

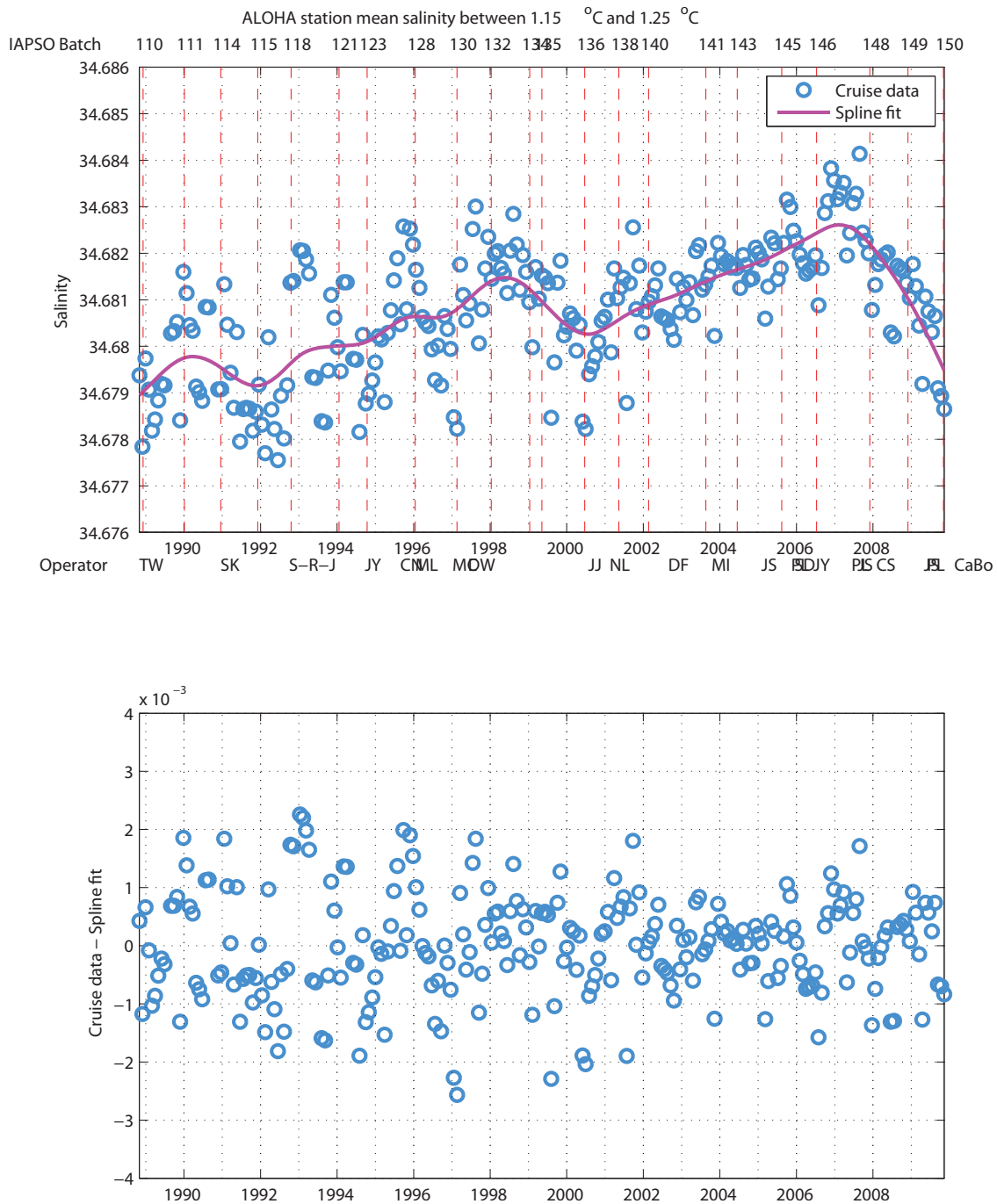
**Hawaii Ocean Time-series  
Salinity Measurement Quality Review 2000 – 2007  
(HOT-114 – HOT-190)**

Craig Nosse, Paul Lethaby and Cameron Fumar  
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# 1 Introduction

The Physical Oceanography (PO) component of the Hawaii Ocean Time-series (HOT) has been responsible for the high quality measurement of salinity for over 18 years at Station ALOHA (A Long-term Oligotrophic Habitat Assessment). Over this time period there has been an increasing trend in mean salinity observed in the deep water (see Figure 1). Until recently the net change has been small, about 0.003 psu which is close to the manufacturer's stated accuracy of the salinometer when calibrated with standard seawater. With the increase now at 0.004 psu a close inspection of the quality of salinity measurements would seem prudent in order to be confident that the trend is real. The aim of this report is to continue some of the work done in the Salinity Sample History Report ([http://www.soest.hawaii.edu/HOT\\_WOCE/sal-hist-report/salthistoryreport.htm](http://www.soest.hawaii.edu/HOT_WOCE/sal-hist-report/salthistoryreport.htm)) by Shimi Rii, in particular the standardization section, to ensure that systematic and random errors are not responsible for apparent signals seen in the time-series. The scope of this report concerns salinity data from HOT-114 (when the RS232 interface was added to the Guildline Autosol 8400B SN: 63903) to HOT-190.



**Figure 1 [Upper] Mean salinity (blue) between 1.15°C and 1.25°C at Station ALOHA from October 1988 through November 2009 and a cubic spline fit overlaid (magenta). The use of different IAPSO standard seawater batches are indicated with the vertical red dashes. Autosal operator initials are shown. [Lower] Difference between mean salinity cruise data and the cubic spline fit.**

## 2 Standardization

The methodology we use in the HOT program to analyze salinity samples is documented in the *Autosal Measurement and Salinity Data Processing Guide* (S.Ashgar et al., latest update: 2007).

### 2.1 Autosal drift

The procedure for standardizing the salinometer involves measuring a bottle of standard seawater (IAPSO), and if the reading differs by more than  $\pm 0.00003$  conductivity units from the stated value of the IAPSO, the standardization knob is adjusted until the reading equals that of the IAPSO. It is important to record the initial reading of the IAPSO along with the change in the standardization knob setting (SKS) so the drift of the Autosal can be monitored. In some cases this was not done, for example from HOT-152 to HOT-156 and from HOT-185 to HOT-189.

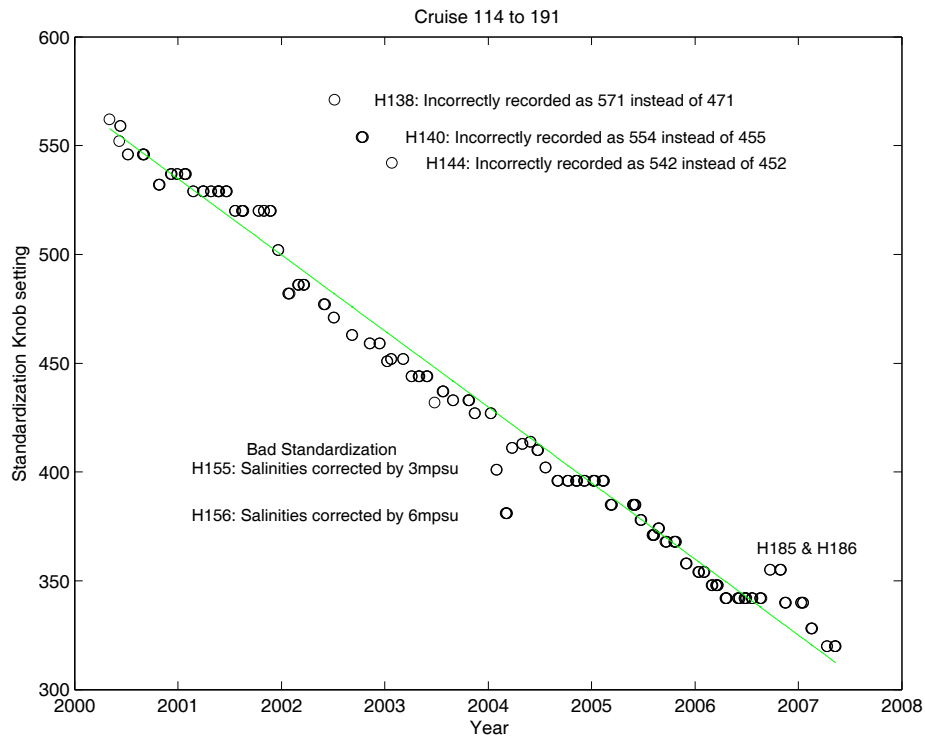
Plotting the change in SKS at standardization with time indicates the approximate drift of the Autosal and highlights potential problems in standardization or data entry. Data used for Figure 2 were read directly from HOT-114 (when the computer interface was first used) to HOT-190 raw data files rather than reading them from the salinity reports. This eliminated human typographical errors made in transcribing the data to the salinity reports.

However, human error in the actual reading and recording of the SKS still exists. Some of these errors were transposed digits and incorrectly entered data in the pre-run setup, as indicated in Figure 2 (i.e. during HOT-138, HOT-140 and HOT-144) and were subsequently corrected.

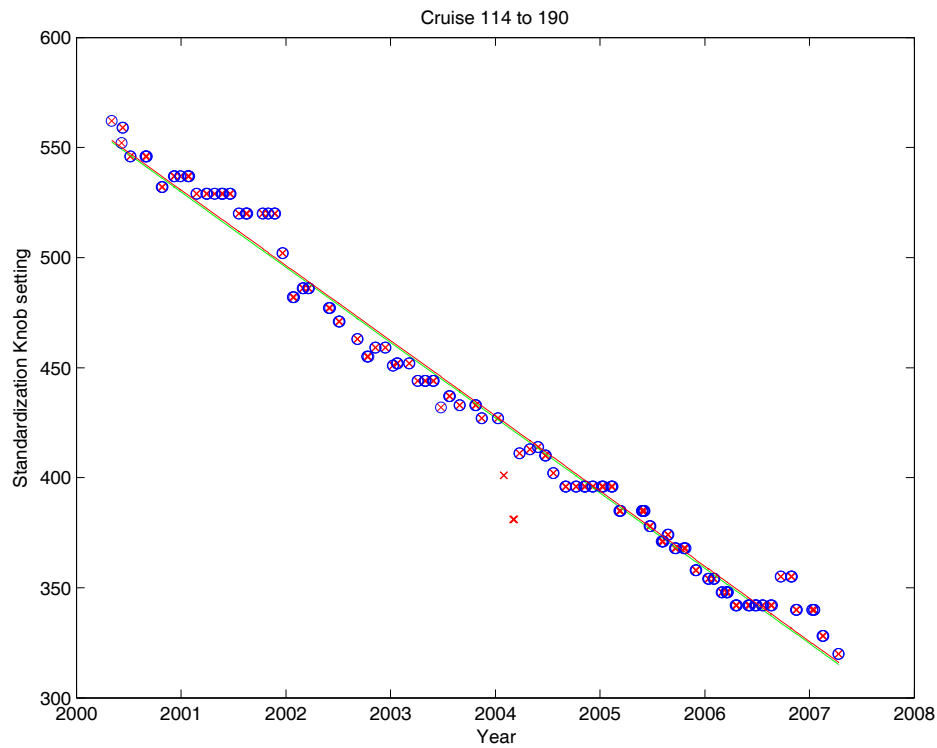
The large changes in SKS applied during the standardizations for HOT-155 and HOT-156 were due to operator inexperience. Initial IAPSO readings were not recorded by this operator until HOT-157 when it appears that the poor standardization was finally noticed and corrections were made to the measured salinities and the standardizing protocol was followed.

The changes in the SKS during HOT 185 and HOT-186 will be examined in a later section (Section 2.4)

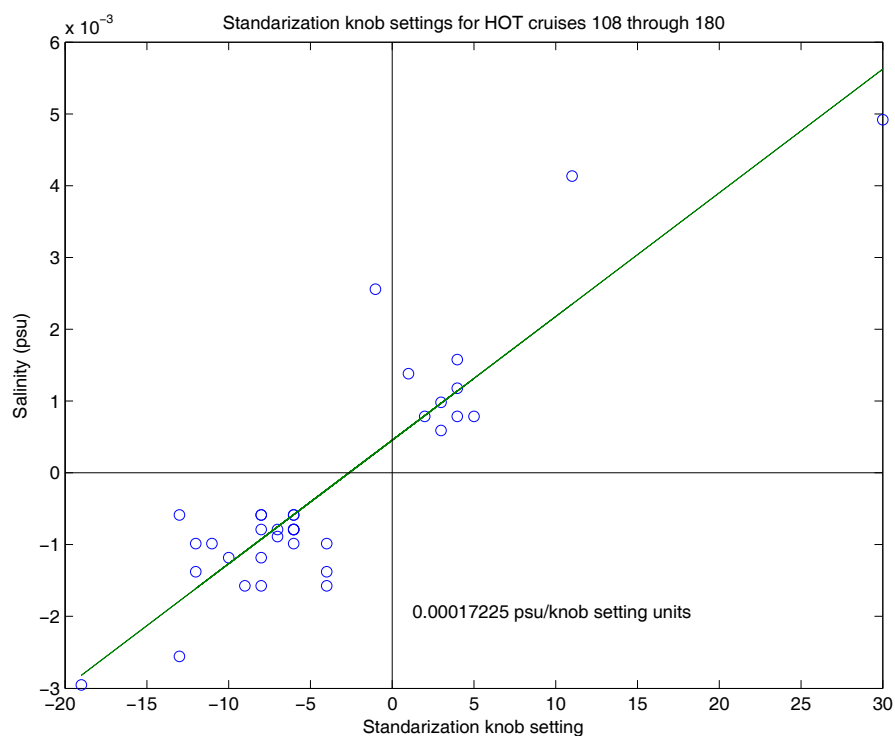
Figure 3 show the changes in SKS after data have been corrected and outliers removed.



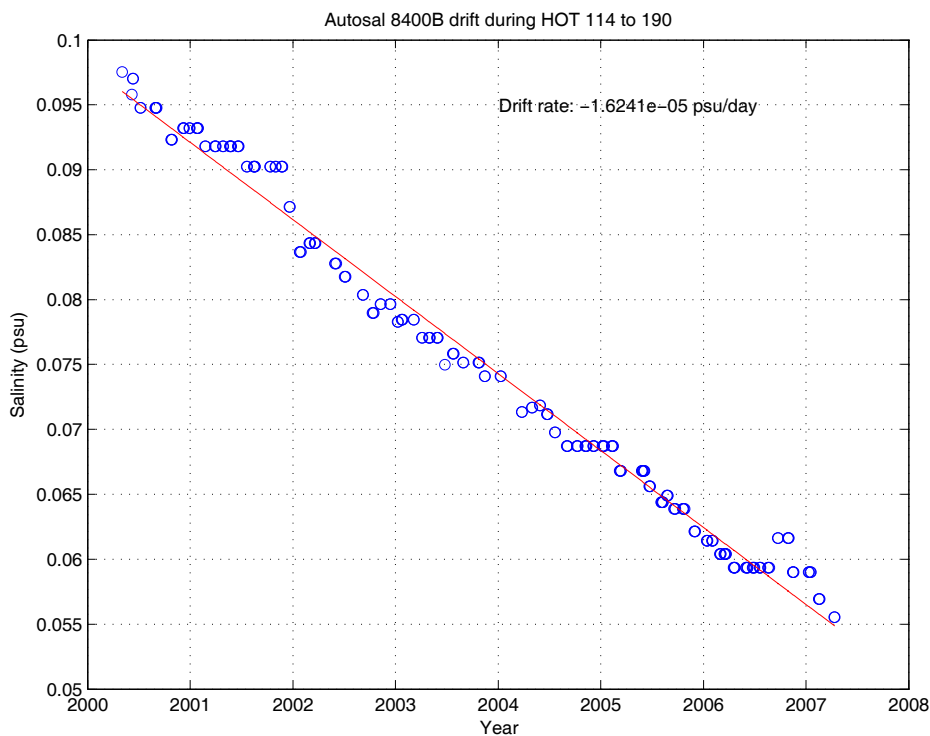
**Figure 2** Changes in standardization knob setting for cruises *HOT-114* through *HOT-190*.



**Figure 3** Changes in standardization knob setting for cruises *HOT-114* through *HOT-190* with corrections made where possible and bad SKS (red x's) ignored.



**Figure 4** Changes in the Autosol's Standardization knob setting and the corresponding changes in salinity for cruises HOT-108 through HOT-190.



**Figure 5** Same as Figure 3 but with SKS expressed as salinity change.

Using the change in SKS between consecutive cruises and the corresponding change in IAPSO salinity readings during standardizing, an equivalent change in salinity per SKS can be determined (Figure 4). Using data from HOT-108, when the autosal 8400B was first used, to HOT-190 (Figure 4) the change was found to be equivalent to  $1.74 \times 10^{-4}$  psu/knob setting unit. Using this relationship the drift rate for the autosal was calculated to be  $-1.62 \times 10^{-5}$  psu day<sup>-1</sup> (Figure 5) corresponding to Figure 3. This is slightly lower than the earlier estimate made by Shimi Rii of  $2.04 \times 10^{-4}$  psu/knob setting units for cruises 108-148, with corresponding drift rate of  $-2.33 \times 10^{-5}$  psu day<sup>-1</sup>. The drift rate over the course of a measurement run (typically 5-7 days) is small enough ( $<0.2$  mpsu) to be negligible.

## 2.2 Measurements of Substandard Water

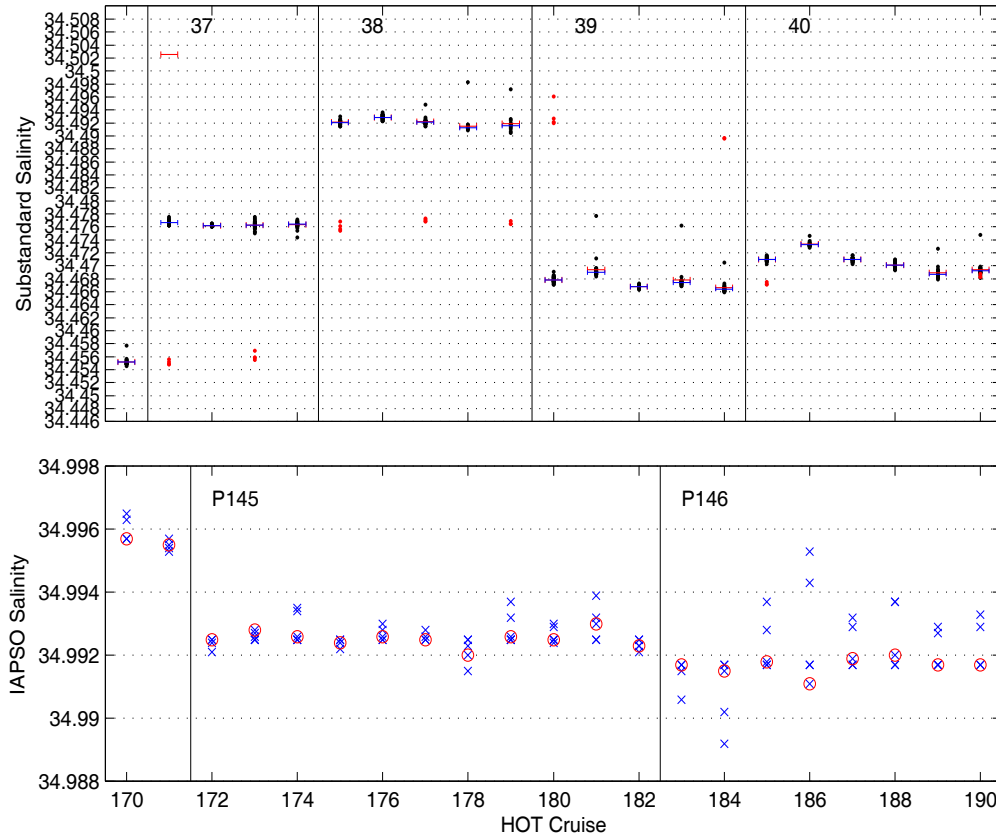
Seawater from 1020 dbar at Station ALOHA has been used as a secondary standard in the HOT program since HOT-24. It has been commonly, but erroneously called substandard water. Approximately 50 liters of homogenized seawater is used for each batch which is stored in a glass carboy capped with a thick layer of oil to prevent evaporation. The carboy is covered to inhibit light from sustaining biological growth. The primary use of substandard water is to monitor electronic drift or sudden change in the salinometer circuitry during the measurement sessions. Frequent use of IAPSO standard water would be prohibitively expensive so the substandard water is used to augment the IAPSO standard. The use of substandard water was a valuable recommendation by Dr. James Swift of SIO to the HOT protocols.

The upper panel of Figure 6 shows the results of substandard water measurements for the 21 cruises covering substandard water batches 37 to 40. The mean substandard salinity for each cruise is indicated with outliers and without outliers as horizontal red and blue bars respectively. Any offsets or corrections based on the substandard data have been applied before computing the mean values. For most cruises these mean values are very similar except for HOT-171 and HOT-173.

HOT-171 had two gross outliers present in the results. These were due to a mechanical problem associated with the suppression knob of the Autosal. The problem was identified and it was noted that sample salinity measurements were not affected at the time. HOT-173 had eight outliers. The majority of outliers are due to contamination during the drawing of the samples and more often than not involve the first substandard sample measured at the beginning of a measurement run or session. A more thorough flushing of the more saline water held at the end of the sampling tube due to evaporation or salt crystal build up is required.

The mean salinity and standard deviations for the measurements of substandard water for each cruise are tabulated in Table 1, with the overall mean salinity for individual batches. During the lifespan of a batch, stored samples from the previous batch are measured in a batch-to-batch comparison. These are usually run at the beginning, midway and end of

the batch's life and compared to the mean of the previous substandard batch, (these are shown in red in Figure 6). Values of the stored subsamples have not had any corrections applied to them. Table 2 shows the mean and standard deviations of the measurements of stored substandards and the differences in salinity from that of the established mean for the corresponding batch. The differences are relatively small at less than 0.8 mpsu with the exception of HOT-184. Measurements of stored substandards were made during the last session of the measurement run for HOT-184 and were subject to an offset which will be discussed in section 2.4.



**Figure 6** [Top panel] Measurements of salinity substandard water for cruises HOT-170 to HOT-190 covering substandard batches 37 to 40. The spread of values for each cruise includes outliers, (some outliers are outside the plotted range). Mean substandard salinity are shown for each cruise including outliers (red horizontal bar), and with outliers removed (blue horizontal bar). Measurements of stored substandard are also shown (red dots). [Lower panel] Measurement of IAPSO water (blue Xs) for same period covering IAPSO batches P145 and P146. Initial readings accepted during the standardization procedure are indicated with the red circles.

**Table 1 Mean salinity and standard deviation of batches of salinity substandard water.**

Batch	Cruise	Month	Day	Year	Mean Salinity (w/o outliers)	Standard deviation (w/o outliers)	Number of substandards measured (w/o outliers)	Number of outliers
37	171	08	01	2005	34.47666	0.00032	36	02
37	172	08	17	2005	34.47622	0.00017	21	00
37	173	09	13	2005	34.47624	0.00029	31	08
37	174	10	12	2005	34.47643	0.00031	26	02
					<b>34.47641</b>		<b>115</b>	
38	175	11	18	2005	34.49206	0.00029	33	02
38	176	01	10	2006	34.49282	0.00031	31	01
38	177	01	28	2006	34.49210	0.00031	26	01
38	178	02	20	2006	34.49122	0.00021	24	01
38	179	03	13	2006	34.49155	0.00057	15	01
					<b>34.49204</b>		<b>129</b>	
39	180	04	17	2006	34.46781	0.00037	33	01
39	181	05	27	2006	34.46898	0.00032	25	02
39	182	06	14	2006	34.46680	0.00028	13	00
39	183	07	13	2006	34.46744	0.00035	21	01
39	184	08	09	2006	34.46643	0.00034	21	01
					<b>34.46764</b>		<b>113</b>	
40	185	09	16	2006	34.47101	0.00029	27	00
40	186	10	28	2006	34.47325	0.00030	23	01
40	187	11	27	2006	34.47096	0.00032	23	00
40	188	01	08	2007	34.47009	0.00048	27	00
40	189	02	14	2007	34.46871	0.00044	21	02
40	190	04	10	2007	34.46921	0.00036	24	02
					<b>34.47056</b>		<b>145</b>	

**Table 2 Mean salinity and standard deviation of measurements of stored salinity substandard water and their difference in salinity from the mean salinity of the corresponding batch.**

Stored Substandard Batch	Current Batch	Cruise	Salinity (w/o outliers)	Standard deviation	Number of substandards measured	Difference
36	37	171	34.45512	0.00036	4	0.00051*
36	37	173	34.45603	0.00061	4	-0.00040*
			<b>34.45558</b>	<b>0.00067</b>	<b>8</b>	<b>0.00005*</b>
37	38	175	34.47597	0.00062	4	0.00044
37	38	177	34.47702	0.00022	4	-0.00061
37	38	179	34.47668	0.00026	4	-0.00026
			<b>34.47656</b>	<b>0.00059</b>	<b>12</b>	<b>-0.00015</b>
38	39	180	34.49227	0.00038	3	-0.00023
38	39	184	34.48965	0.00007	2	0.00239
			<b>34.49122</b>	<b>0.00146</b>	<b>5</b>	<b>0.00082</b>
39	40	185	34.46727	0.00021	3	0.00037
39	40	190	34.46847	0.00029	3	-0.00083
			<b>34.46787</b>	<b>0.00069</b>	<b>6</b>	<b>-0.00023</b>

\* Using a mean of 34.45563 for batch 36

## 2.3 Measurement of Standard water

IAPSO measurements are plotted in Figure 6 in the lower panel for batches P143, P145 and P146. Typically 3-4 IAPSOs are used per measurement run. The initial measurement accepted during standardization is indicated with the red circle. Measurements are accepted if the reading is within  $\pm 0.00003$  conductivity units which equates to  $\pm 0.6$  psu. Results using IAPSO batch P146 indicate that the variability between measured IAPSOs is larger than for those of the previous batch, P145, (see Table 3). This difference although noticeable is small and within the limits to which the salinity of the IAPSO is quoted.

*Table 3 Mean salinity and standard deviation of IAPSO batches P145 and P146.*

HOT Cruises	Batch	K <sub>15</sub>	Salinity	Mean Measured Salinity	Standard Deviation	n samples	Difference
172-182	P145	0.99981	34.9925	34.9927	0.00051	33	0.0002
183-190	P146	0.99979	34.9917	34.9923	0.00137	24	0.0006

## 2.4 Examination of salinity data from HOT-131, 132, 133, & 134

In late 2001 and early 2002 the rate in which the SKS changed increased. In the space of 3 HOT cruises there was a change of 0.007 psu.

## 2.5 Examination of salinity data from HOT-184, 185 & 186

As mentioned earlier changes in SKS with time reflect the linear drift of the autosal electronics with time. During the standardization of HOT-185 the SKS was **increased**, which was contrary to the history of adjustments made during the standardization procedure. At the time of adjustment this was not noted by the salinity operator. Furthermore the salinity of the IAPSO prior to the adjustment was not recorded. HOT cruises 184, 185, and 186 were examined in more detail. A summary of the measurements follows:

### 2.5.1 HOT-184 (Aug 16 – 21, 2006)

- This was the second time that the IAPSO batch P146 was used.
- The SKS remained unchanged at 342 after standardizing.

- During the course of the measurement run the value of the IAPSO fell from 34.9915 to 34.9902 to 34.9892.
- The autosal was shutdown for a scheduled power outage from the 18<sup>th</sup> – 22<sup>nd</sup> August, 2006.
- There was a drop in the value of salinity measured during the last session of approximately 1.8 mpsu.
- Stored samples of substandard from batch #38 were also run during the last session and showed a difference of 2.4 mpsu when compared to the mean salinity of that batch obtained over 5 measurement runs.

### 2.5.2 HOT-185 (Sep 20 – 22, 2006)

- This was the third time that the IAPSO batch P146 was used.
- The SKS was adjusted from 342 to 355. This was upwards (counter to prior experience) and not noted by the operator at the time.
- IAPSO values increased during the course of the measurement run from 34.9918 to 34.9928 to 34.9937
- This was the first time that substandard batch #40 was used.
- Substandard salinities values increased during the course of the measurement run of an order similar to those of the IAPSO values.
- Three stored substandards from batch #39 were run during the determination of the salinity for the new substandard batch #40. Their mean difference was 0.3 mpsu lower than the mean salinity of the previous batch.

### 2.5.3 HOT-186 (Oct 26 – 30, 2006)

- This is the fourth time that IAPSO batch P146 was used.
- IAPSO was incorrectly reported as 34.9918 in the salinity report. The actual value was 34.9911.
- The SKS remained unchanged at 355
- The mean substandard salinity is 2 mpsu higher than that of the previous cruise and of subsequent cruises.
- The IAPSO values increased from 34.9911 to 34.9953 to 34.9943 during the course of the measurement run. This is an increase of slightly over 3 mpsu. This was not noticed as the initial IAPSO reading was incorrectly reported.

The upper left plot in Figure 7 shows the results of the substandard measurements during HOT-184 against time. IAPSO values have been normalized to the mean of the substandard salinity from sessions between day 228 and 232 using the nominal IAPSO salinity. Clearly the drop in substandard values can be seen in the last session that was

started after the interruption due to the power outage. It is hard to determine if the power outage was responsible in the shift in salinity values. The second IAPSO is also lower than the first measurement before the machine was switched off. **It is recommended that interruption during measurement runs be avoided to the maximum extent possible.** Salinities measured during the last session were adjusted by +1.8 mpsu.

The upper right plot in Figure 7 shows results of measurement runs for HOT-185. The IAPSO values were normalized to the mean of the first 7 substandards measured during the first session. These 7 substandards were measured successively in order to establish the salinity of a new batch (#40) of substandard water. Measurements of stored substandard from the previous batch were interlaced between them before actual samples were run. The drift of just under 2 mpsu throughout the measurements in both substandards and IAPSOs can be seen. Measurements of stored substandard from the previous batch were in good agreement ( $<0.4$  mpsu) with the established mean salinity of that batch from over 5 cruises worth of measurements. This would suggest that the salinometer was correctly standardized. However during the standardization procedure the SKS was increased to achieve the IAPSO salinity which is not in the direction historically seen (see *Figur*). **Salinities were adjusted for sessions 2, 3, and 4 by -0.77, -1.50, and -1.30 mpsu respectively.**

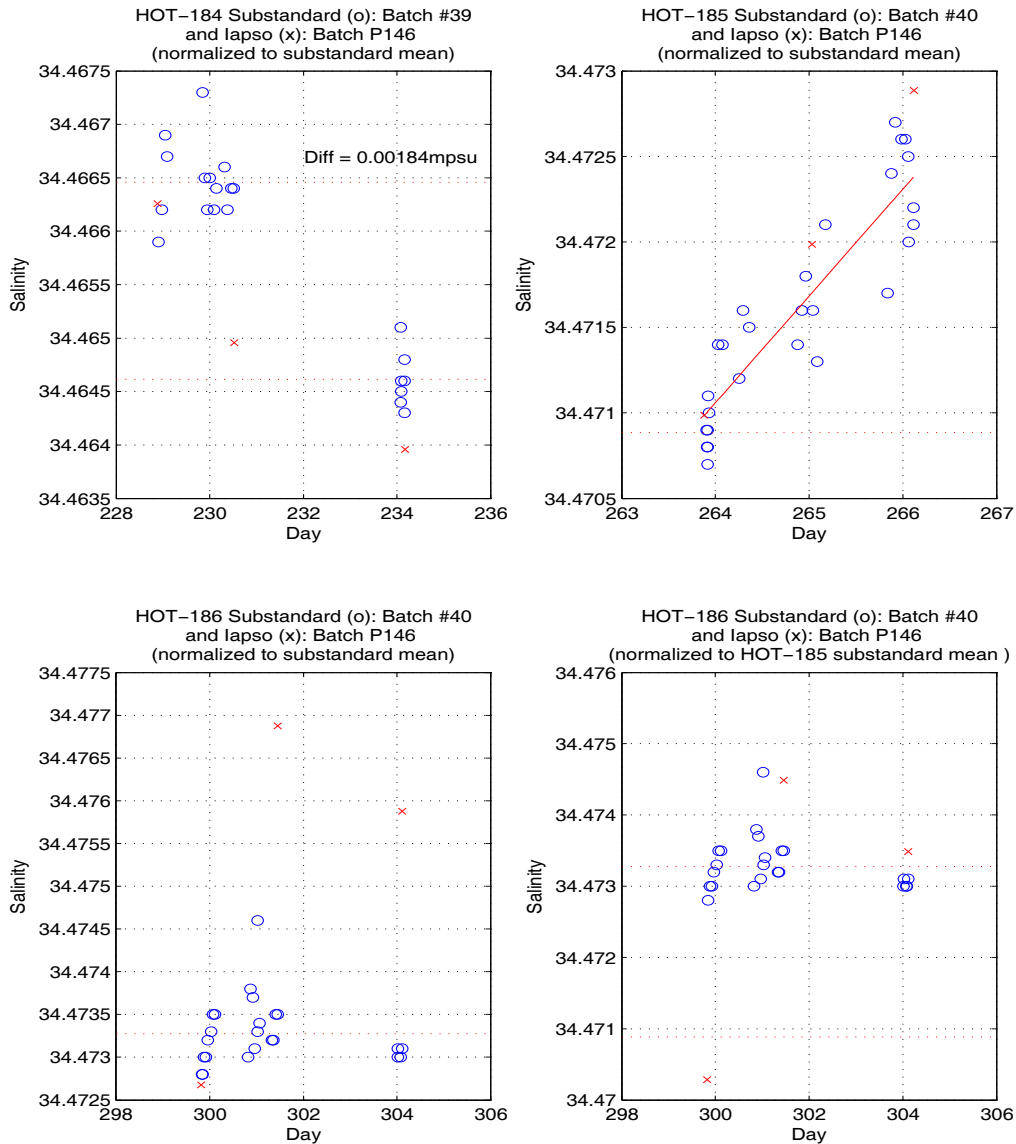
The lower left plot in Figure 7 shows IAPSO and substandard salinities for HOT-186. IAPSO measurements were normalized against the mean substandard salinity from all the sessions during the run. The second and third IAPSO measurements are particularly high ( $\sim 4$  mpsu) when compared with the initial IAPSO and also with the mean of the substandards. It is also of concern that the mean salinity of the substandard measured during HOT-186 was approximately 3 mpsu higher than the mean values subsequently obtained for the batch (excluding HOT-186).

The lower right plot in Figure 7 shows the same as the plot on the lower left only that the IAPSOs have been normalized to the mean of the substandards (corrected) measured during HOT-185. Both the IAPSOs and the substandards appear to be offset by a similar amount if the first IAPSO reading is discarded. During the standardization procedure prior to running HOT-186 salts, the SKS was not adjusted as the IASPO was accepted, being within 0.00003 conductivity ratio units of the nominal value of the IAPSO. Possibly the first IAPSO was bad and the Autosol needed adjusting but based on the acceptable measurement of this one IAPSO it was not done.

#### **2.5.4 Corrections to results of HOT-186**

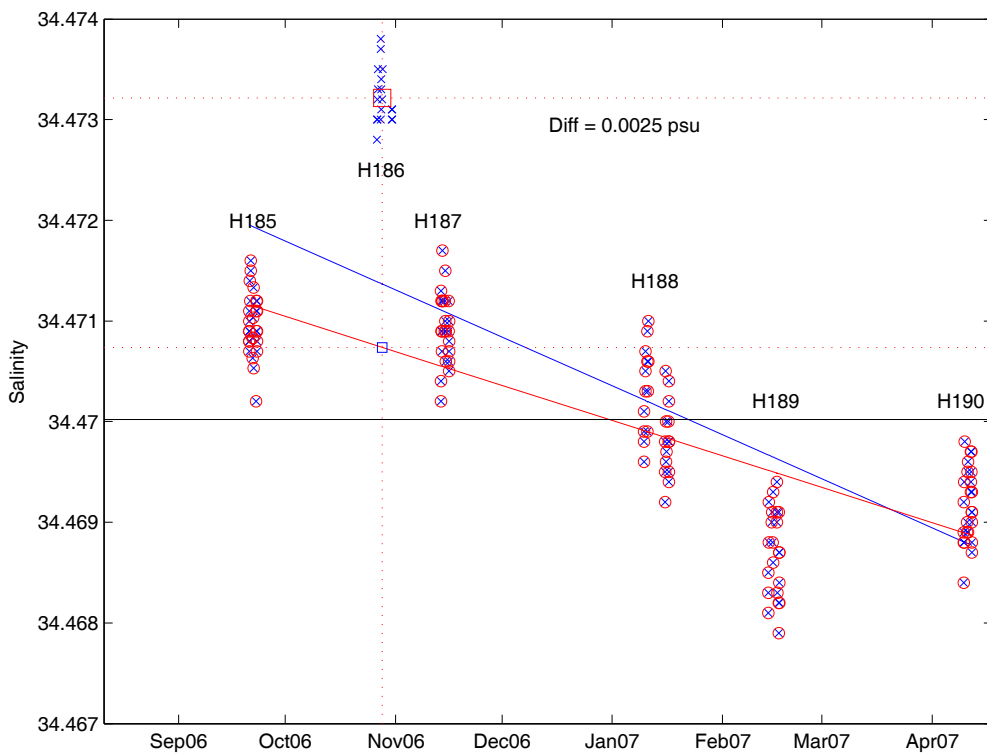
Based on the available data recorded during the measurements sessions of HOT-184, 185, and 186 it is suggested that an offset of -2.5 mpsu be applied to all the measurements made during the HOT-186 run. With 2 out of 3 IAPSO measurements and 23 substandards being higher than expected leads us to the possibility that the Autosol was not standardized correctly. This is most likely due to one bad IAPSO combined with

operator inexperience. Once the Autosol had accepted the IAPSO reading, the high substandard readings should have prompted further substandard measurements to confirm that the autosol was reading high and maybe the measurement of another IAPSO would have further confirmed this. The problem may have been compounded by the fact that the measurements during HOT-185 had a positive drift and that substandard measurements towards the end of the run were not too dissimilar to those measured at the beginning of HOT-186.



**Figure 7** Values of substandard (blue circles) and normalized IAPSOs (red crosses) plotted against time for cruises HOT-184 to 186. The upper left plot show results for HOT-184 and the upper right for HOT-185. The two lower plots are for HOT-186 but with the lower right plot showing IAPSO values normalized to the mean substandard salinity measured during HOT-185.

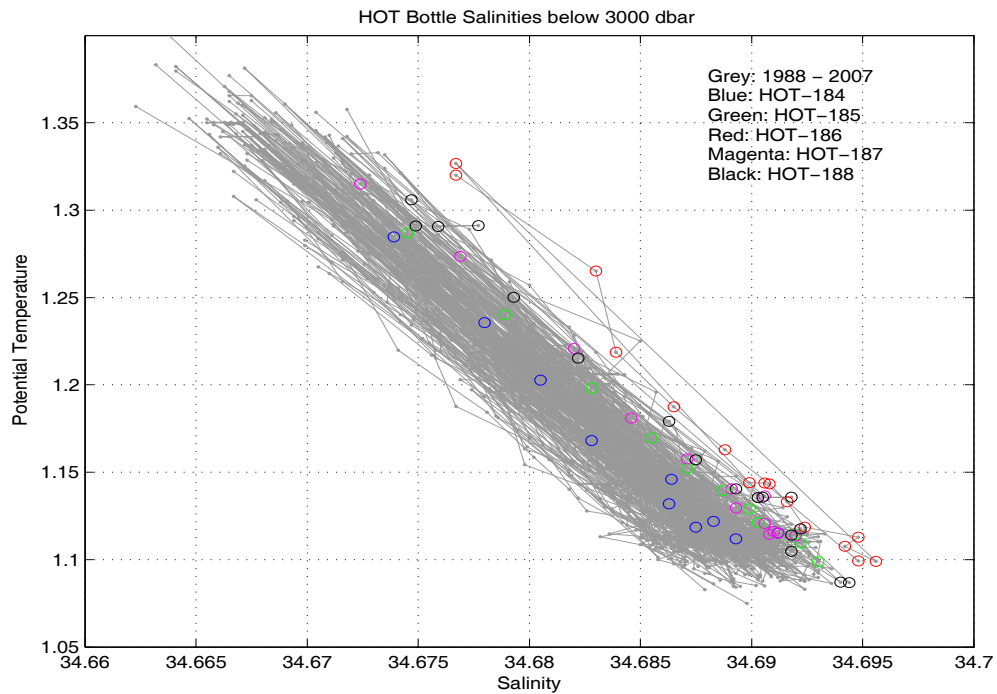
In order to confirm this correction the measurements of HOT-186 were examined with the measurements of other cruises using that batch of substandard more closely. Measurements of batch # 40 taken during HOT-185 -190 are shown in Figure 8 with outliers removed and corrections applied to results of HOT-185 (see p. 11). During the lifespan of the batch the salinity can be seen to decrease slowly with time, which has been regularly observed in previous batches. The reasons for this are still unclear but the change is slight and over the course of one run should not influence the results adversely. The difference of the mean substandard salinity measured during HOT-186 and the fit to the measurements of the other cruise was 2.5 mpsu and it is this value that is used to make the correction.



**Figure 8** Measurements of salinity substandard water for batch #40 used for HOT-185 -190 (outliers removed). Corrections have been made to the measurements taken during HOT-185 (Nov 06). The horizontal black line indicates the mean salinity of the batch excluding the measurements from HOT-186. The blue line is the fit to all the measurements made using the batch #40 and the red line is the fit excluding measurements made for HOT-186.

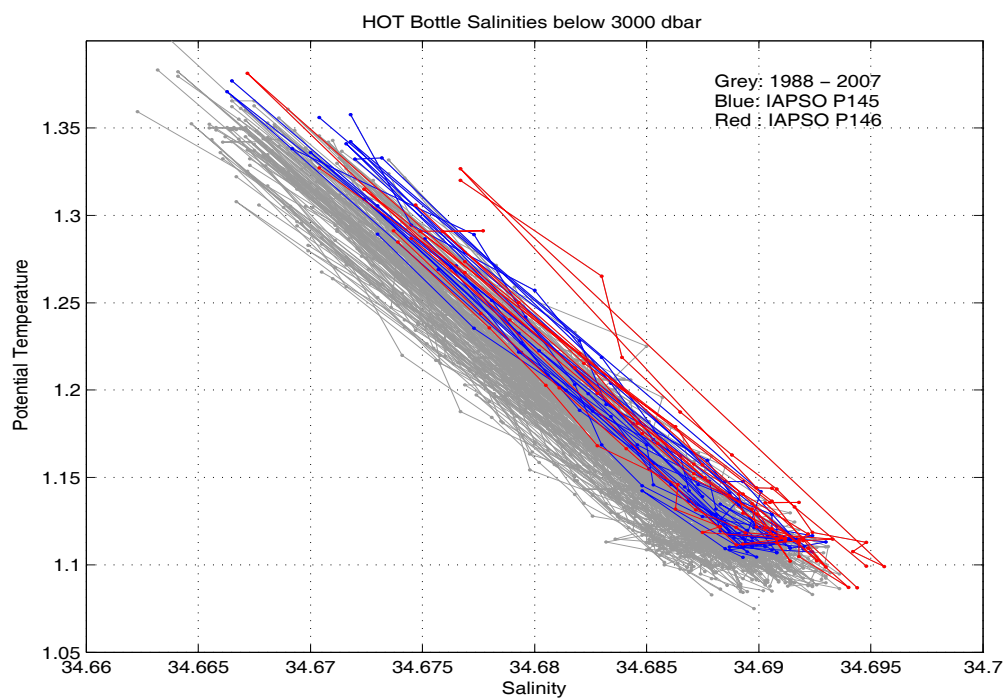
Furthermore, results from HOT-186 were highlighted against salinity measurements below 3000 dbar along with cruises HOT-184 to HOT-188 against the cloud of salinity measurements taken for the entirety of the time-series. Figure 9 indicates that measurements during HOT-186 are biased by an amount similar to the difference seen

with the batch measurements. They clearly stand out against results from adjacent cruises.



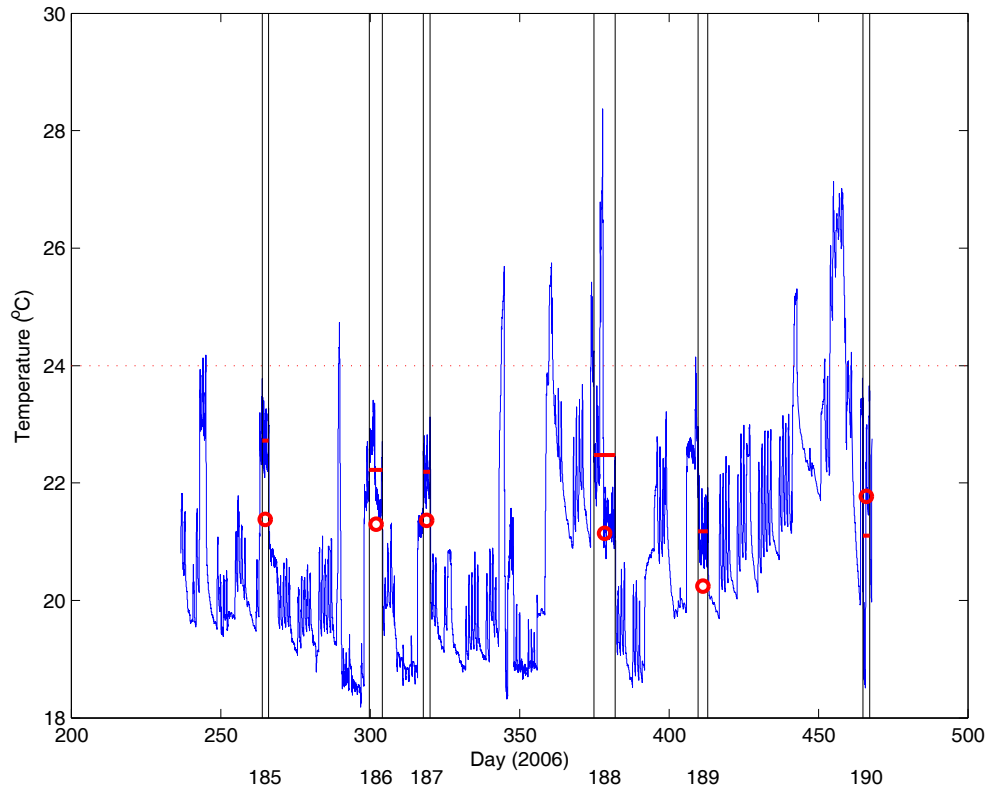
*Figure 9 Bottle salinities below 3000 dbar with salinities from cruises HOT-184 to HOT-188 highlighted.*

As a further check, the measurements using IAPSO batches P145 and P146 are similarly highlighted in Figure 10 and confirm that different IAPSO batches are not contributing to the overall trend in the salinity observed at ALOHA.

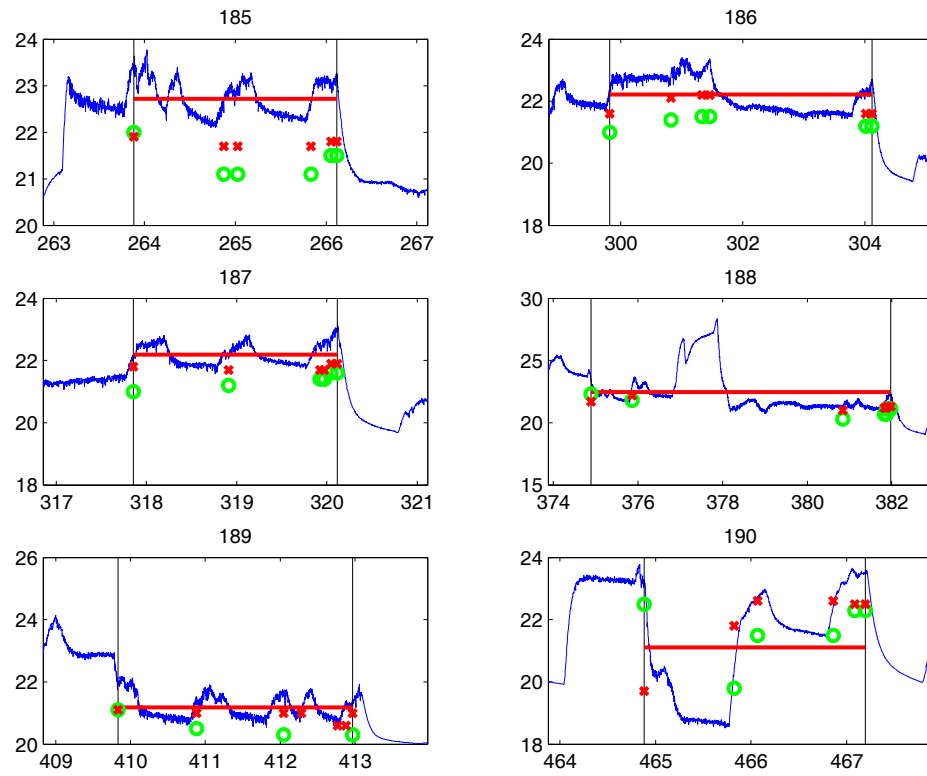


**Figure 10** Bottle salinities below 3000 dbar with salinities measured using IAPSO batches P145 and P146 highlighted.

## 2.6 Room Temperature



*Figure 11 Ambient temperature in Room 427 as measured with a Seabird Microcat sensor for the period 24 August 2006 to XXXX 2007. Salinity measurement sessions for HOT cruises 185 to 190 are indicated with the vertical lines with mean session temperature measured by the microcat plotted as the horizontal red line. The red circle is the mean temperature measured using the temperature probe normally used during measurement runs.*



**Figure 12**

## **2.7 Conclusions**

## **2.8 Recommendations**

## Appendix

**Table 4**

Cruise	Adjust	Pre adjust Reading	Adjusted reading	Pre SKS	SKS	IAPSO batch	Comments	
HOT-148	N	1.99982	1.99983	444	444	P141		
HOT-149	Y	1.99991	1.99986	444	432	P141		
HOT-150	Y	1.99982	1.99986	432	437	P141		
HOT-151	Y	1.99992	1.99985	436	433	P141		
HOT-152	N	X	1.99986	433	433	P141		
HOT-153	Y	X	1.99985	433	427	P141		
HOT-154	N	X		427	427	P141		
HOT-155	Y	X	1.99986	427	401	P141		
HOT-156	Y	X	1.99986	401	386	P141		
HOT-157	Y	1.99961	1.99986	381	411	P141		
HOT-158	Y	1.99983	1.99987	411	413	P141		
HOT-159	Y	1.99979	1.99986	413	414	P141		
HOT-160	Y	1.99992	1.99987	414	410	P141		
HOT-161	Y	1.99986	1.99978	410	402	P143		
HOT-162	Y	1.99982	1.99978	402	396	P143		
HOT-163	N	1.99978		396	396	P143		
HOT-164	N	1.99979		396	396	P143		
HOT-165	N	1.99979		396	396	P143		
HOT-166	N	1.99980		396	396	P143		
HOT-167	N	1.99982		396	396	P143		
HOT-168	Y	1.99983	1.99978	396	385	P143		
HOT-169	N	1.99980		385	385	P143		
HOT-170	Y	1.99982	1.99978	385	378	P143		
HOT-171	Y	1.99982	1.99977	378	371	P143		
HOT-172	Y	1.99959	1.99962	371	374	P145		
HOT-173	Y	1.99965	1.99962	374	368	P145		
HOT-174	N	1.99962	1.99962	368	368	P145		
HOT-175	Y	1.99968	1.99962	368	358	P145		
HOT-176	Y	1.99969	1.99961	358	354	P145		
HOT-177	N	1.99961		354	354	P145		
HOT-178	Y	1.99965	1.99962	354	348	P145		
HOT-179	N	1.99962		348	348	P145		
HOT-180	Y	1.99967	1.99962	348	342	P145		
HOT-181	N	1.99965		342	342	P145		
HOT-182	N	1.99961		342	342	P145		
HOT-183	N	1.99956		342	342	P146		
HOT-184	N	1.99956		342	342	P146		
HOT-185	Y	X		342	355	P146		
HOT-186	N	1.99955		355	355	P146		
HOT-187	Y	X	1.99959	355	340	P146		
HOT-188	N	1.99959		340	340	P146		
HOT-189	Y	X	1.99958	340	328	P146		
HOT-190	Y	1.99967	1.99958	328	320	P146		

