

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

Anonymous Referee #1

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The flow spectrophotometric method presented in this manuscript represents a promising step forward in the routine underway measurement of pH on ships of opportunity, an important activity in the context of ocean acidification. I recommend that the authors consider revision in respect of the following points before publication.

P1342: The authors state in the first paragraph of section 2 that an advantage of the total pH scale is that absolute values can be compared. This is only true where the pH is measured on the total scale, i.e. using Tris/seawater buffers calibrated on the total scale, or indicators whose pK value has been determined on the total scale. That the total scale is widely used does not necessarily guarantee that measurements are

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made on the total scale: authors may find it convenient to convert measurements on other scales to the total scale in order to facilitate comparison. This point should be made clearer.

P1350: The comparison between the flow spectrophotometric measurements and the benchtop spectrophotometric measurements appears to be incomplete. The authors state that the CRM was supplied in relatively small volumes, which did not allow the temperature control for the flow system to stabilise sufficiently. This is of course a problem which must be addressed if flow systems of this type become widely used. It should, however, be possible to make a comparison between the two spectrophotometric methods using a larger batch of locally produced TRIS buffer, which would give added confidence that the flow system itself does not show an offset relative to the benchtop system.

P1351: The pH values measured at 25C are converted to in situ temperature using CO₂ system software. Irrespective of the software used, conversion of pH between different temperatures requires either that another CO₂ system parameter has been measured, or that one such value is assumed (usually alkalinity estimated from salinity). It should be made clear what assumptions were used in the correction of pH to in situ temperature.

P1351: Reliable conversion of pH values from the NBS scale to a concentration scale requires that the fH value, which is specific to each electrode pair, be known. Here the conversion appears to have been carried out using an estimated fH value: this should be clarified in the text.

A point of detail: Practical Salinity is dimensionless, so the “unit” psu should be deleted throughout.

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