

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

Intercalibration  
8903

Dissolved organic carbon,  
and aluminium fractions



# NIVA - REPORT

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Abstract:  
Ten laboratories in ten countries participated in the third intercalibration, 8803. Based on the general target accuracies of  $\pm 20\%$ , all the results were acceptable for dissolved organic carbon. Acceptable results for the aluminium fractions are varying from 50 to 75%. Differences in the methods used by the participating laboratories, are obviously the main reason for the great deviations between their results. To obtain comparable results for aluminium fractions, exactly the same method must be used by every laboratory.

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

**INTERCALIBRATION 8903**

**Dissolved organic carbon,  
and aluminium fractions**

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

NIVA, Oslo, April 1989

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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 third intercalibration test, called 8803, included the determination of dissolved organic carbon, in addition to different fractions of aluminium: total aluminium, reactive aluminium, labile aluminium and non-labile aluminium.

## **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 1st of november 1988. Most of the participating laboratories received the samples within one or two weeks, except for two laboratories receiving the samples after about three weeks.

## **RESULTS**

Ten laboratories (in ten countries) participated in this third 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.

Table 1. Survey of the results of intercalibration 8803.

Parameter, method	True values		Number of labs.		Median		Mean/standard deviation				Relative Std.dev.		Relative Error	
	A	B	TOT	U	A	B	Mean	Sdev	Mean	Sdev	A	B	A	B
Total organic carbon All methods	11.45	9.75	6	0	11.45	9.75	11.57	0.67	9.77	0.73	5.8	7.5	1.0	0.2
Total aluminium All methods	397.5	357.8	8	0	397.5	357.8	404.0	44.8	350.2	30.7	11.1	8.8	1.6	-2.1
Reactive aluminium All methods	274.5	251.5	8	0	274.5	251.5	282.0	63.4	262.4	55.2	22.5	21.1	2.7	4.3
Non-labile aluminium All methods	157.0	130.5	5	1	157.0	130.5	154.8	8.2	138.8	24.9	5.3	17.9	-1.4	6.3
Labile aluminium All methods	209.0	189.5	6	0	209.0	189.5	193.0	56.8	169.7	39.9	29.4	23.5	-7.7	-10.5

U = omitted result

FIG. 1. TOTAL ORGANIC CARBON (TOC) ALL METHODS

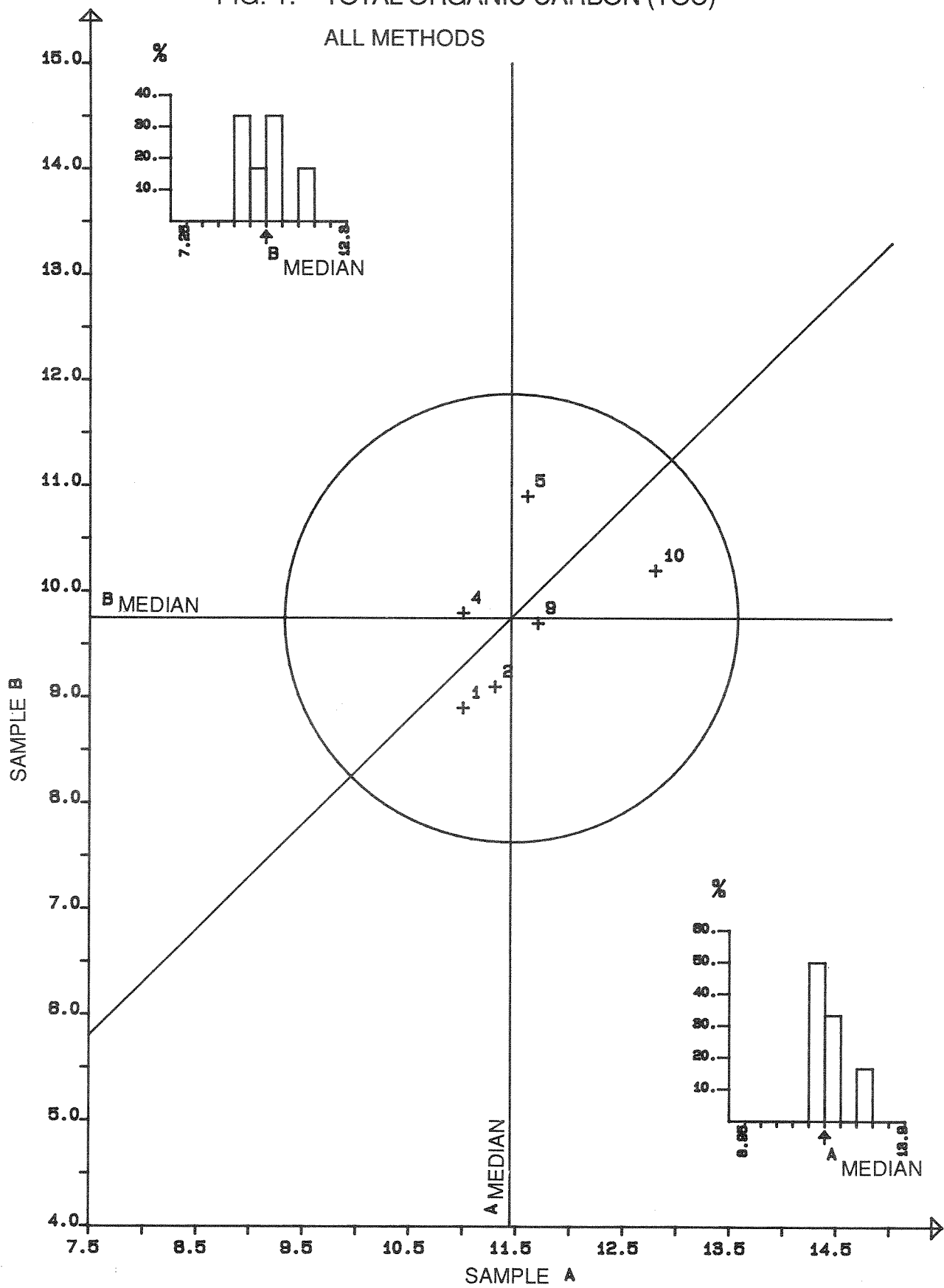


FIG. 2 TOTAL ALUMINIUM ALL METHODS

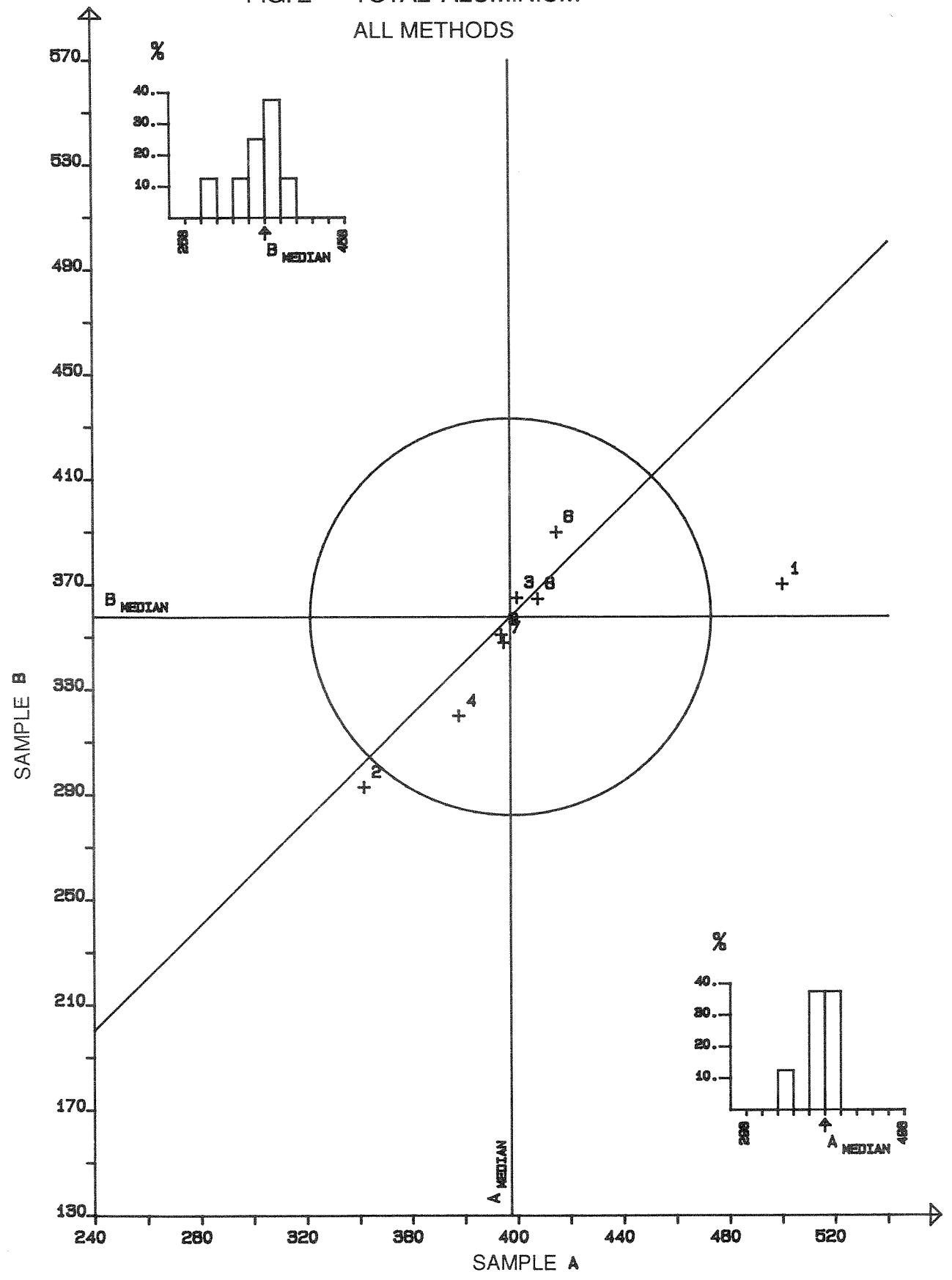




FIG. 3 REACTIVE ALUMINIUM  
ALL METHODS

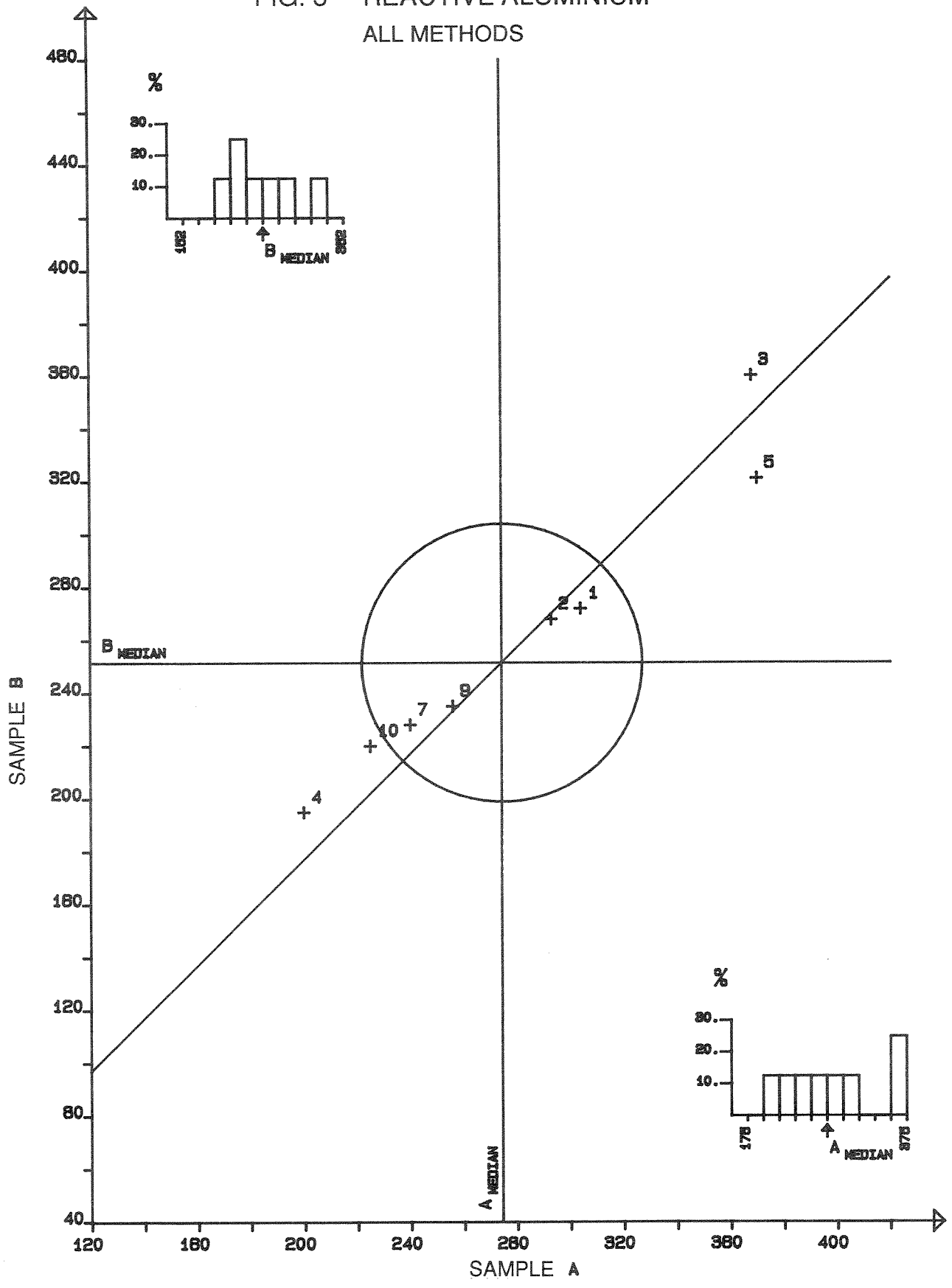


FIG. 4 LABILE ALUMINIUM  
ALL METHODS

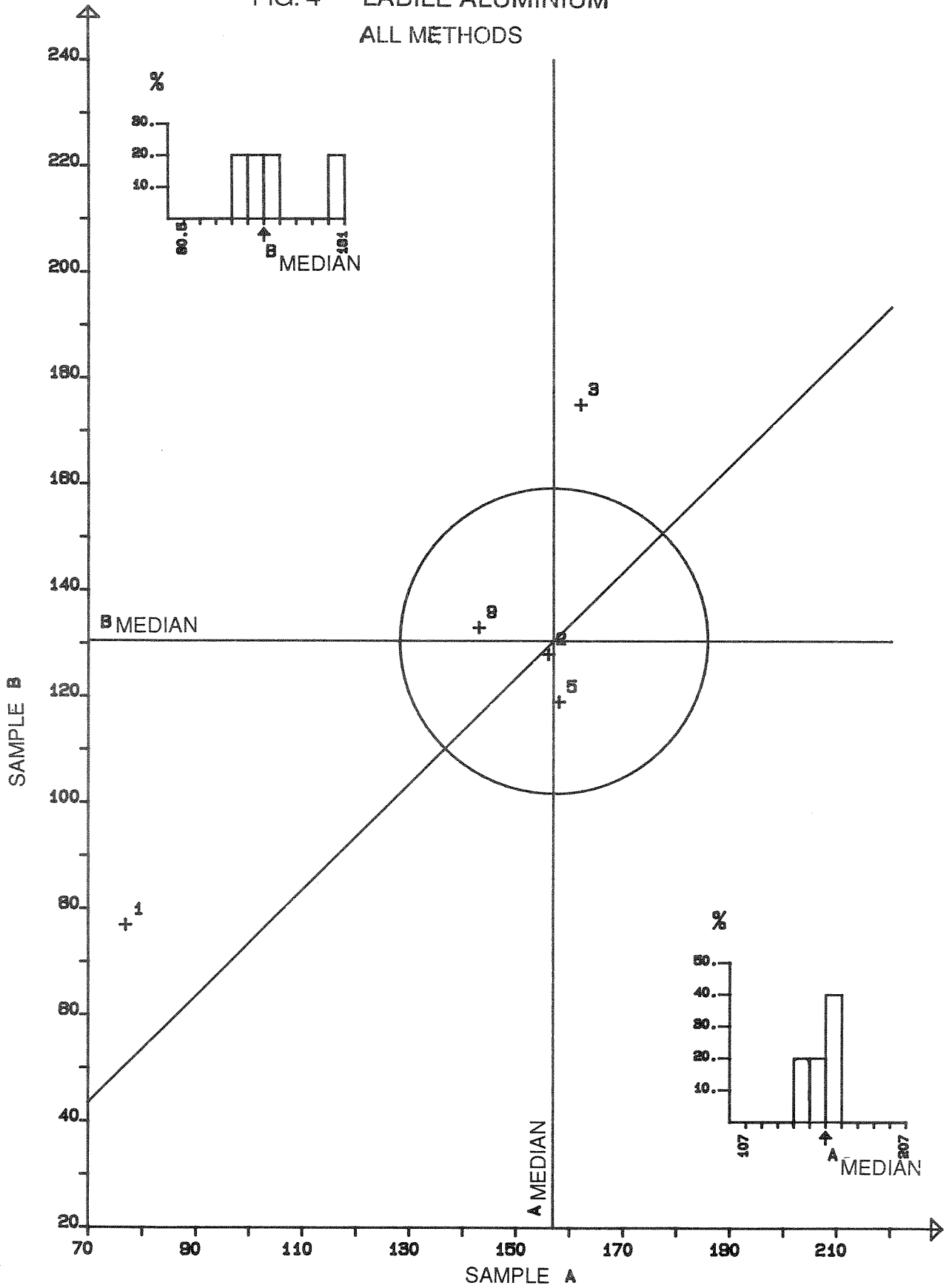
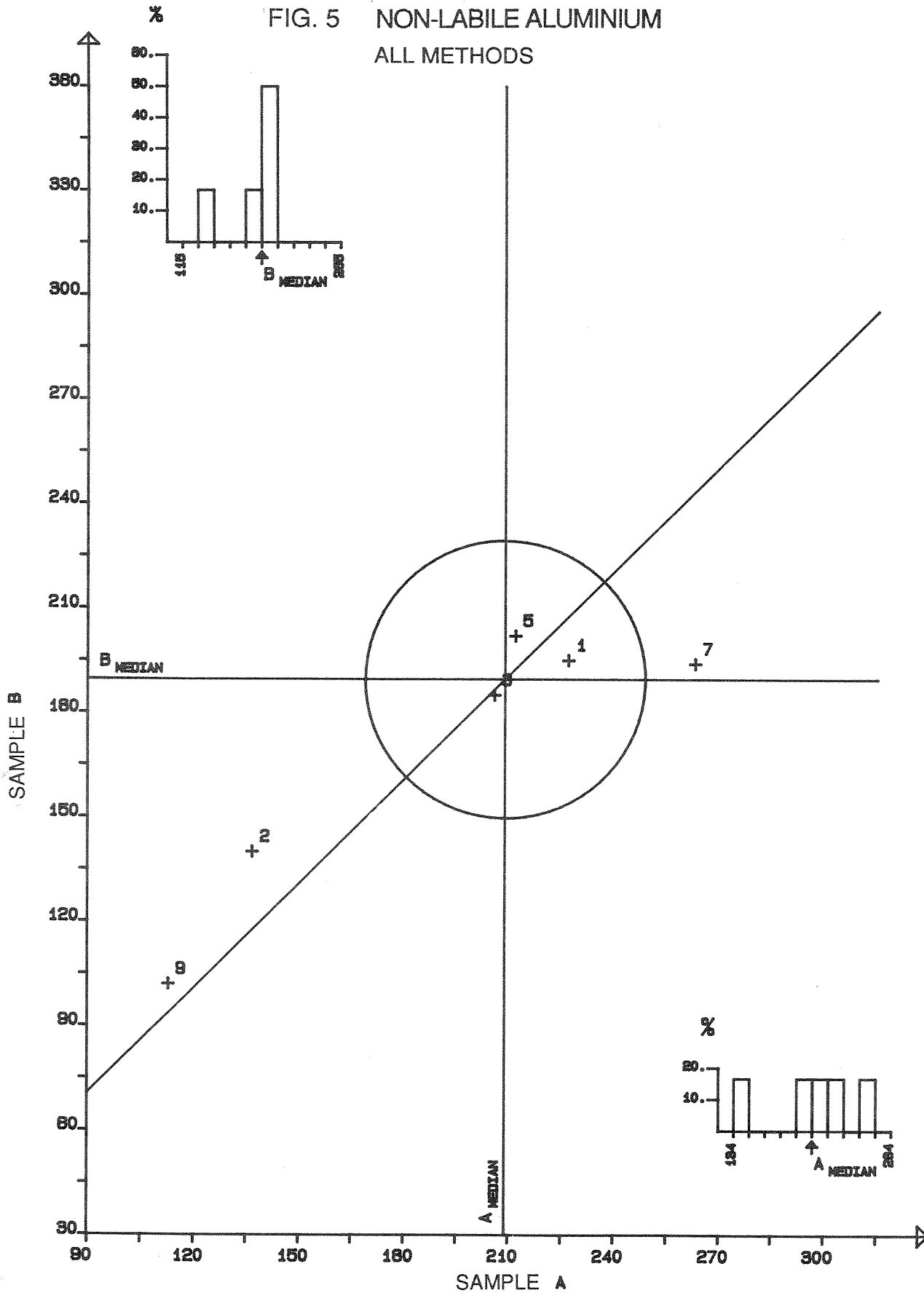


FIG. 5 NON-LABILE ALUMINIUM  
ALL METHODS



The analytical results are illustrated in the figures 1 - 5, 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 - 10.

### Dissolved organic carbon

Six laboratories reported analytical results for dissolved organic carbon, and these results are presented in figure 1 and table 6 (appendix 4). At least three of the laboratories have used carbon-analyzers based on digestion with peroxodisulfate in combination with UV-irradiation. One laboratory used an instrument based on catalyzed combustion at 680 °C. Chemical oxygen demand was determined at one of the laboratories, who calculated a value for DOC by dividing the COD result with the factor 2,67. One of the participants has not given any informations about the instrument system used for the DOC determination.

The quality of the analytical results for this parameter is satisfactory, because everyone of the participants produced results within the general acceptance limit of 20 %.

### Total aluminium

Nine laboratories reported analytical results for total aluminium, of which eight used the graphite furnace technique for the determination step. One laboratory stated that Zeeman correction had been applied, another laboratory diluted the samples 1:10 before the determination step, while one laboratory gave no informations at all about the analytical method used. The results are presented in figure 2 and in table 7 (appendix 4).

In sample A, laboratory no. 1 reported too high value for total aluminium, while the results for sample B is normal. The rest of the laboratories are located along the 45° line, which indicates that the differences between their results are mainly of systematic nature. Seven of the reported result pairs are located within the circle representing the general acceptance limit of 20 % of the median value.

A few of the participants presented additional results showing that the total aluminium values are increasing during the storage time of acidified samples, although the increase is a little less than 10 percent after about one week. Therefore, it is essential that the samples are acidified some days before the determination of total aluminium.

### **Reactive aluminium**

The results reported for this parameter are presented in figure 3 and table 8 (appendix 4). Figure 3 is showing that the deviations between the laboratories are clearly systematic, and must be due to differences between the methods used for the determination. Most of the laboratories determined aluminium photometrically after complexation with pyrocatechol violet (5), while others used the method of Barnes (8).

The reported values for this aluminium fraction are dependent on the chemical conditions in the reaction mixture. Most methods are based on the direct determination of aluminium in a non-acidified sample, preferably accomplished as soon as possible after sampling. However, there are some methods based on acid pretreatment of the sample, then the results will be dependent on how long the acidified sample is stored before the aluminium content is determined. Such acidification is no digestion method, but it will lead to some dissolution of complexes and even particulate matter. The results must be expected to increase when the pretreatment time is increased.

As an example of this acidification effect, is given the results for "acid reactive" aluminium in the samples A and B (table 4), determined at NIVA as a part of the control analysis programme. Addition of sulfuric acid, and storage for at least one week, is leading to an "acid reactive" aluminium content about 40-50 µg/l higher than the reactive aluminium determined in the non-acidified sample.

### **Non-labile aluminium**

The analytical results for non-labile aluminium received from the participants, are presented in figure 4 and table 9 (appendix 4).

Five laboratories reported results for this parameter, and most of them have indicated that they determined non-labile aluminium according to the automated method of Røgeberg and Henriksen (5), which

is based on the method of Driscoll (6). By this method non-labile aluminium is the fraction that passes through a cation exchange column (figure 6), and consists of monomeric alumino-organic complexes. Different resins have different exchange properties, and also the resin form will affect the results. Some of the information received from the participants, indicate that different resin forms have been used for this intercalibration. Thus one laboratory informed that they used the hydrogen form of a strongly acid cation exchanger, while another laboratory used the sodium form of the same ion exchanger (for further comments, see page 15).

However, two other techniques have also been referred to. One lab (no. 2) used the equilibrium dialysis method of B.D. LaZerte et al. (7). Another laboratory (no. 7) extracted the aluminium fraction according to Barnes (8), who complexed aluminium with 8-hydroxy-quinoline, and extracted the aluminium-oxinate complex into methyl-isobutyl-ketone, prior to analysis by atomic absorption.

The observed differences between the reported results are obviously caused by the application of different methods, or slightly different modifications of a method, for the determination of non-labile aluminium.

### Labile aluminium

The reported results for labile aluminium are presented in figure 5 and in table 10 (appendix 4). Only six laboratories have calculated these values.

When an untreated sample passes through the cation exchange column, the labile aluminium fraction is kept back on the resin. This parameter is therefore determined as the difference between the reactive and the non-labile aluminium fractions, and the results of this parameter, therefore, are dependent on both of these determinations.

### **DISCUSSION**

The general rule for target accuracies, outlined in the Manual for Chemical and Biological Monitoring (1), is used as acceptance limit for the results of this intercalibration test. These limits are corresponding to either the detection limit of the method, or 20 % of the true value, whichever being the greater. In table 2 are presented

an evaluation of the results of this intercalibration, which is numbered 8803.

As opposed to dissolved organic carbon, where all result pairs are located within the acceptance limit, the analytical results of the aluminium fractions are largely exposed to deviations caused by the analytical method used for the determination.

Table 2. Evaluation of the results of intercalibration 8903.

Parameter	Acceptance limit	Number of results	Number of acceptable results	Percent acceptable results
Dissolved organic carbon	20 %	6	6	100
Total aluminium	20 %	8	6	75
Reactive aluminium	20 %	8	4	50
Non-labile aluminium	20 %	5	3	60
Labile aluminium	20 %	6	3	50
Total		33	21	67

The treatment of natural samples by ion exchange column, allows us to distinguish between different forms of aluminium on the basis of their kinetic and thermodynamic properties. The programme centre has chosen to use the definitions outlined by Driscoll (6) for the aluminium species (figure 6), well aware of the fact that some other laboratories may use slightly different definition systems.

Many monomeric aluminium complexes exchanges readily, as do low molecular weight polynuclear species, but the reactions are definitely dependent on both reaction time and the acidity of the solution. Measurement of non-labile monomeric aluminium in natural waters has been reported to be dependent on the flow rate of the solution through the column, in addition to chemical conditions in the solutions during the determination. Therefore the results for aluminium species produced by different laboratories would be expected to differ considerably if the laboratories are not applying exactly the same method for the determination.

The ion exchanger shall be strongly acid, but the question is whether it shall be on the hydrogen form, the sodium form, or a combination of hydrogen and sodium form. The available literature may be rather confusing on this point, because the different forms have been recommended by different authors.

Figure 6. Schematic representation of aluminium fractions (Driscoll, (6)).

Aluminium measurement	← Total reactive aluminium, acid digested →		
	← Total monomeric aluminium no acid digestion →		
	← Cation exchange treated, monomeric aluminium →		
Aluminium fraction	Non-labile monomeric aluminium	Labile monomeric aluminium	Acid soluble aluminium
Fraction composition	↓ Monomeric alumino-organic complexes	↓ Free aluminium, monomeric aluminium sulfate, fluoride, and hydroxide complexes	↓ Colloidal polymeric aluminium, strong alumino-organic complexes

The hydrogen form of the cation exchanger is leading to a distinct acidification of the sample when passing through the column, because the metal ions are exchanged with  $H^+$  ions. When pH of the sample are decreasing, some of the non-labile aluminium may be transferred to labile aluminium, which in turn are kept back on the column, and thus leading to a lower result for non-labile aluminium. Natural alumino-organic complexes exhibit a range of stabilities, thus the degree of acidification is decisive to what extent this reaction may go.

Using the sodium form of the exchanger, the pH of the samples are observed to increase a little. It is supposed that this phenomenon is brought about by the exchange of the acid cations, e.g.  $Al^{+++}$  and



$\text{Fe}^{++}/\text{Fe}^{+++}$ , with sodium ions with neutral reaction.

A combination of hydrogen and sodium form of the cation exchanger will retain the original pH of the sample much better. One laboratory (no. 9) informed explicitly that they used the sodium form of the cation exchanger, mixed up with with one percent of the hydrogen form, and the column was treated with sodium chloride before use. In this case only a small increase of the pH value was observed when the sample passed through the column.

The non-exchangeable aluminium initially present in the samples of this intercalibration, is assumed to be mainly associated with organic matter. The fact that the laboratories used different modifications and even different methods for the determination of aluminium fractions, may explain some of the differences between the reported results of the aluminium species.

To attain comparable results from different laboratories, it is absolutely necessary that all the laboratories are using precisely the same method.

**LITERATURE**

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APPENDIX

**APPENDIX 1****Participants of intercalibration 8803, and their code numbers.**

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

## APPENDIX 2

### PREPARATION AND CONTROL ANALYSES OF THE SAMPLES

A working solution of aluminium were prepared by dilution of 100 mL stock solution (BDH "Spectrosil", 1000 mg/L) to 1000 mL with deionized water.

The two sample solutions were prepared from natural water, collected in a brooklet from Hellerudmyra, a marsh area located outside Oslo, Norway. 25 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  $\mu\text{m}$  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 filtrate. A 10 L portion of the filtrate was transferred to a polyethylene container and stored (sample A). Another 8 L portion of the filtrate was transferred to a second polyethylene container, then 2 L deionized water and 3 ml the 100 mg/l working solution of aluminium was added (sample B).

Table 4. Summary of the control analyses. Concentrations are given in  $\mu\text{g/L}$  for aluminium, and mg/L for organic carbon.

Parameter	Sample A		Sample B	
	mean	sdev.	mean	sdev.
Dissolved organic carbon	11.8	0.17	9.8	0.19
Total aluminium	413	20.4	352	14.2
Reactive aluminium	256	11.0	235	7.7
(Acid-reactive aluminium	307	13.8	272	11.6)
Non-labile aluminium	115	7.2	90.5	5.6
Labile aluminium	141	8.3	145	5.4

During the following week the solutions were shaken several times. Then 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.

During the intercalibration period, eight 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 January 1989.

The control analyses confirm that the stability of the sample solutions were acceptable during the intercalibration period, and a summary of the control results is presented in table 4.

## 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 - 5).

The graphical presentation creates a possibility 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 - 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  $45^{\circ}$  line. This is reflecting the fact that many laboratories - due to systematic deviations - have attained too low or too high values for both samples.

The acceptance limit of the results, may be represented by a circle with its centrum at the intersection of the two straight lines in the diagram (true or median values). The distance between the centrum of the circle, and the mark representing the laboratory, is a measure of the total error of the results. The distance along the  $45^{\circ}$  line is giving the magnitude of the systematic error, while the distance perpendicular to the  $45^{\circ}$  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 6 - 10. Results being omitted from the calculations, are marked with the letter "U".

## APPENDIX 4

Table 5. The results of the participating laboratories

	DOC, mg/l		Total Al, µg/l		Reactive Al, µg/l	
	A	B	A	B	A	B
1	11.0	8.9	500.	370.	304.	272.
2	11.3	9.1	342.	293.	293.	268.
3	-	-	400.	365.	368.	360.
4	11.0	9.8	378.	320.	200.	195.
5	11.6	10.9	-	-	370.	321.
6	-	-	415.	390.	-	-
7	-	-	395.	348.	240.	228.
8	-	-	407.9	364.6	-	-
9	11.7	9.7	394.	351.	256.	235.
10	12.8	10.2	-	-	225.	220.

	Non-labile Al, µg/l		Labile Al, µg/l	
	A	B	A	B
1	77.	77.	227.	195.
2	156.	128.	137.	140.
3	162.	175.	206.	185.
4	-	-	-	-
5	158.	119.	212.	202.
6	-	-	-	-
7	-	-	263.	194.
8	-	-	-	-
9	143.	133.	113.	102.
10	-	-	-	-



**Table 6. Statistics, dissolved organic carbon.**

Analytical method: all methods

Unit: mg/l

-----  
Sample A

Number of participants:	6	Range:	1.80
Number of omitted results:	0	Variance:	0.45
True value:	11.45	Standard deviation:	0.67
Mean value:	11.57	Relative standard deviation:	5.8 %
Median value:	11.45	Relative error:	1.0 %

Analytical results in ascending order:

4	11.0	5	11.6
1	11.0	9	11.7
2	11.3	10	12.8

-----  
Sample B

Number of participants:	6	Range:	2.00
Number of omitted results:	0	Variance:	0.53
True value:	9.75	Standard deviation:	0.73
Mean value:	9.77	Relative standard deviation:	7.5 %
Median value:	9.75	Relative error:	0.2 %

Analytical results in ascending order:

1	8.9	4	9.8
2	9.1	10	10.2
9	9.7	5	10.9

**Table 7. Statistics, total aluminium.**

Analytical method: all methods

Unit:  $\mu\text{g/l}$ -----  
Sample A

Number of participants:	8	Range:	158
Number of omitted results:	0	Variance:	2045
True value:	397.5	Standard deviation:	44.8
Mean value:	404.0	Relative standard deviation:	11.1 %
Median value:	397.5	Relative error:	1.6 %

Analytical results in ascending order:

2	342	3	400
4	378	8	407.9
9	394	6	415
7	395	1	500

-----  
Sample B

Number of participants:	8	Range:	97
Number of omitted results:	0	Variance:	948
True value:	357.8	Standard deviation:	30.7
Mean value:	350.2	Relative standard deviation:	8.8 %
Median value:	357.8	Relative error:	-2.1 %

Analytical results in ascending order:

2	293	8	364.6
4	320	3	365
7	348	1	370
9	351	6	390

**Table 8. Statistics, reactive aluminium.**

Analytical method: all methods

Unit:  $\mu\text{g/l}$ -----  
Sample A

Number of participants:	8	Range:	170
Number of omitted results:	0	Variance:	3974
True value:	274.5	Standard deviation:	63.4
Mean value:	282.0	Relative standard deviation:	22.5 %
Median value:	274.5	Relative error:	2.7 %

Analytical results in ascending order:

4	200	2	293
10	225	1	304
7	240	3	368
9	256	5	370

-----  
Sample B

Number of participants:	8	Range:	165
Number of omitted results:	0	Variance:	2933
True value:	251.5	Standard deviation:	55.2
Mean value:	262.4	Relative standard deviation:	21.1 %
Median value:	251.5	Relative error:	4.3 %

Analytical results in ascending order:

4	195	2	268
10	220	1	272
7	228	5	321
9	235	3	360

**Table 9. Statistics, labile aluminium.**

Analytical method: all methods

Unit:  $\mu\text{g/l}$ -----  
Sample A

Number of participants:	5	Range:	21.0
Number of omitted results:	1	Variance:	84.3
True value:	157.0	Standard deviation:	8.2
Mean value:	154.8	Relative standard deviation:	5.3 %
Median value:	157.0	Relative error:	-1.4 %

Analytical results in ascending order:

1	77 U	5	158
9	143	3	162
2	156		

-----  
Sample B

Number of participants:	5	Range:	47.0
Number of omitted results:	1	Variance:	566
True value:	130.5	Standard deviation:	24.9
Mean value:	138.3	Relative standard deviation:	17.9 %
Median value:	130.5	Relative error:	6.3 %

Analytical results in ascending order:

1	77 U	9	133
5	119	3	175
2	128		

**Table 10. Statistics, non-labile aluminium.**

Analytical method: all methods

Unit:  $\mu\text{g/l}$ 

-----

## Sample A

Number of participants:	6	Range:	126
Number of omitted results:	0	Variance:	1982
True value:	209.0	Standard deviation:	56.8
Mean value:	193.0	Relative standard deviation:	29.4 %
Median value:	209.0	Relative error:	-7.7 %

Analytical results in ascending order:

9	113	5	212
2	137	1	251
3	206	7	370

-----

## Sample B

Number of participants:	6	Range:	92
Number of omitted results:	0	Variance:	893
True value:	189.5	Standard deviation:	39.9
Mean value:	169.7	Relative standard deviation:	23.5 %
Median value:	189.5	Relative error:	-10.5 %

Analytical results in ascending order:

9	102	7	194
2	140	1	195
3	185	5	202

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