Supporting Information for:

Title:

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

Authors:

Katharina Seelmann1,∗, Steffen Aßmann2, Arne Körtzinger1,3

1GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany

2Kongsberg Maritime Contros GmbH, Kiel, Germany

3Christian-Albrechts-Universität zu Kiel, Kiel, Germany

∗corresponding author: kseelmann@geomar.de

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

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

\\helmholtz\users\FB2\CH\kseelmann\Daten\MATLAB\For Paper\Data_timeseries\Compare.tif

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)

|  |  |
| --- | --- |
|  | (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

|  |  |  |
| --- | --- | --- |
|  | (S2) | |
|  |  | |
|  | (S3) |

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

Uncertainty of bias *u*(bias)

|  |  |  |
| --- | --- | --- |
| Corrected data: | |  |
| **measurement Counter** | ***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 | % |

|  |  |
| --- | --- |
|  | (S4) |
|  | | | (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 %