

CONVENTION ON LONG-RANGE
TRANSBOUNDARY AIR POLLUTION
INTERNATIONAL CO-OPERATIVE
PROGRAMME ON ASSESSMENT AND
MONITORING OF ACIDIFICATION
IN RIVERS AND LAKES

●
Intercalibration

8802

pH, κ_{25} , HCO_3 , NO_3 ,
 SO_4 , Cl, Ca, Mg, Na, K



NIVA - REPORT

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Abstract: <p>Ten laboratories in nine countries participated in the second intercalibration, 8802. Based on the general target accuracies of $\pm 20\%$, all the results were acceptable for conductivity, nitrate, sulfate and sodium. For chloride, calcium, magnesium and potassium, one or two laboratories have reported results outside the general limit. Better comparability is necessary for pH and alkalinity.</p>

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AND MONITORING OF ACIDIFICATION OF RIVERS AND LAKES

INTERCALIBRATION 8802

pH, K_{25} , HCO_3 , NO_3 , SO_4 ,
Cl, Ca, Mg, Na, K

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

NIVA, Oslo, August 1988

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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 second intercalibration test, called 8802, included the determination of pH, conductivity, alkalinity, nitrate, sulfate, chloride, calcium, magnesium, sodium, and potassium, in spiked, natural water samples.

ACCOMPLISHMENT OF THE INTERCALIBRATION

Preparation of the sample solutions is described in appendix 2. In the same place is also given a summary of the results from the control analyses.

The samples were mailed from the Programme Centre on the 8th of march. Unfortunately, the participating laboratories received the samples at very different point of time, the mailing periode varying from a few days to seven weeks (US and Canada).

RESULTS

Ten laboratories in nine countries participated in this second 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. This method, and a description of the statistical treatment of the analytical data, are briefly cited in appendix 3.

The median value determined from the analytical results of the participating laboratories, were selected as the true value for each parameter.

The analytical results are illustrated in the figures 1 - 10, where each laboratory is represented by a cross and an identification

numbers. 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 - 17.

pH

In spite of the well known problems connected to the evaluation of pH intercalibration results for natural water samples, pH was selected as one of the chemical parameters of this intercalibration. The control analysis carried out at the Programme Centre, however, proved that the samples were rather stable. During three months storage the pH value varied less than ± 0.05 units.

The reported pH values are presented in figure 1 and table 8 (appendix 4). All the laboratories applied an electrometric method for the determination of pH. The date of analysis, and the difference between the pH value reported and the median value, was compared, but there is no evidence for any correlation between the deviation and the storage time. This is in agreement with the results of the control analyses. The spread of the points along the 45 degree line in figure 1 is a typical pattern where the deviations from the true value are systematic. To illustrate the magnitude of the deviations, a circle with radius 0.2 pH units is drawn in figure 1. In spite of the fact that the radius of this circle is corresponding to twice the general target accuracy, only 50 % of the results are located within the circle.

In addition to possible storage effects, deviating pH values may be due to errors in the instrument or the electrodes. Small effects may also be caused by variations in the temperature. Much greater effects may be observed if the sample is stirred during the measurement, especially in low conductivity solutions like samples A and B.

Table 3. Survey of the results of intercalibration 8802.

PARAMETER METHOD	TRUE VALUES		NUMBER OF LABS. TOT U	MEDIAN		MEAN/STANDARD DEVIATION				RELATIVE STD. DEV.		RELATIVE ERROR	
	A	B		A	B	MEAN	SDEV	MEAN	SDEV	A	B	A	B
PH ELECTROMETRY	6.73	6.72	10 0	6.73	6.72	6.77	0.24	6.76	0.24	3.5	3.5	0.7	0.5
CONDUCTIVITY ELECTROMETRY	3.99	4.12	10 0	3.99	4.12	3.95	0.11	4.08	0.11	2.7	2.6	-1.0	-1.0
ALKALINITY ALL METHODS	88.0	76.0	10 1	88.0	72.0	85.7	14.1	74.7	9.6	16.5	12.9	-2.7	-1.8
ELECTROMETRIC TITRATION			7 1	88.0	75.0	87.3	15.3	74.0	10.2	17.5	13.8	-0.8	-2.6
GRAN PLOT TITRATION			3 0	80.0	70.0	82.3	13.7	76.0	10.4	16.6	13.7	-6.4	0.0
NITRATE-NITROGEN ALL METHODS	413.5	422.5	10 0	413.5	422.5	415.1	22.1	424.2	25.5	5.3	6.0	0.4	0.4
PHOTOMETRY (AUTO ANALYZER)			6 0	404.5	411.5	408.2	24.7	411.3	20.6	6.0	5.0	-1.3	-2.6
ION CHROMATOGRAPHY			4 0	426.0	442.0	425.5	14.3	443.5	20.5	3.4	4.6	2.9	5.0
SULFATE ALL METHODS	6.92	6.93	10 0	6.92	6.93	6.84	0.23	6.91	0.22	3.3	3.2	-1.1	-0.3
ION CHROMATOGRAPHY			9 0	6.94	6.90	6.84	0.24	6.90	0.23	3.5	3.4	-1.2	-0.5
THORIN METHOD (AUTO ANALYZER)			1 0	6.90	7.00							-0.3	1.0
CHLORIDE ALL METHODS	1.97	2.50	10 1	1.97	2.50	1.97	0.07	2.54	0.16	3.6	6.5	-0.2	1.5
ION CHROMATOGRAPHY			9 1	1.96	2.49	1.96	0.07	2.53	0.17	3.8	6.9	-0.4	1.2
PHOTOMETRY (AUTO ANALYZER)			1 0	2.00	2.60							1.5	4.0
CALCIUM ALL METHODS	3.20	3.21	10 0	3.20	3.21	3.20	0.22	3.19	0.20	6.7	6.4	-0.1	-0.7
ATOMIC ABSORPTION (FLAME)			8 0	3.20	3.23	3.19	0.24	3.20	0.23	7.5	7.1	-0.4	-0.4
ICP EMISSION SPECTROMETRY			2 0	3.23	3.15							1.1	-2.0
MAGNESIUM ALL METHODS	0.62	0.69	10 0	0.62	0.69	0.63	0.09	0.68	0.11	14.9	16.1	1.1	-1.0
ATOMIC ABSORPTION (FLAME)			8 0	0.61	0.69	0.62	0.10	0.68	0.12	16.4	18.2	-0.6	-1.1
ICP EMISSION SPECTROMETRY			2 0	0.67	0.69							8.1	-0.7
SODIUM ALL METHODS	2.33	2.43	10 0	2.33	2.43	2.30	0.20	2.42	0.14	8.6	5.9	-1.1	-0.6
ATOMIC ABSORPTION (FLAME)			8 0	2.33	2.43	2.32	0.12	2.40	0.14	5.4	5.9	-0.5	-1.1
ATOMIC EMISSION			1 0	2.60	2.60							11.6	7.0
ICP EMISSION SPECTROMETRY			1 0	1.91	2.33							-18.0	-4.1
POTASSIUM ALL METHODS	1.00	0.93	10 1	1.00	0.93	0.99	0.04	0.92	0.04	3.9	3.9	-0.9	-0.7
ATOMIC ABSORPTION (FLAME)			8 0	1.00	0.93	0.99	0.04	0.93	0.04	4.1	4.1	0.4	-1.0
ATOMIC EMISSION SPECTROMETRY			1 0	1.00	0.90							0.0	-3.2
ICP EMISSION SPECTROMETRY			1 1	<0.6	<0.6								

U = OMITTED RESULTS

FIG. 1 pH ELECTROMETRY

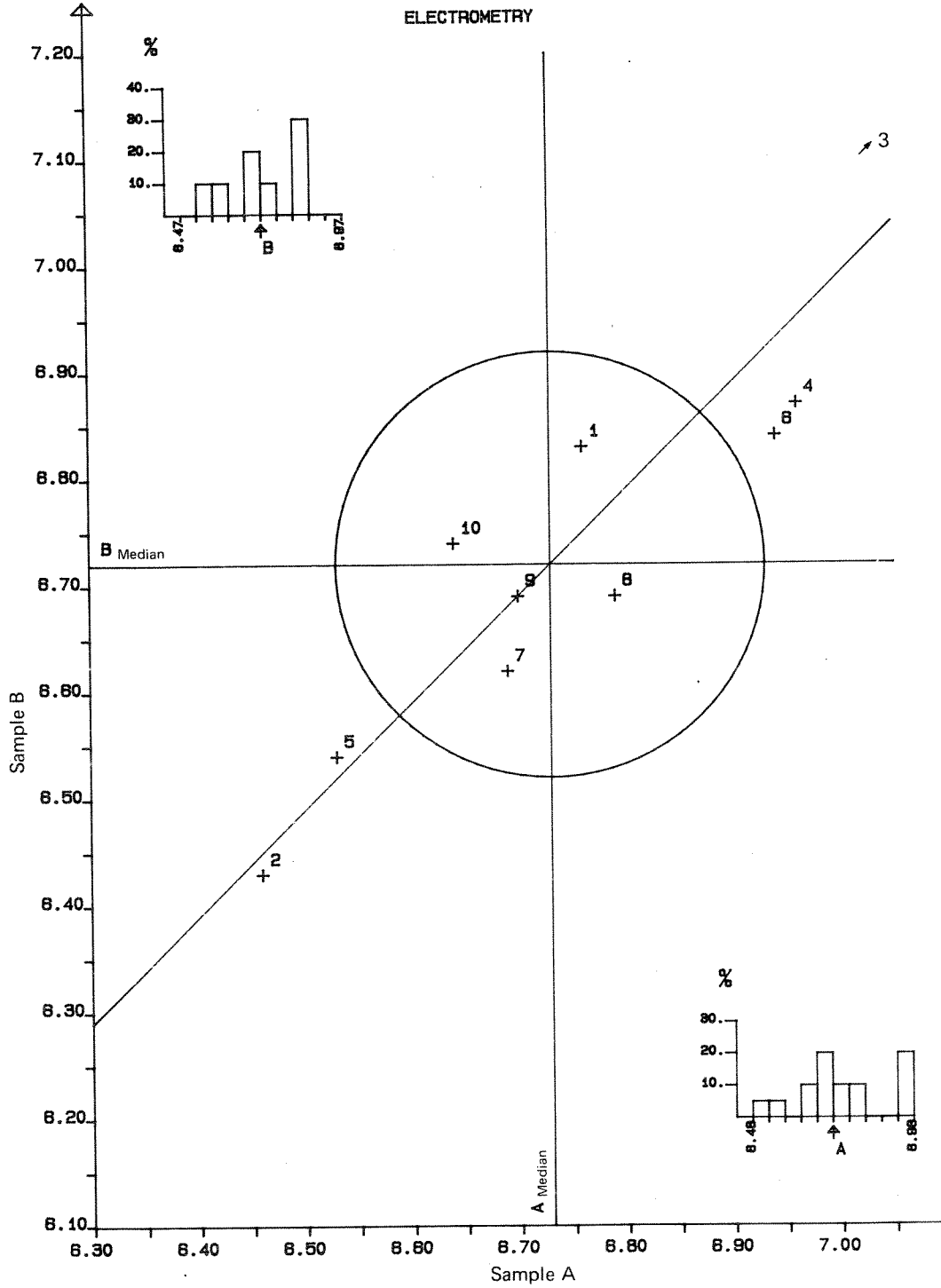


FIG. 2 CONDUKTIVITY ELECTROMETRY

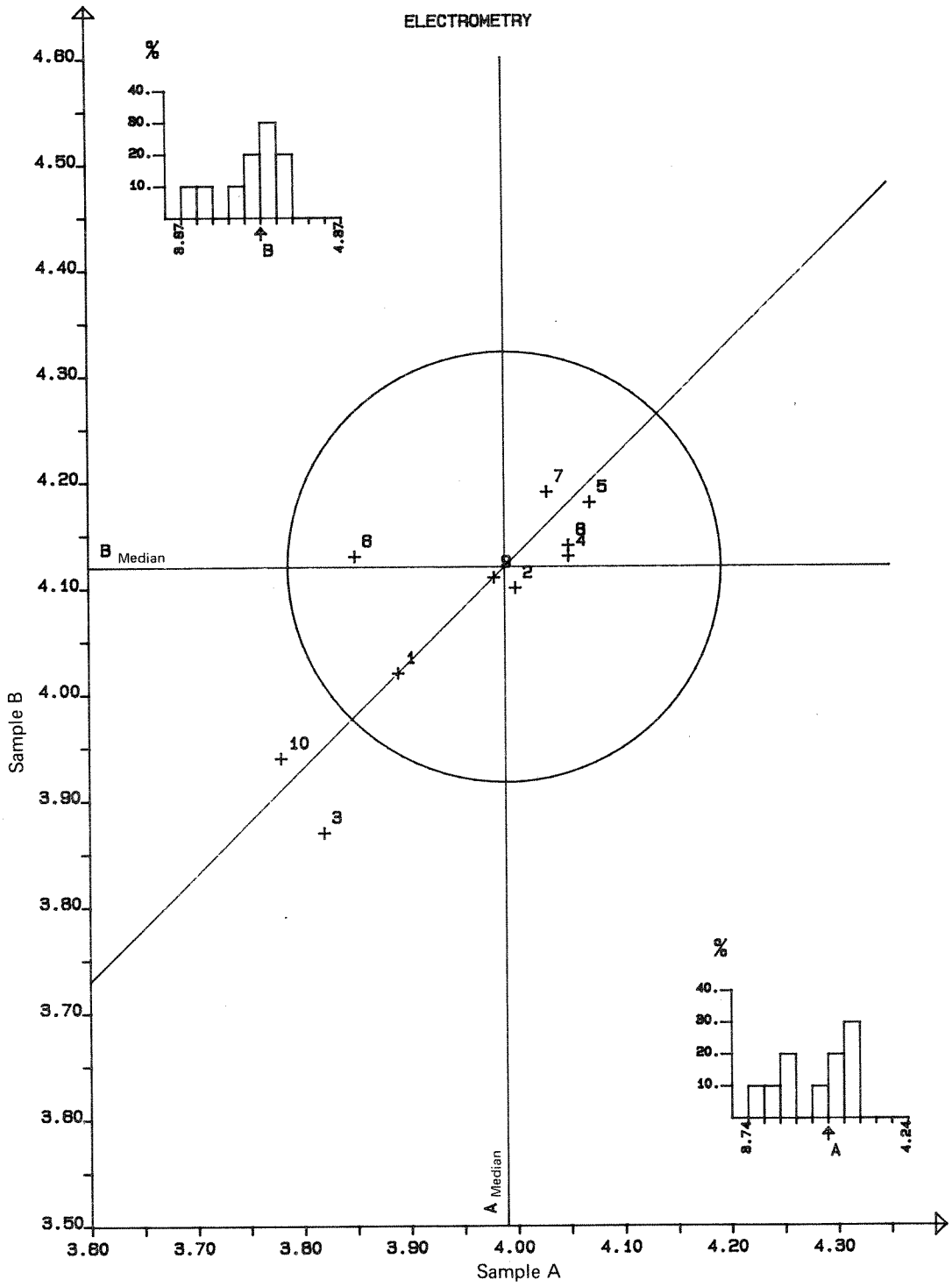


FIG. 3 ALKALINITY ALL METHODS

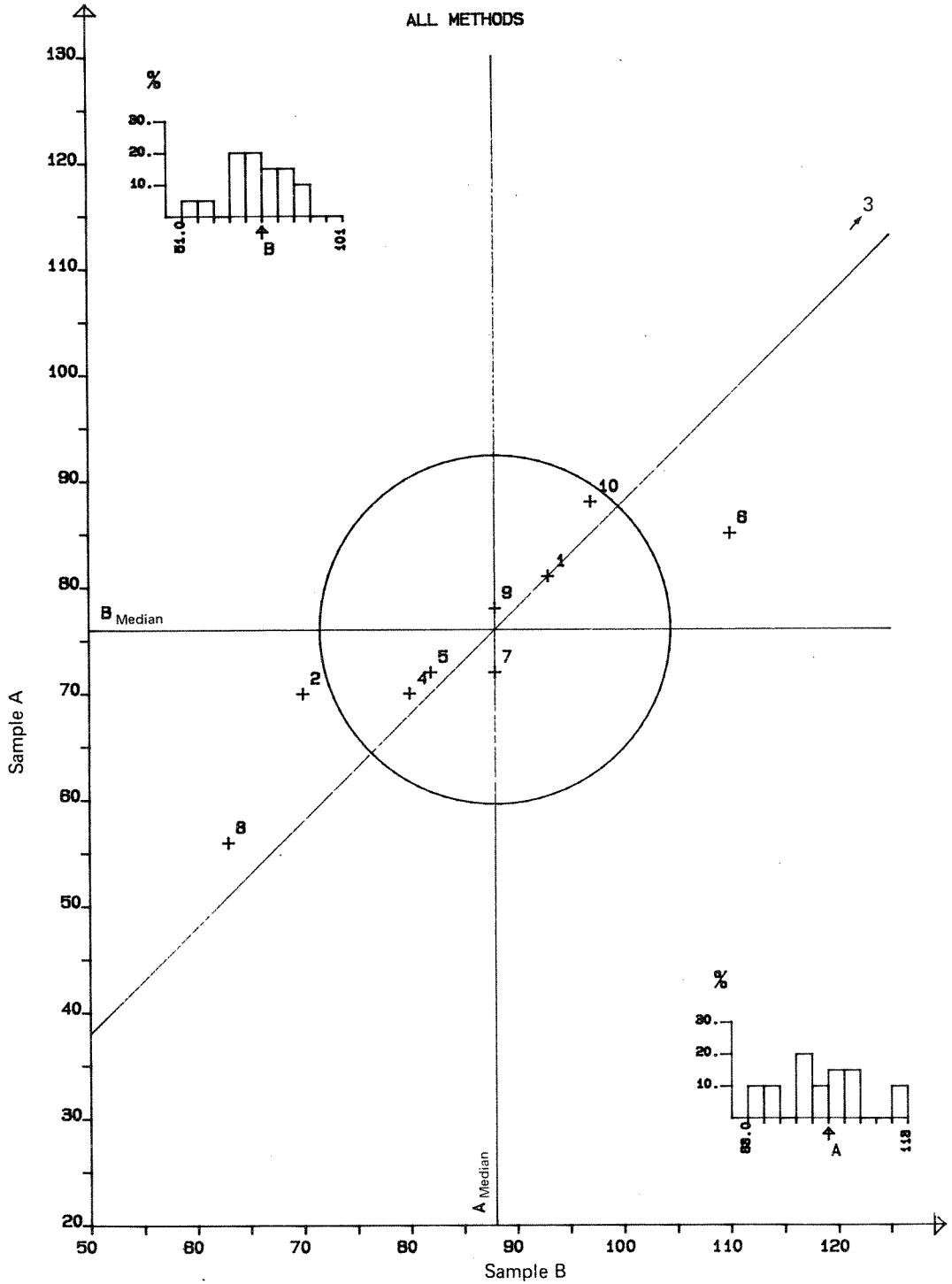


FIG. 4 NITRATE - NITROGEN
ALL METHODS

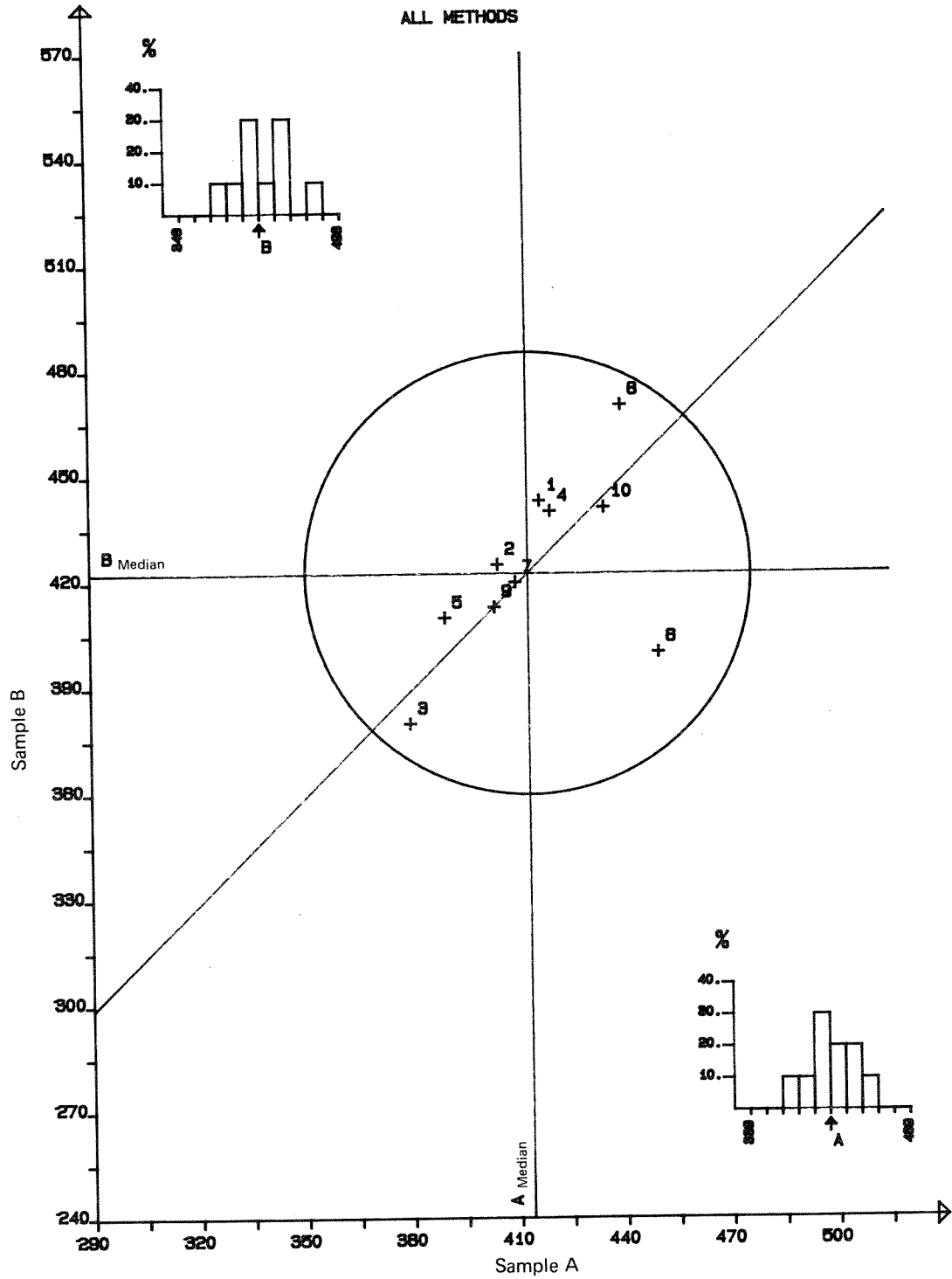


FIG. 5 SULFATE ALL METHODS

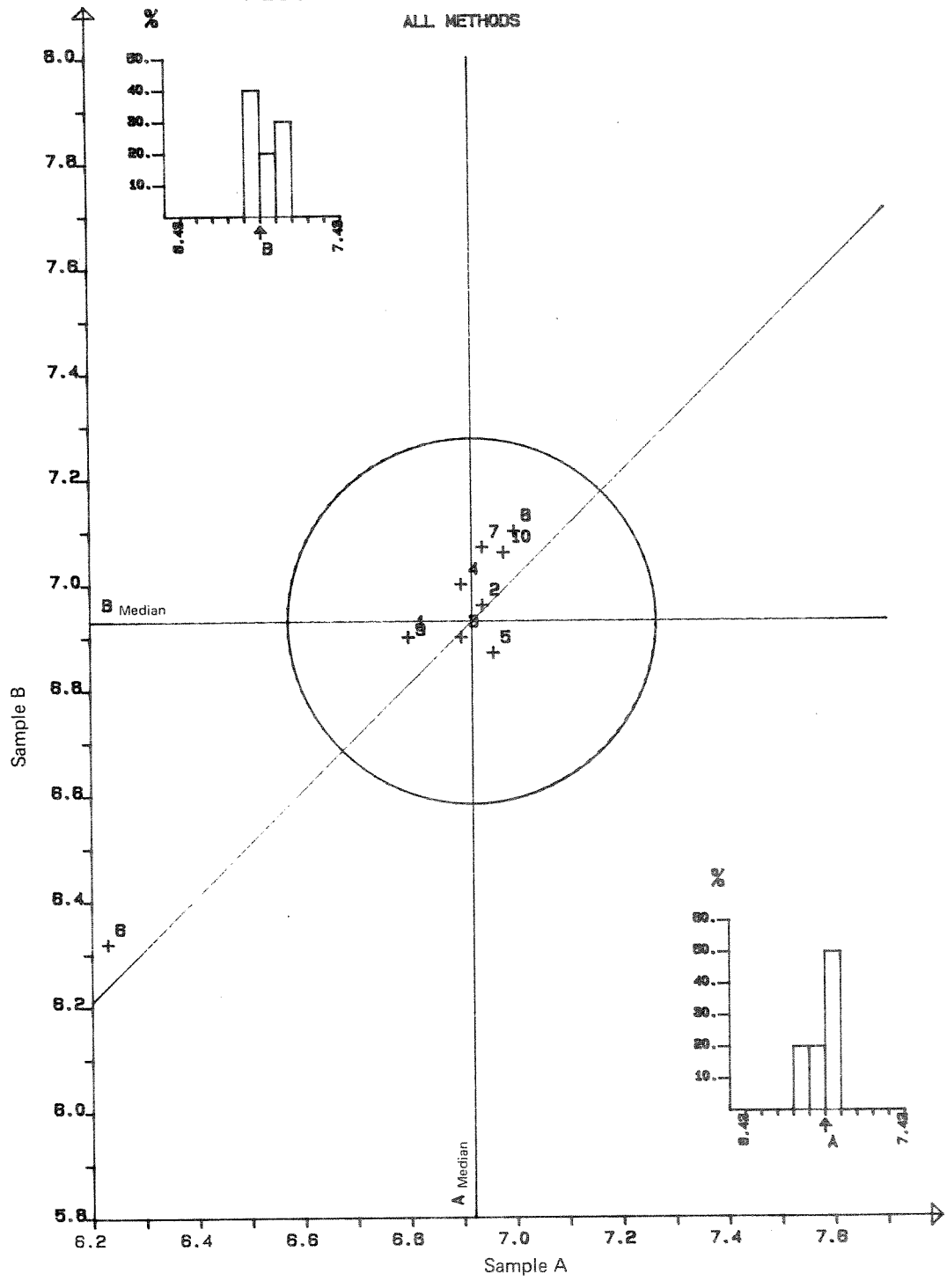


FIG. 6 CHLORIDE ALL METHODS

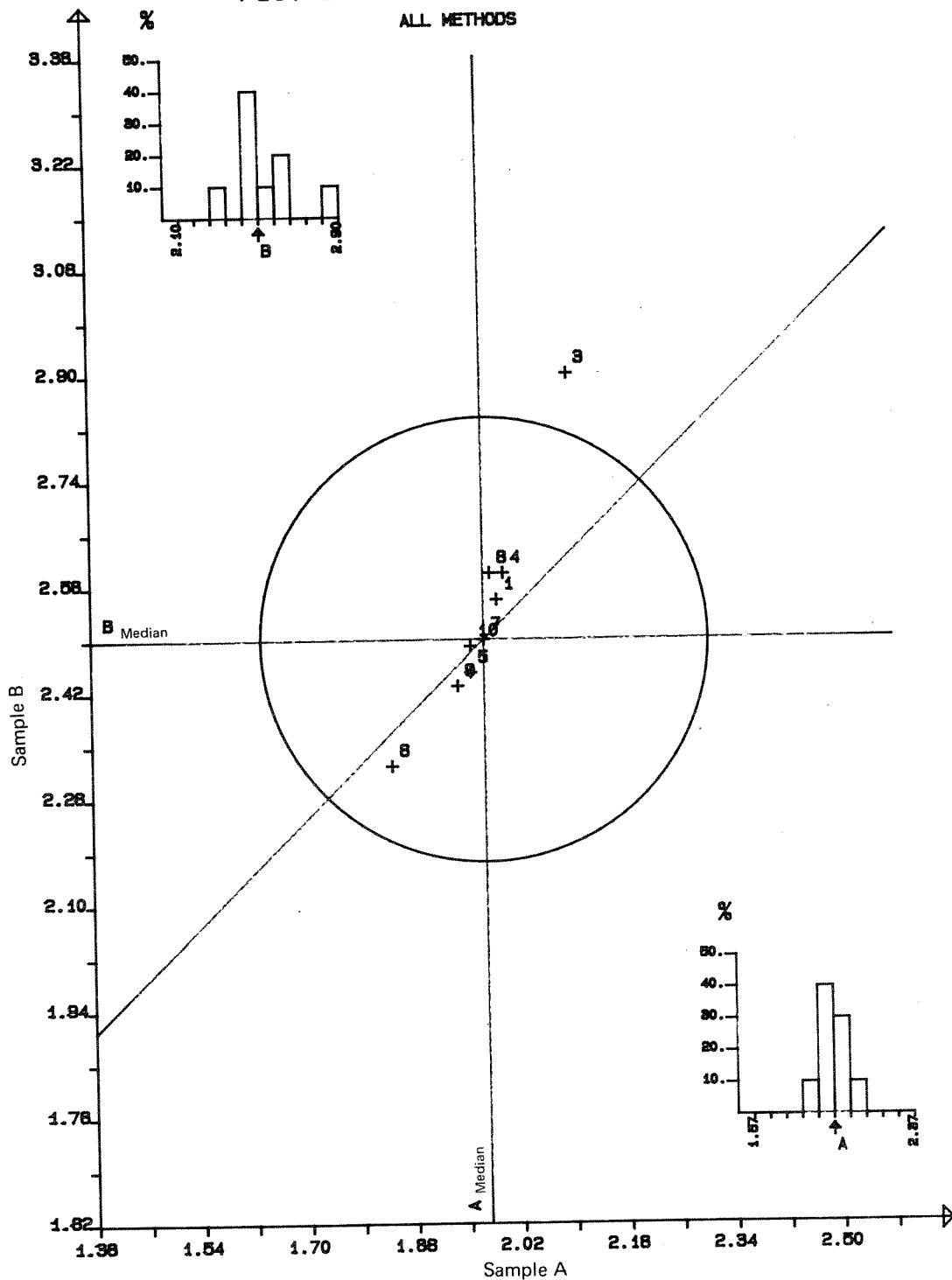


FIG. 7 CALCIUM ALL METHODS

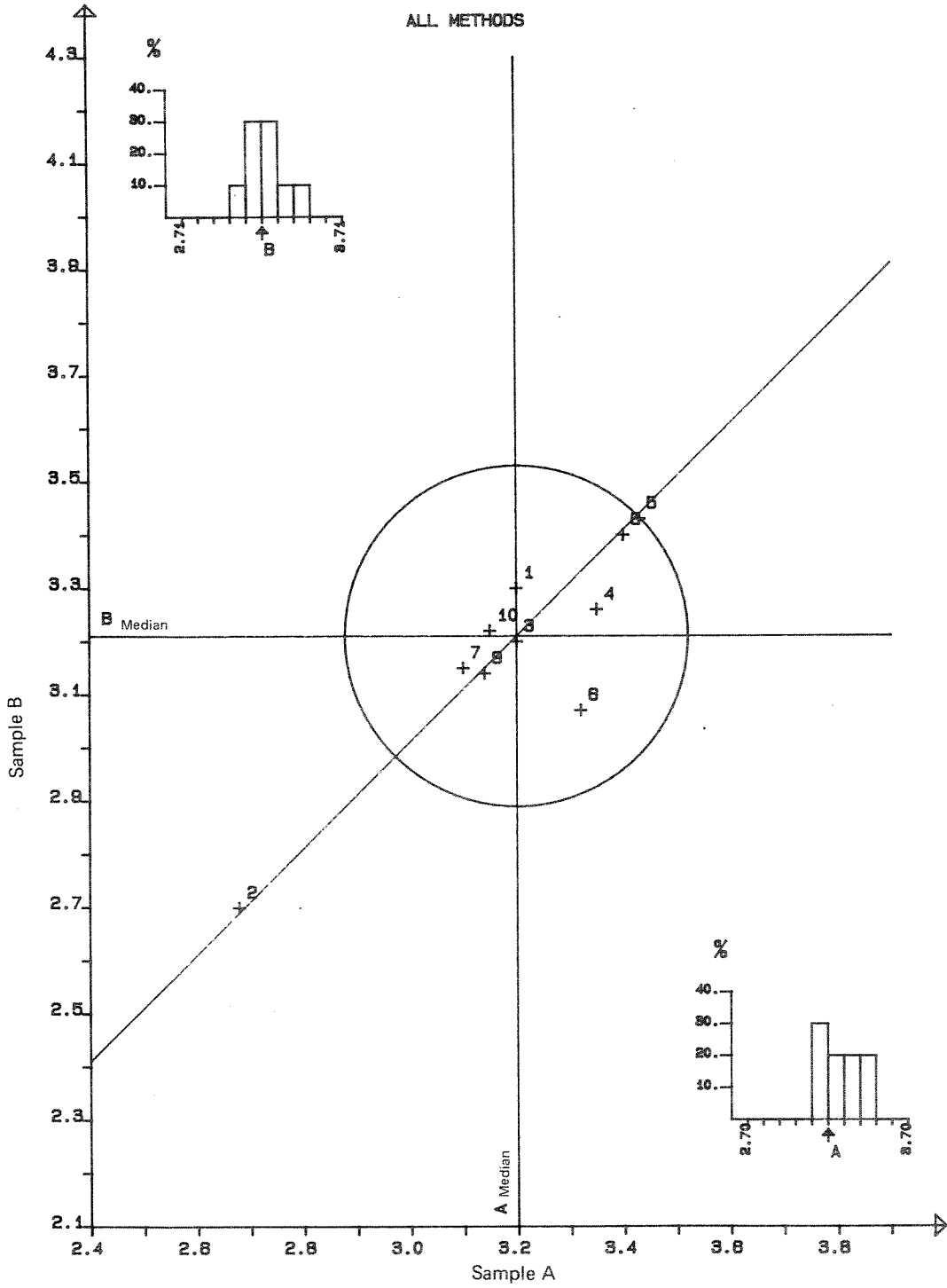


FIG. 8 MAGNESIUM ALL METHODS

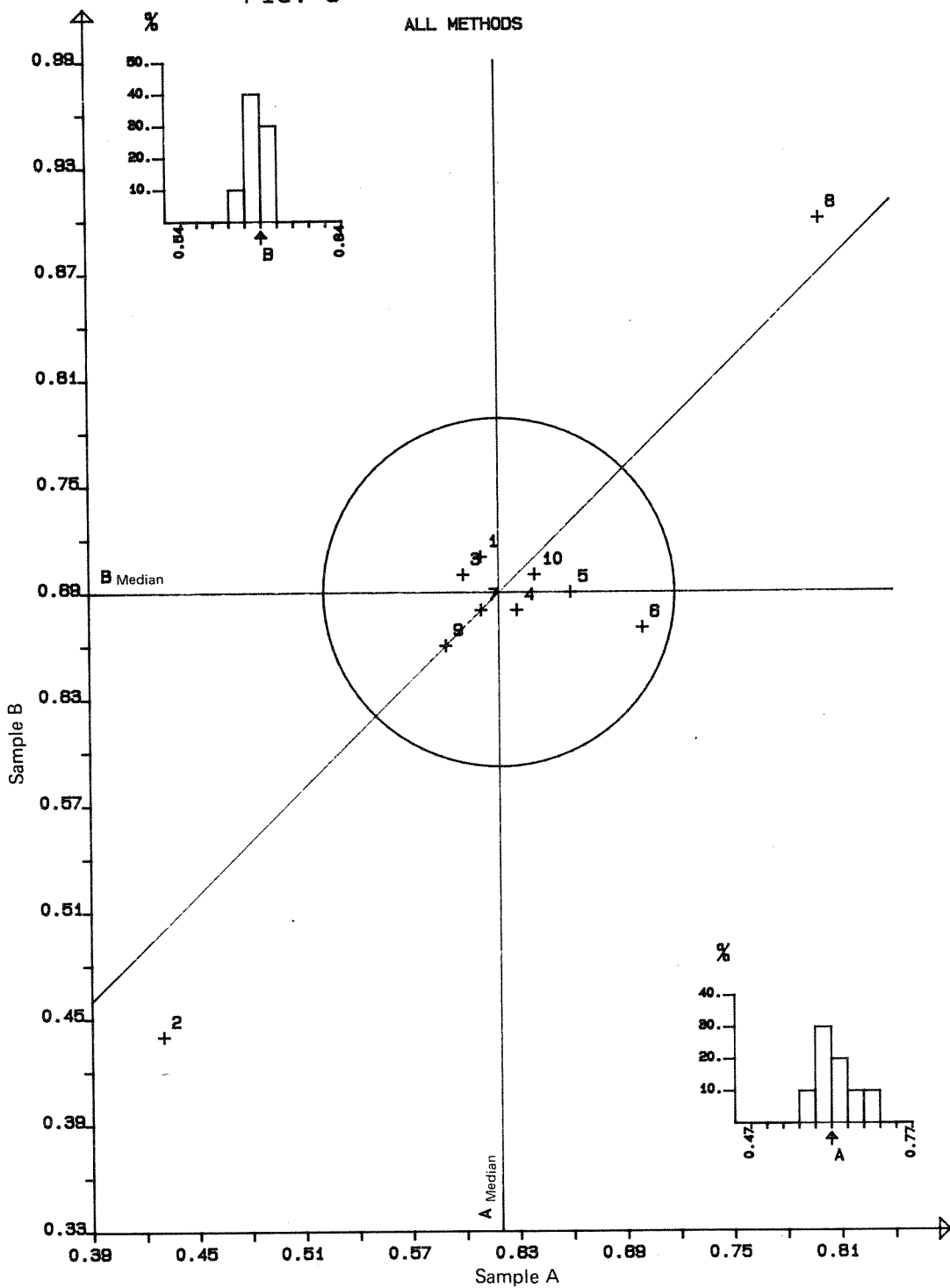


FIG. 9 SODIUM ALL METHODS

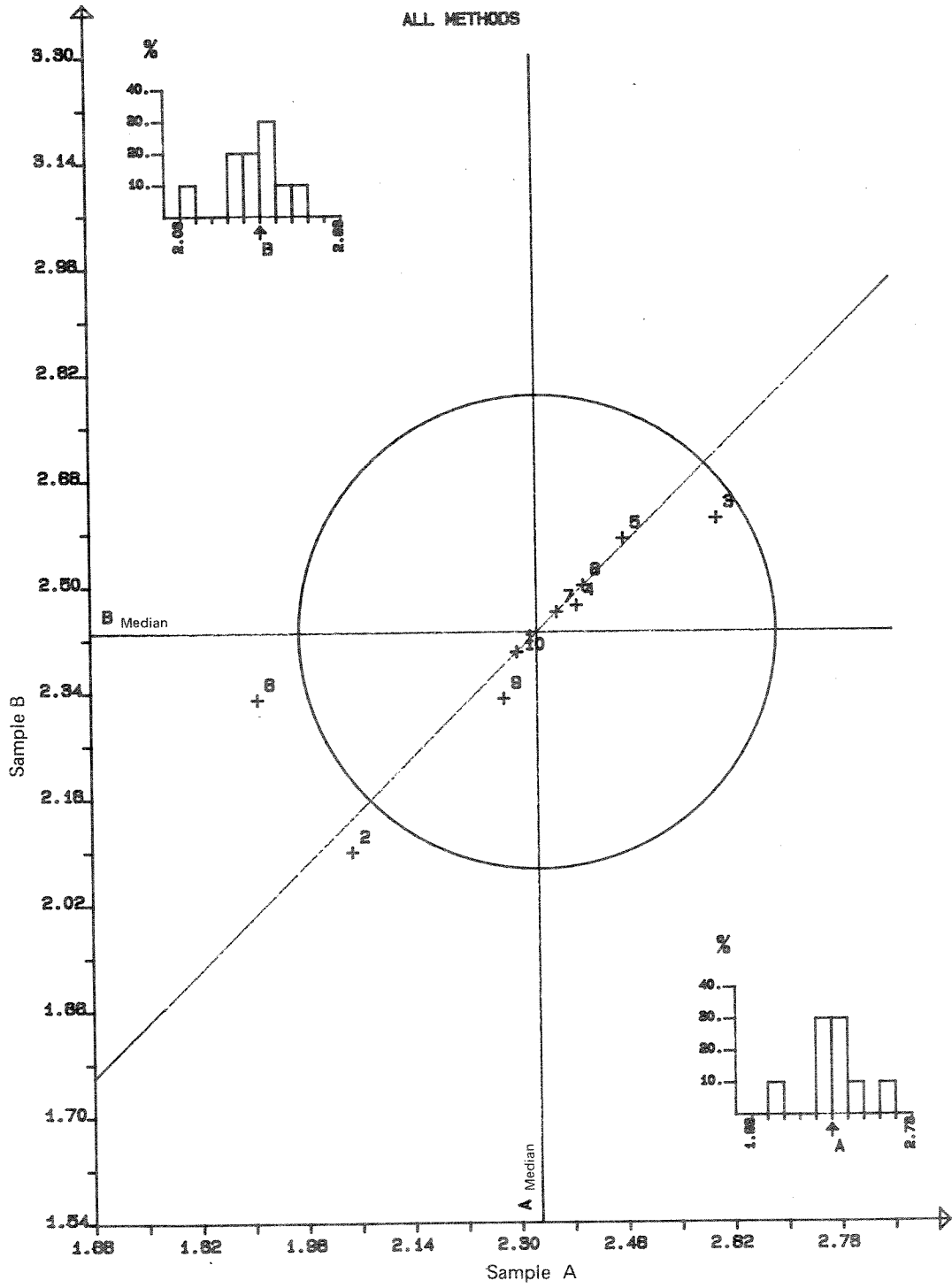


FIG. 10 POTASSIUM
ALL METHODS

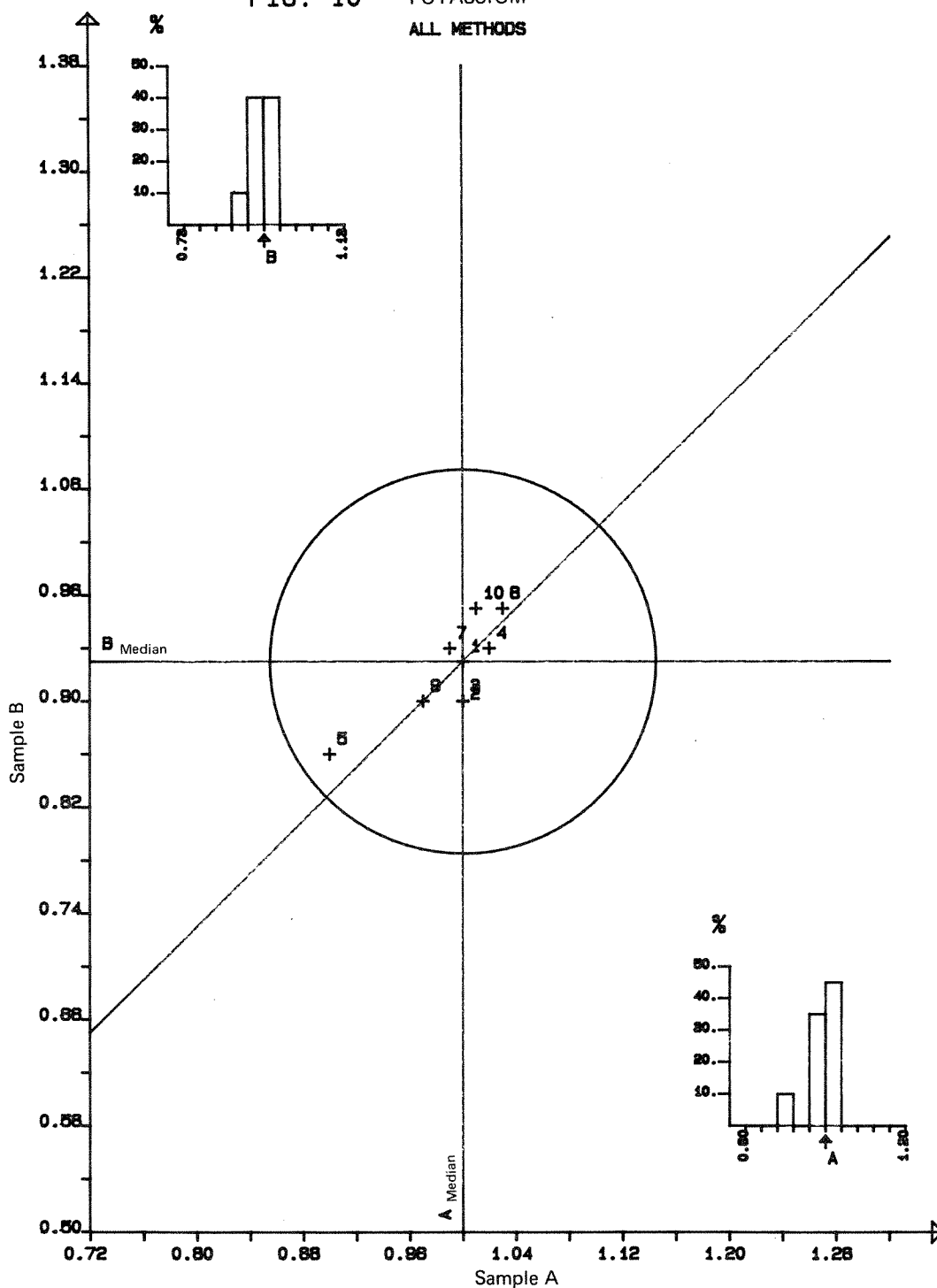


FIGURE 11. IONIC BALANCE

SAMPLE A

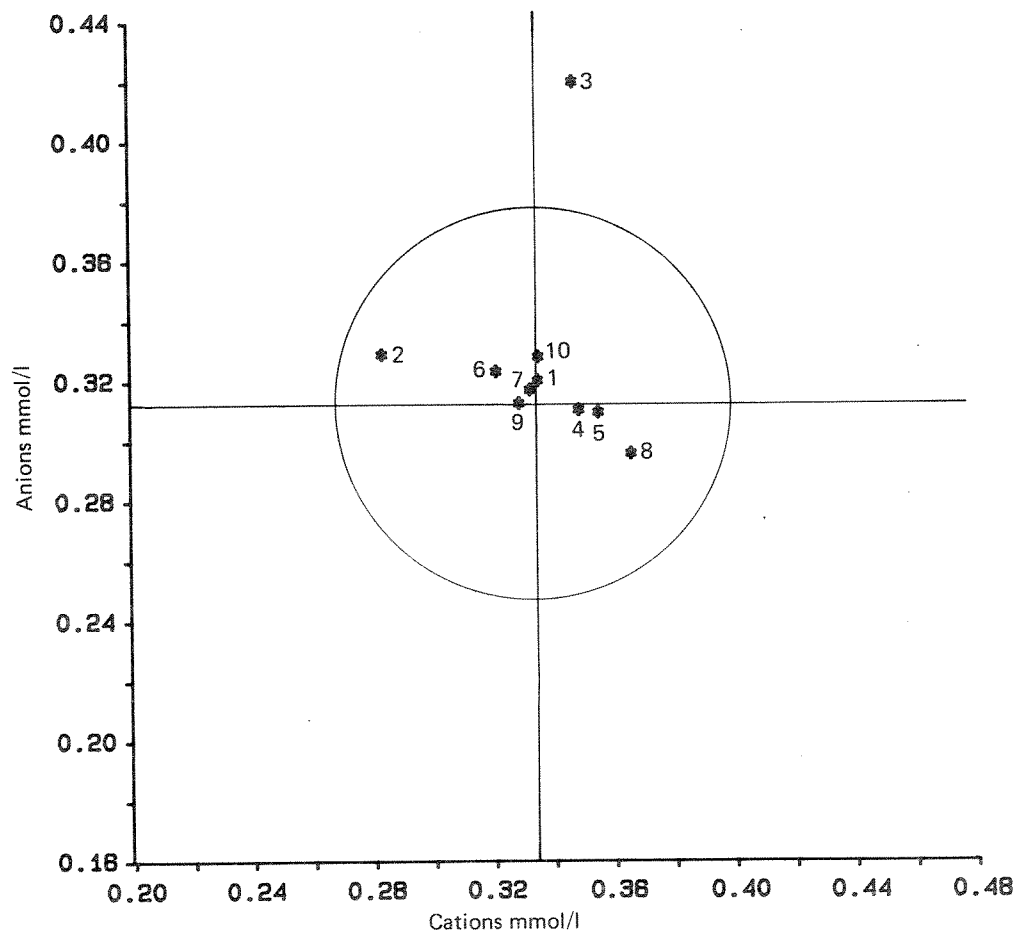
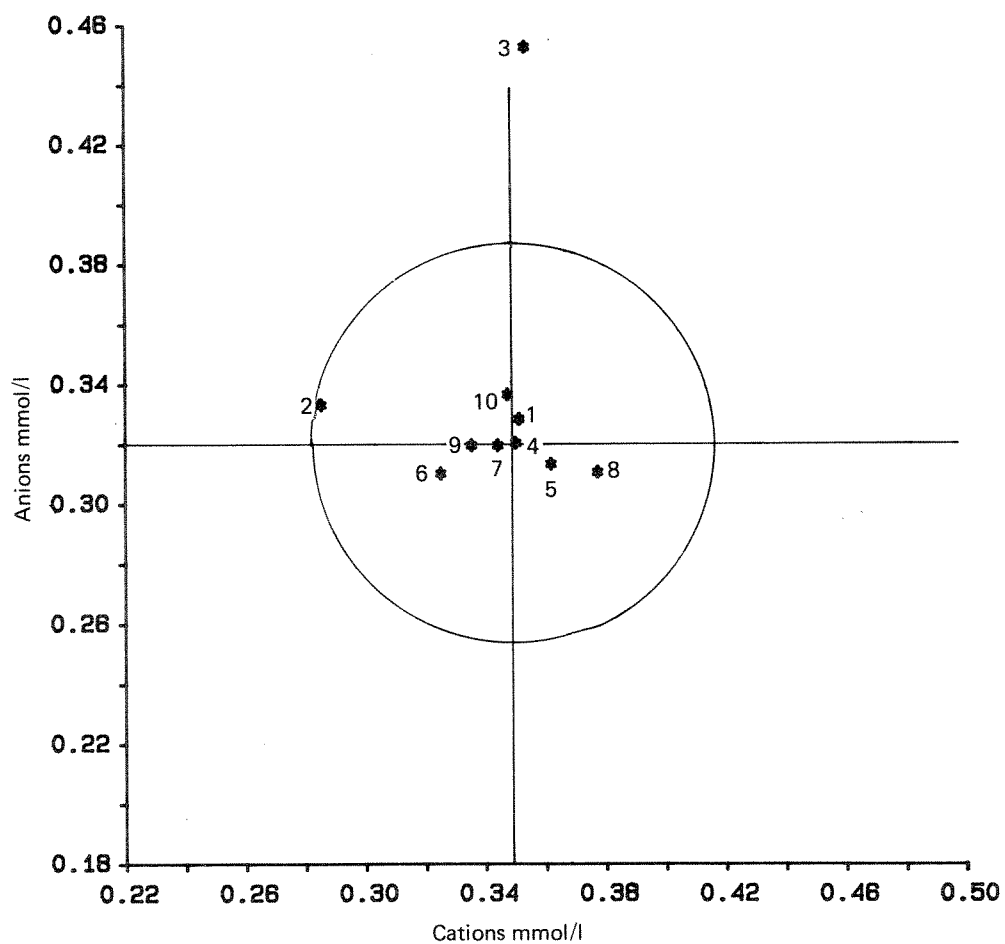


FIGURE 12. IONIC BALANCE

SAMPLE B



Conductivity

The conductivity results are presented in figure 2 and table 9 (appendix 4). Some correspondance was necessary to clarify the units of the reported results. All the laboratories applied an electrometric method for the determination of conductivity.

A very good agreement between the results of the participating laboratories was achieved. The general suggestion for target accuracy is 20 %. However, as demonstrated in figure 2, the reported conductivity values - with exception of two pairs of results - are gathered within the 5 % limit, represented by the circle of the figure.

Alkalinity

The alkalinity results - given in $\mu\text{mol/L}$ - are presented in figure 3, and the reported values are given in table 10. Some of the participants are more familiar with the unit mg/L CaCO_3 . To transform the $\mu\text{mol/L}$ values to mg/L , the value is divided by 10. Seven of the participating laboratories determined alkalinity by electrometric titration, while the remaining three laboratories used Gran plot titration. There is no significant difference between the results of these two methods.

The general target accuracy of 20 percent is represented by the circle in figure 3. Four pair of results are lying outside this limit. Deviating results may arise from different ways of defining the end point of the titration (4). This effect is most distinct in solutions with low alkalinity.

Nitrate

The nitrate results are presented in figure 4, and the reported values are given in table 11. Six laboratories determined nitrate by an automated photometric method, while the four others used ion chromatography.

The statistical information given in table 1 shows that there is a systematic difference between the two methods, the deviation between the median values being about 5 percent. Still, the results are well within the general target accuracy, even lying within the 15 percent limit represented by the circle in figure 4.

Sulfate

The sulfate results are presented in figure 5 and table 12. With one exception all the laboratories were using ion chromatography for the determination of sulfate. One laboratory used an automated, photometric method based on dissociation of the barium-thorin complex.

The comparability of the results is excellent, nine of the result pairs lying well within a 5 percent limit, represented by the circle in figure 5. The systematically low result pair is lying within a 15 percent limit.

Chloride

The chloride results are presented in figure 6, and the reported values are given in table 13. With one exception all the laboratories determined chloride using ion chromatography. One laboratory used an automated, photometric version of the mercury thiocyanate method. All the results are lying within the general 20 percent limit; eight of the result pairs even being within a 10 percent limit illustrated by the circle in figure 6.

Calcium

The calcium results are presented in figure 7, and the reported values are given in table 14. Eight of the laboratories used atomic absorption spectrometry for the determination, while two laboratories determined calcium with ICP emission spectrometry.

Only one lab achieved systematically low results, and is outside the general accuracy limit of 20 percent. The result pairs of the other laboratories are gathered within a ten percent limit, represented by the circle in figure 7.

Magnesium

The magnesium results are presented in figure 8, and the reported values are given in table 15. The majority of the participant used atomic absorption spectrometry for the determination of magnesium. Only two laboratories used ICP emission spectrometry for this purpose.

Two of the laboratories have reported values being outside the acceptance limits, one result pair being systematically too low and the other one too high. The remaining result pairs are located within a 15 percent limit, represented by the circle in figure 8.

Sodium

The sodium results are presented in figure 9, and the reported values are given in table 16. Seven laboratories used atomic absorption spectrometry for the determination. Among the remaining laboratories two were using ICP emission spectrometry, and one atomic emission spectrometry. All the results are within the general limit of 20 percent, represented by the circle in figure 9.

Potassium

The potassium results are presented in figure 10, and the reported values are given in table 17. One laboratory determined potassium by ICP emission spectrometry, all the others were using atomic absorption spectrometry. All the result pairs were lying well within a limit of 15 percent, represented by the circle in figure 10.

Ionic balance

The ionic balance were calculated by adding together the molar concentrations of the major anions (alkalinity, nitrate, sulfate, and chloride) and the major cations (calcium, magnesium, sodium, and potassium), respectively, based on the reported values. For this purpose, results reported as "less than X" were put equal to the determination limit X.

The calculated values of the sum of the anions and the sum of the cations, are presented in the figures 11 and 12 for the samples A and B, respectively. The calculated values are given in table 2. A limit of 10 % is represented by the circle in the figures. Only one laboratory has deviating results, the anion sum being systematically too high.

For the samples A and B, there are a mean difference of 0.022 and 0.029 mmol/L between the sum of cations and the sum of anions, respectively. This is due to the fact that the major inorganic ions only have been taken into consideration in these calculations. This particularly will affect the anion sum, as the content of total organic carbon is about 3.5 mg/L, and the concentration of organic anions, therefore, should be significant.

Table 26. Ionic balance calculations. The sums of the anion and the cation concentrations are given in mmol/L.

Lab.no	Sample A		Sample B	
	Anion	Cation	Anion	Cation
1	0.3205	0.3355	0.3285	0.3513
2	0.3292	0.2835	0.3333	0.2853
3	0.4200	0.3477	0.4526	0.3534
4	0.3106	0.3490	0.3205	0.3501
5	0.3098	0.3555	0.3134	0.3617
6	0.3235	0.3217	0.3103	0.3250
7	0.3173	0.3328	0.3197	0.3442
8	0.2960	0.3662	0.3107	0.3772
9	0.3129	0.3292	0.3197	0.3353
10	0.3284	0.3357	0.3367	0.3475
median	0.3139	0.3356	0.3201	0.3487

CONCLUSION

The general rule for target accuracies, as outlined in the Manual for Chemical and Biological Monitoring (1), are used as a basis for the evaluation of the results. This rule correspond to an acceptance limit equal to the detection limit or 20 % of the true value, whatever being the greater. An exception is pH where the target accuracy is 0,1 units.

In table 3 are presented an evaluation of the results of this inter calibration, with the acceptance limits used, and the percentage of acceptable results.

Table 3. Evaluation of the results of intercalibration 8802.

Parameter	General limit	Acceptable results	Special limit	Acceptable results
pH	0.1	30 %	0.2	50 %
Conductivity	20 %	100 %	5 %	80 %
Alkalinity	20 %	60 %		
Nitrate	20 %	100 %	10 %	70 %
Chloride	20 %	90 %	10 %	70 %
Sulfate	20 %	100 %	10 %	90 %
Calcium	20 %	90 %	10 %	90 %
Magnesium	20 %	80 %	10 %	70 %
Sodium	20 %	100 %	10 %	70 %
Potassium	20 %	90 %	10 %	80 %

For conductivity, nitrate, sulfate and sodium, all the results are within the limits based on the general target accuracy. For chloride, calcium, magnesium, and potassium, one or two laboratories have reported values outside the general limit. By some improvement of the routine analytical method, these laboratories should attain acceptable results. In table 3 there is also given an example of an interpretation based on narrower limits (the so-called special limits in table 3). The high percentage of acceptable results with these limits, indicates that there might be only a small problem to achieve all the results even within these limits.

For pH and alkalinity the picture is more serious. It is possible that

a normalization of the analytical methods used at the different laboratories might lead to an improvement. Better comparability is necessary for these two parameters.

LITERATURE

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APPENDIX

APPENDIX 1

PARTICIPANTS OF INTERCALIBRATION 8802 AND THEIR CODE NUMBERS.

1. Consiglio Nazionale delle Ricerche, Pallanza, Italia.
2. National Institute for Physical Planning and Construction Research, Dublin, Ireland.
3. Bayerische Landesamt für Wasserwirtschaft, München, Federal Republic of Germany.
4. National Board of Waters and Environment, Helsinki, Finland.
5. National Environment Protection Board, Uppsala, Sweden.
6. Institute d'Hygiène et d'Epidémiologie, Bruxelles, Belgium.
7. National Water Quality Laboratory, Burlington, Canada.
8. Ontario Ministry of Environment, Rexdale, Canada.
9. Norwegian Institute for Water Research, Oslo, Norway.
10. Lockheed Emsco, Las Vegas, USA.

APPENDIX 2

PREPARATION AND CONTROL ANALYSES OF THE SAMPLES

Stock solutions were prepared by dissolution of exactly weighted amounts of "pro analysi" quality chemicals, and made up to 1000 mL with deionized water. In table 4 the concentrations of the chemical parameters in these solutions are given.

Table 4. Preparation of stock solutions

Solution no.	Compound	Amount, g/L	Concentration
I	NaHCO_3	7,0975	0,0845 mol/L = 1943 mg/L Na
II	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	5,327	0,02161 mol/L = 525 mg/L Mg = 2076 mg/L SO_4
III	KNO_3	3,6725	0,03632 mol/L = 1421 mg/L K = 508 mg/L $\text{NO}_3\text{-N}$
IV	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	1,8125	0,01232 mol/L = 494 mg/L Ca = 874 mg/L Cl

The two sample solutions were prepared from natural water, collected at the lake Maridalsvannet, a water supply lake located outside Oslo, Norway. 60 litres of raw water was collected in a polyetylen container and stored at room temperature for a couple of weeks at the laboratory. During this stabilization time suspended matter settled.

The required volume of this solution was filtered through 0,45 μm membrane filter, and two 20 L portions of the filtrate was transferred to polyethylene containers. Small aliquots were removed from the filtrate for determination of background concentrations of the constituents of interest.

Two water samples (A and B) were prepared by addition of small volumes of the stock solutions to the 20 L portions of the filtrate, to adjust the concentrations of the major ions (table 5). During the following

week the solutions were shaken several times. Then the solutions were transferred to 1 L polyethylene bottles with screw cap. These samples were stored at room temperature until mailing to the participating laboratories.

Table 5. Adjustment of concentrations of the major ions.

Stock solution	Volume ml		Parameter	Concentration increase		
	A	B		Sample A	Sample B	
I	10	8	Alkalinity	42	34	$\mu\text{mol/L}$
			Sodium	0.97	0.78	mg/L
II	4	5	Sulfate	0.42	0.52	mg/l
			Magnesium	0.11	0.13	mg/L
III	9	8	Nitrate	229	203	$\mu\text{g/L}$
			Potassium	0.64	0.57	mg/L
IV	5	6	Chloride	0.22	0.26	mg/L
			Calcium	0.12	0.15	mg/L

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 six weeks after the reporting deadline of this intercalibration.

The control analyses confirm that the sample solutions were stable during the intercalibration period, and a summary of the control results is presented in table 6.

Table 6. Summary of the control analysis.

Parameter	Sample A		Sample B	
	mean	sdev.	mean	sdev.
pH	6.70	0.027	6.69	0.042
Kond mS/m	3.98	0.048	4.11	0.058
Alk $\mu\text{mol/L}$	88	1.5	78	2.6
$\text{NO}_3\text{-N}$ $\mu\text{g/L}$	404	14.6	413	9.9
SO_3 mg/L	6.8	0.16	6.9	0.12
Cl^4 mg/L	1.93	0.05	2.43	0.08
Ca mg/L	3.14	0.017	3.14	0.026
Mg mg/L	0.59	0.011	0.66	0.019
Na mg/L	2.28	0.071	2.33	0.068
K mg/L	0.97	0.017	0.90	0.008

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 1 is plotted against the result of sample 2 (see figs. 1 - 10).

The graphical presentation makes it possible to distinguish between random and systematic errors affecting the results. The two straight lines drawn in the diagram are representing the true values of the samples; or the median value of the results from all the participating laboratories when the true value is not known. The diagram is 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 errors - 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 for the total error of the results. The distance along the 45° line is giving the magnitude 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 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 $\pm 50\%$, are omitted from the statistical calculations. The remaining results are used for the calculation of the mean value (\bar{x}) and the standard deviation (s). Now the pairs of results where one or both of the values are lying outside $\bar{x} \pm 3 \cdot s$, are omitted. The remaining results are used for a final calculation, the results of which are presented in the tables 8 - 17. The results being

omitted from the calculations, are marked with the letter "U".

Table 7. The individual result of the participants.

	PH		KOND MS/M		ALK MMOL/L		NO3-N MIKG/L		CL MG/L	
	A	B	A	B	A	B	A	B	A	B
1	6.76	6.83	3.89	4.02	93.0	81.0	417.	443.	1.99	2.56
2	6.46	6.43	4.00	4.10	70.0	70.0	405.	425.	3.04	3.12
3	7.28	7.30	3.82	3.87	190.	200.	380.	380.	2.10	2.90
4	6.96	6.87	4.05	4.13	80.0	70.0	420.	440.	2.00	2.60
5	6.53	6.54	4.07	4.18	82.0	72.0	390.	410.	1.95	2.45
6	6.94	6.84	3.85	4.13	110.	85.0	450.	400.	1.83	2.31
7	6.69	6.62	4.03	4.19	88.0	72.0	410.	420.	1.97	2.50
8	6.79	6.69	4.05	4.14	63.0	56.0	440.	470.	1.98	2.60
9	6.70	6.69	3.98	4.11	88.0	78.0	404.	413.	1.93	2.43
10	6.64	6.74	3.78	3.94	97.0	88.0	435.	441.	1.95	2.49

	SO4 MG/L		CA MG/L		MG MG/L		NA MG/L		K MG/L	
	A	B	A	B	A	B	A	B	A	B
1	6.80	6.90	3.20	3.30	0.61	0.71	2.30	2.40	1.00	0.93
2	6.94	6.96	2.68	2.70	0.43	0.44	2.05	2.10	1.00	0.90
3	6.90	6.90	3.20	3.20	0.60	0.70	2.60	2.60	1.00	0.90
4	6.90	7.00	3.35	3.26	0.63	0.68	2.39	2.47	1.02	0.94
5	6.96	6.87	3.43	3.43	0.66	0.69	2.46	2.57	0.90	0.86
6	6.23	6.32	3.32	3.07	0.70	0.67	1.91	2.33	-	-
7	6.94	7.07	3.10	3.15	0.61	0.68	2.36	2.46	0.99	0.94
8	7.00	7.10	3.40	3.40	0.80	0.90	2.40	2.50	1.03	0.97
9	6.80	6.90	3.14	3.14	0.59	0.66	2.28	2.33	0.97	0.90
10	6.98	7.06	3.15	3.22	0.64	0.70	2.30	2.40	1.01	0.97

Table 8. Statistics, pH

Analytical method: Electrometry

Unit:

Sample A

Number of participants:	10	Range:	0.82
Number of omitted results:	0	Variance:	0.06
True value:	6.73	Standard deviation:	0.24
Mean value:	6.77	Relative standard deviation:	3.5 %
Median	6.73	Relative error:	0.7 %

Analytical results in ascending order:

2	6.46	:	9	6.70	:	6	6.94
5	6.53	:	1	6.76	:	4	6.96
10	6.64	:	8	6.79	:	3	7.28
7	6.69						

Sample B

Number of participants:	10	Range:	0.87
Number of omitted results:	0	Variance:	0.06
True value:	6.72	Standard deviation:	0.24
Mean value:	6.76	Relative standard deviation:	3.5 %
Median	6.72	Relative error:	0.5 %

Analytical results in ascending order:

2	6.43	:	9	6.69	:	6	6.84
5	6.54	:	10	6.74	:	4	6.87
7	6.62	:	1	6.83	:	3	7.30
8	6.69						

Table 9. Statistics, Conductivity

Analytical method: Electrometry

Unit: mS/m (25 °C)

Sample A

Number of participants:	10	Range:	0.29
Number of omitted results:	0	Variance:	0.01
True value:	3.99	Standard deviation:	0.11
Mean value:	3.95	Relative standard deviation:	2.7 %
Median	3.99	Relative error:	-1.0 %

Analytical results in ascending order:

10	3.78	:	9	3.98	:	4	4.05
3	3.82	:	2	4.00	:	8	4.05
6	3.85	:	7	4.03	:	5	4.07
1	3.89						

Sample B

Number of participants:	10	Range:	0.32
Number of omitted results:	0	Variance:	0.01
True value:	4.12	Standard deviation:	0.11
Mean value:	4.08	Relative standard deviation:	2.6 %
Median	4.12	Relative error:	-1.0 %

Analytical results in ascending order:

3	3.87	:	9	4.11	:	8	4.14
10	3.94	:	4	4.13	:	5	4.18
1	4.02	:	6	4.13	:	7	4.19
2	4.10						

Table 10. Statistics, Alkalinity

Analytical method: All methods

Unit: $\mu\text{mol/L}$ -----
Sample A

Number of participants:	10	Range:	47.0
Number of omitted results:	1	Variance:	198.8
True value:	88.0	Standard deviation:	14.1
Mean value:	85.7	Relative standard deviation:	16.5 %
Median	88.0	Relative error:	-2.7 %

Analytical results in ascending order:

8	63.0	:	7	88.0	:	10	97.0
2	70.0	:	9	88.0	:	6	110.
4	80.0	:	1	93.0	:	3	190. U
5	82.0						

Sample B

Number of participants:	10	Range:	32.0
Number of omitted results:	1	Variance:	92.8
True value:	76.0	Standard deviation:	9.6
Mean value:	74.7	Relative standard deviation:	12.9 %
Median	72.0	Relative error:	-1.8 %

Analytical results in ascending order:

8	56.0	:	5	72.0	:	6	85.0
2	70.0	:	9	78.0	:	10	88.0
4	70.0	:	1	81.0	:	3	200. U
7	72.0						

U = omitted results

Table 11. Statistics, Nitrate

Analytical method: All methods

Unit: $\mu\text{g/L}$ (as N)-----
Sample A

Number of participants:	10	Range:	70.0
Number of omitted results:	0	Variance:	486.1
True value:	413.5	Standard deviation:	22.1
Mean value:	415.1	Relative standard deviation:	5.3 %
Median	413.5	Relative error:	0.4 %

Analytical results in ascending order:

3	380.	:	7	410.	:	10	435.
5	390.	:	1	417.	:	8	440.
9	404.	:	4	420.	:	6	450.
2	405.						

Sample B

Number of participants:	10	Range:	90.0
Number of omitted results:	0	Variance:	652.0
True value:	422.5	Standard deviation:	25.5
Mean value:	424.2	Relative standard deviation:	6.0 %
Median	422.5	Relative error:	0.4 %

Analytical results in ascending order:

3	380.	:	7	420.	:	10	441.
6	400.	:	2	425.	:	1	443.
5	410.	:	4	440.	:	8	470.
9	413.						

Table 12. Statistics, Sulfate

Analytical method: All methods

Unit: mg/L (as SO₄)-----
Sample A

Number of participants:	10	Range:	0.77
Number of omitted results:	0	Variance:	0.05
True value:	6.92	Standard deviation:	0.23
Mean value:	6.84	Relative standard deviation:	3.3 %
Median	6.92	Relative error:	-1.1 %

Analytical results in ascending order:

6	6.23	:	4	6.90	:	5	6.96
1	6.80	:	7	6.94	:	10	6.98
9	6.80	:	2	6.94	:	8	7.00
3	6.90						

Sample B

Number of participants:	10	Range:	0.78
Number of omitted results:	0	Variance:	0.05
True value:	6.93	Standard deviation:	0.22
Mean value:	6.91	Relative standard deviation:	3.2 %
Median	6.93	Relative error:	-0.3 %

Analytical results in ascending order:

6	6.32	:	9	6.90	:	10	7.06
5	6.87	:	2	6.96	:	7	7.07
1	6.90	:	4	7.00	:	8	7.10
3	6.90						

Table 13. Statistics, Chloride

Analytical method: All methods

Unit: mg/L

Sample A

Number of participants:	10	Range:	0.27
Number of omitted results:	1	Variance:	0.01
True value:	1.97	Standard deviation:	0.07
Mean value:	1.97	Relative standard deviation:	3.6 %
Median	1.97	Relative error:	-0.2 %

Analytical results in ascending order:

6	1.83	:	7	1.97	:	4	2.00
9	1.93	:	8	1.98	:	3	2.10
5	1.95	:	1	1.99	:	2	3.04 U
10	1.95						

Sample B

Number of participants:	10	Range:	0.59
Number of omitted results:	1	Variance:	0.03
True value:	2.50	Standard deviation:	0.16
Mean value:	2.54	Relative standard deviation:	6.5 %
Median	2.50	Relative error:	1.5 %

Analytical results in ascending order:

6	2.31	:	7	2.50	:	8	2.60
9	2.43	:	1	2.56	:	3	2.90
5	2.45	:	4	2.60	:	2	3.12 U
10	2.49						

U= omitted results

Table 14. Statistics, Calcium

Analytical method: All methods

Unit: mg/L

Sample A

Number of participants:	10	Range:	0.75
Number of omitted results:	0	Variance:	0.05
True value:	3.20	Standard deviation:	0.22
Mean value:	3.20	Relative standard deviation:	6.7 %
Median	3.20	Relative error:	-0.1 %

Analytical results in ascending order:

2	2.68	:	1	3.20	:	4	3.35
7	3.10	:	3	3.30	:	8	3.40
9	3.14	:	6	3.32	:	5	3.43
10	3.15						

Sample B

Number of participants:	10	Range:	0.73
Number of omitted results:	0	Variance:	0.04
True value:	3.21	Standard deviation:	0.20
Mean value:	3.19	Relative standard deviation:	6.4 %
Median	3.21	Relative error:	-0.7 %

Analytical results in ascending order:

2	2.70	:	3	3.20	:	1	3.30
6	3.07	:	10	3.22	:	8	3.40
9	3.14	:	4	3.26	:	5	3.43
7	3.15						

Table 15. Statistics, Magnesium

Analytical method: All methods

Unit: mg/L

Sample A

Number of participants:	10	Range:	0.37
Number of omitted results:	0	Variance:	0.01
True value:	0.62	Standard deviation:	0.09
Mean value:	0.63	Relative standard deviation:	14.9 %
Median	0.62	Relative error:	1.1 %

Analytical results in ascending order:

2	0.43	:	1	0.61	:	5	0.66
9	0.59	:	4	0.63	:	6	0.70
3	0.60	:	10	0.64	:	8	0.80
7	0.61						

Sample B

Number of participants:	10	Range:	0.46
Number of omitted results:	0	Variance:	0.01
True value:	0.69	Standard deviation:	0.11
Mean value:	0.68	Relative standard deviation:	16.1 %
Median	0.69	Relative error:	-1.0 %

Analytical results in ascending order:

2	0.44	:	4	0.68	:	10	0.70
9	0.66	:	5	0.69	:	1	0.71
6	0.67	:	3	0.70	:	8	0.90
7	0.68						

Table 16. Statistics, Sodium

Analytical method: All methods

Unit: mg/L

Sample A

Number of participants:	10	Range:	0.69
Number of omitted results:	0	Variance:	0.04
True value:	2.33	Standard deviation:	0.20
Mean value:	2.30	Relative standard deviation:	8.6 %
Median	2.33	Relative error:	-1.1 %

Analytical results in ascending order:

6	1.91	:	10	2.30	:	8	2.40
2	2.05	:	7	2.36	:	5	2.46
9	2.28	:	4	2.39	:	3	2.60
1	2.30						

Sample B

Number of participants:	10	Range:	0.50
Number of omitted results:	0	Variance:	0.02
True value:	2.43	Standard deviation:	0.14
Mean value:	2.42	Relative standard deviation:	5.9 %
Median	2.43	Relative error:	-0.6 %

Analytical results in ascending order:

2	2.10	:	10	2.40	:	8	2.50
6	2.33	:	7	2.46	:	5	2.57
9	2.33	:	4	2.47	:	3	2.60
1	2.40						

Table 17. Statistics, Potassium

Analytical method: All methods

Unit: mg/L

Sample A

Number of participants:	10	Range:	0.13
Number of omitted results:	1	Variance:	0.00
True value:	1.00	Standard deviation:	0.04
Mean value:	0.99	Relative standard deviation:	3.9 %
Median	1.00	Relative error:	-0.9 %

Analytical results in ascending order:

6	<0.6	:	3	1.00	:	10	1.01
5	0.90	:	2	1.00	:	4	1.02
9	0.97	:	1	1.00	:	8	1.03
7	0.99						

Sample B

Number of participants:	10	Range:	0.11
Number of omitted results:	1	Variance:	0.00
True value:	0.93	Standard deviation:	0.04
Mean value:	0.92	Relative standard deviation:	3.9 %
Median	0.93	Relative error:	-0.7 %

Analytical results in ascending order:

6	<0.6	:	9	0.90	:	4	0.94
5	0.86	:	1	0.93	:	8	0.97
2	0.90	:	7	0.94	:	10	0.97
3	0.90						

U = omitted results