United Nations
Educational, Scientific and
Cultural Organization

Intergovernmental
Oceanographic
Commission

SCOR

IAPSO

The International Thermodynamic Equation of Seawater – 2010

A scientific summary for policy makers

For bibliographic purposes, this document should be cited as follows:

The International Thermodynamic Equation of Seawater – 2010: A Summary for Policy Makers. IOC, SCOR and IAPSO, 2011 (IOC. Brochures Series)

TEOS-10 is published in the IOC Manuals and Guides Series:
IOC, SCOR and IAPSO, 2010: The International Thermodynamic Equation of Seawater – 2010: Calculation and use of thermodynamic properties. (Manuals and Guides, 56.) (English), 196 pp. (IOC/2010/MG/56)

Designer: Eric Loddé

(IOC/BRO/2010/7)

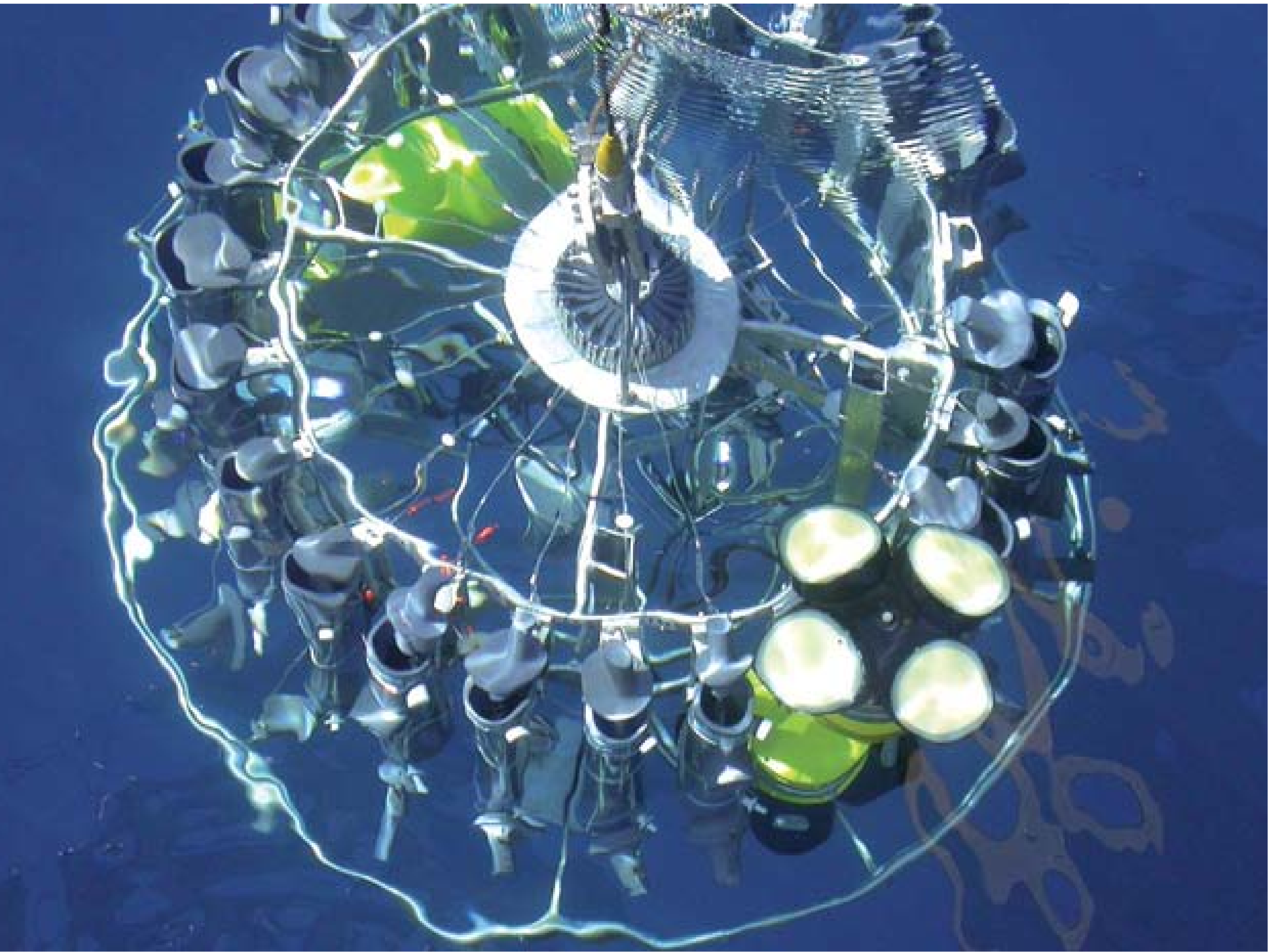
Printed in France

TEOS-10: A new way to look at water

Seawater composition is a critical factor, along with temperature and pressure, in determining the density of the ocean and calculating its potential to contain and disperse energy. How these variables relate to each other is the basis for the new Thermodynamic Equation of Seawater – 2010 (referred to as TEOS-10).

The Intergovernmental Oceanographic Commission (IOC) of the United Nations Educational, Scientific, and Cultural Organization (UNESCO), the Scientific Committee on Oceanic Research (SCOR), the International Association for the Physical Sciences of the Oceans (IAPSO), and the International Association for the Properties of Water and Steam (IAPWS) have all endorsed the new thermodynamic approach, TEOS-10.

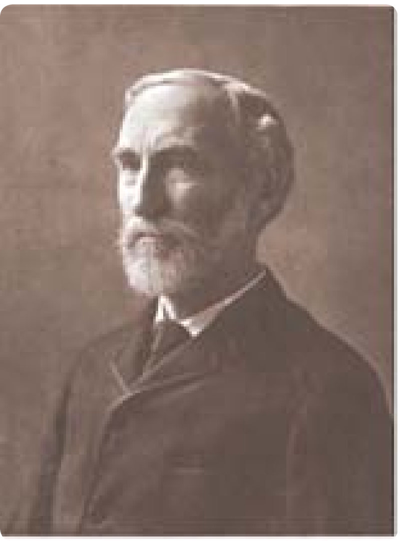
This new method of analyzing seawater provides mutually consistent expressions for density, potential temperature, entropy, enthalpy, sound speed, chemical potential, as well as other seawater properties — and provides an update to the *Equation of State of Seawater*, which UNESCO endorsed in 1980 (referred to as EOS-80). Unlike the previous equation, however, the thermodynamic approach is also applicable to freshwater, ice, and water vapor.



Working Group 127

The people behind the equation

> **"An equation giving internal energy in terms of entropy and specific volume, or more generally any finite equation between internal energy, entropy and specific volume, for a definite quantity of any fluid, may be considered as the fundamental thermodynamic equation of that fluid, as from it… may be derived all the thermodynamic properties of the fluid (so far as reversible processes are concerned)."**
>
> ***~ J. W. Gibbs, 1873***



Josiah Willard Gibbs

The group tasked with developing the new set of highly accurate and comprehensive formulas used in TEOS-10, the SCOR/IAPSO Working Group 127, began work in 2005 and included:

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* Member of the original committee on EOS-80

As previous studies have noted, the EOS-80 equation was missing a mathematical component -- a Gibbs function which physicists had determined for a variety of fluids, except seawater. Named after American theoretical physicist, chemist, and mathematician Josiah Willard Gibbs (1839-1903), a Gibbs function defines a fluid in terms of its energy and heat transfer, or thermodynamics. One of the first requirements the working group had to address was incorporating a Gibbs function into the new equation for seawater. The fundamental work of Rainer Feistel at Leibniz Institute for Baltic Sea Research led to the development of a Gibbs free energy function that is the backbone of the new thermodynamic equation of state (TEOS-10). Because the composition of seawater is different in different locations around the world, another aspect of the new equation is the provision of a practical way to account for these spatial variations. Merging the different seawater properties into one equation, the working group has mixed 19th-century theory with 21st-century computer algorithms.

Practical vs. Absolute Salinity

A fundamentally different approach to determining what's in seawater

In 1978, oceanographers agreed to use conductivity as the universal method for estimating the salinity of seawater. UNESCO endorsed this method, and incorporated the 1978 Practical Salinity Scale into its 1980 equations for calculating the density of seawater (EOS-80).

Prior to the Practical Salinity Scale, oceanographers had primarily calculated salinity using titration methods that measured the most common salt ion: chlorine (see box on page 7: The search for salinity). The conductivity method improved accuracy, as it tracked all the ions in the sea and not just chloride. But calculating salinity from conductivity, as opposed to traditional chemical analysis, required sacrificing the definition of salinity. This is because conductivity measures only free-floating ions or electrolytes, the same dissolved salts that are found in sports drinks, for example. In fact, any non-conductive material, such as dissolved silicon dioxide, is simply ignored when it comes to practical salinity.

Since seawater conductivity can only be precisely related to salinity for a particular chemical composition, applying the 1978 Practical Salinity Scale to seawater of different compositions can lead to errors. These errors are small in the open ocean, but are much larger than the typical precision of modern measurements.

Water from the North Atlantic with a salinity of about 35 parts of salt per thousand parts water has traditionally been used as a control for comparing other water samples. But as the water from the Atlantic ocean travels around the world, the composition of the seawater changes as a consequence of the biogeochemical differences in the environment. Sinking particles remineralize, adding calcium, carbon and nutrients like silicic acid and nitrate. Once seawater comes into coastal areas, its composition will also change as it mixes with river waters, which have dissolved ions in very different combinations from seawater. Some of these added molecules add to the conductivity, but not in the same way as the original set of ions.

Unlike the Practical Salinity Scale, which accounts only for ions, the new Absolute Salinity incorporates non-electrolytes using tables that account for how these additional substances vary region by region. Once again, the latitude and longitude at which seawater samples are taken will play an important role in calculating salinity. Unlike the Practical Salinity Scale -- which, as a reference scale, has no unit of measure -- Absolute Salinity is a new variable within the thermodynamic description and is part of the International System of Units.

A Taste for Salt

'In chemistry, any positive and negative ion bound together is called a salt,' explains molecular geneticist and chemosensation (taste and smell) expert Hiroaki Matsunami of Duke University in the USA. In the ocean, salts dissolve into free-floating negative and positive ions, also known as electrolytes. These charged particles are what make it possible for electricity to flow through water. The same ions that make up the salt used in foods — sodium (Na^+) and chloride (Cl^-) — account for more than 86% by weight of the 11 major ions in the sea and are what gives the ocean its salty taste. Dried, these ions form table salt and get sprinkled over food.

After chloride and sodium, the ocean's next most common ions are sulfate (SO_4^{2-}) and magnesium (Mg^{2+}). How would the ocean taste if these ions were more common? 'I tasted magnesium sulfate and it tasted really bad but I wouldn't call it bitter,' Matsunami says of the ingredient used in bath salts.

Present Practice for Data Storing Stays the Same

Data stored in national and international databases should, as a matter of principle, be measured values rather than derived quantities. Consistent with this, the working group recommends continuing to store the measured (*in situ*) temperature rather than the derived quantity, potential temperature. Similarly they recommend that Practical Salinity (S_P) continue to be the salinity variable that is stored in such databases since S_P is closely related to the measured values of conductivity. This recommendation has the very important advantage that there is no change to the present practice and so there is less chance of transitional errors occurring in national and international databases because of the adoption of Absolute Salinity (S_A) in oceanography (for more see page 9: Data Representations: Meta data requirements of TEOS-10).

In 2010, the algorithm for calculating salinity incorporated for the first time more information than is contained in measurements of seawater conductivity. The more accurate way of identifying Absolute Salinity everywhere in the ocean was devised and incorporated into TEOS-10. The new equation incorporated the location of the conductivity measurements with chemical analysis from those regions into a new Absolute Salinity calculation. The working group also redefined how the properties of seawater are calculated using this new Absolute Salinity method and combining it with the principles behind thermodynamics to form a single new thermodynamic equation for seawater.

The re-evaluation of the 1980s equations provided seawater with a 'Gibbs function'. The previous mathematical equations for determining the properties of seawater had not accounted for water's ability to transfer heat from warmer to cooler currents. Nor did the old equations set a standard for comparing how difficult such a transfer of energy might be, based on the water's inherent pressure and volume. The thermodynamic equation of seawater replaces the old equations with a recipe of computer algorithms that modellers crave.


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On 24 June 2009, the 25th Assembly of UNESCO's Intergovernmental Oceanographic Commission (IOC) recommended that the oceanographic community adopt TEOS-10.

The TEOS-10 method has already become an industrial standard, approved by IAPWS. For example, any company interested in providing drinking water for desert cities near the coast, is required to use the new method of calculation in building seawater desalination plants. The thermodynamic equation uses IAPWS-08 and IAPWS-06 as the official descriptions for seawater and ice.

Under TEOS-10 it is recognized that the composition of seawater varies around the world and that the thermodynamic properties of seawater are more accurately represented as functions of Absolute Salinity than of Practical Salinity. These new international standards were adopted while recognizing that the techniques for estimating Absolute Salinity will likely improve over the coming decades. The algorithm for evaluating Absolute Salinity in terms of Practical Salinity, latitude, longitude and pressure will be updated on the website www.TEOS-10.org following peer-reviewed publications. Users of this software should always state in their published work which version of the software was used to calculate Absolute Salinity.

Motivation for an Updated Thermodynamic Description of Seawater

The Practical Salinity Scale and EOS-80, which expresses the density of seawater as a function of Practical Salinity, temperature, and pressure, have served the oceanographic community for 30 years.

In recent years, however, the following aspects of the thermodynamics of seawater, ice, and moist air became apparent and suggested that it was time to redefine the properties of these substances.

- Several aspects of the International Equation of State of Seawater (EOS-80) were not consistent. The thermodynamic approach eliminates this problem.
- In 1995 the International Association for the Properties of Water and Steam developed a more accurate and more broadly applicable thermodynamic description of pure water. Also higher accuracy measurements have been made of several properties of seawater such as (i) heat capacity, (ii) sound speed and (iii) the temperature of maximum density. These have been incorporated into the new thermodynamic description of seawater.
- Oceanographers now have a better understanding of how variation in the composition of seawater can change seawater density in the different ocean basins. In order to further progress this aspect of seawater, a standard model of seawater composition is needed to serve as a generally recognised reference for theoretical and chemical investigations.
- The increasing emphasis on the ocean as being an integral part of the global heat engine points to the need for accurate expressions for the entropy, enthalpy and internal energy of seawater so that heat fluxes can be more accurately determined in the ocean and across the interfaces between the ocean and the atmosphere and ice (entropy, enthalpy and internal energy were not available from EOS-80).
- The need for a thermodynamically consistent description of the interactions between seawater, ice and moist air; in particular, the need for accurate expressions for the latent heats of evaporation and freezing, both at the sea surface and in the atmosphere.
- The 1968 temperature scale was revised in 1990 and TEOS-10 incorporates this revision as well as the latest update from the International Union of Pure and Applied Chemistry for the atomic weights of the elements.

Practical Salinity vs. Absolute Salinity Part II: How the Relationship Works Together

The salinity input to the TEOS-10 Gibbs function requires knowledge of the Absolute Salinity of seawater (S_A), which is based upon the Reference Salinity of seawater (S_R). The Reference Salinity is our best estimate of the Absolute Salinity of the seawater that was used to develop the Practical Salinity Scale (S_P), the equation of state, and the other thermodynamic properties of seawater. Reference Salinity is related to Practical Salinity by

$$S_R = S_P\,(35.16504/35.000)\ \mathrm{g\,kg^{-1}}$$

and Absolute Salinity is related to Reference Salinity by

$$\delta S_A = S_R + \delta S_A$$

where δS_A is due to the added solutes in seawater in deep waters resulting from the dissolution of $CaCO_3$(soluble) and SiO_2(soluble), CO_2, and nutrients like NO_3 and PO_4 from the oxidation of plant material. The δS_A values due to the added solutes are estimated from the differences between the measured densities of seawater samples compared with the densities calculated from the TEOS-10 equation of state at the same Reference Salinity, temperature, and pressure.

The values of δS_A in the ocean can be estimated for waters at given longitude, latitude, and depth using correlations of δS_A and the concentration of $Si(OH)_4$ in the waters. Other methods of estimating δS_A are also available in cases where the composition changes are measured or can be modelled. The δS_A values can then be used to calculate all the thermodynamic properties of seawater in the major ocean basins using the new TEOS-10.

Improving the accuracy
of climate models

The new thermodynamic equation for seawater also allows climate models to better account for changes in density and heat transfer in the ocean. Early tests of the use of the new equation show an estimated 1% change in how the ocean circulates heat from the equator to the poles. The change in the West to East temperature difference in the equatorial Pacific is about 0.1°C, and this is another aspect which is expected to be a valuable improvement in climate modelling.

The fundamental properties of seawater — salinity, temperature and pressure, along with the freezing and boiling points, heat capacity, speed of sound and density — are intricately tied together. Being able to measure salinity is important, as salinity levels are indicators of climate change. They indicate how much freshwater is evaporating from the oceans. For instance, parts of the Atlantic Ocean appear to be getting saltier. A possible explanation could be that trapped heat from higher atmospheric concentrations of CO_2 is causing more seawater to evaporate than before, leaving the salt behind.

Salinity levels affect water density. Density especially determines whether a current rises towards the surface or sinks towards the seafloor, as the denser the seawater, the deeper it will sink. Density depends on temperature, pressure and the amount of dissolved material in the water. Knowing the density of seawater is crucial to monitoring the Earth's climate. The ocean transports heat via currents collectively called the ocean conveyor belt in a process known as thermohaline circulation. In the Arctic and Southern oceans, cool and salty waters sink to form deep water currents. Over thousands of years, these currents travel around the world until they reach areas of upwelling which bring them to the surface. Once at the surface, the sun-warmed, rain-freshened currents head back


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to the poles, where the formation of ice allows the cycle to continue.

Several factors influence ocean circulation patterns: wind, rain, seafloor topography, the properties of the surrounding water, as well as the position and distance of the moon and the rotation of the Earth. Ocean circulation models include all of these factors and the computer algorithms that generate the models take weeks to run. Climate change models, which incorporate the ocean's ability to transport heat, take even longer. To see what model works best, what fits with the Earth's climate record from the past then run the model forward a century or two can take the best part of a year, on the world's fastest supercomputers.

The Search for Salinity

'The exact chemical composition of seawater is unknown at the present time,' says Frank Millero of the Rosenstiel School of Marine and Atmospheric Science at the University of Miami in Florida (USA) and a member of the SCOR/IAPSO Working Group 127. It is not for want of trying. Marine scientists have been searching for the 'magic formula' for measuring salinity for more than 150 years.

As early as 1865, Danish marine geochemist Georg Forchhammer found 27 different substances in seawater he sampled from different regions of the ocean. 'Next to chlorine, oxygen and hydrogen, sodium is the most abundant element in seawater,' he wrote. Other major substances he found included sulphuric acid, soda, potash, lime and magnesia. 'Those which occur in less but still determinable quantity are silica, phosphoric acid, carbonic acid and oxide of iron,' he concluded. His tables were used until 1902 when Danish oceanographer Martin Knudsen filtered and distilled North Atlantic water as a seawater standard that all marine scientists could use to calibrate their instruments easily and compare their samples from around the world with a control.

In the 1930s, the introduction of instruments that could measure seawater's electrical conductivity set oceanographers scrambling to determine whether chemical analysis or the new physical analysis worked better to determine salinity. Conductivity won and by the mid-1970s, deploying a rosette of sampling tubes equipped with conductivity, temperature and depth recorders (CTDs) was becoming a routine part of oceanographic cruises. To maintain consistency, a change to the international standard for seawater was made in the 1970s that allowed oceanographers to compare conductivity to a Practical Salinity Scale.

Unlike the Practical Salinity Scale, which accounts only for ions, the new Absolute Salinity will incorporate non-electrolytes using tables that account for how these additional substances vary region by region. Once again, the latitude and longitude at which the seawater samples are taken will play an important role in calculating salinity.

Advantages of TEOS-10

The more prominent advantages of TEOS-10 compared with EOS-80 are:

- The Gibbs function approach allows the calculation of internal energy, entropy, enthalpy, potential enthalpy and the chemical potentials of seawater as well as the freezing temperature, and the latent heats of freezing and of evaporation. These quantities were not available from the International Equation of State 1980 but are essential for the accurate accounting of "heat" in the ocean and for the consistent and accurate treatment of air-sea and ice-sea heat fluxes. For example, a new temperature variable, Conservative Temperature, can be defined as being proportional to potential enthalpy and is a valuable measure of the "heat" content per unit mass of seawater for use in physical oceanography and in climate studies, as it is approximately two orders of magnitude more conservative than both potential temperature and entropy.
- For the first time the influence of the spatially varying composition of seawater can systematically be taken into account through the use of Absolute Salinity. In the open ocean, this has a non-trivial effect on the horizontal density gradient computed from the equation of state, and thereby on the ocean velocities and heat transports calculated via the "thermal wind" relation.
- The thermodynamic quantities available from the new approach are totally consistent with each other, and can now account for properties such as speed of sound and the compressibility of water with depth.
- The new salinity variable, Absolute Salinity, is measured in SI units. Moreover the treatment of freshwater fluxes in ocean models will be consistent with the use of Absolute Salinity, but is only approximately so for Practical Salinity.
- The Reference Composition of standard seawater supports marine physicochemical studies such as the solubility of sea salt constituents, alkalinity, pH, and ocean acidification from rising concentrations of atmospheric CO_2.

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Data Representations:

Metadata requirements of TEOS-10 and Absolute Salinity Anomaly

The working group strongly recommends that oceanographers continue to report salinity to national databases as Practical Salinity, determined on the Practical Salinity Scale of 1978 (suitably updated to ITS-90 temperatures as described in appendix E of the TEOS-10 manual).

There are three very good reasons for continuing to store Practical Salinity rather than Absolute Salinity in such data repositories:

1. Practical Salinity is an (almost) directly measured quantity whereas Absolute Salinity is generally a derived quantity. Practical Salinity is directly calculated from measurements of conductivity, temperature and pressure, whereas Absolute Salinity is derived from a combination of these measurements plus other measurements and correlations that are not yet well established. Practical Salinity is preferred over the measured *in situ* conductivity value because of its conservative nature with respect to changes of temperature and pressure, or dilution with pure water.

2. It is imperative that confusion is not created in national databases where a change in the reporting of salinity may be mishandled at some stage and later be misinterpreted as a real increase in the ocean's salinity. This second point argues strongly for no change in present practice in the reporting of Practical Salinity in national databases of oceanographic data.

3. The algorithms for determining the best estimate of Absolute Salinity of seawater with non-standard composition are immature and will undoubtedly change in the future, so storing Absolute Salinity in national databases is not recommended. Storage of an intermediate value, the Reference Salinity, (S_R, defined to give the best estimate of Absolute Salinity of Standard Seawater), would also introduce confusion in the stored salinity values without providing any real advantage over storing Practical Salinity. Values of Reference Salinity obtained from suitable observational techniques (for example, by direct measurement of the density of Standard Seawater) should be converted to corresponding numbers of Practical Salinity for storage. The practice of storing one type of salinity in national databases (Practical Salinity, S_P) but using a different type of salinity in publications (Absolute Salinity, S_A) is analogous to the present practice with temperature; *in situ* temperature (t) is stored in databases (since it is a measured quantity) but the temperature variable that is used in publications is a calculated quantity: potential temperature under EOS-80 or conservative temperature under TEOS-10.

Dr Steve Rintoul and Stephanie Barrett, CSIRO.

In order to improve the determination of Absolute Salinity oceanographers need to begin collecting and storing values of the salinity anomaly $\delta S_A = S_A - S_R$ based on measured values of density (such as can be measured with a vibrating tube densimeter). The 4-letter GF3 code DENS is currently defined for *in situ* measurements or computed values from EOS-80. It is recommended that the density measurements made with a vibrating beam densimeter be reported with the GF3 code DENS along with the laboratory temperature (TLAB in °C) and laboratory pressure (PLAB, the sea pressure in the laboratory, usually 0 dbar). From this information and the Practical Salinity of the seawater sample, the absolute salinity anomaly $\delta S_A = S_A - S_R$ can be calculated using an inversion of the TEOS-10 equation for density to determine S_A. For completeness, it is advisable to also report δS_A under the new GF3 code DELS.

Using the TEOS-10:
Algorithms and Programmes

The computer software to calculate the various thermodynamic quantities is available from two separate libraries, the Seawater-Ice-Air (SIA) library and the Gibbs-SeaWater (GSW) library. The functions in the SIA library are generally available in basic-SI units, both for their input parameters and for the outputs of the algorithms. Some additional routines are included in the SIA library in terms of other commonly used units for the convenience of users. The SIA library takes significantly more computer time to evaluate most quantities (approximately a factor of 65 more computer time for many quantities, comparing optimized code in both cases) and provides significantly more properties than does the GSW library. The SIA library uses the world-wide standard for the thermodynamic description of pure water substance (IAPWS-95). Since this is defined over extended ranges of temperature and pressure, the algorithms are long and their evaluation time-consuming. The GSW library uses the Gibbs function of Feistel (2003) (IAPWS-09) to evaluate the properties of pure water, and since this is valid only over the restricted ranges of temperature and pressure appropriate for the ocean, the algorithms are shorter and their execution is faster. The GSW library is not as comprehensive as the SIA library; for example, the properties of moist air are only available in the SIA library. In addition, computationally efficient expressions for density ρ in terms of Conservative Temperature (rather than in terms of *in situ* temperature) involving just 25 coefficients are also available.

The input and output parameters of the GSW library are in units which oceanographers will find more familiar than basic SI units. We expect that oceanographers will mostly use this GSW library because of its greater simplicity and computational efficiency, and because of the more familiar units compared with the SIA library. The library name GSW (Gibbs-SeaWater) has been chosen to be similar to, but different from the existing "sw" (Sea Water) library which is already in wide circulation. Both the SIA and GSW libraries, together with the TEOS-10 Manual and this summary are available from the website www.TEOS-10.org. Initially the SIA library is being made available in Visual Basic and FORTRAN while the GSW library is available in MATLAB.

Images

Cover: A CTD onboard the R/V *Knorr* during the RAPID/MOCHA Mooring cruise in 2005. The world's first trans-basin mooring array across the North Atlantic Ocean at 26 N, the array has been continuously measuring Atlantic meridional overturning circulation since 2004. The project is a joint effort of the National Oceanography Centre, Southampton UK and the Rosenstiel School of Marine and Atmospheric Science at the University of Miami, USA. Credit: Rosenstiel School of Marine and Atmospheric Science.

Page 1: A CTD and lowered acoustic Doppler current profiler hovering just below the sea surface was taken south of Timor from the *Southern Surveyor* in August 2003. Credit: Ann Gronell Thresher.

Page 2: Josiah Willard Gibbs (1839-1903) Courtesy Wiki Images

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Sampling in the Southern Ocean

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