

A PRECISE AND RAPID ANALYTICAL PROCEDURE FOR ALKALINITY DETERMINATION

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ABSTRACT

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A potentiometric analytical method is proposed for the determination of the alkalinity of seawater. The precision is 0.1% and each determination takes 3 min. The technique is very easy to use, even on board ship since it is carried out in open flasks. A polynomial equation is also proposed which greatly simplifies the theoretical expression.

INTRODUCTION

Many marine scientists have considered the specific alkalinity as a constant chemical parameter in oceanic water. When glass electrodes for potentiometric measurements appeared, they were used for alkalinity measurements using techniques such as the Gran Plot (Gran, 1952). These procedures clearly showed slight variations in the specific alkalinity in the oceans of the world.

A precise method is interesting for two reasons: firstly, alkalinity would be useful for distinguishing water masses, mainly in the surface water, where it could replace temperature as a conservative parameter (Perez et al., 1986). Secondly, together with pH, it could be related with other nutrients (total nitrogen, phosphate and oxygen) for studying the processes of sedimentation-oxidation of organic matter in mixing water masses. The method must also be easy to carry out at the same time as the nutrient salts are analysed on board ship and simple enough for workers not specialised in the carbon system.

Alkalinity, expressed as equivalents per kilogram of seawater, does not depend on temperature and pressure. A variety of procedures has been used including the classical titration with an indicator proposed by Gripenberg (1936), and the 'method of pH' (Anderson and Robinson, 1946) using a single point potentiometric titration, which was later modified by Culberson et al. (1970).

The potentiometric titration methods (Dyrssen, 1965; Dyrssen and Sillen, 1967) based on the Gran Plot reached a great precision (0.17% in alkalinity determinations or 0.68% in total carbon determinations (Edmond, 1970). A more sophisticated method, which takes into account the prevailing reactions, was used by Hansson and Jagner (1973). They evaluated the equivalence points by a modified Gran Plot. If the dissociation constants of minor species which contribute to alkalinity are known, it is possible to obtain a complete theoretical expression of the potentiometric titration curve (Dickson, 1981; Johansson and Wedborg, 1982), and fitting the non-linear experimental curve to the theoretical expression it is possible to accurately evaluate alkalinity and total carbonate (0.08% and 0.20%, respectively).

All the potentiometric methods require that the titration be carried out in a closed system, since it takes at least 15min to complete. When planning an oceanographic cruise it must be remembered that the time of analysis on board must be as short as possible and that this time should be similar for the different parameters to be determined, to optimise the amount of data obtained. Owing to biological activity the sample may not be stored longer than one day. Thus, it is necessary to find less sophisticated and more rapid methods. Non-linear methods have not been used in oceanographic cruises. On the contrary the linearised Gran Plot technique has been used with an automatic titrator. This method has been applied during some cruises (Almgren et al., 1977; Takahashi et al., 1981).

METHOD

The method proposed here is a modification of the 'pH method' consisting of a titration of the sample (250 cm³) to a final (NBS) pH close to 4.44. The titration is carried out in an open flask (with the area of the interface as small as possible, usually < 8 cm²). The time of titration is about 3 min, so that, practically, there is no loss of CO₂. A series of

samples is also taken for pH measurements before and independently of the titration. On the molinity scale, the alkalinity is given by

$$A = 2 \cdot C_{\text{CO}_3} + C_{\text{HCO}_3} + C_{\text{B(OH)}_4} + C_{\text{OH}}^{\text{T}} - C_{\text{H}}^{\text{T}} \quad (1)$$

and taking into account the carbonic acid, boric acid and water equilibria, the following expression (Skirrow, 1975) can be written

$$C_{\text{T}} = (A + D) \cdot E \quad (2)$$

where D and E are the following expressions

$$D = \frac{a'_{\text{H}}}{f_{\text{H}}^{\text{T}}} - \frac{B_{\text{T}} \cdot K'_{\text{B}}}{K'_{\text{B}} + a'_{\text{H}}} - \frac{K_{\text{W}} \cdot f_{\text{H}}^{\text{T}}}{a'_{\text{H}}} \quad (3)$$

and

$$E = \frac{1 + (a'_{\text{H}} / K'_1) + (K'_2 / a'_{\text{H}})}{1 + (2K'_2 / a'_{\text{H}})} \quad (4)$$

and, as there is no loss of COs, the following expression is obtained by equilization of the initial and final values of C_{T} .

$$A = N_{\text{HCl}} \cdot V_{\text{HCl}} / W + \frac{D_f \cdot E_f \cdot (1 + V_{\text{HCl}} / W) - E_i \cdot (D_i + N_{\text{HCl}} \cdot V_{\text{HCl}} / W)}{E_i - E_j} \quad (5)$$

where i and f are the initial and final values of titration, V_{HCl} and N_{HCl} are, respectively, the added volume and molarity (0.1M) of hydrochloric acid and W is the mass of the sample (on board a Knudsen pipette is used to measure the volume ($\pm 0.02 \text{ cm}^3$) and the mass is then calculated as a function of salinity and temperature).

The salinity and temperature of the sample to be titrated must be known to determine the dissociation constants and B_{T} . Constants K'_1 and K'_2 are given by Mehrbach et al. (1973), K'_{B} by Lyman (1956) and K_{W} by Dickson and Riley (1979). Pérez and Fraga (1987) give an expression to calculate f_{H}^{T} obtained from the determinations of Mehrbach et al. (1973), and they discuss the use of f_{H}^{T} to evaluate the systematic error in pH determination in seawater.

Calculations are rapid and easy to carry out with a microcomputer. The experimental procedure of this method is also rapid and easy.

MATERIAL

Sodium tetraborate decahydrate (Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, Merck p.a.) was used as standard. It was in isopiestic equilibrium with a solution saturated with both sodium chloride and sucrose.

The hydrochloric acid ($\approx 0.1 \text{ M}$) was potentiometrically titrated vs. borax to a final pH of 5.3 ± 0.05 .

pH measurements were carried out with a combined glass electrode (Metrohm E-121) with Ag/AgCl (KCl 3M) as reference. To standardize the electrode, we used a phosphate buffer (NBS-7.413), assuming the theoretical slope. Determinations of f_{H}^{T} were carried out to evaluate the systematic errors in the pH measurements. These errors are due to variations in the residual liquid-junction potential.

A pH meter Metrohm E-510 was used with an automatic burette (Metrohm 415) and an impulsomat (Metrohm E-473) for the potentiometric titrations.

DIFFUSION OF CARBON DIOXIDE DURING THE TITRATION

The $\text{CO}_{2(\text{g})}$ interchange is kinetically controlled by diffusion through the interface since the speed of dehydration of H_2CO_3 is greater than the rate of diffusion. The rate of diffusion of the gas across the interface is given by

$$J = K_d \cdot \Delta P_{\text{CO}_2} \quad (6)$$

where K_d is the velocity constant of transference, with a value of $20 \cdot 10^{-6} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{min}^{-1} \cdot \text{atm}^{-1}$ (Skirrow, 1975), ΔP_{CO_2} is the difference in CO_2 partial pressure between the two phases. This difference is calculated from the CO_2 solubility in seawater (Weiss, 1974).

Usually seawater titrations are carried out in a beaker of 400 cm^3 volume and an interface surface of 46 cm^2 or, preferably, in a conical flask of 280 cm^3 volume and an interface surface of 8 cm^2 . The titration consists of the following steps:

- (1) 0.25 min to equilibrate the electrodes in the sample;
- (2) 1-1.5 min to add 90% of the acid;
- (3) 0.5 min to add the rest of the acid and pre-stabilisation of final pH; and

(4) 0.5 min to stabilize and read the final pH. This latter interval is also used to fill the burette for the following determinations.

To evaluate, the loss of CO₂, in a more logical way, we need to calculate the effective time the solution is subject to a fixed partial pressure. The P_{co2} has a linear increase on adding HCl, in the second step. Thus, ΔP_{co2} can be taken as the maximum value (0.06 atm) and the effective time, at most, equals a half of the time consumed in the second step, more of the time consumed in the third and fourth ones. The solutions will be then 1.75min at a partial pressure of 0.06 atm approximately. Taking into account eq. 6

$$\begin{aligned} \Delta C_T &= -K_d \cdot (\Delta P_{co2}) \cdot S \cdot t \\ &= -0.020 \text{ mmol} \cdot \text{atm}^{-1} \cdot \text{min}^{-1} \cdot \text{cm}^{-2} \cdot 0.06 \text{ atm} \cdot 1.75 \text{ min} \cdot 46 \text{ cm}^2 \\ &= -80.10 \cdot 10^{-6} \text{ mol} \dots 4\% \text{ of } C_T \end{aligned} \quad (6a)$$

which gives rise to a systematic error of - 0.11% in alkalinity. These systematic errors are calculated including in eq. 5 the loss of C_T (if 4% of C_T lost, E_i changes to 0.96 E_i). Using conical flasks this error would decrease to 0.02% because the interface is six times smaller.

To confirm these estimates of C_T loss, two kinds of experiments were devised. In the first set of experiments, seawater was titrated with HCl and the final solution was allowed to lose CO₂ for some time while maintaining the pH constant by adding HCl (experiments 1-5, Table I). In the second set of experiments HCl was not added and the increase of pH was measured after some time (experiments 7-10, Table I). The alkalinity of the sample was determined from the data of the first step. The values of C_T and C'_T are, respectively, the total inorganic carbon of the sample at the final point of titration (pH = pH_f) and after some time (pH = pH'_f). They are calculated using eqs. 2-4 taking into account the alkalinity (= A - V_{HCl} · N_{HCl}/W) and pH at both points. When comparing losses of CO₂ per unit time (ΔC_T/t), a decrease directly influenced by a decrease of the interface area is observed and the losses are similar to those estimated from eq. 6 (-45 · 10⁻⁶ mol kg⁻¹ of C_T min⁻¹). In fact, as some CO₂ is lost, the partial pressure in the vicinity of the solution is greater than the atmospheric one. This can be clearly seen in experiment 10 (Table I).

Thus the possible error introduced in the determination of alkalinity (eq. 5) by loss of CO₂ during titration is < 0.05%, if titrations are carried out with interface surfaces < 8 cm².

REPRODUCIBILITY

The mean error was estimated by carrying out repeated measurements of alkalinity on the sample that was stored in a plastic container of 25 l volume. The electrode was standardized with NBS buffer 7.413 (normally once a day on board) and it remained in seawater for more than 30 min to obtain the best stabilization of the residual liquid-junction potential. When this time had elapsed the pH of the sample was measured and repeated titrations were carried out, as in practice.

After the system was considered stable, 23 detailed measurements were made as shown in Table II, obtaining a reproducibility of the method better than 0.1%.

This same experiment was repeated 21 days later to test the reproducibility in time (electrode standardization). It is assumed that sample alkalinity does not vary since the volume is great enough and remains stored in a closed container. Table III shows that values of alkalinity and pH are perfectly reproduced within the experimental errors.

ACCURACY

Five prior measurements of alkalinity in the same water sample were carried out both by the classical method (Gripenberg, 1936) modified to use a glass electrode, as well as by the new method proposed here, giving 2360 ± 7 and $2364 \pm 2 \mu\text{mol kg}^{-1}$, respectively. The classical method is troublesome for the following reasons: it is not so accurate, the time of titration is longer and it has, in addition, the inconvenience of having to boil the sample.

To confirm the method, we prepared different standard solutions similar to natural seawater. The preparation of synthetic water is inconvenient due to the presence of nutrients as impurities of major salts. This gives rise to seawater with an unstable carbonic system due to the possibility of photosynthesis. Besides this, it is easier to

obtain natural seawater with very low nutrient concentrations. In these solutions the residual alkalinity must be known ($< 50 \mu\text{mol kg}^{-1}$) after being neutralized and free of CO_2 . This residual alkalinity is determined, either by measuring the pH (NBS) after seawater has reached the equilibrium at atmospheric CO_2 pressure and then calculating the alkalinity through the equations of the carbonic system equilibrium (Skirrow, 1975), or by measuring the pH after further additions of HCl , with the alkalinity obtained as the intercept on the ordinate when the acid concentration of the sample vs. hydrogen ion activity (a_{H^+}) is plotted.

After the seawater was neutralized and free of CO_2 and the alkalinity was known, we obtained some seawater standards with alkalinities similar to natural seawater by adding fixed amounts of NaHCO_3 or Na_2CO_3 . Some of these standards are somewhat unstable (24h) due to the possible precipitation of CaCO_3 .

Using seawaters with the following salinities and alkalinities:

SW1: $S = 34.5$ and $A = 33 \mu\text{mol kg}^{-1}$

SW2: $S = 34.2$ and $A = 0.5 \mu\text{mol kg}^{-1}$

SW3: $S = 35.2$ and $A = 2317.4 \mu\text{mol kg}^{-1}$

SW4: $S = 35.4$ and $A = 0.1 \mu\text{mol kg}^{-1}$

a series of standard solutions was prepared as follows:

- (1) 0.37525 g of NaHCO_3 + 1026.08 g of SW1;
- (2) 0.40780 g of NaHCO_3 + 2072.04 g of SW2;
- (3) 0.38282 g of NaHCO_3 + 1010.28 g of SW2;
- (4) 0.27067g of Na_2CO_3 + 2067.74g of SW3;
- (5) 0.21427 g of NaHCO_3 + 1040.2 g of SW3; and
- (6) 0.19456g of Na_2CO_3 + 752.63g of SW4 + 34.20g of HCl .

The amount of pure NaHCO_3 is calculated weighting the Na_2CO_3 resulting from heating to 520°C .

Titrations carried out with these standards (Table IV) clearly show that the error of method is $< 0.1\%$.

SIMULATION OF ERROR IN THE CALCULATION OF ALKALINITY AND TOTAL INORGANIC CARBON

It is necessary to know the experimental parameters most influencing alkalinity measurements. The results expressed in Table V are obtained by introducing the measurement error of each experimental parameter into the calculation processes (Eqs. 1-5).

The concentration of total inorganic carbon is calculated from alkalinity and initial pH of the sample. Thus, the experimental error in that concentration is greatly influenced by errors of the initial pH apart from that propagated by alkalinity (Table V). The table shows the influence of dissociation constants of carbonic and boric acid, water and the activity coefficient of hydrogen ions. The values shown in Table V are taken from UNESCO (1983). These determinations are affected by the same residual liquid-junction potential. To use these constants and to introduce no systematic error when measuring alkalinity and total inorganic carbon, the pH measurements must be affected by this residual liquid-junction potential.

Although uncertainties in K_w and K'_B do not influence the alkalinity, K'_B influences the determination of total inorganic carbon.

Other bases such as phosphate and silicate ions may also contribute to alkalinity in seawater. Phosphate is present in natural seawater, mainly as HPO_4 ($\text{pK}_1 = 1.6$, $\text{pK}_2 = 6.1$ and $\text{pK}_3 = 9.1$; Dickson and Riley, 1979) and its contribution is practically equivalent for equivalent to alkalinity, thus it does not introduce errors in the titrated alkalinity. On the other hand, the second and third dissociation constants are close to those of carbonic acid. The contribution to total carbonate, as calculated in eq. 2 is practically mole for mole. If the phosphate ion is not taken into account in these equations, a systematic (mathematical) error appears in total carbonate which equals the phosphate concentration. Since the silicate ion ($\text{pK}_1 = 9.5$) has a constant three times smaller than K'_2 , it does not significantly contribute to the alkalinity; the contribution to total carbonate being 1/12 of the total silicate concentration at pH 8.4 and 1/50 at pH 7.8.

POLYNOMIAL EQUATION

Calculation of alkalinity from the experimental parameters requires the use of many equations; this is really tedious, although not difficult. The simplification of calculations for the following range of experimental parameters seems convenient:

- (1) Initial pH 7.8-8.4.
- (2) Final pH 4.0-4.6. The pH_f appears in this interval after addition of 94% of the equivalent volume of HCl.
- (3) Salinity 20-40.
- (4) Specific alkalinity from 40 to 80 $\mu\text{mol g}^{-1}$ of salt.
- (5) Titration temperature 10-25°C.
- (6) HCl molarity 0.07-0.13 M.

The alkalinity neutralized in the titration is

$$A_N = V_{\text{HCl}} \cdot N_{\text{HCl}} / W \cdot 10^6 \text{ (}\mu\text{mol kg}^{-1}\text{)}$$

The system of equations (2-5), which also involves those equations that define the equilibrium constants, can be reduced to

$$A = A_N - 15.5 + 0.52 (S - 30) + 213.5 (\text{pH}_f - 4.4) \\ + 0.002276 (A_N - 2000) + 302.9 (\text{pH}_f - 4.4)^3 \\ + 0.04310 (\text{pH}_f - 4.4) (A_N - 2000) \quad (7)$$

for the intervals mentioned above, through a minimization process by least squares. If the titration is carried out in a temperature range of 15-22°C, this equation gives the alkalinity with an error of $\pm 3 \mu\text{mol kg}^{-1}$.

Isolines of error using the proposed eq. 7 vs. the theoretical one, are represented in Figs. 1 and 2. Almost the whole error area ($\pm 0.1\%$) covers the zone of basic variables used in the calculations.

This equation greatly simplifies the alkalinity titrations. When the titrations are run at a temperature of about 20°C in a flask with a surface of interface $< 8 \text{ cm}^2$ and HCl of a known molarity is added (not more than 2 rain must be used) until pH_f within the range 4.0-4.6 is reached, the neutralized alkalinity is calculated, and using data of salinity and pH_f , we obtain the alkalinity of the sample through eq. 7.

DISCUSSION

This method is good for the analysis of a large number of samples, since it is much more rapid than any of the methods described in the bibliography. An exception may be the potentiometric method described with linear fitting proposed by Dickson (1981), which is more accurate and precise (0.08% compared with 0.1%, Johansson and Wedborg, 1982). However, the time used is five times longer and the standardization more sophisticated. The potentiometric Gran Plot method, which was proposed by Edmond (1970), presents a similar precision (0.17%) but the time used is also longer (15-20 min).

The method described here is an improvement on that proposed by Culberson et al. (1970), which improves, at the same time, the method of Anderson and Robinson (1946). It is simpler and more precise due to suppression of the step which eliminates the CO₂ in the final pH measurement. Equation 5 may be simplified in an approximate way for comparison with the expression given by Culberson et al.

$$A = N_{\text{HCl}} \cdot V_{\text{HCl}}/W + a'_{\text{H}}(1 + V_{\text{HCl}}/W)/f^{\text{T}}_{\text{H}} + K'_{\text{1}} \cdot \left(\frac{(1 + V_{\text{HCl}}/W)}{f^{\text{T}}_{\text{H}}} - \frac{C_{\text{T}}}{a'_{\text{H}}} \right)$$

The last term does not appear in the conventional pH-method, because in its final conditions the pH_f is lower (≈ 3) or CO₂ is eliminated.

The method proposed here was applied to 3000 samples collected off the coasts of Galicia and Portugal during the cruises "Galicia-V", "Galicia-VI", "Galicia-VII" and "Galicia-VIII" and good results were obtained (Fraga et al., 1985). In addition, it enables one to study mixing of water masses, using the type values of alkalinity for different water masses. In a first approach an error of 0.15% was obtained for water bodies off Galician and Portuguese coasts.

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LIST OF SYMBOLS

Concentration units are given in moles per kilogram of seawater (mol kg^{-1} , molality scale, Whitfield and Jagner, 1981), which do not depend on pressure and temperature.

A	total alkalinity in mol kg^{-1} (UNESCO, 1985)
A_{sp}	specific alkalinity (A/S), in $\mu\text{mol g}^{-1}$ of salt
A_{N}	neutralized alkalinity in $\mu\text{mol kg}^{-1}$ in the titration ($= V_{\text{HCl}} \cdot N_{\text{HCl}} / W$)
A'_{H}	apparent activity of hydrogen ions, $a_{\text{H}}(\text{NBS})$
B_{T}	total borate
C_{T}	total inorganic carbon
f_{H}^{T}	apparent activity coefficient of total hydrogen ions
K'_{1}, K'_{2}	apparent constants of carbonic acid
K'_{B}	apparent constant of boric acid
K_{W}	stoichiometric constant of water
N_{HCl}	molarity of hydrochloric acid
$\text{pH}(\text{NBS})$	scale of apparent activity of hydrogen ions
pH_{i}	$\text{pH}(\text{NBS})$ of the sample
pH_{f}	$\text{pH}(\text{NBS})$ of the sample at the final point of titration
S	salinity
t	temperature in $^{\circ}\text{C}$
V_{HCl}	volume of hydrochloric acid in cm^3
W	mass of the seawater sample

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TABLE I

The loss of total inorganic carbon (C_T) as $CO_{2(g)}$ through the interface after reaching the end point of titration

Exp.	Titration data					Titration results of		After titration				Loss per min ($\Delta C_T \text{min}^{-1}$)	Area (cm^2)
	Initial			Final		A	C_T	Experimental			Calculated		
	S	t	pH_{15}	pH_f	V_{HCl}			Time	V'_{HCl}	pH'_f	C'_T		
1	29.01	18.3	8.233	4.468	4.851	1936	1696	7.6	4.867	4.468	1409	38	46
2	32.67	18.3	8.233	4.470	5.396	2161	1870	30	5.451	4.470	1010	28	46
3	34.77	18.3	8.192	4.470	5.706	2290	1989	9	5.723	4.470	1696	33	46
4	35.30	18.5	7.818	4.467	5.706	2295	2149	16	5.737	4.467	1677	30	46
5	35.41	18.4	7.818	4.424	5.670	2269	2125	16	5.696	4.424	1659	30	46
6	35.41	18.4	7.818	4.340	5.734	2275	2130	21	5.734	4.378	1681	23	46
7	35.41	18.4	7.818	4.195	5.837	2280	2133	18	5.837	4.202	1961	9.6	8
8	35.41	18.4	7.818	4.427	5.694	2274	2134	16	5.694	4.432	2041	5.8	8
9	35.41	18.4	7.818	4.420	5.677	2271	2126	14	5.677	4.428	2004	8.7	8
10	35.41	18.4	7.818	4.422	5.728	2272	2127	12	5.728	4.429	2005	9.3	8
								17	5.728	4.432	1988	8.2	8
								28	5.728	4.438	1935	6.9	8

C_T (in $\mu\text{mol kg}^{-1}$) is calculated from the alkalinity (in $\mu\text{mol kg}^{-1}$) and pH_f of the sample. In experiments 1 to 5 more V_{HCl} (in ml) is added to keep pH constant (= pH_f). In experiments 6-10 the pH changes due to loss of CO_2 . C'_T is the carbon present after some time (in min) of the titration and it is calculated through the pH'_f and the alkalinity at that moment of titration. $(N_{\text{HCl}}/W) = 400 \mu\text{mol kg}^{-1}\text{ml}^{-1}$.

TABLE II

Experiments carried out to determine the reproducibility of the proposed method

Exp.	pH _f	V _{HCl}	A
1	4.440	4.833	2284.4
2	4.442	4.830	2283A
3	4.431	4.839	2284.8
4	4.443	4.832	2284.4
5	4.453	4.825	2283.7
6	4.428	4.837	2283.1
7	4.450	4.829	2284.9
8	4.450	4.826	2283.2
9	4.444	4.827	2282.2
10	4.128	5.002	2282.8
11	4.441	4.830	2282.9
12	4.433	4.840	2285.8
13	4.458	4.824	2284.1
14	4.442	4.832	2284.4
15	4.444	4.830	2283.9
16	4.418	4.848	2286.0
17	4.212	4.963	2288.6
18	4.463	4.823	2284.9
19	4.440	4.832	2283.9
20	4.312	4.903	2286.5
21	4.450	4.829	2284.9
22	4.458	4.825	2284.9
23	4.427	4.843	2285.8
			2284.5 ± 1.4 (23)

Precision on alkalinity = $1.412284.5 = 0.06\%$.

For every sample, S = 34.64, pH_i = 8.148 at 17.6°C (pH₁₆ = 8.182), W = 255.9g. N_{HCl} . 0.1209M.

TABLE III

Experiments carried out (21 days after the experiment described in Table II) to determine the reproducibility of the proposed method

Exp.	pH _f	V _{HCl}	A
1	4.416	4.848	2285.8
2	4.386	4.863	2285.7
3	4.416	4.850	2286.7
4	4.412	4.850	2285.8
5	4.381	4.868	2286.9
6	4.423	4.847	2287.0
7	4.418	4.855	2289.6
8	4.318	4.900	2286.6
9	4.415	4.845	2284.1
10	4.417	4.848	2286.0
11	4.302	4.903	2284.0
			2286.2 ± 1.5 (11)

Precision on alkalinity = $1.5/2286.2 = 0.07\%$.

For every sample $S = 34.64$, $\text{pH}_i = 8.168$ at 16.2°C ($\text{pH}_{15} = 8.184$) and $W = 255.9$. $N_{\text{HCl}} = 0.1209\text{M}$. V_{HCl} and A are expressed in cm^3 and $\mu\text{mol kg}^{-1}$, respectively.

TABLE IV

Accuracy of method using various standard solutions. The alkalinity is expressed in $\mu\text{mol kg}^{-1}$

Standard	Number of analysis	Values		Error (%)
		Exp.	Theoretical	
1	4	4319	4319	0
2	4	4653	4660	- 0.15
3	4	6822	6828	- 0.09
4	5	2470	2470	0
5	3	2454	2452	0.08
6	6	2307	2308	- 0.04

TABLE V

Influence of the directly measured parameter and constant used in the determination of the alkalinity and total inorganic carbon

Parameter	Assumed error	Consequent error in parameter determined	
		%A	% C _T
Titrant concentration	0.1%	0.1	0.1
Mass or volume of the sample	0.01%	- 0.01	- 0.01
Titrant volume	0.02%	0.02	0.02
Salinity	0.003%	0.0005	0.0023
Titration temperature	0.1	0.005	- 0.005
pH _i	0.005	0.0025	0.02
pH _f	0.005	- 0.025	0.03
log f ^l _H	0.010	0.05	0.06
log K' ₁	0.015	0.075	0.06
log K' ₂	0.03	0.015	0.25
log K' _B	0.03	0.015	0.12
log K' _w	0.010	0.00005	- 0.002
Neglecting 1 μM phosphate		- 0.0002	+ 1 μM
Neglecting 20 μM silicate		0.0001	+ 1 μM

Fig. 1. Differences (in μmolkg⁻¹) at different salinities and temperatures, between alkalinity evaluated through the polynomial equation (expression 7) and the theoretical equation set (expressions 3-5), using pH_i = 8, pH_f = 4.4, N_{HCl} = 0.1M and Asp = 66 μmolg⁻¹.

Fig. 2. Differences (in μmolkg⁻¹) at different initial and final pH between alkalinity evaluated through the polynomial equation (expression 7) and the theoretical equations (eqs. 3-5), using t = 20°C, S = 35, N_{HCl} = 0.1M and A_N = 2000 μmolkg⁻¹.