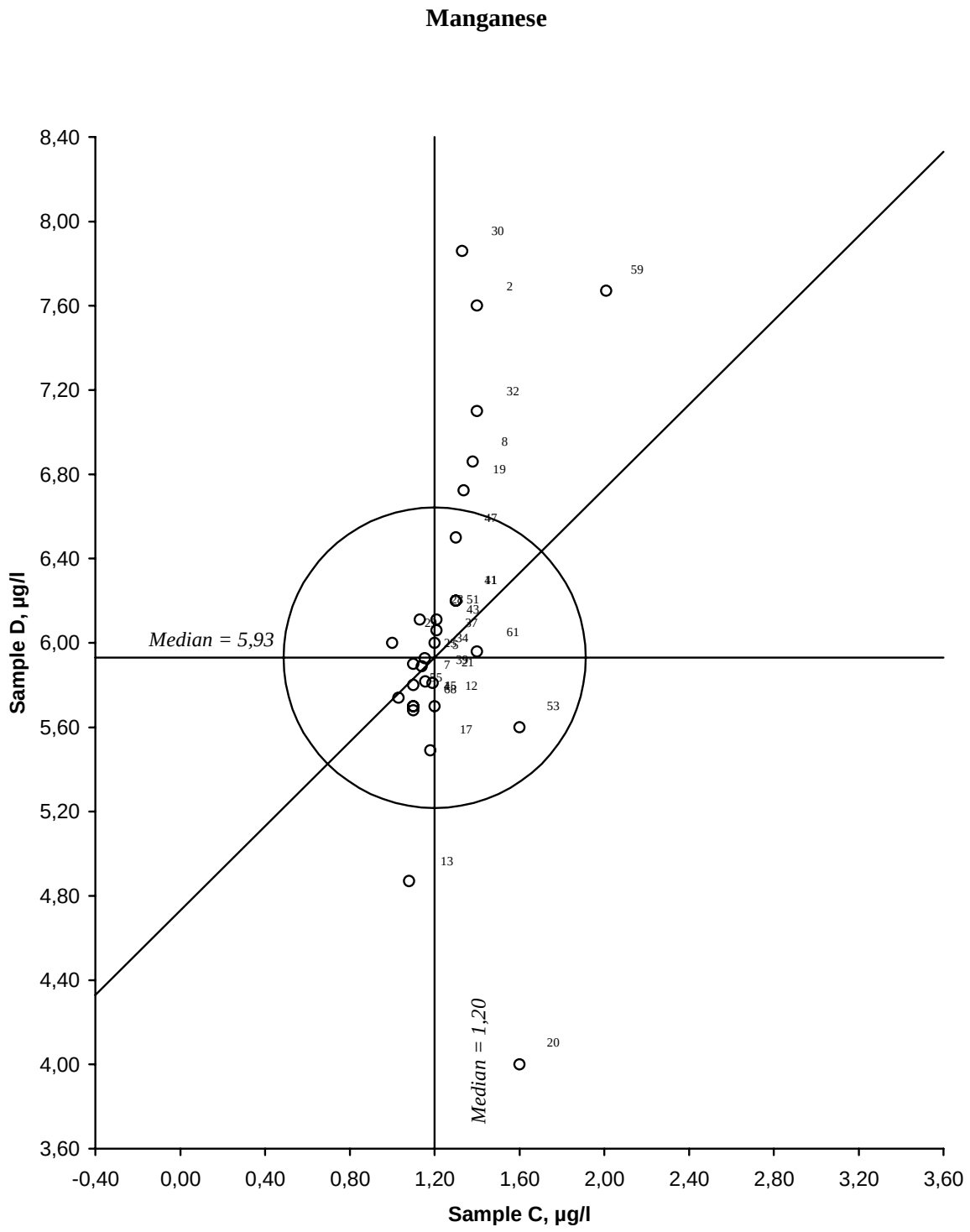

Figure 12. Youden diagramme for manganese, sample pair CD
Acceptance limit, given by the circle, is 20 %

Cadmium

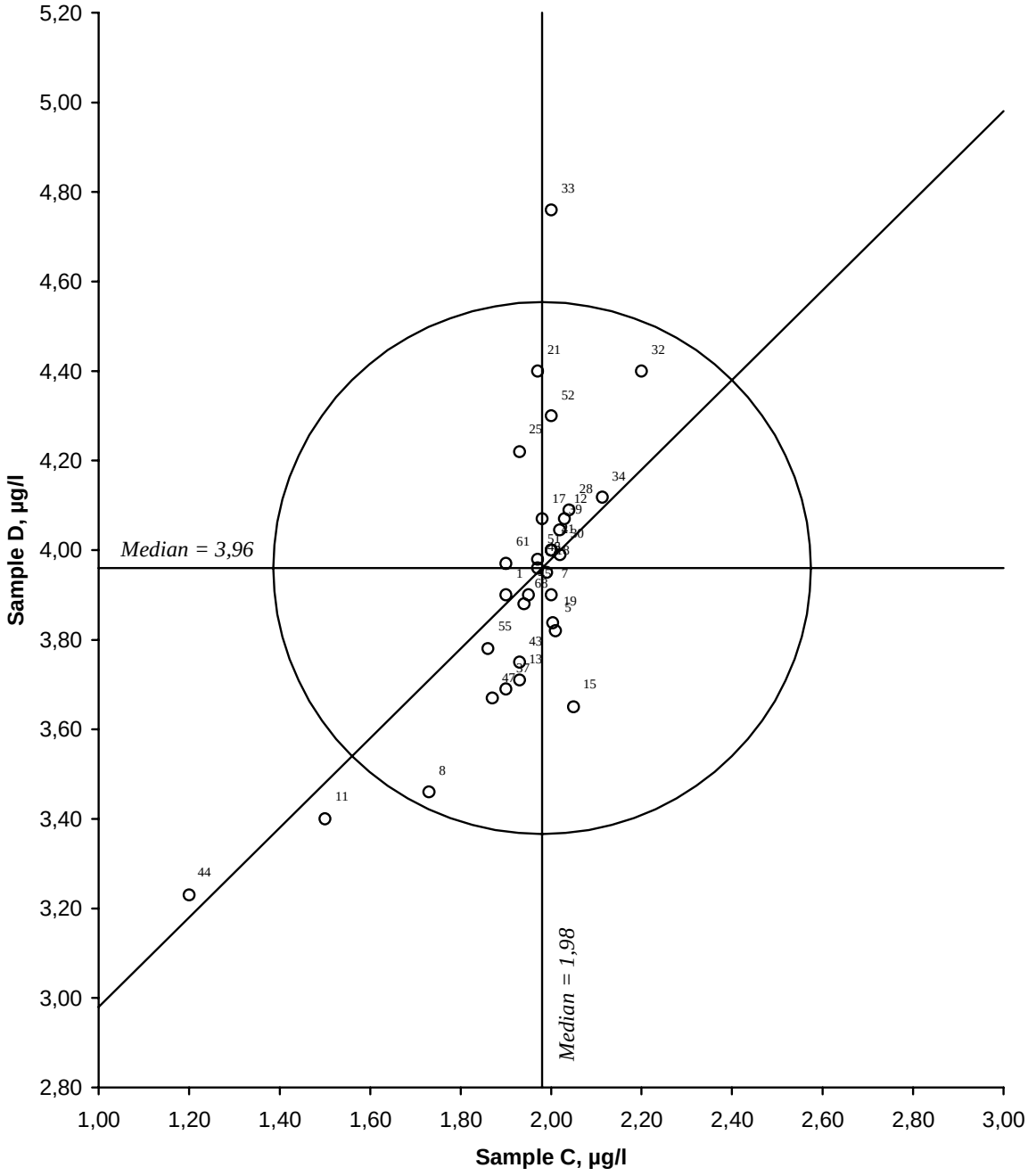

Figure 13. Youden diagramme for cadmium, sample pair CD
Acceptance limit, given by the circle, is 20 %

Lead

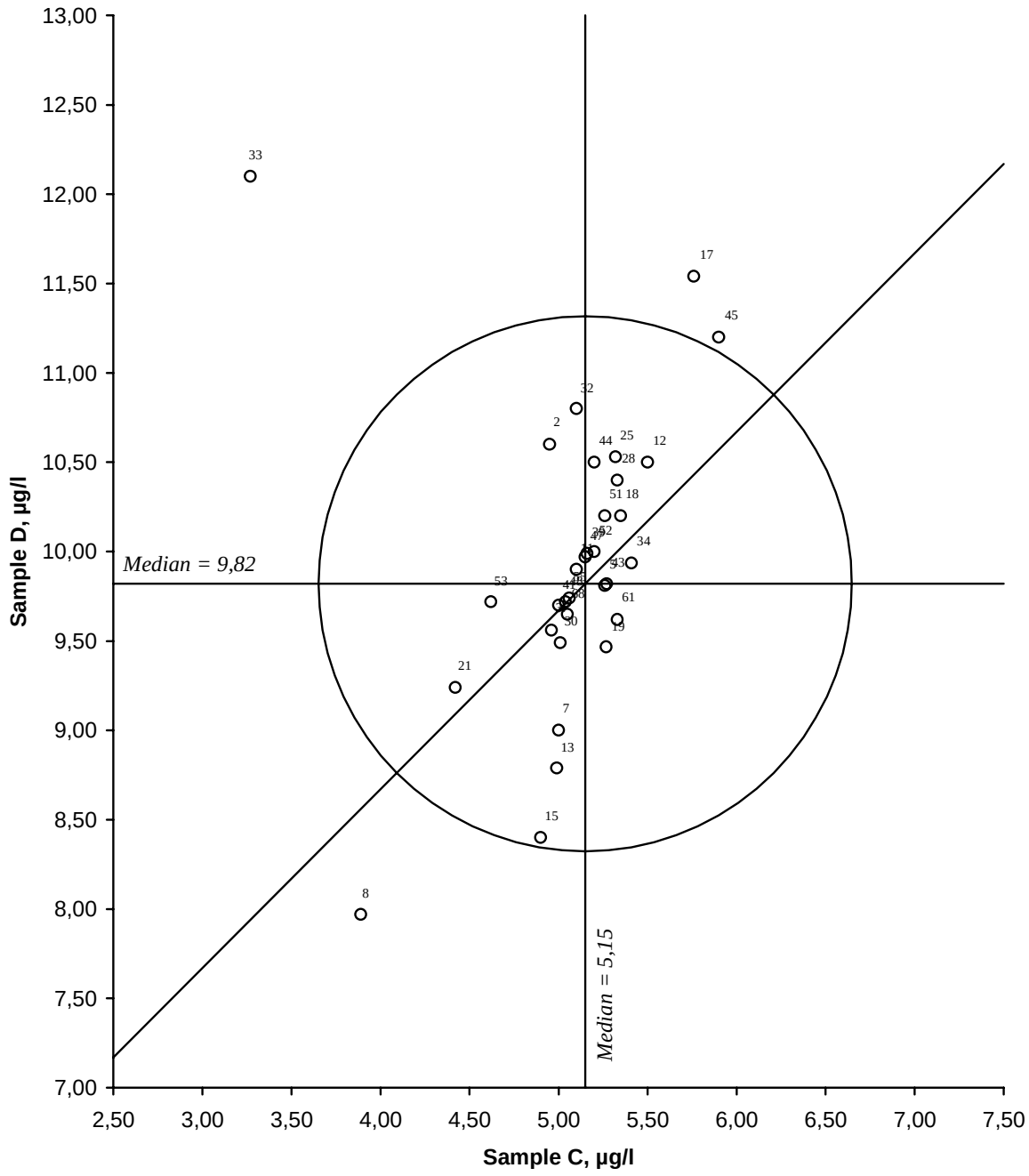

Figure 14. Youden diagramme for lead, sample pair CD
Acceptance limit, given by the circle, is 20 %

Copper

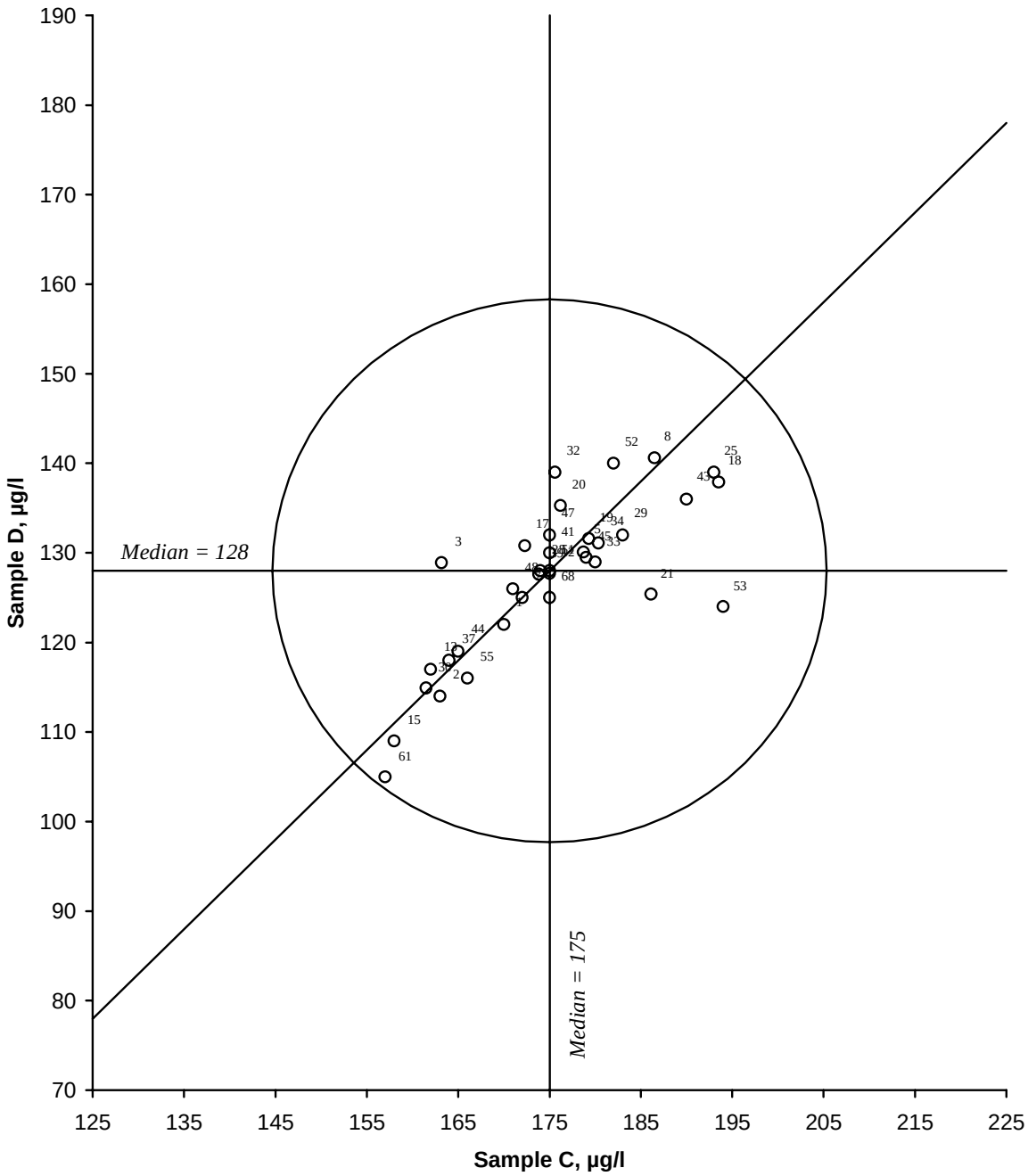

Figure 15. Youden diagramme for copper, sample pair CD
Acceptance limit, given by the circle, is 20 %

Nickel

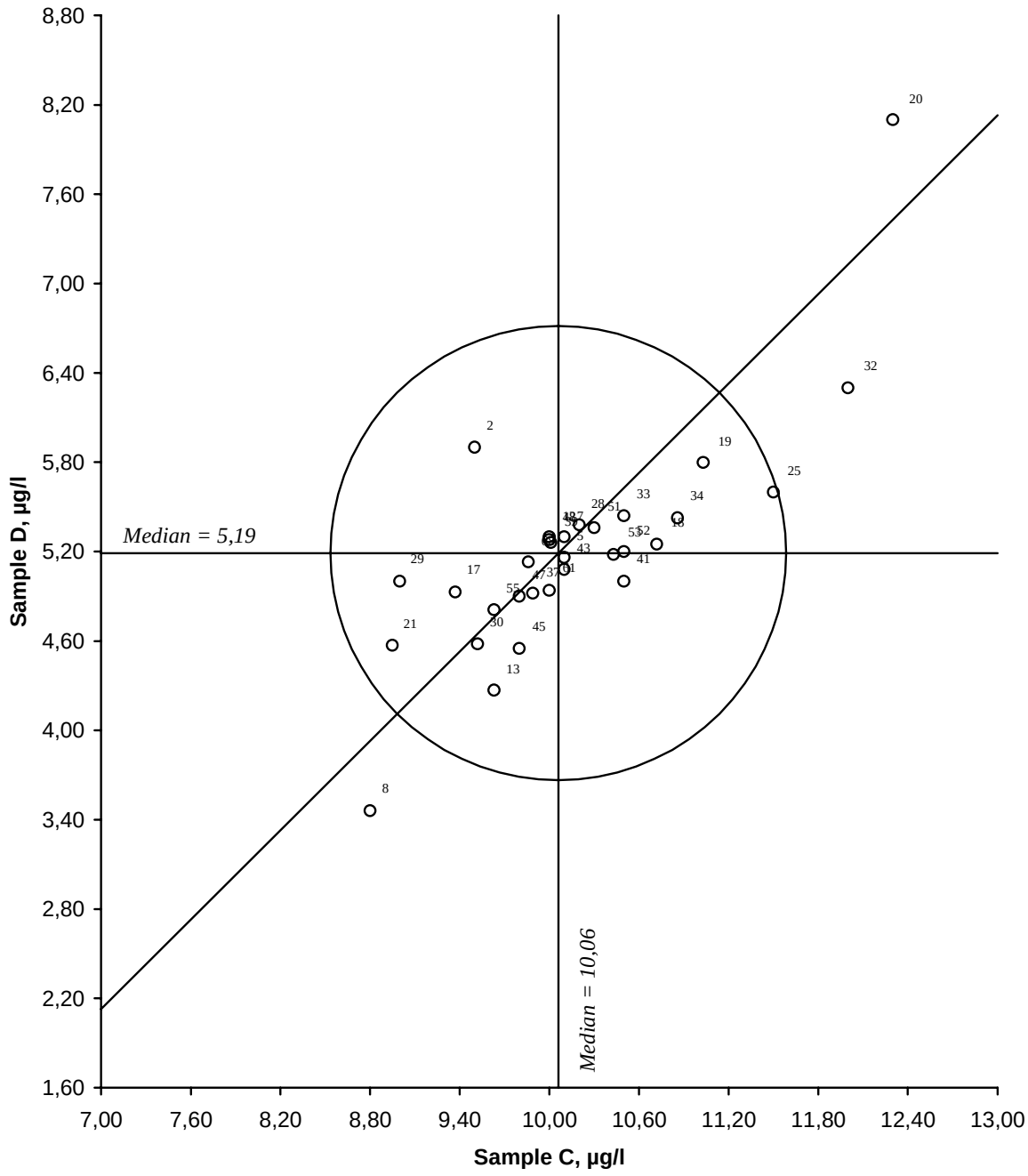

Figure 16. Youden diagramme for nickel, sample pair CD
Acceptance limit, given by the circle, is 20 %

Zinc

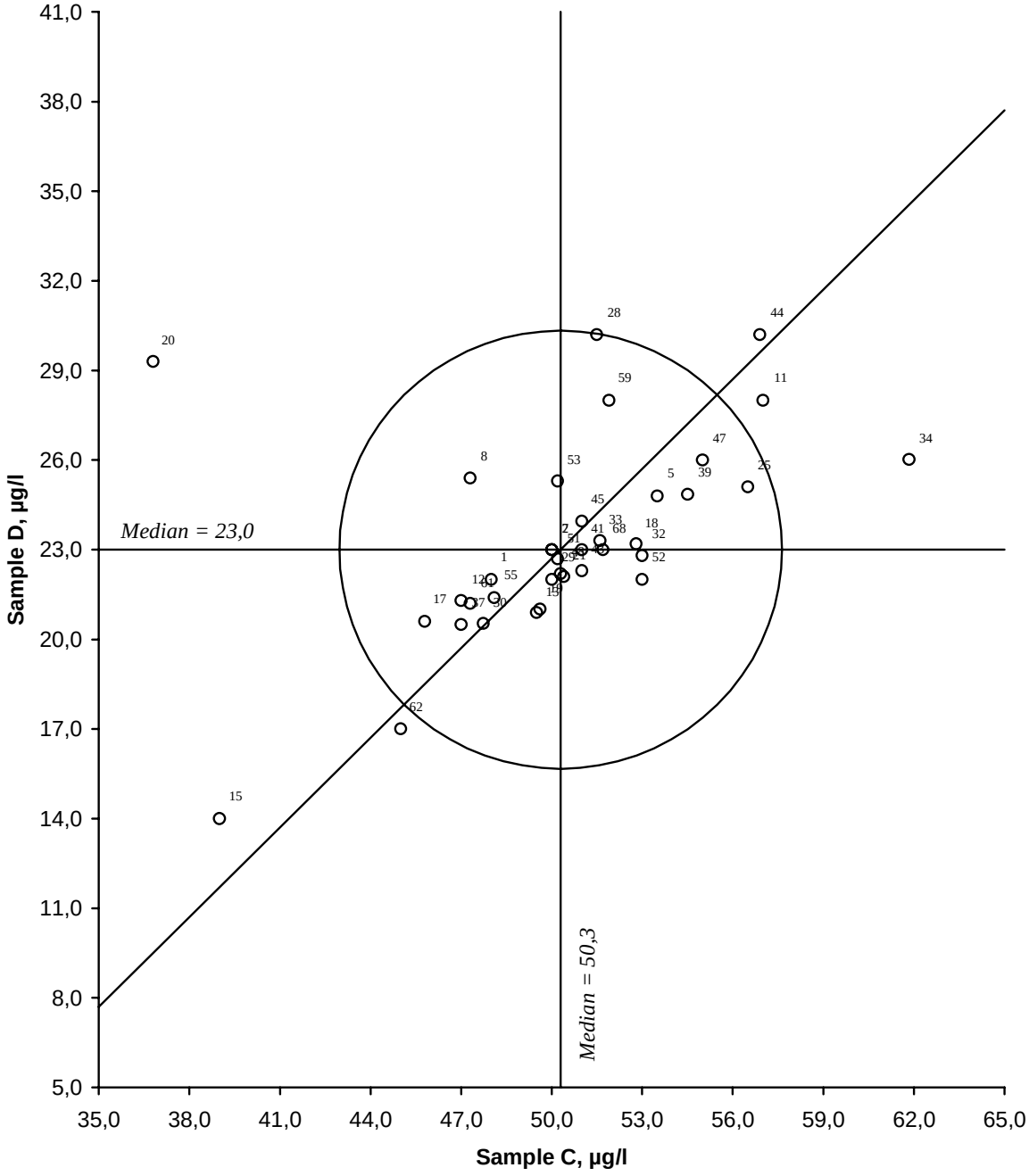

Figure 17. Youden diagramme for zinc, sample pair CD
Acceptance limit, given by the circle, is 20 %

sample. Especially 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, it is possible that the equilibrium of the samples may be influenced by variations in pressure and temperature when they are mailed by air 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 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 these 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), eight more results located 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 demand.

4.3 Alkalinity

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 5.3. 46 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, 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. Four laboratories 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 5,4 gave results mainly located within the acceptance circle.

The overall result for alkalinity in this intercomparison is a little worse than in the last intercomparison, only half of the results being acceptable. A possible reason for this is the fact that samples with rather 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 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 two laboratories gave acceptable results. One laboratory using photometric method reported the results in a wrong unit, and the results were corrected to µg/l after clarification with the laboratory.

This time 81 % of the results are evaluated as acceptable, which is about the same as in the last intercomparison. One probable reason for this may be that the concentrations of nitrate-nitrogen were rather high in this intercomparison. 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. 40 out of 51 laboratories determined chloride by ion chromatography. The greatest deviations are observed for a potentiometric method. The results determined with the argentometric method were too low, while somewhat varying and systematically high results were reported for the mercurimetric method.

84 % acceptable results in this intercomparison is the highest score for the last four intercomparisons.

4.6 Sulphate

The sulphate 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 40 of 51 laboratories for the determination of the sulphate content. Seven laboratories used a photometric method based on the dissociation of the barium-thorin complex, the results, on average, being comparable to the ion chromatographic method. Only one out of three result pairs were acceptable for the nephelometric method. One laboratory used ICP-AES for the determination of total sulphur, and then recalculated the result to mg/l sulphate.

86 % acceptable result pairs is representing the highest score for the last four 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. 56 laboratories reported results for calcium, and 14 of them used the traditional flame atomic absorption spectrometry for the determination. The ICP technique is used by 15 laboratories, and two of these used ICP-MS. An increasing number of laboratories, this time 19, used ion chromatography. One laboratory using a photometric method for the determination of calcium produced results being about the half of the true value.

80 % acceptable result pairs is comparable to the intercomparison last year.

4.8 Magnesium

The magnesium results are presented in Figure 8, and the reported values are given in Table 5.8. One quarter of the participants are still using flame atomic absorption spectrometry for the determination of magnesium. ICP atomic emission spectrometry was used by 12 laboratories, and 20 laboratories used ion chromatography. Systematic errors are dominating the results being outside the acceptance limit. This time, 80 % of the results are located inside the target accuracy of ± 20 %. The great deviations observed for the photometric method 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. Only 11 laboratories used flame atomic absorption spectrometry for the determination this time, and ICP-AES was used by 10 laboratories. However, in many laboratories the ion chromatographic technique becomes increasingly more popular in routine determination of the alkaline metals, thus 20 participants used ion chromatography in this intercomparison. Five laboratories used flame photometry. 87 % 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, only 11 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. 75 % of the result pairs are considered acceptable this time.

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, 69 % of the result pairs are located inside this circle. 36 laboratories submitted results for iron, of which 15 and 11 used ICP-AES and ICP-MS, respectively, while 6 and 3 used flame and graphite furnace atomic absorption, respectively.

Some laboratories using ICP-AES have rather high detection limits, and thus four participants 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. The large difference in concentration between sample C and D, D being ten times more concentrated than C, is probably the reason why the results are widely spread along the C axis compared to the D axis. The ICP-AES results are somewhat higher than the ICP-MS results, especially for sample D with the highest concentration.

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. Only 59 % of the result pairs are located inside this circle, which is rather low compared to former intercomparisons, however, the concentrations used this time are lower than normal. 37 laboratories submitted results for manganese, of which 14 and 13 used ICP-AES and ICP-MS, respectively, while 4 and 6 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. The dominating spreadout along the D axis for this metal too is probably caused by the fact that the sample D has markedly higher concentration than sample C.

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, 76 % of the result pairs are located inside this circle. 38 laboratories submitted results for cadmium, of which 9 and 14 used ICP-AES and ICP-MS, respectively, while 13 used graphite furnace atomic absorption. There are no significant differences between the results determined by the different methods for cadmium. An exception is FAAS which is not a sensitive enough method. However, 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. 78 % of the result pairs are located inside this circle. 36 laboratories submitted results for lead, of which 8 and 14 used ICP-AES and ICP-MS, respectively, while 13 used graphite furnace atomic absorption. Flame atomic absorption is not sensitive enough to determine these low lead concentrations. There are only small differences between the results determined by the different methods for lead, however, the ICP-AES method is probably a little less sensitive for the low concentrations used in these samples. The deviating results are affected by both systematic and random errors.

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. 95 % of the result pairs are located inside this circle, which is very good. Rather high concentrations used for copper this time are most probably a reason for the good results. 37 laboratories submitted results for copper, of which 11 used ICP-AES and 14 used ICP-MS, while 7 and 5 used graphite furnace and flame atomic absorption, respectively. The deviating results are affected mainly by systematic errors.

4.16 Nickel

The results for nickel are illustrated in Figure 16, and the values reported by the participants are given in Table 5.16. The target accuracy is ± 20 %, and is represented by the great circle in Figure 16. This time, as much as 80 % of the result pairs are located inside this circle. The increased concentration in this intercomparison compared to earlier may be the reason for the increased number of accepted results. 35 laboratories submitted results for nickel, of which 10 and 13 used ICP-AES and ICP-MS, respectively, while 10 used graphite furnace atomic absorption. Both result pairs for FAAS were excluded. 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, 82 % of the result pairs are located inside this circle. 38 laboratories submitted results for zinc, of which 14 and 13 used ICP-AES and ICP-MS, respectively, while 2 and 9 used flame and graphite furnace atomic absorption, respectively. 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 they determine 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 0418 is presented, based on the target accuracy (except for pH and conductivity), where the number and percentage of acceptable results are given. 77 % of the results submitted by the participants are acceptable when compared to the acceptance limits given above. By improvement of the routine analytical method, the laboratories should be able to obtain even 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 the measurement is performed 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 problem is well demonstrated for the equilibration method, which normally gives results quite higher than the other methods. This time there were only minor differences between the pH results produced during stirring the solution and no stirring of the solution.

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 %. Still the number of acceptable results for conductivity is 80 % (Table 2). If we increase the acceptance limit to the target value, the number of acceptable results would increase to 95 %. It is still 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.

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 a little weaker than in the last intercomparison, probably because the concentrations of bicarbonate in the samples used this time is rather low. Also for this parameter there is some confusion among the participants about the unit.

Table 2. Evaluation of the results of intercomparison 0418. N is the number of result pairs reported, and n is the number of acceptable results within the given target accuracy.

Analyte and unit	Sample-pair	True value 1	True value 2	Accept. limit %	N Tot.	n Accept.	% accepatble res. for intercal. 0418	0317	0216	0115
pH	AB	6,63	6,86	2,9*	60	34	57	57	66	58
Conductivity, mS/m	AB	3,4	4,36	10¤	60	49	80	82	75	82
Alkalinity, mmol/l	AB	0,096	0,139	20	46	24	52	58	53	76
Nitrate+nitrite-nitrogen, µg/l	AB	283	340	20	54	44	81	82	59	77
Chloride, mg/l	AB	2,92	3,57	20	51	43	84	81	66	79
Sulphate, mg/l	AB	3,3	4,26	20	51	44	86	83	76	82
Calcium, mg/l	AB	3,15	3,55	20	56	45	80	77	62	82
Magnesium, mg/l	AB	0,49	0,736	20	56	45	80	79	67	75
Sodium, mg/l	AB	1,88	2,96	20	53	46	87	92	88	93
Potassium, mg/l	AB	0,33	0,48	20	53	40	75	70	73	85
Iron, µg/l	CD	18	202	20	36	25	69	51	71	41
Manganese, µg/l	CD	1,2	5,93	20	37	22	59	36	76	64
Cadmium, µg/l	CD	1,98	3,96	20	38	29	76	60	63	66
Lead, µg/l	CD	5,15	9,82	20	36	28	78	49	59	51
Copper, µg/l	CD	175	128	20	37	35	95	83	73	75
Nickel, µg/l	CD	10,06	5,19	20	35	28	80	68	68	68
Zinc, µg/l	CD	50,3	23	20	38	31	82	76	64	53
Total					798	612	77	(71)	(68)	(71)

* 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 nitrate + nitrite 81 % of the result pairs are acceptable. This is comparable to the results last year, and the nitrate concentrations in this intercomparison are rather high. In some few 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 fraction of acceptable results are 80 % for both variables. For the other major ions, chloride, sulphate, sodium and potassium, the number of acceptable results are high as usual.

The heavy metals iron, manganese, cadmium, lead, copper, nickel, and zinc were included in this intercomparison Programme. The best results were obtained for copper, zinc and nickel, where 95, 82 and 80 % of the results, respectively, are acceptable. For these elements the concentrations were well above the detection limits of the most sensitive methods used, especially for copper the concentrations are very high. 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, in the cases where the results are close to the detection limit. In such cases it is important that the steering committee decides what target detection limit should be obtained by the laboratories.

6. Conclusion

63 laboratories submitted results for this intercomparison. The best results were reported for the analytical variables copper, sodium and sulphate, where 95, 87 and 86 % of the results, respectively, were acceptable. The worst results were observed for alkalinity, pH and manganese. The different methods used for pH and alkalinity are probably the major reason for the great spread in the results produced, while the concentrations are rather low for manganese.

Overall, 77 % of the evaluated results were located within the general target accuracy of ± 20 %, or the special accuracy limit for pH and conductivity. Thus, more than two thirds of the reported results are acceptable. The low fraction of acceptable results for some variables, may in part be explained by the rather low concentrations used for these analytical variables. When the concentrations are close to the detection limits for some of the methods used by the participants, it must be expected that the spread of the results will be greater than ± 20 %.

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 for the determination of pH, therefore it is necessary to use some wider acceptance limit for this variable.

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	Finnish Forest Research Institute	Vantaa	Finland
2	Estonian Environment Research Centre	Tallinn	Estonia
3	Water Sources Laboratory	Bucuresti	Romania
4	Umweltbundesamt, Analytic 1	Vienna	Austria
5	Bayerishes Landesamt für Wasserwirtschaft	München	Germany
6	Hiiumaä Environmental Laboratory	Kärdla	Estonia
7	CNR Istiuto Studio degli Ecosistemi	Pallanza	Italy
8	Geological Survey of Estonia	Tallinn	Estonia
9	Tallinn Technical University	Tallinn	Estonia
10	Laboratorio Biologico Provinciale	Laives	Italy
11	Joint Research Centre	Vilnius	Lithuania
12	Environmental Protection Agency	Dublin	Ireland
13	Istituto Agrario di St. Michele all'Adige	St. Michele	Italy
14	Soil Science and Plant Nutrition Dept.	Firenze	Italy
15	Polish Academy of Sciences, Botany	Krakow	Poland
16	EAWAG Limnological Research Center	Kastanienbaum	Switzerland
17	Institute for Ecology of Industrial Areas	Katowice	Poland
18	Amt der Kärntner Landesregierung	Klagenfurt	Austria
19	Vlaamse Milieumaatschappij	Antwerpen	Belgium
20	Water Pollution Observation Laboratory	Minsk	Belarus
21	Latvian Laboratory Department	Riga	Latvia
22	Freshwater Institute	Winnipeg	Canada
23	ELA Satellite Laboratory	Winnipeg	Canada
24	Staatliche Umweltbetriebsgesellschaft	Chemnitz	Germany
25	CNR – Water Research Institute	Brugherio	Italy
26	National Institute of Biology	Ljubljana	Slovenia
27	Adirondac Lake Survey Corporation	Ray Brook	USA
28	Umweltbundesamt – Messnetz	Langen	Germany
29	Umweltbundesamt – Dienstgebaude Langen	Langen	Germany
30	Charles University Dept. of Hydrobiology	Blatna	Czech Republic
31	Hubnan Institute of Environmental Science	Changsha	P.R. China
32	ISSeP Colfontaine	Wasmes	Belgium
33	T.G.Masaryk Water Research Institute	Praha	Czech Republic
34	LMTG/CNRS	Toulouse	France
35	Institute of Environmental Protection	Warsawa	Poland
36	Ontario Ministry of Environment	Etobicoke	Canada
37	Swedish University of Agricultural Sciences	Uppsala	Sweden
38	University of Barcelona	Vielha Leida	Spain
39	Freshwater Fisheries Laboratory	Pitlochry	Scotland
40	Laboratory of Hydrochemistry, Limn. St.	Rannu	Estonia
41	Tartu Environmental Research	Tartu	Estonia
42	River Biology Laboratory of EAU	Tartu	Estonia
43	Landesumweltamt NRW	Essen	Germany
44	Yantai Environmental Monitoring Centre	Yantai	P.R. China
45	Centre for Ecology & Hydrology	Wallington	United Kingdom
46	Virumaa Environmental Research Ltd.	Jõhvi	Estonia

Identity	Laboratory	City	Country
47	Cola Science Center, INEP	Apatity	Russia
48	The Environment Agency NLS Laboratory	Llanelli	United Kingdom
49	University of Helsinki, Physical Geography	Helsinki	Finland
50	SLU, Skoglig Marklära	Uppsala	Sweden
51	Finnish Environment Institute Research Lab.	Helsinki	Finland
52	ZAO “ROSSA”	Moscow	Russia
53	Ecoanalytical Laboratory	Syktyvkar	Russia
54	Swedish Environment Research Institute	Gothenburg	Sweden
55	Norwegian Institute for Air Research	Kjeller	Norway
56	Universität Innsbruck, Zoologie & Limnol.	Innsbruck	Austria
57	Acid Deposition and Oxidant Res. Center	Niigata City	Japan
58	Hydrobiological Institute	Ceske Budejovice	Czech Republic
59	Analist Sercise S.R.L.	Bucuresti	Romania
60	Universidad de Granada, Instituto del Agua	Granada	Spain
61	University of Maine, Env. chem.. Lab.	Orono	USA
62	Chemical Laboratory of CGS	Praha	Czech Republic
63	Centre for Marine Analytical Ref. & Stds.	Trivandrum	India
64	Bundesanstalt für Fischereiwirtschaft	Mondsee	Austria
65	M;inistry of Environment	Dorset	Canada
66	Finnish Forest Research Institute	Rovaniemi	Finland
67	Kymi Environmental Laboratory	Kouvola	Finland
68	Norwegian Institute for Water Research	Oslo	Norway

Number of participating laboratories (N) from the different countries being represented in intercomparison 0418.

Country	N	Country	N
Austria	4	Japan	1
Belarussia	1	Latvia	1
Belgium	2	Lithuania	1
Canada	4	Norway	2
China	2	Poland	3
Czech Republic	4	Romania	2
Estonia	8	Russia	3
Finland	5	Slovenia	1
France	1	Spain	2
Germany	5	Sweden	3
India	1	Switzerland	1
Ireland	1	United Kingdom	3
Italy	5	USA	2

Appendix B.

Preparation of samples

The sample solutions were prepared from tap water collected from the lake Maridalsvannet, located outside Oslo, Norway. Tap water was filtrated through 0,45 µm membrane filter and the filtrate collected in polyethylene containers and stored at room temperature for several weeks at the laboratory. 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 in May 2004, a few weeks before mailing the samples to the participants. The last sample was analyzed at the end of July 2004. 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	6,75	0,073	6,96	0,055
Conductivity mS/m	3,19	0,046	4,12	0,043
Alkalinity mmol/l	0,096	0,005	0,141	0,001
Nitrate/nitrite µg/l	264	6,3	329	6,3
Chloride mg/l	2,88	0,03	3,66	0,08
Sulphate mg/l	3,39	0,02	4,35	0,13
Calcium mg/l	3,60	0,05	3,96	0,03
Magnesium mg/l	0,525	0,019	0,798	0,026
Sodium mg/l	1,91	0,05	2,99	0,07
Potassium mg/l	0,320	0,008	0,473	0,013
	Sample C		**Sample D**	
Iron, µg/l	17,5	5,0	202,5	5,0
Manganese, µg/l	1,15	0,06	5,89	0,29
Cadmium, µg/l	1,96	0,02	3,91	0,06
Lead, µg/l	5,09	0,06	9,69	0,04
Copper, µg/l	174,,8	3,1	125,5	2,1
Nickel, µg/l	10,01	0,14	5,16	0,11
Zinc, µg/l	51,03	0,73	22,85	0,79

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 straight lines drawn in the diagram are representing the true values of the samples; or - as in this case, when the true value is not known - the median value of the results from the participating laboratories. The results being omitted in the statistical calculations are not used in the determination of the median value and thus the true value. 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	6,63	6,75	3,47	4,40			286	344
2	6,80	6,89	3,39	4,14	0,16	0,22	300	360
3	6,57	6,59	1,16	0,90	0,32	0,40	346	223
5	6,41	6,54	3,38	4,35			298,3	353,2
6	7,84	7,94	2,28	2,79	0,20	0,30	292	353
7	6,63	6,88	3,35	4,31	0,096	0,143	297	350
8	6,10	6,70	3,09	3,95	0,18	0,21		
9	6,35	6,60	4,0	5,3	0,134	0,179	308	340
10	6,56	6,78	3,43	4,36	0,098	0,135	276	340
11	6,74	6,96	3,32	4,26	0,057	0,103	298,8	359,7
12	5,93	7,42	3,50	4,40	0,08	0,09	265	296
13	6,45	6,65	3,49	4,38	0,108	0,164		
14	7,3	7,5	3,7	4,5			226,1	314,2
15	6,48	6,62	3,15	4,02			254	325
16			3,65	4,52	0,117	0,139	361	267
17	6,44	6,66	3,71	4,41				
18	5,80	5,90	3,60	4,60	0,36	0,43	283	340
19	5,92	6,32	3,39	4,18			286	335
20	6,79	6,97	3,573	4,457	0,075	0,113	304	311
21	6,75	7,03	3,43	4,38	0,150	0,160	290	340
22	7,31	7,52	3,5	4,4	0,096	0,138	289	335
23	6,59	6,86	3,3	4,3			305	338
24	6,7	6,9	3,73	4,49	0,16	0,21	310	350
25	6,71	6,86	3,40	4,38	0,089	0,140	262	344
26	6,66	6,87	3,4	4,5	0,108	0,150	282	331
27	6,690	6,900	3,31	4,30	0,099	0,141	264	339
28								
29			3,43	4,36			270	350
30	6,52	6,73	3,61	4,54	0,097	0,144		
31	6,64	6,83	3,78	4,70	0,142	0,175	374	360
32	6,72	6,96	3,41	4,36			217	300
33	6,34	6,765	3,61	4,49	0,132	0,217	189	267
34	6,50	6,67	3,22	4,14	0,086	0,125	228	312
36	6,69	7,00	3,40	4,30			293	347
37	6,52	6,60	3,29	4,25	0,088	0,135	214	240
39	6,64	6,91	3,30	4,20	0,92	0,137	266	336
40	6,78	6,94	3,51	3,84	0,140	0,170	275	328
41	6,73	6,94	3,35	4,26	0,096	0,139	273	340
42	6,85	6,80	3,42	4,13			260	330
43	6,83	6,93	3,49	4,46			270	350
44	6,62	6,82					209	278
45	6,61	6,84	3,70	4,60			286	345
46	6,60	6,86	3,45	4,34	0,104	0,139		
47	6,62	6,86	2,95	3,89	0,084	0,131	289	375

Lab.	pH		Cond, mS/m		Alk, mmol/l		NO3+NO2, µg/l	
	A	B	A	B	A	B	A	B
48	6,59	6,86	3,31	4,31	0,0441	0,0646	333	340
49	6,83	6,94	3,35	4,30	0,089	0,126	250	342
50	6,21	6,60	3,45	4,40	0,130	0,177		
51	6,67	6,93	3,191	4,370	0,090	0,136	293	353
52	6,78	6,96	3,50	4,50	< 0,1	0,13	259	328
53	6,71	6,94	3,37	4,29	0,12	0,16	337	351
54	6,68	6,86	3,37	4,37	0,084	0,13		
55	6,63	6,85	3,0	3,9			275	354
56	6,75	6,92	3,40	4,37	0,091	0,133	266	350
57	6,58	6,78	3,40	4,35	0,129	0,174	299	345
58	6,43	6,63	3,3	4,3	0,085	0,130	260	350
59	6,37	6,70	3,41	4,31	0,12	0,16	287	332
61	6,87	7,07	3,33	4,27	0,098	0,145		
62	6,65	6,86	3,84	4,37	0,090	0,134	316	287
63	5,55	6,85	3,40	4,40			18	22
65	6,63	6,84	3,08	4,04	0,084	0,131	268	336
66	6,88	7,11	3,4	4,36	0,098	0,143	292	351
67	6,6	6,9	3,5	4,4	0,100	0,147	283	334
68	6,77	6,99	3,20	4,14	0,088	0,136	265	330

Lab.	Cl, mg/l		SO4, mg/l		Ca, mg/l		Mg, mg/l	
	A	B	A	B	A	B	A	B
1					2,86	3,18	0,459	0,708
2	2,78	3,32	3,41	4,04	2,96	3,84	0,482	0,716
3	21,2	28,3	3,0	2,0	3,0	3,2	0,36	0,49
5	2,98	3,57	3,40	4,26	3,13	3,47	0,50	0,75
6	1,2	1,6	2,0	2,4	1,5	2,0	0,30	0,48
7	2,99	3,64	3,44	4,43	3,15	3,60	0,48	0,75
8	0,48	0,48	0,79	1,25	0,86	1,05	0,76	0,87
9	4,2	5,3			2,98	3,57	0,90	1,08
10	2,86	3,57	2,85	3,91	3,03	3,66	0,47	0,74
11			3,1	3,6	3,61	3,53	1,14	1,17
12	2,514	3,117	3,088	3,988	3,59	4,03	0,608	0,916
13					3,53	3,80	0,54	0,80
14	2,86	3,51	3,30	4,25	3,54	3,95	0,48	0,73
15	2,84	3,34	3,20	4,05	4,02	4,44	0,57	0,81
16	2,78	3,00	3,23	4,13	3,33	3,66	0,41	0,65
17					3,24	3,57	0,45	0,71
18	3,0	3,7	3,42	4,38	3,17	3,43	0,51	0,74
19	2,883	3,567	3,477	4,496	3,522	3,636	0,478	0,708
20	2,99	3,74	5,90	6,99	1,51	1,66	0,52	0,82
21	2,98	3,51	3,44	4,33	3,04	3,47	0,50	0,74
22	2,88	3,64	3,30	4,23				
23								
24	2,60	3,24	3,11	3,99	3,0	3,3	0,50	0,71
25	2,96	3,69	3,43	4,48	2,93	3,22	0,50	0,76
26	2,87	3,49	3,25	4,22	3,61	4,04	0,48	0,75
27	2,84	3,52	3,17	4,14	3,10	3,51	0,48	0,71
28								
29	3,08	3,65	3,38	4,26	3,14	3,47	0,49	0,73
30								
31	2,876	3,853	1,091	1,526	3,629	4,015	0,565	0,837
32	2,44	3,10	3,19	4,10	3,55	4,01	0,51	0,76
33	3,36	3,43	3,17	3,93	3,07	3,57	0,481	0,733
34	2,63	3,27	3,37	4,34	2,98	3,32	0,48	0,77
36								
37	3,15	4,00	3,26	4,32	3,19	3,55	0,52	0,74
39	3,01	3,65	3,32	4,28	7,62	8,28	0,933	1,37
40	3,12	3,53	3,9	4,5	3,50	3,54	0,52	0,79
41	2,98	3,43	3,32	4,26	3,22	3,47	0,541	0,752
42								
43	2,88	3,40	3,46	4,36	3,07	3,44	0,480	0,736
44	3,01	3,67	3,19	4,13				
45	2,9	3,6	3,3	4,4	3,2	3,55	0,5	0,7
46	2,70	3,38	2,9	3,7	3,81	3,81	0,30	0,36
47	2,99	3,59	3,38	4,12	2,97	3,28	0,50	0,72

Lab.	Cl, mg/l		SO4, mg/l		Ca, mg/l		Mg, mg/l	
	A	B	A	B	A	B	A	B
48	3,90	4,40	3,21	4,41	3,14	3,53	0,487	0,714
49	2,99	3,57	3,41	4,37	3,29	3,67	0,480	0,730
50					3,09	3,52	0,48	0,73
51	2,92	3,60	3,35	4,36	2,75	3,11	0,47	0,71
52	2,72	3,34	3,09	4,05	2,9	2,9	0,42	0,61
53	3,07	3,75	7,66	7,93	3,04	3,53	0,491	0,738
54	2,8	3,4	3,3	4,3	3,0	3,3	0,53	0,80
55	3,00	3,31	3,39	4,35	4,58	4,94	0,57	0,89
56	3,06	3,65	3,30	4,24	3,22	3,61	0,49	0,74
57	3,01	3,66	3,39	4,37	3,74	4,17	0,53	0,80
58	3,10	3,80	3,42	4,39	2,76	3,15	0,43	0,65
59	9,78	9,64	5,80	7,15	2,89	3,10	0,50	0,71
61					3,21	3,61	0,46	0,72
62	2,81	3,40	3,21	4,19	3,22	3,57	0,49	0,73
63	1,6	1,9	3,2	4,1	3,60	4,11	0,44	0,70
65					3,14	3,48	0,485	0,730
66	2,924	3,621	3,384	4,475	3,404	3,757	0,524	0,780
67	2,95	3,62	3,25	4,34	3,15	3,48	0,48	0,72
68	2,90	3,75	3,41	4,54	3,63	3,99	0,54	0,81

Lab.	Na, mg/l		K, mg/l		Fe, µg/l		Mn, µg/l	
	A	B	A	B	C	D	C	D
1	1,62	2,77	0,308	0,485	15	202	1,1	5,7
2	1,72	2,75	0,32	0,473	< 50	249	1,4	7,6
3	1,43	2,22	0,35	0,36	35,1	206,2	34,8	9,6
5	1,93	3,03	0,36	0,48	18,7	215	1,14	5,89
6					140	220		
7	1,94	3,01	0,32	0,48	17	202	1,1	5,8
8	1,99	3,19	0,38	0,70			1,38	6,86
9								
10	1,87	2,97	0,31	0,47				
11	1,9	2,9	0,37	0,54	20	220	1,3	6,2
12	1,78	2,87	0,318	0,477	6,7	186,2	1,2	5,7
13	1,62	2,45	0,54	0,50	20,4	179	1,08	4,87
14	1,88	2,94	0,33	0,48				
15	2,02	2,31	0,17		18	149	4,0	5,9
16	1,74	2,61	0,38	0,44				
17	1,88	2,90	0,32	0,45	17,21	189,4	1,18	5,49
18	1,95	3,0	< 0,6	< 0,6	12,0	221,0	< 2	6,59
19	2,409	3,694	0,333	0,511	16,5	205,2	1,337	6,723
20	2,24	3,48	0,440	0,680			1,60	4,00
21	1,90	2,98	0,33	0,49	16,12	195,3	1,19	5,81
22								
23								
24	1,9	2,8	0,34	0,48				
25	1,88	2,96	0,32	0,441	19,7	205	1,1	5,9
26	1,72	2,75	0,38	0,52				
27	1,94	3,02	0,33	0,48				
28							1,13	6,11
29	1,67	2,68	0,34	0,50	20	208	1	6
30					21	225	1,33	7,86
31	1,888	2,971	0,320	0,477				
32	2,73	4,25	0,37	0,53	17,3	188,0	1,4	7,1
33	1,99	3,10	0,232	0,418	< 20	201	< 5	5,6
34	1,83	2,88	0,32	0,54	17,00	198,03	1,154	5,927
36								
37	2,00	3,21	0,35	0,59	30	218	1,2	6,0
39	1,95	3,15	0,351	0,508	4,24	184,05	1,156	5,817
40								
41	1,98	3,14	0,342	0,472	19,3	214	1,3	6,2
42								
43	1,94	3,04	0,337	0,492	18,1	201	1,21	6,06
44	1,63	2,57	0,328	0,517				
45	1,8	2,9	0,30	0,40	17,7	206	1,1	5,7
46								
47	1,79	2,94	0,33	0,48	19,1	212	1,3	6,5

Lab.	Na, mg/l		K, mg/l		Fe, µg/l		Mn, µg/l	
	A	B	A	B	C	D	C	D
48	1,88	2,97	0,308	0,492	19	202	< 2	5,72
49	1,51	3,02	0,35	0,49				
50	1,94	3,00	0,32	0,51				
51	1,85	2,92	0,33	0,46	16,4	201	1,21	6,11
52	1,8	2,8	0,30	0,46	18	215	< 5	5,6
53	1,85	2,88	0,497	0,686	28,6	212,6	1,6	5,6
54	1,9	3,1	0,34	0,50				
55	1,97	3,04	0,34	0,50	< 20	203	1,03	5,74
56	1,83	2,83	0,32	0,47				
57	1,89	2,98	0,33	0,49				
58	1,84	2,89	0,33	0,48				
59	1,86	2,91	0,37	0,64	53	272	2,01	7,67
61	1,74	2,68	0,29	0,45	17,3	199	1,40	5,96
62	1,92	3,01	0,35	0,19	< 50	240	< 5	5,0
63	2,20	4,00	0,70	1,30	3,5	3,5		
65	1,96	3,05	0,345	0,505				
66	1,879	2,950	0,338	0,488				
67	1,86	2,99	0,30	0,46				
68	1,95	3,02	0,32	0,47	20	200	1,10	5,68

Lab.	Cd, µg/l		Pb, µg/l		Cu, µg/l		Ni, µg/l	
	C	D	C	D	C	D	C	D
1	1,9	3,9	-15,00	-15,00	170	122	< 8	< 8
2	2,0	4,0	4,95	10,6	163	114	9,5	5,9
3	3,0	5,3			163,2	128,9	16,9	10,6
5	2,01	3,82	5,26	9,81	178,7	130,1	10,1	5,16
6								
7	2,0	3,9	5	9	172	125	10,1	5,3
8	1,73	3,46	3,89	7,97	186,5	140,6	8,80	3,46
9								
10								
11	1,5	3,4	5,1	9,9				
12	2,03	4,07	5,5	10,5	175,0	127,7	10,0	5,3
13	1,93	3,71	4,99	8,79	162	117	9,63	4,27
14								
15	2,05	3,65	4,90	8,40	158	109		
16								
17	1,98	4,07	5,76	11,54	172,3	130,8	9,37	4,93
18	1,99	3,95	5,35	10,2	193,5	137,9	10,72	5,25
19	2,004	3,838	5,268	9,467	179,3	131,6	11,03	5,798
20	3,30	5,50	13,7	18,8	176	135	12,30	8,10
21	1,97	4,40	4,42	9,24	186,1	125,4	8,95	4,57
22								
23								
24								
25	1,93	4,22	5,32	10,53	193	139	11,5	5,6
26								
27								
28	2,04	4,09	5,33	10,4	174	128	10,2	5,38
29	< 4	5,0	< 15	< 15	183	132	9	5
30	2,02	3,99	5,01	9,49	161,5	114,9	9,52	4,58
31								
32	2,2	4,4	5,1	10,8	175,6	139,0	12,0	6,3
33	2,00	4,76	3,27	12,1	180	129	10,5	5,44
34	2,113	4,118	5,409	9,936	180,4	131,1	10,858	5,427
36								
37	1,90	3,69	4,96	9,56	164,0	118,0	9,89	4,92
39	2,019	4,045	5,16	9,99	173,8	127,6	10,01	5,26
40								
41	2,0	4,0	5,0	9,7	175	130	10,5	5,0
42								
43	1,93	3,75	5,27	9,82	190	136	10,1	5,08
44	1,20	3,23	5,20	10,5	165	119		
45	1,95	3,9	5,9	11,2	179	130	9,8	4,55
46								
47	1,87	3,67	5,15	9,97	175	132	9,8	4,9

Lab.	Cd, µg/l		Pb, µg/l		Cu, µg/l		Ni, µg/l	
	C	D	C	D	C	D	C	D
48	1,97	3,96	5,04	9,72	171	126	10,0	5,28
49								
50								
51	1,97	3,98	5,26	10,2	175	128	10,30	5,36
52	2,0	4,3	5,2	10,0	182	140	10,5	5,2
53	1,34	2,42	4,62	9,72	194	124	10,43	5,18
54								
55	1,86	3,78	5,06	9,74	166	116	9,63	4,81
56								
57								
58								
59	6,73	10,41	109	126	437	360	17,4	17,1
61	1,90	3,97	5,33	9,62	157	105	10,0	4,94
62								
63	0,38	0,51			2	2	0,51	0,53
65								
66								
67								
68	1,94	3,88	5,05	9,65	175	125	9,86	5,13

Lab.	Zn, µg/l	
	C	D
1	48	22
2	50	23
3	75,6	37,9
5	53,5	24,8
6		
7	50	23
8	47,3	25,4
9		
10		
11	57	28
12	47,0	21,3
13	49,5	20,9
14		
15	39	14
16		
17	45,8	20,6
18	52,8	23,2
19	49,62	21,01
20	36,8	29,3
21	50,4	22,1
22		
23		
24		
25	56,5	25,1
26		
27		
28	51,5	30,2
29	50	22
30	47,74	20,53
31		
32	53,0	22,8
33	51,6	23,3
34	61,84	26,02
36		
37	47,0	20,5
39	54,51	24,85
40		
41	51	23
42		
43	51,0	22,3
44	56,9	30,2
45	51	24
46		
47	55	26

Lab.	Zn, µg/l	
	C	D
48	50,3	22,2
49		
50		
51	50,2	22,7
52	53	22
53	50,2	25,3
54		
55	48,1	21,4
56		
57		
58		
59	51,9	28,0
61	47,3	21,2
62	45,0	17,0
63		
65		
66		
67		
68	51,7	23,0

Table 5.1. Statistics - pH

Sample A

Number of participants	60	Range	1,39
Number of omitted results	3	Variance	0,06
True value	6,63	Standard deviation	0,24
Mean value	6,62	Relative standard deviation	3,6%
Median value	6,63	Relative error	-0,2%

Analytical results in ascending order:

63	5,55	U	23	6,59		53	6,71	
18	5,80	U	48	6,59		25	6,71	
19	5,92		46	6,60		32	6,72	
12	5,93		67	6,60		41	6,73	
8	6,10		45	6,61		11	6,74	
50	6,21		44	6,62		56	6,75	
33	6,34		47	6,62		21	6,75	
9	6,35		65	6,63		68	6,77	
59	6,37		7	6,63		52	6,78	
5	6,41		1	6,63		40	6,78	
58	6,43		55	6,63		20	6,79	
17	6,44		39	6,64		2	6,80	
13	6,45		31	6,64		43	6,83	
15	6,48		62	6,65		49	6,83	
34	6,50		26	6,66		42	6,85	
30	6,52		51	6,67		61	6,87	
37	6,52		54	6,68		66	6,88	
10	6,56		27	6,69		14	7,28	
3	6,57		36	6,69		22	7,31	
57	6,58		24	6,70		6	7,84	U

Sample B

Number of participants	60	Range	1,20
Number of omitted results	3	Variance	0,04
True value	6,86	Standard deviation	0,21
Mean value	6,86	Relative standard deviation	3,0%
Median value	6,86	Relative error	0,0%

Analytical results in ascending order:

18	5,90	U	44	6,82		56	6,92	
19	6,32		31	6,83		43	6,93	
5	6,54		45	6,84		51	6,93	
3	6,59		65	6,84		53	6,94	
50	6,60		63	6,85	U	40	6,94	
9	6,60		55	6,85		49	6,94	
37	6,60		48	6,86		41	6,94	
15	6,62		47	6,86		52	6,96	
58	6,63		62	6,86		32	6,96	
13	6,65		46	6,86		11	6,96	
17	6,66		23	6,86		20	6,97	
34	6,67		25	6,86		68	6,99	
59	6,70		54	6,86		36	7,00	
8	6,70		26	6,87		21	7,03	
30	6,73		7	6,88		61	7,07	
1	6,75		2	6,89		66	7,11	
33	6,77		24	6,90		12	7,42	
10	6,78		27	6,90		14	7,50	
57	6,78		67	6,90		22	7,52	
42	6,80		39	6,91		6	7,94	U

U = Omitted resultat

Table 5.2. Statistics - conductivity, mS/m

Sample A

Number of participants	60	Range	0,89
Number of omitted results	3	Variance	0,03
True value	3,40	Standard deviation	0,18
Mean value	3,41	Relative standard deviation	5,3%
Median value	3,40	Relative error	0,4%

Analytical results in ascending order:

3	1,16	U	49	3,35		1	3,47	
6	2,28	U	54	3,37		43	3,49	
47	2,95		53	3,37		13	3,49	
55	3,00		5	3,38		52	3,50	
65	3,08		2	3,39		12	3,50	
8	3,09		19	3,39		67	3,50	
15	3,15		25	3,40		22	3,50	
51	3,19		36	3,40		40	3,51	
68	3,20		57	3,40		20	3,57	
34	3,22		56	3,40		18	3,60	
37	3,29		26	3,40		33	3,61	
23	3,30		66	3,40		30	3,61	
58	3,30		63	3,40		16	3,65	
39	3,30		59	3,41		14	3,70	
48	3,31		32	3,41		45	3,70	
27	3,31		42	3,42		17	3,71	
11	3,32		21	3,43		24	3,73	
61	3,33		29	3,43		31	3,78	
41	3,35		10	3,43		62	3,84	
7	3,35		46	3,45		9	4,00	U

Sample B

Number of participants	60	Range	0,86
Number of omitted results	3	Variance	0,03
True value	4,36	Standard deviation	0,18
Mean value	4,32	Relative standard deviation	4,1%
Median value	4,36	Relative error	-0,9%

Analytical results in ascending order:

3	0,90	U	49	4,30		25	4,38	
6	2,79	U	27	4,30		63	4,40	
40	3,84		23	4,30		67	4,40	
47	3,89		58	4,30		22	4,40	
55	3,90		7	4,31		1	4,40	
8	3,95		48	4,31		12	4,40	
15	4,02		59	4,31		17	4,41	
65	4,04		46	4,34		20	4,46	
42	4,13		57	4,35		43	4,46	
2	4,14		5	4,35		24	4,49	
34	4,14		32	4,36		33	4,49	
68	4,14		66	4,36		26	4,50	
19	4,18		29	4,36		52	4,50	
39	4,20		10	4,36		14	4,50	
37	4,25		62	4,37		16	4,52	
41	4,26		51	4,37		30	4,54	
11	4,26		56	4,37		18	4,60	
61	4,27		54	4,37		45	4,60	
53	4,29		13	4,38		31	4,70	
36	4,30		21	4,38		9	5,30	U

U = Omitted resultat

Table 5.3. Statistics - alkalinity, mmol/l

Sample A

Number of participants	46	Range	0,085
Number of omitted results	11	Variance	0,000
True value	0,096	Standard deviation	0,019
Mean value	0,100	Relative standard deviation	19,2%
Median value	0,096	Relative error	3,9%

Analytical results in ascending order:

52	-0,100	U	56	0,091	57	0,129	
48	0,044	U	7	0,096	50	0,130	
11	0,057		41	0,096	33	0,132	U
20	0,075		22	0,096	9	0,134	
12	0,080		30	0,097	40	0,140	
65	0,084		61	0,098	31	0,142	
47	0,084		10	0,098	21	0,150	U
54	0,084		66	0,098	24	0,160	U
58	0,085		27	0,099	2	0,160	U
34	0,086		67	0,100	8	0,180	U
37	0,088		46	0,104	6	0,200	U
68	0,088		26	0,108	3	0,320	U
25	0,089		13	0,108	18	0,360	U
49	0,089		16	0,117	39	0,920	U
62	0,090		59	0,120			
51	0,090		53	0,120			

Sample B

Number of participants	46	Range	0,089
Number of omitted results	11	Variance	0,000
True value	0,139	Standard deviation	0,020
Mean value	0,142	Relative standard deviation	13,9%
Median value	0,139	Relative error	1,8%

Analytical results in ascending order:

48	0,065	U	51	0,136	59	0,160	
12	0,090		39	0,137	U	13	0,164	
11	0,103		22	0,138	40	0,170	
20	0,113		41	0,139	57	0,174	
34	0,125		46	0,139	31	0,175	
49	0,126		16	0,139	50	0,177	
54	0,130		25	0,140	9	0,179	
58	0,130		27	0,141	24	0,210	U
52	0,130	U	66	0,143	8	0,210	U
47	0,131		7	0,143	33	0,217	U
65	0,131		30	0,144	2	0,220	U
56	0,133		61	0,145	6	0,300	U
62	0,134		67	0,147	3	0,400	U
37	0,135		26	0,150	18	0,430	U
10	0,135		53	0,160			
68	0,136		21	0,160	U		

U = Omitted resultat

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

Sample A

Number of participants	54	Range	185
Number of omitted results	3	Variance	1120
True value	283	Standard deviation	33
Mean value	281	Relative standard deviation	11,9%
Median value	283	Relative error	-0,8%

Analytical results in ascending order:

63	18	U	65	268	66	292	
33	189		43	270	51	293	
44	209		29	270	36	293	
37	214	U	41	273	7	297	
32	217		40	275	5	298	
14	226		55	275	11	299	
34	228		10	276	57	299	
49	250		26	282	2	300	
15	254		67	283	20	304	
52	259		18	283	23	305	
58	260		19	286	9	308	
42	260		45	286	24	310	
25	262		1	286	62	316	
27	264		59	287	48	333	
12	265		22	289	53	337	
68	265		47	289	3	346	U
56	266		21	290	16	361	
39	266		6	292	31	374	

Sample B

Number of participants	54	Range	108
Number of omitted results	3	Variance	535
True value	340	Standard deviation	23
Mean value	335	Relative standard deviation	6,9%
Median value	340	Relative error	-1,6%

Analytical results in ascending order:

63	22	U	59	332	57	345	
3	223	U	67	334	36	347	
37	240	U	22	335	29	350	
16	267		19	335	58	350	
33	267		39	336	7	350	
44	278		65	336	24	350	
62	287		23	338	56	350	
12	296		27	339	43	350	
32	300		21	340	53	351	
20	311		10	340	66	351	
34	312		18	340	6	353	
14	314		48	340	51	353	
15	325		41	340	5	353	
40	328		9	340	55	354	
52	328		49	342	11	360	
42	330		25	344	2	360	
68	330		1	344	31	360	
26	331		45	345	47	375	

U = Omitted resultat

Table 5.5. Statistics - chloride, mg/l

Sample A

Number of participants	51	Range	1,46
Number of omitted results	6	Variance	0,05
True value	2,92	Standard deviation	0,22
Mean value	2,93	Relative standard deviation	7,6%
Median value	2,92	Relative error	0,4%

Analytical results in ascending order:

8	0,48	U	26	2,87		47	2,99	
6	1,20	U	31	2,88		18	3,00	
63	1,60	U	22	2,88		55	3,00	
32	2,44		43	2,88		44	3,01	
12	2,51		19	2,88		39	3,01	
24	2,60		45	2,90		57	3,01	
34	2,63		68	2,90		56	3,06	
46	2,70		51	2,92		53	3,07	
52	2,72		66	2,92		29	3,08	
16	2,78		67	2,95		58	3,10	
2	2,78		25	2,96		40	3,12	
54	2,80		21	2,98		37	3,15	
62	2,81		5	2,98		33	3,36	
15	2,84		41	2,98		48	3,90	
27	2,84		7	2,99		9	4,20	U
10	2,86		49	2,99		59	9,78	U
14	2,86		20	2,99		3	21,20	U

Sample B

Number of participants	51	Range	1,40
Number of omitted results	6	Variance	0,06
True value	3,57	Standard deviation	0,24
Mean value	3,55	Relative standard deviation	6,8%
Median value	3,57	Relative error	-0,7%

Analytical results in ascending order:

8	0,48	U	41	3,43		39	3,65	
6	1,60	U	26	3,49		56	3,65	
63	1,90	U	14	3,51		29	3,65	
16	3,00		21	3,51		57	3,66	
32	3,10		27	3,52		44	3,67	
12	3,12		40	3,53		25	3,69	
24	3,24		19	3,57		18	3,70	
34	3,27		49	3,57		20	3,74	
55	3,31		10	3,57		53	3,75	
2	3,32		5	3,57		68	3,75	
52	3,34		47	3,59		58	3,80	
15	3,34		45	3,60		31	3,85	
46	3,38		51	3,60		37	4,00	
54	3,40		67	3,62		48	4,40	
43	3,40		66	3,62		9	5,30	U
62	3,40		22	3,64		59	9,64	U
33	3,43		7	3,64		3	28,30	U

U = Omitted resultat

Table 5.6. Statistics - sulphate, mg/l

Sample A

Number of participants	51	Range	1,05
Number of omitted results	7	Variance	0,03
True value	3,30	Standard deviation	0,17
Mean value	3,30	Relative standard deviation	5,1%
Median value	3,30	Relative error	-0,1%

Analytical results in ascending order:

8	0,79	U	48	3,21		55	3,39	
31	1,09	U	16	3,23		57	3,39	
6	2,00	U	26	3,25		5	3,40	
10	2,85		67	3,25		49	3,41	
46	2,90		37	3,26		68	3,41	
3	3,00	U	54	3,30		2	3,41	
12	3,09		14	3,30		58	3,42	
52	3,09		56	3,30		18	3,42	
11	3,10		22	3,30		25	3,43	
24	3,11		45	3,30		7	3,44	
33	3,17		39	3,32		21	3,44	
27	3,17		41	3,32		43	3,46	
44	3,19		51	3,35		19	3,48	
32	3,19		34	3,37		40	3,90	
63	3,20		47	3,38		59	5,80	U
15	3,20		29	3,38		20	5,90	U
62	3,21		66	3,38		53	7,66	U

Sample B

Number of participants	51	Range	0,94
Number of omitted results	7	Variance	0,04
True value	4,26	Standard deviation	0,21
Mean value	4,23	Relative standard deviation	4,9%
Median value	4,26	Relative error	-0,7%

Analytical results in ascending order:

8	1,25	U	16	4,13		43	4,36	
31	1,53	U	27	4,14		51	4,36	
3	2,00	U	62	4,19		57	4,37	
6	2,40	U	26	4,22		49	4,37	
11	3,60		22	4,23		18	4,38	
46	3,70		56	4,24		58	4,39	
10	3,91		14	4,25		45	4,40	
33	3,93		5	4,26		48	4,41	
12	3,99		41	4,26		7	4,43	
24	3,99		29	4,26		66	4,48	
2	4,04		39	4,28		25	4,48	
15	4,05		54	4,30		19	4,50	
52	4,05		37	4,32		40	4,50	
63	4,10		21	4,33		68	4,54	
32	4,10		67	4,34		20	6,99	U
47	4,12		34	4,34		59	7,15	U
44	4,13		55	4,35		53	7,93	U

U = Omitted resultat

Table 5.7. Statistics - calcium, mg/l

Sample A

Number of participants	56	Range	1,27
Number of omitted results	5	Variance	0,08
True value	3,15	Standard deviation	0,29
Mean value	3,23	Relative standard deviation	8,9%
Median value	3,15	Relative error	2,6%

Analytical results in ascending order:

8	0,86	U	33	3,07		16	3,33	
6	1,50	U	43	3,07		66	3,40	
20	1,51	U	50	3,09		40	3,50	
51	2,75		27	3,10		19	3,52	
58	2,76		5	3,13		13	3,53	
1	2,86		29	3,14		14	3,54	
59	2,89		65	3,14		32	3,55	
52	2,90		48	3,14		12	3,59	
25	2,93		7	3,15		63	3,60	
2	2,96		67	3,15		26	3,61	
47	2,97		18	3,17		11	3,61	
9	2,98		37	3,19		31	3,63	
34	2,98		45	3,20		68	3,63	
54	3,00		61	3,21		57	3,74	
3	3,00		62	3,22		46	3,81	
24	3,00		41	3,22		15	4,02	
10	3,03		56	3,22		55	4,58	U
53	3,04		17	3,24		39	7,62	U
21	3,04		49	3,29				

Sample B

Number of participants	56	Range	1,54
Number of omitted results	5	Variance	0,09
True value	3,55	Standard deviation	0,31
Mean value	3,58	Relative standard deviation	8,5%
Median value	3,55	Relative error	0,9%

Analytical results in ascending order:

8	1,05	U	5	3,47		10	3,66	
20	1,66	U	65	3,48		16	3,66	
6	2,00	U	67	3,48		49	3,67	
52	2,90		27	3,51		66	3,76	
59	3,10		50	3,52		13	3,80	
51	3,11		48	3,53		46	3,81	
58	3,15		53	3,53		2	3,84	
1	3,18		11	3,53		14	3,95	
3	3,20		40	3,54		68	3,99	
25	3,22		37	3,55		32	4,01	
47	3,28		45	3,55		31	4,02	
54	3,30		9	3,57		12	4,03	
24	3,30		62	3,57		26	4,04	
34	3,32		17	3,57		63	4,11	
18	3,43		33	3,57		57	4,17	
43	3,44		7	3,60		15	4,44	
21	3,47		61	3,61		55	4,94	U
41	3,47		56	3,61		39	8,28	U
29	3,47		19	3,64				

U = Omitted resultat

Table 5.8. Statistics - magnesium, mg/l

Sample A

Number of participants	56	Range	0,198
Number of omitted results	7	Variance	0,001
True value	0,490	Standard deviation	0,038
Mean value	0,496	Relative standard deviation	7,7%
Median value	0,490	Relative error	1,2%

Analytical results in ascending order:

6	0,300	U	43	0,480		18	0,510	
46	0,300	U	34	0,480		37	0,520	
3	0,360	U	50	0,480		20	0,520	
16	0,410		33	0,481		40	0,520	
52	0,420		2	0,482		66	0,524	
58	0,430		65	0,485		57	0,530	
63	0,440		48	0,487		54	0,530	
17	0,450		62	0,490		13	0,540	
1	0,459		56	0,490		68	0,540	
61	0,460		29	0,490		41	0,541	
10	0,470		53	0,491		31	0,565	
51	0,470		47	0,500		15	0,570	
19	0,478		24	0,500		55	0,570	
67	0,480		59	0,500		12	0,608	
7	0,480		45	0,500		8	0,760	U
14	0,480		21	0,500		9	0,900	U
26	0,480		5	0,500		39	0,933	U
27	0,480		25	0,500		11	1,140	U
49	0,480		32	0,510				

Sample B

Number of participants	56	Range	0,306
Number of omitted results	7	Variance	0,003
True value	0,736	Standard deviation	0,054
Mean value	0,745	Relative standard deviation	7,3%
Median value	0,736	Relative error	1,2%

Analytical results in ascending order:

46	0,360	U	61	0,720		32	0,760	
6	0,480	U	29	0,730		25	0,760	
3	0,490	U	49	0,730		34	0,770	
52	0,610		50	0,730		66	0,780	
16	0,650		62	0,730		40	0,790	
58	0,650		14	0,730		57	0,800	
63	0,700		65	0,730		54	0,800	
45	0,700		33	0,733		13	0,800	
19	0,708		43	0,736		15	0,810	
1	0,708		53	0,738		68	0,810	
17	0,710		56	0,740		20	0,820	
27	0,710		10	0,740		31	0,837	
24	0,710		18	0,740		8	0,870	U
51	0,710		21	0,740		55	0,890	
59	0,710		37	0,740		12	0,916	
48	0,714		5	0,750		9	1,080	U
2	0,716		26	0,750		11	1,170	U
67	0,720		7	0,750		39	1,370	U
47	0,720		41	0,752				

U = Omitted resultat

Table 5.9. Statistics - sodium, mg/l

Sample A

Number of participants	53	Range	0,98
Number of omitted results	2	Variance	0,02
True value	1,88	Standard deviation	0,16
Mean value	1,87	Relative standard deviation	8,4%
Median value	1,88	Relative error	-0,8%

Analytical results in ascending order:

3	1,43	53	1,85	50	1,94	
49	1,51	67	1,86	43	1,94	
13	1,62	59	1,86	7	1,94	
1	1,62	10	1,87	39	1,95	
44	1,63	66	1,88	18	1,95	
29	1,67	48	1,88	68	1,95	
26	1,72	25	1,88	65	1,96	
2	1,72	17	1,88	55	1,97	
61	1,74	14	1,88	41	1,98	
16	1,74	31	1,89	33	1,99	
12	1,78	57	1,89	8	1,99	
47	1,79	54	1,90	37	2,00	
52	1,80	24	1,90	15	2,02	
45	1,80	21	1,90	63	2,20	U
56	1,83	11	1,90	20	2,24	
34	1,83	62	1,92	19	2,41	
58	1,84	5	1,93	32	2,73	U
51	1,85	27	1,94			

Sample B

Number of participants	53	Range	1,47
Number of omitted results	2	Variance	0,06
True value	2,96	Standard deviation	0,24
Mean value	2,93	Relative standard deviation	8,3%
Median value	2,96	Relative error	-1,1%

Analytical results in ascending order:

3	2,22	17	2,90	27	3,02	
15	2,31	45	2,90	68	3,02	
13	2,45	59	2,91	49	3,02	
44	2,57	51	2,92	5	3,03	
16	2,61	14	2,94	55	3,04	
61	2,68	47	2,94	43	3,04	
29	2,68	66	2,95	65	3,05	
26	2,75	25	2,96	33	3,10	
2	2,75	10	2,97	54	3,10	
1	2,77	48	2,97	41	3,14	
24	2,80	31	2,97	39	3,15	
52	2,80	21	2,98	8	3,19	
56	2,83	57	2,98	37	3,21	
12	2,87	67	2,99	20	3,48	
53	2,88	18	3,00	19	3,69	
34	2,88	50	3,00	63	4,00	U
58	2,89	62	3,01	32	4,25	U
11	2,90	7	3,01			

U = Omitted resultat

Table 5.10. Statistics - potassium, mg/l

Sample A

Number of participants	53	Range		0,090
Number of omitted results	9	Variance		0,000
True value	0,330	Standard deviation		0,021
Mean value	0,333	Relative standard deviation		6,4%
Median value	0,330	Relative error		0,8%

Analytical results in ascending order:

18	-0,600	U	7	0,320	65	0,345	
15	0,170	U	50	0,320	62	0,350	U
33	0,232	U	44	0,328	49	0,350	
61	0,290		21	0,330	37	0,350	
67	0,300		47	0,330	3	0,350	
52	0,300		58	0,330	39	0,351	
45	0,300		14	0,330	5	0,360	
48	0,308		51	0,330	11	0,370	
1	0,308		57	0,330	32	0,370	
10	0,310		27	0,330	59	0,370	
12	0,318		19	0,333	16	0,380	
25	0,320		43	0,337	26	0,380	
56	0,320		66	0,338	8	0,380	U
17	0,320		24	0,340	20	0,440	U
34	0,320		55	0,340	53	0,497	U
31	0,320		29	0,340	13	0,540	U
68	0,320		54	0,340	63	0,700	U
2	0,320		41	0,342			

Sample B

Number of participants	53	Range		0,280
Number of omitted results	9	Variance		0,002
True value	0,480	Standard deviation		0,043
Mean value	0,487	Relative standard deviation		8,9%
Median value	0,480	Relative error		1,5%

Analytical results in ascending order:

18	-0,600	U	12	0,477	13	0,500	U
15	0,000	U	31	0,477	55	0,500	
62	0,190	U	7	0,480	65	0,505	
3	0,360		5	0,480	39	0,508	
45	0,400		27	0,480	50	0,510	
33	0,418	U	24	0,480	19	0,511	
16	0,440		58	0,480	44	0,517	
25	0,441		47	0,480	26	0,520	
61	0,450		14	0,480	32	0,530	
17	0,450		1	0,485	11	0,540	
67	0,460		66	0,488	34	0,540	
52	0,460		57	0,490	37	0,590	
51	0,460		21	0,490	59	0,640	
68	0,470		49	0,490	20	0,680	U
10	0,470		43	0,492	53	0,686	U
56	0,470		48	0,492	8	0,700	U
41	0,472		29	0,500	63	1,300	U
2	0,473		54	0,500			

U = Omitted resultat

Table 5.11. Statistics - iron, µg/l

Sample C

Number of participants	36	Range	9,0
Number of omitted results	13	Variance	4,1
True value	18,0	Standard deviation	2,0
Mean value	17,9	Relative standard deviation	11,3%
Median value	18,0	Relative error	-0,3%

Analytical results in ascending order:

2	-50,0	U	34	17,0		41	19,3	
62	-50,0	U	7	17,0		25	19,7	
55	-20,0	U	17	17,2		29	20,0	
33	-20,0	U	32	17,3		11	20,0	
63	3,5	U	61	17,3		68	20,0	
39	4,2	U	45	17,7		13	20,4	
12	6,7	U	52	18,0		30	21,0	
18	12,0		15	18,0	U	53	28,6	U
1	15,0		43	18,1		37	30,0	U
21	16,1		5	18,7		3	35,1	U
51	16,4		48	19,0		59	53,0	U
19	16,5		47	19,1		6	140,0	U

Sample D

Number of participants	36	Range	46,0
Number of omitted results	13	Variance	122,1
True value	202,0	Standard deviation	11,0
Mean value	204,5	Relative standard deviation	5,4%
Median value	202,0	Relative error	1,2%

Analytical results in ascending order:

63	3,5	U	51	201,0		53	212,6	U
15	149,0	U	33	201,0	U	41	214,0	
13	179,0		7	202,0		5	215,0	
39	184,1	U	1	202,0		52	215,0	
12	186,2	U	48	202,0		37	218,0	U
32	188,0		55	203,0	U	11	220,0	
17	189,4		25	205,0		6	220,0	U
21	195,3		19	205,2		18	221,0	
34	198,0		45	206,0		30	225,0	
61	199,0		3	206,2	U	62	240,0	U
68	200,0		29	208,0		2	249,0	U
43	201,0		47	212,0		59	272,0	U

U = Omitted resultat

Table 5.12. Statistics - manganese, µg/l

Sample C

Number of participants	37	Range	0,60
Number of omitted results	8	Variance	0,02
True value	1,20	Standard deviation	0,15
Mean value	1,23	Relative standard deviation	12,4%
Median value	1,20	Relative error	2,7%

Analytical results in ascending order:

33	-5,00	U	28	1,13		30	1,33	
62	-5,00	U	5	1,14		19	1,34	
52	-5,00	U	34	1,15		8	1,38	
18	-2,00	U	39	1,16		32	1,40	
48	-2,00	U	17	1,18		61	1,40	
29	1,00		21	1,19		2	1,40	
55	1,03		12	1,20		53	1,60	
13	1,08		37	1,20		20	1,60	
7	1,10		43	1,21		59	2,01	U
68	1,10		51	1,21		15	4,00	U
45	1,10		47	1,30		3	34,80	U
25	1,10		11	1,30				
1	1,10		41	1,30				

Sample D

Number of participants	37	Range	3,86
Number of omitted results	8	Variance	0,54
True value	5,93	Standard deviation	0,73
Mean value	6,03	Relative standard deviation	12,2%
Median value	5,93	Relative error	1,7%

Analytical results in ascending order:

20	4,00		7	5,80		11	6,20	
13	4,87		21	5,81		41	6,20	
62	5,00	U	39	5,82		47	6,50	
17	5,49		5	5,89		18	6,59	U
33	5,60	U	25	5,90		19	6,72	
52	5,60	U	15	5,90	U	8	6,86	
53	5,60		34	5,93		32	7,10	
68	5,68		61	5,96		2	7,60	
12	5,70		29	6,00		59	7,67	U
45	5,70		37	6,00		30	7,86	
1	5,70		43	6,06		3	9,60	U
48	5,72	U	51	6,11				
55	5,74		28	6,11				

U = Omitted resultat

Table 5.13. Statistics - cadmium, µg/l

Sample C

Number of participants	38	Range	0,70
Number of omitted results	7	Variance	0,01
True value	1,98	Standard deviation	0,12
Mean value	1,96	Relative standard deviation	6,0%
Median value	1,98	Relative error	-1,1%

Analytical results in ascending order:

29	-4,00	U	13	1,93		19	2,00	
63	0,38	U	68	1,94		5	2,01	
44	1,20	U	45	1,95		39	2,02	
53	1,34	U	51	1,97		30	2,02	
11	1,50		21	1,97		12	2,03	
8	1,73		48	1,97		28	2,04	
55	1,86		17	1,98		15	2,05	
47	1,87		18	1,99		34	2,11	
1	1,90		7	2,00		32	2,20	
37	1,90		2	2,00		3	3,00	U
61	1,90		52	2,00		20	3,30	U
25	1,93		33	2,00		59	6,73	U
43	1,93		41	2,00				

Sample D

Number of participants	38	Range	1,36
Number of omitted results	7	Variance	0,08
True value	3,96	Standard deviation	0,28
Mean value	3,96	Relative standard deviation	7,0%
Median value	3,96	Relative error	-0,1%

Analytical results in ascending order:

63	0,51	U	68	3,88		17	4,07	
53	2,42	U	7	3,90		28	4,09	
44	3,23	U	45	3,90		34	4,12	
11	3,40		1	3,90		25	4,22	
8	3,46		18	3,95		52	4,30	
15	3,65		48	3,96		21	4,40	
47	3,67		61	3,97		32	4,40	
37	3,69		51	3,98		33	4,76	
13	3,71		30	3,99		29	5,00	U
43	3,75		2	4,00		3	5,30	U
55	3,78		41	4,00		20	5,50	U
5	3,82		39	4,05		59	10,41	U
19	3,84		12	4,07				

U = Omitted resultat

Table 5.14. Statistics - lead, µg/l

Sample C

Number of participants	36	Range	2,01
Number of omitted results	5	Variance	0,13
True value	5,15	Standard deviation	0,36
Mean value	5,12	Relative standard deviation	7,1%
Median value	5,15	Relative error	-0,6%

Analytical results in ascending order:

29	-15,00	U	30	5,01		19	5,27	
1	-15,00	U	48	5,04		43	5,27	
33	3,27	U	68	5,05		25	5,32	
8	3,89		55	5,06		28	5,33	
21	4,42		32	5,10		61	5,33	
53	4,62		11	5,10		18	5,35	
15	4,90		47	5,15		34	5,41	
2	4,95		39	5,16		12	5,50	
37	4,96		44	5,20		17	5,76	
13	4,99		52	5,20		45	5,90	
41	5,00		51	5,26		20	13,70	U
7	5,00		5	5,26		59	109,00	U

Sample D

Number of participants	36	Range	3,57
Number of omitted results	5	Variance	0,55
True value	9,82	Standard deviation	0,74
Mean value	9,87	Relative standard deviation	7,5%
Median value	9,82	Relative error	0,5%

Analytical results in ascending order:

1	-15,00	U	41	9,70		18	10,20	
29	-15,00	U	48	9,72		28	10,40	
8	7,97		53	9,72		12	10,50	
15	8,40		55	9,74		44	10,50	
13	8,79		5	9,81		25	10,53	
7	9,00		43	9,82		2	10,60	
21	9,24		11	9,90		32	10,80	
19	9,47		34	9,94		45	11,20	
30	9,49		47	9,97		17	11,54	
37	9,56		39	9,99		33	12,10	U
61	9,62		52	10,00		20	18,80	U
68	9,65		51	10,20		59	126,00	U

U = Omitted resultat

Table 5.15. Statistics - copper, µg/l

Sample C

Number of participants	37	Range	37
Number of omitted results	2	Variance	98
True value	175	Standard deviation	10
Mean value	175	Relative standard deviation	5,7%
Median value	175	Relative error	0,0%

Analytical results in ascending order:

63	2	U	17	172		33	180	
61	157		39	174		34	180	
15	158		28	174		52	182	
30	162		47	175		29	183	
13	162		41	175		21	186	
2	163		68	175		8	187	
3	163		12	175		43	190	
37	164		51	175		25	193	
44	165		32	176		18	194	
55	166		20	176		53	194	
1	170		5	179		59	437	U
48	171		45	179				
7	172		19	179				

Sample D

Number of participants	37	Range	36
Number of omitted results	2	Variance	76
True value	128	Standard deviation	9
Mean value	127	Relative standard deviation	6,9%
Median value	128	Relative error	-0,8%

Analytical results in ascending order:

63	2	U	21	125		19	132	
61	105		48	126		29	132	
15	109		39	128		47	132	
2	114		12	128		20	135	
30	115		51	128		43	136	
55	116		28	128		18	138	
13	117		3	129		25	139	
37	118		33	129		32	139	
44	119		45	130		52	140	
1	122		41	130		8	141	
53	124		5	130		59	360	U
7	125		17	131				
68	125		34	131				

U = Omitted resultat

Table 5.16. Statistics - nickel, µg/l

Sample C

Number of participants	35	Range	3,05
Number of omitted results	6	Variance	0,45
True value	10,06	Standard deviation	0,67
Mean value	10,13	Relative standard deviation	6,6%
Median value	10,01	Relative error	0,7%

Analytical results in ascending order:

1	-8,00	U	68	9,86		33	10,50	
63	0,51	U	37	9,89		52	10,50	
8	8,80	U	48	10,00		41	10,50	
21	8,95		12	10,00		18	10,72	
29	9,00		61	10,00		34	10,86	
17	9,37		39	10,01		19	11,03	
2	9,50		5	10,10		25	11,50	
30	9,52		7	10,10		32	12,00	
13	9,63		43	10,10		20	12,30	U
55	9,63		28	10,20		3	16,90	U
45	9,80		51	10,30		59	17,40	U
47	9,80		53	10,43				

Sample D

Number of participants	35	Range	2,03
Number of omitted results	6	Variance	0,18
True value	5,19	Standard deviation	0,42
Mean value	5,17	Relative standard deviation	8,2%
Median value	5,18	Relative error	-0,5%

Analytical results in ascending order:

1	-8,00	U	29	5,00		51	5,36	
63	0,53	U	41	5,00		28	5,38	
8	3,46	U	43	5,08		34	5,43	
13	4,27		68	5,13		33	5,44	
45	4,55		5	5,16		25	5,60	
21	4,57		53	5,18		19	5,80	
30	4,58		52	5,20		2	5,90	
55	4,81		18	5,25		32	6,30	
47	4,90		39	5,26		20	8,10	U
37	4,92		48	5,28		3	10,60	U
17	4,93		7	5,30		59	17,10	U
61	4,94		12	5,30				

U = Omitted resultat

Table 5.17. Statistics - zinc, µg/l

Sample C

Number of participants	38	Range	25,0
Number of omitted results	1	Variance	21,0
True value	50,3	Standard deviation	4,6
Mean value	50,4	Relative standard deviation	9,1%
Median value	50,3	Relative error	0,1%

Analytical results in ascending order:

20	36,8	7	50,0	59	51,9	
15	39,0	2	50,0	18	52,8	
62	45,0	29	50,0	32	53,0	
17	45,8	53	50,2	52	53,0	
12	47,0	51	50,2	5	53,5	
37	47,0	48	50,3	39	54,5	
8	47,3	21	50,4	47	55,0	
61	47,3	45	51,0	25	56,5	
30	47,7	43	51,0	44	56,9	
1	48,0	41	51,0	11	57,0	
55	48,1	28	51,5	34	61,8	
13	49,5	33	51,6	3	75,6	U
19	49,6	68	51,7			

Sample D

Number of participants	38	Range	16,2
Number of omitted results	1	Variance	10,8
True value	23,0	Standard deviation	3,3
Mean value	23,3	Relative standard deviation	14,1%
Median value	23,0	Relative error	1,3%

Analytical results in ascending order:

15	14,0	21	22,1	39	24,9	
62	17,0	48	22,2	25	25,1	
37	20,5	43	22,3	53	25,3	
30	20,5	51	22,7	8	25,4	
17	20,6	32	22,8	47	26,0	
13	20,9	41	23,0	34	26,0	
19	21,0	68	23,0	11	28,0	
61	21,2	2	23,0	59	28,0	
12	21,3	7	23,0	20	29,3	
55	21,4	18	23,2	28	30,2	
1	22,0	33	23,3	44	30,2	
29	22,0	45	24,0	3	37,9	U
52	22,0	5	24,8			

U = Omitted resultat