An Overview of the IAPSO Standard Seawater Service

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Salinity Measurement

History and Definitions
Forchhammer (1865)

In 1865, Johan Georg Forchhammer found that the ratio of major salts in samples of seawater from various locations was constant. This constant ratio is known as Forchhammer's Principle, or the Principle of Constant Proportions

\[ S = 1.812Cl \]
Dittmar (1884)

- Dittmar (1884) analyzed 70 seawater samples collected at various depths for the major oceans during the cruise of the H.M.S. Challenger (1873-1876).

- \( S = 1.8058\text{Cl} \)
Knudsen (1900)

Martin Hans Christian Knudsen (born February 15, 1871 in Hansmark, died May 27, 1949 in Copenhagen) was a Danish physicist who taught and conducted research at the Technical University of Denmark

\[ S = 1.805C_l + 0.03 \]
Salinity from Conductivity Ratio
Cox (1967)

\[ S = a + a_1 R_{15} + a_2 R_{15}^2 + a_3 R_{15}^3 + a_4 R_{15}^4 + a_5 R_{15}^5 \]

Various natural seawaters

10 to 30 C
Brown & Allentoft (1966)

\[ S = A + BR_{15} + CR_{15}^2 + DR_{15}^3 + ER_{15} \]

Various natural seawaters evaporated or weight diluted with pure water.

0 to 35 C
JPOTS (1978)

\[
S = a_0 + a_1 R_T^{1/2} + a_2 R_T + a_3 R_T^{3/2} + a_4 R_T^2 + a_5 R_T^{5/2} + (T-15) \left\{ b_0 + b_1 R_T^{1/2} + b_2 R_T + b_3 R_T^{3/2} + 1 + K(T-15) \right\} + b_4 R_T^2 + b_5 R_T^{5/2}\]

All temperatures according to the International Practical Temperature Scale 1968 (IPTS68)
Conductivity Ratio

Rt = \frac{\text{Conductivity of seawater at temp. t plus 1 atm.}}{\text{Conductivity of defined KCl soln. at same temp. & press.}}
A seawater of practical salinity 35 has a conductivity ratio of unity at 15°C with a KCl solution containing a mass of 32.4356 grams KCl in a mass of 1 kilogram of solution.
The Practical Salinity Scale

- Practical Salinity is calculated from this scale which is based on a series of laboratory controlled determinations.
- It has no units or dimension. The algorithms in PSS78 were adjusted to eliminate... *ppt, parts per thousand, \( \%_00 \), p.s.u.*
- IAPSO Standard Seawater is the only internationally accepted transfer standard.
- Chlorinity is an independent chemical parameter not linked with salinity.
PSS78: validity of equation

- Salinity: 2 to 42 (now extended to 50)
- Temperature: -2 to +35 °C
- Pressure: Atmospheric
IAPSO Standard Seawater
History

- Founded in Denmark, 1901, Martin Knudsen
- Transferred to Frede Hermann, Denmark, 1947
- Transferred to IOS, Wormley, UK, 1974, Fred Culkin
- Transferred to Ocean Scientific International, 1989, Paul Ridout
Early Batches

- Chlorinity
- Chemical parameter
- Limited accuracy
- Dependent on purity of chemicals
Salinity from Chlorinity

Primary Standard Seawater (stored in glass)

Titration with AgNO3

IAPSO Standard Seawater (transfer standard)
Current Batches

- Conductivity ratio
- Borosilicate bottles
- 3 year shelf life
- Reusable bottles
Salinity from Conductivity

- Defined KCl solution (primary std)
- Conductivity ratio measurement
- IAPSO Standard Seawater (transfer standard)
Why Choose KCl?

- Accepted standard in electrical conductivity
- High Purity (Poisson 1980)
- Consistent Batches (Dauphinee et al 1980)
KCl Purity

• Major impurity claimed to be NaCl (Lewis, 1980)

• Recent batches (Aristar) show N to be major impurity which is decomposed on fusion
Standard Seawater Preparation

- Surface seawater collected from Atlantic Ocean
- Transferred to 5000 litre tank (PVC lined)
- Mixed and re-circulated for several weeks
- Salinity adjusted with deionised water to 34.995
- Filtered to 0.2 um
- UV irradiated
Bottling

Manifold system with ‘point of fill’ filtration
• Bottle one batch of approx. 8000 bottles
• Store bottles for minimum 2 months
• Samples taken throughout the batch for calibration
Calibration

- SSW calibrated on a modified Autosal
- Temperature measured to 1 milli-degree
- Autosal calibrated with defined KCl
- High precision weighing and preparation
- Calibrate 1 bottle in every 130
KCl Calibration Curve

\[ y = 33.588x - 1.1525 \]
Seawater batches

- **P-series**: normal Std. seawater, $S=35$. *This is the main single point calibration standard*

- **38H-series**: high salinity, $S=38$
- **30L-series**: low salinity, $S=30$
- **10L-series**: low salinity, $S=10$

*These standards are used in addition to P-series to make corrections for salinometer offset away from salinity 35*
Distribution

• IAPSO Standard Seawater used in all major oceanographic laboratories worldwide
• Improves the comparability of salinity data
• Only standard recognised by all the international bodies
B. OCEANIC SECTION

IAPSO Standard Seawater: Definition of the Uncertainty in the Calibration Procedure, and Stability of Recent Batches.

Sheldon Bacon, Fred Culkin, Nigel Higgs, and Paul Ridout
pp. 1785–1799

Papers to appear in forthcoming issues can be found online at
http://www.ametsoc.org/journal_abstracts/index.cfm
Reliability of IAPSO SSW

• Expanded uncertainty in conductivity ratio is less than $1 \times 10^{-5}$

  (based on a coverage factor of 2)
Largest Uncertainties

• KCl conductivity solution measurement (salinometer)

• Solvent conductivity in KCl solutions (CO$_2$ saturation)

• New SSW conductivity ratio (salinometer)
Reliability of IAPSO SSW

• Recent batches (P130 –P144) show no ‘offset’, within the same range of uncertainty, over a period of years.
Reliability of IAPSO SSW

• There was no ‘lot dependency’ of uncertainties in the KCl used for SSW calibration

• (we should study further KCl impurities)
Reliability of IAPSO SSW

- There was no ‘within batch’ variability at the time of production
SCOR Working Group 127- suggestions

- Practical Salinity $\times 1.004710 = $ Absolute Salinity

- PSS78 $\rightarrow$ PSS2008

- Adjusted to ITS90

- Calculated for standard Atlantic Seawater
Summary

• Conductivity remains the high precision method for measurement of Practical Salinity

• IAPSO Standard Seawater is the only internationally recognised standard for Practical Salinity

• Density may be calculated from salinity