Supporting Information for:

Title:

Characterization of a novel autonomous analyzer for seawater total alkalinity: Results from laboratory and field tests

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Comparison of measured underway *A*T data with calculated *A*T data

(Compare subsection “Field experiments” in section “Results and discussion” in main text)



Figure S1: Time-series of the *A*T values of a) the M133 cruise and b) the MSM 68/2 cruise, where the black filled circles represent the *A*T values of the analyzer and the red filled circles represent the calculated *A*T values based on the parameterization described by Lee et al. (2006).

Standard uncertainty *u*(c) approximation in the laboratory

(Compare subsection “Laboratory experiments” in section “Results and discussion” in main text)

Systematic component of the uncertainty *u*(bias)

*u*(bias) = RMSElinearRegression

*u*(bias) = 1.0 µmol kg-1 (absolute)

***u*(bias) = 0.04399898 %** (relative)

Random component of the uncertainty *u*(RW)

*u*(RW) = *σ*Laboratory

*u*(RW) = 1.5 µmol kg-1 (absolute)

***u*(RW) = 0.06599847 %** (relative)

Relative combined laboratory standard uncertainty *u*(c)

|  |  |
| --- | --- |
| $$u\left(c\right)=\sqrt{u(RW)^{2}+u(bias)^{2}}$$ | (S1) |

*u*(c) = 0.1887 %

Standard uncertainty *u*(c) approximation in the field (using CRM)

(Compare subsection “Field experiments” in section “Results and discussion” in main text)

Information to CRM Batch No. 160 and calculation of uncertainty of the reference sample *u*(Cref)

*A*T,CRM = 2212.44 ± 0.67 µmol kg-1 (certified value of the CRM Batch No. 160, provided by A. G. Dickson)

*u*(Cref) = (0.67 / 2214.44) x 100 %

***u*(Cref) = 0.03028331 %**

Uncertainty *u*(Corr) of drift correction

**Figure S2:** Bias (Δ*A*T) between measured *A*T and *A*T,CRM as a function of the measurement counter for drift correction purposes

|  |  |
| --- | --- |
| $$RMSE=\sqrt{\frac{\sum\_{}^{}\left(A\_{T,fitted}-A\_{T,measured}\right)^{2}}{n-2}}$$ | (S2) |
|  |  |
| $$u\left(Corr\right)=\frac{RMSE}{A\_{T,CRM}}×100\%$$ | (S3) |

***u*(Corr) = 0.078085733 %**

Uncertainty of bias *u*(bias)

|  |  |
| --- | --- |
| Corrected data: |  |
| **measurementCounter** | ***A*T,corr (µmol kg-1)** |  |
|  |
| 5 | 2211.5 |  |
| 109 | 2212.8 |  |
| 250 | 2211.1 |  |
| 310 | 2211.8 |  |
| 400 | 2213.4 |  |
| 459 | 2213.6 |  |
| 551 | 2213.5 |  |
| 604 | 2211.0 |  |
| 669 | 2213.5 |  |
| 748 | 2212.5 |  |
| 831 | 2211.8 |  |
| 882 | 2215.4 |  |
| 964 | 2211.5 |  |
| 1115 | 2212.8 |  |
| 1164 | 2210.2 |  |
|  |  |  |
| **mean of *A*T,corr** | 2212.4 | µmol kg-1 |
| ***s*bias** | 1.33603259 | µmol kg-1 |
| 0.06038729 | % |
| **n** | 15.0 |  |
| **bias to certified value of CRM** | -8.22E-14 | % |

|  |  |
| --- | --- |
| $$bias= \frac{A\_{T,mean}-A\_{T,CRM}}{A\_{T,CRM}}×100\%$$ | (S4) |
| $$u\left(bias\right)=\sqrt{bias²+\frac{s\_{bias}²}{\sqrt{n}}+u\left(Cref\right)^{2}+u(Corr)^{2}}$$ | (S5) |

*u*(bias) = 0.0891965 %

Uncertainty of the precision *u*(RW)

*u*(RW) = *σ*Field

*u*(RW) = 1.2 µmol kg-1 (absolute)

***u*(RW) = 0.05423876 %** (relative)

Relative combined standard uncertainty *u*(c)

Using equation S1

*u*(c) = 0.1044 %