**Ocean Science
Discussions**

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

A. Dickson (Referee)

adickson@ucsd.edu

Received and published: 5 August 2011

TITLE: Spectrophotometric high-precision seawater pH determinations for use in underway measuring systems

AUTHORS: S. Aßmann, C. Frank, & A. Körtzinger

COMMENTS:

This is an interesting paper that seeks to describe a convenient system for autonomously measuring the pH of seawater on a flowing stream of seawater. The difficulty with pH as a carbon system parameter in seawater is that it is temperature (and

pressure) dependent, thus the pH of a particular sample of seawater will change as the temperature is changed. In this system, this is addressed by making measurements at a constant temperature (25.00 °C).

The system incorporates a number of enhancements, all of which have been utilized in other contexts but which have been brought together here to provide a potentially useful measuring system. These are: (i) the use of a CCD spectrophotometer appropriately calibrated for nonlinearities together with a white LED as the light source; (ii) the use of the Peltier effect to control solution temperature; and (ii) the estimation of pH perturbation due to adding indicator dye from measurements over a range of indicator concentrations on the trailing edge of a pulse of indicator dye added to the sample stream.

There are clearly still a number of problems in the implementation of the system (the existence of which are acknowledged in the manuscript): any bubbles (p. or particles in the flow stream can compromise the data quality (p. 1354); the system cannot cope with rapid changes in the temperature of the flowing sample stream (inferred from the comments on p. 1350); there are other, perhaps unidentified, problems that are addressed by rejecting a proportion of the data (p. 1349, p. 1351) that is far larger than would be expected; as yet the system does not automatically account for the effect of salinity on the indicator properties.

All in all, a good paper that should be published!

However, I have a number of comments that, if addressed, should make the paper still clearer and more helpful to readers.

1. Recent papers alluded to in the text (Yao et al, 2007; Liu et al., 2011) have shown that all commercially available sources of m-cresol purple supply a compound that is contaminated with small amounts of colored compounds. As a result, this throws in doubt the previously published values for the extinction coefficient ratios and pK of this indicator dye (Clayton & Byrne, 1993) that were used in this paper.

Furthermore, these papers also show clearly that the error in the measured pH that is inherent in using such an impure dye is itself pH dependent, and varies from manufacturer to manufacturer (and perhaps from lot to lot). Thus the statements about accuracy for the operation of this system, using dye obtained from Sigma Aldrich) are too optimistic. The check at a single pH, using a Tris buffer, indicates a discrepancy of about 0.01 in pH, yet this is apparently dismissed. All in all, this needs more discussion.

2. The pH offset observed between a bench-top spectrophometer (Perkin Elmer, Lambda) and the CCD spectrophotometer described here was observed at a single pH (Tris buffer, pH $\sim$ 8.1). There are some questions that come to mind: (a) Is this necessarily a consistent offset over the range of pH in consideration? (b) What is the source of this discrepancy? (c) Which spectrophotometer (if either) is "right"? (I note that in the response to another reviewer, further data with a smaller discrepancy are given. Nevertheless, my questions still hold.)

3. The system seems capable of good repeatabilty (0.0007, Fig. 7). How might its longer-term reproducibility be assessed?

4. There are numerous things that will contribute to the overall uncertainty of a pH measurement made using this system: the reproducibility, the effects of dye impurities, the uncertainty of the dye calibration (extinction coefficient ratios and pK), photometric error in the spectrometer, error in the dye perturbation correction, errors in temperature control/ measurement, . . . , Unfortunately, this manuscript does not really address the implications of these at all. It simply states that the method has "an accuracy of better than 0.0018 pH units", surely an over-optimistic statement. The estimates of accuracy need to be reconsidered.

5. The decision to measure pH at a single temperature (25 °C) will surely have some consequences. For example, what is the coldest (or warmest) water than can be brought to 25 °C (within the necessary tolerance) by the system at the 10 mL min–1 flow rate. The data shown refer to July in the North Sea ($\sim$ 15 °C ?).

6. The comparison with a glass electrode system calibrated infrequently using low ionic strength buffers tells one more about the problems of such a system (and about the difficulty in estimating total hydrogen ion concentration from such measurements) than about the behavior of the proposed measurement sensor system I fear. I'd leave this out.

7. The comments about the need to ignore a significant proportion of the data are problematic. For example, with a Normal distribution one would not expect 1% of measurements to exceed 6 sigma, but rather about 3.4 ppm! (p. 1349); similarly the observation that 5% of the measurements are rejected during normal measurement (p. 1351) calls out for further comment.

8. Finally, there are a number of small typos (e.g., Arne Körtzinger's name is spelled wrong in the list of authors) that should be found and fixed.

Interactive comment on Ocean Sci. Discuss., 8, 1339, 2011.