CONVENTION ON LONG-RANGE
TRANSBOUNDARY AIR POLLUTION

2465

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

Intercalibration
9004

pH and alkalinity

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

NIVA – REPORT

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Abstract:

Eleven laboratories in ten countries participated in intercalibration 9004, especially designed for testing of pH and alkalinity determination. The estimate of a total error of ± 0,2 pH units seems to be a reasonable assessment of the accuracy of routine determination of pH. Measurement without stirring the solution is recommended. Regarding the determination of alkalinity, the Gran plot titration method is strongly recommended.

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

INTERCALIBRATION 9004

pH and alkalinity

Oslo, August 1990

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

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 fourth intercalibration test, called 9004, was particularly designed for determination of pH and alkalinity. The idea was to compare the routine methods, used at different laboratories, to other standardized or normalized methods.

ACCOMPLISHMENT OF THE INTERCALIBRATION

Preparation of samples

The sample solutions were prepared from natural water, one sample was collected in the outlet of the lake Maridalsvannet, the other sample was collected in a brooklet from Hellerudmyra, a marsh area. Both sampling sites are located outside Oslo, Norway. 25 litres of raw water were collected in polyetylen containers and stored for several weeks at room temperature at the laboratory. During this stabilization time suspended matter settled. The required volume of these solutions was filtered through 0,45 μm membrane filter. Small aliquots were removed from the filtrate for the the determination of background concentrations of the constituents of interest.

Two water samples (A and B) were prepared from the lake filtrate, and two samples (C and D) were prepared from the marsh water. 10 liter portions of the filtrate were transferred to polyetylene 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. After these additions the solutions were stored for some weeks for further stabilization. During this period aliquotes were taken regularly from the four solutions to control the stability of pH and alkalinity.

A few days before mailing, the solutions were transferred to 1/2 L polyetylene 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 end of march 1990. A summary of the control results is presented in table 4, appendix 2. The control analyses confirmed that the stability of the sample solutions were acceptable during the intercalibration period.

Mailing

The samples were mailed from the Programme Centre on the 7th of february 1990. 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 fast as possible after the arrival at the laboratory.

RESULTS

Eleven laboratories (in ten countries) participated in this fourth intercalibration test. 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.

The median value determined from the analytical results of 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 - 10, where each laboratory is represented by a cross and an identification number. A survey of the results is presented in table 1. The individual results of the participants are presented in table 5 (appendix 4), sorted in order of increasing identification number. More extensive statistical informations are presented in the tables 6 - 15.

Table 1. Survey of the results of intercalibration 9004.

Parameter, method	Sample pair	True values		Number of data		Median		Mean value/standard deviation				Relative Std. dev.		Relative error	
		1	2	Tot.	U	1	2	1 Mean	1 S.dev.	2 Mean	2 S.dev.	1	2	1	2
pH, without stirring	AB	5.80	6.47	11	0	5.80	6.47	5.90	0.35	6.47	0.21	6.0	3.3	1.7	-0.0
pH, without stirring	CD	6.70	7.02	11	0	6.70	7.02	6.70	0.17	7.03	0.15	2.6	2.2	0.1	0.1
pH, during stirring	AB	5.77	6.44	11	0	5.77	6.44	5.84	0.37	6.42	0.16	6.3	2.5	1.2	-0.3
pH, during stirring	CD	6.67	6.99	11	0	6.67	6.99	6.64	0.14	6.97	0.12	2.1	1.8	-0.4	-0.3
pH, air equilibration	AB	6.17	6.81	6	0	6.17	6.81	5.87	0.68	6.46	1.07	11.6	16.6	-4.8	-5.2
pH, air equilibration	CD	7.09	7.39	6	0	7.09	7.39	6.70	0.95	6.93	1.07	14.2	15.4	-5.5	-6.2
Alkalinity, routine method	AB	13.0	75.5	8	4	13.0	75.5	13.3	1.5	75.3	2.1	11.3	2.7	1.9	-0.3
Alkalinity, routine method	CD	358.5	675.0	8	0	358.5	675.0	340.3	57.0	653.1	125.5	16.8	19.2	-5.1	-3.2
Alkalinity, Gran plot	AB	16.5	75.4	8	0	16.5	75.4	17.4	3.7	76.9	6.2	21.4	8.1	-1.4	-0.5
Alkalinity, Gran plot	CD	366.5	675.5	8	0	366.5	675.5	371.8	12.3	682.2	17.6	3.3	2.6	1.4	1.0

U = Excluded results

FIG. 1 PH

WITHOUT STIRRING

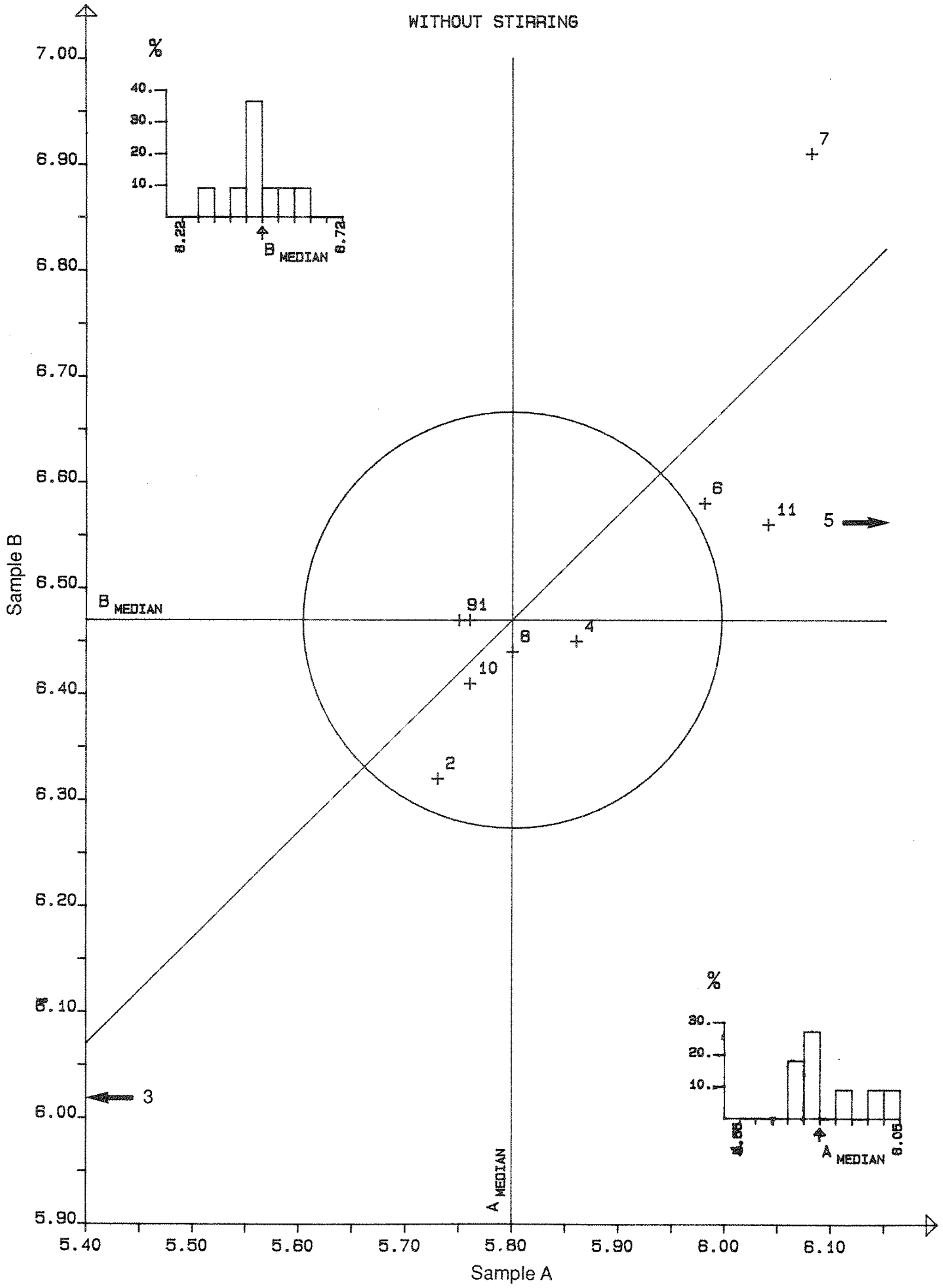


FIG. 2 PH

WITHOUT STIRRING

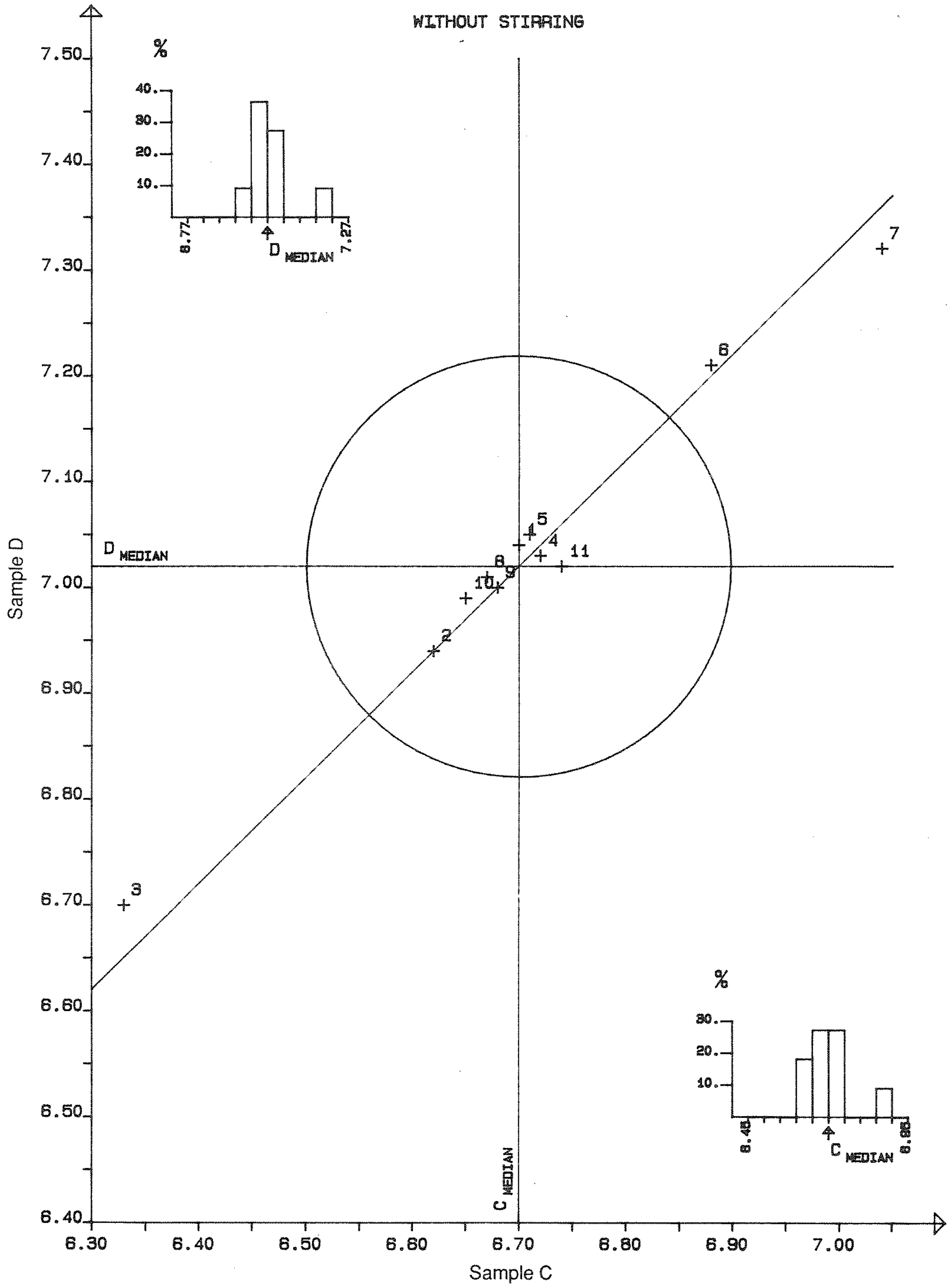


FIG. 3 PH

WITH STIRRING

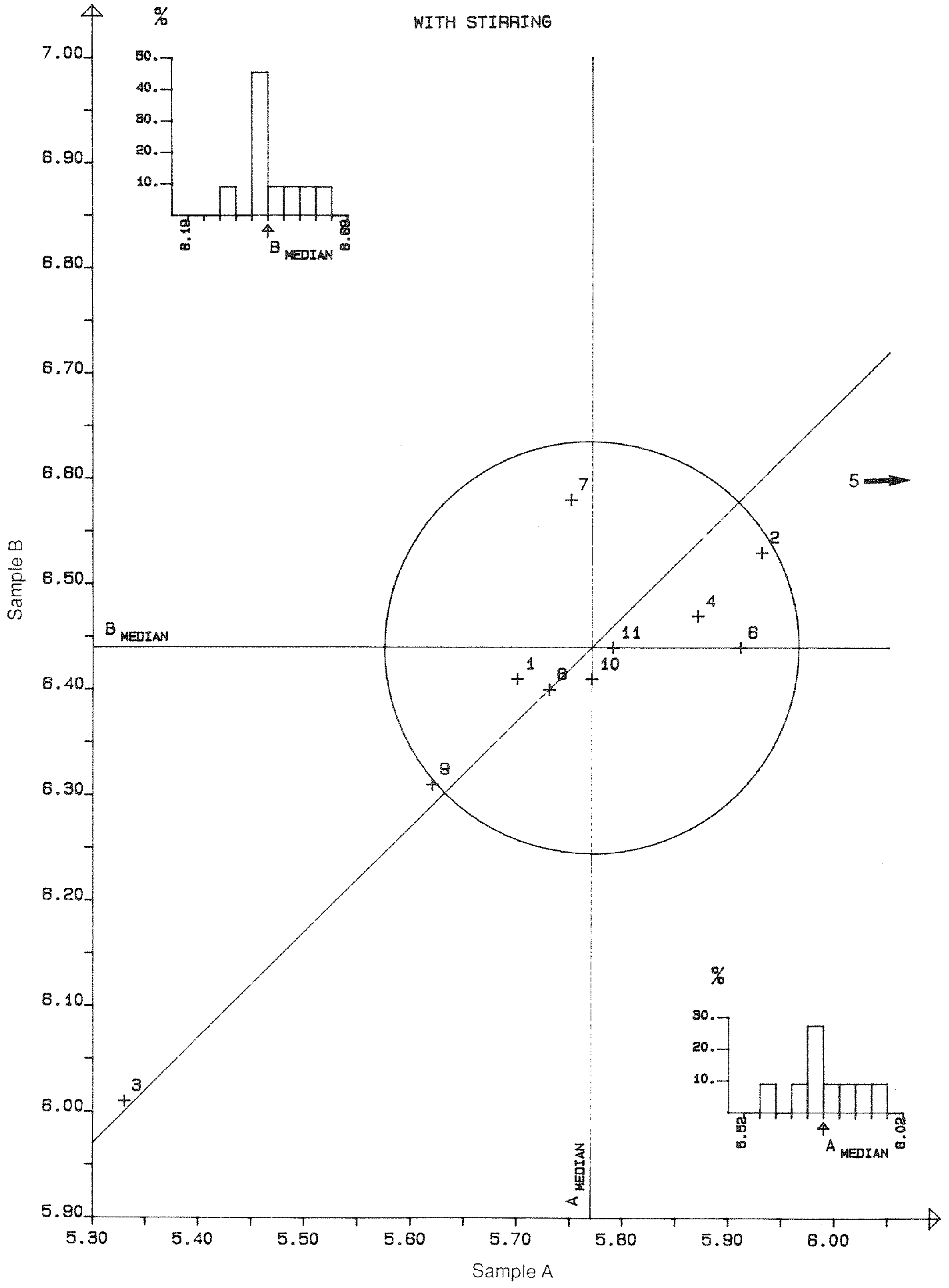


FIG. 4 PH

WITH STIRRING

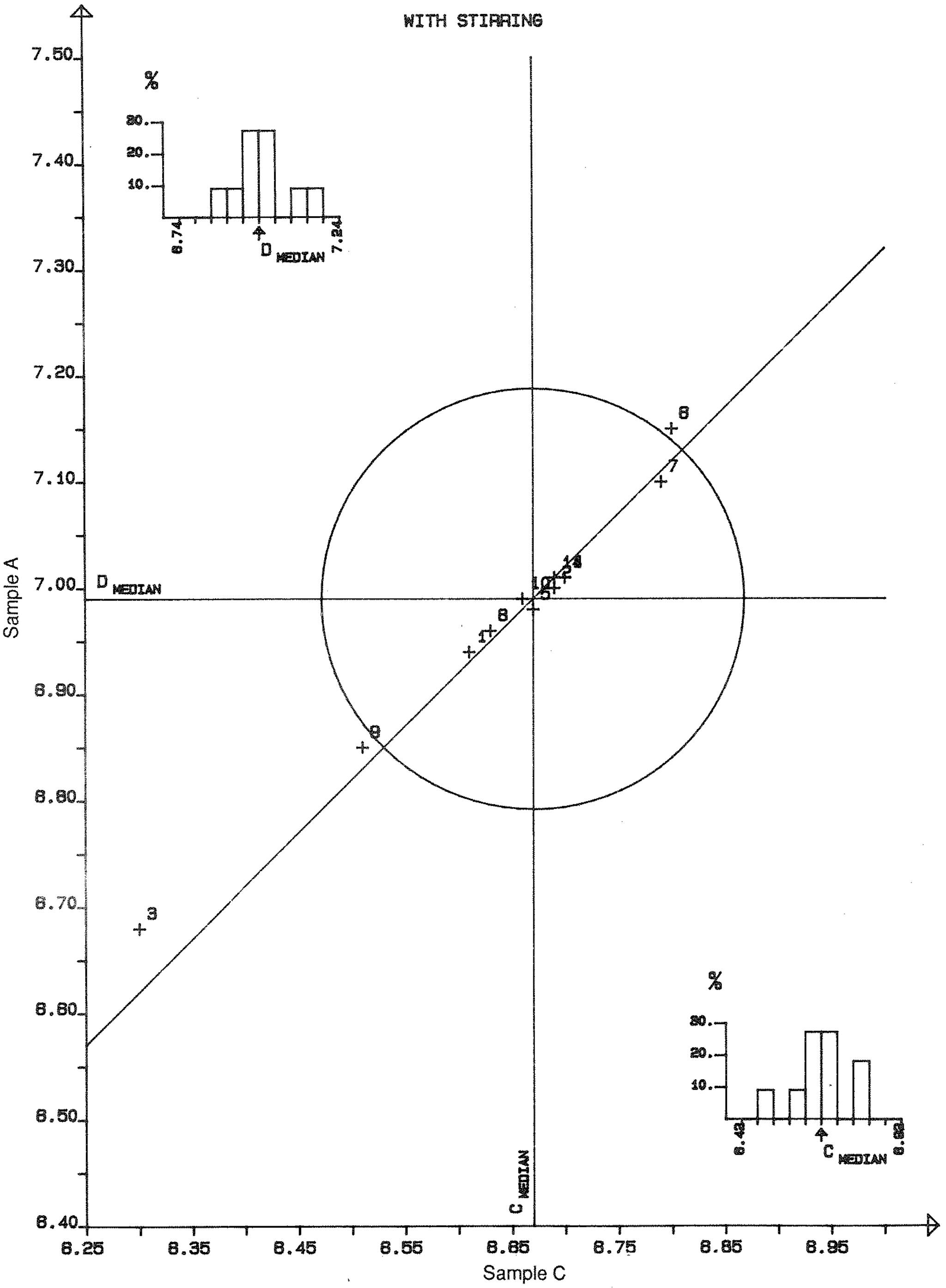


FIG. 5 PH

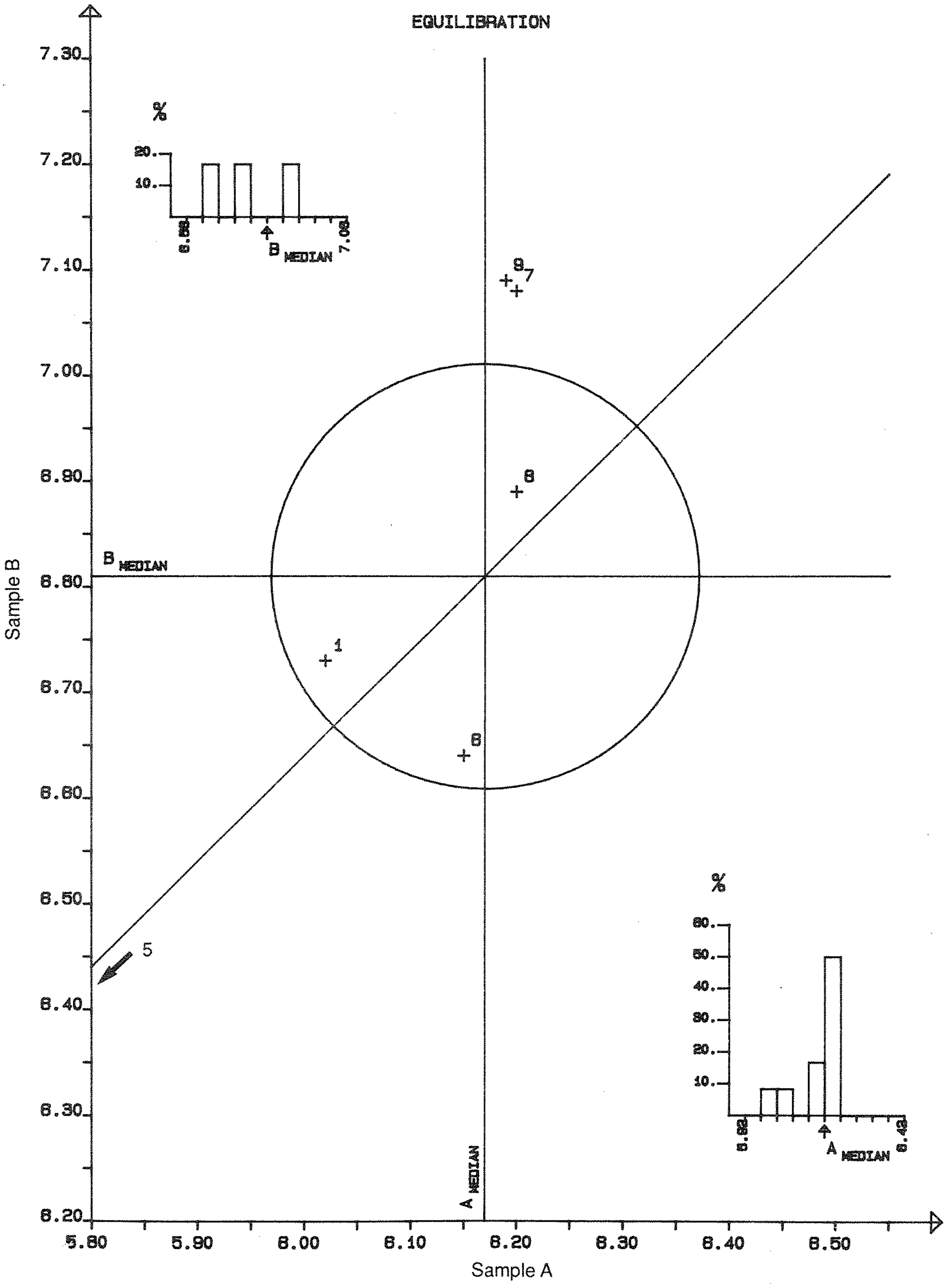

EQUILIBRATION
Sample B
Sample A
7.30
7.20
7.10
7.00
6.90
6.80
6.70
6.60
6.50
6.40
6.30
6.20
5.80
5.90
6.00
6.10
6.20
6.30
6.40
6.50
B MEDIAN
A MEDIAN
9
7
8
1
6
5
%
20.
10.
6.58
7.08
B MEDIAN
%
60.
50.
40.
30.
20.
10.
5.92
6.42
A MEDIAN

FIG. 6 PH
EQUILIBRATION

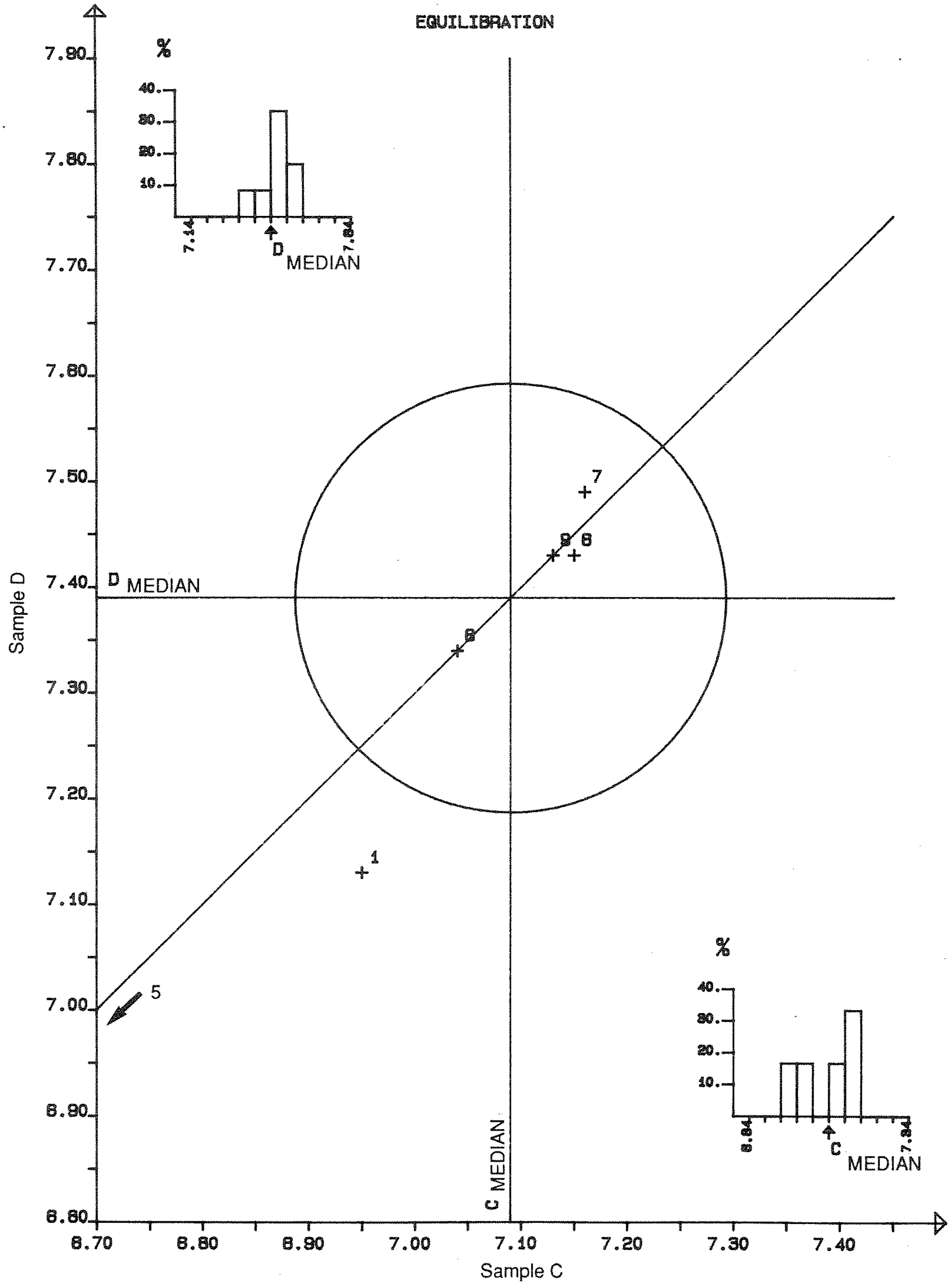
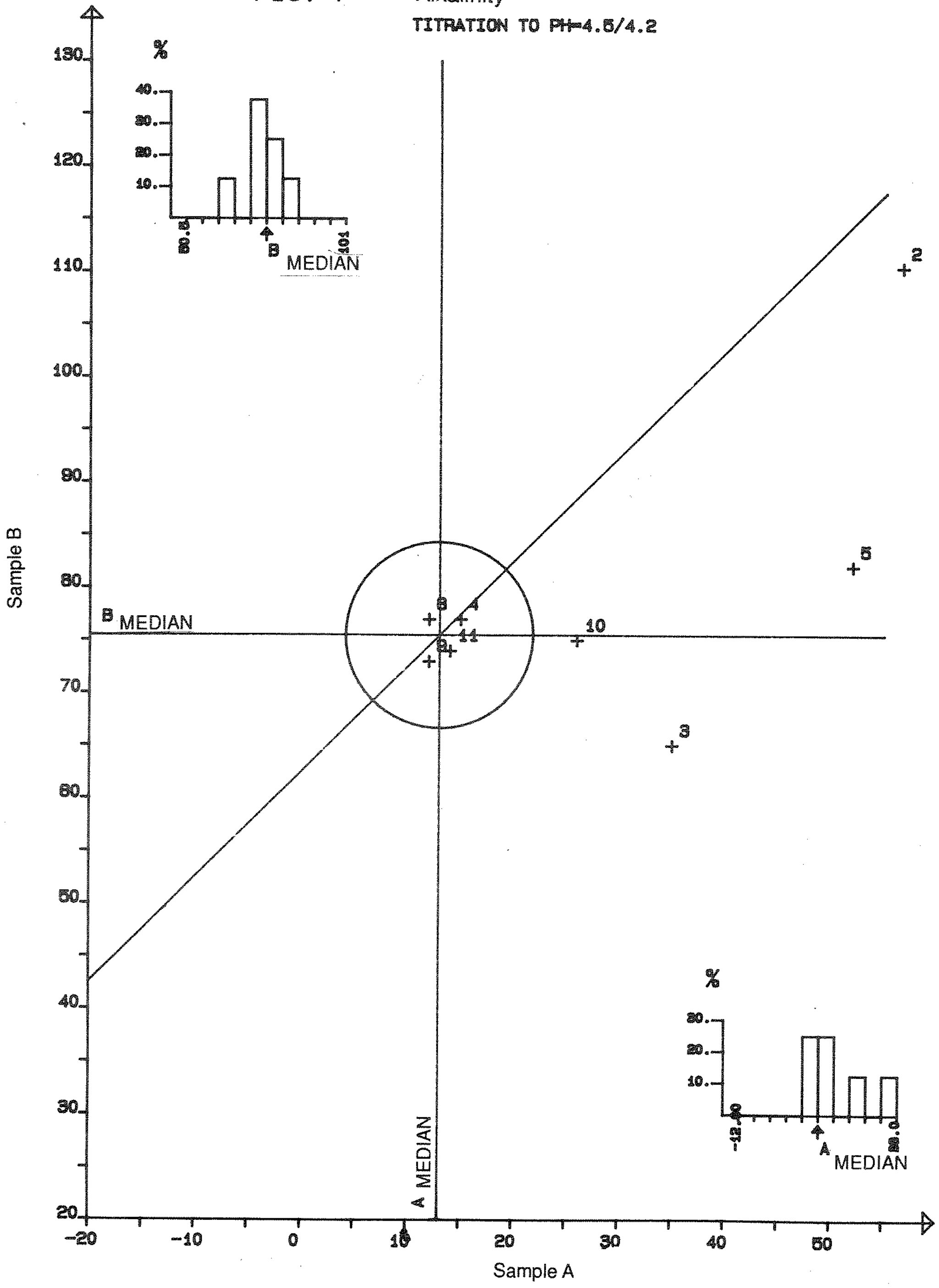


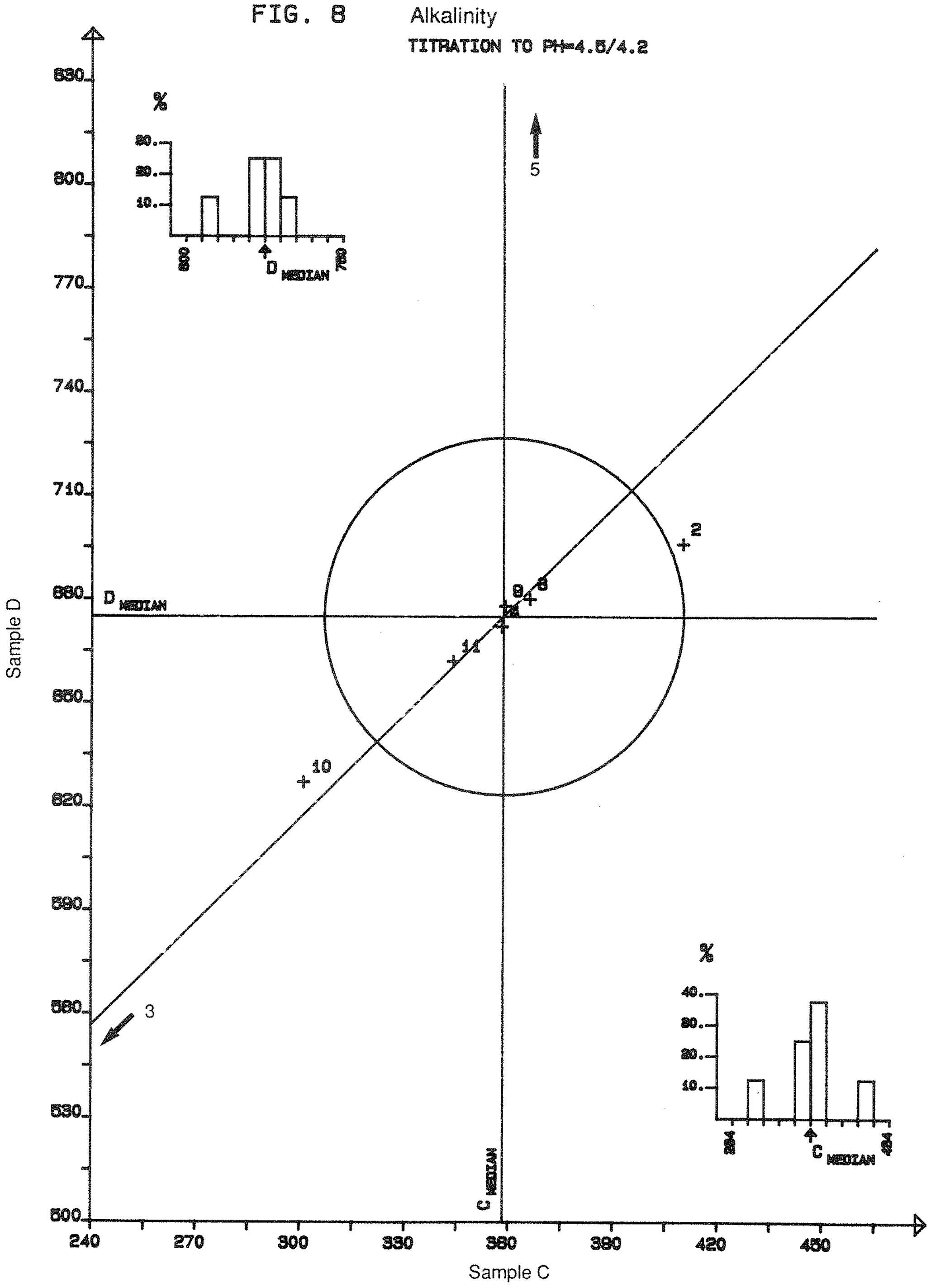
FIG. 7



Alkalinity

TITRATION TO PH=4.5/4.2

FIG. 8



Alkalinity

TITRATION TO PH=4.5/4.2

FIG. 9 Alkalinity

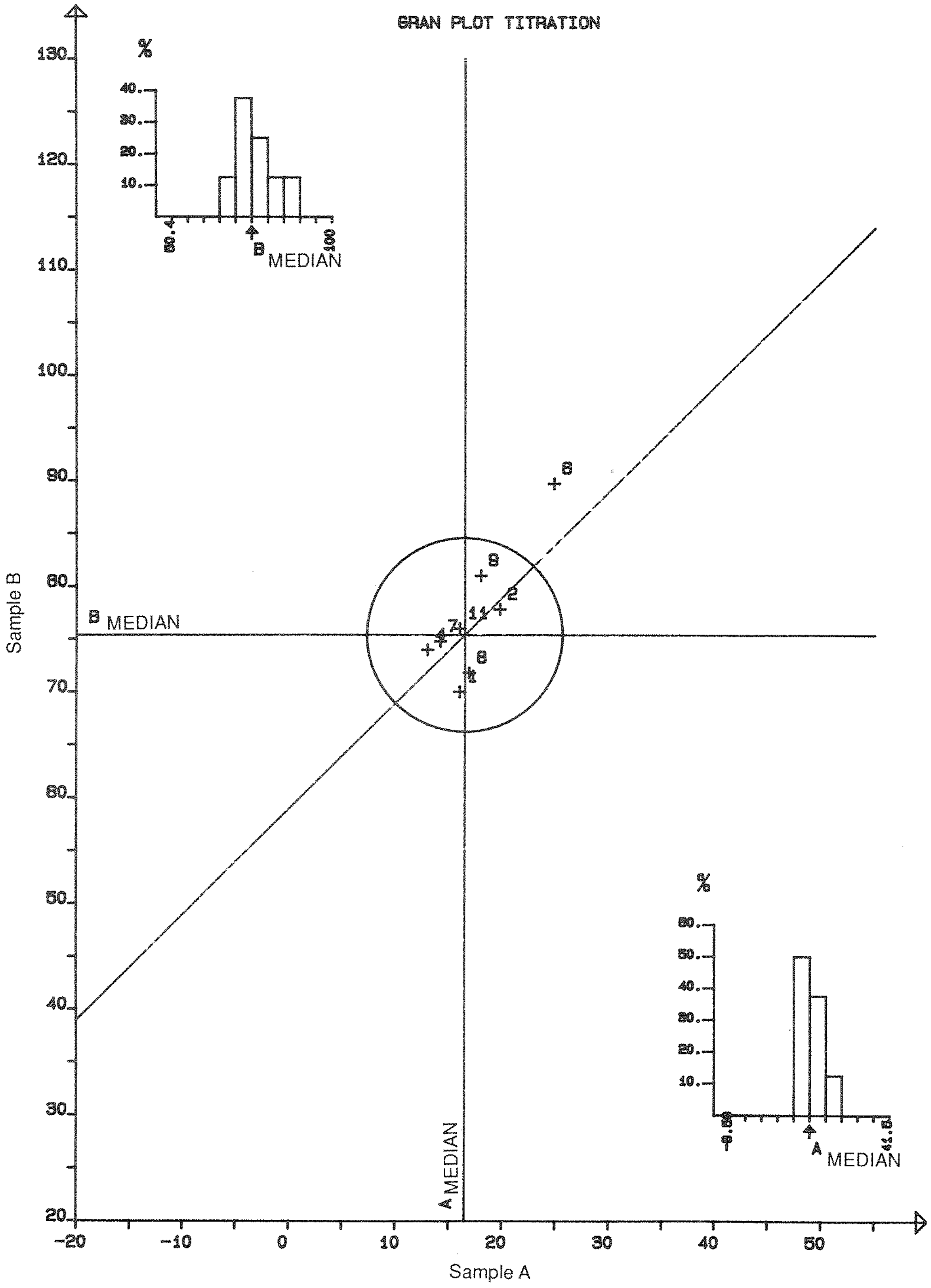
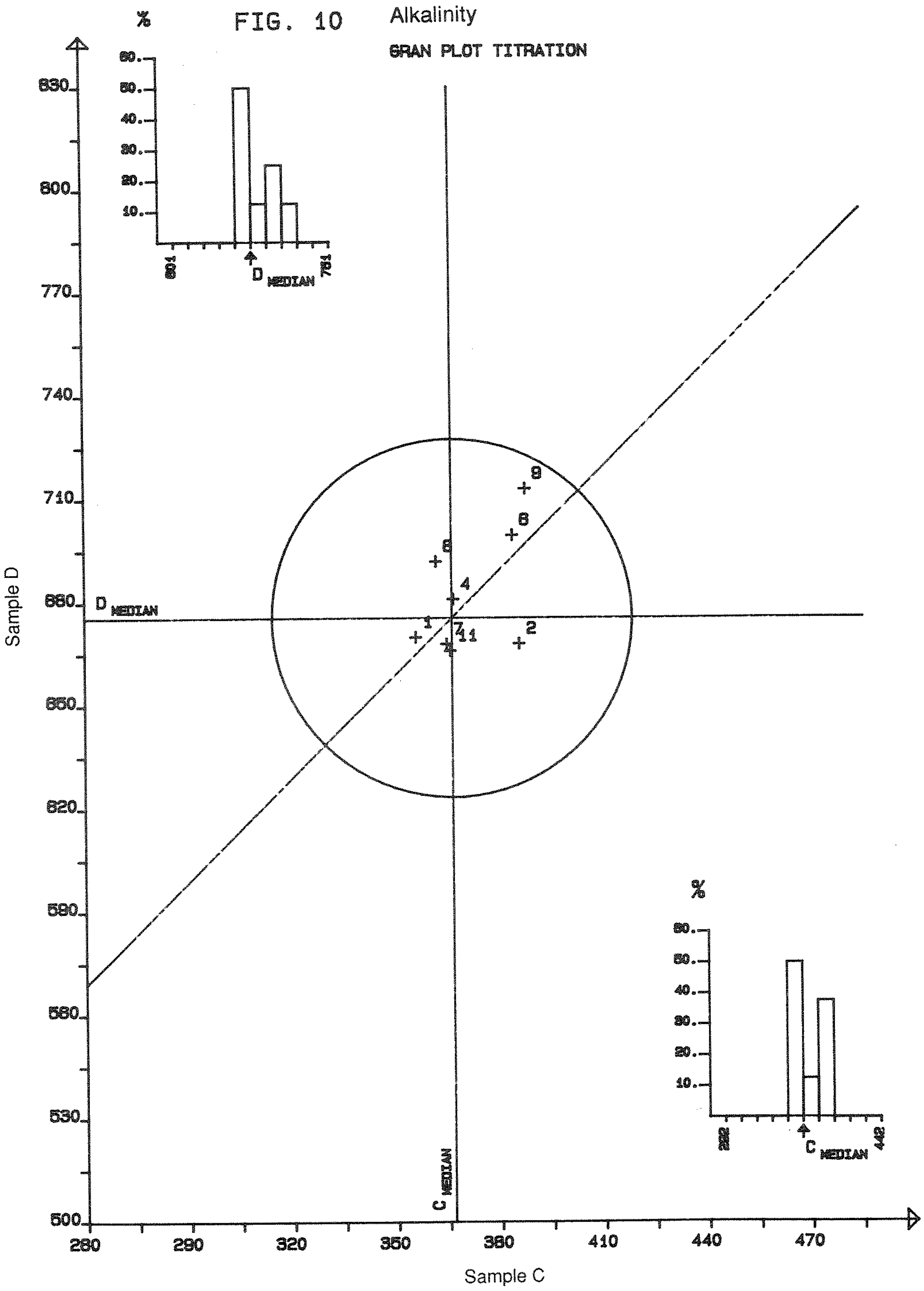


FIG. 10


Alkalinity
GRAN PLOT TITRATION
%
60.
50.
40.
30.
20.
10.
601
D MEDIAN
761
830
800
770
740
710
680
650
620
590
560
530
500
Sample D
D MEDIAN
C MEDIAN
1
2
4
5
6
7
9
11
260
290
320
350
380
410
440
470
Sample C
%
60.
50.
40.
30.
20.
10.
282
C MEDIAN
442

DETERMINATION OF pH

The participants were asked to determine pH in the test solutions by three different methods, of which two are involving some physical pretreatment of the sample.

Measurement without stirring

The simplest method is the direct determination, where the sample is transferred to an open vessel, and pH is determined as soon as the signal is stabilized. Eleven laboratories reported results for pH determined by this method, and the results are presented in the figures 1 and 2, and the tables 6 and 7 (appendix 4). Five and three laboratories have reported results which are outside the limits of ± 0.2 pH units for the sample pairs AB and CD, respectively.

Measurement during stirring

The participants were asked to measure pH of the samples during stirring of the solutions. This method is used for routine measurements at some laboratories, and it has been reported that the pH values usually are lower than when measured in quiescent solutions, especially in low conductivity water samples. A few laboratories have reported that they stopped the stirring of the test solution before reading the pH meter, while most of the participants have not specified specified the details of the procedure they used. The results are presented in the figures 3 and 4, and in the tables 8 and 9 (appendix 4). Three laboratories reported results which are outside the limit of ± 0.2 pH units.

Measurement after air equilibration

By this method the laboratories were asked to equilibrate the samples by treating them with air before the determination of pH. They should use the following method: Allow a sample aliquote to reach room temperature. Standard 300 ppm CO_2 bottled air is bubbled gently through the sample for 20 minutes while stirring with a clean teflon stirring bar on a magnetic stirrer. Rinse the electrode with deionized water before immersing it in 20 ml of the bubbled solution, and stir with a clean stirring bar for at least 60 sconds. After rinsing the electrode with a small portion of the bubbled sample, transfer 50 ml of the bubbled sample solution to a small flask and measure pH in a non-stirred solution.

Only six of the participating laboratories reported results determined by this method, and, unfortunately some of the laboratories have used compressed air instead of 300 ppm CO_2 standard gas. The results are presented in the figures 5 and 6, and in the tables 10 and 11 (appendix 4).

Discussion

When comparing the results of sample pair AB (figures 1, 3 and 5) with the corresponding results for sample pair CD (figures 2, 4 and 6), it is obvious that the random errors are dominating the picture for sample pair AB, as the results are spread out from the 45^0 line. For sample pair CD the results are located along, and close to, the 45^0 line in the figures, which is typical for measurements where systematic errors are dominating. This observation is common for all three methods used for the pH measurement at this intercalibration.

The main chemical difference between the sample pairs, are the higher ionic strength and buffer capacity in the samples C and D compared to A and B. Sample pair AB are made from a typical low conductivity surface water, while CD are made from marsh water with rather high content of humic substances. To the latter samples phosphate and hydrogencarbonate was added to adjust both pH and alkalinity, this addition also increase the buffer capacity of the samples. Obviously the random errors are increasing when the conductivity and buffer capacity are decreasing. This is in accordance to observations published earlier (4,5,9). There is no evidence in the intercalibration data, that changing the measuring procedure itself may improve the results.

The median values of the results reported by the participating laboratories, are given in table 2. By comparison of the median for the different methods, we find a very small difference between pH measured during stirring and in quiescent solutions. According to these results, the stirring process are lowering the pH value by only 0.03 pH units. The individual results presented in table 4, show that the differenc between results produced by these two methods are small in nearly all laboratories. However, at four laboratories the differences between the methods are up to about 0.3 pH units. Unfortunately, there is no information indicating whether the laboratories have read the pH meter during stirring, or when the signal was stabilized after stirring.

Table 2. The median values of the reported results from the participating laboratories. N - no stirring, D - during stirring, E - equilibration before measurement.

Sample	N	D	E	D-N	E-N
A	5.80	5.77	6.17	-0.03	0.37
B	6.47	6.44	6.81	-0.03	0.34
C	6.70	6.67	7.09	-0.03	0.39
D	7.02	6.99	7.39	-0.03	0.37

The idea at this intercalibration was that the pH value, measured by the second method, should be read during stirring, because it has been reported that stirring very often are lowering the result. This effect is most pronounced in solutions of low ionic strength, and with old electrodes (4,5). It has been proposed that registration of the difference between pH values in quiescent and stirred solutions may be used for quality control of the pH measuring equipment. If the difference is not significant, i.e. less than 0.05 pH units, this is taken as a proof of that the instrumental system is working satisfactory (5). However, there are only certain electrodes for which this demand will be fulfilled. This fact may be a possible explanation for the observed differences between the methods reported by the participants in this intercalibration.

By equilibration of the samples before reading the pH value, it should be possible to eliminate differences caused by non-equilibrium CO_2 conditions in the samples. However, for the samples used here, this is obviously not the way to go to improve the comparability of the results. The mean difference from measurement in quiescent solution was 0.37 pH units. There are a rather great spread of the results, and this may be due to the lack of experience in using this method at many laboratories. The lacking experience may also explain why only six laboratories returned results for this method.

ALKALINITY

The participants were asked to determine alkalinity by two methods: their own routine method normally used at the laboratory, and the Gran plot titration method. Three laboratories apply the Gran plot method for routine determinations of alkalinity, and therefore they reported results for this method only.

The results of the routine method are presented in the figures 7 and 8 and in the tables 12 and 13, while the results of the Gran plot method are shown in the figures 9 and 10, and in the tables 14 and 15 (appendix 4).

The routine method used by the participating laboratories are based on acidimetric titration to pH = 4.5 and 4.2 (6). Thus most participants applied electrometric titration with hydrochloric acid, but one laboratory titrated with sulfuric acid using methyl orange as indicator. Eight laboratories reported results for this method, of which four result pairs are located outside the general acceptance limit of 20 % and 10 %, respectively, for the sample pair AB and CD. If the acceptance limits are extended to the general target of ± 20% for sample pair CD, only two data pairs will be located outside this limit.

For the Gran plot titration method, on the other hand, only one result pair (sample AB) is located outside the same limits. The spread of the points within the diagrams 9 and 10 is characterized by the influence of random errors. This is contrary to the results of the routine method, where the results are located close to the 45^0 line and therefore are dominated by systematic errors. The most possible reason for the systematic deviation between the results determined with the routine method, may be the differences in the practical analytical procedure followed by each participant.

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. For pH the 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. This acceptance limit is in accordance to other intercalibration studies of the pH determination (9). For alkalinity, the limits of 20 % and 10 % have been used for the sample pairs AB and CD, respectively. In table 2 are presented an evaluation of the results of intercalibration 9004, based on these acceptance limits.

Table 3. Evaluation of the results of intercalibration 9004.

Parameter	Sample pair	Acceptance limit	Number of results	Number of acceptable results	Percent acceptable results
pH, without stirring	AB CD	0.2 0.2	11 11	6 8	55 73
pH, during stirring	AB CD	0.2 0.2	11 11	9 8	82 73
pH, after equilibr.	AB CD	0.2 0.2	6 6	3 4	50 67
Alkalinity, pH=4.5/4.2	AB CD	20 % 10 %	8 8	4 4	50 50
Alkalinity, Gran plot	AB CD	20 % 10 %	8 8	7 8	88 100
Total			88	61	69

In earlier intercalibrations (7,8), 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. The best solution of this problem would be that all the participants agreed upon using exactly the same method - and did apply it - but this situation will probably be difficult to obtain. It was therefore suggested that different methods should be used at this intercalibration, to elucidate what differences between results may be expected when different methods are used.

The analytical results from the pH measurements may vary considerably, even when the equipment and the general analytical procedure are identical. Such variations are 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.

Considerable bias errors may be due to preparation of standards, as well as inaccuracies associated with the measurement. When pH is determined, stirring and agitation of the test solution can produce a streaming potential, the magnitude of which is a function of the type of electrode used, as well as of the ionic strength of the solution. Although streaming potential changes in solutions of high ionic strength usually are negligible, changes greater than 0.5 pH units while stirring precipitation samples have been reported (4). Care in the selection and initial testing of electrodes will improve the quality of results. Most important, however, is the unambigous description of preparation and measurement procedures, securing that exactly the same procedure is followed each time pH is determined.

This intercalibration does not allow any single procedure to be identified, which is clearly more suitable than others for the routine determination of pH in natural waters. However, as measurement on quiescent solutions resulted in almost identical readings for all kinds of electrodes used (4), we recommend that measurement without stirring should be used for routine determinations of pH. In addition, an internal quality control procedure should be adopted to secure that the instrument system is working satisfactory (5).

On the basis of the results of this intercalibration - regarding the determination of alkalinity - it seems to be easier to obtain acceptable comparability between results by using the Gran plot titration method. This method is therefore strongly recommended in connection to this international co-operation programme on assessment and monitoring of acidification.

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 seem to be a reasonable assessment of the accuracy which might be achieved routinely when commercial equipment is used.

To obtain better comparability between results, the method used at different laboratories must be improved.

Regarding pH measurement, there is no clear evidence in the intercalibration data here, that changing the measuring procedure itself may improve the results. However, 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.

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APPENDIX 1

Participants of intercalibration 9004, and their code numbers

1. National Agency of Environmental Protection, Silkeborg, Denmark.
2. Ontario Ministry of Environment, Dorset, Canada.
3. National Institute for Physical Planning and Construction Research, Dublin, Ireland.
4. National Board of Waters and Environment, Helsinki, Finland.
5. Institute d'Hygiene et d'Epidemiologie, Bruxelles, Belgium.
6. Bayerische Landesamt für Wasserwirtschaft, München, Federal Republic of Germany.
7. University of Maine, Environmental Chemistry Lab., Orono, USA.
8. Norwegian Institute for Water Research, Oslo, Norway.
9. Consiglio Nazionale delle Ricerche, Pallanza, Italia.
10. National Environment Protection Board, Uppsala, Sweden.
11. National Water Quality Laboratory, Burlington, Canada.

APPENDIX 2

Table 4. Summary of the control analyses

The analytical results for alkalinity are given in µmol/l.

Parameter	Sample A		Sample B	
	mean	sdev.	mean	sdev.
pH, without stirring	5.83	0.027	6.47	0.019
pH, during stirring	5.77	0.024	6.43	0.024
pH, after equilibration	6.16	0.024	6.96	0.045
Alkalinity, pH=4.5/4.2	15.3	1.9	104.5	4.2
Alkalinity, Gran plot	16.4	1.7	72.0	0.8

Parameter	Sample C		Sample D	
	mean	sdev.	mean	sdev.
pH, without stirring	6.69	0.013	7.01	0.008
pH, during stirring	6.61	0.019	6.91	0.029
pH, after equilibration	7.11	0.044	7.37	0.031
Alkalinity, pH=4.5/4.2	391	3.4	708	5.1
Alkalinity, Gran plot	359	1.7	692	1.5

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 figs. 1 - 10).

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 6 - 15. Results being omitted from the calculations, are marked with the letter "U".

APPENDIX 4

TABLE 5. THE RESULTS OF THE PARTICIPATING LABORATORIES.

Lab. no.	pH - no stirring				pH - during stirring			
	A	B	C	D	A	B	C	D
1	5.76	6.47	6.70	7.04	5.70	6.41	6.61	6.94
2	5.73	6.32	6.62	6.94	5.93	6.53	6.69	7.00
3	5.35	6.02	6.33	6.70	5.33	6.01	6.30	6.68
4	5.86	6.45	6.72	7.03	5.87	6.47	6.70	7.01
5	6.78	6.51	6.71	7.05	6.83	6.60	6.67	6.98
6	5.98	6.58	6.88	7.21	5.91	6.44	6.80	7.15
7	6.08	6.91	7.04	7.32	5.75	6.58	6.79	7.10
8	5.80	6.44	6.67	7.01	5.73	6.40	6.63	6.96
9	5.75	6.47	6.68	7.00	5.62	6.31	6.51	6.85
10	5.76	6.41	6.65	6.99	5.77	6.41	6.66	6.99
11	6.04	6.56	6.74	7.02	5.79	6.44	6.69	7.01

Lab. no.	pH - after equilibration			
	A	B	C	D
1	6.02	6.73	6.95	7.13
2	-	-	-	-
3	-	-	-	-
4	-	-	-	-
5	4.49	4.30	4.77	4.77
6	6.15	6.64	7.15	7.43
7	6.20	7.08	7.16	7.49
8	6.20	6.89	7.04	7.34
9	6.19	7.09	7.13	7.43
10	-	-	-	-
11	-	-	-	-

Lab. no.	Alkalinity, μmol/l Titration to pH = 4,5 and 4,2				Alkalinity, μmol/l Gran plot titration			
	A	B	C	D	A	B	C	D
1	-	-	-	-	16.0	70.0	356.	670.
2	56.6	110.4	410.	696.	19.8	77.8	386.	668.
3	35.0	65.0	220.	380.	-	-	-	-
4	15.0	77.0	358.	672.	13.0	74.0	367.	681.
5	52.0	82.0	364.	830.	-	-	-	-
6	-	-	-	-	24.9	89.7	384.2	699.5
7	-	-	-	-	14.2	74.8	365.	668.
8	12.0	77.0	366.	680.	16.9	71.8	362.	692.
9	12.0	73.0	359.	678.	18.0	81.0	388.	713.
10	26.0	75.0	301.	627.	-	-	-	-
11	14.0	74.0	344.	662.	16.0	76.0	366.	666.

Table 6. Statistics, pH

Analytical method: electrometric, without stirring

Unit:

Sample A

Number of participants:	11	Range:	1.43
Number of omitted results:	0	Variance:	0.12
True value:	5.80	Standard deviation:	0.35
Mean value:	5.90	Relative standard deviation:	5.96 %
Median value:	5.80	Relative error:	1.71 %

Analytical results in ascending order:

3	5.35	:	10	5.76	:	11	6.04
2	5.73	:	8	5.80	:	7	6.08
9	5.75	:	4	5.86	:	5	6.78
1	5.76	:	6	5.98			

Sample B

Number of participants:	11	Range:	0.89
Number of omitted results:	0	Variance:	0.04
True value:	6.47	Standard deviation:	0.21
Mean value:	6.47	Relative standard deviation:	3.26 %
Median value:	6.47	Relative error:	-0.04 %

Analytical results in ascending order:

3	6.02	:	4	6.45	:	11	6.56
2	6.32	:	9	6.47	:	6	6.58
10	6.41	:	1	6.47	:	7	6.91
8	6.44	:	5	6.51			

TABLE 7. STATISTICS, pH

```
Analytical method: electrometric, without stirring

Unit:

----------------------------------------------------------------------

Sample C

Number of participants:      11    Range:                        0.71
Number of omitted results:    0    Variance:                     0.03
True value:                6.70    Standard deviation:           0.17
Mean value:                6.70    Relative standard deviation: 2.57 %
Median value:              6.70    Relative error:              0.05 %

Analytical results in ascending order:

       3     6.33     :     9     6.68     :    11     6.74
       2     6.62     :     1     6.70     :     6     6.88
      10     6.65     :     5     6.71     :     7     7.04
       8     6.67     :     4     6.72

----------------------------------------------------------------------


Sample D

Number of participants:      11    Range:                        0.62
Number of omitted results:    0    Variance:                     0.02
True value:                7.02    Standard deviation:           0.15
Mean value:                7.03    Relative standard deviation: 2.19 %
Median value:              7.02    Relative error:              0.12 %

Analytical results in ascending order:

       3     6.70     :     8     7.01     :     5     7.05
       2     6.94     :    11     7.02     :     6     7.21
      10     6.99     :     4     7.03     :     7     7.32
       9     7.00     :     1     7.04

----------------------------------------------------------------------
```

TABLE 8. STATISTICS, pH

```
Analytical method: electrometric, during stirring

Unit:

----------------------------------------------------------------------

Sample A

Number of participants:      11    Range:                        1.50
Number of omitted results:    0    Variance:                     0.13
True value:                5.77    Standard deviation:           0.37
Mean value:                5.84    Relative standard deviation: 6.29 %
Median value:              5.77    Relative error:              1.20 %

Analytical results in ascending order:

        3     5.33     :     7     5.75     :     6     5.91
        9     5.62     :    10     5.77     :     2     5.93
        1     5.70     :    11     5.79     :     5     6.83
        8     5.73     :     4     5.87

----------------------------------------------------------------------


Sample B

Number of participants:      11    Range:                        0.59
Number of omitted results:    0    Variance:                     0.03
True value:                6.44    Standard deviation:           0.16
Mean value:                6.42    Relative standard deviation: 2.48 %
Median value:              6.44    Relative error:             -0.34 %

Analytical results in ascending order:

        3     6.01     :    10     6.41     :     2     6.53
        9     6.31     :     6     6.44     :     7     6.58
        8     6.40     :    11     6.44     :     5     6.60
        1     6.41     :     4     6.47

----------------------------------------------------------------------
```

TABLE 9. STATISTICS, pH

Analytical method: electrometric, during stirring

Unit:

Sample C

Number of participants: 11
Number of omitted results: 0
True value: 6.67
Mean value: 6.64
Median value: 6.67

Range: 0.50
Variance: 0.02
Standard deviation: 0.14
Relative standard deviation: 2.08 %
Relative error: -0.44 %

Analytical results in ascending order:

3	6.30	:	10	6.66	:	4	6.70
9	6.51	:	5	6.67	:	7	6.79
1	6.61	:	2	6.69	:	6	6.80
8	6.63	:	11	6.69			

Sample D

Number of participants: 11
Number of omitted results: 0
True value: 6.99
Mean value: 6.97
Median value: 6.99

Range: 0.47
Variance: 0.02
Standard deviation: 0.12
Relative standard deviation: 1.78 %
Relative error: -0.29 %

Analytical results in ascending order:

3	6.68	:	5	6.98	:	11	7.01
9	6.85	:	10	6.99	:	7	7.10
1	6.94	:	2	7.00	:	6	7.15
8	6.96	:	4	7.01			

TABLE 10. STATISTICS, pH

```
Analytical method: electrometric, equilibration

Unit:

----------------------------------------------------------------------

Sample A

Number of participants:       6    Range:                         1.71
Number of omitted results:    0    Variance:                      0.47
True value:                6.17    Standard deviation:            0.68
Mean value:                5.87    Relative standard deviation:11.61 %
Median value:              6.17    Relative error:               -4.78 %

Analytical results in ascending order:

        5     4.49      :     6     6.15      :     8     6.20
        1     6.02      :     9     6.19      :     7     6.20

----------------------------------------------------------------------


Sample B

Number of participants:       6    Range:                         2.79
Number of omitted results:    0    Variance:                      1.15
True value:                6.81    Standard deviation:            1.07
Mean value:                6.46    Relative standard deviation:16.59 %
Median value:              6.81    Relative error:               -5.21 %

Analytical results in ascending order:

        5     4.30      :     1     6.73      :     7     7.08
        6     6.64      :     8     6.89      :     9     7.09

----------------------------------------------------------------------
```

Table 11. Statistics, pH

```
Analytical method: electrometric, equilibration

Unit:

----------------------------------------------------------------------

Sample C

Number of participants:       6    Range:                         2.39
Number of omitted results:    0    Variance:                      0.90
True value:                7.09    Standard deviation:            0.95
Mean value:                6.70    Relative standard deviation:14.16 %
Median value:              7.09    Relative error:               -5.5  %

Analytical results in ascending order:

        5     4.77     :     8     7.04     :     6     7.15
        1     6.95     :     9     7.13     :     7     7.16

----------------------------------------------------------------------


Sample D

Number of participants:       6    Range:                         2.72
Number of omitted results:    0    Variance:                      1.14
True value:                7.39    Standard deviation:            1.07
Mean value:                6.93    Relative standard deviation:15.39 %
Median value:              7.39    Relative error:               -6.2  %

Analytical results in ascending order:

        5     4.77     :     8     7.34     :     9     7.43
        1     7.13     :     6     7.43     :     7     7.49

----------------------------------------------------------------------
```

TABLE 12. STATISTICS, ALKALINITY

```
Analytical method: titration to pH = 4,5 and 4,2

Unit: µmol/l

--------------------------------------------------------------------

Sample A

Number of participants:       8   Range:                        3.00
Number of omitted results:    4   Variance:                     2.25
True value:                13.0   Standard deviation:           1.50
Mean value:                13.3   Relative standard deviation:11.32 %
Median value:              13.0   Relative error:               1.92 %

Analytical results in ascending order:

        8    12.0        :     4    15.0         :     5    52.0  U
        9    12.0        :    10    26.0  U      :     2    56.6  U
       11    14.0        :     3    35.0  U

--------------------------------------------------------------------


Sample B

Number of participants:       8   Range:                        4.00
Number of omitted results:    4   Variance:                     4.25
True value:                75.5   Standard deviation:           2.06
Mean value:                75.3   Relative standard deviation: 2.74 %
Median value:              75.5   Relative error:              -0.33 %

Analytical results in ascending order:

        3    65.0  U     :    10    75.0  U     :     5    82.0  U
        9    73.0        :     8    77.0        :     2   110.4  U
       11    74.0        :     4    77.0

--------------------------------------------------------------------
U = Excluded results
```

TABLE 13. STATISTICS, ALKALINITY

```
Analytical method: titration to pH = 4,5 and 4,2

Unit: µmol/l

----------------------------------------------------------------------

Sample C

Number of participants:       8    Range:                         190.
Number of omitted results:    0    Variance:                    3253.4
True value:               358.5    Standard deviation:            57.0
Mean value:               340.3    Relative standard deviation: 16.8 %
Median value:             358.5    Relative error:              -5.1 %

Analytical results in ascending order:

       3   220.        :     4   358.       :     8   366.
      10   301.        :     9   359.       :     2   410.
      11   344.        :     5   364.

----------------------------------------------------------------------


Sample D

Number of participants:       8    Range:                          450.
Number of omitted results:    0    Variance:                     15740.
True value:               675.0    Standard deviation:            125.5
Mean value:               653.1    Relative standard deviation::19.2 %
Median value:             675.0    Relative error:               -3.2 %

Analytical results in ascending order:

       3   380.        :     4   672.       :     2   696.
      10   627.        :     9   678.       :     5   830.
      11   662.        :     8   680.

----------------------------------------------------------------------
U = excluded results
```

TABLE 14. STATISTICS, ALKALINITY

```
Analytical method: Gran plot titration

Unit: µmol/l

----------------------------------------------------------------------

Sample A

Number of participants:       8    Range:                      11.9
Number of omitted results:    0    Variance:                   13.73
True value:                16.5    Standard deviation:          3.71
Mean value:                17.4    Relative standard deviation:21.36 %
Median value:              16.5    Relative error:             -1.39 %

Analytical results in ascending order:

        4    13.0        :     11    16.0        :     2    19.8
        7    14.2        :      8    16.9        :     6    24.9
        1    16.0        :      9    18.0

----------------------------------------------------------------------


Sample B

Number of participants:       8    Range:                      19.7
Number of omitted results:    0    Variance:                   38.39
True value:                75.4    Standard deviation:          6.20
Mean value:                76.9    Relative standard deviation: 8.06 %
Median value:              75.4    Relative error:             -0.45 %

Analytical results in ascending order:

        1    70.0        :      7    74.8        :     9    81.0
        8    71.8        :     11    76.0        :     6    89.7
        4    74.0        :      2    77.8

----------------------------------------------------------------------
```

TABLE 15. STATISTICS, ALKALINITY

```
Analytical method: Gran plot titration

Unit: µmol/l

----------------------------------------------------------------------

Sample C

Number of participants:       8     Range:                      32.0
Number of omitted results:    0     Variance:                  152.4
True value:               366.5     Standard deviation:        12.34
Mean value:               371.8     Relative standard deviation: 3.32 %
Median value:             366.5     Relative error:             1.44 %

Analytical results in ascending order:

         1   356.       :   11   366.       :    2   386.
         8   362.       :    4   367.       :    9   388.
         7   365.       :    6   384.2

----------------------------------------------------------------------


Sample D

Number of participants:       8     Range:                      47.0
Number of omitted results:    0     Variance:                  308.6
True value:               675.5     Standard deviation:        17.57
Mean value:               682.2     Relative standard deviation: 2.57 %
Median value:             675.5     Relative error:             0.99 %

Analytical results in ascending order:

        11   666.       :    1   670.       :    6   699.5
         2   668.       :    4   681.       :    9   713.
         7   668.       :    8   692.

----------------------------------------------------------------------
```