An Evaluation of Some Recent Batches of IAPSO Standard Seawater

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(Manuscript received 1 December 1998, in final form 22 June 1999)

ABSTRACT

The authors examine changes in the salinity of the International Association for the Physical Sciences of the Ocean standard seawater (SSW) as used in seven cruises between 1991 and 1997. Ten batches of SSW were used during this time—several more than once—such that a clear demonstration of the effect of aging over months and years on SSW salinity can be made. Thus, the authors demonstrate that simple ''offsets'' intended to ''correct'' SSW salinity changes are inappropriate. Interest in intercruise salinity compatibility is high, as scientists attempt to reconcile section measurements made during the World Ocean Circulation Experiment among experiments. SSW salinity changes are one source of salinity differences of $O(0.001)$ between sections. Herein, the authors provide a demonstration of how SSW measurements can be collated to generate a batch-by-batch history of SSW salinity evolution for more accurate sample salinity evaluation.

1. Introduction

With the stringent standards imposed on deep-sea salinity measurements by the World Ocean Circulation Experiment (WOCE) (WCRP 1988a,b), interest has been increasing in an attempt to verify or determine the salinity of the International Association for the Physical Sciences of the Ocean (IAPSO) standard seawater (SSW), which is used routinely in salinometer calibration. References describing the history, production, and calibration of IAPSO SSW can be found in Culkin and Ridout (1998, hereafter CR98). The WOCE Hydrographic Programme Office (WHPO) (1994) has stated that for water sample analysis, 0.002 salinity accuracy can be expected, given individual samples analyzed to an accuracy of 0.001 and given an SSW salinity known to 0.001. If the salinity of SSW is known nearly exactly, then the absolute accuracy of sample measurements may approach 0.001. This issue becomes important as scientists seek to identify climate change in the deepest and most slowly varying waters of the world. For example, Bryden et al. (1996) inspect deep northeast Atlantic water-mass characteristics at 24°30′N using data from 1957, 1981, and 1992, and find that any differences are either at the limits of best measurement accuracy or (potentially, in the case of the earliest data) attributable to instrumental problems or to the calibration of SSW in chlorinity (up to batch P90, labeled 7 May 1980).

It is known that some early batches of IAPSO SSW showed unpredictable changes in conductivity (Mantyla 1980, 1987, 1994). In this article, we use at-sea measurements of SSW salinity from selected United Kingdom WOCE cruises to add to the debate about the salinity of more recent batches of SSW. In particular, we stress the points made by CR98: SSW salinity is correct to measurement accuracy when produced, but unpredictable changes to SSW salinity can result from aging. The following analyses demonstrate how cruise data can be put to good use to determine these age-related changes. Also, we will quote salinity values generally to four decimal places. The appropriateness of this will be discussed in the final section, in light of the evidence discussed herein.

2. Cruise data analyses

In this section, we analyze SSW salinities using data from seven cruises: RRS *Charles Darwin* cruise 62 (1991) (Gould 1992); RRS *Discovery* cruises 199 (1992–1993) (Saunders 1993), 201 (1993), (Pollard 1994), 213 (1995) (Pollard 1995), and 230 (1997) (Bacon 1998); and RRS *James Clark Ross* cruises 10 (1995) (Heywood and King 1996) and 16 (1996) (B. King 1998, personal communication). The preceding references are the cruise reports, which contain details of instruments, operations, etc. Salinity analyses were based on the method described in the relevant WHPO (1994) report, with some modifications. In particular: 1) On all cruises except RRS *Charles Darwin* 62, sample intake into the salinometer was effected by a peristaltic-type pump manufactured by Ocean Scientific International, Ltd.

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TABLE 1. IAPSO standard seawater details. Salinity is calculated (to four decimal places) from the label K15 using the standard PSS78 formulation (UNESCO 1981). Dates of use correspond to the RRS *Charles Darwin* cruise 62 (August 1991); the RRS *Discovery* cruises 199 (January 1993), 201 (April 1993), 213 (January 1995), and 230 (August 1997); and the RRS *James Clark Ross* cruises 10 (April 1995) and 16 (November 1996).

Batch	Production date	Label K15	Salinity	Dates of use
P115	6 Feb. 1991	0.99986	34.9945	Aug. 1991, Jan. 1993, Apr. 1993, Jan. 1995
P116	10 Jul. 1991	0.99981	34.9925	Jan. 1993, Apr. 1993
P120	6 May 1992	0.99985	34.9941	Jan. 1993, Apr. 1993, Apr. 1995
P121	8 Sep. 1992	0.99985	34.9941	Apr. 1993
P124	18 Jan. 1994	0.99990	34.9961	Jan. 1995
P125	1 Aug. 1994	0.99982	34.9929	Jan. 1995, Apr. 1995, Nov. 1996
P128	18 Jul. 1995	0.99986	34.9945	Aug. 1997
P130	21 Mar. 1996	0.99997	34.9988	Nov. 1996, Aug. 1997
P131	10 Dec. 1996	0.99986	34.9945	Aug. 1997
P132	9 Apr. 1997	0.99993	34.9972	Aug. 1997

(OSIL) 2) The salinometer standardization dial (Rs set) was left untouched (though it was altered once; please see section 2c). This enables the following of long-term drift in the salinometer response, as is demonstrated below.

We note from the cruise reports that all salinity analyses were carried out to WOCE standards. In particular, for deep samples, duplicate sample salinity differences always had a standard deviation of 0.0010 or less. All analyses reported here were carried out on Guildline Autosal salinometers, Models 8400 and 8400A.

During the seven cruises, a total of 10 batches of SSW were used—some more than once. In Table 1, we summarize the batches used, their label conductivity ratios (K15) and salinities, the batch production dates, and the dates used. Below, we refer to a quantity we call ‘‘apparent salinity’’ (AS). This quantity is obtained by treating all standards used during a cruise as samples. Then their salinities are calculated in the usual manner on the practical salinity scale of 1978 (PSS78) (UNESCO 1981). This calculation requires the input of a standardization value, which we provide by choosing an arbitrary but sensible value, which can be the first standard value or the mean of a range of standards, or other input. This is an apparent and not a true salinity. Apparent salinity shows long-term drifts during a cruise. We can be confident that these are the result of changes in the behavior of the salinometer. Thus, 1) AS represents the ‘‘performance history’’ of the salinometer, and 2) AS enables us to extract valuable information on salinity *differences* between different batches of SSW used during the same cruise. Where a change of batch exists, there will be a step in AS that conforms to the label salinity difference between the batches. Additionally, for convenience, we choose to center AS on zero, by subtracting a suitable mean.

Mean salinity differences between batches of SSW are described herein. In most of our measurements, the standard deviation of the difference about the mean is generally 0.0004 or better, so that the standard error of the mean difference is 0.0002, or better, for more than six measurements. We describe error estimation only for those cases that are different from this.

a. RRS Charles Darwin *62*

Salinity measurements during the RRS *Charles Darwin* cruise 62 were standardized solely with batch P115. Although we can make no interbatch comparisons, we can compare the bottle salinities with the salinity predicted by Mantyla’s (1994, M94 hereafter) latitude-dependent θ–S relationship for the deep northeast Atlantic, after the manner of Saunders (1986), who used the deep ocean as a natural calibration tank. We set the latitude to the northern extremity of M94’s range of validity, 50°N, while the actual station latitudes were 51°–53°N. The difference is not significant in terms of the formulation results. Cruise stations 6–10 and 70–78 (Gould 1992) were used. Figure 1 shows that there is no significant difference between the cruise θ–S relationship and M94’s prediction (for $2.1 < \theta < 2.4$°C, the mean difference is 0.0001, and the standard deviation is 0.0011, excluding the two outlying points), which gives us confidence that batch P115’s label value of K15 was still valid at a batch age of 6 months.

It is possible to reverse the above argument. M94’s θ–S relationship was based on calibration using 4-month-old batch P108 (McCartney et al. 1991). We can thus state that the label salinity of this batch was most probably valid at the time of use.

b. RRS Discovery *199*

During RRS *Discovery* cruise 199, batch P120 was the primary standard; batches P115 and P116 were also carried. So we can estimate the difference in salinities between these batches. At the time of the cruise, batch P115 was 23 months old, batch P116 was 18 months old, and batch P120 was 9 months old. The standardization history is shown in Fig. 2, in which are indicated two comparison sets: the first, about the middle of the cruise when 16 ampoules of batch P115 were analyzed

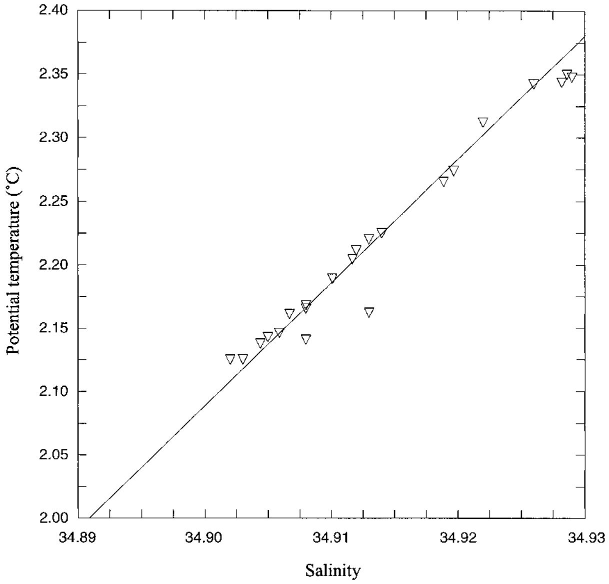

FIG. 1. Deep θ–S bottle data from RRS *Charles Darwin* cruise 62. Stations are in the northeastern North Atlantic east of the Mid-Atlantic Ridge between 51° and 53°N. The line shows the θ–S relationship predicted by Mantyla's (1994) formulation for 50°N latitude.

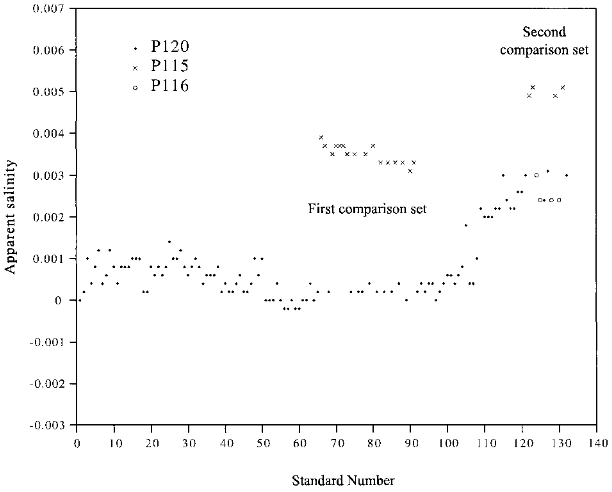

FIG. 2. Salinity standardization history from RRS *Discovery* cruise 199. Standard seawater batches are identified by the key at top left. Apparent salinity is referenced to an arbitrary zero. The comparison sets are discussed in the text.

against 12 ampoules of batch P120, and the second, when 4 ampoules each of the three batches were analyzed. By interleaving standard measurements, any drift in the salinometer response is removed when the mean salinity difference is calculated. We demonstrate the calculation for one case next, but note first that the measurements shown in Fig. 2 were made during 6 weeks, and the long-term drift of the salinometer can be seen clearly. The instrument was very stable, with AS varying slowly and by less than 0.003 overall. We cannot tell whether the short-term variability of amplitude, approximately ±0.0005 about the long-term drift, is due to the salinometer or to within-batch SSW variability, or to a combination of both.

We use the first comparison set. We denote the label salinity by the batch number and the subscript L, and denote the measured salinity difference by the batch numbers and the subscript M. The inferred salinity change from the label salinity is denoted by C, with the batch number subscript. The superscript indicates the comparison set number. Using the values from Table 1, we have (1), which gives the expected salinity difference between the batches based on the label values of K15. Using the data in Fig. 2, we have (2), which gives the measured salinity difference of the two batches at the time of use:

$$\mathrm{P120}_L - \mathrm{P115}_L = -0.0004 \quad \text{and} \tag{1}$$

$$(\mathrm{P120} - \mathrm{P115})^1_M = -0.0033. \tag{2}$$

Now (2) can be reexpressed in terms of label salinities and inferred salinity changes:

$$(\mathrm{P120}_L + C^1_{120}) - (\mathrm{P115}_L + C^1_{115}) = -0.0033, \tag{3}$$

such that when we substitute the difference of label salinities from (1) we have an expression for the difference in salinity changes as measured at the time of use:

$$C^1_{120} - C^1_{115} = -0.0029. \tag{4}$$

We can do the same for the second comparison set, such that $C^2_{120} - C^2_{115} = -0.0017$ and $C^2_{120} - C^2_{116} = -0.0013$ (and $C^2_{116} - C^2_{115} = -0.0004$). From our measurements, we can produce only expressions for differences in salinity changes. However, we can turn to CR98 for some reference values for true salinity changes over time. Batch P120 was remeasured by OSIL (the producers of IAPSO SSW) at the same time as it was being used on RRS *Discovery* 199. OSIL found that batch P120 had freshened by 0.000 01 in K15, equivalent in salinity to $C_{120} = -0.0004$. Thus, we can say that (coincidentally) both batch P115 and batch P116 had aged by similar amounts, such that at the time of use they both appeared higher in salinity than their label values: $C_{115} = 0.0013$–0.0025 and $C_{116} = 0.0009$–0.0021. There is an ambiguity of about 0.001 in the P120–P115 comparison results from the two sets, for which we can offer no explanation. Nevertheless, we present additional examples of P115 and P116 herein that support these results.

c. RRS Discovery *201*

During RRS *Discovery* cruise 201, four batches of SSW were used. See Fig. 3 for the salinometer standardization history. Batch P121 was the newest at 7 months old, batch P120 was 11 months old, batch P116 was 21 months old, and batch P115 was 26 months old. We have made one change to the standard measurements as presented in Pollard (1994). During the cruise, while batch P120 was being used, the Guildline conductivity

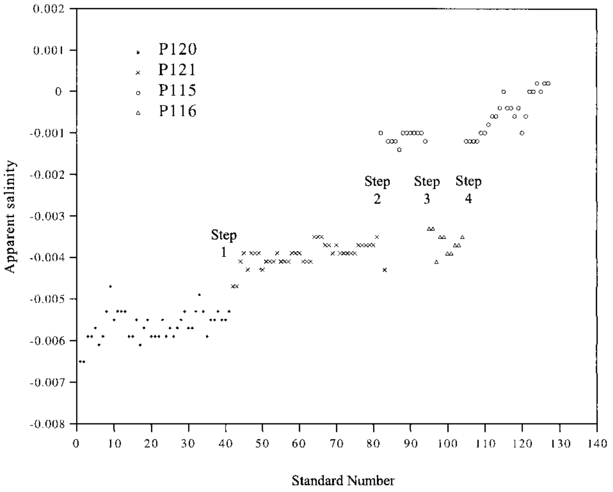

FIG. 3. Salinity standardization history from RRS *Discovery* cruise 201. Standard seawater batches are identified by the key at top left. Apparent salinity is referenced to an arbitrary zero. Changes in batch number are indicated by ordered steps.

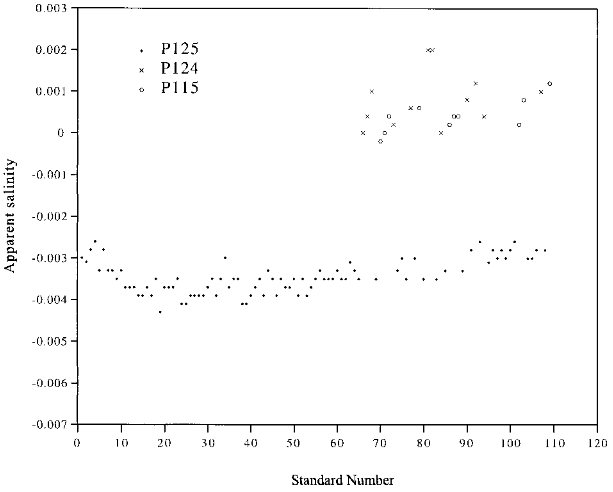

FIG. 4. Salinity standardization history from RRS *Discovery* cruise 213. Standard seawater batches are identified by the key at top left. Apparent salinity is referenced to an arbitrary zero.

ratio (equal to 2K15) began to hover around 1.999 99/2.000 00, which is inconvenient because continual changing of the range setting from 1.9 to 2.0 is needed. Furthermore, although we have never observed any bias at the decade change in our instruments, Mantyla (1987) has. So it is prudent to avoid the decade change. Therefore the standardization dial was adjusted after standard number 33. In Fig. 3, we have removed the effect of this change by offsetting the measurements before the change by an amount equal to the difference between the six measurements before and the six measurements after the change. Care was taken during the cruise to ensure that there were no untoward effects from the change. This does not affect the calculations described herein.

Standard batches were used in groups, as shown in Fig. 3. To calculate differences in apparent salinity between batches, we take the difference between the mean of the six values before and the six values after each change in the batch (or step in Fig. 3). This is to obviate, as far as possible, the effects of long-term drift in the salinometer that would be incorporated into the calculation if the means of all measurements of each batch were used. With the same notation as above, except that superscript now means ‘‘step number,’’ we find that $C^1_{121} - C^1_{120} = 0.0011$, $C^2_{121} - C^2_{115} = -0.0022$, $C^3_{116} - C^3_{115} = -0.0006$, and $C^4_{116} - C^4_{115} = -0.0006$. We refer again to CR98, where we see that at the time of use, P121, the newest batch, had not changed its salinity. Therefore, we find that batch P120 was 0.0011 fresh, batch P115 was 0.0022 higher in salinity, and batches P116 (both estimates) were 0.0014 higher in salinity. Batch P120 thus appears slightly fresher than CR98’s measurements (where it remains 0.0004 fresh), while the estimates for changes in batches P115 and P116 are within the ranges found on RRS *Discovery* 199.

d. RRS Discovery *213*

During the RRS *Discovery* cruise 213, the three SSW batches were P115 (by now 4 years old), P124 (12 months old), and P125 (the newest, 5 months old). There appeared to be difficulties with salinometer stability at the start of the cruise for about the first week, as discussed in Pollard (1995). So Fig. 4 shows the salinometer standardization history excluding the first 27 measurements. The three batches were interleaved toward the end of the cruise. We generate difference statistics using 22 ampoules of batch P125, 12 of batch P124, and 10 of batch P115, from which we find $C_{125} - C_{124} = -0.0007$, $C_{125} - C_{115} = -0.0019$, and $C_{124} - C_{115} = -0.0012$, respectively. Comparing with CR98, these figures are consistent, with batch P125 being unchanged at the time of use, batch P124 being 0.0007 higher in salinity, and batch P115 being 0.0020 higher in salinity. The batch P115 value is again consistent with the values noted above. The greater scatter of batch P124 measurements results in the standard deviation of the relevant differences being 0.0008 (standard error 0.0002).

e. RRS James Clark Ross *10*

Salinity analysis during the RRS *James Clark Ross* cruise 10 was based on batch P125 (8 months old at the time), with some ampoules of batch P120 (36 months old) interleaved as a cross-check. The salinometer standardization history is shown in Fig. 5, from which we can see greater short-term scatter in AS than in RRS *Discovery* and RRS *Darwin* results. We believe this to be due, among other things, to the absence of a constant temperature laboratory on the ship. Ambient temperature control was dependent on the ship’s air conditioning system, which resulted in laboratory temperature fluctuations of about ±3°C. By excluding outliers and se-

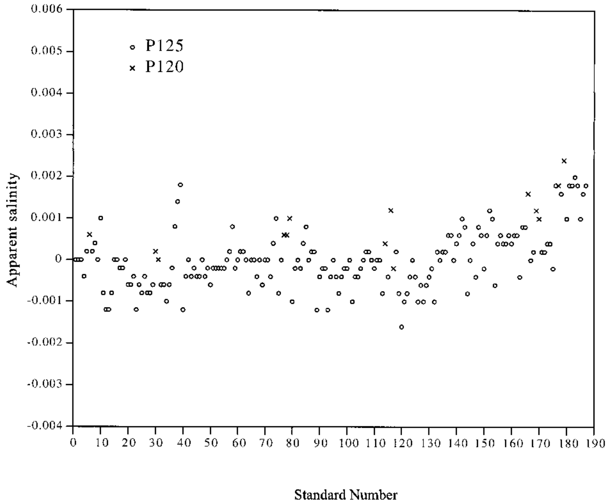

FIG. 5. Salinity standardization history from RRS *James Clark Ross* cruise 10. Standard seawater batches are identified by the key at top left. Apparent salinity is referenced to an arbitrary zero.

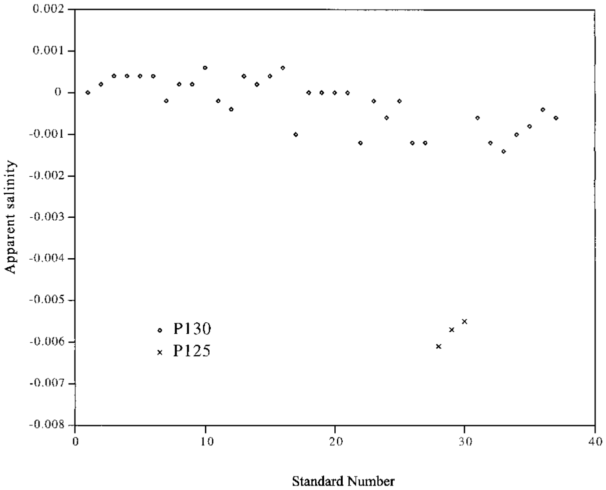

FIG. 6. Salinity standardization history from RRS *James Clark Ross* cruise 16. Standard seawater batches are identified by the key at bottom left. Apparent salinity is referenced to an arbitrary zero.

lecting adjacent batch P120–P125 pairs, we can reduce the noise to an acceptable level. Twelve such pairs result, with $C_{125} - C_{120} = 0.0003$ and the standard deviation of the salinity differences being 0.0009, so that the standard error of the mean difference is 0.0003. We see from CR98 that batch P125 was between 0.000 01 and 0.000 02 low in K15 (0.0004–0.0008 fresh), so that batch P120 was 0.0007 to 0.0011 fresh. We assign the mean salinity change of -0.0009 to batch P120, with an error of 0.0005 from the uncertainty in batch P125 and with a standard error of the mean salinity difference. Similarly, we set the batch P125 salinity change to -0.0006 ± 0.0002.

f. RRS James Clark Ross *16*

The RRS *James Clark Ross* cruise 16 was based on batch P130 (7 months old), with 3 ampoules of batch P125 (now 27 months old) included for comparison. See Fig. 6 for the salinometer standardization history. In the year and a half between cruise 10 and cruise 16, temperature control improved somewhat. In addition, a smaller number of more experienced operators were employed for salinity analysis. The reduction in scatter is evident. The salinity difference between batches P125 and P130 was calculated using six measurements of batch P130 on either side of the three of batch P125, resulting in $C_{130} - C_{125} = 0.0010$, with a standard deviation of 0.0006 and an a standard error of 0.0004 (assuming three degrees of freedom) of the mean salinity difference. There is no measurement of batch P130 in CR98, but assuming it to have been of label salinity at 7 months age, batch P125 appears now to be 0.0010 fresh. Ten months later at 17 months (see section 2g), batch P130 appeared to be 0.0007 higher in salinity. If batch P130 were 0.0004 higher in salinity—a typical measured change over 7 months in CR98—then batch P125 would be 0.0006 fresh. We assign the mean of these estimates (-0.0008) to the salinity change of batch P125 and add the range to the standard error to produce an error of ± 0.0006. Similarly, we set the batch P130 salinity change to 0.0002 ± 0.0002.

g. RRS Discovery *230*

On the RRS *Discovery* cruise 230, we used batches P128 (the oldest, 25 months old), P130 (17 months old), P131 (9 months old), and P132 (the newest, 4 months old). Batches were used in groups. So we calculate mean differences from steps (using six measurements from each side of the step, as before) except for the final comparison set, which was interleaved. The standardization history is shown in Fig. 7. The results are as follows: $C^1_{130} - C^1_{128} = -0.0008$, $C^2_{131} - C^2_{130} = 0.0000$, $C^3_{132} - C^3_{131} = -0.0008$, $C^4_{130} - C^4_{128} = -0.0011$, $C^4_{131} - C^4_{130} = -0.0005$, and $C^4_{132} - C^4_{131} = -0.0001$. We assume that batch P132 was at its label salinity, so that batch P131 appears 0.0001 or 0.0008 higher in salinity, batch P130 appears 0.0006 or 0.0008 higher in salinity, and batch P128 appears 0.0016 or 0.0017 higher in salinity. These difference calculations are generally very consistent, but for batch P131 they are a little less consistent. However, as can be seen in Fig. 7, the measurements of batch P131 were more scattered than the measurements of the other batches (the standard deviation of the differences is 0.0009), which at the time of the cruise led us to cease using batch P131. CR98 offer no SSW measurements beyond batch P129. So we can compare our batch P128 measurements with CR98's P128 measurements when batch P128 was 9 months old, at which time it had grown higher in K15 by 0.000 02—equivalent to 0.0008 in salinity. Our measurements were

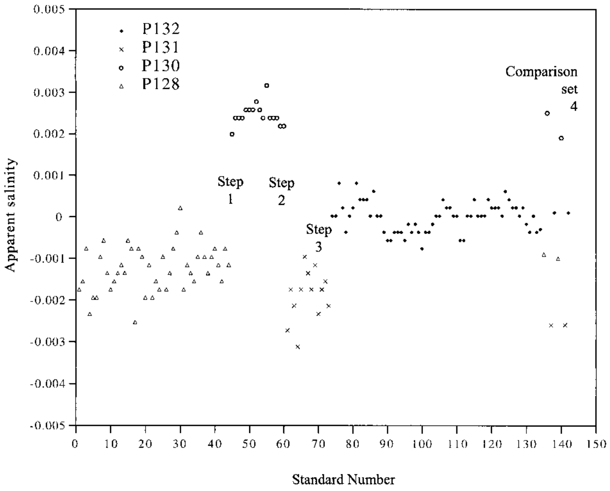

FIG. 7. Salinity standardization history from RRS *Discovery* cruise 230. Standard seawater batches are identified by the key at top left. Apparent salinity is referenced to an arbitrary zero. Steps number the batch changes described in the text. The comparisons made within the final group of measurements (set 4) are numbered in the same sequence.

made an additional 17 months after CR98's measurements.

Batch P128 was used as standard while the ship was in the eastern North Atlantic at 41°30′N. Therefore, we can examine the θ–S relationship in the same way it is examined in section 2a, using M94 again for the 41°30′N latitude. The results are shown in Fig. 8, which incorporates data from stations 20–36 (Bacon 1998). The mean salinity offset for $2.1 < \theta < 2.4$°C is -0.0019 (the standard deviation is 0.0009; samples minus M94 estimate), which is nearly identical to our inferences noted above (a standard of too-high salinity results in overcorrected measurements that thereby appear fresh).

3. Discussion

Combining our measurements with those of CR98, we have demonstrated how the salinity of ampoules of SSW can evolve with time. In Table 2, we summarize the changes by batch and age. All of the measurements are consistent, including the comparisons with Mantyla's (1994) deep northeast Atlantic water-mass relationship. The data of Table 2 are plotted in Fig. 9 as salinity change versus age. It is notable that for particular batches in which multiple estimates of salinity changes with time (over months and years) are available (for example, batch P115), these changes appear smoothly evolutionary—that is, not noisy or jumpy. This alone is suggestive of skill in our measurements. CR98 recommend that SSW should not be stored for longer than 96 weeks (22 months). Figure 9, however, demonstrates that to obtain the highest quality data, SSW should not be stored for than 12 months, when all estimates of salinity change lie within ±0.001.

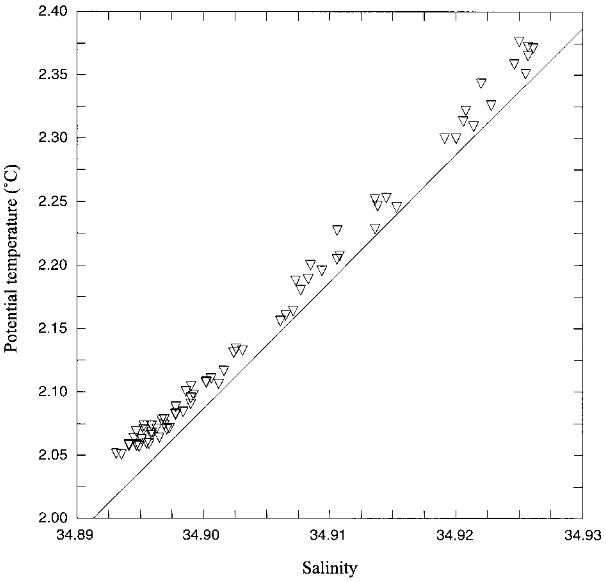

FIG. 8. Deep θ–S bottle data from RRS *Discovery* cruise 230 (uncorrected). Stations are in the eastern North Atlantic along 41°30′N. The line shows the θ–S relationship predicted by Mantyla's (1994) formulation for 41°30′N.

TABLE 2. Changes in salinity values of IAPSO standard seawater with age. Sources of error values and incorporation of CR98 data are detailed in the notes.

Batch	Age (months)	Salinity change ± error	Notes
P115	6	0.0001 ± 0.0002	(1)
	23	0.0019 ± 0.0006	(2)
	26	0.0022 ± 0.0002	(3)
	48	0.0020 ± 0.0002	(3)
P116	18	0.0015 ± 0.0006	(2)
	21	0.0014 ± 0.0002	(4)
P120	9	−0.0004 ± 0.0002	(5)
	11	−0.0007 ± 0.0004	(6)
	36	−0.0009 ± 0.0005	(7)
P121	7	0.0000 ± 0.0002	(5)
P124	12	0.0007 ± 0.0002	(3)
P125	5	0.0000 ± 0.0002	(5)
	8	−0.0006 ± 0.0002	(7)
	27	−0.0008 ± 0.0006	(8)
P128	25	0.0017 ± 0.0002	(1) and (2)
P130	7	0.0002 ± 0.0002	(8)
	17	0.0007 ± 0.0001	(2)
P131	9	0.0004 ± 0.0004	(2)
P132	4	0.0000 ± 0.0002	(9)

(1) Mean difference and standard error about M94 line.

(2) Mean value is average of extremes; range covers extremes.

(3) Single estimate; error is standard error of mean difference (section 2).

(4) Two equal estimates; error is standard error of mean difference (section 2).

(5) Value from CR98; error is CR98 measurement precision.

(6) Mean and range of section 2c and CR98 estimates.

(7) See section 2e.

(8) See section 2f.

(9) Assumed as (5).

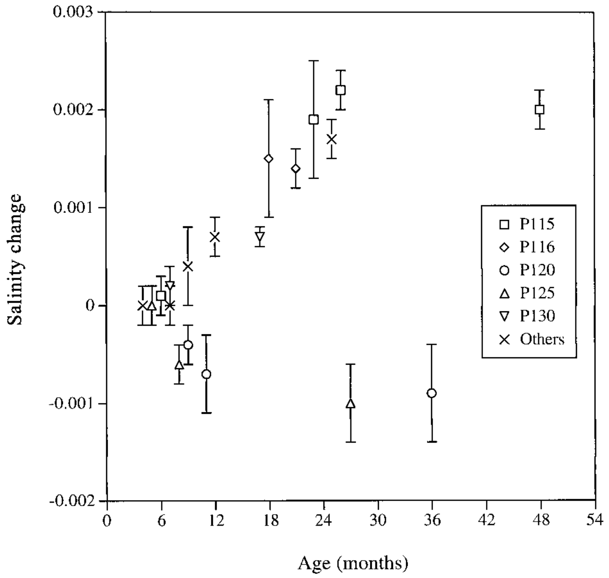

FIG. 9. All standard seawater salinity changes are plotted against age. The data values are given in Table 2. The key shows five batches plotted with individual symbols; all other batches are plotted with one symbol.

In Fig. 9, salinity appears to evolve along two branches: one in which batches freshen, and one in which they grow higher in salinity. Mantyla (1980) and CR98 suggest that increased conductivity could be due to microbial activity and a change in the pH of the SSW. They suggest that decreased conductivity could be due to dissolution of the glass ampoule. In the latter case, there is more dissolved material in the SSW, but the measured salinity is lower because the silica is nonconductive. Interestingly, the two branches remain separate, suggesting that the two effects do not alternate or run in tandem—at least in our relatively small number of SSW histories.

The question of the accuracy of our values for SSW salinity change remains slightly open, however. This is related also to the issue of quoting salinities to four decimal places. For this study's measurements, we quoted above the basic standard error of the mean salinity differences of 0.0002. With many (similar) measurements of the same quantity, the precision is therefore statistically meaningful. It is of doubtful use, though, when applied to individual sample measurements. On the one hand, the unexplained difference in section 2a of 0.0010 in estimates of batch P115 drift is not covered by this (±0.0002) range. On the other hand, some of the estimates appear to have the lower error of 0.0002, such as the three independent sources of batch P128 salinity. Table 2 gives the best likely error for each set of measurements, as explained in section 2.

We cannot find in the literature an estimate of the accuracy of the determination of the label salinity in IAPSO SSW. The *precision* of the determination of K15 is 0.000 01. So the accuracy in salinity cannot be better than ±0.0002. At this stage, we claim for our own estimates of SSW salinity a worst accuracy of 0.0005. It should be remembered that this must be added (in an rms sense) to the approximate 0.0007–0.0010 accuracy of the ''routine best practice'' at-sea individual sample salinity determination to obtain the true accuracy of oceanic salinity measurement. True accuracy of salinity measurement of 0.001, as required by WOCE, is probably just within reach of best practice, but as seen in Fig. 9, we might expect uncorrected between-cruise differences in salinity to be possibly over 0.003 if old batches of SSW were used.

Early batches of SSW may have suffered from salinity changes that we would now consider unacceptably large. There may also have been a problem with the batches being calibrated in chlorinity but not in conductivity, leading to an at least partially correctable error (or offset) when used as a conductivity standard (Mantyla 1980). We do not believe this to be the case for more modern batches. However, Aoyama et al. (1998, A98 hereafter) persist in the adoption of the notion of offset in terms of a fixed error in SSW salinity. There are some noteworthy discrepancies between A98's claims and ours.

First, A98's accuracies are formulated in terms of measurement precision and within-batch variability: it is not clear whether the latter may be measurement error. We operate salinometers at the very limit of their measurement capacity. It is not easy to tell whether short-term variability as seen in AS (for example, see section 2b) is ''within-batch variability'' or instrument noise, or some combination of the two. Our experience of salinometer operations inclines us to believe that short-term instrument variability is generally the dominant cause, although we occasionally see high SSW variability, as in the case of batch P131 in section 2g.

Second, there are important individual differences between A98's offsets and our age-dependent salinity changes. In particular, 1) A98 claim that batch P120 is over 0.002 fresh. It may have been so when they measured it, but it is not appropriate to apply this as a blanket correction to all cruises that used batch P120, such as RRS *Discovery* 199 and 201, when we show it to have been ca. 0.0005–0.0010 fresh. 2) They claim batch P128 to be correct (0.0001 different from label salinity), whereas we show with some confidence that at the time of use on RRS *Discovery* 230, batch P128 was 0.0015–0.0020 higher in salinity. There are further discrepancies between values for batch P116—our values are 0.0015 higher in salinity, and A98's are 0.0001 higher in salinity—for batch P121, which is correct according to CR98 and 0.0009 fresh according to A98, and for batch P124, which is correct, according to our measurements and 0.0007 fresh according to A98. Other batches used in this study were not available to A98.

Third, we note that 9 of the 10 newest batches analyzed by A98 had negative offsets, with a mean of −0.0008, which is an unlikely bias for fresh batches calibrated to the KCl standard. Adding 0.0008 to A98's batches P116, P120, P121, and P124 brings A98's results closer to this study's results. Thus, we suspect that A98's measurements (at least those of more recent batches) have a negative bias in salinity on the order of 0.001.

We caution against the uncritical use of such offsets, which have been applied already in a study of WOCE section crossings by Gouretski and Jancke (1998). Gouretski and Jancke (1998) find that the application of the offsets of A98 results in a decrease of mean absolute section-to-section salinity difference from 0.0023 to 0.0019, wherein individual differences are decreased in 32 cases but *increased* in 20 cases. We believe that the cases of worsening are caused at least partly by the application of corrections inappropriate to the age of the SSW batch used on the relevant section cruises.

Finally, although SSW errors are not the only source of salinity bias, we would encourage all groups involved in at-sea salinity measurement to perform the kind of analysis shown here. It requires that the salinity standardization dial on the salinometers remains unchanged throughout each cruise. In addition, the dial must be set sufficiently low enough that any reasonable salinometer drift would not cause the measured double conductivity ratio of the SSW to impinge on the 1.9–2.0 decade change. By combining all such results, salinity histories could be generated for each batch of SSW, as long as no extraneous effects intervene, such as CR98's suggestion that storage conditions may be important. Corrections derived from such histories would allow the highest accuracy absolute salinity measurements to be obtained throughout the World Ocean.

Acknowledgments. The authors thank the two anonymous referees, one of whom, in particular, provided some very helpful comments.

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