NOTES AND CORRESPONDENCE

Standard Seawater Comparisons Updated

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ABSTRACT

Salinity adjustments that may reconcile differences in results from different expeditions are presented. These corrections are based upon batch-to-batch differences in Standard Seawater (SSW) after comparison with KCl-derived standards.

Earlier SSW comparisons have shown that the chlorinity/conductivity relationship is not the same for all batches. Salinometers were standardized in terms of conductivity, while SSW was formerly labeled in terms of chlorinity. Labeling of SSW in terms of conductivity relative to a standard KCl solution was expected to eliminate SSW batch-to-batch differences. New SSW comparisons, presented below, reveal that while conductivity-labeled SSW batch-to-batch differences have been reduced, significant differences between batches persist. The new results have been adjusted relative to the KCl standard as defined by the Practical Salinity Scale, 1978. In the past, it had not been possible to make absolute corrections to expedition salinities to account for SSW systematic errors because no absolute reference standard was available. It is now possible to account for SSW errors relative to a reproducible KCl standard.

1. Introduction

Electrical conductivity comparisons of Standard Seawater (SSW) batches P29 to P84 were summarized in 1980 (Mantyla, 1980); this report extends the intercomparisons to batch P102. Prior to SSW batch P91 (prepared 10 March 1980), SSW was certified for chlorinity only, although in practice SSW has been treated as a conductivity standard to standardize salinometers. However, earlier comparisons between SSW batches by Poisson et al. (1978) and others have shown that the chlorinity-conductivity relationship was not the same for all batches; they recommended that SSW should be calibrated relative to a potassium chloride solution. That recommendation resulted in a new practical salinity scale defined in terms of a standard KCl solution having a conductivity equivalent to SSW = 35‰ (Cl = 19.37394‰). A special issue of the IEE Journal of Oceanic Engineering (Dauphinee, 1980) contains papers that discuss the rationale for the new salinity scale and also show the measurements used to establish the Practical Salinity Scale 1978 (PSS78). Starting with batch P91, SSW has been labeled in terms of the conductivity ratio, K_{15}, of SSW relative to standard KCl solution (32.4356 g kg^{-1}). Chlorinity is also provided on the label, but is regarded as an independent variable. With SSW being labeled in terms of conductivity, batch-to-batch discrepancies were expected to be eliminated. As will be shown in the following, the new labeling has improved the consistency between batches, but significant differences between batches remain.

2. Methods

The double conductivity ratio was measured for 46 different batches of SSW (run in random order) in July 1985. Additional runs were made two months later on nine of the batches. The experiments were done on two different model 8400 Guildline Autosal salinometers. SSW batch P96 was used to standardize both machines and additional ampules of P96 were run periodically during the experiments. The repeated runs on P96 verified that the salinometers did not drift during either experiment. All double conductivity readings were made on the same suppression dial setting (1.9) in order to avoid possible discontinuities between the 1.9 and 2.0 settings. A similar procedure was used by Dauphinee (Poisson et al., 1978) and is currently used by the Standard Seawater Service (F. Culkin, private communication, 1985). An example of a discontinuity between suppression dial settings is shown in Fig. 1. If undetected, such machine errors would result in systematic offsets for salinities greater than 35 compared to salinities less than 35 run on the same machine. From comparisons of relative salinity errors for SSW batches above and below 35*S* in each of the experiments listed in Mantyla (1980), the problem does not seem to have occurred in the previous SSW comparison experiments. Salinometer discontinuities have, however, been detected on expeditions (Transient Tracers in the Ocean Expedition, R. T. Williams, personal communication, 1985; Ajax Expedition, Scripps Institution of Oceanography Reference 85-24).

Conductivity salinities from the 1985 S.I.O. exper-

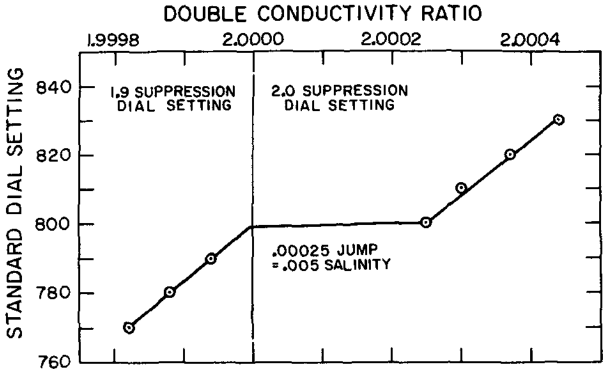

FIG. 1. Example of discontinuity between suppression dial settings detected on one of SIO's older Autosal salinometers. The salinometer was filled with SSW and the double conductivity ratio recorded at uniform increments of standard dial settings. The jump between the 1.9 and 2.0 suppression dial setting results in a salinity error of 0.005*S* for salinity samples that are less than 35 when the salinometer is calibrated with SSW that is greater than 35. The salinometer has since been repaired. This type of salinometer error has been detected on other types of salinometers also.

iments were calculated from the algorithms for the Practical Salinity Scale, 1978 (UNESCO, 1981). The differences between the new PSS78 and the old UNESCO (1966) salinity scales are less than 0.001 between 34 and 36 salinity; thus, the results from the present experiment may be compared directly with earlier results. The expected salinities for SSW batches prior to P91 were calculated from the chlorinity listed on each ampule with the equation $S = 1.80655$ Cl; and the expected salinities for SSW batches P91 to P102 were calculated from the labeled K_{15} conductivity ratios using the PSS78 equations.

The precision of the analyses as inferred from the 15 repeat runs on P96 was $0.2 \times 10^{-3}S\,(1\sigma)$ comparable to the $0.4 \times 10^{-3}S$ precision estimates from earlier experiments by Mantyla (1980) and Millero et al. (1977). Several ampules from older batches contained visible particles or greasy coatings inside the ampule. Also, one ampule of P101 had a hairline crack in the ampule and was very high in salinity. All of the ampules containing obvious contaminants (P35, P37, P54, and P56) gave erroneous results and have been omitted. One ampule of P96 was also very high without obvious reason and is also omitted from the following.

3. Results

Table 1 summarizes the results from the 1985 SSW comparison experiments. The difference between the measured salinity (relative to P96) and the expected salinity from each ampule label is shown, as well as the usual SSW label information. The standard deviation of replicate runs is also given, where appropriate.

It is of interest to compare the last 12 batches labeled with K_{15} values with the previous 12 batches labeled with chlorinity only. Both groups have similar mean offsets relative to P96, -1.1×10^{-3}, $\sigma = 0.8 \times 10^{-3}$ for the K_{15} group and -0.9×10^{-3}, $\sigma = 1.8 \times 10^{-3}$ for the Cl group, but the chlorinity group has twice as much scatter as the K_{15} group. The last 12 batches calculated from the labeled *chlorinity* also have a standard deviation of 1.9×10^{-3}, so the increased scatter from the older batches is not just a consequence of deterioration with age (believed to occur in some batches). Thus the PSS78 change to a conductivity standard *has* improved the SSW batch-to-batch agreement. However, the disagreement between the K_{15} labeled SSW batches is still greater ($\sigma = 0.8 \times 10^{-3}$) than can be attributed to modern measurement precision ($\sigma = 0.2 \times 10^{-3}$, based upon the repeated runs on P96); the disagreement between P92 and P96 is nearly 0.003. The source of the discrepancy between batches is most likely due to changes in the natural seawater used to prepare SSW after preparation and distribution by the Standard Seawater Service (Chen and Gordon, 1979; Mantyla, 1980).

SSW batch P79 was one of the primary batches used to establish the concentration of the new KCl standard (Perkin and Lewis, 1980; Dauphinee et al., 1980; Culkin and Smith, 1980; Poisson, 1980); it was also the batch used in the S.I.O. 1979 experiment as the reference for comparisons of batches P29 to P84. In the present experiment, the repeated runs on P79 show greater scatter than in the 1979 experiment and also P79 now appears to be higher in salinity. Figure 2a illustrates the results from both the 1985 (solid line and triangles) experiment relative to P96 and the 1979 (dashed line and circles) experiment relative to P79. Figure 2b shows the change in salinity offsets between the 1979 and 1985 for SSW batches common to both experiments. The mean difference between the two experiments is zero, with several old and recent batches showing no significant change; thus, both experiments may be compared directly. However, several batches show greater change than can be explained by experimental error. Some older batches are now lower in conductivity salinity. Solution of silica from the glass ampules, precipitation of inorganic material or formation of organic films all lower the conductivity salinity. Any or all of these possibilities could be responsible for the lower conductivity of some of the older batches. Batches P77, P78, P79, P80 and P82 are now higher in conductivity salinity (although P81, P83 and P84 are not). Oxidation of organic material and a lowering of the pH of the SSW would result in increased conductivity salinity. It appears that batch P79 is not a stable batch and the results of the S.I.O. 1979 experiment, which assumed P79 to be correct relative to the new KCl standard, may be offset because P79 (prepared in 1977) could also have changed between the time of the KCl − P79 comparison and the 1979 S.I.O. experiment. SSW batch P96 does not appear to be rep-

TABLE 1. Differences of measured salinity (S_{MEAS}) and SSW label derived salinity (S_{LABEL}) referred to batch P96, July 1985 and September 1985 (in bold face) SIO experiments.

Batch	Preparation date (d-mo-yr)	Cl	S_{Cl}	K_{15}	$S_{K_{15}}$	$(S_{MEAS} - S_{LABEL}) \times 10^3$	Mean $\Delta S \times 10^3$	Std. dev.
P36	23/24-9-62	19.375	35.0019			−2.4	−2.4	—
P40	26/27-10-63	19.375	35.0019			−2.0	−2.0	—
P41	7/8-11-64	19.373	34.9983			−0.8	−0.8	—
P42	30-5-65	19.376	35.0037			−4.1	−4.1	—
P43	12-2-66	19.373	34.9983			−4.5	−4.5	—
P44	13-2-66	19.374	35.0001			−0.4	−0.4	—
P45	3-12-66	19.376	35.0037			−2.8	−2.8	—
P46	4-12-66	19.377	35.0055			−4.9	−4.9	—
P47	15/16-4-67	19.374	35.0001			−2.0	−2.0	—
P52	18/19-10-69	19.3705	34.9938			−0.4	−0.4	—
P59	6-8-72	19.377	35.0055			−1.0	−1.0	—
P61	26-11-72	19.3785	35.0082			−2.7	−2.7	—
P63	3-6-73	19.375	35.0019			−4.1	−4.1	—
P70	18-9-75	19.375	35.0019			−1.1	−1.1	—
P73	12-6-76	19.375	35.0019			−1.6	−1.6	—
P76	7-4-77	19.376	35.0037			1.5, **1.1**, **0.7**	1.1	0.4
P77	14-4-77	19.3755	35.0028			0.8, **0.7**, **1.0**	0.8	0.2
P78	20-9-77	19.377	35.0055			3.8, **2.1**, **1.5**, **3.8**, **1.5**, **1.0**, **1.3**, **1.5**, **1.2**, **1.9**, **1.7**	1.9	1.0
P79	24-9-77	19.376	35.0037			1.3, 0.4, 1.8, 3.0, **1.5**, **2.7**, **1.7**, **2.1**	1.8	0.8
P80	23-3-78	19.378	35.0073			3.0, 2.7, **2.4**, **2.6**, **2.3**, **2.3**	2.6	0.3
P81	15-4-78	19.3695	34.9920			−1.0, 0.0, **0.1**, **0.9**	−0.4	0.6
P82	10-5-78	19.3705	34.9938			1.0	1.0	—
P83	11-10-78	19.3755	35.0028			−1.5	−1.5	—
P84	14-10-78	19.376	35.0037			−1.7, −1.3	−1.5	—
P85	25-4-79	19.3760	35.0037			−2.3, −2.1	−2.2	—
P86	28-4-79	19.3770	35.0055			−2.7, −2.3	−2.5	—
P87	29-11-79	19.375	35.0019			−2.0, −1.8	−1.9	—
P88	1-12-79	19.3760	35.0037			−2.1, −2.3	−2.2	—
P89	3-12-79	19.3745	35.0010			−1.4	−1.4	—
P90	7-5-80	19.3755	35.0028			−3.4, −2.5, **−3.4**, **−3.3**, **−3.8**, **−3.9**	−3.4	0.5
P91	10-5-80	(19,376	35.0037)	1.00007	35.0027	−2.3, −2.0	−2.2	—
P92	29-10-81	(19.372	34.9965)	0.99988	34.9953	−2.8, −2.7, −2.4, **−2.5**, −3.0	−2.7	0.2
P93	31-10-81	(19.373	34.9983)	0.99990	34.9961	−1.7, −1.4	−1.6	—
P94	18-11-81	(19.373	34.9983)	0.99992	34.9969	−1.6, −1.3	−1.4	—
P95	8-3-83	(19.373	34.9983)	0.99997	34.9988	−0.4, −0.2	−0.3	—
P96 (Ref. Std.)	3-3-83	(19.375	35.0019)	1.00006	35.0023	**0.1**, 0.2, 0.1, −0.3, 0.2, 0.1, 0.2, 0.2, −0.4, **−0.1**, **−0.2**, **0.0**, **0.0**, **0.0**, **0.5**	0.0	0.2
P97	3-3-83	(19.374	35.0001)	1.00002	35.0008	−0.3, −0.5	−0.4	—
P98	3-3-83	(19.3725	34.9974)	0.99993	34.9973	−0.6, 0.1	−0.4	—
P99	27-7-84	(19.3745	35.0010)	0.99997	34.9988	**−1.7**, −1.5	−1.6	—
P100	29-11-84	(19.376	35.0037)	1.00003	35.0012	**−1.5**, −1.5	−1.5	—
P101	4-6-85	(19.377	35.0055)	1.00002	35.0008	**−0.7**	−0.7	—
P102	29-11-84	(19.3755	35.0028)	1.00001	35.0004	**−1.0**, −0.9	−1.0	—

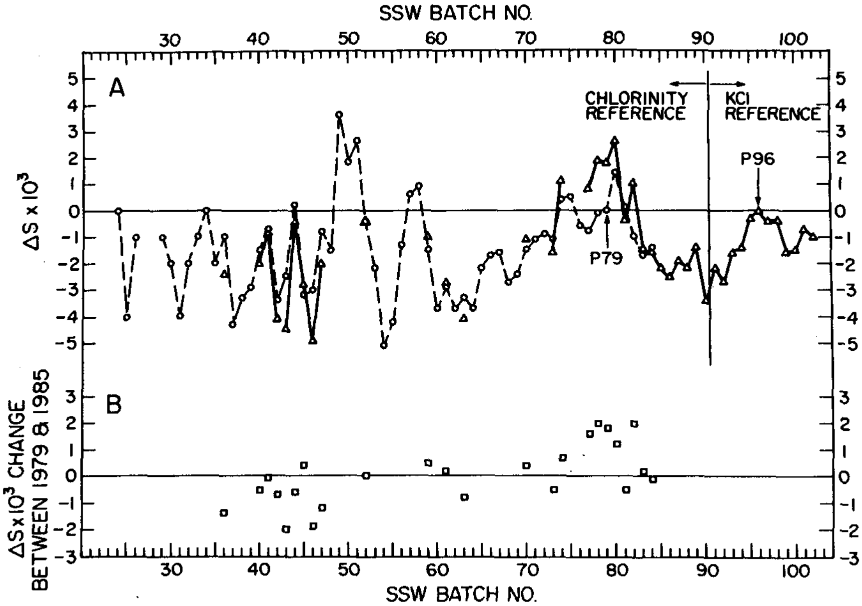

FIG. 2. a) Relative comparisons between various batches of SSW. Dashed line and circles: results of Mantyla (1980, Fig. 4) summary, relative to SSW batch P79. Solid line and triangles: SSW differences relative to batch P96, as reported in this work. Differences are calculated from the experimental results minus labeled values, $\Delta S \times 10^3$. Batches prior to P91 were labeled in terms of chlorinity; recent batches are labeled in terms of conductivity ratio determined from comparisons with KCl solutions. b) change in ΔS between the 1979 and 1985 experimental results.

resentative of the KCl labeled batches (P91 − P102) either; all of the other KCl labeled batches would be lower in conductivity salinity than expected from the labeled value if P96 were correct. There is nothing special about batch P96; it was used as the reference in the 1985 S.I.O. experiments simply because it was the most recent batch available in quantity at S.I.O. Since SSW batches P91 to P102 were all prepared with reference to standard KCl solutions, all are equally valid. Past SSW comparisons have consistently shown similar relative batch-to-batch differences, but it has not been possible to assign absolute errors to the various SSW batches because selection of any particular batch of SSW as the reference would have been arbitrary. Since batches P91 to P102 were all prepared with reference to the newly defined KCl standard, the mean from those batches should be used as the absolute reference to establish SSW batch-to-batch offsets. Results from the 1979 S.I.O. summary (Mantyla, 1980), an unpublished 1982 S.I.O. experiment, and the present experiment have been offset to the KCl standard and are shown in Table 2. The last column in Table 2 lists the consensus of the three experiments, weighted towards the earlier experiments in order to reflect conditions when the batches were relatively new and likely to have been used on expeditions; it is the correction that may be used to correct expedition salinities for relative SSW errors.

4. Discussion

Secular changes in bottom water characteristics close to source regions have been noted by Foster and Middleton (1979), Brewer et al. (1983) and Swift (1984); mid-depth changes at lower latitudes have also been observed in the North Atlantic by Roemmich and Wunsch (1984). The high precision of modern oceanographic measurements makes the detection of secular changes in active regions of the ocean feasible. However, Worthington's (1981) fine-scale volumetric census of the world ocean indicates that there are large areas where the abyssal characteristics are quite uniform. Great accuracy in oceanographic measurements is required in those regions, both to detect secular changes and to be able to merge data from different expeditions for regional studies. One source of systematic error that has occurred on expeditions is due to relative batch-to-batch differences in SSW. Mantyla (1980) showed two examples where abyssal θ–S agreement was improved when SSW differences were accounted for. The 0.005 relative error between batches P80 and P90 observed in the present experiment has been confirmed at sea on the TTO expedition (R. T. Williams, personal communication, 1985); both batches were used on the expedition. The TTO data report (S.I.O. Reference 86-15) lists salinities relative to batch P80. Saunders (1986) noted salinity differences between modern cruises that

TABLE 2. Summary of $(S_{MEAS} - S_{LABEL}) \times 10^3$ from various experiments adjusted to the PSS78 KCl standard.

Batch	SIO[a] 1979	SIO[b] 1982	SIO[c] 1985	"MEAN"[d]	Batch (Cont.)	1979	1982	1985	"MEAN"
P29	0			0	P66	−0.5			0
P30	−1			−1	P67	−0.4			0
P31	−3			−3	P68	−1.5	−1.4		−1
P32	−2			−2	P69	−1.2			−1
P33	0			0	P70	−0.3		0.1	0
P34	1			1	P71	0.1			0
P35	−1			−1	P72	0.3			0
P36	0	0.2	−1.2	0	P73	0.1		−0.4	0
P37	−3.1			−3	P74	1.6			2
P38	−2.1			−2	P75	1.7			2
P39	−1.7			−2	P76	0.6		2.3	1
P40	−0.3		−0.8	0	P77	0.4		2.0	1
P41	0.5	−0.1	0.4	0	P78	1.1	1.6	3.1	1
P42	−2.2		−2.9	−2	P79	1.2	1.9	3.0	1
P43	−1.3		−3.3	−1	P80	2.6	2.4	3.8	3
P44	1.4		0.8	1	P81	1.3	0.8	0.8	1
P45	−2.0		−1.6	−2	P82	0.2	0.9	2.2	0
P46	−1.8		−3.7	−2	P83	−0.5	0.2	−0.3	0
P47	0.4		−0.8	0	P84	−0.2	−1.1	−0.3	0
P48	−0.3			0	P85		−0.9	−1.0	−1
P49	4.8			5	P86		−1.4	−1.3	−1
P50	3.0			3	P87			−0.7	−1
P51	3.8	3.2		4	P88			−1.0	−1
P52	0.8		0.8	1	P89			−0.2	0
P53	−1.0			−1	P90		−1.8	−2.2	−2
P54	−3.9			−4	P91			−1.0	−1
P55	−3.0			−3	P92			−1.5	−2
P56	−0.1			0	P93			−0.4	0
P57	1.8			2	P94			−0.2	0
P58	2.1			2	P95			0.9	1
P59	−0.3	0.8	0.2	0	P96			1.2	1
P60	−2.5			−3	P97			0.8	1
P61	−1.7		−1.5	−2	P98			0.8	1
P62	−2.5			−3	P99			−0.4	0
P63	−2.1		−2.9	−2	P100			0.3	0
P64	−2.6			−3	P101			0.5	0
P65	−1.0			−1	P102			0.2	0

[a] From Mantyla (1980).
[b] Unpublished SIO experiment.
[c] This work, run 17 July and 18 September 1985.
[d] Recommended SSW correction weighted towards early comparisons to correspond to likely date of SSW use.

occupied deep stations in the Northeast Atlantic Basin; those differences are reduced by a factor of two when SSW relative batch errors are accounted for. The 0.003 difference between P92 and P96 has also been confirmed by deep θ–S comparisons between two expeditions in the North Pacific (Talley, personal communication, 1986). Marathon Expedition (unpublished data) used batch P92 and Trans-Pacific Section—47°N (unpublished data) used batch P96 as a reference standard. Undetected systematic errors may still occur if the samples are run on a faulty salinometer such as shown in Fig. 1; that type of error happens most often when the SSW batch is greater than 35S and the target salinity is less than 35 (typical of abyssal world ocean waters, Worthington, 1980). Deep-basin salinity comparisons in regions remote from fresh bottom water sources are a last resort for detecting cruise-to-cruise salinity errors.

5. Conclusions

That relative SSW batch-to-batch errors occur has been well documented by several studies. The SSW errors are now known to have resulted in systematic errors in expedition salinity results. The results from this study now provide a means to correct one source of systematic salinity error relative to a known and repeatable KCl standard. The source of the various SSW errors remains somewhat speculative, but there are indications (Mantyla, 1980) that disagreement between SSW batches might be minimized by reducing the dissolved organic matter in the natural seawater used to prepare SSW. Alternatively, standard reference solutions of KCl might be prepared, but even the effects of solution of the container may be detectable with the sensitivity of modern salinometers. For the present, the prudent course would be to continue monitoring

SSW batch-to-batch comparisons, preferably by more than one laboratory, and to report which batch of SSW was used to determine expedition salinities.

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