Ocean Science

Discussions

Open Access

**OSD**

Interactive
comment

# *Interactive comment on* "Impact of impurities in bromocresol green indicator dye on spectrophotometric total alkalinity measurements" *by* Katharina Seelmann et al.

Katharina Seelmann et al.

kseelmann@geomar.de

**Reply to the comments of Anonymous Referee 1 (received on 17 Jan 2020)**

First, we thank the Anonymous Referee for the evaluation of our manuscript and constructive suggestions and comments. We answer each comment point-by-point in the following text. All manuscript changes based on these comments can be found in the supplements with marked differences to the previous version. Furthermore, all lines named in the following answers refer to the supplemented changed manuscript.

**Comment #1:** Firstly, the paper justifies the effort on the assumption that impurities in

Printer-friendly version

Discussion paper

BCG indicator impact spectrophotometric total alkalinity measurements. It seems to be good paper. Three things were true that led to spectrophotometric pH requiring BCG purification are the impurities in dyes, the impurities cause drift in total alkalinity for the system used for the novel autonomous analyser CONTROS HydroFIAr TA and lastly no two sets of dye had the same impurities. On a similar note, the authors claim that BCG with impurity quantities higher than 6% provided AT values, which failed fundamental quality requirements but still conclude that to gain optimal AT measurements, an Indicator purification is not necessarily required as long as the purchased dye has a purity level of at least 98 % and they are able to provide quality measurements to avoid identified issues. I don't see how this is true. Purification of dye is expensive but then it is not strictly recommended by the author to carryout high quality measurements. I guess with high quality measurements nothing should be compromised.

**Answer #1:** You are totally right by saying "with high quality measurements nothing should be compromised". But we also think that there must be a reasonable balance between the effort to achieve high-quality measurements and their costs. Most users of spectrophotometric $A_T$ analyzers (no matter if they work at research institutes, industry, or somewhere else) are dependent on a certain budget for their measurements. Additionally, they are maybe not able to perform indicator purifications because they do not have the necessary facilities at hand. Consequently, they have to use unpurified BCG as long as there is no commercial provider for purified BCG. Our results show that the quality $A_T$ measurements based on unpurified BCG is fully comparable to those made with purified BCG as long as the impurity quantity does not exceed a certain level (see Table 4). We also show that there is at least one provider of BCG who can routinely fulfill this requirement (there could be others, but during our study we were not able to figure them out). These are the reasons why we do not strictly recommend a purification of BCG to gain high-quality measurements. At the same time, however, we want the reader to be aware of the fact that the impurity level of their purchased BCG is not unimportant at all. We changed the abstract and parts of the manuscript in order to better address this (see supplement).

**Comment #2:** I think there are benefits to this approach, but the authors need to be clearer and accurately spell out what they are as stated in abstract (line 6- 7) that impurities and quality of impurities do impact the drift behaviour of the analyser.

**Answer #2:** Yes, there are benefits to this approach which are stated in lines 298 - 299 of the supplemented manuscript. But in comparison to "high-purity" BCG purchased from TCI, which can be used without any extra work, the gained benefits are not significant enough to justify the need and corresponding effort of indicator purification (it does not measurably improve the precision and accuracy of the measurements). In our opinion, there is no reason why a smaller linear drift is principally better than a somewhat larger **linear** drift as both of them are easily correctable by regular reference measurements. The only thing to avoided is a non-linear drift behavior which we found for the less pure commercial BCG products, hence no need to inform the scientific community about this issue. We changed the cost-benefit analysis (lines 299 - 300) to better address this statement. Of course, in comparison to "low-purity" BCG, purification is beneficial. But we think that the readers of this manuscript would prefer to buy a slightly more expensive unpurified BCG than have extra work with the purification (providing they have the facilities to purify BCG). In addition, we added a hint that the drift pattern should be assessed for each batch of BCG from the same supplier. This procedure ensures that batch to batch variability in purity is monitored (see lines 311 - 313).

**Comment #3:** So my question is that how accurate are these total alkalinity measurements using the analyser and are they taken into account when the total alkalinity is determined.

**Answer #3:** Our previous work with this analyzer (Seelmann et al., 2019) revealed a relative analyzer uncertainty of 0.08 % under laboratory conditions. This was determined by the same standard addition experiment as described in this work (see Sect. 2.2.3). And yes, the uncertainty of the $A_T$ measurements was taken into account (manuscript was changed to address this, see lines 195 - 196).

**Comment #4:** Second, assessment: I have concerns that characterisation of the pure BCG and impure BCG would results in separate values for the extinction coefficients. I don't see any section in paper that shows the characterisation of pure BCG was conducted.

**Answer #4:** A full characterization of the purified BCG was beyond the scope of the study and therefore, not conducted. Of course, it is beyond a doubt that purified BCG might have different extinction coefficients than impure BCG (similar to mCP). In our study, all $A_T$ values were calculated using the coefficients reported by Breland and Byrne (1993). However, Li et al. (2013) investigated the influence of different BCG constants and coefficients on the measured AT value and concluded that they are insignificant (also with regard to indicator impurities). The reason for that is the calibration of the system with CRM as it was also done during our measurements (the measurement principle of the CONTROS HydroFIA$^®$ TA follows a similar procedure like it is described by Li et al. (2013)). Therefore, any uncertainties regarding the coefficients are taken into account for subsequent measurements. And the measurement quality both with purified and unpurified "high-purity" BCG is entirely sufficient for a spectrophotometric analyzer also without a characterization. However, by using "low-purity" BCG, this calibration seems to reach its limits as the measurement uncertainty impairs. That is why we added the statement "the usage of "low-purity" BCG is not recommended" (see line 265). Otherwise a characterization of "low-purity" BCG instead of purified BCG would be necessary. And this procedure seems to be senseless, because there is no need of using "low-purity" BCG as "high-purity" BCG is available. Finally, we concluded that a characterization was not necessary. We included the section "BCG characterization" in the "Cost-benefit analysis" section (line 314 - 327) to justify our decision.

**Comment #5:** If the paper is accepted for publication, I hope the authors could make their points clear so the reader could make proper decision for their research needs.

**Answer #5:** We hope that we could clarified all unclear points named by Referee with

our changes.

**Comment #6:** There are typos in the manuscript which I feel needs to be restructured. Specifically Line 3 influences from impurities. I believe it should read as influences of impurities.

**Answer #6:** Changed (see line 3)

**Comment #7:** Line 8: Could you please specify the kind of drift. Whether there is change in total alkalinity or how the drift is caused by the impurities.

**Answer #7:** Added this information (see lines 10 – 12 and 184 - 187)

**Comment #8:** Lines 40 describe to described

**Answer #8:** Changed (see line 45)

**Comment #9:** Section 2.2 It is stated that all analysis were carried out in air conditioned labs. My question is based on the temperature range for the instrument and sample what was the approximate temperature conditions. As I believe that most of the indicators have a temperature range where they are most effective and work the best.

**Answer #9:** The CONTROS HydroFIA$^{®}$ TA has an internal sample temperature control where the measured sample is constantly temperature controlled to $25.0 \pm 0.1$ °C which is the ideal temperature for BCG (the used characteristics by Breland and Byrne (1993) were carried out at 25°C). The temperature control is realized by a Peltier element and temperature measurement directly behind the cuvette. Therefore, the temperature of the seawater sample is independent of the room temperature. This information has now been added to the manuscript (see line 104).

**Comment #10:** Line 106-107 was the purified BCG prepared using the sodium salt in order to make sure that samples and indicators are of similar ionic strength?

**Answer #10:** Yes, we prepared the purified BCG solution in deionized water and added

C5

a certain amount of sodium hydroxide solution to transfer the BCG into the sodium salt (in solution). Information to this were added in the manuscript (lines 123 - 129).

**Comment #11:** Line 120 Equation 2 shows how the precision was calculated. It would be nice to show in the form of an equation how the total alkalinity for the samples was calculated as well.

**Answer #11:** Equation 2 (now Equ. 4) does not show how the precision is calculated. It shows how the accuracy is calculated. See lines 142 – 145 ("The root mean square error (RMSE) ... gave us information about the measuring accuracy. It was calculated by..."). The precision was calculated by the standard deviation. However, we decided against an equation for the standard deviation as this is a common statistical tool. General calculation equations for $A_T$ were added to the manuscript (see lines 105 - 114).

**Comment #12:** Line 144 additionally could be changed to 'in addition to'

**Answer #12:** Changed (see lines 166)

**Comment #13:** Line 178 reset to 'resets'.

**Answer #13:** Changed (see lines 203)

**Comment #14:** What is the frequency of cleaning the analyser? Could you specify please. And are standard runs or CRM used in between runs to maintain the calibration.

**Answer #14:** The frequency of cleanings depends on the application of the analyzer and cannot be stated in detail. For example: the more measurements are carried out with the analyzer the higher is the frequency of cleanings. That of course differs from user to user. Furthermore, there is a dependency on the measured water matrix as well, e.g. high turbidity coastal water requires more often cleanings. We made a recommendation based on our experiences (see lines 204 - 210)

**Comment #15:** Line 189 to 191. There is something wrong and it is difficult to understand. Probably reword or restructure the sentences so that it is easy to understand. I don't understand how the characters the author is mentioning in this section.

**Answer #15:** Reworded the sentences for a hopefully better understanding (see lines 223 - 226)

**Comment #16:** Was pure BCG characterised?

**Answer #16:** No (please see Answer 4)

**Comment #17:** Line 199 Figure 5 appears on page 12. Could it be moved closer to where it is mentioned in the text for easier referral?

**Answer #17:** Unfortunately, the placement of the figures is automatically performed by LaTeX, which was used for preparing the manuscript (using the Copernicus LaTeX template). We tried to move it, but it was not possible. Unfortunately, the movement of the figure is shown as a change in the manuscript by using the tool "latexdiff" (see caption of Fig. 5 and lines 266 – 269). Please ignore these changes. However, we think that the placement of the figures will be improved during the typesetting progress.

**Comment #18:** Line 204 Author refers to paper by Seelmann et al., 2019 and refers to accuracies I when compared to CRM. It would be nice to at least state some values here so that it is easier for the readers to follow though.

**Answer #18:** Added (see lines 239 – 240 and 243). We also added the requirements and the typical performance of the analyzer in Table 4 for a better comparison.

**Comment #19:** Lines 215 reword the sentence probably.

**Answer #19:** Reworded the sentence (see lines 249 - 252)

**Comment #20:** Line 217- 229 how the total alkalinity measurement deteriorates. This section is a bit confusing as the author tries to show total alkalinity and with that talks about the precision and accuracy. Could the author be more specific? Probably with

the help of equation or something how their system compares to other studies.

**Answer #20:** Please see Table 4 (page 13) in the changed manuscript (changed because of a previous comment). There is a comparison of the measurement uncertainties for purified, "high-purity" and "low-purity" BCG. Additionally, the fundamental $A_\mathrm{T}$ quality requirements reported by Dickson et al. (2007) can be found there in addition to the typical performance of the analyzer found during our previous study (Seelmann et al., 2019). It is obvious that the measurement quality (especially accuracy) deteriorates with increasing impurity level.

**Comment #21:** Line 245 what does FC refer to in this section.

**Answer #21:** FC means flash chromatography. This abbreviation was firstly explained in the Introduction section. But we added an additional explanation there (see line 287)

**Comment #22:** Line 250 with BCG i.e. can be changed to 'using BCG'

**Answer #22:** Changed (see line 293)

**Comment #23:** Lines 257 delete 'be'

**Answer #23:** Deleted (see line 301)

Please also note the supplement to this comment:
https://www.ocean-sci-discuss.net/os-2019-126/os-2019-126-AC1-supplement.pdf

Interactive comment on Ocean Sci. Discuss., https://doi.org/10.5194/os-2019-126, 2020.