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SALINITY INTERCALIBRATION JONSDAP 76

by

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CONTENTS

I. SUMMARY

Seven institutes from six countries around the North Sea took 390 salinity samples for a salinity intercalibration exercise during JONSDAP 76.

For samples in glass bottles, a mean dispersion in duplicates of 0.03°/oo S was found, between salinities of samples determined (soon) after collection at the institutes and salinities of corresponding samples measured after 7-10 months at NIOZ. Evidence points to two major sources of variation:

spread over 9 series; 233 samples were send to NIOZ. The proposal send to the participants January 1976 incorrectly called it "a salinometer-procedures intercalibration". The contents of the proposal made it quite clear to experts that it was a field test in which all errors from filling the bottles at sea up to and including calculation and administration of salinities were involved. Each institute took a series of replicate samples in their own bottles. One or two bottles were measured at the institutes and the other single or duplicate samples were send to NIOZ.

First results were given in a preliminary report prepared for the JONSDAP 76 workshop organized May 1977 in Bergen, Norway.

III. SAMPLES

1. Sampling

At least one sample from the replicates taken at sea in the period March-June 1976 was carried through the routine procedures of the institute and the other samples were send to NIOZ and processed by procedures described in this report.

2. Samples and bottles received at NIOZ

From March 1976 till January 1977 233 bottles were received belonging to nine series. The greater part was packed in wooden cases; in cardboard cases broken bottles were often found. After arrival a firsthand visual and administrative inspection followed. Caps were controlled and sometimes screwed a little tighter.

Several bottle types were encountered. Bottletype was coded with three one digit numbers (a b c).

a = bottle material : 1=glass, 2=polythene (thinwalled)

b = cap material : 1=hard plastic, 2=aluminium

c = cap insert mat. : 1=polythene, 2=rubber, 3=absent

Bottle condition (BC) was coded as follows:

1 = bottle broken

2 = cap broken, insert intact

3 = salt erusts (section 4.2)

4 = o.k.

Some general information has been gathered in the next table.

Table I.

Number of samples, salinity range, bottletype

Serie	Number of bottles		Bottles broken	Salinity range °/oo	Bottle type
	Inst.	NIOZ			
1	13	28	-	34.8-35.2	111
2	40	40	-	35.0-35.3	111
3	9	18	2	34.9-35.1	111
4	-*	24	6	34.5-35.2	113
5	28	56	-	25.3-35.1	113
6	24	24	-	35.0-35.1	113
7	20	20	-	35.0-35.7	211
8	17	17	-	35.0-35.2	111
9	6	6	-	34.9-35.1	122
1-9	157	233	8		
	390				

* Due to a sad accident the technician responsible at the institute for the exercise died and the administrative details could not be recovered.

IV. ESTIMATING SALINITY

1. Institute's salinometer procedure and salinities

In Table II a short summary is given of the information provided by the institutes. The description of measurement procedures differed widely in length and care for details. The instructions were seldom very complete. All institutes used laboratory inductive salinometers (Brown and Hamon, 1961).

Table II

Salinometers and procedures

Serie	Salinometer manufacturer	ISSW used N/time or N/M samples	SSSW used	Calculation includes Flush corr.	Drift corr.	Int. Oceanogr. Tables used
1	Autolab Ind.	5-1/day	1/10	no	yes	yes
2	Beckman	2/5days	1/20	yes	yes	yes
3	Beckman	2/5days	1/20	yes	yes	yes
5	Hytech	1/2days	1/50	no	no	yes
6	Autolab Ind.	1/50	1/50	yes	no	yes
7	G.M.MFG.Instr. Corp.	1/day	1/1?	yes	yes	no
8	Autolab Ind.	1/hour	not used	yes	yes	yes
9	Autolab Ind.	1/hour	not	yes	yes	yes

ISSW = IAPSO Standard Sea Water, SSSW = sub-standard sea water.

The results are tabulated in Appendix 2.

Replicate results are to be found on the same row.

2. NIOZ salinometer procedure and salinities

Contrary to the original announcement a Guildline Autosal 8400 salinometer (from the Royal Netherlands Meteorological Institute was used. All determinations were carried out January 18-20, 1977.

Thermostat temperature was 24°C. IAPSO Standard Sea Water batch P 72 and a filtered batch of seawater taken from the salinity maximum in the Southern Bight of the North Sea with salinity 34.69°/oo was used as substandard.

Before starting a determination, the bottle was shaken, the cap (and insert) removed, the presence of salt crusts in the threaded section of the bottle mouth noted, this part wiped clean and a measurement performed after four flushes. Ten consecutive readings were taken and a mean and standard deviation calculated. In case an upwards or downwards trend appeared, another flush and ten readings were taken. A standard deviation of 1-2 in the last decimal place (exceptional 3) corresponding

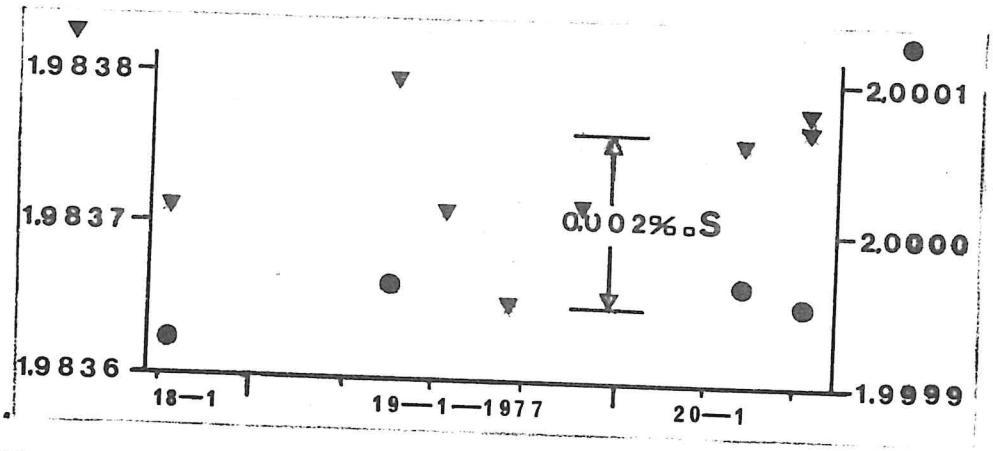

Figure 1. Standard Sea Water (●) and substandard sea water (▼) readings ($G_t = 2xR_t$) during NIOZ conductivity ratio determinations.

to 0.0002-0.0003°/oo S was found. After initial standardization drift control was effected with Standard Sea Water and substandard sea water. In figure 1 standard readings are given.

Maximum drift in the measuring period was 0.003°/oo S. The accumulated drift was only 0.0015°/oo S. In four cases a ratio standard reading/substandard reading could be obtained. The ratios fell within 1.00816 ± 0.00001^5. The instrument was not restandardized in between but the readings of standards were noted and the drift calculation formula adapted accordingly. After applying appropriate corrections and using the International Oceanographic Tables Vol 1. for converting conductivity ratios to salinity, the accuracy of the salinity estimates is believed to be better than ± 0.001 °/oo S. Again salinities are tabulated in Appendix 2.

V. STATISTICS

In the tables of Appendix 2. all estimated salinities and salinity differences (d_i) are given under the headings SALINITY and DELTA-S. Three differences are tabulated. Institutes duplicates (1-2), NIOZ duplicates (3-4) and difference between Institute and NIOZ ((1+2)-(3+4)). In the last difference a systematic part may be present and therefore signs are given.

The formula for the mean systematic difference (MSD) between Institute and NIOZ (rightmost value in the row "MEAN") is therefore

$$MSD = 1/N \sum_{1}^{N} ((S_1+S_2)/2 - (S_3+S_4)/2)$$

To test the hypothesis that MSD differs significant from zero, analysis of variance or/and Student's t-test was applied. Significance was tested one sided with a 95% confidence interval.

The mean dispersion (MDP) in duplicates is defined through the next formulas

$$MDP = 1/N\sqrt{\sum_{1}^{N} d_i^2/2} \quad (1) \text{ or } MDP = 1/N\sqrt{\sum_{1}^{N} (d_i - MSD)^2/2} \quad (2).$$

Dispersion in duplicates (DP) is given in formula (3)

$$DP = \sqrt{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2} = \sqrt{\frac{\Sigma d_i^2}{2}} \quad (3)$$

and is given in the lower part of the tables (S1-2 etc.). Again analysis of variance was used to test the significance of differences between MDP's.

VI. RESULTS

1. Systematic difference between Institute and NIOZ

They are gathered in the next table.

Table III.

Systematic difference (MSD) in salinity

Serie	Syst. Difference Inst. - NIOZ	Significant ?	Bottle type
1	-0.03	yes	111
2	+0.006	no	111
5	-0.03	yes	113
6	-0.011	yes	113
7	-0.3	yes	211
8	-0.005	no	111
9	+0.005	yes	122

Serie 3 is not taken into account. "Statistically" spoken, it is a bad serie.

2. Mean dispersion in duplicates

Three kinds should be considered:

a. between Institute and NIOZ (calculated after removal of a systematic difference)

b. within Institute duplicates

c. within NIOZ duplicates.

Table IV.

Mean dispersion in duplicates (MDP) ($^{o}/_{oo}$S)

Serie	Inst. - NIOZ	Serie	Inst. - Inst.	Serie	NIOZ - NIOZ
1	0.030			1	0.039
2	0.039	2	0.045	2	0.047
				4	0.007
5	0.031			5	0.030
6	0.017	6	0.013	6	0.022
7	0.14				
8	0.027				
9	0.002				

MSD-serie 6 NIOZ-NIOZ appears to be significantly higher than MSD-serie 6 Inst.-Inst.

These values completed with 90% confidence intervals are given in figure 2. This figure is given on the next page.

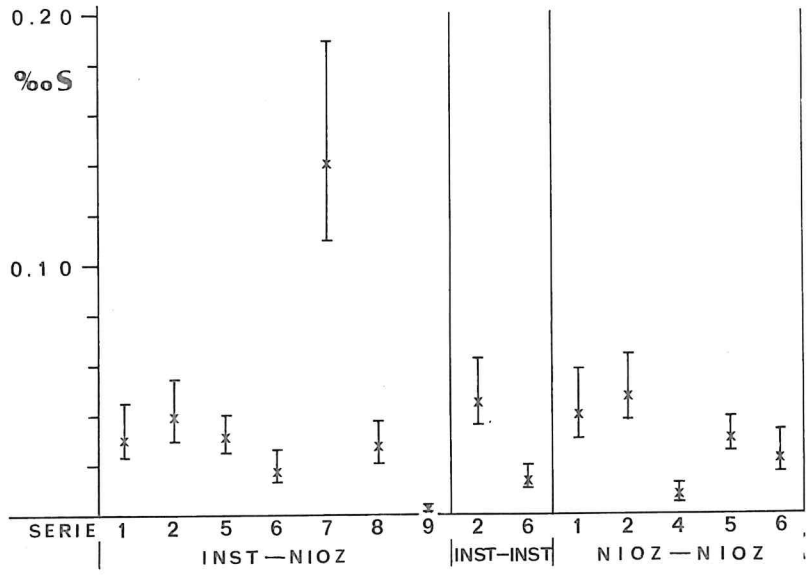

Figure 2. Mean dispersion in duplicate salinity estimates (MDP) with 90% confidence interval.

VII. DISCUSSION

Generally the main sources of error in estimating salinity are:

a. source salinity and initial bottle salinity are not equal within 1:50000 due to insufficient rinsing of the sample bottle.
b. sample bottle salinity changes with time due to dissolution of wall material and/or the exchange of water and/or salt with the exterior.
c. salinometer is in poor condition.
d. measuring procedure is unable to estimate conductivity ratio with the desired precision.
e. conductivity-salinity relation used is incorrect.
f. administration is in error.

1. Intercalibration results

1.1 Mean dispersion in duplicates (MDP)

First looking to the MDP found for Inst. - NIOZ, and excluding the results for series 7 and 9, a range of 0.017-0.039 is found, which is really alarming (see also figure 2). Roughly the same range is seen within Institute and within NIOZ MDP. The large values found within Institute strongly suggest that this unfortunate large dispersion was already present after filling the bottles and did not occur or did only partly occur during storage. If this is true, a major source of lack in precision is incomplete rinsing of the sample bottles (or even a lack of preservation in short term storage).

On the other hand serie 9 tells us that a really low (0.002 $^{o}/_{oo}$ S) MSTDV can be achieved routinely. A glass bottle with aluminium cap and flat rubber insert is evidently able to preserve salinity satisfactory for a period of nine months. In the JONSDAP 73 salinity intercalibration (one case omitted) no MSD was found and MDP was 0.01$^{o}/_{oo}$ S. Storage time was 1-6 weeks.

The conductivity-salinity estimate is capable to give an accuracy of a few 0.001$^{o}/_{oo}$ S. However if you don't want to spent time to measure conductivity ratio correctly, please don't give salinity in three decimal places.

1.2 Systematic differences (MSD) between Institute and NIOZ salinities

In five out of seven cases a significant difference is found. They range from as low as +0.005$^{o}/_{oo}$ S to as high as -0.3$^{o}/_{oo}$ S. In the latter case the bottle material (thin walled polythene) is most probably the cause (Johnston, 1964 and 1969). Some other differences are negative too. Salinometers are known to

show systematic differences of several 0.01°/oo S at 38°/oo S (Grasshof and Hermann, 1975). However such differences seem less likely at mean salinities close to 35°/oo S. The view that negative MSD is caused by long term storage with accompanying loss of water (vapor) is supported in the literature (Johnston, 1964 and 1969) but not supported by the fact that series with the same bottletype (111) not always show significant MSD. Series 5 and 6 (bottletype 113) both show MSD. Serie 9 is certainly the best one. This MSD is lower than could be proven for all series due to their higher MDP's.

2. Salinometer procedures

Doubtful procedures still exist. In one case substandard sea water was not used. This results in an unnecessary high consumption of IAPSO standard sea water and/or insufficient drift control. Standard sea water should be flushed directly into the salinometer cell and no intermediate bottle or beaker should be used. In several cases the frequency of substandard sea water use was low.

More seriously many institutes advocate the use of a "flush corrected" conductivity ratio. No warning is given that this method gives rise to salinity estimates of lower precision. At least one order of magnitude precision can be lost. The basic mistake is the opinion that a drainage factor can be accurately determined and does not vary in practice. A drainage factor is highly dependent on drainage time and wetting conditions of the cell wall. It can easily change $\pm$ 20%.

The drift correction is not always applied.

And last but not least one of the institutes does not seem to apply the International Oceanographic Tables Vol 1 to convert conductivity ratio to salinity.

VIII. LITERATURE

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APPENDIX 1

Participating institutes

Institute for Marine Environmental Research, Plymouth, England (R.H. Bruce)
Fisheries Laboratory, Lowestoft, England (S.R. Jones)
Marine Laboratory, Aberdeen, Scotland (J.A. Adams)
Geofisisk Institutt, Bergen, Norway (G. Furnes)
Institute of Marine Research, Gothenburg, Sweden (J.O. Bladh)
Deutsches Hydrographisches Institut, Hamburg, B.R.D. (K. Huber, G. Becker)
Université de Liège, Oostende, Belgium (H. Picard)

APPENDIX 2

All values given in the tables are in $^{o}/_{oo}$ S,except N, which is the number of observations.

Bottle condition (BC) is coded:

1 = bottle broken

2 = cap broken (insert intact)

3 = salt crusts

4 = o.k.

****S E R I E 1.**** *BOTTLETYPE 111*

--INSTITUTE--	-------NIOZ--------				
--SALINITY----	----SALINITY+BC			------DELTA-S------	
					-- --
			ABS	ABS	1+ 3+
1	2	3	4	1-2	3-4	2 , - 4
35.146		35.222 4	35.159 3		.063	-.045
35.145		35.175 3	35.153 4		.022	-.019
35.172		35.226 4	35.162 4		.064	-.022
35.177		35.238 3	35.184 3		.054	-.034
35.104		35.156 3	35.109 4		.047	-.028
35.127		35.136 4	35.169 4		.033	-.026
35.060		35.064 3	35.067 4		.003	-.006
35.098		35.129 3	35.109 3		.020	-.021
34.893		34.893 4	34.900 4		.007	-.004
35.008		35.012 4	35.010 4		.002	-.003
34.879		34.876 3	34.886 4		.010	-.002
34.921		34.928 4	35.002 4		.074	-.044
		34.936 3	34.868 3		.068	
34.867		35.019 3	34.890 3		.129	-.088
MEAN 35.046	******	35.072	35.048			-.026
N 13	0	14	14	0	14	13
S1-2;S3-4;S1-2-3-4				*****	.039	.030

****S E R I E 2.**** *BOTTLETYPE 111*

--INSTITUTE--		-------NIOZ--------				------DELTA-S------		
--SALINITY---		---SALINITY+BC						-- --
1	2	3		4		ABS 1-2	ABS 3-4	1+ 3+ 2 - 4
35.205	35.169	35.155	3	35.172	3	.036	.017	.023
35.222	35.223	35.162	3	35.213	3	.001	.051	.035
35.206	35.162	35.160	3	35.193	3	.044	.033	.007
35.129	35.191	35.132	3	35.143	3	.062	.011	.022
35.158	35.203	35.168	3	35.224	3	.045	.056	-.016
35.176	35.128	35.262	3	35.135	3	.048	.127	-.047
35.110	35.130	35.113	3	35.172	3	.020	.059	-.023
35.160	35.242	35.165	3	35.164	3	.082	.001	.037
35.161	35.169	35.171	3	35.162	3	.008	.009	-.002
35.205	35.118	35.142	3	35.124	3	.087	.018	.028
35.360	35.163	35.160	3	35.324	3	.197	.164	.019
35.201	35.175	35.171	3	35.158	3	.026	.013	.023
35.128	35.146	35.116	3	35.152	3	.018	.036	.003
35.149	35.106	35.052	3	35.205	3	.043	.153	-.001
35.102		35.142	3					-.040
35.208	35.121	35.110	3	35.154	3	.087	.044	.033
35.049	35.051	35.044	3	35.063	3	.002	.019	-.004
35.170	35.164	35.151	3	35.184	3	.006	.033	-.001
35.072	35.052	35.044	3	35.044	3	.020	0.000	.018
35.087	35.099	35.085	3	35.086	3	.012	.001	.007
35.116		35.117	3					-.001
MEAN 35.161	35.148	35.134		35.162				.006
N 21	19	21		19		19	19	21
S1-2;S3-4;S1-2-3-4						.045	.047	.039

****S E R I E 3.**** *BOTTLETYPE 111*

--INSTITUTE--	-------NIOZ--------			------------------		
--SALINITY---	---SALINITY+BC			------DELTA-S------		
						-- --
				ABS	ABS	1+ 3+
1	2	3	4	1-2	3-4	2 - 4
35.113		35.114 4	35.115 4		.001	-.001
35.108		35.118 4	35.859 2			-.010
35.109		35.114 4	35.117 4		.003	-.007
35.108		35.647 2	35.340 2			
35.109		35.116 4	0.000 1			-.007
35.112		35.117 4	35.112 4		.005	-.003
35.112		35.198 2	0.000 1			
35.108		35.190 4	35.116 4		.074	-.045
34.983		35.116 4	35.115 4		.001	-.133
MEAN 35.096	******	35.192	35.253			-.029
N 9	0	9	7	0	5	7
S1-2;S3-4;S1-2-3-4				*****	.023	.034

****S E R I E 4.**** *BOTTLETYPE 113*

--INSTITUTE--	-------NIOZ--------			------------------		
--SALINITY---	---SALINITY+BC			------DELTA-S------		
						-- --
				ABS	ABS	1+ 3+
1	2	3	4	1-2	3-4	2 - 4
		0.000 1	0.000 1			
		35.080 4	35.086 4		.006	
		35.075 4	35.076 4		.001	
		34.562 4	34.558 4		.004	
		34.563 4	0.000 1			
		35.081 4	35.078 4		.003	
		34.572 4	34.560 4		.012	
		35.216 4	0.000 1			
		35.187 4	0.000 1			
		34.579 4	0.000 1			
		35.204 4	35.185 4		.019	
		35.192 4	35.184 4		.008	
MEAN ******	******	34.937	34.961			*****
N 0	0	11	7	0	7	0
S1-2;S3-4;S1-2-3-4				*****	.007	*****

****S E R I E 5.**** *BOTTLETYPE 113*

--INSTITUTE--		-------NIOZ--------				------------------	
--SALINITY---		---SALINITY+BC				-----DELTA-S-----	
							-- --
						ABS	ABS 1+ 3+
1	2	3		4		1-2	3-4 2 - 4
25.383		25.379	4	25.381	4		.002 .003
31.272		31.273	4	31.269	4		.004 .001
33.446		33.477	4	33.463	4		.014 -.024
34.674		34.694	3	34.690	3		.004 -.018
31.898		31.883	3	31.923	3		.040 -.005
31.890		31.893	3	31.888	3		.005 -.001
31.901		31.899	3	31.894	3		.005 .004
32.859		32.953	3	32.860	3		.093 -.048
33.217		33.301	3	33.193	3		.108 -.030
34.367		34.367	3	34.369	3		.002 -.001
34.549		34.557	3	34.597	3		.040 -.028
34.824		34.835	3	34.828	3		.007 -.007
34.882		34.902	3	34.887	3		.015 -.012
34.950		35.147	3	35.122	3		.025 -.184
35.029		35.039	3	35.069	3		.030 -.025
35.056		35.072	3	35.069	3		.003 -.014
35.122		35.120	3	35.157	3		.037 -.016
35.179		35.184	3	35.185	3		.001 -.005
32.019		32.002	3	32.082	3		.080 -.023
31.988		32.081	3	32.077	3		.004 -.091
33.946		33.976	3	33.985	3		.009 -.035
34.452		34.456	3	34.486	3		.030 -.019
34.768		34.831	3	34.816	3		.015 -.056
34.945		35.007	3	35.051	3		.044 -.084
35.022		34.999	3	35.000	3		.001 .022
35.017		35.047	3	35.039	3		.008 -.026
32.397		32.460	3	32.415	3		.045 -.041
35.179		35.199	3	35.315	3		.116 -.078
MEAN 33.580	******	33.608		33.611			-.030
N 28	0	28		28		0	28 28
S1-2;S3-4;S1-2-3-4						*****	.030 .031

****S E R I E 8.**** *BOTTLETYPE 111*

--INSTITUTE-- / --SALINITY---	-------NIOZ-------- / ---SALINITY+BC			------------------ / ------DELTA-S------		
				ABS	ABS	1+ 3+
1	2	3	4	1-2	3-4	2 - 4
35.170		35.180	3			-.010
35.202		35.178	3			.024
35.203		35.178	3			.025
35.188		35.168	3			.020
35.187		35.170	3			.017
35.068		35.055	3			.013
35.133		35.191	3			-.058
35.137		35.200	3			-.063
35.167		35.158	3			.009
35.170		35.167	3			.003
35.180		35.286	3			-.106
35.163		35.147	3			.016
35.166		35.148	3			.018
35.173		35.229	3			-.056
35.182		35.155	3			.027
35.181		35.165	3			.016
35.188		35.175	3			.013
MEAN 35.168	******	35.174	******			-.005
N 17	0	17	0	0	0	17
S1-2;S3-4;S1-2-3-4				*****	*****	.027

****S E R I E 9.**** *BOTTLETYPE 122*

--INSTITUTE-- / --SALINITY---	-------NIOZ-------- / ---SALINITY+BC			------------------ / ------DELTA-S------		
				ABS	ABS	1+ 3+
1	2	3	4	1-2	3-4	2 - 4
35.137		35.133	4			.004
35.147		35.139	4			.008
35.169		35.161	4			.008
34.992		34.992	4			0.000
34.995		34.991	4			.004
35.073		35.070	4			.003
MEAN 35.086	******	35.081	******			.005
N 6	0	6	0	0	0	6
S1-2;S3-4;S1-2-3-4				*****	*****	.002