



The Physical Definition of Salinity: A Chemical Evaluation

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was mixed with seawater (i.e. source water, having a known concentration of chloride). For this reason I suggest that biologists should report the chlorinity of coastal seawater samples (or more precisely the halide content), not in relation to salinity but as indicative of the salt water content of their samples. Eventually a useful comparative biological description of seawater, particularly in coastal environments, might be obtained by analogy with agricultural practices. For example the notation 27-14-0 gives the nutrient content in terms of nitrogen, phosphorus, and potassium of an agricultural fertilizer. A similar technique could be applied to a seawater sample to give, say, halogen, total nitrogen, and pH values, which would be more biologically

informative than salinity reported to three decimal places.

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The physical definition of salinity: A chemical evaluation¹

The concern of Parsons (1982) is justified in that definitions of salinity based on electrical conductivity are strictly valid only for open ocean salinities and that extrapolations to estuarine waters are often made without sufficient concern for physical chemical principles. However, it may be possible to push the conductimetric measurement of salinity in estuaries closer toward infinite dilution than he suggests.

Millero has investigated the physical chemistry of estuarine water and made theoretical (Millero 1975) and experimental (Millero et al. 1976) comparisons between river waters and diluted seawater. By diluting standard seawater to equivalent total solid concentrations of various average river waters, he com-

pared densities in the seawater range of 0-35‰, with the lowest concentration samples equivalent to 0, 0.7, and 1.4‰ salinity. Agreement between river water and diluted seawater was ± 3 ppm density ($\text{g}\cdot\text{cm}^{-3}$) which is equivalent to $\pm 0.003 \sigma_t$. He concluded that the densities (and other physical chemical properties) of seawater diluted with pure water could be used in rivers and estuaries (Millero 1975). He showed that natural waters and seawater diluted with pure water having the same concentrations of dissolved solids have nearly equal conductivities.

Therefore, on the basis of theory and laboratory experiments, the conductimetric measurement of salinity in estuaries should be accurate to salinities $< 5\text{‰}$. However, an important consideration arises in mathematical translations between conductivity and salinity and between salinity and chlorinity.

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Table 1. Comparison of salinity computed from third-order (S_1) and fifth-order (S_2) equations. Data from Delaware estuary, November 1980.

Temp (°C)	Conductivity (mmho)	S_1	S_2
		(%o)	
7.03	0.116	-0.63	0.004
8.53	0.268	-0.50	0.12
8.10	0.511	-0.28	0.31
8.36	0.816	-0.01	0.55
8.84	1.433	0.53	1.03
8.22	3.270	2.21	2.56
8.29	5.050	3.83	4.07
8.17	7.579	6.18	6.31
7.10	11.928	10.60	10.63
6.83	16.620	15.38	15.37
7.74	21.972	20.33	20.32
8.32	27.181	25.26	25.25
8.79	30.237	28.03	28.02
8.45	32.912	31.08	31.08

In the former case, many salinity-temperature-conductivity (STD) systems are programmed with a third-order polynomial based on the work of Brown and Allentoft (1966). This equation, for conversion from temperature-corrected conductivity ratio (R), is

$$S(\%o) = -0.73469 + 32.28071R + 3.4775R^2 - 0.02395R^3. \quad (1)$$

A fifth-order equation used with the new definition of seawater (Cox et al. 1967) is

$$S(\%o) = -0.08966 + 28.2972R + 12.80832R^2 - 10.67869R^3 + 5.98624R^4 - 1.32311R^5. \quad (2)$$

At oceanic salinities, these two equations give the same results; at low salinities, they differ considerably and the third-order one actually gives negative results. Table 1 gives a comparison with data from the Delaware estuary. Therefore an STD for estuarine waters should use Eq. 2 rather than Eq. 1.

In the mathematical translation between chlorinity and salinity, the new definition

$$S(\%o) = 1.80655Cl\%o \quad (3)$$

has replaced the old equation (see Cox et al. 1967)

$$S(\%o) = 1.805Cl\%o + 0.03. \quad (4)$$

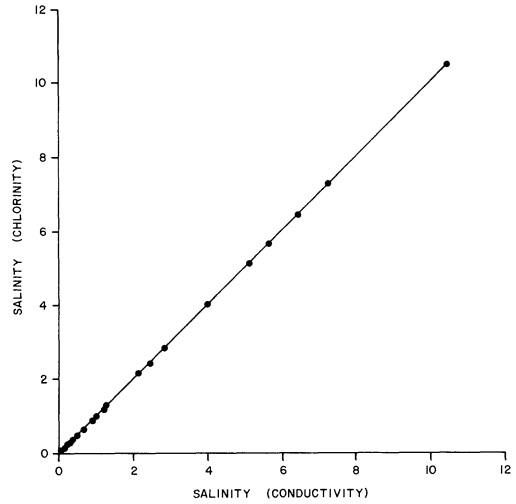


Fig. 1. Comparison of salinity from chlorinity titration and from conductivity measurement. Equation for curve is $y = 0.99881x + 0.01488$ with $r^2 = 0.99991$. This is based on $n = 33$, 12 points of $<0.25\%o$ appear as a single point on figure.

In low salinity regimes of estuaries, it appears that Eq. 4 is more appropriate (Millero 1975). Thus, one must be aware of the mathematical translations used when measuring conductivity in estuaries.

The question of how well conductivity represents chlorinity is perhaps examined best in individual estuaries. We have been working in the Delaware estuary, which has a low pH (6.5–7.2), moderate dissolved organic content (311–436 $\mu\text{M C}$), and very high nutrients (nitrate of 86–178 μM) in the freshwater reaches. The ranges represent samples from 0 to 5‰ salinity. Figure 1 shows salinity from conductivity (Eq. 2) plotted against salinity from chlorinity (Eq. 4) done by silver nitrate titration for the upper estuary. These data are from six cruises from July 1979 to January 1981. The figure shows clearly that chlorinity and conductivity measurements in the Delaware estuary are similar to salinities below 0.5‰.

A potential problem with conductivity measurements in estuaries is that the constant proportionality of the major constituents may not hold at the dilute end of an estuary, due to a markedly different

major constituent composition of the river. This does not seem to be a problem in the Delaware. In other rivers it might cause a discrepancy at low salinities, but this must be demonstrated. If this were indeed the case, chlorinity titrations would then give a more accurate estimate of the chloride content. However, conductivity might give a better estimate of the total dissolved solids. In a case where river ions contribute significantly to conductivity, the total solids content—not the chlorinity—might be more desirable to know. In such a situation, chloride content will not represent the oceanic contribution to the total dissolved solids.

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The practical salinity scale 1978: A reply to comments by T. R. Parsons

During its meeting in Sidney, British Columbia, in September 1980 the UNESCO/ICES/SCOR/IAPSO Joint Panel on Oceanographic Tables and Standards made its final deliberations on the proposed “Practical salinity scale 1978 and the international equation of state of seawater 1980.” A full report on this meeting is available (UNESCO 1981*a*) and the sponsoring organizations have endorsed this work in principle. Parsons (1982) has raised an important point as to the “reality” of the salinity definition, when seawater is strongly diluted by river water or runoff, such as in estuaries. I here present some relevant excerpts from the joint panel’s report, explaining first the need for these new definitions, as well as the various caveats to the application of the equations, particularly in situations when deviations from the mean composition of seawater can be substantial.

A new equation of state was considered desirable because recently acquired data indicated slight discrepancies with the Knudsen–Ekman equation of state of seawater. There is a systematic difference in the specific volume of the order of $8.7 \times 10^{-6} \text{ cm}^3 \cdot \text{g}^{-1}$ in the Knudsen equation for atmospheric pressure, but this difference increases to $33 \times 10^{-6} \text{ cm}^3 \cdot \text{g}^{-1}$ at 500 bars and $89 \times 10^{-6} \text{ cm}^3 \cdot \text{g}^{-1}$ at 1,000 bars pressure in the Ekman equation for elevated pressures (Grasshoff 1976).

A new salinity scale was considered necessary so that all oceanographers using conductivity-temperature-depth instruments would be able to report their observations in a consistent manner. The existing international tables (UNESCO 1966), giving salinity as a function of conductivity ratio, do not go below 10°C, which makes them unsuited for use in most CTD applications. Salinity calcula-