

## ***Interactive comment on “Spectrophotometric high-precision seawater pH determination for use in underway measuring systems” by S. Aßmann et al.***

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Dear Prof. Dickson,  
thank you very much for you comments. We will include the points in the final version of our manuscript as discussed beneath.

1. Applying an impure indicator dye is surely not very reliable within an accuracy of  $\pm 0.01$  pH units as Yao et al. (2007) and Liu et al. (2011) showed. We will include a more detailed view on this issue which will be more in depth than the short discussion on page 1350.

C525

2. (a) We compared our system to a SOP described in Dickson et al. (2007) using a bench-top spectrometer. The offset is only true for one pH value (pH of the CRM TRIS buffer) and is expected to be in the range of 0.001 pH units over the whole pH range of the indicator.  
(b) There are some differences in the pH determination. The bench-top system uses discrete samples and only a few points (at least two) for correction of the indicator perturbation. It takes some time (20 s) for a single measurement due to the wavelength scan. A whole pH determination takes at least 5 min while the underway system takes at most 1 min. Thus the up-take of CO<sub>2</sub> from the atmosphere can change the pH of the sample during one pH determination. The underway system uses Flow Injection Analysis (FIA) where the indicator is injected into the sample stream. As FIA systems are highly reproducible so that any changes in the sample due to a change in the environment (e.g. air CO<sub>2</sub> concentration) will change all parts of the sample in the absolutely same way. However the PTFE tubing used in this setup is not absolutely gas tight which may lead to a small error.  
The reproducibility of the FIA is therefore a very large advantage compared to the sample handling with the bench-top system. However the stray light in the mini spectrometer of the underway system may cause an error which depends on the absorption of the sample-indicator mixture of the single spectra.  
An other issue is the temperature control of the bench-top system. Here the temperature is only assured to be  $25\text{ °C} \pm 0.1\text{ °C}$  while the underway system is much more stable.  
(c) Because of the reasons mentioned above it is not possible for us to say which pH determination is the *right* one. The bench-top system is the only reference which can be taken for a direct comparison of the performance of a newly developed sensor. For us the handling of the sample is the biggest problem with the bench-top spectrometer while this is absolutely no issue

C526

with the FIA system. The bench-top spectrometer has less problems with stray light inside the spectrometer so we could much more rely on this data. However we are not able to combine the the FIA system with the bench-top system due to limitations of this spectrometer.

As a well specified and widely accepted SOP exists using the bench-top system is assumed to be the more accurate method.

3. The long-term precision is assessed using stable (one year) CRM buffers. These TRIS buffers are measured over a longer period (month). Up to now we only have measurements over two month. During that time the system was further optimized which changes slightly its behavior. Over these two month the precision of the system was found to be  $\pm 0.0026$  pH units.

4. We will include a more detailed and differentiated discussion of the uncertainty. The accuracy will be given in comparison to the CRM, which should be a realistic value.

$$\Delta \text{pH} = +0.0081$$

$$\text{pH}_{\text{CRM}} = 8.0893$$

$$\text{pH}_{\text{underway}} = 8.0974$$

5. The ability to bring the sample to  $25.00^\circ\text{C}$  is limited by the power of the Peltier (60 W). However we can not imagine any temperature in natural waters which may be a problem here (last cruise the temperature of the sample was about  $18^\circ\text{C}$  and the power needed to change the temperature of the sample was about 3 W). It would take 18 W to bring sample water of  $0^\circ\text{C}$  to  $25^\circ\text{C}$ . The most problematic point actually was a sample temperature too near to  $25^\circ\text{C}$  which was problematic due to the necessary changes in the polarity of the current for the Peltier element. However this problem has also been solved. The actual restriction is that the difference between the temperature of the heat exchanger ( $25^\circ\text{C}$ ) and the temperature in the surrounding air. This difference should not exceed

C527

$\approx 28^\circ\text{C}$ , because the Peltier elements cannot handle such high temperature differences. Thus the working condition may vary from approx.  $0^\circ\text{C}$  to  $50^\circ\text{C}$ .

6. We would like to keep this comparison, because it gives a quick first view of the behavior of the sensor. You can clearly see that there is no smoothing in the peak resolution and the *real* data frequency is high. This is especially important for steep pH gradients (e.g. near the coast). But you are right, in detail this comparison is problematic.
7. This is a misunderstanding I guess. To omit 1 % of the data during one injection is caused by outliers due to particles or air bubbles. This does not follow the mathematical distribution and its probability is much higher. In this case 1 %. The pH value can still be calculated with sufficient precision. Here only two of approx. 200 spectra during one indicator injection are removed.

Removing of approx. 5 % of the data due to high errors during an indicator correction or high temperature fluctuation also is caused by air bubbles or sediment load. All pH values exceeding a certain value of error during the correction for indicator perturbation are discarded (about 5 %). Our experience is that this filter eliminates nearly all outliers (pH values) of a time series.

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