International Council
for the Exploration of the Sea

C.M. 1986/C:31
Hydrography Committee

Report of
DHI/ICES Salinometer Intercalibration Exercise

1 INTRODUCTION

Recently there has been considerable discussion on the accuracy of salinity measurement using laboratory salinometers. Potential problems were highlighted at last year's special session of the Hydrography Committee which dealt with the current procedures for collecting and processing hydrographic data. It was clear from this that oceanographer's had to remain vigilant in their quest to obtain the best possible data, within the limits of available instrumentation.

In order to assess the absolute accuracy of their Guildline "Autosal 8400" salinometer the DHI, Hamburg initiated plans for the intercalibration of salinometers within the Federal Republic of Germany. Since there were clear benefits in extending this exercise internationally, the Hydrography Committee Chairman, motivated by the 1985 special session requested the DHI to extend its intercalibration exercise. As a result invitations by the Chairman were sent out to all potentially interested participants in the exercise, using the ICES committee and working group mailing lists.

1.1 Preparation and despatch of the samples

During different voyages of DHI ships, several 40 l plastic containers were filled with water from one station each in the Atlantic (S >35.5), the North Sea (S ~ 34.9), and the Baltic Sea (S ~ 24), and stored in darkness. Two of these water samples from each of these areas were then filled into one 65 l barrel. The sample with the lowest salinity (S ~ 8) was made from North Sea water with the addition of distilled water.

From 15 to 17 January, 1986, the bottles were filled with salt water. Before filling, the contents of the 65 l barrels were rolled around by means of a submersible pump for at least 1 h, so that complete mixing within the container was attained. The walls of the container were free of salt crystals and water droplets. During the filling, mixing was likewise ensured within the barrel.

The water was exclusively filled into absolutely new, frequently washed sample bottles (200 cm^3), whereby they were rinsed twice with sample water. The bottles were immediately closed, after filling, with a plastic cap and a screw-on lid, and then sorted into the prepared transportation cartons. The cartons were lined on all sides with styropore, between the bottles was also styropore. In only one case were we informed that sample bottles were broken during transport.

The despatch by post, apart from subsequent requests, took place from 17 to 21 January, 1986. Some of the Federal German participants received the samples by messenger.

The almost simultaneous analysis of the samples by the participating Institutes, which was at first intended, could not be realised because of late postal delivery, organisational problems, and defective salinometers.

Participants were requested to analyse each sample supplied to them three times, and calculate salinity from conductivity ratio using the PSS78 algorithms. They were also requested to supply other details, such as salinometer make and serial number, and also the Standard Sea water Batch used. Results completed on a proforma designed and distributed by the DHI were then returned to both DHI and the Service Hydrographique, for statistical analysis.

2 Data Evaluation

2.1 Relative performance of different instruments

Table 1 is a list of Instruments, and institutes (in alphabetical order) that took part in the exercise. Of the 43 instruments, 28 were of the Guildline "auto-sal" type. Because the precision and resolution of this instrument is higher by several factors than that of the other instruments involved, preliminary statistical , treatment was undertaken with the "Autosals" and non-"Autosals" forming separate groups. It was also decided, at a very early stage, that one of the instruments, instrument 'X', performed so badly that it had to be excluded from the analysis. The measurements from this instrument deviated non-systematically by as much as 0.8. The manufacturer of instrument 'X' has been informed of the apparently poor performance of its product.

A statistical description, which compares the performance of the two groups of instruments is provided in Table 2, using the statistical package SPSS. The basic input data to this analysis was the mean values of each of the three samples analysed at each salinity level. Thus a total of approximately 255 and 90 values were available from measurements from the "autosal" and non-"autosal" respectively (Instrument 'X' excluded). The histograms in this Table show only the distribution of values close to the mean (as indicated), but the statistics include the full range of values. The following observations can be made from Table 2.

a) The overall mean values for the two groups of instruments agreed to within .01, except at the 35.5 level.

b) If the three values at 35.415 (Table 2H) are excluded, the mean values of this group also come within this range. These apparently anomalous values were obtained from the instrument used at the Chemical department of the Kiel Institute. Their instrument was re-checked by samples used previously at the Physics department of this Institute, and values close (within .007) of the mean values were measured. This suggests the possibility of sample contamination, which must cast some doubt on the validity of many of the conclusions in this report.

c) All of the value distributions were non-Guassian, precluding the possibility of conducting many types of standard statistical analysis.

d) The distribution of "Autosal" values was much more highly peaked around the median (mean) value than the non-"autosal" values, in accordance with the high precision capability of the "Autosal".

e) The spread of values away from the mean tended to be greater for the "Autosal" which resulted in the standard deviation from the two groups of measurements being similar.

f) At all 4 levels the "Autosal" exhibited higher maximum values. Indeed, especially on levels 23.6 and 35.5, the "Autosal" exhibited a predominance of scattered high values, but this was not so clearly apparent amongst the fewer non-"Autosal" measurements. This fact was noted by a number of the "Autosal" operators, who referred to the presence of "rogue" samples. This distribution of the "rogue" samples does, however, suggest a problem related to the instrument itself.

2.2 Effect of different Standard sea-water batches

Table 3 shows that 11 of the instruments were standardised using IAPSO sea water batch 95 (8 March 1983). The remaining instruments were standardised using 16 other batch numbers (including one using "Moscow" (sub)standard water). The batch dates ranged from 18 October 1969 to 11 October 1985. Because of the large number of batches used it was not possible to determine statistically whether there was any bias arising from this factor. It was clear however that any bias that may have occurred was well within the noise level of the measurements.

2.3 Performance of individual instruments

One of the main objectives of the exercise was to provide an indication to each of the participants some measure of their relative performance. This was done by calculating the mean and standard deviation for each level of those values lying within one standard deviation of the whole series. The results of this calculation are depicted in the 4 parts of Table 4, which are plotted relative to this mean and standard deviation. Values deviating by more that 5 standard deviations are indicated by arrows, and this implies unacceptable performance. The details of the relevant "Lab no."'s indicated in these plots have been distributed with a copy of this report to the participant concerned. Some outliers, ie values outwith one standard deviation are associated with the same instrument on more than one of the four levels calibrated, suggesting poor instrument performance. (Instrument 'X' falls within this category). There are a small number of cases where a particular instrument may have only a poor performance on only one of the levels and, as already indicated, the possibilty of sample contamination at some stage could be responsible for this. However a clear result is that at least 8 instruments were fairly persistently within 0.001 of the mean at each level. All of these instruments were of the "Autosal" type and confirm the manufacturer's claim concerning the potential capability of this equipment. However the relatively high number of outliers, even from the "Autosal", does not allow for complacency, and oceanographers must remain firm in their resolve to acquire salinity data, which form the basis for accurate calibration of CTDs of the highest possible accuracy.

It is intended to stage another, similar, exercise in the near future. This will pay more attention to the method of distribution of samples, in order to remove any possibility of sample contamination which casts some doubt on some of the above findings.

2.4 Acknowledgements

Many people contributed much hard work to ensure the smooth running of this exercise, in particular the participant's who allowed themselves to be put on the "carpet", and the DHI personnel who had to accomplish much in a short time.

G. Becker, E.-G. Schmidt (DHI) and H. Dooley, K. Jancke (ICES Secretariat) were responsible for analysing the data and preparing this report.

TABLE 1

Salinometer intercomparison - list of participating institutions

Ins. type	Institution	
Autosal 8400A	Alfred-Wegner-Institut	Bremerhaven
Autosal 8400	Atlantic Oceanographic Laboratory	Bedford
AGE Minisal	Atlantic Oceanographic Laboratory	Bedford
Autosal 8400	Biol. Anst. Helgoland	Helgoland
Autosal 8400A	Biol. Anst. Helgoland Litoralstation	List
Autosal 8400	Bundesforschungsanst. f Fischerei	Hamburg
Plessey 6230 N	Danmarks Fiskeri- og Havund.	Hirtshals
Autosal 8400	DHI	Hamburg
Autosal 8400	DHI	Hamburg
Autosal 8400	DHI	Hamburg
Autosal 8400	Finnish Institue of Marine Rsearch	Helsinki
Autolab Induct	Fisheries Laboratory	Lowestoft
Autosal 8400	Geophys. Inst. of Phys. Oceanogr.	Copenhagen
Autosal 8400	Groenlands Fiskeri- og Miljo.	Copenhagen
Autosal 8400	Hydrografisk Lab	Charlottenlund
Autosal 8400	Hydrographer of the Navy	Taunton
Autosal 8400	Hydrographer of the Navy	Taunton
Autosal 8400	IFREMER	Brest
Autosal 8400	Inst. f. Ang. Physik	Kiel
Industria Imc	Inst. f. Marine Research Fisheries	Bergen
Autosal 8400 A	Inst. f. Meeresk. Abt. Meeresphysik	Kiel
Beckmann	Inst. f. Meeresk.Abt. Meereschemie	Kiel
Autosal 8400	Inst. f. Meeresk. Abt. Meeresphysik	Kiel
Autosal 8400	Inst. f. Meereskunde	Hamburg
Autosal 8400	Inst. f. Umweltphysik	Heidelberg
Autosal 8400	Inst. Hidrografico	Lisboa
Plessey 6230 N	Inst. Meteor.i Gospodarki Wodnej	Gdynia
601 MkIII	Institute of Marine Research	Rostock
Autosal 8400	IOS	Wormley
Autosal 8400	IOS	Wormley
Beckman RS7b	IOS,Bidston Observatory	Birkenhead
Tsurumi Seiki	Kristinebergs Marine Biol. St.	Fiskebaeckskil
Autosal 8400A	Lab. de Chimie Oceanographique	Brest
Autosal 8400	Marine Lab. DAFS	Aberdeen
Autosal 8400	Marine Research Institute	Reykjavik
Beckman RS7B	MUMM	Oostende
Tsurumi Seiki	NAEP Mar. Pol. Laboratory	Charlottenlund
Autosal 8400	NOAA Northeast Fisheries Center	Woods Hole
Tsurumi Seiki	RIVO Netherl. Inst. Fishery Invest.	IJmuiden
Autosal 8400 A	SMBA Dunstaffnage Mar. Res. Lab.	Oban
Plessey 6230N	SMHI Oceanographical laboratory	Goeteborg
Hytech 6220	SMHI Oceanographical laboratory	Goeteborg
Industria Ind	SMHI technical Dept.	Norrkoeping

TABLE 2 (A-D)

```
COUNT   MIDPOINT    ONE SYMBOL EQUALS APPROXIMATELY  1.00 OCCURRENCE

    0     8.565                      Autosal
    0     8.575
    0     8.585
    0     8.595
    0     8.605
    0     8.615
    3     8.625  ***
    3     8.635  ***
   12     8.645  ************
   50     8.655  **************************************************
   13     8.665  *************
    0     8.675
    1     8.685  *
    0     8.695
    0     8.705
    0     8.715
    0     8.725
    0     8.735
    1     8.745  *
    0     8.755
    1     8.765  *
                 I....+....I....+....I....+....I....+....I....+....I
                 0        10        20        30        40        50
                           HISTOGRAM FREQUENCY

MEAN           8.655    STD ERR        0.002    MEDIAN        8.653
MODE           8.654    STD DEV        0.018    VARIANCE      0.000
KURTOSIS      22.443    S E KURT       1.979    SKEWNESS      4.068
S E SKEW       0.263    RANGE          0.135    MINIMUM       8.625
MAXIMUM        8.760    SUM          726.998

Valid Cases       84    Missing Cases      2
```

Table 2A

```
COUNT   MIDPOINT    ONE SYMBOL EQUALS APPROXIMATELY  0.20 OCCURRENCES

    0     8.565                      non Autosal
    0     8.575
    0     8.585
    0     8.595
    0     8.605
    0     8.615
    1     8.625  *****
    3     8.635  ***************
    6     8.645  ******************************
    8     8.655  ****************************************
    7     8.665  ***********************************
    0     8.675
    3     8.685  ***************
    1     8.695  *****
    0     8.705
    0     8.715
    1     8.725  *****
    0     8.735
    0     8.745
    0     8.755
    0     8.765
                 I....+....I....+....I....+....I....+....I....+....I
                 0         2         4         6         8        10
                           HISTOGRAM FREQUENCY

MEAN           8.658    STD ERR        0.004    MEDIAN        8.657
MODE           8.645    STD DEV        0.021    VARIANCE      0.000
KURTOSIS       2.916    S E KURT       1.951    SKEWNESS      1.310
S E SKEW       0.427    RANGE          0.102    MINIMUM       8.625
MAXIMUM        8.727    SUM          259.733

Valid Cases       30    Missing Cases      2
```

Table 2B

```
COUNT   MIDPOINT    ONE SYMBOL EQUALS APPROXIMATELY  1.00 OCCURRENCE

    0    23.485                      Autosal
    0    23.495
    0    23.505
    0    23.515
    0    23.525
    0    23.535
    0    23.545
    0    23.555
    0    23.565
    2    23.575  **
   42    23.585  ******************************************
   32    23.595  ********************************
    2    23.605  **
    1    23.615  *
    0    23.625
    2    23.635  **
    1    23.645  *
    0    23.655
    0    23.665
    1    23.675  *
    2    23.685  **
                 I....+....I....+....I....+....I....+....I....+....I
                 0        10        20        30        40        50
                           HISTOGRAM FREQUENCY

MEAN          23.594    STD ERR        0.002    MEDIAN       23.589
MODE          23.587    STD DEV        0.020    VARIANCE      0.000
KURTOSIS      12.878    S E KURT       1.979    SKEWNESS      3.549
S E SKEW       0.261    RANGE          0.108    MINIMUM      23.579
MAXIMUM       23.687    SUM         2005.487

Valid Cases       85    Missing Cases      1
```

Table 2C

```
COUNT   MIDPOINT    ONE SYMBOL EQUALS APPROXIMATELY  0.20 OCCURRENCES

    0    23.485                      non Autosal
    0    23.495
    0    23.505
    0    23.515
    0    23.525
    0    23.535
    2    23.545  **********
    0    23.555
    1    23.565  *****
    2    23.575  **********
    6    23.585  ******************************
    8    23.595  ****************************************
    6    23.605  ******************************
    2    23.615  **********
    0    23.625
    1    23.635  *****
    1    23.645  *****
    0    23.655
    0    23.665
    1    23.675  *****
    0    23.685
                 I....+....I....+....I....+....I....+....I....+....I
                 0         2         4         6         8        10
                           HISTOGRAM FREQUENCY

MEAN          23.585    STD ERR        0.011    MEDIAN       23.592
MODE          23.589    STD DEV        0.061    VARIANCE      0.004
KURTOSIS      20.624    S E KURT       1.952    SKEWNESS     -4.069
S E SKEW       0.421    RANGE          0.393    MINIMUM      23.285
MAXIMUM       23.678    SUM          731.147

Valid Cases       31    Missing Cases      1
```

Table 2D

TABLE 2 (E-H)

```
 COUNT   MIDPOINT    ONE SYMBOL EQUALS APPROXIMATELY  1.50 OCCURRENCES

     0    34.855                      Autosal
     0    34.865
     0    34.875
     0    34.885
     0    34.895
     0    34.905
     0    34.915
     0    34.925
     0    34.935
     0    34.945
    63    34.955  ******************************************
    11    34.965  *******
     3    34.975  **
     0    34.985
     0    34.995
     0    35.005
     0    35.015
     3    35.025  **
     4    35.035  ***
     0    35.045
     0    35.055
     0    35.060
                  I....+....I....+....I....+....I....+....I....+....I
                  0        15        30        45        60        75
                              HISTOGRAM FREQUENCY

MEAN        34.966   STD ERR       0.003   MEDIAN      34.958
MODE        34.957   STD DEV       0.024   VARIANCE     0.001
KURTOSIS    10.385   S E KURT      1.979   SKEWNESS     3.184
S E SKEW     0.261   RANGE         0.140   MINIMUM     34.951
MAXIMUM     35.091   SUM        2972.114

Valid Cases     85   Missing Cases     2
```

Table 2E

```
 COUNT   MIDPOINT    ONE SYMBOL EQUALS APPROXIMATELY  0.40 OCCURRENCES

     0    34.855
     0    34.865
     0    34.875
     0    34.885
     0    34.895
     0    34.905
     0    34.915
     0    34.925
     2    34.935  *****
     7    34.945  *****************
    13    34.955  ********************************
     7    34.965  *****************
     0    34.975
     0    34.985
     0    34.995
     0    35.005
     1    35.015  ***
     0    35.025
     0    35.035
     0    35.045
     1    35.055  ***
     0    35.060
                  I....+....I....+....I....+....I....+....I....+....I
                  0         4         8        12        16        20
                              HISTOGRAM FREQUENCY

MEAN        34.959   STD ERR       0.004   MEDIAN      34.956
MODE        34.949   STD DEV       0.023   VARIANCE     0.001
KURTOSIS    11.842   S E KURT      1.952   SKEWNESS     3.224
S E SKEW     0.421   RANGE         0.121   MINIMUM     34.934
MAXIMUM     35.055   SUM        1083.722

Valid Cases     31   Missing Cases     2
```

Table 2F

```
 COUNT   MIDPOINT    ONE SYMBOL EQUALS APPROXIMATELY  0.40 OCCURRENCES

     0    35.405                      Autosal
     0    35.415
     0    35.425
     0    35.435
     0    35.445
     0    35.455
     0    35.465
     0    35.475
     0    35.485
     2    35.495  *
    61    35.505  *****************************************
    11    35.515  *******
     1    35.525  *
     1    35.535  *
     0    35.545
     2    35.555  *
     2    35.565  *
     1    35.575  *
     1    35.585  *
     1    35.595  *
     0    35.605
                  I....+....I....+....I....+....I....+....I....+....I
                  0        15        30        45        60        75
                              HISTOGRAM FREQUENCY

MEAN        35.516   STD ERR       0.003   MEDIAN      35.507
MODE        35.507   STD DEV       0.027   VARIANCE     0.001
KURTOSIS    12.302   S E KURT      1.979   SKEWNESS     3.383
S E SKEW     0.261   RANGE         0.150   MINIMUM     35.497
MAXIMUM     35.647   SUM        3018.820

Valid Cases     85   Missing Cases     1
```

Table 2G

```
 COUNT   MIDPOINT    ONE SYMBOL EQUALS APPROXIMATELY  0.40 OCCURRENCES

     0    35.405                      non Autosal
     3    35.415  ***************
     0    35.425
     0    35.435
     0    35.445
     0    35.455
     0    35.465
     3    35.475  ***************
     1    35.485  *****
    10    35.495  **************************************************
     9    35.505  *********************************************
     4    35.515  ********************
     0    35.525
     0    35.535
     0    35.545
     0    35.555
     0    35.565
     0    35.575
     0    35.585
     0    35.595
     1    35.605  *****
                  I....+....I....+....I....+....I....+....I....+....I
                  0         2         4         6         8        10
                              HISTOGRAM FREQUENCY

MEAN        35.494   STD ERR       0.006   MEDIAN      35.499
MODE        35.499   STD DEV       0.035   VARIANCE     0.001
KURTOSIS     4.914   S E KURT      1.952   SKEWNESS     0.033
S E SKEW     0.421   RANGE         0.195   MINIMUM     35.414
MAXIMUM     35.609   SUM        1100.320

Valid Cases     31   Missing Cases     1
```

Table 2H

TABLE 3

Standard Sea Water Batches

Batch no	Date	No.of instr
52	18/10/69	1
66		1
72	22/05/76	1
81	15/04/78	1
86	28/04/79	2
88	01/12/79	1
92	29/10/81	3
93	31/10/81	3
94	18/11/81	3
95	08/03/83	11
96	03/03/83	1
97	03/03/83	1
99	27/07/84	4
100	29/11/84	4
102	04/06/85	2
103	11/10/85	3
MOS		1

TABLE 4

Salinity Intercalibration ICES 1986

Smean=8.653 Ssdev= .007

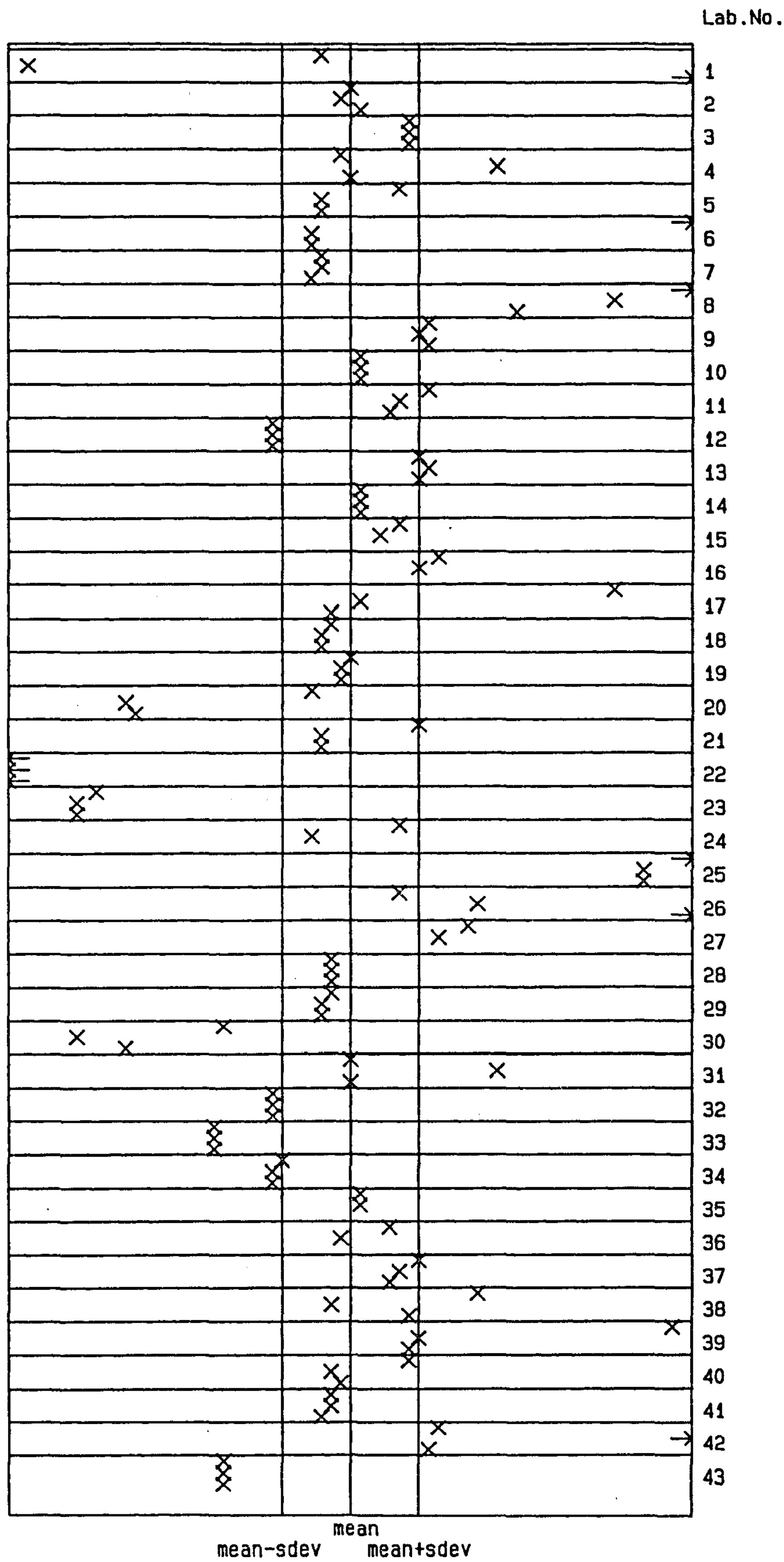
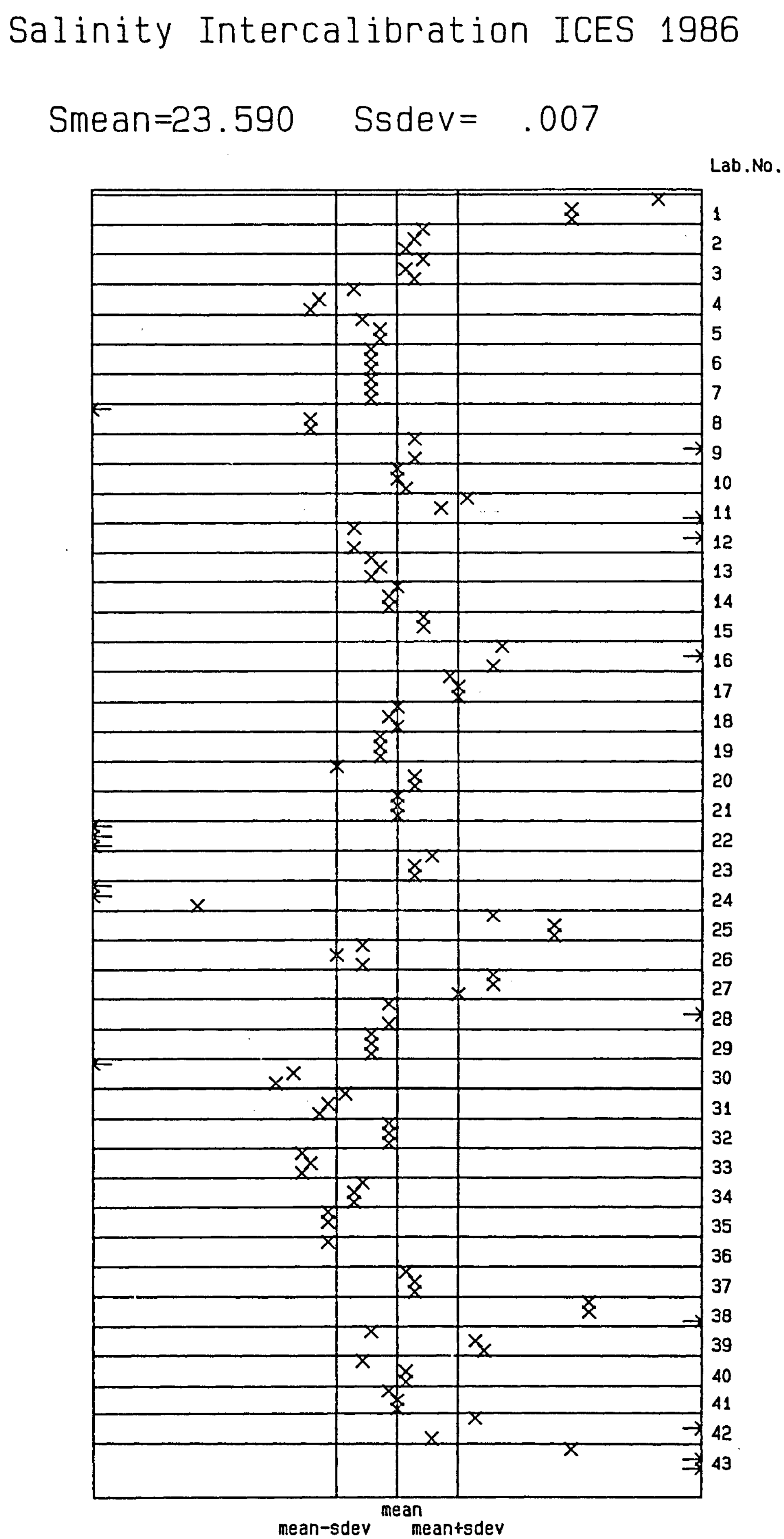


TABLE 4 (ctd)


Salinity Intercalibration ICES 1986
Smean=23.590 Ssdev= .007
Lab.No.
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10
11
12
13
14
15
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38
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41
42
43
mean
mean-sdev
mean+sdev

TABLE 4 (ctd)

Salinity Intercalibration ICES 1986

Smean=34.958   Ssdev= .005

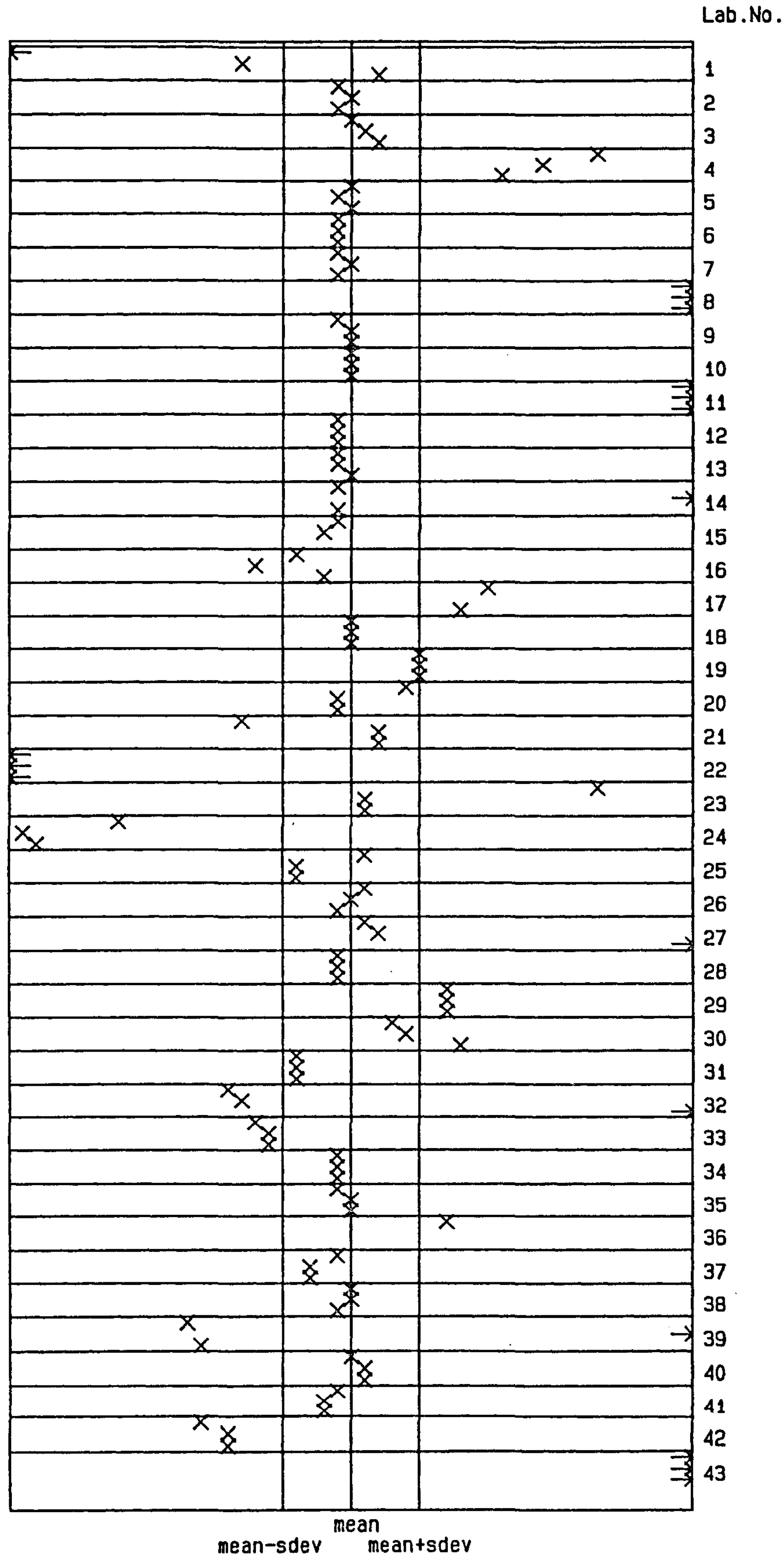
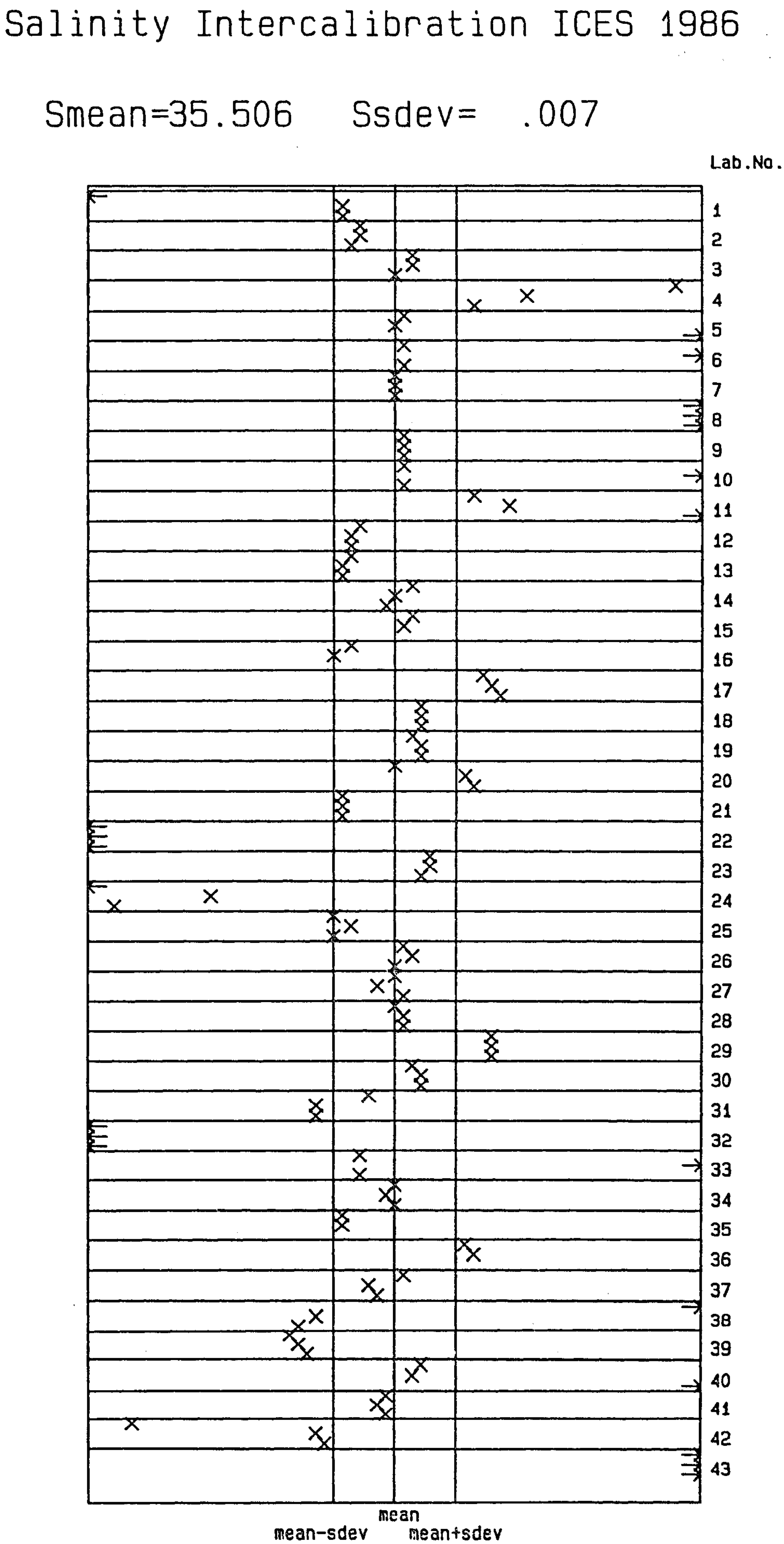


TABLE 4 (ctd)


Salinity Intercalibration ICES 1986
Smean=35.506 Ssdev= .007
Lab.No.
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41
42
43
mean
mean-sdev
mean+sdev