Salinity and Chlorinity

In the chapter on chemical oceanography the composition of the dissolved constituents in sea water is considered in detail. Our present interest is only in the more abundant substances whose concentration will affect the physical properties. It has been found that, *regardless of the absolute concentration, the relative proportions of the different major constituents are virtually constant*, except in regions of high dilution (low salinity), where minor deviations may occur. From this rule it follows that any one of the major constituents may be used as a measure of the others and of the total amount of salt, and that water samples having the same total salt content, regardless of their source, are virtually identical in their physical properties.

Owing to the complexity of sea water, it is impossible by direct chemical analysis to determine the total quantity of dissolved solids in a given sample. Furthermore, it is impossible to obtain reproducible results by evaporating sea water to dryness and weighing the residue, because certain of the materials present, chiefly chloride, are lost in the last stages of drying. These difficulties can be avoided by following a technique yielding reproducible results which, although they do not represent the total quantity of dissolved solids, do represent a quantity of slightly smaller numerical value that is closely related and by definition is called the salinity of the water. This technique was established by an International Commission (Forch, Knudsen, and Sörensen, 1902), and on the basis of its work the salinity is defined as *the total amount of solid material in grams contained in one kilogram of sea water when all the carbonate has been converted to oxide, the bromine and iodine replaced by chlorine, and 'all organic matter completely oxidized*.

The determination of salinity by the method of the International Commission is rarely if ever carried out at the present time because it is too difficult and slow, but, owing to the constant composition of the dissolved solids, the determination of any of the elements present in relatively large quantity can be used as a measure of the other elements and of the salinity. Chloride ions make up approximately 55 per cent of the dissolved solids and can be determined with ease and

accuracy by titration with silver nitrate, using potassium chromate as indicator.

The empirical relationship between salinity and chlorinity, as established by the International Commission, is

$$\text{Salinity} = 0.03 + 1.805 \times \text{Chlorinity}.$$

[Equation]

The chlorinity that appears in this equation is also a *defined* quantity and does not represent the actual amount of chlorine in a sample of sea water. Both salinity and chlorinity are always expressed in grams per kilogram of sea water—that is, in parts per thousand, or per mille, for which the symbol ‰ is used.

Chlorinity. In the titration with silver nitrate, bromides and iodides are precipitated together with the chlorides, but in the computation it is assumed that they are chlorides. Chlorinity was therefore originally defined as *the total amount of chlorine, bromine, and iodine in grams contained in one kilogram of sea water, assuming that the bromine and the iodine had been replaced by chlorine*. This definition introduces a chlorine-equivalent that is dependent upon the atomic weights used in preparing the standard solutions. Since the time of the work of the International Commission, there have been changes in the atomic weights, and the relation between salinity and chlorinity as defined above is no longer strictly true. In order to retain this relationship and to avoid apparent changes in the chlorinity of sea water it has fortunately been possible to redefine chlorinity so that it is independent of changes in atomic weights.

The primary standard used in the determination of chlorinity is so-called "Normal Water" (*Eau de mer normale*), prepared by the Hydrographical Laboratories in Copenhagen, Denmark, and distributed to all oceanographic institutions. Some of these institutions made their own secondary standards by means of the Normal Water. As a result of world conditions the preparation of Normal Water has temporarily been taken over by the Woods Hole Oceanographic Institution.

Normal Water is sea water whose chlorinity has been adjusted to about 19.4 ‰ and accurately determined by either direct or indirect comparisons with the original standard prepared in 1902. Hence, the chlorinities of all batches have been independent of changes in the atomic weights. A new primary standard (Urnormal-1937), prepared in 1937, will be used to establish the chlorinity of future batches of Normal Water for general distribution (Jacobsen and Knudsen, 1940). Comparison with earlier series of Normal Water showed the chlorinity of the new standard to be 19.381 ‰. As a more absolute method should be available with which to check future Normal Water preparations, the 1937 primary standard was analyzed, using extremely pure "atomic weight silver." The equivalent amount of silver necessary to precipitate the halides was determined and the ratio of chlorinity to silver was found to be 0.3285233. On this basis a new definition of chlorinity was

introduced: *The number giving the chlorinity in grams per kilogram of a sea-water sample is identical with the number giving the mass in grams of "atomic weight silver" just necessary to precipitate the halogens in* 0.3285233 *kilogram of the sea-water sample.* By this redefinition the chlorinity has been made independent of changes in atomic weights, whereas the chlorine-equivalent, for which the original definition is retained, may vary slightly as the atomic weights are modified. The empirically established relationship between chlorinity and salinity (p. 51) remains valid and, according to the new definition of chlorinity, will never be affected by modification of the atomic weights.

The ratio of chlorine to silver, using the 1940 atomic weights (Ag = 107.880 and Cl = 35.457), is 0.3286707. Hence the ratio of chlorine-equivalent to the chlorinity is:

$$\frac{0.3286707}{0.3285233} = 1.00045.$$

[Equation]

This ratio is important when computing the chemical composition of sea water of given chlorinity, as the chlorine-equivalent will be greater than the indicated chlorinity. It must also be taken into account when preparing standard chloride solutions or when direct gravimetric analyses are made to determine the halide content of sea water. It is of interest to see how closely this ratio corresponds to the change which could be expected from the modification of the atomic weights. According to Jacobsen and Knudsen (1940) the indicated chlorinity of the Normal Water should be increased by 0.0094 ‰ to take this modification into account. This procedure gives a ratio between chlorine-equivalent and chlorinity of 1.000485, which is in good agreement with that given above.

When dealing with the chemistry of sea water, other substances are generally determined and reported on a volume basis, wherefore it is convenient to introduce *chlorosity* (*Cl*) (Intern. Assn. Phys. Oceanogr., 1939), which is the property corresponding to the chlorinity expressed as grams per 20°-liter (p. 169). Chlorosity is obtained by multiplying the chlorinity of a water sample by its density at 20°. Table 8 gives the corresponding values of chlorosity for chlorinities between 15.00 and 21.00 ‰.

Methods for Obtaining Salinity, Other than Titration with Silver Nitrate. The salinity can also be determined from the density of a water sample at a given temperature or by measuring either the electrical conductivity or the refractive index, both of which depend upon the salinity. The character of these properties will be dealt with below, but their application to salinity determinations will be briefly discussed here.

Determinations of *density* are appropriately included under methods for obtaining salinity, because such determinations are generally made at

atmospheric pressure and at room temperature and will thus differ from, the density of the water sample at the locality where it was

collected, but from the density thus observed the density at 0°C is computed, and from the latter the salinity can be found by means of Knudsen's Hydrographical Tables (p. 56). Determinations of density are rarely made, as it is difficult and time consuming to obtain an accuracy comparable to that obtained from the chlorinity titration, which is about ±0.00001. The methods used can be classified in two groups. In one, the mass of an accurately known volume of water at a definite temperature is determined, for example, by using a pycnometer bottle. In the second group, some form of hydrometer or float is used, and the density is computed from the weight of the hydrometer and the volume of the displaced water. The common form of stem hydrometer is generally not sufficiently accurate except when dealing with coastal waters, where great differences in density are found in short distances. The chain hydrometer of Hans Pettersson (1929) gives greater accuracy, but not as high as desirable. Nansen (1900) developed a hydrometer of total immersion which is very sensitive but which requires a water sample of at least 300 ml. The buoyancy is adjusted by the addition or removal of small weights until the hydrometer neither sinks nor rises in the sample, the temperature of which must be known within ±0.02°. Another type of instrument makes use of a sinker suspended in the water sample from one arm of a delicate chemical balance (Cummings, 1932). The "weight" of the sinker in a sample at a known temperature is determined, and from this the density may be computed. In all instances various corrections must be applied and the original sources consulted before any such determinations are attempted. Thompson (1932) has described the methods in some detail and gives many references.

CORRESPONDING VALUES OF CHLORINITIES AND CHLOROSITIES

| Chlorinity, ‰	15.00	16.00	17.00	18.00	19.00	20.00	21.00
Chlorosity, g/L	15.28	16.32	17.37	18.41	19.46	20.51	21.57
	.28	.32	.37	.41	.46	.51	.57

Measurements of the electrical conductivity have been employed on board the *Carnegie* and by the U. S. Coast Guard as the routine method for obtaining salinities. Owing to the relatively high concentration of the ions and the effect that temperature has upon the

conductivity, the apparatus and the technique employed are rather complicated (Wenner, Smith, and Soule, 1930; Soule, 1932). These instruments are standardized empirically, using sea-water samples of *known salinity* (determined by silver nitrate titrations against Normal Water), and the values for the unknown samples are obtained by interpolation. In order to obtain

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results of adequate accuracy, extreme care must be taken to control the temperature of the conductivity cells, and the resistance must be measured very accurately. A simplified diagram of the type of circuit used in electrical conductivity measurements on sea water is shown in fig. 12. *A* and *B* represent two similar electrolytic cells. *R* is a variable resistance in series with *B*, the cell used for the unknown sample. *A* contains sea water of known chlorinity or a standard potassium chloride solution of approximately the same conductance. *C* and *D* are fixed resistances and *S* is a slide-wire resistance. *H* is a source of alternating current of frequency between 600 to 1000 cycles per second at a potential of about 0.5 to 1.0 volt. *T* represents the telephone receiver used to establish the balance of the bridge. Two cells are used to eliminate small temperature effects. For details concerning the circuit and the various instruments the original references cited above should be consulted.

According to Thomas, Thompson, and Utterback (1934) the Grinnel Jones conductivity bridge may be used with Washburn pipette-type cells, the constants of which are determined with standard potassium chloride solutions.
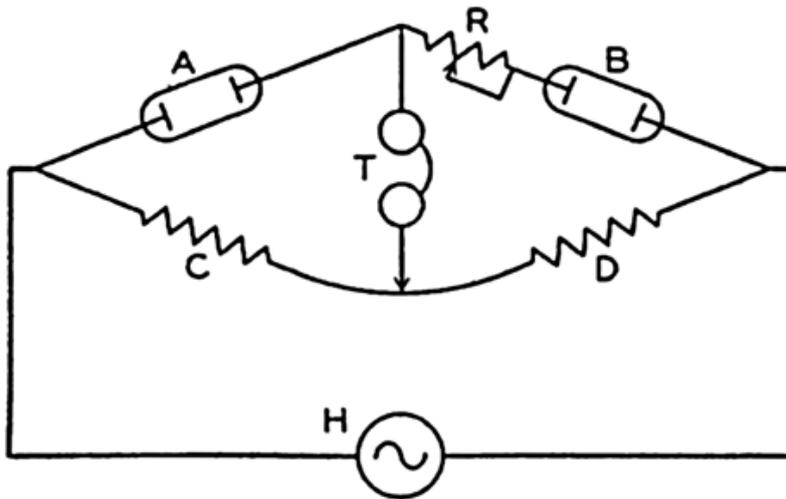
Circuit used in measurements of the electrical conductivity as a means of obtaining the salinity of sea water. Symbols are explained in the text.

[Full Size]

The *refractive index* of sea water, which will be discussed later (p. 70) in greater detail, varies only slightly within the ranges of temperature and salinity encountered in the sea, but, in an interferometer, differences in refractive index can be measured with extreme accuracy. At a given temperature such differences depend only upon the salinity, and special types of interferometers have therefore been developed for indirect determinations of salinity, using water of *known salinity* as a standard. Monochromatic light must be used because the refractive index varies with the wave length. This method of determining salinity has not been widely used.