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1. INTRODUCTION

The method used for measuring the salinity of seawater samples during the World Ocean Circulation Experiment (WOCE) Hydrographic Program (WHP) revisit cruises of the R/V *Mirai* of the Japan Agency for Marine-Earth Science and Technology is described. Since 1978, oceanographers have used the Practical Salinity Scale (PSS78), which defines salinity as the ratio of the electrical conductivity of a seawater sample to the conductivity of a potassium chloride standard solution in which the mass fraction of potassium chloride is 32.4356×10^{-3} (UNESCO, 1981). Practical salinity has some disadvantages; for example, it is not expressed in SI units, it is a non-conservative value in the context of physical oceanography, and its range is limited from 2 to 42. Millero et al. (2008) recently proposed a new definition of salinity called absolute salinity, which is also derived from a conductivity ratio but is a conservative value with units of g/kg. Absolute salinity is going to be used in scientific studies. Although both salinity definitions use the conductivity ratio, the methods for calculating the salinity from the ratio differ; therefore, only the method for measuring the conductivity ratio is described in this chapter. The method for converting conductivity ratios to salinities is described by McDougall et al. in “The International Thermodynamic Equation of Seawater – 2010” published by IOC, SCOR, and IAPSO (2010).

The method described here is a modification of the technique described by Stalcup (1991). Salinities for tens of thousands of samples were measured by the method during the WHP revisit cruises of the R/V *Mirai*. The method is one of the best methods which provide excellent precision onboard. The precision of this method inferred from repeat runs on standard seawater (SSW) of the International Association for the Physical Sciences of the Ocean (IAPSO) during the cruises was about 0.00001 for double conductivity ratio.

2. SAMPLE BOTTLES

Samples for salinity measurement were collected and stored in 250-ml brown borosilicate glass bottles (Figure 1) with GL32 screw caps with PTFE liners (without cones). In contrast, Stalcup (1991) used 120-ml bottles with Poly-Seal cones; because evaporation was probably greater under our conditions owing to the lack of cones, we used the larger, 250-ml bottles to minimize possible errors caused by evaporation. An experiment to estimate the evaporation is described in the cruise report of PR1S (http://whpo.ucsd.edu/data/repeat/pacific/pr01/pr01c/pr01_cdo.txt). We tested the integrity of the bottles by storing samples in them for about 3 months. The double conductivity ratio of the samples increased linearly with storage time, and the difference between the original and final values was 0.00007, which is equivalent to 0.0014 in salinity, during this period (Figure 2).

3. SAMPLE COLLECTION AND ESTABLISHMENT OF TEMPERATURE EQUILIBRIUM

Each bottle was rinsed three times with sample water, and then the water was allowed to overflow the bottle for few seconds. Excess water was poured out until the water was level with the shoulder

of the bottle. This procedure left enough headspace to prevent breakage due to expansion of the cold samples. The caps were also thoroughly rinsed and then tightly screwed onto the bottles. The sealed bottles were rinsed with fresh water (cap side up) and dried on a towel to prevent formation of salt crystals around the cap. The bottles were stored upside down in a carrying case and brought to the laboratory for temperature equilibration. Samples were stored at least 12 hours in the laboratory where the salinity was to be measured (or stored in a laboratory at the same temperature as that where the salinity was to be measured). Because sample temperature is crucial for high accuracy (large differences in sample temperature can easily make the bath temperature of the salinometer unstable), special care was taken with the temperature equilibration process.

4. METHOD

The measurements were conducted with a Guildline Autosal laboratory salinometer (Model 8400B; Figure 3). The Autosal is the only salinometer that can be used at sea that can provide salinity data that meets WOCE standards. Conductivity (ratio) can be measured with this instrument. PSS78 is eventually going to be replaced by the absolute salinity, but because both scales require measurement of conductivity ratios, the method for salinity measurement described herein will still be applicable even after the new scale is approved by IAPSO and widely accepted by the scientific community.

4.1 Installation of instruments

The instruments should be installed in an air-conditioned laboratory. Knapp and Stalcup (1987) clearly showed that the temperature of the room strongly affects the measurement precision. The technical manual for the Autosal (provided by Guildline) indicates that the room temperature should be within -2 and $+1$ °C of the bath temperature. We obtained the best measurement precision when the room temperature was lower than the bath temperature. So, the room temperature was controlled not to exceed bath temperature by air conditioner in the laboratory.

The power supply is also an important factor. The voltage and frequency have to match the settings of the Autosal. A regulated power supply should be used, especially in a ship's laboratory.

Special care should be taken to make sure that the salinometer is electrically grounded. In particular, the tube coming from the conductivity cell drain must be electrically isolated from any ground source, otherwise unexpected noise may occur during measurement.

4.2 Maintenance

The technical manual for the Autosal specifies that it should be checked and maintained periodically. During the cruises, we faced the following problems, which could have been avoided if the instrument had been properly checked and maintained before the cruises:

1. Leakage of sample seawater from a pinhole in the heat exchanger.
2. Poor rotation of the impeller and consequent overheating of the impeller motor.
3. Leakage of sample seawater from the tube attached to the conductivity cell due to faulty tubing. The Teflon tube on the top panel of Autosal contacted the impeller drive belt, which cut the tube. Seawater leaking from the tube short-circuited the motor start capacitor.
4. Insufficient sealing of the cell fill tube caused contamination of the sample seawater in the cell. The double conductivity ratio decreased gradually during readings. Sample seawater also

tween the power supply frequency and settings of Autosal, that is, the power supply frequency was 60 Hz even though settings of Autosal was suitable for 50Hz. Readings were also unstable when it ran in 100 V even though the required power supply voltage was 115 V.

4.3 Data acquisition system

Aoyama et al. (2002) developed a data acquisition system for determining a double conductivity ratio and monitoring the bath and ambient temperatures, and we used the basically same system for our measurements (Figure 4). Two digital platinum resistance thermometers (Model 9540) were used to measure temperature: one placed in the bath of the Autosal to measure the bath temperature, and the other placed beside the Autosal to measure the ambient temperature. The Autosal and thermometers were connected to a laptop computer through Binary Coded Decimal output and GP-IB interfaces, respectively. When the function dial was turned to the 'read' setting, 31 readings of the double conductivity ratio were acquired after a pause of 5 seconds (Table 1). Acquisition of the 31 readings took about 10 seconds. The median and standard deviation of the 31 readings of the double conductivity ratio were calculated and the median was accepted as a measured double conductivity ratio of the sample only in case the standard deviation was less than 0.00001. The temperature was taken to be the values measured before readings of the double conductivity ratio.

The Autosal was modified by the addition of a peristaltic-type sample intake pump (provided by OSIL) equipped with a valve. By turning the valve, we could choose between the sample, the standard, and the sub-standard.

4.4. Standard seawater (SSW)

The IAPSO SSW is widely used as a standard for oceanographic observations. SSW is provided in glass bottles by OSIL. The label on each bottle of SSW contains information on the SSW electrical conductivity ratio, the salinity according to PSS78, the date of preparation, and the batch number. However, studies by Mantyla (1980, 1987, 1994) have shown differences among old ampoules of SSW with batch numbers of P1–P90, mainly variations in the relationship between chlorinity and conductivity (Salinity was defined as a function of chlorinity before PSS78 was adopted.) Inconsistency among recent SSW batches has been greatly reduced (Kawano et al., 2006), but it still exists. The reason for the inconsistency is not clear; Kawano et al. (2005) suggested differences among the electrical conductivity ratios of solutions made from various potassium chloride reagents. Bacon et al. (2000) explained the differences in terms of an aging effect. A recent study by Bacon et al. (2007) demonstrated that there is no inconsistency among SSW batches stocked by OSIL for at least 2 years; Bacon et al. therefore suggested that transport of SSW may affect its conductivity.

Because the reason for the inconsistency among batches is not yet clear, the newest single batch of SSW available should be used during a cruise to avoid any potential problems. Comparing the newest batch with the previously used batch before a cruise would also be a good idea. The batch number of the SSW used as a standard during a cruise should be recorded and subsequently included in the cruise report.

4.5 Sub-standard seawater

Approximately 20 L of seawater were collected from a deep layer, gravity filtered through a membrane filter (Millipore HA, pore size 0.45 μm) and calibrated against IAPSO standard seawater to periodically monitor the conditions of the Autosol. We refer to this seawater as “sub-standard seawater” in this paper. The sub-standard seawater was stored in an aged cubitainer with no headspace and stirred for at least 24 hours before use. Aged cubitainers showed less chloride dissolution and less increase of conductivity of sub-standard seawater. The sub-standard seawater was pumped into the conductivity cell directly from the container through Teflon tubing. Even though care was taken to keep the containers sealed, the conductivity of sub-standard seawater gradually increased over time, so it could not be used as an alternative to SSW; it was used for auxiliary measurements only.

4.6 Measurement procedure

4.6.1 Warm-up

To ensure precise measurements, the Autosol was allowed to warm up for about 24 hours after it was switched on, so that the bath temperature could stabilize. After the bath temperature stabilized, sub-standard seawater was analyzed repeatedly until the readings remained unchanged. Repeated runs of sub-standard seawater should always be done before daily sample measurements are taken.

4.6.2 Standardization

After the Autosol was warmed up, it was standardized according to the procedure described in the technical manual. More than one bottle of SSW should be used for standardization. The setting obtained by standardization should remain unchanged during the measurement and should not be touched during the cruise. The standardization setting should be changed only when the readings for the double conductivity ratio deviate widely from the real value (for example, 0.0001 which is equivalent to about 0.002 in salinity). This kind of deviation rarely happens during a 30–40-day cruise, except when the conductivity cell is removed for cleaning. If the readings for SSW deviate widely over a short period, the Autosol should be maintained and checked again according to the procedure described in the technical manual.

4.6.3 Determination of double conductivity ratio

The double conductivity ratio (along with temperature) was sampled for the sixth and seventh fillings of the conductivity cell. If the difference between the double conductivity ratios obtained for these two fillings was smaller than 0.00002, the average of the two double conductivity ratios was used to calculate the salinity. If the difference was greater than or equal to 0.00003, we measured an additional filling of the cell. If the double conductivity ratio obtained for the additional filling did not satisfy the criterion specified above, we measured two additional fillings of the cell, and the median of the double conductivity ratios for the five fillings was used to calculate the salinity.

4.6.4 Sample measurement

After standardization, samples were measured in the order shown in Table 2 by the procedure described in the technical manual. Bottles of SSW were measured at every station, and sub-standard

seawater was measured every six samples in case of a sudden drift in the Autosol. Daily measurement finished with an SSW measurement. Samples were stirred gently by turning the bottles around (rather than by shaking them) by hand before the measurement so as to disrupt any possible stratification in the bottles. Shaking the bottles produces small air bubbles, which can adhere to the electrode of the conductivity cell and destabilize the readings.

If the double conductivity ratio of the sub-standard seawater varied unacceptably from the previously measured value, we measured SSW to determine whether the variation was due to a change of the conditions of the Autosol.

Because different settings on the suppression dial could be a source of error, the settings should not be changed. For example, the suppression dial should be set to 2.0 if the salinities of the samples are expected to range from 33.05 to 36.97. If the setting of the suppression dial is changed, the difference between the double conductivity ratios measured at the different settings must be checked. The difference should be nearly negligible (or 0.00001–0.00002 at most) if the Autosol has been properly maintained and calibrated.

4.7 Cleaning of the conductivity cell

Salinity measurements were typically conducted for 16 hours a day during our WHP revisit cruises. To avoid the introduction of air bubbles and to avoid insufficient filling of the side arms of the conductivity cell, we pumped soapy water (1% Contaminon; Wako Pure Chemical Industries) or 1% ethanol or both into the cell to clean it after the daily measurements were completed. This procedure is not recommended by Stalcup (1991), but it worked well in our laboratory. After these solutions were pumped into the cell and allowed to remain there for a couple of minutes, the cell was thoroughly rinsed with ultra-pure water until the double conductivity ratio became almost zero. The warm-up procedure (repeated runs of sub-standard seawater) was followed the next day prior to daily measurements.

Complete cleaning of the cell by removal and disassembly of the cell during the cruise should be undertaken only as a last resort, because this procedure often leads to a change in the stand-by value and the SSW readings. Sometimes, re-standardization by changing the potentiometer for standardization control was necessary, and this procedure sometimes resulted in difficulties with linear correction and replicate analysis mentioned in section 4. Completely cleaning the cell routinely after a cruise or between cruise legs is recommended.

5. QUALITY CONTROL

Various factors such as changes in condition of the electric circuit of the instrument, stratification in sample bottles, imperfect sealing of sample bottles, withdrawal of samples in an inappropriate manner, withdrawal of samples from the wrong Niskin bottle, and air bubbles overlooked during measurement can be sources of error. Thus quality-control measures are required to help prevent the generation of inaccurate data, and to estimate the accuracy and precision of the salinity data. We used the following steps for quality control during our WHP revisit cruises.

5.1 Plotting differences between CTD salinity and Autosol salinity

Plotting the differences between CTD salinity and Autosol salinity versus depth (pressure) is useful

for finding “bad” measurements. The differences may not be uniform and may not vary linearly with depth. Therefore several profiles should be plotted on the same graph. The differences will fall within the small range at each depth so “bad measurements” can be found easily in deep layers. In many cases, the differences shallower than 1000 m tend to be scattered, so it is difficult to find “bad” measurements (Figure 5).

5.2 Linear correction using repeated runs of SSW

Plots of the double conductivity ratio of SSW versus time may exhibit a trend. For example, Figure 6 shows the result of repeated runs of SSW during the cruise conducted in 2005 to re-occupy the eastern part of the WHP-P3 line. The double conductivity ratio gradually decreased over a period of 22 days. The trend was calculated by the least-squares method, and the measured double conductivity ratios of SSW and sampled seawater were corrected to compensate for the trend. After the correction (Figure 5 below), the standard deviation of the double conductivity ratio for SSW was 0.00012, which is equivalent to 0.0002 in salinity. The trend will not necessarily be negative. For example, the trend was almost zero during the P6 revisit cruise in 2003, and it was positive during the western part of the P3 cruise in 2005 (not shown here). The standard deviation derived from repeated runs of SSW during the cruise conducted from 2001 to 2007 by R/V Mirai ranged from 0.0002 to 0.0004 in salinity (equivalent to 0.00001 to 0.00002 in double conductivity ratio) measured with the Autosal.

5.3 Replicate analysis

The performance of the Autosal can be determined from the standard deviation of the double conductivity ratio for SSW. However, various factors not related to the instrument, such as stratification in sample bottles, imperfect sealing of sample bottles, and withdrawal of samples in an inappropriate manner, represent other sources of error. Therefore, the actual uncertainty of bottle salinity should be evaluated by some method that accounts for the process of sample withdrawal, sample storage, and other potential sources of error. We estimated the overall precision by comparing the double conductivity ratios for replicate samples, that is, pairs of samples drawn from the same Niskin bottle. Because the difference between the salinity values for the replicates of samples at depths less than 1000 m tended to be scattered (probably because of stratification in the Niskin bottle), drawing replicates from depths below 1000 m was better for obtaining true estimates.

Figure 7 shows a histogram of differences in salinity for replicates. During our WHP revisit cruises, we draw samples for replicate analysis at six layers per station. The standard deviation of differences in salinity between replicates was usually larger than that calculated from repeat runs of SSW, that is, about 0.0002 to 0.0004 in salinity.

6. REFERENCES

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Table 1. Example of acquired 31 readings.

No.	Smpl. No.	Date&Time	Double conductivity ratio	
1	9999	2007/08/15	20:26:42	1.98199
2	9999	2007/08/15	20:26:42	1.98199
3	9999	2007/08/15	20:26:43	1.98199
4	9999	2007/08/15	20:26:43	1.98198
5	9999	2007/08/15	20:26:43	1.98199
6	9999	2007/08/15	20:26:44	1.98199
7	9999	2007/08/15	20:26:44	1.98198
8	9999	2007/08/15	20:26:44	1.98198
9	9999	2007/08/15	20:26:45	1.98199
10	9999	2007/08/15	20:26:45	1.98199
11	9999	2007/08/15	20:26:45	1.98198
12	9999	2007/08/15	20:26:46	1.98198
13	9999	2007/08/15	20:26:46	1.98198
14	9999	2007/08/15	20:26:46	1.98198
15	9999	2007/08/15	20:26:47	1.98198
16	9999	2007/08/15	20:26:47	1.98198
17	9999	2007/08/15	20:26:47	1.98198
18	9999	2007/08/15	20:26:48	1.98198
19	9999	2007/08/15	20:26:48	1.98198
20	9999	2007/08/15	20:26:48	1.98198
21	9999	2007/08/15	20:26:48	1.98198
22	9999	2007/08/15	20:26:49	1.98198
23	9999	2007/08/15	20:26:49	1.98198
24	9999	2007/08/15	20:26:49	1.98198
25	9999	2007/08/15	20:26:50	1.98199
26	9999	2007/08/15	20:26:50	1.98199
27	9999	2007/08/15	20:26:50	1.98198
28	9999	2007/08/15	20:26:51	1.98198
29	9999	2007/08/15	20:26:51	1.98198
30	9999	2007/08/15	20:26:51	1.98198
31	9999	2007/08/15	20:26:52	1.98198

Table 2. Measurement order

SSW
Sub-standard
Sample 1 of Stn. A
Sample 2 of Stn. A
Sample 3 of Stn. A
Sample 4 of Stn. A
Sample 5 of Stn. A
Sample 6 of Stn. A
Sub-standard
Sample 7 of Stn. A
Sample 8 of Stn. A
Sample 9 of Stn. A
Sample 10 of Stn. A
Sample 11 of Stn. A
Sample 12 of Stn. A
Sub-standard
...
Sample XX of Stn. A
Sub-standard
SSW
Substandard
Sample 1 of Stn. B
Sample 2 of Stn. B
Sample 3 of Stn. B
Sample 4 of Stn. B
Sample 5 of Stn. B
Sample 6 of Stn. B
Sub-standard
...
Sample XX of Stn. XX
Sub-standard
SSW



Figure 1. Salinity sample bottle.

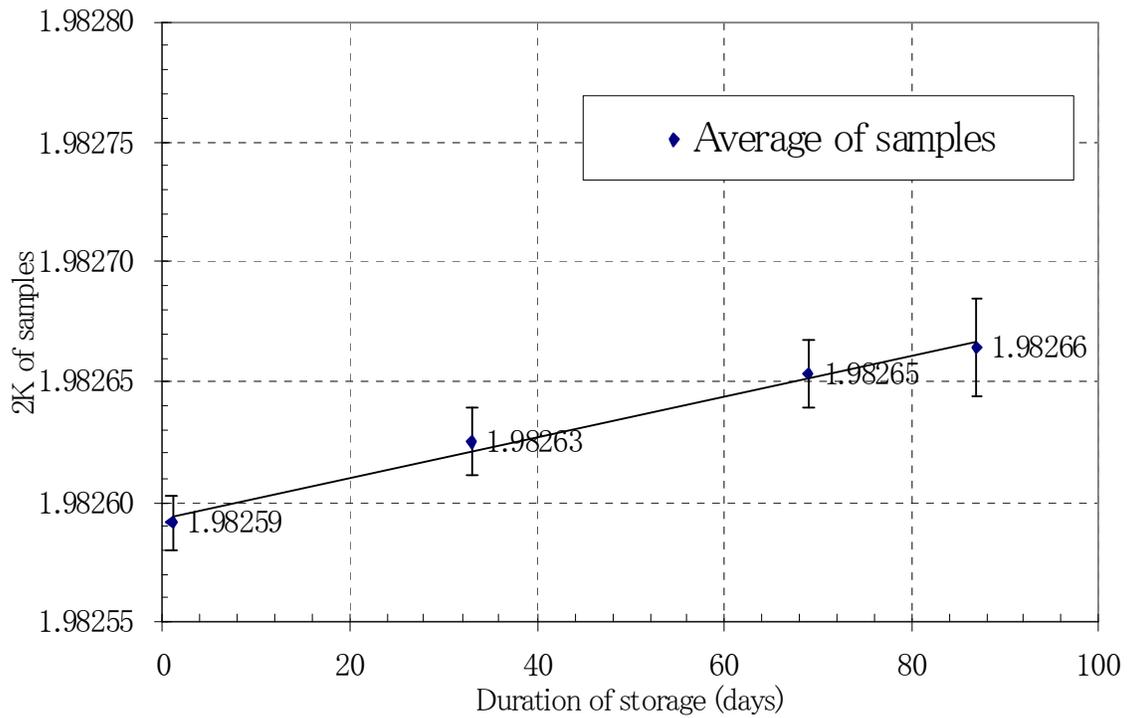


Figure 2. Effect of sample storage on double conductivity ratio. Forty samples were drawn from the same Niskin bottle; 10 samples each were measured after 1, 33, 69, and 87 days of storage. Error bars show the standard deviation for each set of 10 samples. This experiment was conducted by Marine Works Japan, Ltd., and the results are given in an unpublished report to JAMSTEC. Samples were stored in the air-conditioned ship's laboratory where the salinity was to be measured.

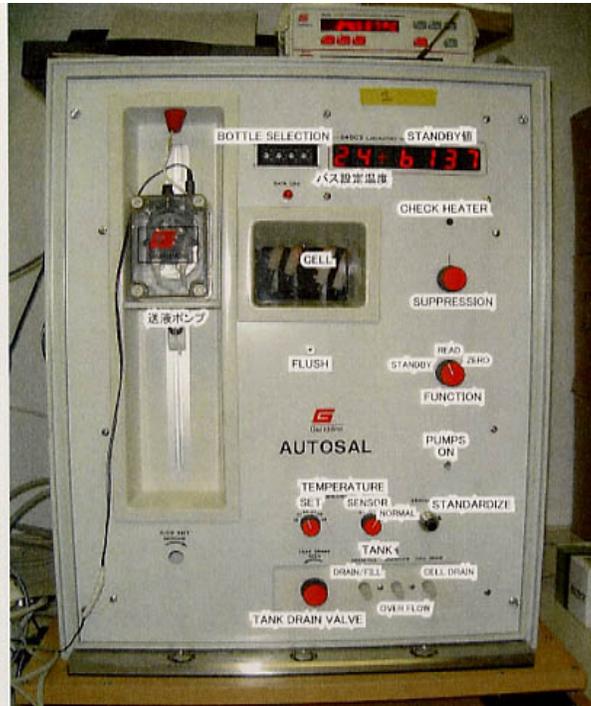


Figure 3. Guideline Autosal salinometer 8400B.

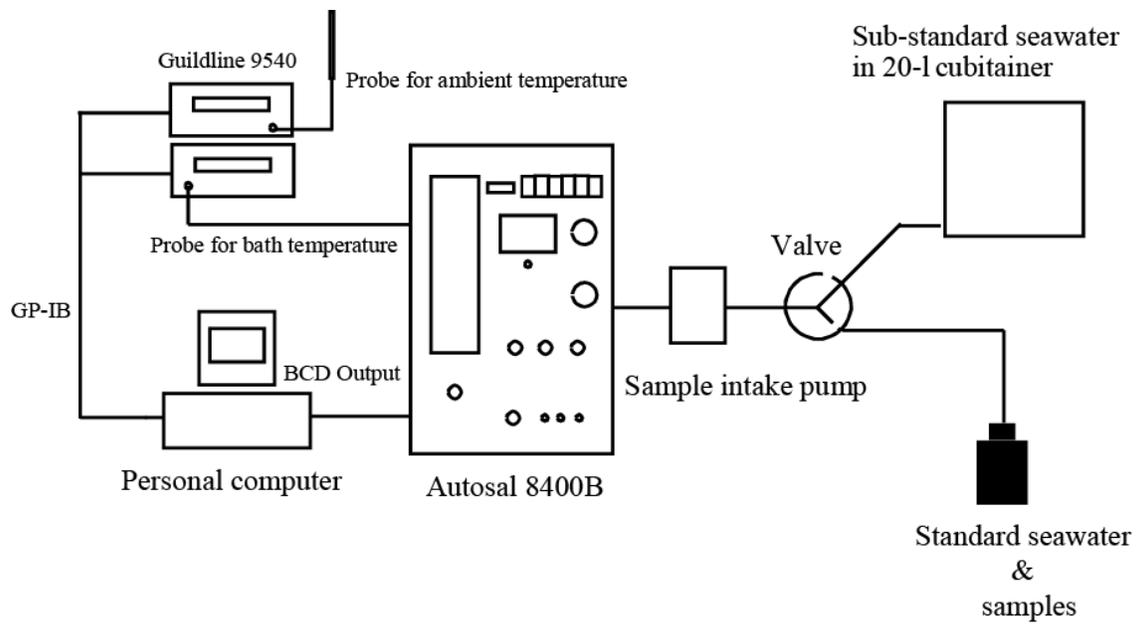


Figure 4. Schematic of measuring system.

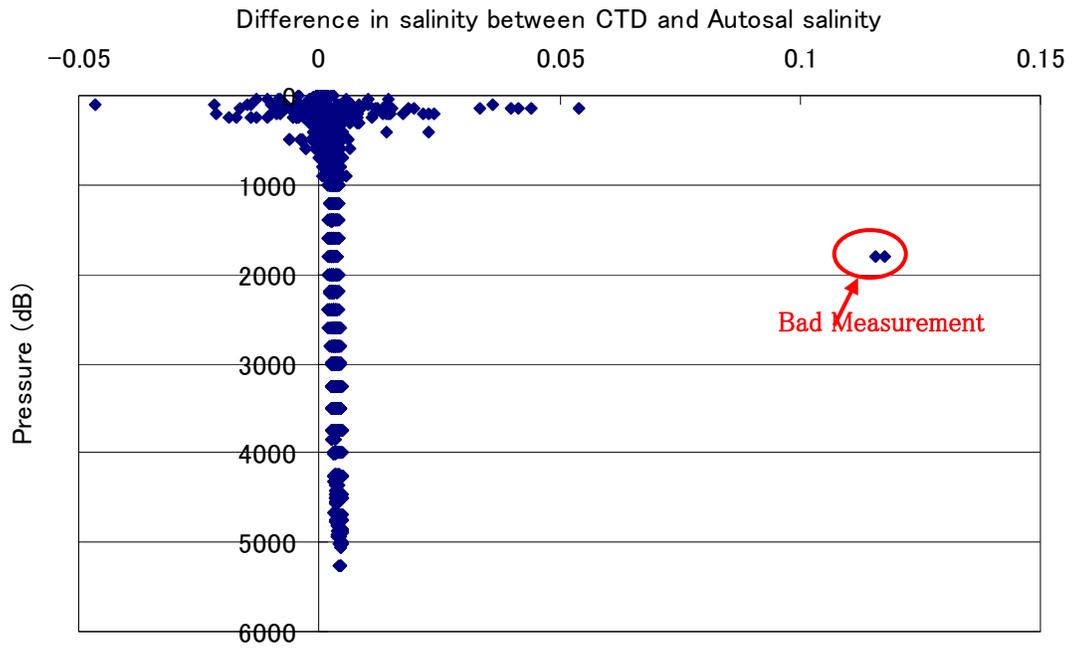


Figure 5. Vertical profiles of differences in salinity between CTD and Autosal salinity.

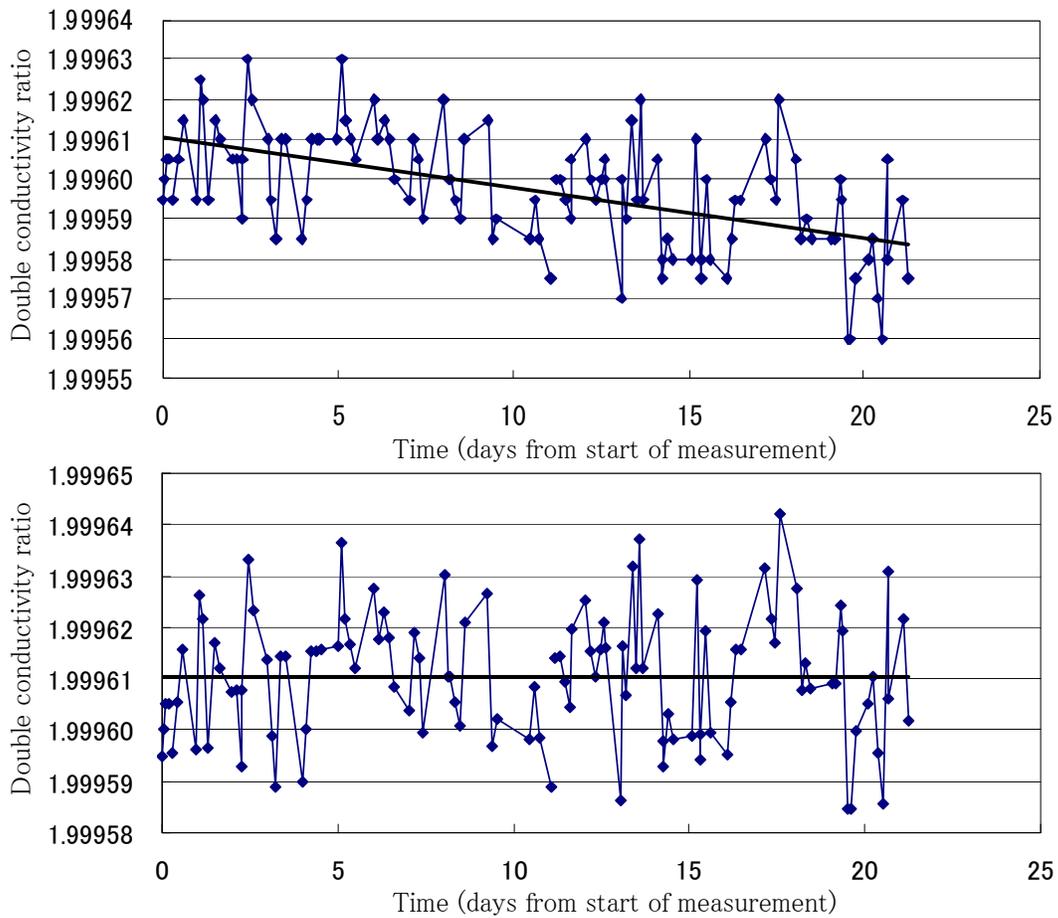


Figure 6. Temporal variation of double conductivity ratio for repeated runs of SSW (batch number P145, conductivity ratio 0.99981, double conductivity ratio 1.99962) during the 2005 cruise to re-occupy the eastern

part of the WHP-P3 line before correction (above) and after correction (below). The trend (solid black line) was calculated by the least-squares method.

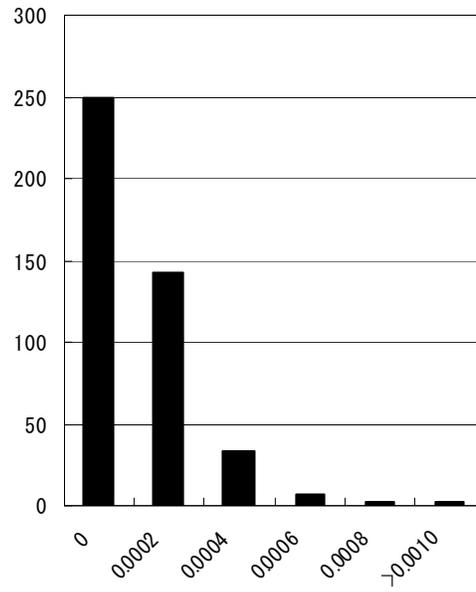


Figure 7. A histogram of the absolute difference between replicates.