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DETERMINATION OF CARBONATE SATURATION OF SEAWATER WITH A CARBONATE SATUROMETER¹

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ABSTRACT

A mathematical model has been established for the implementation of the Weyl saturometer, to obtain quantitative data on the degree of saturation (IP:K'sp) of calcite and aragonite to within $\pm 2\%$ when the chlorinity and pH of the measured seawater are known. The method also enables carbonate alkalinity to be estimated to within $\pm 10\%$ of values obtained by titration. Nomograms are given for the determination of degree saturation and total CO₂ for seawater of known pH, where a change in potential has been measured after exposing a calibrated glass electrode to a slurry of calcium carbonate in the original seawater.

INTRODUCTION

The carbonate saturometer, originally suggested by Weyl (1961), can be used to detect the degree of saturation of natural waters with respect to carbonate. The basic configuration of the saturometer is simple, consisting of a glass electrode that is used to measure the pH of the test solution before and after equilibrating it with a specific carbonate solid. Weyl also developed some mathematical relations that can be used for the calibration of the saturometer. His calibration procedure is, however, quite complex. It consists of titrating a sample of the solution with a strong acid and a strong base and monitoring the output of the glass electrode when small amounts of bicarbonate are added along the titration curve. For seawater, an auxiliary function can be calculated that may replace part of the titration procedure, but an acid-base titration is still required for each water sample studied. The titration information is used to calculate a calibration chart that relates the differential output of the glass electrode to the amount of carbonate that was dissolved into, or precipitated from,

the test solution during equilibration with the solid phase. This calibration curve is not universal and has to be performed on each sample.

Although the carbonate saturometer has been used by a number of investigators (Chave et al. 1962; Chave and Schmalz 1966; Schmalz and Chave 1963; Chave and Suess 1967; Schmalz and Swanson 1969), none of them has used the cumbersome calibration procedure suggested by Weyl. Instead, the output of the saturometer has been used as a relative measure for the degree of carbonate saturation.

We propose a mathematical model for seawater where one can directly use the readings of the saturometer to calculate the degree of saturation of the solution with respect to carbonate. Moreover, this information is often enough to permit calculation of the concentration of the carbonate species and the alkalinity of the test solution, if some reasonable assumptions are made.

BASIC ASSUMPTIONS AND MATHEMATICAL DERIVATION

Our model is based on the following three assumptions:

1. The total alkalinity of seawater is the sum of the borate alkalinity and carbonate alkalinity. We are neglecting here the contribution of the hydrogen ion and hydroxyl ion to the alkalinity as well as other protolytic ions such as sulfide. This assumption

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appears to be valid for normal seawater in the pH range of 7 to 9 (Skirrow 1965).

2. The ratio of boron to chlorinity is constant for normal seawater (Culkin 1965). At any rate, small errors in the estimation of this ratio have negligible effects on our calculation.

3. The ratio of calcium to chlorinity is constant for normal seawater (Culkin 1965). We shall examine below the effect on our results when this ratio varies.

From the first assumption, we obtain:

$$\text{TA} = \text{BA} + \text{CA}, \quad (1)$$

where TA = total alkalinity; BA = borate alkalinity; and CA = carbonate alkalinity.

The carbonate alkalinity is related to the carbonate ions by:

$$\text{CA} = [\text{HCO}_3^{1-}] + 2[\text{CO}_3^{2-}], \quad (2)$$

where $[\text{HCO}_3^{1-}]$ = bicarbonate ion concentration (free and complexed) [mole/liter], and $[\text{CO}_3^{2-}]$ = carbonate ion concentration (free and complexed) [mole/liter].

The borate alkalinity is related to the total boron, ΣB , in the solution by the equation (Skirrow 1965)

$$\text{BA} = \Sigma\text{B} \frac{K'_B}{K'_B + a\text{H}}, \quad (3)$$

where K'_B = apparent dissociation constant of boric acid, and $a\text{H}$ = activity of the hydrogen ion [moles/liter].

Assume now that X [moles/liter] of CaCO_3 dissolved (for precipitation X should be taken as a negative value); as a result, the total alkalinity of the solution will change by $2X$ and equation (1) can be rewritten as:

$$\text{TA} + 2X = \text{BA}_s + \text{CA}_s, \quad (4)$$

where s stands for saturation—the value after the solution is exactly saturated with CaCO_3 . Namely:

$$\text{BA}_s = \Sigma\text{B} \frac{K'_B}{K'_B + a\text{H}_s}. \quad (5)$$

The carbonate alkalinity is related to the total CO_2 in the solution by equation (6) (Skirrow 1965):

$$\text{CA} = \Sigma\text{CO}_2 \left[\frac{1 + (2K'_2/a\text{H})}{1 + (K'_2/a\text{H}) + (a\text{H}/K'_1)} \right], \quad (6)$$

where K'_1 = first apparent dissociation constant of carbonic acid, and K'_2 = second apparent dissociation constant of carbonic acid.

After saturation, the carbonate and total calcium ionic product should equal the apparent solubility product of the relevant carbonate ($K'\text{sp}$). Namely:

$$[\text{CO}_3^{2-}]_s \times [\text{Ca}]_s = K'\text{sp}; \quad (7)$$

where (Skirrow 1965):

$$[\text{CO}_3^{2-}] = \text{CA} \left[\frac{K'_2}{a\text{H} + 2K'_2} \right]. \quad (8)$$

The alkalinity balance before saturation can, therefore, be described by equations (1), (3), and (6):

$$\text{TA} = \Sigma\text{B} \frac{K'_B}{K'_B + a\text{H}} + \Sigma\text{CO}_2 \left[\frac{1 + (2K'_2/a\text{H})}{1 + (K'_2/a\text{H}) + (a\text{H}/K'_1)} \right], \quad (9)$$

and after saturation by equations (4), (5), and (6):

$$\text{TA} + 2X = \Sigma\text{B} \frac{K'_B}{K'_B + a\text{H}_s} + (\Sigma\text{CO}_2 + X) \times \left[\frac{1 + (2K'_2/a\text{H}_s)}{1 + (K'_2/a\text{H}_s) + (a\text{H}_s/K'_1)} \right]. \quad (10)$$

Also, from equations (6), (7), and (8):

$$K'\text{sp} = ([\text{Ca}] + X) (\Sigma\text{CO}_2 + X) \times \left[\frac{1 + (2K'_2/a\text{H}_s)}{1 + (K'_2/a\text{H}_s) + (a\text{H}_s/K'_1)} \right] \times \left[\frac{K'_2}{a\text{H} + 2K'_2} \right]. \quad (11)$$

The last three equations can now be solved for three unknowns, X , ΣCO_2 , and TA. They can then be expressed in terms of the parameters M , P , U , Q , and R which have $a\text{H}$ as a variable.

Thus, U is defined from equation (5), M from equation (6), and P from equation (8); and U_s , M_s , and P_s are defined as above, only for $a\text{H}_s$.

Equations (9), (10), and (11) can now be written as

$$\text{TA} = \Sigma\text{B} \times U + \Sigma\text{CO}_2 \times M; \quad (12)$$

$$TA + 2X = \Sigma B \times U_s + (\Sigma CO_2 + X) \times M_s; \quad (13)$$

$$K'_{sp} = ([Ca] + X)(\Sigma CO_2 + X)M_s P_s. \quad (14)$$

Eliminating TA and solving for ΣCO_2 :

$$\Sigma CO_2 = \frac{X(2 - M_s) - \Sigma B(U_s - U)}{M_s - M}. \quad (15)$$

Inserting ΣCO_2 in (14) and reducing terms yields

$$([Ca] + X)[X(2 - M) - \Sigma B(U_s - U)] = \frac{K'_{sp}}{M_s P_s}(M_s - M). \quad (16)$$

Or:

$$X^2 + X \left\{ \frac{[Ca] - \Sigma B(U_s - U)}{2 - M} \right\} - \frac{K'_{sp}(M_s - M)}{M_s P_s(2 - M)} - \frac{\Sigma B[Ca](U_s - U)}{(2 - M)} = 0. \quad (17)$$

We define:

$$Q = \left\{ [Ca] - \frac{\Sigma B(U_s - U)}{2 - M} \right\}; \quad (18)$$

$$R = \frac{K'_{sp}(M_s - M)}{M_s P_s(2 - M)} + \frac{\Sigma B \times [Ca] \times (U_s - U)}{2 - M}. \quad (19)$$

Equation (17) can now be written as:

$$X^2 + XQ - R = 0, \quad (20)$$

which has the solution:

$$X = \frac{-Q + (Q^2 + 4R)^{\frac{1}{2}}}{2}. \quad (21)$$

The positive square root value was taken since X should be able to assume both positive and negative values.

X can now be used to solve equation (14) for ΣCO_2 , yielding:

$$\Sigma CO_2 = \frac{K'_{sp}}{M_s P_s([Ca] + X)} - X. \quad (22)$$

Using ΣCO_2 , TA can be calculated from equation (12):

$$TA = \Sigma B \times U + \Sigma CO_2 \times M. \quad (23)$$

The molal concentrations of boron and

calcium are calculated from the relations (Culkin 1965):

$$\Sigma B = \frac{0.237}{10.82} \times d \times Cl\% \quad (\text{mmoles/liter}), \quad (24)$$

$$[Ca] = \frac{21.3}{40.08} \times d \times Cl\% \quad (\text{mmoles/liter}) \quad (25)$$

(d = the density of the tested seawater).

It is evident, therefore, that the pH values before and after saturation are sufficient to determine the degree of saturation of the solution. The saturation ratios, namely the ratio of ionic product (IP) of the original solution to the apparent solubility product (K'_{sp}) can be derived from the above, yielding:

$$\frac{IP}{K'_{sp}} = \frac{[Ca] \Sigma CO_2 \times M \times P}{K'_{sp}}. \quad (26)$$

These computations show that a knowledge of only the salinity of the solution and its pH values before and after saturation is sufficient to describe the seawater completely with respect to the carbonate system.

RESULTS

The calculations might be too lengthy to carry out by hand, but they can be readily programmed. By use of a computer program, we have calculated the degree of calcite saturation (IP : K'_{sp}), total dissolved carbon dioxide (ΣCO_2), and carbonate alkalinity (CA), under different conditions of pH, temperature, and salinity. Figure 1 was prepared by calculating the degree of saturation of seawater with respect to calcite for a salinity of 35‰ at 25°C. The values for boron-to-chlorinity ratio and calcium-to-chlorinity ratio were determined by equations (24) and (25). The value of K'_{sp} for calcite was taken as 0.54 [mmole/liter]² (McIntyre 1965). The apparent dissociation constants are from the data of Lyman (1957).

The abscissa units are millivolts and correspond to the potential change of the glass electrode's output (Δv), namely, the difference between the output after saturation and the output of the electrode when im-

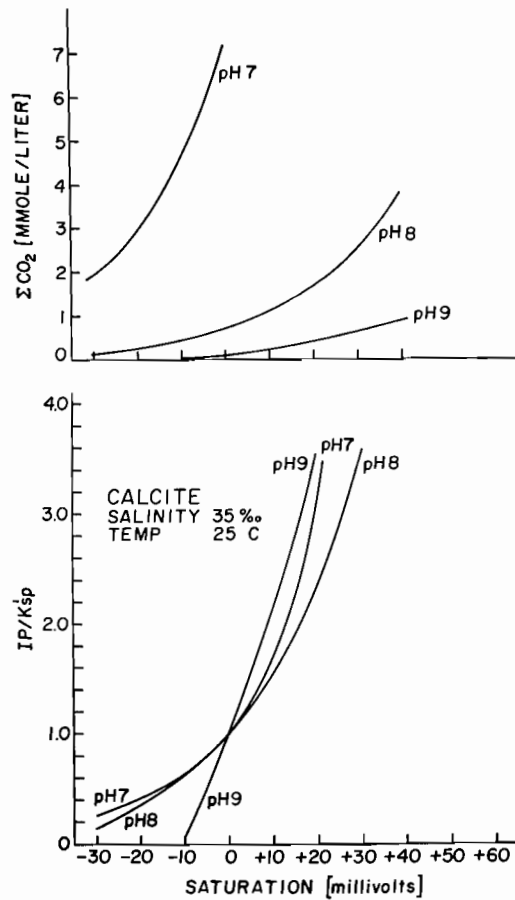


FIG. 1. Nomogram for determination of IP : K'sp and ΣCO₂ from saturometer experiment. Curves are for saturation with respect to calcite for seawater of 35‰ salinity at 25C.

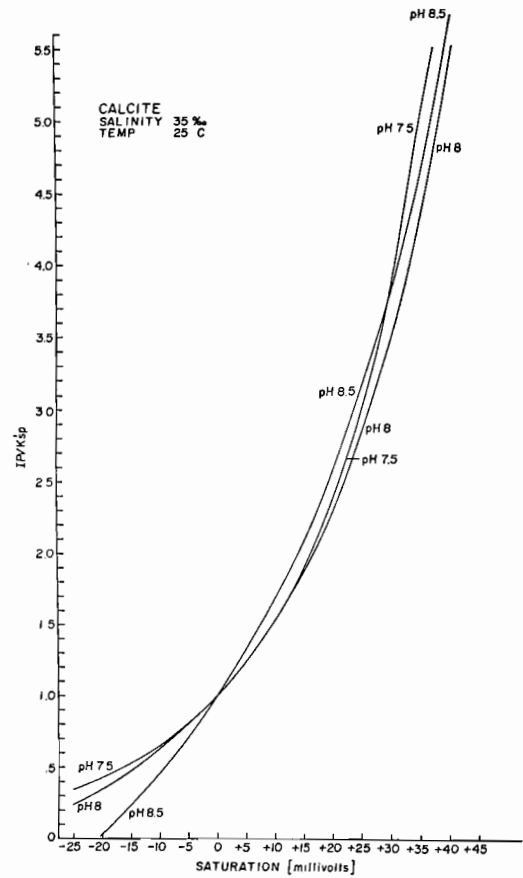


FIG. 2. Expanded nomogram for determination of IP : K'sp from a saturometer experiment. Curves are for saturation with respect to calcite for seawater of 35‰ salinity at 25C.

mersed in the original solution. This is related to pH in the following way,

$$aH_s = [aH] \times 10^{(-\Delta v / SL)}, \quad (27)$$

where Δv = output potential shift (volts), and SL = response of glass electrode (Δv : ΔpH).

It is evident from Fig. 1 that the sensitivity of the saturometer depends on the pH of the original solution. Maximum sensitivity is around pH 8 and falls off toward higher and lower values. This can be explained by the fact that the first equivalence point of seawater (Dyrssen and Sillen 1967) is near pH 8. Around this point, seawater has minimum buffering capacity, and an

addition of relatively small amounts of carbonate will change the pH markedly. The buffer capacity at pH 7 and 9 is larger, and the addition of the same amount of carbonate will change the pH value by a smaller amount. Figure 1 also represents the total CO₂ of the test solution as a function of the shift in potential of a solution in contact with calcite calculated by equation (22). Once the ΣCO₂ and pH of the solution are known, the concentrations of the different carbonate species can be calculated (Skirrow 1965).

Since the sensitivity of the saturometer depends on the pH of the original solution, one should avoid using the output of the

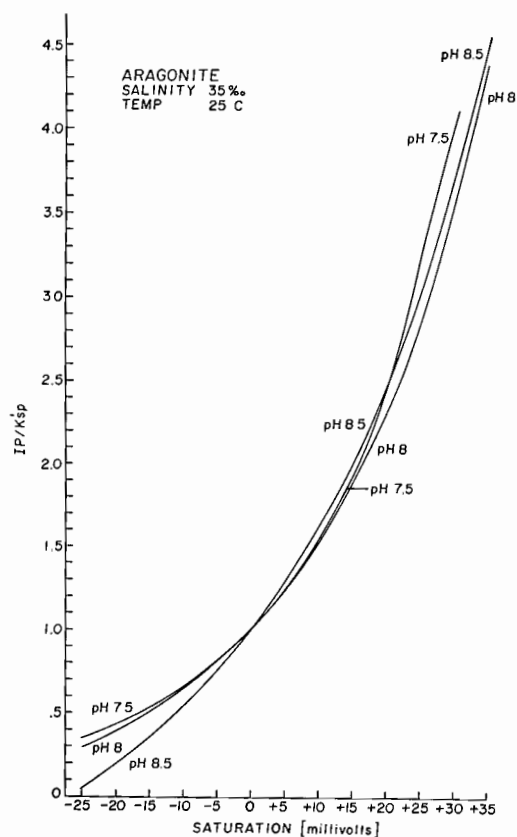


FIG. 3. Expanded nomogram for determination of $IP : K'sp$ from a satrometer experiment. Curves are for saturation with respect to aragonite for seawater of 35‰ salinity at 25C.

satrometer as a relative measure of degree of saturation. The same output shift for two solutions with different pH does not indicate that the two solutions are at the same degree of saturation. However, the pH values of natural seawater are generally limited to the range pH 7.5–8.5. Fortunately, the satrometer has its maximum sensitivity at this range as can be seen from expanded nomograms (Figs. 2 and 3). For a supersaturated solution ($IP : K'sp > 1$), the three lines (for pH 7.5, 8.0, and 8.5) are relatively close together. This indicates that at this particular range the satrometer is relatively insensitive to an error in the pH measurement.

One can also read the nomogram of Fig. 1 backward to obtain (from information on

ΣCO_2 and pH) the degree of saturation of the solution. The pH of surface ocean waters is around 8.2, whereas the total dissolved CO_2 is in the range 2 mmole/liter (Li 1967). It is evident, therefore, that surface seawater is inevitably supersaturated with respect to calcite, with the ratio $IP : K'sp$ in the range 3–5.

Our calculations depend on an a priori knowledge of a number of variables related to the test solutions. Table 1 was prepared to check the sensitivity of the calculated values to small differences in these variables that may arise from experimental techniques. The first line corresponds to a model solution of chlorinity 19‰, pH 8, 25 mv satrometer output, at 25C. In the lines below we have assumed an error in one of the parameters. The three calculated results, ΣCO_2 , carbonate alkalinity (CA), and degree of saturation ($IP : K'sp$) correspond, therefore, to the expected error when one of the variables is reported in error.

Table 1 clearly indicates that the computed value of the saturation ratio ($IP : K'sp$) is fairly insensitive to errors in these parameters. This result is only sensitive to an error in the reading of the satrometer (mv saturation), and for an error of 1 mv, the resulting error will be approximately 4%. In our laboratory, we estimate the error of measurement to be 0.5 mv, namely 2% error in the value for the ratio. This error is small, and in any case there will always be a positive answer to the question whether the solution is supersaturated or undersaturated. The output of the satrometer will always be positive for a supersaturated solution, negative for an undersaturated solution, and zero for a saturated solution.

The values of the calculated concentrations of the carbonate species are more sensitive to an error in the variables that are used during the calculations. In particular, the results are sensitive to an error in the pH value of the solution and the calcium-to-chlorinity ratio. An error of 0.1 pH unit in this particular range will result in an error of approximately 22% in the total CO_2 value and 21% in the carbonate alkalinity ratio. A practical pH measure-

TABLE 1. Estimation of errors in the calculated values as a function of errors in the data

Data						Results					
pH	Saturation (mv)	Temp (°C)	Cl %	B:Cl (10 ⁻³)	Ca:Cl (10 ⁻³)	IP : K'sp	*	ΣCO ₂ (mmole/liter)	*	CA (meq/liter)	*
8.0	25	25	19	0.237	21.3	2.84	0	1.99	0	2.12	0
8.1(0.1)†	26(1)†					2.85	-0.35	1.62	22.1	1.75	21.0
		26(1)†				2.96	-4.0	2.08	-4.3	2.21	-4.1
			20(1)†			2.83	0.35	1.90	4.7	2.03	4.4
				0.261(10)‡		2.84	<0.18	1.91	4.1	2.04	3.9
					23.4(10)‡	2.84	<0.18	2.00	-0.5	2.12	<0.2
								1.81	9.9	1.93	9.8

* Per cent error in "results."

† Error in "data."

‡ Per cent error in "data."

ment can probably determine the pH value to within 0.03 pH units (Pytkowicz, Kester, and Burgener 1966). This might result in an error of approximately 7% in the calculated carbonate concentrations.

The calculated carbonate concentrations are also fairly sensitive to an error in estimation of the calcium-to-chlorinity ratio. Here there is actually a one-to-one relationship, and an error of 1% in the ratio will result in 1% error in the calculated values. This is because any error in the value of calcium concentration will be compensated, during the calculation, by a proportional change in the carbonate ion concentration. It has been observed, however, that during a typical saturometer experiment the amount of CaCO₃ that will be dissolved or precipitated will be in the order of 0.2 mmole/liter, which is approximately 2% of the total calcium concentration in seawater. One might postulate, therefore, that if calcium variations in the oceans are a result of CaCO₃ equilibrium, the maximum expected variation of calcium will be about 2%.

It is evident from Table 1 that by using the information from a saturometer experiment, made with moderate precision, one should be able to calculate the saturation ratio (IP : K'sp) with an estimated error of 2-3%. Under these same conditions, one should be able to estimate the concentrations of the carbonate species with an error of approximately 10%. It should be emphasized that our error estimations are applicable only to natural seawater in the pH range of 7.5 to 8.5.

LABORATORY AND FIELD TESTS OF MODEL

We have experimentally tested our model by performing the saturometer experiment and comparing the value of carbonate alkalinity calculated from these data to an independent carbonate alkalinity determination. The saturometer experiment was carried out by equilibrating the test solution with reagent grade calcite powder. Enough calcite was introduced to surround the glass electrode bulb completely. The response of the glass electrode was measured by two standard buffer solutions kept at the same temperature as the test solution (Bates 1961). This measured response was later used in the calculations (equation 27).

The carbonate alkalinity measurement was performed by the method of Dyrssen and Sillen (1967). These independently determined values were later compared to the calculated values from the saturometer experiment.

Two seawater solutions were tested, one supersaturated and one undersaturated with respect to calcite. The first was a filtered natural surface seawater collected over the coral reef in southeast Oahu, Hawaii. The second solution was an artificial seawater sample whose pH was adjusted to approximately 7.73. This artificial seawater was prepared to contain a low concentration of calcium, and the calcium-to-chlorinity ratio was adjusted to approximately half the natural value.

Table 2 summarizes the results of these tests. The degree of saturation (IP : K'sp) for the natural seawater was 3.90 and for

TABLE 2. Comparison of laboratory measurements on a natural and artificial seawater with model calculations

Solution	Temp (°C)	Salinity (‰)	pH	Saturation (mv)	Glass electrode response ($\Delta mv/\Delta pH$)	Ca : Cl	Calculated IP : K'_{sp}	Carbonate alkalinity (mmole/liter)		
								Calcu- lated, CA ₁	Mea- sured, CA ₂	CA ₁ -CA ₂ (%)
Natural surface seawater (Hawaii)	22.0	34.56	8.16	32	57.6	21.3	3.93	2.41	2.57	+6.6
Artificial seawater (see text)	22.5	33.90	7.743	-4.2	57.4	10.6	0.83	2.38	2.18	+8.3

the artificial seawater, 0.83. The calculated values for the carbonate alkalinity approach the values of the independently determined values with a maximum deviation of 8.3% in the case of the artificial seawater.

We have also tested our method of calculation against an independent set of data from the literature. Schmalz and Swanson (1969) made saturometer measurements on surface seawater to study the diurnal variation in carbonate saturation. Beside performing the saturometer experiment, they also made carbonate alkalinity determinations (Strickland and Parsons 1965). The alkalinity values were used to calculate the partial pressures of CO₂. However, the pH values of the tested solution, the results of the saturometer measurement, and a rough estimate of the salinity should be sufficient—according to the above discussion—to fully characterize the seawater with respect to the degree of saturation and the concentrations of the carbonate species. To check this hypothesis, we have used the pH values and the saturometer data of Schmalz and Swanson for their study on Eniwetok reef water to calculate the saturation ratio, concentrations of the carbonate species, and carbonate alkalinity. The last parameter was then compared with the reported values by back-calculating the carbonate alkalinity from their report (using the same procedure they used) and comparing this value to our result (Table 3). The saturometer measurement was performed with respect to oolite aragonite sand by Schmalz and Swanson. In our calculations, we used the

apparent solubility product of aragonite as reported by McIntyre (1965).

Table 3 shows generally good agreement between the calculated and measured value of carbonate alkalinity. In the majority of the data points, the differences are no more than 5%. In a number of cases (e.g., last data point), the discrepancy is larger—up to 20%. These should be attributed to inconsistency in the values of pH, mv saturation, and carbonate alkalinity reported in their measurements. In some cases, it appears that the carbonate alkalinity is irregular; in other cases, we would suspect the saturometer values. For example, for the data point of 14 August, 1100 hours, we obtained 1.73 mmole/liter of the total CO₂. This value is relatively low and might result from an error in the saturometer value. In any case, we can conclude from the majority of the data points that our method of calculation results in carbonate alkalinity values which are in good agreement with the measured values of Schmalz and Swanson.

CONCLUSION

We have shown that in many cases the pH value of seawater, the saturometer value, and approximate information on the chlorinity make possible calculation of the saturation ratio (IP : K'_{sp}) as well as a close approximation of the concentration of the carbonate species. The accuracy for the saturation ratio is reasonably good and it should be possible to calculate this value to within 2% when pH and saturometer values are recorded with moderate precision. The

TABLE 3. Comparison of model calculations with independent carbonate alkalinity determination

Schmalz and Swanson (1969)					Results of calculations				
Date	Time (hours)	$p\text{CO}_2^*$ ($\times 10^3$ atm)	Saturation* (mv)	pH*	Carbonate alkalinity† (CA_1 , mmole/liter)	Carbonate alkalinity (CA_2 , mmole/liter)	ΣCO_2	IP : K'sp	$\text{CA}_1 - \text{CA}_2$ (%)
7-8 Aug	2000	0.257	27.8	8.292	2.34	2.30	2.03	3.22	1.7
	2300	0.278	25.6	8.257	2.22	2.23	1.98	2.93	-0.5
	0200	0.304	22.6	8.196	2.10	2.18	1.98	2.58	-3.8
	0500	0.326	21.7	8.170	2.10	2.21	2.00	2.48	-5.2
	0800	0.304	22.6	8.196	2.10	2.19	1.98	2.58	-4.3
	1100	0.252	26.1	8.292	2.29	2.15	1.90	3.00	6.1
	1400	0.235	30.4	8.309	2.35	2.49	2.18	3.59	-5.9
	1700	0.248	27.9	8.300	2.25	2.28	2.00	3.24	-1.3
	1900	0.296	22.6	8.220	2.11	2.10	1.88	2.59	0.5
13-14 Aug	2000	0.298	23.4	8.248	2.34	2.07	1.84	2.68	11.5
	2400	0.320	23.0	8.208	2.28	2.18	1.96	2.62	4.4
	0630	0.398	20.0	8.135	2.27	2.20	2.00	2.31	3.1
	1100	0.320	20.0	8.208	2.28	1.92	1.73	2.32	15.8
	1400	0.281	26.1	8.257	2.24	2.27	2.02	2.99	-1.4
	1700	0.272	26.1	8.265	2.16	2.24	1.99	3.00	-3.7
	2000	0.289	23.0	8.248	2.28	2.03	1.81	2.63	11.0
	2000	0.315	26.5	8.208	2.25	2.51	2.26	3.03	-11.6
18-19 Aug	2300	0.381	22.2	8.158	2.38	2.30	2.10	2.53	3.4
	0300	0.381	20.0	8.143	2.24	2.16	1.97	2.31	3.1
	0700	0.376	22.2	8.158	2.35	2.30	2.10	2.53	2.1
	1200	0.363	25.2	8.187	2.42	2.47	2.24	2.87	-2.1
	1500	0.263	29.6	8.283	2.12	2.51	2.22	3.46	-18.4
	1700	0.250	30.0	8.309	2.50	2.44	2.15	3.53	2.4
	2200	0.298	30.0	8.237	2.30	2.76	2.47	3.50	-20.0

* Estimated from graphs.

† Calculated from $p\text{CO}_2$.

method presented appears to be superior for direct determination of the saturation ratio with respect to a given carbonate. The major advantage of this method might be the direct implementation of the saturation experiment *in situ*, using a high pressure glass electrode (Ben-Yaakov and Kaplan 1968). Such an experiment should give high accuracy in the determination of the degree of saturation of the ocean with respect to a given CaCO_3 . In addition, one should also be able to obtain fair estimations of the concentrations of the carbonate species. Clearly, for high pressure calculations, one should take into account the pressure coefficients of the apparent solubility products and apparent dissociation constants (Pytkowicz, Disteché, and Disteché 1967; Pytkowicz and Fowler 1967; Culberson and Pytkowicz 1968).

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