2591

CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

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

Intercalibration 9105

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

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

NIVA – REPORT

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Abstract:

21 laboratories in 15 countries participated in intercalibration 9105. Based on the general target accuracy of ± 20 %, 90 - 100 % of the results were acceptable for all the main components, only 0 - 2 result pairs lying outside the accuracy limit. Most results are even lying within much narrower limits. For pH only 35 % of the result pairs were acceptable in relation to the target accuracy of ± 0.1 units. The deviations observed for pH are caused by systematic errors.

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Project leader

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

INTERCALIBRATION 9105

pH, κ_{25}, HCO_3^-, NO_3^- + NO_2^-, Cl^-, SO_4^{--},
Ca^{++}, Mg^{++}, Na^+, K^+ and TOC

Oslo, June, 1991

Written at the Programme Centre, Norwegian Inst. for Water Research.

SUMMARY

Intercalibration 9105 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-April 1991, and included determination of the major ions in two natural water samples spiked with solutions of stoichiometric compounds with known concentrations. The participants were asked to determine pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium and total organic carbon.

The samples were sent to 24 laboratories, and 21 submitted results to the Programme Centre. 15 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 nearly all parameters, only one or two laboratories reported results lying outside the general target accuracy of ± 20 %.

pH makes an exception, where the accuracy limit was extended to ± 0.2 units. 67 % of the result pairs were included by this limit, in contrary to only 35 % within the target accuracy of ± 0.1 units, given in the Manual (1). The deviating results are dominated by systematic errors.

CONTENTS

INTRODUCTION

As stated in "Manual for Chemical and Biological Monitoring" (1), between-laboratory quality control is necessary in a multilaboratory programme to assure clear identification and control of the bias between analyses carried out by individual participants of the programme. Such biases may arise through the use of different analytical methods, errors in the laboratory standards, 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 fifth intercalibration test, called 9105, included the determination of the main components: pH, conductivity, alkalinity, nitrate + nitrite, chloride, sulfate, calcium, magnesium, sodium, potassium and total organic carbon, in spiked, natural water samples.

ACCOMPLISHMENT OF THE INTERCALIBRATION

Preparation of the sample solutions is described in Appendix 2. There, also the results of the control analyses performed at the Programme Centre are summarized.

The samples were mailed from the Programme Centre on the 28th of february 1991. 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 within four weeks after the arrival at the laboratory.

RESULTS

The samples were sent to 24 laboratories. The 21 laboratories who submittet results to the Programme Centre, are representing 15 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. A short description of this method and the statistical treatment of the analytical data, are presented in Appendix 3.

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Table 1. Survey of the results of intercalibration 9105.

Parameter Method	Sample pair	True values 1	True values 2	Number of data Tot.	Number of data U	Median 1	Median 2	Mean value/std. 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	7.24	7.32												
Electrometry				21	1	7.24	7.32	7.30	0.21	7.39	0.20	2.9	2.8	0.8	0.9
Conductivity	AB	6.57	6.21												
Electrometry				20	1	6.57	6.21	6.55	0.21	6.19	0.20	3.2	3.2	-0.3	-0.3
Alkalinity	AB	15.0	17.9												
All methods				20	1	15.00	17.90	15.37	1.30	18.26	1.32	8.5	7.2	2.5	2.0
Gran plot titration				12	0	15.00	17.90	15.13	0.68	18.09	0.70	4.5	3.9	0.9	1.1
Electrometric titration				6	0	15.00	17.84	14.82	3.38	17.82	3.19	22.8	17.9	-1.2	-0.5
Ion chromatography				2	0	15.25	17.75	15.25		17.75				1.0	-0.8
Nitrate nitrogen	AB	638.	518.												
All methods				20	1	638.0	518.0	636.5	24.5	513.2	20.1	3.8	3.9	-0.2	-0.9
Ion chromatography				14	0	639.5	515.0	637.4	28.4	506.8	36.6	4.5	7.2	-0.1	-2.2
Photometry				6	0	621.5	514.8	622.8	28.6	509.1	21.3	4.6	4.2	-2.4	-1.7
Chloride	AB	3.30	2.50												
All methods				20	1	3.30	2.50	3.32	0.25	2.45	0.15	7.4	6.1	0.7	-1.9
Ion chromatography				18	1	3.32	2.50	3.33	0.26	2.45	0.15	7.8	6.2	0.9	-2.1
Argentometric titration				1	0	3.30	2.60	3.30		2.60				0.0	4.0
Photometry				1	0	3.20	2.40	3.20		2.40				-3.0	-4.0
Sulfate	AB	6.90	5.19												
All methods				20	0	6.90	5.19	6.87	0.38	5.13	0.35	5.5	6.9	-0.4	-1.2
Ion chromatography				19	1	6.91	5.20	6.89	0.38	5.18	0.26	5.6	4.9	-0.2	-0.1
Photometry				1	0	6.60	4.10	6.60		4.10				-4.6	-21.

Calcium	AB	3.21	2.46											
All methods				20	1	3.21	2.46	3.24	0.14	2.50	0.14	4.3	5.8	1.1	1.4
Atomic absorption				13	0	3.22	2.46	3.26	0.15	2.49	0.14	4.5	5.7	1.7	1.2
ICP emission				4	0	3.16	2.50	3.18	0.09	2.50	0.12	2.9	4.6	-0.9	1.6
Ion chromatography				3	0	3.10	2.31	3.06	0.37	2.28	0.46	12.0	20.2	-4.8	-7.2
Magnesium	AB	0.83	0.57											
All methods				20	0	0.83	0.57	0.82	0.06	0.57	0.05	7.1	9.3	-1.1	0.1
Atomic absorption				13	0	0.83	0.57	0.83	0.05	0.57	0.04	6.4	6.3	-0.1	0.5
ICP - emission				4	0	0.84	0.59	0.84	0.04	0.61	0.06	5.0	9.9	1.5	7.5
Ion chromatography				3	0	0.75	0.50	0.76	0.08	0.51	0.06	9.9	11.9	-8.4	-11.
Sodium	AB	7.61	8.79											
All methods				20	0	7.61	8.79	7.53	0.36	8.64	0.42	4.8	4.9	-1.0	-1.7
Atomic absorption				16	0	7.63	8.80	7.56	0.39	8.66	0.46	5.2	5.4	-0.7	-1.5
Ion chromatography				2	0	7.57	8.72	7.57		8.72				-0.5	-0.8
ICP emission				1	0	7.38	8.37	7.38		8.37				-3.0	-4.8
Flame emission				1	0	7.22	8.39	7.22		8.39				-5.1	-4.6
Potassium	AB	1.42	1.15											
All methods				20	0	1.42	1.15	1.43	0.08	1.15	0.07	5.6	6.5	0.4	-0.3
Atomic absorption				16	0	1.43	1.15	1.44	0.07	1.16	0.07	4.6	6.1	1.4	0.7
Ion chromatography				2	0	1.43	1.13	1.43		1.13				0.7	-1.7
ICP emission				1	0	1.21	0.98	1.21		0.98				-15.	-15.
Flame emission				1	0	1.40	1.16	1.40		1.16				-1.4	0.9
Total organic carbon (TOC)	AB	23.4	13.0											
All methods				12	0	23.35	13.00	24.23	3.22	13.66	1.66	13.3	12.2	3.6	5.1

U = Excluded results

FIG. 1 pH

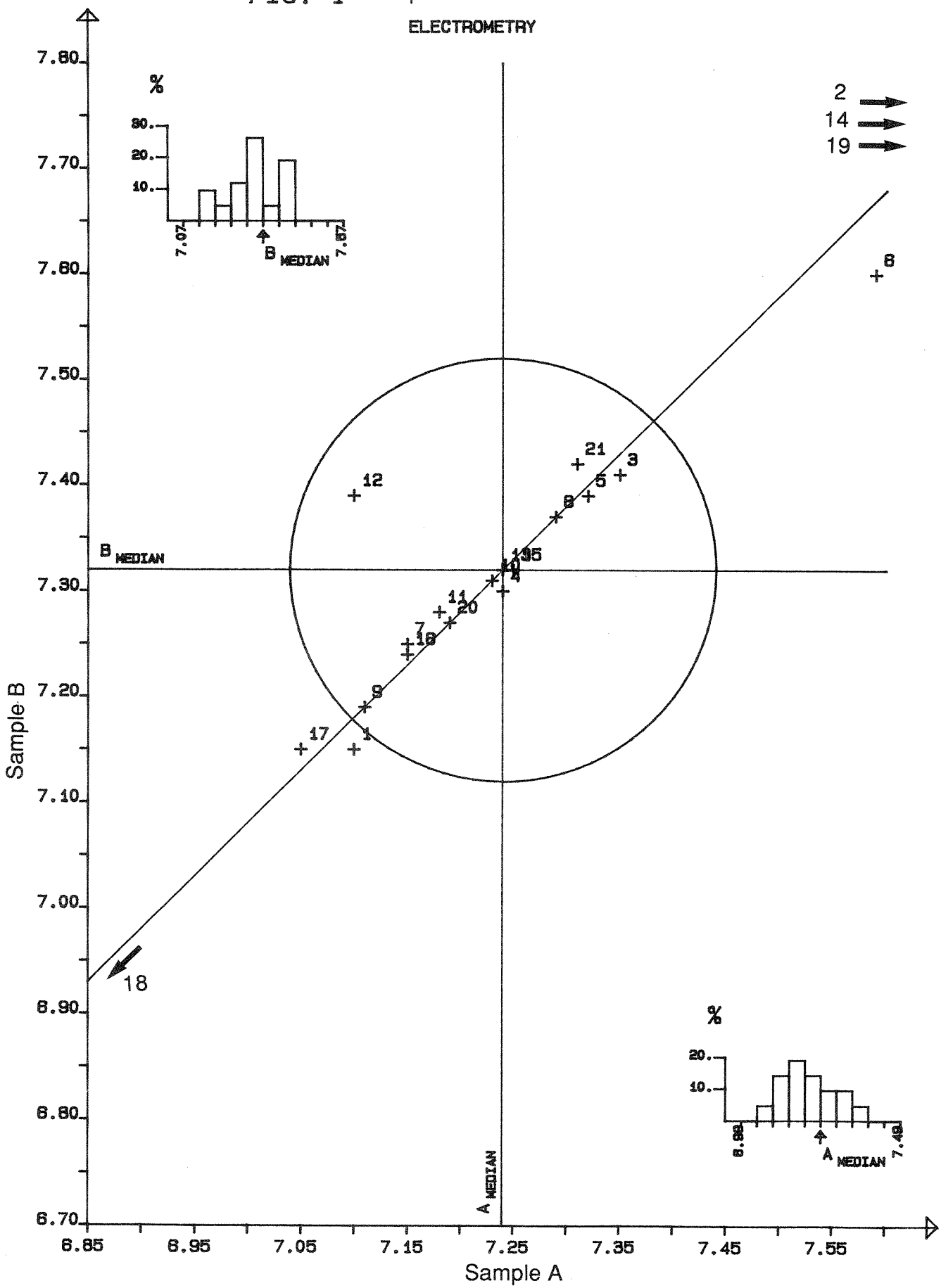

ELECTROMETRY
%
30.
20.
10.
7.07
B MEDIAN
7.87
2
14
19
8
21
3
5
12
B MEDIAN
135
11
20
7
18
9
17
1
18
%
20.
10.
6.88
A MEDIAN
7.49
A MEDIAN
7.80
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
6.90
6.80
6.70
Sample B
6.85
6.95
7.05
7.15
7.25
7.35
7.45
7.55
Sample A

FIG. 2 Conduktivity

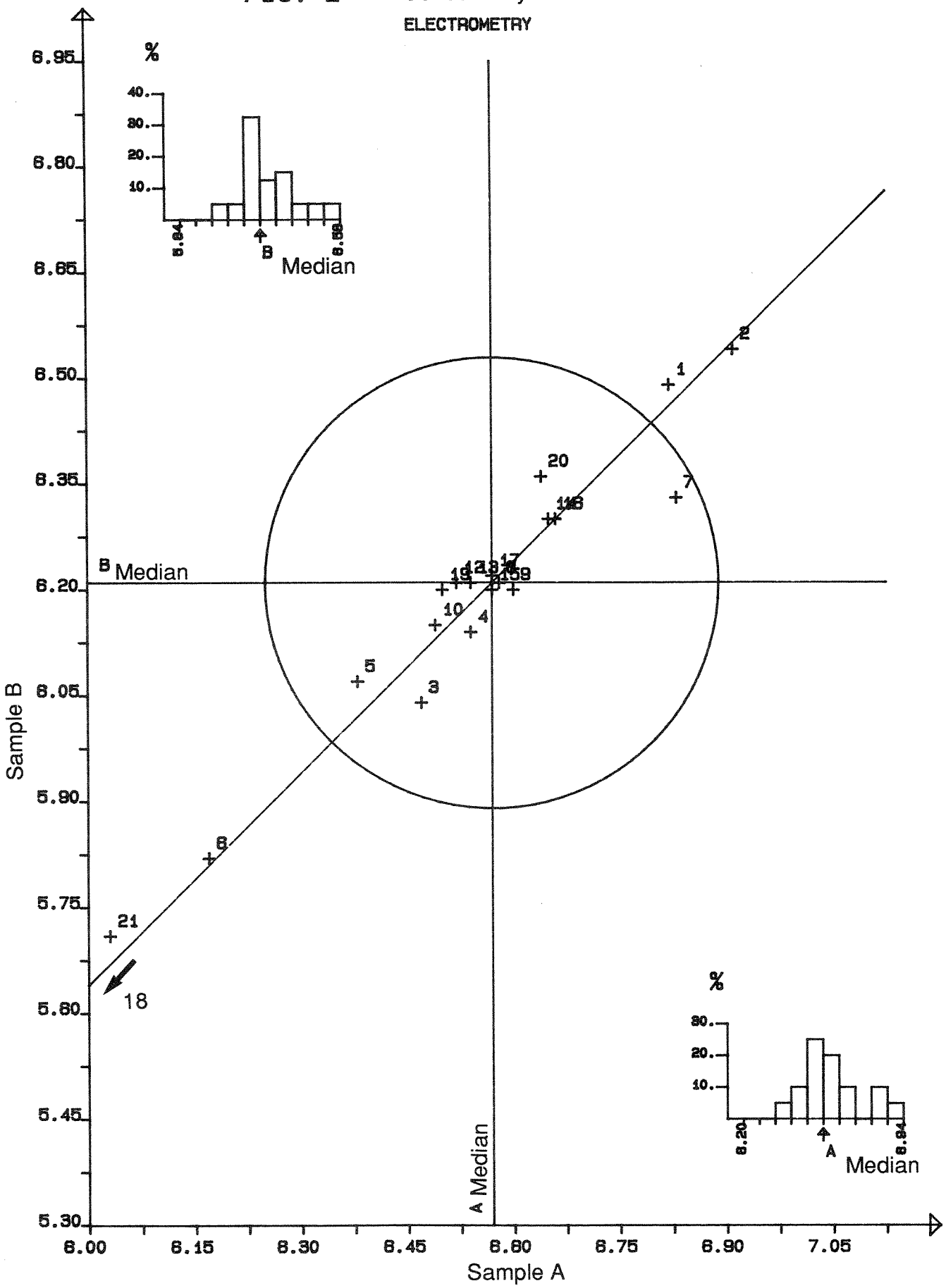


FIG. 3

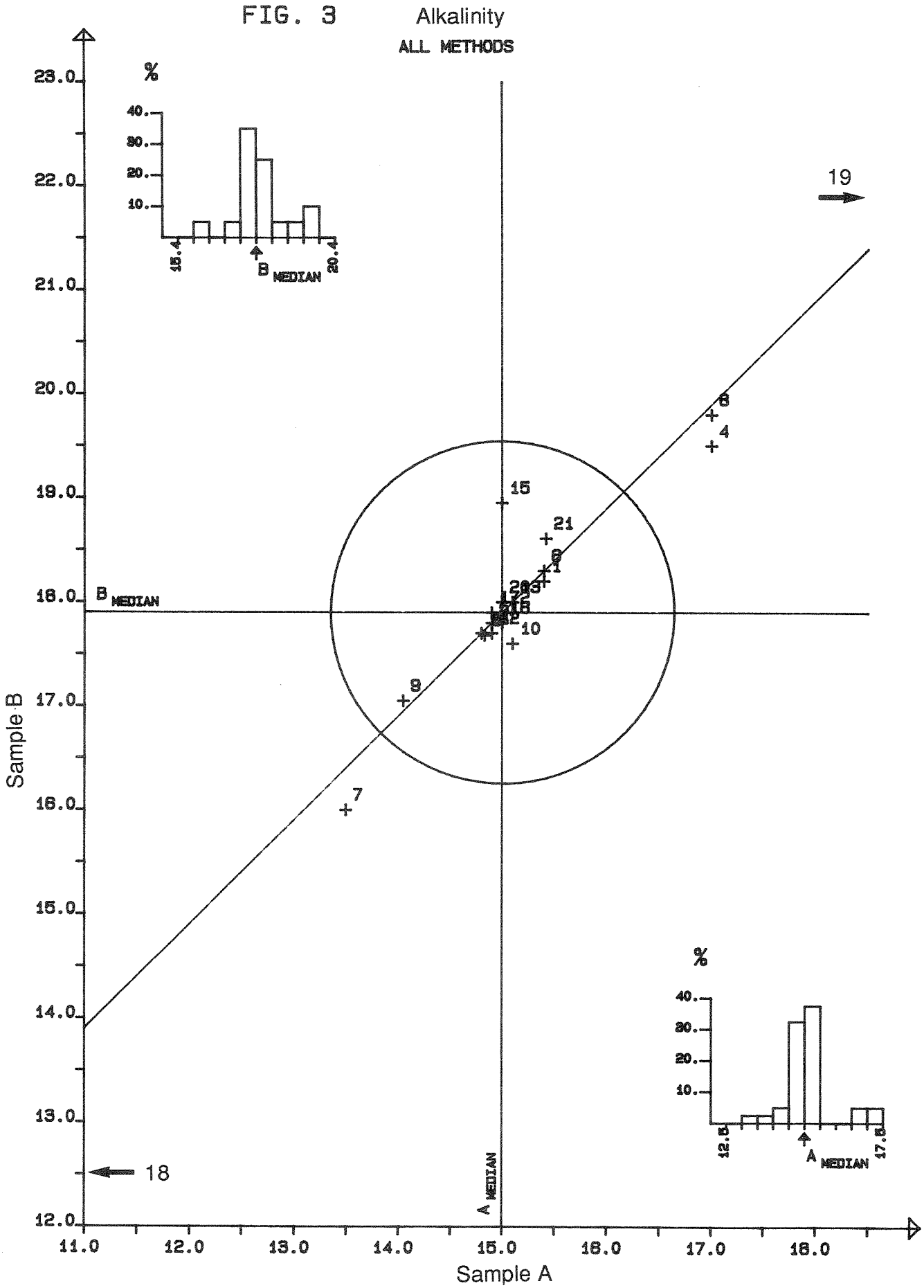

Alkalinity
ALL METHODS
%
40.
30.
20.
10.
15.4
B MEDIAN
20.4
19
18
B MEDIAN
A MEDIAN
Sample B
Sample A
23.0
22.0
21.0
20.0
19.0
18.0
17.0
16.0
15.0
14.0
13.0
12.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
15
21
9
1
3
10
9
7
8
4
%
40.
30.
20.
10.
12.5
A MEDIAN
17.5

FIG. 4 Nitrate + Nitrite

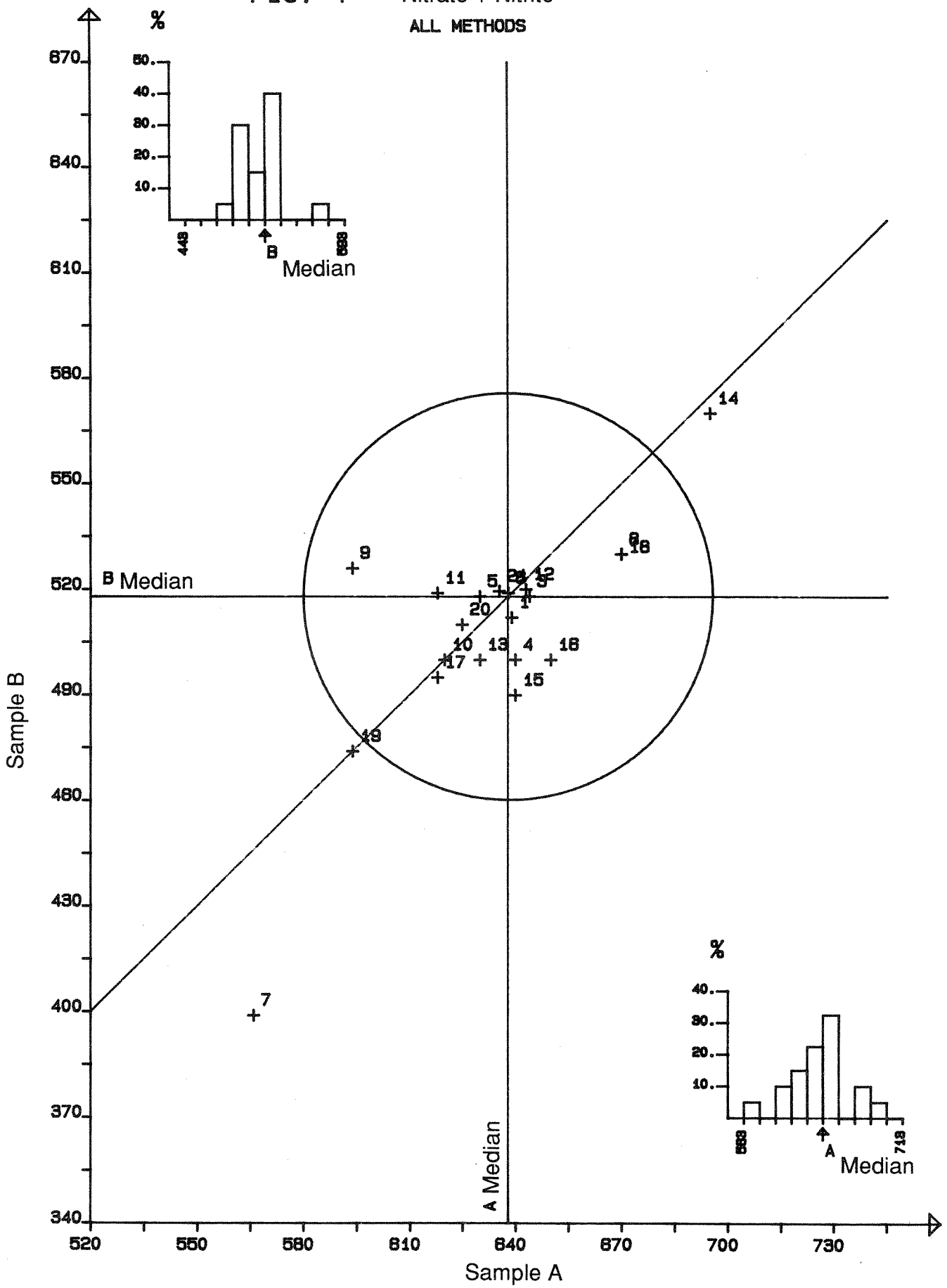


FIG. 5

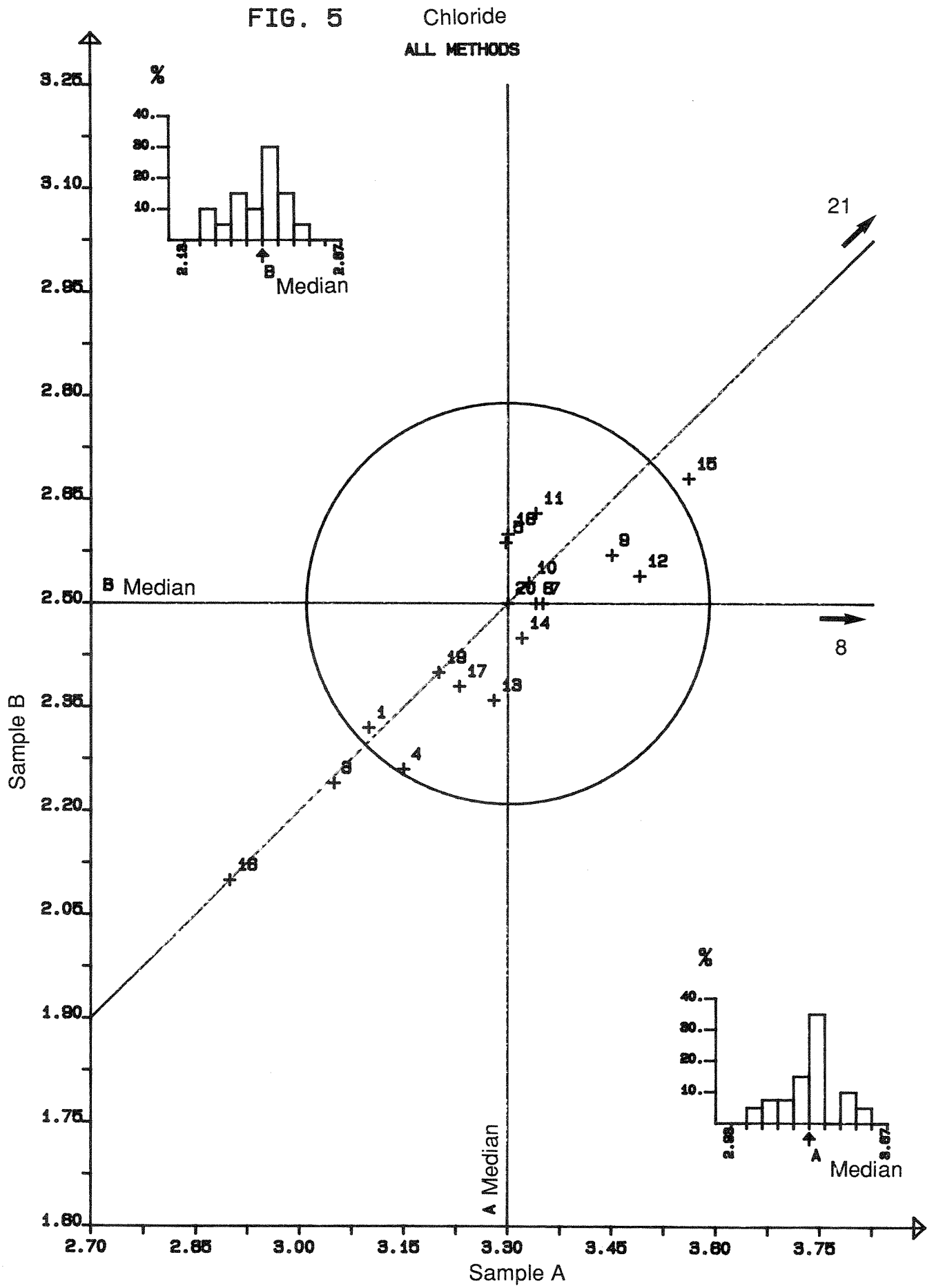

Chloride
ALL METHODS
%
40.
30.
20.
10.
2.13
B
2.87
Median
21
8
B Median
A Median
Sample B
Sample A
3.25
3.10
2.95
2.80
2.65
2.50
2.35
2.20
2.05
1.90
1.75
1.60
2.70
2.85
3.00
3.15
3.30
3.45
3.60
3.75
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

FIG. 7

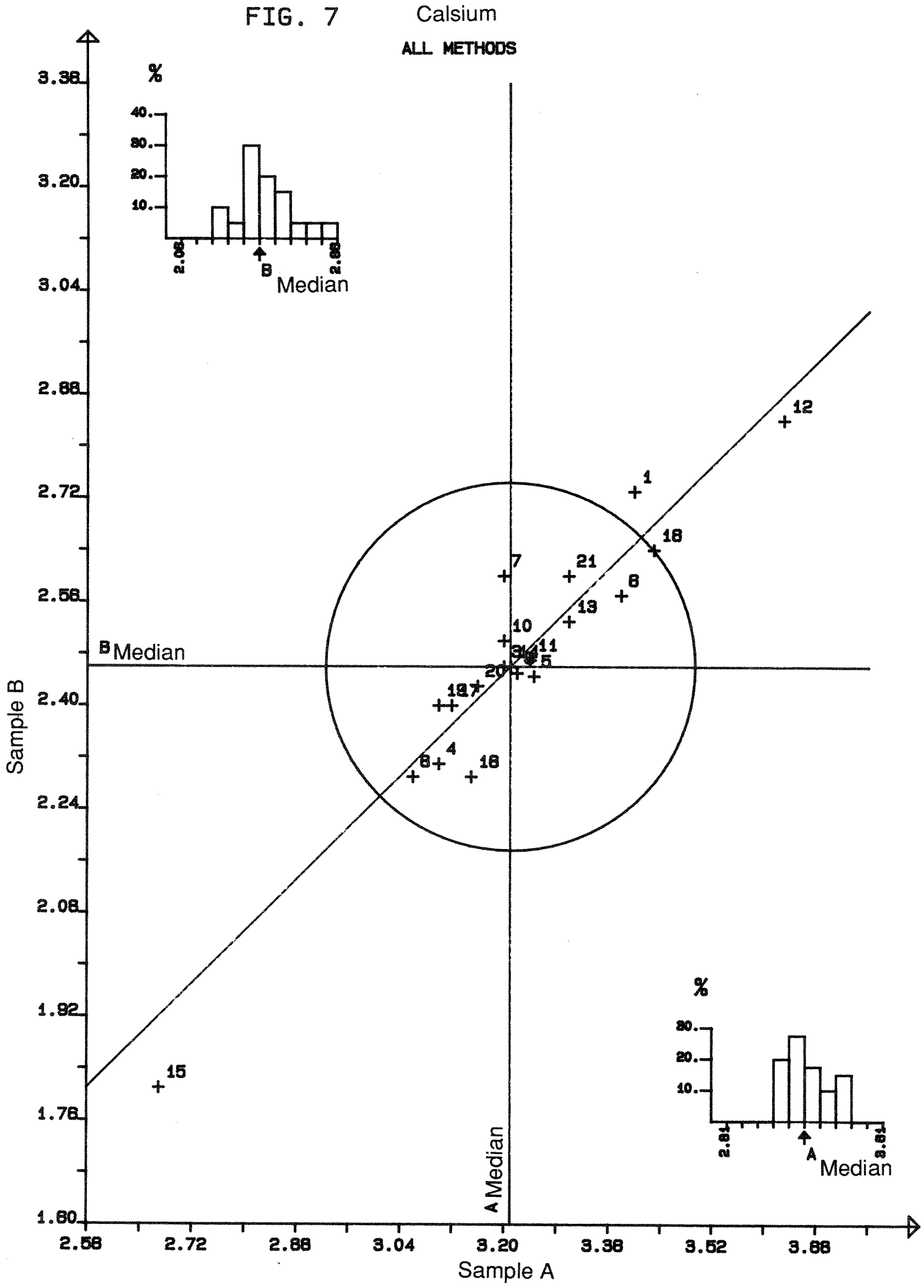

Calsium
ALL METHODS
%
40.
30.
20.
10.
2.56
B
2.88
Median
3.36
3.20
3.04
2.88
2.72
2.56
2.40
2.24
2.08
1.92
1.76
1.60
B Median
Sample B
12
1
18
7
21
8
13
10
11
5
20
4
18
15
A Median
%
30.
20.
10.
2.81
A
3.61
Median
2.56
2.72
2.88
3.04
3.20
3.36
3.52
3.68
Sample A

FIG. 6

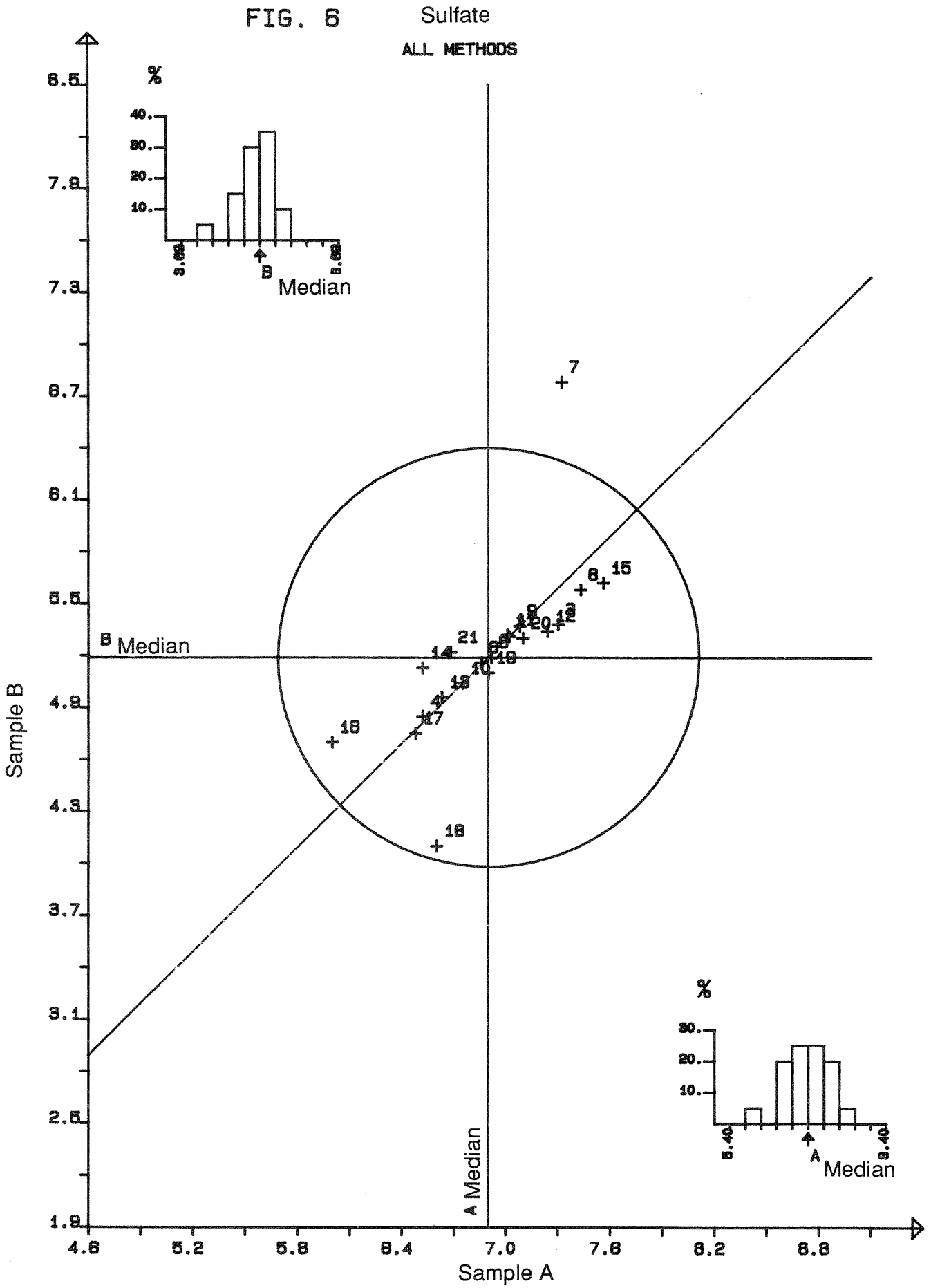

Sulfate
ALL METHODS
%
40.
30.
20.
10.
B
Median
B Median
A Median
Sample B
Sample A
8.5
7.9
7.3
6.7
6.1
5.5
4.9
4.3
3.7
3.1
2.5
1.9
4.6
5.2
5.8
6.4
7.0
7.6
8.2
8.8
7
8
15
21
14
18
16
18
%
30.
20.
10.
A
Median

FIG. 8 Magnesium

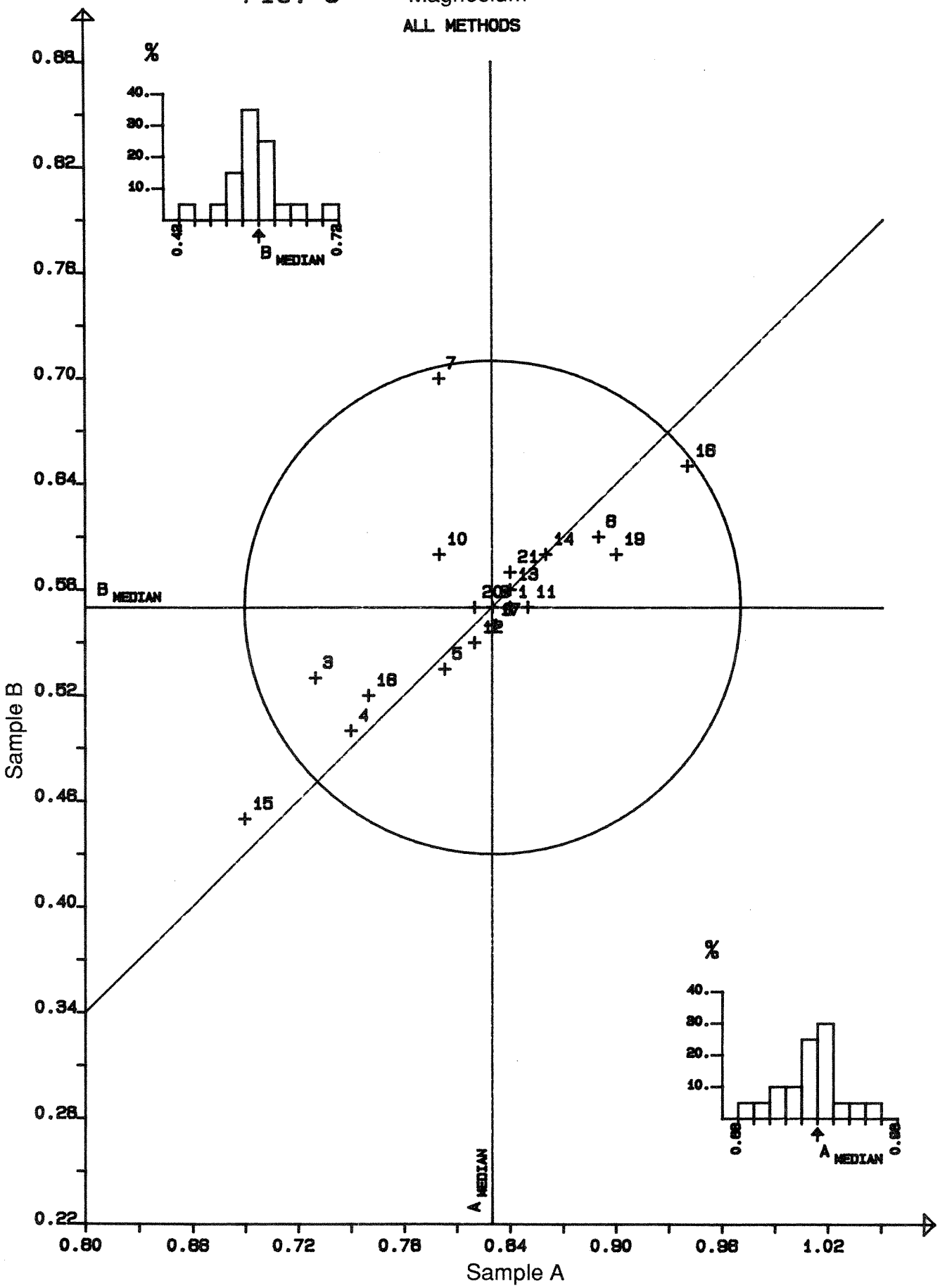


FIG. 9

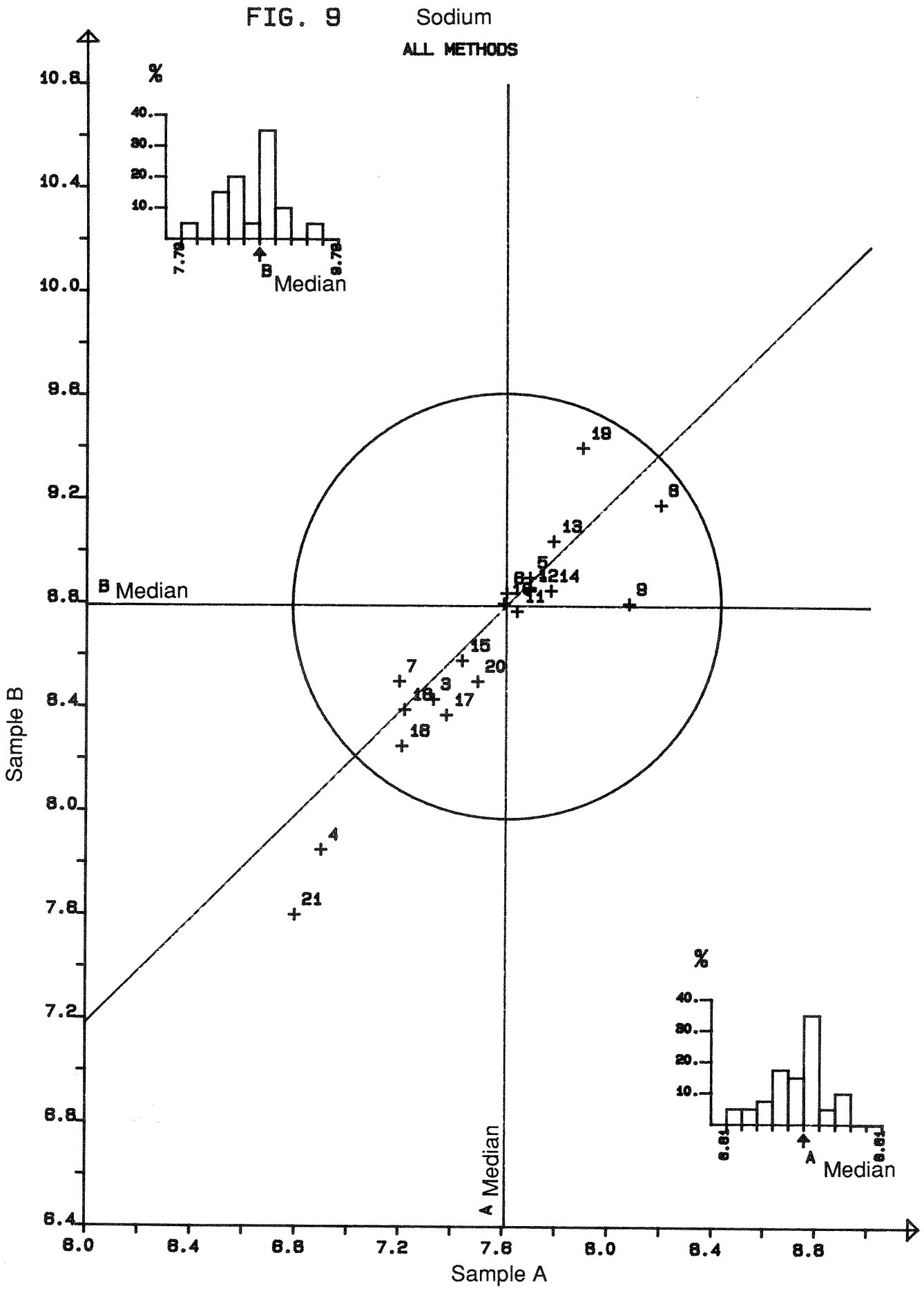

Sodium
ALL METHODS
%
40.
30.
20.
10.
7.78
B
8.78
B Median
10.8
10.4
10.0
9.6
9.2
8.8
8.4
8.0
7.6
7.2
6.8
6.4
Sample B
19
8
13
5
12
14
11
9
15
7
20
3
17
16
4
21
%
40.
30.
20.
10.
6.81
A
8.81
A Median
6.0
6.4
6.8
7.2
7.6
8.0
8.4
8.8
Sample A

FIG. 10 Potassium

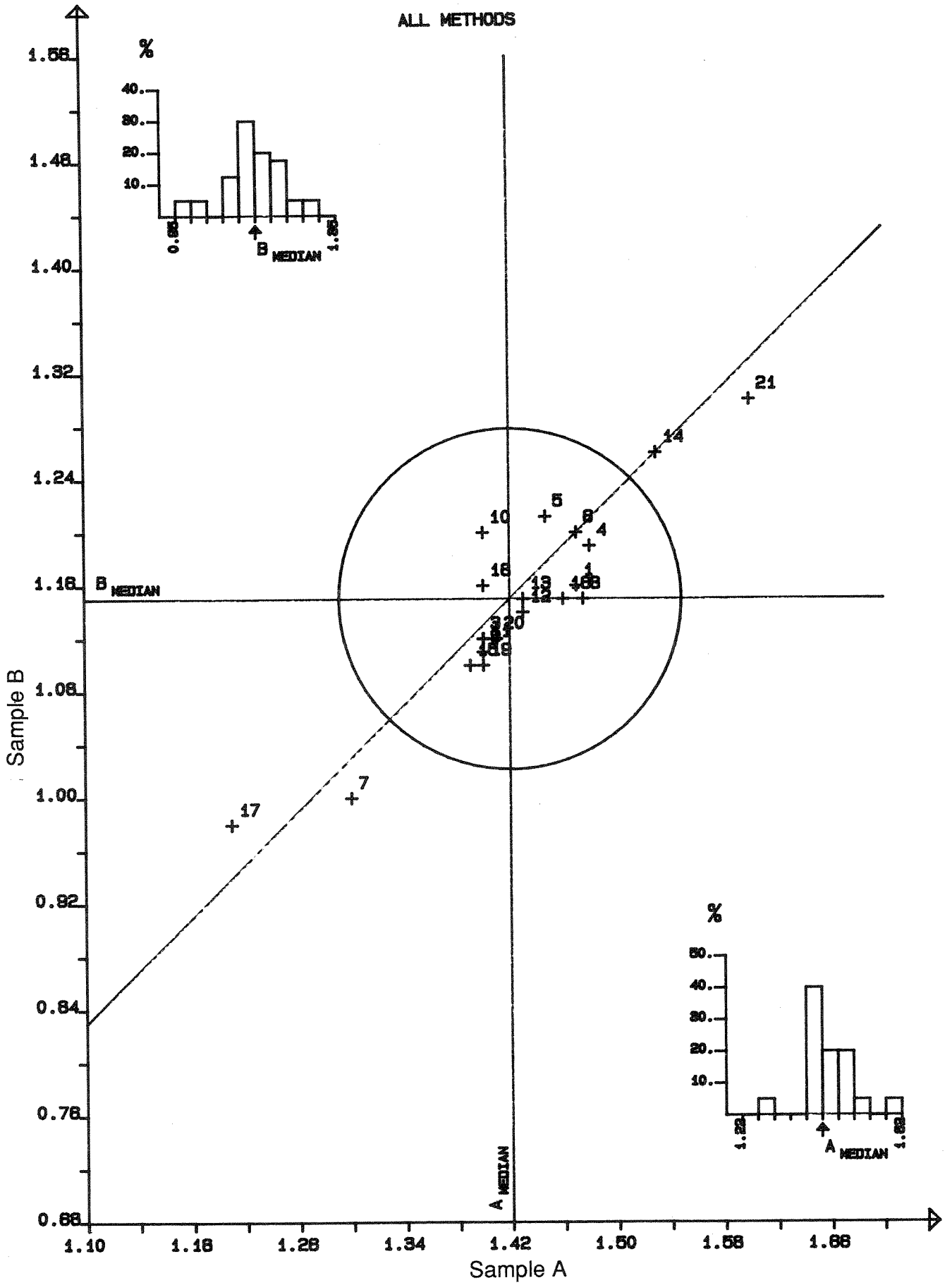
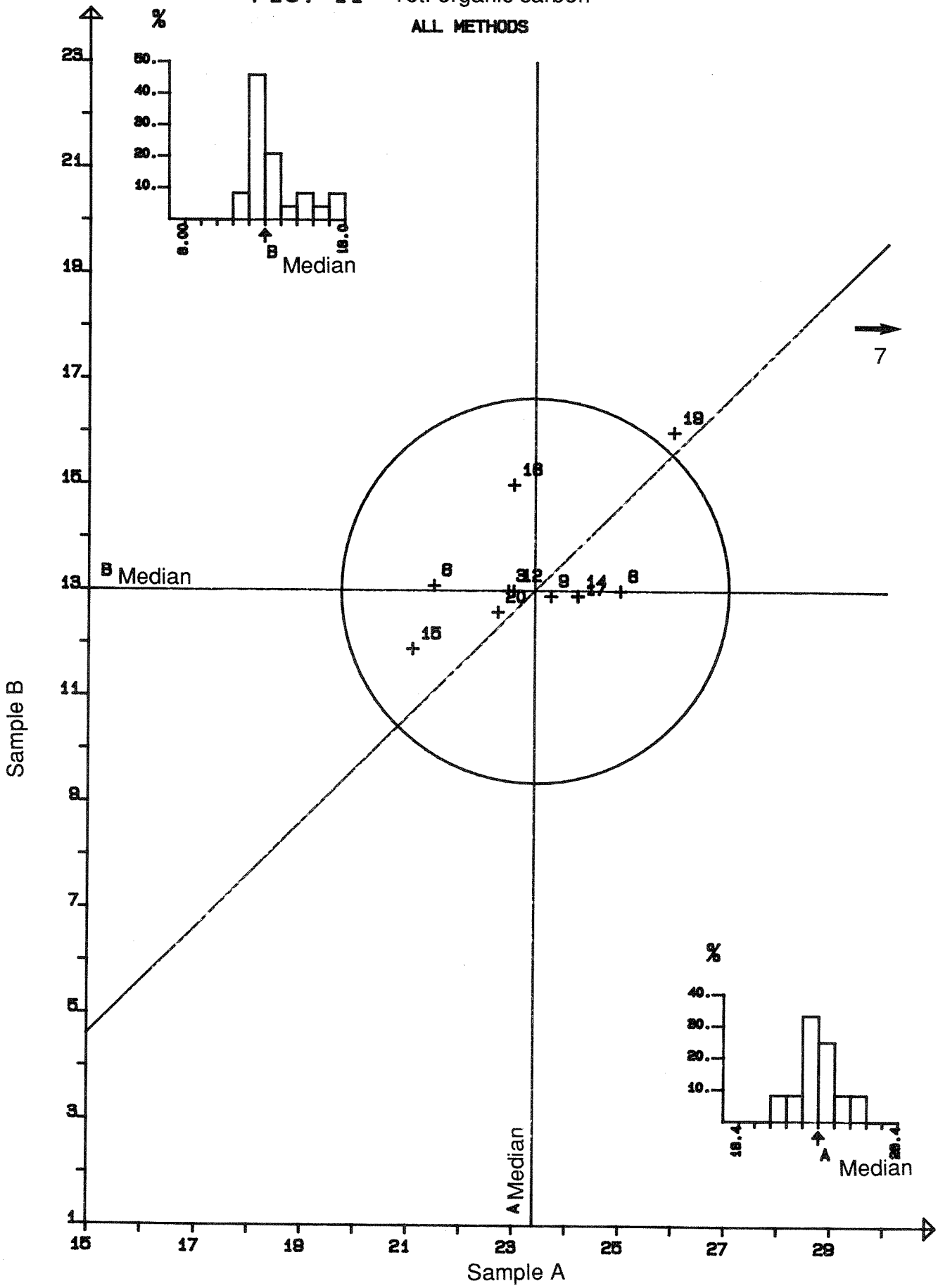


FIG. 11 Tot. organic carbon



The median value determined from the analytical results submitted by the participating laboratories, was selected as the "true value" for each parameter, because the real "true value" is not known exactly.

The results are illustrated in the Figures 1 - 11, where each laboratory is represented by a cross and an identification number. The circle is representing the special accuracy limit, defined below. A survey of the results is presented in Table 1. The individual results of the participants are presented in Table 7 (Appendix 4), sorted in order of increasing identification number. More extensive statistical informations are presented in the Tables 8 - 18.

pH

The reported pH results are presented in Figure 1 where the radius of the circle is 0.2 pH units, and in Table 8 (Appendix 4).

The participating laboratories determined pH in the test solutions by their own routine method. All the laboratories applied an electometric method for the determination of pH, but rather incomplete informations were given about the details of the procedures used. Thus we do not know whether the solution was stirred, before or during reading the meter, or not. Stirring may reduce the measured pH value.

The dato of analysis, and the difference between the result reported and the "true value", was compared, but there is no evidence for any correlation between the deviation from the "true value" and the storage time. This is in agreement with the control analyses carried out at the Programme Centre, which proved that the samples were rather stable. During three months storage the pH varied not more than ± 0.1 pH units.

The spread of the points along the 45^0 line in Figure 1 is a typical pattern when the deviations from the "true" value are of systematic character. Such variations are observed even when the equipment and the general analytical procedure are identical, and may be due to the working procedure of the analyst, different sample handling at the laboratories, and the amount of CO_2 dissolved in the sample, etc.

Deviating pH values may be due to errors in the instrument, or more likely, in the electrodes. Small effects may also be caused by variations in the temperature. Greater effects may be observed if the solution is stirred during reading the meter. Different kind of electrodes may give rise to different readings, especially the gel electrodes may give too low results in low conductivity solutions (4).

Conductivity

The conductivity results are presented in Figure 2 where the radius of the circle is 5 %, and in Table 9 of Appendix 4. Some correspondance was necessary to clarify the units of the reported results. Many laboratories reported the results in the units they use routinely, instead of the requested mS/m at 25 ^{0}C. All participants applied an electrometric method for the measurement of conductivity.

A very good agreement between the results of the participating laboratories was achieved. All laboratories, except one, is within the general target of ± 20 %, and only four result pairs are outside a limit of ± 5 %, represented by the circle in Figure 1. One reason for deviating results may be due to lacking temperature correction, as the conductivity is changing with 1% per ^{0}C at room temperature.

Alkalinity

The alkalinity results are presented in Figure 3, and the reported values are given in Table 10 (Appendix 4). Also for this parameter some correspondance was necessary to clarify the units of the reported results.

Twelve of the participants determined alkalinity by Gran plot titration, which was shown in intercalibration 9004 to give the best comparability between the results of different laboratories. Some modifications of electrometric titration was used by six laboratories, and two used ion chromatography. There is no significant difference between the mean values of these methods.

The circle in Figure 3 is representing a limit of ± 10 %, and five result pairs are lying outside this limit, while only two laboratories are outside the general target limit of ± 20 %. Deviating results may arise from different ways of defining the end point of the titration (5), an effect which is more distinct in solutions of low alkalinity.

Nitrate + nitrite

The results for this parameter are presented in Figure 4, and the reported values are given in Table 11 (Appendix 4). Fourteen laboratories determined this parameter by ion chromatography, while the six others applied different modifications of a photometric method, in most cases an automated version.

There is no significant systematic differences in the mean values of these two methods. All result pairs, except one, are well within the target accuracy of ± 20 %. Also, only three result pairs are outside the ± 10 % limit represented by the circle in Figure 4.

Chloride

The chloride results are presented in Figure 5, and the reported values are given in Table 12 (Appendix 4). Most of the the laboratories determined chloride by ion chromatography. One laboratory used a photometric version of the mercury thiocyanate method, and one laboratory used argentometric titration. Only two of the results are lying outside the general limit of 20 %, fifteen result pairs even being within a 10 % limit illustrated by the circle in Figure 5.

Sulfate

The sulfate results are presented in Figure 6 and Table 13 (Appendix 4). Most of the laboratories applied ion chromatography for the determination of this parameter. One laboratory used a photometric method based on dissociation of the barium-thorin complex.

Only one of the result pairs are outside the general accuracy target of ± 20 %, represented by the circle in Figure 6.

Calcium

The calcium results are presented in Figure 7, and the reported values are given in Table 14. Thirteen of the participants used atomic absorption spectrometry for the determination of this metal, while four laboratories determined calcium with ICP emission spectrometry, and three laboratories used ion chromatography.

Only one laboratory achieved systematically low results, and is outside the general accuracy limit of ± 20 %. 16 of the result pairs are even gathered within a ± 10 % limit, represented by the circle in Figure 7. There is no significant difference between results determined by the different methods.

Magnesium

The magnesium results are presented in Figure 8, and the reported values are given in Table 15. The majority of the participating laboratories used atomic absorption spectrometry for the determination of magnesium. Four laboratories used ICP emission spectrometry for this purpose, and three laboratories ion chromatography.

One laboratory have reported results lying outside the general acceptance limit of ± 20 %, represented by the circle in Figure 8.

Sodium

The sodium results are presented in Figure 9, where the circle is representing an acceptance limit of ± 10 %, and the reported values are given in Table 16. 16 laboratories used atomic absorption spectrometry for this determination. Among the remaining laboratories, two applied ion chromatography, one ICP emission technique and one flame emission. All the results are within the general limit of ± 20 %, and only two result pairs are outside the aspecial limit of ± 10 %.

Potassium

The potassium results are presented in Figure 10, where the diameter of the circle is representing an acceptance limit of ± 10 %. The reported values are given in Table 17. 16 participants determined potassium with atomic absorption spectrometry. Among the remaining laboratories, two used ion chromatography, one ICP emission technique and one flame emission. All the result pairs, except one, are lying within the general target limit of ± 20 %.

Total organic carbon

The results of this parameter are presented in Figure 11, and the reported values are given in Table 18 (Appendix 4). Only 12 out of 21 participants determined this parameter, ten of these laboratories being within the general accuracy target of ± 20 %. The result for this parameter are normally expected to vary between laboratories, as the instruments used for the determination may be based on quite different oxidation methods: UV combustion, UV combined with peroxodisulfate, or high temperature combustion. These techniques does not always produce comparable results. As the main organic compound in the samples A and B are easily oxidable, it was not expected any

great deviations between the different methods for these samples. Very few informations were given by the laboratories with respect to what kind of instruments had been used.

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 values. Laboratories where the results for one or more of these ions were missing, were omitted from the calculations.

Table 2. Ionic balance calculations. The sums of the anion and cation concentrations, and the difference between theese concentrations, are given in mmol/l. Laboratories where the results for one or more ions are missing, was omitted from the calculations.

Lab. no.	Sample A			Sample B		
	Anions	Cations	Diff.	Anions	Cations	Diff.
1	0.5869	0.6113	0.0244	0.5762	0.5982	0.0220
3	0.5803	0.5744	-0.0059	0.5654	0.5617	-0.0037
4	0.6100	0.5544	-0.0556	0.5900	0.5283	-0.0617
5	0.5798	0.6000	0.0202	0.5737	0.5834	0.0097
6	0.5903	0.6105	0.0202	0.5806	0.5936	0.0130
7	0.5570	0.5719	0.0149	0.5598	0.5826	0.0228
8	0.6584	0.6155	-0.0429	0.6193	0.5891	-0.0302
9	0.5679	0.6162	0.0484	0.5625	0.5803	0.0178
10	0.5804	0.5919	0.0115	0.5636	0.5876	0.0239
12	0.5928	0.6201	0.0273	0.5736	0.6011	0.0275
13	0.5772	0.6092	0.0320	0.5652	0.5966	0.0314
14	0.5747	0.6085	0.0338	0.5703	0.5893	0.0190
15	0.6032	0.5492	-0.0540	0.6062	0.5287	-0.0775
16	0.5528	0.5994	0.0466	0.5484	0.5735	0.0251
17	0.5679	0.5759	0.0081	0.5590	0.5550	-0.0040
18	0.4582	0.5696	0.1114	0.4463	0.5517	0.1054
19	0.6679	0.6082	-0.0598	0.6573	0.6061	-0.0511
20	0.5852	0.5874	0.0022	0.5769	0.5665	-0.0104
21	0.6085	0.5705	-0.0380	0.6127	0.5421	-0.0706
Mean val.	0.5692	0.5922	0.0230	0.5565	0.5748	0.0183

UThe calculated values are given in table 2, where the difference between the concentrations of cations and anions also is given. Only one laboratory has clearly deviating results, the anion sum being systematically too low compared to the cation sum, which is likely due to the systematically low alkalinity results. For the samples A and B, there are a mean difference of 0.023 and 0.018 mmol/l, respectively, between the sum of cations and the sum of anions. If the concentration of organic anions had been taken into account in the anion sum, the difference should have been almost zero.

DISCUSSION

The general rule for target accuracies, outlined in the Manual for Chemical and Biological Monitoring (1), shall normally be used as acceptance limits for the results of the intercalibration test. These limits are corresponding to either the detection limit of the method, or 20 % of the true value, whichever being the greater. To visualize the results of the participants in a better way, we have in many cases chosen to use some special limits instead of the general target in the Figures 1 - 11.

In Table 3 an evaluation of the results of this intercalibration is presented, based on two different target accuracies: the general target accuracy defined by the Manual, and some special limits. For pH the general target accuracy is 0.1 unit. By evaluation of the results of this intercalibration we have extended the acceptance limits for pH to ± 0.2 units, because of the great spread of the results for this parameter. It is probably easier to obtain a better comparability between the laboratories if pH is measured in solutions being at least 1 - 2 units away from neutrality.

For the remaining parameters, 90 -100 % of the result pairs is lying within the general target limit of ± 20 %. For these parameters only one or two laboratories are outside the acceptance limit, and by some improvement of the routine analytical method, these laboratories should obtain results with better comparability to the others in this laboratory group.

In Table 3 an example of an evaluation based on narrower limits is also given (the so-called special limits). The high percentage of acceptable results even within these limits, indicates that there might be a minor problem to achieve all the results within these limits.

Table 3. Evaluation of the results of intercalibration 9105. N is number of result pairs reported, n is number of acceptable results within the given acceptance limit.

Parameter	N	General limit	Acceptable results n	%	Special limit	Acceptable results n	%
pH	21	0.1	7	35	0.2	14	67
Conductivity	20	20 %	19	95	5 %	15	75
Alkalinity	20	20 %	18	90	10 %	15	75
Nitrate+nitrite	20	20 %	19	95	10 %	17	85
Chloride	20	20 %	18	90	10 %	15	75
Sulfate	20	20 %	19	95	10 %	14	70
Calcium	20	20 %	19	95	10 %	16	80
Magnesium	20	20 %	19	95	10 %	12	60
Sodium	20	20 %	20	100	10 %	18	90
Potassium	20	20 %	19	95	10 %	16	80
Tot. org. carbon	12	20 %	10	83	10 %	7	58
Total	213		187	88		159	75

In earlier intercalibrations (6,7), the greatest deviations between the results of the participating laboratories have been observed for the parameters pH and alkalinity. To obtain better comparability between results, the methods used at the different laboratories must be improved. As indicated in intercalibration 9004 (8) we recommend that measurement without stirring the solution during reading the meter, should be used for routine determinations.

Considerable bias errors may be due to preparation of standards, as well as inaccuracies associated with the measurement. Most important, therefore, is the unambigous description of preparation of solutions and of measurement procedures, securing that exactly the same procedure is followed each time the determination is performed. The best solution of this problem would be that all the participants agreed upon using exactly the same method - and really do apply it.

CONCLUSIONS

Under conditions where directions have been given with respect to

equipment and measuring procedures, the estimate of a total error of ± 0.2 pH units seems to be a reasonable assessment of the accuracy which might be achieved routinely when commercial equipment is used. We recommend that measurement without stirring the solution should be used for routine determinations.

The Gran plot method is strongly recommended for the alkalinity determination in connection to this international co-operation programme on assessment and monitoring of acidification.

For the other parameters most laboratories are within the general target accuracy limit of ± 20 %. Generally only one or two laboratories are outside this limit, and these laboratories should improve the method to obtain better comparability.

LITERATURE

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APPENDIX 1

Participants of intercalibration 9105, and their code numbers

1. Bundesinstitut für Fischereiwirtschaft, Mondsee, Austria.
2. US Geological Survey, Lakewood, USA.
3. DAFS, Freshwater Fisheries Laboratory, Pitlochry, Scotland.
4. National Institute for Physical Planning and Construction Research, Dublin, Ireland.
5. Centre de Geochimie de la Surface, Strasbourg, France.
6. University of Maine, Environmental Chemistry Lab., Orono, USA.
7. Kärntner institut für Seewasser Forschung, Klagenfurt, Austria.
8. Ontario Ministry of Environment, Rexdale, Canada.
9. National Board of Waters and Environment, Helsinki, Finland.
10. Consiglio Nazionale delle Ricerche, Pallanza, Italia.
11. National Water Quality Laboratory, Burlington, Canada.
12. US Geological Survey, Arvado, USA.
13. Geological Survey, Praha, Czechoslovakia.

14 Freshwater Institute, Winnipeg, Canada.

15. National Agency of Environmental Protection, Silkeborg, Denmark.
16. Universität Innsbruck, Innsbruck, Austria.
17. National Environment Protection Board, Uppsala, Sweden.
18. Research Centre for Water Research Development, Budapest, Hungary.
19. Bayerische Landesamt für Wasserwirtschaft, München, Germany.
20. Norwegian Institute for Water Research, Oslo, Norway.
21. Universitat de Barcelona, Barcelona, Spain.

APPENDIX 2

Preparation of samples

The sample solutions were prepared from natural water, collected in the outlet of the lake Maridalsvannet, a water supply lake located outside Oslo, Norway. 50 litres of raw water were collected in polyethylen containers and stored for several weeks at room temperature at the laboratory. During this stabilization period suspended matter settled. The required volume was filtered through 0,45 µm membrane filter. Small aliquots were removed from the filtrate for the determination of background concentrations of the constituents of interest.

Table 4. Preparation of stock solutions.

Solution number	Compound	Amount g/l	Concentration
I	$NaHCO_3$	13.917	0.1657 mol/l 3808 mg/l Na
II	$MgSO_4.7H_2O$	10.722	1058 mg/l Mg 4179 mg/l SO_4
III	KNO_3	7.178	2776 mg/l K 994 mg/l NO_3-N
IV	$CaCl_2.2H_2O$	4.028	1098 mg/l Ca 1943 mg/l Cl
V	Sucrose	63.898	26.905 mg/l C

The stock solutions were prepared by dissolution of exactly weighed amounts of stoichiometric compounds of quality "pro analysi", and made up to 1000 ml with deionized water. In Table 4 are given the concentrations of the chemical parameters in the stock solutions.

Two water samples (A and B) were prepared from the lake filtrate. 20 liter portions of the filtrate were transferred to two polyethylene containers. The pH of the samples were adjusted by addition of an

appropriate amount of disodium-hydrogenphosphate. The alkalinity were adjusted by addition of small amounts of sodiumhydrogencarbonate solution. Small volumes of the stock solutions were added to the 20 liter portions to adjust the concentrations of the major ions (Table 5). After these additions the solutions were stored for two weeks for further stabilization. During this period aliquotes were taken regularly from the four solutions to control the stability of pH and alkalinity.

Table 8. Adjustment of concentrations of the major ions.

Stock solution	Volume, ml A	B	Parameter	Increase, mg/l A	B
I	50	40	Alkalinity	15.5	13.2
			Sodium	7.62	6.09
II	8	4	Magnesium	0.42	0.17
			Sulfate	1.67	0.67
III	10	8	Nitrate	0.398	0.318
			Potassium	1.11	0.89
IV	10	5	Chloride	0.78	0.39
			Calcium	0.44	0.22
V	20	10	TOC	21.5	10.8

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

Sample control analyses

During the intercalibration period, six sets of samples were randomly selected from the batch for control analysis. The determinations were carried out by the laboratory at the Programme Centre, the first sample set being analyzed two weeks before mailing of samples to the participants. The last sample set was analyzed at the beginning of May 1991. A summary of the control results is presented in Table 6. The control analyses confirmed that the stability of the sample solutions

were acceptable during the intercalibration period.

Table 6. Summary of the control analyses

Parameter	Sample A		Sample B	
	mean	sdev.	mean	sdev.
pH	7.26	0.09	7.32	0.07
Conductivity, mS/m 25°C	6.65	0.02	6.32	0.05
Alkalinity, mg/l $CaCO_3$	15.9	0.10	18.6	0.33
Nitrate+nitrite, µg/l N	629	13	511	10
Chloride, mg/l Cl	3.14	0.13	2.38	0.18
Sulfate, mg/l SO_4	6.70	0.24	5.10	0.10
Calcium, mg/l Ca	3.21	0.05	2.46	0.05
Magnesium, mg/l Mg	0.81	0.005	0.560	0.007
Sodium, mg/l Na	7.40	0.20	8.46	0.09
Potassium, mg/l K	1.41	0.011	1.11	0.013
Tot. org. carbon mg/l C	24.4	1.191	12.7	0.23

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 - 11).

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 45^0 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 stright 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 45^0 line is giving the magnitude of the systematic error, while the distance perpendicular to the 45^0 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 the 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 one or both of the values are lying outside $x \pm 3 \cdot s$, are omitted. The remaining results are used for a final calculation, the results of which are presented in the Tables 8 - 18. Results being omitted from the calculations, are marked with the letter "U".

APPENDIX IV

Table 7. The results of the participating laboratories.

Lab.no.	pH		COND mS/m		ALK mg/l	
	A	B	A	B	A	B
1	7.10	7.15	6.82	6.49	15.4	18.2
2	7.72	7.86	6.91	6.54	15.1	17.9
3	7.35	7.41	6.47	6.04	14.83	17.68
4	7.24	7.30	6.54	6.14	17.0	19.5
5	7.32	7.39	6.38	6.07	14.9	17.8
6	7.59	7.60	6.17	5.82	15.4	18.3
7	7.15	7.25	6.83	6.33	13.5	16.0
8	7.29	7.37	6.58	6.21	17.0	19.8
9	7.11	7.19	6.60	6.20	14.05	17.05
10	7.23	7.31	6.49	6.15	15.1	17.6
11	7.18	7.28				
12	7.10	7.39	6.52	6.21	14.9	17.7
13	7.24	7.32	6.54	6.21	15.1	18.0
14	7.70	7.78	6.65	6.30	14.8	17.7
15	7.25	7.32	6.57	6.20	15.0	18.95
16	7.15	7.24	6.66	6.30	15.0	17.8
17	7.05	7.15	6.57	6.22	14.9	17.9
18	5.5	5.7	5.1	4.9	9.0	12.5
19	7.72	7.74	6.5	6.2	19.6	22.5
20	7.19	7.27	6.64	6.36	15.0	18.1
21	7.31	7.42	6.03	5.71	15.42	18.61

Lab.no.	NO3-N+NO2-N µg/l		CL mg/l		SO4 mg/l	
	A	B	A	B	A	B
1	639.	512.	3.10	2.32	7.02	5.31
2						
3	644.	518.	3.05	2.24	7.30	5.38
4	640.	500.	3.15	2.26	6.52	4.85
5	630.	518.	3.30	2.59	6.92	5.19
6	638.	519.	3.34	2.50	6.86	5.16
7	566.	399.	3.35	2.50	7.32	6.78
8	670.	530.	4.12	2.47	7.43	5.58
9	594.	526.	3.45	2.57	7.08	5.37
10	620.	500.	3.33	2.53	6.75	5.04
11	618.	519.	3.34	2.63	7.01	5.32
12	643.	520.	3.49	2.54	7.24	5.34
13	630.	500.	3.28	2.36	6.63	4.96
14	695.	570.	3.32	2.45	6.52	5.13
15	640.	490.	3.56	2.68	7.56	5.62
16	650.	500.	2.90	2.10	6.00	4.70
17	618.	495.	3.23	2.38	6.48	4.75
18	670.	530.	3.3	2.6	6.6	4.1
19	594.	474.	3.2	2.4	6.9	5.1
20	625.	510.	3.3	2.5	7.1	5.3
21	635.5	519.5	4.11	3.37	6.68	5.22

Lab.no.	CA mg/l		MG mg/l		NA mg/l	
	A	B	A	B	A	B
1	3.40	2.73	0.84	0.57	7.70	8.86
2						
3	3.20	2.46	0.73	0.53	7.33	8.43
4	3.10	2.31	0.75	0.50	6.90	7.85
5	3.25	2.44	0.80	0.53	7.70	8.90
6	3.38	2.57	0.89	0.61	7.61	8.84
7	3.20	2.60	0.80	0.70	7.20	8.50
8	3.06	2.29	0.83	0.56	8.20	9.18
9	3.22	2.45	0.83	0.57	8.08	8.80
10	3.20	2.50	0.80	0.60	7.60	8.80
11	3.24	2.47	0.85	0.57	7.65	8.77
12	3.62	2.84	0.82	0.54	7.70	8.85
13	3.30	2.53	0.84	0.58	7.79	9.04
14	3.21	2.46	0.86	0.60	7.78	8.85
15	2.67	1.81	0.69	0.45	7.44	8.58
16	3.43	2.64	0.94	0.65	7.21	8.25
17	3.12	2.40	0.83	0.56	7.38	8.37
18	3.15	2.29	0.76	0.52	7.22	8.39
19	3.1	2.4	0.9	0.6	7.9	9.4
20	3.16	2.43	0.82	0.57	7.5	8.5
21	3.3	2.60	0.84	0.59	6.8	7.6

Lab.no.	K mg/l		TOC mg/l	
	A	B	A	B
1	1.47	1.16		
2				
3	1.40	1.12	22.9	13.0
4	1.48	1.19		
5	1.45	1.21		
6	1.47	1.20	21.5	13.1
7	1.30	1.00	33.5	17.6
8	1.48	1.15	25.0	13.0
9	1.40	1.11	23.7	12.9
10	1.40	1.20		
11	1.40	1.12		
12	1.43	1.14	23.0	13.0
13	1.43	1.15		
14	1.53	1.26	24.2	12.9
15	1.39	1.10	21.1	11.9
16	1.46	1.15		
17	1.21	0.98	24.2	12.9
18	1.40	1.16	23.	15.
19	1.4	1.1	26.	16.
20	1.41	1.12	22.8	12.6
21	1.6	1.3		

TABLE 8. STATISTICS, pH

Analytical method: Electrometry

Unit:

Sample A

Number of participants:	21	Range:	0.67
Number of omitted results:	1	Variance:	0.05
True value:	7.24	Standard deviation:	0.21
Mean value:	7.30	Relative standard deviation:	2.92 %
Median value:	7.24	Relative error:	0.82 %

Analytical results in ascending order:

18	5.50 U	:	11	7.18	:	21	7.31
17	7.05	:	20	7.19	:	5	7.32
1	7.10	:	10	7.23	:	3	7.35
12	7.10	:	4	7.24	:	6	7.59
9	7.11	:	13	7.24	:	14	7.70
7	7.15	:	15	7.25	:	2	7.72
16	7.15	:	8	7.29	:	19	7.72

Sample B

Number of participants:	21	Range:	0.71
Number of omitted results:	1	Variance:	0.04
True value:	7.32	Standard deviation:	0.20
Mean value:	7.39	Relative standard deviation:	2.76 %
Median value:	7.32	Relative error:	0.92 %

Analytical results in ascending order:

18	5.70 U	:	11	7.28	:	12	7.39
17	7.15	:	4	7.30	:	3	7.41
1	7.15	:	10	7.31	:	21	7.42
9	7.19	:	13	7.32	:	6	7.60
16	7.24	:	15	7.32	:	19	7.74
7	7.25	:	8	7.37	:	14	7.78
20	7.27	:	5	7.39	:	2	7.86

U = Omitted results

TABLE 9. STATISTICS, CONDUCTIVITY

Analytical method: Electrometry

Unit: mS/m (25 °C)

Sample A

Number of participants:	20	Range:	0.88
Number of omitted results:	1	Variance:	0.04
True value:	6.57	Standard deviation:	0.21
Mean value:	6.55	Relative standard deviation:	3.16 %
Median value:	6.57	Relative error:	-0.29 %

Analytical results in ascending order:

18	5.10 U	:	12	6.52	:	20	6.64
21	6.03	:	13	6.54	:	14	6.65
6	6.17	:	4	6.54	:	16	6.66
5	6.38	:	17	6.57	:	1	6.82
3	6.47	:	15	6.57	:	7	6.83
10	6.49	:	8	6.58	:	2	6.91
19	6.50	:	9	6.60	:		

Sample B

Number of participants:	20	Range:	0.83
Number of omitted results:	1	Variance:	0.04
True value:	6.21	Standard deviation:	0.20
Mean value:	6.19	Relative standard deviation:	3.17 %
Median value:	6.21	Relative error:	-0.25 %

Analytical results in ascending order:

18	4.90 U	:	9	6.20	:	14	6.30
21	5.71	:	19	6.20	:	16	6.30
6	5.82	:	15	6.20	:	7	6.33
3	6.04	:	12	6.21	:	20	6.36
5	6.07	:	13	6.21	:	1	6.49
4	6.14	:	8	6.21	:	2	6.54
10	6.15	:	17	6.22	:		

U = Omitted results

TABLE 10. STATISTICS, ALKALINITY

Analytical method: All methods

Unit: mg/l $CaCO_3$

Sample A

Number of participants:	20	Range:	6.10
Number of omitted results:	1	Variance:	1.69
True value:	15.00	Standard deviation:	1.30
Mean value:	15.37	Relative standard deviation:	8.45 %
Median value:	15.00	Relative error:	2.46 %

Analytical results in ascending order:

18	9.00 U	:	12	14.9	:	6	15.4
7	13.5	:	15	15.0	:	1	15.4
9	14.05	:	16	15.0	:	21	15.42
14	14.8	:	20	15.0	:	8	17.0
3	14.83	:	2	15.1	:	4	17.0
5	14.9	:	10	15.1	:	19	19.6
17	14.9	:	13	15.1	:		

Sample B

Number of participants:	20	Range:	6.50
Number of omitted results:	1	Variance:	1.74
True value:	17.90	Standard deviation:	1.32
Mean value:	18.26	Relative standard deviation:	7.22 %
Median value:	17.90	Relative error:	2.03 %

Analytical results in ascending order:

18	12.5 U	:	16	17.8	:	6	18.3
7	16.0	:	5	17.8	:	21	18.61
9	17.05	:	17	17.9	:	15	18.95
10	17.6	:	2	17.9	:	4	19.5
3	17.68	:	13	18.0	:	8	19.8
14	17.7	:	20	18.0	:	19	22.5
12	17.7	:	1	18.2	:		

U = Omitted results

TABLE 11. STATISTICS, NITRATE + NITRITE-NITROGEN

Analytical method: All methods

Unit: µg/l N

Sample A

Number of participants:	20	Range:	101.
Number of omitted results:	1	Variance:	598.
True value:	638.0	Standard deviation:	24.5
Mean value:	636.5	Relative standard deviation:	3.84 %
Median value:	638.0	Relative error:	-0.24 %

Analytical results in ascending order:

7	566.	U	:	13	630.	:	12	643.
9	594.		:	5	630.	:	3	644.
19	594.		:	21	635.5	:	16	650.
17	618.		:	6	638.	:	18	670.
11	618.		:	1	639.	:	8	670.
10	620.		:	4	640.	:	14	695.
20	625.		:	15	640.	:		

Sample B

Number of participants:	20	Range:	96.0
Number of omitted results:	1	Variance:	404.
True value:	518.0	Standard deviation:	20.1
Mean value:	513.2	Relative standard deviation:	3.92 %
Median value:	518.0	Relative error:	-0.93 %

Analytical results in ascending order:

7	399.	U	:	13	500.	:	21	519.5
19	474.		:	20	510.	:	12	520.
15	490.		:	1	512.	:	9	526.
17	495.		:	3	518.	:	18	530.
10	500.		:	5	518.	:	8	530.
16	500.		:	6	519.	:	14	570.
4	500.		:	11	519.	:		

U = Omitted results

TABLE 12. STATISTICS, CHLORIDE

Analytical method: All methods

Unit: mg/l Cl

Sample A

Number of participants:	20	Range:	1.22
Number of omitted results:	1	Variance:	0.06
True value:	3.30	Standard deviation:	0.25
Mean value:	3.32	Relative standard deviation:	7.43 %
Median value:	3.30	Relative error:	0.65 %

Analytical results in ascending order:

16	2.90	:	5	3.30	:	7	3.35	
3	3.05	:	18	3.30	:	9	3.45	
1	3.10	:	20	3.30	:	12	3.49	
4	3.15	:	14	3.32	:	15	3.56	
19	3.20	:	10	3.33	:	21	4.11	U
17	3.23	:	11	3.34	:	8	4.12	
13	3.28	:	6	3.34	:			

Sample B

Number of participants:	20	Range:	0.58
Number of omitted results:	1	Variance:	0.02
True value:	2.50	Standard deviation:	0.15
Mean value:	2.45	Relative standard deviation:	6.06 %
Median value:	2.50	Relative error:	-1.86 %

Analytical results in ascending order:

16	2.10	:	14	2.45	:	9	2.57	
3	2.24	:	8	2.47	:	5	2.59	
4	2.26	:	7	2.50	:	18	2.60	
1	2.32	:	6	2.50	:	11	2.63	
13	2.36	:	20	2.50	:	15	2.68	
17	2.38	:	10	2.53	:	21	3.37	U
19	2.40	:	12	2.54	:			

U = Omitted results

TABLE 13. STATISTICS, SULFATE

Analytical method: All methods

Unit: mg/l SO_4

Sample A

Number of participants:	20	Range:	1.56
Number of omitted results:	1	Variance:	0.14
True value:	6.90	Standard deviation:	0.38
Mean value:	6.87	Relative standard deviation:	5.52 %
Median value:	6.90	Relative error:	-0.38 %

Analytical results in ascending order:

16	6.00	:	10	6.75	:	20	7.10
17	6.48	:	6	6.86	:	12	7.24
4	6.52	:	19	6.90	:	3	7.30
14	6.52	:	5	6.92	:	7	7.32 U
18	6.60	:	11	7.01	:	8	7.43
13	6.63	:	1	7.02	:	15	7.56
21	6.68	:	9	7.08	:		

Sample B

Number of participants:	20	Range:	1.52
Number of omitted results:	1	Variance:	0.12
True value:	5.19	Standard deviation:	0.35
Mean value:	5.13	Relative standard deviation:	6.85 %
Median value:	5.19	Relative error:	-1.21 %

Analytical results in ascending order:

18	4.10	:	14	5.13	:	12	5.34
16	4.70	:	6	5.16	:	9	5.37
17	4.75	:	5	5.19	:	3	5.38
4	4.85	:	21	5.22	:	8	5.58
13	4.96	:	20	5.30	:	15	5.62
10	5.04	:	1	5.31	:	7	6.78 U
19	5.10	:	11	5.32	:		

U = Omitted results

TABLE 14. STATISTICS, CALCIUM

Analytical method: All methods

Unit: mg/l Ca

Sample A

Number of participants:	20	Range:	0.57
Number of omitted results:	1	Variance:	0.02
True value:	3.21	Standard deviation:	0.14
Mean value:	3.24	Relative standard deviation:	4.28 %
Median value:	3.21	Relative error:	1.08 %

Analytical results in ascending order:

15	2.67 U	:	3	3.20	:	13	3.30
8	3.06	:	7	3.20	:	21	3.30
4	3.10	:	10	3.20	:	6	3.38
19	3.10	:	14	3.21	:	1	3.40
17	3.12	:	9	3.22	:	16	3.43
18	3.15	:	11	3.24	:	12	3.63
20	3.16	:	5	3.25	:		

Sample B

Number of participants:	20	Range:	0.55
Number of omitted results:	1	Variance:	0.02
True value:	2.46	Standard deviation:	0.14
Mean value:	2.50	Relative standard deviation:	5.76 %
Median value:	2.46	Relative error:	1.44 %

Analytical results in ascending order:

15	1.81 U	:	5	2.44	:	6	2.57
8	2.29	:	9	2.45	:	7	2.60
18	2.29	:	14	2.46	:	21	2.60
4	2.31	:	3	2.46	:	16	2.64
17	2.40	:	11	2.47	:	1	2.73
19	2.40	:	10	2.50	:	12	2.84
20	2.43	:	13	2.53	:		

U = Omitted results

TABLE 15. STATISTICS, MAGNESIUM

Analytical method: All methods

Unit: mg/l Mg

Sample A

Number of participants:	20	Range:	0.25
Number of omitted results:	0	Variance:	0.00
True value:	0.83	Standard deviation:	0.06
Mean value:	0.82	Relative standard deviation:	7.08 %
Median value:	0.83	Relative error:	-1.05 %

Analytical results in ascending order:

15	0.69	:	12	0.82	:	21	0.84
3	0.73	:	20	0.82	:	11	0.85
4	0.75	:	9	0.83	:	14	0.86
18	0.76	:	17	0.83	:	6	0.89
10	0.80	:	8	0.83	:	19	0.90
7	0.80	:	1	0.84	:	16	0.94
5	0.80	:	13	0.84	:		

Sample B

Number of participants:	20	Range:	0.25
Number of omitted results:	0	Variance:	0.00
True value:	0.57	Standard deviation:	0.05
Mean value:	0.57	Relative standard deviation:	9.28 %
Median value:	0.57	Relative error:	0.13 %

Analytical results in ascending order:

15	0.45	:	8	0.56	:	19	0.60
4	0.50	:	1	0.57	:	14	0.60
18	0.52	:	11	0.57	:	10	0.60
3	0.53	:	9	0.57	:	6	0.61
5	0.53	:	20	0.57	:	16	0.65
12	0.55	:	13	0.58	:	7	0.70
17	0.56	:	21	0.59	:		

TABLE 16. STATISTICS, SODIUM

Analytical method: All methods

Unit: mg/l Na

Sample A

Number of participants:	20	Range:	1.40
Number of omitted results:	0	Variance:	0.13
True value:	7.61	Standard deviation:	0.36
Mean value:	7.53	Relative standard deviation:	4.76 %
Median value:	7.61	Relative error:	-0.99 %

Analytical results in ascending order:

21	6.80	:	15	7.44	:	12	7.70
4	6.90	:	20	7.50	:	14	7.78
7	7.20	:	10	7.60	:	13	7.79
16	7.21	:	6	7.61	:	19	7.90
18	7.22	:	11	7.65	:	9	8.08
3	7.33	:	1	7.70	:	8	8.20
17	7.38	:	5	7.70	:		

Sample B

Number of participants:	20	Range:	1.80
Number of omitted results:	0	Variance:	0.18
True value:	8.79	Standard deviation:	0.42
Mean value:	8.64	Relative standard deviation:	4.91 %
Median value:	8.79	Relative error:	-1.73 %

Analytical results in ascending order:

21	7.60	:	7	8.50	:	14	8.85
4	7.85	:	15	8.58	:	1	8.86
16	8.25	:	11	8.77	:	5	8.90
17	8.37	:	10	8.80	:	13	9.04
18	8.39	:	9	8.80	:	8	9.18
3	8.43	:	6	8.84	:	19	9.40
20	8.50	:	12	8.85	:		

TABLE 17. STATISTICS, POTASSIUM

Analytical method: All methods

Unit: mg/l K

Sample A

Number of participants:	20	Range:	0.39
Number of omitted results:	0	Variance:	0.01
True value:	1.42	Standard deviation:	0.08
Mean value:	1.43	Relative standard deviation:	5.58 %
Median value:	1.42	Relative error:	0.36 %

Analytical results in ascending order:

17	1.21	:	18	1.40	:	1	1.47
7	1.30	:	19	1.40	:	6	1.47
15	1.39	:	20	1.41	:	8	1.48
3	1.40	:	13	1.43	:	4	1.48
11	1.40	:	12	1.43	:	14	1.53
9	1.40	:	5	1.45	:	21	1.60
10	1.40	:	16	1.46	:		

Sample B

Number of participants:	20	Range:	0.32
Number of omitted results:	0	Variance:	0.01
True value:	1.15	Standard deviation:	0.07
Mean value:	1.15	Relative standard deviation:	6.51 %
Median value:	1.15	Relative error:	-0.34 %

Analytical results in ascending order:

17	0.98	:	20	1.12	:	4	1.19
7	1.00	:	12	1.14	:	10	1.20
15	1.10	:	13	1.15	:	6	1.20
19	1.10	:	8	1.15	:	5	1.21
9	1.11	:	16	1.15	:	14	1.26
11	1.12	:	1	1.16	:	21	1.30
3	1.12	:	18	1.16	:		

TABLE 18. STATISTICS, TOTAL ORGANIC CARBON

Analytical method: All methods

Unit: mg/l C

Sample A

Number of participants:	20	Range:	12.4
Number of omitted results:	0	Variance:	10.4
True value:	23.40	Standard deviation:	3.22
Mean value:	24.23	Relative standard deviation:	13.3 %
Median value:	23.35	Relative error:	3.56 %

Analytical results in ascending order:

15	21.1	:	18	23.0	:	17	24.2
6	21.5	:	12	23.0	:	8	25.0
20	22.7	:	9	23.7	:	19	26.0
3	22.9	:	14	24.2	:	7	33.5

Sample B

Number of participants:	12	Range:	5.70
Number of omitted results:	0	Variance:	2.76
True value:	13.00	Standard deviation:	1.66
Mean value:	13.66	Relative standard deviation:	12.2 %
Median value:	13.00	Relative error:	5.06 %

Analytical results in ascending order:

15	11.9	:	14	12.9	:	6	13.1
20	12.6	:	3	13.0	:	18	15.0
9	12.9	:	12	13.0	:	19	16.0
17	12.9	:	8	13.0	:	7	17.6
