CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

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

Intercalibration 9307

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

Prepared by the Programme Centre,
Norwegian Institute for Water Research

NIVA

NIVA - REPORT

Norwegian Institute for Water Research NIVA

Report No.:	Sub-No.:
Serial No.:	**Limited distrib.:**
2948	

Main Office	Regional Office, Sørlandet	Regional Office, Østlandet	Regional Office, Vestlandet	Akvaplan-NIVA A/S
P.O. Box 69, Korsvoll	Televeien 1	Rute 866	Thormøhlensgt 55	Søndre Tollbugate 3
N-0808 Oslo 8	N-4890 Grimstad	N-2312 Ottestad	N-5008 Bergen	N-9000 Tromsø
Norway	Norway	Norway	Norway	Norway
Phone (47) 22 18 51 00	Phone (47) 37 04 30 33	Phone (47) 62 57 64 00	Phone (47) 55 32 56 40	Phone (47) 77 68 52 80
Telefax (47) 22 18 52 00	Telefax (47) 37 04 45 13	Telefax (47) 62 57 66 53	Telefax (47) 55 32 88 33	Telefax (47) 77 68 05 09

Report Title:	Date:	Printed:
Intercalibration 9307. pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, total aluminium, reactive and non-labile aluminium, dissolved organic carbon, and chemical oxygen demand.	September	NIVA 1993
	Topic group: Analysis	
Author(s): Håvard Hovind	Geographical area:	
	Pages: 50	Edition: 100

Contractor:	Contractors ref.:
Department of Environment, Norway	86001

Abstract:

26 laboratories in 19 countries participated in intercalibration 9307. Based on the general target accuracy of ± 20 %, 81 % of the results were acceptable. However, for pH only 52 % of the result pairs were acceptable in relation to the target accuracy of ± 0.1 units. A total error of ± 0.2 units seems to be a reasonable assessment of the accuracy between laboratories.

4 keywords, Norwegian

1. Interkalibrering
2. Sur nedbør
3. Kvalitetskontroll
4. Overvåking

4 keywords, English

1. Intercalibration
2. Acid precipitation
3. Quality Control
   Monitoring

Project manager

Håvard Hovind

For the Administration

Merete Johannessen

ISBN82-577-2370-3

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

INTERCALIBRATION 9307

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

Oslo, september, 1993

Written at the Programme Centre, Norwegian Institute for Water Research

SUMMARY

Intercalibration 9307 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 intercalibration was performed in April-May 1993, 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, reactive and non-labile aluminium (2), dissolved organic carbon and chemical oxygen demand (COD-Mn).

The samples were sent to 32 laboratories, and 26 submitted results to the Programme Centre. 19 countries were represented in this laboratory group.

As "true" value for each parameter was selected the median value of the results received from the participants. For most parameters only 2 - 4 laboratories reported results lying outside the general target accuracy of ± 20 %. Some of these laboratories are obviously using methods not being precise enough for the concentrations of the samples used here, and should select more sensitive methods. Reducing the accuracy limit to ± 10 %, still two third of the laboratories are inside the limits.

For pH the accuracy limit was extended to ± 0.2 units. 72 % of the result pairs were included by this special limit, while only 52 % of the results were within the target accuracy of ± 0.1 units, given in the Manual (1). A total error of ± 0.2 units for pH measurements seems to be a reasonable assessment of the accuracy between laboratories.

The concentrations of alkalinity and non-labile aluminium were to close to the detection limits to be evaluated by the Youden method.

CONTENTS

Summary	2
Introduction	4
Accomplishment of the intercalibration	4
Results	4
pH	22
Conductivity	22
Alkalinity	23
Nitrate + nitrite	23
Chloride	23
Sulfate	23
Calcium	24
Magnesium	24
Sodium	24
Potassium	24
Total aluminium	25
Reactive aluminium	25
Non-labile aluminium	25
Dissolved organic carbon	26
Chemical oxygen demand, COD-Mn	26
Ionic balance	26
Discussion	27
Conclusion	28
Literature	29
Appendix 1 Participants of intercalibration 9307	30
Appendix 2 Preparation of samples.	31
Sample control analyses	31
Appendix 3 Treatment of analytical data	32
Appendix 4 The results of the participating laboratories	33
Appendix 5 Ionic balance calculations	50

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 (3,4), which is briefly described in Appendix 3. This seventh intercalibration test, called 9307, 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, reactive and non-labile aluminium (2), 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.

The samples were mailed from the Programme Centre on the April 2nd, 1993. Nearly all the participating laboratories received the samples within one or two weeks. 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 32 laboratories. The 26 laboratories who submitted results to the Programme Centre, are representing 19 countries. The results from one laboratory was excluded, because they reported results for one sample only, and we need results for a sample pair to evaluate the results by the Youden technique. 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 (3,4). 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 different laboratories. The real "true value" is not known exactly for the natural samples used in this intercalibration. 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 text continues on page 22)

Tabell 1. Statistical summary of the intercalibration 9307.

Parameters and methods	Sample pair	True value		Number of laboratories		Median		Mean value / standard deviation				Relative std. deviation, %		Relative error, %	
		1	2	Total	Excl.	1	2	Sample 1		Sample 2		1	2	1	2
pH	AB	4.92	5.38	25	1	4.92	5.38	4.91	0.12	5.35	0.13	2.3	2.5	-0.4	-0.5
Conductivity, mS/m	AB	3.26	3.96	24	2	3.26	3.96	3.22	0.18	3.95	0.21	5.7	5.3	-1.2	-0.3
Alkalinity, mg/l	AB	0.98	1.59	19	17	0.98	1.59	0.98		1.59				-0.5	0
Gran plot				12	10	0.98	1.59	0.98		1.59				-0.5	0
Not dokumented				7	7										
Nitrate+nitrite, µg/l	AB	107	261	24	3	107	261	110	11	261	21	10.1	8.1	2.6	0
Photom. autoan.				20	2	107	261	111	12	262	22	10.4	8.6	3.5	0.3
Ion chromatogr.				3	1			104		251				-2.8	-3.8
FIA				1	0			103		268				-3.7	2.7
Chloride, mg/l	AB	3.1	4.8	24	3	3.1	4.8	3.08	0.18	4.80	0.32	5.8	6.7	-0.6	-0.1
Ion chrom.				21	1	3.1	4.8	3.09	0.18	4.81	0.33	5.8	6.8	-0.3	0.1
Photom. autoan.				1	0			2.90		4.60				-6.5	-4.2
Argent. titration				2	2			2.38		2.59				-23.2	-46
Sulfate, mg/l	AB	6.2	6.0	24	2	6.2	6.0	6.1	0.4	6.0	0.4	5.8	6.0	-1.0	0
Ion chromatogr.				21	0	6.2	6.0	6.1	0.4	6.0	0.4	5.9	6.2	-0.9	0
Photometry				2	1			6		6				-3.2	0
Nephelometry				1	1			2.5		0.8				-60.5	-86.7
Calcium, mg/l	AB	1.11	3.05	23	2	1.11	3.05	1.12	0.08	3.08	0.19	7.1	6.2	0.7	1.1
FAAS				16	2	1.14	3.08	1.13	0.09	3.08	0.18	7.7	5.9	1.4	1.1
ICP				2	0			1.11		3.01				-0.5	-1.5
EDTA titrnation				3	0	1.08	3.0	1.09	0.1	2.99	0.02	9.2	0.7	-1.5	-1.9
Ion chromatogr.				2	0			1.11		3.31				0	8.5

Magnesium, mg/l	AB	0.35	0.48	23	2	0.35	0.48	0.35	0.04	0.47	0.03	10.3	6.5	-0.5	-1.8
FAAS				17	1	0.35	0.48	0.35	0.03	0.48	0.02	9.5	5.2	-0.3	-1
ICP				2	1			0.40		0.50				14.3	4.2
EDTA titration				2	0			0.35		0.47				-1.4	-3.1
Ion chromatogr.				2	0			0.32		0.44				-8.6	-9.4
Sodium, mg/l	AB	2.11	2.15	23	1	2.11	2.15	2.15	0.23	2.2	0.21	10.6	9.5	1.8	2.1
FAAS				15	1	2.07	2.12	2.11	0.19	2.12	0.14	9.2	6.5	0	-1.2
ICP				1	0			2.50		2.70				18.5	25.6
Flame photom.				5	0	2.18	2.21	2.19	0.33	2.29	0.27	15.2	11.8	3.6	6.4
Ion chromatogr.				2	0			2.14		2.22				1.2	3
Potassium, mg/l	AB	0.255	0.40	23	2	0.255	0.40	0.255	0.027	0.40	0.024	10.6	5.9	0	0.7
FAAS				16	1	0.25	0.40	0.25	0.022	0.40	0.025	8.7	6.2	-1.8	0.8
ICP				1	0			0.30		0.40				17.6	0
Flame Photom.				4	0	0.265	0.42	0.25	0.034	0.41	0.022	13.5	5.3	-2	2.5
Ion chromatogr.				2	1			0.3		0.37				17.6	-7.5
Aluminium, µg/l	AB	429	191	11	1	429	191	425	41	191	24	9.7	12.5	-0.9	-0.1
FAAS				9	1	429	191	430	30	190	20	7.0	10.6	0.3	-0.5
ICP				2	0			406		195				-5.4	1.8
Al, reactive, µg/l	AB	399	148	10	3	399	148	372	80	147	35	21.6	23.7	-6.8	-0.9
Photometry				9	2	399	148	372	80	147	35	21.6	23.7	-6.8	-0.9
Not documented				1	1			138		92				-65.4	-37.8
Al, illabile, µg/l	AB	10	20	7	6	10	20	10		20				0	0
Photometry				6	5			10		20				0	0
Not documented				1	1			23		38				130	90
Org. carbon, mg/l	AB	1.3	3.8	17	4	1.3	3.8	1.3	0.1	3.8	0.2	6.7	5.3	0.7	-0.1
Combustion				13	2	1.3	3.8	1.3	0.1	3.8	0.2	7.8	5.6	0.9	0.1
UV/S_2O_8				3	0	1.3	3.7	1.3	0	3.8	0.2	0	5.5	0	-0.9
Photometry				1	1			1.3		1.5				0	-60.5
Oxyg.dem. mg/l *	AB	1.1	4.5	7	3	1.1	4.5	1.0	0.2	4.5	0.6	20.2	12.9	-5.7	1.0

* Chemical oxygen demand, permanganate oxidation

Fig. 1. pH

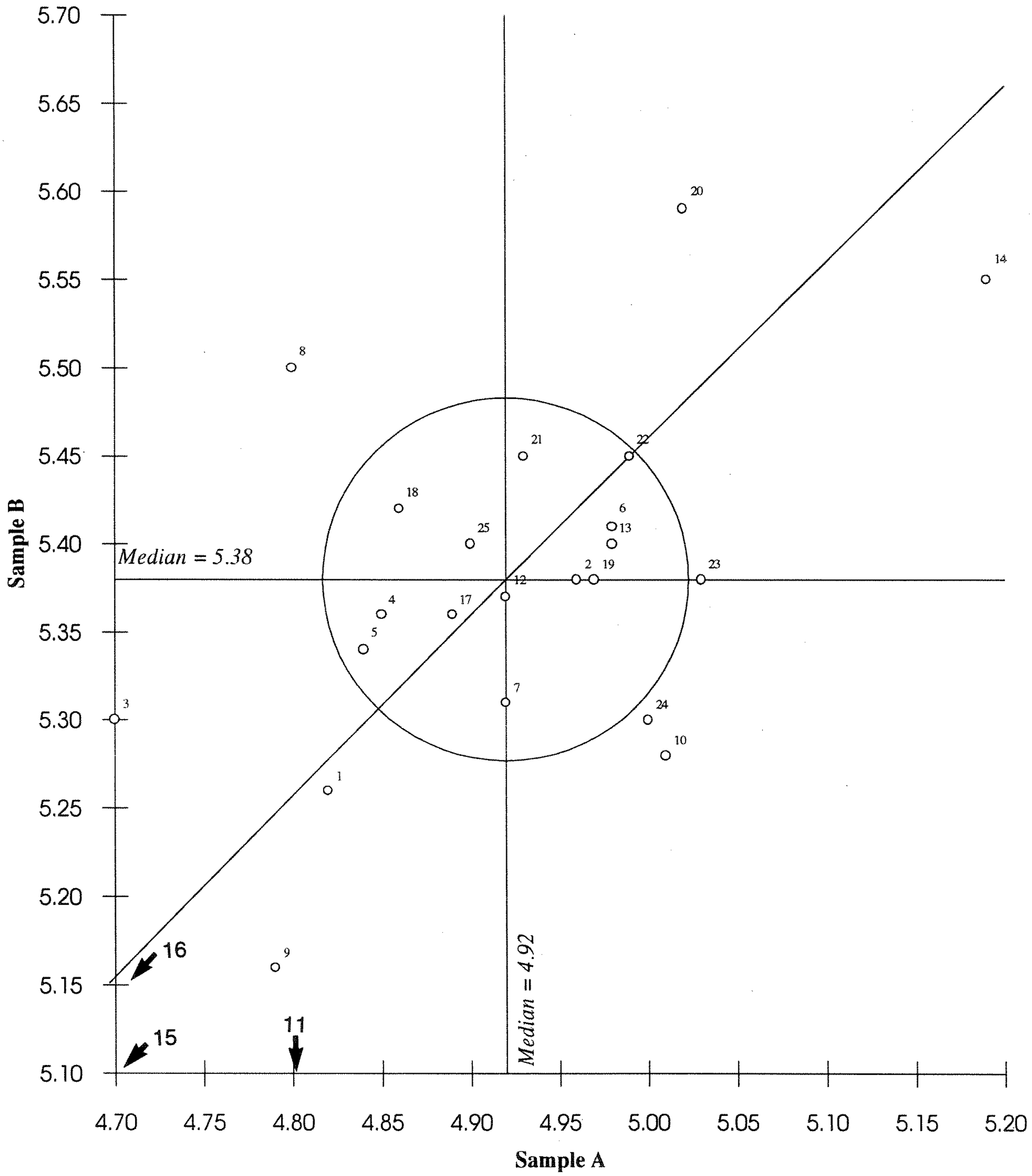

Sample B
Sample A
Median = 5.38
Median = 4.92
5.70
5.65
5.60
5.55
5.50
5.45
5.40
5.35
5.30
5.25
5.20
5.15
5.10
4.70
4.75
4.80
4.85
4.90
4.95
5.00
5.05
5.10
5.15
5.20
16
15
11

Fig. 2. Conductivity

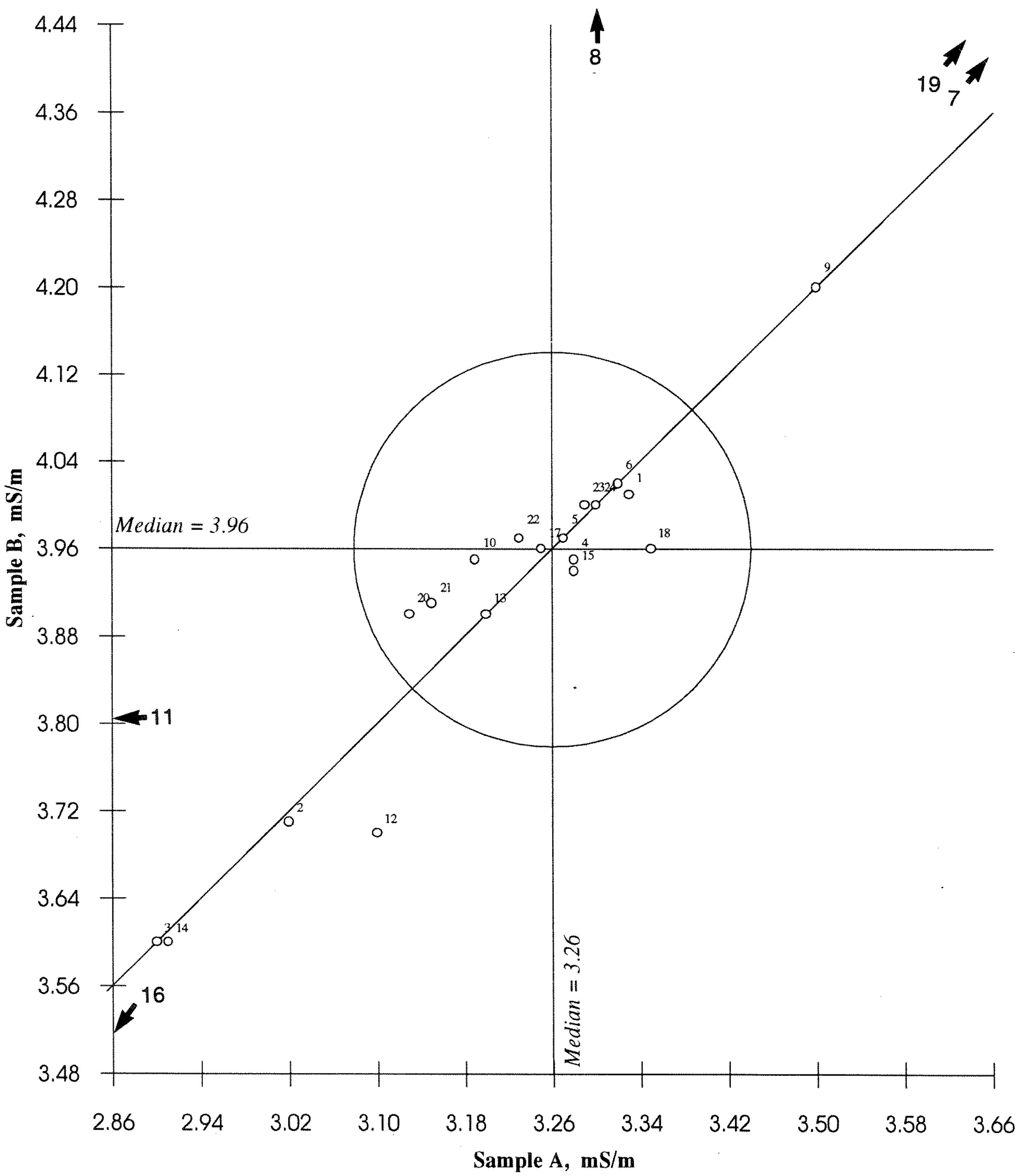


Fig. 3. Alkalinity

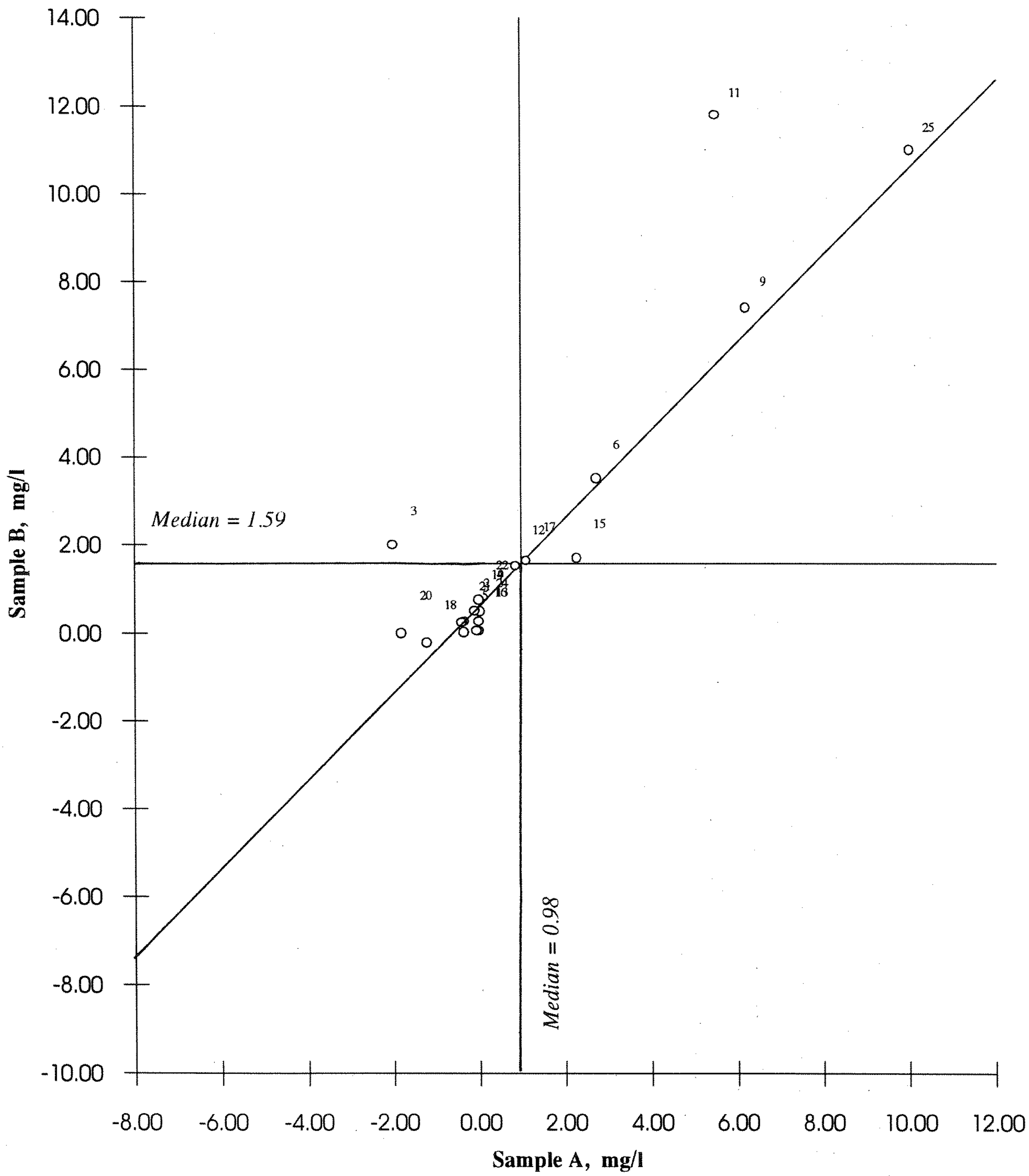


Fig. 4. Nitrate + nitrite-nitrogen

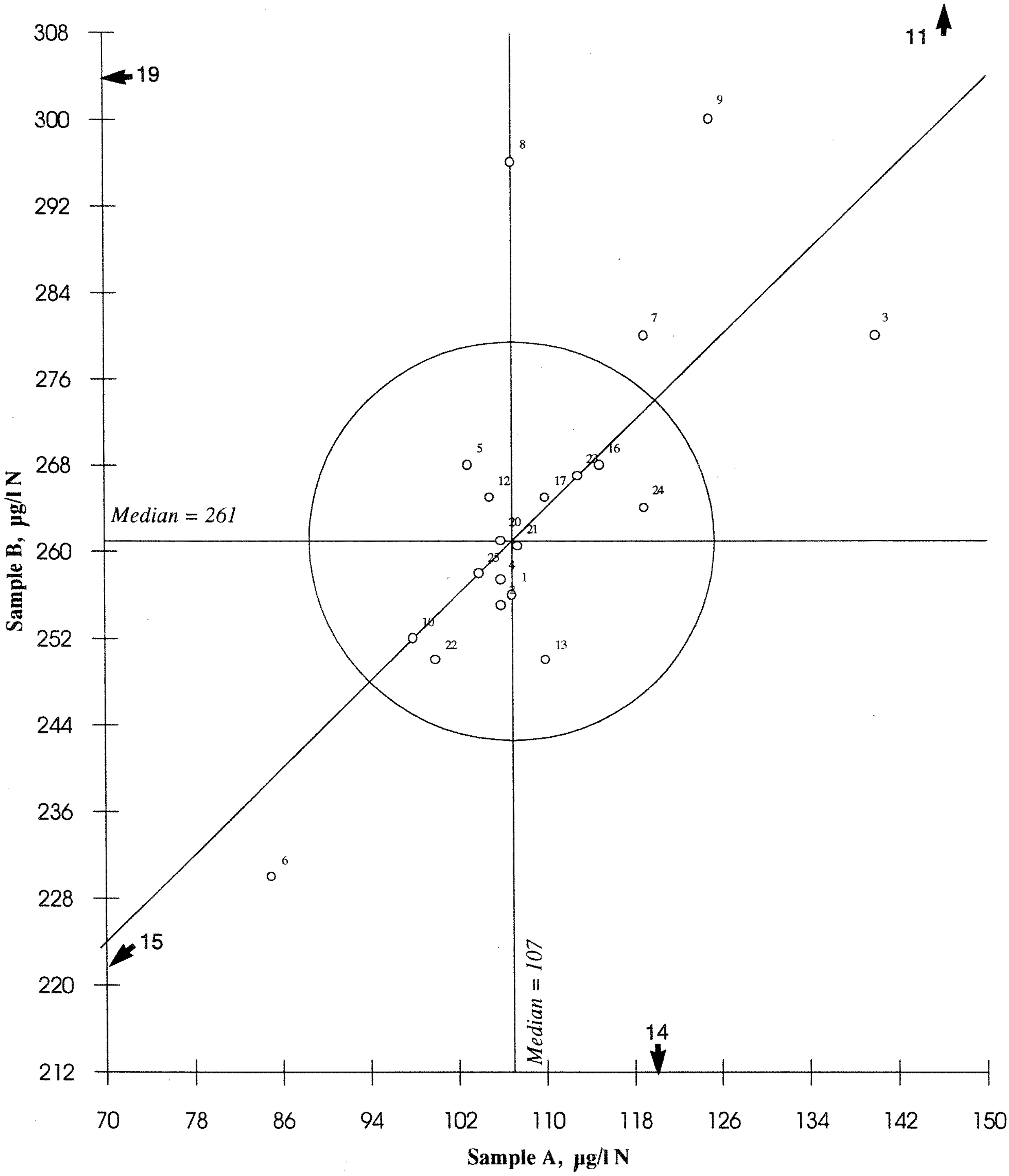


Fig. 5. Chloride

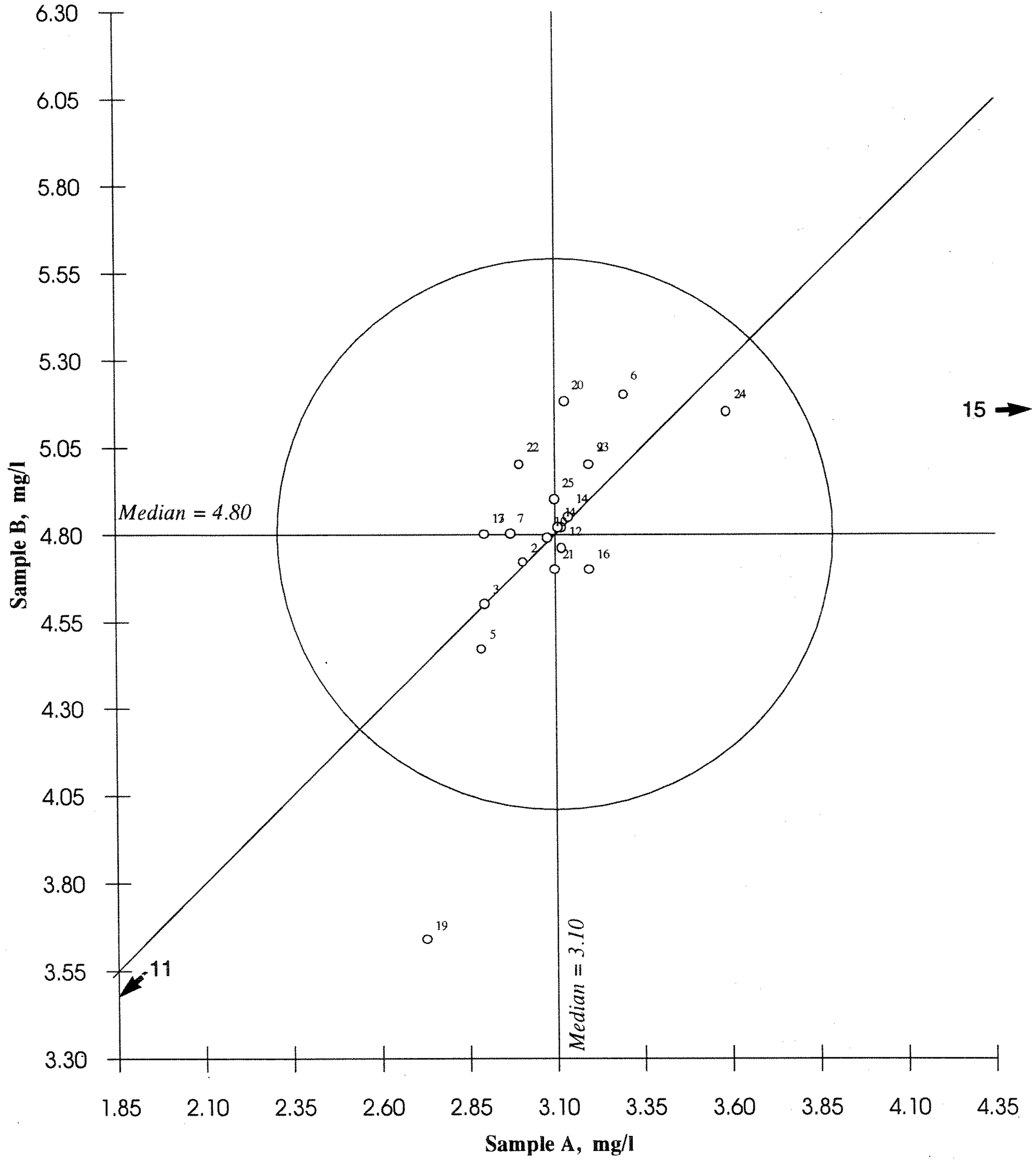


Fig. 6. Sulfate

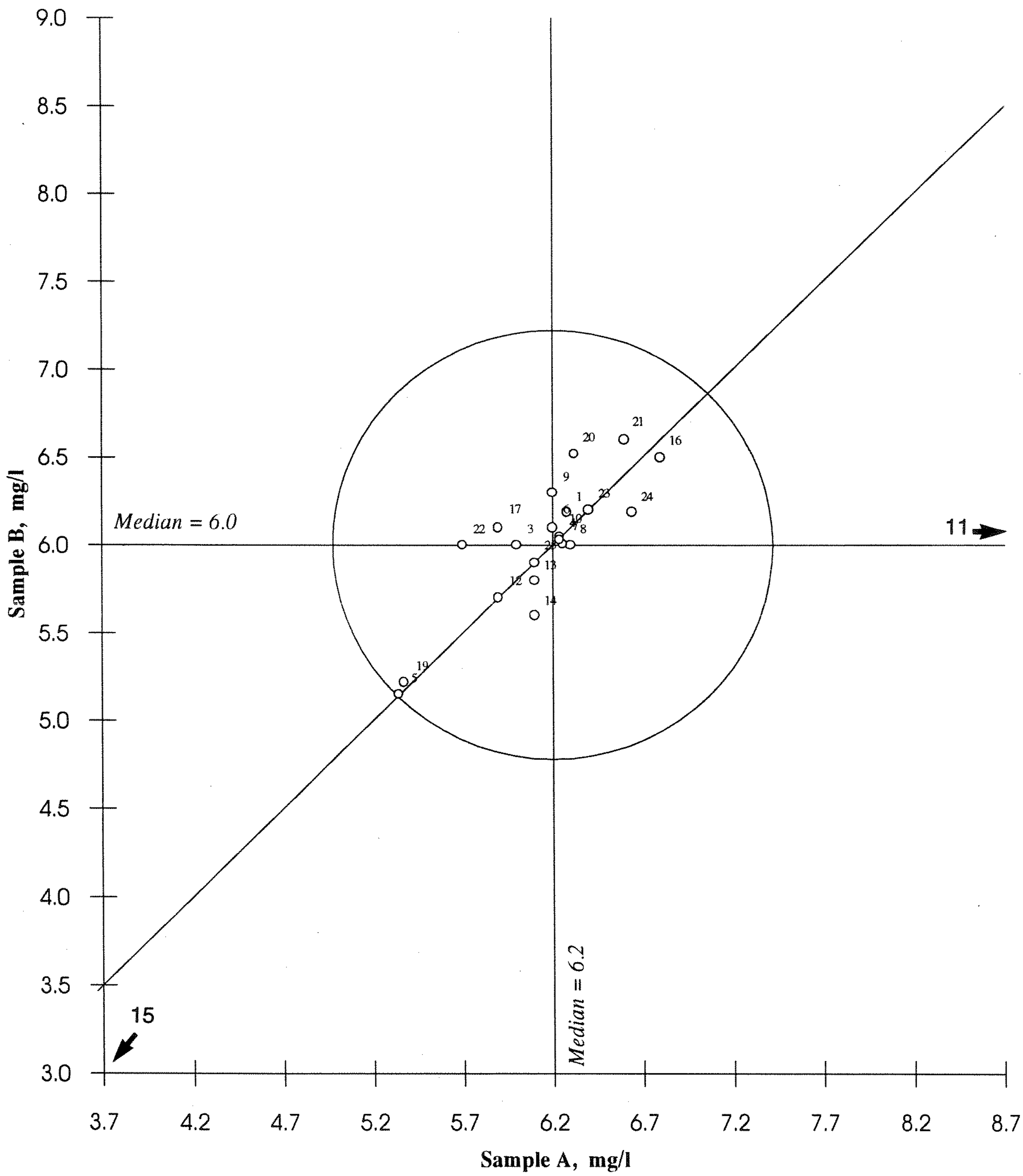


Fig. 7. Calcium

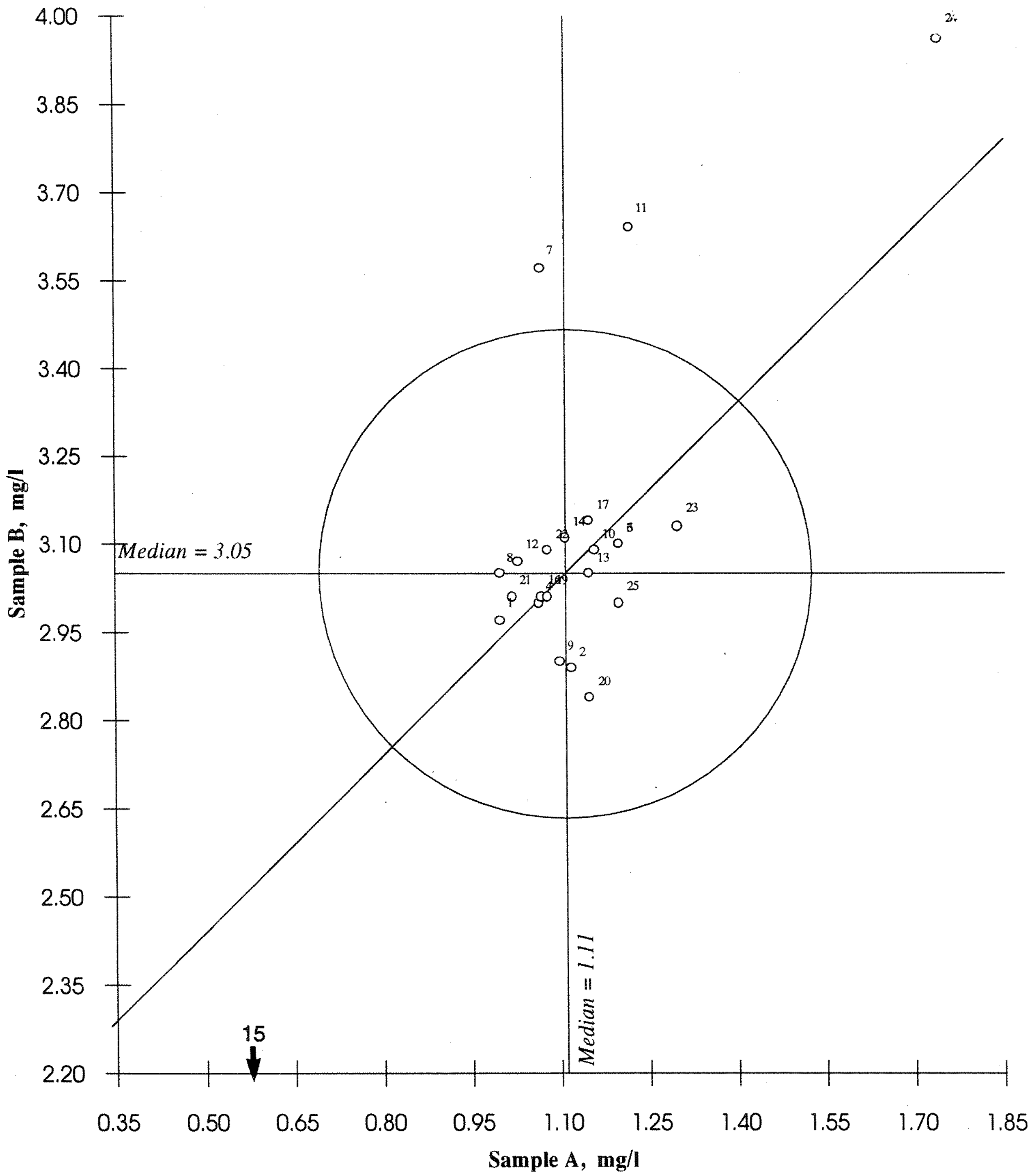


Fig. 8. Magnesium

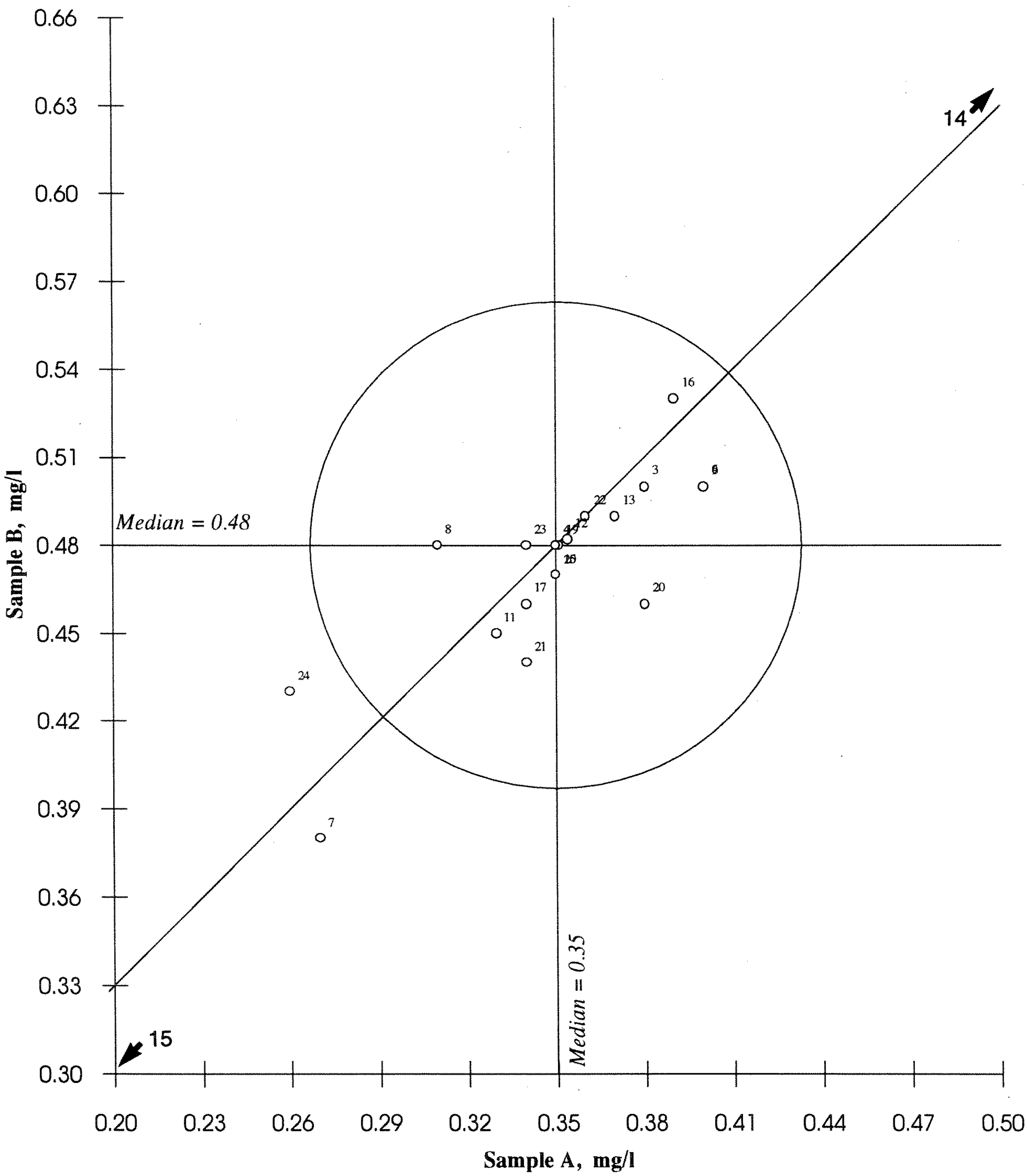
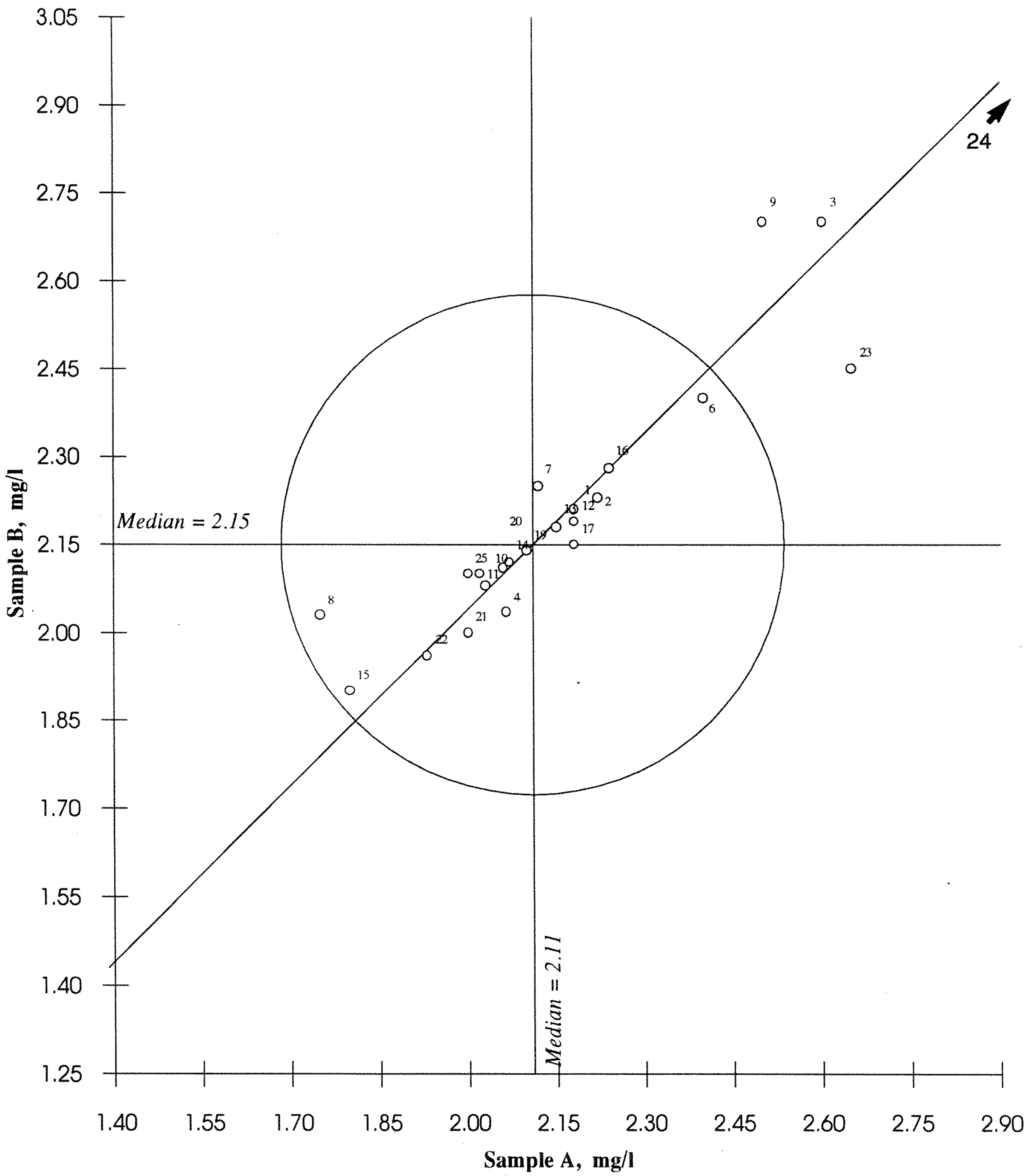


Fig. 9. Sodium



3.05
2.90
2.75
2.60
2.45
2.30
2.15
2.00
1.85
1.70
1.55
1.40
1.25
Sample B, mg/l
1.40
1.55
1.70
1.85
2.00
2.15
2.30
2.45
2.60
2.75
2.90
Sample A, mg/l
Median = 2.15
Median = 2.11
24
9
3
23
6
16
7
1
12
2
13
20
17
19
14
25
10
11
8
4
21
22
15

Fig. 10. Potassium

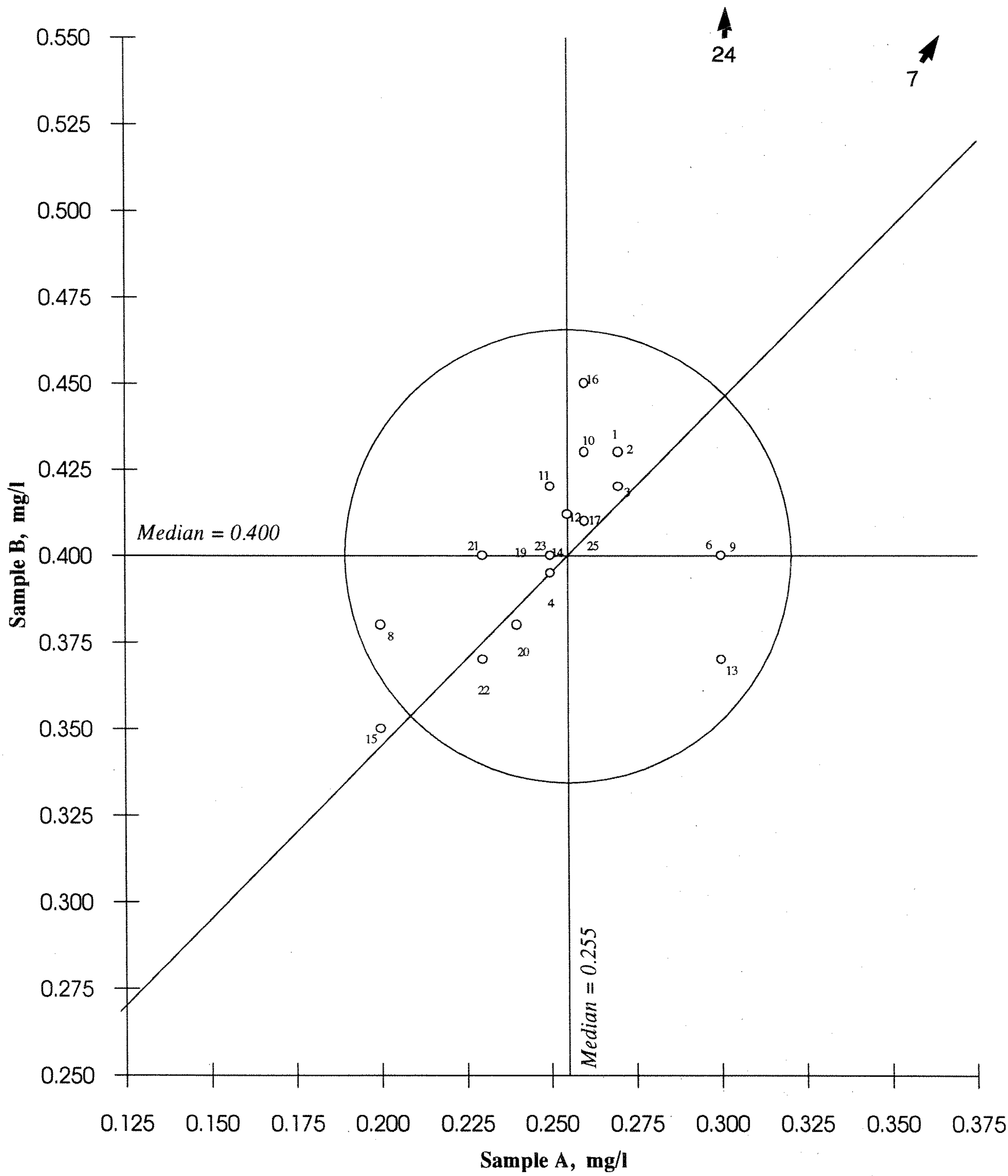


Fig. 11. Aluminium

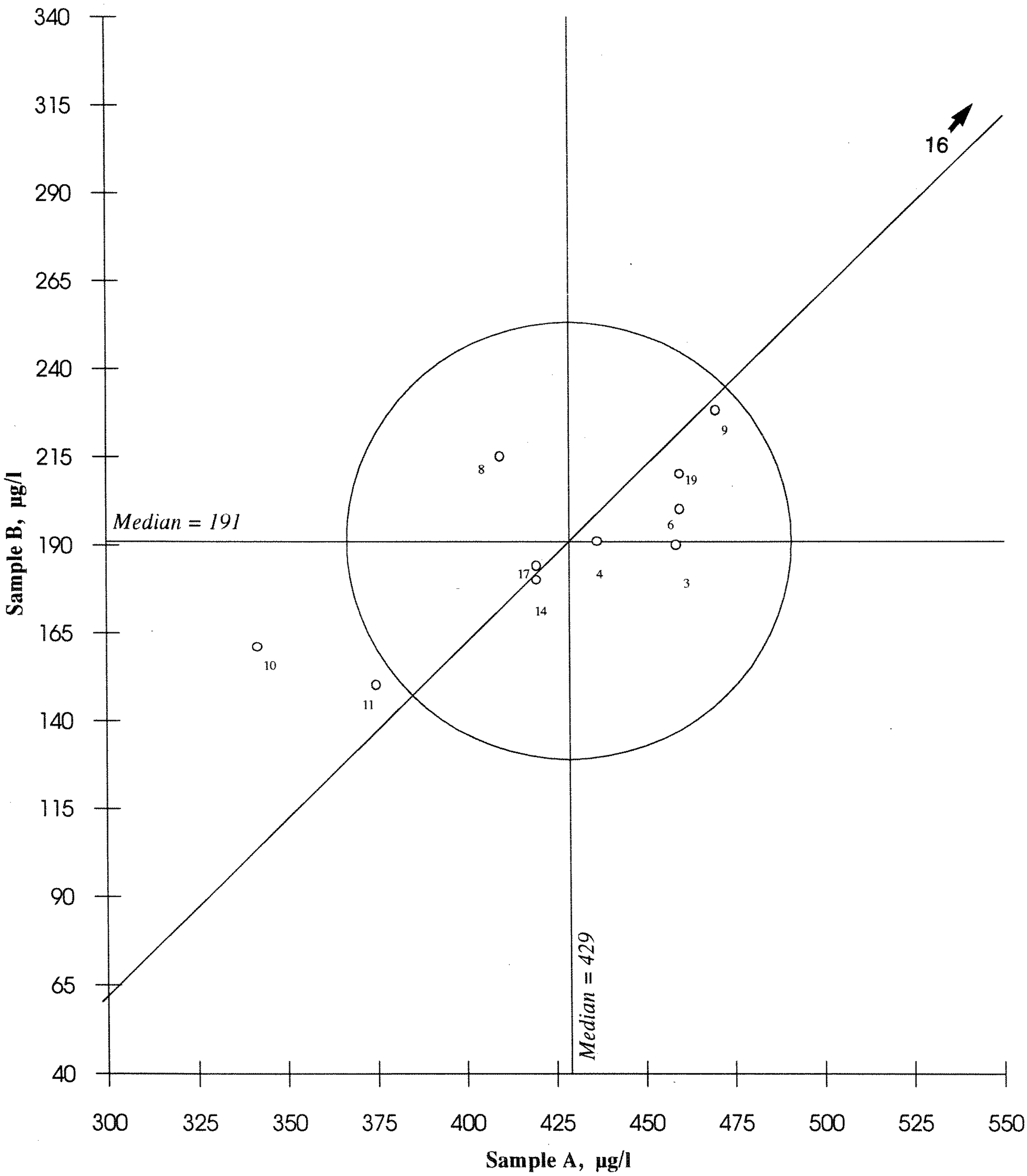


Fig. 12. Aluminium, reactive

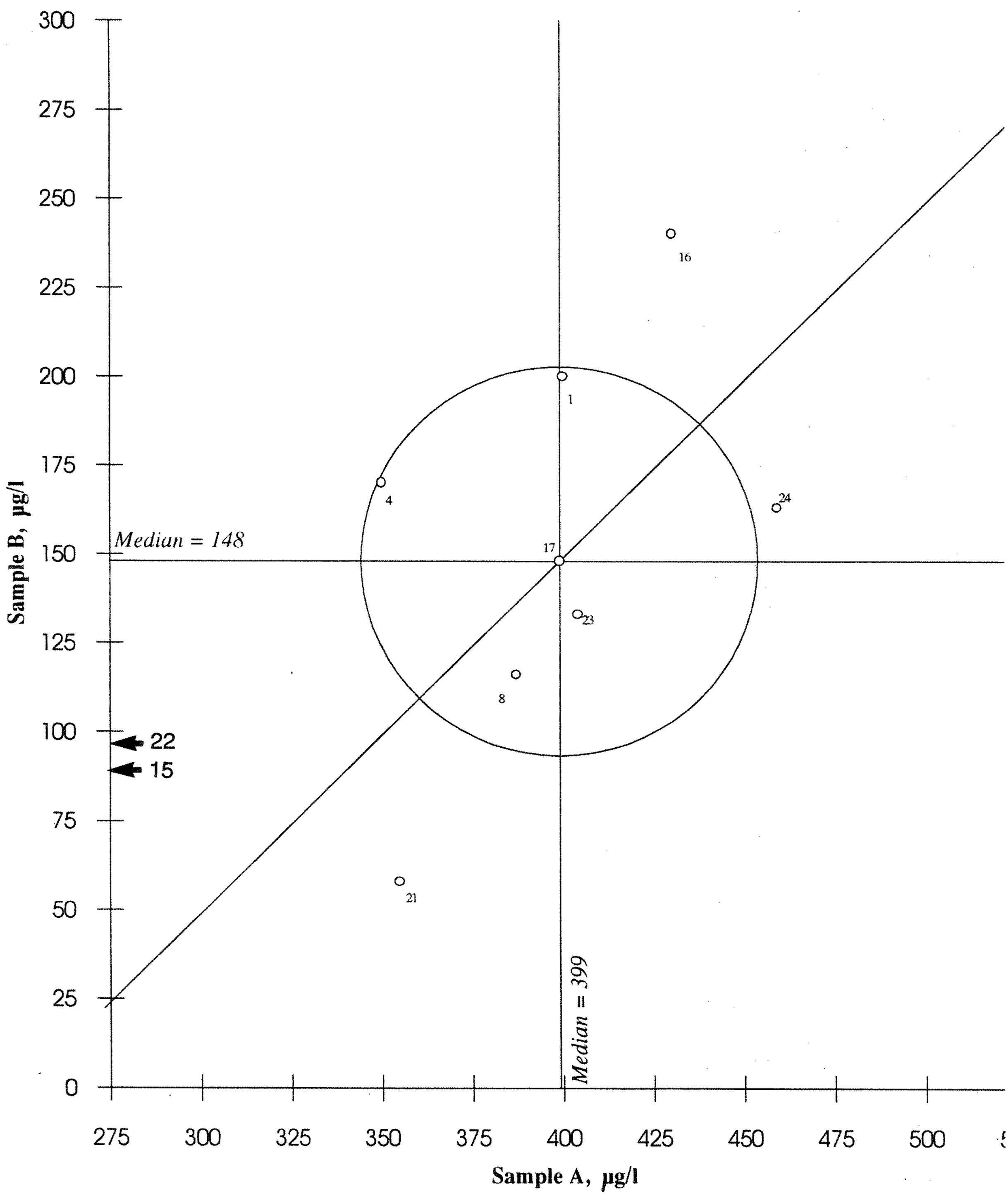


Fig. 13. Aluminium, non-labile

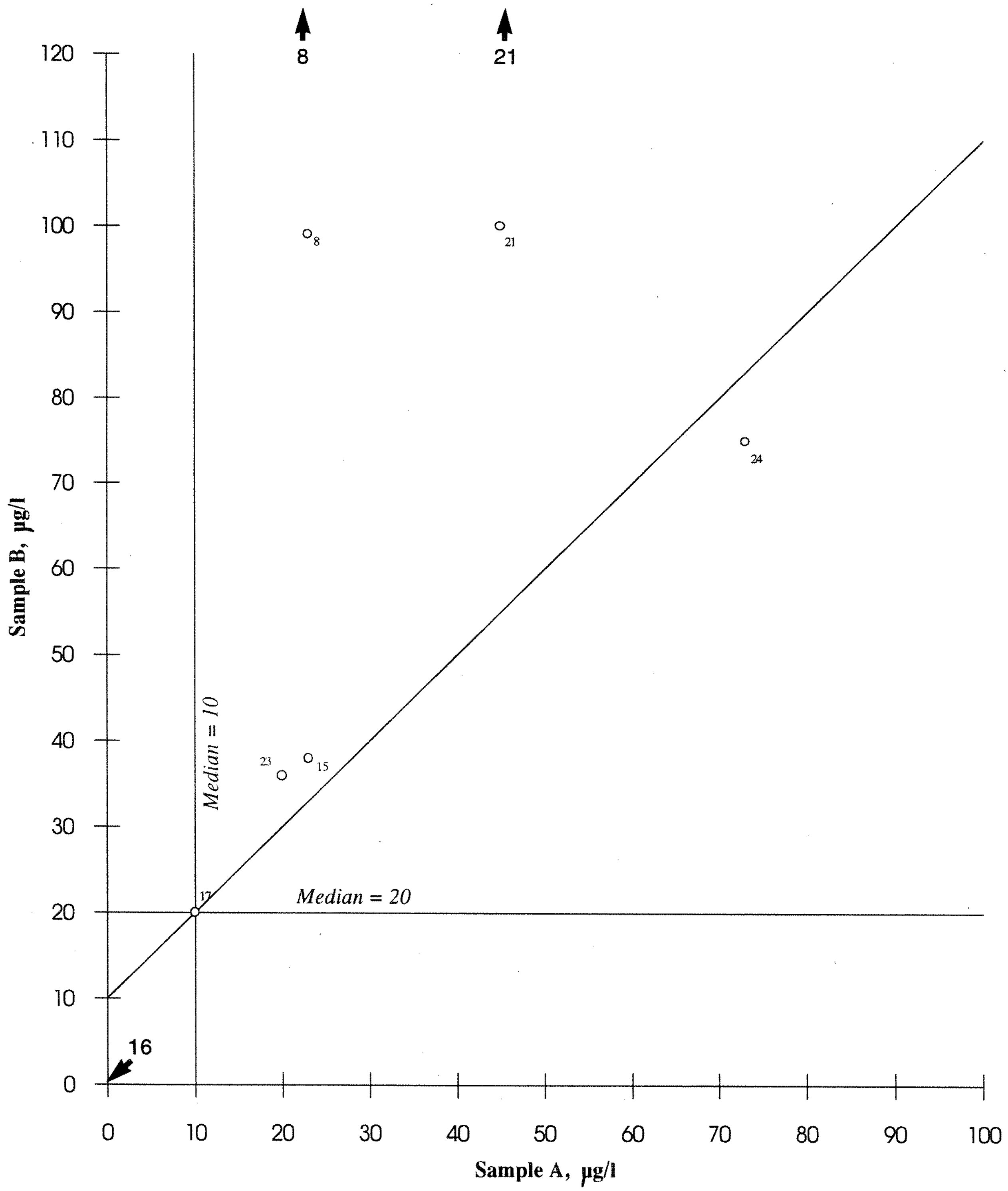


Fig. 14. Dissolved organic carbon

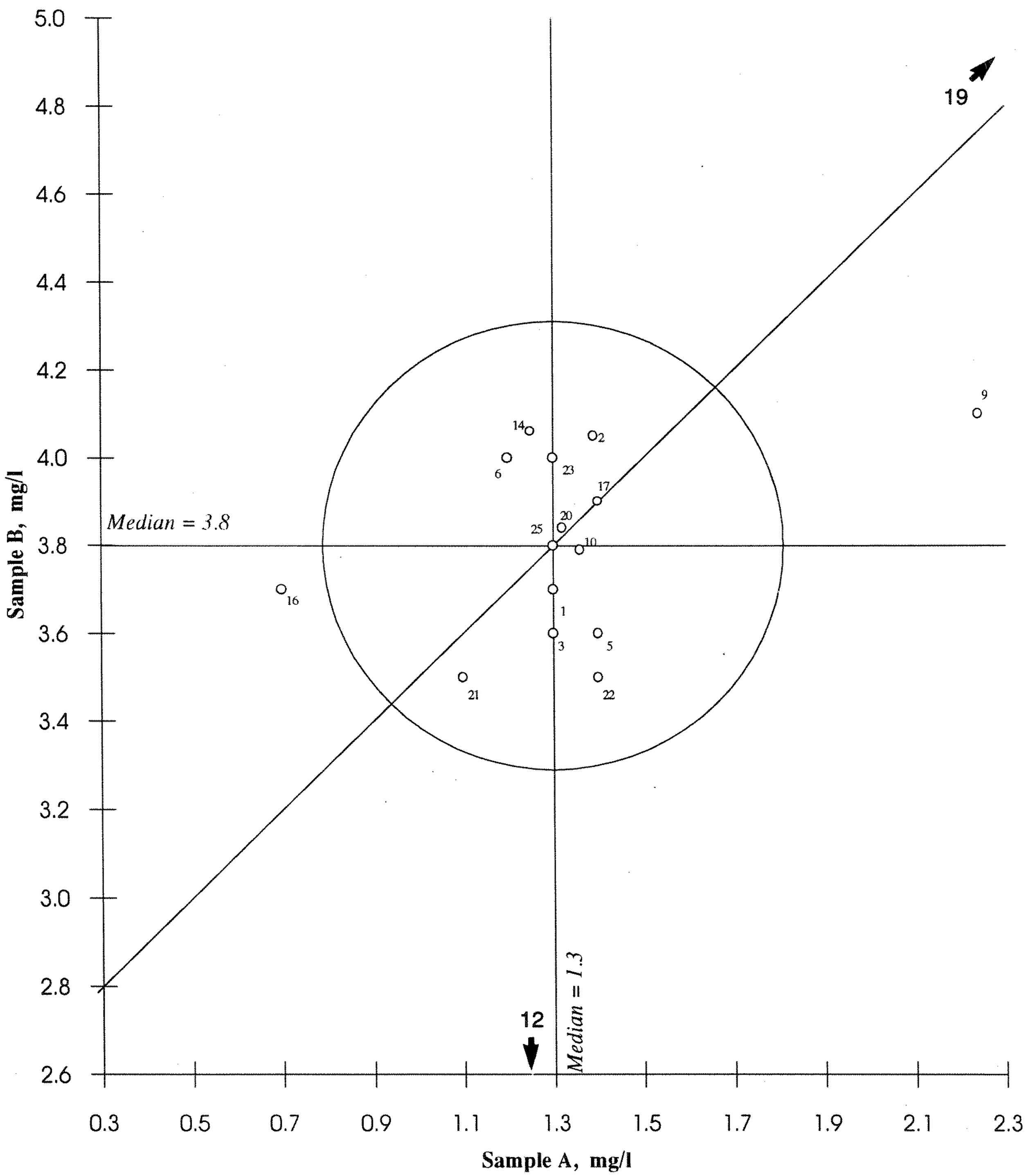
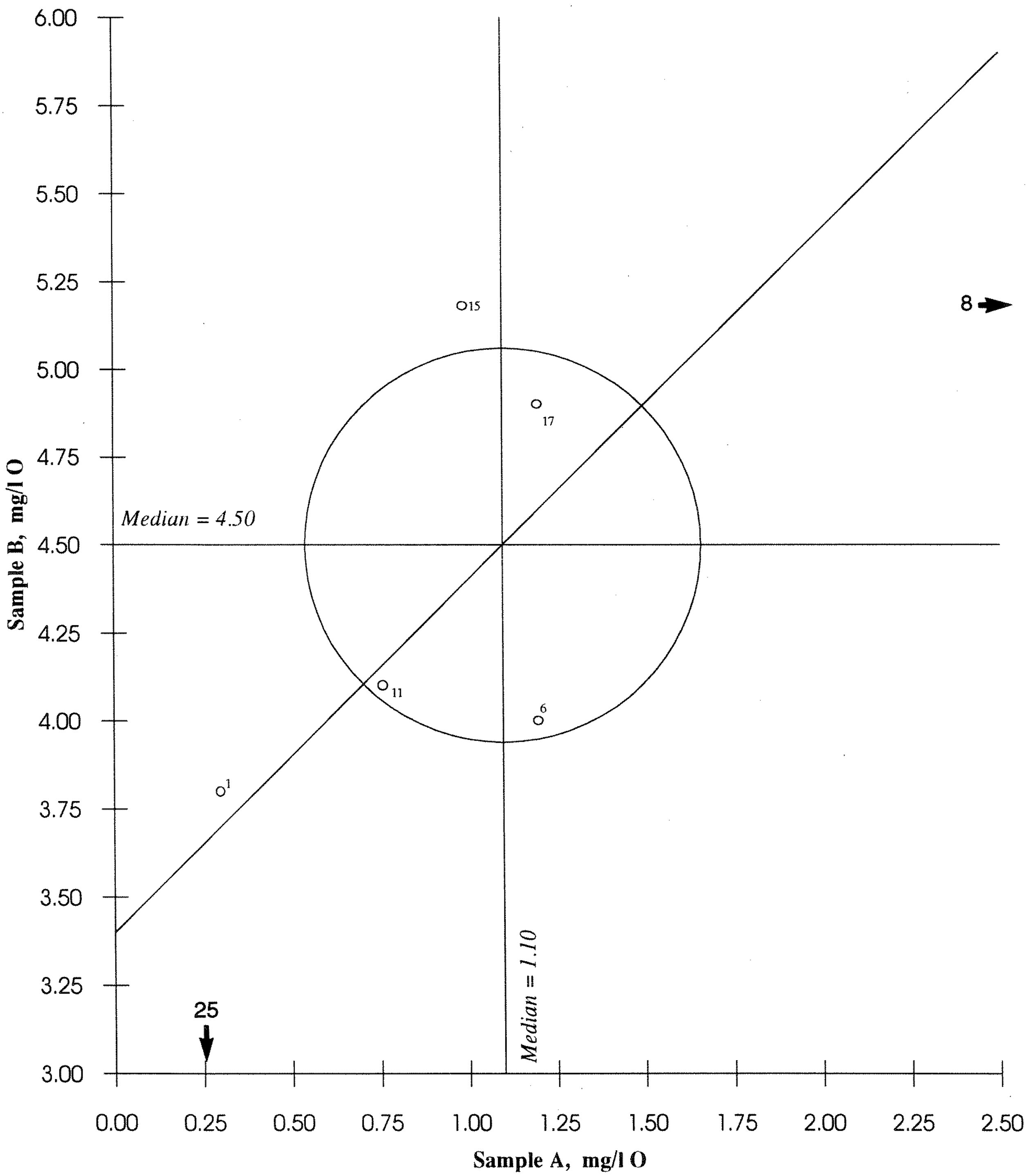


Fig. 15. Chemical oxygen demand



The results are illustrated in Figure 1 - 15, 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 intercalibration 9307 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 - 19.

pH

The reported results for pH are graphically presented in Figure 1, where the radius of the great circle is 0.1 pH units, and visualizes the degree of comparability of pH results between the laboratories. The reported pH values are given in Table 5 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; however, incomplete informations have been given by the participants about the details of the method. Thus we do not know whether some laboratories may have used an equilibration method before the measurement of pH, instead of the "in situ" method used by most laboratories. However, one laboratory informed that they equilibrated the solutions in 350 ppm CO_2 before the measuring pH. The results of this laboratory was a little 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 will thus 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. The pCO_2 effect on pH should be rather small in the acid samples used in this intercalibration.

The control analyses carried out at the Program Centre proved that the samples were stable when stored within the laboratory. However, we must have in mind that 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 (5).

Conductivity

The conductivity results are presented in Figure 2, where the great circle is representing a special accuracy limit of ± 5 %. The reported results are given in Table 6 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. Only one laboratory reported results outside the general target accuracy of ± 20 %. Not more than two result pairs are lying outside the acceptance limit when it is reduced to ± 10 %. The great circle in Figure 2 is representing a special limit of ± 5 %.

Alkalinity

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 7 in Appendix 4. The alkalinity values in the natural water samples used in this intercalibration are very low, the reported results being less than zero or even negative at some laboratories (acidity is reported), and greater than zero at other laboratories. Therefore, it is not possible to evaluate these results in the traditional way, described in Appendix 3.

Nitrate + nitrite

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

The circle in Figure 4 is representing a general target accuracy of ± 20 %.

Chloride

The chloride results are presented in Figure 5, and the reported results are given in Table 9 (Appendix 4). Most laboratories determined chloride by ion chromatography, and one laboratory used an automated photometric version of the mercury thiocyanate method. Two laboratories used argentometric titration for this determination, however, this method is not sensitive enough for the concentrations in these samples.

The great circle in Figure 6 are representing a general target accuracy of ± 20 % of the mean of the true values of the sample pair. Only three result pairs are lying outside this limit.

Sulfate

The sulfate results are illustrated in Figure 6, and the reported values are given in Table 10 (Appendix 4). Most laboratories applied ion chromatography for the determination of this parameter, while two laboratories used an automated photometric method based on the dissociation of the barium-thorin complex. One laboratory used a nephelometric method for the determination, however, the results reported for this method were too low.

An accuracy limit of ± 20 % is represented by the circle in Figure 6. Only 2 result pairs are lying outside this general target accuracy.

Calcium

The calcium results are illustrated in Figure 7, and the reported values are given in Table 11 in Appendix 4. More than half of the participants used atomic absorption spectrometry for the determination of this metal. Among the remaining laboratories two used ICP, two used ion chromatography, and three laboratories applied a volumetric titration method for the determination of calcium.

A general target accuracy of ± 20 % is represented by the great circle in Figure 7. Only four result pairs are lying outside this limit. Even when the narrower special target accuracy of ± 10 % is used, the same four laboratories are the only ones outside the target limit.

Magnesium

The magnesium results are presented in Figure 8, and the reported values are given in Table 12 in Appendix 4. The majority of the participants used atomic absorption spectrometry for the determination of magnesium. Two laboratories used ICP emission spectrometry, two used ion chromatography, and two applied a volumetric titration method for this determination.

Only four laboratories reported values lying outside the general acceptance limit of ± 20 %, which is represented by the great circle in Figure 8.

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 13 (Appendix 4). Most laboratories used flame atomic absorption spectrometry for this determination, while five laboratories used flame emission spectrometry. Only one laboratory used ICP emission spectrometry, and ion chromatography was used by two laboratories.

Four result pairs are lying outside the general target accuracy of ± 20 %, and all four result pairs are systematically too high.

Potassium

The potassium results are presented in Figure 10. The great circle in Figure 10 is representing a general acceptance limit of ± 20 %. The reported values are given in Table 14 in Appendix 4. As for sodium, most laboratories used flame atomic absorption spectrometry for the determination of this element, while four laboratories used flame emission spectrometry. One laboratory used ICP emission technique, and ion chromatography was used by two laboratories.

Three laboratories reported results lying outside the general target accuracy limit of ± 20 %.

Total aluminium

The results for total aluminium are illustrated in Figure 11, and the reported values are given in Table 15 (Appendix 4). The great circle in Figure 12 are representing the general accuracy target of ± 20 %. Most laboratories used atomic absorption spectrometry for the determination of aluminium, while two laboratories used ICP.

Three laboratories have reported results lying outside the general target accuracy limit of ± 20 %.

Reactive aluminium

The results reported for this parameter are represented in Figure 12 and Table 16 (Appendix 4). The deviations between the results of the participating laboratories are mainly systematic, in addition there are a contribution from random errors causing the small circles in the figure to be located a certain distance away from the 45 ° line. Most of the laboratories have reported that they determined aluminium photometrically after complexation with pyrocatechol violet (6), however, exact informations about the method used are lacking from some laboratories.

The reported values for this aluminium fraction are 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. However, there are some methods based on acid pretreatment of the sample, then the results are dependent on how long the acidified sample is stored before the aluminium content is determined. Such acidification is no digestion, but it will lead to some dissolution of complexes, and even of some particulate matter. The results must be expected to increase when the storage time is increased in acidified solutions.

Only five out of ten laboratories reported results lying within the general target accuracy limit of ± 20 %.

Non-labile aluminium

The analytical results for non-labile aluminium received from the participants are presented in Figure 13 and Table 17 (Appendix 4). Only seven laboratories reported results for this parameter, and most of them 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 (2). By this method non-labile aluminium is the fraction that passes through a cation exchange column, and consists of monomeric alumino-organic complexes. Different resins have different exchange properties, in addition to the fact that the resin form also will affect the results. Some of the information from the participating laboratories indicate the different resin forms have been used for this determination.

The observed differences between the reported results are obviously caused by the application of different methods, or slightly different modifications of the method. Additionally, the concentration of non-labile aluminium in these samples are very low. Therefore, the Youden technique is not applicable for the evaluation of the results for non-labile aluminium in these samples.

Dissolved organic carbon

The results for this parameter are presented in Figure 14, and the reported values are given in Table 18 (Appendix 4). Only 16 out of 26 laboratories determined this parameter, and very few informations were given with respect to what instrument had been used, and what oxidation principle is used in the instrument. The analytical results for this parameter may be dependent on the combustion principle, even for the samples used in this intercalibration, which was made from natural water containing humic compounds. However, there is no evidence for such differences in the reported results. One laboratory which used a photometric method based on phenolphthalein, reported a very low value for sample B.

The great circle in Figure 14 is representing a general target accuracy of ± 20 %. Four laboratories reported results lying outside this limit.

Chemical oxygen demand, COD-Mn

The results for this parameter are presented in Figure 15, and the reported values are given in Table 19 (Appendix 4). Only 7 out of 26 laboratories determined this parameter, which was included in the intercalibration because there are some laboratories that do not have equipment for the determination of dissolved organic carbon. Random effects are dominating in Figure 15.

Ionic balance

The ionic balance were calculated by adding the molar concentrations of the major anions (nitrate + nitrite, chloride and sulfate), and the major cations (calcium, magnesium, sodium and potassium), respectively, based on the reported results; and then calculating the difference between the sum of anions and the sum of cations. Laboratories where the results for one or more of these ions were missing, were omitted from the calculations.

The calculated values for the sum of anions, the sum of cations, and the difference between the anions and the cations, are given in the Table 20 of Appendix 5. Normally we expect that the cation sum will be greater than the anion sum, as the organic anions are not included in the calculation of the anion sum. However, alkalinity was omitted in these calculations, and may therefore cause low anion values for sample B, where, in fact, the cation sum is greater than the anion sum

Comparing the anion sums and the cation sums for the results reported by the participants, it seems to be a greater spread in the anion sums than the cation sums, indicating that the cations are generally more precisely determined than the anions.

DISCUSSION

The general rule for target accuracies, outlined in the Manual for Chemical and Biological Monitoring (1), shal normally be used as acceptance limits for the results of the intercalibration test. These limits are corresponding to either the detection limit of the method, or 20 % of the true value, whichever is the greater. To visualize the results of the participants in more detail in the Figures 1 - 15, we have in some cases used a special accuracy limit, usually 5 or 10 %, instead of the general target accuracy.

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	N	Limit	n	%
pH	25	0.1	13*	52
		0.2	18	72
Conductivity	24	5 %	14	58
		20 %	22*	82
Nitrate + nitrite-nitrogen	24	10 %	15	63
		20 %	17*	71
Chloride	24	20 %	21	88
Sulfate	24	20 %	22	92
Calcium	23	20 %	19	79
Magnesium	23	20 %	19	79
Sodium	23	20 %	19	79
Potassium	23	20 %	20	87
Aluminium, total	11	20 %	8	73
Aluminium, reactive	10	20 %	5	50
Dissolved organic carbon	17	20 %	13	76
Chemical oxygen demand	7	20 %	3	43
Sum	258		201	81

* Included in the sum of acceptable results

In table 2 an evaluation of the results of this intercalibration is presented, based on the target accuracy. For pH the general target accuracy is 0.1 pH units. If we extend the acceptance limit to ± 0.2 pH units, the number of acceptable results are increased from 52 to 72 %. Compared to earlier intercalibrations a larger part of results are lying within the target accuracy of ± 0.1 pH units. This is probably due to the lower pH in the samples used this time, being more stable than solutions in the circumneutrality.

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. Selection of a more selective method may be necessary for a 2 opr 3 of the laboratories.

In Table 2 is summarized an evaluation of the results of intercalibration 9307, the number and percentage of acceptable results both for the general target acceptance and the selected special limits are given. 77 % 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.

When alkalinity is included in the intercalibration test, it is necessary to select solutions with higher concentrations than in the samples used this time, the concentration should obviously be quite different from the detection limit of the method. The reported results for alkalinity indicate that the methods used by the participants may be different. The same conclusion include the determination of non-labile aluminium.

For the other parameters most laboratories are within the general target accuracy of ± 20 %. Generally, only a very few laboratories reported results outside this limit. In two or three cases this obviously is caused by using methods not being precise enough for the concentrations of the samples used here. These laboratories should improve their methods to obtain a better comparability, or select a more sensitive method.

More detailed informations about the methods is necessary to evaluate the reported results, and indicate possible connections between deviating results and the method used for the analysis.

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. Driscoll, C.T.: A Procedure for the Fractionation of Aqueous Aluminium in Dilute Acidic Waters. Intern. J. Environ. Anal. Chem. 1984, 16, 267-83.

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

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

5. 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).

6. Røgeberg, E.J.S, Henriksen, A.: An Automated Method for Fractionation and Determination of Aluminium Species in Fresh-Waters. Vatten 1985, 41, pp 48 - 53.

APPENDIX 1

Participants of intercalibration 9307.

1. Swedish Environmental Protection Agency, Uppsala, Sweden.
2. Sawyer Environmental Research Center, Orono, Maine, USA.
3. N.V. Waterleidingbedrijf Midden-Nederland, Utrecht, The Netherlands.
4. Geological Survey, Praha, Czechoslovakia.
5. National Environmental Research Institute, Silkeborg, Denmark.
6. Bayerisches Landesamt für Wasserwirtschaft, München, Germany.
7. Environmental Research Unit, Dublin, Ireland.
8. Kola Science Centre, Apatity, Russia.
9. Kärntner Institut für Seewasser Forschung, Klagenfurt, Austria.
10. Centre de Geochimie de la Surface, Strasbourg, France.
11. Environmental and Water Management Consultants, Budapest, Hungary.
12. Ministry of the Environment, Etobicke, Ontario, Canada.
13. C.N.R., Istituto Italiano di Idrobiologia, Pallanza, Italia.
14. University of Barcelona, Dept. of Ecology, Barcelona, Spain.
15. Research and Engineering Institute for Environment, Bucharest, Romania.
16. Sächsisches Landesamt für Umwelt ung Geologie, Radebeul, Germany
17. Norwegian Institute for Water Research, Oslo, Norway.
18. US Geological Survey, Lakewood, Colorado, USA.
19. Institut of Environmental Protection, Warsaw, Poland.
20. Freshwater Institute, Winnipeg, Manitoba, Canada.
21. National Rivers Authority, Llanelli, Great Britain.
22. Universität Innsbruck, Institut für Zoologie, Innsbruck, Austria.
23. National Board of Waters and the Environment, Helsinki, Finland
24. Charles University, Department of Hydrobiology, Praha, Czechoslovakia.
25. Landesamt für Umweltschutz, Karlsruhe, Germany.
26. Landesamt für Wasser und Abfall, Düsseldorf, Germany

APPENDIX 2

Preparation of samples

The sample solutions were prepared from natural water collected at two locations outside Oslo, a small lake named Nepptjern, and the creek Dalebråtbekken. Raw water was collected in polyethylene containers and brought to the laboratory for storage.

For sample A was used the water from the small lake Nepptjern, while sample B was prepared from the creek water. 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.

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	
	Mean	Sdev.	Mean	Sdev.
pH	4.92	0.08	5.37	0.06
Conductivity mS/m	3.18	0.07	3.96	0.05
Alkalinity mmol/l	< 0.2	-	0.4	0.2
Nitrate/nitrite µg/l	110.5	0.6	265	0
Chloride mg/l	2.95	0.1	4.8	0.2
Sulfate mg/l	5.8	0.1	5.9	0.3
Calcium mg/l	1.14	0.03	3.11	0.05
Magnesium mg/l	0.34	0.01	0.465	0.006
Sodium mg/l	2.18	0.03	2.20	0.04
Potassium mg/l	0.24	0.02	0.39	0.03
Aluminium total, µg/l	421	4.8	161	4.2
Al, reactive, µg/l	393	5.5	144	4.8
Al, non-labile, µg/l	26.7	2.3	69.3	4.0
Diss.org. C mg/l	1.28	0.13	3.75	0.13
COD-Mn, mg/l	1.13	0.15	3.75	0.19

Sample control analyses

During the intercalibration 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 some days before mailing of the samples to the participants. The last sample was analyzed at the beginning of May 1992. 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 - 15).

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 - 19. 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	pH	Cond	Cond	Alk	Alk	NO3+NO2	NO3+NO2	Cl	Cl	SO4	SO4	Ca	Ca
	A	B	A	B	A	B	A	B	A	B	A	A	A	B
1	4.82	5.26	3.33	4.01			107	256	3.11	4.82	6.28	6.19	1.00	2.97
2	4.96	5.38	3.02	3.71	-0.33	0.268	106	255	3.01	4.72	6.10	5.90	1.12	2.89
3	4.70	5.30	2.90	3.60	< 2	2	140	280	2.90	4.60	6.00	6.00	1.20	3.10
4	4.85	5.36	3.28	3.95	0.02	0.49	106	257.4	3.12	4.82	6.24	6.03	1.07	3.00
5	4.84	5.34	3.27	3.97	-0.35	0.02	103	268	2.89	4.47	5.34	5.15		
6	4.98	5.41	3.32	4.02	2.74	3.52	85	230	3.30	5.20	6.20	6.10	1.20	3.10
7	4.92	5.31	4.30	4.90			119	280	2.98	4.80	6.26	6.01	1.07	3.57
8	4.80	5.50	3.30	4.40			107	296	3.00	6.90	6.30	6.00	1.00	3.05
9	4.79	5.16	3.50	4.20	6.2	7.4	125	300	3.20	5.00	6.20	6.30	1.10	2.90
10	5.01	5.28	3.19	3.95			98	252	3.08	4.79	6.24	6.05	1.16	3.09
11	4.80	5.05	2.90	3.80	5.5	11.8	162	628	0.00	0.00	12.80	6.04	1.22	3.64
12	4.92	5.37	3.10	3.70	0.85	1.53	105	265	3.12	4.76	5.90	5.70	1.03	3.07
13	4.98	5.40	3.20	3.90	0	0.05	110	250	2.90	4.80	6.10	5.80	1.15	3.05
14	5.19	5.55	2.91	3.60			119	199	3.14	4.85	6.10	5.60	1.11	3.11
15	4.67	5.03	3.28	3.94	2.28	1.71	30.45	175.75	4.76	5.18	2.45	0.80	0.60	1.90
16	4.20	4.70	1.04	1.80	< 0.05	0.05	115	268	3.20	4.70	6.80	6.50	1.07	3.01
17	4.89	5.36	3.25	3.96	1.1	1.65	110	265	2.90	4.80	5.90	6.10	1.15	3.14
18	4.86	5.42	3.35	3.96	-1.21	-0.23								
19	4.97	5.38	3.65	4.45	< 0.1	0.5	43	304	2.73	3.64	5.37	5.22	1.08	3.01
20	5.02	5.59	3.13	3.90	-1.8	0	106	261	3.13	5.18	6.32	6.52	1.15	2.84
21	4.93	5.45	3.15	3.91	-0.4	0.25	107.5	260.5	3.10	4.70	6.60	6.60	1.02	3.01
22	4.99	5.45	3.23	3.97	0	0.75	100	250	3.00	5.00	5.70	6.00	1.08	3.09
23	5.03	5.38	3.29	4.00			113	267	3.20	5.00	6.40	6.20	1.30	3.13
24	5.00	5.30	3.30	4.00	0	0.27	119	264	3.59	5.15	6.64	6.19	1.74	3.96
25	4.90	5.40			10	11	104	258	3.10	4.90	6.10	5.90	1.20	3.00

Lab.no.	Mg	Mg	Na	Na	K	K	Al	Al	Al-R	Al-R	Al-I	Al-I	DOC	DOC	COD-Mn	COD-Mn
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
1	0.34	0.46	2.18	2.21	0.27	0.43			400	200			1.3	3.7	0.3	3.8
2	0.35	0.47	2.22	2.23	0.27	0.43							1.39	4.05		
3	0.38	0.50	2.60	2.70	0.27	0.42	459	190					1.3	3.6		
4	0.35	0.48	2.07	2.04	0.25	0.40	437	191	350	170						
5																
6	0.40	0.50	2.40	2.40	0.30	0.40	460	200					1.4	3.6		
7	0.27	0.38	2.12	2.25	0.42	0.89							1.2	4	1.2	4
8	0.31	0.48	1.75	2.03	0.20	0.38	410	215	387	116	23	99			2.7	4.3
9	0.40	0.50	2.50	2.70	0.30	0.40	470	228					2.24	4.1		
10	0.35	0.47	2.03	2.08	0.26	0.43	342	161					1.36	3.79		
11	0.33	0.45	2.02	2.10	0.25	0.42	375	150							0.76	4.1
12	0.35	0.48	2.18	2.19	0.26	0.41							1.3	1.5		
13	0.37	0.49	2.15	2.18	0.30	0.37										
14	0.73	1.01	2.07	2.12	0.25	0.40	420	180					1.25	4.06		
15	0.18	0.25	1.80	1.90	0.20	0.35			138	92	23	38			0.99	5.18
16	0.39	0.53	2.24	2.28	0.26	0.45	660	330	430	240	230	90	0.7	3.7		
17	0.34	0.46	2.18	2.15	0.26	0.41	420	184	399	148	10	20	1.4	3.9	1.2	4.9
18																
19	0.35	0.48	2.10	2.14	0.25	0.40	460	210					2.4	5.4		
20	0.38	0.46	2.06	2.11	0.24	0.38							1.32	3.84		
21	0.34	0.44	2.00	2.00	0.23	0.40			355	58	45	100	1.1	3.5		
22	0.36	0.49	1.93	1.96	0.23	0.37			205	97			1.4	3.5		
23	0.34	0.48	2.65	2.45	0.25	0.40			404	133	20	36	1.3	4		
24	0.26	0.43	4.52	4.53	0.31	0.56			459	163	73	75				
25	0.35	0.47	2.00	2.10	0.26	0.41							1.3	3.8	0.3	2.7

Table 5. Statistics - pH

Sample A

Analytical method: All
Unit:

Number of participants	25	Range	0.52
Number of omitted results	1	Variance	0.01
True value	4.92	Standard deviation	0.12
Mean value	4.91	Relative Standard deviation	2.30 %
Median value	4.92	Relative error	- 0.20 %

Analytical results in ascending order:

16	4.20	U	18	4.86		6	4.98
15	4.67		17	4.89		22	4.99
3	4.70		25	4.90		24	5.00
9	4.79		12	4.92		10	5.01
8	4.80		7	4.92		20	5.02
11	4.80		21	4.93		23	5.03
1	4.82		2	4.96		14	5.19
5	4.84		19	4.97			
4	4.85		13	4.98			

U = Omitted results

Sample B

Analytical method: All
Unit:-

Number of participants	25	Range	0.56
Number of omitted results	1	Variance	0.02
True value	5.38	Standard deviation	0.13
Mean value	5.35	Relative Standard deviation	2.50 %
Median value	5.38	Relative error	- 0.50 %

Analytical results in ascending order:

16	4.70	U	5	5.34		6	5.41
15	5.03		17	5.36		18	5.42
11	5.05		4	5.36		22	5.45
9	5.16		12	5.37		21	5.45
1	5.26		23	5.38		8	5.50
10	5.28		2	5.38		14	5.55
24	5.30		19	5.38		20	5.59
3	5.30		13	5.40			
7	5.31		25	5.40			

U = Omitted results

Table 6. Statistics - Conductivity

Sample A

Analytical method: All
Unit: mS/m

Number of participants	24	Range	0.75
Number of omitted results	2	Variance	0.03
True value	3.26	Standard deviation	0.18
Mean value	3.22	Relative Standard deviation	5.60 %
Median value	3.26	Relative error	- 1.20 %

Analytical results in ascending order:

16	1.04	U	10	3.19		8	3.30	
11	2.90		13	3.20		24	3.30	
3	2.90		22	3.23		6	3.32	
14	2.91		17	3.25		1	3.33	
2	3.02		5	3.27		18	3.35	
12	3.10		4	3.28		9	3.50	
20	3.13		15	3.28		19	3.65	
21	3.15		23	3.29		7	4.30	U

U = Omitted results

Sample B

Analytical method: All
Unit: mS/m

Number of participants	24	Range	0.85
Number of omitted results	2	Variance	0.04
True value	3.96	Standard deviation	0.21
Mean value	3.95	Relative Standard deviation	5.30 %
Median value	3.96	Relative error	- 0.30 %

Analytical results in ascending order:

16	1.80	U	21	3.91		24	4.00	
14	3.60		15	3.94		23	4.00	
3	3.60		10	3.95		1	4.01	
12	3.70		4	3.95		6	4.02	
2	3.71		18	3.96		9	4.20	
11	3.80		17	3.96		8	4.40	
13	3.90		5	3.97		19	4.45	
20	3.90		22	3.97		7	4.90	U

U = Omitted results

Table 7. Statistics - Alkalinity

Sample A

Analytical method: All
Unit: mg/l

Number of participants	19	Range	0.25
Number of omitted results	17	Variance	0.03
True value	0.98	Standard deviation	0.18
Mean value	0.98	Relative Standard deviation	18.0 %
Median value	0.98	Relative error	- 0.50 %

Analytical results in ascending order:

3	-2.0	U	16	-0.05	U	15	2.28	U
20	-1.8	U	24	0	U	6	2.74	U
18	-1.21	U	22	0	U	11	5.5	U
21	-0.4	U	13	0	U	9	6.2	U
5	-0.35	U	4	0.02	U	25	10	U
2	-0.33	U	12	0.85				
19	-0.1	U	17	1.1				

U = Omitted results

Sample B

Analytical method: All
Unit: mg/l

Number of participants	19	Range	0.12
Number of omitted results	17	Variance	0.01
True value	1.59	Standard deviation	0.08
Mean value	1.59	Relative Standard deviation	5.30 %
Median value	1.59	Relative error	0.00 %

Analytical results in ascending order:

18	-0.23	U	24	0.27	U	3	2.00	U
20	0	U	4	0.49	U	6	3.52	U
5	-0.02	U	19	0.5	U	9	7.4	U
13	0.05	U	22	0.75	U	25	11	U
16	0.05	U	12	1.53		11	11.8	U
21	0.25	U	17	1.65				
2	0.27	U	15	1.71	U			

U = Omitted results

Table 8. Statistics - Nitrate + nitrite-nitrogen

Sample A

Analytical method: All
Unit: µg/l N

Number of participants	24	Range	55
Number of omitted results	3	Variance	123
True value	107	Standard deviation	11
Mean value	110	Relative Standard deviation	10.3 %
Median value	107	Relative error	2.60 %

Analytical results in ascending order:

15	30	U	2	106		23	113	
19	43	U	4	106		16	115	
6	85		20	106		24	119	
10	98		8	107		7	119	
22	100		1	107		14	119	
5	103		21	108		9	125	
25	104		13	110		3	140	
12	105		17	110		11	162	U

U = Omitted results

Sample B

Number of participants	24	Range	101
Number of omitted results	3	Variance	443
True value	261	Standard deviation	21
Mean value	261	Relative Standard deviation	8.10 %
Median value	261	Relative error	0.00 %

Analytical method: All
Unit: µg/l N

Analytical results in ascending order:

15	176	U	4	257		5	268	
14	199		25	258		16	268	
6	230		21	261		7	280	
22	250		20	261		3	280	
13	250		24	264		8	296	
10	252		12	265		9	300	
2	255		17	265		19	304	U
1	256		23	267		11	628	U

U = Omitted results

Table 9. Statistics - Chloride

Sample A

Analytical method: All
Unit: mg/l

Number of participants	24	Range	0.86
Number of omitted results	3	Variance	0.03
True value	3.10	Standard deviation	0.18
Mean value	3.08	Relative Standard deviation	5.80 %
Median value	3.10	Relative error	- 0.60 %

Analytical results in ascending order:

11	0.00	U	22	3.00		20	3.13	
19	2.73		2	3.01		14	3.14	
5	2.89		10	3.08		23	3.20	
13	2.90		25	3.10		9	3.20	
17	2.90		21	3.10		16	3.20	
3	2.90		1	3.11		6	3.30	
7	2.98		12	3.12		24	3.59	
8	3.00	U	4	3.12		15	4.76	U

U = Omitted results

Analytical method: All
Unit: mg/l

Number of participants	24	Range	1.56
Number of omitted results	3	Variance	0.10
True value	4.80	Standard deviation	0.32
Mean value	4.80	Relative Standard deviation	6.70 %
Median value	4.80	Relative error	- 0.10 %

Analytical results in ascending order:

11	0.00	U	10	4.79		23	5.00	
19	3.64		13	4.80		22	5.00	
5	4.47		17	4.80		9	5.00	
3	4.60		7	4.80		24	5.15	
21	4.70		4	4.82		15	5.18	U
16	4.70		1	4.82		20	5.18	
2	4.72		14	4.85		6	5.20	
12	4.76		25	4.90		8	6.90	U

U = Omitted results

Table 10. Statistics - Sulfate

Sample A

Analytical method: All
Unit: mg/l

Number of participants	24	Range	1.50
Number of omitted results	2	Variance	0.10
True value	6.20	Standard deviation	0.40
Mean value	6.21	Relative Standard deviation	5.70 %
Median value	6.20	Relative error	- 1.00 %

Analytical results in ascending order:

15	2.5	U	25	6.1		1	6.3	
5	5.34		2	6.1		8	6.3	
19	5.4		14	6.1		20	6.3	
22	5.7		9	6.2		23	6.4	
12	5.9		6	6.2		21	6.6	
17	5.9		10	6.2		24	6.6	
3	6.0		4	6.2		16	6.8	
13	6.1		7	6.3		11	12.8	U

U = Omitted results

Sample B

Analytical method: Alle
Unit: mg/l

Number of participants	24	Range	1.4
Number of omitted results	2	Variance	0.1
True value	6.00	Standard deviation	0.4
Mean value	6.00	Relative Standard deviation	6.00 %
Median value	6.00	Relative error	0.00 %

Analytical results in ascending order:

15	0.8	U	8	6.0		17	6.1
5	5.15		22	6.0		24	6.2
19	5.2		3	6.0		1	6.2
14	5.6		7	6.0		23	6.2
12	5.7		4	6.0		9	6.3
13	5.8		11	6.0	U	16	6.5
25	5.9		10	6.1		20	6.5
2	5.9		6	6.1		21	6.6

U = Omitted results

Table 11. Statistics - Calcium

Sample A

Analytical method: All
Unit: mg/l

Number of participants	23	Range	0.30
Number of omitted results	2	Variance	0.01
True value	1.11	Standard deviation	0.08
Mean value	1.12	Relative Standard deviation	7.10 %
Median value	1.11	Relative error	0.70 %

Analytical results in ascending order:

15	0.60	U	22	1.08	10	1.16	
8	1.00		19	1.08	25	1.20	
1	1.00		9	1.10	6	1.20	
21	1.02		14	1.11	3	1.20	
12	1.03		2	1.12	11	1.22	
4	1.07		13	1.15	23	1.30	
7	1.07		17	1.15	24	1.74	U
16	1.07		20	1.15			

U = Omitted results

Sample B

Analytical method: All
Unit: mg/l

Number of participants	23	Range	0.80
Number of omitted results	2	Variance	0.04
True value	3.05	Standard deviation	0.19
Mean value	3.08	Relative Standard deviation	6.30 %
Median value	3.05	Relative error	1.10 %

Analytical results in ascending order:

15	1.90	U	19	3.01	3	3.10	
20	2.84		16	3.01	14	3.11	
2	2.89		8	3.05	23	3.13	
9	2.90		13	3.05	17	3.14	
1	2.97		12	3.07	7	3.57	
25	3.00		10	3.09	11	3.64	
4	3.00		22	3.09	24	3.96	U
21	3.01		6	3.10			

U = Omitted results

Table 12. Statistics - Magnesium

Sample A

Analytical method: All
Unit: mg/l

Number of participants	23	Range	0.15
Number of omitted results	2	Variance	0.00
True value	0.35	Standard deviation	0.04
Mean value	0.35	Relative Standard deviation	10.3 %
Median value	0.35	Relative error	- 0.50 %

Analytical results in ascending order:

15	0.18	U	1	0.34		13	0.37	
24	0.26		10	0.35		3	0.38	
7	0.27		25	0.35		20	0.38	
8	0.31		2	0.35		16	0.39	
11	0.33		4	0.35		9	0.40	
23	0.34		19	0.35		6	0.40	
21	0.34		12	0.35		14	0.73	U
17	0.34		22	0.36				

U = Omitted results

Sample B

Analytical method: All
Unit: mg/l

Number of participants	23	Range	0.15
Number of omitted results	2	Variance	0.00
True value	0.48	Standard deviation	0.03
Mean value	0.47	Relative Standard deviation	6.40 %
Median value	0.48	Relative error	- 1.80 %

Analytical results in ascending order:

15	0.25	U	10	0.47		22	0.49	
7	0.38		25	0.47		13	0.49	
24	0.43		2	0.47		9	0.50	
21	0.44		8	0.48		6	0.50	
11	0.45		23	0.48		3	0.50	
17	0.46		19	0.48		16	0.53	
1	0.46		4	0.48		14	1.01	U
20	0.46		12	0.48				

U = Omitted results

Table 13. Statistics - Sodium

Sample A

Analytical method: All
Unit: mg/l

Number of participants	23	Range	0.90
Number of omitted results	1	Variance	0.05
True value	2.11	Standard deviation	0.23
Mean value	2.15	Relative Standard deviation	10.8 %
Median value	2.11	Relative error	1.80 %

Analytical results in ascending order:

8	1.75	4	2.07	2	2.22	
15	1.8	14	2.07	16	2.24	
22	1.93	19	2.10	6	2.40	
25	2.00	7	2.12	9	2.50	
21	2.00	13	2.15	3	2.60	
11	2.02	12	2.18	23	2.65	
10	2.03	17	2.18	24	4.52	U
20	2.06	1	2.18			

U = Omitted results

Sample B

Analytical method: All
Unit: mg/l

Number of participants	23	Range	0.80
Number of omitted results	1	Variance	0.04
True value	2.15	Standard deviation	0.21
Mean value	2.20	Relative Standard deviation	9.70 %
Median value	2.15	Relative error	2.10 %

Analytical results in ascending order:

15	1.90	20	2.11	7	2.25	
22	1.96	14	2.12	16	2.28	
21	2.00	19	2.14	6	2.40	
8	2.03	17	2.15	23	2.45	
4	2.04	13	2.18	9	2.70	
10	2.08	12	2.19	3	2.70	
25	2.10	1	2.21	24	4.53	U
11	2.10	2	2.23			

U = Omitted results

Table 14. Statistics - Potassium

Sample A

Analytical method: All
Unit: mg/l

Number of participants	23	Range	0.10
Number of omitted results	2	Variance	0.001
True value	0.255	Standard deviation	0.027
Mean value	0.255	Relative Standard deviation	10.6 %
Median value	0.255	Relative error	0.00 %

Analytical results in ascending order:

8	0.20	14	0.25	1	0.27	
15	0.20	11	0.25	3	0.27	
22	0.23	12	0.255	13	0.30	
21	0.23	10	0.26	9	0.30	
20	0.24	25	0.26	6	0.30	
23	0.25	17	0.26	24	0.31	U
19	0.25	16	0.26	7	0.42	U
4	0.25	2	0.27			

U = Omitted results

Sample B

Analytical method: All
Unit: mg/l

Number of participants	23	Range	0.10
Number of omitted results	2	Variance	0.001
True value	0.40	Standard deviation	0.024
Mean value	0.403	Relative Standard deviation	5.90 %
Median value	0.40	Relative error	0.70 %

Analytical results in ascending order:

15	0.35	21	0.40	3	0.42	
22	0.37	6	0.40	10	0.43	
13	0.37	19	0.40	2	0.43	
8	0.38	14	0.40	1	0.43	
20	0.38	25	0.41	16	0.45	
4	0.395	17	0.41	24	0.56	U
23	0.40	12	0.412	7	0.89	U
9	0.40	11	0.42			

U = Omitted results

Table 15. Statistics - Aluminium, total

Sample A

Analytical method: All
Unit: µg/l

Number of participants	11	Range	128
Number of omitted results	1	Variance	1715
True value	429	Standard deviation	41
Mean value	425	Relative Standard deviation	9.90 %
Median value	429	Relative error	1.30 %

Analytical results in ascending order:

10	342	14	420	19	460	
11	375	4	437	9	470	
8	410	3	459	16	660	U
17	420	6	460			

U = Omitted results

Sample B

Analytical method: All
Unit: µg/l

Number of participants	11	Range	78
Number of omitted results	1	Variance	571
True value	191	Standard deviation	24
Mean value	191	Relative Standard deviation	12.5 %
Median value	191	Relative error	- 0.10 %

Analytical results in ascending order:

11	150	3	190	8	215	
10	161	4	191	9	228	
14	180	6	200	16	330	U
17	184	19	210			

U = Omitted results

Table 16. Statistics - Aluminium, reactive

Sample A

Analytical method: All
Unit: µg/l

Number of participants	10	Range	254
Number of omitted results	8	Variance	6451
True value	399	Standard deviation	80
Mean value	372	Relative Standard deviation	20.1 %
Median value	399	Relative error	- 6.80 %

Analytical results in ascending order:

15	138	U	8	387	16	430	
22	205		17	399	24	459	U
4	350		1	400			
21	355	U	23	404			

U = Omitted results

Sample B

Analytical method: Alle
Unit: µg/l

Number of participants	10	Range	103
Number of omitted results	3	Variance	1209
True value	148	Standard deviation	35
Mean value	147	Relative Standard deviation	23.5 %
Median value	148	Relative error	- 0.90 %

Analytical results in ascending order:

21	58	U	23	133	1	200	
15	92	U	17	148	16	240	U
22	97		24	163			
8	116		4	170			

U = Omitted results

Table 17. Statistics - Aluminium, non-labile

Sample A

Analytical method: All
Unit: µg/l

Number of participants	7	Range	0
Number of omitted results	6	Variance	0
True value	10	Standard deviation	0
Mean value	10	Relative Standard deviation	0.0 %
Median value	10	Relative error	0.0 %

Analytical results in ascending order:

16	1	U	8	23	U	24	73	U
17	10		15	23	U			
23	20	U	21	45	U			

U = Omitted results

Sample B

Analytical method: All
Unit: µg/l

Number of participants	7	Range	0
Number of omitted results	6	Variance	0
True value	20	Standard deviation	0
Mean value	20	Relative Standard deviation	0.0 %
Median value	20	Relative error	0.0 %

Number of participants	7	Range	0
Number of omitted results	6	Variance	0
True value	20	Standard deviation	0
Mean value	20	Relative Standard deviation, %	0.0
Median value	20	Relative error	0.0

Analytical results in ascending order:

16	0	U	15	38	U	21	100	U
17	20		24	75	U			
23	36	U	8	99	U			

U = Omitted results

Table 18. Statistics - Dissolved organic carbon

Sample A

Analytical method: All
Unit: mg/l

Number of participants	17	Range	0.3
Number of omitted results	4	Variance	0.0
True value	1.3	Standard deviation	0.1
Mean value	1.3	Relative Standard deviation	6.80 %
Median value	1.3	Relative error	0.70 %

Analytical results in ascending order:

16	0.7	U	25	1.3	5	1.4	
21	1.1		1	1.3	22	1.4	
6	1.2		3	1.3	17	1.4	
14	1.3		20	1.3	9	2.2	U
12	1.3	U	10	1.4	19	2.4	U
23	1.3		2	1.4			

U = Omitted results

Sample B

Analytical method: All
Unit: mg/l

Number of participants	17	Range	0.6
Number of omitted results	4	Variance	0.0
True value	3.8	Standard deviation	0.2
Mean value	3.8	Relative Standard deviation	5.3 %
Median value	3.8	Relative error	- 0.10 %

Analytical results in ascending order:

12	1.5	U	1	3.7	6	4.0	
22	3.5		10	3.8	2	4.1	
21	3.5		25	3.8	14	4.1	
5	3.6		20	3.8	9	4.1	U
3	3.6		17	3.9	19	5.4	U
16	3.7	U	23	4.0			

U = Omitted results

Table 19. Statistics - Chemical oxygen demand

Sample A

Analytical method: All
Unit: mg/l O

Number of participants	7	Range	0.4
Number of omitted results	3	Variance	0.0
True value	1.1	Standard deviation	0.2
Mean value	1.0	Relative Standard deviation	19.1 %
Median value	1.1	Relative error	- 5.7 %

Analytical results in ascending order:

25	0.3	U	15	1.0		8	2.7	U
1	0.3	U	6	1.2				
11	0.8		17	1.2				

U = Omitted results

Sample B

Analytical method: All
Unit: mg/l O

Number of participants	7	Range	1.2
Number of omitted results	3	Variance	0.3
True value	4.5	Standard deviation	0.6
Mean value	4.5	Relative Standard deviation	13.0 %
Median value	4.5	Relative error	1.0 %

Analytical results in ascending order:

25	2.7	U	11	4.1		15	5.2	
1	3.8	U	8	4.3	U			
6	4.0		17	4.9				

U = Omitted results

APPENDIX 5

Ionic balance calculations.

Table 20. Calculation of ionic balance for the intercalibration 9307. The sums of the anions and the cations concentrations, and the difference between these sums, are given in mmol/l. Laboratories where the result for one or more ions are missing, was omitted from the calculations.

	Sample A			Sample B		
Lab. no.	**Anions**	**Cations**	**Differ.**	**Anions**	**Cations**	**Differ.**
1	0.226	0.180	0.047	0.283	0.293	-0.010
2	0.219	0.188	0.031	0.274	0.291	-0.017
3	0.217	0.211	0.006	0.275	0.324	-0.049
4	0.225	0.178	0.047	0.280	0.288	-0.008
6	0.228	0.205	0.023	0.290	0.310	-0.020
7	0.223	0.179	0.044	0.281	0.330	-0.050
8	0.223	0.157	0.067	0.341	0.290	-0.051
9	0.228	0.204	0.024	0.294	0.314	-0.020
10	0.224	0.182	0.042	0.279	0.294	-0.015
11	0.278	0.182	0.096	0.171	0.321	-0.0150
12	0.218	0.182	0.036	0.272	0.299	-0.027
13	0.217	0.189	0.028	0.274	0.297	-0.023
14	0.224	0.212	0.012	0.268	0.341	-0.073
15	0.187	0.128	0.060	0.175	0.207	-0.032
16	0.240	0.190	0.050	0.287	0.304	-0.017
17	0.212	0.187	0.026	0.281	0.299	-0.017
19	0.192	0.181	0.011	0.233	0.293	-0.060
20	0.227	0.184	0.043	0.301	0.281	0.019
21	0.233	0.172	0.061	0.289	0.284	0.005
22	0.210	0.173	0.037	0.284	0.289	-0.005
23	0.232	0.215	0.017	0.289	0.312	-0.023
24	0.248	0.313	-0.065	0.293	0.444	-0.151
25	0.222	0.182	0.040	0.279	0.290	-0.011
Mean	0.224	0.190	0.034	0.274	0.304	-0.031
Std.dev.	0.018	0.033		0.036	0.040	

Norwegian Institute for Water Research NIVA

P.O.Box 69, Korsvoll N-0808 Oslo, Norway
Phone: + 47 22 18 51 00   Fax: + 47 22 18 52 00

ISBN-82-577-2370-3