Metrological concepts applied to Total Alkalinity measurements in seawater: reference materials, inter-laboratory comparison and uncertainty budget

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Abstract. Total alkalinity (TA) measurements in seawater are crucial for characterizing and monitoring the oceanic carbonate system. While international best practices and guidelines exist, the field still lacks widely available traceable reference materials and a well-established uncertainty budget of the measurement method. In this study, we applied key metrological principles—development of reference materials, inter-laboratory comparison and uncertainty quantification—to TA measurements. We developed two reference materials, including an artificial material with a rigorously characterized reference value and an associated uncertainty budget, being potentially traceable to the International System of units (SI). These materials were tested in an inter-laboratory comparison involving five laboratories and demonstrated the applicability and interest of the reference materials developed for quality control. Additionally, we established an uncertainty budget for the TA measurement method using two metrological approaches. The resulting expanded uncertainty was 5 µmol kg⁻¹ (k = 2) in TA, approaching the 4 µmol kg⁻¹ target set by the Global Ocean Acidification Observing Network for climate monitoring. These findings mark a significant step toward improving the quality and comparability of TA measurements, thereby strengthening long-term ocean carbonate system monitoring.

1 Introduction

Total alkalinity of seawater (TA) represents the excess of proton acceptors over proton donors and can be described in a simplified manner as the buffer capacity of seawater. The exact definition of the total alkalinity is the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$, at 25°C and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$, same conditions) in one kilogram of seawater (Dickson, 1981). This definition, which is the one commonly accepted, is represented in terms of ionic chemical model by Eq. 1.

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}]$$

(1)

$$+2[PO_4{}^{3-}] + [SiO(OH)_3{}^-] + [NH_3] + [HS^-] + [...] - [H^+]_F -$$
$$[HSO_4{}^-] - [HF] - [H_3PO_4] - [...]$$

35   where brackets represent amount contents (mol kg^{-1} sol) and ellipses corresponds to minor species.

Total alkalinity is an essential independently measurable variable contributing to the monitoring of changes in the ocean carbon cycle and ocean acidification, that can be used together with pH$_T$ (total scale), Dissolved Inorganic Carbon (DIC) or partial pressure of CO$_2$ (pCO$_2$) to compute other variables of the ocean carbonate system. Moreover, total alkalinity is a relatively simple variable to monitor thanks to the fact that (1) it is independent from

40   temperature and pressure, unlike pH$_T$ and pCO$_2$, and (2) it isn't affected by atmospheric CO$_2$, unlike DIC, that could come for example from the exposure of the sample to air.

Ensuring the quality of total alkalinity measurement results is of great importance. The Global Ocean Acidification Observing Network and the World Meteorological Organization have fixed a data quality objective corresponding to a standard uncertainty in total alkalinity measurement results being of 1 and 2 µmol kg^{-1}, respectively (GOA-

45   ON, 2019; WMO et al., 2022). These values were chosen in order to highlight climatic variations of total alkalinity relevant to the monitoring of ocean acidification.

Contributing to the objective of achieving comparable TA measurement results, the Scripps Institution of Oceanography currently distributes reference materials constituted of a stabilized natural seawater (Dickson, 2010). These materials are carefully characterized in terms of total alkalinity using the open-cell multi-step

50   potentiometric titration method, whose accuracy has been validated with synthetic solutions constituted of bases such as sodium carbonate, borate or TRIS (Dickson et al., 2003). It is the only laboratory producing reference materials (RMs) for total alkalinity measurements on a regular basis (Acquafredda et al., 2022). However, the RMs distributed aren't fully traceable and aren't given with a rigorously assessed uncertainty. Developing a reference material made in artificial seawater, characterized with a traceable reference method, and with a thoroughly

55   quantified uncertainty that could be distributed together with a natural seawater such as the one from Scripps, might help in improving the trueness of the results. Moreover, the uncertainty budget of the measurement method results is required to ensure the comparability of total alkalinity measurements.

The first aim of the work presented in this paper was thus to develop a reference material produced following the international standards appropriate to the production of reference materials (ISO 17034, 2016; ISO Guide 35:2017,

60   2017). This material is made of artificial seawater with a total alkalinity reference value attributed from knowledge of the composition. The uncertainty budget associated to the reference value is determined following the Guide to the expression of Uncertainty in Measurement (GUM, 'JCGM 100:2008', 2008) and integrates information about stability and homogeneity of the material.

This developed reference material has been tested in an inter-laboratory comparison conducted with five French

65   laboratories conducting TA measurements with the standardized method, being the multi-step potentiometric titration method. Measurements were also performed on a second material, produced similarly to the one from Scripps, being a stabilized natural seawater from the Mediterranean Sea. The second aim of the work presented was, from the inter-laboratory comparison, to study the applicability in quality control for total alkalinity measurements of the artificial and natural solutions developed as reference materials.

70   The third objective of the work presented was to thoroughly establish the uncertainty budget of the standardized measurement method, which is up to date lacking. This paper thus presents for the first time an uncertainty estimation for the open-cell multi-step potentiometric titration method together with Gran's data treatment,

established following the GUM (i.e. bottom-up approach). A comparison with the uncertainty budget obtained from the inter-laboratory comparison results (i.e. top-down approach) is also presented.

2 Materials and methods

2.1 TA measurement method

The titration method has always been the measurement method of choice for the determination of seawater total alkalinity (Greenberg et al., 1932).

The procedure consists in a multi-step addition of acid, with algorithmic determination of the equivalence point from potentiometric data titration curve (Dickson, 1981; Edmond, 1970). This method either can be used in an open or closed cell. This multi-step titration is recognized as the best-practice method for measurements in seawater compared to the single-step method (Dickson et al., 2007). Therefore, this is the procedure chosen and thus the one referring to in the rest of this paper.

The standard procedure as well as the data treatment method for the open-cell multi-step titration has been well described in the literature (Dickson et al., 2003, 2007; Okamura et al., 2014; Wolf-Gladrow et al., 2007), and is detailed in Appendix A.

The measurement model of TA obtained from the titration curve using Gran's method (Gran, 1952) is presented below:

$$TA = \frac{-b}{a} \frac{v_{HCl}}{m_{init}} \tag{2}$$

where v_{HCl} is the acid amount content (mol kg^{-1} sol), m_{init} the mass of sample analysed (g) and coefficients a and b represent, respectively, the slope and the intercept of the linear regression $F1 = a * m_{HCl} + b$.

The Gran function $F1$ is represented by Eq. 3.

$$F1 = (m_{init} + m_{HCl}) \times \exp\left(\frac{E}{\frac{RT}{F}}\right) \tag{3}$$

where m_{HCl} is the mass of acid added (g), E is the potential measured by the glass electrode (V), R the universal gas constant (J mol^{-1} K^{-1}), T temperature of the sample (K), F the Faraday constant (C mol^{-1})

This method gives a first estimation of the total alkalinity. However, errors are introduced when using the Gran's method for seawater analysis due to competing acid-base equilibria in seawater. A method allowing to solve the equivalence point using a nonlinear least-squares (NLLS) regression has thus been developed (Dickson, 1981; Martz, 2005). This method is detailed in Appendix A.

2.2 Development of reference materials

Two reference materials have been developed for the quality control of seawater total alkalinity measurement methods: a stabilized natural seawater and an artificial seawater. This section details the methods applied for the preparation, characterization, stability and homogeneity studies, as well as for the uncertainty quantification of the reference TA value assigned to the artificial solution.

2.2.1 Preparation

Stabilized natural seawater

The natural seawater was collected by the Mediterranean Institute of Oceanography (MIO) during an oceanographic field trip to the Antares station (42°48 N 6°10 E) of the Mediterranean Ocean Observation System for the Environment (MOOSE; Lefevre, 2010). Deep waters of respectively 2000, 1750, 1500 and 1000 meters depth were collected in two plastic containers and homogenized, for a total of 35 liters of seawater. The containers were stored protected from light at 4°C until filtration. 25 liters of the collected seawater were filtered with a 0.2 µm Sartobran filter using a Masterflex peristaltic pump, and gathered from the two containers to one unique container in Nalgene (polycarbonate). 10 ml of a solution of mercuric chloride at 36 g.l⁻¹ were added to the seawater in the Nalgene container, corresponding to the usual concentration of 0.02% saturated $HgCl_2$. The container was stirred to ensure homogeneity of the seawater. The natural seawater was then bottled in 42 ground-neck borosilicate bottles of 500 ml sealed with greased glass stoppers held on with elastic bands.

Artificial seawater

The composition of the artificial seawater was chosen in order to have a total alkalinity of 2500 µmol kg⁻¹ sol, known based on gravimetric information, and with salinity and pH_T values that match those of a natural seawater. To respond to these criteria, the artificial seawater is composed of sodium bicarbonate ($NaHCO_3$), sodium carbonate (Na_2CO_3) and is made in a NaCl matrix. The ratio of $NaHCO_3$ over Na_2CO_3 amount contents to obtain a pH_T close to 8.1 was estimated based on Bjerrum plot of carbonate species and their dissociation constant in a saline media (Wolf-Gladrow et al., 2007). The composition of the artificial solution is given in Table 1.

Table 1: Composition and information about ionic strength (I), absolute salinity and theoretical pH of the artificial solution for total alkalinity reference material

	v (mol kg⁻¹ sol)	b (mol kg⁻¹ H₂O)
$NaHCO_3$ (*Merck, 100.039 %*)	0.0022746	0.0023578
Na_2CO_3 (*Merck, 99.948 %*)	0.0001127	0.0001168
NaCl (*VWR chemicals, 99.945 %*)	0.6000000	0.6219348
I	0.625	
Absolute salinity	35	
Theoretical pH	8.1	

Note: where v is the amount content, expressed in mol kg⁻¹ sol, b is the molality, expressed in mol kg⁻¹ H₂O and I is the ionic strength. The suppliers of the salts and their purity are given in brackets.

The artificial solution was prepared from respective stock solutions of $NaHCO_3$ and Na_2CO_3. The purity of the sodium carbonate and sodium bicarbonate salts used were characterized in terms of purity as bases expressed as sodium carbonate by coulometric analysis performed at the National Metrology Institute of Japan (NMIJ), while the purity of the sodium chloride was characterized by coulometric analysis at the Slovack Metrology Institute (SMU) based on chloride content. The sodium carbonate salt was dried at 280°C for 4 hours and cooled down in a desiccator for 1h before use, to remove potential humidity. This procedure wasn't applied to sodium bicarbonate salt due to the decomposition reaction caused by heat. The same pre-treatment of the salts was applied before characterization at NMIJ and before stock solution preparation at LNE, ensuring that the purity obtained by coulometric analysis is suitable for the solution preparation.

Two batches of artificial seawater solution of respectively 12 and 7 kg were prepared. The first batch (Batch 1) was bottled in equivalent bottles to the one used for the natural seawater (i.e. ground-neck borosilicate bottles of 500 ml sealed with greased glass stoppers maintained with elastic bands). While the second batch (Batch 2) is
140   bottled in *SCHOTT* borosilicate bottles of 500 ml with screw caps containing PTFE coated seals.

The stabilized natural seawater and Batch 1 of the artificial solution were distributed to be studied in the inter-laboratory comparison described in Sect. 2.3. The Batch 2 of the artificial seawater was analysed at LNE, with the objective of comparing the stability of the material for the two methods of bottling.

2.2.2 Characterization

145   The artificial seawater was characterized in terms of total alkalinity based on gravimetric information. Given the composition of Table 1 and the total alkalinity definition (Eq. 1), the alkalinity introduced in the artificial solution is supposed to only come from carbonate and bicarbonate ions, as described by Eq. 4.

$$TA = 2\,v_{Na_2CO_3} + v_{NaHCO_3} \tag{4}$$

where v represents amount contents (mol kg^{-1} sol).

150   However, the impurities contained in the NaCl salt (0.055%) can also contribute to the total alkalinity of the solution. This source of alkalinity is hereafter called background alkalinity (noted $TA_{background}$, expressed in mol kg^{-1} sol).

The final total alkalinity of the artificial solution was thus obtained from Eq. 5.

$$TA = 2\,v_{Na_2CO_3} + v_{NaHCO_3} + TA_{background} \tag{5}$$

155   The background alkalinity was quantified based on the preparation of four solutions with the same amount contents of bicarbonate and carbonate ions while varying the NaCl amount content from 0 to 3 mol kg^{-1} sol (solutions in NaCl matrix of respectively 0, 1, 2 and 3 mol kg^{-1} sol). The total alkalinity of each of the four solutions was determined at LNE from, respectively, the mean of at least three repeatability measurements made using the open-cell multi-step potentiometric titration method, as described in Sect. 2.1, and using the material described
160   Appendix B. The difference of total alkalinity between the measured one and the theoretical value calculated with Eq. 4, was represented in function of the amount content of NaCl for each NaCl amount content present in the four solutions. From this representation was computed a linear regression passing through the origin. The linear regression was forced to pass through the origin as the background alkalinity coming from NaCl impurities is theoretically zero for a solution without NaCl matrix. The measurement results, shown in Fig. 2, support this
165   theory. The linear relation obtained allowed the determination of the background alkalinity for the solution studied (i.e. for a NaCl amount content of 0.6 mol kg^{-1} sol, Table 1). This is further discussed in Sect. 3.1.1.

Batch 1 of the artificial reference material and the stabilized natural seawater were characterized in terms of practical salinity aboard the *Thalassa* oceanographic vessel during the 2023 PIRATA cruise (Bourles et al., 2023; Llido, 2023), using an *OSIL Portasal 8410A* salinometer.

170   The natural seawater was also characterized in terms of dissolved nutrients (i.e. silicates, nitrites, phosphates and nitrates) based on colorimetric determination using a *SEAL AutoAnalyzer 3 HR* at the platform of Analysis of Basic Parameters (PAPB) of the MIO.

2.2.3 Stability and homogeneity studies

Homogeneity

175 Homogeneity estimations were based on TA measurements carried out at LNE, MIO and at the French National Service for Analysis of Oceanic CO_2 Parameters (SNAPO-CO_2) following the standardized multi-step potentiometric titration method. The compatibility of the measurements performed by these three institutes have first been established.

The homogeneity assessment integrates two components: (1) the between-bottle homogeneity, taking into account
180 standard deviation between different bottles of a same batch, and (2) within-bottle homogeneity, taking into account standard deviation within one bottle.

Between-bottle homogeneity of the stabilized natural seawater and of Batch 1 of the artificial seawater was computed from standard deviation of single measurements made consecutively on three bottles of the same batch. It was conducted with the closed-cell multi-step potentiometric titration method at the SNAPO-CO_2.

185 The between-bottle homogeneity of the Batch 2 of the artificial seawater was obtained from the standard deviation of the mean TA values of three different bottles, themselves computed from at least three repeatability measurements. These measurements were made at LNE, using the open-cell multi-step potentiometric titration method.

The within-bottle homogeneity was computed, for the stabilized natural seawater and Batch 1 of the artificial
190 seawater, from the mean of the standard deviations obtained at LNE and MIO, from, respectively, three repeatability measurements made in one bottle. The within-bottle homogeneity of the Batch 2 of the artificial seawater was obtained from the mean of the standard deviations obtained from repeatability measurements of the same three bottles used for between-bottle homogeneity assessment.

Stability

195 The stability of the stabilized natural seawater and Batch 1 of the artificial reference material, both bottled in ground-neck bottles, were followed by each participant to the inter-laboratory comparison over one year, with total alkalinity measurements performed every three months. For the results obtained at each deadline, Grubb's and Cochran's tests were applied to remove eventual outliers and the median of the remaining values are taken to establish the stability over time. The stability over time of the Batch 2 of the artificial seawater, bottled in glass
200 bottles with screw caps, was followed at LNE on the same schedule.

The stability was established with a statistical Student test (t test) highlighting whether there is a significant trend in the evolution of the material or not (ISO Guide 35, 2017). This test is based on the determination of the slope, noted b1, of the regression line of the TA values as a function of time. It computes t_0, defined as being the ratio of the slope on its standard deviation, noted sb1, and compares it to the threshold value tα in the Student's table with
205 n-2 degrees of freedom at a 95% confidence level (Linsinger et al., 2001).

Stability to transport was described as the discrepancy between measurements results obtained at LNE and MIO, LNE being the source laboratory of the artificial reference material and MIO the source of the natural seawater reference material. It isn't computed for the second batch of artificial solution in screw cap bottles that was only tested at LNE.

210 Dissolved nutrients of the stabilized natural seawater and of Batch 1 of the artificial seawater were also analysed at the end of the stability study to highlight an eventual evolution.

2.2.4 Uncertainty estimation of the artificial reference material value

The uncertainty associated to the total alkalinity reference value of the artificial solution was obtained based on the ISO Guide 35 (2017) and takes into account the uncertainties coming from the preparation and the characterization u_{charac}, the homogeneity u_{hom} and the stability u_{stab} (Eq. 6).

$$u_{MR} = \sqrt{u_{charac}^2 + u_{hom}^2 + u_{stability}^2} \tag{6}$$

Preparation and characterization uncertainty

The uncertainty coming from the preparation and characterization was estimated based on Eq. 5 following the law of uncertainty propagation of the Guide to the expression of Uncertainty in Measurement (JCGM 100:2008, 2008). The evaluation of the uncertainties of the different terms in Eq. 5 requires several steps of uncertainty determination.

    (1) The uncertainty of the amount contents of the stock solutions of NaHCO₃ and Na₂CO₃ (v_{stock}) were determined using uncertainty propagation for the following Eq. 7.

$$v_{stock} = \frac{m_{salt}*p*1000}{(m_{salt}+m_{H2O})* M_{salt}} \tag{7}$$

where m_{salt} is the mass of salt of either NaHCO₃ or Na₂CO₃ salts (g), m_{H2O} the mass of water (g), p the purity of the salt and M_{salt} the molar mass of the salt.

The uncertainties on the masses were obtained from the weighing scales calibration, the uncertainty of the purity was known from NMIJ coulometric characterization certificate and uncertainties on the molar masses were taken from IUPAC (Meija et al., 2016).

    (2) The uncertainty of the amount content of NaHCO₃ and Na₂CO₃ in the artificial reference material ($v_{salt_{RM}}$) was determined using the law of uncertainty propagation for Eq. 8.

$$v_{salt_{RM}} = \frac{m_{salt}* v_{stock}}{m_{total}} \tag{8}$$

where m_{total} is the total mass of the reference material ($m_{NaHCO3} + m_{Na2CO3} + m_{NaCl} + m_{H2O}$), in g.

The quantification of the uncertainties of masses and v_{stock} are detailed above.

    (3) The uncertainty associated with the background alkalinity coming from the NaCl matrix also needs to be quantified. The amount content of NaCl introduced in the reference material solution and in each of the four solutions at different NaCl amount contents used to determine the background TA was obtained with Eq. 9, whose term's uncertainties quantification is detailed in the steps above.

$$v_{NaCl} = \frac{m_{NaCl}*1000}{m_{total}* M_{NaCl}} \tag{9}$$

The difference between measured and theoretical total alkalinity $\Delta(TA_{measured} - TA_{theoretical})$ was represented as a function of the amount content of the NaCl of the solutions used to study the background alkalinity, being respectively, 0, 1, 2 and 3 mol kg⁻¹ sol. The uncertainty estimate chosen to be attributed to the measured TA, pending a thorough assessment, was 2 µmol kg⁻¹. Indeed, it is the order of precision reported to be achievable in the literature for TA measurements. Systematic uncertainty sources, as the ones coming from the device, the operator or the procedure are here cancelled. The uncertainty is thus expected to be relatively low. The uncertainty of the theoretical total alkalinity was obtained using the law of uncertainty propagation in Eq. 4, whose term's uncertainties quantification are detailed in step (2) above.

The slope b_b giving the evolution of $\Delta(TA_{measured} - TA_{theoretical})$ in function of v_{NaCl} was obtained by linear
250   regression passing through the origin.

The uncertainty associated to this slope was obtained using the LNE-RegPoly software. LNE-RegPoly estimates
a polynomial of degree k as $y = b_a + b_b x + b_c x^2 + ... + b_k x^k$ using n pairs of points (xi, yi), taking into account the
uncertainties associated with these points. It then propagates the uncertainties from the points to the coefficients
of the polynomial. A second uncertainty component was added to this uncertainty to take into account for the fact
255   that the regression is forced to pass through the origin. Indeed, the residuals were thus slightly bigger. To do so,
the standard deviations of slopes (i) with regular linear regression and (ii) forced to pass through the origin, were
computed from knowledge of the residuals of the regressions. The difference of the standard deviations of
regressions (i) and (ii) was added as an uncertainty component of the slope b_b.

A second approach based on weighted orthogonal distance regression was applied with help of statisticians to
260   compute the uncertainty of the slope b_b (Boggs et al., 1992). This approach yielded a slightly lower uncertainty.
To maximise the uncertainty of the slope, the first approach, described above, was adopted.

Knowing the uncertainties of, respectively, the slope b_b and the amount content of NaCl in the reference material
solution ($v_{NaCl_{RM}}$), the uncertainty on the background total alkalinity is obtained by propagation in Eq. 10.

$$TA_{background} = b_b * v_{NaCl_{RM}} \qquad (10)$$

265   (4) The final step is to propagate the uncertainties quantified in steps (2) and (3) in the Eq. 5, giving the total
alkalinity of the reference material.

Homogeneity uncertainty

The within and between bottles homogeneities were assessed from the homogeneity study described in Sect. 2.2.3.
270   This study highlighted that the determination of the homogeneity is highly dependent on the variability of the
measurement method. It was chosen to neglect the within-bottle homogeneity component, supposed to be
negligible, in the homogeneity uncertainty quantification. The uncertainty relative to homogeneity was obtained,
based on between-bottle homogeneity assessment, from Eq. 11. It is computed for each batch respectively.

$$u_{hom} = \frac{s^2}{N} \qquad (11)$$

275   where s^2 is the standard deviation between the mean TA values measured for each bottle considered in the
homogeneity study and N the number of bottles analysed (i.e. 3 bottles for each batch).

Stability uncertainty

The uncertainty on the stability is obtained from Eq. 12 if no significant trend is established by the t tests described
280   in Sect. 2.2.3, and by Eq. 13 if a significant trend is established. These equations are introduced below.

$$u_{stab} = s_{b1} \cdot t \qquad (12)$$

$$u_{stab} = \sqrt{(\frac{b1 \cdot \frac{t}{2}}{\sqrt{3}})^2 + (s_{b1} \cdot t)^2} \qquad (13)$$

where b_1 corresponds to the slope of the evolution over time, s_{b1} corresponds to the slope standard deviation and
t to the time.

285   The assessment of stability to transport showed no significant discrepancy between the source and recipient
laboratory, this source of uncertainty was thus neglected in the uncertainty budget.

2.3 Inter-laboratory comparison

2.3.1 Protocol of the inter-laboratory comparison

The inter-laboratory comparison (ILC) was conducted with five French laboratories conducting seawater total
290   alkalinity measurements with the standardized measurement method, being the multi-step potentiometric
measurement method (Dickson et al., 2007 - SOP 3a & 3b).

Figure 1 gathers information about the participants to the ILC, including affiliation and measurement methods.

⬤ Open-cell multi-step potentiometric titration

◯ Closed-cell multi-step potentiometric titration

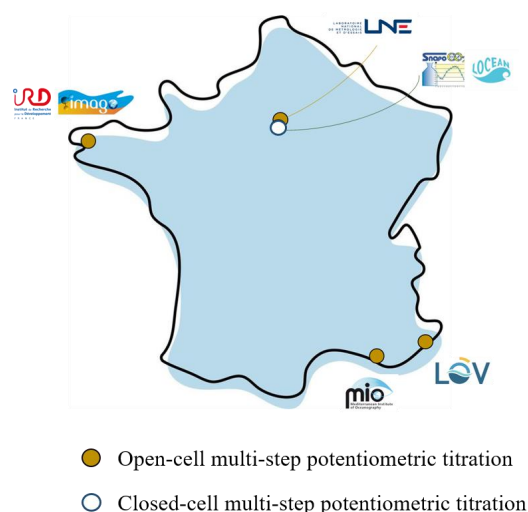



Figure 1: Information concerning the participants to the inter-laboratory comparison

295   The total alkalinity measurements were performed by each participant on the two reference materials developed:
the stabilized natural seawater, and the artificial seawater of known TA. The measurements were performed two
months after the preparation of the artificial seawater, two months after bottling for the natural seawater, and all
the participants completed their measurements within a two weeks period. Each participants performed three
repeatability measurements, within one bottle for LNE, MIO, IMAGO and LOV, and using three bottles for
300   SNAPO-CO$_2$ as the closed-cell measurement method requires a larger volume of sample (around 500 ml).

The amount content of the hydrochloric acid used by MIO, SNAPO-CO$_2$, IMAGO and LOV was calibrated based
on the analyses of a total alkalinity reference material purchased from Scripps Institution of Oceanography. LNE's
hydrochloric acid was a Standard Reference Material purchased from SMU (Slovack metrology institute, ν = 1
mol kg^{-1} sol) diluted gravimetrically.

305   As the artificial reference material didn't contain sulphate and fluoride ions, the data treatment applied was Gran's
regression method. However, for the natural seawater samples, a correction computed from the nonlinear least-
squares regression method was applied to take into account for the matrix.

In addition, the SNAPO-CO$_2$ used the titration data from the closed-cell multi-step potentiometric titration to
compute dissolved inorganic carbon values for the stabilized natural seawater reference material.

310 **2.3.2 Treatment of the inter-laboratory comparison results**

The median value of each sample analysed was obtained from means of the replicate values obtained by each of the five participants, the uncertainty associated to the median was calculated with the method given in Muller (2000).

The Cochran's and Grubbs' statistical tests were used to identify eventual isolated values or outliers due to,

315 respectively, intra-laboratories variances and discrepancy to the mean observation. These values were removed from the ILC results treatment used to quantify trueness and precision of the method. The bias between the mean obtained on the artificial seawater and the reference value obtained with Eq. 5, gives information on the trueness of the measurement method. The precision was computed from the combination of intra- and inter-laboratory variances obtained for the two materials.

320 As all participants realised measurements on the two different solutions developed, the ILC results were presented under a Youden plot (Youden, 1959; ISO 13528, 2022,). The methodology of the Youden plot is as follows:

- The results of each participant is represented on a graph by a single point (Xi, Yi), representing its mean TA value obtained on the natural seawater in the x-axis (Xi) and its mean TA value of the artificial seawater in the y-axis (Yi).

325 - The medians obtained on the two samples are drawn as the centroid (X,Y). Vertical and horizontal lines are drawn from that centroid, representing x-axis and y-axis medians (i.e. natural seawater and artificial seawater median values, respectively).

- A 45° line passing through the centroid (X,Y) is then drawn.

- A 95% confidence circle is finally represented from the centroid with a radius, r, calculated with Eq. 14.

330 $$r = \sqrt{\frac{\sum_i^p ((X_i - Y_i) - \overline{(X_i - Y_i)})^2}{2*(p-1)}} * 2.448 \tag{14}$$

where $\overline{(X_i - Y_i)}$ represents the mean difference (Xi – Yi), p is the number of participants and 2.448 is the factor allowing to obtain a circle with a 95% confidence level (Youden, 1959).

Each participants having a data point (Xi, Yi) outside of the confidence circle is considered as having biased results. The shortest distance of (Xi, Yi) to the 45° line is proportional to random errors for the concerned

335 laboratory, while the distance between that point on the 45° line to the centroid is proportional to systematic errors (Martín et al., 2017).

2.4 Uncertainty estimation of the total alkalinity measurements results

2.4.1 Top-down approach

The uncertainty of the total alkalinity measurement results was established using the top-down approach (i.e. using

340 experimental data from the inter-laboratory comparison exercise), following the ISO standard 21748 "Guidance for the use of repeatability, reproducibility and trueness estimates in measurement uncertainty evaluation" (2017). The uncertainty budget was calculated using Eq. 15 and 16.

As the uncertainty estimates require information about trueness of the method, only the measurement results carried out on the artificial seawater, having a characterized reference value, can be used. Thus, the final

345 uncertainty budget can be attributed to the results obtained with the multi-step potentiometric titration method using the Gran's data treatment. Uncertainties coming from the nonlinear least-squares regression data treatment are not included in the budget.

$$u^2(y) = s_L^2 + s_r^2 + u^2(\hat{\delta}) \tag{15}$$

where $u(y)$ is the estimated measurement result uncertainty, s_L the inter-laboratory standard deviation, s_r the
intra-laboratory standard deviation divided by the square root of the mean number of replicates, and $u(\hat{\delta})$ the
uncertainty associated to the estimated bias of the measurement method (Eq. 16).

$$u^2(\hat{\delta}) = \frac{(s_L^2 + s_r^2) - \left(1 - \frac{1}{n}\right)s_r^2}{p} + u^2(\hat{\mu}) \tag{16}$$

where n is the number of replicates in each laboratory, p the number of laboratories and $u(\hat{\mu})$ the standard
uncertainty of the certified reference value.

2.4.2 Bottom-up approach

The bottom-up approach for the establishment of the uncertainty budget of the total alkalinity measurement results
is hereafter detailed for the open-cell multi-step potentiometric titration method applied at LNE and Gran's data
treatment, following the Guide to Uncertainty in Measurement (JCGM 100:2008, 2008). Details of the
instrumentation for TA measurements performed at LNE are given in Appendix B.

The bottom-up approach involves several steps: the establishment of the measurement model, the uncertainty
quantification of the input variables, the identification of eventual covariances, the propagation of the uncertainty
through the established model and the final expression of the results.

Establishment of the measurement model

The measurement model was established from the measurement and Gran's data treatment methods presented in
Sect. 2.1, represented by Eq. 2 and 3.

Identification and uncertainty quantification of input variables

Table 2 gathers all the input variables identified in the measurement model presented above. It also presents the
sub-sources of uncertainty influencing these input variables and the method allowing their uncertainty
quantification. The sub-sources identification together with their uncertainty quantification methods are based on
the procedure conducted at LNE and instrumentation available there.

**Table 2: Identification and uncertainty quantification method of the input variables involved in the measurement model
of the open-cell multi-step potentiometric titration method conducted at LNE.**

Input variables	Definition	Unit	Sub-sources of uncertainty	Sub-sources uncertainty quantification method
m_{HCl}	Mass of HCl delivered during the titration	g	-HCl density : Densimeter and temperature of the acid accuracies (g/cm3 and °C, respectively) -Volume delivered: burette accuracy (ml)	-Densimeter specification -Temperature probe calibration certificate -Tolerance/√3
m_{init}	Mass of sample analysed	g		-Weighing scale calibration certificate
		V	-Tolerance of the electrode	-Tolerance/√3

E	Potential measured by the glass electrode		-Repeatability	-standard deviation from experimental data
T	Temperature of the sample during the titration	°C	-Resolution -Repeatability -Trueness	-Probe specification - standard deviation from experimental data -Calibration with a certified temperature probe
R	Universal gas constant	J mol^{-1} K^{-1}		(Pratt, 2014)
F	Faraday constant	C mol^{-1}		(Pratt, 2014)
ν_{HCl}	Amount content of the acid titrant	mol kg^{-1} sol	-Stock solution (HCl 1 mol kg^{-1} sol) amount content -Gravimetric dilution	-SMU certificate -Calibration certificate
a and b	Gran's regression coefficients		-m_{HCl} -F1 -Gran's regression method	-As for m_{HCl} above -Law of uncertainty propagation in Eq. 3 -LNE-RegPoly

Uncertainty propagation and expression of the results

375 The final uncertainty on TA results was obtained using the law of uncertainty propagation in Eq. 2. The utilisation of the software LNE-RegPoly for the quantification of the uncertainties of coefficients a and b coming from the linear regression of F1 in function m_{HCl} allowed demonstrating that these two terms are highly correlated. The factor of correlation between a and b, quantified by the software, was integrated in a correlation matrix introduced in the process of uncertainty propagation using partial derivatives.

380 The final uncertainty is expressed as expanded uncertainty using a coverage factor, k, of 2.

3 Results

3.1 Production of reference materials

3.1.1 Characterization

Two reference materials have been produced, an artificial seawater (2 batches) and a stabilized natural seawater.
385 Table 3 presents the characteristics of these two reference materials, established following the methods described in Sect. 2.2.2.

Table 3: Characteristics of the produced reference materials for total alkalinity measurements

Artificial solution			Stabilized natural seawater		
	Batch 1 (Ground neck bottles)	Batch 2 (Screw caps bottles)	Practical salinity[b]		38.533
Absolute salinity[a]	35.189	35.184	Dissolved nutrients (μmol l^{-1})	Silicates	12.37
Ionic strength	0.623	0.623		Nitrites	0.02
Reference Total Alkalinity value (μmol kg^{-1})	2503.64	2503.78		Phosphate	0.40
				Nitrates & nitrites	9.08

[a] The absolute salinity was calculated based on the composition of the solution (g of dissolved salts per kg of solution).

[b] The practical salinity was measured with a salinometer and is based on a conductivity ratio.

Reference values of total alkalinity for the two batches of artificial reference materials are computed from Eq. 5, giving values of respectively 2503.64 and 2503.78 μmol kg^{-1}. These values seem to indicate the reproducibility of the batches preparation. The background alkalinity has been quantified, following the method described in Sect. 2.2.2, to be 3.53 μmol kg^{-1} for both batches, and is included in the reference values given above. Figure 2 represents the results of the quantification of the background alkalinity.

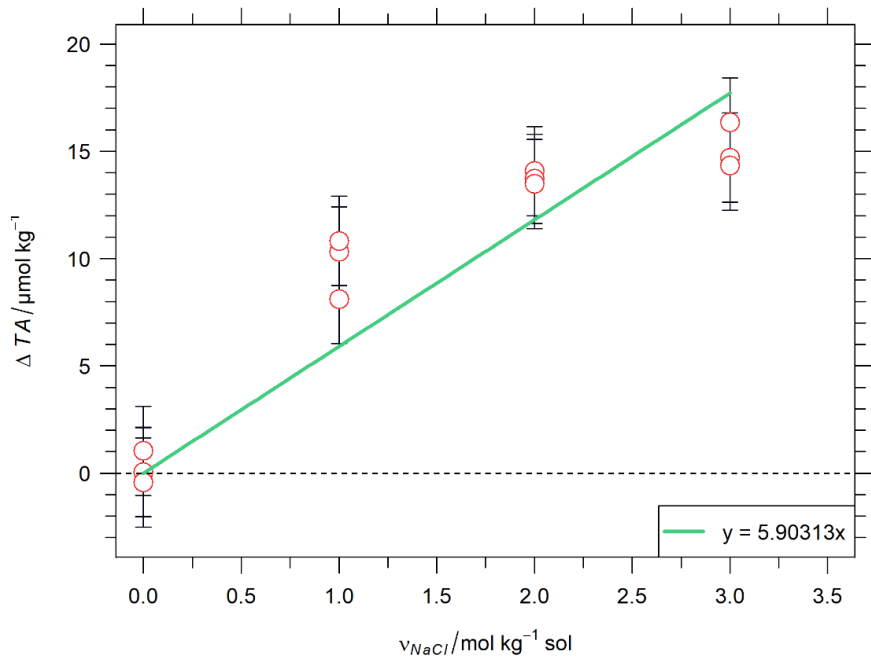



Figure 2: Quantification of background alkalinity coming from the NaCl matrix for the artificial reference material. Where ΔTA represents the difference of total alkalinity between the measured one and the theoretical value calculated with Eq. 4. Red circles represent single TA potentiometric measurements with error bars representing their standard uncertainty, and green straight line represents the slope obtained from linear regression passing through the origin.

3.1.2 Homogeneity, stability studies and uncertainty quantification

Table 4 presents the results of the homogeneity and stability assessments established as described in the Sect. 2.2.3.

Table 4: Results obtained from the homogeneity and stability assessments of the reference materials developed. Numerical values are expressed in µmol kg^{-1}.

405

	Artificial solution		Stabilized natural seawater
	Batch 1 (Ground neck bottles)	Batch 2 (Screw caps bottles)	
Homogeneity			
Between-bottle	1.0820	0.9915	1.6100
Within-bottle	1.3505	1.2859	1.6618
Stability over time			
Slope (b1)	0.8065	0.9325	0.2219
Slope standard deviation (Sb1)	0.2735	0.1341	0.4366
t0 (b1 / Sb1)	2.9485	6.9528	0.5081
tα (Student n-2)	4.3027	3.1824	3.1824
Stability to transport	1.2052	/	1.1781

The between and within bottles standard deviations are in the range $1.0 – 1.7$ µmol kg^{-1}, and seems to be slightly greater for the natural seawater than for the artificial solutions.

Assessments of stability over time show a significant trend (t0 > tα) only for Batch 2 of the artificial reference material. Its stability has been studied up to fourteen months after the preparation, however, the significant trend,
410   and thus instability of the material, was already established after eleven months. The stability study of the stabilized natural seawater and of the 1st batch of artificial seawater doesn't show a significant trend, which seems to indicate a better stability. The stability study on the Batch 1 of the artificial solution had to be interrupted before due to lack of remaining bottles to pursue the study, it was conducted up to eleven months. The stability study of the natural solution was conducted up to fourteen months after bottling. The detail of the alkalinity values used to
415   establish the stability of the materials are given in Appendix C1.

The stability to transport is negligible (discrepancies are in the level of within and between bottles homogeneities reported) and is thus not taken into account in the final uncertainty budget. It is expected that the second batch of artificial solution behaves similarly to transportation as the other materials. Thus, the uncertainty of the second batch is also computed, even if stability to transport study wasn't performed.

420   Table 5 presents the uncertainty budget attributed to the reference values of the artificial reference materials as detailed in Sect. 2.2.4.

Table 5: Uncertainties involved in Eq. 6 for the assessment of total alkalinity reference value's uncertainty of the artificial reference material

	Batch 1 (Ground neck bottles)	Batch 2 (Screw caps bottles)

Characterization and preparation			
ν_{NaHCO_3} (µmol kg^{-1})		5.11E-01	8.06E-01
$\nu_{Na_2CO_3}$ (µmol kg^{-1})		5.53E-02	7.77E-02
Background TA (µmol kg^{-1})		3.09E-01	3.09E-01
Combined u		6.00E-01	8.67E-01
Homogeneity		3.61E-01	3.30E-01
Stability		8.21E-01	9.02E-01
Total			
u (k=1)		1.08E+00	1.29E+00
U (k=2)		2.16E+00	2.59E+00

425 The standard uncertainties of the terms in equations 5 are assessed following the method given in Sect. 2.2.4 and are given in Table 5, corresponding to the "characterization and preparation" uncertainty. The difference of uncertainty coming from the preparation and characterization between the two batches is explained by the fact that the volume of the Batch 1 is higher, allowing to reduce the relative uncertainty of gravimetric preparation.

The uncertainty of stability of the Batch 1 and Batch 2 of the artificial reference material are computed from Eq.
430 12 and 13, respectively, using the t-test information given in Table 4 and for a material shelf life of 3 months (chosen as the ILC was conducted within 3 months after the preparation of the solutions).

The standard uncertainty attributed to the TA reference values of Batch 1 and Batch 2 of the artificial reference material are of 1.08 and 1.29 µmol kg^{-1}, respectively, and were computed from Eq. 6. Which gives a global expanded uncertainty budget (i.e. with a coverage factor, k, of 2) of respectively 2.16 and 2.59 µmol kg^{-1}.

435 **3.2 Inter-laboratory comparison results**

Figure 3 represents, following the method detailed in Sect. 2.3.2, the Youden plot obtained from the results of the inter-laboratory comparison conducted with five laboratories (Fig. 1) for total alkalinity measurements on the two reference materials developed: a stabilized natural seawater and an artificial solution. The total alkalinity values obtained by each participant are presented in Appendix C1, corresponding to the measurements made at the first
440 deadline.

The median value obtained on the stabilized natural seawater is of 2581.43 ± 2.19 µmol kg^{-1} (k=2). The median obtained on the artificial solution is of 2501.61 ± 2.78 µmol kg^{-1} (k=2).

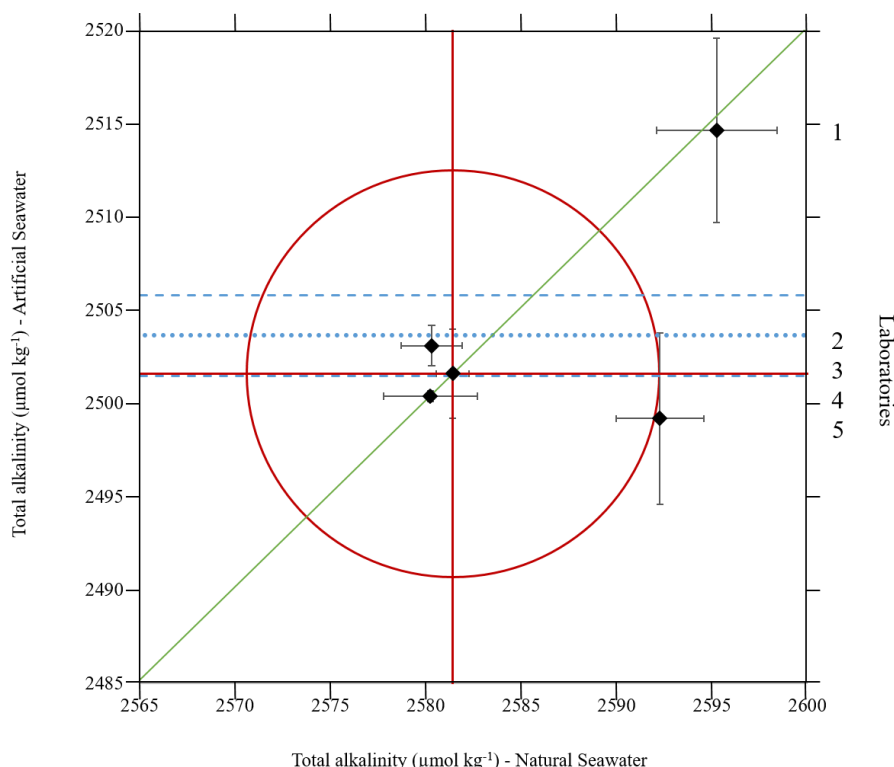



Figure 3: Youden plot of the inter-laboratory comparison conducted on the Stabilized natural seawater (X-axis) and the Artificial seawater, Batch 1 (Y-axis). Where diamonds correspond to the data point (Xi, Yi) of each participant, green straight line corresponds to the 45° line graphical marker, the two straight red horizontal and vertical lines represent the median of total alkalinity results obtained from the five laboratories on the artificial solution and the stabilized natural seawater, respectively, and the red circle represents the 95% confidence level circle. The blue dotted line represents the artificial reference material reference value together with its expanded uncertainty in blue dashed lines.

The Youden plot shows that three laboratories out of five obtained really closed results that are centred around the medians of the two samples (laboratories, 2, 3 and 4). The standard deviation (represented by error bars) obtained by the laboratory 5 on the natural seawater shows that this laboratory obtained results that could be considered compatible according to the 95% confidence circle. Moreover, its error bars obtained on the artificial reference material are compatible with the TA reference value. The laboratory 1, on the other hand, is considered as having biased results according to the 95% confidence circle drawn on the plot. Its proximity with the 45° line clearly indicates that the source of error is systematic (i.e. similar bias to the medians for the two samples).

The value of the laboratory 1 obtained on the artificial seawater was also isolated by Grubb's test. This laboratory was thus not taken into account in the computation of the precision and bias of the measurement method.

The bias between the reference value and the mean value obtained by the four participants selected for the artificial solution is of -2.56 ± 2.44 µmol kg^{-1} (k=2). The precision of the method, s_R, given by the computation of s_L and s_r, being, respectively, inter and intra laboratory variation, is of 1.99 µmol kg^{-1} on the artificial seawater. This precision reaches level of precision reported in the literature (Millero et al., 1998; Bockmon and Dickson, 2015).

However, the precision on the natural seawater is of 5.85 µmol kg^{-1}, which mostly arises from the laboratory 5
465   random error highlighted by the Youden plot in Fig. 3.

3.3 Uncertainty of total alkalinity measurements results with Gran's data treatment

Table 6 presents the uncertainty budget of the total alkalinity measurement results obtained from the inter-
laboratory comparison, i.e. following the top-down approach, as described in Sect. 2.4.1. The uncertainty budget
corresponds to the multi-step potentiometric measurement method and Gran's data treatment, as it was computed
470   from measurements made on the artificial solution. As laboratory 1 was isolated, the uncertainty budget is obtained
from results of the four remaining laboratories. The uncertainties attributed to inter and intra laboratory variation
are, respectively, 1.67 and 1.09 µmol kg^{-1}. The uncertainty attributed to the bias is of 1.22 µmol kg^{-1}. The global
standard uncertainty budget is thus of 2.33 µmol kg^{-1}; giving an expanded uncertainty of 4.67 µmol kg^{-1}.

475   **Table 6: Uncertainty budget of total alkalinity measurement results computed with the top-down approach. Where s_L and s_r represent respectively inter and intra laboratory variation, $u(\hat{\delta})$ the uncertainty of the bias and $u(y)$ the global standard uncertainty.**

Standard uncertainty estimation	
Uncertainty sources	u (k=1)
s_L	1.67E+00
s_r	1.09E+00
$u(\hat{\delta})$	1.22E+00
$u(y)$	2.33E+00

Table 7 presents the uncertainty quantification of all input variables involved in the measurement model of the
multi-step open-cell potentiometric titration procedure with Gran's data treatment. The uncertainty quantification
480   is detailed in Sect. 2.4.2 and is based on LNE's measurement method and apparatus as described in Sect. 2.1 and
Appendix B. The overall total alkalinity uncertainty budget gives a standard uncertainty of 2.63 µmol kg^{-1}, thus
an expanded uncertainty (i.e. with a coverage factor, k, of 2) of 5.26 µmol kg^{-1}.

Table 7: Quantification of the uncertainty sources involved in the Total Alkalinity measurement method and Gran's data treatment following the bottom-up approach.

Input variables	Definition	Unit	Sub-sources of uncertainty		Standard uncertainty (k=1)
m_{HCl}	Mass of HCl delivered during the titration	g	- Densimeter accuracy (g/cm3)	2.00E-05	2.89E-03
			- Acid temperature (°C)	1.25E-01	
			-Volume delivered (ml), burette tolerance	2.89E-03	

m_{init}	Mass of sample analysed	g			1.70E-03
E	Potential measured by the glass electrode	mV	-Tolerance of the electrode	1.15E-01	1.16E-01
			-Repeatability	1.11E-02	
T	Temperature of the sample during the titration	°C	-Resolution	1.00E-01	1.00E-01
			-Repeatability	2.95E-03	
			-Trueness	5.66E-03	
R	Universal gas constant	J/mol.K			1.50E-05
F	Faraday constant	C/mol			8.30E-03
C_{HCl}	Amount content of the acid titrant	mol kg^{-1} sol	- Stock solution (HCl 1 mol kg^{-1} sol) amount content	6.00E-05	1.08E-05
			- Gravimetric dilution: weighing scale calibration	5.09E-03	
a and b	Gran's regression coefficients		- m_{HCl}		2.89E-03
			- F1		= 0.0055 * F1 - 76.39097
			- Gran's regression method	a	5.33E+03
				b	1.59E+04
				corr(a,b)	-0.99889
Total uncertainty budget of total alkalinity (µmol kg^{-1})	u (k=1)				2.63E+00
	U (k=2)				5.26E+00

485

The two uncertainty quantification approaches, i.e. top-down and bottom-up approaches, gave the same level of uncertainty for the total alkalinity measurement results obtained with the standardized measurement method and the Gran's data treatment, being an expanded uncertainty of 5 µmol kg^{-1} (k=2).

4 Discussion

490   **4.1 Development of the artificial reference material**

4.1.1 Composition of the artificial solution

The artificial solution developed for use as a reference material for total alkalinity measurements differs slightly from synthetic solution described in the literature for accuracy checking. Previous studies by Dickson et al. (2003) used solutions composed of either sodium carbonate, TRIS, or borax in an NaCl matrix. In this study, a decision was made to use a combination of sodium carbonate and sodium bicarbonate for two main reasons: (1) to mimic the alkalinity source found in natural seawater, which primarily arises from carbonate and bicarbonate ions, and (2) to achieve a pH level representative of seawater, ensuring that the potential measured by the glass electrode during titration is similar to that of a natural sample.

The addition of NaCl to the solution background helps maintain an ionic strength similar to that of natural seawater. However, it introduces background alkalinity, which complicates the determination of the total alkalinity reference value of the material. Moreover, the zero level of protons defined to measure TA in seawater is based on seawater acid-base chemical equilibria (Schulz et al., 2023). The impact of using a reference material with a simplified matrix must be further investigated, even though the good results obtained in the ILC seem to show that the artificial RM could be adequate.

For the artificial solution, the practical salinity was also measured with a salinometer, highlighting a difference of +2.05 compared to the absolute salinity obtained from knowledge of the composition. The significant discrepancy between both comes from the difference in definition. Absolute salinity is defined as the mass fraction of dissolved material in solution while the practical salinity is defined as the ratio of the conductivity of the solution on the conductivity of a standard KCl solution. For a natural seawater, the discrepancy between both is in the order of 0.2 (Pawlowicz, 2013). The composition of the artificial seawater being composed in high majority of NaCl, explains the higher discrepancy between practical and absolute salinity observed. The definition of absolute salinity may not be adequate for the artificial solution, where it is probably more relevant to compare ionic strengths, which should be of 0.7 mol kg^{-1} for a salinity 35. For the natural solution, only the practical salinity is given due to a lack of knowledge of its exact composition.

Developing an artificial reference material also served as a step forward in eliminating the use of mercuric compounds, which are currently employed to inhibit the growth of microorganisms in natural seawater solutions. This is however tied to the stability of the RM achievable.

4.1.2 Reference value determination

The total alkalinity reference value is determined through the gravimetric preparation of the solution, which is composed of salts previously characterized in terms of base amount content via coulometric analysis. Both the gravimetry and coulometry methods provide SI traceable results. Since the background alkalinity ($TA_{background}$) is carefully quantified, along with its associated uncertainty, the reference TA value assigned to the material may also be considered traceable to the SI units. It however necessitates that NaCl is the only significant source of background alkalinity and the purity of NaHCO$_3$ is correctly assessed.

The determination of background alkalinity resulting from NaCl impurities involves the gravimetric preparation of artificial solutions with varying NaCl concentrations, coupled with TA potentiometric measurements. This approach establishes a relationship between NaCl concentration and background alkalinity, along with its uncertainty (as described in Eq. 10). The linear regression was forced to pass through the origin as the background alkalinity coming from NaCl impurities is zero for a solution without NaCl matrix, this is confirmed by the measurements made with v_{NaCl} = 0 mol kg^{-1} sol (Fig. 2). Initially, an uncertainty of 2 µmol kg^{-1} was chosen for

the TA potentiometric results to quantify $TA_{background}$, which closely matches the final estimated uncertainty obtained through the bottom-up approach (2.63 µmol kg^{-1}). Attributing this final uncertainty to the TA measurements for determining $TA_{background}$ would only marginally increase the uncertainty of the reference value of the material by 1 to 2%, which is negligible. Additionally, considering the presence of systematic errors between

535 measurements (such as the same operator, device, method, acid titrant, etc.), 2 µmol kg^{-1} can be deemed a realistic uncertainty for this purpose.

However, to simplify the determination of the TA reference value, it may be considered to purify the NaCl before use, as suggested by Dickson et al. (2003), who estimated that the resulting $TA_{background}$ could be negligible. Alternatively, removing completely the NaCl background may be a final solution but it should first be investigated

540 whether the difference in salinity with natural samples would introduce other mechanisms that could hinder the artificial solution's applicability for quality control.

4.1.3 Other considerations

Having a reference material such as the developed artificial solution, with a potential for a SI traceable reference value provided alongside a comprehensive uncertainty budget, offers several advantages:

545   (1) It enables the validation of experimental protocols and the Gran's determination of the TA value.

     (2) It facilitates the control of device accuracy

     (3) It assists in qualifying new operators

     (4) It allows for the quantification of acid titrant amount content for laboratories that do not have access to coulometric methods.

550 Another benefit of having an artificial reference material is the ability to provide reference materials for a wide range of total alkalinity values. This is important for end-users to verify that there isn't a linear bias in the measurement method across the studied range of alkalinity.

However, it does not allow for the accuracy verification of TA values obtained using the nonlinear least-squares regression method, which is yet widely applied to natural seawater samples to correct the value considering the

555 acid-base system in the solution. Therefore, it is highly recommended to distribute a second material being a stabilized seawater, as the one from Scripps or the one developed in this study, to ensure the comparability of TA measurements on natural seawater samples.

Having a natural seawater reference material, that is easy to collect during open ocean oceanographic cruises, also offers the availability of a reference material that can be a bit cheaper than the artificial one, which has to be

560 produced in the lab from high purity compounds.

4.2 Homogeneity and stability of the materials

The homogeneity of the material was assessed through potentiometric total alkalinity measurements. However, due to the method's limited precision, it was challenging to detect significant within- and between-bottle inhomogeneity (Table 4). It is anticipated that the homogenization step during material preparation ensures

565 sufficient homogeneity for the intended use. Only the estimation of between-bottle homogeneity was included in the uncertainty budget of the TA reference value of the artificial materials, accounting for 6 to 7% of the final budgets.

The stability studies presented in Table 4 revealed a significant trend in Batch 2 of the artificial solution bottled with screw caps borosilicate bottles, indicating instability. Conversely, Batch 1 of the artificial solution and the

570 stabilized natural seawater, both bottled in ground neck borosilicate bottles, did not exhibit significant instability based on the t-test results (Table 4). This suggests potential better stability with the latter bottles. However, it should be noted that the standard deviation of corresponding slopes is not negligible compared to the slopes themselves. Further stability studies with longer durations could provide clearer insights into the stability of Batch 1 of the artificial solution and the stabilized natural seawater.

575 Dissolved inorganic carbon (DIC) analyses conducted at SNAPO-CO_2 on the natural seawater solution after 2, 8, and 11 months since bottling indicated a mean DIC value of 2385 µmol kg^{-1} with no significant evolution over time. These results are presented in Appendix C2.

However, nutrients analysis performed at MIO revealed an increase in silicate content from 12.1 to 23.2 µmol kg^{-1} for the stabilized natural seawater in the ground neck bottles, representing an increase of about 11 µmol kg^{-1}

580 between months 2 and 14 post-bottling (Appendix C3). Additionally, nutrient analysis on Batch 2 of the artificial seawater indicated a silicate content of 26.5 µmol kg^{-1} 14 months after preparation, despite an initial supposed content of zero. This suggests a release of silicate ions from the borosilicate glass containers, as previously suggested by Mos et al. (2021). The release appears to be more significant from glass bottles with screw caps, which may align with the findings that Batch 2 of the artificial solution was less stable. However, the fact that

585 silicates are also released in glass bottles with ground necks suggests that Batch 1 of the artificial solution and stabilized natural seawater may also lack stability. The increase in alkalinity measured by potentiometric measurements for both solutions is lower than the amount of silicates released, indicating potential secondary processes influencing alkalinity. Improving the stability of the developed materials likely necessitates using different bottling methods, such as employing glass with specific treatments to prevent silicate release. The

590 reference materials distributed by Scripps Institution of Oceanography are known to be more stable, possibly due to differences in glass bottle suppliers. It could also be worthwhile to test storing solutions in polypropylene bottles, as investigations by Mos et al. (2021) suggested better stability, although this may compromise eventual stable DIC values simultaneously.

4.3 Results of the inter-laboratory comparison

595 The results of the inter-laboratory comparison indicate an acceptable agreement among four out of five participants, even though the random error highlighted for laboratory 5 seems to affect the estimated precision of the method. Also, laboratory 1 exhibits a systematic error in Fig. 3, evidenced by an equivalent bias compared to the median for both analysed samples: 13.64 µmol kg^{-1} for the artificial solution and 13.82 µmol kg^{-1} for the stabilized natural seawater. Laboratory 1 later reported that the acid injection system was not functioning properly

600 during the ILC. A leak at the microvalve, leading to inconsistent acid delivery volumes, could explain the observed bias. To address this issue, laboratory 1 subsequently removed the microvalve and replaced it with a microcapillary, which seemed to improve both the precision and accuracy of the measurements.

More broadly, the results of this inter-comparison suggest that:

    (1) The TA reference value assigned to the artificial material based on knowledge of its composition aligns

605   well with TA values measured using the standardized potentiometric titration method. The bias between

the two, being of -2.56 ± 2.44 µmol kg^{-1} (k=2), falls within the expanded uncertainties of the bias and of the reference value (which is of 2.16 µmol kg^{-1}).

(2) In the case of a laboratory showing a systematic bias, the artificial material with a well-characterized reference value might be employed to correct potentiometric measurements by calculating the trueness

610   bias, however this needs further careful investigation.

(3) The closed-cell measurement method, being employed by one of the laboratories among laboratories 2, 3, and 4 in Fig. 3, yields results that are compatible with those obtained using the open-cell measurement method.

These seem to demonstrate that both developed materials could be considered suitable for use in quality controls

615 of the multi-step potentiometric titration method for total alkalinity measurements in seawater.

4.4 Uncertainty estimation

The bottom-up and top-down approaches applied for uncertainty quantification of total alkalinity measurement results obtained from the standardized method and Gran's data treatment yielded really close results, with standard uncertainties of 2.63 and 2.33 µmol kg^{-1}, respectively. This level of uncertainty is coherent regarding the precision

620 of the method reported in the literature, typically ranging between 2 and 4 µmol kg^{-1} (Millero et al*.,* 1998; Bockmon and Dickson, 2015). Moreover, it is close to the data quality objective required by the GOA-ON for monitoring ocean acidification, indicating promising prospects for achieving good data quality for TA results.

However, the uncertainty budget detailed in this paper does not include uncertainty arising from the nonlinear least-squares (NLLS) regression typically applied to natural seawater samples. This remains to be quantified and

625 may slightly increase the uncertainty budget. Quantifying this uncertainty will entail considering several aspects and input variables from the NLLS equation, including:

(1) The uncertainty of practical salinity measurements

(2) Possible discrepancies between total fluoride and total sulphate amount contents computed from salinity and the actual composition of natural seawaters worldwide

630 (3) The uncertainty of dissociation constants of fluoride and sulphate ions

The Monte Carlo approach, as described in GUM Supplement 1 (JCGM 101:2008, 2008), might be pertinent for computing the uncertainty of the NLLS regression as it enables uncertainty computation from the distribution of the regression.

Although the top-down approach appears to provide a realistic evaluation of the uncertainty of TA measurement

635 results, conducting an inter-laboratory comparison with more participants could lead to a more robust uncertainty budget. According to the top-down uncertainty budget (

Table 6), reducing uncertainty would necessitate mitigating the contributions of inter-laboratory deviation and bias uncertainty. This could be achieved through better harmonization of measurement procedures and reducing uncertainty in the reference value of the material, which requires improving material stability.

640 The bottom-up approach, which relies on a detailed identification and quantification of sources of uncertainty in the measurement process, helps identify the main contributions to the overall budget.

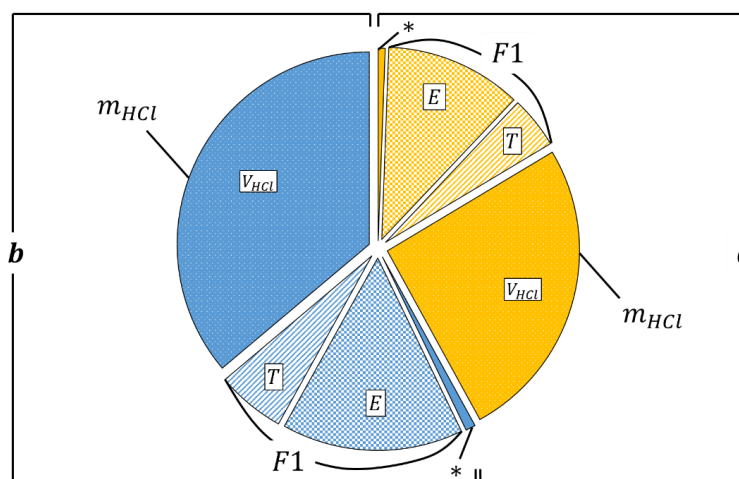



Figure 4: Main sources of uncertainty contributing to the overall budget of total alkalinity measurement results obtained with the open-cell titration measurement method together with Gran's data treatment. With uncertainty sources coming from a and b represented in yellow and blue, respectively right and left hand sides of the figure. The symbol * corresponds to the residuals of Gran's regression.

In Table 7, the main sources identified are the coefficients a and b of Gran's regression, contributing 42% and 58%, respectively, to the uncertainty budget. These components are computed from F1 (Eq. 3) and from the weight of HCl added during titration (m_{HCl}). The main sources of uncertainty influencing F1 are the measured potential (≈72.5%) and temperature (≈27.5%). The main source of uncertainty influencing m_{HCl} is the volume of acid delivered by the burette (nearly 100%). The importance of this parameter on the measurement result was well illustrated by the issue encountered by laboratory 1 during the ILC (Fig. 3, Sect. 4.3). The weight of all of these sources in the overall budget are presented in Fig. 4. Reducing uncertainties in these three components can help diminish the overall budget. However, this is heavily reliant on device resolution and tolerance, and thus depends on the choice of the device and manufacturer. The similarity of the sources of uncertainty influencing a and b in Fig. 4 well illustrates the high correlation between both (corr(a,b) = -0.999).

5 Conclusion

This study explores the application of various metrological tools to measurements of total alkalinity (TA) of seawater using the standardized multi-step potentiometric titration method.

Two batches of an artificial certified reference material with reference TA values of, respectively, 2503.6 ± 2.2 µmol kg^{-1} and 2503.8 ± 2.6 µmol kg^{-1} (k=2) for a shelf-life of three months have been produced, alongside a second reference material comprising stabilized natural seawater. These materials underwent homogeneity and stability studies to comply with ISO standard 17034 "General requirements for the competence of reference material producers" (2016). While the homogeneity study requires more precise measurements to obtain significant information, stability was evaluated to be unsatisfactory due to an increase in TA over time. This might be partly attributed to the release of silicates from the glass container but needs further investigation. Using a different type of bottling is suggested to enhance stability.

An inter-laboratory comparison involving five laboratories indicated that both reference materials could be suitable for quality control of the standardized total alkalinity measurement method.

670   The uncertainty of the multi-step potentiometric measurement method with Gran's data treatment was quantified through both bottom-up and top-down approaches, yielding expanded uncertainties of 5.26 and 4.67 µmol kg^{-1}, respectively. Although slightly higher than required by the GOA-ON (< 4 µmol kg^{-1}) for monitoring ocean acidification, these results are very encouraging for achieving good data quality of TA measurement results. The bottom-up approach helps identify key sources of uncertainty to prioritize for improvement. Quantification of the

675   nonlinear least-squares regression will be necessary to establish the overall uncertainty budget of seawater TA measurement results.

The results presented in this paper represent progress towards ensuring compatibility and accuracy of seawater total alkalinity measurement results.

Appendix A

680   **Standard procedure as well as data treatment method for the open-cell multi-step titration for the determination of seawater total alkalinity.**

A known amount of sample, measured by gravimetry, is placed in an open-cell thermostated at 25°C. The sample is titrated by an HCl solution of known amount content and density. A glass electrode allows the monitoring of the potential during the titration. The glass electrode is first calibrated in total pH scale (noted pH_T) using a TRIS

685   buffer.

The titration is then carried out in two stages. The first stage consists in adding enough HCl to reach a pH_T situated just beyond the endpoint (between pH_T 4 and 3.5). At this pH_T, the predominant weak bases, HCO_3^- and CO_3^{2-}, are converted to CO_2. This CO_2 is removed by agitation and by bubbling of air through the solution for around 6 minutes. A further addition of HCl, in a series of small increments, allows reaching a pH_T of about 3. At this pH_T,

690   all proton acceptors are consumed. The data given by the titration (i.e. measured potential, temperature and volume of HCl added) during the second stage is used to compute the total alkalinity. Data are taken only for this range of pH_T as it is low enough to neglect residual bicarbonate ions and high enough so that the Nernst equation still holds true (Dickson et al., 2007).

An initial estimate of the total alkalinity is obtained from the titration curve using Gran's method (Gran, 1952).

695   This is a highly effective method for the determination of the equivalence point in potentiometric titrations.

At each point of the titration, the amount content of hydrogen ions v_H (mol kg^{-1} sol) can be described by Eq. A1.

$$v_H = \frac{m_{HCl}\, v_{HCl} - m_{init}\, TA}{m_{HCl} + m_{init}} \tag{A1}$$

where m_{HCl} is the mass of acid added (g), v_{HCl} the acid amount content (mol kg^{-1} sol), and m_{init} the mass of sample analysed (g).

700   In the range of pH_T corresponding to the second stage of the titration, the following equation is valid (Eq. A2):

$$\frac{m_{HCl}\, v_{HCl} - m_{init}\, TA}{m_{HCl} + m_{init}} = [H^+] + [HSO_4^-] + [HF] \approx [H^+]_T \tag{A2}$$

The glass electrode has been calibrated in total pH:

$$[H^+]_T = \exp\left(\frac{E - E°}{\frac{RT}{F}}\right) = cst\, \exp\left(\frac{E}{\frac{RT}{F}}\right) \tag{A3}$$

where E is the potential measured by the glass electrode (V), $E°$ its reference potential (V), R the universal gas constant (J mol^{-1} K^{-1}), T the temperature of the sample (K), F the Faraday constant (C mol^{-1}) and *cst* and undefined constant.

From Eq. A2 and A3, the Eq. A4 is computed.

$$(m_{init} + m_{HCl}) \times \exp\left(\frac{E}{\frac{RT}{F}}\right) = \frac{-TA\, m_{init} + m_{HCl}\, v_{HCl}}{cst} \tag{A4}$$

The left-hand side of this equation defines the Gran function F1 (Eq. A5).

$$F1 = (m_{init} + m_{HCl}) \times \exp\left(\frac{E}{\frac{RT}{F}}\right) \tag{A5}$$

F1 is plotted as a function of the amount of HCl added for each point of the second stage of the titration, and TA is thus obtained with Eq. A6.

$$TA = \frac{-b}{a}\frac{v_{HCl}}{m_{init}} \tag{A6}$$

where coefficients a and b represent, respectively, the slope and the intercept of the linear regression $F1 = a * m_{HCl} + b$.

This method gives a first estimation of the total alkalinity. However, errors are introduced when using the Gran's method for seawater analysis due to competing acid-base equilibria in seawater. A method allowing to solve the equivalence point by curve fitting has thus been developed (Dickson, 1981; Martz, 2005). This method consists in an iterative process where the standard potential of the glass electrode (E°) is calculated from the estimation of TA obtained by the Gran's method. A nonlinear least-squares (NLLS) regression is then used to refine the values of E° and TA. The refinement in E° first allows the calculation of the factor $f = [H^+]_T/[H^{+'}]_T$, where $[H^{+'}]_T$ is obtained from the refinement in E° and Eq. A3. f is then itself used to determine a new value of TA using Eq. A7.

$$TA + \frac{S_T}{1+\frac{K_S Z}{f[H^{+'}]_T}} + \frac{F_T}{1+\frac{K_F}{f[H^{+'}]_T}} + \frac{m_{init} + m_{HCl}}{m_{init}}\frac{f[H^{+'}]_T}{Z} - \frac{m_{HCl}\, v_{HCl}}{m_{init}} = 0 \tag{A7}$$

where S_T is the total sulphate amount content (mol kg^{-1} sol), F_T the total fluoride ion amount content (mol kg^{-1} sol), K_s the dissociation constant of $[HSO_4{}^-]$, K_F the dissociation constant of hydrogen fluoride, and $Z = 1 + \frac{S_T}{K_s}$.

The nonlinear least-squares regression consists in computing how much the left-hand side of Eq. A7 differs from zero. The residuals are squared and the sum of squares is minimized by adjusting f and TA using an algorithm. By applying this method, the errors in Ks are negligible (Dickson et al., 2007).

Appendix B

Instrumentation for total alkalinity measurements performed at LNE

The measurement of total alkalinity at LNE was made using the titration system and the 888 Titrando electroburette from *Methrom*, associated with the 801 Stirrer agitation system. A thermostated glass cell with a capacity of 50-150 ml was used. The volume of the samples analysed was of 100 ml. This cell was connected to a *LAUDA* Eco Gold bath to control the temperature of the cell. The setpoint was fixed in order to obtain a temperature of 25 ± 0.2°C in the cell. The temperature was maintained stable, i.e. the temperature acquired during the whole titration had a standard deviation within 0.05°C. The potential measurement was carried out with a *Metrohm Ecotrode Plus*

glass electrode (ref: 6.0262.100) and the temperature with the *Metrohm* temperature probe (ref: 6.1110.100). The data acquisition software used was Tiamo 2.4.

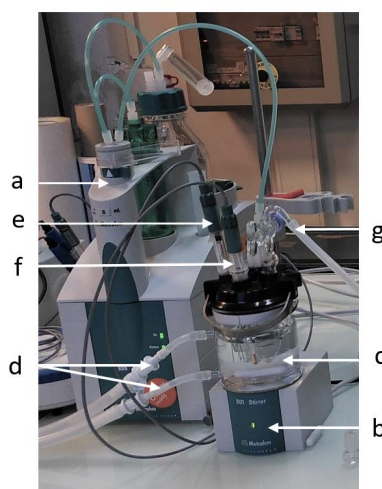
The airflow for CO_2 degassing was obtained from a compressed air tank connected to an inlet system in the cell. Figure B1 illustrates the description of the setup.

740

Figure B1: Description of LNE's total alkalinity measurement setup. With a) Burette and titration system, b) Magnetic stirrer, c) Thermostated cell, d) Tubing connected to the water bath, e) Glass electrode, f) Temperature probe, and g) Air inlet for degassing.

The hydrochloric acid used was a Standard Reference Material (SRM) at 1 mol kg^{-1} sol prepared and characterized

745 by coulometry at the Slovenský Metrologický Ústav (Slovak Institute of Metrology, SMU). It was diluted by mass to 0.1 mol kg^{-1} sol before its use as acid titrant; it wasn't prepared in an NaCl matrix. It is often recommended that the HCl solution is prepared in an NaCl matrix in order to keep the ionic strength, and thus the activity coefficients, constant during the titration. However, Okamura et al. (2014) has indicated that using HCl solution containing no NaCl has a negligible effect on the TA results (about -0.2 µmol kg^{-1}). The density of the titrant solution was

750 measured with a DMA 4500M *Anton Paar* densimeter.

The mass of the analyzed sample was weighed on a calibrated 2 kg balance with a resolution of 0.1 mg.

The data treatment was performed as described in Appendix A, with an R routine written based on the function "alkalinity" of the package seacarb (Gattuso et al., 2021).

The glass electrode was calibrated with a TRIS buffer prepared and characterized with the Harned cell

755 measurement method at LNE. Its linearity over a range of pH was checked with NBS buffers of pH 4, 7 and 12.

The electroburette and the temperature probe are calibrated once a year.

The accuracy of the method was controlled either with a reference material purchased from Scripps or with a synthetic solution prepared gravimetrically at LNE.

Appendix C

760 **C1: Total Alkalinity measurement results of all participants to the inter-laboratory comparison (µmol kg⁻¹), including the stability monitoring over time. The "Mean" corresponds to the mean value of replicates, with standard deviation reported as "SD".**

Laboratory		1		2		3		4		5	
	Time after solution preparation (months)	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Artificial reference material - Batch 1	2	2514.6	4.9	2503.1	1.1	2501.6	2.4	2500.4	0.3	2499.2	4.6
	5	2516.8	0.7			2502.1	1.6	2499.2	1.8	2487.5	0.5
	8	2506.5	0.7			2506.5	0.6	2510.5	1.2	2522.5	3.4
	11	2507.1	1.9			2510.2	1.9	2505.4	1.3	2502.8	5.8

Laboratory		LNE	
	Time after solution preparation (months)	Mean	SD
Artificial reference material - Batch 2	2	2503.7	0.6
	5	2504.6	1.5
	8	2509.3	0.6
	11	2512.9	0.7
	14	2513.5	2.3

Laboratory		1		2		3		4		5	
	Time after solution bottling (months)	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Natural Reference Material	2	2595.3	3.2	2580.3	1.6	2581.4	0.9	2580.2	2.5	2592.3	2.3
	5	2593.3	0.4			2583.5	0.9	2582.0	1.4	2573.5	1.4
	8	2592.5	0.6	2583.7	1.6	2581.2	0.4	2588.1	0.6	2603.4	5.9
	11	2590.5	0.6	2590.3	1.0	2589.7	1.4	2587.0	0.7	2573.5	0.3
	14	2580.3	1.8			2582.0	1.8	2585.1	2.2	2577.4	0.8

C2: Dissolved Inorganic Carbon measurement results performed at the SNAPO-CO₂ (µmol kg⁻¹), including the stability monitoring over time. The "Mean" corresponds to the mean value of replicates, with standard
765 **deviation reported as "SD".**

Laboratory		SNAPO-CO2	
	Time after solution bottling (months)	Mean	SD
Natural Reference Material	2	2384.9	1.2
	8	2384.4	2.2
	11	2385.5	1.1

C3: Nutrients measurement results performed at the MIO (µmol l⁻¹), including the stability monitoring over time. The "Mean" corresponds to the mean value of replicates, with standard deviation reported as "SD".

Laboratory	MIO

Natural Reference Material	Time after solution bottling (months)	silicates		nitrites		phosphates		nitrates+nitrites	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD
	2	12.4	0.1	0.02	0	0.40	0.01	9.08	0.03
	11	21.9	-	0.00	-	0.75	-	9.32	-
	14	23.8	0.0	0.01	0	0.45	0.01	8.79	0.09

Artificial Reference Material - Batch 2	Laboratory	MIO			
		silicates	nitrites	phosphates	nitrates + nitrites
	Time after solution preparation (months)	Mean	Mean	Mean	Mean
	14	27.1	0.03	0.03	0.4

Data availability

The data are presented in the main manuscript or in Appendix.

Authors' contribution

G.C.: Conceptualization, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft preparation; S.A., T.C. & J.F.: Investigation, Methodology, Writing – review and editing; P.F.: Funding acquisition, Supervision, Writing – review and editing; T.W.: Conceptualization, Investigation, Methodology, Supervision, Writing – review and editing

Competing interests

The authors declare that they have no conflict of interest.

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