Salinity

The concept of salinity was introduced as a measure of the salt content of seawater. A simple basic measure is the mass ratio of dissolved salts to seawater. This ratio cannot be accurately or conveniently measured so a different measure (scale) is used. JPOTS recommends that the mass ratio be called absolute salinity to distinguish it from the practical scale salinity.

Sørensen (1902) introduced a salinity scale based on evaporating seawater to dryness. Knudsen used this procedure to establish a relationship between salinity and chlorinity using 9 samples of natural seawater:

\[ S = 0.03 + 1.805 \, C1 \]

Chlorinity could be determined by chemical titration and used to estimate salinity. Note that the composition changes with salinity and the equation is not conservative for addition and removal of pure water.

The introduction and subsequent widespread use of electrical conductivity in the 1950's to estimate salinity led to a reconsideration of the salinity scale. To achieve conservation for addition and removal of pure water salinity must be proportional to chlorinity. To be consistent with historical data, the new scale was chosen to coincide with the previous scale at 35°/oo salinity. The result is

\[ S = 1.80655 \cdot C1 \]

To relate this salinity scale to conductivity, Cox determined a regression formula (least squares) between electrical conductivity ratio \( R_{15} \) at 15°C and chlorinity for a large number (135) of natural seawater samples including mid range samples made by mixing Baltic and Red Sea Waters. After replacing chlorinity by salinity using the proportionality factor 1.80655 the resulting formula is:

1969 salinity scale

\[
S^0/\text{oo} = -0.08996 + 28.29720 \, R_{15} + 12.80832 \, R_{15}^2 \\
-10.67869 \, R_{15}^3 + 5.98624 \, R_{15}^4 - 1.32311 \, R_{15}^5
\]

The ratio \( R_{15} \) is determined relative to standard seawater for which absolute conductivity is known by precise measurements. (The absolute conductivity measurements were not made because of development problems with the laboratory apparatus.)
Problems arose with the 1969 salinity scale. The $R_{15}$ determinations are based on natural (or mixed) seawater samples of variable composition. The salinity-chlorinity conversion assumes fixed ratios. This is inconsistent. The scale is not reproducible. Since the salt ratios are time dependent, samples from the same geographical points would not yield the same relationship between conductivity and chlorinity. The single point necessary to fix the scale was tied to standard seawater through chlorinity and not absolute conductivity. In 1978 at the 10th meeting of JPOTS, the panel introduced a KCl conductivity standard to fix the salinity scale at 35$^0/_{oo}$. The new practical salinity scale is fixed at 35$^0/_{oo}$ salinity by reference to conductivity of a potassium chloride solution at 15°C containing a mass of 32.4357 gms KCl in a mass of 1 kilogram of solution. This point coincides with the 1969 scale and Knudsen scale by using chlorinity to find the 35$^0/_{oo}$ point for the particular batch of standard seawater used. In future, the 35$^0/_{oo}$ salinity may not be related precisely to chlorinity by the ratio 1.80655 because of long-term compositional changes in the oceans. Having fixed the 35$^0/_{oo}$ point, other salinities can be produced precisely by addition (by dilution with distilled water) or removal (by evaporation) of water from the standard seawater. Such samples were used to develop a relationship between salinity and $R_{15} = C(S,15,0)/C(35,15,0)$ which is proposed as the new practical salinity scale. This relationship is:

$$S^0/_{oo} = 0.0080 - 0.1692 R_{15}^{1/2} + 25.3851 R_{15} + 14.0941 R_{15}^{3/2}$$
$$-7.0261 R_{15}^2 + 2.7081 R_{15}^{5/2}$$
$$1^0/_{oo} \leq S \leq 42^0/_{oo}$$

The new practical salinity scale is defined with fixed ionic ratios (by using standard seawater only) referenced to a readily reproduced fixed standard of conductivity (KCl). The formula for determining salinity has been extended to other temperatures in terms of the ratio $R_T = C(S,T,O)/C(35,T,O)$

$$S^0/_{oo} = 0.0080 - 0.1692 R_T^{1/2} + 25.3851 R_T + 14.0941 R_T^{3/2}$$
$$-7.0261 R_T^2 + 2.7081 R_T^{5/2}$$
$$+ \frac{(T - 15)}{1 + 0.0162 (T - 15)} [0.0005 - 0.0056 R_T^{1/2} - 0.0066 R_T]$$
$$-0.0375 R_T^{3/2} + 0.0636 R_T^2 - 0.0144 R_T^{5/2}]$$
$$-2^\circ C \leq T \leq 35^\circ C \quad S. D. = 0.0007^0/_{oo}$$

For CTD measurements, electrical conductivity of seawater $C(S,T,P)$ can be written in the ratio form

$$C(S,T,P) = C(S,T,P) \cdot C(S,T,O) \cdot C(35,T,O) \cdot C(35,15,0)$$
$$C(S,T,O) \cdot C(35,T,O) \cdot C(35,15,0)$$
$$= R_P \cdot R_T \cdot r_T \cdot C(35,15,0)$$

or dividing by $C(35,15,0)$ to obtain the conductivity ratio $R(S,T,P) = C(S,T,P)/C(35,15,0)$
\[ R(S,T,P) = R_p \cdot R_T \cdot r_T \]

WG 10 (JPOTS) accepted and proposes the relationship

\[
\begin{align*}
    r_T &= 0.676612 + 2.00557 \times 10^{-2} T + 1.10558 \times 10^{-4} T^2 \\
    &\quad - 7.04373 \times 10^{-7} T^3 + 1.11940 \times 10^{-9} T^4 \\
    &\quad - T^5 \leq T \leq 35^\circ C
\end{align*}
\]

for the temperature dependence. The ratio \( R_p \) is still under investigation by Bradshaw and Schleicher at W.H.O.I. and should be determined by end of 1978. This will complete the definition of the practical salinity scale for the full range of oceanic variables of conductivity ratio, temperature and pressure.

**EQUATION OF STATE FOR SEAWATER**

An equation of state for seawater (EOS) using the new practical salinity and the IPTS–68 for temperature has been constructed from 5 data sets obtained by 3 laboratories. Only part of the EOS has been adopted by JPOTS. Questions remain about the EOS for seawater at atmospheric pressure because of discrepancies with a 6-th data set obtained recently by Poisson in France. The discrepancies are small ~ \( 10 \times 10^{-6} \text{ cm}^3/\text{gm} \) but occur in the oceanic range of temperatures and salinities. It is expected that these will be resolved by March 1979.

The EOS is in the form

\[ v(S,T,p) = v(S,T,0) [1 - p/K(S,T,p)] \]

where \( v \) is specific volume \( \text{cm}^3/\text{gm} \), \( p \) pressure in bars and \( K \) is secant bulk modulus in bars. Note: the form is identical to that used by Ekman (1908). He used mean compression \( \mu = 1/K \).

The EOS has been developed in 4 parts:

1. density of pure water at 1 atmosphere (adopted)
2. density difference of seawater at one atm (not adopted)
3. specific volume difference of pure water at elevated pressure (adopted)
4. specific volume difference from 1 atm difference for seawater and from pure water at elevated pressures (adopted)

The EOS has the form (in terms of bulk modulus \( K \)):

\[
K_p = \frac{p v^O}{(v^O - v^P)} = K^O + A_p + B_p^2
\]

\[
K^O = K^O_w + a S + b S^{3/2} \quad \text{(All coefficients are polynomials in } T)\]

\[
A = A_w + c S + d S^{3/2}
\]
\( B = B_w + eS \)

and at 1 atm

\[
\rho(S,T,0) = 1/\nu(S,T,0) = \rho_w + A_0 S + B_0 S^{3/2} + C_0 S^2
\]

S.D. = \( 4.3 \times 10^{-6} \) cm\(^3\)/gm for pure water

= \( 9.0 \times 10^{-6} \) cm\(^3\)/gm for seawater

JPOTS has not accepted any formulas for other properties except for

- freezing point of seawater (8th report JPOTS)
- partial pressure of dissolved oxygen (Weiss eqn)

In particular, JPOTS has not recommended or proposed formulas for computing

- sound speed
- adiabatic lapse rate or potential temperature
- specific heat

These and other physical and chemical properties of seawater need to be evaluated by JPOTS.

References


