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Interactive comment on "Technical Note: How long can seawater oxygen samples be stored before titration?" *by* M. Lankhorst et al.

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Abstract

This response refers to comment osd-11-C1121-2014 received for the following paper in *Ocean Science Discussions*:
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1 Comments from referees/public

The two key points of criticism made in this comment are that the number of samples is too small and that the samples from the two expeditions were treated differently. A

larger number of samples is requested, as is an experimental setup that is dedicated to the question at hand. Other points of major criticism are that:

- eliminating all samples with known problems leaves too few data points to reach any conclusion,
- the acid experiment is pointless,
- duplicate samples are not reported,
- sampling in the upper ocean from separate Niskin bottles introduces scatter that should have been avoided,
- blank determinations are not reported.

On a more positive note, the topic as such is called interesting and further investigation is encouraged.

2 Authors' response

The small sample number and experimental setup are explained in our response to the first referee comment, C1116. Basically, the results we are presenting are results ancillary to the primary purpose of the data collection, which was calibration and validation of the SBE and AADI sensors. That said, the statistics presented in table 3 of the original manuscript show that the effect of storage appears to be less than a certain threshold, and quantifying an upper bound for this threshold constitutes the novel result from our manuscript. Figure 1 then demonstrates that this threshold is sufficiently small to be useful in our particular application, which is the sensor cal/val.

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The number of samples is sufficient to compute means and standard deviations which support this conclusion (table 3). Several of the samples that are called out as suspicious in tables 1/2 of the original manuscript are still used, because the data themselves do not appear anomalous. The likely reason is that these are the ones where bubbles were noted in the samples, and that the bubbles formed when the samples warmed to room temperature before sampling from gases other than oxygen (meaning that the bubbles are not an indication of anything wrong).

The reason for trying the acid experiment is mentioned in the original manuscript (page 4, lines 6 onward). We asked several experts whether storage of these samples might be acceptable, and got very different answers. One answer was that perhaps the samples would keep better if this acid was added. We chose to include this aspect in the manuscript, because we show that at least within our large error bars, the acid procedure does not make a difference, which we in turn use as an argument against it (it is a risky procedure that can ruin the sample).

While it is correct that repeat samples from identical Niskin bottles were not taken, it is unclear to us how that would change the results presented in the manuscript.

The rationale for separate Niskin bottles is outlined in our response to comment C1114.

Blanks and standards were obtained in all titrations and applied to the data values.

The review contains an itemized list of “specific comments”, to which we respond as follows:

1. Yes, this is the sulfuric acid.
2. The manuscript consistently uses ml/l throughout. While we would have preferred to use micromol/kg, we decided to stick with ml/l because the original procedural documents for the titration are given in ml/l. Wherever a different unit is presented in the manuscript, it is a quote from an external document, for which we give the equivalent in ml/l. We believe no changes are needed.

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3. Yes, collection means transfer from a Niskin bottle into the Erlenmeyer flask through a tygon tube, trying to avoid splashes and bubbles. The flask volumess were around 130 ml and individually calibrated. There is 1 ml of each of the MnCl2 and NaI+NaOH solutions, put in one after the other. The amount of sulfuric acid was 2 ml. The ODF website indicates that their analysis uses KIO3 as the standard, which is the same as what was used for the on-board samples. Blanks were performed in all cases.
4. See above for rationale for the acid.
5. We will refer to the lab websites.
6. We will refer to the lab websites. Yes, the equipment was different. The biggest difference is that ODF has an automated end-point detection for the titration, whereas the on-board samples were titrated visually.

We can easily make the suggested improvements to figure 1 and tables 1 and 2. The accuracies of the sensors are provided by the vendors as the greater of a constant number X or a percentage Y% of the measurement value. For small values, this amounts to X, and will increase to Y as the numbers get higher, hence the shape of the green shading.

3 Authors' changes in manuscript

Based on this set of review comments, we propose the following changes in the manuscript:

- See proposed changes to title and text in response to other reviewer comment, meant to address the key criticisms of low sample number and statistical significance of result

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- Add references to chem lab websites, which contain info about equipment used
- Figure 1: better distinction between squares and dots
- Tables 1 and 2: add maximum pressure of casts

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