

Salinity Measurements

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This report describes the collection and measurement of salinity samples during “blue water” oceanographic cruises. The technique described below has been successfully used at sea for over twenty years and presently yields salinity measurements which, when interpolated to deep potential temperature surfaces, have a standard deviation of about 0.0010. Although numerous modifications to this technique are possible, this method has consistently produced tens of thousands of high quality salinity measurements from throughout the world oceans.

1. Salinity Sample Bottles

The bottles in which the salinity samples are collected and stored are 120 ml Boston Round, flint glass bottles with screw caps equipped with Poly-Seal cones to prevent leakage and evaporation. The integrity of these bottles has been tested by storing salinity samples in them for up to six months. During this period the salinity of the water changed by less than 0.001. The Poly-Seal inserts deform with extended use and are replaced every 2-3 years. The bottles are replaced every 8-10 years. The salinity sample bottles are kept in “tote” cases containing enough bottles for a typical CTD station. Each case is identified alphabetically and the bottles within each case are sequentially numbered to match the numbers on the Rosette sampler bottles. Other groups report success with a variety of sample bottles including type III soda-glass bottles with a capacity of 200 ml and separate cones for sealing the caps.

2. Salinity Sample Collection

During the collection of each salinity sample the bottle number is matched with the corresponding Rosette sampler number. This routine minimizes the chance of collecting samples out of sequence or misidentifying their source. Each bottle is rinsed three times with 30-40 ml of sample water and is then filled only to the shoulder of the bottle. This leaves about 3 cc airspace to provide for the expansion of cold samples. The cap is thoroughly rinsed before it is tightly screwed onto the bottle. For best results these samples should be analysed as soon as they reach laboratory temperature. However, if the sample must be stored for some time before analysis, both the cap and the neck of the bottle should be dried to prevent the formation of salt crystals within the threads of the cap which could contaminate the sample when the bottle is opened. Care is taken while collecting the sample to avoid contamination from droplets of surface water dripping from the outside of the Rosette sampling bottles or from rain, etc.

3. Sample Temperature Equilibration

After all of the salinity samples from a station have been collected they are stored in the same temperature controlled laboratory in which the salinity measurements are made. Samples should equilibrate to room temperature before they are analysed if the highest accuracies are to be achieved. Thermal equilibration is typically reached within 4-5 hours, but can be accelerated by providing good air flow around the bottles or by carefully immersing them in a water bath.

4. Guildline Autosol Salinometer

Recent discussions with representatives from several oceanographic laboratories produced a consensus that the Guildline Autosol Salinometer is the only instrument presently capable of providing the required accuracy in salinity measurements made during WOCE cruises. Guildline states that this salinometer has a resolution of 0.0002 and an accuracy of ± 0.003 in salinity. They point out, however, that accuracies of ± 0.001 are possible when special care is taken in handling the samples and when the measurements are made in a laboratory in which the temperature is maintained about 1-2°C below that of the Autosol bath temperature. This higher accuracy is required to meet WOCE recommendations of ± 0.001 .

The “standard Autosol” analytical technique for measuring salinity samples is fully described in the Guildline Autosol Operating manual and should be followed closely to achieve the recommended WOCE accuracy. Some laboratories employ modifications to this technique which appear to be an attempt to compensate for the effects of either poor temperature stability within their laboratories or malfunctioning salinometers.

Autosol salinometers that are competently maintained and calibrated (as described in the Guildline Service manual) are capable of routinely measuring salinities to the WOCE standard when the analyses are conducted as recommended in the Guildline Operating manual. However, when laboratory temperatures change by more than 1-2°C during the course of the analyses a measurable drift in the standardization of the salinometer can be recorded. Attempts to compensate for this drift by frequent standardizations may not provide WOCE accuracy. The proper electrical alignment, calibration and maintenance of the salinometer are also critical to the achievement of salinity measurements accurate to ± 0.001 . Older Autosols, especially those with poor maintenance records, may be incapable of consistently providing measurements of the highest accuracy. Experience has shown that model 8400 Autosols, which have been used extensively in shipboard laboratories, have a useful life expectancy of about 10-12 years. At about this age many of the electronic components begin to fail and the overall reliability of the instrument begins to deteriorate. The reduced dependability tends to degrade the accuracy of the salinities determined with these instruments and, if the highest accuracies are required, newer instruments should be substituted.

The thermistors used to regulate the bath temperature in both the 8400 and 8400A models begin to fail after 5-7 years of continuous use. In most instances the resistance of one of the matched pair of thermistors begins to slowly change and produces a drift in the bath temperature. This temperature drift is reflected in a concomitant change in the standardization value of the salinometer. Occasionally one thermistor may fail suddenly and produce an immediate change of several degrees in the bath temperature and a large jump in the standardization value. Guildline recommends measuring the bath temperature every two weeks to monitor the condition of the thermistors and the temperature control circuit. A daily drift in the standardization value indicates that the salinometer is in need of repair and/or calibration.

Figure 1 (upper), (Knapp and Stalcup, 1987) is included here to illustrate and emphasize the deleterious effect of changing laboratory temperatures on salinity measurements made with an Autosol salinometer. During Atlantis II cruise #107, Leg 10 in 1980, the shipboard laboratory temperature varied from about 17° to almost 24°C during which the standardization of the Autosol 8400 salinometer changed by 0.003. Standardizations made when the laboratory temperature was cool produced LOW readings while HIGH readings resulted when the laboratory temperature was elevated. Compare these data to those shown in Figure 1 (lower) collected during Moana Wave cruise #893, Leg 1 in 1989. All of the salinity measurements made during this leg of the cruise were made with an Autosol 8400A in a “constant temperature” laboratory in which the temperature was 22°C, $\pm 1^\circ\text{C}$. Changes in the daily standardization of the salinometer used during this leg were less than ± 0.0005 . It is obvious that the daily standardizations during this cruise adequately tracked the drift of the salinometer.

Figure 1 clearly shows that a well maintained and calibrated Autosol 8400A salinometer drifts less than a few units per week when operated within a constant temperature environment. This experience has been duplicated on numerous cruises during the past several years using five 8400A Autosols and appears attainable by most hydrographic groups.

Although the Autosol 8400A Salinometer is remarkably stable and relatively easy to operate, several problems may occur which can reduce the accuracy of the conductivity measurements. Before attempting to analyse salinity samples to an accuracy of 0.001 the operator must thoroughly study both the Guildline Autosol Operating and Service manuals and undergo at-sea training by an analyst skilled in the sea-going collection and measurement of salinity samples. Special attention should be given to section 6.5 in the Operating Manual which describes the procedures to be followed to attain the highest accuracy. Although many of the following topics are described in the Autosol manuals and in Knapp and Stalcup (1987) they are included here to emphasize their importance.

4.1 Installation

When the salinometer is initially installed in the laboratory it is critically important that the cell overflow tubing be electrically isolated from any ground source. This tubing should also be as short as possible and arranged so that saltwater does not remain in the tubing after the conductivity cell is flushed. Best results are obtained when the salinometer is installed facing fore-and-aft instead of athwartships.

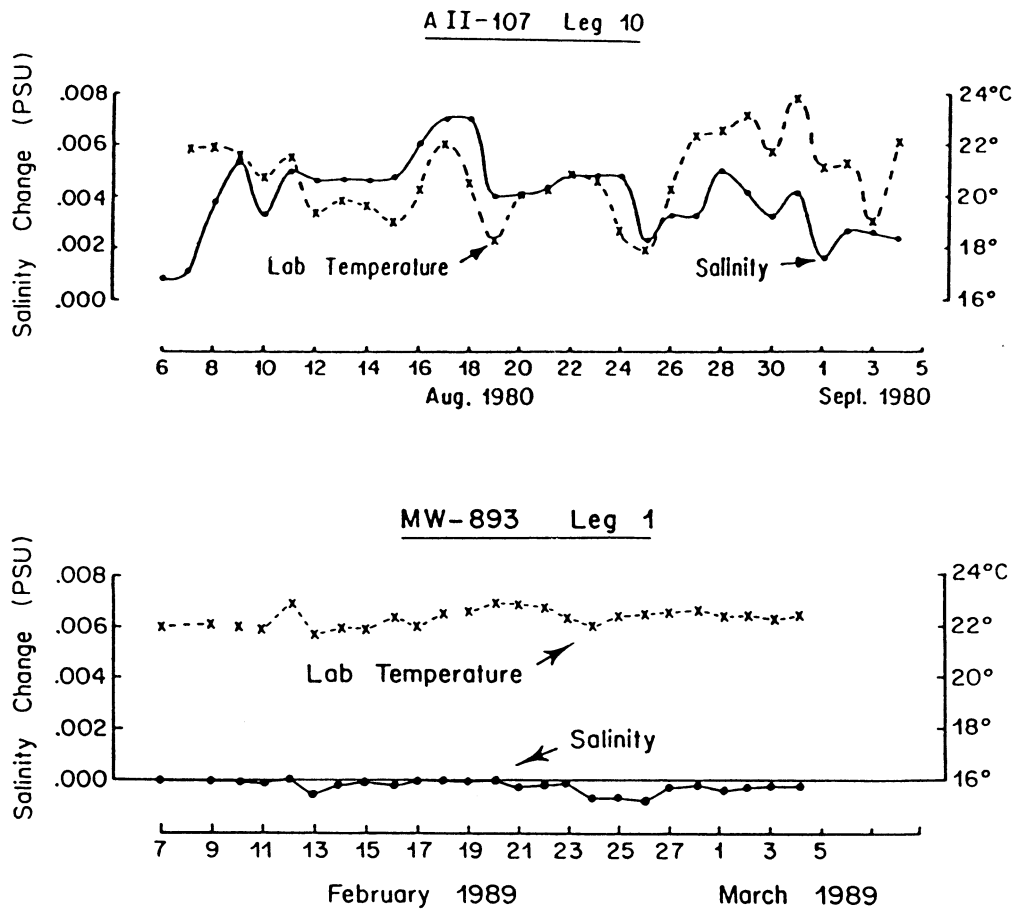


Figure 1: The upper and lower portions of this figure illustrate the changes made to the Autosal Salinometer during standardizations (PSU) and the laboratory temperatures (Celsius) during Leg 10 of *Atlantis II* Cruise #107 in 1980, and Leg 1 of *Moana Wave* Cruise #893 in 1989, respectively. During the *Atlantis II* cruise, changes of approximately 3° C in the laboratory temperature resulted in a change of about 0.003 in the standardization value. The <1° C changes in laboratory temperatures during the *Moana Wave* cruise resulted in changes of <0.001 in the salinometer standardizations.

4.2 Conductivity Cell Filling Rate

The cell filling rate is adjusted so that the sample reaches bath temperature while flowing through the heat exchanger. If cold (warm) samples must be analysed the flow rate must be readjusted.

4.3 Frequency of Standardization

The Autosol should be standardized with IAPSO SSW at the beginning of each station to measure the effect of electrode drift or changes in the bath temperature. However, if ambient temperatures are constant to within 1°C and standardizations over the course of several days show drifts of less than 1 or 2 units, then one has demonstrated that less frequent standardizations are adequate to measure instrument drift. We find that daily standardizations reliably monitor the performance of our instruments and that if more frequent standardizations are required the salinometer is probably in need of repair and recalibration.

The Autosol zero and standby readings are recorded at each station to monitor the stability of the electronics during use. A zero reading which exceeds ± 5 units indicates that the instrument needs to be calibrated as described in Section 3.4 of the Service Manual. A change in the standby number of two or three units is most likely the result of a small change in the laboratory temperature since the last standardization, and the instrument should be standardized with SSW as described in Section 6.6.2 of the Operating Manual. A larger change in the standby number is indicative of problems with the Autosol and the instrument may need to be repaired and recalibrated. The heater lamps should be observed daily to see that they are both lighted when heat is called for by the bath temperature control circuit. Burned out heater lamps must be replaced so that the correct bath temperature is maintained.

Each vial of SSW should be at laboratory temperature and be thoroughly shaken to eliminate gradients. When beginning with distilled water in the cell it must be flushed at least 10 times with SSW (or seawater near 35) before attempting to read the conductivity value. Several read-flush cycles are made until successive conductivity ratios agree to within less than 3 units. If this value differs by more than 3-4 units from twice the K15 value printed on the vial of SSW, then additional vials must be used to validate the apparent drift in the Autosol. Historically about 5% of IAPSO SSW vials contain water with a conductivity ratio more than 5 units different from that printed on the label. Whenever successive vials of SSW indicate an instrumental drift has occurred the standardization potentiometer is adjusted so that the conductivity ratio reading equals twice the K15 value on the SSW vial. When measuring a sample the display should be stable to within ± 2 units before a reading is recorded. If the display is not stable, or if the standby value has changed by more than 5 units since the last standardization, then the instrument is not functioning as it should. This salinometer may not be capable of measuring salinities to ± 0.001 and is probably in need of repair and/or calibration.

The function of the two thermistors used to control the bath temperature can be checked by switching the Temperature Sensor Switch from “NORM” to “CK1” and “CK2”. If the heater lamps do not begin to cycle normally after 2-3 minutes, in either of the switch positions, it is likely that the resistance of one thermistor has changed and the bath is no longer at the specified temperature.

4.4 Conductivity Cell Cleaning

Air bubbles or incompletely filled side-arms in the conductivity cell are indications that the interior of the cell is dirty. Attempts to ‘clean’ the cell by pumping soapy water through it or soaking the cell with various solutions invariably meet with failure and may result in a change in the standardization value. Attempts to clean the cell by pumping a weak acid solution through the cell will polarize the electrodes and seriously affect the calibration of the salinometer. For best results the cell should be carefully removed and disassembled for cleaning as described in the operation manual. A bottle brush and a cleaning solution (SparKleen) are used to thoroughly clean the interior of the glass cell. The platinum electrodes can be cleaned by gently agitating it in the cleaning solution. The cell will stay clean longer if it is kept filled with distilled water when not in use. However, when starting with fresh water in the cell, it must be rinsed at least 10 times with sample salt water before it can be used to measure salinity to ± 0.001 .

4.5 Autosal Calibration

The maintenance schedule described in the Guildline Autosal Service manual suggests that the bath temperature be verified every two weeks during shipboard use. This check requires a stable sensor capable of measuring temperature to 0.001°C . At least once a year, and before each major oceanographic cruise, the Autosal should be calibrated as described in the Guildline Service manual in section 3.4. A simple check for a discontinuity between suppression dial settings can be performed at sea by filling the cell with a sample in which the conductivity ratio is near the upper limit of the suppression switch setting used to measure samples, i.e. 1.9+9995. Increase the suppression switch by one unit and note the new reading. If the sum of the new reading, i.e. 2.0-0005, is not the same as the first, a discontinuity is present and the instrument must be recalibrated as described in the Service manual.

4.6 Standardization

IAPSO Standard Seawater is used to standardize the salinometer. The vial of SSW should be at laboratory temperature and thoroughly shaken before use. Following the instructions in the Autosal manual, the cell is filled and flushed at least ten times before a reading is attempted. The non-blinking, positive digits on the Autosal display should be set to twice the K15 conductivity ratio printed on the label of the SSW vial using the standardization potentiometer. Once the instrument has been standardized and in operation for several days, any changes in the standardization value should be suspect and confirmed

with additional vials of SSW. The most likely cause of an apparent shift in calibration is a bad vial of SSW. Shipboard experience in a temperature controlled laboratory has shown that well maintained Autosol salinometers are stable ($\pm 2-3$ units or about ± 0.0005) for several weeks.

4.7 Sample Measurement

Each seawater sample must be thoroughly shaken to remove conductivity gradients and be within a degree or so of laboratory temperature before the conductivity ratio is measured. Carefully wipe both the filling tube and the rubber stopper on the salinometer with lint-free tissue to remove traces of the previous sample. Guildline states that, when starting with distilled water in the cell and attempting to measure water with a salinity of 35, 3 flushes are required to yield values within 0.100, 7 flushes to within 0.010 and 10 flushes to within 0.001. Salinity differences between successive samples collected during a typical hydrographic station require an average of 3-4 rinses to yield high quality salinity measurements.

4.8 Radio Interference

Shipboard radio transmissions can be a source of electrical noise in the Autosol which is recognizable by highly unstable conductivity values. Conductivity ratio readings which do not stabilize to $\pm 1-2$ units within 10-20 seconds may be caused by radio interference.

5. IAPSO Standard Seawater

Standard Seawater prepared by Ocean Scientific International Ltd. (OSI) is the recognized standard for the calibration of instruments measuring conductivity (salinity). This water is natural surface water which has been collected in the North Atlantic and carefully filtered and diluted with distilled water to yield seawater with a conductivity ratio near unity and a salinity near 35. The seawater is sealed in glass vials and labeled with the date, batch number, K15 value and chlorinity. Mantyla (1987) has compared batches of this seawater (P-29 to P-102) and found inter-batch differences as great as about ± 0.003 in some of the older batches. Since batch P- 93 however, inter-batch differences have not exceeded about 0.001.

It is recommended that a single batch of SSW be used during each cruise and that it be identified in the cruise report. It is the responsibility of the salinity analyst and chief scientist to ensure that the quality of the salinity observations are the highest attainable. It follows, therefore, that the inter-batch differences described by Mantyla (1987) should be used to correct the final salinities before they are reported. It has also been noted that the conductivity of some Standard Seawater changes with time. Vials more than 4-5 years old should be compared with fresher Standards to determine possible changes in conductivity due to aging. We have used SSW batch P-97 since 1983 and, after numerous comparisons

with fresher batches, have never detected any change in the conductivity of this batch. Additional standards with salinity values of 10, 30 and 38 are available from OSI to provide better calibrations for salinity measurements near these values. The use of substandards to conserve SSW when standardizing the salinometer is not recommended.

6. Data Quality Control

Scatter plots of the CTD potential temperature (Θ) *versus* the water sample salinity values should be prepared soon after each CTD station is completed. This provides an initial assessment of the quality of both the salinity sample collection procedure and the analytical technique. A typical plot of the data presents Θ (0 to 30° C) *versus* salinity (34.5 to 37.5) on a 8" x 10" graph. The deep samples are also plotted at a higher resolution where Θ varies from 0 to 4° C and salinity from 34.4 to 35.1. Station data which are geographically and hydrographically similar are grouped together to define the local Θ /S relationship. Deep oceanic gradients are generally minimal so that small differences from the established Θ /S curve are more readily apparent in the $\Theta = 0$ -4° C plot. This plot provides the best assessment of the quality of the salinity measurements. Duplicate samples are collected from some stations and analysed to assess the reproducibility of the salinity measurements.

Salinity values are also compared with historical data from the same area. However, it is important to remember that Mantyla (1987) has shown that some of the older batches of SSW had inter-batch differences as great as 0.003. During a recent cruise in the western Pacific, for instance, the salinity measurements were compared with those measured during two earlier cruises. One cruise averaged 0.002 higher and the other 0.002 lower than the modern measurements. When the historical salinity measurements were corrected for the inter-batch differences measured by Mantyla (1987) all three cruises were in agreement.

7. Record Keeping

Complete records of all the salinity measurements and standardizations made during the cruise should be maintained. For each station the Ship-Cruise ID, station and cast numbers, date and time, operator's name and IAPSO Standard Seawater batch number, conductivity value and correction applied to the data are recorded together with the Autosal Salinometer serial number, bath temperature, zero reading, standby number and average room temperature during the measurements. For each sample the "tote" case ID, sample bottle number, double conductivity ratio value, calculated salinity and quality indicator are recorded. A separate record is also kept of problems noted with each of the Rosette sampling bottles. This information is used to provide a history of the performance of each bottle.

8. Accuracy

During all of the WOCE cruises the participants are expected to measure salinity with an accuracy of ± 0.001 . Based on salinity measurements made during the recent Moana Wave cruise #893 in 1989, described earlier in this report, this requirement seems routinely attainable with an Autosal 8400A. During this cruise 216 CTD stations were occupied along 10°N , from the Philippines to Costa Rica. At most CTD stations 24 salinity samples were collected throughout the water column to calibrate the CTD conductivity sensor. At each of these stations salinities were interpolated to a potential temperature of 1.4°C . With the linear trend removed from these data the standard deviation of the interpolated salinity is about 0.001 in each of the major oceanic basins crossed during the cruise. Forty-three duplicate samples were collected at the same depth from separate sampling bottles. The standard deviation of differences between these samples is 0.0010.

9. References

- Knapp, G.P. and M.C. Stalcup 1987. Progress in the measurement of salinity and oxygen at the Woods Hole Oceanographic Institution. *WHOI Tech. Rept.*, **WHOI 87-4**, 27 pp.
- Mantyla, A.W. 1987. Standard seawater comparisons updated. *J. Phys. Oceanogr.*, **17**,4, 543-548.