ICP-WATERS REPORT 64/2001

Intercomparison 0115:

pH, K_{25}, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, aluminium - reactive and nonlabile, TOC, COD-Mn, Fe, Mn, Cd, Pb, Cu, Ni and Zn

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

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Abstract

77 laboratories received samples for the intercomparison 0115, and 72 laboratories in 26 countries submitted results. Three sample sets were used, one for the determination of major ions, one for organic matter and aluminium fractions, and one for heavy metals. Based on the general target accuracy of ± 20 %, 71 % of the results were considered acceptable. 93 % of the result pairs were acceptable for sodium and 85 % for potassium. For pH only 58 % of the result pairs were acceptable in relation to the extended target accuracy of ± 0.2 units. Normalization of the analytical methods used is necessary to improve the comparability for pH. For the aluminium fractions it was decided not to evaluate the reported results, because of the great spread of the results in combination with very few results for this analytical variable in the samples C and D. Determination of heavy metals was included in the intercomparison for the second time, with fairly good results for copper and nickel. For iron, lead, and zinc the fraction of acceptable result pairs were 41 - 53 %, this low acceptance may be due to the low concentrations used for these metals. For the heavy metals it should be discussed whether an absolute acceptance limit should be used instead of the general target of ± 20 % when the concentrations are close to the detection limit of the recommended method.

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Project manager

Håvard Hovind

Håvard Hovind

Research manager
Head of research department

Rainer Lichtenthaler

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CONVENTION ON LONG-RANGE
TRANSBOUNDARY AIR POLLUTION

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

Intercomparison 0115

pH, Cond, HCO_3^-, NO_3^-+NO_2^-, Cl^-, SO_4^{--}
Ca^{++}, Mg^{++}, Na^+, K^+, Al, Al-R, Al-I, DOC,
COD-Mn, Fe, Mn, Cd, Pb, Cu, Ni, and Zn

Prepared by the Programme Centre
Norwegian Institute for Water Research
Oslo, August 2001

Preface

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

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

We here report the results from the 15th intercomparison of chemical analysis.

Oslo, August 2001

Håvard Hovind

Contents

1. Summary

Intercomparison 0115 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 2001, and included the determination of major ions and metals in natural water samples. The participants were asked to determine pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, total aluminium, reactive and non-labile aluminium, dissolved organic carbon, chemical oxygen demand (COD-Mn), iron, manganese, cadmium, lead, copper, nickel and zinc.

Three sample sets were prepared for this intercomparison, one for the determination of the major ions, one for aluminium fractions and unspecific organic matter, and the third for the heavy metals. 104 laboratories were invited to participate in this intercomparison, and the samples were sent to 77 laboratories who accepted to participate. 72 laboratories submitted results to the Programme Centre before the final statistical treatment of the data. 26 countries were represented in this laboratory group (see Appendix A, page 48).

The median value of the results received from the participants was selected as "true" value for each variable. For the aluminium fractions results were received from rather few laboratories. As the analytical values from the participants are widely spread out, it is difficult to define a good estimate of the "true" value, and it was decided not to evaluate these analytical variables. For the remaining variables, 71 % of the result pairs were regarded as acceptable, the target limit being the median value ± 20 %, except for pH and conductivity where the acceptance limits were ± 0,2 units and ± 10 %, respectively.

For pH, the accuracy limit was extended from 0,1 to ± 0.2 units, but still only 58 % of the result pairs were included using this special limit. A total error of ± 0.2 units for pH measurements seems to be a more reasonable assessment of the accuracy between laboratories, than the target limit of ± 0.1 units. The reason for the great spreading of pH results is mainly due to the fact that different routines are used for measurement by the participants, leading to systematically different results. It is terefore 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 best results were obtained for sodium and potassium, with 93 % and 85 % of the result pairs being acceptable, respectively. Rather poor comparability was observed for iron, lead and zinc, the number of acceptable results being between 41 and 53 %. However, the concentrations of these elements are close to the detection limit for the methods used. To improve the comparability of the results for these variables, it is necessary to normalize the analytical methods used.

For the second time in this intercomparison programme, the heavy metals iron, manganese, cadmium, lead, copper, nickel, and zinc were included. The best results were obtained for copper where 75 % of the results were acceptable. For this element the concentrations were at least somewhat higher than the detection limit of the most sensitive methods used. For the metals nickel, cadmium and manganese, 68, 66 and 64 % of the results were acceptable.

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 fifteenth intercomparison test, called 0115, included the determination of the major components and some other ions in natural water samples: pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, total aluminium, reactive and non-labile aluminium, dissolved organic carbon, chemical oxygen demand (COD-Mn), 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 2000 it was decided that three sample sets should be included in this intercomparison, one sample pair for the determination of the major ions, one sample pair for aluminium fractions and unspecific organic compounds, and one for the heavy metals.

The samples were mailed from the Programme Centre on May 21 and the following days, 2001. Most of the participating laboratories received the samples within one week, with some few exceptions. Two laboratories did not receive the first sample set, and had to be supplied with an extra set. Thus one laboratory was not able to return the results to the Programme centre in due time for the statistical calculations. To ensure that the effect of possible alterations in the solutions is minimized, the participants were asked to analyze the samples as soon as possible, and return the analytical results within one month after the samples arrived at the laboratory. Most results were received within the end of June, the last results included in the report were received in the beginning of August.

4. Results

104 laboratories were invited to participate in the intercomparison, and 77 laboratories accepted and received samples. The 72 laboratories who submitted results to the Programme Centre, are representing 26 countries. It was a problem that some laboratories submitted the results several weeks after the deadline, and a reminder letter had to be mailed to some few participants. A survey of the participants and their code numbers are listed in Appendix 1. Here are also included a table illustrating how many laboratories are participating from each country (see page 48). Two of the laboratories also sent a double set of results, representing

different departments of the institute, these result sets are included as different laboratories in the report.

The analytical results received from the laboratories were treated by the method of Youden (2, 3). A short description of this method, and the statistical treatment of the analytical data, are presented in Appendix 3. The purpose of this test is to evaluate the comparability of the analytical results produced by the laboratories participting in the International Cooperative Programme. The real "true value" is not known exactly for the natural 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 are producing systematically different results.

The results are illustrated in Figure 1 - 23, where each laboratory is represented by a small circle and an identification number. Some laboratories with strongly deviating results may be located outside the plot. The great circle in the Figures are representing a selected accuracy limit, either the general target limit of ± 20 % of the mean true values of the sample pair, or a special accuracy limit defined in the sections below. A survey of the results of intercomparison 0115 is presented in Table 1. The individual results of the participants are presented in Table 4 in the Appendix, sorted in order of increasing identification number. More extensive statistical informations are presented in the Tables 5.1 - 5.23 in the Appendix.

4.1 pH

The reported results for pH are graphically presented in Figure 1, where the radius of the circle is 0.2 pH units, and visualizes the degree of comparability between the pH results from the participating laboratories. The values reported by the laboratories are given in Table 5.1.

The participating laboratories determined pH in the test solutions using their own routine method. An electrometric method was used by all laboratories. 69 laboratories reported results for pH, of this group 34 indicated that they read the pH value during stirring the solution. The stirring are normally lowering the observed pH result. In this intercomparison the median values are only slightly lowered in the stirred samples compared to the non-stirred samples (see Table 1), the differences are small and are not statistically significant. The standard deviation of the results from laboratories using stirred samples are somewhat higher than the results read in the non-stirred solutions.

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. Two laboratories that equilibrated the solutions by bubbling with air containing 350 ppm CO_2 before reading the pH value, reported far higher results than the other laboratories, the pH-values are roughly half a unit higher than obtained with the two other methods. These results should not be evaluated by comparing them to the mean value of all the reported results, because this method is systematically different from the two other methods. The information obtained by pH measurement after equilibrating the solution, is different from pH-values read directly, or during stirring the sample.

(The text continues on page 35)

Table 1. Statistical summary of intercomparison 0115

Analytical variable and method	Sample pair	True value 1	True value 2	Total No.	Labs. exclud.	Median 1	Median 2	Mean Sample 1	St.dev. Sample 1	Mean Sample 2	St.dev. Sample 2	Rel.std.av. % 1	Rel.std.av. % 2	Relative error % 1	Relative error % 2
pH	AB	7,15	7,24	69	1	7,15	7,24	7,14	0,21	7,23	0,19	2,9	2,6	-0,1	-0,2
No stirring				32	1	7,18	7,25	7,17	0,16	7,23	0,14	2,2	1,9	0,3	-0,1
Stirring				34	0	7,14	7,24	7,09	0,22	7,20	0,22	3,1	3,0	-0,8	-0,6
Equilibration				2	0			7,58		7,59				6,0	4,8
Not documented				1	0			6,96		7,21				-2,7	-0,4
Conductivity, mS/m	AB	4,70	5,98	65	5	4,70	5,98	4,68	0,22	5,95	0,25	4,7	4,3	-0,5	-0,5
Alkalinity, mmol/l	AB	0,270	0,357	53	2	0,270	0,357	0,266	0,045	0,349	0,056	17,1	16,0	-1,5	-3,0
Gran plot titration				27	1	0,270	0,357	0,260	0,038	0,349	0,050	14,7	14,4	-3,5	-3,1
End point titration				7	0	0,289	0,382	0,292	0,031	0,383	0,028	10,7	7,3	8,3	6,4
End point 5.6				1	0			0,263		0,353				-2,6	-1,9
End point 5.4				1	0			0,266		0,357				-1,5	-0,8
End point 4.5				11	0	0,270	0,350	0,278	0,052	0,355	0,061	18,9	17,1	2,8	-1,5
Colorimetry				2	1			0,300		0,350				11,1	-2,8
Not documented				4	0	0,209	0,272	0,214	0,068	0,274	0,081	31,6	29,8	-20,6	-24,0
Nitrate + nitrite-nitrogen, µg/l	AB	223	291	60	6	223	291	219	22	286	25	9,9	8,9	-1,7	-1,9
Autoanalyzer				19	2	228	300	225	16	289	28	7,2	9,6	1,0	-0,7
Photometry, manual				9	1	224	289	221	33	295	34	14,8	11,6	-0,8	1,4
Ion chromatography				28	3	221	287	217	21	282	19	9,5	6,8	-2,6	-3,0
Hydrazine				2	0			211		299				-5,4	2,6
Cap. electrophoresis				1	0			214		265				-4,0	-8,9
Photometry, other				1	0			175		231				-21,5	-20,6
Chloride, mg/l	AB	2,20	3,08	61	3	2,20	3,08	2,21	0,21	3,05	0,30	9,6	9,9	0,5	-0,9
Ion chromatography				47	1	2,20	3,09	2,19	0,20	3,05	0,30	9,2	9,9	-0,4	-1,1
Autoanalyzer				2	0			2,46		3,27				11,6	6,2
Argentometry				4	2			2,11		2,68				-4,1	-13,1
Manual, Hg				6	0	2,22	3,08	2,33	0,26	3,16	0,26	11,0	8,3	5,9	2,5
Cap. electrophoresis				1	0			2,11		3,01				-4,0	-2,2
Potentiometry				1	0			2,20		3,05				0,0	-1,0

Table 1. Statistical summary of intercomparison 0115

Analytical variable and method	Sample pair	True value 1	True value 2	Total No.	Labs. exclud.	Median 1	Median 2	Mean Sample 1	St.dev. Sample 1	Mean Sample 2	St.dev. Sample 2	Rel.std.av. % 1	Rel.std.av. % 2	Relative error % 1	Relative error % 2
pH	AB	7,15	7,24	69	1	7,15	7,24	7,14	0,21	7,23	0,19	2,9	2,6	-0,1	-0,2
No stirring				32	1	7,18	7,25	7,17	0,16	7,23	0,14	2,2	1,9	0,3	-0,1
Stirring				34	0	7,14	7,24	7,09	0,22	7,20	0,22	3,1	3,0	-0,8	-0,6
Equilibration				2	0			7,58		7,59				6,0	4,8
Not documented				1	0			6,96		7,21				-2,7	-0,4
Conductivity, mS/m	AB	4,70	5,98	65	5	4,70	5,98	4,68	0,22	5,95	0,25	4,7	4,3	-0,5	-0,5
Alkalinity, mmol/l	AB	0,270	0,357	53	2	0,270	0,357	0,266	0,045	0,349	0,056	17,1	16,0	-1,5	-3,0
Gran plot titration				27	1	0,270	0,357	0,260	0,038	0,349	0,050	14,7	14,4	-3,5	-3,1
End point titration				7	0	0,289	0,382	0,292	0,031	0,383	0,028	10,7	7,3	8,3	6,4
End point 5.6				1	0			0,263		0,353				-2,6	-1,9
End point 5.4				1	0			0,266		0,357				-1,5	-0,8
End point 4.5				11	0	0,270	0,350	0,278	0,052	0,355	0,061	18,9	17,1	2,8	-1,5
Colorimetry				2	1			0,300		0,350				11,1	-2,8
Not documented				4	0	0,209	0,272	0,214	0,068	0,274	0,081	31,6	29,8	-20,6	-24,0
Nitrate + nitrite-nitrogen, µg/l	AB	223	291	60	6	223	291	219	22	286	25	9,9	8,9	-1,7	-1,9
Autoanalyzer				19	2	228	300	225	16	289	28	7,2	9,6	1,0	-0,7
Photometry, manual				9	1	224	289	221	33	295	34	14,8	11,6	-0,8	1,4
Ion chromatography				28	3	221	287	217	21	282	19	9,5	6,8	-2,6	-3,0
Hydrazine				2	0			211		299				-5,4	2,6
Cap. electrophoresis				1	0			214		265				-4,0	-8,9
Photometry, other				1	0			175		231				-21,5	-20,6
Chloride, mg/l	AB	2,20	3,08	61	3	2,20	3,08	2,21	0,21	3,05	0,30	9,6	9,9	0,5	-0,9
Ion chromatography				47	1	2,20	3,09	2,19	0,20	3,05	0,30	9,2	9,9	-0,4	-1,1
Autoanalyzer				2	0			2,46		3,27				11,6	6,2
Argentometry				4	2			2,11		2,68				-4,1	-13,1
Manual, Hg				6	0	2,22	3,08	2,33	0,26	3,16	0,26	11,0	8,3	5,9	2,5
Cap. electrophoresis				1	0			2,11		3,01				-4,0	-2,2
Potentiometry				1	0			2,20		3,05				0,0	-1,0

Analytical variable And method	Sample pair	True value 1	True value 2	Total No.	Labs. exclud.	Median 1	Median 2	Mean Sample 1	St.dev. Sample 1	Mean Sample 2	St.dev. Sample 2	Rel.std.av. % 1	Rel.std.av. % 2	Relative error % 1	Relative error % 2
Sulfate, mg/l	AB	3,2	3,6	61	3	3,2	3,6	3,1	0,3	3,6	0,4	10,9	10,5	-1,6	-1,0
Ion chromatography				48	0	3,2	3,6	3,2	0,3	3,6	0,3	7,9	8,8	0,1	-0,9
Photometry				7	2	2,9	3,3	2,7	0,5	3,3	0,7	17,4	20,8	-16,0	-9,2
Nephelometry				3	0	3,4	4,1	3,1	0,9	4,1	0,3	28,8	7,8	-1,7	12,7
ICP				1	0			2,9		3,3				-9,4	-8,9
Cap. electrophoresis				1	0			3,2		3,7				0,3	1,4
Gravimetry				1	1			3,7		5,5				15,6	52,8
Calcium, mg/l	AB	2,55	3,20	65	2	2,55	3,20	2,56	0,26	3,22	0,28	10,3	8,8	0,5	0,6
FAAS				25	1	2,53	3,16	2,47	0,27	3,15	0,25	10,8	7,9	-3,1	-1,7
ICP				18	0	2,55	3,19	2,57	0,20	3,21	0,20	7,6	6,1	0,9	0,4
EDTA				6	0	2,75	3,22	2,78	0,20	3,32	0,44	7,3	13,3	9,1	3,9
Ion chromatography				15	1	2,56	3,37	2,60	0,31	3,31	0,35	12,1	10,6	2,1	3,4
ICP-MS				1	0			2,57		3,18				0,8	-0,6
Magnesium, mg/l	AB	0,44	0,53	63	6	0,44	0,53	0,45	0,05	0,54	0,06	10,3	10,4	1,2	2,0
FAAS				25	0	0,44	0,53	0,43	0,02	0,53	0,04	4,3	7,1	-1,9	0,7
ICP				18	2	0,44	0,54	0,45	0,06	0,54	0,08	12,8	14,0	3,2	2,2
EDTA				4	2			0,54		0,57				22,7	6,6
Ion chromatography				15	2	0,43	0,53	0,45	0,05	0,55	0,06	11,1	10,7	1,7	4,0
ICP-MS				1	0			0,42		0,51				-4,8	-3,2
Sodium, mg/l	AB	6,22	8,16	61	1	6,22	8,16	6,27	0,49	8,26	0,54	7,7	6,5	0,7	1,2
FAAS				18	1	6,18	8,10	6,14	0,47	8,16	0,46	7,7	5,7	-1,4	0,0
ICP				16	0	6,28	8,19	6,28	0,55	8,28	0,57	8,8	6,9	1,0	1,5
AES				12	0	6,14	7,95	6,14	0,45	7,99	0,48	7,3	6,0	-1,3	-2,0
Ion chromatography				14	0	6,37	8,44	6,52	0,41	8,56	0,55	6,2	6,4	4,9	4,9
ICP-MS				1	0			6,14		8,29				-1,3	1,6
Potassium, mg/l	AB	0,35	0,55	61	6	0,35	0,55	0,35	0,04	0,55	0,04	10,9	7,7	1,3	0,5
FAAS				19	2	0,36	0,56	0,36	0,02	0,56	0,03	6,9	5,5	2,1	1,9
ICP				14	2	0,35	0,56	0,36	0,02	0,56	0,04	6,5	6,7	2,3	2,2
AES				12	1	0,33	0,52	0,35	0,06	0,53	0,06	18,0	11,3	0,1	-3,2
Ion chromatography				15	1	0,35	0,55	0,35	0,04	0,55	0,04	12,5	7,9	0,4	0,3
ICP-MS				1	0			0,35		0,55				0,0	-0,7

Analytical variable and method	Sample pair	True value 1	True value 2	Total No.	Labs. exclud.	Median 1	Median 2	Mean Sample 1	St.dev. Sample 1	Mean Sample 2	St.dev. Sample 2	Rel.std.av. % 1	Rel.std.av. % 2	Relative error % 1	Relative error % 2
Aluminium, µg/l	CD	81	130	28	4	81	130	82	10	128	19	11,7	14,5	1,5	-1,9
FAAS				2	0			80		135				-1,9	3,8
GFAAS				4	0	83	131	80	8	132	22	9,5	17,1	-1,5	1,2
ICP				14	3	81	131	85	10	130	16	11,7	12,4	4,3	0,3
ICP-MS				3	0	85	127	88	10	135	15	11,2	11,2	8,6	3,6
Photometry				5	1	78	100	75	11	107	19	14,5	18,1	-7,1	-17,9
Aluminium, µg/l	EF	105	134	23	1	105	134	103	16	129	22	15,4	16,8	-2,1	-3,5
FAAS				1	0			110		139				4,8	3,7
GFAAS				3	1			98		128				-6,7	-4,9
ICP				9	0	113	141	116	8	145	12	7,2	8,2	10,0	8,6
ICP-MS				7	0	101	130	99	9	125	12	8,9	9,3	-6,2	-6,8
Photometry				3	0	70	91	75	11	89	17	14,9	18,5	-28,4	-33,3
Aluminium, reactive, µg/l	CD	45	73	13	4	45	73	42	9	73	15	22,4	20,3	-5,8	-0,4
Photometry, PCV				12	3	45	73	42	9	73	15	22,4	20,3	-5,8	-0,4
Photometry, other				1	1			-135		-135				-400,0	-284,9
Aluminium, nonlabile, µg/l	CD	34	54	11	3	34	54	33	10	53	14	29,0	25,6	-1,9	-2,0
Photometry, PCV				10	2	34	54	33	10	53	14	29,0	25,6	-1,9	-2,0
Photometry, other				1	1			-135		-135				-497,1	-350,0
Dissolved org. carbon, mg/l	CD	5,5	5,5	29	2	5,5	5,5	5,6	0,9	5,5	1,0	15,9	17,5	1,0	0,1
Combustion				16	1	5,6	5,5	5,7	0,9	5,7	1,0	16,4	18,2	3,5	4,3
UV/S2O8				12	0	5,3	5,2	5,4	0,8	5,2	0,8	15,4	15,2	-2,0	-5,2
Not documented				1	1			9,3		8,7				68,4	58,5
Chem. oxygen demand, mg/l	CD	6,0	6,1	17	0	6,0	6,1	6,1	0,6	6,1	0,7	10,4	11,8	1,6	0,6
Iron, µg/l	EF	26,3	45,0	37	6	26,3	45,0	26,8	4,7	44,6	8,2	17,7	18,4	1,9	-0,8
FAAS				2	0			23,0		35,0				-12,5	-22,2
GFAAS				7	1	27,9	51,4	26,7	6,3	47,4	13,1	23,5	27,7	1,6	5,3
ICP				14	1	26,3	45,0	27,1	3,2	44,5	4,2	11,7	9,3	3,0	-1,1
ICP-MS				10	2	26,5	43,4	25,4	5,2	43,4	9,3	20,4	21,4	-3,3	-3,6
Photometry				4	2			34,5		52,0				31,2	15,6

Analytical variable and method	Sample pair	True value 1	True value 2	Total No.	Labs. exclud.	Median 1	Median 2	Mean Sample 1	St.dev. Sample 1	Mean Sample 2	St.dev. Sample 2	Rel.std.av. % 1	Rel.std.av. % 2	Relative error % 1	Relative error % 2
Manganese, µg/l	EF	5,6	1,6	36	8	5,6	1,6	5,7	0,5	1,6	0,2	8,1	15,1	1,8	-0,9
FAAS				2	1			6,3		2,3				12,5	43,8
GFAAS				9	3	6,1	1,7	6,0	0,6	1,7	0,2	10,7	10,5	6,8	4,4
ICP				14	3	5,6	1,6	5,7	0,4	1,5	0,3	7,2	17,1	1,0	-5,2
ICP-MS				10	0	5,5	1,6	5,5	0,3	1,5	0,1	5,6	6,4	-1,4	-3,7
Photometry				1	1			7,0		5,0				25,0	212,5
Kadmium, µg/l	EF	1,08	3,00	35	3	1,08	3,00	1,08	0,16	3,00	0,43	15,0	14,2	0,2	-0,1
GFAAS				17	1	1,08	3,00	1,08	0,19	2,93	0,51	17,2	17,5	-0,1	-2,5
ICP				7	1	0,95	2,92	1,05	0,18	2,92	0,34	17,6	11,5	-2,9	-2,6
ICP-MS				11	1	1,11	3,10	1,11	0,11	3,16	0,29	10,2	9,0	2,6	5,3
Bly, µg/l	EF	3,1	6,9	35	8	3,1	6,9	3,0	0,5	7,0	1,2	18,0	16,5	-3,5	1,0
GFAAS				18	3	3,1	7,2	3,0	0,7	7,1	1,5	24,1	21,7	-4,5	2,2
ICP				6	4			2,7		6,6				-11,6	-4,2
ICP-MS				11	1	3,1	6,9	3,1	0,1	6,9	0,4	4,8	5,5	-0,4	0,2
Kopper, µg/l	EF	29,1	11,7	36	4	29,1	11,7	28,9	3,0	11,5	1,1	10,4	9,7	-0,8	-1,4
FAAS				2	1			22,1		7,7				-24,2	-34,6
GFAAS				13	0	29,1	11,6	28,6	3,1	11,6	0,8	10,9	7,1	-1,6	-0,8
ICP				10	2	29,4	11,9	29,7	3,3	11,7	1,1	11,1	9,6	2,1	-0,2
ICP-MS				11	1	29,1	11,6	29,2	1,9	11,7	0,8	6,6	7,0	0,3	0,3
Nikkel, µg/l	EF	2,4	6,1	34	6	2,4	6,1	2,3	0,3	6,1	0,5	13,2	7,9	-2,8	0,3
GFAAS				13	1	2,4	6,1	2,3	0,4	6,1	0,6	15,6	9,8	-3,0	0,7
ICP				10	4	2,3	6,1	2,4	0,4	6,0	0,4	18,3	7,3	-1,1	-1,6
ICP-MS				11	1	2,3	6,1	2,3	0,1	6,2	0,4	5,9	6,1	-3,5	1,0
Zinc, µg/l	EF	23,6	12,4	36	7	23,6	12,4	23,9	3,0	12,7	2,0	12,6	15,5	1,4	2,2
FAAS				7	4	25,0	14,0	25,8	4,8	14,0	4,0	18,6	28,9	9,5	12,7
GFAAS				5	2	20,0	11,5	22,1	4,1	12,1	1,9	18,7	15,9	-6,2	-2,7
ICP				13	0	23,3	12,2	23,0	1,8	11,9	1,2	8,0	10,0	-2,7	-4,0
ICP-MS				11	1	24,6	13,2	25,2	3,0	13,5	1,8	12,1	13,7	6,7	8,5

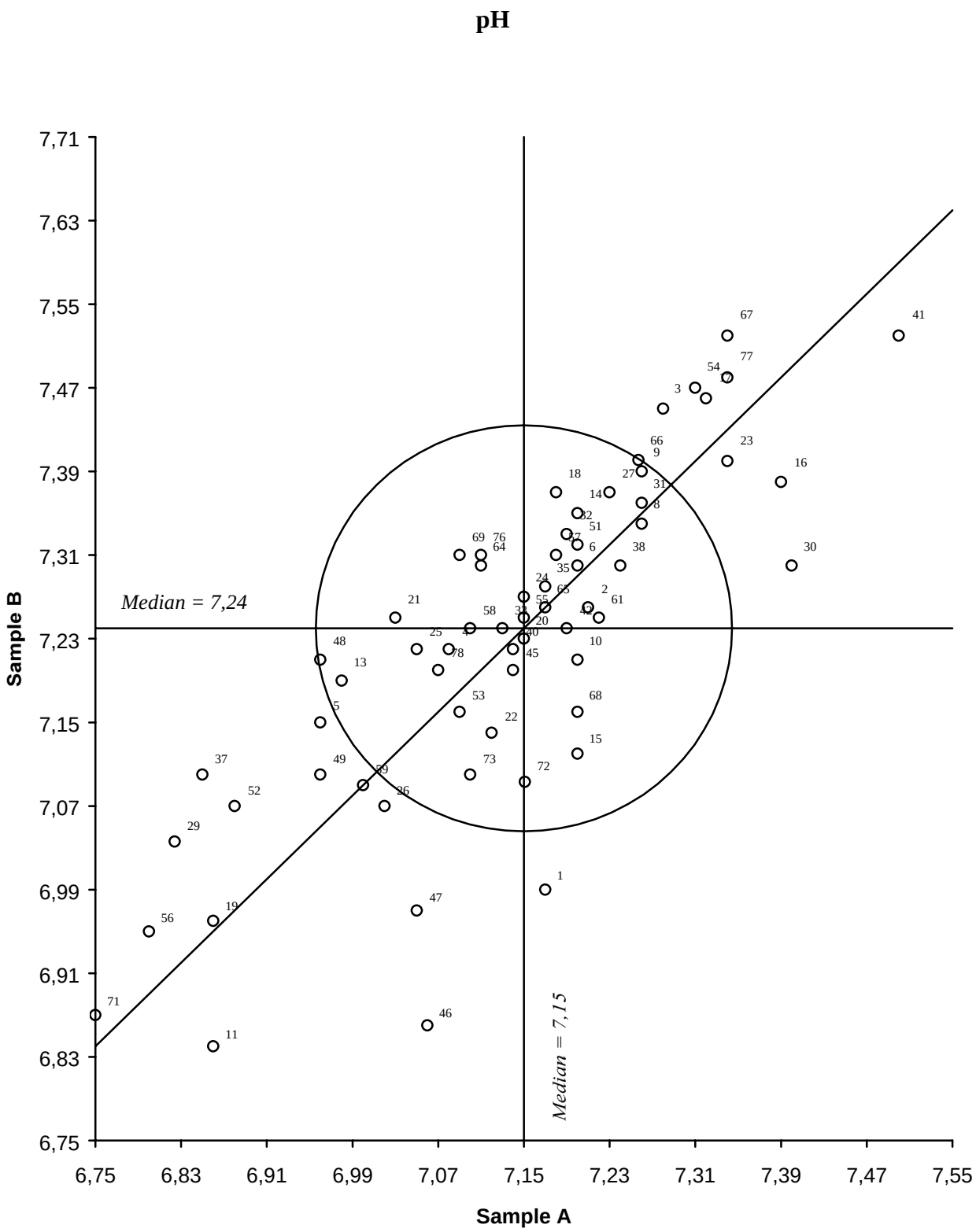

Figure 1. Youdendiagramme for pH, sample pair AB.
Acceptance limit given by the circle is 0,2 pH units.

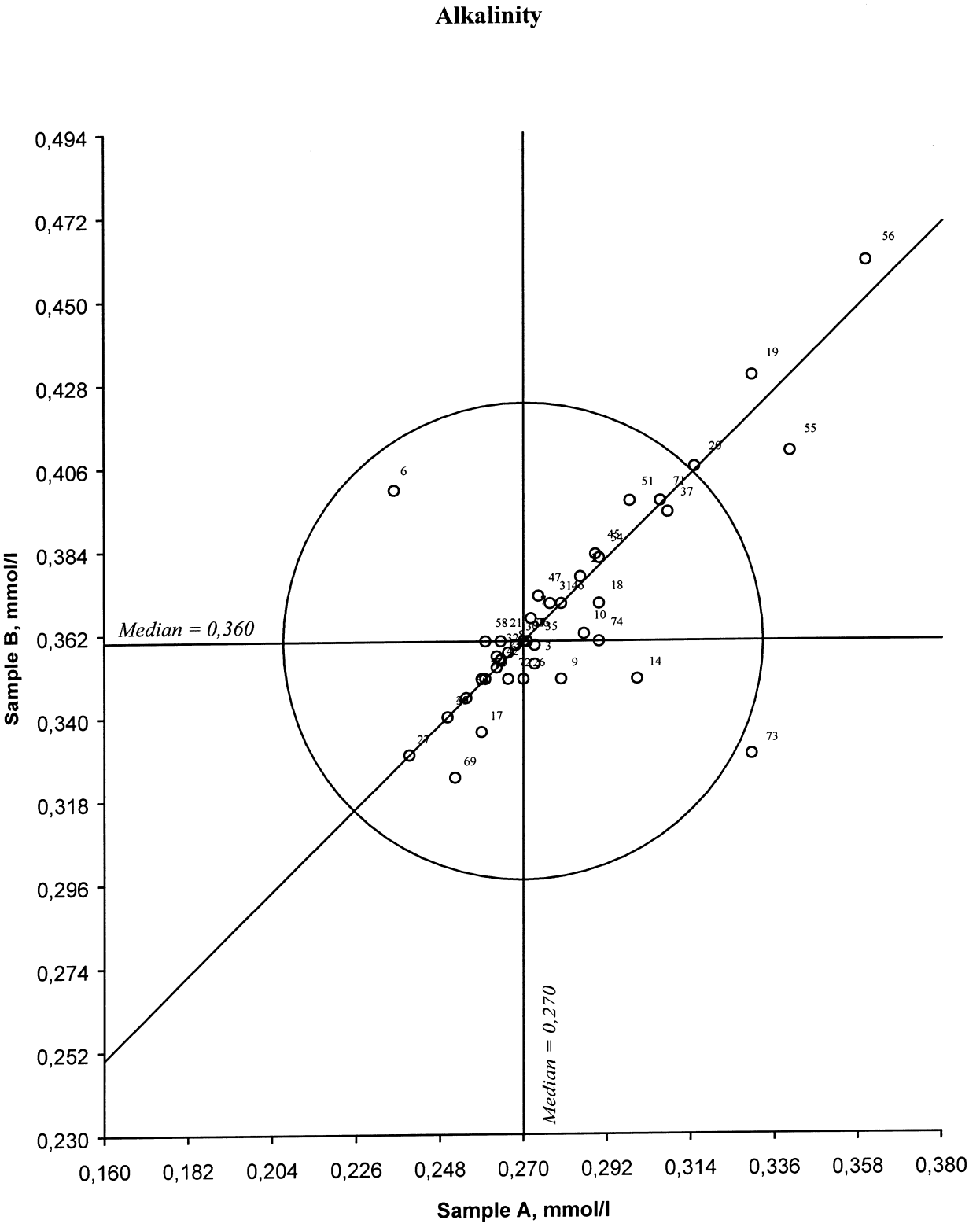

Figure 3. Youdendiagramme for alkalinity, sample pair AB.
Acceptance limit given by the circle is 20 %.

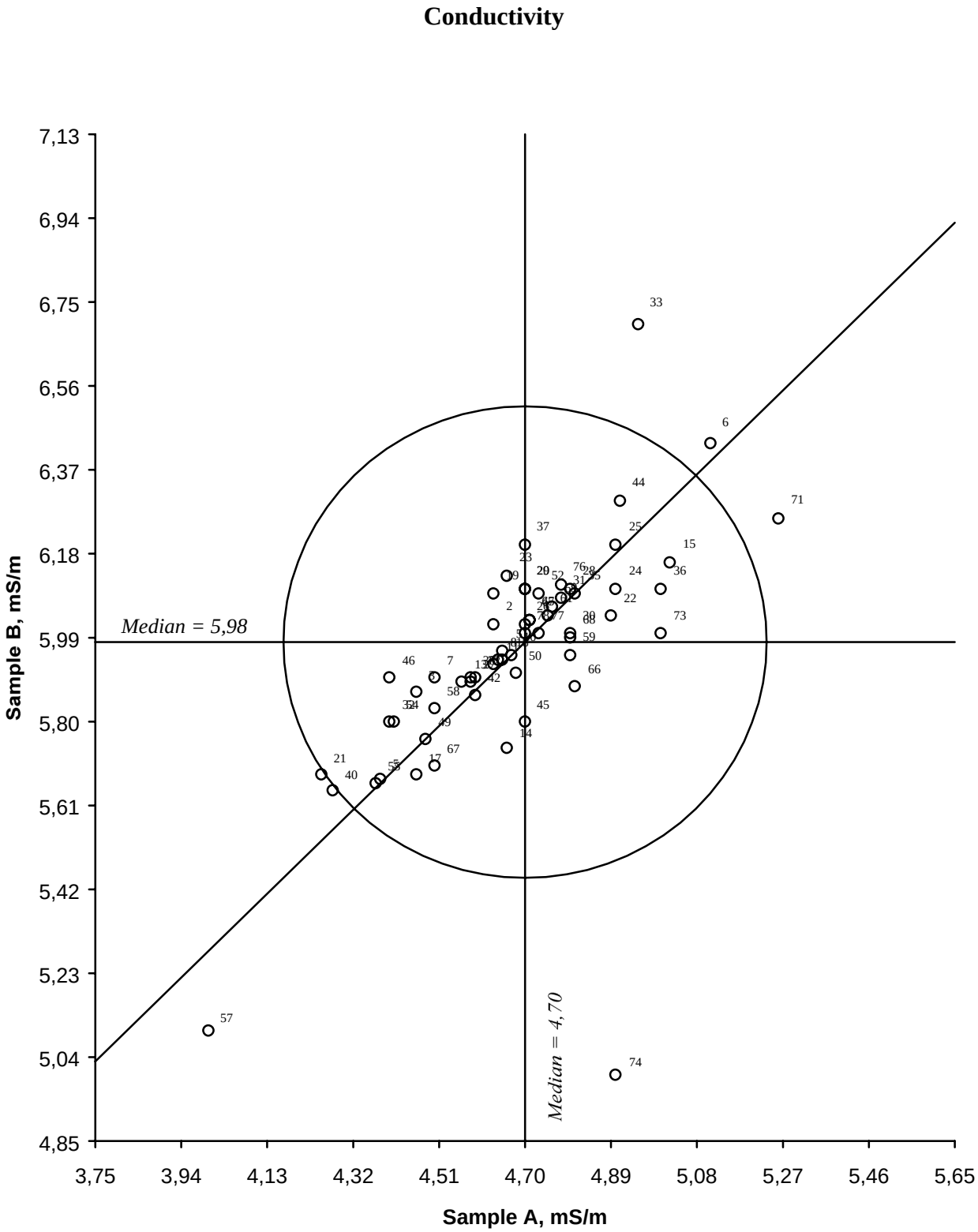

Figure 2. Youdendiagramme for conductivity, sample pair AB. Acceptance limit given by the circle is 10 %.

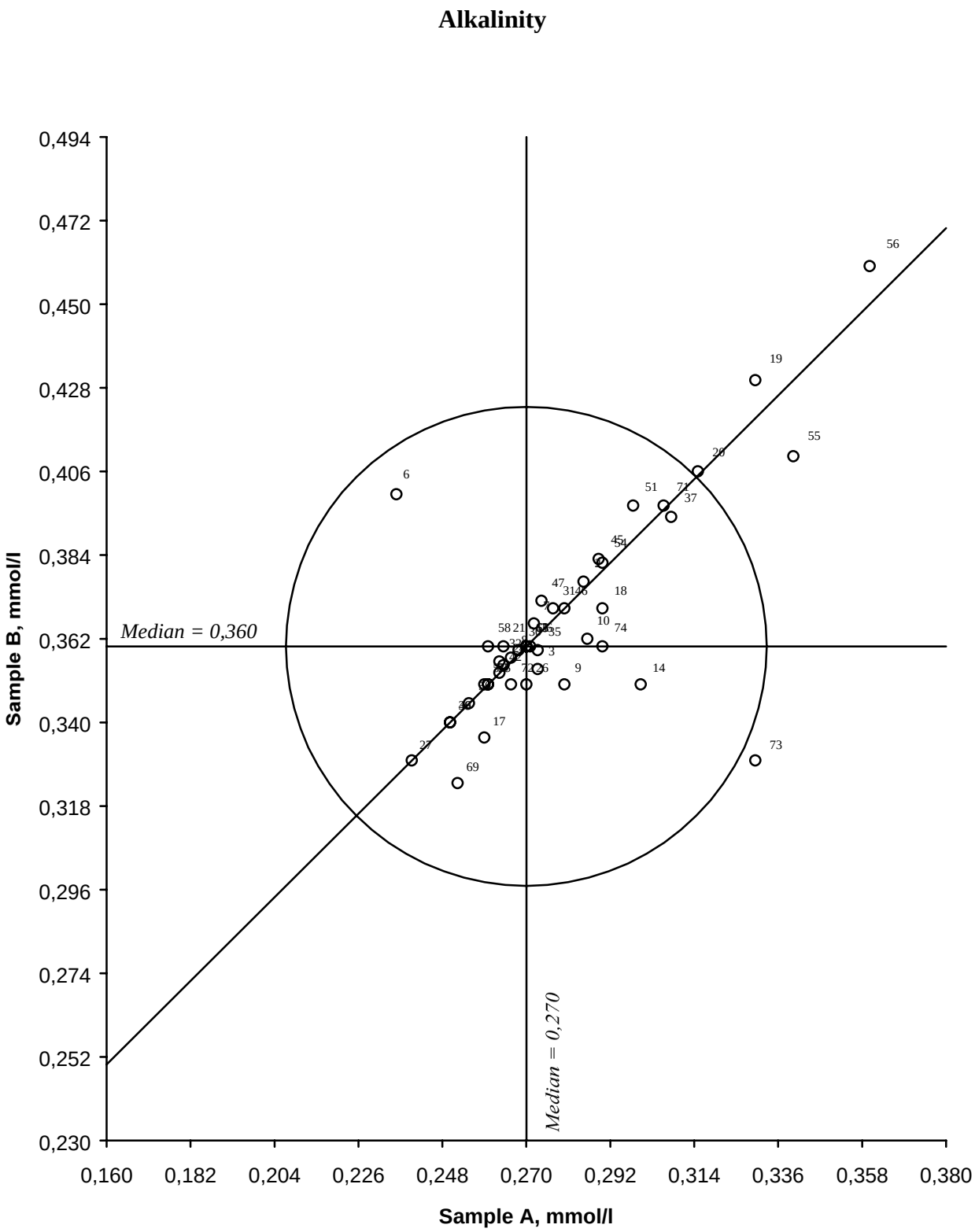

Figure 3. Youdendiagramme for alkalinity, sample pair AB. Acceptance limit given by the circle is 20 %.

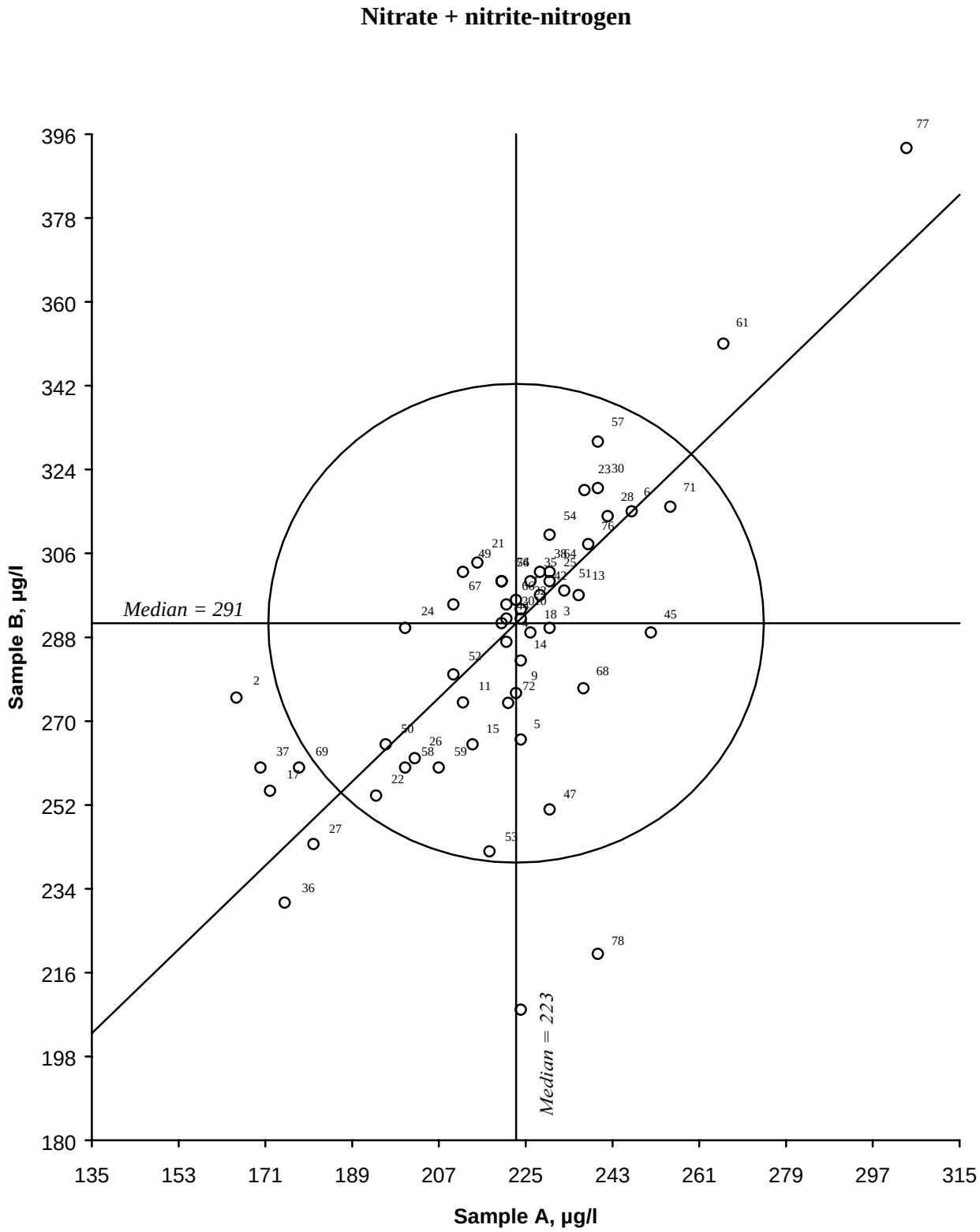

Figure 4. Youdendiagramme for nitrate+nitrite-nitrogen, sample pair AB. Acceptance limit given by the circle is 20 %.

Chloride

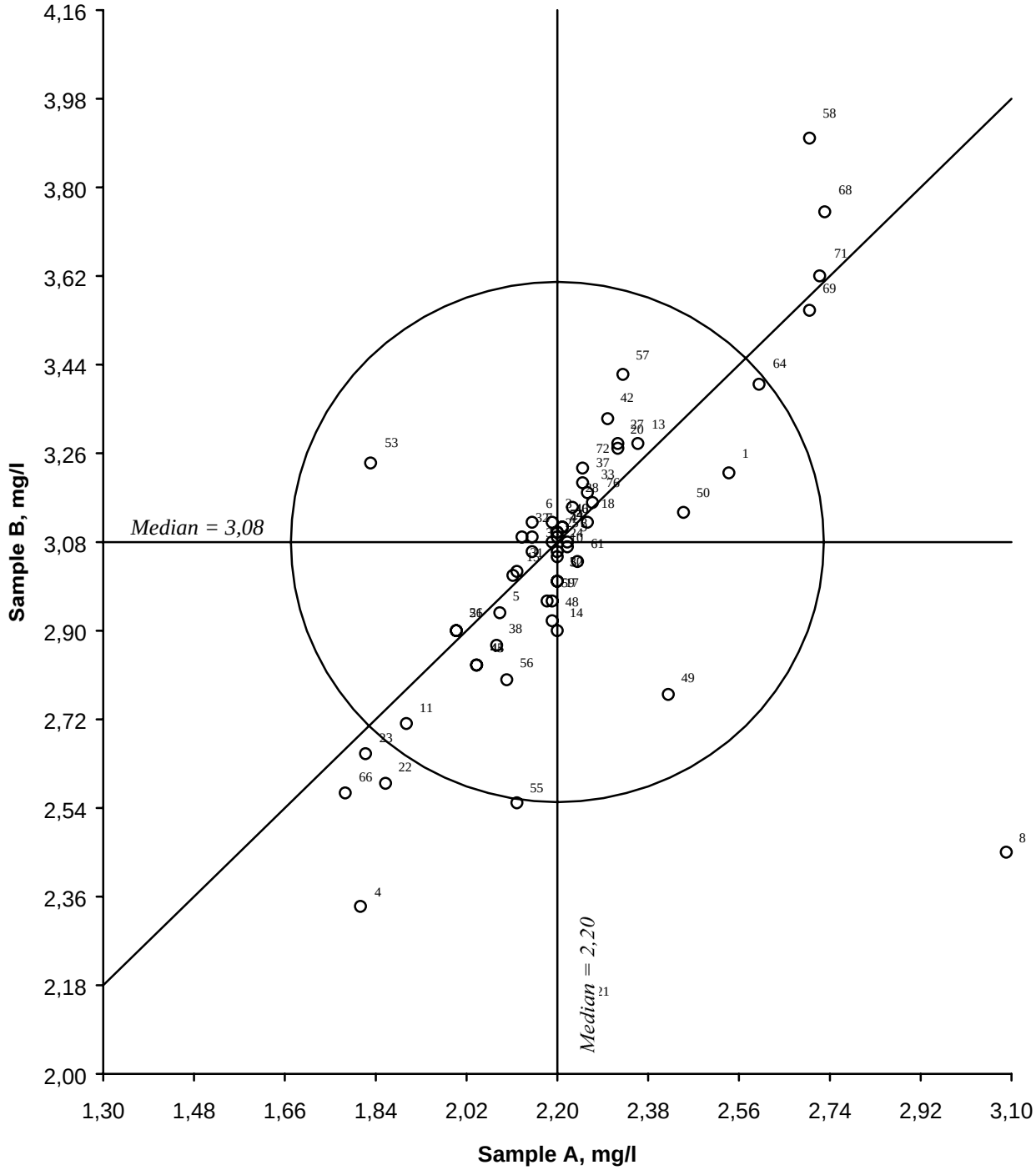

Figure 5. Youdendiagramme for chloride, sample pair AB. Acceptance limit given by the circle is 20 %.

Sulfate

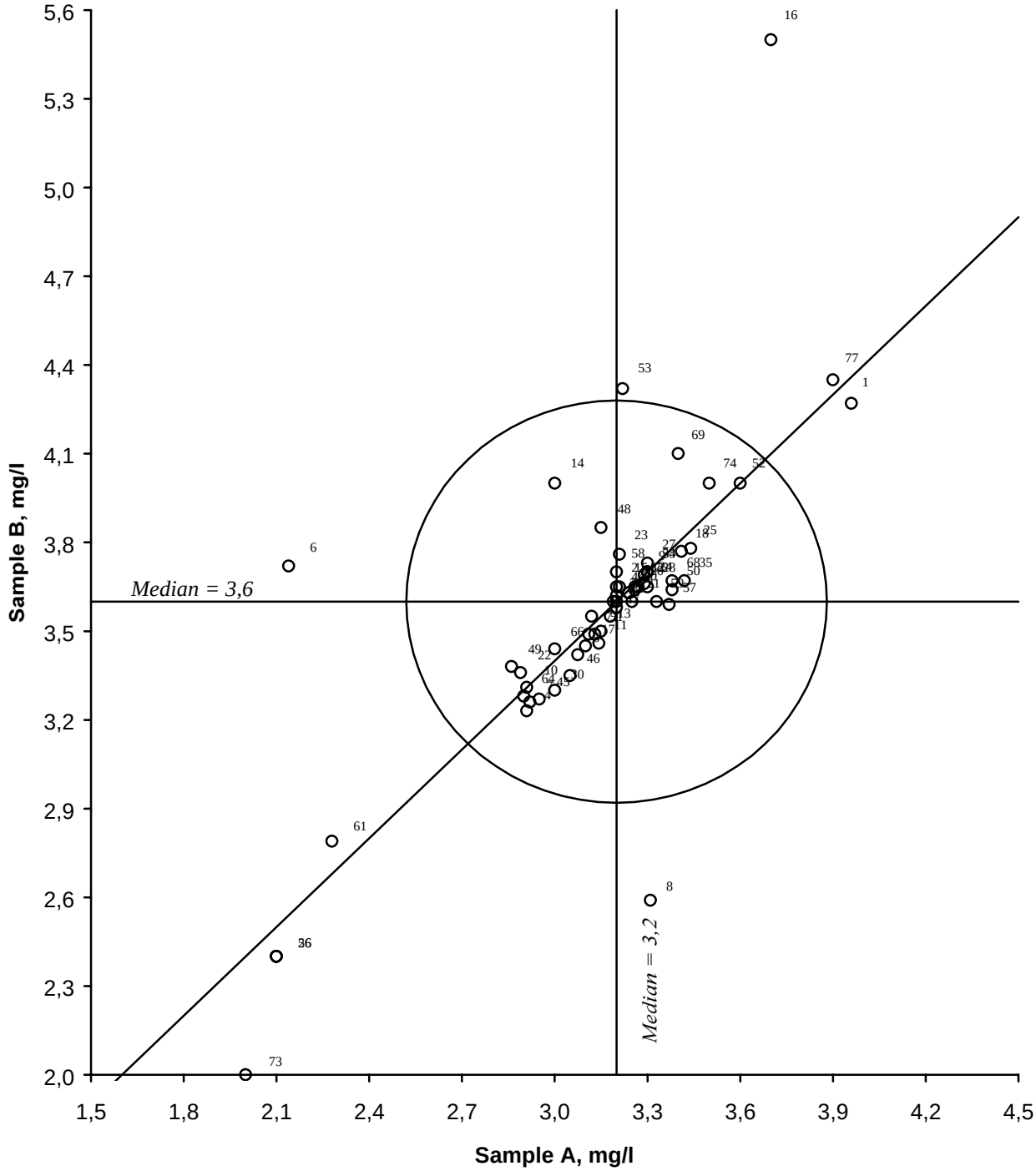

Figure 6. Youdendiagramme for sulfate, sample pair AB. Acceptance limit given by the circle is 20 %.

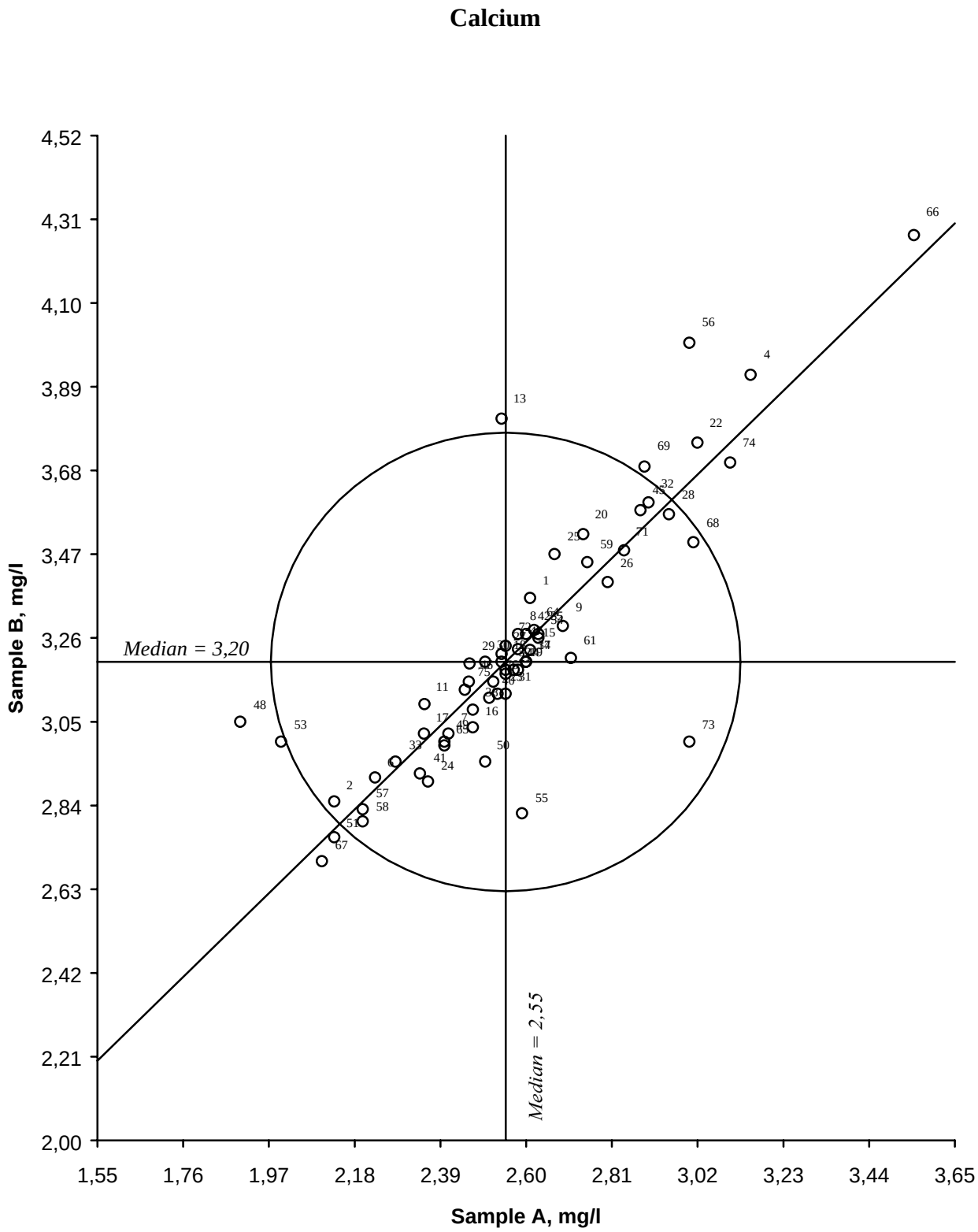

Figure 7. Youdendiagramme for calcium, sample pair AB. Acceptance limit given by the circle is 20 %.

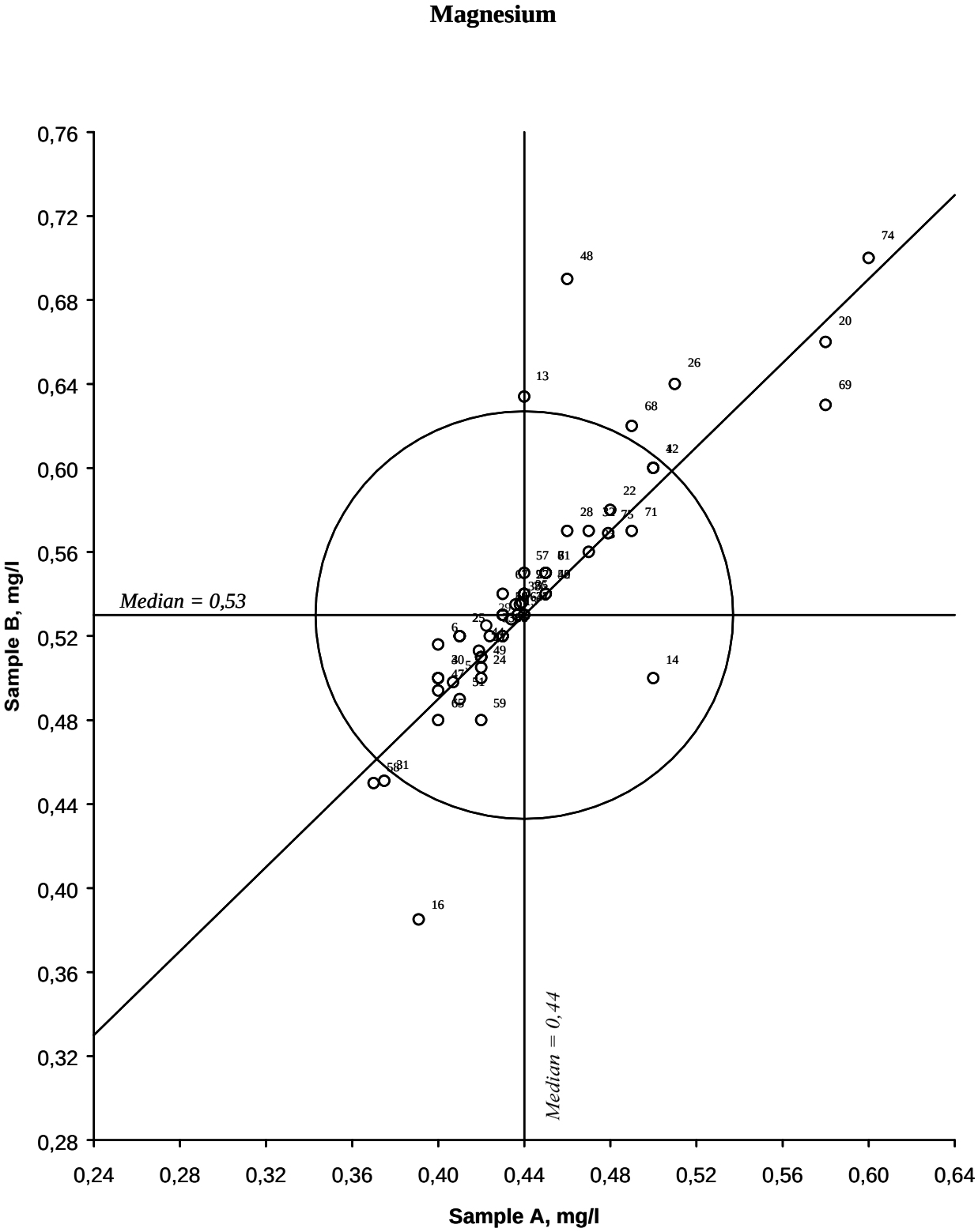

Figure 8. Youdendiagramme for magnesium, sample pair AB. Acceptance limit given by the circle is 20 %.

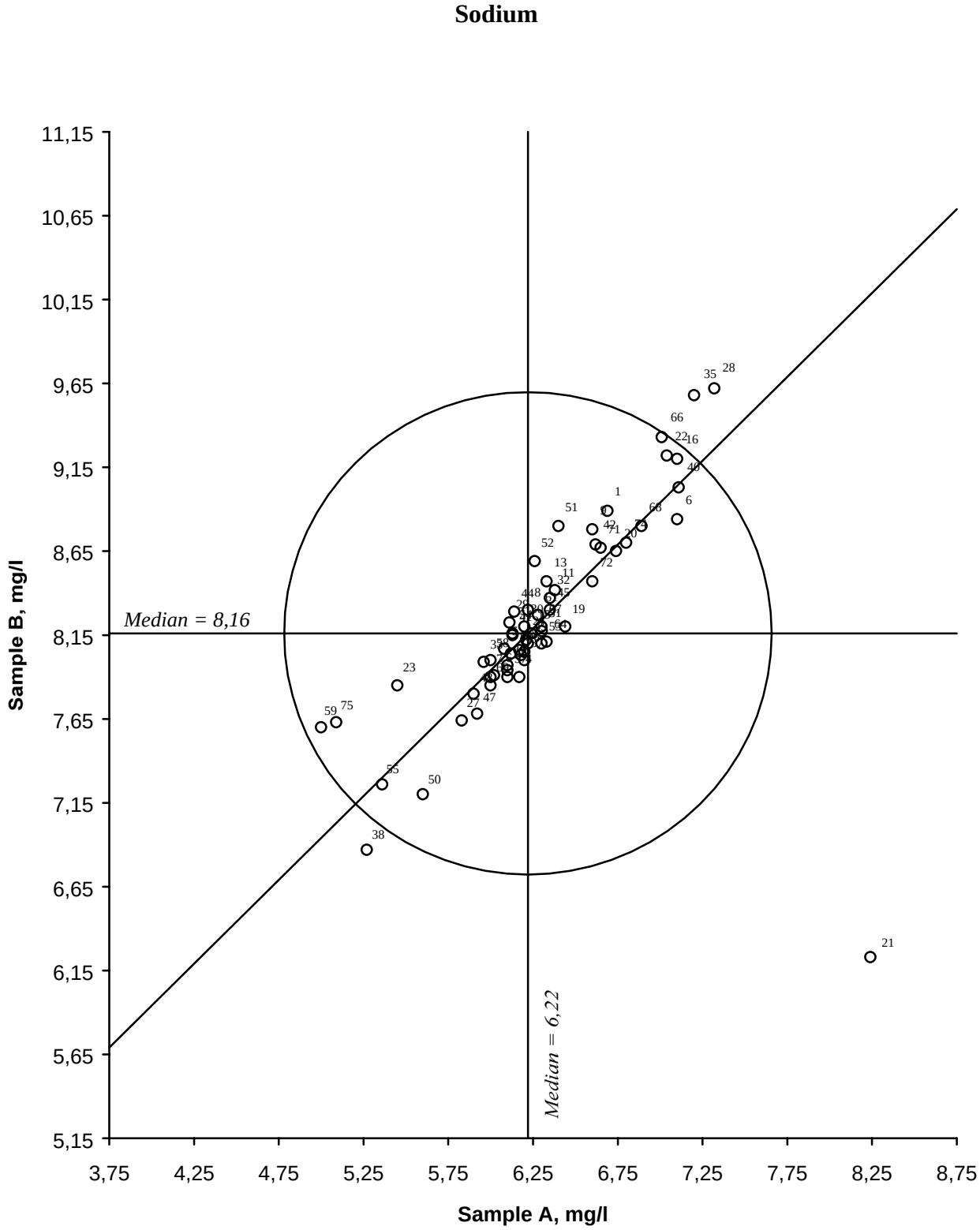

Figure 9. Youdendiagramme for sodium, sample pair AB.
Acceptance limit given by the circle is 20 %.

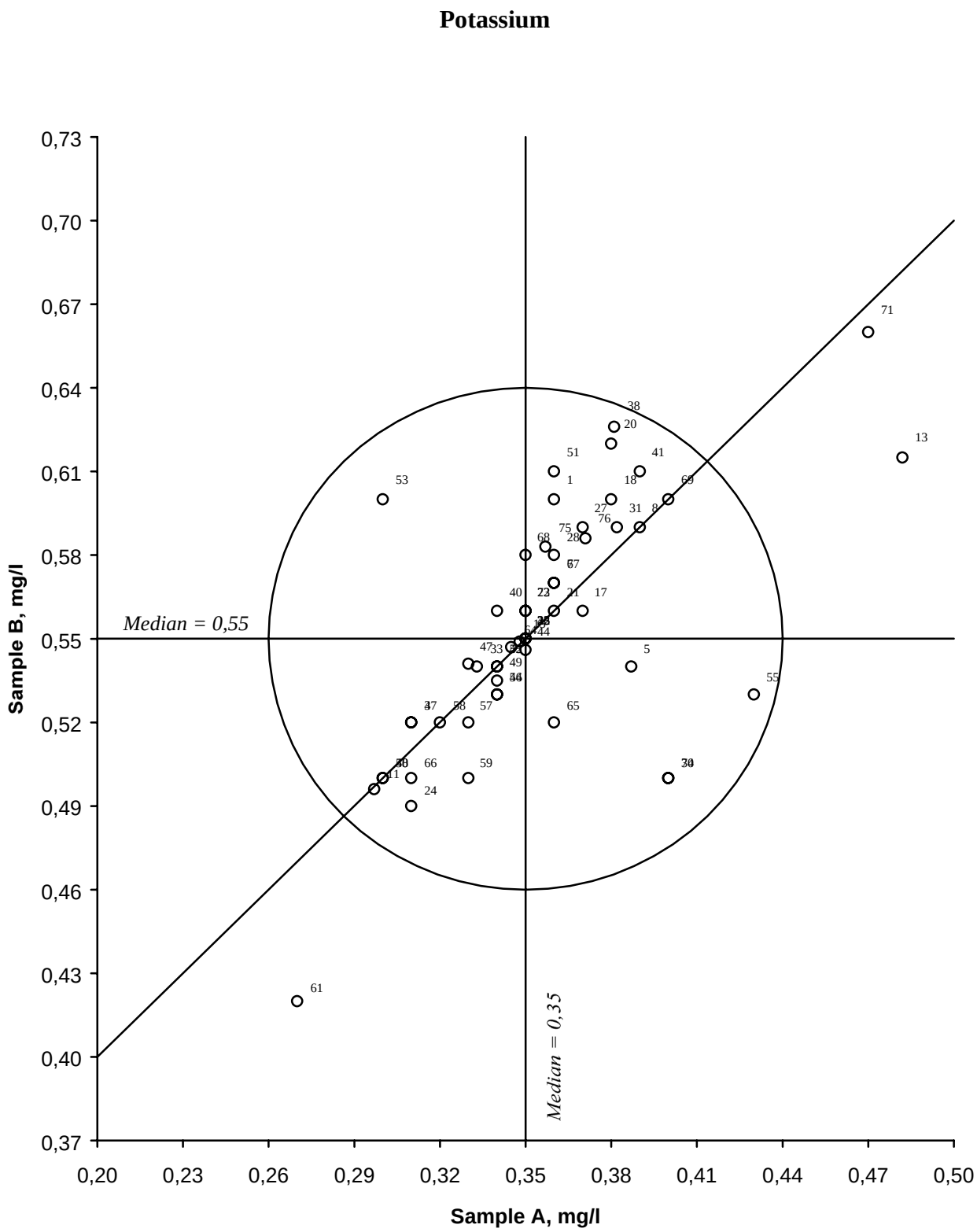

Figure 10. Youdendiagramme for potassium, sample pair AB.
Acceptance limit given by the circle is 20 %.

Aluminium

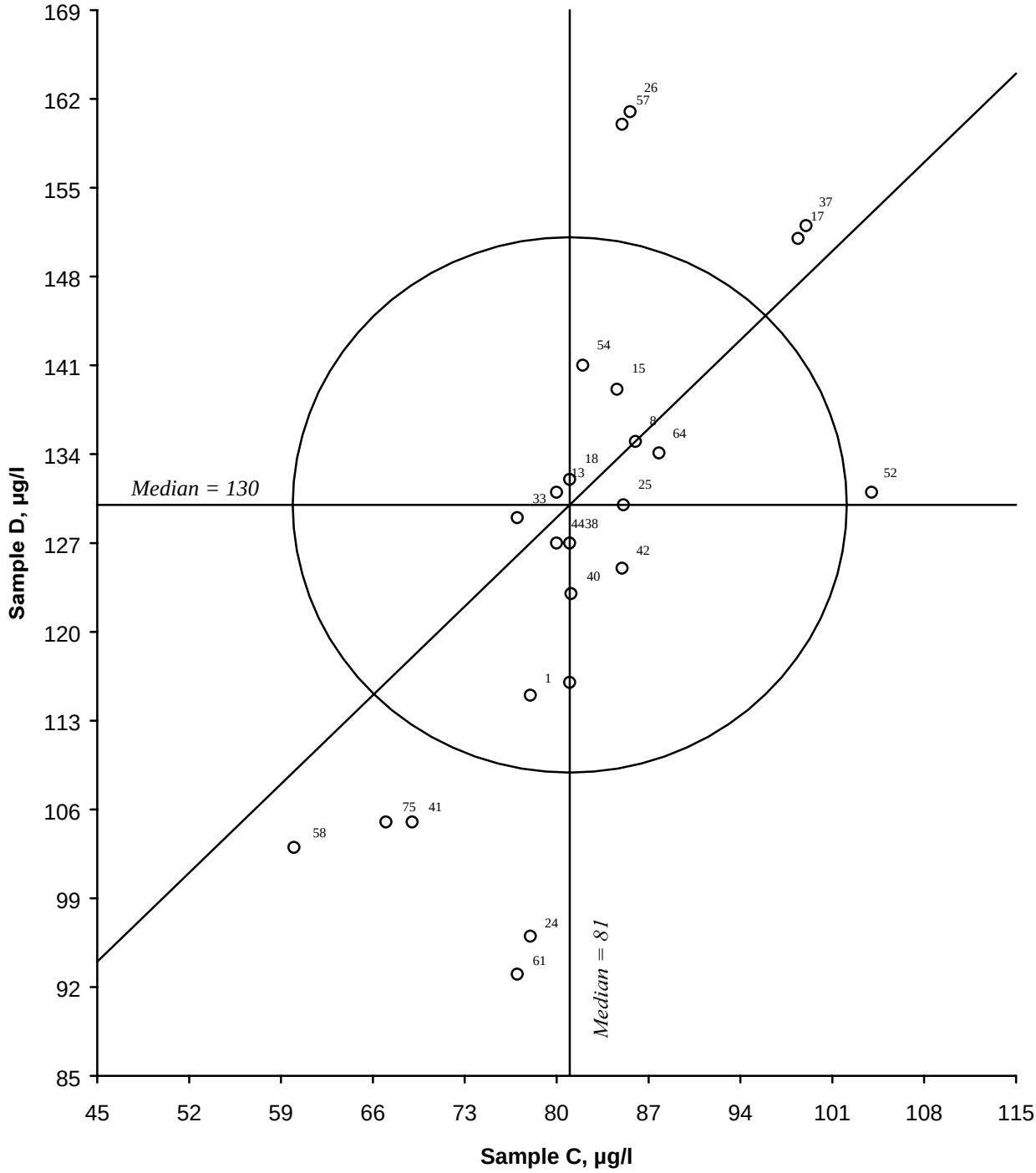

Figure 11. Youdendiagramme for aluminium, sample pair CD.
Acceptance limit given by the circle is 20 %.

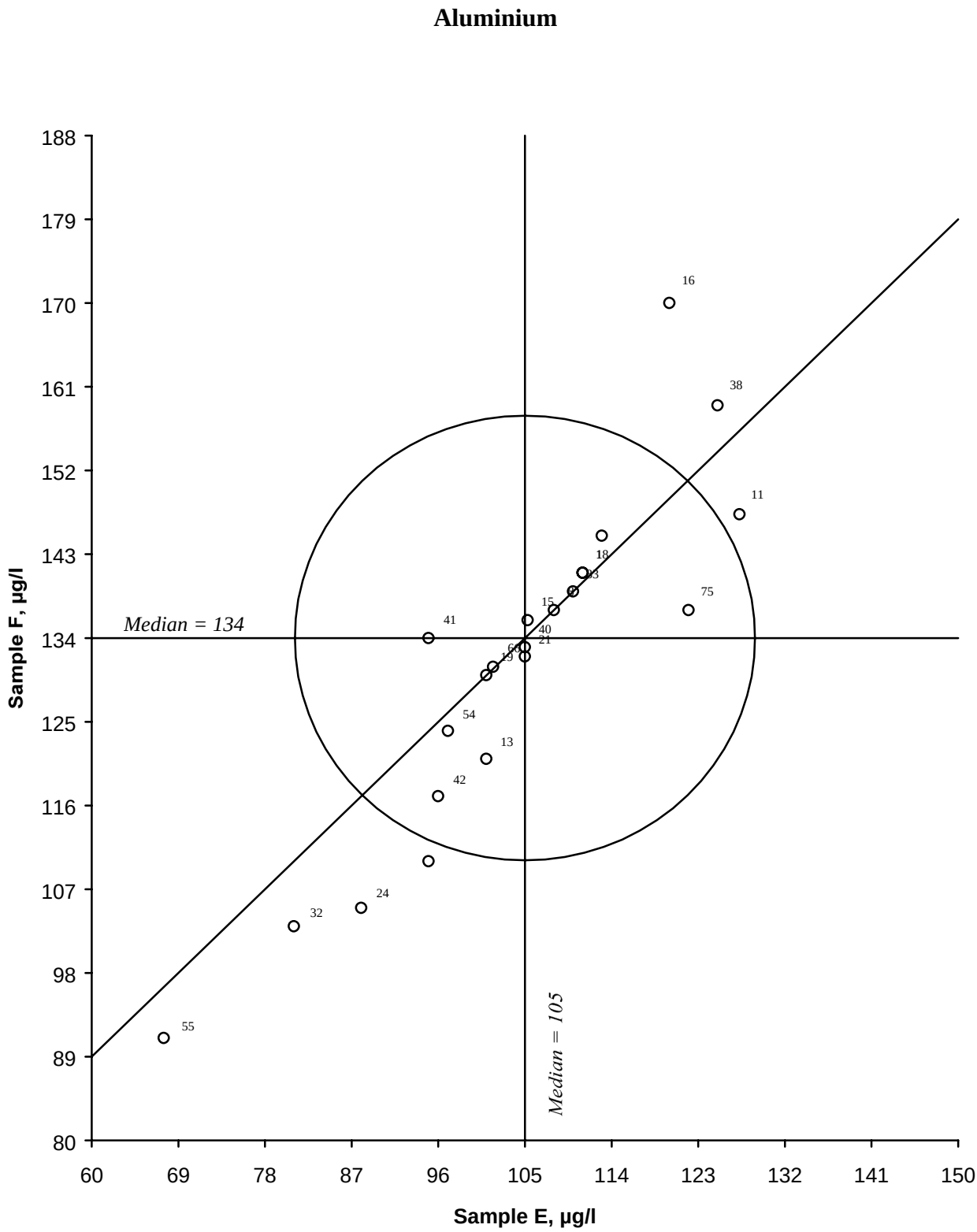

Figure 12. Youdendiagramme for aluminium, sample pair EF.
Acceptance limit given by the circle is 20 %.

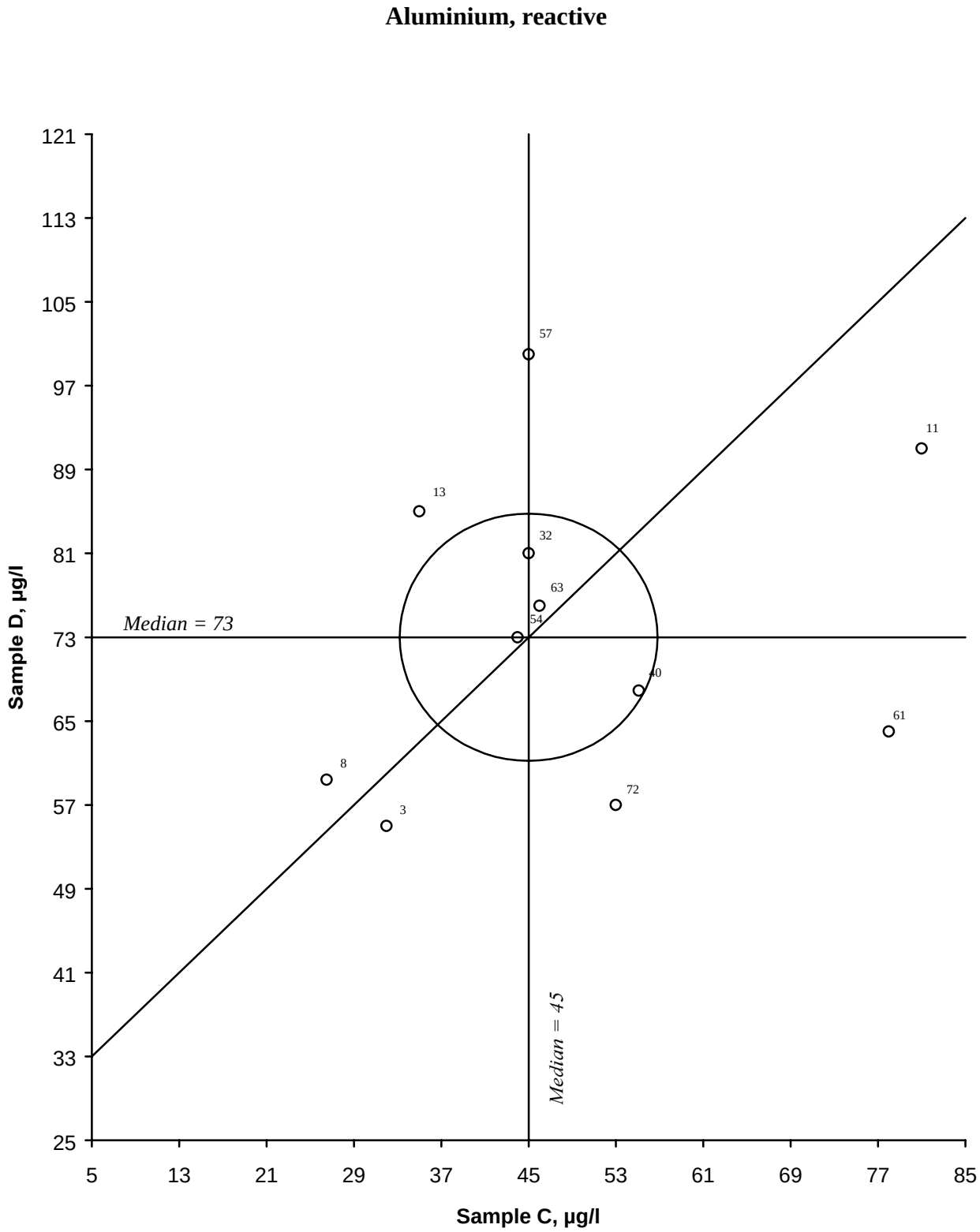

Figure 13. Youdendiagramme for aluminium, reactive, sample pair CD. Acceptance limit given by the circle is 20 %.

Aluminium, nonlabile

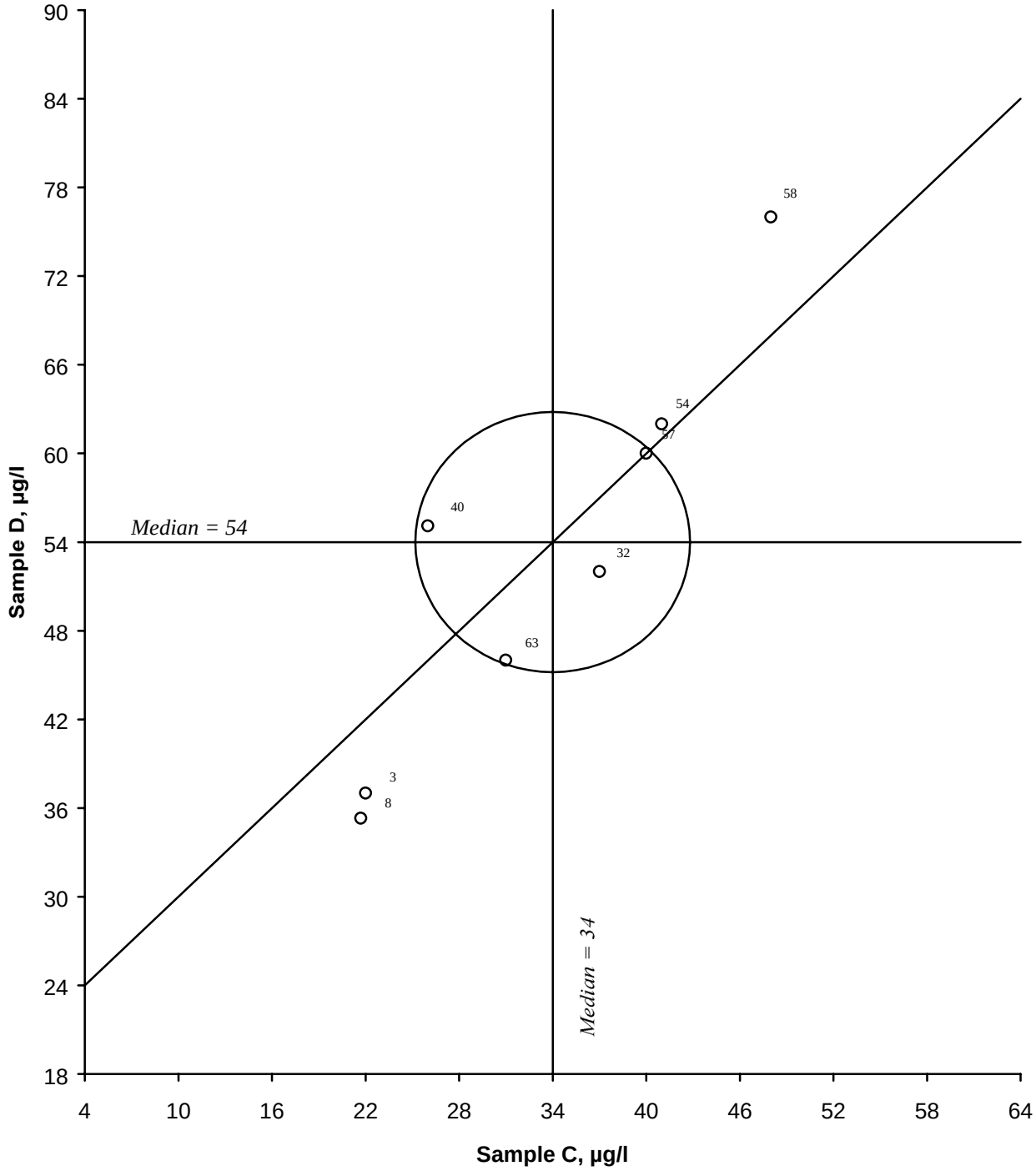

Figure 14. Youdendiagramme for aluminium, nonlabile, sample pair CD. Acceptance limit given by the circle is 20 %.

Dissolved organic carbon

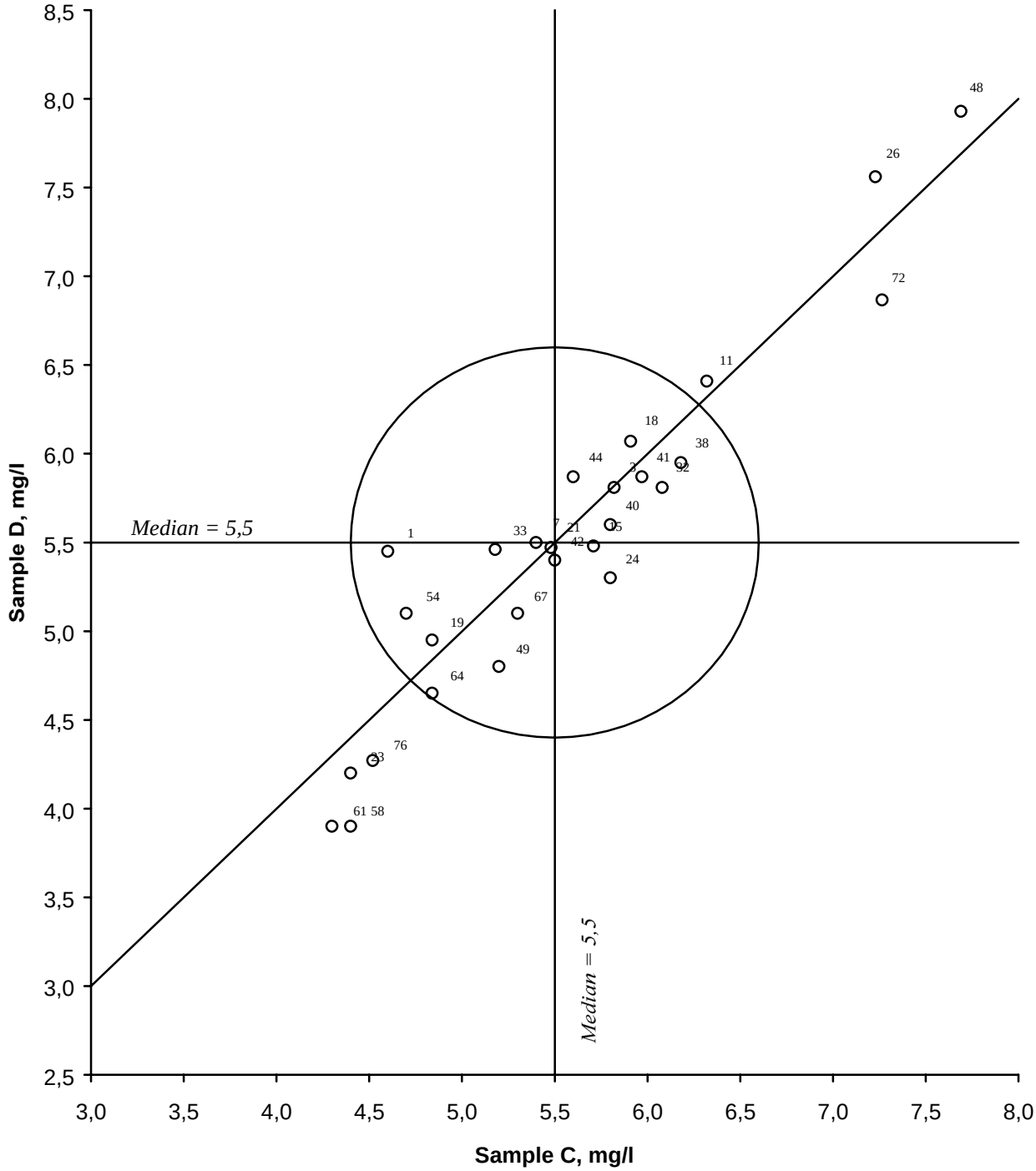

Figure 15. Youdendiagramme for dissolved organic carbon, sample pair CD. Acceptance limit given by the circle is 20 %.

Chemical oxygen demand

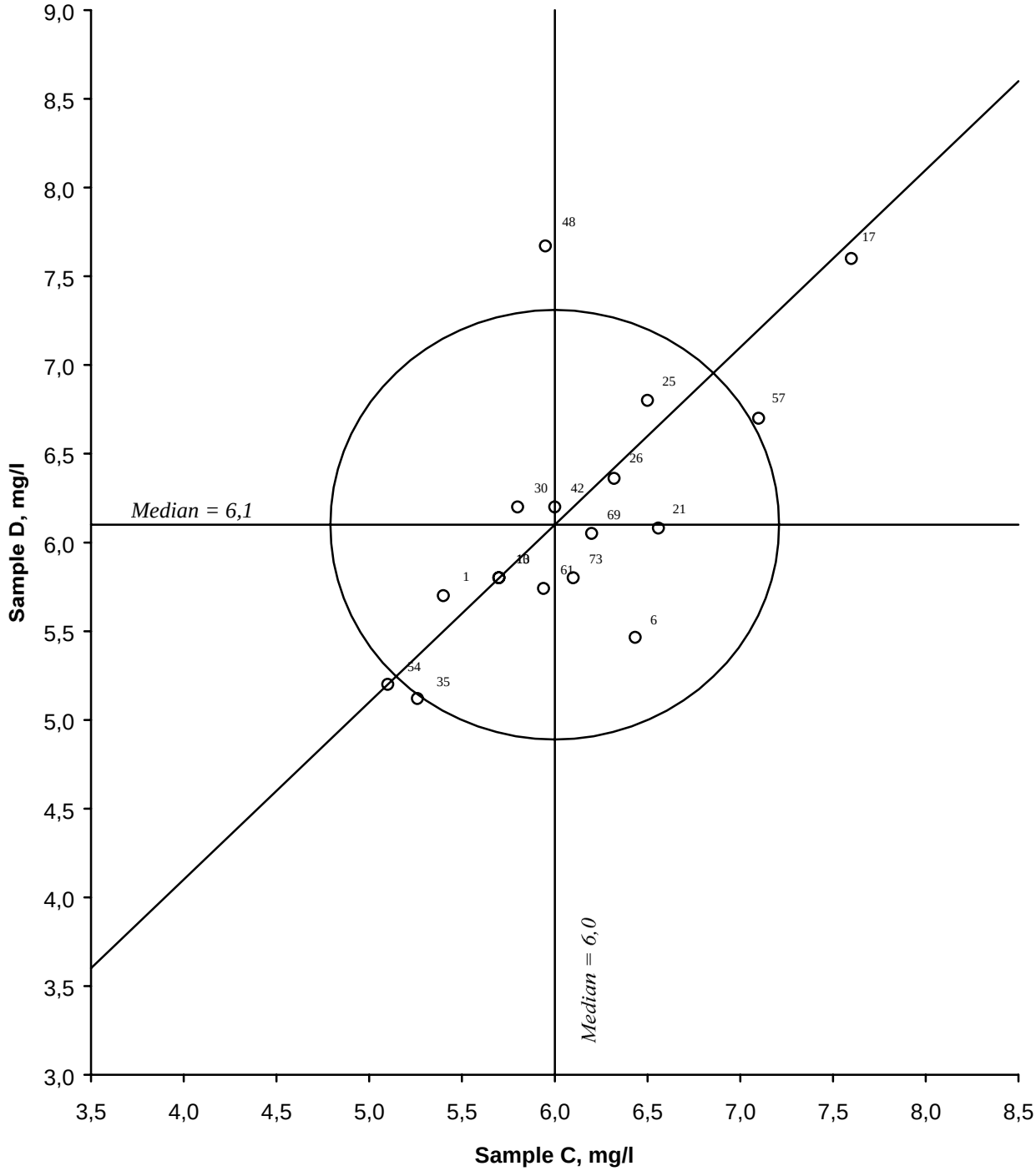

Figure 16. Youdendiagramme for chemical oxygen demand, sample pair CD. Acceptance limit given by the circle is 20 %.

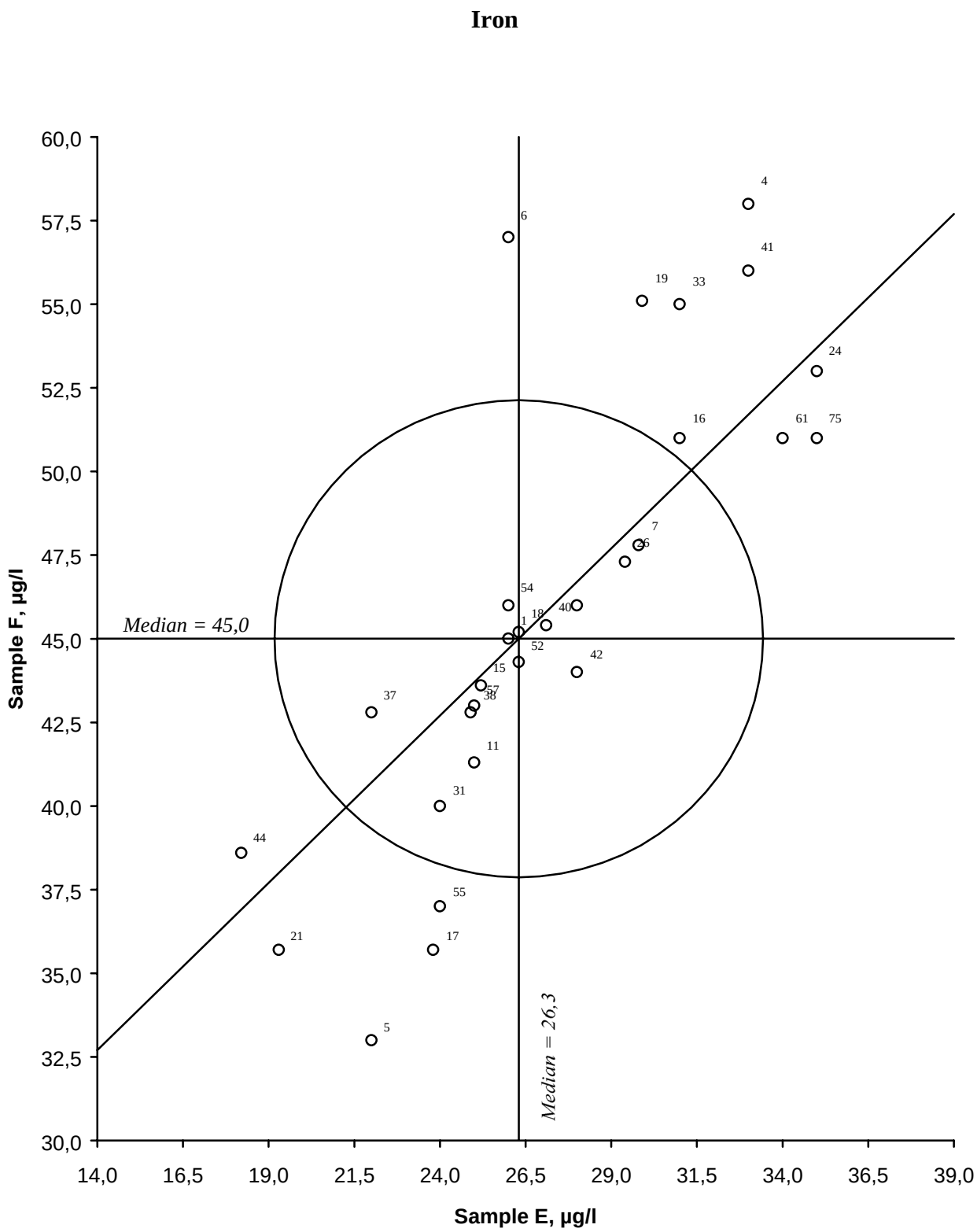

Figure 17. Youdendiagramme for iron, sample pair EF.
Acceptance limit given by the circle is 20 %.

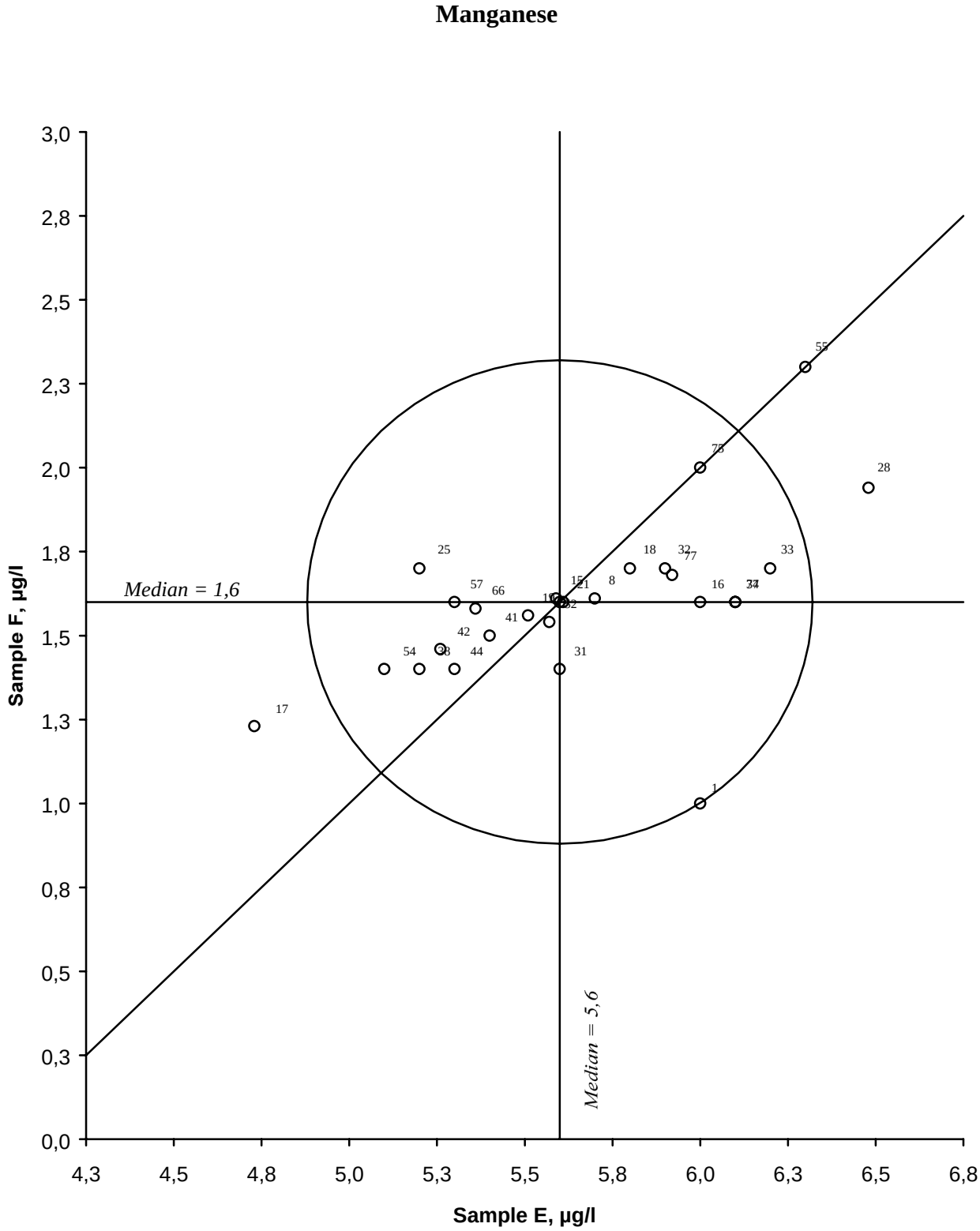

Figure 18. Youdendiagramme for manganese, sample pair EF.
Acceptance limit given by the circle is 20 %.

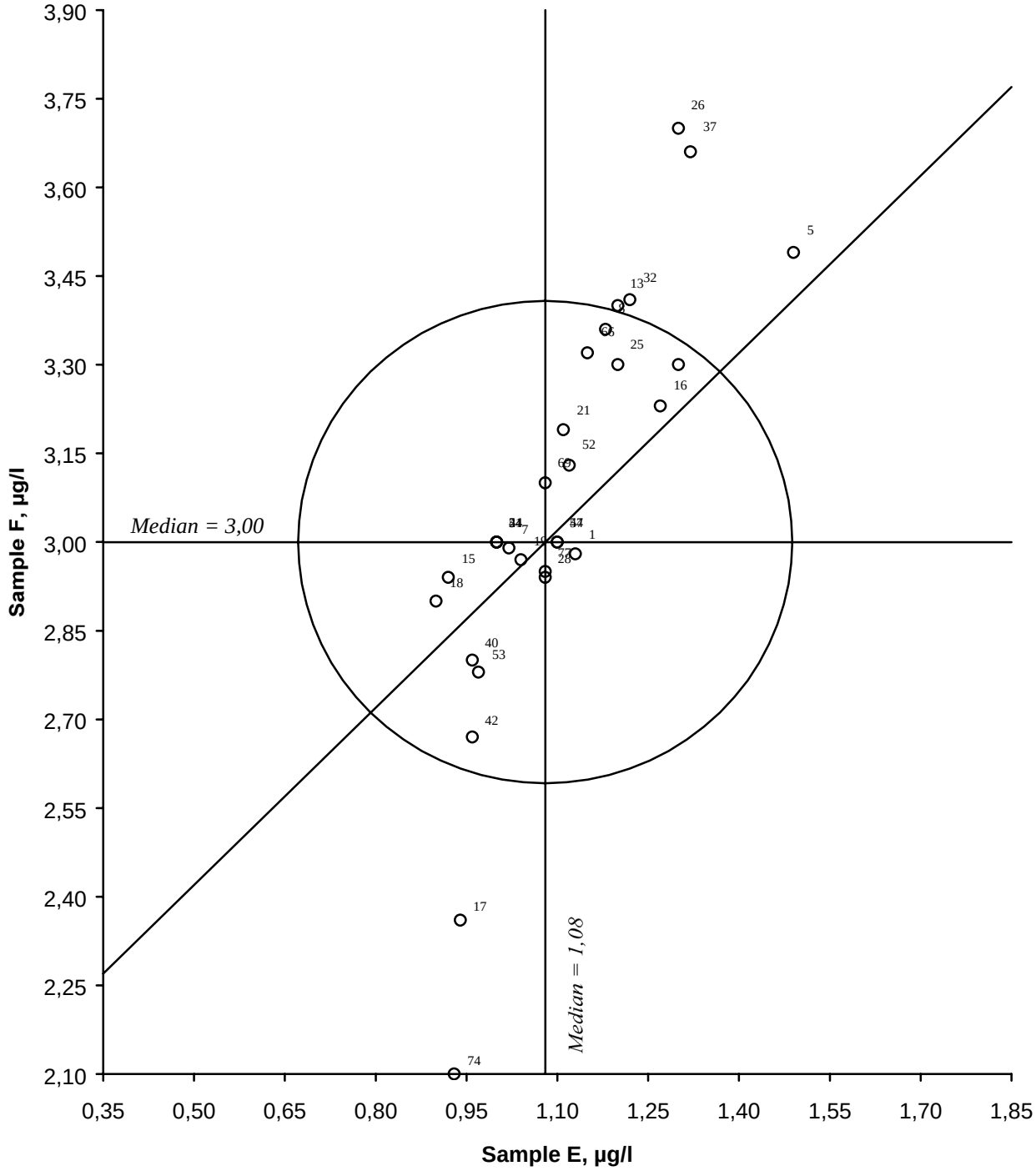

Figure 19. Youdendiagramme for cadmium, sample pair EF.
Acceptance limit given by the circle is 20 %.

Bly

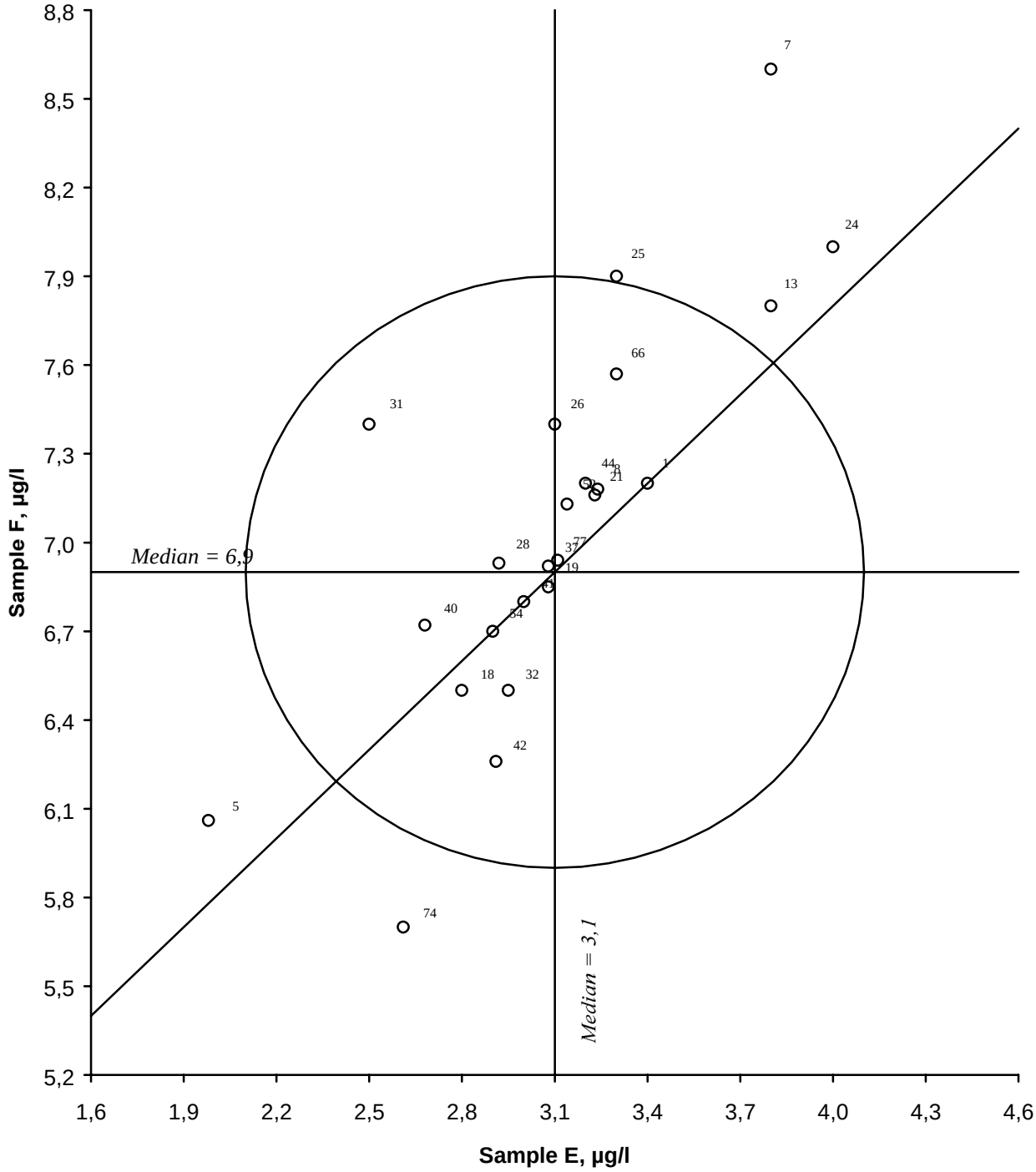

Figure 20. Youdendiagramme for lead, sample pair EF.
Acceptance limit given by the circle is 20 %.

Kopper

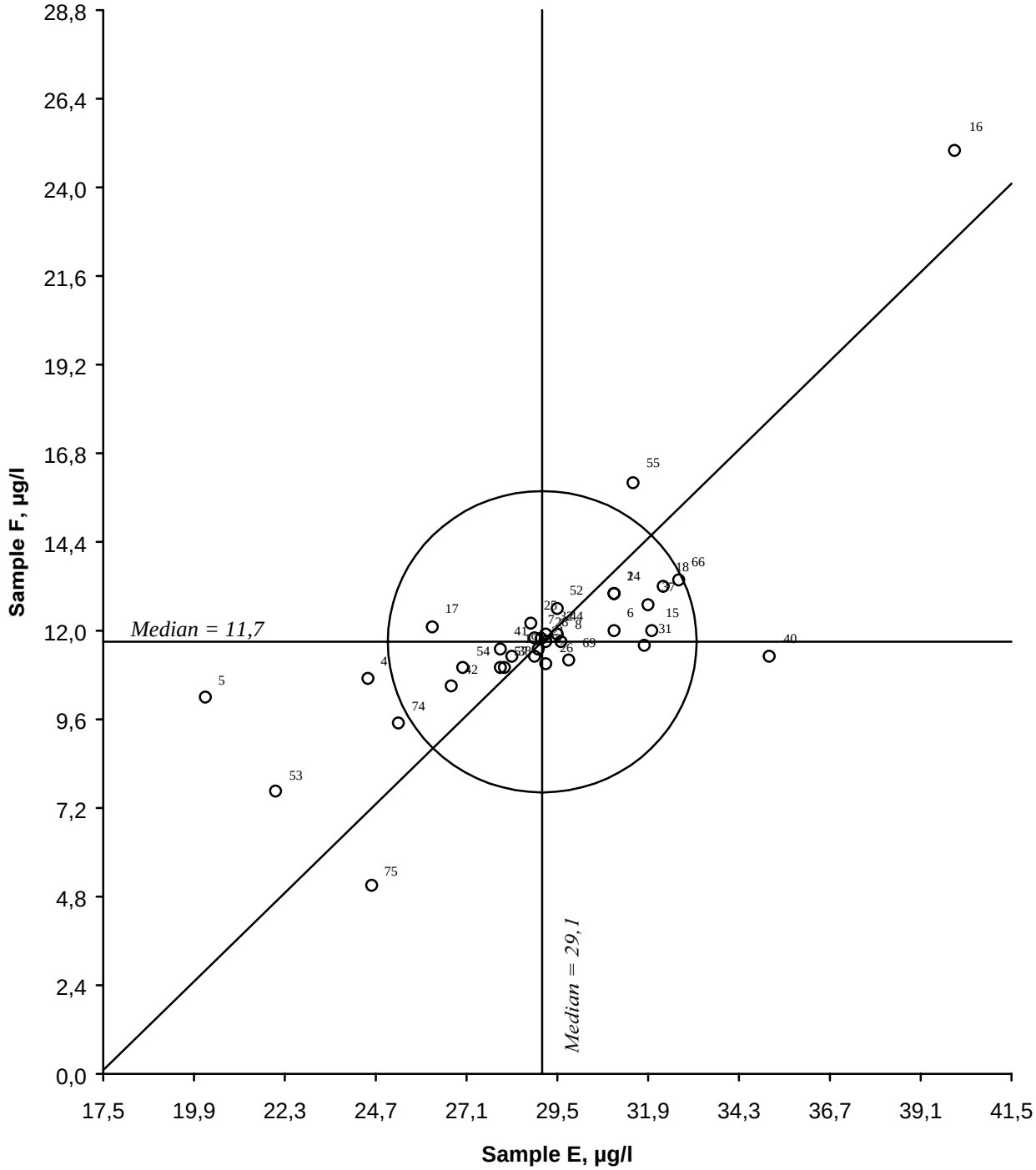

Figure 21. Youdendiagramme for copper, sample pair EF.
Acceptance limit given by the circle is 20 %.

Nikkel

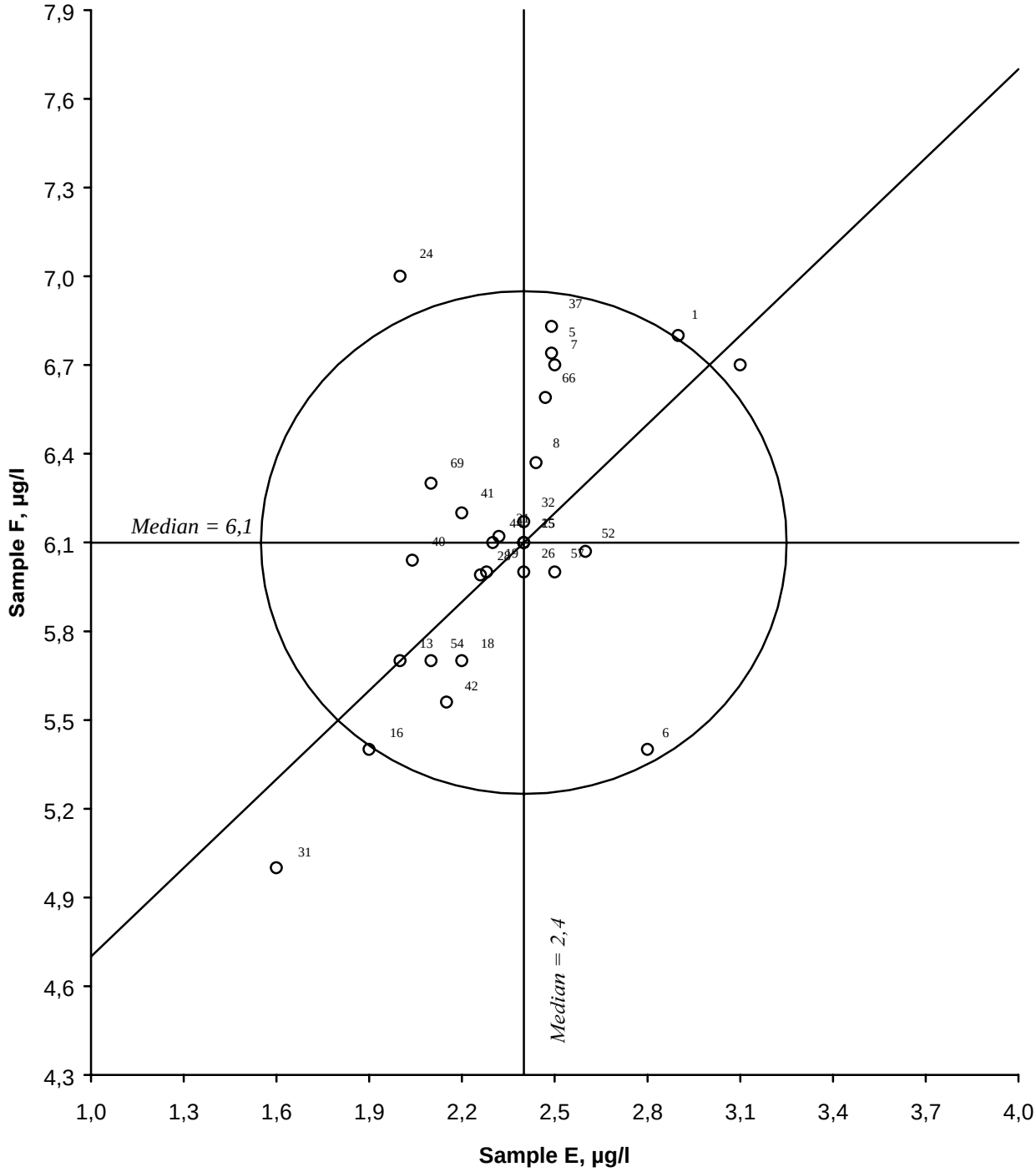

Figure 22. Youdendiagramme for nickel, sample pair EF.
Acceptance limit given by the circle is 20 %.

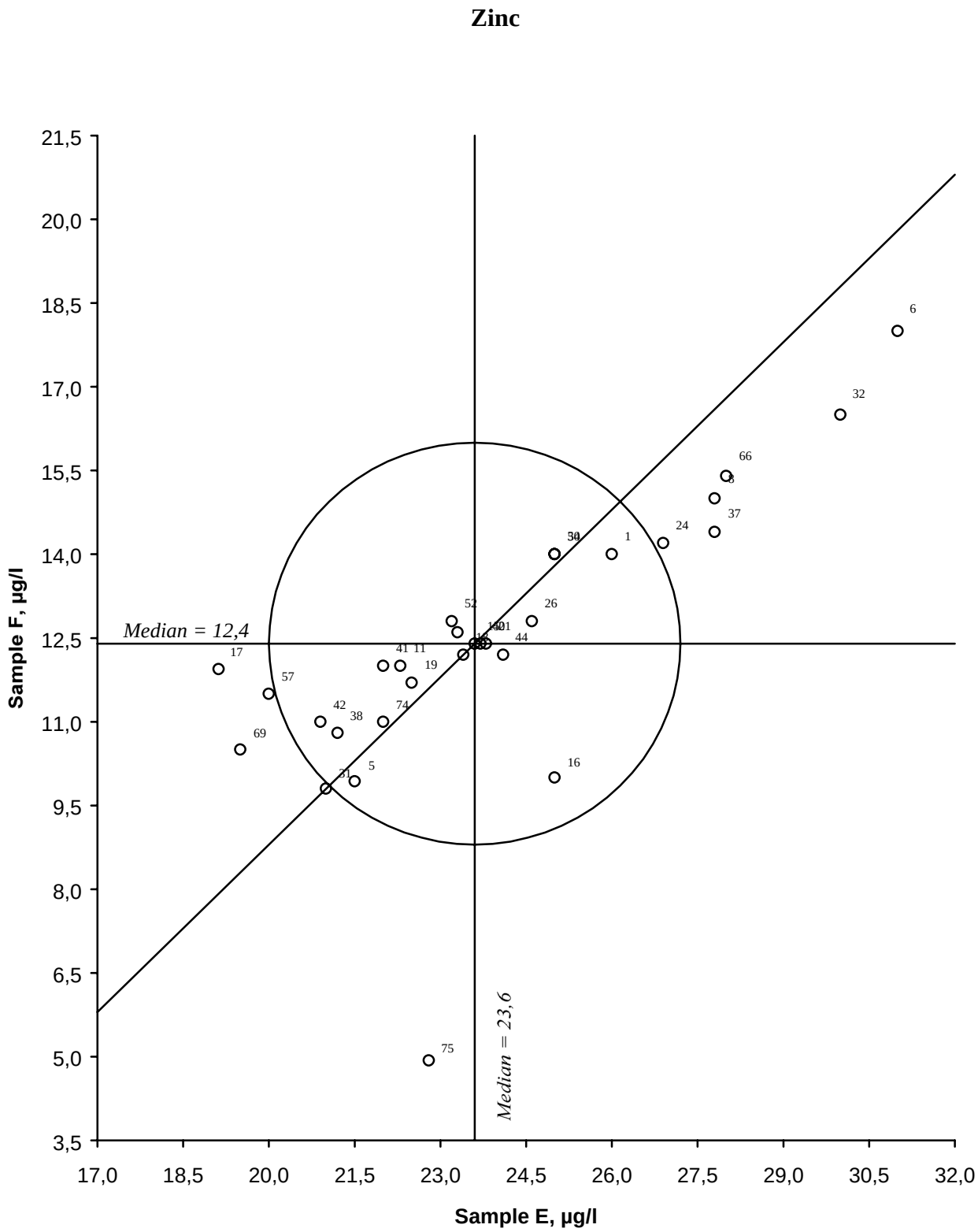

Figure 23. Youdendiagramme for zinc, sample pair EF.
Acceptance limit given by the circle is 20 %.

The control analyses carried out at the Program Centre proved that the samples were stable when stored at our laboratory. However, the equilibrium of the samples may be influenced by variations in pressure and temperature when they are mailed to the participants.

Some systematic deviations observed in Figure 1 may also be due to errors in the instrument, or more likely the electrodes, as different electrodes may give rise to different results (4, 5). The main reason for the differences in the reported results, however, is probably connected to the small differences in the analytical methods used by the participants. Random errors are affecting the results to a greater degree for pH than many other variables, illustrated in Figure 1 by the spread of the small circles away from the 45° line.

4.2 Conductivity

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

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

4.3 Alkalinity

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 5.3. 53 laboratories reported results for alkalinity, and about one half of the participants used the Gran plot titration method suggested in the Manual (1). The others used end point titration, either to pH = 4.5 and 4.2, or to one certain pH value only (4.5, 5.4, or 5.6). Two laboratories used colorimetric methods.

The results for alkalinity are spread out along the 45 ° line, most result pairs being very close to this line, as illustrated in Figure 3, indicating that systematic effects are the dominating reason for the differences between the results. This is most likely due to the different methods used by the laboratories. By a closer examination of the results, a certain connection between the method used and the location in Figure 3 was observed. The laboratories using the Gran plot titration reported results normally located close to the centrum of the circle, with some exceptions, two laboratories reported one good result and one strongly devatin one, three laboratories reported systematically far too low results for both samples. With one exception all the results determined by the end point titration to pH 4.2 or 4.5 alone, are located in the

upper right part of Figure 3, beeing systematically too high. The end point titration to pH 5.6 or 5.4 gave results mainly located within the acceptance circle.

The overall result for alkalinity in this intercomparison is better than in earlier intercomparisons, as two third of the results are acceptable. A probable reason for this is the fact that samples with higher alkalinity have been used for this intercomparison. The alkalinity value varies significantly with the end-point pH used for the titration. In waters containing high concentrations of total inorganic carbon, the equivalence point is close to pH = 5.4. In this case, the relative error introduced by assuming a fixed end-point pH, is negligible. However, at lower alkalinities normally encountered in areas sensitive to acidification, the “total fixed end-point method” may overestimate the true alkalinity or the “equivalence” alkalinity.

4.4 Nitrate + nitrite

The results reported for this parameter are presented in Figure 4, and the reported results are given in Table 5.4. The circle in Figure 4 represents a general target accuracy of ± 20 %. Ion chromatography is used by an increasing number of laboratories, and is now used by nearly half of the participants. The others are determining this analytical variable by photometric methods, most of these laboratories are using an automated version of the cadmium reduction method. There is no significant difference between the results determined by the different methods, however, the concentrations from the determination with automated cadmium reduction method are systematically slightly higher than the results determined by ion chromatography.

There has been problems with the stability of this analytical variable in the two latest intercomparisons, due to the instability of nitrate in the samples used. This time however, the results are more "normal" because 77 % of the results are acceptable. The control analyses at the Programme Centre also demonstrated that these samples were stable with respect to the content of nitrate and nitrite, throughout the 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. The target accuracy of ± 20 % is represented by the great circle in figure 5. 47 out of 61 laboratories determined chloride by ion chromatography. The greatest deviations are observed for the manual photometric methods, and the argentometric method which have too high detection limit. The latter method is not sensitive enough for many of the acid rain samples. One laboratory determined chloride with capillary electrophoresis, the results being acceptable.

4.6 Sulfate

The sulfate results are illustrated in Figure 6, and the reported values are given in Table 5.6. The circle is representing the target accuracy of ± 20 %. Ion chromatography is used by 48 of 61 laboratories for the determination of the sulfate content. Seven laboratories used a photometric method based on the dissociation of the barium-thorin complex, two of these

result pairs deviated too much from the true value. One laboratory used capillary electrophoresis, the results being acceptable.

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. 65 laboratories reported results for calcium, and 25 of them used flame atomic absorption spectrometry for the determination. ICP and ICP-MS techniques are used by 18 and 1 laboratories, respectively, and 15 laboratories used ion chromatography. The complexometric titration method, used by six laboratories, is not sensitive enough for this kind of samples, and some of the laboratories using this method reported results clearly affected by random errors.

4.8 Magnesium

The magnesium results are presented in Figure 8, and the reported values are given in Table 5.8. Most of the participants are still using flame atomic absorption spectrometry for the determination of magnesium. ICP emission spectrometry and ICP-MS was used by 18 and 1 laboratories, respectively, and 15 laboratories used ion chromatography. Systematic errors are dominating the results being outside the acceptance limit, as much as 82 % of the results are located inside the target accuracy of ± 20 %. The great deviations observed for manual titrations indicate that the concentrations of the samples used in this intercomparison are rather low for this technique. The most used methods give comparable results.

4.9 Sodium

The sodium results are presented in Figure 9, where the great circle is representing the general target accuracy of ± 20 %. The reported values are given in Table 5.9. Most laboratories used flame atomic absorption spectrometry for this determination. However, in many laboratories the ion chromatographic techniques are slowly taking over the routine determinations of the alkaline metals, thus 14 participants used this technique. ICP was used by 16 laboratories, and 12 used flame photometry. The relative standard deviation was greatest for the results produced with flame photometry. As much as 93 % of the result pairs are located within the general target accuracy of ± 20 %.

4.10 Potassium

The potassium results are presented in Figure 10. The great circle is representing the target acceptance limit of ± 20 %. The reported values are given in Table 5.10. As for sodium, many laboratories used flame atomic absorption spectrometry for the determination of this element, and emission spectrometry is used by the same number of laboratories. The greatest deviations observed in Figure 10 are mainly of systematic nature. Only one laboratory reported results as less than the detection limit.

4.11 Aluminium

The results for aluminium are illustrated in Figure 11 for sample pair CD, and Figure 12 for sample pair EF, and the reported values are given in Table 5.11 and 5.12, respectively. The great circle is representing the general target accuracy of ± 20 %. More than half of the laboratories used ICP and ICP-MS techniques, the results for both methods giving more or less comparable results. Five and three of the participants, respectively, used photometry for the determination of aluminium in the samples CD and EF, the results being considerably lower than for the other methods. Most of the deviating results are dominated by systematic errors, even if some few results are affected by random errors, especially in sample set CD.

4.12 Reactive aluminium

The results for reactive aluminium are illustrated in Figure 13, and the reported values are given in Table 5.13. Thirteen laboratories reported results for reactive aluminium, and twelve of these used the pyrocathechol violet method. The results are dominated by systematic effects, probably caused by the differences in the analytical method used. As very few laboratories determine this analytical variable, and the results are very spread out, it is not possible to do a proper evaluation of these results. The "true" values, therefore, are considered indicative only.

The reported values for this aluminium fraction are strongly dependent on the chemical conditions in the reaction mixture. Most methods are based on the direct determination of aluminium in a non-acidified sample, preferably accomplished as soon as possible after sampling. By these methods acid is added as a part of the determination step. However, there are some methods based on acid pretreatment of the sample, then the results are dependent on how long time the acidified samples have been stored before the aluminium content is determined. Such acidification is no digestion, but will lead to dissolution of complexes and even dissolution of some particulate matter containing aluminium. The results are expected to increase towards an upper limit when the pretreatment time is prolonged.

4.13 Non-labile aluminium

The results for non-labile aluminium are illustrated in Figure 14, and the reported values are given in Table 5.14. The situation is very much alike what we observe for reactive aluminium. Most laboratories have indicated that they determined non-labile aluminium according to the automated method of Røgeberg and Henriksen (6), which is based on the method of Driscoll (7). By this method non-labile aluminium is the fraction that passes through a cation exchange column, and consists of monomeric alumino-organic complexes (see Figure 16, page 32).

Some of the informations given by the participants indicate that different resin forms have been used for this intercomparison, and it is well known that different resins have different exchange properties, and therefore will affect the results. Thus, the main problem is the systematic deviations observed between the participating laboratories, indicating that the laboratories have applied different methods or slightly different modifications of a method, affecting the analytical results strongly. It is not possible to evaluate the analytical results properly when the result pairs are very spread out, and only few laboratories determine this analytical variable. Therefore, the “true” values and the 20 % circle in Figure 14 have to be considered as indicative only.

4.14 Dissolved organic carbon

The results for this variable are presented in Figure 15, and the reported values are given in Table 5.15. 29 laboratories determined this analytical variable in the sample pair CD. 16 laboratories used a combustion technique, and a wet oxidation technique with UV and peroxodisulfate was used by twelve laboratories. For the samples used in this intercomparison there is no evidence for any significant differences between the reported results determined with these two methods.

The great circle in Figure 15 is representing the general target accuracy of ± 20 %, and 19 laboratories reported results located inside this limit. This is a little less than the last intercomparison.

4.15 Chemical oxygen demand, COD-Mn

Several participating laboratories are not equipped with carbon analyzer, therefore this analytical variable is included in the intercomparison. The results for this parameter are presented in Figure 16, and the reported values are given in Table 5.16. Only 17 of the laboratories determined this parameter. Twelve of the result pairs are located within the circle representing the target accuracy of ± 20 %.

4.16 Iron

The results for iron 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, only 41 % of the result pairs are located inside this circle. 37 laboratories submitted results for iron, of which 14 and 10 used ICP and ICP-MS, respectively, while 2 and 7 used flame and graphite furnace atomic absorption, respectively. Only four laboratories used photometric methods. There is no significant difference between the results determined by the different methods for iron. The deviating results are mainly affected by systematic errors, however, the low concentrations in the samples used this time have obviously increased the effect of the random errors, as may be demonstrated by the spread out of the results from the 45° line.

4.17 Manganese

The manganese results are illustrated in Figure 18, and the values reported by the participants are given in Table 5.18. The target accuracy is ± 20 %, and is represented by the great circle in Figure 18. 64 % of the result pairs are located inside this circle, this is less than the intercomparison run last year, however, the concentrations this time are much closer to the detection limits of some of the methods used. 36 laboratories submitted results for manganese, of which 14 and 10 used ICP and ICP-MS, respectively, while 2 and 9 used flame and graphite furnace atomic absorption, respectively. Only one laboratory used a photometric method. There is no significant difference between the results determined by the different methods for manganese. The deviating results are mainly affected by systematic errors.

4.18 Cadmium

The results for cadmium are illustrated in Figure 19, and the values reported by the participants are given in Table 5.19. The target accuracy is ± 20 % and is represented by the great circle in Figure 19, 66 % of the result pairs are located inside this circle. 35 laboratories submitted results for cadmium, of which 7 and 11 used ICP and ICP-MS, respectively, while 17 used graphite furnace atomic absorption. There is no significant difference between the results determined by the different methods for cadmium, even if the results produced with ICP - on average - is clearly lower than those produced with ICP-MS. The deviating results are affected by both systematic and random errors.

4.19 Lead

The results for lead are illustrated in Figure 20, and the values reported by the participants are given in Table 5.20. The target accuracy is ± 20 %, and is represented by the great circle in Figure 20, only 51 % of the result pairs are located inside this circle. 33 laboratories submitted results for lead, of which 6 and 11 used ICP and ICP-MS, respectively, while 18 used graphite furnace atomic absorption. There is no significant difference between the results determined by the different methods for lead, however, the ICP method is probably too less sensitive for the low concentrations used in these samples. The deviating results are affected by both systematic and random errors. The concentration is close to the detection limit of the method used at some of the laboratories, and three laboratories reported their results as below their detection limit.

4.20 Copper

The copper results are illustrated in Figure 21, and the values reported by the participants are given in Table 5.21. The target accuracy is ± 20 %, and is represented by the great circle in Figure 21, 67 % of the result pairs are located inside this circle. 36 laboratories submitted results for copper, of which 10 and 11 used ICP and ICP-MS, respectively, while 13 and 2 used graphite furnace and flame atomic absorption, respectively. There is no significant difference between the results determined by the different methods for copper, except that the results from the flame method is clearly lower than for the other methods. The deviating results are affected mainly by systematic errors.

4.21 Nickel

The results for nickel are illustrated in Figure 22, and the values reported by the participants are given in Table 5.22. The target accuracy is ± 20 %, and is represented by the great circle in Figure 22, This time as much as 68 % of the result pairs are located inside this circle. 34 laboratories submitted results for nickel, of which 10 and 11 used ICP and ICP-MS, respectively, while 13 used graphite furnace atomic absorption. There is no significant difference between the results determined by the different methods for nickel, however, many laboratories using ICP reported results as less than a value representing their detection limit. The deviating results are affected mainly by systematic errors.

4.22 Zinc

The results for zinc are illustrated in Figure 23, and the values reported by the participants are given in Table 5.23. The target accuracy is ± 20 %, and is represented by the great circle in Figure 23, only 53 % of the result pairs are located inside this circle. 36 laboratories submitted results for zinc, of which 13 and 11 used ICP and ICP-MS, respectively, while 7 and 5 used flame and graphite furnace atomic absorption, respectively. The results determined by ICP-MS are slightly higher than for ICP, and the results determined with flame atomic absorption are higher than the graphite furnace. The deviating results are affected by both systematic and random errors, some too high values indicate that contamination may be a problem for some laboratories when determining the zinc concentration.

5. Discussion

The general rule for target accuracies, outlined in the Manual for Chemical and Biological Monitoring (1), shall normally be used as acceptance limits for the results of the intercomparison test. These limits are corresponding to either the detection limit of the method, or 20 % of the true value, whichever being the greater.

In Table 2 an evaluation of the results of intercomparison 0015 is presented, based on the target accuracy (except for pH and conductivity), where the number and percentage of acceptable results are given. 71 % of the results submitted by the participants are acceptable when compared to the acceptance limits given above, i.e. on average, nearly one out of three result pairs is located outside the acceptance limit. By improvement of the routine analytical method, the laboratories should be able to obtain more comparable results.

For pH, the general target accuracy is ± 0.1 pH units (1), and far less than 50 % of the result pairs are found within these accuracy limits. However, we have chosen to extend the acceptance limit to ± 0.2 pH units, because of the great spread of the results for these two samples which are close to neutrality, and therefore are supposed not to be completely in CO_2-equilibrium. Even with this acceptance limit only 58 % of the result pairs are evaluated as acceptable.

Problems with poor comparability between the reported results for pH arise probably from the fact that the pH results are much more affected by the method used, when measuring in nearly neutral solutions. This problem has been demonstrated through several earlier intercomparisons, and will remain as a problem as long as different methods for pH determination are used by the participating laboratories. Therefore, it should be discussed whether a different approach should be used for the comparison of the results, for instance different “true values” for pH, one for each method? This is especially important for the equilibration method, which is definitely different from the others.

Because of the high precision of the reported results for conductivity in earlier intercomparisons, we reduced the acceptance limit for this analytical variable to ± 10 %. The number of acceptable results for conductivity, 82 %, is much better than the last

intercomparison (Table 2), and is comparable to the acceptance level observed earlier. If we increase the acceptance limit to the target value, five more result pairs would be inside the circle, and the number of acceptable results would increase to 89 %. It is a problem that many laboratories report their results in the units they normally use at their laboratory, and not in the unit asked for, mS/m.

Table 2. Evaluation of the results of intercomparison 0115. N is the number of result pairs reported, and n is the number of acceptable results within the given target accuracy. Numbers in brackets are not icluded in the evaluation.

Analyte and unit	Sample pair	True value 1	True value 2	Accept. limit, %	N	n	% accepatble res. for intercal. 0115	0014	9913	9812
pH	AB	7,15	7,24	2,7 *	69	40	58	57	57	55
Conductivity, mS/m	AB	4,7	5,98	10 ¤	65	53	82	64	81	90
Alkalinity, mmol/l	AB	0,27	0,36	20	54	40	74	46	63	60
Nitrate + nitrite-nitrogen, µg/l	AB	223	291	20	60	46	77	51	31	85
Chloride, mg/l	AB	2,2	3,08	20	61	48	79	73	87	73
Sulfate, mg/l	AB	3,2	3,6	20	61	50	82	72	87	82
Calcium, mg/l	AB	2,55	3,2	20	65	53	82	55	78	70
Magnesium, mg/l	AB	0,44	0,53	20	63	47	75	58	78	75
Sodium, mg/l	AB	6,22	8,16	20	61	57	93	91	89	92
Potassium, mg/l	AB	0,35	0,55	20	61	52	85	76	77	72
Aluminium, µg/l	CD	81	130	20	28	14	57	50	73	53
Aluminium, µg/l	EF	105	134	20	23	15	57	60		
Aluminium, reactive µg/l	CD	45	73	20	(13)	(4)	(31)	58	17	33
Aluminium, nonlabile, µg/l	CD	34	54	20	(11)	(4)	(36)	40	50	33
Dissolved org. carbon, mg/l	CD	5,5	5,5	20	29	19	66	89	83	82
Chem. oxygen demand, mg/l	CD	6	6,1	20	17	12	71	73	77	67
Iron, µg/l	EF	26,3	45	20	37	15	41	74	-	-
Manganese, µg/l	EF	5,6	1,6	20	36	23	64	75	-	-
Cadmium, µg/l	EF	1,08	3	20	35	23	66	65	-	-
Lead, µg/l	EF	3,1	6,9	20	35	18	51	47	-	-
Copper, µg/l	EF	29,1	11,7	20	36	27	75	67	-	-
Nickel, µg/l	EF	2,4	6,1	20	34	23	68	42	-	-
Zinc, µg/l	EF	23,6	12,4	20	36	19	53	47	-	-
Total					1017	723	71	(63)	(72)	(74)

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

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

For nitrate + nitrite 77 % of the result pairs are acceptable, this is better than the two last years, when the samples proved to be unstable for nitrate. We have not yet found any good explanation to the observed effect on nitrate + nitrite the two last years, however, the control analyses performed at the Programme Centre proved that the samples were stable for nitrate + nitrite this time.

If the determination of aluminium fractions should be evaluated, it seems necessary that the laboratories normalize their analytical methods to improve the comparability for these variables. There are some confusions about what aluminium fractions should be determined. The intention in this intercomparison was to compare the results for the variables printed in bold in the scheme presented in Figure 24. There have obviously been reported some results for other fractions than we asked for. The Programme Centre has chosen the definitions of aluminium species given by Driscoll (7), however, other laboratories may use a slightly different definition system. The non-exchangeable aluminium initially present in the samples of this intercomparison, is assumed to be associated with organic matter. The fact that the laboratories used different modifications and even different methods for the determination of aluminium species, may explain the great spread observed between the results for the different aluminium fractions. The labile monomeric aluminium is the fraction being of most interest in acid rain problems, and should therfore be calculated as a separate analytical variable in the future.

Figure 24. Schematic representation of aluminium fractions according to Driscoll (7).

	Total aluminium acid digested		
Aluminium measurement	**Reactive aluminium** Total monomeric aluminium, no acid digestion		
	Monomeric aluminium, cation exchange treated		
Aluminium fraction	**Non-labile monomeric aluminium**	Labile monomeric aluminium	Acid soluble aluminium
Fraction composition	Monomeric alumino-organic complexes	Free aluminium, monomeric aluminiumsulfate, Fluoride and hydroxide complexes	Colloidal polymeric aluminium, strong alumino-organic complexes

For calcium and magnesium a greater fraction of the result pairs are acceptable in this intercomparison, and the % acceptance is now comparable to some earlier intercomparisons. For sodium and potassium the fraction of acceptable results, and the concentrations, are comparable to earlier intercomparisons. For the other major constituents, some more results are acceptable to earlier intercomparisons. One possible explanation for this observation may be that the concentrations are partly higher than usual. Some of the laboratories that reported results outside the acceptance limits used methods being different from the major group of

participants, some of the methods used may not be sensitive enough for samples typically analyzed for acid rain monitoring.

The heavy metals iron, manganese, cadmium, lead, copper, nickel, and zinc were included in this intercomparison Programme for the second time. The best results were obtained for copper, nickel and cadmium, where 75, 68 and 66 % of the results are acceptable. For these elements the concentrations were at least a little higher than the detection limit of the most sensitive methods used. For the rest of the heavy metals, less results were acceptable. However, the concentrations of these elements are closer to the detection limit for the methods used, and even below this limit for some of the laboratories. Therefore, it should be discussed whether absolute acceptance limits should be used instead of the relative one (20 %) used in this intercomparison, when the results are close to the detection limit. If so, it is important that it is decided what target detection limit should be obtained by the laboratories.

6. Conclusion

72 laboratories submitted results for this intercomparison. The best results were reported for the analytical variables sodium and potassium, where 93 and 85 % of the results were acceptable. The worst results were observed for the aluminium fractions, however, the methods used by some of the participants may not allways be directly comparable, therefore a great spread of the analytical values may be expected. Therefore, the aluminium fractions are not evaluated this time. To improve the comparability of the analytical results for aluminium fractions, it may be necessary to normalize the analytical methods and the determination techniques used for these determinations, for instance to meet the operational definitions given in Figure 24.

Overall, 71 % of the evaluated results were located within the general target accuracy of ± 20 %, or the special accuracy limit for pH and conductivity. The reason for the overall worse results this time compared to som earlier intercomparisons, is in part explained by the introduction of seven heavy metals, where the number of acceptable results for three elements are rather low. When the concentrations are close to the detection limit of some of the methods used by the participants, it must be expected that the spread of the results will be more than ± 20 % for many of the participants.

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

A total error of ± 0.2 pH units seems to be a reasonable assessment of the accuracy for pH measurements when near neutral water samples - which are not in CO_2 equilibrium - are analyzed. There are obviously systematic differences between the methods used by the participating laboratories. On the next meeting, it should therefore be discussed whether we are continuing to use only one “true value” for all the pH results, or to have different “true value” for each method.

7. Literature

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Appendices

A The participating laboratories

B Preparation of samples

C Treatment of analytical data

D The results of the participating laboratories

Appendix A.

The participating laboratories

Identity	Laboratory	City	Country
1	Bayerische Landesamt fur Wasserwirtschaft	München	Germany
2	CNR Istituto Italiano di Idrobiologia	Pallanza	Italy
3	US Environmental Protection Agency	Corvallis, OR	USA
4	Forest Research Institute, Karelian Res. Centre	Petrozavodsk	Russia
5	Latvian Hydrometeorological Agency	Riga	Latvia
6	Institute of Biology, Lab.of Analytical Chem.	Syktyvkar	Russia
7	Freshwater Institute	Winnipeg	Canada
8	Stocholm University, ITM	Stockholm	Sweden
9	University of Helsinki, Lab. of Phys. Geography	Helsinki	Finland
10	Lapland Regional Environment Centre	Rovaniemi	Finland
11	Finnish Forest Research Institute	Rovaniemi	Finland
13	Tartu Environmental Researches	Tartu	Estonia
14	Vortsjarv Limnological St.	Rannu, Tartu Co.	Estonia
15	Institute of Environmental Protection	Warsawa	Poland
16	The Railway Sanitary and Epidem. Service	Katowice	Poland
17	Institute for Ecology of Industrial Areas	Katowice	Poland
18	Umweltbundesamt - Dienst-gebaude Langen	Langen	Germany
19	Umweltbundesamt, Analytic 1	Vienna	Austria
20	National Institute of Biology	Ljublana	Slovenia
21	Finnish Environment Institute Research Lab.	Helsinki	Finland
22	ISSeP Colfontaine	Paturages	Belgium
23	D.R. Ambiente Alentejo	Santo André	Portugal
24	Laboratorio Studi Ambientali SPAA	Paradiso	Switzerland
25	Estonian Environment Research Centre	Tallinn	Estonia
26	T.G.Masaryk Water Research Institute	Praha	Czech Republic
27	University of Alberta	Edmonton	Canada
28	Vlaamse Milieumaatschappij	Antwerpen	Belgium
29	Forest Ecosystem Research Group	Belfield, Dublin	Ireland
30	North Ostrobothnian Regional Env. Centre	Oulu	Finland
31	Chemical Laboratory of CGU	Praha	Czech Republic
32	Freshwater Fisheries Laboratory	Perthshire	United Kingdom
33	Swedish Environment Research Institute (IVL)	Stockholm	Sweden
35	Kymi Environmental Laboratory LTD	Kouvola	Finland
36	Institute of Zoology	Sofia	Bulgaria
37	Istituto Agrario di S. Michele all'Adige	S.Michele Adige	Italy
38	Finnish Forest Research Institute, Central Lab.	Vantaa	Finland
40	University of Maine, George Mitchell Center	Orono, MA	USA
41	Toulouse University	Toulouse	France
42	Swedish University of Agricultural Sciences	Uppsala	Sweden
44	Swiss Federal Institute for FSL	Birmensdorf	Switzerland
45	CNR - IRSA	Brugherio	Italy
46	Institute of Meterology and Geophysics	Innsbruck	Austria
47	Institut für Zoologie und Limnologie	Innsbruck	Austria
48	Laboratory of Ecological Chemistry, ABIET	Baikalsk	Russia

49	Dorset Research Centre	Dorset, Ontario	Canada
50	Universite de Metz	Metz, Borny	France
51	Laboratorio Biologico Provinciale APPA-BZ	Laives	Italy
52	Landesumweltamt NRW	Essen	Germany
53	Centre for Marine Anal. Reference & Standards	Trivandrum	India
54	Norwegian Institute for Water Research	Oslo	Norway
55	Geological Survey of Estonia	Tallinn	Estonia
56	Tallinn Technical University	Tallinn	Estonia
57	Kola Science Centre	Apatity	Russia
58	Academy of Sciences Hydrobiological Institute	Budejovice	Czech Republic
59	Polish Academy of Sciences Institute of Botany	Krakow	Poland
61	Northern Water Problems Institute	Petrozavodsk	Russia
63	University of Stockholm	Delsbo	Sweden
64	The Environment Agency, NLS Laboratory	Llanelli, Dyfed	U. Kingdom
65	Charles University, Dept. of Hydrobiology	Prague	Czech Republic
66	Environmental Protection Agency	Co. Dublin	Ireland
67	Ontario Ministry of Environment	Etobicoke	Canada
68	Universita degli Studi di Siena	Siena	Italy
69	Environ. Prot. Ministry, Joint Research Centre	Vilnius	Lithuania
71	Aquatische Oecologie en Milieubiologie	Nijmegen	Netherlands
72	Adirondac Lake Survey Corporation	Ray Brook, NY	USA
73	Viruuma Environment Research Ltd	J'ohvi	Estonia
74	Staatliche Umweltbetriebs-gesellschaft	Chemnitz	Germany
75	Centre de Geochimie de la Surface, Lab. II	Strasbourg	France
76	Centre de Geochimie de la Surface	Strasbourg	France
77	Food and Environment Agency	Torshavn	Faroe Islands
78	Freshwater Institute, ELA Sattelite Lab.	Winnipeg	Canada
79	Tartu Environmental Researches, Section II	Tartu	Estonia

Number of participating laboratories (N) from the different countries being represented in intercomparison 0115.

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

Appendix B.

Preparation of samples

The sample solutions were prepared from natural water collected from the lake Maridalsvannet, located outside Oslo, Norway. Raw water was collected in polyethylene containers and brought to the laboratory for storage. These containers were stored at room temperature for several weeks at the laboratory. During this stabilization period suspended matter settled. The solutions were filtrated through 0,45 µm membrane filter, and small aliquots were removed from the filtrate to determine the concentrations of the analytical variables of interest.

The samples were prepared by spiking the filtrated water with stock solutions of stoichiometric compounds containing the major ions, or heavy metals. The samples E and F 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.

Table 3. Summary of the control analyses.

Analytical variable	**Sample A**		**Sample B**	
	Mean	Std. dev.	Mean	Std. dev.
pH	7,20	0,020	7,25	0,03
Conductivity mS/m	4,71	0,052	5,91	0,021
Alkalinity mmol/l	0,279	0,001	0,369	0,005
Nitrate/nitrite µg/l	228	2,9	303	5,8
Chloride mg/l	2,17	0,06	3,10	0,00
Sulfate mg/l	3,23	0,12	3,67	0,06
Calcium mg/l	2,55	0,09	3,17	0,09
Magnesium mg/l	0,43	0,015	0,52	0,020
Sodium mg/l	6,10	0,11	7,98	0,24
Potassium mg/l	0,34	0,006	0,53	0,006
	Sample C		Sample D	
Aluminium, µg/l	88	9,8	141	6,0
Reactive aluminium µg/l	43	2,3	75	4,7
Non-labile aluminium, µg/l	38	5,2	61	4,0
Dissolved organic carbon, mg/l	4,6	0,12	5,1	0,50
COD-Mn, mg/l	5,2	0,12	5,3	0,15
	Sample E		Sample F	
Aluminium, µg/l	101	6,3	131	9,8
Iron, µg/l	26	0,0	49	5,1
Manganese, µg/l	5,5	0,47	1,5	0,17
Cadmium, µg/l	1,11	0,12	3,04	0,07
Lead, µg/l	3,1	0,21	7,0	0,67
Copper, µg/l	29,7	2,5	12,0	1,0
Nickel, µg/l	2,2	0,15	6,1	0,67
Zinc, µg/l	26,0	1,0	14,7	1,2

Sample control analyses

During the intercomparison period, four sets of samples were randomly selected from the batch for control analyses. The determinations were carried out by the laboratory at the Programme Centre, the first sample set being analyzed at the end of April 2001, a few weeks before mailing the samples to the participants. The last sample was analyzed at the end of July 2001. 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.

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 - 23).

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

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

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

The statistical treatment of the analytical results was accomplished in this way: Pairs of results where one or both of the values are lying outside the true value ± 50 %, are omitted from the statistical calculations. The remaining results are used for the calculation of the mean value (x) and the standard deviation (s). Now the pairs of results where both of the values are lying outside $x \pm 3s$, are omitted. The remaining results are used for a final calculation, the results of which are presented in the tables 5.1 - 5.23. Results being omitted from the calculations, are marked with the letter "U".

Appendix D.

Table 4. The results of the participating laboratories.

Lab. No.	pH		Cond, mS/m		Alk, mmol/l		NO3+NO2, µg/l		Cl, mg/l		SO4, mg/l	
	A	B	A	B	A	B	A	B	A	B	A	B
1	7,17	6,99	5,60	7,80			484	527	2,54	3,22	4,0	4,3
2	7,21	7,26	4,63	6,02	0,285	0,377	165	275	2,22	3,08	3,2	3,7
3	7,28	7,45	4,46	5,87	0,273	0,354	230	290	2,19	3,12	3,2	3,6
4	7,08	7,22					221	287	1,81	2,34	2,9	3,2
5	6,96	7,15	4,38	5,67	0,259	0,350	224	266	2,09	2,94	3,1	3,4
6	7,20	7,30	5,11	6,43	0,236	0,400	247	315	2,15	3,12	2,1	3,7
7	7,66	7,65	4,50	5,90	0,272	0,366	223	296	2,15	3,09	2,9	3,3
8	7,26	7,34	4,64	5,94	0,266	0,357			3,09	2,45	3,3	2,6
9	7,26	7,39	6,20	6,00	0,280	0,350	223	276	2,22	3,07	3,3	3,7
10	7,20	7,21	4,67	5,95	0,286	0,362	224	292	2,20	3,05	2,9	3,3
11	6,86	6,84	4,63	5,93			212	274	1,90	2,71	3,1	3,5
13	6,98	7,19	4,56	5,89	0,270	0,360	236	297	2,36	3,28	3,2	3,5
14	7,20	7,35	4,66	5,74	0,300	0,350	224	283	2,20	2,90	3,0	4,0
15	7,20	7,12	5,02	6,16			214	265	2,11	3,01	3,2	3,7
16	7,39	7,38	0,02	0,02	0,520	0,620	1160	930	6,00	8,00	3,7	5,5
17	7,32	7,46	4,46	5,68	0,259	0,336	172	255	2,19	2,96	3,1	3,5
18	7,18	7,37	4,65	5,94	0,290	0,370	226	289	2,26	3,12	3,4	3,8
19	6,86	6,96	4,63	6,09	0,330	0,430						
20	7,15	7,23	4,70	6,10	0,315	0,406	221	292	2,32	3,27	3,3	3,6
21	7,03	7,25	4,25	5,68	0,264	0,360	215	304	2,25	2,14	3,3	3,6
22	7,12	7,14	4,89	6,04			194	254	1,86	2,59	2,9	3,4
23	7,34	7,40	4,66	6,13	0,160	0,210	237	320	1,82	2,65	3,2	3,8
24	7,15	7,27	4,90	6,10	0,264	0,355	200	290	2,20	3,06	3,3	3,7
25	7,05	7,22	4,90	6,20	0,260	0,350	230	300	2,19	3,08	3,4	3,8
26	7,02	7,07	4,70	6,02	0,270	0,350	202	262	2,00	2,90	2,1	2,4
27	7,23	7,37	4,58	5,89	0,240	0,330	181	244	2,32	3,28	3,3	3,7
28	6,53	6,69	4,80	6,10			242	314	2,23	3,15	3,3	3,7
29	6,82	7,04	4,70	6,10	0,150	0,200						
30	7,40	7,30	4,80	6,00	0,268	0,359	240	320	2,20	3,00	3,0	3,3
31	7,26	7,36	4,78	6,08	0,277	0,370	626	447	2,12	3,02	3,2	3,6
32	7,19	7,33	4,40	5,80	0,263	0,356	224	294	2,13	3,09	3,3	3,7
33	7,13	7,24	4,95	6,70					2,26	3,18	3,3	3,7
35	7,17	7,28	4,81	6,09	0,273	0,359	226	300	2,15	3,06	3,4	3,7
36	6,37	6,80	5,00	6,10	0,250	0,340	175	231				
37	6,85	7,10	4,70	6,20	0,308	0,394	170	260	2,25	3,20	3,2	3,6
38	7,24	7,30	4,58	5,90			228	302	2,08	2,87	3,2	3,6
40	7,14	7,22	4,28	5,64	0,140	0,185			2,21	3,11	3,2	3,6
41	7,50	7,52										
42	7,19	7,24	4,59	5,86	0,263	0,353	228	297	2,30	3,33	3,1	3,6
44	7,59	7,72	4,91	6,30			220	291	2,04	2,83	3,2	3,6
45	7,14	7,20	4,70	5,80	0,289	0,383	251	289	2,04	2,83	3,0	3,3
46	7,06	6,86	4,40	5,90	0,280	0,370	224	208	2,21	3,11	3,1	3,4

Lab. No.	pH		Cond, mS/m		Alk, mmol/l		NO3+NO2, µg/l		Cl, mg/l		SO4, mg/l	
	A	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**	**A**	**B**
47	7,05	6,97	4,71	6,03	0,274	0,372	230	251	2,20	3,09	3,2	3,6
48	6,96	7,21					92	128	2,19	2,92	3,2	3,9
49	6,96	7,10	4,48	5,76	0,250	0,340	212	302	2,42	2,77	2,9	3,4
50	6,68	6,86	4,68	5,91	0,255	0,345	196	265	2,45	3,14	3,4	3,6
51	7,20	7,32	4,65	5,96	0,298	0,397	233	298	2,00	2,90	3,1	3,5
52	6,88	7,07	4,73	6,09			210	280	2,20	3,00	3,6	4,0
53	7,09	7,16			0,165	0,220	218	242	1,83	3,24	3,2	4,3
54	7,31	7,47	4,41	5,80	0,290	0,382	230	310	2,20	3,10	3,3	3,7
55	7,15	7,25	4,37	5,66	0,340	0,410			2,19	2,55	<2,0	<2,0
56	6,80	6,95	6,00	7,50	0,360	0,460	220	300	2,10	2,80	2,1	2,4
57	7,18	7,31	4,00	5,10	0,264	0,555	240	330	2,33	3,42	3,4	3,6
58	7,10	7,24	4,50	5,83	0,260	0,360	200	260	2,70	3,90	3,2	3,7
59	7,00	7,09	4,80	5,95			207	260	2,18	2,96	3,3	3,6
61	7,22	7,25	4,75	6,04	0,270	0,360	266	351	2,24	3,04	2,3	2,8
63												
64	7,11	7,30	3,40	4,80	0,132	0,170	230	302	2,60	3,40	2,9	3,3
65	7,17	7,26	4,71	6,03	0,270	0,360						
66	7,26	7,40	4,81	5,88	0,150	0,190	221	295	1,78	2,57	3,0	3,4
67	7,34	7,52	4,50	5,70			210	295				
68	7,20	7,16	4,80	5,99	0,280	0,361	237	277	2,79	3,75	3,4	3,7
69	7,09	7,31	4,76	6,06	0,252	0,324	178	260	2,70	3,55	3,4	4,1
71	6,75	6,87	5,26	6,26	0,306	0,397	255	316	2,72	3,62		
72	7,15	7,09	4,59	5,90	0,266	0,350	221	274	2,25	3,23	3,1	3,5
73	7,10	7,10	5,00	6,00	0,330	0,330					2,0	2,0
74	7,70	7,10	4,90	5,00	0,290	0,360	220	300	2,20	3,10	3,5	4,0
75												
76	7,11	7,31	4,78	6,11	0,271	0,360	238	308	2,27	3,16	3,3	3,7
77	7,34	7,48	4,73	6,00	0,260	0,350	304	393	<1,00	<1,00	3,9	4,4
78	7,07	7,20	4,70	6,00			240	220				
79												

Lab. No.	Ca, mg/l		Mg, mg/l		Na, mg/l		K, mg/l		Al, µg/l		Al, µg/l	
	A	B	A	B	A	B	A	B	C	D	E	F
1	2,61	3,36	0,50	0,60	6,69	8,89	0,36	0,60	78	115	111	141
2	2,13	2,85	0,41	0,52	6,20	8,05	0,35	0,55				
3												
4	3,15	3,92	0,40	0,50	6,17	7,90	0,31	0,52				
5	0,32	0,68	0,41	0,50	6,08	8,07	0,39	0,54				
6	2,23	2,91	0,40	0,52	7,10	8,84	0,89	1,26				
7	2,41	3,02	0,45	0,55	6,00	7,90	0,36	0,57				
8	2,58	3,27	0,45	0,55	6,22	8,30	0,39	0,59	86	135	108	137
9	2,69	3,29	0,44	0,54	6,60	8,78	1,55	2,44				
10												
11	2,35	3,09	0,76	0,63	6,38	8,42	0,30	0,50	<106	125	127	147
13	2,54	3,81	0,44	0,63	6,33	8,47	0,48	0,62	80	131	101	121
14	2,60	3,20	0,50	0,50								
15	2,61	3,23	0,43	0,53	6,24	8,16	0,35	0,55	85	139	105	136
16	2,47	3,04	0,39	0,39	7,10	9,20	1,54	1,52			120	170
17	2,35	3,02	0,42	0,51	6,12	8,04	0,37	0,56	98	151		
18	2,54	3,20	0,43	0,53	6,10	7,97	0,38	0,60	81	132	111	141
19	2,58	3,18	<1,00	<1,00	6,44	8,20	<1,00	<1,00			101	130
20	2,74	3,52	0,58	0,66	6,74	8,65	0,38	0,62				
21	2,55	3,17	0,44	0,53	8,24	6,23	0,36	0,56			105	132
22	3,02	3,75	0,48	0,58	7,04	9,22	0,52	0,57				
23	2,53	3,12	0,47	0,56	5,45	7,85	0,35	0,56				
24	2,36	2,90	0,42	0,50	6,21	8,12	0,31	0,49	78	96	88	105
25	2,67	3,47	0,41	0,52	6,10	7,94	0,35	0,55	85	130	177	203
26	2,80	3,40	0,51	0,64	6,18	8,03	0,35	0,55	86	161		
27	2,54	3,22	0,44	0,54	5,83	7,64	0,37	0,59				
28	2,95	3,57	0,46	0,57	7,32	9,62	0,36	0,58				
29	2,46	3,20	0,42	0,53	6,11	8,23			37	65		
30	2,50	3,20	0,40	0,50	6,20	8,20	0,40	0,50				
31	2,55	3,12	0,38	0,45	6,30	8,17	0,38	0,59				
32	2,90	3,60	0,47	0,57	6,35	8,37	0,35	0,55			81	103
33	2,28	2,95	0,42	0,52	5,96	7,99	0,33	0,54	77	129	110	139
35	2,63	3,27	0,44	0,54	7,20	9,58	0,18	0,30				
36												
37	2,60	3,20	0,44	0,53	6,20	8,00	0,31	0,52	99	152		
38	2,47	3,08	0,44	0,54	5,27	6,87	0,38	0,63	81	127	125	159
40	2,51	3,11	0,45	0,54	7,11	9,03	0,34	0,56	81	123	105	133
41	2,34	2,92	0,42	0,51	6,13	8,15	0,39	0,61	69	105	95	134
42	2,60	3,27	0,50	0,60	6,62	8,69	0,35	0,55	85	125	96	117
44	2,57	3,18	0,42	0,51	6,14	8,29	0,35	0,55	80	127		
45	2,88	3,58	0,43	0,52	6,35	8,30	0,34	0,54				
46	2,46	3,15	0,43	0,53			0,34	0,53				
47	2,58	3,23	0,40	0,49	5,92	7,68	0,33	0,54				
48	1,90	3,05	0,46	0,69	5,90	7,80	0,30	0,50	<20	<20		
49	2,40	3,00	0,42	0,51	6,22	8,10	0,34	0,54				
50	2,50	2,95	0,43	0,53	5,60	7,20	0,30	0,50				

Lab. No.	Ca, mg/l		Mg, mg/l		Na, mg/l		K, mg/l		Al, µg/l		Al, µg/l	
	A	B	A	B	A	B	A	B	C	D	E	F
51	2,13	2,76	0,41	0,49	6,40	8,80	0,36	0,61				
52	2,55	3,18	0,45	0,54	6,26	8,59	0,34	0,54	104	131		
53	2,00	3,00			6,30	8,10	0,30	0,60				
54	2,63	3,26	0,43	0,52	6,13	8,16	0,34	0,53	82	141	97	124
55	2,59	2,82	0,61	0,94	5,36	7,26	0,43	0,53			68	91
56	3,00	4,00	1,20	1,20								
57	2,20	2,83	0,44	0,55	6,10	7,90	0,33	0,52	85	160		
58	2,20	2,80	0,37	0,45	6,00	8,00	0,32	0,52	60	103		
59	2,75	3,45	0,42	0,48	5,00	7,60	0,33	0,50				
61	2,71	3,21	0,45	0,55	6,28	8,27	0,27	0,42	77	93	70	72
63												
64	2,62	3,28	0,44	0,53	6,33	8,11	0,35	0,55	88	134		
65	2,40	2,99	0,40	0,48	6,17	8,06	0,36	0,52				
66	3,55	4,27	0,69	0,82	7,01	9,33	0,31	0,50			102	131
67	2,10	2,70	0,43	0,54	6,30	8,20	0,36	0,57				
68	3,01	3,50	0,49	0,62	6,89	8,80	0,35	0,58				
69	2,89	3,69	0,58	0,63	6,00	7,85	0,40	0,60				
71	2,84	3,48	0,49	0,57	6,65	8,67	0,47	0,66				
72	2,55	3,24	0,44	0,54	6,60	8,47	0,35	0,56				
73	3,00	3,00										
74	3,10	3,70	0,60	0,70	6,80	8,70	0,40	0,50	129	163		
75	2,45	3,13	0,48	0,57	5,09	7,63	0,36	0,58	67	105	122	137
76	2,52	3,15	0,44	0,54	6,02	7,91	0,37	0,59				
77												
78												
79									81	116	113	145

Lab. No.	Al-R, µg/l		Al-I, µg/l		DOC, mg/l		COD-Mn, mg/l		Fe, µg/l		Mn, µg/l	
	C	D	C	D	C	D	C	D	E	F	E	F
1					4,6	5,5	5,4	5,7	26,0	45,0	6,0	1,0
2												
3	32	55	22	37	5,8	5,8						
4									33,0	58,0	12,9	10,9
5									22,0	33,0		
6							6,4	5,5	26,0	57,0	8,4	5,4
7					5,4	5,5			29,8	47,8	6,2	<2,0
8	27	59	22	35					3,4	25,1	5,7	1,6
9												
10							5,7	5,8				
11	81	91	67	73	6,3	6,4			25,0	41,3	4,3	-3,0
13	35	85			9,0	8,0	5,7	5,8				
14												
15					5,7	5,5			25,2	43,6	5,6	1,6
16									31,0	51,0	6,0	1,6
17							7,6	7,6	23,8	35,7	4,7	1,2
18					5,9	6,1			26,3	45,2	5,8	1,7
19					4,8	5,0			29,9	55,1	5,5	1,6
20												
21					5,5	5,5	6,6	6,1	19,3	35,7	5,6	1,6
22												
23					4,4	4,2						
24					5,8	5,3			35,0	53,0		
25							6,5	6,8	72,7	71,5	5,2	1,7
26					7,2	7,6	6,3	6,4	29,4	47,3	5,5	<5,0
27												
28											6,5	1,9
29					9,3	8,7						
30							5,8	6,2			8,0	2,0
31									24,0	40,0	5,6	1,4
32	45	81	37	52	6,1	5,8			27,0	28,7	5,9	1,7
33					5,2	5,5			31,0	55,0	6,2	1,7
35							5,3	5,1				
36												
37									22,0	42,8	6,1	1,6
38					6,2	6,0			24,9	42,8	5,2	1,4
40	55	68	26	55	5,8	5,6			27,1	45,4	<10,0	<10,0
41					6,0	5,9			33,0	56,0	5,4	1,5
42					5,5	5,4	6,0	6,2	28,0	44,0	5,3	1,5
44	<135	<135	<135	<135	5,6	5,9			18,2	38,6	5,3	1,4
45												
46												
47												
48					7,7	7,9	6,0	7,7				
49					5,2	4,8						
50												

Lab. No.	Al-R, µg/l		Al-I, µg/l		DOC, mg/l		COD-Mn, mg/l		Fe, µg/l		Mn, µg/l	
	C	D	C	D	C	D	C	D	E	F	E	F
51												
52									26,3	44,3	5,6	1,5
53									15,5	23,4		
54	44	73	41	62	4,7	5,1	5,1	5,2	26,0	46,0	5,1	1,4
55									24,0	37,0	6,3	2,3
56												
57	45	100	40	60			7,1	6,7	25,0	43,0	5,3	1,6
58			48	76	4,4	3,9						
59												
61	78	64			4,3	3,9	5,9	5,7	34,0	51,0	7,0	5,0
63	46	76	31	46								
64	86	129	82	115	4,8	4,7						
65												
66									1,7	19,6	5,4	1,6
67					5,3	5,1						
68												
69							6,2	6,1	50,9	71,3	6,8	1,4
71												
72	53	57			7,3	6,9						
73							6,1	5,8	330,0	400,0		
74									<30,0	<30,0	6,1	1,6
75									35,0	51,0	6,0	2,0
76					4,5	4,3						
77											5,9	1,7
78												
79									28,0	46,0	5,6	1,6

Lab. No.	Cd, µg/l		Pb, µg/l		Cu, µg/l		Ni, µg/l		Zn, µg/l	
	E	**F**	**E**	**F**	**E**	**F**	**E**	**F**	**E**	**F**
1	1,13	2,98	3,4	7,2	31,0	13,0	2,9	6,8	26,0	14,0
2										
3										
4			5,0	8,8	24,5	10,7			37,5	17,5
5	1,49	3,49	2,0	6,1	20,2	10,2	2,5	6,7	21,5	9,9
6	1,13	5,00	3,2	10,1	31,0	12,0	2,8	5,4	31,0	18,0
7	1,02	2,99	3,8	8,6	28,9	11,8	2,5	6,7	31,9	22,4
8	1,18	3,36	3,2	7,2	29,6	11,7	2,4	6,4	27,8	15,0
9										
10										
11	<16,00	<16,00	<427,0	<427,0	<33,0	<33,0	<66,0	<66,0	22,3	12,0
13	1,20	3,40	3,8	7,8	28,9	11,3	2,0	5,7		
14										
15	0,92	2,94	5,7	1,7	32,0	12,0	2,4	6,1	23,6	12,4
16	1,27	3,23	0,6	4,8	40,0	25,0	1,9	5,4	25,0	10,0
17	0,94	2,36			26,2	12,1	1,3	1,8	19,1	11,9
18	0,90	2,90	2,8	6,5	32,3	13,2	2,2	5,7	23,4	12,2
19	1,04	2,97	3,1	6,9	28,3	11,3	2,3	6,0	22,5	11,7
20										
21	1,11	3,19	3,2	7,2	29,0	11,5	2,3	6,1	23,8	12,4
22										
23										
24	1,00	3,00	4,0	8,0	31,0	13,0	2,0	7,0	26,9	14,2
25	1,20	3,30	3,3	7,9	28,8	12,2	2,4	6,1	20,0	<10,0
26	1,30	3,70	3,1	7,4	29,2	11,1	2,4	6,0	24,6	12,8
27										
28	1,08	2,94	2,9	6,9	29,1	11,8	2,3	6,0	13,7	<4,3
29										
30									25,0	14,0
31	0,93	1,85	2,5	7,4	31,8	11,6	1,6	5,0	21,0	9,8
32	1,22	3,41	3,0	6,5	29,2	11,9	2,4	6,2	30,0	16,5
33										
35										
36										
37	1,32	3,66	3,1	6,9	31,9	12,7	2,5	6,8	27,8	14,4
38			<10,0	<10,0	28,1	11,0	<4,5	4,7	21,2	10,8
40	0,96	2,80	2,7	6,7	35,1	11,3	2,0	6,0	23,7	12,4
41	1,00	3,00	3,0	6,8	28,0	11,5	2,2	6,2	22,0	12,0
42	0,96	2,67	2,9	6,3	26,7	10,5	2,2	5,6	20,9	11,0
44	1,10	3,00	3,2	7,2	29,5	11,9	2,3	6,1	24,1	12,2
45										
46										
47										
48										
49										
50										

Lab. No.	Cd, µg/l		Pb, µg/l		Cu, µg/l		Ni, µg/l		Zn, µg/l	
	E	**F**	**E**	**F**	**E**	**F**	**E**	**F**	**E**	**F**
51										
52	1,12	3,13	3,1	7,1	29,5	12,6	2,6	6,1	23,2	12,8
53	0,97	2,78	1,6	3,7	22,1	7,7			4,7	0,8
54	1,00	3,00	2,9	6,7	27,0	11,0	2,1	5,7	25,0	14,0
55	0,63	2,09	<2,0	3,7	31,5	16,0	<3,0	<3,0	45,0	14,0
56										
57	1,10	3,00	2,0	5,0	28,0	11,0	2,5	6,0	20,0	11,5
58										
59										
61										
63										
64										
65										
66	1,15	3,32	3,3	7,6	32,7	13,4	2,5	6,6	28,0	15,4
67										
68										
69	1,08	3,10	4,7	10,4	29,8	11,2	2,1	6,3	19,5	10,5
71										
72										
73										
74	0,93	2,10	2,6	5,7	25,3	9,5	<2,0	3,2	22,0	11,0
75	1,03	0,01	4,0	0,0	24,6	5,1	2,0	0,1	22,8	4,9
76										
77	1,08	2,95	3,1	6,9						
78										
79	1,30	3,30			29,2	11,7	3,1	6,7	23,3	12,6

Table 5.1. Statistics - pH

Sample A

Number of participants	69	Range	1,17
Number of omitted results	1	Variance	0,04
True value	7,15	Standard deviation	0,21
Mean value	7,14	Relative standard deviation	2,9%
Median	7,15	Relative error	-0,1%

Analytical results in ascending order:

36	6,37 U	69	7,09	6	7,20
28	6,53	58	7,10	15	7,20
50	6,68	73	7,10	51	7,20
71	6,75	64	7,11	2	7,21
56	6,80	76	7,11	61	7,22
29	6,82	22	7,12	27	7,23
37	6,85	33	7,13	38	7,24
19	6,86	45	7,14	66	7,26
11	6,86	40	7,14	8	7,26
52	6,88	55	7,15	31	7,26
5	6,96	20	7,15	9	7,26
49	6,96	24	7,15	3	7,28
48	6,96	72	7,15	54	7,31
13	6,98	1	7,17	17	7,32
59	7,00	65	7,17	67	7,34
26	7,02	35	7,17	77	7,34
21	7,03	18	7,18	23	7,34
25	7,05	57	7,18	16	7,39
47	7,05	32	7,19	30	7,40
46	7,06	42	7,19	41	7,50
78	7,07	14	7,20	44	7,59
4	7,08	68	7,20	7	7,66
53	7,09	10	7,20	74	7,70

Sample B

Number of participants	69	Range	1,03
Number of omitted results	1	Variance	0,04
True value	7,24	Standard deviation	0,19
Mean value	7,23	Relative standard deviation	2,6%
Median	7,24	Relative error	-0,2%

Analytical results in ascending order:

28	6,69	68	7,16	64	7,30
36	6,80 U	13	7,19	69	7,31
11	6,84	78	7,20	76	7,31
50	6,86	45	7,20	57	7,31
46	6,86	10	7,21	51	7,32
71	6,87	48	7,21	32	7,33
56	6,95	25	7,22	8	7,34
19	6,96	40	7,22	14	7,35
47	6,97	4	7,22	31	7,36
1	6,99	20	7,23	27	7,37
29	7,04	58	7,24	18	7,37
52	7,07	42	7,24	16	7,38
26	7,07	33	7,24	9	7,39
59	7,09	55	7,25	23	7,40
72	7,09	61	7,25	66	7,40
73	7,10	21	7,25	3	7,45
37	7,10	65	7,26	17	7,46
49	7,10	2	7,26	54	7,47
74	7,10	24	7,27	77	7,48
15	7,12	35	7,28	67	7,52
22	7,14	6	7,30	41	7,52
5	7,15	38	7,30	7	7,65
53	7,16	30	7,30	44	7,72

U = Omitted resultat

Table 5.2. Statistics - Conductivity, mS/m

Sample A

Number of participants	65	Range	1,26
Number of omitted results	5	Variance	0,05
True value	4,70	Standard deviation	0,22
Mean value	4,68	Relative standard deviation	4,7%
Median	4,70	Relative error	-0,5%

Analytical results in ascending order:

16	0,02 U	11	4,63	76	4,78
64	3,40 U	19	4,63	68	4,80
57	4,00	8	4,64	28	4,80
21	4,25	51	4,65	59	4,80
40	4,28	18	4,65	30	4,80
55	4,37	23	4,66	66	4,81
5	4,38	14	4,66	35	4,81
46	4,40	10	4,67	22	4,89
32	4,40	50	4,68	74	4,90
54	4,41	29	4,70	25	4,90
3	4,46	78	4,70	24	4,90
17	4,46	37	4,70	44	4,91
49	4,48	45	4,70	33	4,95
67	4,50	26	4,70	36	5,00
58	4,50	20	4,70	73	5,00
7	4,50	65	4,71	15	5,02
13	4,56	47	4,71	6	5,11
27	4,58	77	4,73	71	5,26
38	4,58	52	4,73	1	5,60 U
72	4,59	61	4,75	56	6,00 U
42	4,59	69	4,76	9	6,20 U
2	4,63	31	4,78		

Sample B

Number of participants	65	Range	1,70
Number of omitted results	5	Variance	0,06
True value	5,98	Standard deviation	0,25
Mean value	5,95	Relative standard deviation	4,3%
Median	5,98	Relative error	-0,5%

Analytical results in ascending order:

16	0,02 U	72	5,90	69	6,06
64	4,80 U	7	5,90	31	6,08
74	5,00	38	5,90	52	6,09
57	5,10	50	5,91	19	6,09
40	5,64	11	5,93	35	6,09
55	5,66	18	5,94	29	6,10
5	5,67	8	5,94	28	6,10
21	5,68	59	5,95	36	6,10
17	5,68	10	5,95	20	6,10
67	5,70	51	5,96	24	6,10
14	5,74	68	5,99	76	6,11
49	5,76	77	6,00	23	6,13
54	5,80	73	6,00	15	6,16
45	5,80	9	6,00 U	37	6,20
32	5,80	30	6,00	25	6,20
58	5,83	78	6,00	71	6,26
42	5,86	2	6,02	44	6,30
3	5,87	26	6,02	6	6,43
66	5,88	47	6,03	33	6,70
13	5,89	65	6,03	56	7,50 U
27	5,89	22	6,04	1	7,80 U
46	5,90	61	6,04		

U = Omitted resultat

Table 5.3. Statistics - Alkalinity, mmol/l

Sample A

Number of participants	53	Range	0,220
Number of omitted results	2	Variance	0,002
True value	0,270	Standard deviation	0,045
Mean value	0,266	Relative standard deviation	17,1%
Median	0,270	Relative error	-1,5%

Analytical results in ascending order:

64	0,132 U	32	0,263	46	0,280
40	0,140	21	0,264	9	0,280
29	0,150	24	0,264	2	0,285
66	0,150	57	0,264	10	0,286
23	0,160	8	0,266	45	0,289
53	0,165	72	0,266	74	0,290
6	0,236	30	0,268	18	0,290
27	0,240	61	0,270	54	0,290
36	0,250	26	0,270	51	0,298
49	0,250	65	0,270	14	0,300
69	0,252	13	0,270	71	0,306
50	0,255	76	0,271	37	0,308
5	0,259	7	0,272	20	0,315
17	0,259	35	0,273	19	0,330
58	0,260	3	0,273	73	0,330
77	0,260	47	0,274	55	0,340
25	0,260	31	0,277	56	0,360
42	0,263	68	0,279	16	0,520 U

Sample B

Number of participants	53	Range	0,275
Number of omitted results	2	Variance	0,003
True value	0,360	Standard deviation	0,056
Mean value	0,349	Relative standard deviation	16,0%
Median	0,359	Relative error	-3,0%

Analytical results in ascending order:

64	0,170 U	72	0,350	10	0,362
40	0,185	5	0,350	7	0,366
66	0,190	42	0,353	31	0,370
29	0,200	3	0,354	18	0,370
23	0,210	24	0,355	46	0,370
53	0,220	57	0,355	47	0,372
69	0,324	32	0,356	2	0,377
27	0,330	8	0,357	54	0,382
73	0,330	35	0,359	45	0,383
17	0,336	30	0,359	37	0,394
36	0,340	21	0,360	51	0,397
49	0,340	76	0,360	71	0,397
50	0,345	61	0,360	6	0,400
26	0,350	74	0,360	20	0,406
9	0,350	13	0,360	55	0,410
14	0,350	65	0,360	19	0,430
25	0,350	58	0,360	56	0,460
77	0,350	68	0,361	16	0,620 U

U = Omitted resultat

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

Sample A

Number of participants	60	Range	101
Number of omitted results	5	Variance	469
True value	223	Standard deviation	22
Mean value	219	Relative standard deviation	9,9%
Median	223	Relative error	-1,7%

Analytical results in ascending order:

48	92 U	74	220	3	230
2	165	44	220	54	230
37	170	56	220	25	230
17	172	4	221	51	233
36	175	20	221	13	236
69	178	66	221	68	237
27	181	72	221	23	237
22	194	7	223	76	238
50	196	9	223	78	240
58	200	46	224	30	240
24	200	10	224	57	240
26	202	32	224	28	242
59	207	5	224	6	247
67	210	14	224	45	251
52	210	35	226	71	255
11	212	18	226	61	266
49	212	42	228	77	304 U
15	214	38	228	1	484 U
21	215	64	230	31	626 U
53	218	47	230	16	1160 U

Sample B

Number of participants	60	Range	131
Number of omitted results	6	Variance	647
True value	291	Standard deviation	25
Mean value	286	Relative standard deviation	8,9%
Median	291	Relative error	-1,9%

Analytical results in ascending order:

48	128 U	9	276	25	300
46	208	68	277	74	300
78	220	52	280	56	300
36	231	14	283	49	302
53	242	4	287	64	302
27	244	18	289	38	302
47	251	45	289	21	304
22	254	3	290	76	308
17	255	24	290	54	310
69	260	44	291	28	314
58	260	20	292	6	315
59	260	10	292	71	316
37	260	32	294	23	320
26	262	67	295	30	320
15	265	66	295	57	330
50	265	7	296	61	351
5	266	13	297	77	393 U
72	274	42	297	31	447 U
11	274	51	298	1	527 U
2	275	35	300	16	930 U

U = Omitted resultat

Table 5.5. Statistics - Chloride, mg/l

Sample A

Number of participants	61	Range	0,95
Number of omitted results	3	Variance	0,04
True value	2,20	Standard deviation	0,21
Mean value	2,21	Relative standard deviation	9,6%
Median	2,20	Relative error	0,5%

Analytical results in ascending order:

77	<1 U	55	2,19	37	2,25
66	1,78	48	2,19	18	2,26
4	1,81	25	2,19	33	2,26
23	1,82	17	2,19	76	2,27
53	1,83	3	2,19	42	2,30
22	1,86	47	2,20	20	2,32
11	1,90	10	2,20	27	2,32
51	2,00	24	2,20	57	2,33
26	2,00	52	2,20	13	2,36
45	2,04	74	2,20	49	2,42
44	2,04	54	2,20	50	2,45
38	2,08	30	2,20	1	2,54
5	2,09	14	2,20	64	2,60
56	2,10	46	2,21	58	2,70
15	2,11	40	2,21	69	2,70
31	2,12	2	2,22	71	2,72
32	2,13	9	2,22	68	2,79
35	2,15	28	2,23	8	3,09 U
7	2,15	61	2,24	16	6,00 U
6	2,15	21	2,25		
59	2,18	72	2,25		

Sample B

Number of participants	61	Range	1,76
Number of omitted results	3	Variance	0,09
True value	3,08	Standard deviation	0,30
Mean value	3,05	Relative standard deviation	9,9%
Median	3,08	Relative error	-0,9%

Analytical results in ascending order:

77	<1 U	52	3,00	50	3,14
21	2,14	30	3,00	28	3,15
4	2,34	15	3,01	76	3,16
8	2,45 U	31	3,02	33	3,18
55	2,55	61	3,04	37	3,20
66	2,57	10	3,05	1	3,22
22	2,59	35	3,06	72	3,23
23	2,65	24	3,06	53	3,24
11	2,71	9	3,07	20	3,27
49	2,77	25	3,08	27	3,28
56	2,80	2	3,08	13	3,28
44	2,83	32	3,09	42	3,33
45	2,83	7	3,09	64	3,40
38	2,87	47	3,09	57	3,42
14	2,90	74	3,10	69	3,55
51	2,90	54	3,10	71	3,62
26	2,90	46	3,11	68	3,75
48	2,92	40	3,11	58	3,90
5	2,94	18	3,12	16	8,00 U
17	2,96	3	3,12		
59	2,96	6	3,12		

U = Omitted resultat
U = Omitted resultat

Table 5.6. Statistics - Sulfate, mg/l

Sample A

Number of participants	61	Range	1,9
Number of omitted results	3	Variance	0,1
True value	3,2	Standard deviation	0,3
Mean value	3,1	Relative standard deviation	10,9%
Median	3,2	Relative error	-1,6%

Analytical results in ascending order:

55	< 2 U	51	3,1	9	3,3
73	2,0 U	11	3,1	54	3,3
26	2,1	48	3,2	27	3,3
56	2,1	13	3,2	33	3,3
6	2,1	47	3,2	28	3,3
61	2,3	38	3,2	8	3,3
49	2,9	31	3,2	59	3,3
22	2,9	58	3,2	57	3,4
64	2,9	2	3,2	50	3,4
4	2,9	37	3,2	68	3,4
10	2,9	44	3,2	69	3,4
7	2,9	15	3,2	18	3,4
45	3,0	23	3,2	35	3,4
30	3,0	53	3,2	25	3,4
66	3,0	3	3,2	74	3,5
14	3,0	40	3,2	52	3,6
46	3,1	21	3,3	16	3,7 U
5	3,1	20	3,3	77	3,9
17	3,1	32	3,3	1	4,0
72	3,1	76	3,3		
42	3,1	24	3,3		

Sample B

Number of participants	61	Range	2,0
Number of omitted results	3	Variance	0,1
True value	3,6	Standard deviation	0,4
Mean value	3,6	Relative standard deviation	10,5%
Median	3,6	Relative error	-1,0%

Analytical results in ascending order:

55	< 2 U	13	3,5	68	3,7
73	2,0 U	42	3,6	9	3,7
26	2,4	47	3,6	33	3,7
56	2,4	31	3,6	54	3,7
8	2,6	57	3,6	58	3,7
61	2,8	38	3,6	6	3,7
4	3,2	21	3,6	27	3,7
7	3,3	59	3,6	23	3,8
45	3,3	37	3,6	18	3,8
64	3,3	44	3,6	25	3,8
30	3,3	3	3,6	48	3,9
10	3,3	40	3,6	74	4,0
46	3,4	20	3,6	14	4,0
22	3,4	50	3,6	52	4,0
49	3,4	15	3,7	69	4,1
5	3,4	28	3,7	1	4,3
66	3,4	76	3,7	53	4,3
17	3,5	2	3,7	77	4,4
11	3,5	32	3,7	16	5,5 U
72	3,5	24	3,7		
51	3,5	35	3,7		

U = Omitted resultat

Table 5.7. Statistics - Calcium, mg/l

Sample A

Number of participants	65	Range	1,25
Number of omitted results	2	Variance	0,07
True value	2,55	Standard deviation	0,26
Mean value	2,56	Relative standard deviation	10,3%
Median	2,55	Relative error	0,5%

Analytical results in ascending order:

5	0,32 U	50	2,50	64	2,62
48	1,90	30	2,50	54	2,63
53	2,00	40	2,51	35	2,63
67	2,10	76	2,52	25	2,67
2	2,13	23	2,53	9	2,69
51	2,13	18	2,54	61	2,71
57	2,20	27	2,54	20	2,74
58	2,20	13	2,54	59	2,75
6	2,23	21	2,55	26	2,80
33	2,28	72	2,55	71	2,84
41	2,34	31	2,55	45	2,88
17	2,35	52	2,55	69	2,89
11	2,35	44	2,57	32	2,90
24	2,36	19	2,58	28	2,95
49	2,40	47	2,58	56	3,00
65	2,40	8	2,58	73	3,00
7	2,41	55	2,59	68	3,01
75	2,45	14	2,60	22	3,02
46	2,46	37	2,60	74	3,10
29	2,46	42	2,60	4	3,15
16	2,47	1	2,61	66	3,55 U
38	2,47	15	2,61		

Sample B

Number of participants	65	Range	1,30
Number of omitted results	2	Variance	0,08
True value	3,20	Standard deviation	0,28
Mean value	3,22	Relative standard deviation	8,8%
Median	3,20	Relative error	0,6%

Analytical results in ascending order:

5	0,68 U	40	3,11	35	3,27
67	2,70	31	3,12	42	3,27
51	2,76	23	3,12	64	3,28
58	2,80	75	3,13	9	3,29
55	2,82	46	3,15	1	3,36
57	2,83	76	3,15	26	3,40
2	2,85	21	3,17	59	3,45
24	2,90	44	3,18	25	3,47
6	2,91	52	3,18	71	3,48
41	2,92	19	3,18	68	3,50
33	2,95	29	3,20	20	3,52
50	2,95	37	3,20	28	3,57
65	2,99	18	3,20	45	3,58
49	3,00	30	3,20	32	3,60
73	3,00	14	3,20	69	3,69
53	3,00	61	3,21	74	3,70
17	3,02	27	3,22	22	3,75
7	3,02	15	3,23	13	3,81
16	3,04	47	3,23	4	3,92
48	3,05	72	3,24	56	4,00
38	3,08	54	3,26	66	4,27 U
11	3,09	8	3,27		

U = Omitted resultat

Table 5.8. Statistics - Magnesium, mg/l

Sample A

Number of participants	63	Range	0,23
Number of omitted results	5	Variance	0,00
True value	0,44	Standard deviation	0,05
Mean value	0,45	Relative standard deviation	10,3%
Median	0,44	Relative error	1,2%

Analytical results in ascending order:

19	< 1 U	46	0,43	8	0,45
58	0,37	54	0,43	40	0,45
31	0,38	50	0,43	48	0,46
16	0,39	18	0,43	28	0,46
47	0,40	45	0,43	23	0,47
30	0,40	67	0,43	32	0,47
65	0,40	15	0,43	75	0,48
4	0,40	38	0,44	22	0,48
6	0,40	64	0,44	68	0,49
5	0,41	76	0,44	71	0,49
51	0,41	35	0,44	14	0,50
2	0,41	9	0,44	42	0,50
25	0,41	57	0,44	1	0,50
44	0,42	13	0,44	26	0,51
41	0,42	27	0,44	69	0,58
24	0,42	21	0,44	20	0,58
59	0,42	72	0,44	74	0,60
17	0,42	37	0,44	55	0,61 U
49	0,42	7	0,45	66	0,69 U
33	0,42	61	0,45	11	0,76 U
29	0,42	52	0,45	56	1,20 U

Sample B

Number of participants	63	Range	0,32
Number of omitted results	5	Variance	0,00
True value	0,53	Standard deviation	0,06
Mean value	0,54	Relative standard deviation	10,4%
Median	0,53	Relative error	2,0%

Analytical results in ascending order:

19	< 1 U	25	0,52	8	0,55
16	0,39	33	0,52	57	0,55
58	0,45	29	0,53	23	0,56
31	0,45	15	0,53	75	0,57
59	0,48	50	0,53	71	0,57
65	0,48	46	0,53	28	0,57
51	0,49	21	0,53	32	0,57
47	0,49	18	0,53	22	0,58
5	0,50	64	0,53	42	0,60
4	0,50	37	0,53	1	0,60
14	0,50	38	0,54	68	0,62
24	0,50	76	0,54	11	0,63 U
30	0,50	35	0,54	69	0,63
49	0,51	9	0,54	13	0,63
41	0,51	27	0,54	26	0,64
17	0,51	40	0,54	20	0,66
44	0,51	67	0,54	48	0,69
6	0,52	52	0,54	74	0,70
45	0,52	72	0,54	66	0,82 U
54	0,52	7	0,55	55	0,94 U
2	0,52	61	0,55	56	1,20 U

U = Omitted resultat

Table 5.9. Statistics - Sodium, mg/l

Sample A

Number of participants	61	Range	2,32
Number of omitted results	1	Variance	0,24
True value	6,22	Standard deviation	0,49
Mean value	6,27	Relative standard deviation	7,7%
Median	6,22	Relative error	0,7%

Analytical results in ascending order:

59	5,00	54	6,13	11	6,38
75	5,09	44	6,14	51	6,40
38	5,27	4	6,17	19	6,44
55	5,36	65	6,17	9	6,60
23	5,45	26	6,18	72	6,60
50	5,60	37	6,20	42	6,62
27	5,83	30	6,20	71	6,65
48	5,90	2	6,20	1	6,69
47	5,92	24	6,21	20	6,74
33	5,96	49	6,22	74	6,80
69	6,00	8	6,22	68	6,89
58	6,00	15	6,24	66	7,01
7	6,00	52	6,26	22	7,04
76	6,02	61	6,28	16	7,10
5	6,08	53	6,30	6	7,10
25	6,10	67	6,30	40	7,11
57	6,10	31	6,30	35	7,20
18	6,10	13	6,33	28	7,32
29	6,11	64	6,33	21	8,24 U
17	6,12	32	6,35		
41	6,13	45	6,35		

Sample B

Number of participants	61	Range	2,75
Number of omitted results	1	Variance	0,29
True value	8,16	Standard deviation	0,54
Mean value	8,26	Relative standard deviation	6,5%
Median	8,16	Relative error	1,2%

Analytical results in ascending order:

21	6,23 U	17	8,04	11	8,42
38	6,87	2	8,05	72	8,47
50	7,20	65	8,06	13	8,47
55	7,26	5	8,07	52	8,59
59	7,60	53	8,10	20	8,65
75	7,63	49	8,10	71	8,67
27	7,64	64	8,11	42	8,69
47	7,68	24	8,12	74	8,70
48	7,80	41	8,15	9	8,78
69	7,85	15	8,16	51	8,80
23	7,85	54	8,16	68	8,80
7	7,90	31	8,17	6	8,84
4	7,90	67	8,20	1	8,89
57	7,90	19	8,20	40	9,03
76	7,91	30	8,20	16	9,20
25	7,94	29	8,23	22	9,22
18	7,97	61	8,27	66	9,33
33	7,99	44	8,29	35	9,58
58	8,00	8	8,30	28	9,62
37	8,00	45	8,30		
26	8,03	32	8,37		

U = Omitted resultat

Table 5.10. Statistics - Potassium, mg/l

Sample A

Number of participants	61	Range	0,21
Number of omitted results	6	Variance	0,00
True value	0,35	Standard deviation	0,04
Mean value	0,35	Relative standard deviation	10,9%
Median	0,35	Relative error	1,3%

Analytical results in ascending order:

19	< 1 U	40	0,34	27	0,37
35	0,18 U	64	0,35	76	0,37
61	0,27	15	0,35	20	0,38
11	0,30	2	0,35	18	0,38
48	0,30	25	0,35	38	0,38
53	0,30	26	0,35	31	0,38
50	0,30	44	0,35	5	0,39
4	0,31	42	0,35	8	0,39
37	0,31	68	0,35	41	0,39
24	0,31	23	0,35	74	0,40
66	0,31	72	0,35	69	0,40
58	0,32	32	0,35	30	0,40
47	0,33	75	0,36	55	0,43
59	0,33	1	0,36	71	0,47
57	0,33	67	0,36	13	0,48
33	0,33	21	0,36	22	0,52 U
46	0,34	65	0,36	6	0,89 U
49	0,34	28	0,36	16	1,54 U
52	0,34	7	0,36	9	1,55 U
45	0,34	51	0,36		
54	0,34	17	0,37		

Sample B

Number of participants	61	Range	0,24
Number of omitted results	6	Variance	0,00
True value	0,55	Standard deviation	0,04
Mean value	0,55	Relative standard deviation	7,7%
Median	0,55	Relative error	0,5%

Analytical results in ascending order:

19	< 1 U	45	0,54	68	0,58
35	0,30 U	5	0,54	75	0,58
61	0,42	52	0,54	76	0,59
24	0,49	47	0,54	31	0,59
11	0,50	44	0,55	27	0,59
59	0,50	64	0,55	8	0,59
50	0,50	15	0,55	1	0,60
74	0,50	2	0,55	69	0,60
66	0,50	25	0,55	53	0,60
48	0,50	42	0,55	18	0,60
30	0,50	26	0,55	41	0,61
65	0,52	32	0,55	51	0,61
57	0,52	21	0,56	13	0,62
4	0,52	72	0,56	20	0,62
58	0,52	17	0,56	38	0,63
37	0,52	23	0,56	71	0,66
46	0,53	40	0,56	6	1,26 U
55	0,53	22	0,57 U	16	1,52 U
54	0,53	7	0,57	9	2,44 U
49	0,54	67	0,57		
33	0,54	28	0,58		

U = Omitted resultat

Table 5.11. Statistics - Aluminium, µg/l

Sample C

Number of participants	28	Range	44
Number of omitted results	4	Variance	92
True value	81	Standard deviation	10
Mean value	82	Relative standard deviation	11,7%
Median	81	Relative error	1,5%

Analytical results in ascending order:

11	< 106 U	44	80	25	85
48	< 20 U	13	80	26	86
29	37 U	79	81	8	86
58	60	38	81	64	88
75	67	18	81	17	98
41	69	40	81	37	99
33	77	54	82	52	104
61	77	15	85	74	129 U
24	78	42	85		
1	78	57	85		

Sample D

Number of participants	28	Range	68
Number of omitted results	4	Variance	344
True value	130	Standard deviation	19
Mean value	128	Relative standard deviation	14,5%
Median	130	Relative error	-1,9%

Analytical results in ascending order:

48	< 20 U	11	125 U	8	135
29	65 U	42	125	15	139
61	93	44	127	54	141
24	96	38	127	17	151
58	103	33	129	37	152
75	105	25	130	57	160
41	105	13	131	26	161
1	115	52	131	74	163 U
79	116	18	132		
40	123	64	134		

U = Omitted resultat

Table 5.11. Statistics - Aluminium, µg/l

Sample E

Number of participants	23	Range	60
Number of omitted results	1	Variance	250
True value	105	Standard deviation	16
Mean value	103	Relative standard deviation	15,4%
Median	105	Relative error	-2,1%

Analytical results in ascending order:

55	68	19	101	1	111
61	70	13	101	18	111
32	81	66	102	79	113
24	88	21	105	16	120
41	95	40	105	75	122
57	95	15	105	38	125
42	96	8	108	11	127
54	97	33	110	25	177 U

Sample F

Number of participants	23	Range	98
Number of omitted results	1	Variance	475
True value	134	Standard deviation	22
Mean value	129	Relative standard deviation	16,8%
Median	134	Relative error	-3,5%

Analytical results in ascending order:

61	72	19	130	33	139
55	91	66	131	1	141
32	103	21	132	18	141
24	105	40	133	79	145
57	110	41	134	11	147
42	117	15	136	38	159
13	121	8	137	16	170
54	124	75	137	25	203 U

U = Omitted resultat

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

Sample C

Number of participants	13	Range	29
Number of omitted results	4	Variance	90
True value	45	Standard deviation	9
Mean value	42	Relative standard deviation	22,4%
Median	45	Relative error	-5,8%

Analytical results in ascending order:

44	< 135 U	32	45	61	78 U
8	27	57	45	11	81 U
3	32	63	46	64	86 U
13	35	72	53		
54	44	40	55		

Sample D

Number of participants	13	Range	45
Number of omitted results	4	Variance	217
True value	73	Standard deviation	15
Mean value	73	Relative standard deviation	20,3%
Median	73	Relative error	-0,4%

Analytical results in ascending order:

44	< 135 U	40	68	11	91 U
3	55	54	73	57	100
72	57	63	76	64	129 U
8	59	32	81		
61	64 U	13	85		

U = Omitted resultat

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

Sample C

Number of participants	11	Range	26
Number of omitted results	3	Variance	94
True value	34	Standard deviation	10
Mean value	33	Relative standard deviation	29,0%
Median	34	Relative error	-1,9%

Analytical results in ascending order:

44	< 135 U	63	31	58	48
8	22	32	37	11	67 U
3	22	57	40	64	82 U
40	26	54	41		

Sample D

Number of participants	11	Range	41
Number of omitted results	3	Variance	183
True value	54	Standard deviation	14
Mean value	53	Relative standard deviation	25,6%
Median	54	Relative error	-2,0%

Analytical results in ascending order:

44	< 135 U	32	52	11	73 U
8	35	40	55	58	76
3	37	57	60	64	115 U
63	46	54	62		

U = Omitted resultat

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

Sample C

Number of participants	29	Range	3,4
Number of omitted results	2	Variance	0,8
True value	5,5	Standard deviation	0,9
Mean value	5,6	Relative standard deviation	15,9%
Median	5,5	Relative error	1,0%

Analytical results in ascending order:

61	4,3	67	5,3	41	6,0
58	4,4	7	5,4	32	6,1
23	4,4	21	5,5	38	6,2
76	4,5	42	5,5	11	6,3
1	4,6	44	5,6	26	7,2
54	4,7	15	5,7	72	7,3
19	4,8	24	5,8	48	7,7
64	4,8	40	5,8	13	9,0 U
33	5,2	3	5,8	29	9,3 U
49	5,2	18	5,9		

Sample D

Number of participants	29	Range	4,0
Number of omitted results	2	Variance	0,9
True value	5,5	Standard deviation	1,0
Mean value	5,5	Relative standard deviation	17,5%
Median	5,5	Relative error	0,1%

Analytical results in ascending order:

58	3,9	42	5,4	41	5,9
61	3,9	1	5,5	38	6,0
23	4,2	33	5,5	18	6,1
76	4,3	21	5,5	11	6,4
64	4,7	15	5,5	72	6,9
49	4,8	7	5,5	26	7,6
19	5,0	40	5,6	48	7,9
67	5,1	3	5,8	13	8,0 U
54	5,1	32	5,8	29	8,7 U
24	5,3	44	5,9		

U = Omitted resultat

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

Sample C

Number of participants	17	Range	2,5
Number of omitted results	0	Variance	0,4
True value	6,0	Standard deviation	0,6
Mean value	6,1	Relative standard deviation	10,4%
Median	6,0	Relative error	1,6%

Analytical results in ascending order:

54	5,1	61	5,9	6	6,4
35	5,3	48	6,0	25	6,5
1	5,4	42	6,0	21	6,6
13	5,7	73	6,1	57	7,1
10	5,7	69	6,2	17	7,6
30	5,8	26	6,3		

Sample D

Number of participants	17	Range	2,6
Number of omitted results	0	Variance	0,5
True value	6,1	Standard deviation	0,7
Mean value	6,1	Relative standard deviation	11,8%
Median	6,1	Relative error	0,6%

Analytical results in ascending order:

35	5,1	73	5,8	26	6,4
54	5,2	10	5,8	57	6,7
6	5,5	69	6,1	25	6,8
1	5,7	21	6,1	17	7,6
61	5,7	30	6,2	48	7,7
13	5,8	42	6,2		

U = Omitted resultat

Table 5.16. Statistics - Iron, µg/l

Sample E

Number of participants	37	Range	19,5
Number of omitted results	6	Variance	22,4
True value	26,3	Standard deviation	4,7
Mean value	26,8	Relative standard deviation	17,7%
Median	26,3	Relative error	1,9%

Analytical results in ascending order:

74	< 30 U	57	25,0	19	29,9
66	1,7 U	15	25,2	33	31,0
8	3,4 U	1	26,0	16	31,0
53	15,5	54	26,0	41	33,0
44	18,2	6	26,0	4	33,0
21	19,3	52	26,3	61	34,0
5	22,0	18	26,3	24	35,0
37	22,0	32	27,0	75	35,0
17	23,8	40	27,1	69	50,9 U
55	24,0	79	28,0	25	72,7 U
31	24,0	42	28,0	73	330,0 U
38	24,9	26	29,4		
11	25,0	7	29,8		

Sample F

Number of participants	37	Range	34,6
Number of omitted results	6	Variance	67,7
True value	45,0	Standard deviation	8,2
Mean value	44,6	Relative standard deviation	18,4%
Median	45,0	Relative error	-0,8%

Analytical results in ascending order:

74	< 30 U	37	42,8	16	51,0
66	19,6 U	57	43,0	75	51,0
53	23,4	15	43,6	24	53,0
8	25,1 U	42	44,0	33	55,0
32	28,7	52	44,3	19	55,1
5	33,0	1	45,0	41	56,0
17	35,7	18	45,2	6	57,0
21	35,7	40	45,4	4	58,0
55	37,0	79	46,0	69	71,3 U
44	38,6	54	46,0	25	71,5 U
31	40,0	26	47,3	73	400,0 U
11	41,3	7	47,8		
38	42,8	61	51,0		

U = Omitted resultat

Table 5.17. Statistics - Manganese, µg/l

Sample E

Number of participants	36	Range	2,1
Number of omitted results	8	Variance	0,2
True value	5,6	Standard deviation	0,5
Mean value	5,7	Relative standard deviation	8,1%
Median	5,6	Relative error	1,8%

Analytical results in ascending order:

40	< 10 U	19	5,5	1	6,0
11	4,3 U	52	5,6	74	6,1
17	4,7	15	5,6	37	6,1
54	5,1	31	5,6	33	6,2
38	5,2	79	5,6	7	6,2 U
25	5,2	21	5,6	55	6,3
42	5,3	8	5,7	28	6,5
44	5,3	18	5,8	69	6,8
57	5,3	32	5,9	61	7,0 U
66	5,4	77	5,9	30	8,0 U
41	5,4	75	6,0	6	8,4 U
26	5,5 U	16	6,0	4	12,9 U

Sample F

Number of participants	36	Range	1,3
Number of omitted results	8	Variance	0,1
True value	1,6	Standard deviation	0,2
Mean value	1,6	Relative standard deviation	15,1%
Median	1,6	Relative error	-0,9%

Analytical results in ascending order:

40	< 10 U	41	1,5	77	1,7
26	< 5 U	52	1,5	25	1,7
11	< 3 U	19	1,6	33	1,7
7	< 2 U	66	1,6	18	1,7
1	1,0	74	1,6	32	1,7
17	1,2	16	1,6	28	1,9
54	1,4	37	1,6	75	2,0
31	1,4	21	1,6	30	2,0 U
69	1,4	57	1,6	55	2,3
38	1,4	79	1,6	61	5,0 U
44	1,4	15	1,6	6	5,4 U
42	1,5	8	1,6	4	10,9 U

U = Omitted resultat

Table 5.18. Statistics - Kadmium, µg/l

Sample E

Number of participants	35	Range	0,86
Number of omitted results	3	Variance	0,03
True value	1,08	Standard deviation	0,16
Mean value	1,08	Relative standard deviation	15,0%
Median	1,08	Relative error	0,2%

Analytical results in ascending order:

11	< 16 U	24	1,00	6	1,13 U
55	0,63	7	1,02	66	1,15
18	0,90	75	1,03 U	8	1,18
15	0,92	19	1,04	25	1,20
74	0,93	77	1,08	13	1,20
31	0,93	69	1,08	32	1,22
17	0,94	28	1,08	16	1,27
42	0,96	44	1,10	26	1,30
40	0,96	57	1,10	79	1,30
53	0,97	21	1,11	37	1,32
41	1,00	52	1,12	5	1,49
54	1,00	1	1,13		

Sample F

Number of participants	35	Range	1,85
Number of omitted results	3	Variance	0,18
True value	3,00	Standard deviation	0,43
Mean value	3,00	Relative standard deviation	14,2%
Median	3,00	Relative error	-0,1%

Analytical results in ascending order:

11	< 16 U	77	2,95	16	3,23
75	0,01 U	19	2,97	79	3,30
31	1,85	1	2,98	25	3,30
55	2,09	7	2,99	66	3,32
74	2,10	57	3,00	8	3,36
17	2,36	54	3,00	13	3,40
42	2,67	44	3,00	32	3,41
53	2,78	24	3,00	5	3,49
40	2,80	41	3,00	37	3,66
18	2,90	69	3,10	26	3,70
28	2,94	52	3,13	6	5,00 U
15	2,94	21	3,19		

U = Omitted resultat

Table 5.19. Statistics - Bly, µg/l

Sample E

Number of participants	35	Range	2,5
Number of omitted results	8	Variance	0,3
True value	3,1	Standard deviation	0,5
Mean value	3,0	Relative standard deviation	18,0%
Median	3,1	Relative error	-3,5%

Analytical results in ascending order:

11	< 427 U	42	2,9	8	3,2
38	< 10 U	28	2,9	25	3,3
55	< 2 U	32	3,0	66	3,3
16	0,6 U	41	3,0	1	3,4
53	1,6	37	3,1	13	3,8
5	2,0	19	3,1	7	3,8
57	2,0	26	3,1	75	4,0 U
31	2,5	77	3,1	24	4,0
74	2,6	52	3,1	69	4,7 U
40	2,7	6	3,2	4	5,0 U
18	2,8	44	3,2	15	5,7 U
54	2,9	21	3,2		

Sample F

Number of participants	35	Range	6,4
Number of omitted results	8	Variance	1,3
True value	6,9	Standard deviation	1,2
Mean value	7,0	Relative standard deviation	16,5%
Median	6,9	Relative error	1,0%

Analytical results in ascending order:

11	< 427 U	18	6,5	44	7,2
38	< 10 U	54	6,7	26	7,4
75	0,0 U	40	6,7	31	7,4
15	1,7 U	41	6,8	66	7,6
53	3,7	19	6,9	13	7,8
55	3,7 U	37	6,9	25	7,9
16	4,8 U	28	6,9	24	8,0
57	5,0	77	6,9	7	8,6
74	5,7	52	7,1	4	8,8 U
5	6,1	21	7,2	6	10,1
42	6,3	8	7,2	69	10,4 U
32	6,5	1	7,2		

U = Omitted resultat

Table 5.20. Statistics - Kopper, µg/l

Sample E

Number of participants	36	Range	14,9
Number of omitted results	4	Variance	9,0
True value	29,1	Standard deviation	3,0
Mean value	28,9	Relative standard deviation	10,4%
Median	29,1	Relative error	-0,8%

Analytical results in ascending order:

11	< 33 U	19	28,3	69	29,8
5	20,2	25	28,8	24	31,0
53	22,1	13	28,9	1	31,0
4	24,5	7	28,9	6	31,0
75	24,6 U	21	29,0	55	31,5 U
74	25,3	28	29,1	31	31,8
17	26,2	32	29,2	37	31,9
42	26,7	26	29,2	15	32,0
54	27,0	79	29,2	18	32,3
41	28,0	44	29,5	66	32,7
57	28,0	52	29,5	40	35,1
38	28,1	8	29,6	16	40,0 U

Sample F

Number of participants	36	Range	5,7
Number of omitted results	4	Variance	1,2
True value	11,7	Standard deviation	1,1
Mean value	11,5	Relative standard deviation	9,7%
Median	11,7	Relative error	-1,4%

Analytical results in ascending order:

11	< 33 U	19	11,3	6	12,0
75	5,1 U	40	11,3	15	12,0
53	7,7	13	11,3	17	12,1
74	9,5	41	11,5	25	12,2
5	10,2	21	11,5	52	12,6
42	10,5	31	11,6	37	12,7
4	10,7	79	11,7	24	13,0
38	11,0	8	11,7	1	13,0
57	11,0	28	11,8	18	13,2
54	11,0	7	11,8	66	13,4
26	11,1	32	11,9	55	16,0 U
69	11,2	44	11,9	16	25,0 U

U = Omitted resultat

Table 5.21. Statistics - Nickel, µg/l

Sample E

Number of participants	34	Range	1,5
Number of omitted results	6	Variance	0,1
True value	2,4	Standard deviation	0,3
Mean value	2,3	Relative standard deviation	13,2%
Median	2,4	Relative error	-2,8%

Analytical results in ascending order:

11	< 66 U	69	2,1	8	2,4
38	< 4,5 U	42	2,2	66	2,5
55	< 3 U	18	2,2	5	2,5
74	< 2 U	41	2,2	37	2,5
17	1,3 U	28	2,3	57	2,5
31	1,6	19	2,3	7	2,5
16	1,9	44	2,3	52	2,6
75	2,0 U	21	2,3	6	2,8
24	2,0	26	2,4	1	2,9
13	2,0	25	2,4	79	3,1
40	2,0	15	2,4		
54	2,1	32	2,4		

Sample F

Number of participants	34	Range	2,0
Number of omitted results	6	Variance	0,2
True value	6,1	Standard deviation	0,5
Mean value	6,1	Relative standard deviation	7,9%
Median	6,1	Relative error	0,3%

Analytical results in ascending order:

11	< 66 U	54	5,7	41	6,2
55	< 3 U	28	6,0	69	6,3
75	0,1 U	19	6,0	8	6,4
17	1,8 U	57	6,0	66	6,6
74	3,2 U	26	6,0	7	6,7
38	4,7 U	40	6,0	79	6,7
31	5,0	52	6,1	5	6,7
16	5,4	44	6,1	1	6,8
6	5,4	15	6,1	37	6,8
42	5,6	25	6,1	24	7,0
18	5,7	21	6,1		
13	5,7	32	6,2		

U = Omitted resultat

Table 5.22. Statistics - Zinc, µg/l

Sample E

Number of participants	36	Range	11,9
Number of omitted results	7	Variance	9,0
True value	23,6	Standard deviation	3,0
Mean value	23,9	Relative standard deviation	12,6%
Median	23,6	Relative error	1,4%

Analytical results in ascending order:

53	4,7 U	11	22,3	30	25,0
28	13,7 U	19	22,5	54	25,0
17	19,1	75	22,8 U	1	26,0
69	19,5	52	23,2	24	26,9
25	20,0 U	79	23,3	37	27,8
57	20,0	18	23,4	8	27,8
42	20,9	15	23,6	66	28,0
31	21,0	40	23,7	32	30,0
38	21,2	21	23,8	6	31,0
5	21,5	44	24,1	7	31,9 U
74	22,0	26	24,6	4	37,5 U
41	22,0	16	25,0	55	45,0 U

Sample F

Number of participants	36	Range	8,2
Number of omitted results	7	Variance	3,8
True value	12,4	Standard deviation	2,0
Mean value	12,7	Relative standard deviation	15,5%
Median	12,4	Relative error	2,2%

Analytical results in ascending order:

25	< 10 U	19	11,7	30	14,0
28	< 4,3 U	17	11,9	55	14,0 U
53	0,8 U	11	12,0	54	14,0
75	4,9 U	41	12,0	1	14,0
31	9,8	18	12,2	24	14,2
5	9,9	44	12,2	37	14,4
16	10,0	21	12,4	8	15,0
69	10,5	15	12,4	66	15,4
38	10,8	40	12,4	32	16,5
42	11,0	79	12,6	4	17,5 U
74	11,0	26	12,8	6	18,0
57	11,5	52	12,8	7	22,4 U

U = Omitted resultat