OCEANOLOGICA ACTA 1979 - VOL. 2 - N° 3

The history of standard seawater

Standard Seawater
Primary Standard Seawater
Standard Seawater Service
Chlorinity
Salinity
Eau Normale
Eau Normale Primaire
Service de l'Eau Normale
Chlorinité
Salinité

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Received 17/11/1978, in revised form 18/12/1978, accepted 2/1/1979.

ABSTRACT

A standard seawater, to be used in all salinity determinations, was first recommended to oceanographers by Martin Knudsen in 1899. The history of how the standard was developed over the past 70 years or so, in such a way that continuity was maintained in all chlorinity and salinity determinations, is described in this paper. Discussion of the Primary Standard and of the history of the Standard Seawater Service are also included.

Oceanol. Acta, 1979, **2**, 3, 355-364.

RÉSUMÉ

L'histoire de l'eau normale.

L'utilisation d'une eau normale pour toutes les mesures de salinité fut recommandée aux océanographes pour la première fois par Martin Knudsen en 1899. Le présent article décrit la façon dont cette eau normale fut mise au point, au cours de ces 70 dernières années, de façon à ce que soit maintenue une continuité dans toutes les mesures de chlorinité et de salinité. L'Eau Normale Primaire ainsi que l'histoire du Service de l'Eau Normale sont également évoquées.

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INTRODUCTION

Unquestionably one of the most important and, indeed, one of the most frequently studied parameters of seawater is the salinity or salt content. Data centres today contain the results of millions of salinity determinations. The fact that most of these data, obtained by different workers over a long period of time, can be compared with a fair degree of confidence is due largely to the dedication and efforts of two Danish hydrographers, Martin Knudsen and Frede Hermann, who between them supplied the oceanographic community with a salinity standard for more than seventy years. The idea of a standard seawater, to be used in all salinity determinations, was conceived at the end of the 19th century by Knudsen who organized and directed what later became known as the Standard Seawater Service.

Following Knudsen's death in 1940 Helge Thomsen took over the administrative responsibilities of the Service until 1959 when he was succeeded as Director of the Service by Knudsen's former assistant, Hermann. The scientific responsibility for the preparation of the standard water, however, rested with Hermann from 1947 until 1974, a period in which heavy demands were made on him because of the considerable expansion which took place in oceanography during this period. Hermann met all these demands and maintained supplies of a very high quality standard, with the minimum of help, and his untimely death in 1977 came as a severe shock to his many friends.

Over the years standard seawater has been used by physicists, chemists, biologists and engineers, all of whom came to expect that their demands would be met. Perhaps few of them realized that they were being served, not by a commercial organization, but in the main by one man who also had research interests. It is for their enlightenment and to pay tribute to the work of Knudsen and Hermann that this historical account has been written.

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THE BASIS OF THE SALINITY DETERMINATION

The determination of salinity as carried out for the past eighty years or so is based on two facts. Firstly, the proportions of the major constituents of seawater are almost constant throughout the major oceans, and secondly, the major constituent, chloride, is the one which can be determined most accurately and precisely (by titration or precipitation with silver nitrate). The methods which are used for the determination of chloride do not differentiate between chloride and the small amount of bromide which is also present in seawater, so in practice the two halides are determined together and calculated as chloride to give what is called chlorinity.

Perhaps the first relevant discovery in the story was the fact that when silver nitrate solution is added to a solution of a chloride, such as seawater, a white precipitate of silver chloride is formed. This reaction was used by Robert Boyle in the 17th century to distinguish between fresh or brackish waters, which contain little or no chloride, and seawater. By the beginning of the 19th century several other major constituents of seawater had been discovered. Five of these elements were determined in seawater samples from various sources by Marcet (1819) who also determined total dissolved salts by evaporating a sample to dryness and weighing the residue. As a result of this work, Marcet 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 the first statement that the composition of seawater is constant, or nearly so, and it was confirmed by a number of other workers between 1820 and 1865.

Studies of ocean circulation which were carried out later in the 19th century involved investigating the distribution of salinity and density. Consequently there was a need for a better method of determining total dissolved salts than the tedious and unreliable one of evaporating a sample to dryness and weighing the residue. This is where the concept of constant composition of seawater became useful because it meant that the total dissolved salts could be estimated from the concentration of any one constituent once the relationship between the two had been established. The constituent chosen to estimate total dissolved salts by this means was chloride (plus bromide), simply because it was the easiest to determine accurately, and it was first used in hydrographic work by the Danish chemist 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. Forchhammer's work confirmed Marcet's findings and he established that the total dissolved salts could be obtained by multiplying the chloride content by the factor 1.812, a relationship which he used in tracing water masses, particularly the Gulf Stream. Incidentally, Forchhammer also introduced the term "salinity" for total dissolved salts.

Mention should also be made here of another major classical study carried out in the 19th century, viz. that by Dittmar (1884) who analysed seawater samples collected during the Challenger Expedition (1873-1876). Dittmar is the one who is usually credited with firmly establishing the constancy of composition of seawater, although it should be pointed out that he also established that there were some small deviations from constancy, particularly in the proportions of calcium. It is also interesting to note that Dittmar's coefficient of 1.805 8 for converting chloride to salinity is remarkably close to the value of 1.806 55 which is used today.

By the end of the 19th century a number of countries, mainly European, were collecting salinity data and carrying out studies in physical oceanography. The use of the chloride titration and a coefficient for converting chloride content into salinity were widely accepted and hydrographic tables were available. However, there was some lack of uniformity, both in the method of analysis and in the value of the coefficient (1.806-1.829) used. Consequently, results obtained by different workers were not always comparable.

THE CHLORINITY DETERMINATION

Basically, only two methods have been used to any great extent for the routine determination of chlorinity of seawater. In the Mohr method (Mohr, 1856) the seawater is titrated with a silver nitrate solution of known strength to the point where all the chloride and bromide have been precipitated, as detected by indicators which change colour when a slight excess of silver has been added. The Volhard method, which was introduced later (Volhard, 1874), 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 indicator.

An important point concerning the standardization of the silver nitrate solution, which is necessary in both methods, should be emphasized here. Silver nitrate is not a good primary standard, because it cannot be dried without decomposition, which means that it is not possible to prepare a silver nitrate solution of known strength simply by dissolving a weighed quantity of crystals in a given volume of water. The usual practice has always been to prepare a solution of approximately the desired concentration and then standardize this against a reliable standard of known composition, such as potassium chloride. In these days of accurately calibrated analytical balances, highly purified chemicals and readily available chloride-free water for preparing solutions this is probably not too difficult, but it should be borne in mind when considering the problems involved in the determination of chlorinity in the 19th century. Another important point about this procedure, which will be mentioned again later, is that it involves the use of atomic weights (relative atomic masses), the accepted values of which are subject to revision periodically.

THE NEED FOR A STANDARD WATER

Towards the end of the 19th century there was a

Martin Knudsen, 1891-1949.

considerable growth in hydrographic investigations and this led the participating European countries to convene a preparatory conference in Stockholm in 1899 to establish the International Council for the Exploration of the Sea (ICES). By this time Knudsen had improved the Mohr method of chlorinity determination by developing special burettes and pipettes. He had 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 standardize the silver nitrate solutions used in Danish hydrographic work. In effect, this was referring all chlorinity determinations to one standardization, thus giving greater internal consistency. He therefore submitted to the Stockholm Conference a "Proposal about an international institution for procuring standard water" (Conférence Internationale, 1899 *a*).

In his proposal Knudsen stressed the importance of the measurement of salinity of seawater in physical, climatological and biological investigations and maintained that the measurement could be carried out by titration with an accuracy of 0.04‰ but that this was not generally achieved by the methods then in use. Usually a few titrations were carried out by weighing and all volumetric titrations were then referred to these. Knudsen pointed out that titration by weighing was at that time a fairly difficult operation which it was almost impossible to carry out often enough to obtain the desired accuracy and he thought that the errors in salinity determinations were usually as high as 0.10 to 0.15‰. From his own investigations on the "Ingolf" Expeditions of 1895 and 1896, however, Knudsen knew that some Atlantic water types differed by only 0.10 to 0.25‰ in salinity so there was a need for greater accuracy in salinity determination than that usually obtained.

Obviously, better homogeneity could be obtained in salinity determinations if all water samples were examined in one laboratory but Knudsen realized that this would not be very practical. Instead he proposed that all interested nations should contribute to the establishment of an institution for procuring a standard water. This institution would prepare (and standardize in terms of its chlorinity) the standard water and distribute samples to interested laboratories, together with a statement of the physical and chemical qualities (properties) of the standard. These laboratories would then determine the halogen content (chlorinity) of their own samples simply by comparison with the standard water by titration, thus eliminating a number of sources of error.

The success of such a scheme depended heavily upon the physical and chemical properties of the standard water being determined with great accuracy, implying that the work should be carried out by experienced physicists and chemists with considerable instrumental resources at their disposal. Knudsen suggested that the new institution should have a staff consisting of a manager, a physicist, a chemist and two assistants. A detailed consideration of the programme of work which Knudsen deemed necessary shows that this was by no means an unduly large staff. To start with it would be necessary to obtain a quantity of open Atlantic seawater and investigate its physical and chemical properties, by which Knudsen meant:

"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.".

Some of the water would then be sealed in glass tubes and examined at intervals to find out if any alteration had taken place, for instance by interaction between the glass and the water. The results of these investigations would be used to decide if seawater was a suitable standard. Similar investigations would be carried out on an artificially produced seawater to find out if this offered any advantages. After these investigations, which Knudsen expected to take about two years, it would be possible to decide not only what should be the future standard for use in the determination of the halogen content of seawater but also what should be chosen as standard in determining the other physical and chemical qualities of seawater, if the investigations had shown that use of a reference standard should be preferred to an absolute determination.

In his proposal Knudsen carefully emphasized that the institution was not to deal with general hydrography, such as the study of hydrographical variations. He thought, however, that the institution should use the knowledge and practice which it would obtain by investigation of the standard water to carefully investigate water from different places "for the determination of the qualities and mark of different waters, that the general hydrography can be able to use the results of the Institution".

Knudsen's proposal has been reported here in some detail, to some extent in his own words, because so much of what he achieved in later years is suggested in it. Persuasive though his arguments were, Knudsen's proposal was not accepted in its entirety by the Conference. Knudsen himself later expressed his opinion that the members of the Conference had not seen clearly the advantage of using a standard water for all titrations (Knudsen, 1903) and one may surmize also that the Conference was reluctant to accept the considerable expense which would have been involved. Whatever the reasons, the proposal for the establishment of an institution devoted to the preparation and study of a standard water was not accepted, but some of Knudsen's other ideas were, though in modified forms. For instance, it was resolved to charge Knudsen with the task of experimentally revising certain hydrographic tables (Conférence Internationale, 1899 *d*). It was proposed that the relationship between the quantity of halogen contained in the (sea) water and the density of the water should be carefully investigated by an experimental examination of the tables prepared by Knudsen (Knudsen, 1899). A revision of the tables compiled by Makaroff, Krümmel *et al.*, as well as a definitive determination of the relationship between density and salinity, was also urgently needed. These investigations were to be carried out at the Technical University in Copenhagen under the direction of a committee consisting of Murray, Knudsen, Pettersson, Nansen, Krümmel, Dickson and Makaroff. The means for carrying out the work were to be solicited from learned societies in the countries concerned. This resolution was the background to the determination of constants and the compilation of the Hydrographical Tables, a formidable task undertaken by Knudsen and his collaborators during the following 2 years.

Despite his doubts, Knudsen's arguments for a standard water evidently found favour with the members of the Conference, as is shown by the following quotation from the hydrographical programme which they agreed upon (Conférence Internationale, 1899 *b*).

"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".

A footnote explains this further:

"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".

Thus, the need for a standard water for use in all chlorinity titrations was established.

THE INTERNATIONAL STANDARD SEAWATER

The central bureau from which standard samples would be sent, which is mentioned in the hydrographical programme quoted in the previous section, refers to a proposal by Fridtjof Nansen, one of the Norwegian delegates to the Stockholm Conference, that a Central Laboratory should be established in connection with the Central Bureau of the organization (ICES). This Central Laboratory would carry out a number of important investigations of general interest to the hydrographic and biological research and would also have the responsibility for supplying standard water. Nansen's proposal was incorporated in a recommendation from the Conference (Conférence Internationale, 1899 *c*).

Knudsen appears to have accepted the decisions of the Stockholm Conference gracefully and far from being discouraged he set about preparing samples of standard water to avoid some of the delay which would be involved in setting up the Central Laboratory. 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 (experience has shown that it 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 founded".

It should be stressed that preparation of standard water was nothing new to Knudsen. Prior to the Stockholm Conference he had made five different batches of such standards for use in Danish hydrographic work. The standard water prepared in 1900 in connection with the constant determinations was therefore designated No. VI. A description of the preparation of No. VI (and applicable also to later batches) was given by Forch *et. al.* (1902) and again in more detail by Knudsen (1903). Suffice to say here that the chlorinity of this batch was determined by the Danish chemist Sørensen who prepared a sample of potassium chloride, weighed it, corrected the weight for buoyancy in air and used this for the titrimetric standardization of a solution of silver nitrate. This solution was then used for the titration of the chlorinity of the samples of seawater to be used as standard water. *The chlorinity of standard water No. VI, and of all following standards which were referred to it, is thus based upon the chlorine in Sørensen's sample of potassium chloride and therefore depends upon the values of atomic weights which he used.*

About 80 tubes of standard water No. VI were prepared in April 1900 and random samples were investigated with regard to chlorinity (by Volhard titration and by a gravimetric method) and specific gravity. Periodic checks of the specific gravity revealed an increase of 0.015 in σ_0 over 2 years which was attributed to dissolution of the glass. This did not affect the chlorinity significantly, as the glass did not contain any chlorine. It did mean, however, that the water in the tubes was of little value as a density standard, though this is less true of the modern standard water which is stored in a more resistant glass.

This first standard water for international use was distributed to Russia, Sweden, Norway, Finland and Germany and it was used for all Danish titrations between May 1900 and August 1902, by which time the stock was nearly exhausted. ICES had just been established and international cooperation was beginning to gain momentum but the Central Laboratory had not yet been opened. Knudsen was therefore asked to prepare a new supply of standard water. As before, water taken from the Atlantic, having a chlorinity of 19.50‰, was used. This water was diluted with an appropriate quantity of distilled water, to give a chlorinity nearer to that of standard No. VI, as had been laid down previously (Knudsen 1903), before it was sealed in tubes. Of the 201 tubes prepared in this batch, which was designated VI *a*, 168 were distributed free of charge to the member countries of ICES, a few were used for determination of chlorinity, using standard VI as reference, and density, and the remainder were dispatched to the Central Laboratory which opened in Christiania (now Olso) in 1902.

In the meantime a second preparatory conference had been held in Christiania in 1901 at which Knudsen presented a provisional report on the determination of the constants of seawater and the compilation of the Hydrographical Tables. A resolution from the Conference read as follows.

"The Conference recognizes the extreme value of Dr. Martin Knudsen's Hydrographic Tables and expresses its cordial thanks to him for his admirable work" (Conférence Internationale, 1901 *a*).

In the hydrographic programme the use of Knudsen's Tables was directly prescribed (Conférence Internationale, 1901 *b*).

"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".

It was further prescribed that "The same standard seawater shall be employed in all cases for standardizing the solutions used for chlorine determinations".

In the autumn of 1902 the Central Laboratory was opened, with V. W. Ekman and C.J.J. Fox as assistants. In the first report from the laboratory the preparation in July 1903 of about 100 tubes of standard water (VI *b*), standardized by comparison with Knudsen's standard water VI *a*, was mentioned. This was obviously a provisional venture and the report stressed that steps had been taken for the preparation of a primary standard water to be compared directly with Knudsen's water VI. It was intended that this primary standard should be used to standardize subsequent batches of standard water, presumably because stocks of water VI were running low.

Before the new primary standard could be prepared and analysed it became necessary to prepare two more batches (VI *c* and VI *d*, about 250 tubes of each) for general distribution. In December 1903, however, about 120 tubes of seawater were reserved as the primary standard. Probably because light conditions during the winter months were not suitable for accurate chlorinity determinations, the analyses were delayed, but finally in October 1905 the chlorinity of the new Primary Standard (designated P) was established as 19.448 2‰ by direct comparison with Knudsen water VI. In the following two years four other batches of standard water (P1-P4) were prepared and analysed at the Central Laboratory.

THE STANDARD SEAWATER SERVICE

The responsibilities of the Central Laboratory were numerous (Went, 1972) but unfortunately it had a relatively short life. In 1908 Nansen decided that he no longer wished to continue as director and it was decided to close down the Laboratory. The Council (ICES) agreed that, whereas the further elaboration of special problems in future must be entrusted to the specialists of the various countries, there remained "practical charges, in which all the hydrographers are concerned, e.g., the preparation of normal (standard) water. It seems natural to hand over again to Docent M. Knudsen this task and to decide that, to defray part of the expenses, those who want the normal water, will in future contribute to its cost". Knudsen agreed to direct, on behalf of the Council, the preparation and distribution of the standard seawater and the remaining stocks (83 tubes of P and 49 tubes of P4) were transferred from the Central Laboratory to Copenhagen in September 1908.

Knudsen's reports to ICES in the following few years revealed that standard seawater was becoming widely adopted for the determination of salinity. Four more batches (P5-P8) of standard water were prepared in Copenhagen in the years leading up to the outbreak of war in 1914, at which point Knudsen assumed responsibility for the Standard Seawater Service in a personal capacity in order to release the Council of financial responsibility. Under this arrangement a further seven batches (P9-P15) were prepared in the period 1920-1937.

For each standard seawater in the series P5-P15 the link with the original Knudsen VI was maintained. Usually six tubes of a new batch were used, three of them being compared with Primary Standard P and three with a previously produced batch, usually the latest. The comparison was carried out by the Volhard method, as modified by Sørenson (Forch, *et. al.*, 1902), and the agreement between these comparisons was such that the results were considered accurate to the third decimal place. All the analyses on batches P5-P15 were carried out by J. P. Jacobsen, one of Knudsen's collaborators in the work on the seawater constants and the Hydrogra-

Frede Evan Hermann, 1917-1977.

phic Tables and, incidentally, Hydrographer to ICES from 1926-1946.

During the second world war the demand for standard seawater was fairly limited but nevertheless it became necessary to produce a new batch (P16) in 1943. The preparations for this were made by Frede Hermann, with some guidance from J. P. Jacobsen, and Hermann also made the chlorinity analyses. Previously, as an undergraduate, Hermann had assisted in the work connected with the 1937 Primary Standard, and from 1941, when he joined the Danish Hydrographical Laboratory as Knudsen's assistant, until the end of 1974 he was in charge of the preparation of the standard seawater.

In 1947 at the age of 76, having on his own responsibility prepared and supplied standard seawater since 1914, Martin Knudsen felt that this responsibility should be taken over by some competent scientific body interested in the matter, in order to secure continuity in the work. He therefore proposed to the Association International d'Océanographie Physique (AIOP) that this organization should take over the responsibility for the preparation of standard seawater and support the preparation financially so that it could be sold at a price allowing the users to obtain it more freely. The proposal was adopted at the Oslo meeting of AIOP in August 1948. Under this new arrangement another batch (P17) of standard water was prepared in late 1948. In February 1949 Knudsen issued a circular announcing the new arrangements and the availability of P17.

A few months later Martin Knudsen passed away and an era in the history of the Standard Seawater service ended. Because of his foresight, however, the Service was able to continue. At the request of AIOP, Helge Thomsen took over the administrative responsibilities and Hermann continued to prepare the standard and carry out the analyses. This arrangement continued, with the annual demand for the standard increasing gradually, until 1959 when Thomsen informed the Secretary of AIOP that he wished to retire as Director of the Standard Seawater Service. Thomsen's proposal of Hermann as his successor was welcomed by AIOP in view of Hermann's expertise and long association with the Service and Hermann took over full responsibility in January 1960.

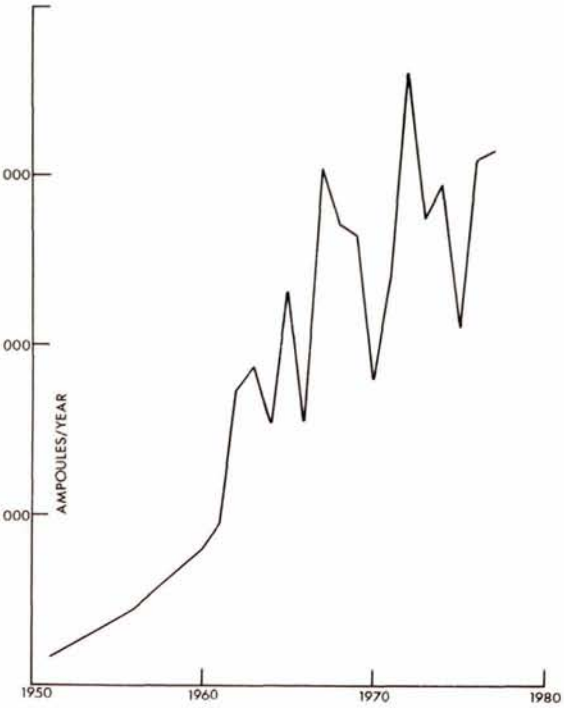
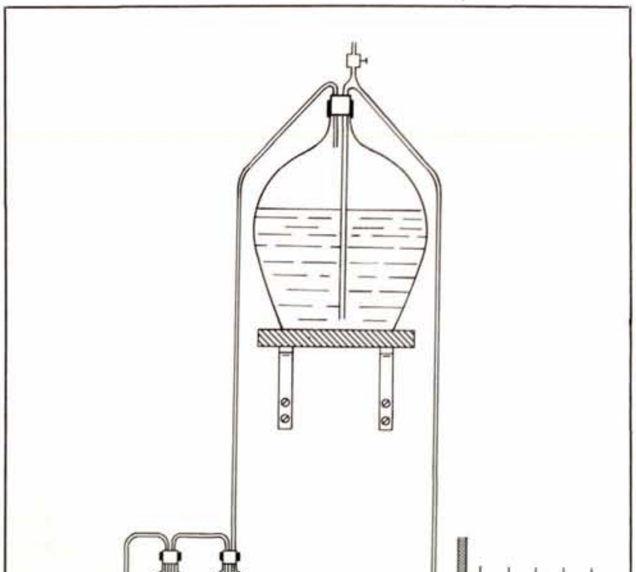


Figure 1
Annual sales of standard seawater.

From 1960 onwards there was considerable expansion in oceanography throughout the world, with a corresponding increase in the demand for standard seawater (Fig. 1), rising to more than 30 000 in some years. The changes which were forced upon Hermann in this period included the use of a 4 000 l tank (a far cry from the 30 l or so which Knudsen found adequate at first), and various improvements in the circulation and filtration systems, all of which enabled him to produce batches of 9 000 ampoules. Collection of seawater, which in some years amounted to 2 000 gallons, had to be arranged well in advance and for this Hermann had an amicable arrangement with a Danish shipping line. Washing and drying of the ampoules and labelling, packing and dispatch of the filled ampoules were dealt with by a part-time helper. Preparation of the seawater (mixing, filtering, diluting, etc.) which took several weeks for each batch, was dealt with by Hermann and his laboratory assistant. The major organizational problem was usually the filling session when the water was transferred from the large tank to the ampoules in which it was sold. Once the water had been diluted to the desired salinity (35‰) it was necessary to transfer as much of it as possible to the ampoules in one operation. For this Hermann hired a team of twenty-four people, consisting of family, friends and colleagues, to work at weekends. These filling sessions were an impressive sight to the newcomer, a hive of activity with everyone working non-stop to keep production flowing. Every stage of the operation, filling, sealing, packing, was watched keenly by Hermann to ensure that standards (of work) were maintained. Nor did Hermann's responsibilities end when the water was in the ampoules because he then had to determine the chlorinity of each batch by a very precise analytical method (Hermann, Culkin, 1978). As the Service had to cover running costs, he was also expected to balance the books, a task in which he was helped for many years by his secretary Miss Lemvig.

From the start the preparation of the standard has remained the same in principle though there have been some changes in detail. The water has usually been collected at the surface in the North Atlantic and transported in glass carboys or, more recently, polythene containers to the Standard Seawater Service premises. It is then pumped through filters into the storage tank and circulated through the filters for 2-3 weeks to achieve thorough mixing. During this period the seawater is gradually diluted with distilled water to give a final salinity near to 35‰ and the temperature is raised to ca. 26°C so that when it is finally transferred to glass ampoules (at 20-24°C) the seawater is slightly undersaturated with dissolved air. In earlier years filter papers were used to remove particulate matter but more recently membrane filters of pore size ca. 0.3 μm have been used in an attempt to eliminate bacteria. For sealing the seawater in the glass ampoules the method used today is similar to the one described by Knudsen in 1903, though the scale is now much bigger of course (Fig. 2). The water is pumped from the storage tank to a manifold or horizontal glass tube on the filling table. Each outlet from the manifold is fitted with a small length of rubber tubing into which is inserted one (open) end of a clean dry ampoule. The ampoule is almost filled with seawater and then the rubber tubing is closed by means of a clamp (*c* in Fig. 2 *a*) while the upper tip of the ampoule is sealed by drawing off in an air/acetylene flame. After cooling, the ampoule is inverted and the second tip is sealed. By operating two filling benches, each handling 48 ampoules at a time, it is possible to produce about 7 000 ampoules of standard seawater in a day.

Although the Service was always operated from Denmark until 1975 it was accommodated in a number of locations When the Service was first transferred from Christiania to Copenhagen in 1908 the standard was probably prepared in the Hydrographic Laboratory of the Danish Commission for Marine Investigations (then co-located with ICES at Jens Kofoeds Gade 2) according to the address on the labels of batches P5-P8. In 1914, when Knudsen took over the responsibility in a personal capacity, the Service moved to the Laboratoire Hydrographique which had premises in the Technical University (Polyteknisk Laereanstalt) where Knudsen as a professor in the University of Copenhagen had his laboratories. On Knudsen's retirement from the University in 1941 the Service was transferred to Charlottenlund Castle near Copenhagen which, from 1936, was the seat of the Danish Institute for Marine Research (Danmarks Fiskeri og Havundersøgelser) as well as the ICES headquarters. Batch P16, under the name of Professor Knudsen and batches P17 onwards, under the name of "Association d'Océanographie Physique, Dépôt d'Eau Normale", were prepared at this



◀ Figure 2 *a*
Early equipment for preparing standard seawater.

Figure 2 *b*
Present day equipment for preparing standard seawater.

address. When space could no longer be made available in the Castle the Service finally moved to rented accommodation at Mariendalsvej in Copenhagen where it remained until it was transferred to England in 1974.

Thus, from a laboratory scale beginning, the Standard Seawater Service expanded into a fairly large operation. It developed to the stage where it was not a full-time occupation for one man but it was sufficiently time-consuming to interfere seriously with other activities such as research. For many years Hermann successfully combined the two but he had considerable responsibility as head of the Danish Hydrographical Laboratory and this fact, together with some personal problems, led to his decision in 1973 to retire from the Service. He therefore proposed to IAPSO (formerly AIOP) that the responsibility for operating the Service should be passed to F. Culkin, who had collaborated with him in the chlorinity calibrations for several years. With financial help from IAPSO the equipment and stocks were transferred from Charlottenlund to Wormley at the end of 1974 and production was re-commenced in 1975. For the next $2^1/_2$ years the Service was operated along the same lines as in Denmark, i.e., as a separate non-profit making organization, responsible to IAPSO The disadvantages of this system, relying as it did on a great deal of part-time help, led to the decision in 1977 to transfer the responsibility for general administration of the Service to the appropriate sections of the Institute of Oceanographic Sciences and to leave only the preparation and analyses of the standard to the scientific staff.

THE PRIMARY STANDARD

Although the use of a standard water of known chlorinity obviated the need for individual laboratories to prepare their own potassium chloride solutions, all chlorinities to the present day can be traced back to potassium chloride and the 1900 atomic weights.

Among the standard waters which Knudsen prepared for his own work was the batch designated standard-water VI. The chlorinity of this water was determined by Sørensen, both by a gravimetric method and by titration with silver nitrate solution. At that time 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 chlorinity, Sørensen used pure potassium chloride to standardize his silver nitrate solutions and the chlorinity of 19.380‰ which he obtained for standard-water VI was based on the values of atomic weights adopted in 1900. The chlorinities of all subsequent Normal or Standard seawaters prepared between 1902 and 1937 were then determined, directly or indirectly, by comparison with standard water VI. The sequence of comparisons is fully described by Jacobsen and Knudsen (1940) who claimed that Sørensen's method would not introduce an error greater than 0.001‰ in such a comparison. Nevertheless, when a new Primary Standard was prepared in 1937 some fundamental changes were proposed.

In 1936 when stocks of the 1900 Primary Standard were running low Knudsen submitted a "Report on Standard-Water" to ICES (ICES, 1936) explaining the situation. He stressed that it was necessary for future determinations of chlorinity to be secured in a similar way as before and consequently that the preparation and distribution of standard water be continued. It was therefore necessary to produce a new Primary Standard. As the subject was also of interest to countries outside ICES (the standard was, by then, being distributed to 37 countries), Knudsen expressed his intention to propose to the Association International d'Océanographie Physique (AIOP) that the organization be charged with the task of directing the preparation of the new Primary Standard and the physical and chemical investigations involved, and that AIOP should defray the expenses of assistance, etc., in connection with the work and publish a report on it. Knudsen further put forward the idea that, when the work on the Primary Standard was finished, the preparation of the ordinary standard should go on as hitherto under his direction, but that when he no longer wished to keep the responsibility the Primary Standard should be at the disposal of the Council, which could then charge the Danish Hydrographic Laboratory, or some other competent institution or person in Copenhagen, with the preparation and distribution of the ordinary standard seawater.

This proposal by Knudsen was approved by the ICES Statutory Meeting in 1936 and also by the AIOP Executive Committee (AIOP, 1937) who adopted it as follows:

"A scheme was considered for the preparation of a new primary standard seawater, the details of which had been circulated to members of the Executive Committee in June 1936. It was agreed to make a grant of £ 350 to Pr. Knudsen towards the cost of assistance and apparatus. The Executive Committee authorized Pr. Knudsen to prepare and distribute ordinary samples of standard seawater based on this primary standard, and reserved, the right to authorize all modifications of this arrangement."

The new Primary Standard was prepared in 1937 and designated Urnormal or Primary Standard 1937. The chlorinity was determined by Inger Knudsen by direct comparison with Primary Standard P and some of the earlier standard seawaters, taking the chlorinities of these as known. In describing the preparation of the new Primary Standard, Jacobsen and Knudsen (1940) pointed out that a tube of seawater was probably not the best standard for maintaining continuity over a long period of time. Another unsatisfactory point was the fact that the definition of chlorinity made it dependent on the ratios of certain atomic weights which meant that, if the definition were strictly adhered to, there would be breaks in the chlorinity determinations every time the accepted values of atomic weights changed. Jacobsen and Knudsen (1940) argued, therefore, that a far better standard would be pure silver (Atomgewichtssilber) and they proposed a new definition of chlorinity, based on the following measurements and reasoning.

1) Let Ag denote the number giving the mass (in grams) of Atomgewichtssilber just necessary to precipitate the halogens in 1 kg of seawater sample of which the chlorinity expressed in $^0/_{00}$ 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.

Thus Cl = k. Ag grams Atomgewichtssilber – (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 19.381 $0^0/_{00}$, as determined by Inger Knudsen by comparison with previous standards, was adopted for Urnormal 1937, thus ensuring continuity between past (as far back at 1902) and future chlorinity determinations.

3) Investigations carried out by Pr. Otto Hönigschmid in München established that 58.994 28 g Atomgewichtssilber were necessary and sufficient to precipitate the halogens in 1 kg of Urnormal 1937.

4) Substituting these values in equation (1):

$$19.381\,0^0/_{00} = k \times 58.994\,28 \text{ g Atomgewichtssilber}$$

or $\mathrm{Cl} = 0.328\,523\,4\ \mathrm{Ag}^0/_{00}$.

The new definition thus 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 0.328 523 4 kg of the seawater sample".

This definition has the advantage of being independent of accepted values of atomic weights and the use of pure silver as the ultimate standard provides a continuous link beween all chlorinity determinations. It is obvious, however, that it would not be practicable to calibrate every batch of standard seawater against pure silver. In practice every few years the Standard Seawater Service prepares a small number of ampoules of seawater and determines the chlorinity against pure silver (some of which was prepared by Hönigschmid for the 1937 determinations). These ampoules of seawater are regarded as the practical Primary Standard against which the chlorinity of ordinary standard seawater is determined.

THE RELIABILITY OF STANDARD SEAWATER

For a solution such as seawater, calibrated in terms of one of its chemical constituents or physical properties, to be satisfactory as a standard, two major requirements must be met.

1) The calibration must be carried out by a method which is at least as accurate as the method for which the standard is intended.

2) The calibration should not change significantly during a reasonable period of storage.

In assessing the reliability of standard seawater as a salinity standard it must be borne in mind that the methods of salinity determination have changed drastically in recent years. Standard seawater was originally intended as a chlorinity standard and as such it meets the above-mentioned requirements very satisfactorily. For many years the chlorinity calibration was carried out by the Volhard method which was considerably more accurate and precise than the volumetric methods in routine use. In 1969 a combined gravimetric/potentiometric method (Hermann, Culkin, 1978), which was much simpler operationally than the Volhard, was adopted and tested independently at both Charlottenlund and Wormley on all batches of standard produced between 1969 and 1974. Agreement between the two laboratories was usually better than 1×10^{-4} in the chlorinity value, with a standard deviation of $\pm 2\text{-}3 \times 10^{-4}$, which is more than adequate. Storage of the standard in glass ampoules also presents no problems from the point of view of chlorinity, as glass contains no halogens and the small amount of silica which does dissolve, even from the most resistant glass, has a negligible effect on the chlorinity.

In the past 15-20 years the chlorinity titration has been almost completely replaced, as a means of determining salinity, by the measurement of electrical conductivity. The present practice is to fill the salinometer cell with standard seawater and adjust the instrument to read the conductivity corresponding to the certified chlorinity. This means that standard seawater is now being used as a conductivity standard, although it is only calibrated in terms of chlorinity. The conductivity method also assumes that the conductivity/chlorinity relationship is the same, or nearly so, for all batches of standard. Recent investigations carried out in four different laboratories (Millero *et al.*, 1977; Poisson *et. al.*, 1978) have shown that this assumption is valid for most batches. These studies, of more than twenty different batches of standard seawater, prepared in the period 1962-1975, revealed variations in pH and dissolved silicate content but only four batches (prepared in 1967-1969) had unacceptably high conductivities (equivalent to 0.004-$0.007^0/_{00}$ in salinity). At least one of these batches was found some time after its preparation to be contaminated by bacteria (Hermann, personal communication) and it is possible that oxidation of dissolved organic matter to CO_2 by the bacteria increased the conductivity during storage. Steps have been taken in recent years to avoid a recurrence of this problem by filtering the seawater through a membrane filter at the preparation stage.

The evidence, suggests, therefore, that standard seawater is a reliable standard for conductivity and, incidentally, for density measurements. Nevertheless, the preparation of the standard almost certainly involves some disturbance of its CO_2 system, on which the conductivity is very dependent, and for some time there has been a strong feeling that if the seawater is to be used as a conductivity standard then it should be calibrated in conductivity as well as chlorinity. Development of an instrument for measuring the absolute conductivity of seawater to 1 in 10^5 has proved exceedingly difficult, although such an instrument is now in operation at

Wormley. A simpler proposal (UNESCO 1978) that the conductivity of each batch should be measured relative to a defined potassium chloride solution is under consideration by the Joint Panel on Oceanographic Tables and Standards and a proposal may be formulated in the near future.

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