DEVELOPMENTS IN THE STANDARDISATION OF OCEAN SALINITY

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The salt content or salinity of the oceans is one of the most measured parameters in oceanography. Its importance has long been recognised in studies of water mass movements in the open ocean. Improving knowledge of sea surface salinity is leading to a better estimation of the global hydrological cycle which, ultimately, will contribute towards a better understanding of climate change.

As a result of global warming, increased amounts of fresh water are being evaporated from the ocean surface and transported to higher latitudes, giving rise to increased surface salinities in some areas of the oceans. The Ocean Observations Panel for Climate, OOPC, and its predecessors examined the usefulness of sea surface salinity data in the context of climate change detection. They state that "At high latitude, sea surface salinity is known to be critical for decadal and longer time scale variations associated with deep-ocean over turning and the hydrological cycle. In the tropics and, in particular, the western Pacific, Indonesian Seas and in upwelling zones salinity is also believed to be important."

Salinity is important in other aspects of marine science. SONAR (sound navigation and ranging) is influenced by water density and hence the salinity of the seawater in applications such as seabed mapping, submarine detection and bathymetry. Salinity has a considerable influence as an ecological factor on marine organisms, affecting algal blooms, movement of fish stocks, shellfish productivity and aquaculture.

Early work in measuring the saltiness of the sea involved techniques utilising weighing after evaporation (Boyle,1693; see Birch, 1965), 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. This work was supported further by Dittmar (1884) who analysed over 75 samples from the Challenger Expedition (1872-1876) to establish the theory of 'Constant Composition of Seawater'. Further work by Knudsen et al (1902) resulted in a new definition which stated that Salinity was "The total amount of solid material in grams contained in one kilogram of seawater when all of the carbonate has been converted to oxide, all the bromine and iodine replaced by chlorine and all the organic material oxidised".

Towards the end of the 19th century the Danish physicist and hydrographer Martin Knudsen prepared sealed glass tubes of seawater to standardise the silver nitrate solutions used in Danish hydrographic work. In 1899 when a preparatory conference took place in Stockholm to establish the International Council for the Exploration of the Seas (ICES), Knudsen submitted a proposal for an international institution for the procurement of standard water (Conference Internationale, 1899). Key features of his proposal were the collection of open Atlantic seawater, detailed determination of the total salinity and testing of sealed glass tubes for maintaining the integrity of the standard. The Norwegian explorer, Fridtjof Nansen

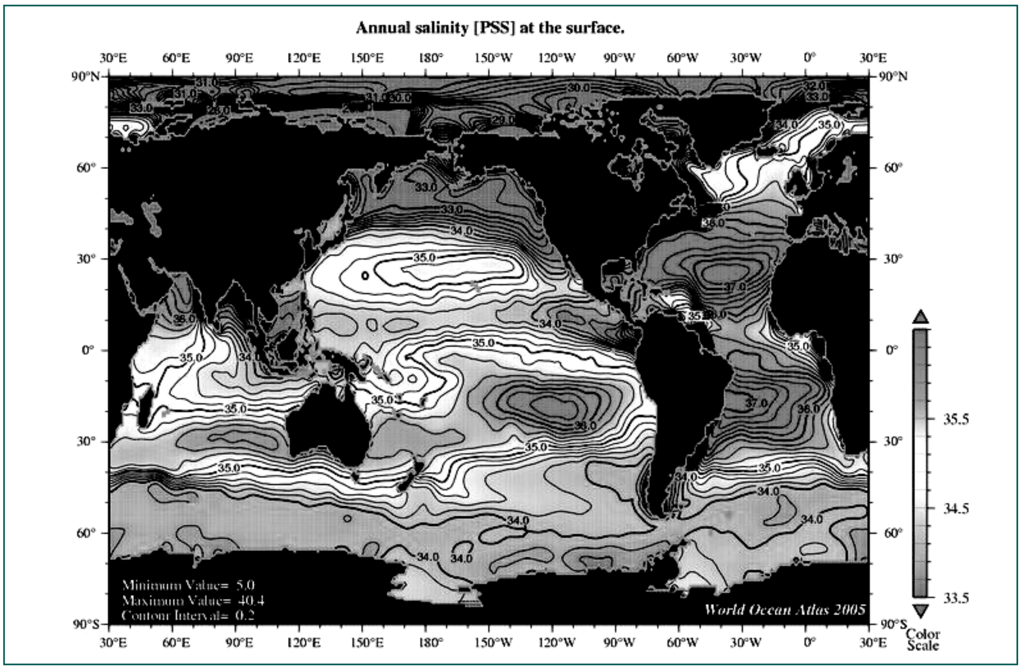

Fig 1 Sea surface annual salinity (Antonov et al, 2006)

proposed to the Conference that a Central Laboratory be set up in connection with ICES for the supply of standard seawater. In April 1900 about 80 tubes of 'Standard Water No VI' and random samples were investigated for chlorinity and specific gravity by the Danish chemist, Sørensen. When Nansen relinquished this responsibility in 1908, Knudsen agreed to direct the Standard Seawater Service on behalf of the Council and then in 1914 he assumed personal responsibility for its operation.

Fig 2 An ampoule of Standard Seawater from 1902 (© P Ridout)

In 1947, at the age of 76, Knudsen suggested that the Association Internationale d'Oceanographie Physique (AIOP) take over responsibility for the Service in order to secure its future. His foresight was appreciated soon after when Knudsen died and, at the request of AIOP, Helge Thomsen took over administrative responsibility with Knudsen's assistant, Frede Hermann, preparing and calibrating the standards. When Thomsen retired in 1960 Hermann took over full responsibility and the requirement for standards increased dramatically as oceanographic science expanded around the world. Scaling up of the seawater collection, processing and calibration was necessary to meet the demand which peaked at around 30,000 ampoules of standard per annum. Hermann retired in 1974 and responsibility for the Service passed to Fred Culkin, a UK marine chemist who had collaborated with him on chlorinity titrations for several years. With support from IAPSO (formerly AIOP) all the equipment, which included a 5000 litre tank, circulation pumps, filling manifold and stocks of ampoules were transferred to the Institute of Oceanographic Sciences (IOS) in Wormley, Surrey, UK. Much of the knowledge and analytical techniques involved in the production of this important standard had been transferred via word of mouth and handwritten notes so when Hermann died a year or so later Fred Culkin essentially was the only person who had the knowledge to produce Standard Seawater. By way of mitigation and to ease the workload, IOS employed Paul Ridout to understudy Fred Culkin and take over the day-to-day operation of the service with Culkin remaining as its director. At that time Standard Seawater was still calibrated using a high precision potentiometric titration of the seawater total halide with silver nitrate solution to give Chlorinity.

In 1978 the break with chlorinity was sealed with the introduction of a new conductivity-based definition of salinity by the Joint Panel on Oceanographic Tables and Standards (JPOTS). This new definition states that 'a seawater of salinity 35 has a conductivity ratio of unity with a solution of 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).

Fig 3: Fred Culkin and Paul Ridout at OSIL.

This gave rise to the introduction of the Practical Salinity Scale 1978 (PSS78) and the term Practical Salinity.

With the change in definition to Practical Salinity in 1978 came the need to determine the calibration of Standard Seawater in conductivity ratio. This was achieved using high precision weighings of KCl and measurement of conductivity ratio on a modified laboratory salinometer (Guildline Autosal). For a while the standard seawater label showed both conductivity ratio (K15) and chlorinity until Batch P113 (1990) when chlorinity was discontinued and replaced with the calculated value for Practical Salinity. In 1989 the Service was transferred, for the first time in its history, to a private company, Ocean Scientific International Ltd (OSIL) and the company's founder, Paul Ridout, took over as Director of the IAPSO Standard Seawater Service. Fred Culkin retired from IOS but continued in a consultancy role with OSIL until his death in February 2011. There were some concerns in 1989 with regard to the long-term stability of a commercial operation but in effect the Service has never been more secure with now, 22 years on, 3 analysts trained in the calibration and the methodology fully documented under an ISO9001:2008 quality system. In 2000, following almost a decade of testing, the traditional glass ampoule was replaced by a pharmaceutical grade glass bottle which offered an improved shelf-life (to 3 years) and a more robust container which required less packaging and was easier to use.

OSIL has continued to publish the results of ageing on the batches of P-series (Culkin and Ridout, 1997) and the statistical uncertainty of the calibration (Bacon et al 2007) and continues to archive samples from each batch. This archive contains seawater collected from the Atlantic Ocean since 1901.

Standard Seawater is identified by a batch number with the prefix 'P'. This originates from Knudsen's early work when in 1905 a new Primary Standard was established by direct comparison with Knudsen water VI. In the following two years, four more batches (P1-P4) were prepared. In the early years the demand was somewhat limited with Batch P17 being produced in 1948. The Service operated by OSIL has now reached Batch P153 and supplies the standards to marine scientists in over 75 countries. Seawater chemist, Nigel Higgs, carries out the day-to-day preparation and calibration of the standards with Paul Ridout as the Service Director. (More information is available at www.osil.co.uk).

Some countries (eg Japan, Russia, China) have produced

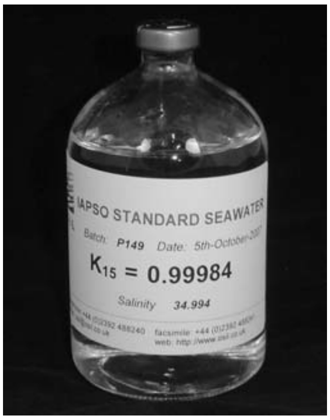

Fig 4: IAPSO Standard Seawater (© P Ridout)

their own standards for various reasons. The Japanese standard manufacture was discontinued in favour of the IAPSO standard which is now imported from OSIL and distributed in Japan. Seawater salinity standards have also been produced in Russia and China as secondary standards, calibrated against the IAPSO standard, for distribution only in those countries. The IAPSO Standard Seawater Service (at IOS and OSIL), with some support from the World Ocean Circulation Experiment (WOCE), the International Oceanographic Commission and Unesco, has worked closely with scientists from both the Russian and Chinese laboratories to maintain comparability between the primary (IAPSO) standard and these secondary standards.

Recent work by the SCOR/IAPSO Working Group 127 (WG127) has resulted in improved algorithms and descriptions of the thermodynamic properties of seawater (TEOS-10). In order to achieve higher accuracy a salinity variable was required which more accurately represented Absolute Salinity than the conductivity-based Practical Salinity. Absolute Salinity essentially represents the total dissolved salts whereas Practical Salinity is calculated from only the conductive components. This can lead to density anomalies (for example due to silicate which is non-conductive) between different oceans which affects high precision mathematical models of water mass movement models widely used in climate studies. As a result of the WG127 work the term Reference Salinity (SR) has been introduced which represents the best available estimate of the Absolute Salinity (SA) of an artificial seawater solution with a Reference Composition that has stoichiometry in molar fractions based on the most accurate determinations of IAPSO Standard Seawater constituents and the 2005 atomic weights of IUPAC (Millero et al, 2008). From a practical point of view the value of SR can be related to the Practical Salinity, SP by ….

$$\mathbf{SR = (35.16504/35)\ g\ Kg^{-1}\ x\ S_P}$$

Absolute Salinity offers several advantages over Practical Salinity for oceanographic purposes including its expression in SI units (g Kg^{-1}), no limitations by scale (as in PSS78), improved ocean models (as SA is truly conservative), reduced density errors in the Equation of State for seawater. Hence, new algorithms have been formulated for density, enthalpy, entropy, potential temperature and sound speed in terms of Absolute Salinity, temperature and pressure (Feistel, 2008).

Practical Salinity remains the preferred parameter for measuring and storing salinity data. This maintains the link with measurements made in the past and reduces the possibility of mislabelled salinity data from a wide range of sources. All instrumentation (*in situ* and laboratory) for the measurement of Practical Salinity are conductivity based and the algorithms in software and firmware can remain in place thereby reducing the potential for confused datasets. Reference Salinity is calculated as an SI-based extension of Practical Salinity and as a best estimate of Absolute Salinity by practising research oceanographers. With regard to the IAPSO Standard Seawater Service, work is currently under way in a joint European project to profile the density of each new batch.

Our understanding of global salinity depends largely on data from laboratory salinometers and instruments at sea such as buoys, drifters, towed platforms, autonomous underwater vehicles and moorings. The WOCE programme involved scientists from 33 countries and produced the largest salinity dataset ever, so comparability of that data was crucial to its success. As subsequent ocean circulation projects related to climate change (eg CLIVAR) collect even more salinity data, the need for comparability remains a top priority.

Fig 5: An instrument buoy used to measure salinity at sea.

The NASA satellite mission Aquarius SAC-D, due to be launched in June 2011, has an overarching scientific goal to quantify and understand the linkages among ocean circulation, the global water cycle, and climate by accurately measuring sea surface salinity. The accuracy and subsequent value of these satellite data will depend crucially on the high quality data produced by *in situ* sampling and measurement.

Data centres contain the results of millions of salinity determinations carried out and used by chemists, physicists, biologists and engineers from all over the world. The comparability of these data is largely due to the widespread use of a single source calibration standard for salinity, IAPSO Standard Seawater.

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