

***Interactive comment on “Technical Note: Highly precise quantitative measurements of total dissolved inorganic carbon from small amounts of seawater using a common gas chromatographic system: an alternative method compared to established detection systems” by T. Hansen et al.***

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The authors describe a GC-based approach to measuring total dissolved inorganic carbon in seawater. The GC approach is similar to that used for at least 30 years to measure CO<sub>2</sub> in air (i.e., using an acidic drying agent, together with hydrogen and a nickel catalyst to ensure reduction of CO<sub>2</sub> to methane and subsequent detection with an FID); the use of a cold-trap to "focus" the CO<sub>2</sub> from an acidified seawater

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sample is essentially that of Wong (1970), though – it appears – automated. The authors' contribution has been to put a system together from commercially available components that achieves this measurement relatively straightforwardly. They also indicate that – with care – it may be practical to filter samples for this measurement (a practice that is usually not done for high-quality measurements).

So what might make this a "better" method? The prime aspect that the authors emphasize is that it provides a good estimate of total dissolved inorganic carbon from a relatively small sample of seawater (10 mL). This is – in part – because typically only 0.200 mL of sample are injected into the stripping chamber for analysis; the balance of the sample acts to mitigate the likelihood of significant CO<sub>2</sub> loss / gain occurring during handling and to allow for replication, if desired. I should point out here that two commercially available systems for measurement of the total dissolved inorganic carbon in seawater (the Airica from Marianda, and the AS-C3 from Apollo SciTech Inc.) also claim in their specifications that small sample sizes (~1 mL) are used, and one explicitly states that "less than 10 mL of sample is required." (This contrasts to the comment – p. 4449, line 19 – suggesting that at least 250 mL are needed.)

The authors also suggest that cost is a significant advantage of their system (noting the significant cost of the LiCor 7000 for IR systems – though it is practical to use the much cheaper LiCor 840 with only some degradation of precision – Ludger Mintrop, Marianda, personal communication). I should like to take this opportunity to point out that choosing a system based on acquisition cost alone is ill-advised; it is recommended that the full costs – including the (usually dominant) personnel costs for operation and maintenance of the equipment, in addition to the acquisition and operating costs – be compared. (I note that the analysis time for a single sample – excluding time for changing samples – is 14.5 min: Fig. 2.)

However, it is the description of the method itself, and the characterization of its performance, that I feel still need some improvement. The instrumental description is quite vague and ill-organized, possibly making it difficult for other laboratories to replicate as

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it neither provides a clear statement of the components used, nor does it guide other labs as to the component specifications that are key to achieving the results detailed here. Thus I believe that this section (describing the system) could benefit from careful planning and reorganization to assist such readers.

Also, the statement is made that: "Method validation was done in agreement with the terminology for accuracy and precision (RSC, 2003)." I disagree. That – admittedly short – document differs from the authors in a number of key aspects. For example, it states: "Because precision depends on the conditions of measurement, the conditions must be specified when referring to an estimate of precision." The authors do not do this. (I feel that their precisions are all estimated under repeatability conditions and would be better estimated as a pooled value.) Furthermore, the RSC document is at pains to state, "an estimate of uncertainty is probably the most appropriate means of expressing the accuracy of results" and also "An estimate of uncertainty must incorporate what is known about random effects and what is known about uncertainties associated with systematic effects on the measurement process." Granted this is non-trivial (see for example "Quantifying Uncertainty in Analytical Measurements", EURACHEM / CITAC Guide CG 4, 2012), but would be a much more useful guide to the method than the (I suspect over-optimistic) comment that: "Our technique is able to provide . . . an accuracy of  $\pm 1.2$  mol/kg . . ."

Thus, although I believe that this is a potentially useful approach, particularly as there is a need for measurements of total dissolved inorganic carbon in seawater that can achieve adequate quality from a small original sample volume, I feel it could have been presented far more effectively, and that it should not be published in its current form.

I detail below a list of further comments (that should not be considered exhaustive) that the authors should consider when preparing a revision.

p. 4441, line 3. I would dispute that the need is for "precise" measurements, instead I would assert we need measurements of known "uncertainty" that can therefore be

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compared reliably both within and between laboratories.

p. 4442. A variety of "precisions" are stated. I am not convinced that they are really comparable, as I would note that the numbers given for the precision of coulometric analysis are those found from repeated analyses of separate bottles of CO<sub>2</sub> in seawater reference materials over a period of months, whereas the precision in Stoll et al. seems to be a repeatability (based on a single analyzer run).

p. 4444, section 2.2 I am surprised (given my own experience with using Na<sub>2</sub>CO<sub>3</sub> as a calibration standard) that it was not dried (at >270 °C) nor is any comment noted about care with regard to static when weighing or transferring. I also could not find a Sartorius SR2 balance with a simple web search, so feel it would be desirable to indicate the balance accuracy for this 4 mg weighing.

p. 4444, section 2.3. "samples were collected by hydrostatic pressure into 10 mL vials" – It is not clear what this means. Perhaps pneumatic pressure was used to force the sample through the tube?

p. 4445, line 4. The use of 20 microliters of saturated HgCl<sub>2</sub> solution in a 10 mL sample will change the total dissolved inorganic carbon by about 0.2% (4 micromol per kg at a level of 2000 micromol/kg). Was this dilution adjusted for?

p. 4445, line 20. "After the gas pressure inside the measurement chamber was close to zero . . ." – Surely not! Is this the amount of CO<sub>2</sub> remaining in the measurement chamber?

p. 4446, line 12-13. ". . . were always blank corrected (5 micromol  $\pm$  1.8)." – Should this not be micromol/kg? Also, it is not clear what the relevance of the phrase "200 microliters of DI water which was used for the preparation of the sodium carbonate solution" is. Does that mean that that solution has a necessarily higher "blank"?

p. 4446, line 13-14. "sample temperature and salinity were taken into account" I'd guess this is for a density estimate, but it doesn't say so.

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p. 4446, section 2.7.1 suggests that different volumes of both the internal standard and the "Dickson standard" were injected to achieve a range of values; however, the first sentence of section 3 implies that "different concentrations" of internal standard were used together with "different volumes" of Dickson standard. Which is correct?

p. 4447, section 3. I found this confusing. The first paragraph seems to describe the data of Fig. 3, providing the least-squares parameters describing the line which is, apparently, based on two separate Na<sub>2</sub>CO<sub>3</sub> solutions and the Dickson standard. However, the statement regarding the "precision" seems to be based on Na<sub>2</sub>CO<sub>3</sub> solutions alone. Also, I am not clear as to the significance of the "intercept" (equivalent to about 10 micromol/kg?), particularly in the light of the comment about blank correction on the previous page.

The second paragraph then describes Fig. 4, with the mean of the 9? measurements on the "original" (not subsampled but from the same bottle?) Dickson standard seeming to be identical to the certified value. Is this a lucky accident or were the data adjusted to indicate that the other handling methods only result in small average deviations? Also where does the number chosen as an "accuracy" come from? The average deviation of all these 27 data from the certified value? As the RSC document the authors quote is at pains to state, "an estimate of uncertainty is probably the most appropriate means of expressing the accuracy of results".

p. 4448, Paragraph 3 of section 3 discusses Fig. 5, again treating its "precision" as a separate concept for statistical analysis. I really believe that all the replicate data given in this paper should be combined to provide a single estimate of the measurement repeatability (a pooled standard deviation). I do not believe that any of the estimates given are really significantly different one from another as the individual numbers of degrees of freedom are typically small. (You could confirm my assertion with a series of F-tests.)

p. 4448, line 22. The assertion is made that other methods have not been "validated"

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over an equivalent concentration range. This is not really very convincing. First, Goyet & Snover based their results on a calibration curve over a wide range of total inorganic carbon concentrations; second, even the coulometric method has been shown to be linear over a larger range than stated here, and it too is an integrative method thus is unlikely not to work just as well (in absolute terms) at lower concentrations.

Fig 2. I'd have the time axis in minutes (with one decimal place); this seems to be the inherent time step.

Fig. 3 A plot like this is an almost useless approach to displaying good-quality linear data where the size of the symbol significantly exceeds the measurement repeatability. I suggest plotting the deviations from a straight line as a function of total inorganic carbon concentration, possibly scaled to indicate the discrepancy in concentration units.

Figs 4 & 5 & 6 would be even clearer as tabular material (and then some of the text might also not be needed).

Fig 6. It seems a pity that the two parts of this plot are not on the same scale as this confuses any comparison of precision.

Finally, I don't believe there is a 1:1 correspondence between citations, and the bibliographic list of references. The authors should check this more carefully.

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