CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

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

Intercomparison 9408

pH, k_{25}, HCO_3, $NO_3 + NO_2$, Cl, SO_4, Ca, Mg, Na, K, total aluminium, TOC and COD-Mn

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Prepared by the Programme Centre,
Norwegian Institute for Water Research

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Abstract:

26 laboratories in 17 countries participated in intercomparison 9408. Based on the general target accuracy of ± 20 %, 81 % of the results were acceptable. However, for pH only 54 % and 59 % of the result pairs in the two sample sets were acceptable in relation to the extended target accuracy of ± 0.2 units. A total error of ± 0.2 units for pH measurements seems to be a reasonable assessment of the accuracy between laboratories. 23 laboratories determined the analytical variables in both the low and high concentration sample pairs. Two laboratories analyzed the low concentration samples only, and one laboratory analyzed the high concentration samples only. The part of acceptable results are approximately the same for both sample pairs.

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2. Sur nedbør	2. Acid precipitation
3. Kvalitetskontroll	3. Quality Control
4. Overvåking	4. Monitoring

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INTERNATIONAL CO-OPERATIVE PROGRAMME FOR ASSESSMENT AND MONITORING OF ACIDIFICATION OF RIVERS AND LAKES

INTERCOMPARISON 9408

pH, κ_{25}, HCO_3^-, $NO_3^- + NO_2^-$, Cl^-, SO_4^{--}
Ca^{++}, Mg^{++}, Na^+, K^+, Al, DOC and COD-Mn

Oslo, October, 1994

Written at the Programme Centre, Norwegian Institute for Water Research

SUMMARY

Intercomparison 9408 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 1994, and included the determination of major ions in two sets of natural water samples. The participants were asked to determine pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, total aluminium, dissolved organic carbon and chemical oxygen demand (COD-Mn).

Two sample sets with different concentrations were prepared for this intercomparison, one set with low concentrations and one set with high concentrations. The idea was that every participant might select the sample set that fitted best for the routine method used. However, 23 laboratories determined the analytical variables in both sample sets, 5 laboratories asked for the low concentration samples only, and one laboratory asked for the high concentration sample set. The number of acceptable results are approximately the same for both sample pairs.

The samples were sent to 29 laboratories, and 26 submitted results to the Programme Centre. 17 countries were represented in this laboratory group. From one laboratory we received the results too late to include them in this report.

As "true" value for each parameter was selected the median value of the results received from the participants. For most parameters only 2 - 5 laboratories reported results lying outside the general target accuracy of ± 20 %.

For pH the accuracy limit was extended to ± 0.2 units. 54 and 59 % of the result pairs were included by this special limit for the sample sets AB and CD, respectively. A total error of ± 0.2 units for pH measurements seems to be a reasonable assessment of the accuracy between laboratories for samples which are approximately neutral.

CONTENTS

INTRODUCTION

As stated in "Manual for Chemical and Biological Monitoring" (1), between-laboratory quality control is necessary in 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 through the 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 eighth intercomparison test, called 9408, included the determination of the main components and some other ions in natural water samples: pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, total aluminium, dissolved organic carbon and chemical oxygen demand (COD-Mn).

ACCOMPLISHMENT OF THE INTERCALIBRATION

The preparation of the sample solutions is described in Appendix 2. The results of the control analyses performed at the Programme Centre are also summarized in the same place. On the Task Force meeting in 1993 it was decided that two sample sets should be included in this intercomparison, one sample pair with low concentrations of most analytical variables, and one sample pair with higher concentrations. The idea was that laboratories using less sensitive methods routinely, should also have the possibility to analyze samples with concentrations fitting to the routine method.

The samples were mailed from the Programme Centre on June 16th, 1994. Nearly all the participating laboratories received the samples within one week. 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 four weeks after the samples arrived at the laboratory.

RESULTS

The samples were sent to 29 laboratories. The 26 laboratories who submitted results to the Programme Centre, are representing 17 countries. One laboratory returned the results too late to be included in this report. This time it was a problem that many laboratories submitted the results several weeks after the deadline. A survey of the participants and their code numbers are listed in Appendix 1.

The analytical results received from the laboratories were treated by the method of Youden (2,3). A short description of this method, and the statistical treatment of the analytical data, are presented in Appendix 3.

(The text continues on page 35)

Table 3. Statistical summary of the intercomparison 9408

Analytical variable and methods	Sample pair	True value 1	True value 2	Number of labs Total	Number of labs Excl.	Median 1	Median 2	Mean and standard deviation 1		Mean and standard deviation 2		Relative std. dev. 1	Relative std. dev. 2	Relative error, % 1	Relative error, % 2
pH	AB	7.57	6.53	24	0	7.57	6.53	7.56	0.21	6.59	0.26	2.8	4	-0.1	0.9
Electr.				22	0	7.54	6.52	7.52	0.15	6.54	0.2	2	3.1	-0.7	0.2
Equilib.				2	0			8.05		7.18				6.3	10
pH	CD	6.91	6.99	22	1	6.91	6.99	6.95	0.23	7.07	0.26	3.3	3.6	0.6	1.2
Electr.				20	0	6.91	6.99	6.91	0.13	7.03	0.14	1.9	2	0.1	0.5
Equilib.				2	1			7.84		8.1				13.5	15.9
Conductivity	AB	8.2	3.38	23	4	8.2	3.38	8.19	0.19	3.36	0.09	2.4	2.6	-0.1	-0.6
Conductivity	CD	23.45	38	21	3	23.45	38	23.35	0.64	37.72	1.02	2.7	2.7	-0.4	-0.7
Alkalinity	AB	33.3	4.13	22	2	33.3	4.13	33.22	1.33	4.44	0.92	4	20.7	-0.2	7
Alk/Gran				13	1	33.55	4.1	33.44	0.98	4.21	0.72	2.9	17	0.4	1.9
Alktitrn.				9	1	33.3	4.2	32.88	1.75	4.77	1.13	7.9	23.7	-0.4	15.5
Alkalinity	CD	22.7	41	21	0	22.7	41	23.64	3.77	42.99	7.38	16	17.2	4.1	4.9
Alk/Gran				11	0	22.85	42.5	23.9	3.51	44.54	7.32	14.7	16.4	5.3	8.6
Alktitrn.				10	0	20.75	37.45	23.34	4.21	41.29	7.45	18	18	2.8	0.7
Nitrate + nitrite-N	AB	149	1138	23	1	149	1137	154.6	23.6	1136	107.1	15.2	9.4	3.8	-0.2
Autoanal.				7	0	146	1200	150	11	1186	84	7.6	7.1	0.5	4.3
Photom.				1	1			64		479				-57	-57.9
IC				13	0	149	1136	158.4	29.2	1119	117.3	18.9	10.5	3.8	-1.7
FIA				1	0			158		1110				6	-2.4
Hydrazine				1	0			137		1030				-8.1	-9.4

Nitrate + nitrite-N	CD	2841	3912	23	3	2841	3912	2766	384	3794	501	13.9	13.2	-2.6	-3
Autoanal.				9	2	2860	4000	2875	78	4013	166	2.7	4.1	1.2	2.6
Photom.				1	1			5704		7191				100.8	83.8
IC				11	0	2869	3920	2875	179	3882	233	6.2	6	1.2	-0.8
FIA				1	0			2750		3730				-3.2	-4.6
Hydrazine				1	0			2830		3500				-0.4	-10.5
Chloride	AB	1.4	1	23	4	1.4	1	1.4	0.2	1	0.1	12.6	6.8	-0.8	0.3
IC				19	2	1.4	1	1.4	0.2	1	0.1	11	7.2	1	0.4
AA				3	1			1.2		1				-16.1	-1
Argent.				1	1			0.3		0.1				-79.8	-85.9
Chloride	CD	22.18	35.4	23	4	22.18	35.4	22.28	1.05	35.2	2.03	4.7	5.8	0.5	-0.6
IC				19	3	22.24	35.45	22.32	1.15	35.26	2.22	5.2	6.3	0.6	-0.4
AA				3	0	22.1	34.9	22.1	0.1	34.9	0.1	0.5	0.3	-0.4	-1.4
Argent.				1	1			2.19		2.12				-90.1	-94
Sulfate	AB	4.22	3.7	23	5	4.22	3.7	4.23	0.26	3.65	0.11	6.1	2.9	0.2	-1.3
IC				19	2	4.2	3.7	4.19	0.22	3.66	0.1	5.3	2.8	-0.6	-1.1
Photom.				4	3			4.8		3.5				13.7	-5.4
Sulfate	CD	15.55	24.32	23	5	15.55	24.37	15.71	0.94	24.43	1.01	6	4.1	1	0.5
IC				19	3	15.5	24.32	15.44	0.53	24.22	0.66	3.5	2.7	-0.7	-0.4
Photom.				4	2			17.9		26.15				15.1	7.5
Calcium	AB	3	2.01	22	0	3	2.01	3.03	0.21	2.03	0.17	6.9	8.2	1.1	0.8
FAAS				13	0	3	2.01	3	0.17	1.99	0.16	5.8	8.1	0	-0.9
ICP				4	0	3	2	2.97	0.13	1.99	0.07	4.2	3.3	-0.9	-1.1
IC				4	0	3.11	2.08	3.16	0.36	2.16	0.24	11.4	11	5.4	7.2
ICP-MS				1	0			3.2		2.1				6.7	4.5
Calcium	CD	15.05	19.65	22	0	15.05	19.65	15.09	1.11	19.89	1.74	7.3	8.8	0.2	1.2
FAAS				13	0	15	19.4	14.8	0.81	19.56	1.5	5.5	7.7	-1.6	-0.4
ICP				4	0	15.25	19.85	14.95	0.78	19.4	1.08	5.2	5.6	-0.7	-1.3
IC				4	0	16.34	21.3	16.41	1.5	21.66	2.4	9.1	11.1	9	10.2
ICP-MS				1	0			14		19				-7	-3.3

Magnesium	AB	0.39	0.3	22	1	0.39	0.3	0.39	0.03	0.3	0.03	7.2	9.9	-0.8	1
FAAS				13	0	0.39	0.3	0.39	0.03	0.3	0.04	8.8	11.9	-0.6	0
ICP				4	0	0.38	0.3	0.37	0.01	0.3	0.01	2.6	2.8	-4	0.3
IC				4	1	0.4	0.31	0.4	0.02	0.32	0.03	3.9	8.3	1.7	6.7
ICP-MS				1	0			0.4		0.3				2.6	0
Magnesium	CD	3	4.57	22	1	3	4.57	3	0.13	4.56	0.26	4.2	5.8	0.1	-0.3
FAAS				13	0	3	4.5	2.98	0.13	4.52	0.29	4.4	6.3	-0.5	-1
ICP				4	0	3.04	4.54	3.02	0.13	4.54	0.24	4.3	5.2	0.7	-0.6
IC				4	1	3.08	4.67	3.1	0.07	4.75	0.23	2.2	4.9	3.4	3.9
ICP-MS				1	0			2.9		4.5				-3.3	-1.5
Sodium	AB	15.2	3.61	22	1	15.2	3.62	15.39	0.74	3.7	0.21	4.8	5.6	1.3	2.5
FAAS				8	0	15	3.62	15.09	0.39	3.66	0.13	2.6	3.7	-0.7	1.4
ICP				6	0	15.4	3.66	15.55	0.9	3.81	0.33	5.8	8.8	2.3	5.5
AES				3	0	15.1	3.6	15.1	0.9	3.67	0.12	6	3.1	-0.7	1.6
IC				4	1	15.4	3.75	15.93	0.92	3.7	0.09	5.8	2.3	4.8	2.5
ICP-MS				1	0			16.1		3.5				5.9	-3
Sodium	CD	25.7	52.4	22	2	25.7	52.4	25.88	0.94	52.83	1.94	3.6	3.7	0.7	0.8
FAAS				8	0	25.21	52	25.48	0.45	52.13	1.08	1.7	2.1	-0.8	-0.5
ICP				6	0	27.05	54.55	26.68	1.3	54.28	2.57	4.9	4.7	3.8	3.6
AES				3	0	25.7	52.9	25.57	0.32	52.37	2.15	1.3	4.1	-0.5	-0.1
IC				4	2			25.9		52.65				0.8	0.5
ICP-MS				1	0			25.1		51.4				-2.3	-1.9
Potassium	AB	0.27	0.27	22	3	0.27	0.27	0.274	0.04	0.268	0.04	12.8	13.8	1.5	-0.7
FAAS				9	0	0.27	0.27	0.267	0.03	0.267	0.02	11.8	8.7	-1.1	-1.1
ICP				4	2			0.33		0.33				20.4	20.4
AES				3	0	0.29	0.26	0.28	0.05	0.27	0.05	16.4	17	3.7	0
IC				4	1	0.25	0.25	0.25	0.02	0.25	0.02	6	6	-6.2	-6.2
ICP-MS				2	0			0.28		0.23				1.9	-14.8

Potassium	CD	7.91	11.8	21	1	7.91	11.8	7.8	0.66	11.57	1.29	8.5	11.2	-1.4	-2
FAAS				9	0	8.1	12.05	8.11	0.35	12.13	0.7	4.3	5.8	2.5	2.8
ICP				4	0	7.6	11.6	7.7	0.76	11.05	2.04	9.9	18.4	-2.7	-6.3
AES				2	0			8.03		11.85				1.5	0.4
IC				4	1	7.04	10.28	6.93	0.93	10.24	1.08	13.4	10.5	-12.4	-13.2
ICP-MS				2	0			7.7		11.75				-2.7	-0.4
Aluminium	AB	166	109	16	0	166	109	159	26	102	20	16.6	20	-4.1	-6.4
FAAS				2	0			158		104				-5.1	-5
GFAAS				5	0	179	115	172	28	110	18	16.1	16	3.9	0.6
ICP				3	0	140	90	139	31	97	31	22.3	31.6	-16.1	-11.3
ICP-MS				3	0	170	108	174	11	109	3	6.4	2.9	5	0.3
Photom.				3	0	147	79	143	29	87	30	20.4	34.9	-13.9	-20.5
Aluminium	CD	148	530	15	2	148	530	140	24	507	69	17	13.5	-5.6	-4.4
FAAS				2	0			144		512				-2.7	-3.5
GFAAS				4	1	152	500	154	13	477	107	8.2	22.5	3.8	-10
ICP				3	1			124		461				-16.6	-13
ICP-MS				3	0	150	566	151	4	560	13	2.8	2.2	2.3	5.7
Photom.				3	0	136	501	122	32	509	57	26	11.2	-17.3	-3.9
Diss. org. carbon	AB	5.4	3.1	14	1	5.4	3.1	5.35	0.41	3.08	0.4	7.62	12.98	0.92	0.65
Combust.				8	1	5.4	3.2	5.34	0.49	2.96	0.49	9.22	16.4	-0.19	-4.52
UV/S2O8				5	0	5.4	3.4	5.4	0.34	3.28	0.22	6.28	6.61	0	5.81
Phenolphthalein				1	0			5.1		3				-15.7	-13.1
Diss. org. carbon	CD	60	109.1	13	0	60	109.1	60.4	5.4	108.3	7	9	6.4	0.7	-0.7
Combust.				7	0	61	109	60.4	2.9	108.1	4	4.9	3.7	0.7	-0.9
UV/S2O8				5	0	57	109.1	59.9	8.6	107.4	10.5	14.3	9.8	-0.1	-1.6
Phenolphthalein				1	0			62.8		114.4				4.7	4.9
Ch. oxygen demand	AB	6.6	3.9	5	0	6.6	3.9	7.1	1.1	3.7	0.6	15.3	17.4	7.4	-4.5
Volum.				5	0	6.6	3.9	7.1	1.1	3.7	0.6	15.3	17.4	7.4	-4.5
Ch. oxygen demand	CD	81.2	154	4	0	81.2	154	79.1	11.7	151	26.1	14.8	17.3	-2.6	-1.9
Volum.				4	0	81.2	154	79.1	11.7	151	26.1	14.8	17.3	-2.6	-1.9

Fig. 1. pH

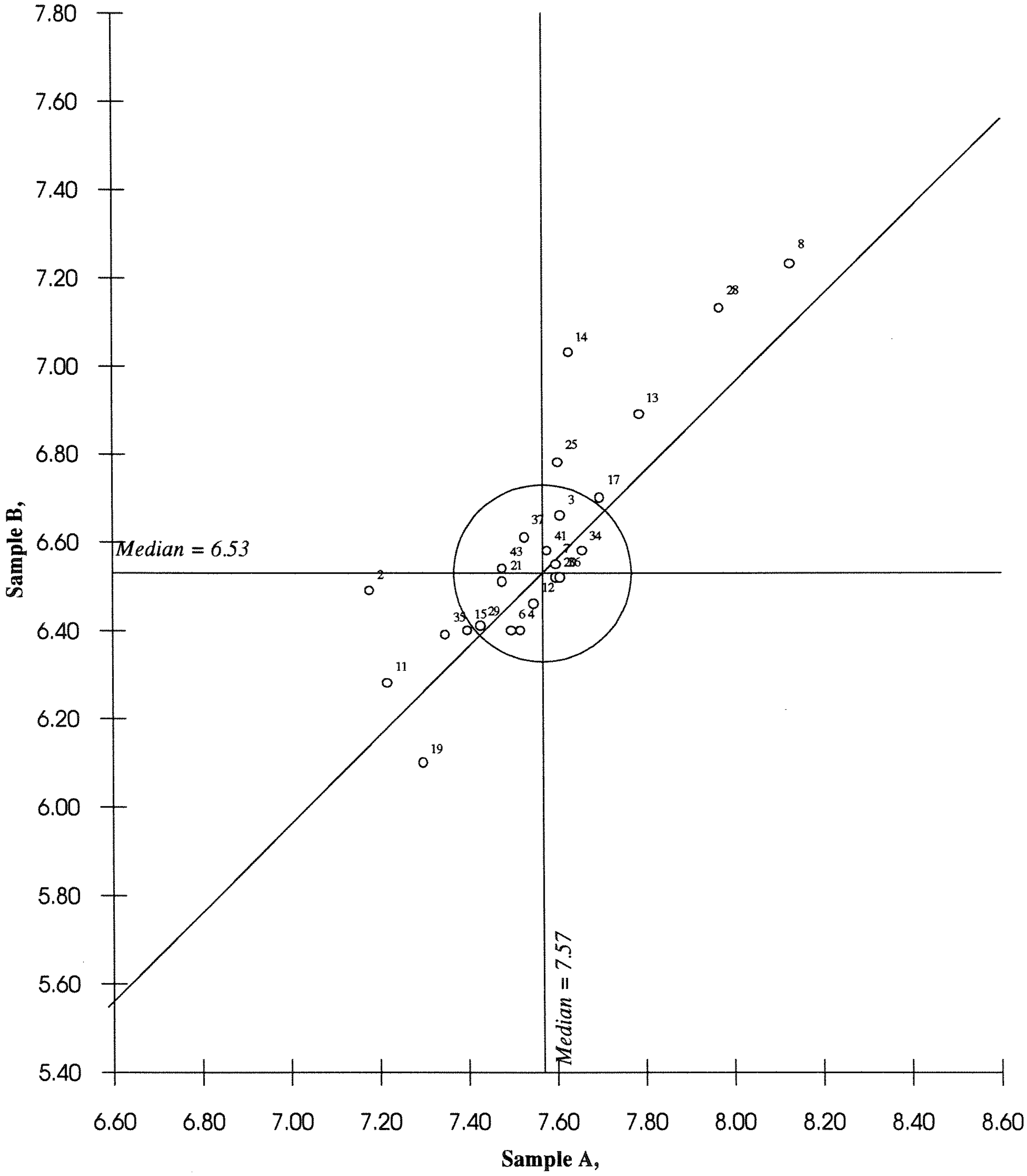
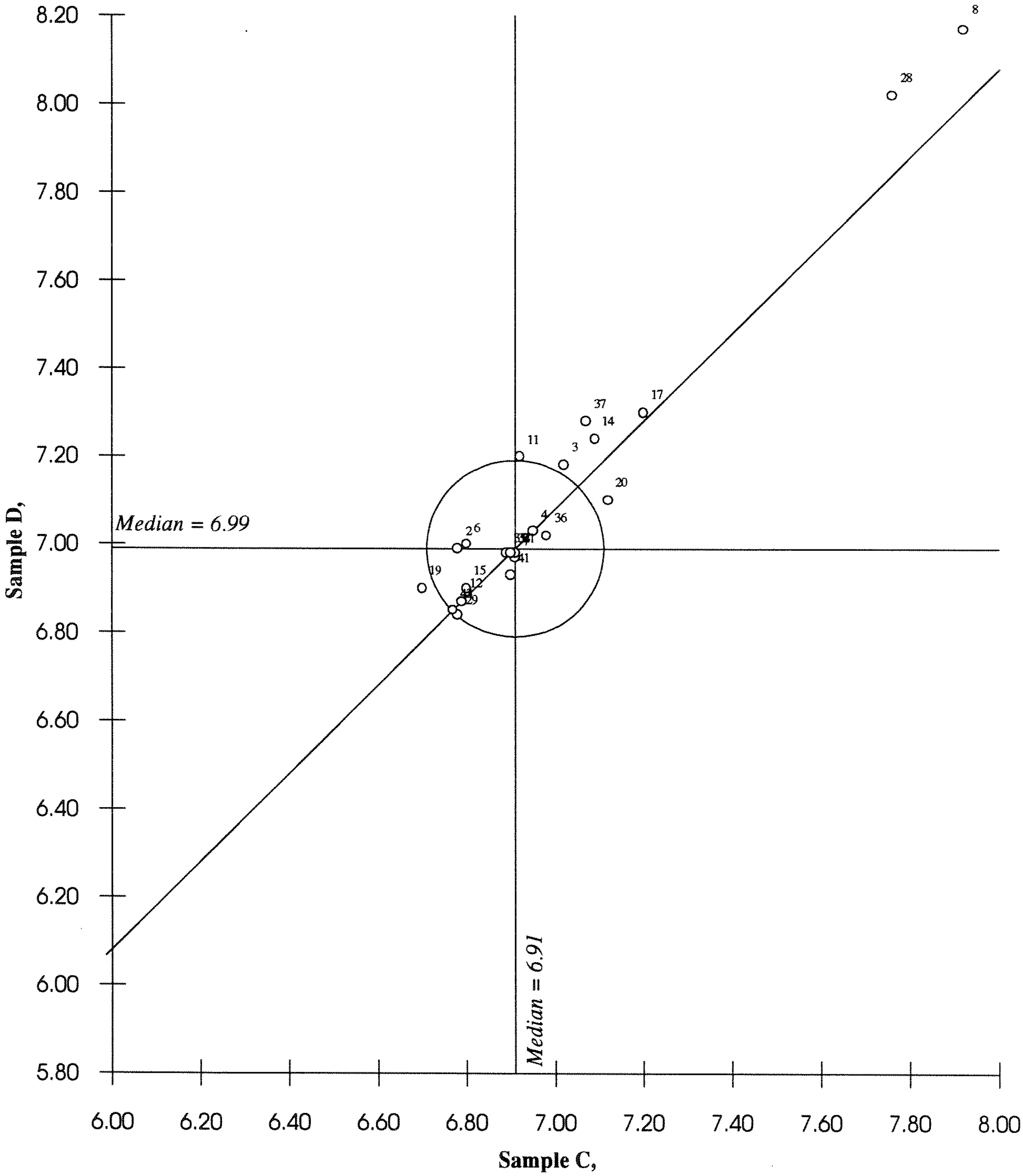

7.80
7.60
7.40
7.20
7.00
6.80
6.60
6.40
6.20
6.00
5.80
5.60
5.40
Sample B,
Median = 6.53
Median = 7.57
6.60
6.80
7.00
7.20
7.40
7.60
7.80
8.00
8.20
8.40
8.60
Sample A,

Fig. 2. pH



8.20
8.00
7.80
7.60
7.40
7.20
7.00
6.80
6.60
6.40
6.20
6.00
5.80
Sample D,
Median = 6.99
Median = 6.91
6.00
6.20
6.40
6.60
6.80
7.00
7.20
7.40
7.60
7.80
8.00
Sample C,
8
28
17
37
14
11
3
20
4
36
2
6
19
15
12
29
41

Fig. 3. Conductivity

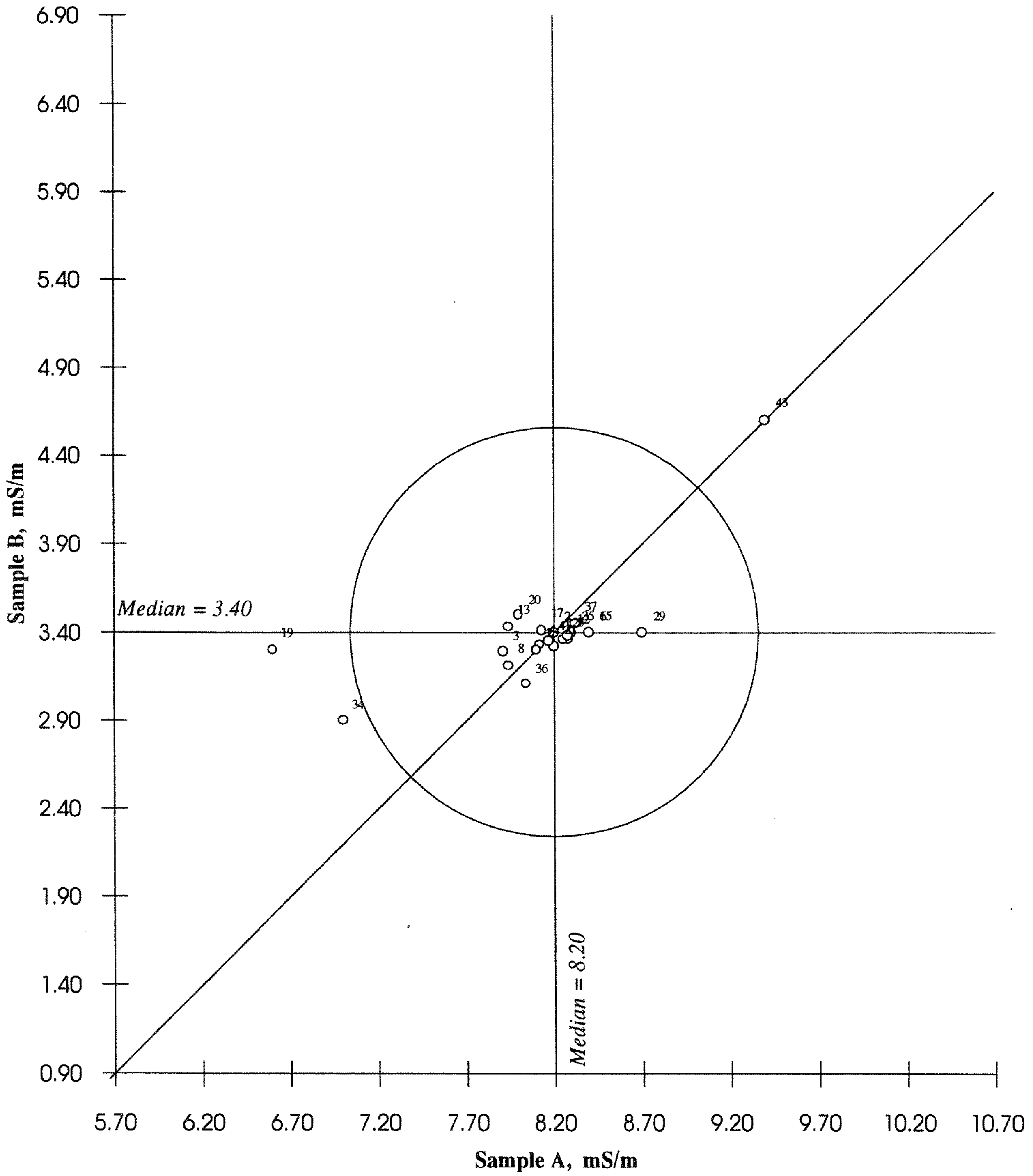


Fig. 4. Conductivity

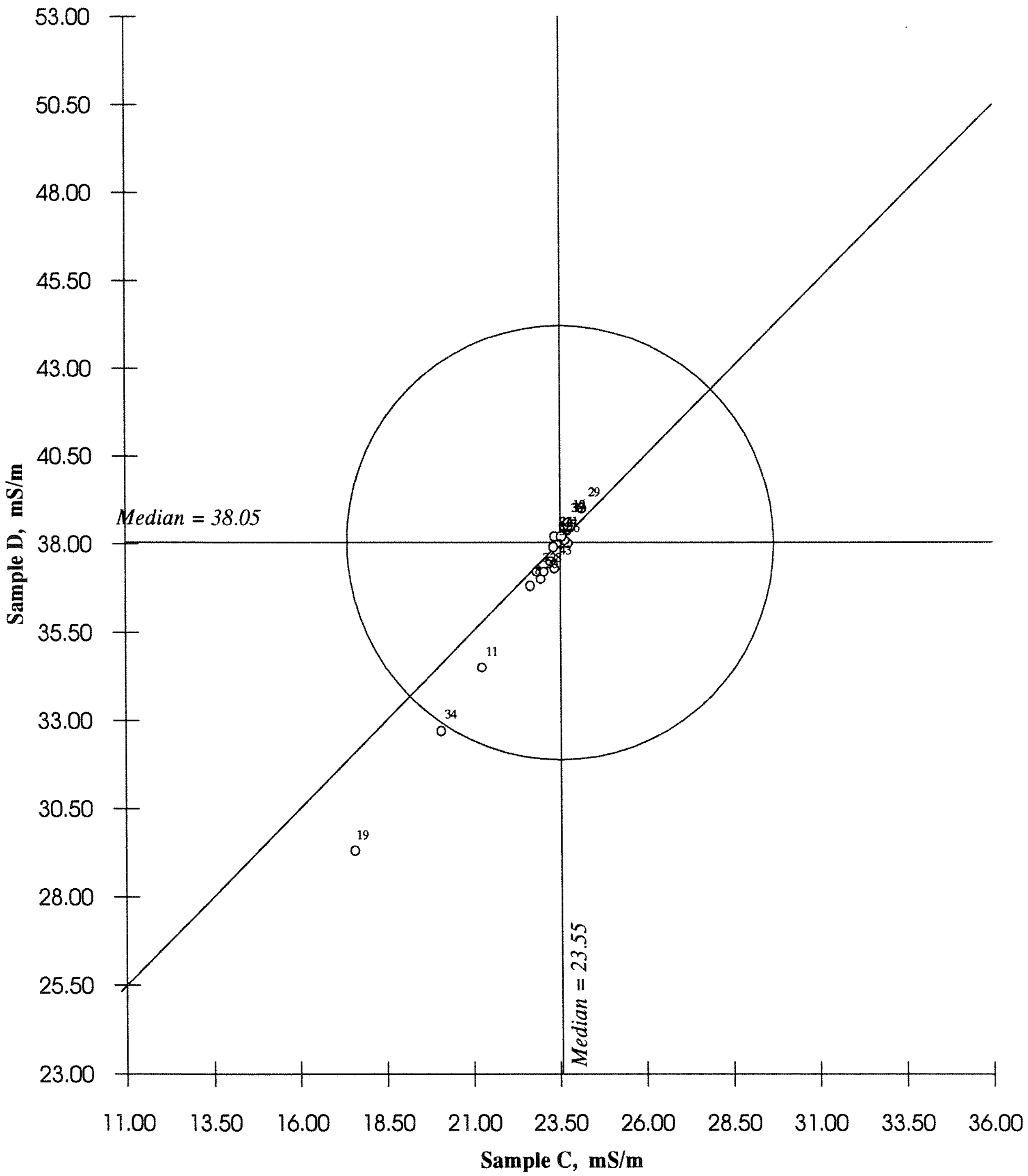


Fig. 5. Alkalinity

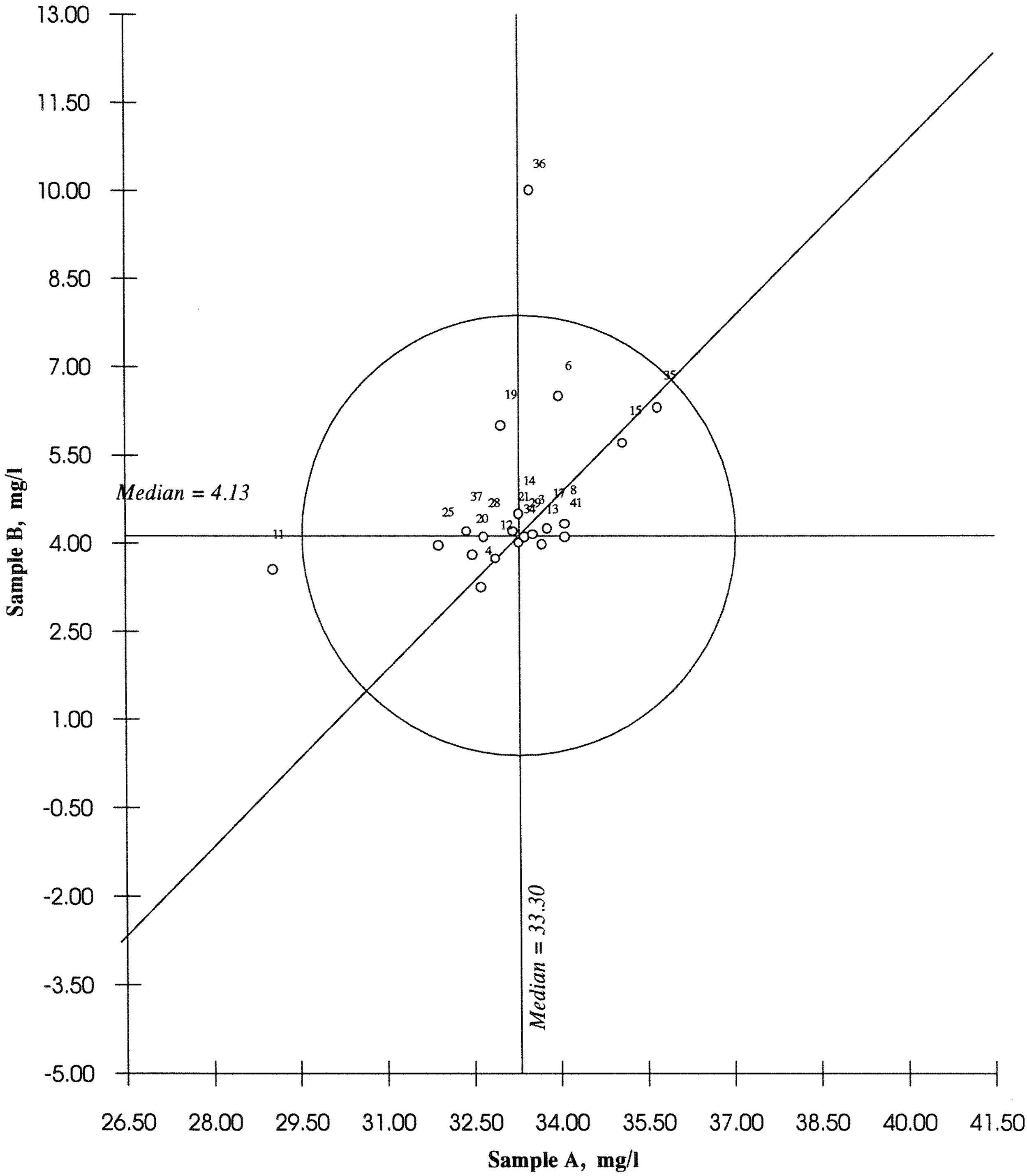


Fig. 6. Alkalinity

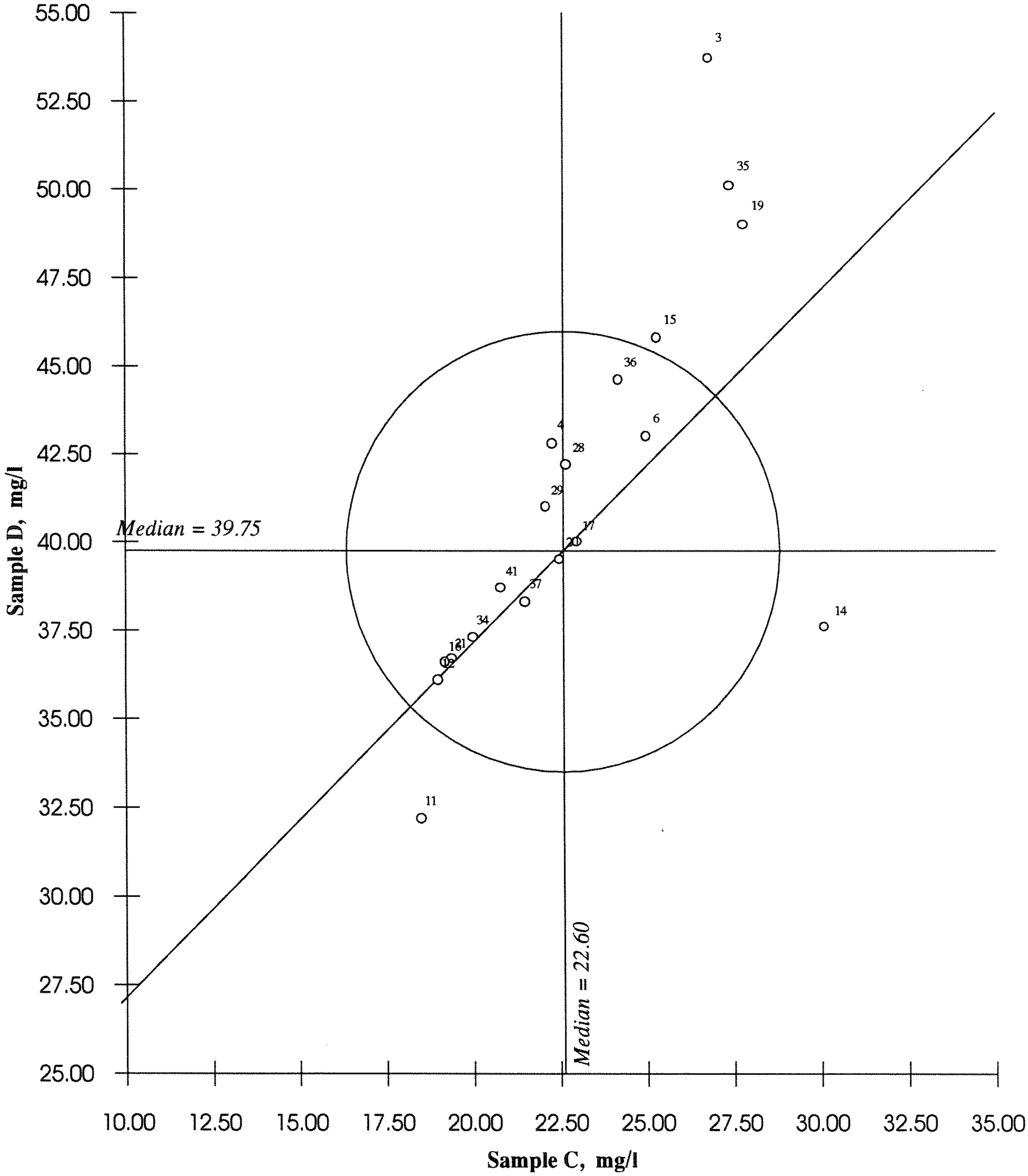


Fig. 7. Nitrate + nitrite-nitrogen

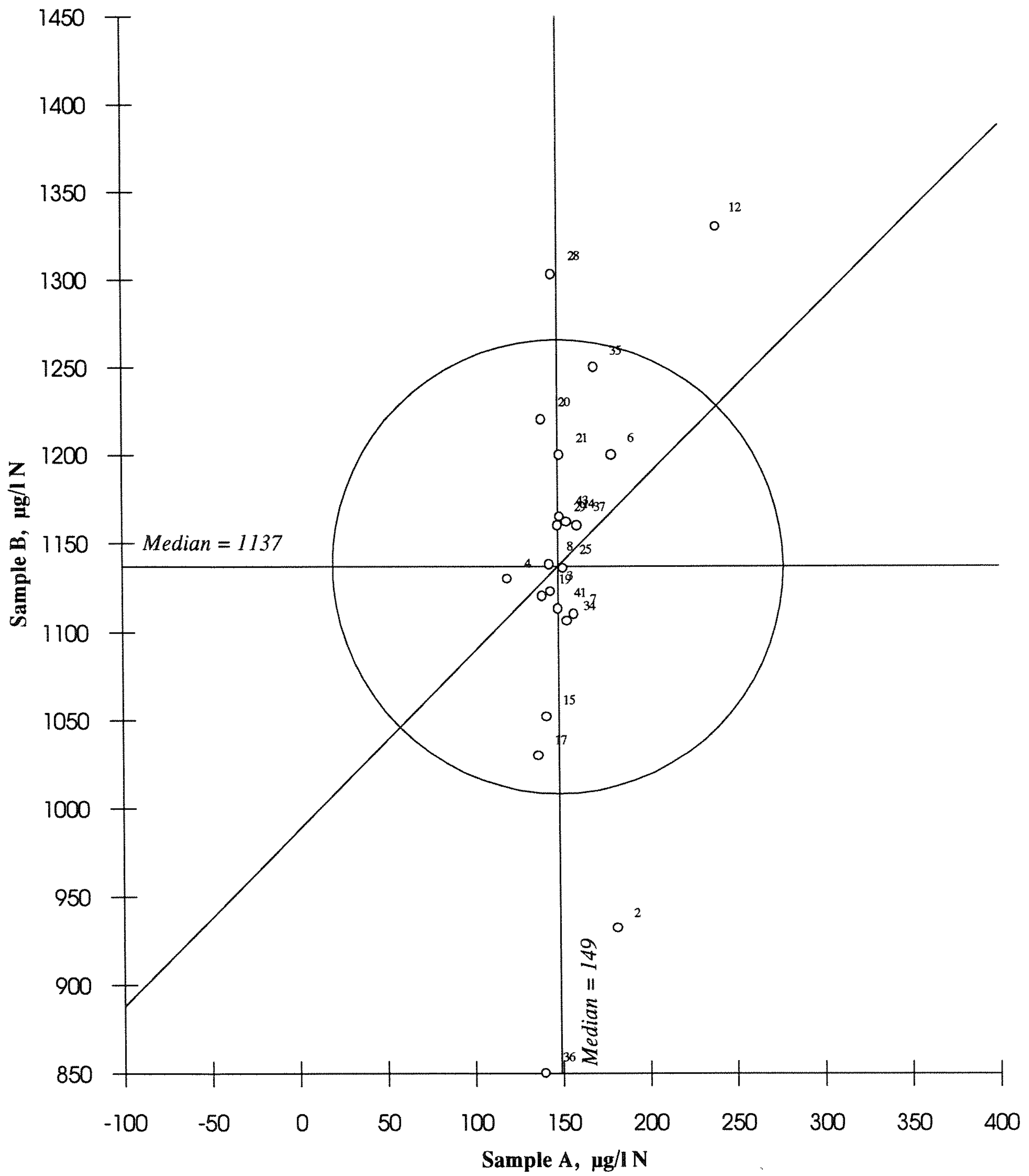


Fig. 8. Nitrate + nitrite-nitrogen

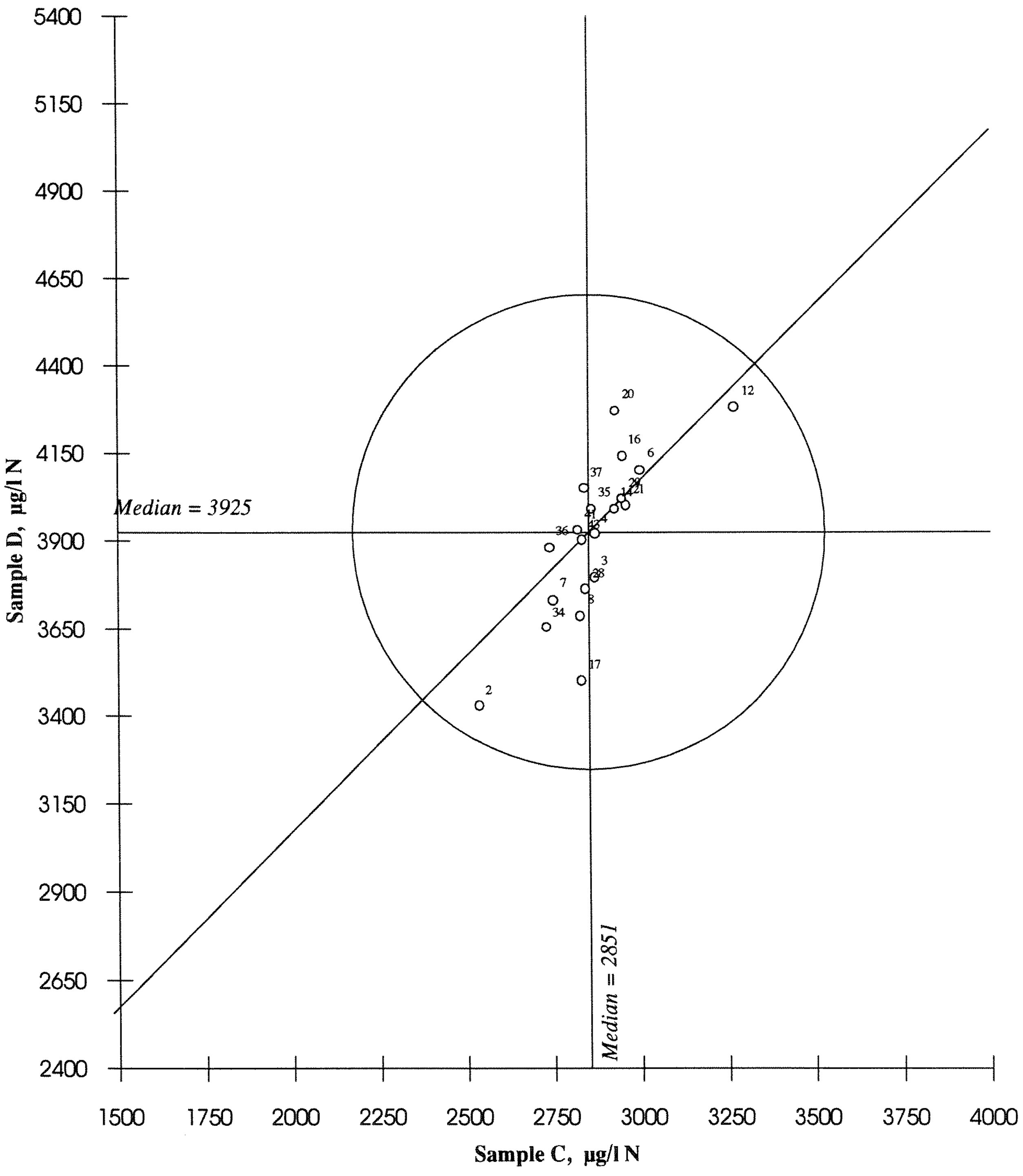


Fig. 9. Chloride

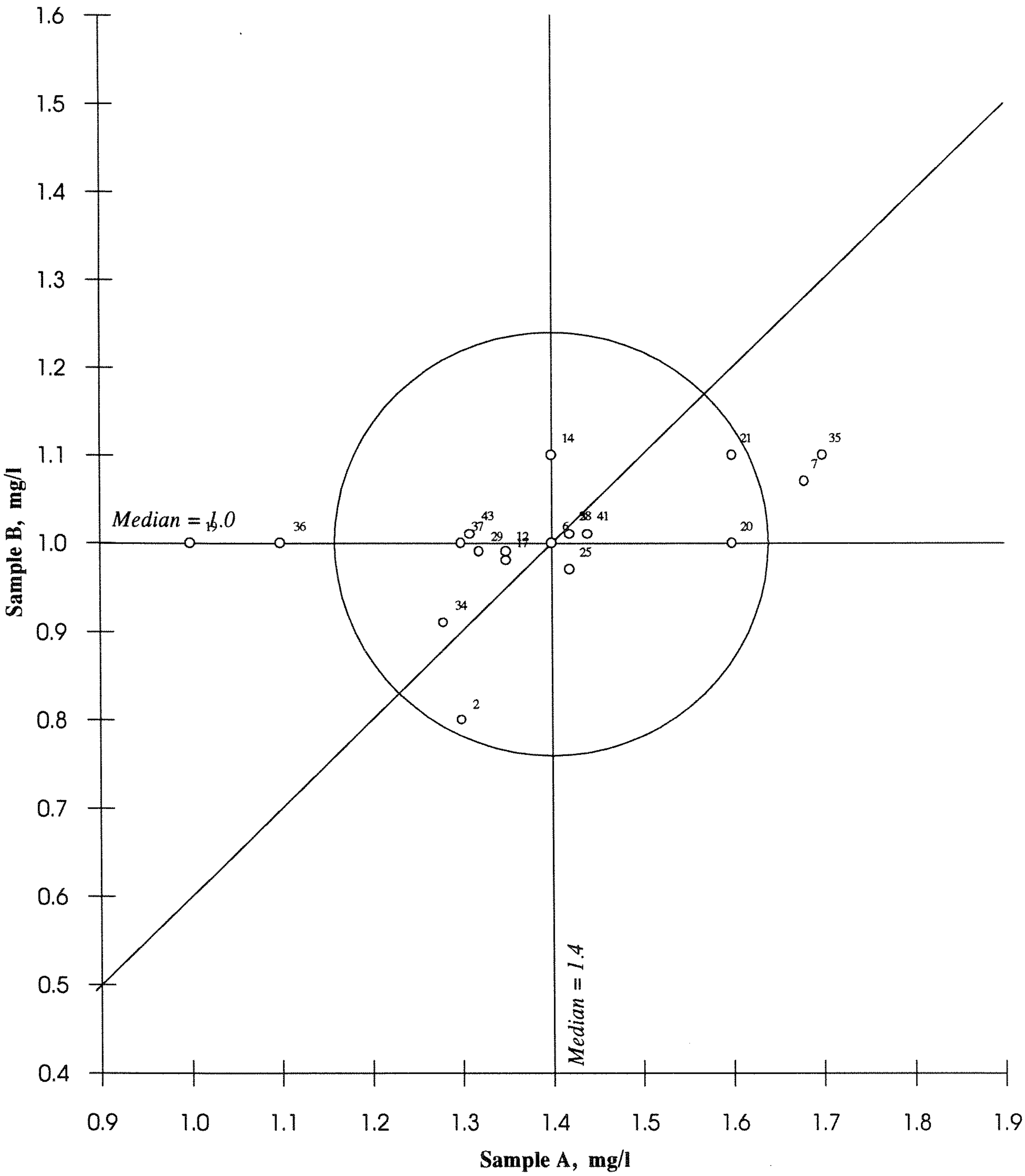


Fig. 10. Chloride

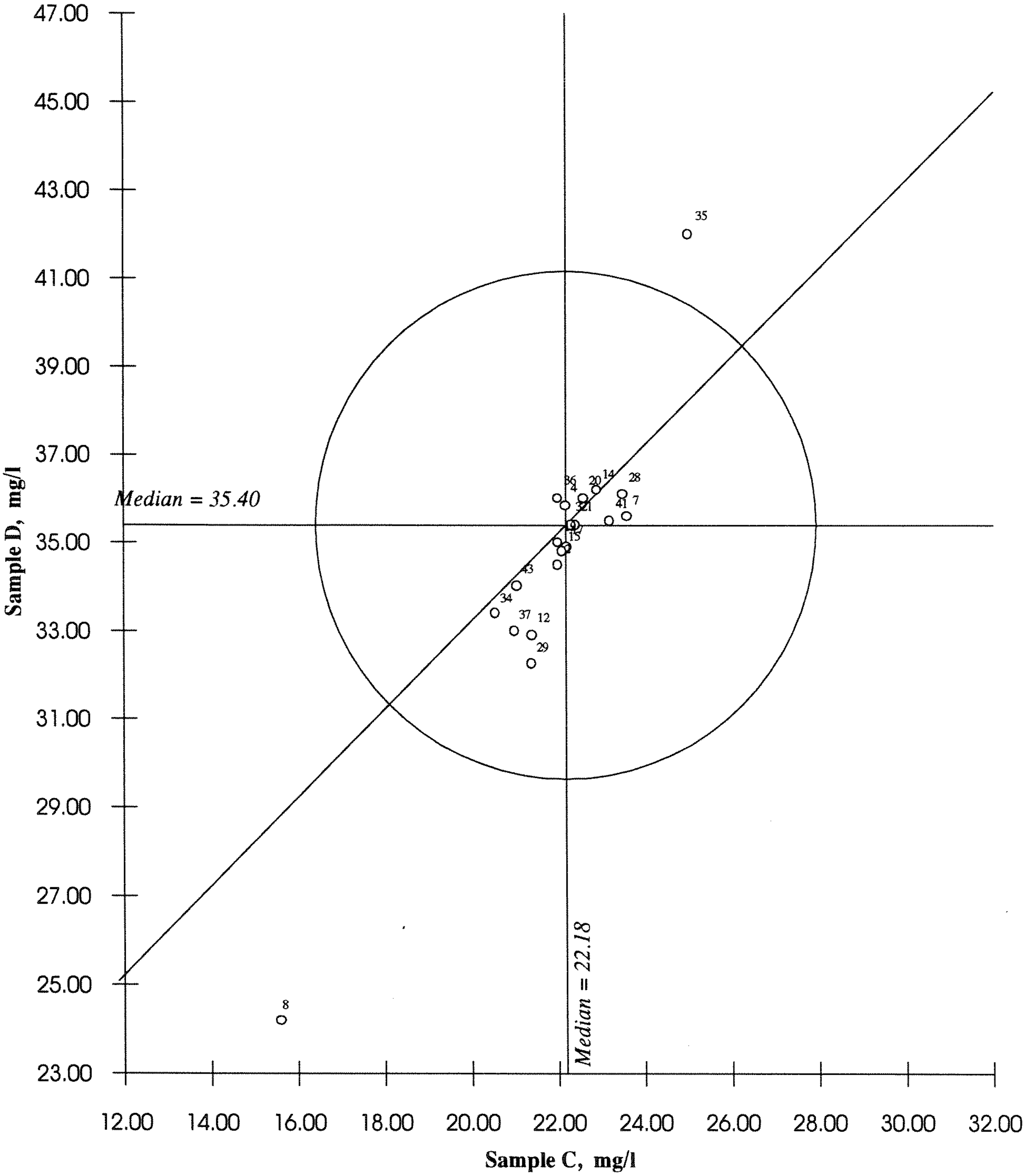


Fig. 11. Sulfate

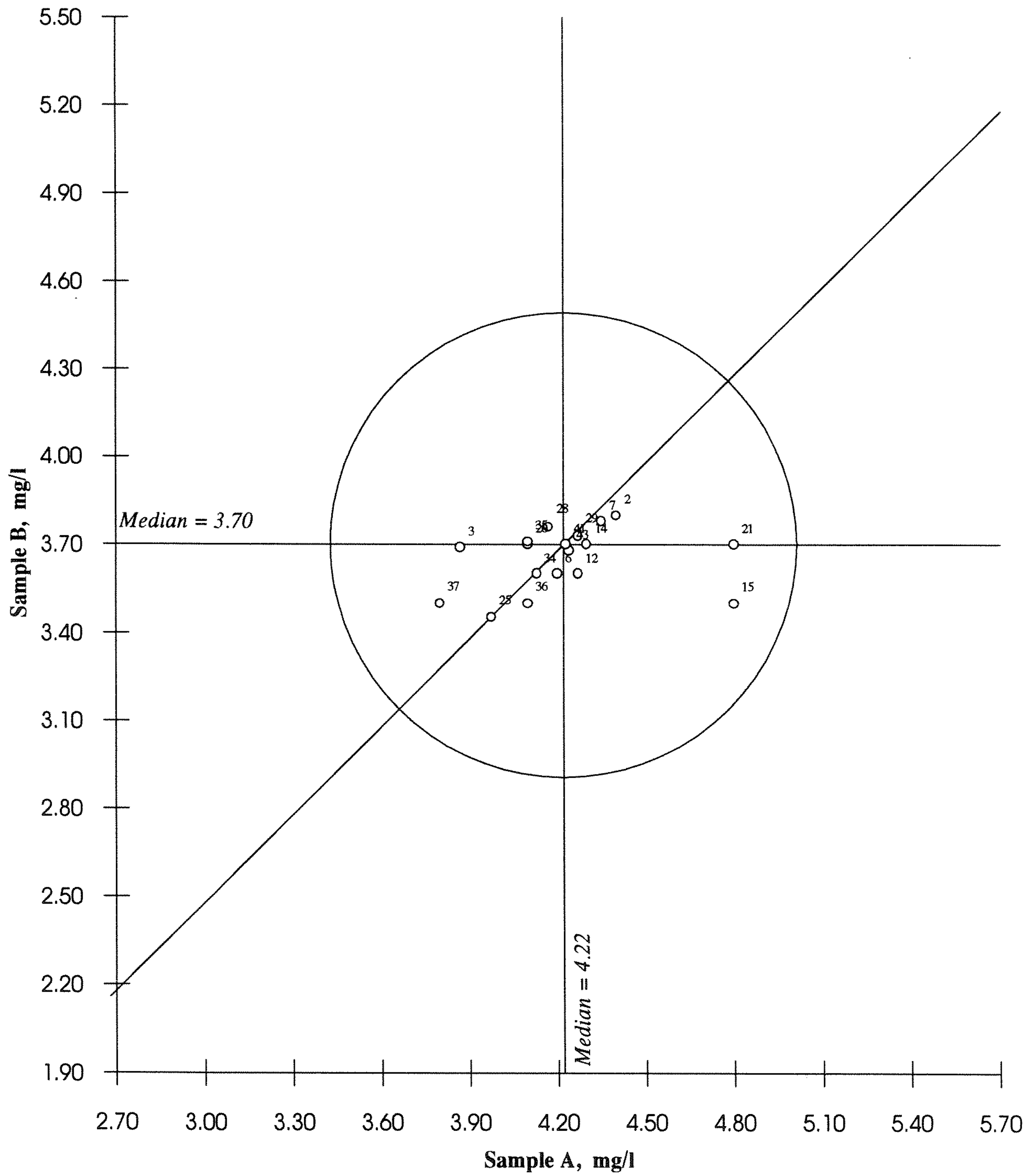


Fig. 12. Sulfate

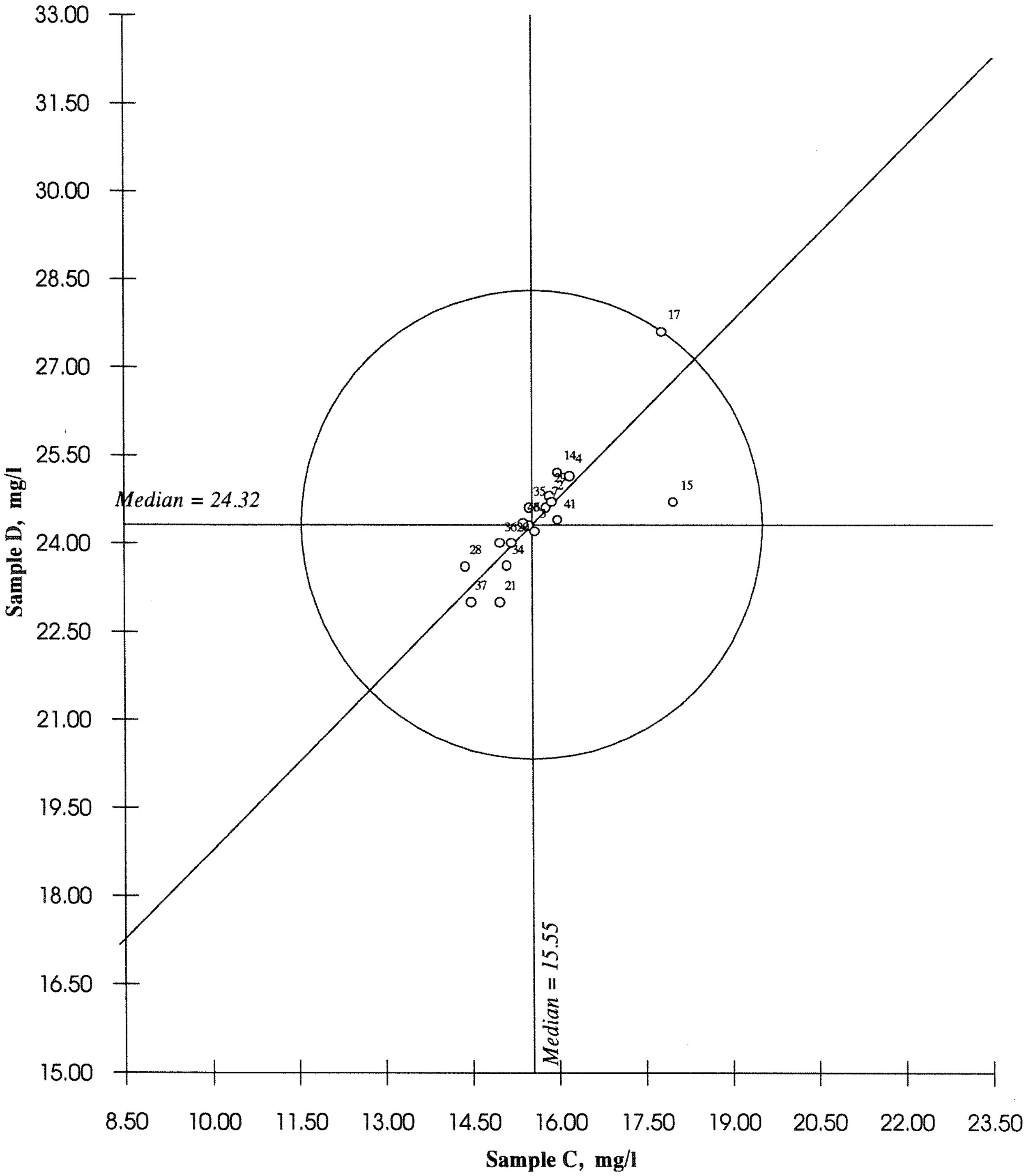


Fig. 13. Calcium

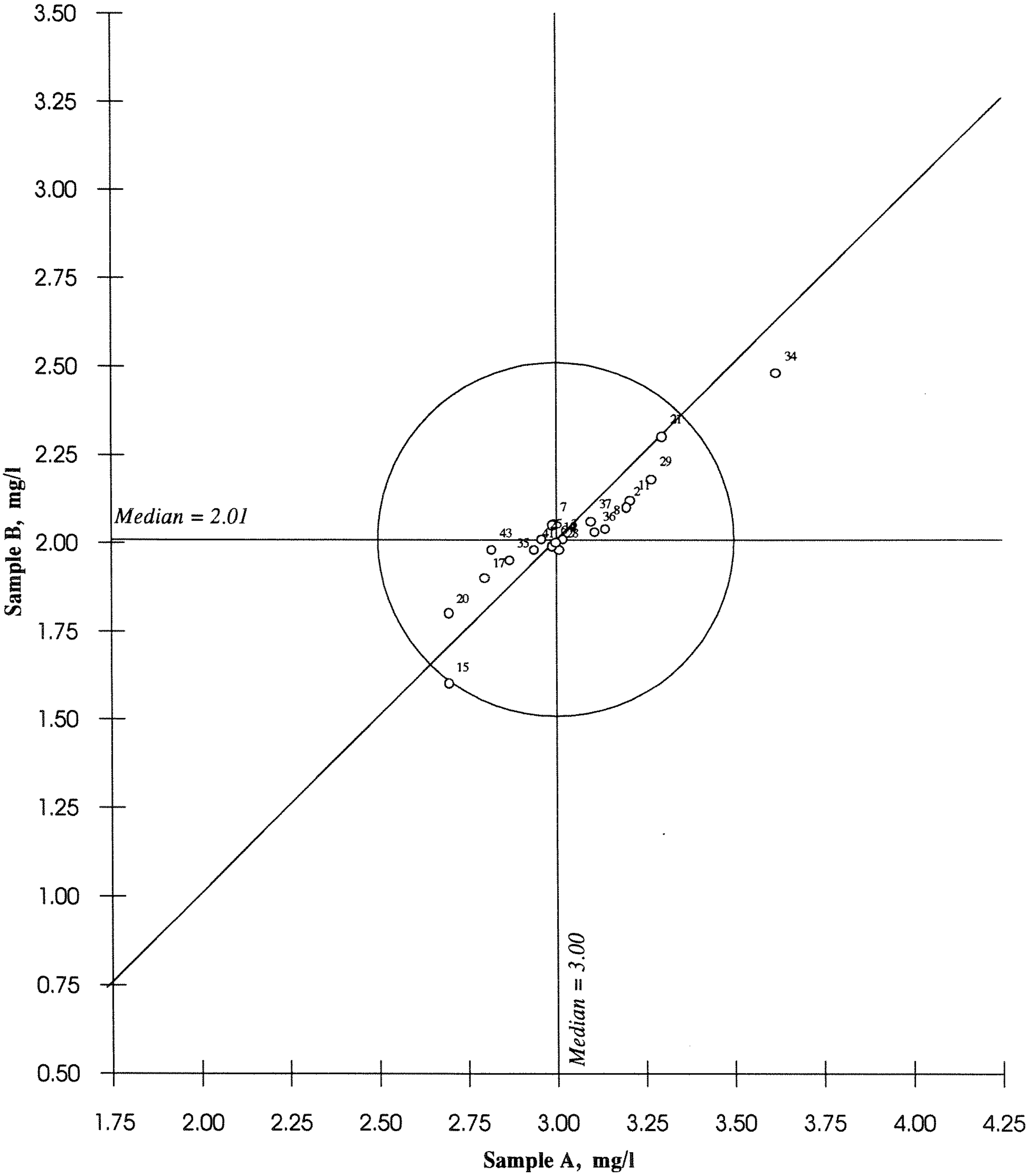


Fig. 14. Calcium

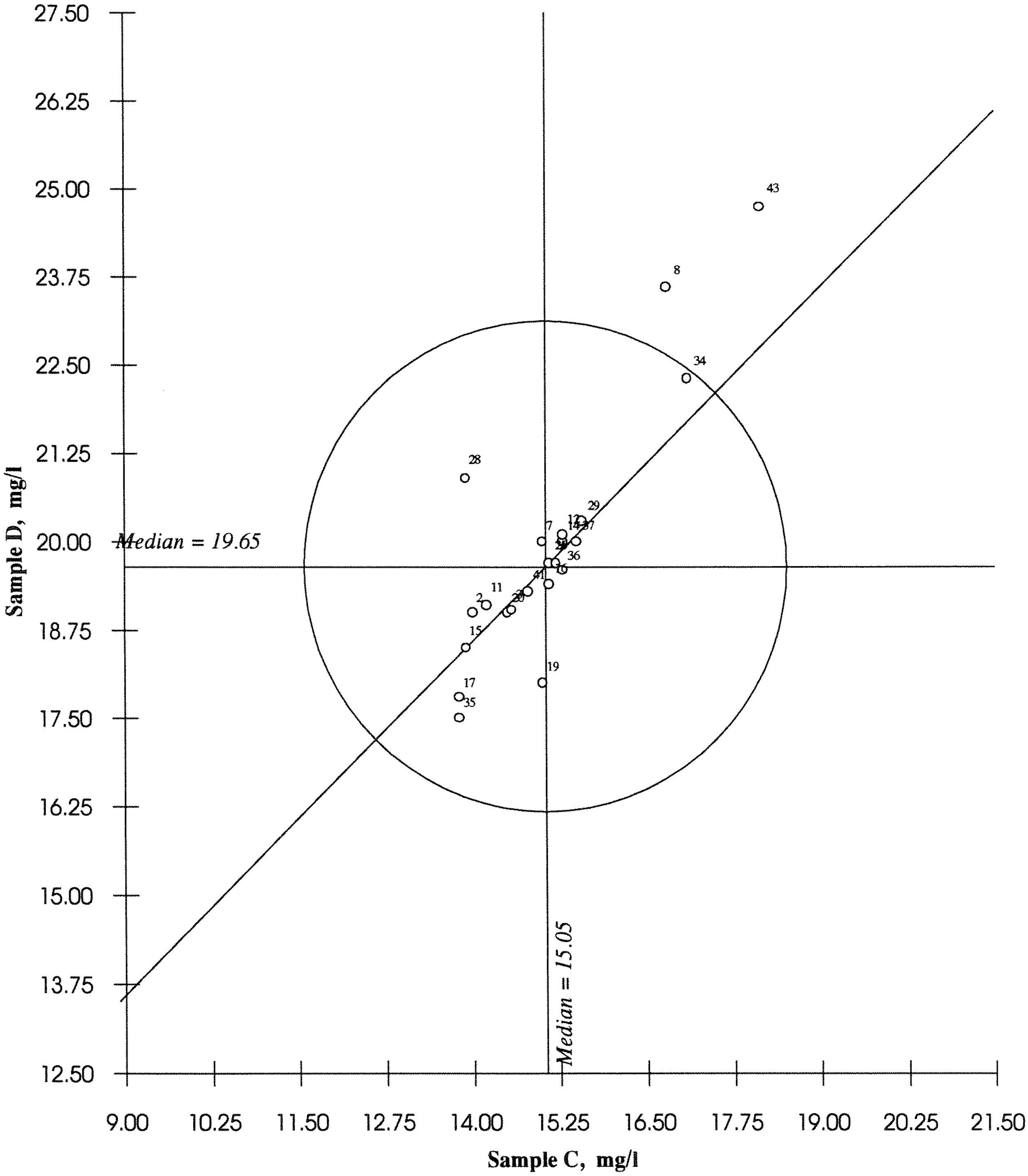


Fig. 15. Magnesium

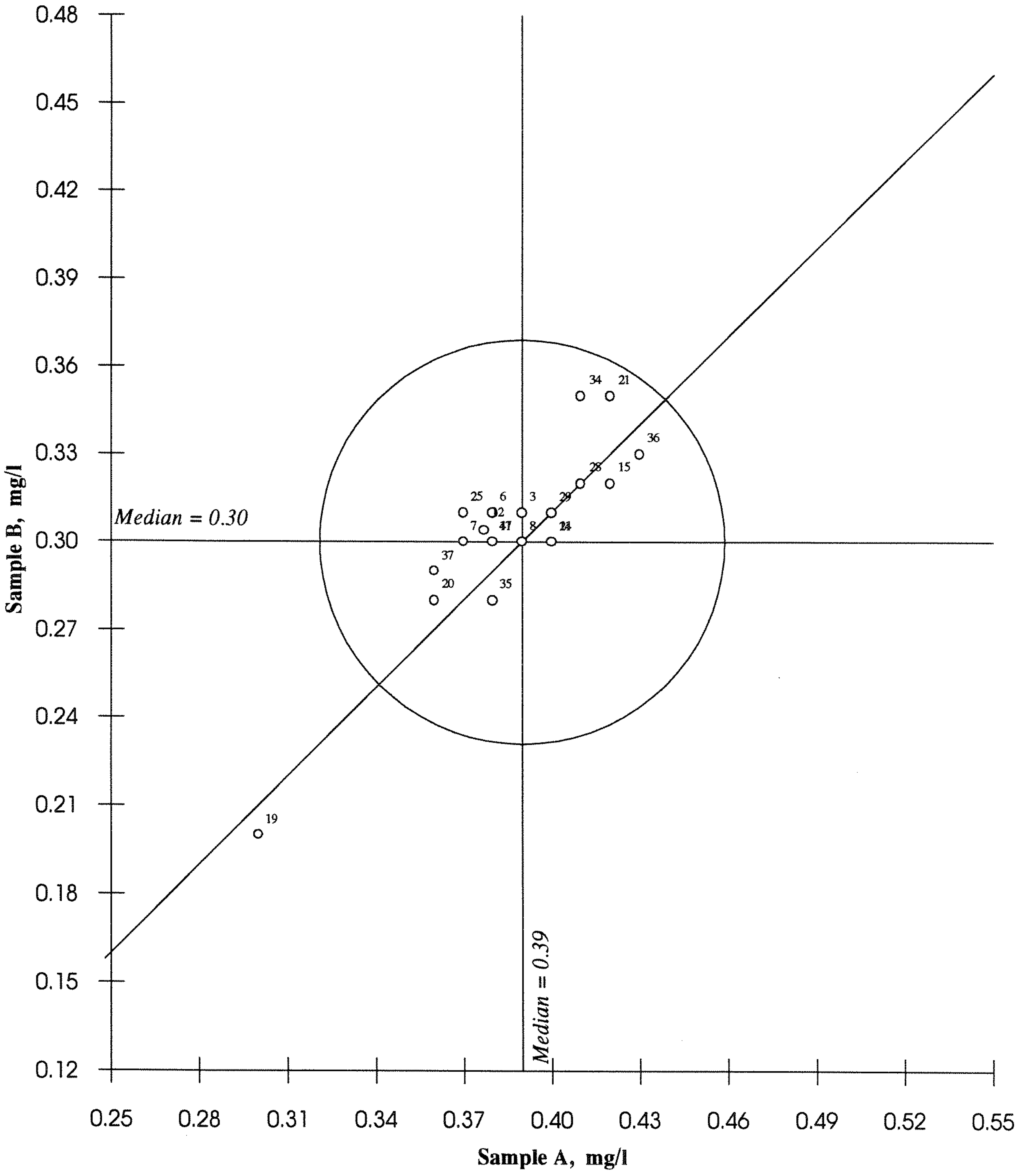


Fig. 16. Magnesium

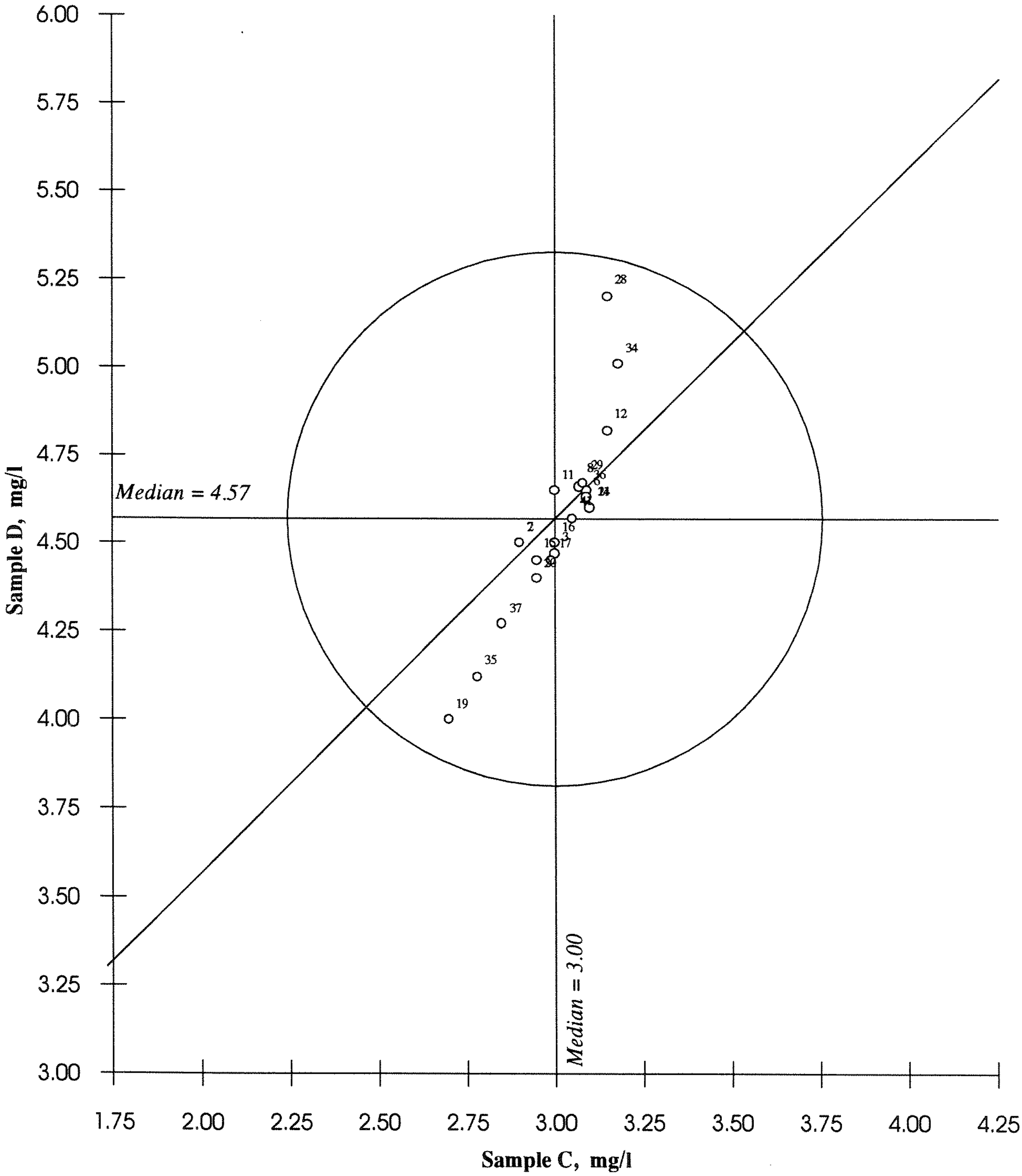


Fig. 17. Sodium

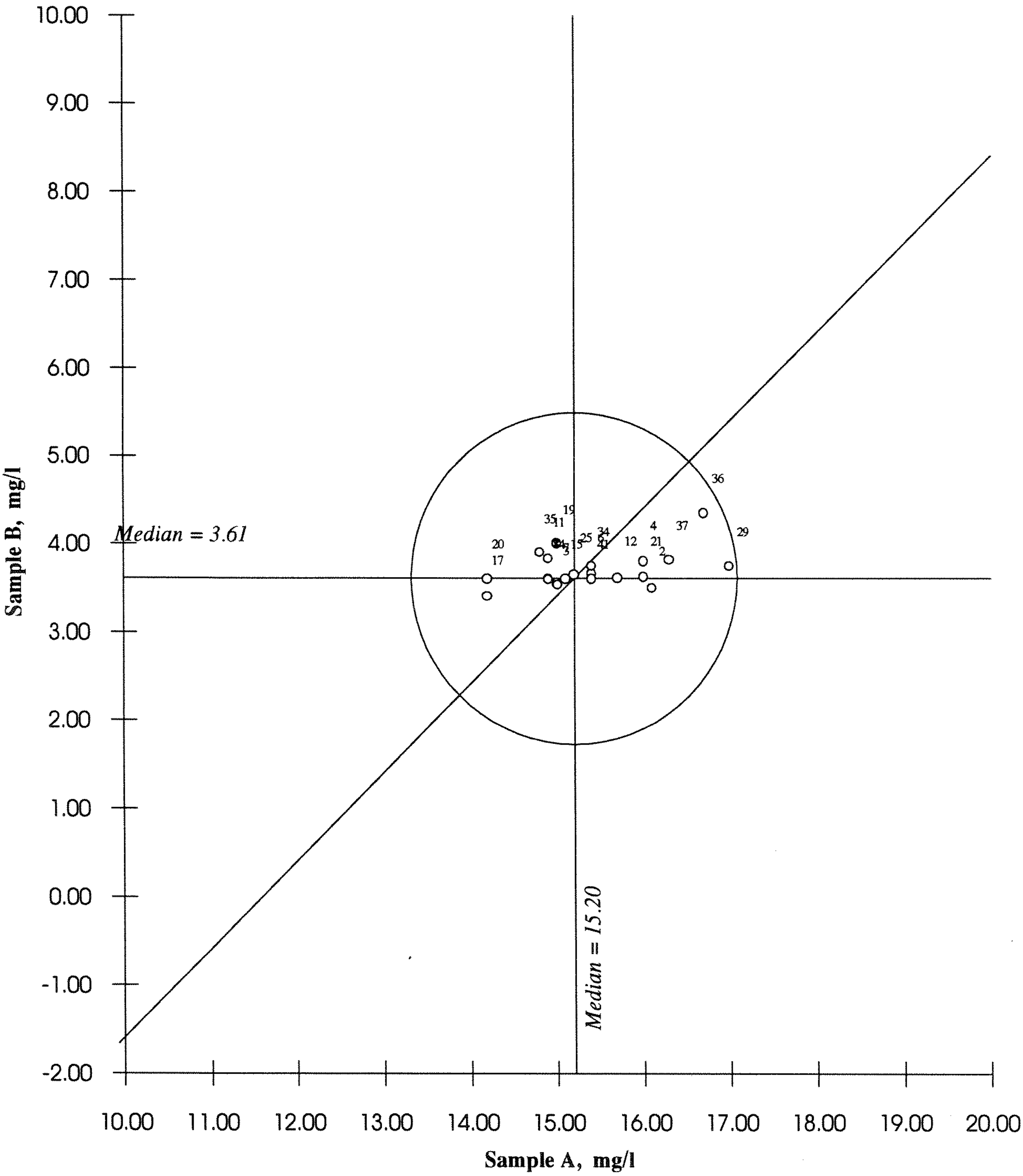


Fig. 18. Sodium

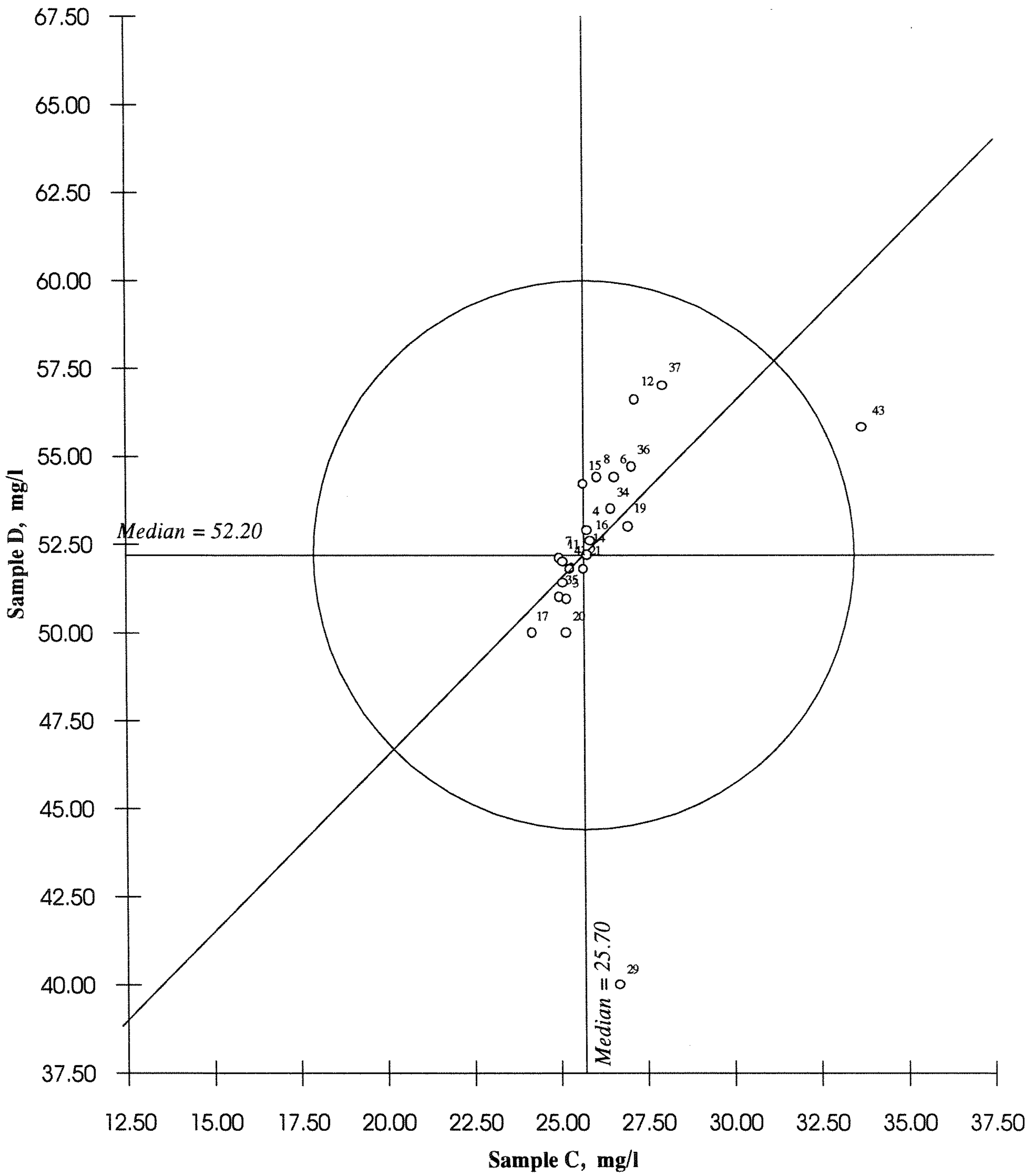


Fig. 19. Potassium

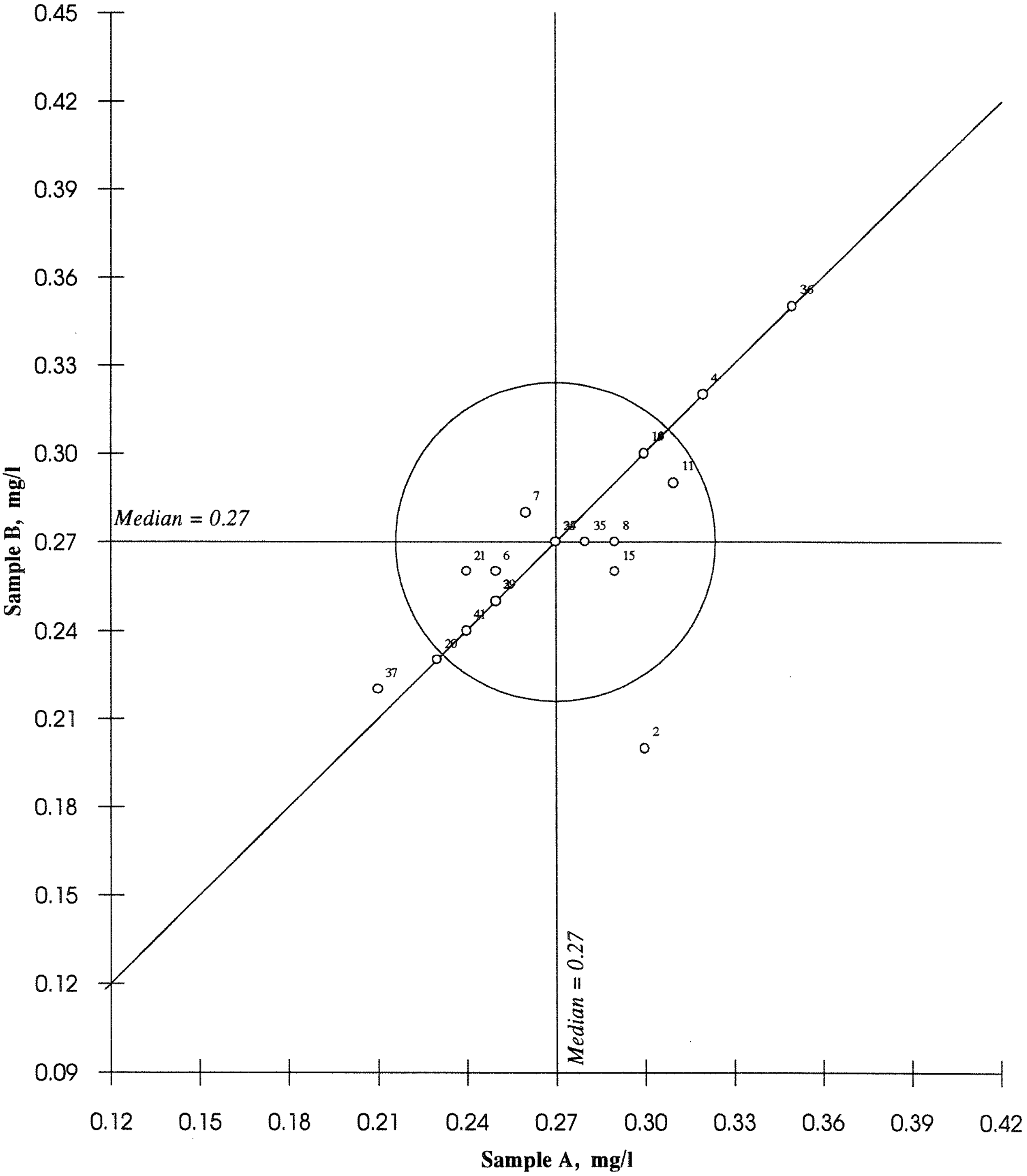


Fig. 20. Potassium

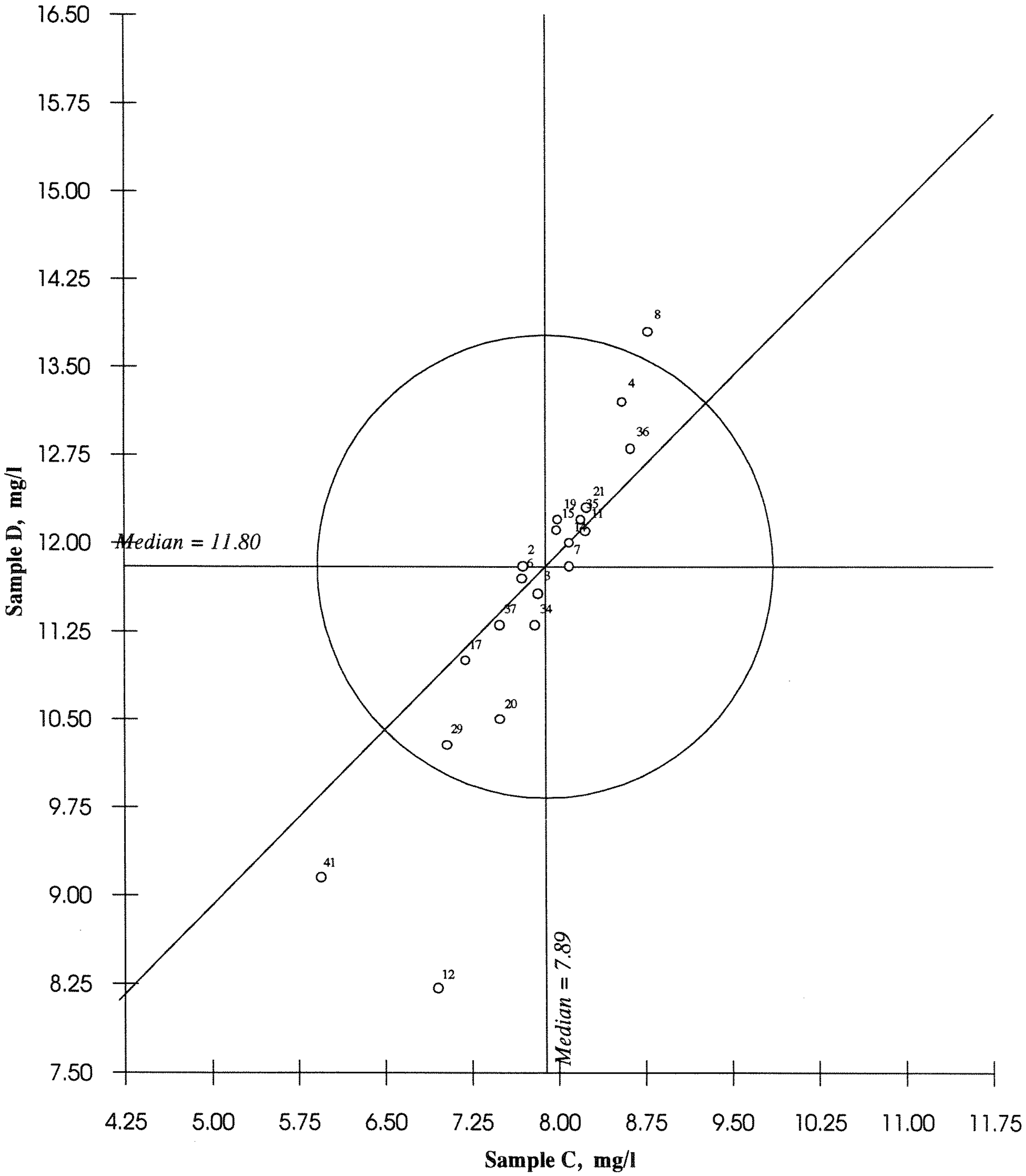


Fig. 21. Aluminium

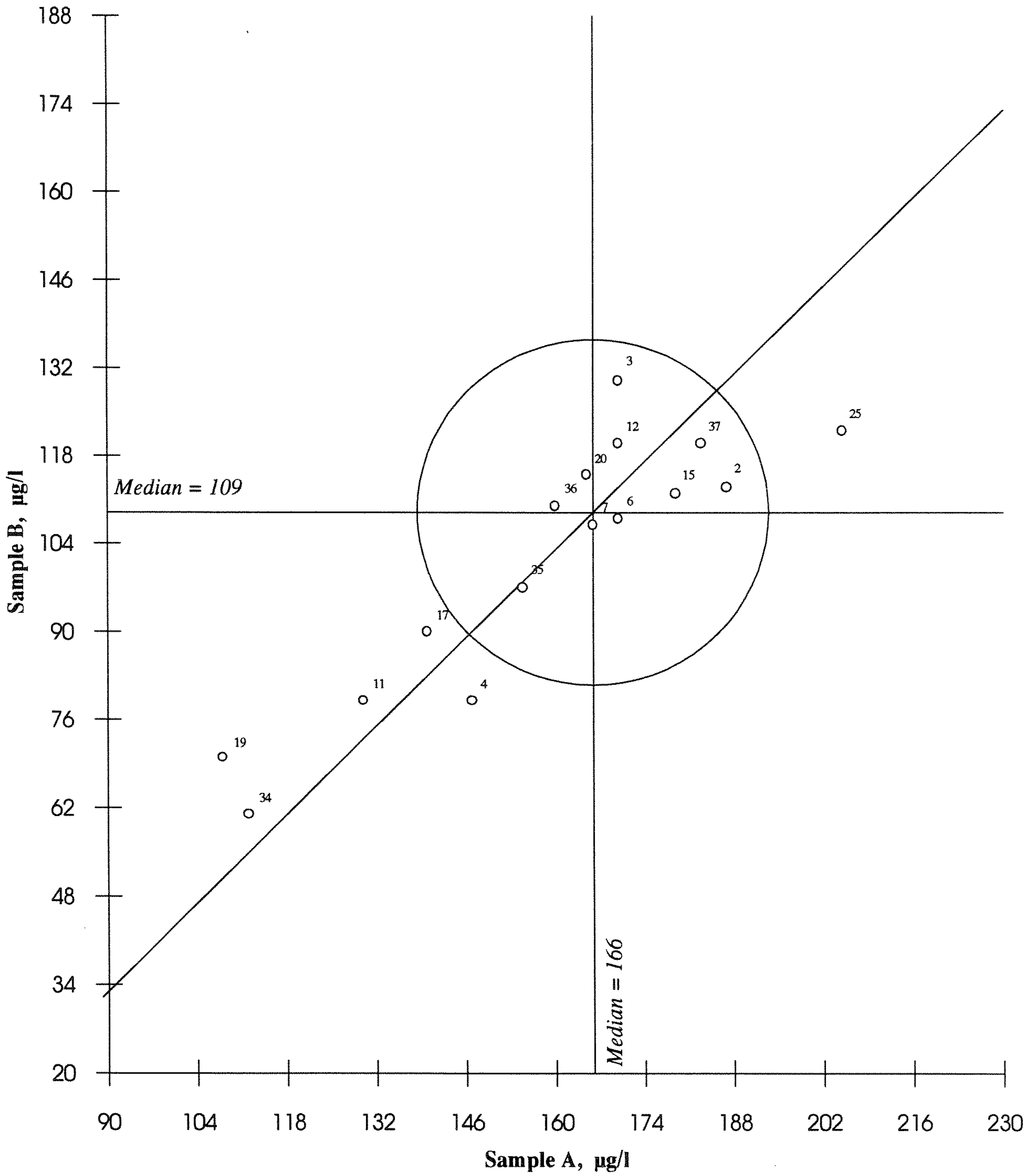


Fig. 22. Aluminium

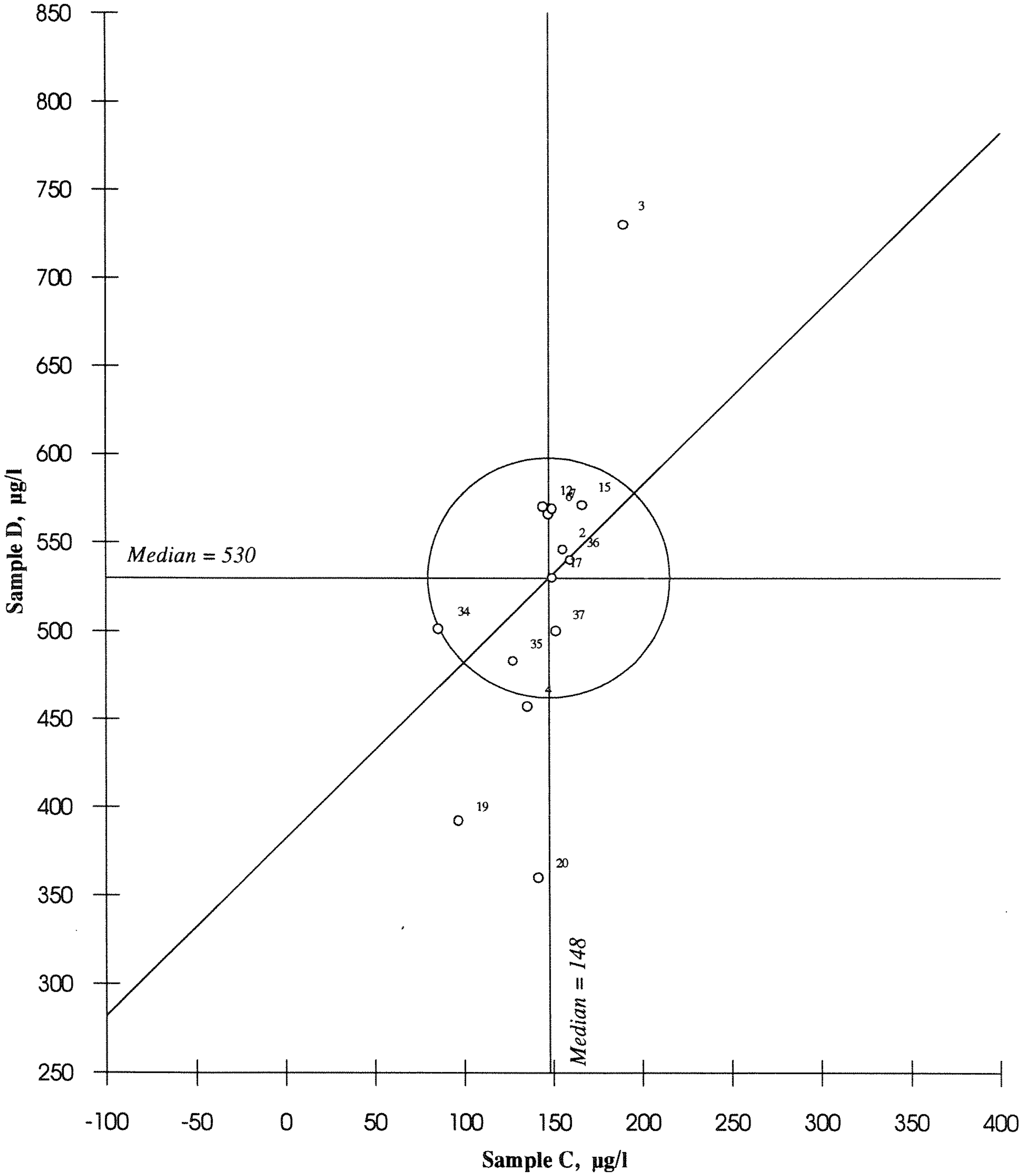


Fig. 23. Dissolved organic carbon

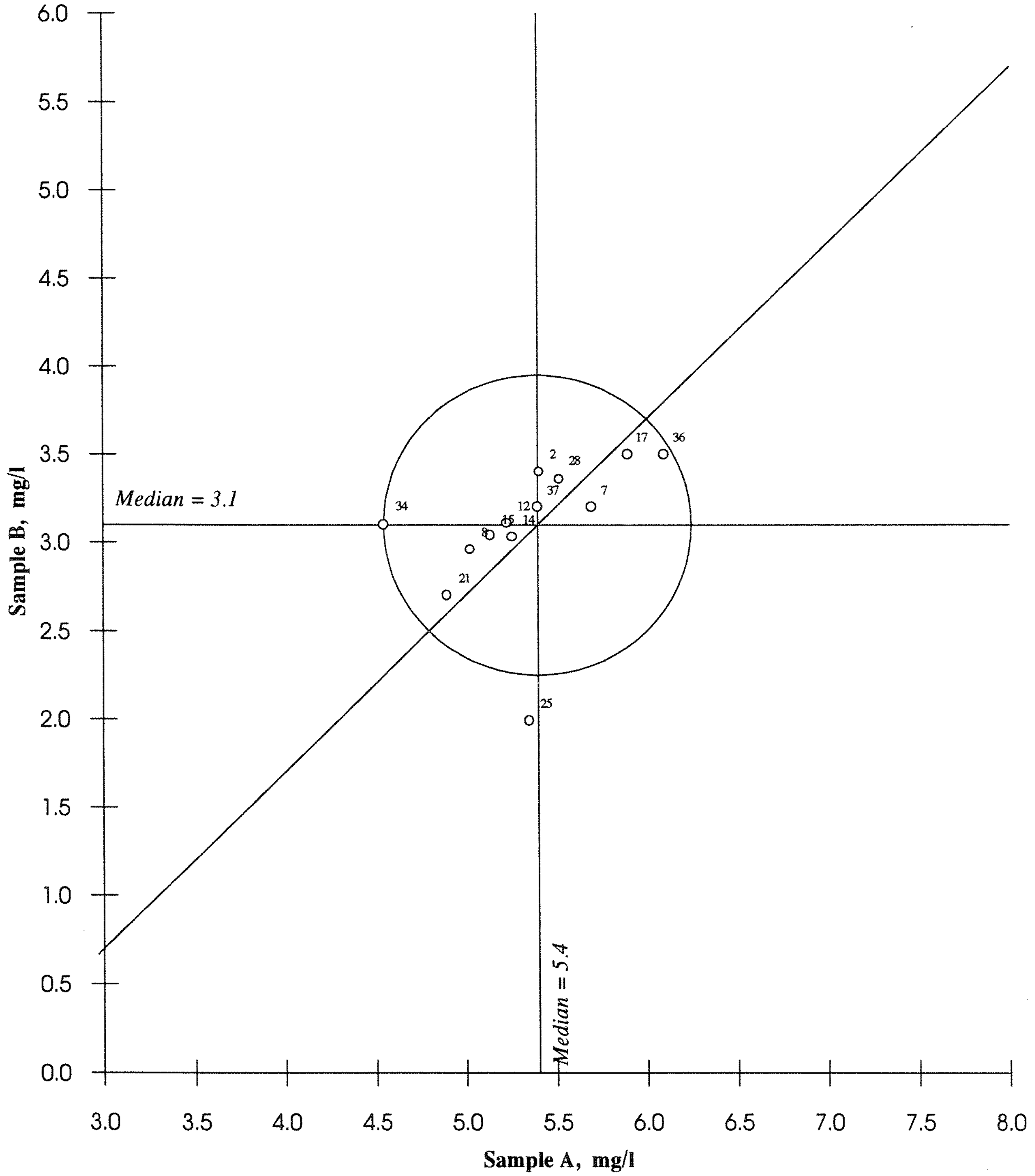


Fig. 24. Dissolved organic carbon

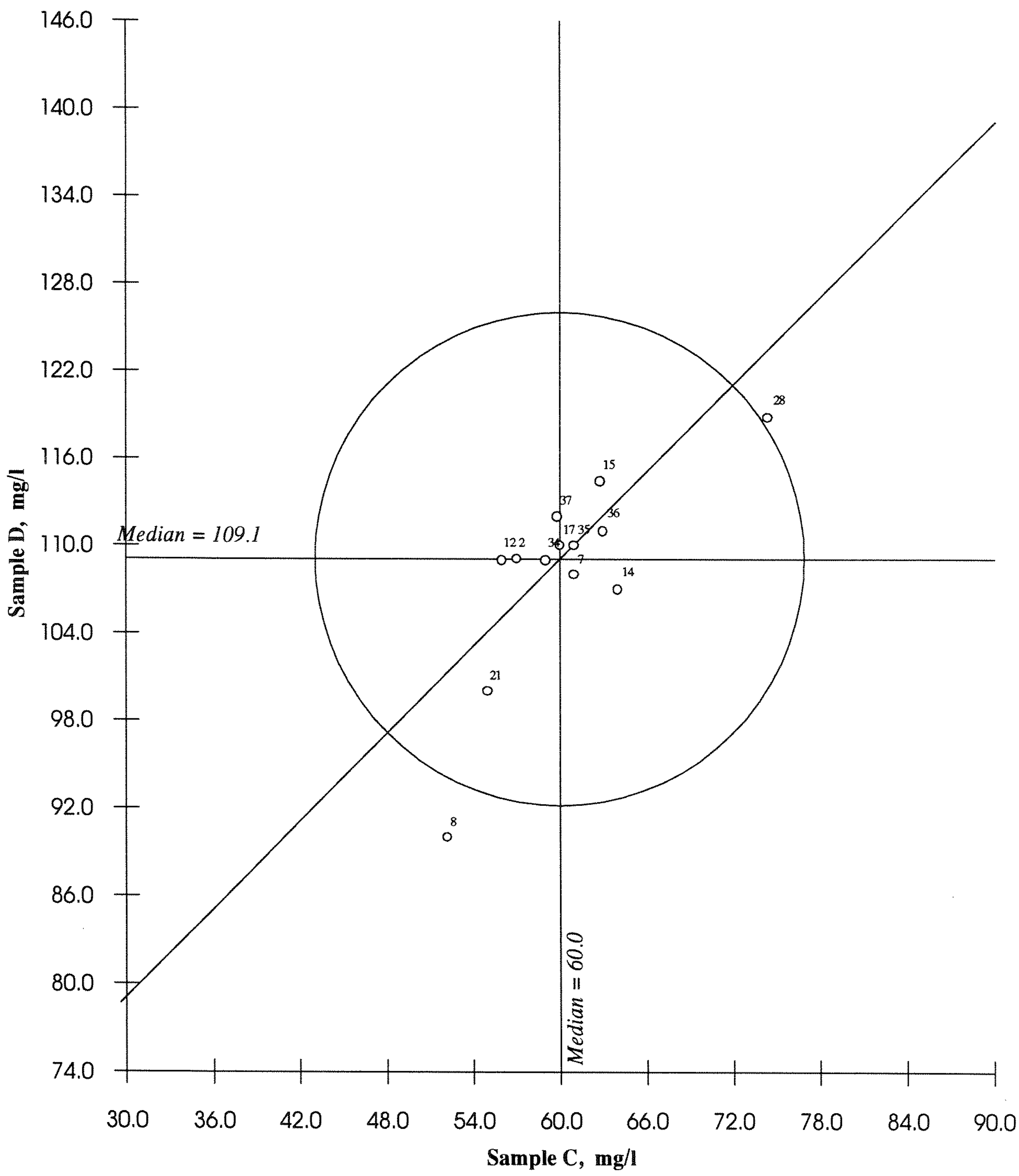


Fig. 25. Chemical oxygen demand

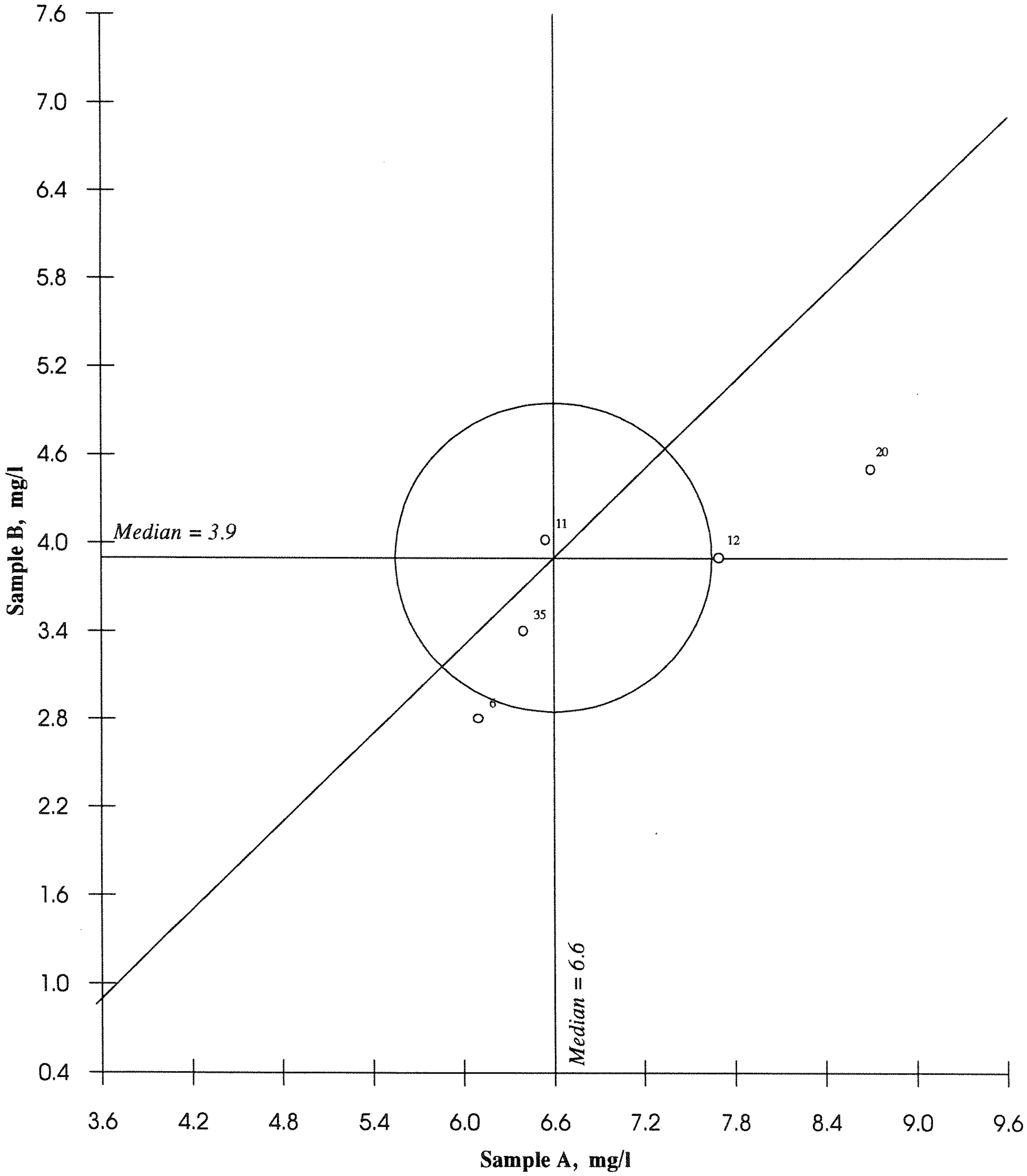
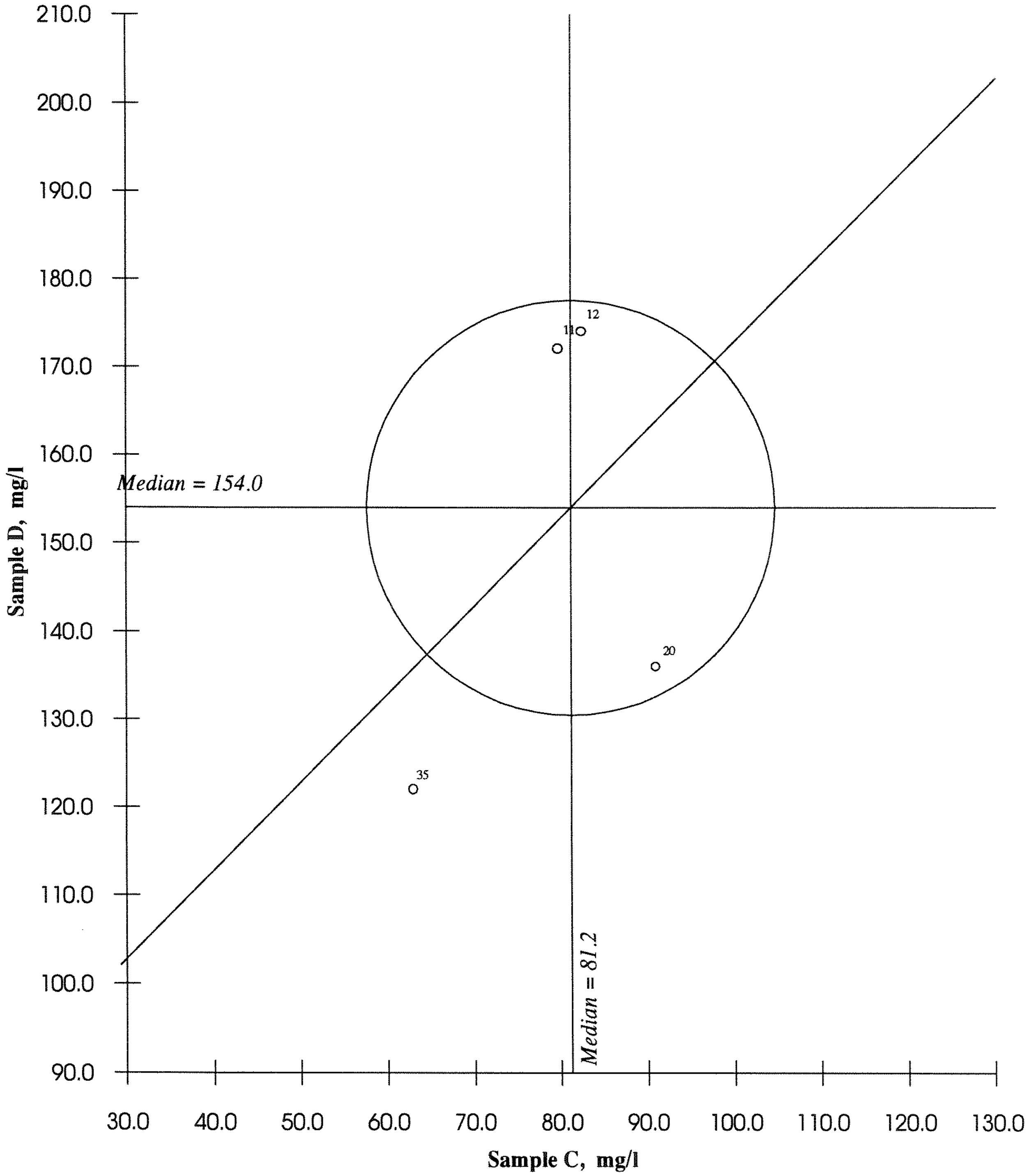


Fig. 26. Chemical oxygen demand



The purpose of this test is to evaluate the comparability of the analytical results produced by different laboratories. The real "true value" is not known exactly for the natural samples used in this intercomparison. Therefore, we selected the median value, determined from the analytical results submitted by the participating laboratories, as the "true value" for each parameter. The median value is considered to be an acceptable estimate of the true value for this purpose.

The results are illustrated in Figure 1 - 26, where each laboratory is represented by a small circle and an identification number. 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 9408 is presented in Table 1. The individual results of the participants are presented in Table 4 in Appendix 4, sorted in order of increasing identification number. More extensive statistical informations are presented in the Tables 5.1 - 5.26.

pH

The reported results for pH are graphically presented in Figure 1 and 2, where the radius of the great circle is 0.2 pH units, and visualizes the degree of comparability between the pH results from the participating laboratories. The reported pH values are given in Table 5.1 and 5.2 in Appendix 4.

The participating laboratories determined pH in the test solutions by their own routine method. An electrometric method was used by all laboratories, informations about the details of the methods was collected in a questionnaire mailed to the laboratories in January this year. Two laboratories informed that they equilibrated the solutions before the measuring pH. The results from these laboratories were somewhat higher than the median values.

It has been demonstrated that the CO_2 concentration of samples in the circumneutral range may be far above the atmospheric equilibrium. The relative high pCO_2 levels thus will lead to large systematic errors, the magnitude of which will vary between the laboratories due to different pCO_2 levels in the samples caused by different storage and handling conditions. This effect may also increase the random error as the samples may contain different amount of excess CO_2. As we used water samples which was approximately neutral, this problem is dominating and is supposed to be the reason for the scatter of results in Figure 1 and 2.

The control analyses carried out at the Program Centre proved that the samples were stable when stored within the laboratory. However, the equilibrium of the samples may be influenced when they are mailed to the participants. Some deviations may also be due to errors in the instrument, or more likely in the electrodes, as different electrodes may give rise to different results (4).

Conductivity

The conductivity results are presented in Figure 3 and 4, where the great circle is representing an accuracy limit of ± 20 %. The reported results are given in Table 5.3 and 5.4 in Appendix 4.

Correspondance with some of the participants was necessary to clarify the results, as some laboratories reported the conductivity results in the units they use routinely, instead of the requested mS/m at 25 °C. Some erratic calculations between different units also were corrected. All participants used an electrometric method for the determination of conductivity.

The laboratories achieved good agreement between the results for this parameter. Four and five laboratories, respectively, reported results for the sample pairs AB and CD lying outside the general target accuracy of ± 20 %. Only one more result would be outside the acceptance limit if it was reduced to ± 10 %.

Alkalinity

The alkalinity results are illustrated in Figure 5 and 6, and the reported results are given in Table 5.5 and 5.6 in Appendix 4. Half of the laboratories used the Gran plot titration suggested in the Manual (1), and the other laboratories used titration to certain pH values. For the sample pair CD the Gran plot titration gave slightly higer results than the traditional titration method.

Nitrate + nitrite

The results reported for this parameter are presented in Figure 7 and 8, and the reported results are given in Table 5.7 and 5.8 in Appendix 4. The most common analytical method used for the determination of this parameter is ion chromatography, even though an automated photometric method is used by many laboratories. There is no significant systematic difference between the results determined by the two methods.

The circle in Figure 7 and 8 is representing a general target accuracy of ± 20 %.

Chloride

The chloride results are presented in Figure 9 and 10, and the reported results are given in Table 5.9 and 5.10 (Appendix 4). Most laboratories determined chloride by ion chromatography, and three laboratories used an automated photometric version of the mercury thiocyanate method. The precision of the results are far better for the more concentrated sample pair CD.

The great circle in Figure 9 and 10 are representing a general target accuracy of ± 20 % of the mean value of the sample pair.

Sulfate

The sulfate results are illustrated in Figure 11 and 12, and the reported values are given in Table 5.11 and 5.12 (Appendix 4). Most laboratories applied ion chromatography for the determination of this parameter, while four laboratories used an automated photometric method based on the dissociation of the barium-thorin complex.

An accuracy limit of ± 20 % is represented by the circle in Figure 11 and 12. About 80 % of the result pairs are lying within this general target accuracy.

Calcium

The calcium results are illustrated in Figure 13 and 14, and the reported values are given in Table 5.13 and 5.14 in Appendix 4. More than half of the participants used flame atomic absorption spectrometry for the determination of this metal. ICP techniques and ion chromatography are used by some few laboratories.

A general target accuracy of ± 20 % is represented by the great circle in Figure 13 and 14. Only two result pairs are lying outside this limit for both sample pairs.

Magnesium

The magnesium results are presented in Figure 15 and 16, and the reported values are given in Table 5.15 and 5.16 in Appendix 4. The majority of the participants used flame atomic absorption spectrometry for the determination of magnesium. ICP emission spectrometry and ion chromatography was used by som few laboratories.

More than 90 % of the laboratories reported values lying within the general acceptance limit of ± 20 %, which is represented by the great circle in Figure 15 and 16.

Sodium

The sodium results are presented in Figure 17 and 18, where the great circle is representing the general target accuracy of ± 20 %. The reported values are given in Table 5.17 and 5.18 (Appendix 4). Most laboratories used flame atomic absorption spectrometry for this determination, however, many laboratories used emission spectrometry.

More than 90 % of the result pairs are lying within the general target accuracy of ± 20 %.

Potassium

The potassium results are presented in Figure 19 and 20. The great circle is representing a general acceptance limit of ± 20 %. The reported values are given in Table 5.19 and 5.20 in Appendix 4. As for sodium, most laboratories used flame atomic absorption spectrometry for the determination of this element, however, emission spectrometry is used by some of the laboratories.

Total aluminium

The results for total aluminium are illustrated in Figure 21 na 22, and the reported values are given in Table 5.21 and 5.22 (Appendix 4). The great circle is representing the general accuracy target of ± 20 %. Most laboratories used atomic absorption spectrometry or ICP techniques for the determination of aluminium.

The determination of this analytical variable is less precise, even thoug the systematic errors are dominating the picture.

Dissolved organic carbon

The results for this parameter are presented in Figure 23 and 24, and the reported values are given in Table 5.23 and 5.24 (Appendix 4). Only 14 and 13 out of 26 laboratories determined this parameterin the sample pairs AB and CD, respectively. A combustion technique is used by most laboratories, however, five laboratories used the wet oxidation method with peroxodisulphate. There is no evidence for any differences in the reported results for these two methods. One laboratory used a photometric method based on phenolphthalein.

The great circle in Figure 23 and 24 is representing a general target accuracy of ± 20 %. Two laboratories reported results lying outside this limit.

Chemical oxygen demand, COD-Mn

The results for this parameter are presented in Figure 25 and 26, and the reported values are given in Table 5.25 and 5.26 (Appendix 4). Only a very few laboratories determined this parameter, which was included in the intercomparison because some laboratories do not have equipment for the determination of dissolved organic carbon. Random effects are dominating in Figure 25 and 26.

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 is the greater.

In table 2 an evaluation of the results of this intercomparison is presented, based on the target accuracy. For pH the general target accuracy is 0.1 pH units. However, we have chosen to extend the acceptance limit to ± 0.2 pH units, because of the great spread of the results for these samples which are nearly neutral. Compared to earlier intercomparisons, a larger part of the results are lying outside the target accuracy of ± 0.1 pH units. This is probably due to the supersaturation of CO_2 in the samples used this time.

Table 2. Evaluation of the results of intercalibration 9307. N is the number of result pairs reported, and n is the number of acceptable results within the given target accuracy.

Parameter	Sample pair	N	Limit	n	%
pH	AB	24	0.2*	13	54
	CD	22	0.2*	13	59
Conductivity	AB	23	20 %	19	83
	CD	21	20 %	18	86
Alkalinity	AB	22	20 %	20	91
	CD	21	20 %	13	62
Nitrate + nitrite-nitrogen	AB	22	20 %	18	82
	CD	22	20 %	19	86
Chloride	AB	23	20 %	19	83
	CD	23	20 %	18	78
Sulfate	AB	23	20 %	18	78
	CD	23	20 %	19	83
Calcium	AB	22	20 %	20	91
	CD	22	20 %	20	91
Magnesium	AB	22	20 %	20	91
	CD	22	20 %	21	95
Sodium	AB	22	20 %	21	95
	CD	22	20 %	20	91
Potassium	AB	22	20 %	19	86
	CD	21	20 %	17	81
Aluminium, total	AB	16	20 %	10	63
	CD	15	20 %	10	67
Dissolved organic carbon	AB	14	20 %	12	86
	CD	13	20 %	11	85
Chemical oxygen demand	AB	5	20 %	2	40
	CD	4	20 %	3	75
Sum		511		413	81

* The accetance limit is extended from 0.1 to 0.2 pH units

For the remaining parameters, 81 % of the result pairs are lying within the general target accuracy of ± 20 %. For these parameters only a few laboratories are outside the acceptance limit, and by some improvement of the routine analytical method, these laboratories should obtain results with better comparablility to the others.

In Table 2 is summarized an evaluation of the results of intercomparison 9408, are given the number and percentage of acceptable results both for the general target acceptance and the selected special limits. 81 % of the results are acceptable when compared to the general acceptance target.

CONCLUSION

A total error of ± 0.2 pH units seems to be a reasonable assessment of the accuracy for pH measurements, which might be achieved routinely when commercial equipment is used.

For the other analytical variables most laboratories have reported results within the general target accuracy of ± 20 %. Generally, only a very few laboratories reported results outside this limit. These laboratories should improve their methods to obtain a better comparability.

Two sample sets with different concentrations were prepared for this intercomparison, one set with low concentrations and one set with high concentrations. The idea was that every participant might select the sample set that fitted best for the routine method used at his or her laboratory. However, most laboratories asked for both sample pairs, thus 23 laboratories have determined the analytical variables in both sample sets. Five laboratories asked for the low concentration samples only, of which two returned their results, and one laboratory asked for the high concentration samples.

LITERATURE

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

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

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

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

APPENDIX 1

Participants of intercomparison 9408.

No.	Name of laboratory	City	Country
2	Kärntner Institut für Seewasser Forschung	Klagenfurt	Austria
3	Czech Geological Survey Prague	Prague	Czech Republic
4	National Environmental Research Institute	Silkeborg	Denmark
6	Geological Survey of Finland	Espoo	Finland
7	Nat. Board of Waters and the Environment	Helsinki	Finland
8	University of Maine	Orono	USA
11	VITUKI Consult Rt	Budapest	Hungary
12	Swedish University for Agricultural Sciences	Uppsala	Sweden
13	US Geological Survey	Lakewood	USA
14	Cetre National de la Recherche Scientifique	Strasbourg	France
15	N.V. Waterleidingbedrijf Midden-Nederland	Utrecht	Netherland
16	Kymen Water and Environment District	Kouvola	Finland
17	Institute of Hydrobiology	Ceské Budejovice	Czech Republic
19	Werkgroep Milieubiologie	Nijmegen	Netherland
20	Kola Science Center	Apatity	Russia
21	Institut für Zoologie, Universtät Innsbruck	Innsbruck	Austria
25	Adirondac Lakes Survey Corporation	Ray Brook	USA
28	Aquatic Chemistry Project	Winnipeg	Canada
29	Charles University	Prague	Czech Republic
34	DAFS Freshwater Laboratory	Pitlochry	Scotland
35	Bayerische Landesamt für Wasserwirtschaft	München	Germany
36	Landesumweltamt Nordrhein Westfalen	Essen	Germany
37	Norwegian Institute for Water Research	Oslo	Norway
41	CNR Istituto Italiano di Idrobiologia	Pallanza	Italy
43	Environmental Research Unit	Dublin	Ireland

APPENDIX 2

Preparation of samples

The sample solutions were prepared from natural water collected at four locations outside Oslo. Raw water was collected in polyethylene containers and brought to the laboratory for storage.

For sample A was used the water from a river called Sørkedalselva, sample B was prepared from water from a creek called Sørbråtbekken, Sample C was collected at a small lake called Svartkulp, while sample D was prepared from the river water Skjærsjøelva. These solutions were stored at room temperature for several weeks at the laboratory. During this stabilization period suspended matter settled. The solutions were filtrated through 0.45 µm membrane filter, and small aliquouts were removed from the filtrate to determine the concentrations of the parameters of interest. The concentrations of samples C and D were increased by the addition of dissolved salts.

A few days before mailing to the participants, the solutions were transferred to 1/2 liter polyethylene bottles with screw cap. These samples were stored at room temperature until mailing to the participating laboratories.

Table 3. Summary of the control analyses.

Parameter	Sample A		Sample B		Sample C		Sample D	
	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.
pH	7.55	0.026	6.66	0.050	7.08	0.031	7.23	0.047
Conductivity mS/m	8.30	0.035	3.42	0.026	23.9	0.100	38.5	0.200
Alkalinity mmol/l	33.7	0.67	4.3	0.41	22.8	1.1	40.6	2.7
Nitrate/nitrite µg/l	157	2.9	1162	7.6	2860	26	3937	23
Chloride mg/l	1.3	0.0	0.9	0.1	21.8	0.3	34.3	1.2
Sulfate mg/l	3.6	0.2	3.4	0.1	14.2	0.6	22.0	1.0
Calcium mg/l	3.06	0.04	2.02	0.03	15.3	0.26	19.8	0.20
Magnesium mg/l	0.37	0.010	0.29	0.006	2.88	0.035	4.34	0.106
Sodium mg/l	16.3	0.15	3.85	0.04	25.3	0.38	52.7	0.58
Potassium mg/l	0.22	0.01	0.23	0.006	7.37	0.12	11.1	0.17
Aluminium total, µg/l	157	12	102	6	143	10	493	12
Diss.org. C mg/l	5.57	0.38	3.13	0.12	58.3	5.0	105.8	6.7

Sample control analyses

During the intercalibration period, three 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 some days before mailing of the samples to the participants. The last sample was analyzed at the middle of June 1994. 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.

APPENDIX 3

Treatment of analytical data

The intercalibration 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 parameter. In a coordinate system the result of sample 2 is plotted against the result of sample 1 (see Figures 1 - 26).

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 cause of error.

The statistical treatment of the analytical results was accomplished in this way: Pairs of results where one or both of the values are lying outside the true value ± 50 %, are omitted from the statistical calculations. The remaining results are used for the calculation of the mean value (x) and the standard deviation (s). Now the pairs of results where both of the values are lying outside x ± 3s, are omitted. The remaining results are used for a final calculation, the results of which are presented in the tables 5.1 - 5.26. Results being omitted from the calculations, are marked with the letter "U".

APPENDIX 4 **Table 4. The results of the participating laboratories.**

Lab. no.	pH A	B	C	D	Conductivity A	B	C	D
2	7.18	6.49	6.78	6.99	8.2	3.4	23.3	37.5
3	7.61	6.66	7.02	7.18	7.91	3.29	22.9	37.2
4	7.52	6.4	6.95	7.03	8.12	3.33	2.32	37.6
6	7.5	6.4	6.8	7	8.4	3.4	23.8	38
7	7.6	6.55	6.91	6.97	8.28	3.36	23.7	38.1
8	8.13	7.23	7.92	8.17	7.94	3.21	22.7	36.8
11	7.22	6.28	6.92	7.2	6.7	9.5	21.3	34.5
12	7.55	6.46	6.79	6.87	8.28	3.38	23.8	38.6
13	7.79	6.89			7.94	3.43		
14	7.63	7.03	7.09	7.24				
15	7.4	6.4	6.8	6.9	8.4	3.4	23.8	38.6
16								
17	7.7	6.7	7.2	7.3	8.13	3.41	23.5	38
19	7.3	6.1	6.7	6.9	6.6	3.3	17.6	29.3
20	7.6	6.52	7.12	7.1	8	3.5	23	37
21	7.48	6.51	6.91	6.98	8.2	3.32	23.4	38.2
25	7.605	6.78			8.25	3.36		
28	7.97	7.13	7.76	8.02	8.1	3.3	23.1	37.2
29	7.43	6.41	6.78	6.84	8.7	3.4	24.2	39
34	7.66	6.58	6.9	6.98	7	2.9	20.1	32.7
35	7.35	6.39	6.89	6.98	8.3	3.4	23.7	38.5
36	7.61	6.52	6.98	7.02	8.04	3.11	23.37	37.9
37	7.53	6.61	7.07	7.28	8.32	3.45	23.8	38.5
41	7.58	6.58	6.9	6.93	8.17	3.35	23.6	38.2
43	7.48	6.54	6.77	6.85	9.4	4.6	23.4	37.3

Lab.no.	Alkalinity A	B	C	D	Nitrate+nitrite A	B	C	D
2	27	14					181.9	932.2
3	33.55	4.15	26.8	53.7	144.6	1122.7	2868.9	3795.1
4	32.65	3.25	22.3	42.8	120	1130	2870	3920
6	34	6.5	25	43	180	1200	3000	4100
7					158	1110	2750	3730
8	34.1	4.33	31.8	60.6	144	1138	2827	3685
11	29.05	3.55	18.5	32.2	64	479	5704	7191
12	32.9	3.74	19	36.1	240	1330	3270	4280
13	33.7	3.98						
14	33.3	4.5	30.1	37.6	154	1162	2926	3990
15	35.1	5.7	25.3	45.8	142	1052	2270	1790
16			19.2	36.6			2950	4140
17	33.8	4.25	23	40	137	1030	2830	3500
19	33	6	27.8	49	140	1120	1260	3640
20	32.5	3.8	22.5	39.5	140	1220	2930	4270
21	33.2	4.2	19.4	36.7	150	1200	2960	4000
25	31.918	3.957			152	1136		
28	32.7	4.1	22.7	42.2	146	1303	2842	3763
29	33.4	4.1	22.1	41	149	1160	2947	4020
34	33.3	4	20	37.3	154	1106	2730	3654
35	35.7	6.3	27.4	50.1	170	1250	2860	3990
36	33.5	10	24.2	44.6	140	850	2740	3880
37	32.4	4.2	21.5	38.3	160	1160	2840	4050
41	34.1	4.1	20.8	38.7	149	1113	2820	3930
43					150	1165	2833	3903

Lab.no.	Chloride A	B	C	D	Sulphate A	B	C	D
2	1.3	0.8	22	34.5	4.4	3.8	15.9	24.7
3	1.42	1.01	22.3	35.4	3.87	3.69	15.6	24.2
4	3.37	2.44	22.18	35.84	7.25	4.89	16.21	25.14
6	1.4	1	40	61	4.2	3.6	15.5	24.3
7	1.68	1.07	23.6	35.6	4.35	3.78	15.8	24.6
8	4.41	3.83	15.6	24.2	1.38	0.97	22.3	34
11	0.283	0.141	2.19	2.12	21.1	14.3	26.4	27.9
12	1.35	0.99	21.4	32.9	4.27	3.6	15.7	49.7
13								
14	1.4	1.1	22.9	36.2	4.3	3.7	16	25.2
15	2.5	1.6	22.1	34.8	4.8	3.5	18	24.7
16			21.6	15.2			33.4	23.8
17	1.35	0.98	22.2	34.9	6.2	5.7	17.8	27.6
19	1	1	22	35	0	0	0	22
20	1.6	1	22.6	36	4.1	3.7	15.2	24
21	1.6	1.1	22.4	35.4	4.8	3.7	15	23
25	1.42	0.97			3.977	3.453		
28	1.42	1.01	23.5	36.1	4.17	3.76	14.4	23.6
29	1.32	0.99	21.38	32.26	4.27	3.73	15.86	24.8
34	1.28	0.91	20.55	33.4	4.13	3.6	15.12	23.62
35	1.7	1.1	25	42	4.1	3.71	15.5	24.6
36	1.1	1	22	36	4.1	3.5	15	24
37	1.3	1	21	33	3.8	3.5	14.5	23
41	1.44	1.01	23.2	35.5	4.23	3.7	16	24.4
43	1.31	1.01	21.05	34.02	4.24	3.68	15.4	24.34

Lab.no.	Calcium A	B	C	D	Magnesium A	B	C	D
2	3.2	2.1	14	19	0.4	0.3	2.9	4.5
3	3.02	2.01	14.56	19.04	0.39	0.31	3	4.47
4								
6	2.99	1.99	15.2	19.7	0.38	0.31	3.09	4.63
7	2.99	2.05	15	20	0.37	0.3	2.9	4.5
8	3.14	2.04	16.8	23.6	0.39	0.3	3.07	4.66
11	3.21	2.12	14.2	19.1	0.4	0.3	3	4.65
12	3	2	15.3	20.1	0.377	0.304	3.15	4.82
13								
14	3	2	15.3	20	0.4	0.3	3.1	4.6
15	2.7	1.6	13.9	18.5	0.42	0.32	2.95	4.45
16			15.1	19.4			3	4.5
17	2.8	1.9	13.8	17.8	0.38	0.3	2.99	4.45
19	3	2	15	18	0.3	0.2	2.7	4
20	2.7	1.8	14.5	19	0.36	0.28	2.95	4.4
21	3.3	2.3	15.1	19.7	0.42	0.35	3.1	4.6
25	2.96	2.01			0.37	0.31		
28	3.01	1.98	13.9	20.9	0.41	0.32	3.15	5.2
29	3.27	2.18	15.58	20.29	0.4	0.31	3.08	4.67
34	3.62	2.48	17.1	22.3	0.41	0.35	3.18	5.01
35	2.87	1.95	13.8	17.5	0.38	0.28	2.78	4.12
36	3.11	2.03	15.3	19.6	0.43	0.33	3.09	4.65
37	3.1	2.06	15.5	20	0.36	0.29	2.85	4.27
41	2.94	1.98	14.8	19.3	0.38	0.3	3.05	4.57
43	2.82	1.98	18.14	24.74	0.22	0.21	3.33	6.89

Lab.no.	Sodium A	B	C	D	Potassium A	B	C	D
2	16.1	3.5	25.1	51.4	0.3	0.2	7.7	11.8
3	15.01	3.53	25.21	50.94	0.25	0.25	7.83	11.57
4	16	3.8	25.8	52.9	0.32	0.32	8.56	13.2
6	15.4	3.66	26.6	54.4	0.25	0.26	7.69	11.7
7	15	3.55	25	52.1	0.26	0.28	8.1	11.8
8	14.9	3.59	26.1	54.4	0.29	0.27	8.78	13.8
11	14.9	3.83	25.1	52	0.31	0.29	8.24	12.1
12	15.7	3.61	27.2	56.6	0.035	0.027	6.96	8.21
13								
14	14.9	3.6	25.8	52.2	0.3	0.3	8.1	12
15	15.1	3.6	25.7	54.2	0.29	0.26	7.99	12.11
16			25.9	52.6				
17	14.2	3.4	24.2	50	0.1	0.2	7.2	11
19	15	4	27	53	0.3	0.3	8	12.2
20	14.2	3.6	25.2	50	0.23	0.23	7.5	10.5
21	16	3.62	25.7	51.8	0.24	0.26	8.25	12.3
25	15.2	3.645			0.27	0.27		
28								
29	16.99	3.75	26.69	40	0.25	0.25	7.04	10.28
34	15.4	3.75	26.5	53.5	0.27	0.27	7.8	11.3
35	14.8	3.9	25	51	0.28	0.27	8.2	12.2
36	16.7	4.35	27.1	54.7	0.35	0.35	8.63	12.8
37	16.3	3.82	28	57	0.21	0.22	7.5	11.3
41	15.4	3.6	25.3	51.8	0.24	0.24	5.95	9.15
43	146.5	3.41	33.72	55.81	0.77	0.54	8.38	22.29

Lab.no.	Aluminium A	B	C	D
2	187	113	156	546
3	170	130	190	730
4	147	79	136	457
6	170	108	148	566
7	166	107	150	569
8				
11	130	79	58	216
12	170	120	145	570
13				
14				
15	179	112	167	571
16				
17	140	90	150	530
19	108	70	97	392
20	165	115	142	360
21				
25	205	122		
28				
29				
34	112	61	86	501
35	155	97	128	483
36	160	110	160	540
37				
41				
43				

	DOC				COC-Mn			
Lab.no.	**A**	**B**	**C**	**D**	**A**	**B**	**C**	**D**
2	5.41	3.4	57	109.1				
3								
4								
6					6.1	2.8		
7	5.7	3.2	61	108				
8	5.03	2.96	52.2	90				
11					6.55	4.02	79.8	172
12	5.23	3.11	56	109	7.7	3.9	82.5	174
13								
14	5.26	3.03	64	107				
15	5.14	3.04	62.8	114.4				
16								
17	5.9	3.5	60	110				
19								
20					8.7	4.5	91	136
21	4.9	2.7	55	100				
25	5.351	1.994						
28	5.52	3.36	74.4	118.8				
29								
34	4.55	3.1	59	109				
35	11.7	5.4	61	110	6.4	3.4	63	122
36	6.1	3.5	63	111				
37	5.4	3.2	59.8	109				
41								
43								

Table 5. 1 . Statistics - pH

Sample A

Analytical method: All
Unit: none

Number of participant:	24	Range	0.95
Number of omitted res	0	Variance	0.04
True value	7.57	Standard deviation	0.21
Mean value	7.56	Relative Standard deviation	2.80%
Median value	7.57	Relative error	-0.10%

Analytical results in ascending order:

2	7.18	6	7.5	36	7.61
11	7.22	4	7.52	3	7.61
19	7.3	37	7.53	14	7.63
35	7.35	12	7.55	34	7.66
15	7.4	41	7.58	17	7.7
29	7.43	20	7.6	13	7.79
21	7.48	7	7.6	28	7.97
43	7.48	25	7.61	8	8.13

Sample B

Analytical method: All
Unit: none

Number of participant:	24	Range	1.13
Number of omitted res	0	Variance	0.07
True value	6.53	Standard deviation	0.26
Mean value	6.59	Relative Standard deviation	4.00%
Median value	6.53	Relative error	0.90%

Analytical results in ascending order:

19	6.1	2	6.49	37	6.61
11	6.28	21	6.51	3	6.66
35	6.39	20	6.52	17	6.7
4	6.4	36	6.52	25	6.78
6	6.4	43	6.54	13	6.89
15	6.4	7	6.55	14	7.03
29	6.41	41	6.58	28	7.13
12	6.46	34	6.58	8	7.23

Table 5. 2 . Statistics - pH

Sample C

Analytical method: All
Unit: none

Number of participant:	22	Range	1.06
Number of omitted res	1	Variance	0.05
True value	6.91	Standard deviation	0.23
Mean value	6.95	Relative Standard deviation	3.30%
Median value	6.91	Relative error	0.60%

Analytical results in ascending order:

19	6.7	41	6.9	37	7.07
43	6.77	34	6.9	14	7.09
29	6.78	7	6.91	20	7.12
2	6.78	21	6.91	17	7.2
12	6.79	11	6.92	28	7.76
6	6.8	4	6.95	8	7.92 U
15	6.8	36	6.98		
35	6.89	3	7.02		

Sample D

Analytical method: All
Unit: none

Number of participant:	22	Range	1.18
Number of omitted res	1	Variance	0.07
True value	6.99	Standard deviation	0.26
Mean value	7.07	Relative Standard deviation	3.70%
Median value	6.99	Relative error	1.20%

Analytical results in ascending order:

29	6.84	35	6.98	11	7.2
43	6.85	34	6.98	14	7.24
12	6.87	2	6.99	37	7.28
19	6.9	6	7	17	7.3
15	6.9	36	7.02	28	8.02
41	6.93	4	7.03	8	8.17 U
7	6.97	20	7.1		
21	6.98	3	7.18		

U = Omitted results

Table 5. 3 . Statistics - Conductivity

Sample A

Analytical method: All
Unit: mS/m

Number of participant:	23	Range	0.79
Number of omitted res	4	Variance	0.04
True value	8.2	Standard deviation	0.19
Mean value	8.19	Relative Standard deviation	2.36%
Median value	8.2	Relative error	0.12%

Analytical results in ascending order:

19	6.6 U	28	8.1	12	8.28
11	6.7 U	4	8.12	35	8.3
34	7 U	17	8.13	37	8.32
3	7.91	41	8.17	6	8.4
13	7.94	21	8.2	15	8.4
8	7.94	2	8.2	29	8.7
20	8	25	8.25	43	9.4 U
36	8.04	7	8.28		

Sample B

Analytical method: All
Unit: mS/m

Number of participant:	23	Range	0.39
Number of omitted res	4	Variance	0.01
True value	3.38	Standard deviation	0.09
Mean value	3.36	Relative Standard deviation	2.62%
Median value	3.38	Relative error	-0.59%

Analytical results in ascending order:

34	2.9 U	41	3.35	15	3.4
36	3.11	7	3.36	17	3.41
8	3.21	25	3.36	13	3.43
3	3.29	12	3.38	37	3.45
19	3.3 U	29	3.4	20	3.5
28	3.3	6	3.4	43	4.6 U
21	3.32	2	3.4	11	9.5 U
4	3.33	35	3.4		

U = Omitted results

Table 5. 4 . Statistics - Conductivity

Sample C

Analytical method: All
Unit: mS/m

Number of participant:	21	Range	2.9
Number of omitted res	3	Variance	0.43
True value	23.45	Standard deviation	0.64
Mean value	23.35	Relative Standard deviation	2.72%
Median value	23.45	Relative error	-0.43%

Analytical results in ascending order:

4	2.32 U	28	23.1	7	23.7
19	17.6 U	2	23.3	35	23.7
34	20.1 U	36	23.37	6	23.8
11	21.3	21	23.4	37	23.8
8	22.7	43	23.4	12	23.8
3	22.9	17	23.5	15	23.8
20	23	41	23.6	29	24.2

Sample D

Analytical method: All
Unit: mS/m

Number of participant:	21	Range	4.5
Number of omitted res	3	Variance	1.1
True value	38	Standard deviation	1.02
Mean value	37.72	Relative Standard deviation	2.68%
Median value	38	Relative error	-0.74%

Analytical results in ascending order:

19	29.3 U	43	37.3	21	38.2
34	32.7 U	2	37.5	41	38.2
11	34.5	4	37.6 U	35	38.5
8	36.8	36	37.9	37	38.5
20	37	17	38	12	38.6
3	37.2	6	38	15	38.6
28	37.2	7	38.1	29	39

U = Omitted results

Table 5. 5 . Statistics - Alkalinity

Sample A

Analytical method: All
Unit: mg/l CaCO3

Number of participant:	22	Range	6.65
Number of omitted res	2	Variance	1.97
True value	33.3	Standard deviation	1.33
Mean value	33.22	Relative Standard deviation	4.00%
Median value	33.3	Relative error	-0.20%

Analytical results in ascending order:

11	29.05	21	33.2	17	33.8
25	31.92	14	33.3	6	34
37	32.4	34	33.3	41	34.1
20	32.5	29	33.4	8	34.1
4	32.65	36	33.5 U	2	34.5 U
28	32.7	3	33.55	15	35.1
12	32.9	13	33.7	35	35.7
19	33				

Sample B

Analytical method: All
Unit: mg/l CaCO3

Number of participant:	22	Range	3.25
Number of omitted res	2	Variance	0.79
True value	4.13	Standard deviation	0.89
Mean value	4.37	Relative Standard deviation	21.50%
Median value	4.13	Relative error	5.70%

Analytical results in ascending order:

4	3.25	41	4.1	14	4.5
11	3.55	28	4.1	15	5.7
12	3.74	3	4.15	19	6
20	3.8	21	4.2	35	6.3
25	3.96	37	4.2	6	6.5
13	3.98	17	4.25	36	10 U
34	4	8	4.33	2	14 U
29	4.1				

U = Omitted results

Table 5. 6 . Statistics - Alkalinity

Sample C

Analytical method: All
Unit: mg/l CaCO3

Number of participant:	21	Range	13.3
Number of omitted res	0	Variance	14.78
True value	22.7	Standard deviation	3.77
Mean value	23.64	Relative Standard deviation	15.95%
Median value	22.7	Relative error	4.14%

Analytical results in ascending order:

11	18.5	29	22.1	15	25.3
12	19	4	22.3	3	26.8
16	19.2	20	22.5	2	27
21	19.4	28	22.7	35	27.4
34	20	17	23	19	27.8
41	20.8	36	24.2	14	30.1
37	21.5	6	25	8	31.8

Sample D

Analytical method: All
Unit: mg/l CaCO3

Number of participant:	21	Range	28.4
Number of omitted res	0	Variance	49.16
True value	41	Standard deviation	7.38
Mean value	42.99	Relative Standard deviation	17.17%
Median value	41	Relative error	4.85%

Analytical results in ascending order:

11	32.2	41	38.7	36	44.6
12	36.1	20	39.5	15	45.8
16	36.6	17	40	19	49
21	36.7	29	41	35	50.1
34	37.3	28	42.2	3	53.7
14	37.6	4	42.8	2	57
37	38.3	6	43	8	60.6

Table 5. 7 . Statistics - Nitrate + nitrite-nitrogen

Sample A

Analytical method: All
Unit: µg/l N

Number of participant:	23	Range	60
Number of omitted res	1	Variance	158
True value	149	Standard deviation	23.6
Mean value	154.6	Relative Standard deviation	15.20%
Median value	149	Relative error	3.76%

Analytical results in ascending order:

11	64 U	3	145	34	154
4	120	28	146	7	158
17	137	29	149	37	160
20	140	41	149	35	170
36	140	21	150	6	180
19	140	43	150	2	182
15	142	25	152	12	240
8	144	14	154		

Sample B

Analytical method: All
Unit: µg/l N

Number of participant:	23	Range	453
Number of omitted res	1	Variance	8498
True value	1138	Standard deviation	107.1
Mean value	1136	Relative Standard deviation	9.42%
Median value	1138	Relative error	-0.17%

Analytical results in ascending order:

11	479 U	19	1120	43	1165
36	850	3	1123	6	1200
2	932	4	1130	21	1200
17	1030	25	1136	20	1220
15	1052	8	1138	35	1250
34	1106	29	1160	28	1303
7	1110	37	1160	12	1330
41	1113	14	1162		

U = Omitted results

Table 5. 8 . Statistics - Nitrate + nitrite-nitrogen

Sample C

Analytical method: All
Unit: µg/l N

Number of participant:	23	Range	733
Number of omitted res	3	Variance	19722
True value	2841	Standard deviation	384
Mean value	2766	Relative Standard deviation	13.90%
Median value	2841	Relative error	-2.64%

Analytical results in ascending order:

19	1260 U	17	2830	20	2930
15	2270 U	43	2833	29	2947
2	2537	37	2840	16	2950
34	2730	28	2842	21	2960
36	2740	35	2860	6	3000
7	2750	3	2869	12	3270
41	2820	4	2870	11	5704 U
8	2827	14	2926		

Sample D

Analytical method: All
Unit: µg/l N

Number of participant:	23	Range	851
Number of omitted res	3	Variance	52154
True value	3912	Standard deviation	501
Mean value	3994	Relative Standard deviation	13.20%
Median value	3912	Relative error	-3.02%

Analytical results in ascending order:

15	1790 U	3	3795	29	4020
2	3429	36	3880	37	4050
17	3500	43	3903	6	4100
19	3640 U	4	3920	16	4140
34	3654	41	3930	20	4270
8	3685	14	3990	12	4280
7	3730	35	3990	11	7191 U
28	3763	21	4000		

U = Omitted results

Table 5. 9 . Statistics - Chloride

Sample A

Analytical method: All
Unit: mg/l

Number of participant:	23	Range	0.7
Number of omitted res	4	Variance	0
True value	1.4	Standard deviation	0.2
Mean value	1.4	Relative Standard deviation	12.50%
Median value	1.4	Relative error	-0.80%

Analytical results in ascending order:

11	0.3 U	17	1.4	20	1.6
19	1	12	1.4	21	1.6
36	1.1	6	1.4	7	1.7
34	1.3	14	1.4	35	1.7
2	1.3	3	1.4	15	2.5 U
37	1.3	25	1.4	4	3.4 U
43	1.3	28	1.4	8	4.4 U
29	1.3	41	1.4		

Sample B

Analytical method: All
Unit: mg/l

Number of participant:	23	Range	0.3
Number of omitted res	4	Variance	0
True value	1	Standard deviation	0.1
Mean value	1	Relative Standard deviation	6.90%
Median value	1	Relative error	0.30%

Analytical results in ascending order:

11	0.1 U	6	1	7	1.1
2	0.8	36	1	14	1.1
34	0.9	19	1	21	1.1
25	1	37	1	35	1.1
17	1	43	1	15	1.6 U
29	1	41	1	4	2.4 U
12	1	3	1	8	3.8 U
20	1	28	1		

U = Omitted results

Table 5. 10. Statistics - Chloride

Sample C

Analytical method: All
Unit: mg/l

Number of participant:	23	Range	4.45
Number of omitted res	4	Variance	1.11
True value	22.18	Standard deviation	1.05
Mean value	22.28	Relative Standard deviation	4.80%
Median value	22.18	Relative error	0.50%

Analytical results in ascending order:

11	2.19 U	36	22	20	22.6
8	15.6 U	2	22	14	22.9
34	20.55	19	22	41	23.2
37	21	15	22.1	28	23.5
43	21.05	4	22.18	7	23.6
29	21.38	17	22.2	35	25
12	21.4	3	22.3	6	40 U
16	21.6 U	21	22.4		

Sample D

Analytical method: All
Unit: mg/l

Number of participant:	23	Range	9.74
Number of omitted res	4	Variance	4.13
True value	35.4	Standard deviation	2.03
Mean value	35.2	Relative Standard deviation	5.70%
Median value	35.4	Relative error	-0.60%

Analytical results in ascending order:

11	2.12 U	2	34.5	4	35.84
16	15.2 U	15	34.8	20	36
8	24.2 U	17	34.9	36	36
29	32.26	19	35	28	36.1
12	32.9	21	35.4	14	36.2
37	33	3	35.4	35	42
34	33.4	41	35.5	6	61 U
43	34.02	7	35.6		

U = Omitted results

Table 5. 11. Statistics - Sulfate

Sample A

Analytical method: All
Unit: mg/l

Number of participant:	23	Range	1
Number of omitted res	5	Variance	0.07
True value	4.22	Standard deviation	0.26
Mean value	4.23	Relative Standard deviation	6.10%
Median value	4.22	Relative error	0.20%

Analytical results in ascending order:

19	0 U	34	4.13	7	4.35
8	1.38 U	28	4.17	2	4.4
37	3.8	6	4.2	21	4.8
3	3.87	41	4.23	15	4.8
25	3.98	43	4.24	17	6.2 U
20	4.1	29	4.27	4	7.25 U
36	4.1	12	4.27	11	21.1 U
35	4.1	14	4.3		

Sample B

Analytical method: All
Unit: mg/l

Number of participant:	23	Range	0.35
Number of omitted res	5	Variance	0.01
True value	3.7	Standard deviation	0.11
Mean value	3.65	Relative Standard deviation	2.80%
Median value	3.7	Relative error	-1.30%

Analytical results in ascending order:

19	0 U	12	3.6	29	3.73
8	0.97 U	43	3.68	28	3.76
25	3.45	3	3.69	7	3.78
36	3.5	20	3.7	2	3.8
37	3.5	14	3.7	4	4.89 U
15	3.5	21	3.7	17	5.7 U
6	3.6	41	3.7	11	14.3 U
34	3.6	35	3.71		

U = Omitted results

Table 5. 12. Statistics - Sulfate

Sample C

Analytical method: All
Unit: mg/l

Number of participant:	23	Range	3.6
Number of omitted res	5	Variance	0.89
True value	15.55	Standard deviation	0.94
Mean value	15.71	Relative Standard deviation	6.10%
Median value	15.55	Relative error	1.00%

Analytical results in ascending order:

19	0 U	6	15.5	41	16
28	14.4	35	15.5	4	16.21
37	14.5	3	15.6	17	17.8
36	15	12	15.7 U	15	18
21	15	7	15.8	8	22.3 U
34	15.12	29	15.86	11	26.4 U
20	15.2	2	15.9	16	33.4 U
43	15.4	14	16		

Sample D

Analytical method: All
Unit: mg/l

Number of participant:	23	Range	4.6
Number of omitted res	5	Variance	1.06
True value	24.32	Standard deviation	1.03
Mean value	24.32	Relative Standard deviation	4.20%
Median value	24.32	Relative error	0.00%

Analytical results in ascending order:

19	22 U	3	24.2	29	24.8
21	23	6	24.3	4	25.14
37	23	43	24.34	14	25.2
28	23.6	41	24.4	17	27.6
34	23.62	7	24.6	11	27.9 U
16	23.8 U	35	24.6	8	34 U
20	24	2	24.7	12	49.7 U
36	24	15	24.7		

U = Omitted results

Table 5. 13. Statistics - Calcium

Sample A

Analytical method: All
Unit: mg/l

Number of participant:	22	Range	0.92
Number of omitted res	0	Variance	0.04
True value	3	Standard deviation	0.21
Mean value	3.03	Relative Standard deviation	7.00%
Median value	3	Relative error	1.10%

Analytical results in ascending order:

20	2.7	7	2.99	8	3.14
15	2.7	14	3	2	3.2
17	2.8	19	3	11	3.21
43	2.82	12	3	29	3.27
35	2.87	28	3.01	21	3.3
41	2.94	3	3.02	34	3.62
25	2.96	37	3.1		
6	2.99	36	3.11		

Sample B

Analytical method: All
Unit: mg/l

Number of participant:	22	Range	0.88
Number of omitted res	0	Variance	0.03
True value	2.01	Standard deviation	0.17
Mean value	2.03	Relative Standard deviation	8.30%
Median value	2.01	Relative error	0.80%

Analytical results in ascending order:

15	1.6	14	2	37	2.06
20	1.8	19	2	2	2.1
17	1.9	12	2	11	2.12
35	1.95	3	2.01	29	2.18
43	1.98	25	2.01	21	2.3
41	1.98	36	2.03	34	2.48
28	1.98	8	2.04		
6	1.99	7	2.05		

Table 5. 14. Statistics - Calcium

Sample C

Analytical method: All
Unit: mg/l

Number of participant:	22	Range	4.34
Number of omitted res	0	Variance	1.22
True value	15.05	Standard deviation	1.11
Mean value	15.09	Relative Standard deviation	7.30%
Median value	15.05	Relative error	0.20%

Analytical results in ascending order:

17	13.8	41	14.8	12	15.3
35	13.8	7	15	37	15.5
15	13.9	19	15	29	15.58
28	13.9	21	15.1	8	16.8
2	14	16	15.1	34	17.1
11	14.2	6	15.2	43	18.14
20	14.5	36	15.3		
3	14.56	14	15.3		

Sample D

Analytical method: All
Unit: mg/l

Number of participant:	22	Range	7.24
Number of omitted res	0	Variance	3.03
True value	19.65	Standard deviation	1.74
Mean value	19.89	Relative Standard deviation	8.90%
Median value	19.65	Relative error	1.20%

Analytical results in ascending order:

35	17.5	41	19.3	12	20.1
17	17.8	16	19.4	29	20.29
19	18	36	19.6	28	20.9
15	18.5	6	19.7	34	22.3
20	19	21	19.7	8	23.6
2	19	7	20	43	24.74
3	19.04	14	20		
11	19.1	37	20		

Table 5. 15. Statistics - Magnesium

Sample A

Analytical method: All
Unit: mg/l

Number of participant:	22	Range	0.13
Number of omitted res	1	Variance	0
True value	0.39	Standard deviation	0.03
Mean value	0.39	Relative Standard deviation	7.20%
Median value	0.39	Relative error	-0.80%

Analytical results in ascending order:

43	0.22 U	6	0.38	11	0.4
19	0.3	41	0.38	34	0.41
20	0.36	35	0.38	28	0.41
37	0.36	8	0.39	21	0.42
7	0.37	3	0.39	15	0.42
25	0.37	29	0.4	36	0.43
12	0.38	14	0.4		
17	0.38	2	0.4		

Sample B

Analytical method: All
Unit: mg/l

Number of participant:	22	Range	0.15
Number of omitted res	1	Variance	0
True value	0.3	Standard deviation	0.03
Mean value	0.3	Relative Standard deviation	10.00%
Median value	0.3	Relative error	1.00%

Analytical results in ascending order:

19	0.2	41	0.3	25	0.31
43	0.21 U	2	0.3	15	0.32
20	0.28	8	0.3	28	0.32
35	0.28	11	0.3	36	0.33
37	0.29	12	0.3	21	0.35
17	0.3	29	0.31	34	0.35
7	0.3	6	0.31		
14	0.3	3	0.31		

U = Omitted results

Table 5. 16. Statistics - Magnesium

Sample C

Analytical method: All
Unit: mg/l

Number of participant:	22	Range	0.48
Number of omitted res	1	Variance	0.02
True value	3	Standard deviation	0.13
Mean value	3	Relative Standard deviation	4.20%
Median value	3	Relative error	0.10%

Analytical results in ascending order:

19	2.7	16	3	14	3.1
35	2.78	3	3	21	3.1
37	2.85	11	3	12	3.15
7	2.9	41	3.05	28	3.15
2	2.9	8	3.07	34	3.18
20	2.95	29	3.08	43	3.33 U
15	2.95	6	3.09		
17	2.99	36	3.09		

Sample D

Analytical method: All
Unit: mg/l

Number of participant:	22	Range	1.2
Number of omitted res	1	Variance	0.07
True value	4.57	Standard deviation	0.26
Mean value	4.56	Relative Standard deviation	5.80%
Median value	4.57	Relative error	-0.30%

Analytical results in ascending order:

19	4	2	4.5	8	4.66
35	4.12	16	4.5	29	4.67
37	4.27	41	4.57	12	4.82
20	4.4	14	4.6	34	5.01
17	4.45	21	4.6	28	5.2
15	4.45	6	4.63	43	6.89 U
3	4.47	36	4.65		
7	4.5	11	4.65		

U = Omitted results

Table 5. 17. Statistics - Sodium

Sample A

Analytical method: All
Unit: mg/l

Number of participant:	22	Range	2.79
Number of omitted res	1	Variance	0.5
True value	15.2	Standard deviation	0.74
Mean value	15.39	Relative Standard deviation	4.80%
Median value	15.2	Relative error	1.25%

Analytical results in ascending order:

20	14.2	3	15.01	21	16
17	14.2	15	15.1	2	16.1
35	14.8	25	15.2	37	16.3
14	14.9	6	15.4	36	16.7
8	14.9	41	15.4	29	16.99
11	14.9	34	15.4	43	146.5 U
7	15	12	15.7		
19	15	4	16		

Sample B

Analytical method: All
Unit: mg/l

Number of participant:	22	Range	0.6
Number of omitted res	1	Variance	0.02
True value	3.61	Standard deviation	0.21
Mean value	3.7	Relative Standard deviation	5.57%
Median value	3.61	Relative error	2.49%

Analytical results in ascending order:

17	3.4	41	3.6	4	3.8
43	3.41 U	15	3.6	37	3.82
2	3.5	12	3.61	11	3.83
3	3.53	21	3.62	35	3.9
7	3.55	25	3.65	19	4
8	3.59	6	3.66	36	4.35
20	3.6	29	3.75		
14	3.6	34	3.75		

U = Omitted results

Table 5. 18. Statistics - Sodium

Sample C

Analytical method: All
Unit: mg/l

Number of participant:	22	Range	3.8
Number of omitted res	2	Variance	0.93
True value	25.7	Standard deviation	0.94
Mean value	25.88	Relative Standard deviation	3.64%
Median value	25.7	Relative error	0.70%

Analytical results in ascending order:

17	24.2	21	25.7	29	26.69 U
7	25	15	25.7	19	27
35	25	4	25.8	36	27.1
2	25.1	14	25.8	12	27.2
11	25.1	16	25.9	37	28
20	25.2	8	26.1	43	33.72 U
3	25.21	34	26.5		
41	25.3	6	26.6		

Sample D

Analytical method: All
Unit: mg/l

Number of participant:	22	Range	7
Number of omitted res	2	Variance	3.81
True value	52.4	Standard deviation	1.94
Mean value	52.83	Relative Standard deviation	3.66%
Median value	52.4	Relative error	0.82%

Analytical results in ascending order:

29	40 U	11	52	6	54.4
20	50	7	52.1	8	54.4
17	50	14	52.2	36	54.7
3	50.94	16	52.6	43	55.81 U
35	51	4	52.9	12	56.6
2	51.4	19	53	37	57
21	51.8	34	53.5		
41	51.8	15	54.2		

U = Omitted results

Table 5. 19. Statistics - Potassium

Sample A

Analytical method: All
Unit: mg/l

Number of participant:	22	Range	0.14
Number of omitted res	3	Variance	0
True value	0.27	Standard deviation	0.04
Mean value	0.274	Relative Standard deviation	12.78%
Median value	0.27	Relative error	1.48%

Analytical results in ascending order:

12	0.04 U	3	0.25	2	0.3
17	0.1 U	7	0.26	19	0.3
37	0.21	34	0.27	11	0.31
20	0.23	25	0.27	4	0.32
21	0.24	35	0.28	36	0.35
41	0.24	8	0.29	43	0.77 U
29	0.25	15	0.29		
6	0.25	14	0.3		

Sample B

Analytical method: All
Unit: mg/l

Number of participant:	22	Range	0.15
Number of omitted res	3	Variance	0
True value	0.27	Standard deviation	0.04
Mean value	0.268	Relative Standard deviation	13.08%
Median value	0.27	Relative error	-0.74%

Analytical results in ascending order:

12	0.03 U	6	0.26	11	0.29
17	0.2 U	21	0.26	14	0.3
2	0.2	15	0.26	19	0.3
37	0.22	35	0.27	4	0.32
20	0.23	8	0.27	36	0.35
41	0.24	34	0.27	43	0.54 U
29	0.25	25	0.27		
3	0.25	7	0.28		

U = Omitted results

Table 5. 20. Statistics - Potassium

Sample C

Analytical method: All
Unit: mg/l

Number of participant:	21	Range	2.68
Number of omitted res	1	Variance	0.41
True value	7.91	Standard deviation	0.66
Mean value	7.8	Relative Standard deviation	8.48%
Median value	7.91	Relative error	-1.39%

Analytical results in ascending order:

41	5.95	2	7.7	35	8.2
12	6.96	34	7.8	11	8.24
29	7.04	3	7.83	21	8.25
17	7.2	15	7.99	43	8.38 U
20	7.5	19	8	4	8.56
37	7.5	7	8.1	36	8.63
6	7.69	14	8.1	8	8.78

Sample D

Analytical method: All
Unit: mg/l

Number of participant:	21	Range	4.99
Number of omitted res	1	Variance	1.47
True value	11.8	Standard deviation	1.29
Mean value	11.57	Relative Standard deviation	11.18%
Median value	11.8	Relative error	-1.95%

Analytical results in ascending order:

12	8.21	3	11.57	35	12.2
41	9.15	6	11.7	19	12.2
29	10.28	7	11.8	21	12.3
20	10.5	2	11.8	36	12.8
17	11	14	12	4	13.2
37	11.3	11	12.1	8	13.8
34	11.3	15	12.11	43	22.29 U

U = Omitted results

Table 5. 21. Statistics - Aluminium

Sample A

Analytical method: All
Unit: µg/l

Number of participant:	16	Range	97
Number of omitted res	0	Variance	700
True value	166	Standard deviation	26
Mean value	159	Relative Standard deviation	15.90%
Median value	166	Relative error	-4.10%

Analytical results in ascending order:

19	108	36	160	15	179
34	112	20	165	37	183
11	130	7	166	2	187
17	140	6	170	25	205
4	147	3	170		
35	155	12	170		

Sample B

Analytical method: All
Unit: µg/l

Number of participant:	16	Range	69
Number of omitted res	0	Variance	419
True value	109	Standard deviation	20
Mean value	102	Relative Standard deviation	18.80%
Median value	109	Relative error	-6.40%

Analytical results in ascending order:

34	61	7	107	37	120
19	70	6	108	12	120
4	79	36	110	25	122
11	79	15	112	3	130
17	90	2	113		
35	97	20	115		

Table 5. 22. Statistics - Aluminium

Sample C

Analytical method: All
Unit: µg/l

Number of participant:	15	Range	81
Number of omitted res	2	Variance	562
True value	148	Standard deviation	24
Mean value	140	Relative Standard deviation	16.00%
Median value	148	Relative error	-5.60%

Analytical results in ascending order:

11	58 U	20	142	37	152
34	86	12	145	2	156
19	97	6	148	36	160
35	128	17	150	15	167
4	136	7	150	3	190 U

Sample D

Analytical method: All
Unit: µg/l

Number of participant:	15	Range	211
Number of omitted res	2	Variance	4710
True value	530	Standard deviation	69
Mean value	507	Relative Standard deviation	12.90%
Median value	530	Relative error	-4.40%

Analytical results in ascending order:

11	216 U	37	500	6	566
20	360	34	501	7	569
19	392	17	530	12	570
4	457	36	540	15	571
35	483	2	546	3	730 U

U = Omitted results

Table 5. 23. Statistics - Dissolved organic carbon

Sample A

Analytical method: All
Unit: mg/l

Number of participant:	14	Range	1.5
Number of omitted res	1	Variance	0.17
True value	5.4	Standard deviation	0.41
Mean value	5.35	Relative Standard deviation	7.62%
Median value	5.4	Relative error	0.92%

Analytical results in ascending order:

34	4.6	14	5.3	7	5.7
21	4.9	25	5.4	17	5.9
8	5	37	5.4	36	6.1
15	5.1	2	5.4	35	11.7 U
12	5.2	28	5.5		

Sample B

Analytical method: All
Unit: mg/l

Number of participant:	14	Range	1.5
Number of omitted res	1	Variance	0.16
True value	3.1	Standard deviation	0.4
Mean value	3.08	Relative Standard deviation	12.98%
Median value	3.1	Relative error	0.65%

Analytical results in ascending order:

25	2	34	3.1	2	3.4
21	2.7	12	3.1	17	3.5
8	3	7	3.2	36	3.5
14	3	37	3.2	35	5.4 U
15	3	28	3.4		

U = Omitted results

Table 5. 24. Statistics - Dissolved organic carbon

Sample C

Analytical method: All
Unit: mg/l

Number of participant:	13	Range	22.2
Number of omitted res	0	Variance	29.3
True value	60	Standard deviation	5.4
Mean value	60.4	Relative Standard deviation	9.00%
Median value	60	Relative error	0.70%

Analytical results in ascending order:

8	52.2	37	59.8	36	63
21	55	17	60	14	64
12	56	7	61	28	74.4
2	57	35	61		
34	59	15	62.8		

Sample D

Analytical method: All
Unit: mg/l

Number of participant:	13	Range	28.8
Number of omitted res	0	Variance	48.4
True value	109.1	Standard deviation	7
Mean value	108.3	Relative Standard deviation	6.40%
Median value	109.1	Relative error	-0.70%

Analytical results in ascending order:

8	90	12	109	37	112
21	100	2	109.1	15	114.4
14	107	17	110	28	118.8
7	108	35	110		
34	109	36	111		

Table 5. 25. Statistics - Chemical oxygen demand

Sample A

Analytical method: All
Unit: mg/l

Number of participant:	5	Range	2.6
Number of omitted res	0	Variance	1.2
True value	6.6	Standard deviation	1.1
Mean value	7.1	Relative Standard deviation	16.40%
Median value	6.6	Relative error	7.40%

Analytical results in ascending order:

6	6.1	11	6.6	20	8.7
35	6.4	12	7.7		

Sample B

Analytical method: All
Unit: mg/l

Number of participant:	5	Range	1.7
Number of omitted res	0	Variance	0.4
True value	3.9	Standard deviation	0.6
Mean value	3.7	Relative Standard deviation	16.60%
Median value	3.9	Relative error	-4.50%

Analytical results in ascending order:

6	2.8	12	3.9	20	4.5
35	3.4	11	4		

Table 5. 26. Statistics - Chemical oxygen demand

Sample C

Analytical method: All
Unit: mg/l

Number of participant:	4	Range	28
Number of omitted res	0	Variance	137.6
True value	81.2	Standard deviation	11.7
Mean value	79.1	Relative Standard deviation	14.40%
Median value	81.2	Relative error	-2.60%

Analytical results in ascending order:

35	63	12	82.5
11	79.8	20	91

Sample D

Analytical method: All
Unit: mg/l

Number of participant:	4	Range	52
Number of omitted res	0	Variance	678.7
True value	154	Standard deviation	26.1
Mean value	151	Relative Standard deviation	16.90%
Median value	154	Relative error	-1.90%

Analytical results in ascending order:

35	122	11	172
20	136	12	174

NIVA

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