Water Sample Salinity Analysis From CTD Bottles and TSG

Sampling

Salinity samples were collected in 200ml glass bottles from each CTD bottle fired at each station. In addition to this, TSG samples were collected every 4 hours. Two crates were set aside for TSG samples. The TSG crates did not have complete sets of sample bottles because some were substituted and re-labelled to make up complete crates for sampling the CTD. Standard procedure for sampling from both the CTD and the TSG was to rinse the sample bottles using sample water from the Niskin bottles on the rosette, and then fill the bottle completely to collect the sample. It was considered good practise to run the samples for the TSG through the hose for approximately 1 minute in order to flush through any water that may have been sitting in the system since the previous sample was taken. The rim and the inside of the lid of each bottle was wiped dry using disposable paper towels to prevent salt crystals forming. Each sample bottle was then sealed with a disposable plastic stopper and its respective screw cap. When a crate was completed it was taken into the constant temperature (CT) laboratory and left for a minimum of 24 hours to equilibrate with the temperature of the laboratory. It was necessary to record the identity of the crate and the time it was placed in the CT lab so that it could be easily identified when a crate was ready to be analysed.

Laboratory Setup

Salinity samples were analysed using a Guildline 8400B laboratory salinometer (S/N 68426) situated in a temperature controlled laboratory. The temperature of the laboratory should have been between 22 -23°C, lower than temperature of the water bath in the Autosal, which in this case was set to 24°C. Over the duration of the cruise the room temperature was recorded in the watchkeeping logs, and was found to fluctuate between 21.5 - 23.5°C. It was possible that these temperatures are slightly erroneous because the thermometer was situated against the casing of the Autosal. When measuring different areas of the room, it was found that the temperature could be as low as 16°C near air conditioning outlets. The same components and setup for the Autosal were used on JC032 as on JC031. The only adjustment was an addition of an on/off switch on the peristaltic pump. The object of this was simply to improve the functionality of the pump for the analyst.

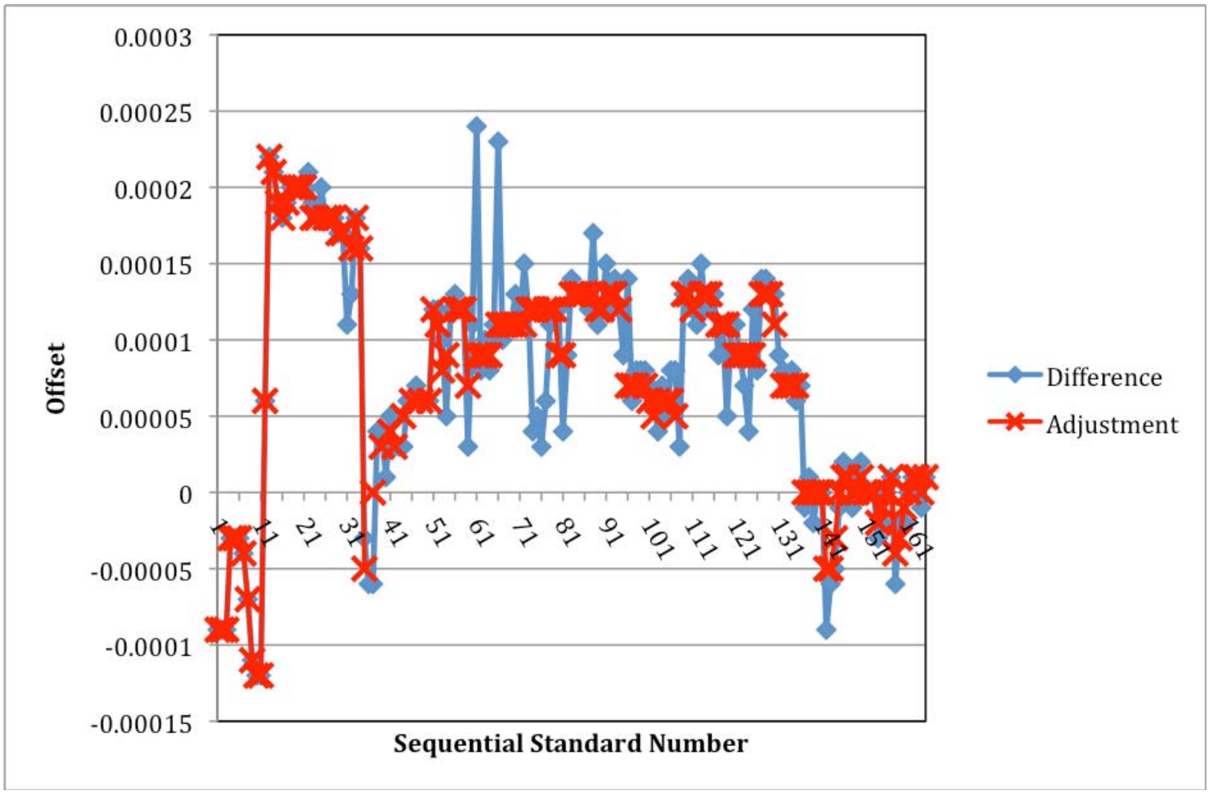
Analysis

Salinity analysis duties were shared between the members of the physics watch. In the beginning there were inevitably a few teething problems in terms of getting new analysts used to the Autosal, either because they had never performed any salinity measurements before, or because they had done so on a different type of salinometer. One of the problems that commonly occurred was failure to alter the suppression settings of the salinometer when necessary. However, this was not a major problem as the values were easily corrected by hand after the analysis was complete. Various changes, which will be discussed in this report, were made to the analysis procedures from the previous cruise (JC031). The number of remaining seawater standards was found to be approximately 170. This meant that the number of standards was limited for the number of stations on this cruise. It was therefore determined that salinity analysis should only be performed when 3 or more crates had equilibrated to room temperature. This way the number of standards used for analyses could be minimised.

Additional methods for ensuring efficient use of standards included flushing the cell in the Autosal with old standard before the usual prescribed three flushes with new standard. The reason behind this was to bring the salinity of the sample in the cell closer to the value of the new standard to increase the likelihood of any previous sample being completely flushed out. When entering bottle numbers into the data logging software, standards were designated 9*nnn*, where '*nnn*' relates to the sequential number of the standard e.g. the first standard used was 9001. This number, along with the times and crates associated with the respective standard were recorded in a standardisation log sheet.

The same standard seawater samples, produced by Ocean Scientific Instruments Ltd. (OSIL), were used throughout the cruise. Batch number: P150, K_{15} ratio: 0.99978, K_{15} ratio x2: 1.99956. Instead of running standardisations and altering the standardization setting on the Autosal (which was set at 490), it was agreed that standards would be run as samples and then adjusted for the difference between the measured value and labelled value. Several Matlab scripts were written to perform the adjustments to the salinities of the bottle samples and the TSG samples.

There were several adjustments to the standardisation setting of the Autosal at the beginning of the cruise. At station 1 the standardisation setting was changed from 490 to 583, this was changed again to 570 at station 4. The standardisation setting was finally changed to 490 when analysing station 10, because it was found that the values were too close to the 2.00000 suppression setting to allow a coherent standardisation to be achieved. After this station it was agreed that the standardisation setting should be kept the same and only to run standards as samples. Doing this meant that the salinity adjustments had to be performed manually using Matlab scripts, which would otherwise have been performed by the data logging software from standardisations.



Comparison of standardisation adjustments and differences.

The graph seen above represents the differences that were calculated between the label value on the standard bottles and the measured value of the standard. Adjustments were made to the calculated differences in order to try and smooth out the readings that were thought to be attributed to noise. It can be seen that there has been considerable drift in the values of the standards measured by the salinometer. These adjustments were made manually to the salinity data, using scripts written in Matlab. (See appendix for table of salinity standard adjustments).

It has been frequently noted by the members of the physics team, that the readings from the salinometer show much less variation (noise) on the 2.00000 suppression as opposed to the 1.90000 suppression. It is thought that this could potentially be an electronic fault which occurs when the suppression switch is put on this setting. The degree of the variability on this suppression has been found to increase at certain times throughout this cruise, but has always returned to periods of relative stability. However, due to the uncertainty that the noise is having on the final average calculated by the software, it was decided that the analysts should record the readings visually, so that efforts could be made to observe how much of an effect the noise was having on the computer calculated average. Findings showed that there was generally a difference between the computer calculated and manually calculated average of approximately 1 or 2 counts (0.00001-0.00002). Despite the noise observed on the salinometer display, this does not appear to hugely affect the calculated average. However, continued visual observation was suggested in order to maintain a record which could be consulted if results produced by the data-logging software continued to appear anomalous.

Specific Observations

This section merely draws attention to specific incidents that are considered to be relevant to the reliability and quality of the salinity samples. This should not only serve as an account of the salinity analysis that has taken place on JC032, but also as an indication of potential problems that may be encountered on future cruises.

Whilst analysing station 10 it was realised by the analyst that the drainage can was overflowing with the drainage pipe dangling in the can. It is believed that this could have caused an electrical circuit which possibly altered the electrical conductivity in the cell, hence leading to comparatively large variation in the data. The issue was explained to the physics team and the situation has thus been rectified by emptying the drainage can at the end of every set of analyses.

For the crate sampled at station 25 both temperature sensors were checked separately on different temperature settings. The temperature sensors are wired in series allowing each of the sensors to operate independently. The two temperature sensors are separated in their calibration by approximately 10-20 millidegrees Celsius. When temperature sensor 1 is selected the heater lamps should stay on temporarily to bring the temperature of the bath up, whereas when sensor 2 is selected the lamps should remain off until the temperature of the bath has fallen sufficiently. When changing between these temperature sensors the lamps should be observed to see how long it takes for them to begin cycling again.

The analysis of station 31 was suspended after the first sample bottle was run and it was decided that the readings being produced by the Autosal were far too variable. The machine was left to settle and was re-run the following day when the readings being produced appeared to be stable. It should be noted the sample, that was originally run before analysis was suspended, was re-run despite the bottle being half empty for several hours, so it is likely that the salinity of this sample may have altered from its original value.

On several occasions, the plastic insert was found to be very loose in the sample bottle. This could have potentially led to some evaporation from the sample which would have altered the salinity. In addition to this, samples were intermittently found to have no plastic inserts. These samples were not analysed on the basis of them being contaminated.

The third sample collected at station 60 was analysed but the last reading taken from the bottle yielded a very high value 8 counts higher than the previous readings. Due to the large variability an additional reading was taken which was found to be within one count of the first two readings, this value was replaced manually in the spreadsheet.

Sample bottle 8 was discarded from the analysis of station 70 due to pieces of blue paper towel found in the sample.

At station 76 a second crate of samples from the bottom -50m bottle (Niskin bottle 2) were collected with the view to assess the stability of the Autosal, however these samples were not actually analysed in the end as the Autosal appeared to have become stable again by this point.

The problem of large variability and instability in the readings from the Autosal continued, consequently, from station 80 onwards it was decided to allow the software to log the data as usual, but to also perform readings using the visual display. The reason for this was so that we could manually filter out the noisy readings from the Autosal, and have a basis for comparison in the variability of the results. It was found that there was generally very little difference in the final averages calculated by the software and the averages calculated from the visual readings taking by the analyst. The averages taken for processing were those calculated by the software, but if the averages had a difference of more than two counts then a note was made in order to flag the result as potentially noisy.

Processing

Various additions were made to the excel spreadsheet files created by the data logging software. However, the files were edited differently according to whether the files contained CTD or TSG data. For TSG samples, the files were amended by adding the collection times of each TSG sample in the following format, '*dddhhmmss*'. For CTD samples unique sample numbers were assigned according to the station number and the position the sample was taken from on the CTD rosette. For example, for the first bottle of station 67 would be recorded as 6701. It was necessary to consult the CTD logsheets to check whether if any bottles were missing due to leaks or misfires. Similarly, special identification numbers were given to standards that were run. This basically consisted of adding another two nines onto the sequential numbers of the standards, e.g. '*999nnn*'. After all the files had been edited accordingly, they were saved as comma delimited csv files.

It was necessary to determine the adjustments to give to the values from each crate due to the choice not to standardise at the beginning of the cruise. From the differences that were determined an adjustment value was chosen according to the variability in adjacent difference values. After these amendments to the files had been made the files could be processed using matlab scripts prepared '*in-house*'. Separate scripts existed for CTD and TSG samples. The difference between these scripts is that the TSG script parses out the data in terms of time whereas the script for the bottle samples sorts the data according to sample number. Both scripts perform the task of applying the adjustments from the standards to the respective datasets.

Assessment

The Guildline 8400B laboratory salinometer had been used heavily used on consecutive cruises, and thus in this regard it has been deemed to provide reliable results. However, it is recommended that certain aspects of this piece of equipment are investigated further, such as the high degree of variability in the readings when the machine is set to the 1.90000 suppression.

Appendix

Table 1: Differences and adjustments calculated for standardisations for each run

Station	Crate	Difference	Adjustment	Run Position	Comments
1	7	-0.00009	-0.00009	?	
2	7	-0.00009	-0.00009	?	
3	7	-0.00009	-0.00009	?	(bottles 41-48)
3	4	-0.00003	-0.00003	?	(bottles 73-77)
4	4	-0.00003	-0.00003	?	
5	6	-0.00003	-0.00003	?	
6	28	-0.00004	-0.00004	?	
7	28&20	-0.00007	-0.00007	?	
8	20&25	-0.00011	-0.00011	?	
9	39	-0.00012	-0.00012	?	
TSG 001	3	-0.00012	-0.00012	?	
10	7	0.00006	0.00006	?	(bottles 25-38)
10	7	0.00022	0.00022	?	(bottles 39-44)
11	28	0.00021	0.00021	?	
12	6	0.00019	0.00019	?	
13	38	0.00018	0.00018	?	
14	4	0.00019	0.00019	?	
15	11	0.0002	0.0002	?	
16	20	0.0002	0.0002	?	
17	39	0.0002	0.0002	?	
18	23	0.0002	0.0002	?	
		0.00021		END	
19	1	0.00019	0.00018	START	
20	1	0.00018	0.00018	END/START	
		0.0002		END	
21	25	0.00018	0.00018	START	
22	25	0.00018	0.00018	END/START	
TSG 002	5	0.00018	0.00018	END/START	
23	11	0.00017	0.00017	END/START	
24	11	0.00017	0.00017	END	
		0.00011		START	
25	4	0.00013	0.00016	MID	
26	25	0.00018	0.00018	MID	

27	6	0.00016	0.00016	END	
28	20	-0.00003	-0.00005	START	Standard left in?
		-0.00006		END	
29	38	-0.00006	0	START	
		0.00004		END	
30	7	0.00004	0.00003	START	
		0.00001		END	
31	23	0.00005	0.00004	START	
32	39	0.00003	0.00003	START	
		0.00003		END	
33	6	0.00003	0.00005	START	
		0.00006		END	
34	25	0.00006	0.00006	START	
		0.00007		END	
35	4	0.00006	0.00006	START	
		0.00006		END	
TSG 003	3	0.00006	0.00006		
36	39	0.00012	0.00012	START	
37	11	0.00012	0.00011	END/START	
38	25	0.0001	0.00008	END/START	
39	28	0.00005	0.00009	END/START	
		0.00012		END	
40	23	0.00013	0.00012	START	
TSG 004	5	0.00012	0.00012	END/START	
41	6	0.00012	0.00012	END/START	
42	20	0.00003	0.00007	END/START	Standard left in?
		0.00011		END	
43	11	0.00024	0.00009	START	
44	39	0.00008	0.00009	END/START	
45	7	0.0001	0.00009	END/START	
46	4	0.00008	0.00009	END/START	
		0.00011		END	
47	1	0.00023	0.00011	START	MilliQ left in?
TSG 005	3	0.0001	0.00011	END/START	
49	23	0.00011	0.00011	END/START	
50	11	0.00011	0.00011	END/START	
51	28	0.00013	0.00011	END/START	
		0.00011		END	
52	20	0.00015	0.00011	START	
53	6	0.00012	0.00012	END/START	Warm standard
54	39	0.00004	0.00012	END/START	Warm standard
55	7	0.00005	0.00012	END/START	Warm standard
		0.00003		END	Warm standard
TSG 006	5	0.00006	0.00012	START	Warm standard
56	25	0.00011	0.00012	END/START	
57	28	0.00012	0.00012	END/START	
58	11	0.00012	0.00009	END/START	
59	20	0.00004	0.00009	END/START	
		0.00009		END	

60	38	0.00014	0.00013	START	
61	11	0.00013	0.00013	END/START	
62	6	0.00013	0.00013	END/START	
63	23	0.00013	0.00013	END/START	
		0.00012		END	
TSG 007	3	0.00017	0.00013	START	
64	25	0.00011	0.00012	END/START	
65	1	0.00012	0.00012	END	
66	28	0.00015	0.00013	START	
67	7	0.00012	0.00013	END/START	
68	11	0.00014	0.00013	END/START	
69	6	0.00012	0.00012	END/START	
		0.00009		END	
70	1	0.00014	0.00007	START	
71	38	0.00006	0.00007	END/START	
TSG 008	5	0.00008	0.00007	END/START	
		0.00008		END	
72	4	0.00008	0.00007	START	
73	25	0.00007	0.00006	END/START	
74	11	0.00006	0.00005	END/START	
75	39	0.00004	0.00006	END/START	
		0.00007		END	
76	20	0.00005	0.00006	START	
77	6	0.00008	0.00006	END/START	
78	38	0.00008	0.00005	END/START	
		0.00003		END	
79	1	0.00013	0.00013	START	
80	11	0.00014	0.00013	END/START	
81	23	0.00012	0.00012	END/START	
		0.00011		END	
82	28	0.00015	0.00013	START	
TSG009	3	0.00012	0.00013	END/START	
83	4	0.00013	0.00013	END/START	
		0.00013		END	
84	39	0.00009	0.00011	START	
85	6	0.00011	0.00011	END/START	
86	25	0.00005	0.00011	END/START	
		0.00011		END	
87	1	0.00011	0.00009	START	
88	23	0.00009	0.00009	END/START	
TSG010	5	0.00007	0.00009	END/START	
89	7	0.00004	0.00009	END/START	
90	6	0.00012	0.00009	END/START	
		0.00008		END	
91	11	0.00014	0.00013	START	
92	28	0.00014	0.00013	END/START	
93	20	0.00013	0.00013	END/START	
94	7	0.00013	0.00011	END/START	

		0.00009		END	
95	6	0.00008	0.00007	START	
96	4	0.00007	0.00007	END/START	
97	38	0.00008	0.00007	END/START	
98	25	0.00006	0.00007	END	
		0.00007			
99	1	-0.00001	0	START	
100	39	0.00001	0	END/START	
101	11	-0.00002	0	END/START	
TSG 11	3	0	0	END/START	
		0	0	END	
102	23	-0.00009	-0.00005	START	
103	6	-0.00006	-0.00005	END/START	
104	20	-0.00005	-0.00003	END/START	
		-0.00001	0	END	
105	4	0.00002	0.00001	START	
106	11	0.00001	0.00001	END/START	
107	1	-0.00001	0	END/START	
		0.00001	0	END	
108	25	0.00002	0.00001	START	
109	7	0	0	END/START	
110	6	0	0	END/START	
		0	0	END	
111	1	-0.00003	-0.00002	START	
TSG 12	5	-0.00002	-0.00001	END/START	
		0	0	END	
112	11	0.00001	0.00001	START	
113	20	-0.00006	-0.00004	END/START	
114	38	-0.00002	-0.00003	END/START	
115	39	-0.00002	-0.00001	END/START	
116	23	0	0	END	
117	23	0.00001	0.00001	START	
TSG 13	3	0.00001	0.00001	END/START	
118	28	-0.00001	0	END/START	
		0.00001	0.00001	END	