The Laboratory Measurement

Salinity is one of the most measured parameters in oceanography. The importance of high quality salinity data has long been recognised in open ocean studies and more recently in coastal and estuarine processes. Much data is collected using in-situ instrumentation (e.g. CTD, multi-probes) but the measurement of salinity in the laboratory remains an important and widely used technique. This article describes developments made to allow the high precision, accurate measurement of Practical Salinity in the laboratory.

In recent years salinity data has provided important information in the study of climate change. Large transects of the ocean using CTD profiles have helped to improve the understanding of ocean circulation and water mass movements which are critical factors in the influence of global weather. Improving our knowledge of sea surface salinity also leads to a better estimation of the global hydrological cycle and will aid in the prediction of possible climate change events such as the weakening of the North Atlantic Conveyor Belt.
Salinity measurement continues to play an important role in other aspects of oceanography. The passage of sound in seawater is dependent on the density and hence the salinity of that water. Activities involving SONAR devices rely, at some stage, on an accurate measurement of salinity in order to obtain meaningful data. Such applications include seabed mapping, submarine detection and bathymetry.
It should be remembered that salinity data is also important in coastal and estuarine waters. Being a natural parameter, which changes significantly with every tidal cycle, salinity can play a useful role in assessing the dynamics of a coastal or estuarine location. Such applications are used, for example, to predict the fate of effluents from industry or sediments during dredging operations.
Salinity also plays an important role in biological processes affecting algal blooms, fish movements, shellfish productivity and aquaculture.

Early Work on Salinity Measurement

Early work in measuring the saltiness of the sea involved taking a known weight of seawater, evaporating the water and weighing the residue (Boyle, 1693; see Birch, 1965). Problems of inaccuracies were soon recognised due to the inability to obtain a dry weight. Many of the crystalline salts are bound up with water and attempts to drive off this water with increased heat resulted in the loss of the more volatile components. Refinements to the analysis included solvent extraction (Lavoisier, 1772) and precipitation (Bergman, 1784). It was Forchhammer (1865) who introduced the term salinity and the concept of measuring one parameter, chloride (in reality, total halide), from which the salinity could be calculated. Its success depended on his concept that the proportions of the major ions dis-solved in seawater were the same throughout the oceans. This work was supported further by Dittmar (1884), who analysed over 75 samples from the Challenger Expedition to establish the theory of 'Constant Composition of Seawater' Further work by Knudsen et al (1902) resulted in a new definition. Salinity was, according to him: "The total amount of solid material in grams contained in one kilogram of sea water when all of the carbonate has been converted to oxide, all the bromine and iodine replaced by chlorine and all the organic material oxidised". It was at this time that Knudsen introduced the Standard Seawater Service to supply (natural) seawater standards to workers measuring salinity. This innovative forethought has led to more than a century of high degree comparability in salinity data from workers world-wide (Culkin and Smed, 1979). This service is currently operated, in the UK, by Ocean Scientific International Ltd which supplies IAPSO Stand-ard Seawater to salinity workers in over 75 countries world-wide who depend on the reliability of this common standard (Culkin and Ridout, 1997).
These methods remained dominant until the 1950s, when conductivity was intro-duced as a practical means to measure salinity. A conductivity-based salinometer was developed for the International Ice Patrol capable of measuring salinity to better than 0.01 ppt (Emery and Thomson, 1998). It contained six thermostatically controlled conductivity cells and was claimed to have reached a precision of 0.003 ppt. (Cox, 1963). Various salinometers were developed during the 1950s and 1960s (e.g. Hamon, 1955) and new relationships were produced for conductivity and salinity (Culkin (1979); Millero et al1977; Poisson et al1978).
For a period of twenty years or so, the chlorinity and the conductivity methods for measuring salinity sat somewhat uncomfortably alongside each other. However, conductivity began to dominate due to improved precision and, most particularly, because it allowed the development of in-situ probes, later to become the traditional CTD (conductivity, temp-erature, depth) device.

Practical Salinity

In 1978, the break with chlorinity was sealed; the Joint Panel on Oceanographic Tables and Standards (JPOTS) introduced a new, conductivity-based definition. This new definition, which is current today, states that 'a seawater of salinity 35 has a conductivity ratio of unity with 32,4356 grams of Potassium Chloride in 1 kilogram of solution at 15 C and 1 atmosphere'. The standard concentration of KCL was derived from measurements carried out on one batch of Standard Seawater, weight diluted and evaporated (Lewis, 1980; see Unesco Technical Papers No. 37, 1981). Also included were measurements of absolute conductivity carried out at the Institute of Oceanographic Sciences, Wormley, UK (Culkin and Smith, 1980).
The introduction of the Practical Salinity Scale 1978 (PSS78) resulted in some significant operational changes which, sadly, have not been fully understood by some workers even now, 25 years later. One change particularly difficult to accept by some has been the abolition of units due to the adoption of a scale. Previous methods had resulted in concentration units such as parts per thousand (ppt) being used but such descriptions now became invalid. The correct way to report Practical Salinity is as a number (e.g. the sample had a salinity of 35), possibly with reference to PSS78. However, the move away from units has proved so difficult for some to accept that a new unit, the Practical Salinity Unit (PSU), has been unofficially introduced. In true terms of the PSS78, the PSU is not valid but it is widely used and often accepted even by the editors of journals.

Modern Salinometers

The first version of the modern, conductive salinometer was developed by Dauphinee in 1975; he produced a four-electrode (platinum) cell located in a temperature-controlled bath. This gave rise to the widely accepted 'industry standard' salinometers (Autosal and Portasal) which are produced by Guildline Instruments Ltd and which achieve a quoted accuracy of +-0.002 in Practical Salinity.

This proved to be important in the World Ocean Circulation Experiment (WOCE) during the 1990s, which produced the largest ever set of high-precision salinity data from the world oceans. This level of accuracy is now being widely accepted as the desirable goal for all salinity data from the open ocean.

Salinity in the Future

It is difficult to envisage how salinity measurement can develop further. A number of workers have expressed a desire for accuracy in the 4th decimal place of salinity. Limitations on the nstrumentation are related mainly to stability of conductivity cells and temperature control. The real question perhaps should be "how meaningful would 4th decimal salinities be in the real world?" Certainly, they would be useless in the dynamic conditions of estuaries and most coastal waters but even in the deep ocean it is extremely doubtful that we could we interpret real differences, or maintain sample integrity, at that level.
There are limitations in converting to density, conductivity-based salinity measurements where there are compositional differences between bodies of water (e.g. silicate affects density but is not detected by conductivity). Some workers have highlighted the value of optical methods, such as refractive index, for salinity measurement but this would, of course, require a change in the current definition. Many advances are taking place in optical measurement, including the development of laser interferometers, which suggest high levels of sensitivity are achievable. But it may be that their value lies more in the provision of data complementary to the conductivity-based salinities.

Acknowledgements

The author is grateful to Dr Fred Culkin and Nigel Higgs for assistance in preparing this manuscript.

Note by the Editor

The submitted article has many references, which were - in consultation with the author - left out to bring the article into the 'culture' of Hydro International.