CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

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

Intercalibration 9206

pH, κ_{25}, HCO_3, NO_3+ NO_2, Cl, SO_4, Ca, Mg, Na, K, Al and DOC

Prepared by the Programme Centre,
Norwegian Institute for Water Research NIVA

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Abstract:

23 laboratories in 18 countries participated in intercalibration 9206. Based on the general target accuracy of ± 20 %, about 80 - 90 % of the results were acceptable for the main components. However, for pH only 30 and 70 % of the result pairs in the two sample sets were acceptable in relation to the target accuracy of ± 0,1 units. Supersaturation with carbondioxide is probably the reason why we observe reduced quality of pH data in circumneutral samples.

4 keywords, Norwegian

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

4 keywords, English

1. Intercalibration
2. Acid precipitation
3. Ionic balance
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INTERNATIONAL CO-OPERATIVE PROGRAMME FOR ASSESSMENT AND MONITORING OF ACIDIFICATION OF RIVERS AND LAKES

INTERCALIBRATION 9206

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

Oslo, september, 1992

Written at the Programme Centre, Norwegian Institute for Water Research

SUMMARY

Intercalibration 9206 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 March-May 1992, 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 organic carbon, and aluminium.

The samples were sent to 26 laboratories, and 23 submitted results to the Programme Centre. 18 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 3 - 5 laboratories reported results lying outside the general target accuracy of ± 20 %.

pH makes an exception, for this parameter the accuracy limit was extended to ± 0,2 units. 57 and 83 % of the result pairs were included by this special limit for the sample pairs AB and CD, respectively, while only 30 and 70 % of the results were within the target accuracy of ± 0,1 units, given in the Manual (1). Especially for samples with pH values near neutrality, the supersaturation of CO_2 leads to greater variation in the results from the different laboratories. Application of a well defined pretreatment method for the samples is probably the only way to improve the comparability for such samples.

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 sixth intercalibration test, called 9206, included the determination of the main components in water: pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium, total organic carbon, and aluminium in natural water samples.

ACCOMPLISHMENT OF THE INTERCALIBRATION

The preparation of the sample solutions is describedi 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 20th of March, 1992. 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 26 laboratories. The 23 laboratories who submitted results to the Programme Centre, are representing 18 countries. 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 purpose of this test is to evaluate the comparability of the analytical results produced by different laboratories. As the real "true value" is not known exactly for the natural samples used here, we selected the median value determined from the analytical results submitted by the participating laboratories as the "true value" for each parameter. Therefore the median value is considered to be an acceptable estimate of the true value for this purpose.

(The text continues on page 30)

TABLE 1. SURVEY OF THE RESULTS OF INTERCALIBRATION.

Parameter/method	Sample pair	True values 1	True values 2	Number of labs. Tot.	Number of labs. Om.	Median value 1	Median value 2	Mean value/standard deviation 1 mean	1 s.dev.	2 mean	2 s.dev.	Relative std. dev. 1	Relative std. dev. 2	Relative error 1	Relative error 2
pH	AB	6.60	7.16	23	1	6.60	7.16	6.56	0.20	7.12	0.23	3.0	3.2	-0.7	-0.6
pH	CD	3.79	4.42	23	1	3.79	4.42	3.79	0.07	4.42	0.08	1.8	1.9	0.1	0.0
Conductivity, all methods	AB	3.00	5.44	22	1	3.00	5.44	2.99	0.12	5.39	0.26	4.0	4.9	-0.5	-0.9
Conductivity, all methods	CD	11.0	3.80	22	1	11.0	3.80	10.9	0.65	3.79	0.24	6.0	6.4	-1.6	-0.3
Alkalinity, all methods	AB	2.37	7.75	20	7	2.37	7.75	2.51	0.41	7.78	0.44	16.2	5.7	5.9	0.4
Nitrate-nitrogen, all methods	AD	220	21.5	22	8	220	21.5	218	12.5	21.4	4.69	5.7	21.9	-1.0	-0.3
Nitrate-nitrogen, all methods	CB	2460	960	22	1	2460	960	2432	89.6	950	59.5	3.7	6.3	-1.3	-1.0
Chloride, all methods	AB	1.88	2.99	22	1	1.88	2.99	1.88	0.15	2.99	0.17	7.8	5.8	-0.1	-0.1
Chloride, all methods	CD	3.31	1.74	22	2	3.31	1.74	3.32	0.24	1.74	0.14	7.1	8.0	0.4	0.1
Sulfate, all methods	AB	5.34	6.89	22	2	5.34	6.89	5.38	0.26	6.88	0.16	4.8	2.3	0.7	-0.2
Sulfate, all methods	CD	8.83	5.90	22	3	8.83	5.90	8.82	0.56	5.85	0.27	6.3	4.7	-0.1	-0.8
Calcium, all methods	AB	2.72	2.84	22	2	2.72	2.84	2.74	0.08	2.82	0.10	3.0	3.4	0.7	-0.5
Calcium, all methods	CD	0.96	1.71	22	4	0.96	1.71	0.96	0.07	1.71	0.07	7.1	4.1	0.2	0.0

Magnesium,	AB	0.46	0.51												
all methods				22	1	0.46	0.51	0.46	0.02	0.51	0.02	4.5	4.4	0.1	0.3
Magnesium,	CD	0.31	0.35												
all methods				22	2	0.31	0.35	0.31	0.02	0.34	0.03	6.8	9.2	0.7	-1.6
Sodium,	AB	1.48	5.48												
all methods				21	3	1.48	5.48	1.50	0.10	5.47	0.20	6.9	3.6	1.3	-0.1
Sodium,	CD	1.96	1.29												
all methods				21	2	1.96	1.29	1.98	0.13	1.29	0.10	6.7	7.7	1.2	-0.0
Potassium,	AB	0.35	0.37												
all methods				20	1	0.35	0.37	0.35	0.03	0.38	0.03	7.7	7.4	0.5	1.5
Potassium,	CD	0.19	0.05												
all methods				20	8	0.19	0.05	0.19	0.02	0.05	0.01	9.4	18.5	-2.5	-4.3
Dissolved organic carbon	AB	2.90	2.24												
all methods				16	1	2.90	2.24	3.00	0.36	2.23	0.44	12.1	19.9	3.5	-0.2
Dissolved organic carbon	CD	6.9	10.1												
all methods				16	1	6.90	10.10	6.93	0.64	10.03	0.77	9.3	7.7	0.4	-0.7
Aluminium	AB	53.0	40.0												
all methods				17	5	53.0	40.0	50.2	11.9	36.2	9.02	23.8	24.9	-5.4	-9.6
Aluminium	CD	296	351												
all methods				17	0	296	351	290	43	350	58	14.8	16.5	-1.9	-0.2
Iron	AB			1	0	13	27								
Iron	CD			1	0	287	217								
Manganese	AB			1	0	2.0	9.0								
Manganese	CD			1	0	19	42								
Ammonium-nitrogen	AB			1	0	<14	462								
Ammonium-nitrogen	CD			1	0	1456	28								
Silicium	AB			1	0	3.30	2.70								
Silicium	AB			1	0	2.64	5.70								

Om. = omitted laboratories

FIG. 1 pH

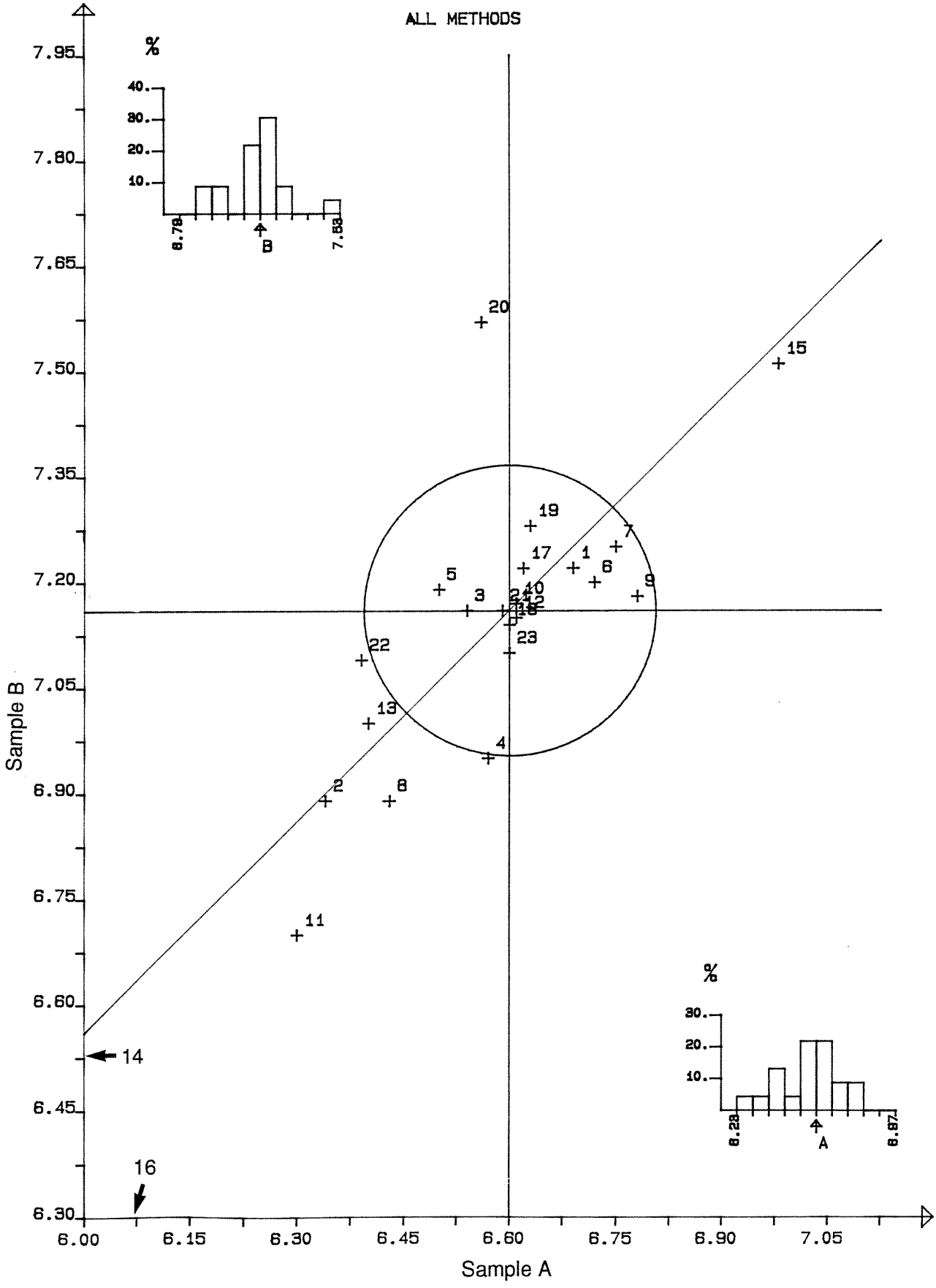

ALL METHODS
%
40.
30.
20.
10.
8.78
B
7.88
7.95
7.80
7.65
7.50
7.35
7.20
7.05
6.90
6.75
6.60
6.45
6.30
Sample B
20
15
19
7
17
1
6
5
3
9
10
23
22
13
4
2
8
11
14
16
%
30.
20.
10.
8.23
A
8.97
6.00
6.15
6.30
6.45
6.60
6.75
6.90
7.05
Sample A

FIG. 2 pH

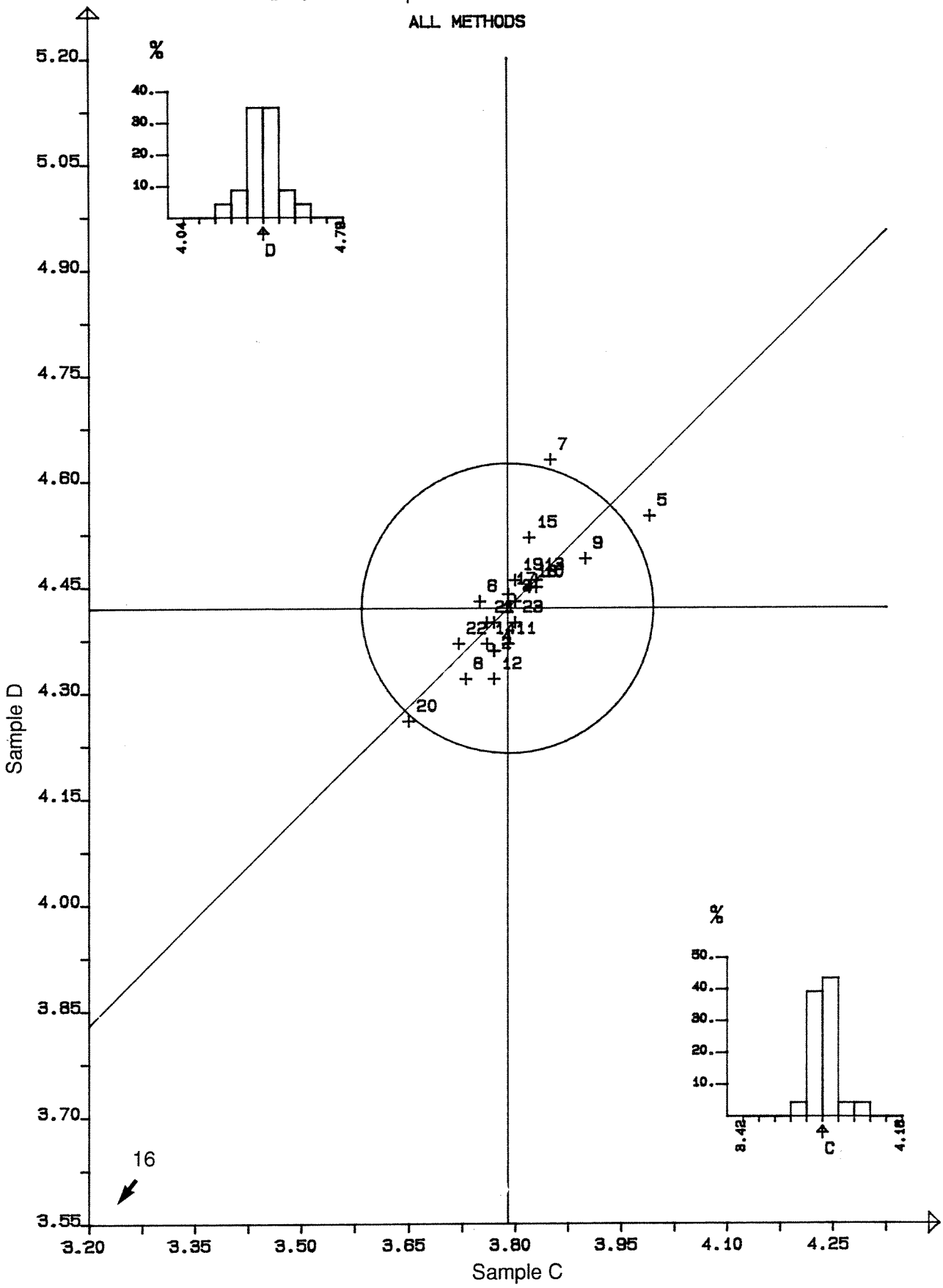

ALL METHODS
%
40.
30.
20.
10.
4.04
D
4.78
5.20
5.05
4.90
4.75
4.60
4.45
4.30
4.15
4.00
3.85
3.70
3.55
Sample D
7
5
15
9
19
6
23
22
11
8
12
20
16
%
50.
40.
30.
20.
10.
3.42
C
4.18
3.20
3.35
3.50
3.65
3.80
3.95
4.10
4.25
Sample C

FIG. 3

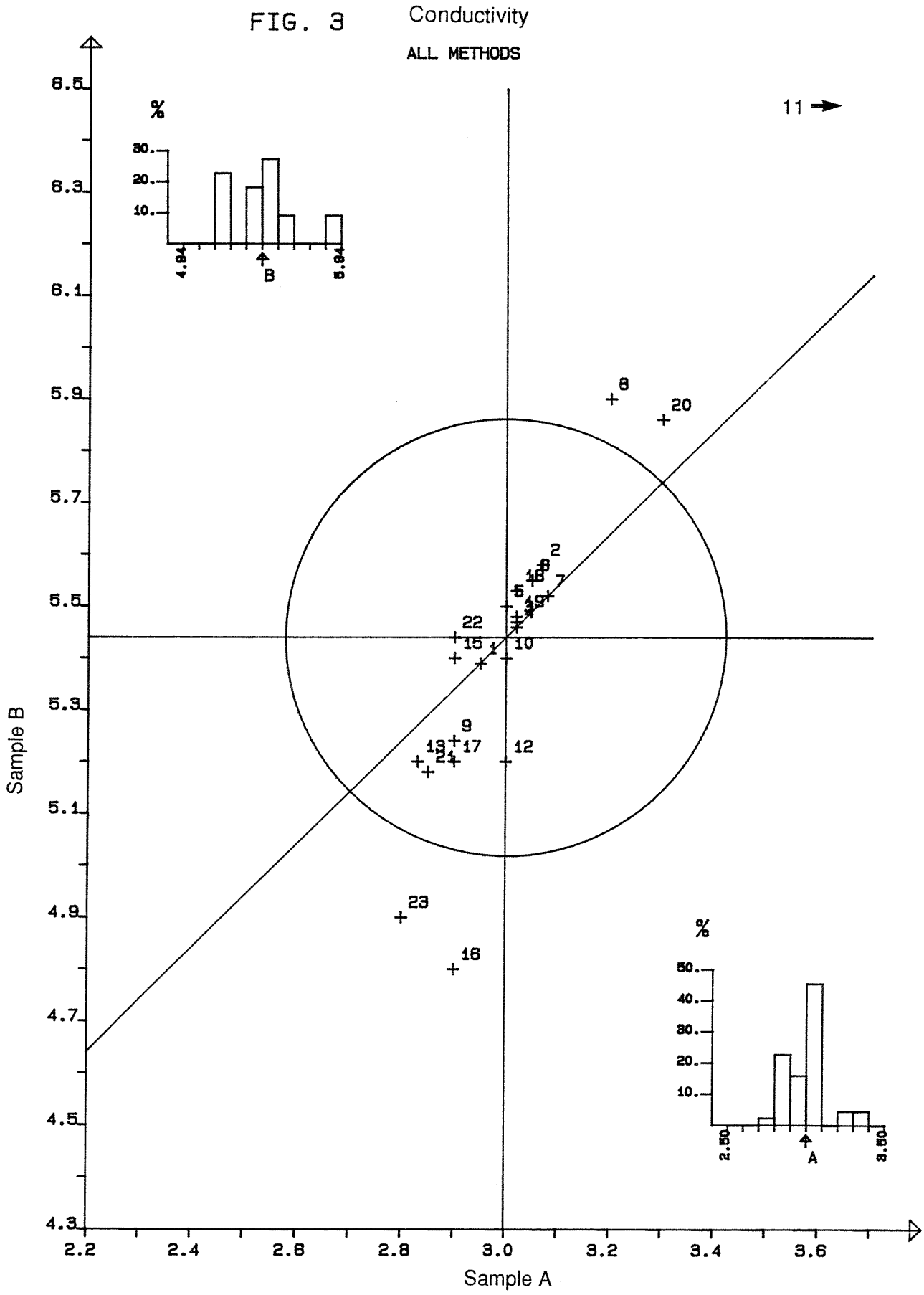

Conductivity
ALL METHODS
11
%
30.
20.
10.
4.84
B
5.84
8
20
2
7
22
15
10
9
13
17
12
24
23
16
%
50.
40.
30.
20.
10.
2.50
A
3.50
Sample B
6.5
6.3
6.1
5.9
5.7
5.5
5.3
5.1
4.9
4.7
4.5
4.3
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
Sample A

FIG. 4

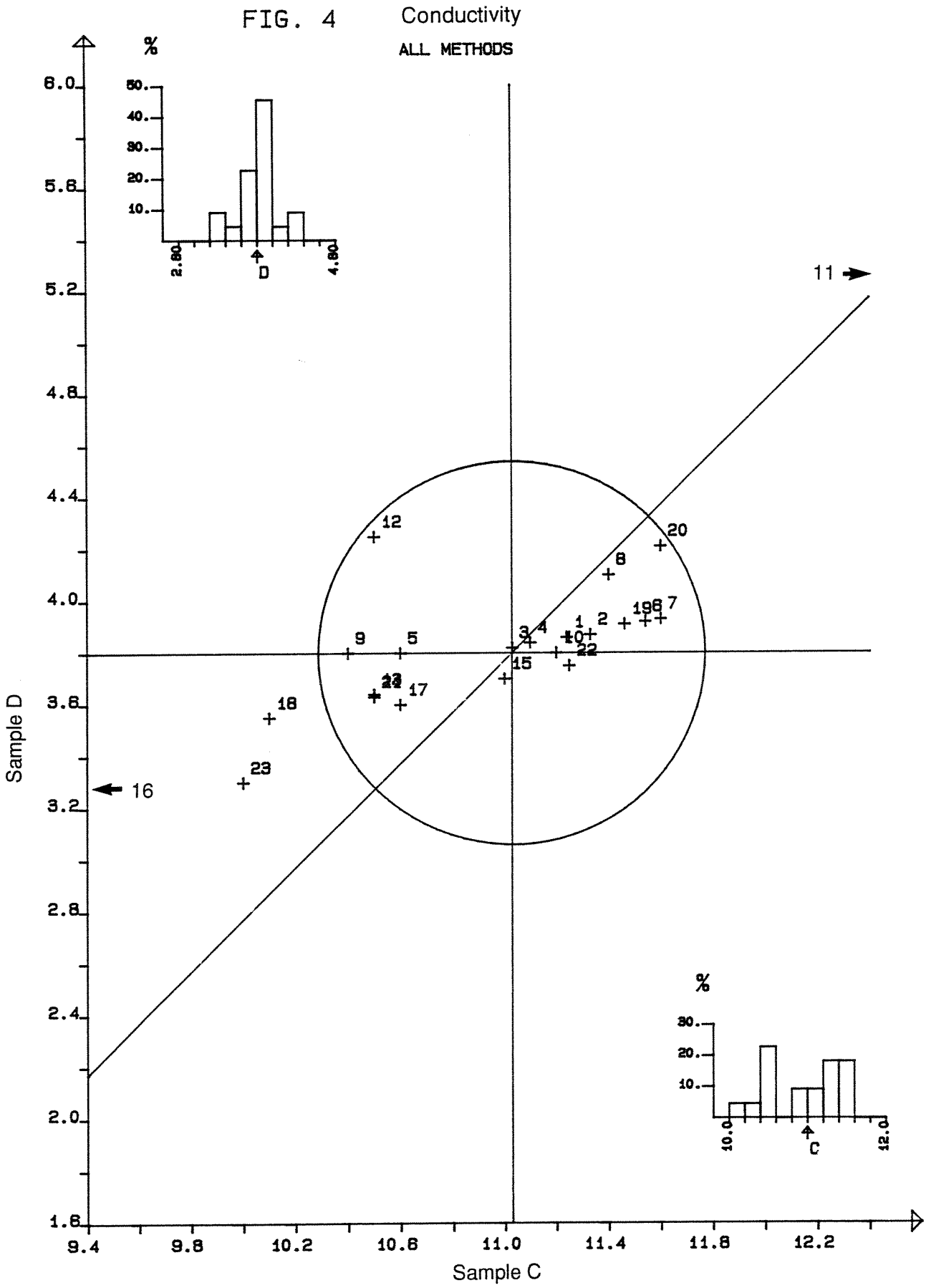

Conductivity
ALL METHODS
%
50.
40.
30.
20.
10.
2.80
D
4.80
11
12
20
8
19
6
7
1
2
3
4
10
9
5
22
15
17
18
23
16
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
Sample D
9.4
9.8
10.2
10.6
11.0
11.4
11.8
12.2
Sample C
%
30.
20.
10.
10.0
C
12.0

FIG. 5 Alkalinity

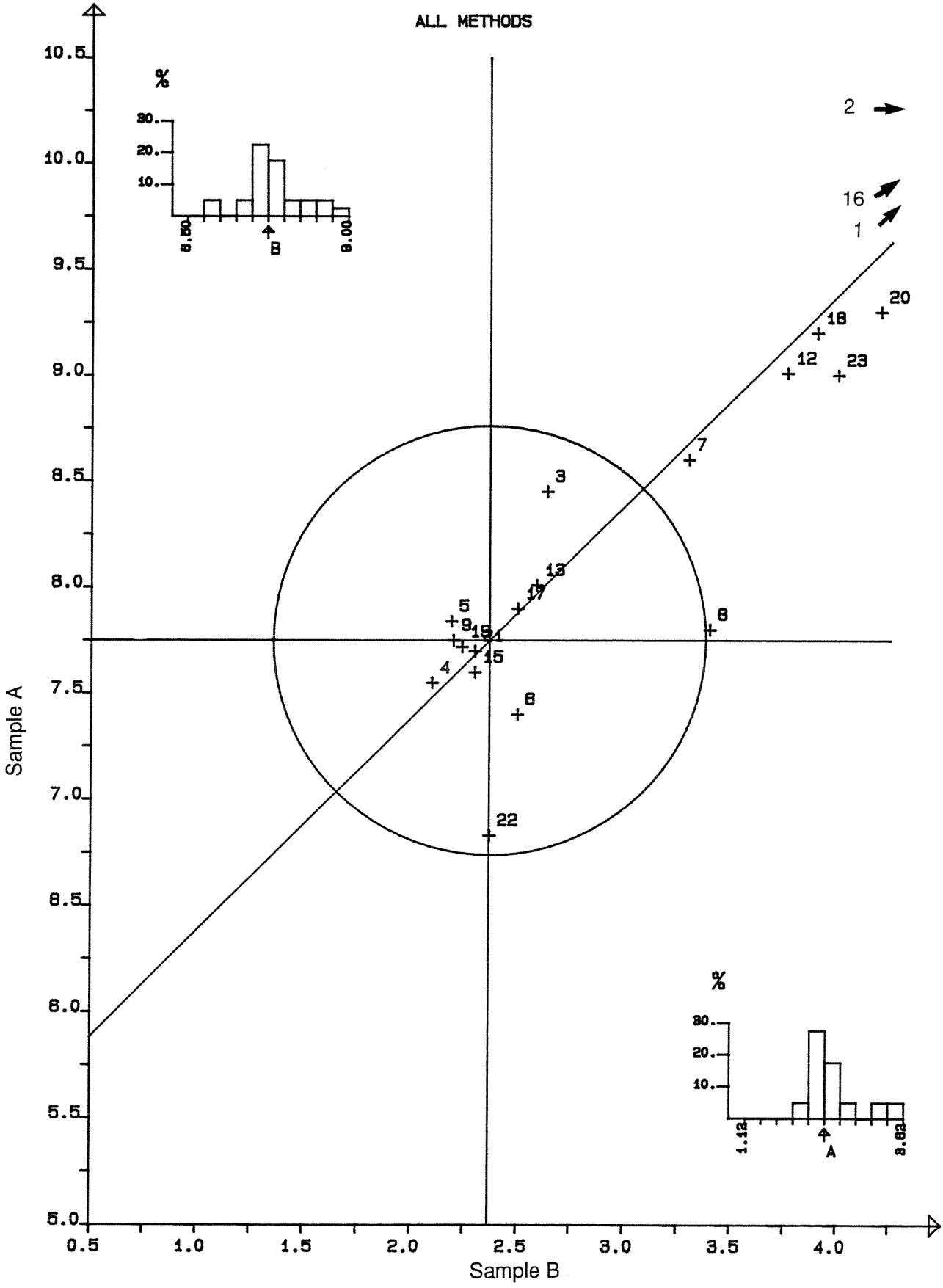


FIG. 6 Nitrate + nitrite

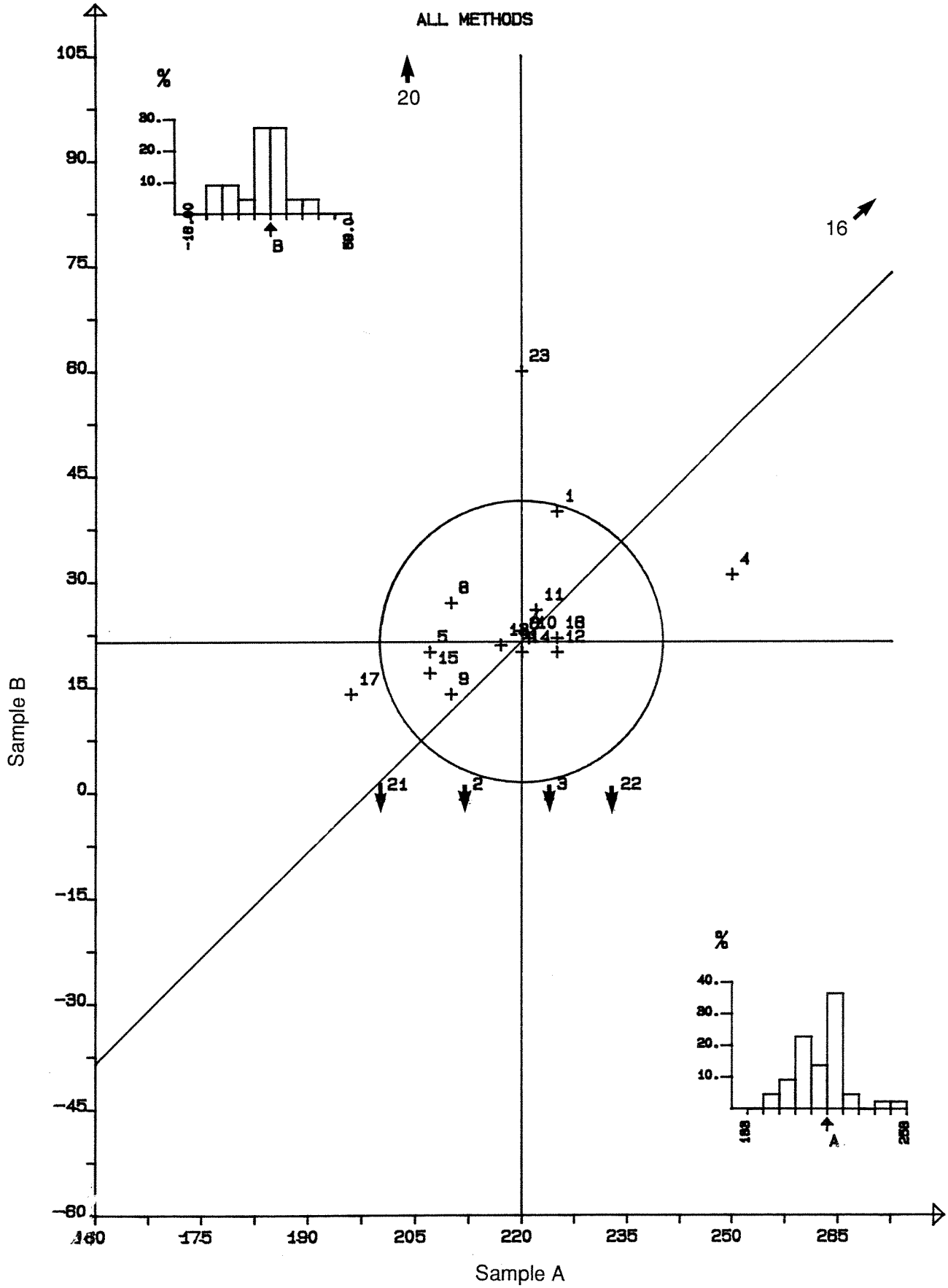


FIG. 7

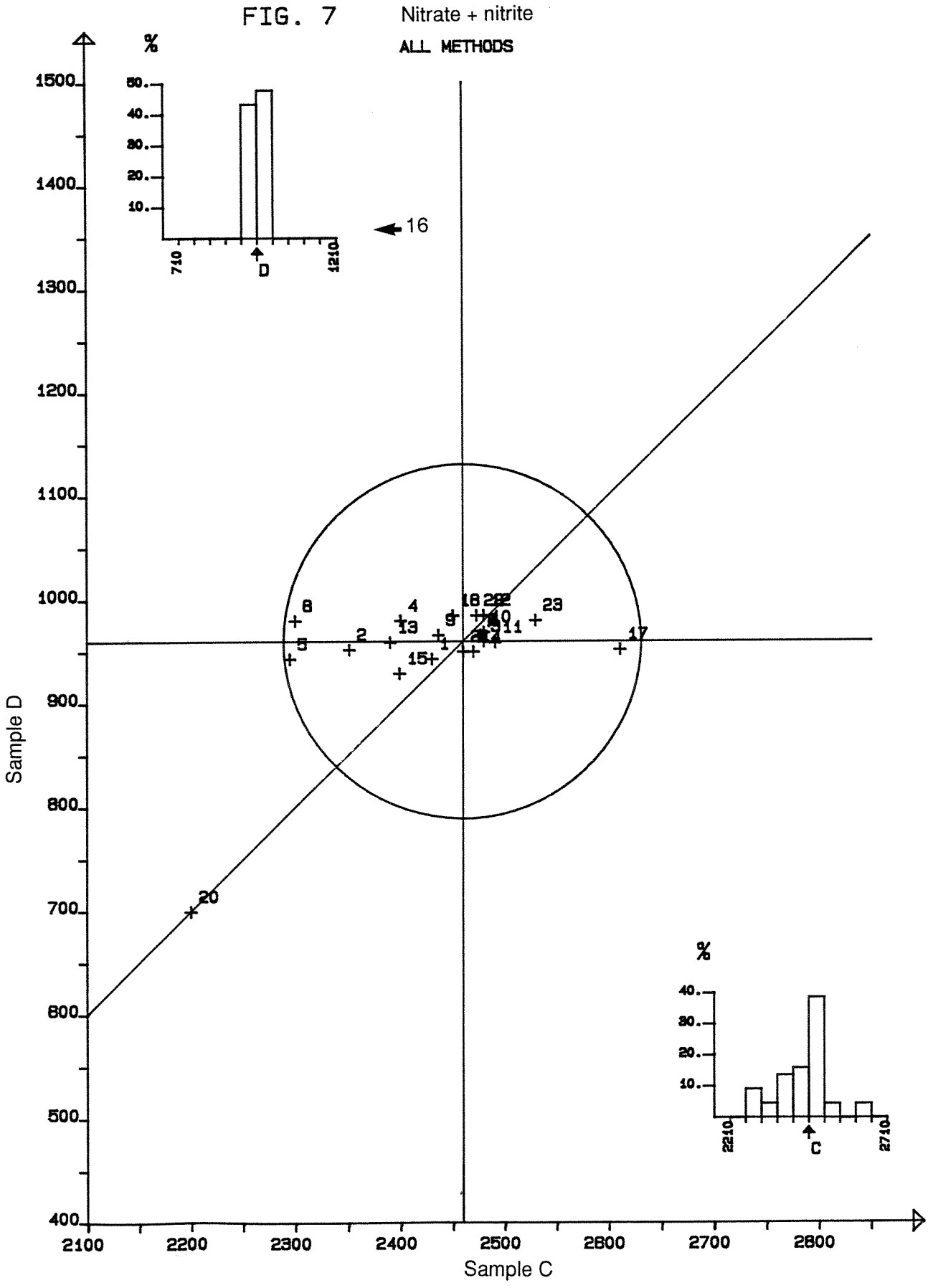

Nitrate + nitrite
ALL METHODS
%
50.
40.
30.
20.
10.
710
D
1210
16
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
Sample D
2100
2200
2300
2400
2500
2600
2700
2800
Sample C
%
40.
30.
20.
10.
2210
C
2710

FIG. 8 Chloride

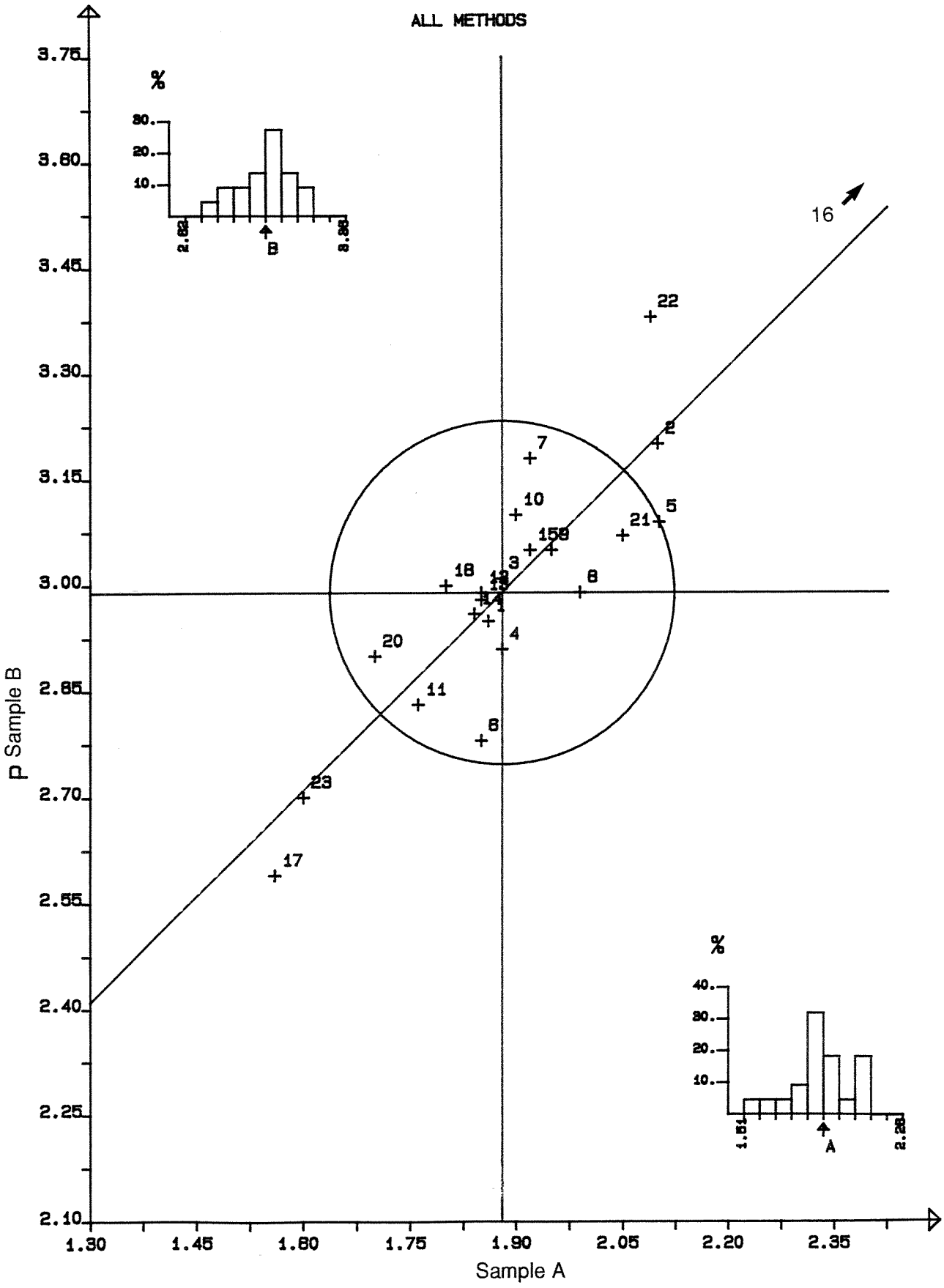


FIG. 9 Chloride

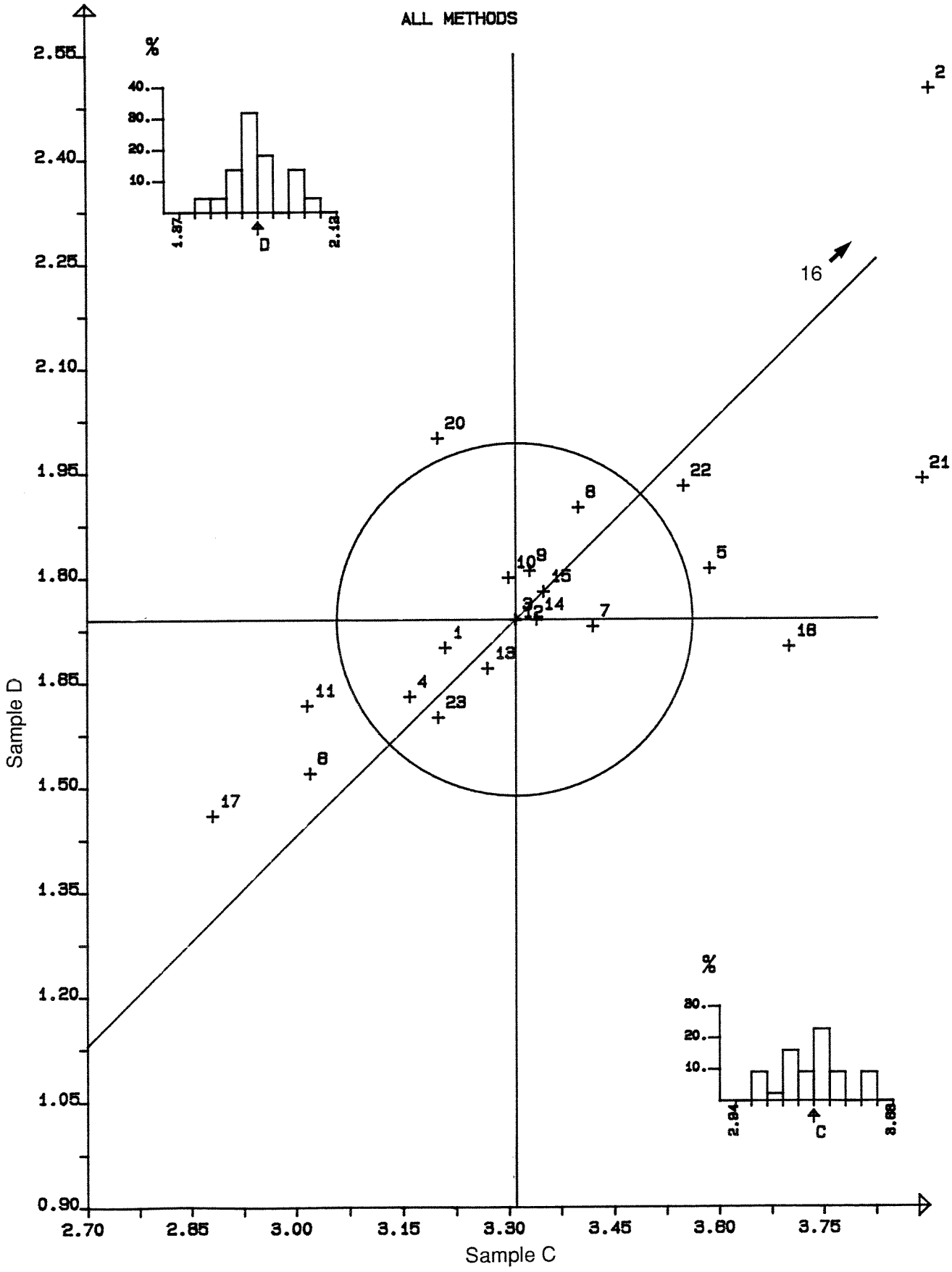


FIG. 10 Sulfate

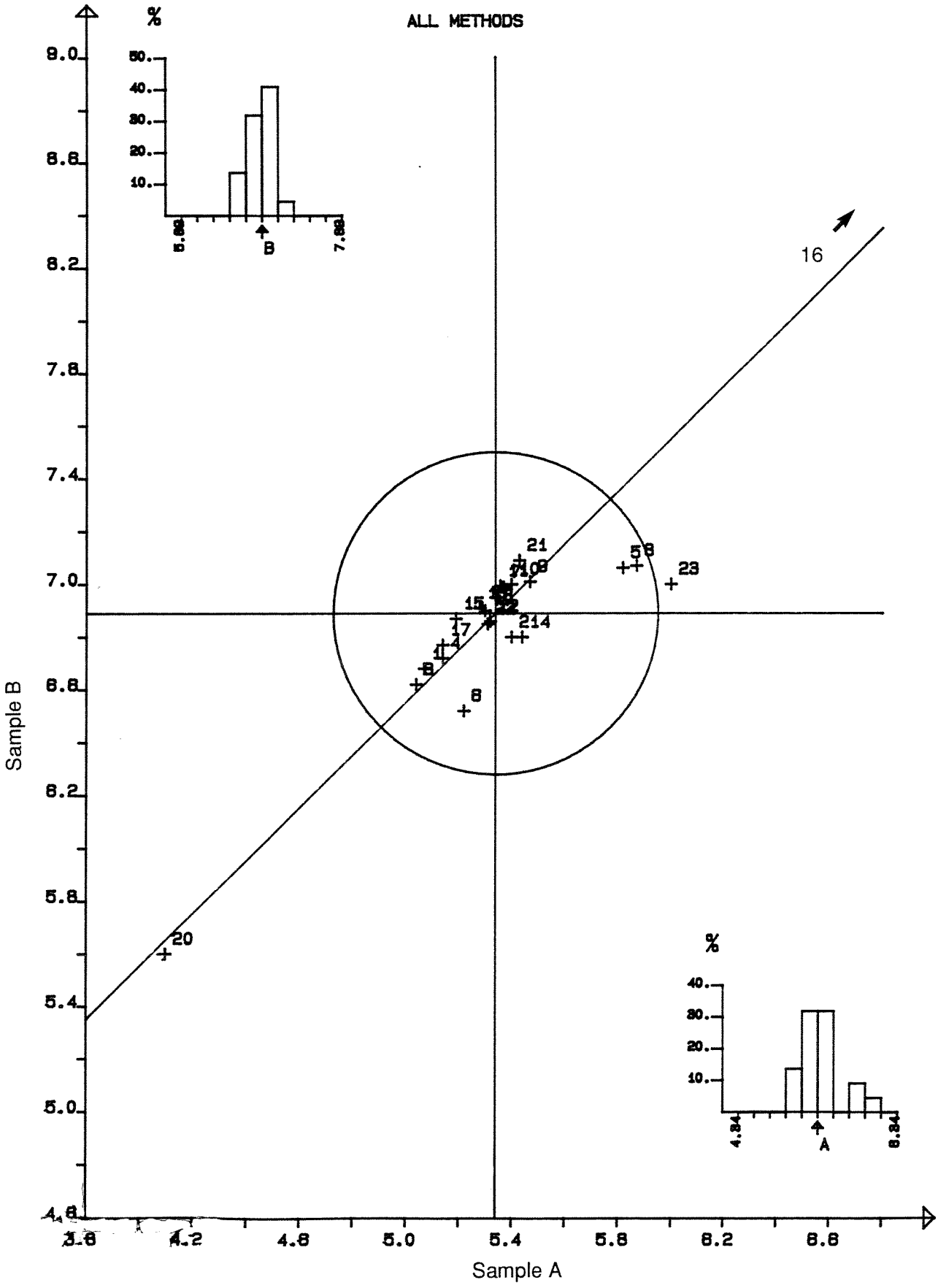


FIG. 11 Sulfate

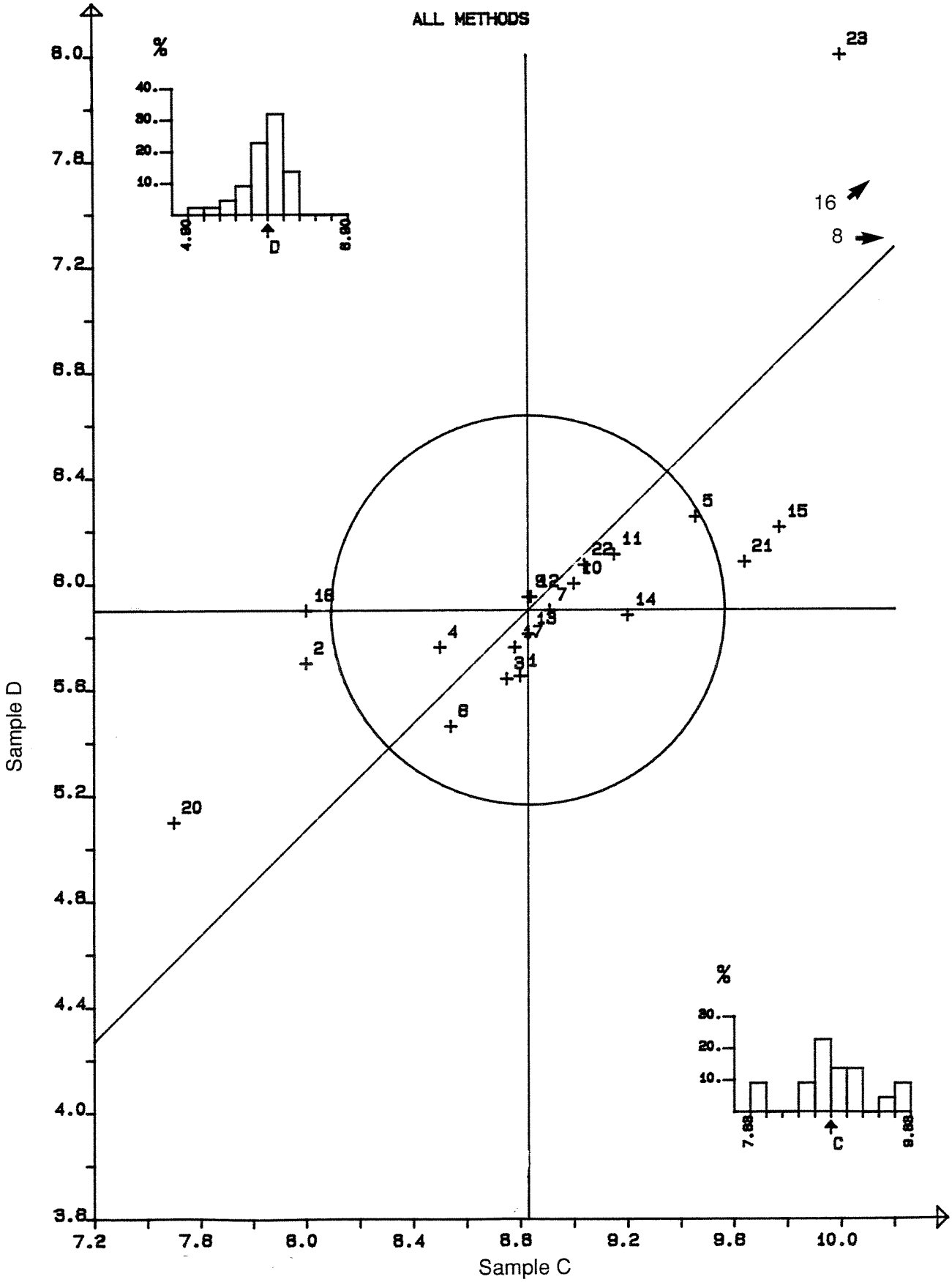


FIG. 12 Calsium

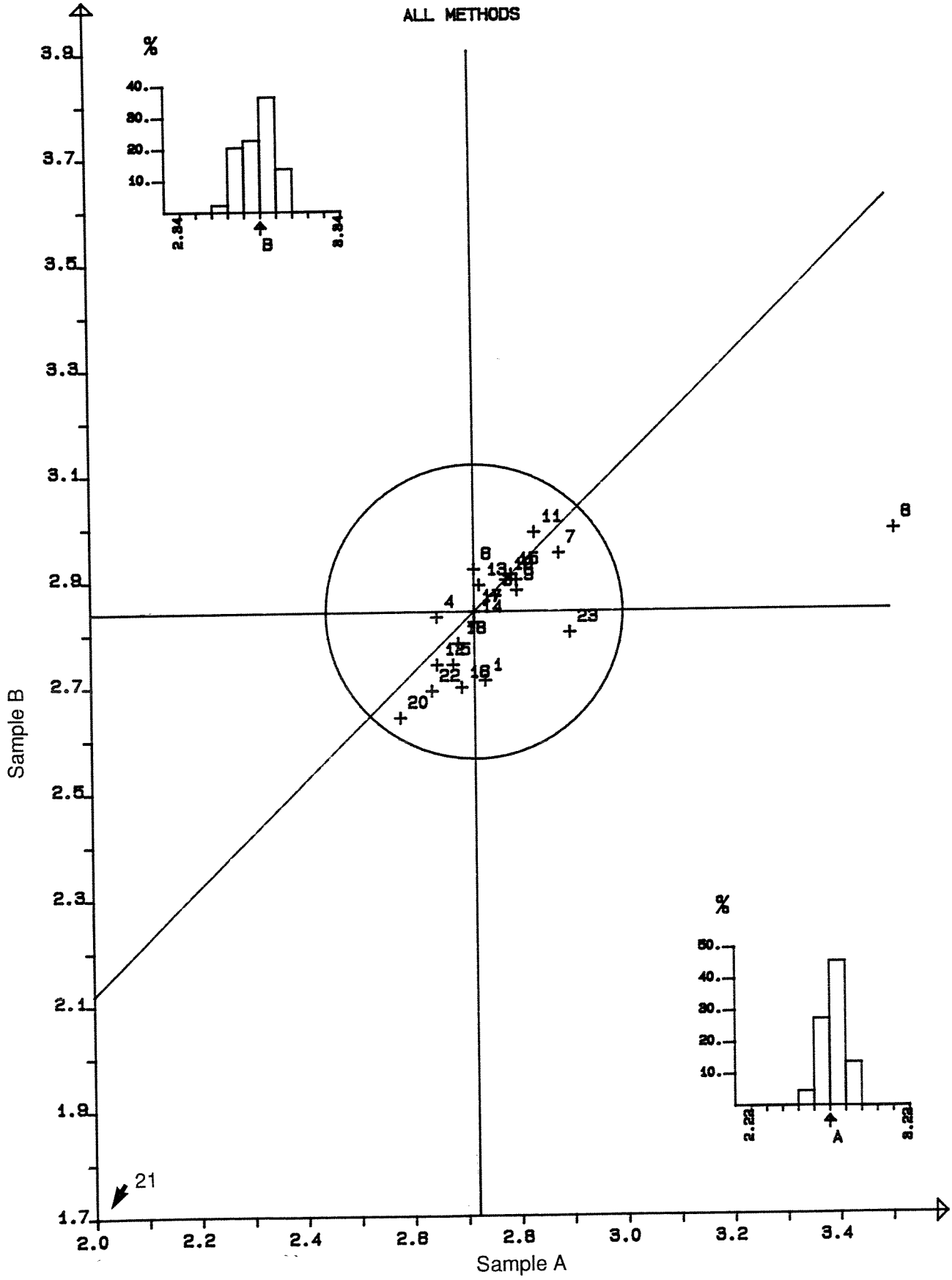


FIG. 13 Calsium

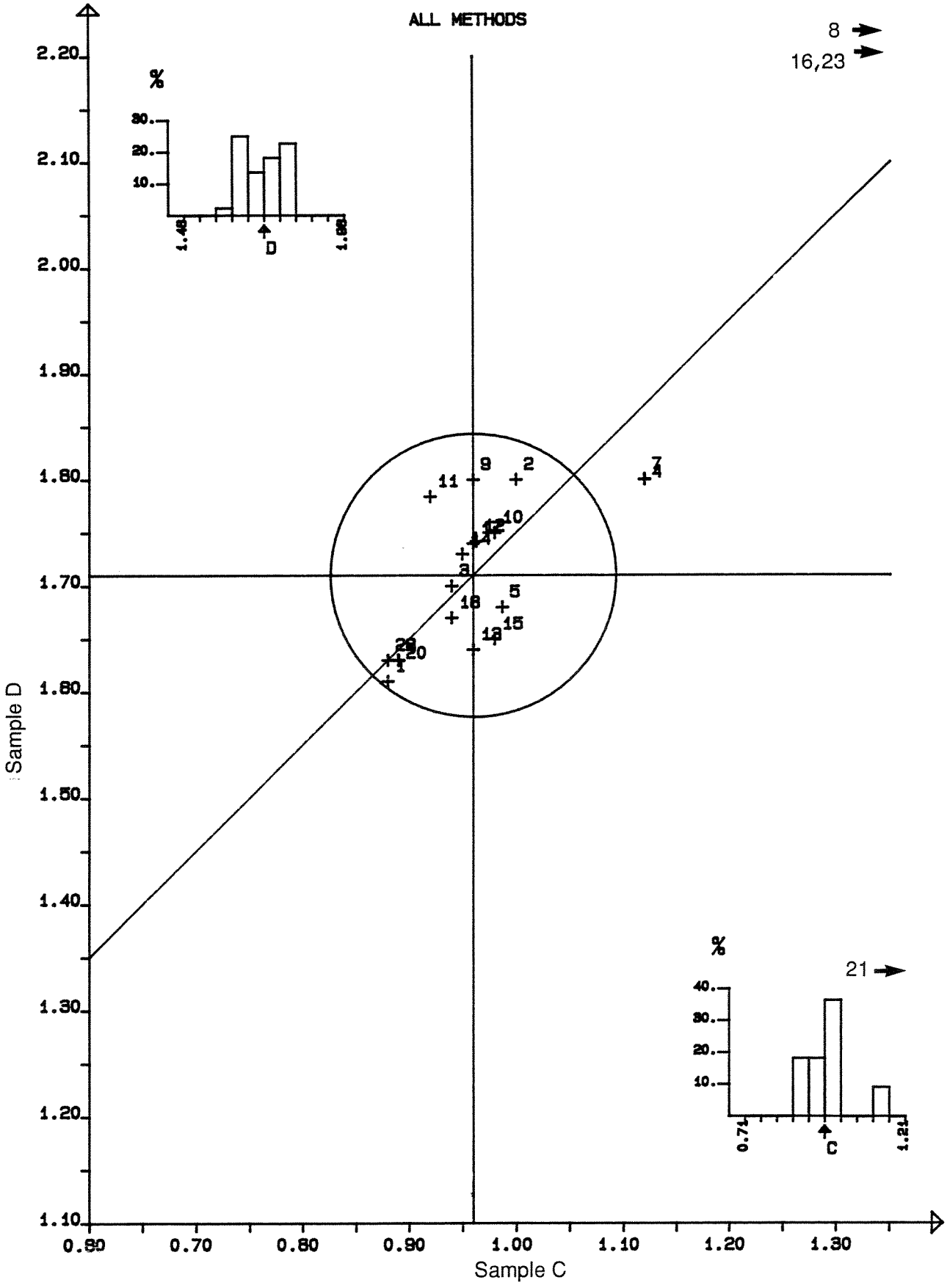


FIG. 14 Magnesium

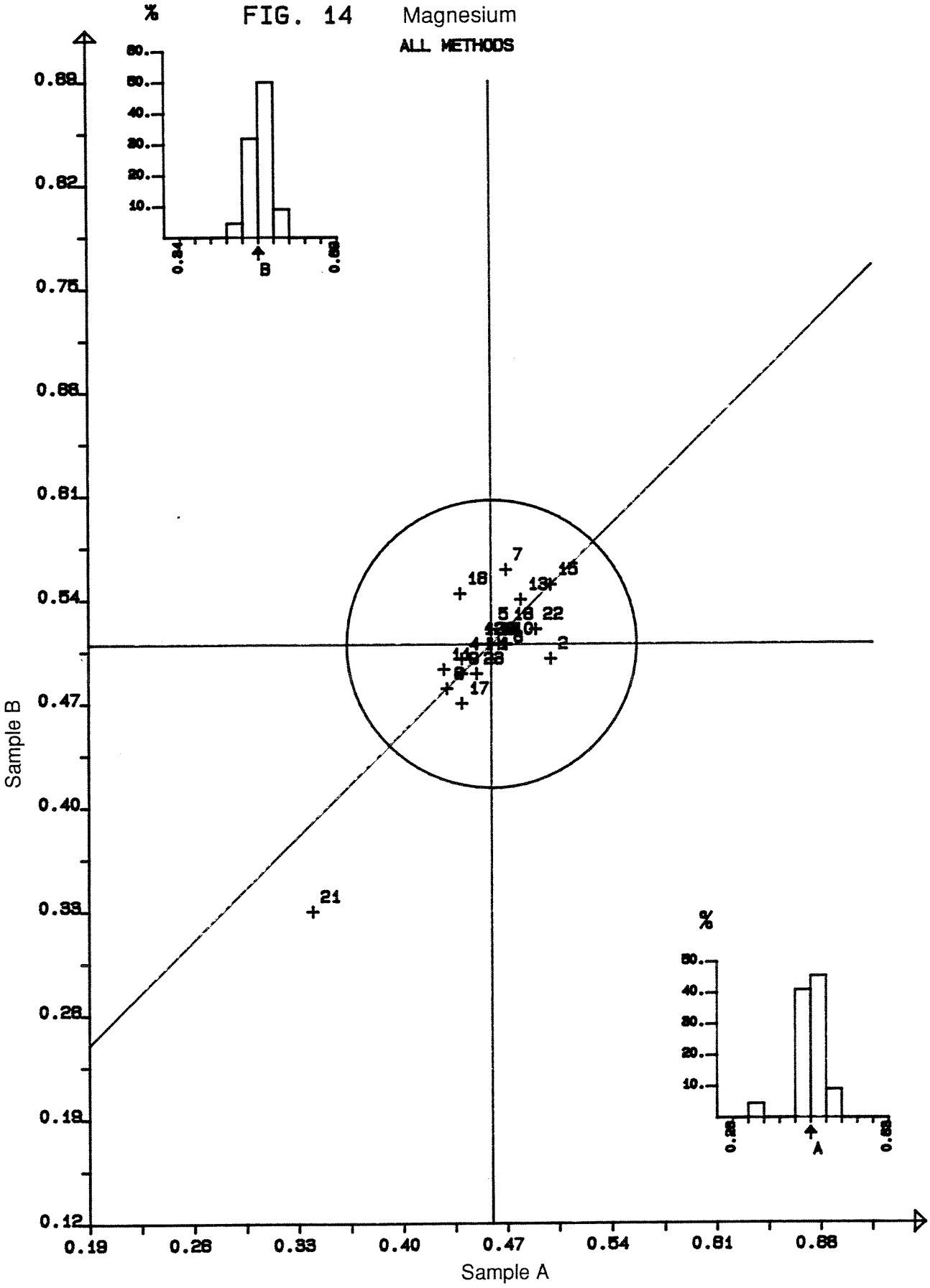


FIG. 15 Magnesium

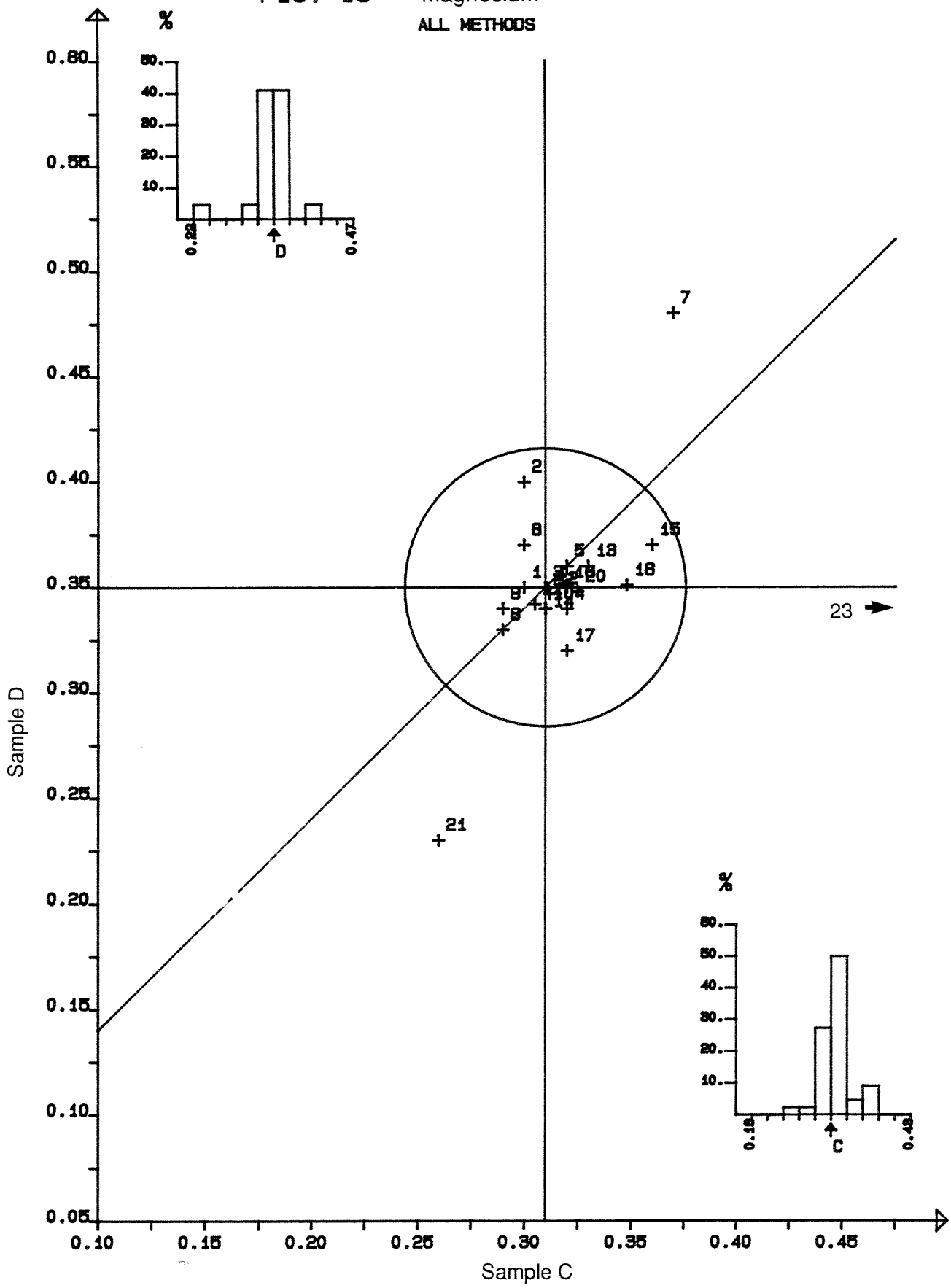


FIG. 16 Sodium

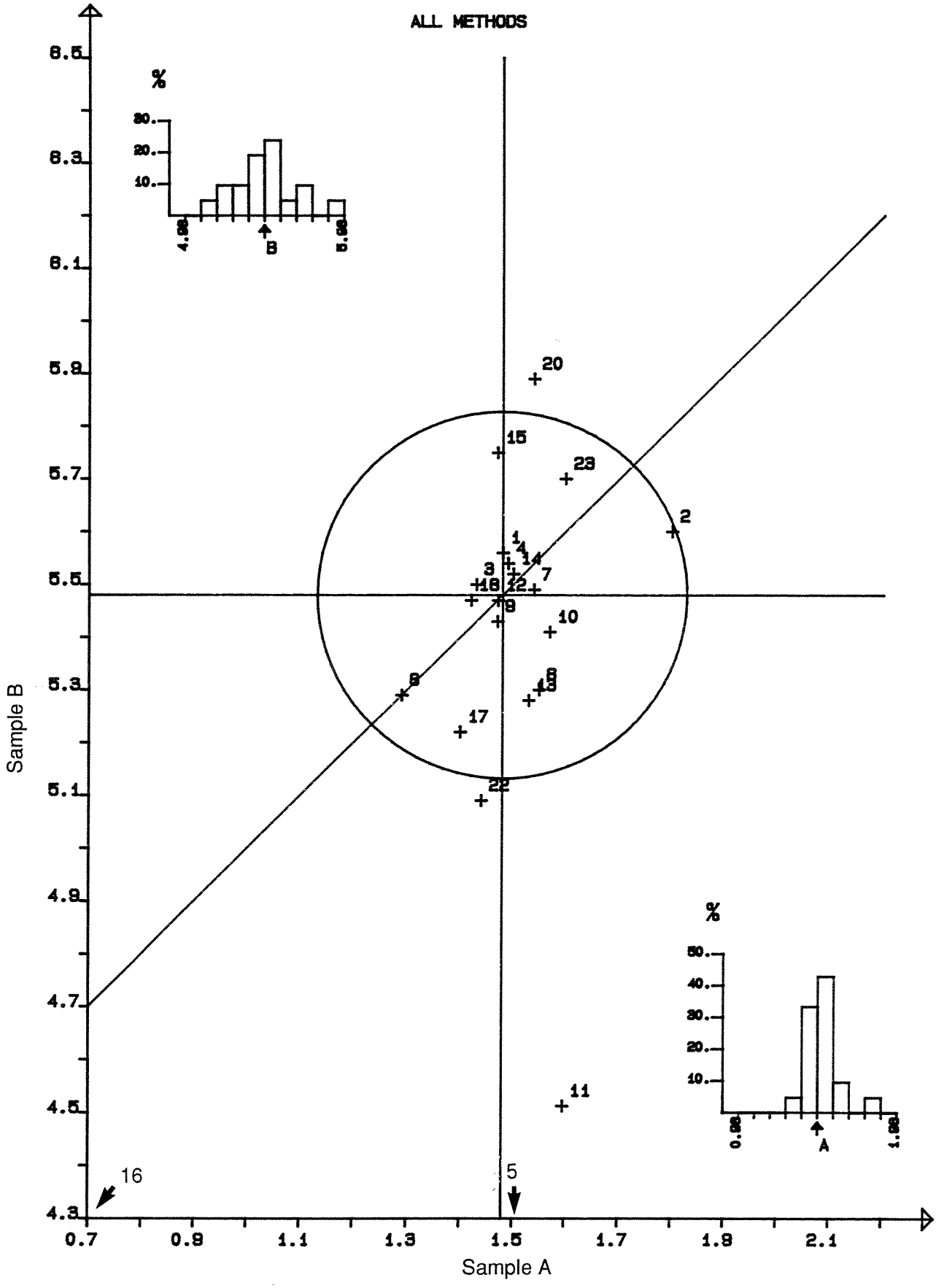


FIG. 17 Sodium

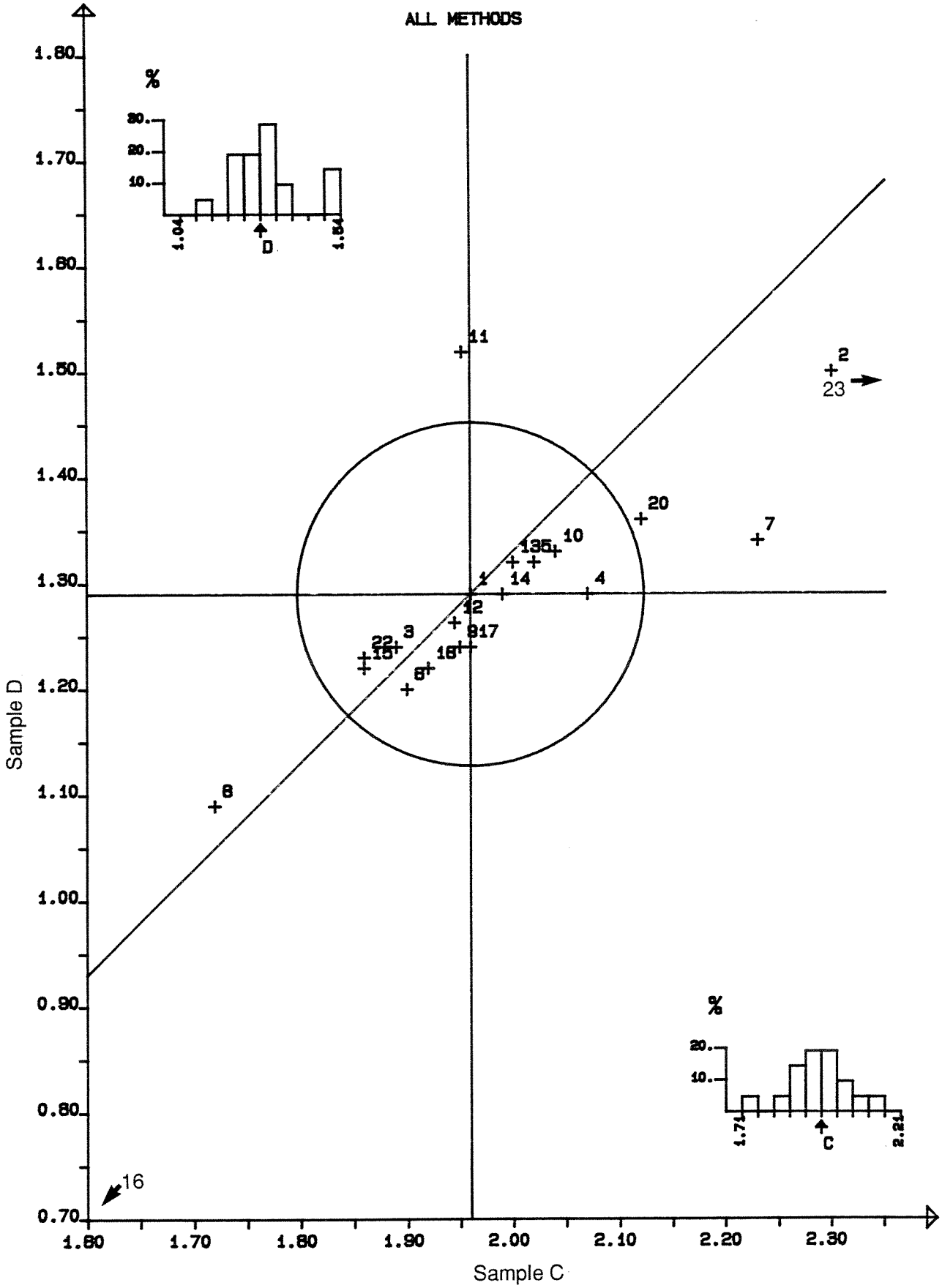


FIG. 18 Potassium

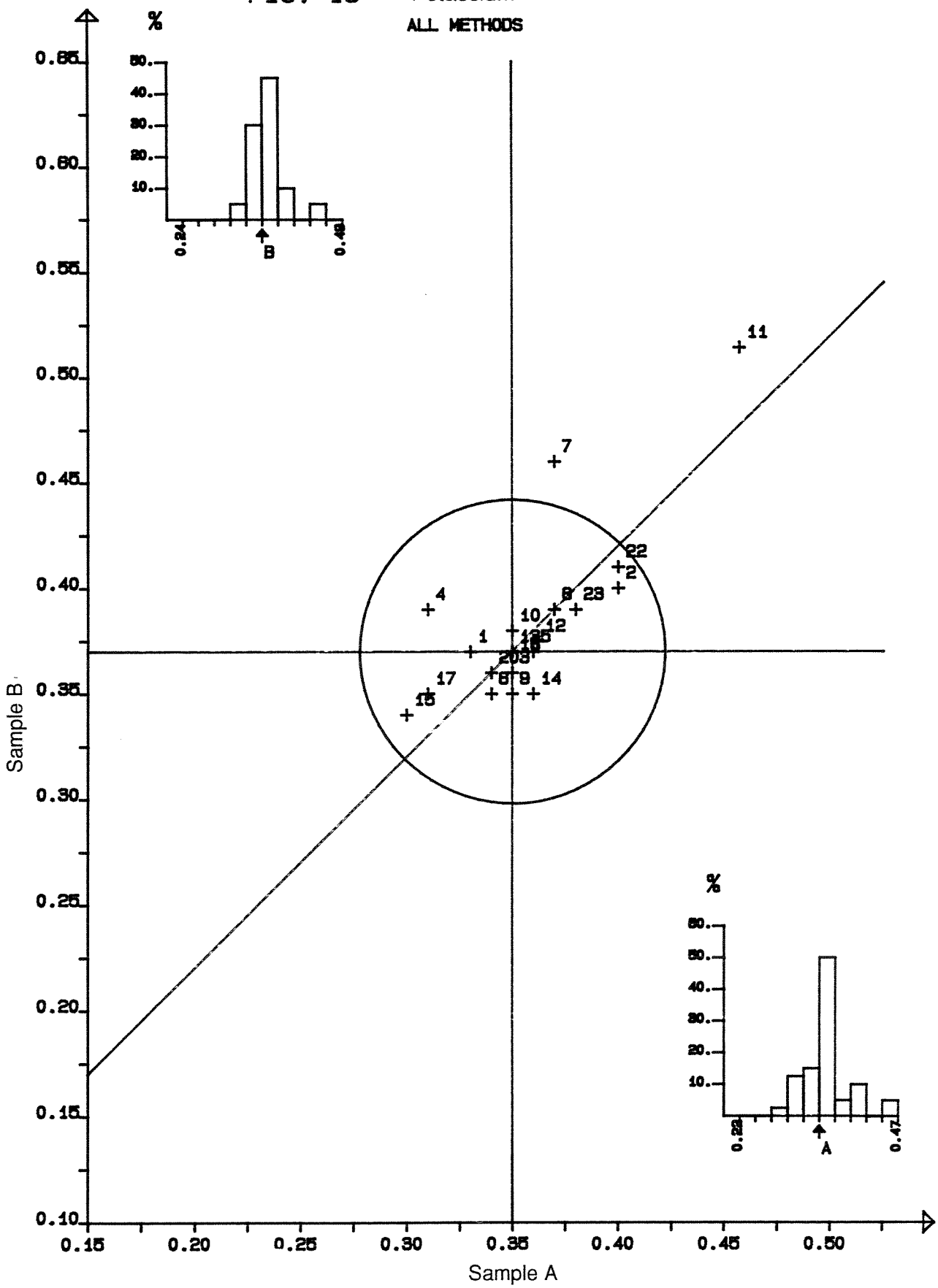


FIG. 19 Potassium

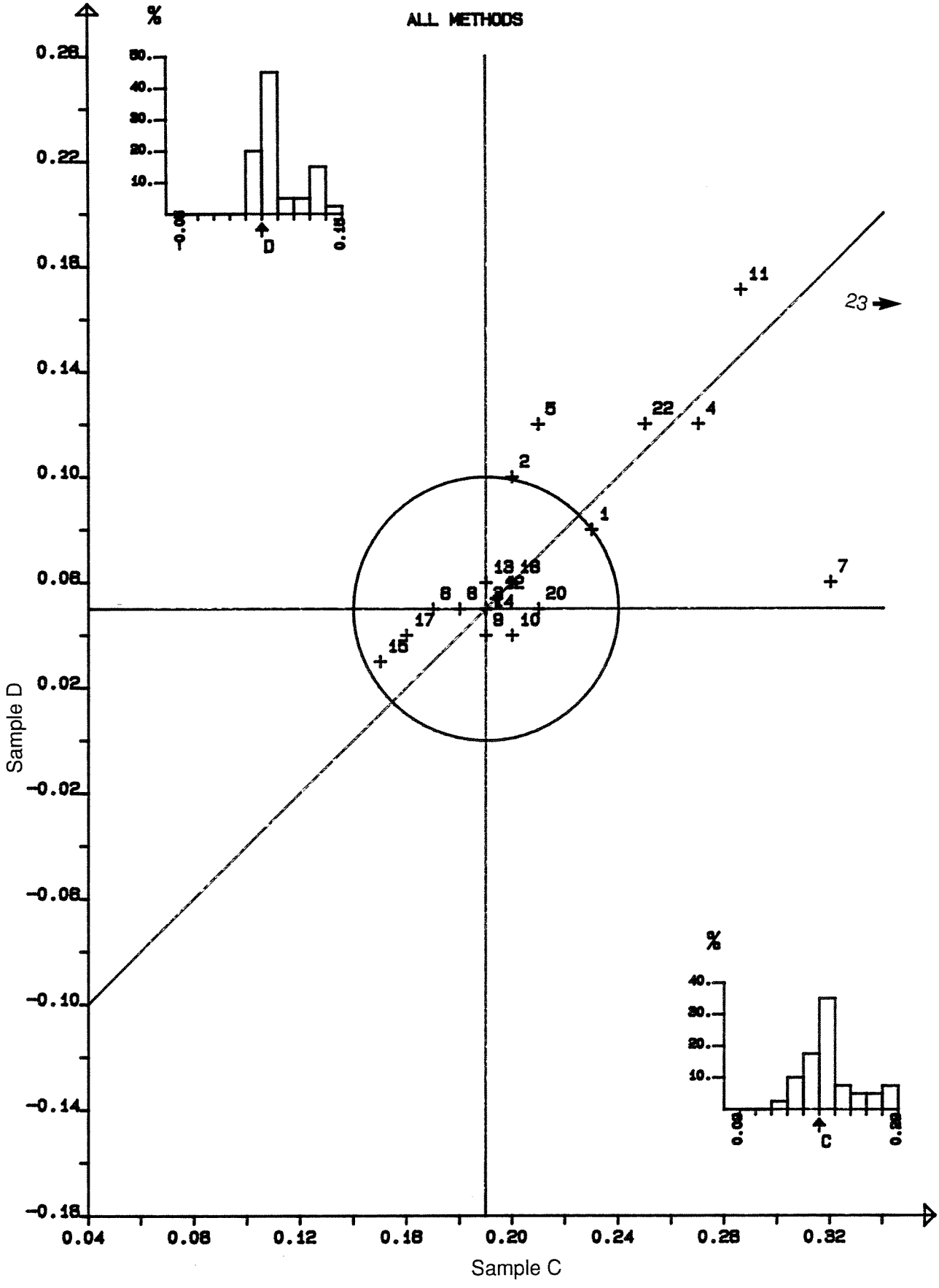


FIG. 20 Dissolved organic carbon

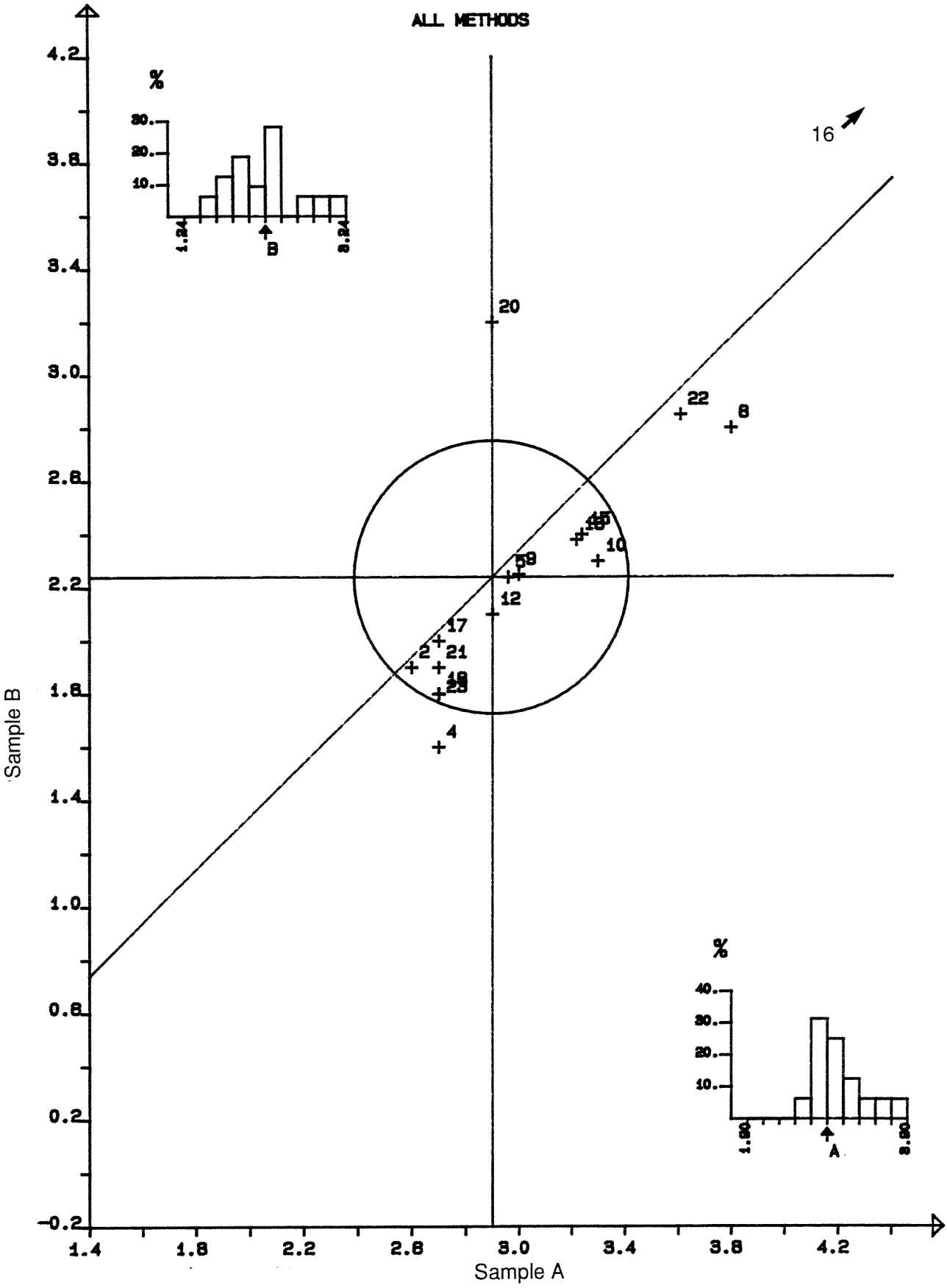


FIG. 21 Dissolved organic carbon

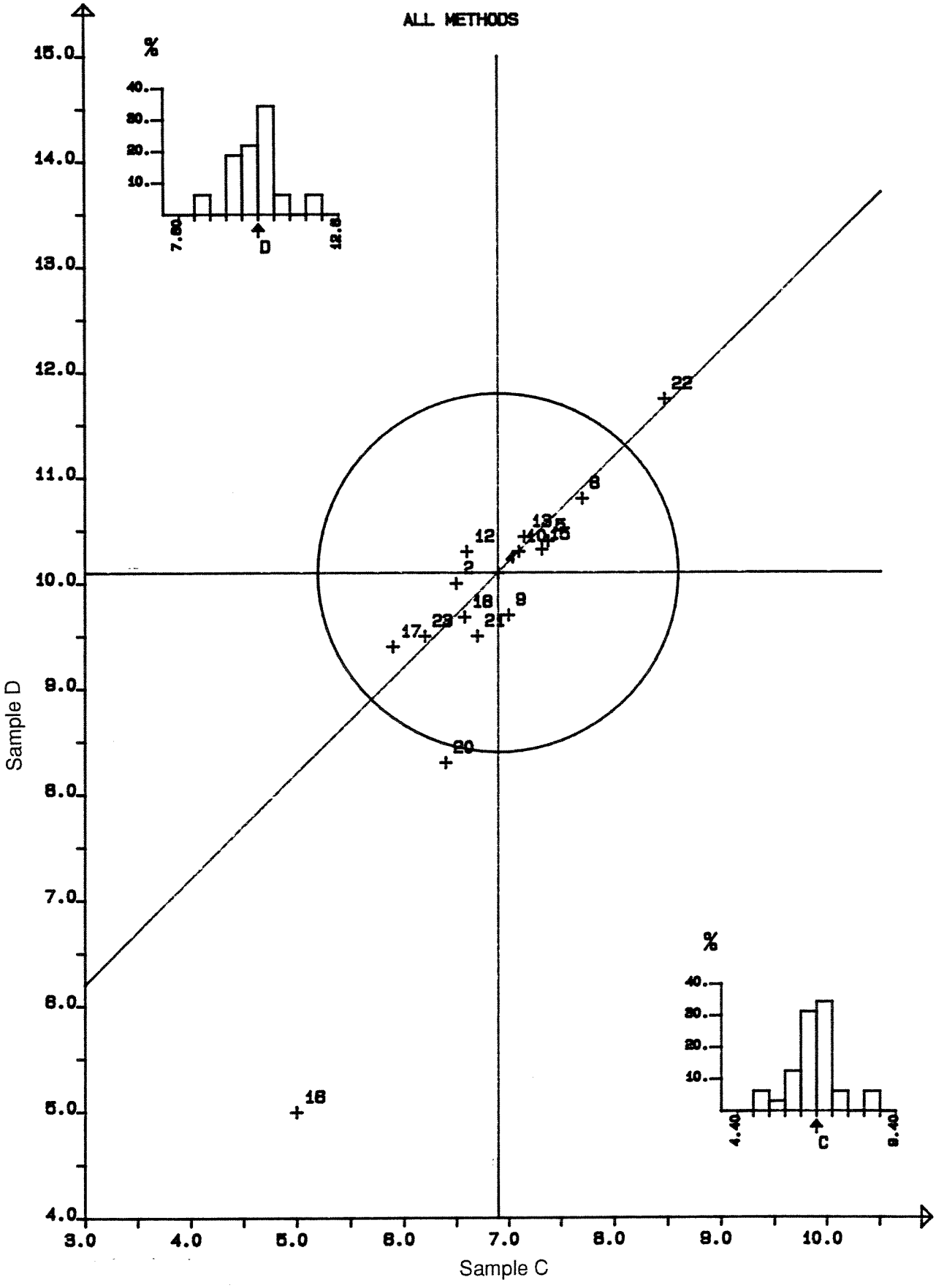


FIG. 22 Aluminium

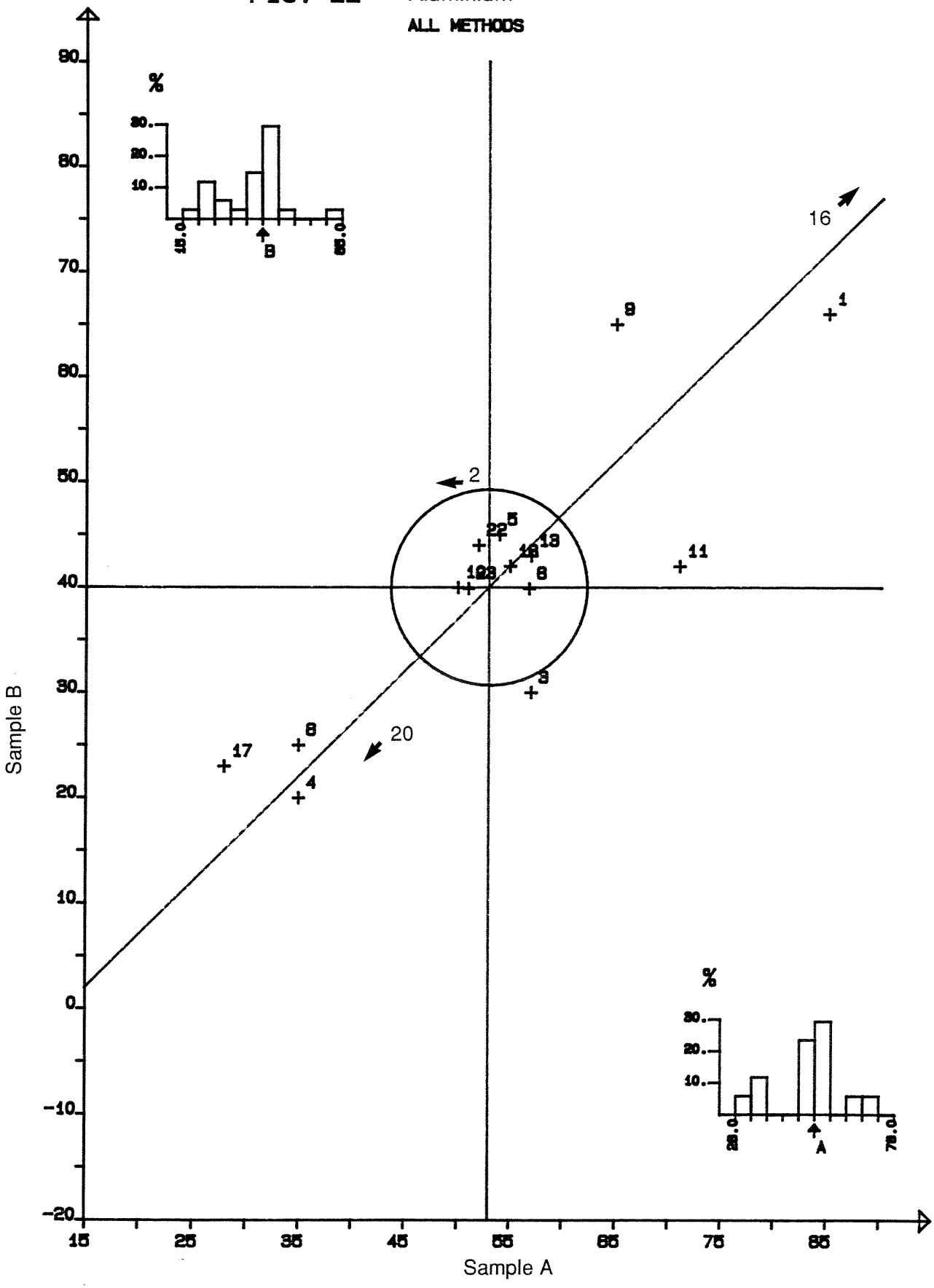
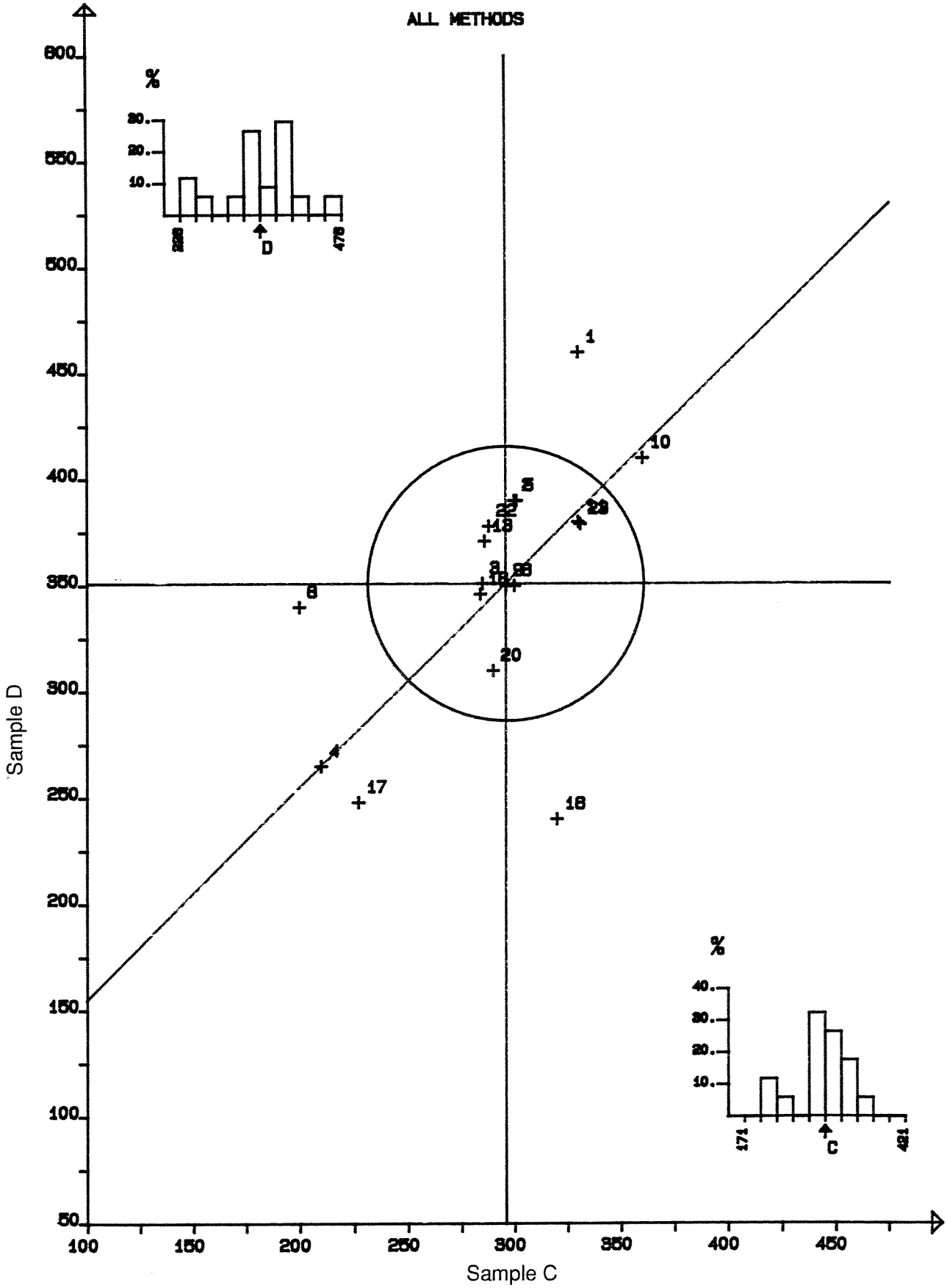


FIG. 23 Aluminium



The results are illustrated in the Figures 1 - 23, where each laboratory is represented by a cross and an identification number. The circle is 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 9206 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 - 27.

pH

The reported pH results are graphically presented in the Figures 1 and 2, where the radius of the circle is 0.2 pH units, and visualizes the degree of comparability of pH results between the laboratories. The reported results are given in the Tables 5 and 6 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, rather 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 of the laboratories. It has been demonstrated that the CO_2 concentration of samples in the circumneutral range may be far above the atmospheric equilibrium (4). 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 is minimal in the more acid sample pairs CD. This is clearly demonstrated in Figure 2 where the precision is far better than in Figure 1.

The control analyses carried out at the Program Centre proved that the samples were stable when stored within one laboratory. However, we must have in mind that possibly quite another situation may arise when the samples 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 the Figures 3 and 4, where the circle is representing a special accuracy limit of ± 10 %. The reported results are given in the Tables 7 and 8 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. An electrometric method was used for the determination by all the participants.

It was achieved a good agreement between the results of the participating laboratories. Only one laboratory reported results outside the general target accuracy of ± 20 % for sample pair AB, and three result pairs are lying outside the same limit for the sample pair CD. Not more than five result pairs are lying outside the special limit when it is reduced to ± 10 % , represented by the circle in the Figures 3 and 4.

One possible reason for systematic deviating results of the proportional kind, may be wrong temperature correction.

Alkalinity

The alkalinity results are illustrated in Figure 5, and the reported results are given in Table 9 in Appendix 4. For this parameter, too, it was necessary with som correspondance to clarify the units of the reported results, and some values had to be recalculated to the requested unit mg/l $CaCO_3$.

Most laboratories determined alkalinity by the Gran plot titration, which has been shown to give the best comparability between the results from different laboratories (6). Some modifications of the electrometric titration method, such as titration to pH = 4,5 only, was used by a few laboratories.

The circle in Figure 5 is representing a limit of ± 20 % of the mean value of the true value of the two samples, and six out of twenty result pairs are lying outside this limit. Deviating results may arise from analytical methods where different ways of defining the end point of the titration (7) have been used, this effect is more pronounced in solutoins of low alkalinity.

Nitrate + nitrite

The results reported for this parameter are presented in the Tables 10 and 11 in Appendix 4. The concentration of nitrate + nitrite is very different in the four samples. The value of evaluating the results by the Youden technique is limited if the concentration in the two samples of a sample pair is quite different, therefore, we have chosen to illustrate the results by combining the samples A and D as one pair (Figure 6), and the samples C and B as the other pair (Figure 7). The evaluation of the results for this parameter is based on this combination of samples.

The most common analytical method used for the determination of this parameter is ion chromatography, although some laboratories used an automated photo-metric method. Two laboratories reported results both for the photometric method and the ion chromatographic technique, for both laboratories the IC results was selected in this intercomparison (it is not possible to register a double set of results for the same sample pair at one laboratory by the computer programme used at the moment). There is no significant systematic difference between the results determined by the two methods.

The circle in Figure 6 is represented by a limit of ± 20 µg/l, while the circle in Figure 7 is representing the special limit of ± 10 %. The random errors are dominating at the low concentrations in the sample pair AD, here four laboratories have reported results as "less than" the determination limit. At higher concentrations, such as in the sample pair CB, only two results are lying outside the general limit.

Chloride

The chloride results are presented in the Figures 8 and 9, and the reported results are given in the Tables 12 and 13 (Appendix 4). Most laboratories determined chloride by ion chromatography, and one laboratory used an automated photometric version of the mercury thiocyanate method. One laboratory used a volumetric method for this determination, however, this method is not sensitive enough for the concentrations of these solutions.

The circles in the Figures 8 and 9 are representing a special limit of ± 10 % of the mean true values of the two samples of a sample pair. Only 2 and 4 result pairs are lying outside the general target accuracy of ± 20 %, for the sample pairs AB and CD, respectively.

Sulfate

The sulfate results are illustrated in the Figures 10 and 11, and the reported values are given in the Tables 14 and 15 (Appendix 4). Most laboratories applied ion chromatography for the determination of this parameter, while ne laboratory used an automated photometric method based on the dissociation of the barium-thorin complex. One laboratory used a gravimetric method for the determination, however, this method is not sensitive enough for the concentration level of these solutions.

A special accuracy limit of ± 10 % is represented by the circle in the Figures 10 and 11. Only 2 and 4 result pairs are lying outside the general target accuracy of ± 20 %, for the sample pairs AB and CD, respectively.

Calcium

The calcium results are illustrated in the Figures 12 and 13, and the reported values are given in the Tables 16 and 17 (Appendix 4). More than half of the participants used atomic absorption spectrometry for the determination of this metal. Among the remaining laboratories some used ICP, and some few used ion chromatography. One laboratory used a volumetric method for the determination, this method is not sensitive enough for the low concentrations in the test solutions used here, especially in the samples C and D.

A special accuracy limit of ± 10 % is representing the circles in the Figures 12 and 13. Only 2 and 4 result pairs are lying outside the general target accuracy of ± 20 %, for the sample pairs AB and CD, respectively.

Magnesium

The magnesium results are presented in the Figures 14 and 15, and the reported values are given in the Tables 18 and 19 (Appendix 4). The majority of the participants used atomic absorption spectrometry for the determination of magnesium. Some laboratories used ICP emission spectrometry or ion chromatography for this purpose.

Only one and three laboratories, respectively, reported values lying outside the general acceptance limit of ± 20 % for the sample pair AB and CD. The general target accuracy is represented by the circles in the Figures 14 and 15.

Sodium

The sodium results are presented in the Figures 16 and 17, where the circle is representing a special acceptance limit of ± 10 %. The reported values are given in the Tables 20 and 21 (Appendix 4). Most laboratories used flame atomic absorption spectrometry for this determination, a couple of laboratories used ICP emission technique, and one flame emission spectrometry. Ion chromatography was used by one laboratory.

Four result pairs are lying outside the general target accuracy of ± 20 % for both sample sets.

Potassium

The potassium results are presented in the Figures 18 and 19. The circle in Figure 18 is representing a general acceptance limit of ± 20 %, while a radius of 0,05 mg/l has been used In Figure 19. The reported values are given in the Tables 22 and 23 in Appendix 4. As for sodium, most laboratories used flame atomic absorption spectrometry for this determination, a couple of laboratories used ICP emission technique, and one flame emission spectrometry. Ion chromatography was used by one laboratory.

The low concentrations in these solutions, especially in sampl D, is the main reason for the spread of the results illustrated in the Figures 18 and 19. Contamination is not expected to be any problem for theis metal. To obtain a reliable precision at this concentration level may be more likely the reason for the deviating results.

Dissolved organic carbon

The results for this parameter are presented in the Figures 20 and 21, and the reported values are given in the Tables 24 and 25 (Appendix 4). Only 16 out of 23 laboratories determined this parameter, and very few informations were given with respect to what instrument had been used, and what oxidation principle the instrument were based upon. It should be well known that the analytical results for this parameter may be dependent on what combustion principle is used in the instrument. The samples was made from natural water samples containing humic compounds, and we expected that there might be a certain spread between the results from different laboratories.

The circle in the Figures 20 and 21 is representing av general acceptance limit of ± 20 %. Compared to the general target accuracy, 69 and 81 % of the result pairs was acceptable for the sample sets AB and CD, respectively.

Aluminium

The results for aluminium are illustrated in the Figures 22 and 23, and the reported values are given in the Tables 26 and 27 (Appendix 4). The circle in the figures are representing the general accuracy target of ± 20 %. The relative precision is worse for for the sample pair AB because of the low concentrations of aluminium in these samples. Only 41 % of the result pairs are acceptable accoprding to the general target accuracy, while 65 % are acceptable in the sample pair CD. Both ICP, atomic absorption and photometric methods have been used for the determination, but there is no detailed informations about the methods.

IONIC BALANCE

The ionic balance were calculated by adding the molar concentrations of the major anions (alkalinity, 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 28 of Appendix 4. 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. Thus the difference should be about 0,02 for sample A (Maridalsvannet), a well studied lake outside Oslo.

Sample B and C have anion sums being greater than the cation sum, this property being much greater in sample C. The reason for this effect is the content of ammonia

in these solutions. The concentration of ammonia-nitrogen has been analyzed by one of the participants, who found 460 µg/l in sample B, and 1450 µg/l in sample C.

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 more detailed, we have in some cases chosen to use some special limits, usually 10 %, instead of the general target, in the Figures 1 - 23.

Table 2. Evaluation of the results of intercalibration 9206. N is the number of result pairs reported, and n is the number of acceptable results within the given acceptance limit. For each parameter the results for sample pairs AB is given first.

Parameter	N	Gen. limit	n	%	Spec. limit	n	%
pH	23	0.1	7	30	0.2	13	57
	23	0.1	16	70	0.2	19	83
Conductivity	22	20 %	21	95	10 %	17	77
	22	20 %	19	86	10 %	17	77
Alkalinity	20	20 %	11	55	10 %	8	40
Nitrate + nitrite-nitrogen	22	20 %	13	59	10 %	9	41
	22	20 %	20	91	10 %	20	91
Chloride	22	20 %	20	91	10 %	17	77
	22	20 %	18	82	10 %	12	55
Sulfate	22	20 %	20	91	10 %	19	86
	22	20 %	18	82	10 %	14	64
Calcium	22	20 %	20	91	10 %	20	91
	22	20 %	18	82	10 %	16	73
Magnesium	22	20 %	21	95	10 %	19	86
	22	20 %	19	86	10 %	16	73
Sodium	21	20 %	18	86	10 %	16	76
	21	20 %	18	86	10 %	14	67
Potassium	20	20 %	18	90	10 %	12	60
	20	20 %	10	50	10 %	6	30
Dissolved organic carbon	16	20 %	11	69	10 %	3	19
	16	20 %	13	81	10 %	10	63
Aluminium	17	20 %	7	41			
	17	20 %	11	65			
Sum	478		367	77			

In table 2 an evaluation of the results of this intercalibration is presented, based on two different target accuracies: the general target accuracy defined by the Manual (1), and some special limits. For pH the general target accuracy is 0.1 pH units. By the evaluation of the results of this intercalibration we have extended the acceptance limit to ± 20 %, because of the great spread of the results for this parameter. The Figures 1 and 2 demonstrate that the comparability between the laboratories is far better for the sample pair CD than AB where pH is about 2 - 3 units away from neutrality.

For the remaining parameters, about 80 % of the result pairs are lying within the general acceptance target of ± 20 %. For these parameters only three - four 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. At one or two laboratories the selection of a more sensitive method is necessary.

In Table 2 is summarized an evaluation of the results of intercalibration 9206, 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.

In earlier intercalibrations (8-10) the greatest deviations between the results of the participating laboratories have been observed for the parameters pH and alkalinity. To obtain better comparability between the results, the methods used at different laboratories must be improved. In the report of intercalibration 9004 (6) we recommended that measurement without stirring the solution during reading the meter, should be used for routine determinations. Obviously the participating laboratories prefer to use their own routine methods for the analysis of the acid rain samples, in spite of the fact that the Manual (1) may suggest that another analytical method being used for these samples. Therefore we have to expect that this spread of the results will persist also in the future. Of course, some analytical errors have to be corrected, and thus will improve the results.

CONCLUSION

Under the conditions defined by the equipment and the measuring procedures used at the different participating laboratories, the estimate of a total error of ± 0.02 pH units seems to be a reasonable assessment of the accuracy, which might be achieved routinely when commercial equipment is used. Especially in vicinity of the circumneutrality we have to expect that the supersaturation of CO_2 will reduce the precision and accuracy of pH measurements i such solutions. In acidified samples where the pH value is at least 1-2 units away from circumneutrality, the accuracy will be improved.

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 a couple of cases this is caused by using methos not being precise enough for the

concentrations of the samples used here. These laboratories should improve their methods to obtain a better comparability.

In the next intercalibration more detailed informations about the methods have to be collected, to evaluate possible connections between deviating results and the method used for the analysis.

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APPENDIX 1

Participants of intercalibration 9206.

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5. US Geological Survey, Denver, Colorado, USA.
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8. Institut d'Hygiene et d'Epidemiologie, Bruxelles, Belgium.
9. Centre de Geochimie de la Surface, Strasbourg, France.
10. National Board of Waters and the Environment, Helsinki, Finland
11. Environmental Research Unit, Dublin, Ireland.
12. Ministry of the Environment, Rexdale, Ontario, Canada.
13. Sawyer Environmental Research Center, Orono, Maine, USA.
14. National Laboratory for Environmental Testing, Burlington, Ontario, Canada.
15. Freshwater Institute, Winnipeg, Manitoba, Canada.
16. Research and Engineering Institute for Environment, Bucharest, Romania.
17. DAFS Freshwater Laboratory, Pitlocry, Scotland.
18. Norwegian Institute for Water Research, Oslo, Norway.
19. US Geological Survey, Co. Dist., Denver, Colorado, USA
20. Institut of Environmental Protection, Warsaw, Poland.
21. National Environmental Research Institute, Silkeborg, Denmark.
22. University of Barcelona, Dept. of Ecology, Barcelona, Spain.
23. N.V. Waterleidingbedrijf Midden-Nederland, Utrecht, The Netherlands.

APPENDIX 2

Preparation of samples.

The sample solutions were prepared from natural water collected at two locations outside Oslo, the lake Maridalsvannet and the outlet of Hellerudmyra marsh area, and from a research area at the southern part of Norway, Risdalsheia. Raw water was collected in polyethylene containers and brought to the laboratory, where two samples were prepared by mixing of natural waters.

For sample A was used the water from the lake Maridalsvannet, while sample B was prepared by mixing three parts of Maridalsvannet with one part of water from Risdalsheia, and adjusting the pH value of the solution with sodium bicarbonate solution. As sample C was used water from the outlet of Hellerudmyra marsh area, and sample D was prepared by mixing one part of water from Hellerudmyra with one part of water from the outlet of a small catchment at Risdalsheia research station.

These solutions were stored at room temperature for several weeks at the laboratory. During this stabilization period suspended matter settled. Then 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 6. Summary of the control analyses.

Parameter	Sample A		Sample B		Sample C		Sample D	
	Mean	Sdev.	Mean	Sdev.	Mean	Sdev.	Mean	Sdev.
pH	6,51	0,09	7,06	0,08	3,83	0,02	4,44	0,01
Conductivity mS/m	3,04	0,03	5,50	0,07	11,1	0,20	3,86	0,04
Alkalinity mmol/l	2,30	0,06	7,62	0,10				
Nitrate/nitrite μg/l	225	0	975	10	2450	0	22	0,6
Chloride mg/l	1,83	0,06	3,00	0,06	3,33	0,06	1,66	0,06
Sulfate mg/l	5,40	0,17	6,80	0,10	8,87	0,21	5,93	0,06
Calcium mg/l	2,66	0,04	2,75	0,03	0,93	0,01	1,66	0,01
Magnesium mg/l	0,46	0,006	0,51	0,006	0,31	0,006	0,35	0,006
Sodium mg/l	1,42	0,01	5,39	0,08	1,89	0,08	1,29	0,006
Potassium mg/l	0,35	0	0,37	0	0,20	0,006	0,05	0,006
Diss.org. C mg/l	2,92	0,23	2,47	0,52	7,3	0,65	10,3	0,58
Aluminium μg/l	47	10	38	4,5	295	11	367	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 methoid 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 - 23).

The graphical presentation creates a possibility to distinguish between random and systematic errors affecting the results. The two stright lines drawn in the diagram are representing the true values of the samples; or - 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 $x \pm 3s$, are omitted. The remaining results are used for a final calculation, the results of which are presented in the tables 5 - 27. Results being omitted from the calculations, are marked with the letter "U".

APPENDIX 4 TABLE 4. THE RESULTS OF THE PARTICIPANTS

Lab. no.	pH		pH		COND mS/m		COND mS/m	
	A	B	C	D	A	B	C	D
1	6.69	7.22	3.77	4.40	2.95	5.39	11.24	3.86
2	6.34	6.89	3.77	4.36	3.07	5.58	11.33	3.87
3	6.54	7.16	3.80	4.43	3.02	5.47	11.03	3.82
4	6.57	6.95	3.77	4.36	3.02	5.46	11.1	3.84
5	6.50	7.19	3.99	4.55	3.0	5.5	10.6	3.8
6	6.72	7.20	3.75	4.43	3.05	5.55	11.54	3.92
7	6.75	7.25	3.85	4.63	3.08	5.52	11.6	3.93
8	6.43	6.89	3.73	4.32	3.2	5.9	11.4	4.1
9	6.78	7.18	3.90	4.49	2.90	5.24	10.4	3.80
10	6.61	7.17	3.83	4.45	3.00	5.40	11.20	3.80
11	6.30	6.70	3.79	4.37	3.80	6.50	13.5	5.30
12	6.61	7.15	3.77	4.32	3.0	5.2	10.5	4.25
13	6.40	7.00	3.83	4.46	2.83	5.20	10.5	3.64
14	6.00	6.53	3.76	4.37				
15	6.98	7.51	3.82	4.52	2.90	5.40	11.0	3.70
16	6.0	6.0	2.3	3.0	2.9	4.8	9.0	3.3
17	6.62	7.22	3.79	4.44	2.9	5.2	10.6	3.6
18	6.60	7.14	3.82	4.45	3.02	5.53	10.1	3.55
19	6.63	7.28	3.80	4.46	3.02	5.48	11.46	3.91
20	6.56	7.57	3.65	4.26	3.30	5.86	11.6	4.21
21	6.59	7.16	3.76	4.40	2.85	5.18	10.5	3.63
22	6.39	7.09	3.72	4.37	2.90	5.44	11.25	3.75
23	6.6	7.1	3.8	4.4	2.8	4.9	10.	3.3

Lab. no.	ALK mg/l		NO_3-N µg/l		NO_3-N µg/l	
	A	B	A	B	C	D
1	5.0	16.0	225	943	2430	40
2	5.10	10.62	212	952	2351	< 21
3	2.64	8.45	224	960	2480	< 50
4	2.10	7.55	250	980	2400	31
5	2.19	7.84	207	943	2295	20
6	2.50	7.40	220	966	2477	23
7	3.3	8.6	220	965	2475	23
8	3.4	7.8	210	980	2300	27
9	2.20	7.75	210	966	2436	14
10			221	969	2480	22
11			222	959	2491	26
12	3.76	9.01	225	985	2480	20
13	2.59	8.01	217	959	2390	21
14			220	950	2470	20
15	2.3	7.6	207	929	2399	17
16	16.24	32.12	308	1358	1389	179
17	2.5	7.9	196	952	2611	14
18	3.9	9.2	225	985	2450	22
19	2.24	7.72				
20	4.2	9.3	200	700	2200	200
21	2.3	7.7	200	950	2460	< 10
22	2.37	6.83	233	985	2473	< ?
23	4.0	9.0	220	980	2530	60

Lab. no.	Cl mg/l		Cl mg/l		SO_4 mg/l		SO_4 mg/l	
	A	B	C	D	A	B	C	D
1	1.86	2.95	3.21	1.70	5.07	6.68	8.80	5.65
2	2.1	3.2	3.9	2.5	5.4	6.8	8.0	5.7
3	1.88	3.01	3.31	1.74	5.04	6.62	8.75	5.64
4	1.88	2.91	3.16	1.63	5.14	6.72	8.50	5.76
5	2.10	3.09	3.59	1.81	5.82	7.06	9.46	6.25
6	1.85	2.78	3.02	1.52	5.22	6.52	8.54	5.46
7	1.92	3.18	3.42	1.73	5.37	6.99	8.91	5.90
8	1.99	2.99	3.40	1.90	5.87	7.07	12.24	7.42
9	1.95	3.05	3.33	1.81	5.47	7.01	8.83	5.95
10	1.9	3.1	3.3	1.8	5.4	7.0	9.0	6.0
11	1.76	2.83	3.02	1.62	5.36	6.99	9.15	6.11
12	1.85	2.99	3.31	1.74	5.32	6.86	8.84	5.95
13	1.85	2.98	3.27	1.67	5.28	6.91	8.83	5.81
14	1.84	2.96	3.34	1.74	5.44	6.80	9.20	5.88
15	1.92	3.05	3.35	1.78	5.19	6.87	9.77	6.21
16	21.08	11.24	14.05	17.37	17.69	19.12	22.62	23.03
17	1.56	2.59	2.88	1.46	5.14	6.77	8.78	5.76
18	1.8	3.0	3.7	1.7	5.3	6.9	8.0	5.9
19								
20	1.7	2.9	3.2	2.0	4.1	5.6	7.5	5.1
21	2.05	3.07	3.89	1.94	5.43	7.09	9.64	6.08
22	2.09	3.38	3.55	1.93	5.31	6.85	9.04	6.07
23	1.6	2.7	3.2	1.6	6	7	10	8

Lab. no.	Ca mg/l		Ca mg/l		Mg mg/l		Mg mg/l	
	A	B	C	D	A	B	C	D
1	2.74	2.71	0.88	1.61	0.46	0.50	0.30	0.35
2	2.8	2.9	1.0	1.8	0.5	0.5	0.3	0.4
3	2.76	2.87	0.94	1.70	0.46	0.51	0.31	0.35
4	2.65	2.83	1.12	1.80	0.44	0.50	0.32	0.34
5	2.68	2.74	0.99	1.68	0.46	0.52	0.32	0.36
6	2.72	2.92	0.89	1.63	0.43	0.48	0.29	0.33
7	2.88	2.95	1.12	1.80	0.47	0.56	0.37	0.48
8	3.51	2.99	1.53	2.22	0.47	0.51	0.30	0.37
9	2.80	2.88	0.96	1.80	0.44	0.49	0.29	0.34
10	2.78	2.90	0.98	1.75	0.47	0.51	0.31	0.34
11	2.83	2.99	0.92	1.78	0.428	0.493	0.305	0.342
12	2.65	2.74	0.96	1.74	0.453	0.506	0.312	0.347
13	2.73	2.89	0.96	1.64	0.48	0.54	0.33	0.36
14	2.72	2.82	0.95	1.73	0.46	0.51	0.31	0.34
15	2.79	2.91	0.98	1.65	0.50	0.55	0.36	0.37
16	2.70	2.70	2.50	2.31	0.439	0.544	0.348	0.351
17	2.72	2.84	0.96	1.74	0.44	0.47	0.32	0.32
18	2.69	2.78	0.94	1.67	0.47	0.52	0.32	0.35
19								
20	2.58	2.64	0.89	1.63	0.458	0.510	0.325	0.348
21	2.03	1.67	1.74	1.34	0.34	0.33	0.26	0.23
22	2.64	2.69	0.88	1.63	0.49	0.52	0.31	0.35
23	2.9	2.8	2.5	2.2	0.45	0.49	0.51	0.34

Lab. no.	Na mg/l		Na mg/l		K mg/l		K mg/l	
	A	B	C	D	A	B	C	D
1	1.48	5.56	1.96	1.29	0.33	0.37	0.23	0.08
2	1.8	5.6	2.3	1.5	0.4	0.4	0.2	0.1
3	1.43	5.50	1.89	1.24	0.35	0.36	0.19	0.050
4	1.49	5.54	2.07	1.29	0.31	0.39	0.27	0.12
5	1.50	2.47	2.02	1.32	0.36	0.37	0.21	0.12
6	1.55	5.30	1.90	1.20	0.34	0.35	0.17	0.05
7	1.54	5.49	2.23	1.34	0.37	0.46	0.32	0.06
8	1.29	5.29	1.72	1.09	0.37	0.39	0.18	0.05
9	1.47	5.43	1.95	1.24	0.35	0.35	0.19	0.04
10	1.57	5.41	2.04	1.33	0.35	0.38	0.20	0.04
11	1.60	4.51	1.95	1.52	0.457	0.514	0.286	0.171
12	1.47	5.47	1.94	1.26	0.362	0.375	0.194	0.054
13	1.53	5.28	2.00	1.32	0.35	0.37	0.19	0.06
14	1.50	5.52	1.99	1.29	0.36	0.35	0.19	0.05
15	1.47	5.75	1.86	1.22	0.30	0.34	0.15	0.03
16	0	2.55	0.50	0				
17	1.40	5.22	1.96	1.24	0.31	0.35	0.16	0.04
18	1.42	5.47	1.92	1.22	0.35	0.37	0.20	0.06
19								
20	1.54	5.89	2.12	1.36	0.34	0.36	0.21	0.05
21								
22	1.44	5.09	1.86	1.23	0.40	0.41	0.25	0.12
23	1.6	5.7	2.8	1.5	0.38	0.39	0.52	0.15

Lab. no.	DOC mg/l		DOC mg/l		Al µg/l		Al µg/l	
	A	B	C	D	A	B	C	D
1					85	66	330	460
2	2.6	1.9	6.5	10.	50	50	300	390
3					57	30	285	351
4	2.7	1.6	6.9	10.1	35	20	210	265
5	2.96	2.24	7.38	10.4	54	45	301	390
6					35	25	300	350
7								
8	3.8	2.8	7.7	10.8	56	39	200	340
9	3.00	2.25	7.00	9.70	65	65	296	350
10	3.3	2.3	7.1	10.3	50	40	360	410
11					71	42	330	380
12	2.90	2.10	6.60	10.3				
13	3.22	2.38	7.15	10.44	57	43	286	371
14								
15	3.24	2.40	7.32	10.32				
16	7	5	5	5	140	160	320	240
17	2.7	2.0	5.9	9.4	28	23	227	248
18	2.70	1.80	6.58	9.68	55	42	284	346
19								
20	2.9	3.2	6.4	8.3	<30	<30	290	310
21	2.7	1.9	6.7	9.5				
22	3.61	2.85	8.47	11.74	52	44	288	378
23	2.7	1.8	6.2	9.5	51	39	331	379

Lab. no.	Fe µg/l		Fe µg/l		Mn µg/l		Mn µg/l	
	A	B	C	D	A	B	C	D
20	13	27	287	217	2	9	19	42

Lab. no.	Zn µg/l		Zn µg/l	
	A	B	C	D
20	6	63	201	14

Lab. no.	NH_4-N µg/l		NH_4-N µg/l		SiO_2 µg/l		SiO_2 µg/l	
	A	B	C	D	A	B	C	D
9	< 14	462	1456	28	3.30	2.70	2.64	5.70

TABLE 5. STATISTICS, pH

All methods

Unit:

Sample A

Number of participants:	23	Range:	0.98
Number of omitted results:	1	Variance:	0.04
True value:	6.60	Standard deviation:	0.20
Mean value:	6.56	Relative standard deviation	3.02 %
Median value:	6.60	Relative error:	-0.68 %

Analytical results in ascending order:

14	6.00	:	3	6.54	:	17	6.62
16	6.00 U	:	20	6.56	:	19	6.63
11	6.30	:	4	6.57	:	1	6.69
2	6.34	:	21	6.59	:	6	6.72
22	6.39	:	18	6.60	:	7	6.75
13	6.40	:	23	6.60	:	9	6.78
8	6.43	:	10	6.61	:	15	6.98
5	6.50	:	12	6.61	:		

Sample B

Number of participants:	23	Range:	1.04
Number of omitted results:	1	Variance:	0.05
True value:	7.16	Standard deviation:	0.23
Mean value:	7.12	Relative standard deviation	3.24 %
Median value:	7.16	Relative error:	-0.62 %

Analytical results in ascending order:

16	6.00 U	:	23	7.10	:	6	7.20
14	6.53	:	18	7.14	:	1	7.22
11	6.70	:	12	7.15	:	17	7.22
8	6.89	:	3	7.16	:	7	7.25
2	6.89	:	21	7.16	:	19	7.28
4	6.95	:	10	7.17	:	15	7.51
13	7.00	:	9	7.18	:	20	7.57
22	7.09	:	5	7.19	:		

U = omitted results

TABLE 6. STATISTICS, pH

All methods

Unit:

Sample C

Number of participants:	23	Range:	0.34
Number of omitted results:	1	Variance:	0.00
True value:	3.79	Standard deviation:	0.07
Mean value:	3.79	Relative standard deviation	1.76 %
Median value:	3.79	Relative error:	0.11 %

Analytical results in ascending order:

16	2.30 U	:	1	3.77	:	18	3.82
20	3.65	:	12	3.77	:	15	3.82
22	3.72	:	4	3.77	:	10	3.83
8	3.73	:	17	3.79	:	13	3.83
6	3.75	:	11	3.79	:	7	3.85
21	3.76	:	19	3.80	:	9	3.90
14	3.76	:	3	3.80	:	5	3.99
2	3.77	:	23	3.80	:		

Sample D

Number of participants:	23	Range:	0.37
Number of omitted results:	1	Variance:	0.01
True value:	4.42	Standard deviation:	0.08
Mean value:	4.42	Relative standard deviation	1.87 %
Median value:	4.42	Relative error:	0.00 %

Analytical results in ascending order:

16	3.00 U	:	22	4.37	:	18	4.45
20	4.26	:	21	4.40	:	13	4.46
8	4.32	:	1	4.40	:	19	4.46
12	4.32	:	23	4.40	:	9	4.49
2	4.36	:	3	4.43	:	15	4.52
4	4.36	:	6	4.43	:	5	4.55
11	4.37	:	17	4.44	:	7	4.63
14	4.37	:	10	4.45	:		

U = omitted results

TABLE 7. STATISTICS, CONDUCTIVITY

All methods

Unit: mS/m 25 °C

Sample A

Number of participants:	22	Range:	0.50
Number of omitted results:	1	Variance:	0.01
True value:	3.00	Standard deviation:	0.12
Mean value:	2.99	Relative standard deviation	4.00 %
Median value:	3.00	Relative error:	-0.46 %

Analytical results in ascending order:

23	2.80	:	1	2.95	:	18	3.02
13	2.83	:	10	3.00	:	6	3.05
21	2.85	:	12	3.00	:	2	3.07
16	2.90	:	5	3.00	:	7	3.08
17	2.90	:	19	3.02	:	8	3.20
9	2.90	:	4	3.02	:	20	3.30
22	2.90	:	3	3.02	:	11	3.80 U
15	2.90	:					

Sample B

Number of participants:	22	Range:	1.10
Number of omitted results:	1	Variance:	0.07
True value:	5.44	Standard deviation:	0.26
Mean value:	5.39	Relative standard deviation	4.87 %
Median value:	5.44	Relative error:	-0.91 %

Analytical results in ascending order:

16	4.80	:	10	5.40	:	7	5.52
23	4.90	:	15	5.40	:	18	5.53
21	5.18	:	22	5.44	:	6	5.55
17	5.20	:	4	5.46	:	2	5.58
13	5.20	:	3	5.47	:	20	5.86
12	5.20	:	19	5.48	:	8	5.90
9	5.24	:	5	5.50	:	11	6.50 U
1	5.39	:					

U = omitted results

TABLE 8. STATISTICS, CONDUCTIVITY

All methods

Unit: mS/m 25°C

Sample C

Number of participants:	22	Range:	2.60
Number of omitted results:	1	Variance:	0.42
True value:	11.0	Standard deviation:	0.65
Mean value:	10.9	Relative standard deviation	5.99 %
Median value:	11.0	Relative error:	-1.59 %

Analytical results in ascending order:

16	9.00	:	5	10.6	:	2	11.33
23	10.0	:	15	11.0	:	8	11.4
18	10.1	:	3	11.03	:	19	11.46
9	10.4	:	4	11.1	:	6	11.54
13	10.5	:	10	11.2	:	20	11.6
21	10.5	:	1	11.24	:	7	11.6
12	10.5	:	22	11.25	:	11	13.5 U
17	10.6	:					

Sample D

Number of participants:	22	Range:	0.95
Number of omitted results:	1	Variance:	0.06
True value:	3.80	Standard deviation:	0.24
Mean value:	3.79	Relative standard deviation	6.41 %
Median value:	3.80	Relative error:	-0.28 %

Analytical results in ascending order:

16	3.30	:	9	3.80	:	19	3.91
23	3.30	:	5	3.80	:	6	3.92
18	3.55	:	10	3.80	:	7	3.93
17	3.60	:	3	3.82	:	8	4.10
21	3.63	:	4	3.84	:	20	4.21
13	3.64	:	1	3.86	:	12	4.25
15	3.70	:	2	3.87	:	11	5.30 U
22	3.75						

U = omitted results

TABLE 9. STATISTICS, ALKALINITY

All methods

Unit: mg/l as $CaCO_3$

Sample A

Number of participants:	20	Range:	1.30
Number of omitted results:	7	Variance:	0.17
True value:	2.37	Standard deviation:	0.41
Mean value:	2.51	Relative standard deviation	16.2 %
Median value:	2.37	Relative error:	5.91 %

Analytical results in ascending order:

4	2.10	:	17	2.50	:	18	3.90 U
5	2.19	:	6	2.50	:	23	4.00 U
9	2.20	:	13	2.59	:	20	4.20 U
19	2.24	:	3	2.64	:	1	5.00 U
15	2.30	:	7	3.30	:	2	5.10 U
21	2.30	:	8	3.40	:	16	16.24 U
22	2.37	:	12	3.76	:		

Sample B

Number of participants:	20	Range:	1.77
Number of omitted results:	7	Variance:	0.19
True value:	7.75	Standard deviation:	0.44
Mean value:	7.78	Relative standard deviation	5.67 %
Median value:	7.75	Relative error:	0.40 %

Analytical results in ascending order:

22	6.83	:	8	7.80	:	12	9.01
6	7.40	:	5	7.84	:	18	9.20 U
4	7.55	:	17	7.90	:	20	9.30 U
15	7.60	:	13	8.01	:	2	10.62 U
21	7.70	:	3	8.45	:	1	16.0 U
19	7.72	:	7	8.60	:	16	32.12 U
9	7.75	:	23	9.00 U	:		

U = omitted results

TABLE 10. STATISTICS, NITRATE + NITRITE

All methods

Unit: µg/l

Sample A

Number of participants:	22	Range:	54.0
Number of omitted results:	8	Variance:	155.9
True value:	220	Standard deviation:	12.5
Mean value:	218	Relative standard deviation	5.71 %
Median value:	220	Relative error:	-0.97 %

Analytical results in ascending order:

17	196.		:	13	217.		:	3	224.	U
20	200.	U	:	7	220.		:	1	225.	
21	200.	U	:	14	220.		:	12	225.	
15	207.		:	6	220.		:	18	225.	
5	207.		:	23	220.	U	:	22	233.	U
8	210.		:	10	221.		:	4	250.	
9	210.		:	11	222.		:	16	308.	U
2	212.	U	:							

Sample D

Number of participants:	22	Range:	17.0
Number of omitted results:	8	Variance:	22.0
True value:	21.5	Standard deviation:	4.69
Mean value:	21.4	Relative standard deviation	21.9 %
Median value:	21.5	Relative error:	-0.33 %

Analytical results in ascending order:

3	< 50	U	:	14	20.0		:	11	26.0	
2	< 21	U	:	5	20.0		:	8	27.0	
21	< 10	U	:	13	21.0		:	4	31.0	
22	< DL	U	:	10	22.0		:	1	40.0	
9	14.0		:	18	22.0		:	23	60.0	U
17	14.0		:	6	23.0		:	16	179.	U
15	17.0		:	7	23.0		:	20	200.	U
12	20.0		:							

U = omitted results

TABLE 11. STATISTICS, NITRATE + NITRITE

All methods

Unit: µg/l

Sample C

Number of participants:	22	Range:	411
Number of omitted results:	1	Variance:	8031
True value:	2460	Standard deviation:	89.6
Mean value:	2432	Relative standard deviation	3.68 %
Median value:	2460	Relative error:	-1.13 %

Analytical results in ascending order:

16	1389.	U	:	1	2430.	:	6	2477.
20	2200.		:	9	2436.	:	12	2480.
5	2295.		:	18	2450.	:	10	2480.
8	2300.		:	21	2460.	:	3	2480.
2	2351.		:	14	2470.	:	11	2491.
13	2390.		:	22	2473.	:	23	2530.
15	2399.		:	7	2475.	:	17	2611.
4	2400.		:					

Sample B

Number of participants:	22	Range:	285
Number of omitted results:	1	Variance:	3539
True value:	960	Standard deviation:	59.5
Mean value:	950	Relative standard deviation	6.26 %
Median value:	960	Relative error:	-1.00 %

Analytical results in ascending order:

20	700.	:	13	959.	:	4	980.	
15	929.	:	11	959.	:	8	980.	
5	943.	:	3	960.	:	23	980.	
1	943.	:	7	965.	:	18	985.	
14	950.	:	9	966.	:	22	985.	
21	950.	:	6	966.	:	12	985.	
2	952.	:	10	969.	:	16	1358.	U
17	952.	:						

U = omitted results

TABLE 12. STATISTICS, CHLORIDE

All methods

Unit: mg/l

Sample A

Number of participants:	22	Range:	0.54
Number of omitted results:	1	Variance:	0.02
True value:	1.88	Standard deviation:	0.15
Mean value:	1.88	Relative standard deviation	7.80 %
Median value:	1.88	Relative error:	-0.07 %

Analytical results in ascending order:

17	1.56	:	12	1.85	:	9	1.95
23	1.60	:	1	1.86	:	8	1.99
20	1.70	:	4	1.88	:	21	2.05
11	1.76	:	3	1.88	:	22	2.09
18	1.80	:	10	1.90	:	2	2.10
14	1.84	:	7	1.92	:	5	2.10
13	1.85	:	15	1.92	:	16	21.08 U
6	1.85	:					

Sample B

Number of participants:	22	Range:	0.79
Number of omitted results:	1	Variance:	0.03
True value:	2.99	Standard deviation:	0.17
Mean value:	2.99	Relative standard deviation	5.79 %
Median value:	2.99	Relative error:	-0.13 %

Analytical results in ascending order:

17	2.59	:	13	2.98	:	21	3.07
23	2.70	:	12	2.99	:	5	3.09
6	2.78	:	8	2.99	:	10	3.10
11	2.83	:	18	3.00	:	7	3.18
20	2.90	:	3	3.01	:	2	3.20
4	2.91	:	9	3.05	:	22	3.38
1	2.95	:	15	3.05	:	16	11.24 U
14	2.96	:					

U = omitted results

TABLE 13. STATISTICS, CHLORIDE

All methods

Unit: mg/l

Sample C

Number of participants:	22	Range:	1.01
Number of omitted results:	2	Variance:	0.06
True value:	3.31	Standard deviation:	0.24
Mean value:	3.32	Relative standard deviation	7.10 %
Median value:	3.31	Relative error:	0.37 %

Analytical results in ascending order:

17	2.88	:	10	3.30	:	7	3.42
11	3.02	:	3	3.31	:	22	3.55
6	3.02	:	12	3.31	:	5	3.59
4	3.16	:	9	3.33	:	18	3.70
20	3.20	:	14	3.34	:	21	3.89
23	3.20	:	15	3.35	:	2	3.90 U
1	3.21	:	8	3.40	:	16	14.05 U
13	3.27	:					

Sample D

Number of participants:	22	Range:	0.54
Number of omitted results:	2	Variance:	0.02
True value:	1.74	Standard deviation:	0.14
Mean value:	1.74	Relative standard deviation	7.98 %
Median value:	1.74	Relative error:	0.05 %

Analytical results in ascending order:

17	1.46	:	7	1.73	:	5	1.81
6	1.52	:	12	1.74	:	8	1.90
23	1.60	:	3	1.74	:	22	1.93
11	1.62	:	14	1.74	:	21	1.94
4	1.63	:	15	1.78	:	20	2.00
13	1.67	:	10	1.80	:	2	2.50 U
18	1.70	:	9	1.81	:	16	17.37 U
1	1.70	:					

U = omitted results

TABLE 14. STATISTICS, SULFATE

All methods

Unit: mg/l

Sample A

Number of participants:	22	Range:	0.96
Number of omitted results:	2	Variance:	0.07
True value:	5.34	Standard deviation:	0.26
Mean value:	5.38	Relative standard deviation	4.76 %
Median value:	5.34	Relative error:	0.72 %

Analytical results in ascending order:

20	4.10 U	:	18	5.30	:	21	5.43
3	5.04	:	22	5.31	:	14	5.44
1	5.07	:	12	5.32	:	9	5.47
17	5.14	:	11	5.36	:	5	5.82
4	5.14	:	7	5.37	:	8	5.87
15	5.19	:	10	5.40	:	23	6.00
6	5.22	:	2	5.40	:	16	17.69 U
13	5.28	:					

Sample B

Number of participants:	22	Range:	0.57
Number of omitted results:	2	Variance:	0.02
True value:	6.89	Standard deviation:	0.16
Mean value:	6.88	Relative standard deviation	2.30 %
Median value:	6.89	Relative error:	-0.21 %

Analytical results in ascending order:

20	5.60 U	:	22	6.85	:	10	7.00
6	6.52	:	12	6.86	:	23	7.00
3	6.62	:	15	6.87	:	9	7.01
1	6.68	:	18	6.90	:	5	7.06
4	6.72	:	13	6.91	:	8	7.07
17	6.77	:	7	6.99	:	21	7.09
2	6.80	:	11	6.99	:	16	19.12 U
14	6.80	:					

U = omitted results

TABLE 15. STATISTICS, SULFATE

All methods

Unit: mg/l

Sample C

Number of participants:	22	Range:	2.27
Number of omitted results:	3	Variance:	0.31
True value:	8.83	Standard deviation:	0.56
Mean value:	8.82	Relative standard deviation	6.32 %
Median value:	8.83	Relative error:	-0.14 %

Analytical results in ascending order:

20	7.50	:	13	8.83	:	14	9.20
18	8.00	:	9	8.83	:	5	9.46
2	8.00	:	12	8.84	:	21	9.64
4	8.50	:	7	8.91	:	15	9.77
6	8.54	:	10	9.00	:	23	10.0 U
3	8.75	:	22	9.04	:	8	12.24 U
17	8.78	:	11	9.15	:	16	22.62 U
1	8.80	:					

Sample D

Number of participants:	22	Range:	1.15
Number of omitted results:	3	Variance:	0.07
True value:	5.90	Standard deviation:	0.27
Mean value:	5.85	Relative standard deviation	4.67 %
Median value:	5.90	Relative error:	-0.82 %

Analytical results in ascending order:

20	5.10	:	14	5.88	:	21	6.08
6	5.46	:	18	5.90	:	11	6.11
3	5.64	:	7	5.90	:	15	6.21
1	5.65	:	12	5.95	:	5	6.25
2	5.70	:	9	5.95	:	8	7.42 U
17	5.76	:	10	6.00	:	23	8.00 U
4	5.76	:	22	6.07	:	16	23.03 U
13	5.81	:					

U = omitted results

TABLE 16. STATISTICS, CALCIUM

All methods

Unit: mg/l

Sample A

Number of participants:	22	Range:	0.32
Number of omitted results:	2	Variance:	0.01
True value:	2.72	Standard deviation:	0.08
Mean value:	2.74	Relative standard deviation	2.98 %
Median value:	2.72	Relative error:	0.66 %

Analytical results in ascending order:

21	2.03 U	:	6	2.72	:	15	2.79
20	2.58	:	17	2.72	:	2	2.80
22	2.64	:	14	2.72	:	9	2.80
12	2.65	:	13	2.73	:	11	2.83
4	2.65	:	1	2.74	:	7	2.88
5	2.68	:	3	2.76	:	23	2.90
18	2.69	:	10	2.78	:	8	3.51 U
16	2.70	:					

Sample B

Number of participants:	22	Range:	0.35
Number of omitted results:	2	Variance:	0.01
True value:	2.84	Standard deviation:	0.10
Mean value:	2.82	Relative standard deviation	3.43 %
Median value:	2.84	Relative error:	-0.54 %

Analytical results in ascending order:

21	1.67 U	:	23	2.80	:	2	2.90
20	2.64	:	14	2.82	:	10	2.90
22	2.69	:	4	2.83	:	15	2.91
16	2.70	:	17	2.84	:	6	2.92
1	2.71	:	3	2.87	:	7	2.95
5	2.74	:	9	2.88	:	11	2.99
12	2.74	:	13	2.89	:	8	2.99 U
18	2.78	:					

U = omitted results

TABLE 17. STATISTICS, CALCIUM

All methods

Unit: mg/l

Sample C

Number of participants:	22	Range:	0.24
Number of omitted results:	4	Variance:	0.00
True value:	0.96	Standard deviation:	0.07
Mean value:	0.96	Relative standard deviation	7.10 %
Median value:	0.96	Relative error:	0.23 %

Analytical results in ascending order:

1	0.88	:	13	0.96	:	2	1.00
22	0.88	:	9	0.96	:	4	1.12
20	0.89	:	17	0.96	:	7	1.12
6	0.89	:	12	0.96	:	8	1.53 U
11	0.92	:	10	0.98	:	21	1.74 U
3	0.94	:	15	0.98	:	23	2.50 U
18	0.94	:	5	0.99	:	16	2.50 U
14	0.95	:					

Sample D

Number of participants:	22	Range:	0.19
Number of omitted results:	4	Variance:	0.00
True value:	1.71	Standard deviation:	0.07
Mean value:	1.71	Relative standard deviation	4.06 %
Median value:	1.71	Relative error:	0.02 %

Analytical results in ascending order:

21	1.34 U	:	5	1.68	:	9	1.80
1	1.61	:	3	1.70	:	2	1.80
20	1.63	:	14	1.73	:	7	1.80
6	1.63	:	17	1.74	:	4	1.80
22	1.63	:	12	1.74	:	23	2.20 U
13	1.64	:	10	1.75	:	8	2.22 U
15	1.65	:	11	1.78	:	16	2.31 U
18	1.67	:					

U = omitted results

TABLE 18. STATISTICS, MAGNESIUM

All methods

Unit: mg/l

Sample A

Number of participants:	22	Range:	0.07
Number of omitted results:	1	Variance:	0.00
True value:	0.46	Standard deviation:	0.02
Mean value:	0.46	Relative standard deviation	4.53 %
Median value:	0.46	Relative error:	0.10 %

Analytical results in ascending order:

21	0.34 U	:	23	0.45	:	10	0.47
11	0.43	:	20	0.46	:	8	0.47
6	0.43	:	14	0.46	:	7	0.47
16	0.44	:	1	0.46	:	13	0.48
9	0.44	:	5	0.46	:	22	0.49
17	0.44	:	3	0.46	:	15	0.50
4	0.44	:	18	0.47	:	2	0.50
12	0.45	:					

Sample B

Number of participants:	22	Range:	0.09
Number of omitted results:	1	Variance:	0.00
True value:	0.51	Standard deviation:	0.02
Mean value:	0.51	Relative standard deviation	4.44 %
Median value:	0.51	Relative error:	0.25 %

Analytical results in ascending order:

21	0.33 U	:	1	0.50	:	18	0.52
17	0.47	:	12	0.51	:	22	0.52
6	0.48	:	14	0.51	:	5	0.52
9	0.49	:	3	0.51	:	13	0.54
23	0.49	:	20	0.51	:	16	0.54
11	0.49	:	10	0.51	:	15	0.55
4	0.50	:	8	0.51	:	7	0.56
2	0.50	:					

U = omitted results

TABLE 19. STATISTICS, MAGNESIUM

All methods

Unit: mg/l

Sample C

Number of participants:	22	Range:	0.10
Number of omitted results:	2	Variance:	0.00
True value:	0.31	Standard deviation:	0.02
Mean value:	0.31	Relative standard deviation	6.79 %
Median value:	0.31	Relative error:	0.65 %

Analytical results in ascending order:

21	0.26	:	14	0.31	:	5	0.32
6	0.29	:	10	0.31	:	20	0.33
9	0.29	:	22	0.31	:	13	0.33
2	0.30	:	12	0.31	:	16	0.35
1	0.30	:	17	0.32	:	15	0.36
8	0.30	:	18	0.32	:	7	0.37 U
11	0.30	:	4	0.32	:	23	0.51 U
3	0.31	:					

Sample D

Number of participants:	22	Range:	0.17
Number of omitted results:	2	Variance:	0.00
True value:	0.35	Standard deviation:	0.03
Mean value:	0.34	Relative standard deviation	9.19 %
Median value:	0.35	Relative error:	-1.60 %

Analytical results in ascending order:

21	0.23	:	11	0.34	:	16	0.35
17	0.32	:	12	0.35	:	5	0.36
6	0.33	:	20	0.35	:	13	0.36
4	0.34	:	1	0.35	:	15	0.37
14	0.34	:	3	0.35	:	8	0.37
9	0.34	:	22	0.35	:	2	0.40
10	0.34	:	18	0.35	:	7	0.48 U
23	0.34 U	:					

U = omitted results

TABLE 20. STATISTICS, SODIUM

All methods

Unit: mg/l

Sample A

Number of participants:	21	Range:	0.51
Number of omitted results:	3	Variance:	0.01
True value:	1.48	Standard deviation:	0.10
Mean value:	1.50	Relative standard deviation	6.93 %
Median value:	1.48	Relative error:	1.32 %

Analytical results in ascending order:

16	0.00 U	:	15	1.47	:	20	1.54
8	1.29	:	12	1.47	:	7	1.54
17	1.40	:	1	1.48	:	6	1.55
18	1.42	:	4	1.49	:	10	1.57
3	1.43	:	14	1.50	:	11	1.60 U
22	1.44	:	5	1.50 U	:	23	1.60
9	1.47	:	13	1.53	:	2	1.80

Sample B

Number of participants:	21	Range:	0.80
Number of omitted results:	3	Variance:	0.04
True value:	5.48	Standard deviation:	0.20
Mean value:	5.47	Relative standard deviation	3.58 %
Median value:	5.48	Relative error:	-0.13 %

Analytical results in ascending order:

5	2.47 U	:	6	5.30	:	14	5.52
16	2.55 U	:	10	5.41	:	4	5.54
11	4.51 U	:	9	5.43	:	1	5.56
22	5.09	:	18	5.47	:	2	5.60
17	5.22	:	12	5.47	:	23	5.70
13	5.28	:	7	5.49	:	15	5.75
8	5.29	:	3	5.50	:	20	5.89

U = omitted results

TABLE 21. STATISTICS, SODIUM

All methods

Unit: mg/l

Sample C

Number of participants:	21	Range:	0.58
Number of omitted results:	2	Variance:	0.02
True value:	1.96	Standard deviation:	0.13
Mean value:	1.98	Relative standard deviation	6.68 %
Median value:	1.96	Relative error:	1.20 %

Analytical results in ascending order:

16	0.50 U	:	12	1.94	:	5	2.02
8	1.72	:	9	1.95	:	10	2.04
15	1.86	:	11	1.95	:	4	2.07
22	1.86	:	1	1.96	:	20	2.12
3	1.89	:	17	1.96	:	7	2.23
6	1.90	:	14	1.99	:	2	2.30
18	1.92	:	13	2.00	:	23	2.80 U

Sample D

Number of participants:	21	Range:	0.43
Number of omitted results:	2	Variance:	0.01
True value:	1.29	Standard deviation:	0.10
Mean value:	1.29	Relative standard deviation	7.69 %
Median value:	1.29	Relative error:	-0.03 %

Analytical results in ascending order:

16	0.00 U	:	9	1.24	:	13	1.32
8	1.09	:	3	1.24	:	10	1.33
6	1.20	:	12	1.26	:	7	1.34
15	1.22	:	14	1.29	:	20	1.36
18	1.22	:	1	1.29	:	2	1.50
22	1.23	:	4	1.29	:	23	1.50 U
17	1.24	:	5	1.32	:	11	1.52

U = omitted results

TABLE 22. STATISTICS, POTASSIUM

All methods

Unit: mg/l

Sample A

Number of participants:	20	Range:	0.10
Number of omitted results:	1	Variance:	0.00
True value:	0.35	Standard deviation:	0.03
Mean value:	0.35	Relative standard deviation	7.73 %
Median value:	0.35	Relative error:	0.48 %

Analytical results in ascending order:

15	0.30	:	9	0.35	:	8	0.37
4	0.31	:	3	0.35	:	7	0.37
17	0.31	:	18	0.35	:	23	0.38
1	0.33	:	10	0.35	:	22	0.40
6	0.34	:	5	0.36	:	2	0.40
20	0.34	:	14	0.36	:	11	0.46 U
13	0.35	:	12	0.36	:		

Sample B

Number of participants:	20	Range:	0.12
Number of omitted results:	1	Variance:	0.00
True value:	0.37	Standard deviation:	0.03
Mean value:	0.38	Relative standard deviation	7.44 %
Median value:	0.37	Relative error:	1.49 %

Analytical results in ascending order:

15	0.34	:	1	0.37	:	8	0.39
6	0.35	:	13	0.37	:	23	0.39
14	0.35	:	18	0.37	:	2	0.40
9	0.35	:	5	0.37	:	22	0.41
17	0.35	:	12	0.38	:	7	0.46
3	0.36	:	10	0.38	:	11	0.51 U
20	0.36	:	4	0.39	:		

U = omitted results

TABLE 23. STATISTICS, POTASSIUM

All methods

Unit: mg/l

Sample C

Number of participants:	20	Range:	0.06
Number of omitted results:	8	Variance:	0.00
True value:	0.19	Standard deviation:	0.02
Mean value:	0.19	Relative standard deviation	9.43 %
Median value:	0.19	Relative error:	-2.46 %

Analytical results in ascending order:

15	0.15	:	3	0.19	:	1	0.23 U
17	0.16	:	12	0.19	:	22	0.25 U
6	0.17	:	2	0.20 U	:	4	0.27 U
8	0.18	:	10	0.20	:	11	0.29 U
13	0.19	:	18	0.20	:	7	0.32 U
14	0.19	:	5	0.21 U	:	23	0.52 U
9	0.19	:	20	0.21	:		

Sample D

Number of participants:	20	Range:	0.03
Number of omitted results:	8	Variance:	0.00
True value:	0.05	Standard deviation:	0.01
Mean value:	0.05	Relative standard deviation	18.5 %
Median value:	0.05	Relative error:	-4.33 %

Analytical results in ascending order:

15	0.03	:	6	0.05	:	2	0.10 U
9	0.04	:	20	0.05	:	5	0.12 U
10	0.04	:	12	0.05	:	4	0.12 U
17	0.04	:	7	0.06 U	:	22	0.12 U
3	0.05	:	18	0.06	:	23	0.15 U
14	0.05	:	13	0.06	:	11	0.17 U
8	0.05	:	1	0.08 U	:		

U = omitted results

TABLE 24. STATISTICS, DISSOLVED ORGANIC CARBON, (DOC)

All methods

Unit: mg/l

Sample A

Number of participants:	16	Range:	1.20
Number of omitted results:	1	Variance:	0.13
True value:	2.90	Standard deviation:	0.36
Mean value:	3.00	Relative standard deviation	12.1 %
Median value:	2.90	Relative error:	3.52 %

Analytical results in ascending order:

2	2.60	:	12	2.90	:	15	3.24
4	2.70	:	20	2.90	:	10	3.30
17	2.70	:	5	2.96	:	22	3.61
18	2.70	:	9	3.00	:	8	3.80
21	2.70	:	13	3.22	:	16	7.00 U
23	2.70	:					

Sample B

Number of participants:	16	Range:	1.60
Number of omitted results:	1	Variance:	0.20
True value:	2.24	Standard deviation:	0.44
Mean value:	2.23	Relative standard deviation	19.9 %
Median value:	2.24	Relative error:	-0.24 %

Analytical results in ascending order:

4	1.60	:	12	2.10	:	15	2.40
18	1.80	:	5	2.24	:	8	2.80
23	1.80	:	9	2.25	:	22	2.85
21	1.90	:	10	2.30	:	20	3.20
2	1.90	:	13	2.38	:	16	5.00 U
17	2.00	:					

U = omitted results

TABLE 25. STATISTICS, DISSOLVED ORGANIC CARBON, (DOC)

All methods

Unit: mg/l

Sample C

Number of participants:	16	Range:	2.57
Number of omitted results:	1	Variance:	0.41
True value:	6.90	Standard deviation:	0.64
Mean value:	6.93	Relative standard deviation	9.25 %
Median value:	6.90	Relative error:	0.39 %

Analytical results in ascending order:

16	5.00 U	:	12	6.60	:	13	7.15
17	5.90	:	21	6.70	:	15	7.32
23	6.20	:	4	6.90	:	5	7.38
20	6.40	:	9	7.00	:	8	7.70
2	6.50	:	10	7.10	:	22	8.47
18	6.58	:					

Sample D

Number of participants:	16	Range:	3.44
Number of omitted results:	1	Variance:	0.59
True value:	10.1	Standard deviation:	0.77
Mean value:	10.0	Relative standard deviation	7.65 %
Median value:	10.1	Relative error:	-0.67 %

Analytical results in ascending order:

16	5.00 U	:	9	9.70	:	15	10.32
20	8.30	:	2	10.0	:	5	10.4
17	9.40	:	4	10.1	:	13	10.44
21	9.50	:	10	10.3	:	8	10.8
23	9.50	:	12	10.3	:	22	11.74
18	9.68	:					

U = omitted results

TABLE 26. STATISTICS, ALUMINIUM

All methods

Unit: µg/l

Sample A

Number of participants:	17	Range:	43.0
Number of omitted results:	5	Variance:	142.3
True value:	53.0	Standard deviation:	11.9
Mean value:	50.2	Relative standard deviation	23.8 %
Median value:	53.0	Relative error:	-5.38 %

Analytical results in ascending order:

20	< 30	U	:	23	51.0	:	3	57.0	
17	28.0		:	22	52.0	:	9	65.0	U
6	35.0		:	5	54.0	:	11	71.0	
4	35.0		:	18	55.0	:	1	85.0	U
10	50.0		:	8	56.8	:	16	140.	U
2	50.0	U	:	13	57.0	:			

Sample B

Number of participants:	17	Range:	25.0
Number of omitted results:	5	Variance:	81.3
True value:	40.0	Standard deviation:	9.02
Mean value:	36.2	Relative standard deviation	24.9 %
Median value:	40.0	Relative error:	-9.63 %

Analytical results in ascending order:

2	< 50	U	:	8	39.9	:	22	44.0	
20	< 30	U	:	23	39.9	:	5	45.0	
4	20.0		:	10	40.0	:	9	65.0	U
17	23.0		:	11	42.0	:	1	66.0	U
6	25.0		:	18	42.0	:	16	160.	U
3	30.0		:	13	43.0	:			

U = omitted results

TABLE 27. STATISTICS, ALUMINIUM

All methods

Unit: µg/l

Sample C

Number of participants:	17	Range:	160
Number of omitted results:	0	Variance:	1849
True value:	296	Standard deviation:	43.0
Mean value:	290	Relative standard deviation	14.8 %
Median value:	296	Relative error:	-1.87 %

Analytical results in ascending order:

8	200.	:	22	288.	:	16	320.
4	210.	:	20	290.	:	11	330.
17	227.	:	9	296.	:	1	330.
18	284.	:	2	300.	:	23	331.
3	285.	:	6	300.	:	10	360.
13	286.	:	5	301.	:		

Sample D

Number of participants:	17	Range:	220
Number of omitted results:	0	Variance:	3332
True value:	351	Standard deviation:	57.7
Mean value:	350	Relative standard deviation	16.5 %
Median value:	351	Relative error:	-0.15 %

Analytical results in ascending order:

16	240.	:	6	350.	:	11	380.
17	248.	:	9	350.	:	2	390.
4	265.	:	3	351.	:	5	390.
20	310.	:	13	371.	:	10	410.
8	340.	:	22	378.	:	1	460.
18	346.	:	23	379.	:		

U = omitted results

APPENDIX 5

Table 28. Ionic balance calculations. The sums of the anions and the cations concentrations, and the difference between these sums, are given in mmom/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	0,274	0,247	-0,027	0,609	0,428	-0,182
2	0,289	0,269	-0,019	0,512	0,440	-0,072
3	0,227	0,247	0,020	0,460	0,434	-0,026
4	0,220	0,241	0,021	0,443	0,433	-0,010
5	0,239	0,246	0,007	0,458	0,296	-0,162
6	0,227	0,247	0,021	0,431	0,425	-0,006
7	0,248	0,259	0,011	0,476	0,444	-0,032
8	0,261	0,279	0,018	0,457	0,431	-0,026
9	0,228	0,249	0,021	0,456	0,429	-0,027
12	0,254	0,242	-0,012	0,478	0,426	-0,051
13	0,229	0,251	0,022	0,456	0,428	-0,029
15	0,223	0,252	0,029	0,447	0,449	0,002
17	0,215	0,241	0,026	0,440	0,416	-0,023
18	0,255	0,243	-0,011	0,482	0,429	-0,054
20	0,232	0,242	0,011	0,434	0,439	0,005
22	0,234	0,245	0,011	0,445	0,409	-0,036
23	0,266	0,261	-0,005	0,472	0,438	-0,034
MEAN	0,242	0,251	0,008	0,468	0,423	-0,045

	Sample C			Sample D		
Lab. no.	Anions	Cations	Differ.	Anions	Cations	Differ.
1	0,447	0,160	-0,288	0,168	0,167	-0,001
2	0,444	0,180	-0,265	0,189	0,190	0,001
3	0,452	0,159	-0,293	0,167	0,169	0,002
4	0,437	0,179	-0,252	0,168	0,177	0,009
5	0,462	0,169	-0,293	0,183	0,174	-0,009
6	0,440	0,155	-0,285	0,158	0,162	0,004
7	0,459	0,192	-0,267	0,173	0,189	0,016
8	0,515	0,180	-0,335	0,210	0,190	-0,020
9	0,452	0,161	-0,290	0,176	0,173	-0,003
12	0,454	0,163	-0,292	0,174	0,172	-0,003
13	0,447	0,170	-0,280	0,170	0,170	0,001
15	0,469	0,163	-0,306	0,181	0,167	-0,014
17	0,450	0,164	-0,287	0,162	0,168	0,006
18	0,446	0,162	-0,284	0,172	0,167	-0,006
20	0,403	0,169	-0,234	0,177	0,171	-0,006
22	0,465	0,157	-0,308	0,181	0,167	-0,014
23	0,479	0,302	-0,177	0,216	0,207	-0,009
MEAN	0,454	0,175	-0,279	0,178	0,175	-0,003

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