Chapter 8
The History of Standard Seawater for Salinity Measurements

Alan Jenkins and Richard Williams

Abstract The history of Standard Seawater, from its beginnings in 1899 by Martin Knudsen, through to its current preparation at Ocean Scientific International Ltd (OSIL), is described in this chapter. Having been used for over 120 years as a reference material in the determination of salinity, how the standard was developed and maintained to allow for continuity is discussed.

Keywords Standard Seawater Service · Salinity · Martin Knudsen · Primary standard · Practical salinity scale 1978 · International Association for the Physical Sciences of the Oceans (IAPSO)

8.1 Introduction

Salinity is one of the most measured, and arguably one of the most important, parameters of seawater. Not only does it have considerable influence on marine organisms and fish stock, it is vital for measuring global water mass movements. The study of this parameter provides key information that aids researchers studying climate change, as well as allowing for the accurate mapping of the seabed.

It was recognised by Martin Knudsen at the end of the nineteenth century that there needed to be an accurate way for researchers to be able to reliably study and compare salinity data. To that end, he introduced Standard Seawater, a chlorinity standard for seawater that could be used to calculate salinity, and went on to direct what became known as the Standard Seawater Service for the better part of 40 years. Following his passing in 1949, Helge Thomson took over the administrative responsibilities until 1959, when he was succeeded by Knudsen's former assistant, Frede Hermann. A considerable expansion to the Service was overseen by Hermann, driven by increased

A. Jenkins · R. Williams (✉)
Ocean Scientific International Ltd., Havant, Hampshire, United Kingdom
e-mail: Richard.Williams@osil.com

A. Jenkins
e-mail: osil@osil.com

M. Aoyama et al. (eds.), *Chemical Reference Materials for Oceanography*, Springer Oceanography, https://doi.org/10.1007/978-981-96-2520-8_8

interest in oceanographic research. From 1974, the Service was directed by Fred Culkin, who, with the aid of many international researchers, helped develop the Practical Salinity Scale 1978 (PSS-78), which allowed for Standard Seawater to be calibrated in terms of conductivity ratio, thus breaking the link between salinity and chlorinity.

When Culkin retired as director in 1989, the Service was transferred to Ocean Scientific International Limited (OSIL), a private company established by Culkin's former colleague Paul Ridout. During the Service's tenure at OSIL, three new Standards with salinity 10, 30 and 38 were introduced to aid researchers operating under different conditions, along with new borosilicate glass bottles to improve Standard longevity and ease of handling. Now, under the directorship of Richard Williams (since 2016), the Standard Seawater Service ships to over 108 countries around the world.

The history of Standard Seawater has been documented in detail previously by Culkin and Smed (1979); this chapter serves as a review of their work and to update developments to the Standard Seawater Service.

8.2 Early Determination of Seawater Salinity

In 1674, British natural philosopher Robert Boyle published his scientific work on ocean salts, "Observations and Experiments about the Saltiness of the Sea". In his work, he shows various experiments that determine the saltiness of the seas around Britain, one such method being:

> Take a clean towel, or any other piece of cloth; dry it well before the sun or before the fire, then weigh it accurately, and note down its weight; dip it in the sea water, and, when taken out, wring it a little till it will not drip when hung up to dry; weigh it in this wet state, then dry it in the sun or at the fire, and when it is perfectly dry, weigh it again: the excess of the weight of the wetted cloth above its original weight, is the weight of the sea water imbibed by the cloth; and the excess of the weight of the cloth after being dried, above its original weight, is the specific gravity of the salt retained by the cloth; and by comparing this weight with the weight of the seawater imbibed by the cloth, we obtain the proportion of salt contained in that species of seawater (Boyle, 1674).

Boyle compiled data pertaining to the saltiness of surface seawater, as well as at depths up to 80 m. In 1693, he demonstrated the use of a solution of silver nitrate to distinguish between fresh and brackish water. He was able to do this owing to the fact that when a silver nitrate solution is added to that containing a chloride, such as seawater, a white precipitate of silver chloride is formed.

From the start of the twentieth century, salinity determination was based on two main facts, namely that the constituents of seawater are constant throughout the major oceans and that chloride, as the major constituent, can be determined with the highest level of accuracy (by titration with silver nitrate).

In 1819, Alexander Marcet (1819) determined that five of the then known major constituents of seawater were present in samples taken from different sources. By

also determining the total dissolved salts by evaporation, he concluded that: "All specimens of seawater contain the same ingredients all over the world, these bearing nearly the same proportions to each other so that they differ only as to the total amounts of their saline contents". This was confirmed later by other researchers.

Later in the nineteenth century, ocean studies required the salinity and density to be more accurately determined. At the time, total dissolved salt content was determined through drying samples and weighing the residue, which was both time-consuming and inaccurate. Based on Marcet's statement that seawater has a constant composition, the Danish geologist and mineralogist Johan Georg Forchhammer was able to demonstrate that by measuring a single constituent of seawater, the total dissolved salt content could be calculated (Forchhammer, 1865). Instead of using the evaporation method, he obtained the total dissolved salts by adding together the weights of a number of individual constituents, which he determined separately. By doing this, not only was he able to confirm Marcet's work, but he was able to show that the total dissolved salts could be calculated by multiplying the chloride content by a factor of 1.812. Forchhammer is also credited with introducing the term "salinity", meaning the concentration of total dissolved salts.

In 1884, German-born chemist Wilhelm Dittmar analysed seawater samples collected during the Challenger Expedition (1873–1876) (Dittmar, 1884). He is most commonly credited with establishing the constancy of seawater composition, having shown the constant proportions of seven major components of seawater (other than hydrogen and oxygen), namely, sodium, calcium, magnesium, potassium, chloride, bromide and sulfate. The work performed by Dittmar led to a coefficient of 1.8058 for converting chloride to salinity, a value that was very close to that used in the mid–late 1900s (1.80655).

Towards the end of the nineteenth century, the number of countries interested in salinity data was increasing, and the use of titrating seawater against a solution of silver nitrate and converting the resulting chloride content to salinity using a coefficient was widely accepted. What was lacking was consistency in both the method of analysis and the value of the coefficient used (1.806–1.829), so comparison of data between research groups was poor.

8.3 Chlorinity Determination

For the determination of chlorinity in seawater, only two methods were used to any great extent, namely, the Mohr method (1856) and the Volhard method (1874).

In the Mohr method, the seawater is titrated against a solution of silver nitrate of known concentration with the end point being when all the chloride, and the small amount of bromide, which is also present in seawater, has been precipitated. An indicator is used that changes colour when a slight excess of silver is detected. The Volhard method, developed nearly 20 years later, involves adding an excess of silver nitrate solution to the seawater sample, filtering off the precipitated silver halides, and

determining the excess of silver in the filtrate by titration with thiocyanate solution, using ferric alum as an indicator.

Both of these methods make use of silver nitrate to precipitate the halide species present in the seawater sample, but it is important to note that silver nitrate cannot be dried without some decomposition occurring. This makes it a poor primary standard as it is not possible to prepare a silver nitrate solution at a known concentration by dissolving it in water.

At the time, the usual practice has always been to prepare a solution of approximately the desired concentration and then standardise this against a reliable standard of known composition, such as potassium chloride. Whilst this is not an issue in current times, with accurately calibrated analytical balances, highly purified chemicals and ultrapure water, but in the nineteenth century this was a major hurdle. It is also important to note that both of these methods require the use of atomic weights to calculate the concentration of solutions, something that is periodically updated as measurements become more accurate.

8.4 Salinity Research in the Early Twentieth Century

In the late nineteenth century, there was considerable growth in hydrographic investigations which led many European countries to convene a preparatory conference in Stockholm (1899) to establish the International Council for the Exploration of the Sea (ICES). By this time, Martin Knudsen (Fig. 8.1) had improved the Mohr method of chlorinity determination by developing special burettes and pipettes, giving a salinity conversion factor of "1.805Cl + 0.03" (Forch et al., 1902). He also prepared a number of sealed tubes of seawater, the chlorinity of which was determined accurately by the Volhard method, and these had been used successfully to standardise the silver nitrate solutions used in Danish hydrographic work. This had the effect of referring all chlorinity determinations to one standardisation, thus giving greater internal consistency. He therefore submitted to the Stockholm Conference a "Proposal about an international institution for procuring standard water" (Conférence Internationale, 1899a).

In this proposal, Knudsen stressed the importance of the measurement of the salinity of seawater in physical, climatological, and biological investigations. Knudsen pointed out that titration by weighing was at that time a fairly difficult operation but maintained that, whilst not generally achieved by methods then in use, the measurement could be carried out with an accuracy of 0.04‰. Given that it was almost impossible to carry out often enough to obtain the desired accuracy, he thought that the current errors in salinity determinations were usually as high as 0.10–0.15‰. From his own investigations on the "Ingolf" Expeditions of 1895 and 1896 to the waters around the Faroes, Iceland, and Greenland, Knudsen knew that some Atlantic water types differed by only 0.10–0.25‰ in salinity so there was a need for greater accuracy (Knudsen, 1899).

Fig. 8.1 Martin Knudsen, 1871–1949 (Thomsen, 1950)

The proposal also suggested that an institution should be established that would prepare and standardise (in terms of chlorinity) the Standard Seawater, and provide a statement of its physical and chemical properties to interested laboratories. These laboratories could then determine the chlorinity of their seawater samples by comparison with the Standard Seawater, thus eliminating a number of sources of error.

In order to achieve this, Knudsen suggested the institution (consisting of a manager, a physicist, a chemist and two assistants) would first need to obtain a quantity of open Atlantic seawater and then investigate its physical and chemical properties:

> A detailed determination of the total salinity and the quantity of the single salts. Determination of carbonic acid, sulphuric acid, alkalinity, specific gravity, etc., the coefficient of refraction and absorption for light with different wavelengths. Determination of the specific electric resistance, the surface tension and the viscosity. Determinations of freezing point, boiling point, etc.

This seawater would then be sealed in glass ampoules and examined at intervals to study its stability. Alongside this, artificially produced seawater will also be studied. Based on these investigations, which Knudsen expected to take 2 years, it would be possible to determine what should be the future standard for determining the halogen content of seawater.

Persuasive though his arguments were, Knudsen's proposal was not accepted in its entirety by the Conference. Whilst the establishment of an institution devoted to the preparation and study of standard water was not accepted, it could be surmised that the Conference was reluctant to accept the considerable cost that would be involved, some of his other ideas were, though in modified forms. For example, Knudsen was

charged with the revision of certain hydrographic tables. (Conférence Internationale, 1899d).

These investigations were carried out at the Technical University in Copenhagen under the direction of a committee consisting of John Murray, Martin Knudsen, Otto Pettersson, Fridtjof Nansen, Otto Krümmel, Henry N. Dickson and Stepan O. Makaroff. Samples of seawater from different parts of the world were collected and the "constants" of seawater were precisely determined, i.e. the relation between the amount of chlorine and the salinity, and between the amount of chlorine and the specific gravity at different temperatures (Thomsen, 1950).

This considerable amount of work was completed and presented at the second ICES at Kristiania (Oslo) in May 1901 (Conférence Internationale, 1901a, 1901b). With these revised hydrographic tables it was possible to determine the chlorine content, salinity and specific gravity of a sample of seawater with great accuracy from a Mohr titration against "Standard Water".

Despite Knudsen's doubts, his arguments for standard water evidently found favour with the members of the Conference:

> The chemical analysis shall be controlled by physical methods and physical determinations by chemical analysis in the following manner. From every collection of samples examined at least three shall be selected and sent to the central bureau. Standard samples shall be sent in return. (Conférence Internationale, 1899b).

The hydrographical programme goes on to say that:

> By Standard water shall be understood samples of filtered seawater, the physical and chemical properties of which are known with all possible accuracy by analysis, and statements of which are sent to the different laboratories, together with samples. In respect to halogen, the ordinary water samples have to be compared with the Standard water by analytical methods.

With that, the Conference established the need for standard water for use in all chlorinity titrations.

8.5 The Beginnings of International Standard Seawater

The Stockholm Conference of 1899 recognised the need for standard water for use in all chlorinity titrations, saying that these samples would be sent out by the central bureau. This relates to a preferred proposal made by one of the Norwegian delegates, Fridtjof Nansen, which said that a Central Laboratory should be established in connection with the Central Bureau of the organisation (International Council for the Exploration of the Sea [ICES]). This Central Laboratory would carry out a number of important investigations of general interest to hydrographic and biological research and would also have the responsibility for supplying standard water. This proposal was incorporated in a recommendation from the Conference (Conférence Internationale, 1899c).

In order to avoid any delay that might result from setting up the Central Laboratory, Knudsen quickly started preparing samples of Standard Water. In describing the

standard water used in hydrographical work up to July 1903, Knudsen gave the following reasons for proceeding (Knudsen, 1903):

(1) Though, in my opinion, the members of the Stockholm Conference did not clearly see the advantage of using a standard water for all titrations, I did not hear a single remark against it, and I myself felt convinced that standard water sooner or later would be a great advantage, perhaps a necessity for hydrographical work.
(2) It did not seem probable to me that the whole international cooperation would begin within a short time (it in fact took three years) and in the meantime it would be useful to have at hand reliable standard water.
(3) The researches done for the determination of the constants of different kinds of seawater would offer a convenient occasion for determining the constants of standard water.
(4) In case I should succeed in carrying through the work of the constants-determination and have compiled some Hydrographical Tables that could be generally adopted, I thought it of importance that the standard water used should be investigated with the same means and methods as used in the researches upon which the tables would be found.

Preparation of standard water was nothing new to Knudsen, he had prepared five different batches prior to the Stockholm Conference for use in Danish hydrographical work. His sixth batch, prepared in 1900 in association with the constant determinations, was designated No. VI. The chlorinity of standard water No. VI (19.380‰) was determined by the Danish chemist Soren Sørensen; he prepared a sample of potassium chloride, weighed it, corrected the weight for buoyancy in air, and used this for the titrimetric standardisation of a solution of silver nitrate. This solution was then used for the titration of the chlorinity of the samples of seawater used as Standard Water (Forch et al., 1902; Knudsen, 1903). The chlorinity of Standard Water No. VI, together with all subsequent standards, which are referred to it, are therefore based upon the chlorine content of Sørensen's sample of potassium chloride and consequently depend upon the atomic weights, which he used (Culkin & Smed, 1979).

In 1901, the second preparatory conference was held in Kristiania (now Oslo). The "extreme value" of the Hydrographical Tables that Knudsen compiled was recognised by the Conference along with his provisional report on the determination of the constants of seawater (Conférence Internationale, 1901b). The hydrographic programme went on to say (Conférence Internationale, 1901a):

> "Preliminary determinations of salinity may be made on board ship with appropriate instruments; but the exact determinations of the salinity and density of water samples shall take place in a scientific laboratory on shore. The ratios between salinity, density and chlorine given in Dr Martin Knudsen's Hydrographic Tables are to be adopted; and the salinity is to be calculated by the use of these Tables from the determinations of chlorine or from the specific gravity". And that "The same standard seawater shall be employed in all cases for standardising the solutions used for chlorine determinations".

About 80 ampoules of Standard Water No. VI were prepared in April 1900, which were analysed with regards to chlorinity (Volhard titration and a gravimetric method) and specific gravity. They were also subjected to periodic checks of the specific gravity over the following two years which showed an increase of 0.015 kg m^{-3} in σ_0, most likely due to the dissolution of the glass used at the time, though as the

glass did not contain any chloride ions the chlorinity was not significantly affected. Unfortunately, this meant that the water in the ampoules could not be used as a density standard, however, the Standard Seawater in modern times is stored using a more resistant glass.

Whilst being called No. VI, this was the first Standard Water for international use and was distributed to Germany, Finland, Norway, Russia and Sweden as well as being used for all Danish titrations. Despite the Central Laboratory not yet being opened, by mid-1902 the stock of Standard Water was running low so Knudsen was asked to prepare a new supply. As before, water was collected from the Atlantic Ocean, which was then diluted with distilled water to give a chlorinity similar to that of standard No. VI before being sealed in ampoules (Knudsen, 1903). 201 Ampoules were prepared, designated VI*a* (Fig. 8.2), with 168 being distributed free of charge to member countries of ICES. Of the remaining ampoules, some were used to determine chlorinity (using standard No. VI as a reference) and density, with the remainder being sent to the Central Laboratory in Kristiania which opened in late 1902.

In July 1903, 100 ampoules of Standard Water (VI*b*) were produced and standardised by comparison with Knudsen's standard VI*a*. It was reported that a new Primary Standard would be produced, which would be compared directly with Knudsen's standard water No. VI, with the intention that this primary standard be used to standardise subsequent batches. However, before this could be prepared, further batches of 250 ampoules of standard water (VI*c* and VI*d*) needed to be produced for general

Fig. 8.2 Ampoules of Standard Seawater No. VI*a* (left) and P86 (right)

distribution. In December 1903, 120 ampoules of seawater were reserved as the Primary Standard, though it wasn't until October 1905 that accurate chlorinity analysis could be carried out. By direct comparison with Knudsen's Standard Water No. VI, the chlorinity of the new Primary Standard (designated P) was established as 19.4482‰. Over the following two years, the Central Laboratory produced four batches of Standard Water (P1–P4).

8.6 The Standard Seawater Service

In 1908, the decision was made to close the Central Laboratory, primarily due to Nansen deciding he no longer wanted to continue as director, and assign most of its responsibility's various national laboratories. The preparation of standard water, which was of interest to all hydrographers, would be handed over to Knudsen. The ICES agreed that in the future, in order to cover part of the expenses those who request the standard water would have to financially contribute. The remaining stocks, 83 ampoules of Primary Standard P and 49 ampoules of P4, were transferred to Knudsen at the Danish Hydrographical Laboratory in Copenhagen.

Reports to the ICES over the following years showed that standard water had become widely adopted for measuring salinity. Batches P5–P8 were produced in the years preceding the outbreak of World War I in 1914. To relieve the ICES of the financial responsibility during the war, Knudsen took over the Standard Seawater Service in a personal capacity, an arrangement that continued after the war.

In the years 1920–1937, batches P9–P15 were produced and analysed by Jacob P. Jacobsen, one of Knudsen's collaborators. Each batch was compared against Primary Standard P as well as the previously produced batch using the Volhard method, with agreement being seen between them to show the results were accurate to the third decimal place. Thus, the link with the original Standard Water No. VI was maintained.

With the ever-increasing demand for Standard Water, it became necessary to prepare a new Primary Standard. At the Council meeting in 1936, Knudsen explained that since the Standard Water had become used worldwide, he intended to propose to the International Association for Physical Oceanography (IAPO) that it should direct the preparation of the new Primary Standard as well as cover the associated expenses. Knudsen and Jacobsen had argued that a new definition of salinity was needed that did not depend on ratios of certain atomic weights (of silver nitrate), and that pure silver (Atomgewichtssilber) should be used, which would have the advantage of being independent of atomic weight values (Jacobsen & Knudsen, 1940).

This was accepted by both the ICES and the IAPO, with the new Primary Standard being produced in 1937. The chlorinity of this new standard, called Urnormal or Primary Standard 1937, was found to be 19.3810‰ by direct comparison with Primary Standard P as well as previous standard water samples (Jacobsen & Knudsen, 1940).

Owing to limited demand during World War II, only one batch (P16) of standard seawater was produced in 1943. Hermann (Fig. 8.3), previously an undergraduate

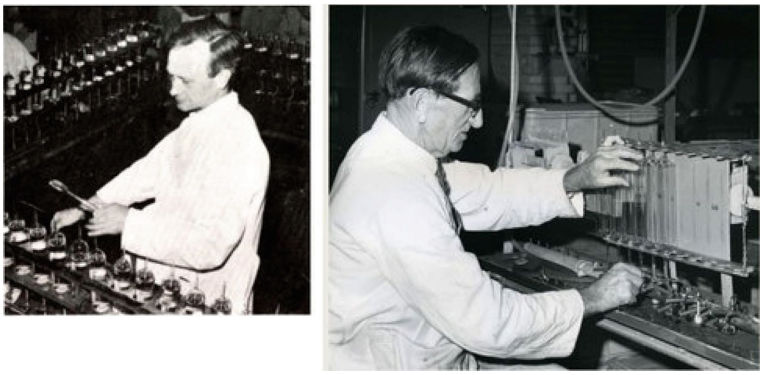

Fig. 8.3 Frede Hermann, 1917–1977 (UK National Oceanography Archives)

who worked on Primary Standard 1937, prepared and analysed P16 with guidance from J.P. Jacobsen.

When Knudsen was approaching his late 70s, he looked to ensure the future continuation of the Standard Seawater Service. Having been responsible for the Service for nearly 40 years, he felt that it should be taken over by a scientific body with interest in the work, so in 1947 he proposed to IAPO that they should undertake future preparations. This was agreed by IAPO at the Oslo meeting in 1948, and under this arrangement batch P17 was produced.

It was the end of an era when, in May 1949, Knudsen passed away. But thanks to his arrangement with IAPO, the Standard Seawater Service was able to continue. At the request of IAPO, Helge Thomsen took over the administrative responsibilities whilst Hermann continued to prepare and analyse the Standard Seawater. Thomsen continued in this role until 1959, overseeing the production of multiple batches (P18–P29), when he made the decision to retire as director of the Service. Given Hermann's long association with the Service, Thomsen proposed that he take over; a decision that was welcomed by IAPO. With Hermann as director from January 1960, the Service saw a large increase in the demand for Standard Seawater, sometimes rising to over 30,000 ampoules per year, in part owing to the considerable expansion in oceanography throughout the world.

For many years, Hermann successfully ran the Seawater Service, producing batches P30–P65, but given his other responsibilities as the head of the Danish Hydrographical Laboratory, he made the decision in 1973 to retire from the Service. He proposed to the International Association for the Physical Sciences of the Oceans (IAPSO, formerly known as IAPO, who updated their name in 1967) that responsibility for running the Service should be passed to Fred Culkin (Fig. 8.4), who had collaborated with him in the chlorinity calibrations for several years. With help from IAPSO, equipment and stock were transferred from Charlottenlund to the Institute of Oceanographic Sciences (IOS) at Wormley (UK) at the end of 1974, with production recommencing in 1975.

Fig. 8.4 Fred Culkin, 1929–2011

Salinometers, instruments that can determine the salinity of seawater using an electrical conductivity method, first began to appear in the 1930s. They worked by measuring the ratio of conductivity between Standard Seawater and a seawater sample, with the ratio being used to calculate the salinity. Over the following decades, salinometers became more readily available and increasingly accurate; In 1961, Bruce Hamon and Neil Brown designed a portable salinometer with a precision of ±0.003‰. Later, in 1975, Tim Dauphinee designed a laboratory salinometer, the Guildline Autosal, which has become synonymous with salinity measurement and is still widely used by oceanographers, reaching accuracies of ±0.002‰.

With the introduction of using conductivity to measure salinity in situ, International Oceanography Tables began to be published that linked conductivity and salinity based on precise determinations of chlorinity (UNESCO, 1965, 1966; Wooster et al., 1969). These tables, and resulting equations, were valid for salinities ranging from 29 to 42‰ at 15 °C, with a correction table for measurements at temperatures from 10 to 31 °C (Brown & Allentoft, 1966; Cox et al., 1967). The equations relied on a conductivity ratio between that of the sample and that of Standard Seawater P31 at 15 °C (chlorinity, 19.374‰).

In 1978, after much research and discussion, the Joint Panel on Oceanographic Tables and Standards (JPOTS) determined that Standard Seawater would be calibrated in terms of its conductivity relative to that of a potassium chloride solution, and that a Practical Salinity Scale would be established (UNESCO, 1978). Intense research from multiple laboratories was used to create the Practical Salinity Scale 1978 (PSS-78) as well as the recommended equation for calculating Practical Salinity

from conductivity ratio which is valid at all temperatures and pressures that were of oceanographic interest (UNESCO, 1979).

With the acceptance of the PSS-78, which was valid from salinity 2 to 42 and temperatures from −2 to 35 °C, the link between salinity and chlorinity was broken.

All the batches up to P90 had been calibrated solely in terms of its chlorinity, but following the official adoption of the Practical Salinity Scale by JPOTS in 1980 (UNESCO, 1981a, 1981b, 1981c), batch P91 and all following batches of Standard Seawater were calibrated in conductivity relative to the defined potassium chloride (KCl) standard and labelled with the appropriate K_{15} value (see Sect. 8.8 for definition) (Culkin & Ridout, 1998). For the following 10 years (to 1990, P113), batches were calibrated to both chlorinity and conductivity ratio.

When Culkin retired as director in 1989, the Service was transferred with IAPSO's agreement to Ocean Scientific International Limited (OSIL), a private company established by former colleague Paul Ridout to produce and distribute Standard Seawater. Culkin joined OSIL as a consultant where he remained actively involved. Alongside the Standard Seawater, having a Practical Salinity of approximately 35, three further standards were introduced around 1990. These had practical salinities of 10, 30 and 38 (batch 10L1, 30L2 and 38H1, respectively), and were intended to aid researchers operating under different conditions (Fig. 8.5).

Batches P112–P137 were produced at OSIL in normal glass ampoules then, in 2000, after 8 years of research and development, Standard Seawater began to be stored in borosilicate bottles. This pharmaceutical-grade glass had several benefits, including improved ease of handling and storage, as well as being much easier to fill. Following a move of OSIL from Wormley to Petersfield, it relocated to Havant at the end of 2006 and under the directorship of Richard Williams now ships Standard Seawater to over 108 countries around the world.

It is a remarkable feature of the Standard Seawater Service that the continuity has been maintained from its inception all the way through to the most recent batch, P169

Fig. 8.5 Current range of IAPSO Standard Seawater (left to right: 10L, 30L, P, 38H)

(2024). IAPSO Standard Seawater remains the only standard for Practical Salinity, which is recognised by all major oceanographic bodies around the world.

8.7 Preparation of Standard Seawater

The general preparation method of Standard Seawater and its transfer into ampoules/bottles has remained largely unchanged since it began, though as demand increased over the years the scale of the production similarly increased.

When Knudsen first began producing Standard Water, he found that a stock of around 50 L was enough to produce enough ampoules for distribution (Fig. 8.6). From 1960, when Hermann oversaw a considerable increase in demand, a stock of 4,000 L was required. With such a large storage tank, and improvements to filtration and circulation, he was able to produce batches of 9,000 ampoules, a far cry from the 80 ampoules of Standard Water No. VI that Knudsen first produced.

Given the large volumes required, surface seawater was collected from a known area in the North Atlantic Ocean well in advance of a new batch being prepared, for which Hermann had an amicable arrangement with a Danish shipping line. The ampoules to be used were washed and dried, and once filled would be labelled, packed and distributed by a part-time helper. The seawater was pumped through filters and stored in a large tank where it was mixed and further filtered. Whilst in the tank, the seawater was slowly diluted with ultra-pure water to the desired salinity, usually just below 35‰, a process that took several weeks. Its temperature was raised to around

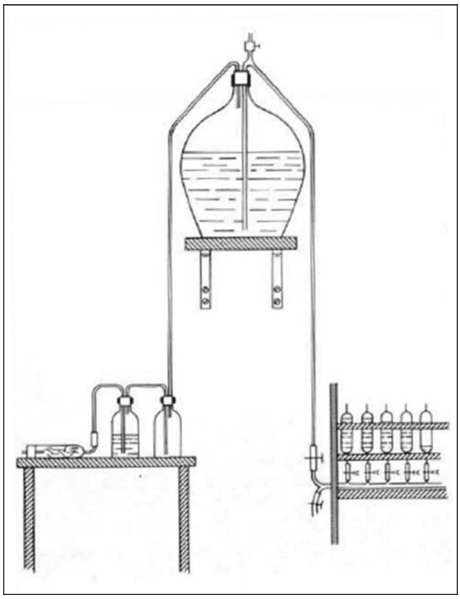

Fig. 8.6 Early equipment for preparing Standard Seawater (Jacobsen & Knudsen, 1940)

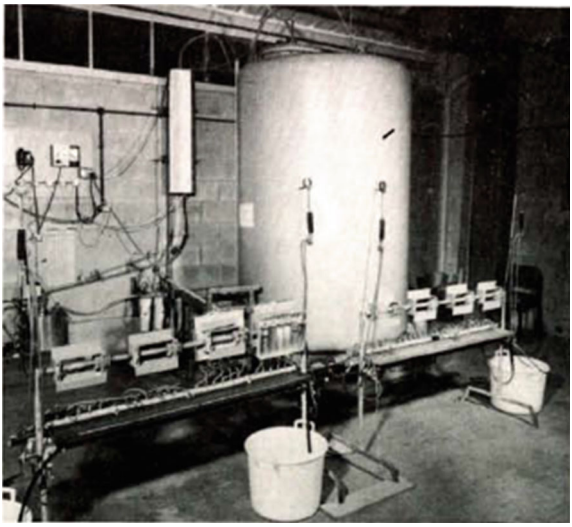

Fig. 8.7 Ampoule filling benches (Culkin & Smed, 1979)

26 °C so that when it was transferred to the glass ampoules (20–24 °C) the seawater was slightly undersaturated with dissolved air.

The seawater was pumped from the storage tank to a horizontal glass tube on the filling table using a powerful pump (whereas Knudsen fed the seawater by gravity). This tube had several outlets to which fitted a clean and unsealed soda-glass ampoule via a rubber tube (Fig. 8.7). The seawater was allowed to fill the ampoule to within 2–3 cm of the top (~275 mL) and then the rubber tubing was closed with a clip and the upper tip of the ampoule was sealed using an acetylene/air flame. After cooling, the ampoule was inverted and similarly sealed, and the seawater in the other tip allowed to drain beforehand. Using this method, and multiple filling benches, it was possible to produce up to 7,000 ampoules in a day.

Over time as technology improved, ultraviolet sterilisation modules were added and filters with smaller pore sizes were introduced, going from the filter papers Knudsen used that remove particulates, to 0.2 μm filters currently used to remove bacteria. By the time the Service moved to the UK at IOS, and later to OSIL, the stock volume had increased to 5,000 L which was stored in a polymer-linked tank (Fig. 8.8).

With the exception of how salinity was measured (chlorinity vs conductivity ratio), this filling process into glass ampoules largely remained the same since Knudsen's first preparations. From the year 2000, having undergone 8 years of research and development, OSIL started producing Standard Seawater batches in pharmaceutical grade Type 1 borosilicate glass bottles as opposed to soda-glass ampoules. Not only did this make the filling process much simpler, but the design made it easier to handle, pack and ship whilst providing a longer shelf-life (3 years) for the Standard. In this case, water is pumped from the storage tank, through a 0.2 μm filter and ultraviolet sterilisation module, to a tube fitted with a number of taps. Bottles are placed on the

Fig. 8.8 5000 L Standard Seawater tank at OSIL

taps and filled to the desired volume (~210 mL) before being sealed with a secure crimp cap over a halo-butyl bung coated with PTFE to provide a totally impervious barrier to evaporation. Over 8,000 bottles are produced in a filling session; after being stored for a minimum of 2 months, samples are taken throughout the batch to be used for calibration.

8.8 Certification of Standard Seawater—The Primary Standard

At the beginning of the twentieth century, it was understood from the work of Marcet (1819), Forchhammer (1865) and Dittmar (1884) that salinity (i.e. total dissolved salts) could be calculated from chlorinity using a conversion coefficient. When Knudsen first prepared his Standard Water, the accepted definition of chlorinity was:

> By chlorinity is understood the mass of chlorine equivalent to the total mass of halogen contained in the mass of 1 kg of seawater.

In determining the chlorinity of Standard Water No. VI in 1900, Sørensen used both gravimetric and titration techniques. The silver nitrate solution that was used

in the titration was standardised against pure potassium chloride using the atomic weights adopted in 1900. The chlorinity of Standard Water No. VI was found to be 19.380‰, with all subsequent Normal or Standard Seawaters up to 1937 being determined either directly or indirectly by comparison to it.

When stocks of the Primary Standard were running low in 1937, a new batch, Primary Standard 1937 (also known as Urnormal), was produced. The chlorinity was determined by Inger Bondorff (formerly Knudsen), Martin Knudsen's daughter, by direct comparison with the previous Primary Standard as well as other standard seawaters. Jacobsen and Knudsen (Jacobsen & Knudsen, 1940) argued that it was unsatisfactory that the definition of chlorinity made it dependent on the ratios of certain atomic weights. This would mean that, if the definition was strictly followed, there would be breaks in the chlorinity determination every time the accepted values of atomic weights changed.

Jacobsen and Knudsen proposed that using a new standard, pure silver (Atomgewichtssilber), would be much better and that a new definition of chlorinity be established based on the following reasoning (Culkin & Smed, 1979):

(1) Let Ag denote the number giving the mass (in grams) of Atomgewichtssilber just necessary to precipitate the halogens of 1 kg of seawater sample of which the chlorinity expressed in ‰ is Cl. It is then natural, by definition, to put Cl proportional to Ag, because Ag is the quantity which can be determined with greater relative accuracy than any other chemical quantity which could be considered in this connection.

$$\text{Thus Cl} = k \times \text{Ag grams Atomgewichtssilber} \tag{8.1}$$

Where k has the same value for all seawater samples and consequently the same as it has for Urnormal 1937.

(2) A chlorinity of 19.3810‰, as determined by Inger Knudsen by comparison with previous standards, was adopted for Urnormal 1937, thus ensuring continuity between past (as far back as 1902) and future chlorinity determinations.

(3) Investigations carried out by Prof. Otto Hönigschmid in Munchen established that 58.99428 g Atomgewichtssilber were necessary and sufficient to precipitate the halogens in 1 kg of Urnormal 1937.

(4) Substituting these values Eq. (8.1):
19.3810‰ = k × 58.99428 g Atomgewichtssilber
Or Cl = 0.3285234 Ag‰".

Thus the new definition of chlorinity became:

> The number giving the chlorinity in per mille of a seawater sample is by definition identical with the number giving the mass with unit gram of Atomgewichtssilber just necessary to precipitate the halogens in 0.3285234 kg of the seawater sample (Jacobsen & Knudsen, 1940).

Whilst this had the advantage of being independent of atomic weight values and providing a continuous link between all chlorinity measurements, the use of pure silver was not feasible for calibrating every batch of standard seawater. Instead, it was more practical to determine the chlorinity of a small number of seawater ampoules against pure silver every few years and then use these ampoules as the practical Primary Standard against which the chlorinity of ordinary standard seawater is determined.

In the early 1970s, the use of in situ electrical conductivity measurements to estimate salinity was increasing. International Oceanographic Tables at the time were based on a relationship between conductivity, chlorinity and salinity, but did not go below temperatures of 10 °C, making them unsuited for in situ measurements (UNESCO, 1966). In 1978–1979, new tables were produced out of intense research from laboratories in Canada, France and the United Kingdom, and were based on the conductivity of a seawater sample relative to that of a potassium chloride solution (UNESCO, 1981a, 1981b, 1981c). From this work, the Joint Panel on Oceanographic Tables and Standards (JPOTS) (appointed by the United Nations Educational, Scientific and Cultural Organization [UNESCO], ICES, Scientific Committee on Oceanic Research [SCOR] and IAPSO) formed the Practical Salinity Scale 1978, which adopted a KCl solution containing 32.4356 g kg^{-1} as the reference standard for salinity determination (UNESCO, 1981a, 1981b, 1981c; Culkin, 1986).

The new definition, as published by UNESCO in 1981, for Practical Salinity became:

> The practical salinity, symbol S, of a sample of seawater, is defined in terms of the ratio K_{15} of the electrical conductivity of the seawater sample at the temperature of 15 °C and the pressure of one standard atmosphere, to that of a potassium chloride (KCl) solution, in which the mass fraction of KCl is 32.4356×10^{-3}, at the same temperature and pressure. The K_{15} value exactly equal to 1 corresponds, by definition, to a practical salinity exactly equal to 35.

So essentially: A seawater sample of Practical Salinity 35 has a conductivity ratio of unity at 15 °C and 1 atmosphere with a KCl solution containing a mass of 32.4356 g KCl in a mass of 1 kg of solution.

The Practical Salinity Scale 1978 was accepted by ICES and IAPSO in 1979, SCOR and JPOTS in 1980, and by the Intergovernmental Oceanographic Commission (IOC) of UNESCO in 1981.

To ensure continuity with the previous scale, the value of Practical Salinity 35 at unity corresponds to a Standard Seawater whose certified chlorinity was 19.3740‰, i.e. its salinity was exactly 35‰ on the previous scale.

Potassium chloride was chosen as the reference standard for a number of reasons. Not only was it the accepted standard used in electrical conductivity measurements, but Merck "Suprapur" KCl had excellent purity and well-documented chemical analysis. It also had good consistency between batches (Dauphinee et al., 1980). The major impurity of this material was found to be sodium chloride, but at the level of interest the molar conductivities of the two salts were sufficiently similar to minimise the effect of the impurity (Lewis, 1980).

Practical Salinity, S_P, is a dimensionless value, i.e. the algorithms of the Practical Salinity Scale 1978 were adjusted to eliminate any units. So whilst research papers may state ppt, ‰ or psu (practical salinity unit), these should not be used. It is sufficient to state, for example, a "Practical Salinity of 34.995".

The Practical Salinity is defined in terms of the ratio R_t (at temperature, t) by the following equation:

$$S_p = a_0 + a_1 R_t^{1/2} + a_2 R_t + a_3 R_t^{3/2} + a_4 R_t^2 + a_5 R_t^{5/2}$$

$$+\frac{(t-15)}{1+k(t-15)}\left\{b_0+b_1R_t^{1/2}+b_2R_t+b_3R_t^{3/2}+b_4R_t^2+b_5R_t^{5/2}\right\}$$

where:

$a_0 = 0.0080$	$b_0 = 0.0005$
$a_1 = -0.1692$	$b_1 = -0.0056$
$a_2 = 25.3851$	$b_2 = -0.0066$
$a_3 = 14.0941$	$b_3 = -0.0375$
$a_4 = -7.0261$	$b_4 = 0.0636$
$a_5 = 2.7081$	$b_5 = -0.0144$
	$k = 0.0162$

This equation, being based on the new International Oceanographic Tables and utilising electrical conductivity measurements, is valid for salinities ranging from 2 to 42 at temperatures of −2 to 35 °C (UNESCO, 1981a, 1981b, 1981c). As it no longer uses chlorinity, its link with salinity is broken and should now be used as an independent chemical parameter.

It should be noted that the salinities calculated at the time were measured on temperatures according to the International Practical Temperature Scale 1968 (IPTS-68). Temperatures based on the more recent International Temperature Scale 1990 (ITS-90) can be converted to IPTS-68 using the below formula (Saunders, 1990):

$$t_{IPTS68} = 1.00024 \times t_{ITS-90}$$

8.9 Standard Seawater Batch Stability

Standard Seawater was originally intended as a chlorinity standard and was calibrated mainly using the Volhard method which was found to be more accurate than other methods in routine use. From 1969, a combined gravimetric/potentiometric titration method (Hermann & Culkin, 1978) was used, which whilst being operationally simpler, was still time-consuming. When the Seawater Service was due to transfer from Copenhagen to the Institute of Oceanographic Sciences, Wormley, UK, independent checks were made by both sites on batches prepared between 1969 and 1974 (Hermann & Culkin, 1972). The agreement between the two laboratories was better than 1×10^{-4}‰ in chlorinity (std dev 2–3 $\times 10^{-4}$) which confirmed the reliability of the calibrations but unfortunately revealed little about its stability (Culkin & Ridout, 1998; Culkin & Smed, 1979). The use of glass ampoules for storing the standard has a negligible effect on its stability; given that the glass contains no halogens, the small amount of silica that might dissolve over time will not alter the chlorinity.

Although the standard was only calibrated in terms of chlorinity, from the late 1950s, chlorinity titration was gradually replaced by electrical conductivity measurements. Batch comparisons of Standard Seawaters prepared from 1937 to 1978 were investigated by six laboratories (Mantyla, 1980; Millero et al., 1977; Park, 1964; Poisson et al., 1978) which showed that the conductivity/chlorinity relationship was largely the same but that some variations did occur. Notably, batches P49–P51 were found to have anomalously high conductivities (equivalent to 0.004–0.007‰ in salinity), which were attributed to bacterial contamination, possibly combined with oil pollution (Culkin & Ridout, 1998). Following the adoption of the Practical Salinity Scale in 1978 and better filtration technologies, agreement between batches reportedly improved (Mantyla, 1987; Takatsuki et al., 1991).

In recent years, there have been numerous studies into the stability of Standard Seawater (Aoyama et al., 2002; Bacon et al., 2000, 2007; Culkin & Ridout, 1998; Kawano et al., 2006, 2012; Mantyla, 1980, 1987, 1994; Takatsuki et al., 1991; Uchida et al., 2020), perhaps most notable are those carried out in conjunction with Ocean Scientific International Ltd (OSIL) who currently operate and maintain the Standard Seawater Service. Culkin and Ridout (1998) demonstrated that conductivity changes over time of various batches of standards stored in ampoules could amount to less than 0.001 in salinity (studied over 96 weeks). When this is compared to the accuracy/precision of 0.002 quoted by Guildline Instruments for their widely used Autosal Salinometers, it would suggest that the stability of the standard is not usually the limiting factor. They also showed that there was a variability of less than 0.00001 in K_{15} of a standard (P123) stored in borosilicate bottles over a period of 158 weeks.

An in-depth study by Bacon et al. (2007) examined batch stability and the uncertainty associated with the Standard Seawater manufacturing process, and determined that the expanded uncertainty of the conductivity ratio to be 1×10^{-5}, based on a coverage factor of 2, at the time of manufacture. It found that there was no discernible "within batch" variability. The study also reported on the Standard Seawater "offsets" from the label conductivity ratio of batches P130–P144 over a period of 5 years after manufacture, and showed that no significant change in label conductivity outside the expanded uncertainty was found. This is in contrast to some other studies, and suggestions were made by Bacon as to why this may be the case, but the use of any "correction tables" intended to allow for offsets in modern Standard Seawater should be treated with great caution.

8.10 Final Thoughts

It has never been more important for the health of the oceans, and of the planet, that researchers are able to reliably compare data. Since its inception at the start of the twentieth century, the Standard Seawater Service has provided the means for oceanographic researchers to collect meaningful salinity data that has been used to monitor the oceans. With a well-documented history, and IAPSO's unswerving support, Standard Seawater remains the only Practical Salinity standard recognised

by all international oceanographic bodies and will continue to provide researchers with a traceable standard.

Acknowledgements This work was greatly improved by comments from staff at Ocean Scientific International Ltd.

Competing Interests The authors have no conflicts of interest to declare that are relevant to the content of this chapter.

References

Aoyama, M., Joyce, T. M., Kawano, T., & Takatsuki, Y. (2002). Standard seawater comparison up to P129. *Deep-Sea Research, 49*, 1103–1114.

Bacon, S., Snaith, H. M., & Yelland, M. J. (2000). An evaluation of some recent batches of IAPSO standard seawater. *Journal of Atmospheric and Oceanic Technology, 17*, 854–861.

Bacon, S., Culkin, F., Higgs, N., & Ridout, P. (2007). IAPSO standard seawater: Definition of the uncertainty in the calibration procedure and stability of recent batches. *Journal of Atmospheric and Oceanic Technology, 24*(10), 1785–1799.

Boyle, R. (1674). *The saltiness of the sea.* London, Printed by E. Fletcher for R. Davis.

Brown, N., & Allentoft, B. (1966). *Salinity, conductivity, and temperature relationships of seawater over the range of 0 to 50 ppt*. Bissett-Berman Corp San Diego CA.

Conférence Internationale. (1899a). *Conférence Internationale pour l'Exploration de la mer*, réunie à Stockholm 1899, XLII–XLVI.

Conférence Internationale (1899b). *Conférence Internationale pour l'Exploration de la mer*, réunie à Stockholm 1899, 6–7.

Conférence Internationale (1899c). *Conférence Internationale pour l'Exploration de la mer*, réunie à Stockholm 1899, 12–13.

Conférence Internationale. (1899d). *Conférence Internationale pour l'Exploration de la mer*, réunie à Stockholm 1899, 16.

Conférence Internationale. (1901a). *Conférence Internationale pour l'Exploration de la mer*, réunie à Kristiania 1901, 4–5.

Conférence Internationale. (1901b). *Conférence Internationale pour l'Exploration de la mer*, réunie à Kristiania 1901, 26.

Cox, R. A., Culkin, F., & Riley, J. P. (1967). The electrical conductivity/chlorinity relationship in natural seawater. *Deep-Sea Research, 14*(2), 203–220.

Culkin, F. (1986). Calibration of standard seawater in electrical conductivity. *Science of the Total Environment, 49*, 1–7.

Culkin, F., & Ridout, P. S. (1998). Stability of IAPSO standard seawater. *Journal of Atmospheric and Oceanic Technology, 15*, 1072–1075.

Culkin, F., & Smed, J. (1979). The history of standard seawater. *Oceanologica Acta, 2*(3), 355–364.

Dittmar, W. (1884). Report on the scientific results of the exploring voyage of H.M.S. Challenger. *Physics and Chemistry*, *1*, HMSO, London.

Dauphinee, T. M., Ancsin J., Klein, H. P., & Phillips, M. J. (1980). The effect of concentration and temperature on the conductivity ratio of potassium chloride solutions to Standard Seawater of salinity 35‰ (Cl 19.3740‰). *IEEE Journal of Oceanic Engineering, OE-5* (1), 17–21.

Forch, C., Knudsen, M., & Sørensen, S. P. L. (1902). Berichte über die Konstantenbestimmungen zur Aufstellungen der hydrografischen Taabellen, K. danske Vidensk. Selsk. Skr., 6, *Raekke, naturvidensk og mathem Afd*., XII, 1 (p. 22).

Forchhammer, G. (1865). On the composition of seawater, at different depths, and in different latitudes. *Philosophical Transactions of the Royal Society of London, 155*, 203–262.

Hermann, F., & Culkin, F. (1972). A check of the analysis of standard seawater. In *International Council for the Exploration of the sea, Hydrography committee Communication CM 1972/C:33* (5 pp.)

Hermann, F., & Culkin, F. (1978). Preparation and chlorinity calibration of standard seawater. *Deep-Sea Research, 25*(12), 1265–1270.

Jacobsen, J. P., & Knudsen, M. (1940). Urnormal 1937 or primary standard sea-water 1937. *Association D'océanographie Physique, Publication Scientifique, 7*, 1–38.

Kawano, T., Aoyama, M., Joyce, T., Uchida, H., Takatsuki, Y., & Fukasawa, M. (2006). The latest batch-to-batch difference table of standard seawater and its application to the WOCE onetime sections. *Journal of Oceanography, 62*, 777–792.

Kawano, T., Takatsuki, Y., & Aoyama, M. (2012). Comparison of some recent batches of IAPSO standard seawater. *Journal of the Japan Society for Marine Surveys and Technology, 12*(2), 49–55.

Knudsen, M. (1899). The Danish "Ingolf" Expedition. *Hydrography, 1*(2), 37–39.

Knudsen, M. (1903). On the standard-water used in the hydrographical work until July 1903. *Cons. Internat. Pour l'Explor. De la Mer*, Pub. De Circ. No. 2 (9 p.).

Lewis, E. L. (1980). The practical salinity scale 1978 and its antecedents. *IEEE Journal of Oceanic Engineering*, *OE-5*(1), 3–8.

Mantyla, A. W. (1980). Electrical conductivity comparisons of standard seawater batches P29 to P84. *Deep-Sea Research, 27A*, 837–846.

Mantyla, A. W. (1987). Standard seawater comparisons updated. *Journal of Physical Oceanography, 17*, 543–548.

Mantyla, A. W. (1994). The treatment if inconsistencies in Atlantic deep water salinity data. *Deep-Sea Research, 41*, 1387–1405.

Marcet, A. (1819). On the specific gravity and temperature in different parts of the ocean and in particular seas, with some account of their saline contents. *Philosophical Transactions of the Royal Society of London, 109*, 161–208.

Millero, F. J., Chetirkin, P., & Culkin, F. (1977). The relative conductivity and density of standard seawaters. *Deep-Sea Research, 24*, 315–321.

Mohr, C. F. (1856). Neue massanalytische Bestimmung des Chlors in Verbindungen. *Annalen der Chemie und Pharmacie, 97*, 335–338.

Park, K. (1964). Reliability of standard seawater as a conductivity standard. *Deep-Sea Research, 11*, 85–87.

Poisson, A., Dauphinee, T., Ross, C. K., & Culkin, F. (1978). The reliability of standard seawater as an electrical conductivity standard. *Oceanologica Acta, 1*, 425–433.

Saunders, P. M. (1990). The international temperature scale of 1990, ITS-90. *WOCE Newsletter, 10*, 10.

Takatsuki, Y., Ayoama, M., Nakano, T., Miyagi, H., Ishihara, T., & Tsutsumida, T. (1991). Standard seawater comparisons of some recent batches. *Journal of Atmospheric and Oceanic Technology, 8*, 895–897.

Thomsen, H. (1950). Martin Knudsen 1871–1949. *ICES Journal of Marine Science, 16*(2), 155–159.

Uchida, H., Kawano, T., Nakano, T., Wakita, M., Tanaka, T., & Tanihara, S. (2020). An expanded batch-to-batch correction for IAPSO standard seawater. *Journal of Atmospheric and Oceanic Technology, 37*(8), 1507–1520.

UNESCO. (1965). *First report of the joint panel on oceanographic tables and standards, Copenhagen, October 1964* (UNESCO Technical Paper in Marine Science, No. 1, 1–9).

UNESCO. (1966). *First report of the joint panel on oceanographic tables and standards, Rome, October 1965* (UNESCO Technical Paper in Marine Science, No. 4, 1–9).

UNESCO. (1978). *Eighth report of the joint panel on oceanographic tables and standards, Woods Hole March 1977* (UNESCO Technical Paper in Marine Science, No. 28, 1–35).

UNESCO. (1979). Ninth report of the joint panel on oceanographic tables and standards, Paris, September 1978 (UNESCO Technical Paper in Marine Science, No. 30, 1–32)

UNESCO. (1981a).*Tenth report of the joint panel on oceanographic tables and standards, Sidney, September 1980* (UNESCO Technical Paper in Marine Science, No. 36, 1–25).
UNESCO. (1981b). *Background papers and supporting data on the Practical Salinity Scale 1978* (Sidney UNESCO Technical Paper in Marine Science, No. 37, 1–144).
UNESCO. (1981c). *International oceanography tables* (UNESCO Technical Paper in Marine Science, No. 39, 1–111).
Wooster, W. S., Arthur, A. J., & Dietrich, G. (1969). Redefinition of salinity. *Limnology and Oceanography, 14*(3):437–438.
Volhard, J. (1874). Über eine neue Methode der massanalytischen Bestimmung des Silbers. *Journal Für Praktische Chemie, 117*, 217–224.