

Supplementary Material

of
On the True and the Perceived Minor Interactions of Dissolved Phosphate and Dissolved Sulphate
and some other constituents with the Alkalinity of Oceanic Seawater
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S1. Nernst equation and various sources of error

The Nernst equation and several sources of error of Titration Alkalinity are described, after Brewer et al. (1986) and Stoll (1994). When using pH-electrodes during a potentiometric titration, it is assumed that the pH electrode in principle follows Nernstian behavior:

$$E = E_0 + (RT/F) \cdot \ln(H^+) \quad (S1)$$

where

E = Potential (in mV (millivolt)) measured by the electrode relative to E_0

E_0 = an arbitrary level of E depending on the electrode used (in mV)

R = Gas constant $8.3144 \text{ (J mol}^{-1} \text{ K}^{-1})$ where K is degree Kelvin

T = Temperature (K)

F = Faraday constant $9.6485 \cdot 10^4 \text{ (C mol}^{-1})$

(H⁺) = the activity of hydrogen ions

Theoretically the slope of this linear equation would be 59.16 mV at 25 °C (Brewer et al., 1986) or 58.16 mV at 20 °C (Stoll, 1994) with every change in pH unit (10-fold increase of H⁺ activity) (Eq. S1).

Deviations from this theoretical slope may occur and are a frequent concern during potentiometric titration (Brewer et al., 1986). In context of the Transient Tracers in the Oceans program (TTO 1981, 1983; Brewer et al., 1985), for the shipboard and shore-based titrations, the practical electrode slopes were determined meticulously (Brewer et al., 1986; their Table 18.3). Effects of deviations from the theoretical response of 59.16 on the derived values of Alkalinity (and DIC) were discussed. In summary, the small deviations from the theoretical response were judged to not constitute sufficient evidence of non-ideal behavior, and, therefore, for all calculated values from the cruise, the Nernstian slope was assumed.

Almost one decade later, for seawater samples (Stoll et al., 1993) collected during the 1989-1990 JGOFS North Atlantic Bloom Experiment, the titrator systems had been constructed following blueprints provided by Brewer and co-workers. Stoll (1994) mentions that deviations from the ideal theoretical response of 58.16 mV at 20 °C can be straightforward denoted by the slope factor f as follows:

$$E = E_0 + (RT/F) \cdot \ln(H^+) \cdot f \quad (S2)$$

Stoll (1994) reported that during JGOFS 1989-1990 cruises, the slope factor f was never deviating from the ideal value, within the error of its determination (0.001). Otherwise, theoretical calculated effects on the Titration Alkalinity due to various errors were given as follows:

Titration Alkalinity
($\mu\text{mol dm}^{-3}$)

$f + 0.001$	- 1
$f - 0.001$	0
$N1 + 0.0001$	+2
$N1 - 0.0001$	- 3
$V0 + 0.1$	- 3
$V0 - 0.1$	+2
$t + 1$	- 3
$t - 1$	+2

Table S1. An example of the theoretical calculated effects on Titration Alkalinity due to errors in the slope factor f , the normality $N1$ of the titration acid, the volume $V0$ (ml) of the titrator cell, and the temperature t (°C) of the thermostated waterjacketed titrator cell (taken from Stoll, 1994). Each titration cell has its own volume, typically in the order of 116 ml. The cell temperature was kept constant at 20 °C \pm 0.2 °C (Stoll et al., 1993). Obviously, for any assumed larger errors of f or $V0$ of the titrated seawater samples, the error of Titration Alkalinity would be larger (Table 3 in Chapter 2 of Stoll, 1994).

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74 75 76 **S2. The GEOSECS expeditions**

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78 The late Professor Broecker (Lamont-Doherty Geological Observatory LDGO and Columbia University, New
79 York) was one of the leading scientists having initiated, implemented and interpreted the GEOSECS Program
80 (Geochemical Ocean Sections Study). This was the first ever program doing large scale ocean sections of the
81 CO₂ system, ancillary parameters notably the major nutrients, and other ocean variables in the three major
82 oceans, Atlantic, Pacific, Indian Oceans. Prof. Broecker was chief scientist or co-chief scientist during five
83 GEOSECS cruise Legs. Similarly, Dr. Takahashi was chief scientist or co-chief scientist during three GEOSECS
84 cruise Legs. The measurements by acid titration of both DIC and Titration Alkalinity were done with the method
85 of Edmond (1970), the latter also serving as chief scientist or associate chief scientist during four expeditions.
86 Dr. Brewer was chief scientist of cruise leg 9 in the Pacific. For other shipboard scientists, chief scientists or
87 associate chief scientists see the resulting Data Report Volumes 1, 3 and 5. For this GEOSECS program some
88 further refinements of the acid titration method for determination of both DIC and Titration Alkalinity were
89 made by the late Arnold Bainbridge, as well as by Bradshaw et al. (1981). The expeditions took place in 1972-
90 1973 in the Atlantic, in 1973-1974 in the Pacific, and in 1977-1978 in the Indian Ocean. Overall, more than 6000
91 seawater samples were analyzed by acid titration for DIC and Titration Alkalinity. The resulting datasets,
92 including all the derived calculated values of the different CO₂ chemical species, were published in three
93 Hydrographic Data Reports Volumes 1, 3 and 5, as well as three Atlases comprising the graphics of Sections and
94 Profiles Volumes 2, 4 and 6, and Volume 7 comprising Shore-Based Data and Graphics. Moreover, independent
95 measurements of DIC were made by gas chromatography, and pCO₂ by infrared gas analyses. This also led to
96 assessments of internal consistency of the measurements (see Data Report Volumes 1, 3 and 5). All seven
97 GEOSECS Volumes were published in print (GEOSECS 1981-1987). The major findings were described in an
98 overview chapter by Campbell (1983).

99 During GEOSECS the acid titration method was used to determine both DIC and Titration Alkalinity. During
100 the Atlantic expedition, the DIC was also determined by shipboard gas chromatography, as well as for a suite of
101 selected stored samples, by infrared gas analysis afterwards in the home laboratory (Takahashi and Bainbridge,
102 1981). The station-by-station average for the difference between the shipboard GC data and shipboard titration
103 data of DIC was reported. The GC based data was in average 15.1 (\pm 9.7) $\mu\text{mol.kg}^{-1}$ greater than the titration-
104 based data. Offsets were also reported between the shore-based infrared data of DIC and the shipboard DIC data
105 of either GC or titration. During GEOSECS (1972-1978) the precision of Titration Alkalinity was reported to be
106 0.1%, that is \sim 2.3 $\mu\text{mol.kg}^{-1}$ such that for almost all samples of all three major oceans, the effect of phosphate in
107 the 0 to \sim 3.3 $\mu\text{mol.kg}^{-1}$ range was at most near the precision of GEOSECS at its time.

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118 119 120 **S3. Historical example of hypothesis of interferences due to unknown protolytes**

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122 During the GEOSECS expeditions in the 1970s the acid titration method was used to determine both DIC and
123 Titration Alkalinity (see Supplementary Information B. The GEOSECS Expeditions). During the Atlantic
124 expedition, the DIC was also determined by shipboard gas chromatography, as well as for a suite of selected
125 stored samples, by infrared gas analysis afterwards in the home laboratory (Takahashi and Bainbridge, 1981).
126 The station-by-station average for the difference between the shipboard GC data and shipboard titration data of
127 DIC was reported. The GC based data was in average $15.1 (\pm 9.7) \mu\text{mol.kg}^{-1}$ greater than the titration-based data.
128 Offsets were also reported between the shore-based infrared data of DIC and the shipboard DIC data of either
129 GC or titration. This, and various other uncertainties, also in the ensuing Pacific and Indian Ocean expeditions,
130 were deemed to lead to some ambiguity in the data of both DIC and Alkalinity.

131 Bradshaw and Brewer (1988) reported for the TTO project (Brewer et al., 1985, 1986), that the titration-
132 based DIC results were $\sim 21 \mu\text{mol kg}^{-1}$ higher than those obtained by gas extraction methods which, unlike the
133 titration method, do not require detailed knowledge of the chemistry of the seawater samples. Possible
134 explanations of these differences were mentioned: an error in the physico-chemical model; a persistent
135 contamination problem; or the presence of an unknown protolyte (HX) in natural seawater. The systematic offset
136 appeared to be largest in the surface waters, where the recently reported very high concentrations of Dissolved
137 Organic Carbon (DOC) by Sugimura and Suzuki (1988) might give rise to higher concentrations of such
138 unknown organic protolytes. At the time ($\sim 1986-1988$), the latter reported DOC data (Sugimura and Suzuki,
139 1988) appeared to be convincing due to a quite remarkable reportedly very significant inverse relationship with
140 Apparent Oxygen Utilization (AOU). This oceanographic consistency between the novel DOC data and the
141 classical well known and very accurate AOU data, was seen by many of the readership as the key evidence, at
142 the time somewhat of a scientific revolution.

143 During the JGOFS expeditions in 1989 and 1990 Stoll et al. (1993) used two independent methods for
144 measurement of DIC, the traditional acid titration and the then quite novel coulometric method (Johnson et al.,
145 1987). Latter coulometric method nowadays is the standard method for DIC. For more than 600 seawater
146 samples there was fair agreement between the two methods (on average 0.6 %). This fair agreement was
147 independent of depth.

148 Eventually the very high DOC data as reported by Sugimura and Suzuki (1988) was demonstrated to be
149 irreproducible by others (e.g., Sharp, 1993; De Baar et al., 1993; among others). This led to a retraction of the
150 dataset of Sugimura and Suzuki (1988) by Suzuki (1993). This retraction was taken after re-evaluation of the raw
151 data on which the papers were based and recognition of inadequate blank subtraction and peak measurement.
152 This retraction did not provide an explanation of the previous reportedly close relationship of DOC and AOU,
153 such that data manipulation of the initial DOC data of Sugimura and Suzuki (1988) cannot be firmly excluded.

154 Some years later, Millero et al. (1993) concluded that the previously reported offset in DIC by titration versus
155 DIC by other method(s), for example as reported by Bradshaw and Brewer (1988), after all is independent of
156 depth and instead is deemed to be due to the non-Nernstian behavior of the electrodes. In other words, according
157 to Millero et al. (1993), the offset would not be due to unknown protolytes.

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