3.3 THE MEASUREMENT OF SALINITY

Early attempts to determine the chemical composition of seawater were hampered by the low sensitivity of analytical techniques. It was not until the early nineteenth century that any order became apparent in the data and the constancy of composition of seawater was first recognized from the few analyses available. During the cruise of HMS *Challenger* from 1872 to 1876, 77 water samples were collected from various depths in nearly all the major oceans and seas, and analysed for the elements chlorine, sodium, magnesium, sulphur, calcium, potassium and bromine. The method used for each element was rigorously tested on synthetic samples, thus giving a check on the reliability of the technique.

Since the nineteenth century, a large number of investigations have been carried out into the ratio of single constituents to salinity. During the mid 1960s, scientists from the British National Institute of Oceanography (now the Institute of Oceanographic Sciences) and the University of Liverpool analysed more than one hundred samples for all the major constituents. In the 1970s, the GEOSECS programme (GEochemical Ocean SECtionS), based in the USA, collected systematic chemical data for all the oceans, using the most accurate analytical techniques available and (more importantly) sampling procedures that minimized contamination. The huge amount of data collected is still being interpreted.

3.3.1 CHEMICAL METHODS OF SALINITY MEASUREMENT

Perhaps the most obvious way of measuring salinity is to take a known amount of seawater, evaporate it to dryness and then weigh the remaining salts (gravimetric determination). Although simple in theory, such a method gives variable and therefore unreliable results, for a number of reasons. The residue left after evaporation is a complex mixture of salts, together with some water of hydration bound to the solids, plus a small amount of organic material. The amount of water left behind can obviously be decreased by thorough drying of the residual salts at elevated temperatures, but this leads to other problems such as (i) decomposition of some of the salts (e.g. loss of HCl from hydrous $MgCl_2$ crystals); (ii) vaporization and decomposition of the organic matter; and (iii) expulsion of CO_2 from carbonate salts. The weight of solid material left behind after evaporation (and hence the measured salinity) thus depends on the conditions employed to drive off the water. Marine chemists in the nineteenth century were well aware of this in their attempts to measure salinity gravimetrically, and devised procedures that gave reasonably reproducible results.

None the less, gravimetric determination of salinity remains both difficult and tedious, and so other methods have been investigated. As you have read in Section 3.1, the concentrations of many major dissolved constituents of seawater bear a constant ratio to the total dissolved salt concentration, so the concentrations of one or more major constituents can be used to deduce the total salinity, S. The easiest constituents to measure are the halides (chloride + bromide + iodide), and this led ultimately to the empirical relationship:

$$S = 1.80655\ Cl \qquad (3.1)$$

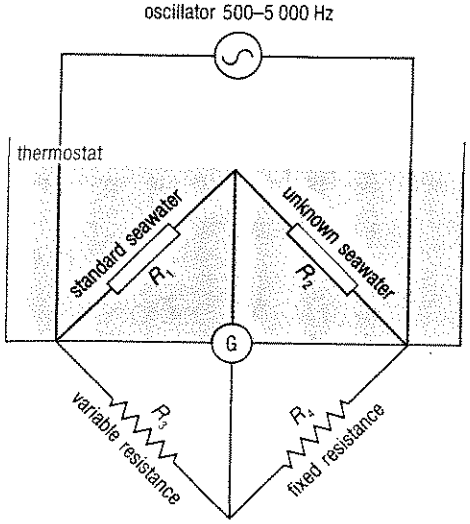

Figure 3.5 A simple bridge circuit for measuring conductivity of seawater samples. R_1 to R_4 represent resistance values, and G is the galvanometer. The thermostat would commonly be a constant-temperature water bath.

where *Cl* is the **chlorinity** of the sample, defined as the concentration of chloride in seawater (in parts per thousand) assuming that the bromide and iodide have been replaced by chloride.

Chlorinity was measured by titration and the salinity determined by substitution in equation 3.1 or tables derived from it. This method was used for determining virtually all salinities from the turn of the century until the mid-1960s. It is rarely used today, having been almost entirely superseded by measurements of electrical conductivity.

3.3.2 PHYSICAL METHODS OF SALINITY MEASUREMENT

Pure water is a poor conductor of electricity. However, the presence of ions in water enables it to carry an electric current. In the 1930s it was established that the electrical **conductivity** of seawater is proportional to its salinity. Conductivity is inversely proportional to resistance.

The first conductivity salinometers employed simple circuits of the type shown in Figure 3.5. In operation, R_3 is adjusted until the current flowing through the galvanometer falls to zero, when the following relationship holds:

$$\frac{R_1}{R_2} = \frac{R_3}{R_4} \quad (3.2)$$

As the values of all the resistances, except R_2, are known, the resistance of the seawater sample can be calculated. For oceanographic work, water of salinity of 35 was generally used as the standard water (R_1) for calibration purposes.

Conductivity is also affected by the temperature of the solution, which can lead to appreciable errors. Physical oceanographers ideally require salinity measurements to be accurate to ±0.001 if possible. To achieve this, conductivity must be measured to 1 part in 40000. A change of this magnitude can be induced by a temperature change of only 0.001°C, so careful control of temperature is essential. Precision thermostating can maintain both sample and standard seawater at the same temperature, but the equipment is then bulky and measurements take a long time, because the sample has to be heated or cooled to working temperature before measurement can begin. Such problems inherent in circuits of the type shown in Figure 3.5 have now been largely circumvented, and modern salinometers are compact and rapid in operation, and can measure salinity to ±0.003‰ or better. Conductivity sensors have been incorporated into *in situ* temperature–salinity instruments for use in shallow waters, and into conductivity–temperature–depth (CTD) probes for use in the deep oceans.

3.3.3 THE FORMAL DEFINITION OF SALINITY

Since the mid-1960s, the definition of salinity has been based (by international agreement) on empirically determined and rather complicated-looking formulations involving a conductivity standard. The formal definition that has been in use since the early 1980s runs as follows.

The practical salinity of a sample of seawater is defined in terms of the conductivity ratio, K_{15}, which is defined by:

$$K_{15} = \frac{\text{conductivity of seawater sample}}{\text{conductivity of standard KCl solution}} \quad ($$

at 15°C and 1 atmosphere pressure, the concentration of the standard K solution being 32.4356g kg^{-1}.

The practical salinity is related to the ratio K_{15} by the following equatio

$$S = 0.0080 - 0.1692\, K_{15}^{1/2} + 25.3851\, K_{15} + 14.0941\, K_{15}^{3/2} - 7.0261\, K_{15}^{2} + 2.7081\, K_{15}^{5/2} \quad (3$$

1 You do not need to remember any details of equation 3.4. Question 3.7 (below) is intended simply to show you how it works.

2 As the definition is a ratio, salinities are nowadays presented simply numbers. It is important to remember that the numbers represent grammes per kilogramme, or parts per thousand by weight.

3 In practice, tables (and, increasingly, computer algorithms) are used for the direct conversion of K_{15} into S, and for converting conductivity ratios at temperatures and pressures of measurement other than 15°C ar 1 atmosphere pressure into K_{15}.

QUESTION 3.7 Use equation 3.4 to answer this question by completing th following sentence. By definition, when $K_{15} = 1$, the practical salinity is exactly equal to...?

Hence there is a 0.5% diff between chemical salinity & practical salinity →

A salinity value determined by conductivity depends on the temperature and pressure at which the conductivity is measured, and is thus somewh removed from the simple but fundamental idea of salinity being the total dissolved salts in a seawater sample. In fact, for open ocean seawater, th two are closely related: the content of total dissolved salts in g per kg of seawater is $1.00510 \times S$, where S is as defined in equation 3.4.

As explained in next chapter chlorinity is ~ conservative moreso than salinity.

Clear Cl
Natural Na
Seawater SO_4
must Mg
Contain Ca
Kippered K
Herrings, HCO_3
a
Briny Br
Boil BO_3
Surrounding Sr
Fishes F

3.4 SUMMARY OF CHAPTER 3

1 The average salinity of seawater is close to 35 parts per thousand (‰ by weight. Eleven ions make up 99.9 per cent of the dissolved constituents: Cl^-, Na^+, SO_4^{2-}, Mg^{2+}, Ca^{2+}, K^+, HCO_3^-, Br^+, $H_2BO_3^-$, Sr^{2} and F^-, in that order. The relative proportions of elements in solution in seawater differ greatly from the proportions in crustal rocks, because of their different solubilities in the solutions formed during terrestrial weathering and sea-floor hydrothermal activity.

2 Salinity varies from place to place in the oceans, but the relative proportions of most major dissolved constituents (their ionic ratios) remain virtually constant. Evaporation and precipitation change the total salinity, but do not affect the constancy of composition.

3 Minor departures from constancy of composition in the open oceans result mainly from the intervention of biological and hydrothermal processes, affecting principally Ca^{2+}, Mg^{2+} and HCO_3^-. Major departures are the result of local conditions, chiefly in shallow near-shore waters, but also where hydrothermal activity occurs. Some major constituents are extracted commercially from seawater, but minor constituents have so far not been successfully extracted on a commercial scale.

4 The vertical and lateral distribution of salinity in the oceans do not change significantly from year to year, but the waters themselves are continually moving in a three-dimensional system of surface and deep currents. Surface salinities in the open oceans are greatest (up to 38) in tropical latitudes, where evaporation exceeds precipitation. They are lower near the Equator (*c.* 35) and in high latitudes (*c.* 33–34), because of greater rainfall and (in high latitudes) melting ice and snowfall. In middle and low latitudes, there is a halocline from the base of the mixed surface layer to about 1000m depth, below which salinities are generally between 34.5 and 35.

5 Gravimetric measurement of salinity is difficult because of decomposition of some of the salts on heating to evaporation. Chemical measurements of salinity, based on titration to determine chlorinity, were standard until the 1960s, but have been almost entirely superseded by electrical conductivity methods. An empirically determined formula is used to convert conductivities, measured against a standard, into salinities.

Now try the following questions to consolidate your understanding of this Chapter.

QUESTION 3.8 Which of the following statements (a)–(e) are true, and which are false?

(a) The relative proportions of elements dissolved in seawater are very similar to those in average crustal rocks.

(b) Salinity can vary from place to place in the oceans, but the ratio of salinity to chlorinity will nearly always remain constant.

(c) The ratio of Ca^{2+} to salinity will fall where there is significant precipitation of calcium carbonate.

(d) Haloclines are regions in which salinity increases with depth.

(e) It is impossible to measure either salinity or temperature to better than one part in a thousand.

QUESTION 3.9 The oceans are not a closed system, and large amounts of dissolved salts are continually being introduced into them from the world's rivers. There are also significant inputs from other sources such as hydrothermal solutions. So how is it that, in general, the constancy of composition of seawater is maintained?