

Salinity Determination

OVERVIEW: This procedure describes the method for the determination of seawater salinity using a Guildline Portasal™ Salinometer (Model 8410).

1. Principle

During a cruise a 24 bottle rosette is used to collect seawater salinity samples of ~225 mL from all bottles closed from pre-designated depths. A Guildline Instruments Portasal™ Salinometer (8410A) makes the precise conductivity comparisons between the water samples and a reference water standard. From these comparisons salinities are then calculated and logged using PC based software that averages data that meet replicate criteria. Concurrent with the water sampling, a Sea-Bird Electronics CTD (SBE 911 plus) profiles in situ data. Data processing software is used to compare the bottle salts to in situ CTD measurements. This is useful to confirm bottle closure, monitor CTD performance, and to select the best salinity data for future comparison.

2. Sample Bottles

Salinity bottles are collected in ~250 ml borosilicate KIMAX-35 bottles. These square cross sectioned bottles have screw tops and lids with separate plastic thimbles to prevent leakage and evaporation. Numbered stackable divider boxes (<http://www.lewis-bins.com/index.cfm?mf=browse.showPart&partClassID=2789&PName=Divider%20Boxes>) hold 24 numbered bottles to match the 24 Niskins on the rosette water sampler. Bottles are filled with previously unused sample water to limit salt crystallization and to pre-leech silicate from the glass.

3. Sample Collection

Numbered salt bottles are drawn from corresponding Niskin bottles and filled to the shoulder after three ~40 ml rinses. The last fill is done without interruption until overflowing; then ~10 ml is poured out over the thimble and the bottle is stoppered and capped. Samples are left to equilibrate to room temperature for >8 hours prior to measurement. Before being placed in the salinometer samples are: gently inverted 3 times to remove any possible stratification, wiped around the bottom of the cap to draw out as much water as possible that may be trapped under and around the cap, wiped around the thimble and threaded neck once the cap is removed to eliminate any excess water or salt precipitate, and flushed by dumping out ~10 ml into a collection bucket.

4. Guildline Portasal™ Salinometer (8410A)

Guildline Portasal Salinometer model 8410A (<http://www.guildline.com/Datasheet/Guildline8410ADatasheet.pdf>) is used to make the precise conductivity comparisons between the water samples and reference water standards. Two of these instruments are taken on each cruise. Guildline specifications state an accuracy of ± 0.003 PSU (same set point temperature as standization and within -2°C and +4°C of ambient), and a precision of 0.0003 PSU.

3. configuring the PORTASAL™

Bath temperature must be within 2 degrees below and 4 degrees above ambient. To check bath temperature set point press the TSET key. Compare set point to actual by pressing ENTER for actual bath temperature. Set point and actual temperature must be within 0.02°C. Press UP ARROW key to view temperatures of the dual bath thermistors (TH1 and TH2). TH1 and TH2 must agree to within 0.04°C.

The Portasal must be powered up for >3 hours to ensure bath temperature regulation has begun before Reference values can be calibrated. While the the FUNCTION switch is in STDBY pressing REF key will display alternating Reference readings plus (+), minus (-), and Reference readings. After several cycles, when + and - values are within 1 unit of each other, pressing the COND key will initiate salinometer self-calibration.

With the FUNCTION switch set to ZERO, pressing the COND key will initiate the ZERO calibration process. When satisfied that the displayed value is stable, press the ZERO key. When the subsequent displayed number is stable (but not necessarily zero) press the COND key. The display should then read 0.00000. Setting the FUNCTION switch back to STDBY will ready the Portasal for Standardization.

4. SubStandard Preparation

Deep sea water is collected on cruises from bottles tripped at depths greater than 300m in 10 liter polyethylene jerry jugs. The seawater is then transferred to 50 liter carboys at the lab for filtration. During the transfer 10 ml hypochlorate (bleach) is added to inhibit biological activity. Concentrated high salinity seawater is prepared by evaporating deep sea water (>300m) by heating the seawater at about 90°C in an oven overnight. A volume of 1800 ml will evaporate down to about 1000 ml in 24 hours, final volume can be adjusted with DI water, this will give a salinity of around 60psu. Filter the concentrate through GF/F filter before using it for adjusting the sub-standard. Filter the deep seawater through GF/F to 46 liter mark. Add 10 ml laundry bleach to inhibit biological activity. Measure the salinity of the filtered water. Adjustment of the substandard salinity is usually done in two steps. For the first adjustment, add concentrate to the filtered sea water to adjust to the desired salinity using the relationship:

$$(\text{vol. sw})(\text{sal. sw}) + (\text{vol. conc.})(\text{sal. conc.}) = (\text{vol. sw} + \text{vol. conc.})(\text{final sal. sub})$$

The salinity of the concentrate will be too high to measure on the salinometer. If you have prepared the concentrate as above you can do your initial adjustment using an estimated salinity of 60 for the concentrate. The final salinity of the sub should be close to your standard value ± 0.015 PSU. For the initial adjustment it works well to add about 90% of the concentrate volume calculated above. Be sure you have thoroughly mixed the solution by stirring gently. A motorized paddle wheel is used to thoroughly stir the mixture. Measure the salinity of the sub after the first adjustment. Using the equation above you can now calculate the apparent salinity of the concentrate, by using the salinity of the concentrate as an unknown, along with the known values for the initial salinity of the seawater, and the adjusted value of the substandard as just measured. Applying the calculated salinity value for the concentrate, use the equation again to calculate a new volume of concentrate to be added to get to the final desired salinity of the substandard. If your initial concentrate addition was too large you may have to dilute with DI water using zero for salinity concentrate in the equation. When you have arrived at the desired salinity for the sub-standard add a layer dimethylpolysiloxane to prevent evaporation resulting in salinity changes.

6. IAPSO Standard Seawater

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Standard Seawater

(<http://www.osil.co.uk/IAPSOSeawater/SeawaterStandards/tabid/113/agentType/View/PropertyID/47/Default.aspx>) 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 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.

7. Wolga Water

In addition to using IAPSO SSW, a batch of aforementioned substandard water has been bottled and sealed in glass vials. This is done to decrease dependence on IAPSO standard while maintaining acceptable standardization accuracies.

8. Standardizing the Portasal with substandard

Before standardization can begin the conductivity cell must be flushed rigorously as it had been filled with detergent or 50% ethanol between uses. To flush, attach the peristaltic pump to the Portasal sampling tube. Turn on both the Portasal and peristaltic pumps, and open the valve on the substandard feed line. Flush repeatedly (~10 flushes) until the cell is free of contamination. It is convenient to do this during Portasal configuration. Begin the salt program on the salt computer, and complete requisite data fields.

With the conductivity cell full of substandard and a stable value being displayed turn the FUNCTION switch to READ. When displayed value is stable press STD key. When the Portasal display reads STD STANDARDIZE press ENTER key. The display will show the conductivity of the standard being used. Press ENTER key to proceed (if values of substandard need to be adjusted use ARROW keys.) The BATCH # will be displayed and should match what is being used. If values need to be changed modify with the ARROW keys, pressing the ENTER key will ready Portasal for standardization. The display will read ENTER WHEN READY, press ENTER key. The Portasal will begin measurement and display a substandard value. When stable press the COND key. This will terminate the standardization and the displayed conductivity ratio should match that of your sub-standard within ± 0.00001 . Pressing the ENTER key on the salt computer will save it to file.

At the beginning of each sample run the Portasal is standardized with substandard. However, every other day IAPSO and Wolga standards are also sampled. All three standards are run before and after the sample run in order to ascertain instrument drift.

9. Salt Data ACQUISITION Program

The SIO-CalCOFI-authored conductivity recording software, PSal.exe, is a Windows-based data acquisition program that records conductivity values from discrete salinity samples. Averaging five or more conductivity readings from the Guildline Portasal, the operator saves a stable reading. The flow cell is flushed and refilled and additional readings are performed. A pair of conductivity values which agree within 0.0010 standard deviation are recorded and salinity calculated. The software compares this calculated bottle measurement to the matching CTD salinity when available. This comparison is a good indicator of sensor performance and bottle sampling accuracy.

The data are saved as salt run files which may contain more than one station. Keeping the salt runs combined is necessary to calculate the drift-over-time calculated from any change in the end standard or substandard reading. The data are also saved in a single, combined, database-friendly csv for database processing (in development).

10. CTD Equipment and Data Processing

A SBE 911+ CTD is equipped with dual conductivity and temperature sensors. These are routinely calibrated (~6 months), but because of superior stability the pressure sensor is calibrated much less frequently (~24 months).

The SBE 11plus Deck Unit applies a real time alignment correction to conductivity during data collection, and the accompanying software generates a marker file for each profile containing CTD data at the instant of each Niskin closure.

Seasoft-processed CTD salinities are processed and imported into station csvs for comparison to bottle salinities.

11. DECODR: Data Entry Compiler & Output Data Reports

CalCOFI-authored Windows program will process the bottle sample conductivity data files generated by the SalReCap.exe data acquisition program. Using beginning and end standards, a linear drift is applied to each conductivity pair before salinity (PSU) is calculated. DECODR combines all stations selected into a single text file for data-quality assessment. When CTD salinities for matching depths are available, DECODR compares the bottle & CTD salinities, calculating & reporting the differences. DECODR, as an option, will save the bottle salinity values into each station's csv. DECODR can generate data products using bottle or CTD data such as IEH or data reports.