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

Anonymous Referee #2

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This is a technical note about how long the oxygen samples collected in order to perform Winkler titration, can be stored before the titration is run. I found this note quite interesting since I am often involved in collecting oxygen sample for calibrating the CTDO sensor and I was not aware of this wide range of time allowed to store the sample. I've been trained long ago that sample cannot be stored longer than 24 hours and this is what I usually do when I measure oxygen at sea. There are two things, however, that I'm concerned the most about this paper. First of all the small number of samples used for the two experiments, this is mentioned in the conclusion and I perfectly agree that more investigation is needed. However, due to this reason I found the conclusion of this paper quite weak. The authors are suggesting that the oxygen can be stored for longer time, up to a month after the sampling, but this needs to be proved and as the authors say it remain to be seen if the results are valid for a larger number of re-

alization. So after reading the manuscript the question "how long the oxygen sample can be store?" still remains. My second concern is: why the choice of setting the two experiments with so different conditions. In my opinion the experiments should have been made with similar conditions, so if in the first cruise the titration of the first Batch was performed after a week and the titration of the second Batch was performed after 1 month, then the time span on the second cruise for the two Batches should have been the same, or at least the reference Batch for both experiments should have had the same storage time, either one week or one day. I actually suggest one day or less storage time for the reference Batch, and the measurements for this Batch should be on board since this is the usual routine. I would recommend the authors major revision before publications, and with major revision I mean to add more data in order to able to answer to the question posed in the title and to set the experiments in a better way. I don't know if that is feasible, but if the conclusion cannot be supported, than the paper should be rejected.

Major comments

Regarding the experiments, the first experiment has only 9 samples, and 4 of them has known problem in the Batch where the acid was added before storing, so they need to be discarded. This points to the fact that the authors cannot really say anything about whether or not adding acid before the storage is possible. In the second experiment there are even less sample and here the acid "experiment" is not even performed. So I don't see any reason to include this part of the experiment.

It is a common procedure to sample double sample in order to be able to calculate the final precision. I don't see any double sample in any of the two experiments, unless you consider as a double the two samples from the 2 Batches. But I won't count that as a double sample since are measured in different time with different conditions. It is normal that at the beginning the difference between the doubles are higher than at the end of the cruise, this is due to the fact that whoever is sampling and measuring the oxygen need to get into the routine, so this goes back to the point that the number of

samples is too small.

Moreover, why choosing so shallow depth (like 3 dbar, 16 dbar and 23 dbar)? At this shallow depth there is much higher variability compared to the deeper ocean and this will add more uncertainties in the results. If the goal was to prove that you can store for longer time the sample before measure them, then I would take the sample at depth where there is not a strong gradient. Especially if the authors decided to take the samples from the reference Batch and from the stored Batch from different Niskin bottles. There is highly chance to close the Niskin bottle at different depth and since the oxygen gradient can be quite high, the difference between the two samples can be quite significant. While contamination of the Niskin bottle from the air is not so likely, especially if the two samples are taken immediately one after the other. Indeed most of the samples in the NH cruise are that shallow and are the one that shows the highest difference between the reference batch and the stored batch.

What about the determination of the blank? Did the authors check by the determination of the blank whether the reagents used have impurities (for example the presence of redox species) that would bias the results? Could that be also a possible reason for the differences between the two cruises and between the Batch 2 and 3 compared with the reference Batch in the NH cruise?

Specific comments

1) P 2448 L 9: Specify already here in the abstract what chemical is added before storage. I guess here is meant sulfuric acid.

2) In the introduction is well described the accuracy of the method, the precision of the instruments etc. However, I suggest to use always the same units and not to switch back and forth with different units. I'll explain better, usually most of the database use μmol/kg as standard unit for oxygen, so I like to see this unit since is the most common one. However, the oxygen sensors usually give the measured oxygen in ml/l, which is also used here for the experiments. So my suggestion is, if the authors want to stick

with ml/l, to describe all the precision and accuracies in ml/l and then use μmol/kg in parenthesis. So:

Page 2448 line 19: "this would amount to 0.006 ml/l" could you say how much that is in μmol/kg

Page 2449 line 3: write (0.003 ml/l or 0.15 μmol/kg)

Page 2449 line 15: 2% or 0.07 ml/l (xxx μmol/kg)

Page 2449 line 17: 5% or 0.19 ml/l (8 μmol/kg)

3) Can you be a bit more detailed about the method?

- Collect water samples transfer to Erlenmeyer flasks: when the authors say transfer to Erlenmeyer flasks, does that mean collecting the water directly from the Niskin bottle into the flasks? If so, are these pre-calibrated flasks. How big they are?

- Add "picking" reagents: how much of the two reagents were used. Did you put the reagents on the same time or first one and then the other?

Add sulfuric acid (how much?)

Did you use the potassium iodate (KIO3) or potassium hydrogen diiodate KH(IO3)2 for the standard? I see that somehow the determination of the standard is mentioned in the discussion (page 2453 between line 16 and 20) but it should be mentioned in the method first. Also did you do the blank?

4) I never heard that the acid could be added before storage. What is the reason? Would be good if the authors can shortly explain why this should be done.

5) P. 2451 L. 21 I think it would be good here to specify which titration equipment was used.

6) P. 2452 Specify also here what kind of titration equipment was used. Was the equipment used to titrate the oxygen on board different from the one used about two weeks

later ashore, what was different?

Figure 1: Make the square symbols a bit bigger, I can barely distinguish with the dots. Also I don't understand in Figure 1 why the shade area in green increases after the O2 concentration is higher than 3.8 ml/l. According to the figure caption the green shading indicates accuracy limits of different electronic sensors, which should be according to what is stated in the introduction between 0.07 ml/l and 0.19 ml/l. So why are they increasing for higher O2 concentration?

Table 1 and 2: Can you specify the maximum depth (or pressure) of the station.

Interactive comment on Ocean Sci. Discuss., 11, 2447, 2014.