Bermuda Biological Station For Research, Inc.
Bermuda Atlantic Time-series Study

Chapter 4. Quality Control and Intercalibration

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1.0 Introduction

The methods described in the next chapters provide the core set of data for the U.S. JGOFS, Bermuda Atlantic Time-series Study (BATS). The continuous CTD data described in Chapter 3 are calibrated by these bottle-collected data. Most of the techniques are standard and widely used. However, there are also numerous ways that the data can be inaccurate, from mechanical failure of the OTE bottles to accidents in the laboratory. Since these kinds of problems are unavoidable, we have set up a series of procedures for checking the BATS data both internally (for consistence with the other TS data) and externally (for consistence with historical data for this area and intercalibrations with other labs). These methods are used primarily to evaluate the salinity, dissolved oxygen, dissolved inorganic carbon, and nutrient data.

The quality control measures that we employ are a combination of formal and informal examinations of the data for inconsistencies and errors. The technicians who are making the measurements are well trained and make the same measurements month to month. They often spot an error in the data set as the number is being generated or as the data are recorded. They know the typical values for a depth and can spot many of the outliers. These points are not automatically discarded. The identification of an aberrant datum, either at this step or in the subsequent examinations, is cause for rechecking the previous steps in the data generation process (sampling, analysis, data entry and calculation, etc.) for inadvertent errors. If no inadvertent error can be found, then a decision must be made. If the datum is out of the bounds of possibility, it is likely to be discarded (see below). Discarded data are maintained in the master data files at BBSR, but will not be reported to U.S. JGOFS and NODC. For these official reportings, the number is replaced by a -9.99.

The next step in data quality control is to graph the data with depth and visually examine the profile. At this step, aberrant points can also become evident as deviations from the continuity of the profile. These deviations are checked as above. The other analyses of samples from the same OTE bottle are also examined to see if they all are aberrant, indicating that the bottle misfired or leaked. If a bottle appears to have leaked then it is appropriately flagged, which automatically prohibits the reporting of all measurements from this bottle.

1.1 Other graphical methods are also employed to examine the data. T-S diagrams are plotted and compared with historical data. Nutrients are plotted against temperature and density and against each other. Nitrate-phosphate plots have proved very useful in identifying both individual and systematic problems in these nutrient data.

The final examination procedure is the comparison with a carefully selected set of data called our QC windows. The original QC windows were compiled by G. Heimerdinger (NODC) from a number of cruises within 200 miles of Bermuda between 1975 and 1985. These are data sets that he feels are of high quality and also reflect the kinds of variation that would be seen at the BATS station. Salinity and oxygen are well represented in this data set, while nutrients are present for only four cruises. These original QC windows have now been superceded by the BATS QC windows which are based on the first 8 years of time-series data. These QC windows are available for all core discrete measurements on both depth and potential temperature intervals. The BATS data are graphically overlaid on the QC data and both systematic and individual variations noted and checked carefully, as above.

The most difficult problems to resolve are small systematic deviations from the QC envelopes. We are unwilling to automatically discard every deviation from the existing data, especially when we can find no reason that a previously reliable analysis should show the deviation. If the measurements were meant to come out invariant, there would be no reason to collect new data. Therefore, we anticipate that some of the data that we report will deviate from the QC envelope and we will then leave it to others to decide whether they agree with the values. We will make efforts to note these deviations in the cruise summaries that accompany each data report. We will not flag individual values.

Finally, we are constantly expanding the methods we use to check the data quality. For many measurements we have added internal standards, sample carry-overs between months and other procedures to prevent accuracy and standardization biases from giving false temporal change. Since the inception of BATS we have regularly been involved in intercomparison efforts with other laboratories and organizations, for a number of core measurements. These exercises have generally shown that sample analyses at BBSR agree well with those at other institutions. At times however, differences between the participating groups have existed which are not resolved due to the inadequacy of the exercise. BATS is now committed to involvement in well-managed, large scale inter-comparison exercises, preferably with use of certified reference materials, and our participation in smaller ad hoc exercises will be reduced.

Chapter 5. Salinity Determination

Updated by: S. Bell (1997); R. Johnson and R. Little (April 1996, April 1994); A. Michaels, R. Dow and N. Bates (April 1991)
Prepared by: A. Michaels and R. Dow (October 1989)
Modified from: Guideline Instruments (1978)

1.0 Scope and field of application

This procedure describes the method for the determination of seawater salinity. The method is suitable for the assay of oceanic levels (0.005–42). This method is a modification of one published by Guildline Instruments (1978).

2.0 Definition

The method determines the practical salinity (S) of seawater samples which is based on electrical conductivity measurements. The Practical Salinity Scale 1978 (PSS 78) defines the practical salinity of a sample of seawater in terms of the conductivity ratio (K_{15}) of the conductivity of the sample at a temperature of 15°C and pressure of one standard atmosphere to that of a potassium chloride (KCl) solution containing 32.4356 g of KCl in a mass of 1 kg of solution.

3.0 Principle

A salinometer is used to measure the conductivity ratio of a sample of seawater at a controlled temperature. The sample is continuously pushed through an internal conductivity cell where electrodes initiate signals that are proportional to the conductivity of the sample. Using an internal preset electrical reference, these signals are converted to a conductivity ratio value. The number displayed by the salinometer is twice the conductivity ratio. The internal reference is standardized against the recognized IAPSO standard seawater.

4.0 Apparatus

Guildline model 8400A Autosal Salinometer. The Autosal has a 4 electrode cell which measures the conductivity ratio of a sample seawater in less than one minute. The salinity range of the instrument is about 0.005–42 and has a stated accuracy of ± 0.003 by the manufacturer. In practice, accuracies of 0.001 are possible.

5.0 Reagents

IAPSO Standard Seawater. Standard seawater for instrument calibration.

6.0 Sampling

6.1 Salinity samples are collected from OTE bottles at 35 depths from 0-4200m. Duplicate deep water samples are taken (>3000m).

6.2 The sample bottles are 250 ml clear borosilicate glass bottles with plastic screw caps. A plastic insert is used in the cap to form an effective airtight seal. Sample remaining after analysis is always left in the bottles to prevent salt crystal buildup due to evaporation and to maintain an equilibrium with the glass. When drawing a new sample, the old water is discarded and the bottle is rinsed three times with new sample water. The bottle is then filled to the shoulder and capped.

6.3 When sampling is complete, the set of salt bottles is taken into the temperature controlled laboratory. The cap of each bottle is momentarily removed, so that the inside of the cap and the threads of the bottle can be quickly dried with a Kimwipe and a clean plastic insert pressed in the bottle mouth. The cap is then replaced and firmly tightened. Samples are stored in the temperature controlled laboratory for later analysis (typically within 1-5 days of collection).

6.4 Every six months, the bottles are acid washed (1 M HCl), and rinsed and filled with Milli-Q water. After this cleaning they are rinsed five times with copious amounts of sample before filling.

7.0 Procedures

7.1 The samples are analyzed on a Guildline AutoSal 8400A laboratory salinometer using the manufacturer's recommended techniques. Samples are not run unless the ambient room temperature is ≤2°C below the salinometer bath temperature.

7.2 The salinometer is calibrated with IAPSO standard seawater. At least two standards are run prior to running the samples. The samples are run only if two standards give identical readings. At the end of the run, two new standards are run to check for instrument drift. The drifts are generally found to be zero. Using this procedure, the instrument can give a salinity precision of ± 0.001-0.002.

8.0 Calculation and expression of results

The calculation of salinity is based on the 1978 definition of practical salinity (UNESCO, 1978). The following gives the necessary computation to calculate a salinity (S) given a conductivity ratio determined by the salinometer:

$$S = a_0 + a_1 R_T^{\frac{1}{2}} + a_2 R_T + a_3 R_T^{\frac{3}{2}} + a_4 R_T^{2} + a_5 R_T^{\frac{5}{2}}$$

$$+ \frac{T - 15}{1 + kT - 15}\left\{ b_0 + b_1 R_T^{\frac{1}{2}} + b_2 R_T + b_3 R_T^{\frac{3}{2}} + b_4 R_T^{2} + b_5 R_T^{\frac{5}{2}} \right\}$$

Where:

a_0	= 0.0080	b_0	= 0.0005
a_1	= -0.1692	b_1	= -0.0056
a_2	= 25.3851	b_2	= -0.0066
a_3	= 14.0941	b_3	= -0.0375
a_4	= -7.0261	b_4	= 0.0636
a_5	= 2.7081	b_5	= -0.0144

k = 0.0162

R_T = conductivity ratio of sample (=0.5 salinometer reading)

T = bath temperature of salinometer (°C)

$$\sum_{i=0}^{5} a_i = 35.0000$$

$$\sum_{i=0}^{5} b_i = 0.0000$$

for:

$$-2°C \leq T \leq 35°C$$

$$2 \leq S \leq 42$$

9.0 Quality assurance

9.1 *Quality control*: The bottle salinities are compared with the downcast CTD profiles to search for possible outliers. The bottle salinities are plotted against potential temperature and overlaid with the CTD data. Historical envelopes from the time-series station are further overlaid to check for calibration problems or anomalous behavior.

9.2 *Quality assessment*: Replicate deep water (>3000m) samples are found to agree in salinity, ±0.001.

9.3 Regular intercalibration exercises are performed with other laboratories.

10.0 References

Guildline Instruments. (1981). Technical Manual for 'Autosal' Laboratory Salinometer Model 8400.

UNESCO. (1978). *Technical Papers in Marine Science*, **28**, 35pp.