Salinity (and Density) in the Ocean

1 What is salinity?

Another quantity useful in characterizing seawater is the amount or concentration of dissolved solids within it. This is a particularly useful thing to know because dissolved solids are conservative, that is, they don’t just vanish during the normal transport and mixing processes (unlike density!). Ideally, then, true salinity ($S_T$) would be defined thus:

True salinity is the amount of dissolved solids in 1 kg of seawater

2 What do we measure instead?

Unfortunately, there is no straightforward and simple way to measure this directly, in part because there are a large number of different elements involved. The most obvious approach - evaporating away the water to leave behind the solids - is rather difficult since at the temperatures necessary to drive off the last traces of pure water various other elements oxidize or vapourize. A complete chemical analysis of the major constituents is possible, but too timeconsuming for routine use.

However, as early as 1819 it was suggested by Marcet that although the absolute amounts of the dissolved salts varied from place to place, their relative concentrations remained fairly constant. In 1865 Forchammer analyzed several hundred samples of surface seawater from all over the globe and also concluded that this was true. However, his methodology was flawed, and it was not until Dittmar in 1884 published a rigorous analysis of 70 samples of seawater from the Challenger expedition that this hypothesis was generally accepted. It is important to remember, however, that the ratios are not exactly constant - only CLOSE to being so. In fact, most of chemical oceanography and a large part of biological oceanography are based around measuring and interpreting changes in these ratios for particular constituents.

In 1899 the International Council for the Exploration of the Sea (ICES) named Knudsen as the chairman of a commission to study the problem of determining salinity and density. A reproducible evaporative technique was found, in which the seawater was first processed with $HCl$. This resulted in the following definition for salinity:

“the weight in grams of dissolved inorganic salts in 1 kg of seawater, when all bromides and iodides are replaced by an equivalent quantity of chlorides, and all the carbonates are replaced by an equivalent quantity of oxides”

Although reproducible, such a definition is still quite difficult to work with on board a ship, and so, based on the apparent constancy of ratios between major constituents, they suggested an alternative measure of salinity based on a chlorinity $Cl(\%\text{o/o})$, defined as

“the chlorine equivalent to the total halide concentration in parts per thousand by weight measured by titration with $AGNO_3$”
This is not exactly the “true” chlorinity since bromides and iodides are also precipitated out in the titration. Based on comparisons of chlorinity with salinity from 9 samples of seawater (6 of which were in the Baltic or North Sea), salinity $S_K$ was then defined in terms of Chlorinity $Cl(\%)$

$$S_K(\%) = 0.03 + 1.805 Cl(\%).$$

(1)
a formulation used until the 1960s. Careful analysis using this titration technique yields salinities with a repeatability of $\pm 0.02\%o$.

The chlorinity determination was to be calibrated through tables produced using Copenhagen “Normal” seawater as a standard. However, the definition of chlorinity was refined in 1937 (by Jacobsen and Knudsen) to take into account changes in various atomic weights and to free it from dependence on the original Copenhagen water:

“the mass in grams of pure silver necessary to precipitate the halogens in 328.5233 grams of water”

based on a new primary standard (named Urnormal-1937).

By the 1960s, problems began to arise with these definitions. The first problem was the salinity-chlorinity relation (1). Note that although chlorinity is conservative, salinity (defined this way) is not. As an extreme example, when $Cl(\%) = 0, S_K (\%) = 0.03$! Further, it was discovered that Baltic waters contain a significant river contribution whose salts have a different ratio with chlorine than does, for example, North Atlantic water (or indeed many other river systems), so that the samples from which (1) was determined were not truly representative of the world ocean. In 1966 a Joint Panel for Oceanographic Tables and Standards (JPOTS), after examining a number of samples of seawater, revised the definition to

$$S_{JPOTS}(\%) = 1.80655 Cl(\%)$$

(2)

which agreed with the old definition at $S = 35$, but would also be conservative. At this point, it should be pointed out that it is best to call the resulting $S_{JPOTS}$ a “practical salinity” measure, because it still contains the effects of iodide and bromide precipitation in the titration method. Millero found in 1976, through a careful and complete analysis of standard seawater that the true salinity $S_T$ was slightly greater than the practical salinity:

$$S_T = 1.00488 S_{JPOTS}(\%)$$

(3)

The second problem arose with introduction of high-quality commercial salinometers based on conductivity measurements. Cox, Culkin, and Riley studied the conductivity/chlorinity relation at a temperature of $15^\circ C$, which, after applying (2), was put forward as a standard for salinity:

$$S_C = -0.08996 + 28.2970 R_{15} + 12.80832 R_{15}^2 - 10.67869 R_{15}^3 + 5.98624 R_{15}^4 - 1.32311 R_{15}^5$$

(4)

where $R_{15}$ is a ratio of conductivities $C_{15}[\text{sample}]/C_{15}[\text{std seawater}]$. Tables were then published giving salinity as a function of conductivity ratio for temperatures above $10^\circ C$, adequate for bench salinometers. However, although the chlorinity of Normal Water (by this time distributed through the Institute of Ocean Sciences in Wormley, England) was strictly defined, its conductivity (and hence $S_C$) was not, with different batches varying in conductivity-derived $S$ by $\pm 0.003\%o$ and sometimes even as much as $\pm 0.01\%o$ from that derived using the chlorinity method. Also, in-situ instruments began to be developed that could measure profiles of conductivity, and since much of the ocean is colder than $10^\circ C$ various other equations began to be used to correct for this effect. Differences in experimental protocols and the kinds of seawater used (normal or natural) in determining these dependencies resulted in somewhat inequivalent and inconsistent procedures. An intercomparison between the equations used by various labs suggested that, even without regard to sampling errors, an intercomparison was not possible to better than $\pm 0.03\%o$. Experiments carried out with samples of Baltic ($\approx 8\%o$) and Mediterranean water ($\approx 38\%o$) showed that while various labs reported quite reproducible results (thermostated bench salinometers giving precisions of $\pm 0.002\%o$), their intercomparison had a scatter of $\pm 0.05\%o$. 

2
By 1975 it was clear that something would have to be done. A new standard was needed that would be a) reproducible, b) conservative, and c) would allow density to be computed to acceptable limits (of which we shall have more to say later).

3 The Practical Salinity Scale of 1978 (PSS-78)

During the late 1970s, the UNESCO/ICES/SCOR/IAPSO Joint Panel on Oceanographic Tables and Standards (JPOTS) developed the “Practical Salinity Scale 1978” (as well as an Equation of State to determine density) and these were adopted as international standards.

PSS-78 first defined a reproducible primary standard for conductivity. A solution of 32.4356g of potassium chloride (Merck “Suprapur” was used) in 1 kg of solution was specified as having a conductivity ratio of 1 and hence a “practical salinity” of 35 at 15°C. This was determined by comparison with a batch of standard seawater of salinity $S_{JPOTS} = 35 \permil$ determined using the older chlorinity-based standard to preserve continuity. Normal Water, standardized in this way, is still used to calibrate bench salinometers at temperatures other than 15°C since the temperature coefficient of conductivity is different for KCl than for seawater. This standard water is now called “IAPSO Standard Seawater” and is purchased from OSIL, a company in the U.K. These vials come in numbered batches and are labelled with their conductivity ratio and their Practical Salinity as determined using PSS-78.

Based on extensive measurements at five different laboratories of dilutions and evaporations of this standard seawater, a formula was developed to determine a “Practical Salinity” $S_P$ (which has no units or $\permil$) based on measurements of the dimensionless conductivity ratio $R$ as a function of salinity, temperature $T$ (using IPTS-68), and gauge pressure $p$:

$$ R = \frac{C(S_P, T, p)}{C(35, 15, 0)} $$  \hspace{1cm} (5)

$$ = \frac{C(S_P, T, p)}{C(S_P, T, 0)} \cdot \frac{C(S_P, T, 0)}{C(35, T, 0)} \cdot \frac{C(35, T, 0)}{C(35, 15, 0)} $$  \hspace{1cm} (6)

$$ = R_p \cdot R_T \cdot r_T $$  \hspace{1cm} (7)

The equations are valid for the range $2 \leq S_P \leq 42$, and $-2^\circ \leq T \leq 35^\circ$C.

The dependence is rewritten in this way for convenience. Salinity determination proceeds by

- standardizing a salinometer using the labelled value of a vial of IAPSO Standard Seawater
- Measuring the conductivity ratio $R$ at a fixed temperature $T$.
- solving for $R_T$ as a function of $R$, $r_T(T)$, and $R_p(R, T, p)$ and computing $S_P = F(R_T, T)$.

Conductivity ratio is used rather than absolute conductivity since the latter is quite difficult to measure, requiring exact knowledge of the dimensions and geometry of the instrument. In fact, we CANNOT measure absolute conductivity in an “SI-traceable” manner to the accuracy that we need for oceanographic research (this was true in the 1970s, and is still true today). “SI-traceability” means that the measurement can be defined in terms of fundamental parameters (like length and electrical current) which are basic parameters in the SI system of units.

For reference, one can take as a DEFINITION that the conductivity of water with $S_P = 35$ at an IPTS-68 temperature of 15°C is:

$$ C(35, 15, 0) = 4.29140 \, \text{S/m} = 42.9140 \, \text{mmho/cm} $$  \hspace{1cm} (8)

although this definition has more digits than the accuracy of the measurement can justify.

One possible disadvantage of using conductivity to determine salinity is that this is strongly dependent on temperature. However, since temperature is often being measured at the same time, this is not usually a practical difficulty.
4 International Thermodynamic Equation of Seawater 2010 (TEOS-10)

Although PSS-78 solved many problems, the Practical Salinity is not in fact a measure of the mass fraction of dissolved material in seawater, even leaving aside the insistence that units are not included. This is, first, because PSS78 numerically scaled a conductivity (ratio) to match the older chlorinity scale for particular samples of seawater. In the century since that scale was defined, we have learned much more about the composition and chemistry of seawater; and it is clear that the numerical values do not match g/kg estimates. Second, the scale was defined on measurements of Standard Seawater, which comes from a particular region of the ocean, and real seawater from anywhere else in the ocean has a slightly different composition. Thus the same conductivity can represent a slightly different mass of dissolved material, depending on the manner in which the additional solute contributes to conductivity. PSS-78 is therefore conservative for IAPSO Standard Seawater, but not for real seawater.

For these reasons, it was deemed useful to delink the numerical values of salinity from the conductivity measurement. In addition, a new thermodynamic formulation for the properties of seawater would allow density, sound speed, and many other properties to be defined in a manner consistent with the thermodynamic relationships between them. SCOR and IAPSO jointly appointed a working group to proceed on this problem. WG-127 (Thermodynamics of Seawater) developed a new method for describing both salinity and the other properties of seawater, and this procedure has now been adopted as a new international standard by the IOC, SCOR, and IAPSO: the Thermodynamic Equation of Seawater 2010 (TEOS-10).

As part of an overall redefinition of the equations dealing with seawater, a new salinity variable was defined in TEOS-10: the Absolute Salinity ($S_A$) of seawater, which represents the best estimate of the true mass fraction of all constituents of seawater which contribute to conductivity and density. Note that this is not exactly the same as the amount of dissolved solids in seawater, since it includes carbon system parameters, some of which enter seawater as dissolved gases, and all of which react with water to a degree.

The best estimate of this mass fraction for IAPSO Standard Seawater with $S_P = 35.000$ is determined from a defined Reference Composition to be 35.16504 g/kg. This Reference Composition can be thought of as an artificial seawater of fixed composition, defined to be as close a match to true Standard Seawater (the stuff bottled by OSIL) as is possible. The mass fraction is measured on the Reference Composition Salinity Scale and is named Reference Salinity $S_R$. Thus for Standard Seawater

$$S_A = S_R \equiv 35.16504/35 \times S_P \approx 1.00471543 \times S_P$$

This definition allows us to continue using the perfectly good existing measurements made on Standard Seawater, but in a well-defined way. Reference Salinity can be specified using mass fraction units (as is done in all other scientific fields).

For real seawater, the Absolute Salinity differs from the Reference Salinity by an anomaly:

$$S_A = S_R + \delta S_A$$

where the anomaly can be as large as 0.02 g/kg in the open ocean, and as much as 0.1 g/kg in coastal areas. This formula now explicitly delinks conductivity and salinity.

The salinity anomaly $\delta S_A$ cannot be determined from a conductivity measurement alone, but is determined from other measurements. There are currently several ways to do this:

1. It can be determined from density anomaly measurements
2. It can be determined from measurements of the macronutrients ($Si(OH)_4$ and $NO_3^-$) and carbon system parameters ($TA$ and $DIC$), since changes in the concentrations of these constituents are the most important variations in the composition of seawater.
3. It can be determined from a lookup table as a function of geographic position and depth. The lookup table itself is based on a database of density anomaly measurements.

5 Techniques

Many techniques have been used to determining salinity. The two most important techniques (on which practical scales have been based), are described below, but for completeness a brief description will be given of some of the others, which are mainly useful in the laboratory. They rely on the fact that many physical parameters depend on both the temperature, which can be readily measured or controlled in the lab, and salinity. Their chief disadvantage is the lack of standards in relating the derived salinities to PSS-78. These methods include:

Density Method Rather than compute density from measurements of salinity, a direct measurement of density can be used to infer salinity. This technique is possible generally only in the laboratory, but can be especially useful when investigating changes in the ratios of constituents. One method of computing density is a vibrating flow densimeter. Seawater is piped through a thin tube contained in a constant temperature jacket (±0.01°C). The density is proportional to the square of the period of vibration. With careful calibration, accuracies of about ±0.004 have been claimed in the derived salinities, and it is hoped that accuracies of ±0.002 are possible, matching the precision of conductivity methods. It is believed that “SI-traceability” is best pursued using this method.

Soundspeed method Soundspeed depends on the salinity and temperature of seawater. As long as temperature is well-regulated, the salinity may be determined from observations of soundspeed. The accuracy of this technique is about ±0.03.

Refractive Index method The refractive index of seawater (i.e. its effect on visible light) can be measured precisely enough to allow for determination of salinity to an accuracy of about ±0.05. Using interference methods, an accuracy of about ±0.001 to ±0.01 is possible. One problem with this kind of technique is that it is difficult to keep optical components clean.

Evaporation to dryness An accuracy of about ±0.01 is possible, although difficult and lengthy.

Chemical analysis A complete analysis of the chemical composition of the major constituents can be used to determine salinity. An accuracy of about ±0.01 is possible.

The two main methods, however, are titration and conductivity-related.

5.1 Chemical Titration

As discussed above, for many years the term “salinity” implicitly referred to the results of a chemical titration of seawater with AgNO₃ (the “Knudsen Method”). The endpoint of the titration is determined visually using potassium chromate as an indicator, although other methods are sometimes employed. Examples include potentiometric endpoints (using a Ag,AgCl electrode), or thermal endpoints for which a titration calorimeter is used.

In all cases, the AgNO₃ solution is standardized using standard seawater. The method has been found to be accurate to about ±0.02%/oo in routine use, although accuracies of about ±0.002%/oo have sometimes been claimed.

5.2 Conductivity

5.2.1 Electrode methods

In this technique, a current is passed through seawater in order to determine its resistance. This resistance can be determined very accurately and stably using a bridge circuit. To prevent polarization problems an alternating current
(AC) is used. One advantage of a bridge circuit is that it works on a null-point principle, rather than the end-point of titrations, which makes it easier to use in practice.

It is important to keep the electrodes clean in order to preserve the calibration. Early electrode-based instruments suffered from stability and drift problems, and were discarded in favour of the inductive methods described next, but these problems appear to be solved and they are the method of choice in modern in-situ instruments.

Electrodes are sometimes mounted inside a glass or quartz tube. This facilitates the use of pumps to minimize spiking problems (see below), and also allows the electrodes to be stored “wet”, reducing stability problems and the tendency for bubbles to be formed when dry surfaces are placed into water. Since the conductivity of air is much smaller than that for seawater, even the presence of very small bubbles can adversely affect the measured salinity\(^1\). Electrodes not kept wet should be washed with fresh water to prevent salt from drying on them between stations.

5.2.2 Inductive methods

In this method, an alternating current is sent through a coil wound around an iron core toroid. This sets up a field in the surrounding water, which can be sensed by windings around a second parallel coil. The sensed field depends on the geometry of the windings and the conductivity of seawater. Usually both coils are potted in resin to preserve the geometry.

The coil should be kept clean, but if the geometry is changed it must be recalibrated. Inductive methods are generally less accurate than modern electrode methods, but are widely used in applications where extreme accuracy is unnecessary (for example, on current meters). The calibration is easy to monitor by looping a piece of wire with a resistor on it through the coils. This does not require a seawater tank. Actual calibration requires the use of a tank, which should be fairly large otherwise the presence of nearby walls can affect the readings.

5.3 Integrated instruments

The first integrated instrument capable of measuring continuous profiles of temperature and conductivity was constructed by Jacobsen in 1948. In the 1950s, Hamon and Brown developed a workable system in which the instrument was lowered using a single-core armoured cable down which power was sent and up which multiplexed signals from the various sensor elements were transmitted. By the 1960s commercial instruments (called STDs) were being widely used.

Since computers were too expensive and unreliable to be used at sea at that time, the salinity computations were carried out using analog circuits built into the instrument. An inductive conductivity cell was used. Accuracy was only good to about ±0.03/o or so, although it could be made better with calibrations against bottle data.

As digital computers became more robust, and the problems with the definition of salinity resolved, a new generation of instruments was developed. These so-called CTDs reported only raw conductivities, which could then be converted into salinities using the algorithms of PSS-78.

Many Canadian institutions used the Guildline CTD. This instrument can determine salinities to an absolute accuracy of about 0.015 (perhaps 0.01 with in-situ calibration). For measurements of vertical gradients precisions of about 0.003 are possible.

Many US labs used the Neil Brown MkIII. Claimed accuracies are about 0.005 in absolute terms, although care must be taken with respect to known drift problems.

\(^1\)This effect is used to advantage by researchers interested in estimating the void fraction in and around breaking waves.
Nowadays there are quite a number of companies marketing CTDs, in a number of different configurations, each of which have certain advantages according to usage. SeaBird Electronics (Seattle) has the most widely known and used products, and is almost the only instrument in routine use for quality measurements these days.

5.4 ...And Their Problems

As mentioned above, the presence of air bubbles in the conductivity cells will result in totally useless data. A CTD should be kept near the surface for several minutes to ‘soak” before beginning a station in order to make sure that no bubbles are present, otherwise air entrained by the CTD and its protective cage may contaminate profiles in the upper few 10s of meters. For this reason, the CTD operator should check that the readings being displayed make sense before continuing with the cast.

Another problem arises because the response times of thermistor and conductivity cells are different. These response times depend on the flushing of the conductivity cell and differences in the physical location of the two sensors. As the CTD is lowered through a sharp interface this can result in so-called salinity spiking. In older instruments (especially the STD) in which the salinity was computed internally there was no solution to this problem other than ignoring these small-scale features. In modern instruments where the salinity is computed digitally, extra filtering can be used to compensate for these differences after the fact. Both time delays and smoothing scales may have to be accounted for. A different solution is to try and match the response times within the instrument. Since that depends to some extent on the flow rate it requires either that the lowering speed of the instrument be controlled (design speeds of about 1 m/s are standard), or that a pumped cell be used.

In order to prevent contamination of the profiles from mixing induced by the instrument casing or the cable by which it is lowered only the downcast is used, and the lowering rate is kept as uniform as possible. Stops to trigger bottles etc. are made during the upcast. This rule can be modified according to circumstances and design details of the particular instrument being used.

6 Density

Until 1980 density was computed from tables prepared for standard seawaters (the “Knudsen tables”, accurate to ±0.02). The values derived were not actually for absolute density $\rho$, but instead measured the specific gravity $\rho/\rho_m$, where $\rho_m$ is the maximum density of pure water, taken to be 1000 kg/m$^3$. Since the specific gravity is always close to 1, a quantity $\sigma$ was defined

$$\sigma = 1000\left(\frac{\rho}{\rho_m} - 1\right)$$

This was loosely referred to as density.

In 1971 Girard and Menache found that $\rho_m$ depended on isotopic content, and the true value is slightly smaller (999.975kg/m$^3$). Thus $\sigma$ determined the old way is about 0.025 units larger than $\sigma$ as currently defined in terms of true density,

$$\sigma = \rho - 1000 \text{ kg/m}^3$$

In practical terms this difference is almost always unimportant, since it is differences in densities that are dynamically important.

True density was then defined by the 1980 International Equation of State (EOS-80) as a function of temperature (IPTS-68), Practical Salinity (PSS-78) and pressure over the range of oceanic interest. The function itself results from an empirical fit to observations, and is highly non-linear.

Although not generally an issue, it should be remembered that both EOS-80 and the original Knudsen tables were derived from Copenhagen normal water (or Standard Seawater), which is very similar to North Atlantic water in
constituent ratios. Although waters of the same true salinity have the same density (within ±0.01 σ units), small differences in the constituent ratios in different oceans mean that waters of the same practical salinity can differ in density, essentially because the true salinity is not simply related to the practical salinity. However, it turns out that these differences are smaller for conductivity-derived salinities than for chlorinity-derived salinities. This is because various ions contribute to the conductivity measurement, partially compensating for the change in their ratios.

In particular, a densities in the Pacific are about 0.016 σ-units greater than those determined from PSS-78/EOS-80 due to the high carbon and macronutrient content there, and those in the Baltic are about 0.035 larger (the comparable values for density derived from chlorinity-based salinities are 0.02 and 0.06). These differences are of some practical importance as trans-oceanic sections are being analyzed for global transports. They may also be important in the operation of neutrally buoyant floats.

The provision of salinity anomalies δSA in the TEOS-10 definition of Absolute Salinity SA allows one to correct for these effects.

7 Further reading

A good starting point for reading about the history of salinity and problems with density calculations are


and the entire issue of IEEE J. Oceanic Eng., Vol OE-5, no. 1, January 1980 which is devoted to PSS-78. Also useful are


which contains many details of the actual composition of sea and river waters, and their effects on various methods of determining density and/or salinity. Finally, conversion between the older scales and PSS-78 is examined in


Information on commercial instruments can be found in the pages and advertisements of *Sea Technology*. There are now quite a few companies marketing CTDs, some of them (e.g. Sea-Bird and General Oceanics) also maintain Web pages, a good starting point is the index to commercial companies at

http://www.mth.uea.ac.uk/ocean/vl/namerica.html

Another is


EOS-80 is listed in various places; the most accessible is probably in Appendix 3 of


The main reference to TEOS-10 is the manual:


which is available at http://www.teos-10.org.