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Stability of IAPSO Standard Seawater

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Abstract

A check of the calibration of 10 batches of IAPSO Standard Seawater (P120-P129) against the defined KCl standard (Practical Salinity Scale 1978) showed differences of less than 0.001 in salinity (equivalent to ca. 0.00003 in K15) during storage periods of up to 96 weeks. An experimental batch stored in borosilicate bottles showed no significant difference from the seawater stored in glass ampoules over a storage period of 158 weeks.

1. Introduction

As large-scale international projects (e.g. WOCE, GOOS, JGOFS, CLIVAR) occupy increasingly important roles in the production of oceanographic data, greater demands are made on the instrumentation used. However, the quality of those data depends on the calibration accuracy of the instruments and so increasing demands are also made on the standards and reference materials. This is particularly true of salinity data for which the need to define their accuracy is essential for an understanding of oceanic profiles.

The reliability of salinity determinations depends on many factors, but one factor common to all laboratory determinations is the IAPSO Standard Seawater which is used to calibrate salinometers. Questions are frequently asked about the reliability of Standard Seawater, its stability and how it should be stored. This paper summarises some of the data and experiences acquired by the IAPSO Standard Seawater Service in the past 25 years.

2. History of Calibration of IAPSO Standard Seawater

A detailed history of Standard Seawater can be found in Culkin & Smed (1979) but it is worth mentioning here the major changes in calibration which have taken place.

When it was first introduced at the end of the 19th century, Standard Seawater was calibrated in chlorinity by titration with silver nitrate solution, using potassium chloride as a reference standard. A subsequent change in the definition of chlorinity (Jacobsen & Knudsen, 1940) led to the adoption of high purity silver as the primary reference standard but, in practice, each batch of Standard Seawater was still calibrated by silver nitrate titration.

In 1978 the Practical Salinity Scale, involving a fundamental change in the definition of salinity, was adopted and potassium chloride again became the reference standard, this time in conductivity. Salinity was defined in terms of electrical conductivity ratio, at 15 °C and 1 atmosphere, relative to a KCl solution containing 32.4356g kg^{-1} (corrected for buoyancy). It should be pointed out that the 15 °C mentioned in the salinity definition is on the temperature scale (IPTS-68) which was in operation at the time. If salinity is eventually redefined to take into account the new temperature scale introduced in 1990 (ITS-90) a small change in the defined concentration of KCl will be necessary but this will not affect the value of K15 for any given seawater. In the meantime, since 1981 the conductivity of each batch of Standard Seawater has been compared with that of defined KCl standard in accordance with the definition, the ratio being designated K15.

3. Early Comparisons of Batches of Standard Seawater

In the years when Standard Seawater was certified in chlorinity and used as a standard for chlorinity titrations, the calibration was carried out by a time-consuming combined gravimetric, potentiometric titration used only by the IAPSO Standard Seawater Service. The only independent check appears to have been that carried out on batches prepared between 1969 and 1974 in preparation for the transfer of the Service from Copenhagen to the Institute of Oceanographic Sciences, Wormley, England (Hermann & Culkin, 1972). The agreement between the two laboratories (s.d 4 - 6 x 10^{-4} in salinity) confirmed the reliability of the calibrations but revealed nothing about the stability of Standard Seawater as neither reaction with the glass ampoules nor bacterial contamination (which had been encountered previously) was likely to alter the chlorinity.

From the late 1950's, chlorinity titration was gradually replaced by measurement of electrical conductivity for determination of salinity, but IAPSO Standard Seawater, although being used as a conductivity standard, continued to be certified in chlorinity. Early comparisons of batches of Standard Seawater prepared between 1937 and 1978 (Park, 1964; Millero et al, 1977; Poisson et al, 1978; Mantyla, 1980), revealed variations in the chlorinity/conductivity relationship and a need for the standard to be calibrated in electrical conductivity.

Significantly, from the point of view of stability, three batches (P49 - P51) were found (Millero et al, 1977, Poisson et al, 1978) to have anomalously high conductivities which were attributed (Hermann, private communication) to bacterial contamination, possibly combined with oil pollution. More recently Mantyla (1987) and Takatsuki et al (1991) reported that agreement between batches had improved since the adoption of a defined KCl solution as reference.

4. Comparisons by the Standard Seawater Service

Although the investigations mentioned above were of high quality, they did not give an absolute measure of change in conductivity as the comparisons were made relative to older batches of Standard Seawater which themselves may have changed. The Practical Salinity Scale 1978, however, provided a means of checking the calibration and stability of Standard Seawater against a reproducible KCl standard. Since batch P91, produced in 1981, all batches of Standard Seawater (i.e. the working standard) have been calibrated in conductivity relative to this defined KCl standard and labelled with the appropriate K15. Details of the procedures for preparing the standard KCl solutions and for calibrating new batches of Standard Seawater have been published (Culkin 1986) and need not be repeated here. During the past few years, however, the opportunity has been taken to check the calibration of the previous two or three batches at the same time that a new batch was being calibrated and the results of these measurements are shown in Table 1.

In addition a study has been made of the stability of Standard Seawater stored in bottles instead of the traditional glass ampoules. The bottles were made from borosilicate glass and closed with chemically resistant plastic stoppers as supplied to the pharmaceutical industry. Batch P123 was chosen for this study and its conductivity ratio, K15, has been regularly measured against the defined KCl standard at intervals since 1993. The results are shown in Table 2.

5. Discussion

It should be borne in mind that the results shown in Tables 1 and 2 were obtained from high quality calibrations of Standard Seawater. The salinometer used (Guildline Autosal 8400B), which was reserved for Standard Seawater calibrations, was serviced regularly and was operated in a temperature-controlled laboratory maintained at 1-2 ° C below the salinometer operating temperature. All ampoules, which had been stored in our warehouse (temperature range 8 - 25 ° C) since preparation, were carefully examined for minute cracks which sometimes develop in a small number of ampoules and which lead to an anomalously high values of conductivity. Also, none of the ampoules showed any visual signs of bacterial contamination such as those which have been reported in the past.

Overall, the repeat determinations agreed to within $\pm$ 0.00002 of the label K_{15} value over storage periods of up to 96 weeks. The mean of 0.00000 is probably fortuitous and suggests that experimental errors in the preparation of the KCl solutions and measurement of conductivities are responsible for most of the differences from the label value. This interpretation is also supported by the fact that the differences seem random, with no trend with age, (see Fig. 1).

For the seawater stored in borosilicate bottles, it can be seen (Table 2), that changes of no more than 0.00001 in K_{15} were observed. This is a slight improvement over the storage changes found for Standard Seawater stored in sealed glass ampoules, but the data set is limited to only one batch of bottles.
A number of factors are thought to affect the long-term stability of Standard Seawater. These include microbial activity and interactions between the seawater and the glass. There is no reason to expect any difference in the potential for microbial activity between ampoules and bottles as both were filled with the same source water, filtered through 0.2 μm pore size cartridges to reduce microbial contamination.
However, there are differences in the glass composition. The ampoules used routinely by the Standard Seawater Service are manufactured from a pharmaceutical grade soda glass, whereas the bottles were made from a more resistant borosilicate glass.

6. Conclusions

The changes with time in the conductivity of Standard Seawater stored in the conventional glass ampoules, if real, amount to less than 0.001 in salinity. This may be compared with the accuracy/precision of 0.002 quoted by Guildline Instruments for their widely used Autosal Salinometers, and suggests that the stability of Standard Seawater is not usually the limiting factor in laboratory salinity determinations. Such discrepancies between batches which do occur are likely to be due to undetected microbial activity, which unfortunately can develop some time after preparation, and reaction with the glass ampoule. Nevertheless, we would recommend that, for high precision salinity determinations, Standard Seawater should be stored at a temperature between 8 and 25 ° C for no longer than 96 weeks (these figures may be revised in the light of longer term studies). Storage at higher ambient temperatures such as may occur in the hold of a ship, may accelerate reaction with the glass and is to be avoided. It is also advisable to prevent freezing of the seawater as this can lead to precipitation of salts which do not readily re-dissolve on thawing.

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References

CULKIN, F & SMED, J, (1978): The History of Standard Seawater. Oceanologica Acta, 2,(3), 355-364.

CULKIN, F, (1986) : Calibration of Standard Seawater in Electrical Conductivity. The Science of the Total Environment, 49, 1 - 7.

HERMANN, F & CULKIN, F, (1972): A Check of the Analysis of Standard Seawater. International Council for the Exploration of the Sea, Hydrography Committee Communication CM 1972/C:33.

JACOBSEN, J P & KNUDSEN, M, (1940): Urnormal 1937 or Primary Standard-Water 1937. Assoc. Oceanog. Phys., Pub. Sci., No. 7, 38p.

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.

MILLERO, F J; CHETIRKIN, P & CULKIN, F, (1977): The Relative Conductivity & Density of Standard Seawaters. Deep-Sea Research, 24, 315-321.

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,(4), 425-433.

TAKATSUKI, Y; AYOAMA, M; NAKANO, T; MIYAGI, H; ISHIHARA T & TSUTSUMIDA, T, (1991): Journal of Atmospheric & Oceanic Technology, 8, 895-897. Standard Seawater comparisons of some recent batches.

UNESCO, (1980): Tenth Report of the Joint Panel on Oceanographic Tables & Standards, Sydney, B.C., 1-5 September 1980. Unesco Technical Papers in Marine Science, No. 36.

Figure Captions

Table 1 : Changes in K15 values of IAPSO Standard Seawaters after storage.

Table 2 : Changes in the K15 value of IAPSO Standard Seawater Batch P123 after storage in ampoules and borosilicate bottles.

Figure 1 : Changes in K15 values of IAPSO Standard Seawaters after storage.

Table 1: Changes in K15 values of IAPSO Standard Seawaters after storage.

Batch	Date	Age (weeks)	Label K15	New K15	(New-Label) x 10^5	No. of checks
P120	6-May-92	0	0.99985			
	8-Sep-92	18		0.99984	-1	3
	19-Jan-93	37		0.99984	-1	2
	8-May-93	52		0.99984	-1	2
	13-Jan-94	88		0.99984	-1	1
P121	8-Sep-92	0	0.99985			
	19-Jan-93	19		0.99985	0	4
	8-May-93	35		0.99985	0	3
	13-Jan-94	70		0.99986	1	1
P122	21-Jan-93	0	0.99991			
	8-May-93	15		0.99991	0	6
	13-Jan-94	51		0.99991	0	2
	27-Jul-94	79		0.99992	1	2
	22-Nov-94	96		0.99991	0	1
P123	10-May-93	0	0.99994			
	13-Jan-94	35		0.99994	0	3
	22-Jul-94	63		0.99995	1	4
	22-Nov-94	80		0.99994	0	3
	7-Feb-95	91		0.99994	0	1
P124	18-Jan-94	0	0.99990			
	27-Jul-94	27		0.99991	1	3
	22-Nov-94	44		0.99990	0	5
	7-Feb-95	55		0.99990	0	1
P125	1-Aug-94	0	0.99982			
	22-Nov-94	16		0.99982	0	6
	7-Feb-95	27		0.99980	-2	4
	18-Jul-95	50		0.99981	-1	2
P126	29-Nov-94	0	0.99987			
	7-Feb-95	10		0.99986	-1	4
	18-Jul-95	33		0.99987	0	2
	21-Nov-95	51		0.99987	0	1
P127	14-Feb-95	0	0.99990			
	18-Jul-95	22		0.99990	0	2
	21-Nov-95	40		0.99991	1	4
	19-Mar-96	57		0.99992	2	3
P128	18-Jul-95	0	0.99986			
	21-Nov-95	18		0.99987	1	7
	19-Mar-96	35		0.99988	2	5
P129	22-Nov-95	0	0.99996			
	19-Mar-96	17		0.99997	1	5
	16-May-96	25		0.99997	1	1

Table 2: Changes in the K15 value of IAPSO Standard Seawater Batch P123 after storage in ampoules and borosilicate bottles.

Date	Age (weeks)	P123 K15 Ampoules	P123 K15 Bottles
10-May-93	0	0.99994	0.99993
13-Jan-94	35	0.99994	0.99993
27-Jul-94	63	0.99995	0.99994
29-Jul-94	64		0.99994
22-Nov-94	80	0.99994	
7-Feb-95	91	0.99994	
21-May-96	158		0.99994

Figure 1: Changes in K15 values of IAPSO Standard Seawaters after storage.