On the Use of a Secondary Standard to Improve Autosal Calibration

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ABSTRACT NO. 751348, PAPER NUMBER IT25T-08

Sea-Bird Electronics is an oceanographic instrumentation and technology company that relies on exceptionally accurate analytical salinity procedures to perform instrument calibrations to WOCE level standards. Sea-Bird uses IAPSO Standard Seawater as its primary salinity standard to generate offset corrections for its Guildline Autosal laboratory salinometers. These corrections are implemented computationally rather than making adjustments to the Autosal electronics. Driven both by the desire for part per million (ppm) accuracy and the high volume of work being performed daily in the calibration facility, Sea-Bird developed an independent secondary seawater standard to run side-by-side with IAPSO primary standard. This added protocol allows for precise tracking of Autosal salinities and subsequent adjustments of Autosal drift. Results have thus far demonstrated that the drift for Sea-Bird's primary Autosal units is minor, typically less than 1-2 ppm over a one-day period. The secondary standard also allows the detection of offsets between batches of primary standard water. An experiment analyzing multiple bottles of primary and secondary standards, including bottles from multiple IAPSO batches, identified a nearly 2 ppm offset between IAPSO Batches P150 and P151. An offset of this magnitude has a significant implication for the accuracy of field data.

INTRODUCTION

Why Use a Secondary Standard?

- Sea-Bird's Autosal is used for several hours per day, 5-6 days per week. There was the traditional concern that the initial calibration with IAPSO Standard Seawater performed at the beginning of a sample run might not hold constant over the entire measurement session.
- The drift of the Autosal over time can be easily measured by running additional samples of IAPSO Standard Seawater and assigning linear drift to the Autosal.
- Developing a secondary standard to monitor Autosal drift has a distinct economic advantage, allowing additional data points at modest cost.

METHODS

Practices to Achieve High-Accuracy, High-Precision Autosal Results

- Autosal computationally rather than mechanically standardized.
  - Offset correction derived from bottle of IAPSO standard water and applied to each subsequent reading.
  - Standardize dial of Autosal NOT adjusted.
- Bath temperature precisely measured with SBE 35 Deep Ocean Standards Thermometer, allowing more accurate salinity
- calculations.
- Room temperature maintained 2-5 °C below Autosal bath temperature (approximately 19-22 °C).
- Before use, Autosal warmed-up with water close to 35 PSU.
- Primary and secondary standard water stored in same room as Autosal, to normalize sample water temperatures.
- Small number of operators used to limit operator bias.
- Room temperature and humidity monitored throughout Autosal run.
- Stand-By and Zero diagnostics monitored.
  Autosal readings recorded with proprietary software to decrease transfer errors.

Creation of Secondary Standard

- Natural seawater filtered and adjusted to be near 35 PSU via dilution with deionized water or evaporation.
- Water siphoned from 55-gallon drum and bottled into sequentially numbered batches of 360 bottles.
- Several of the very first and very last bottles to be filled (6-12 bottles total) are analyzed to determine nominal salinity for that batch.
- Analysis also ensures no drift has occurred during the bottling process itself.
- Batches exhausted by Sea-Bird in approximately 1 month.

RESULTS

Verification of Autosal Practices

Table 1: *Effect of Autosal Bath Temperature Post-Standardization on Salinity of Sea-Bird Secondary Standard Batch SS64.*

Autosal Thermistor	Average Autosal Bath Temperature (°C) (measured by SBE 35 SN 0055)	Average Salinity of SS64 (PSU)
2	23.9918	34.9526
1	24.0069	34.9646
2	23.9917	34.9527
Δ	0.0150	0.0120

Figure 1: *Autosal Warm-Up Time Determination. Effect of Time on Sea-Bird Secondary Standard Batch SS62 Autosal Salinity Readings (Nominal Salinity = 34.9458).*

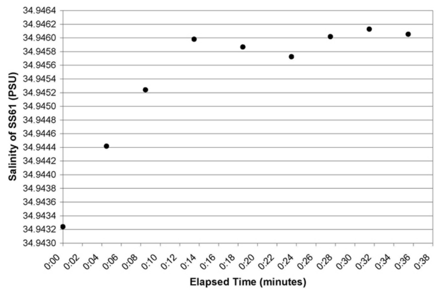
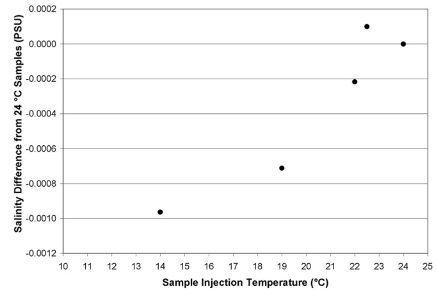


Figure 2: *Effect of Sample Injection Temperatures on Sea-Bird Secondary Standard Batch SS64 Autosal Salinity Readings.*



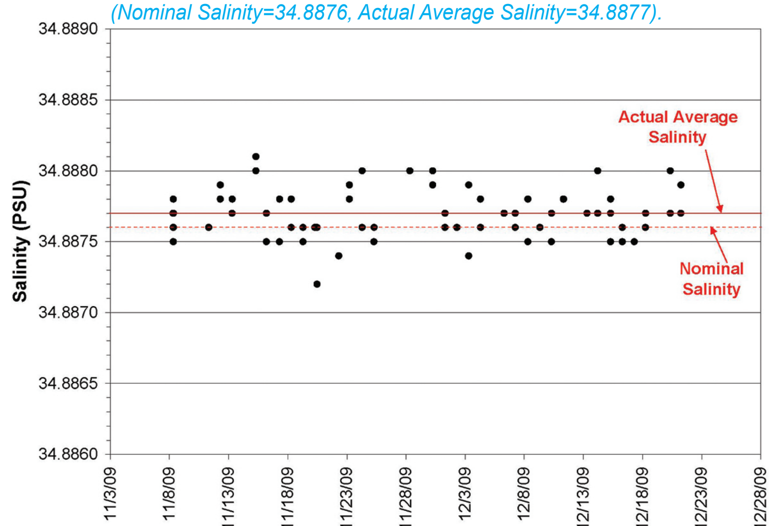
Verification of Autosal Standardization

- After warm-up, standardized Autosal using 1 bottle of IAPSO Standard Seawater to obtain offset correction (difference between IAPSO conductivity reading and labeled conductivity reading).
- Two bottles of secondary standard analyzed and adjusted using current offset correction value. These 2 bottles should be very close to nominal salinity calculated for batch.

Example:

- On 11/19/09, 2*conductivity ratio of IAPSO Standard Seawater Batch P151 was 1.999784. When compared to its labeled K15 conductivity ratio of 1.999940, this produces an offset correction of 0.000156.
- Two subsequent bottles of Secondary Standard Batch 63 were run, and each 2*conductivity reading was increased by 0.000156 before calculating salinity. Combined salinity average from both bottles was 34.8876. This matches nominal salinity for Batch 63.

Figure 3: *Stability of Secondary Standard. First 2 Bottles of Secondary Standard Batch SS63, Analyzed After Acceptable IAPSO Standard (Nominal Salinity=34.8876, Actual Average Salinity=34.8877).*



Correction for Autosal Drift

- An additional bottle of secondary standard analyzed after every 6-9 calibration laboratory sample bottles.
- Salinity of each additional bottle of secondary standard compared to average of first 2 bottles.
- Any systematic drift added computationally as a function of time to salinity values of each sample.

Example:

Average Salinity
34.9721 PSU

Original Salinity
34.5588 PSU
Drift-Corrected Salinity
34.5588 PSU

Original Salinity
34.5580 PSU
Drift-Corrected Salinity
34.5580 PSU

Original Salinity
34.5581 PSU
Drift-Corrected Salinity
34.5581 PSU

Original Salinity
34.8499PSU
Drift-Corrected Salinity
34.8498 PSU

Original Salinity
34.5499 PSU
Drift-Corrected Salinity
34.8498 PSU

Original Salinity
34.5501 PSU
Drift-Corrected Salinity
34.8499 PSU

Salinity
34.9723 PSU

CONCLUSIONS

Autosal Best Practices

- Because a part per thousand difference in the temperature of the Autosal affects salinity approximately 1 ppm, it is important to:
  a. Measure the bath temperature as precisely as possible, as with an SBE 35 Deep Ocean Standards Thermometer.
  b. Keep the bath as stable as possible by keeping the room temperature stable and below the Autosal set point.
- This Autosal requires a warm-up period of at least 15 minutes, before reliably reading salinity to ± 2 ppm.
- Bottle sample temperatures affect salinity 1 ppm at 10 °C below the set point. For best results, samples should be maintained within 2 °C of the Autosal set point of 24 °C.

Secondary Standard Batch Trends

- Sea-Bird is capable of creating small batches of secondary standard using natural seawater that are stable within ± 0.0005 PSU for at least a 1-month time period.
- This stability allows us to see daily shift in the Autosal, which can change dramatically, but is typically less than ±1 ppm when the best practices for Autosal are employed.

IAPSO Within-Batch Variation

- Because of the stability of Sea-Bird's secondary standard and the accuracy achieved using the best practices with the Autosal, the secondary standard can be used to detect anomalous bottles of IAPSO Standard Seawater.

  Example:

  - On 11/11/2009, the 2*conductivity ratio of a bottle of IAPSO Standard Seawater Batch P151 was measured at 1.999779, producing an offset correction of 0.000161.
  - Subsequent bottles of SS63 utilizing this correction ratio produced a salinity average of 34.8867, which is nearly 1 ppm lower than expected.
  - An additional bottle of IAPSO P151 was run, and the 2*conductivity ratio was measured at 1.999718, producing an offset correction of 0.000222.
  - Subsequent bottles of SS63 utilizing the new correction ratio produced a average of 34.8876, which matches the nominal salinity for batch SS63.
  - Therefore, the second bottle of IAPSO was used to standardize the Autosal and the offset correction it produced was considered more accurate.

IAPSO Between-Batch Offset

- As others have observed (i.e. Mantyla, 1997; Aoyama et al., 2002), there can be batch-to-batch offsets of IAPSO Standard Seawater.
- Despite data showing Secondary Standard Batch SS61 was stable within ±1 ppm when the Autosal was standardized properly, the salinity of SS61 shifted dramatically when Sea-Bird began using IAPSO Standard Batch P151.
- Although unclear if the issue is with P150 or P151, the offset between the two may be observable by scientists in the field.

Figure 4: *Average Salinities of First 2 bottles of SS61 Recorded after Standardization with IAPSO Batches P150 and P151.*

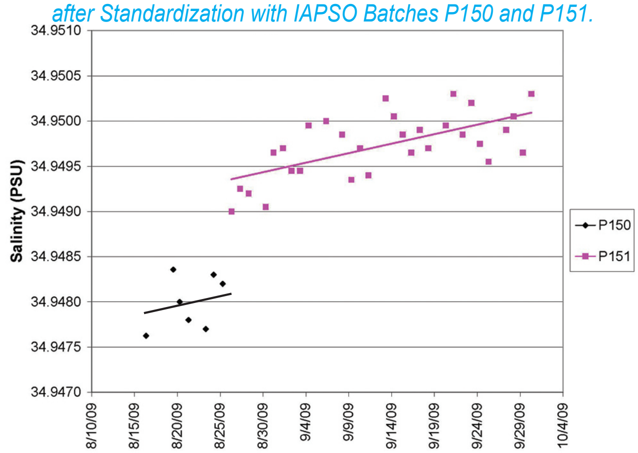
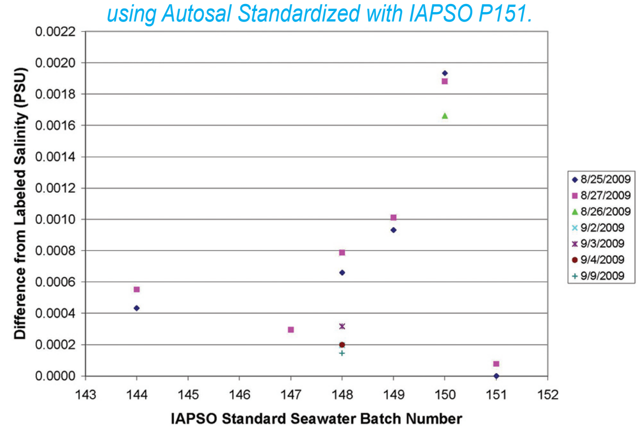


Figure 5: *Experiment Comparing Salinities of various IAPSO Batches to their Labeled Salinities, using Autosal Standardized with IAPSO P151.*



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Mantyla, A., 1987: Standard Seawater Comparisons Updated. Journal of Physical Oceanography, 17, 543-548.