of a chemical species to a different chemical state is measured. The amount converted, in moles, is related to the quantity of electricity by Faraday's constant (96 489 ± 2 coulombs mol^{-1}). The coulometric titration of CO_2 involves the electrolytic generation of a strong base to titrate the weak acid formed by the reaction of CO_2 and ethanolamine. Thus, CO_2 extracted from seawater is quantitatively converted to hydroxyethylcarbamic acid and titrated with OH^- ions electrogenerated by the reduction of H_2O at a platinum cathode. The equivalence point is detected photometrically with thymolphthalein as indicator, and the complete sequence includes neutralization, redox, and complexation reactions.

Neutralization

$$2CO_2 + 2NH_2(CH_2)_2OH \rightarrow 2HO(CH_2)_2NHCOOH$$

$$2HO(CH_2)_2NHCOOH + OH^- \rightarrow 2HOH + 2HO(CH_2)_2NHCOO^-$$

Oxidation—reduction

$$2Ag^0(s) \rightarrow 2Ag^+ + 2e^- \qquad \text{(anode)}$$

$$2HOH + 2e^- \rightarrow H_2 + 2OH^- \qquad \text{(cathode)}$$

Complexation

$$2Ag^+ + 4I^-(\text{saturated KI}) \rightarrow 2AgI_2^- \qquad \text{(anode)}$$

Net reaction

$$Ag^0(s) + 2I^- + CO_2 + NH_2(CH_2)_2OH \rightarrow AgI_2^- + 1/2H_2 + HO(CH_2)_2NHCOO^-$$

To be quantitative, the reduction of H_2O must occur without the involvement of other chemical species and each faraday of electricity must bring about a chemical change corresponding to one equivalent of the analyte. If true, 100% current efficiency is maintained even though the neutralization reaction is secondary to the electrode reaction, i.e., CO_2 does not directly participate in the electron transfer process at the electrode. Descriptively, the cell solution is blue at the equivalence point due to thymolphthalein (blue at pH 10.5 and colorless at pH 9.3 in aqueous solutions). CO_2 drives down the pH and raises the transmittance (%T) which initiates the above sequence by passing current at a low (1—5 mA) or high (50—100 mA) level depending upon the magnitude of %T. The increasing pH indicated by the decreasing %T, as acid is titrated, causes the titration current to pass from high to low to zero as the equivalence point is approached and sensed by the optical detector. During titration, the coulometer passes a current through a very precise and stable calibration

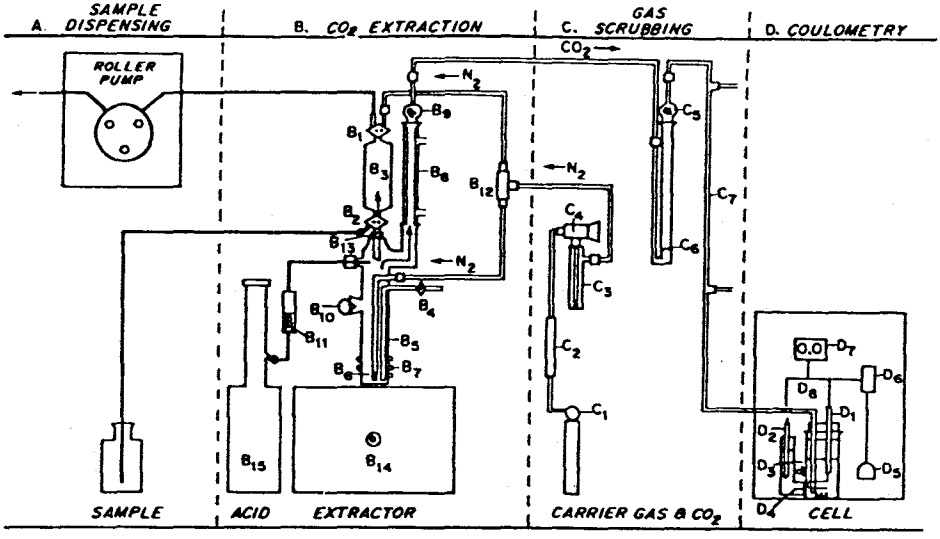

Fig. 1. Schematic diagram for the coulometric determination of TCO_2 showing sample dispensing (A), extraction (B), gas scrubbing (C), and detection (D) systems based on the Coulometrics Inc. Model 5030 scrubber and 5010 coulometer. Process lines transporting liquids are filled in and appear on the left while those conducting gases on the right are open lines. Key to diagram is as follows

(B) CO_2 extraction	
B_1, B_2	three-way stopcocks
B_3	sample pipet of known volume
B_4	one-way stopcock
B_5	extractor–stripper
B_6	glass frit
B_7	heater coil
B_8	condenser
B_9	glass adapter
B_{10}	T14/20 standardization port
B_{11}	check value
B_{12}	union tee connector
B_{13}	thermometer adapter
B_{14}	carbonate carbon apparatus with heater control
B_{15}	repipet
(C) Gas scrubbers	
C_1	N_2 regulator (8 psi)
C_2	ascarite trap
C_3	KOH trap
C_4	flow controller
C_5	glass adapter
C_6	gas scrubber
C_7	gas drier
(D) Coulometry	
D_1	platinum electrode
D_2	silver electrode
D_3	light source (lamp)
D_4	glass frit
D_5	photodetector
D_6	DC current source
D_7	digital readout
D_8	electrical circuit

teflon shell. After the analysis, 5–9 min per replicate, the drain stopcock (B_4) is opened to exhaust the spent sample. Within broad limits, the carrier gas flow rate is not critical. Rates of 100–200 ml min^{-1} were used, with the bulk of the analyses being at a rate of 150 ml min^{-1}.

The coulometer cell is filled with 100 ml of Coulometrics cell solution (300-001) and the anode chamber to a level 6—13 mm below the main chamber with 14—15 ml of anode solution (300-002) and a few crystals of potassium iodide (300-003). The cell solution includes: dimethylsulfoxide (DMSO) as non-aqueous solvent, the electrolyte is tetraethylammonium bromide (TEAB), ethanolamine absorbs CO_2, thymolphthalein is the indicator, with a small amount of water providing the reducible species. The anode solution is essentially a saturated solution of potassium iodide. The exact composition of these solutions (Huffman, 1977) are proprietaries of Coulometrics Inc. The solutions are discarded daily and the cell and frit are cleaned with acetone, being careful not to expose the frit to acids and to wipe the cell dry before use. The cell solution is stirred with a teflon bar (25 mm) during the titration. When the cell is turned on, CO_2 absorbed in the cell solution is titrated to the equivalence point.

Fittings and connections

Process lines are 1/8 in. OD polyallomer tubing (22 pp, Imperial Eastman, Chicago, IL) and the appropriate nylon Swagelok (Crawford Fitting Company, Solon, OH) reducing unions (NY-400-6-200 or NY-500-6-4) or stainless-steel 1/4—1/4 in. Ultra-Torr adapters (SS-4-UT-A-4, Cajon Company, Solon, OH) were used for glass-to-tubing connections. The glass adapters (B_9, C_5, Fig. 1) (129-033, Coulometrics, Inc.) are loosely packed with glass wool, to condense water vapor, and secured with rubber bands at the lugs provided. The sample pipet is joined to the stripper joint (T14/20) with a teflon thermometer adapter (B_{13}) (size 22, K-179800, Kontes, Vineland, NJ) so it can be removed for remote sampling (Niskin bottle, etc.). A stainless-steel check valve (B_{11}, SS-2C, Nupro, Willoughby, OH) between the acid repipet and stripper prevents CO_2 losses from the stripper. Carrier gas flow rates are controlled by a Nupro very fine metering valve (SS-2SA) with vernier handle (NY-IS-S6) mounted at the inlet (C_4) of the KOH trap (C_3).

Determination of accuracy

Anhydrous $CaCO_3$ (Baker and Adamson, Morristown, NJ or National Bureau of Standards [SRM 915]; 99.9% pure) was dispensed into preweighed No. 4 gelatin capsules (07013, Electron Microscopy Sciences, Washington, PA) and weighed to the nearest 0.1 μg C on model 26 and 29 Cahn electrobalances (Cahn Instruments, Inc., Cerritos, CA). Capsules were introduced with forceps through a port (B_{10}) into hot ($\leqslant 75°C$) acidified CO_2-free water, dissolved (ca. 1 min), and analyzed. Carrier gas exiting the port excludes air, while the dissolution time allows reisolation of the sytem without loss of analyte (CO_2). Before weighing, the capsules were equilibrated within the balance weighing chamber with the lamp on to eliminate weighing

TABLE I

The accuracy of coulometric TCO_2 determinations of $CaCO_3$ using the system of Fig. 1 with stock and custom cells without and with the gas drier (C_7, Fig. 1), respectively. All titrations were run at a current of 100 mA, with the same source of $CaCO_3$, and at a carrier gas flow rate of 150 ml min^{-1}

Date (month/day/year)		$CaCO_3$ weights (μg C)		Error	
Weighed	Analyzed	True	Determined	Diff.	%
(A) Stock cell without gas drier					
11/24/82	12/1/82	670.8	672.8	+2.0	0.3
11/24/82	12/1/82	894.2	896.7	+2.5	0.28
11/24/82	12/1/82	306.9	307.0	+0.1	0.03
11/24/82	12/1/82	1162.8	1164.6	+1.8	0.15
12/3/82	12/8/82	418.7	418.4	−0.3	0.07
12/3/82	12/17/82	439.1	439.6	+0.5	0.11
12/3/82	12/15/82	591.5	591.4	−0.1	0.02
12/3/82	12/21/82	628.1	629.8	+1.7	0.27
12/3/82	12/7/82	899.8	901.2	+1.4	0.16
Means		667.9	669.0	+1.1	0.16
(B) Figure 1 cell with gas drier					
6/14/83	6/15/83	925.3	925.3	0.0	0.0
6/14/83	6/15/83	1595.5	1596.5	+0.9	0.06
6/14/83	6/16/83	1174.1	1175.1	+1.0	0.08
6/14/83	6/17/83	1118.4	1117.9	−0.5	0.04
6/14/83	6/20/83	1452.4	1450.1	−2.3	0.15
6/14/83	6/20/83	1415.2	1415.2	0.0	0.0
6/14/83	6/20/83	1467.1	1467.5	+0.4	0.03
6/14/83	6/21/83	1239.4	1238.9	−0.5	0.04
6/14/83	6/21/83	1233.4	1236.0	+2.6	0.21
6/14/83	6/21/83	1263.4	1264.4	+1.0	0.08
Means		1288.4	1288.7	+0.3	0.02

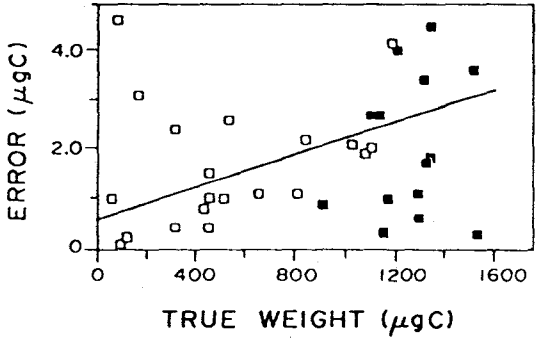

Fig. 2. Comparison of the accuracy of the stock cell at sea (□) with that of the custom cell shown in Fig. 1 in the laboratory (■) at a titration current of 100 mA. The data sets shown are designated CI-83-1 and GSO-2 in Table II.

TABLE II

Summary of the accuracy of the coulometric TCO_2 determination of carbonate carbon under varying analytical conditions during 1983

Source	Period (m/d)	n	Means			Analytical conditions					
			True wt. (μg C)	Error (μg C)	%	ΣCp (mg C)[a]	Solution age (h)[b]	Gas drier[c]	Cell[d]	Maximum current (mA)	$CaCO_3$ source
CI-83-1	3/2—10	18	536.6	+1.5	0.28	6.2	6.4	No	A	100	Reagent
GSO 1	6/15—21	10	1288.4	+0.3	0.02	7.9	4.9	Yes	B	100	Reagent
GSO 2	6/21—7/13	15	1254.4	+2.0	0.16	13.1	5.8	No	B	100	Reagent
GSO 3	7/13—20	5	1503.8	+1.7	0.11	12.3	6.8	No	B	50	NBS[e]
GSO 4	7/22—27	7	1053.2	+0.3	0.03	9.1	4.2	Yes	B	50	NBS
BBS 1	8/10—19	26	1143.6	+1.3	0.11	17.1	7.2	Yes	B	50	NBS
BBS 2	8/10—19	5	1318.7	+4.3	0.33	25.7	10.5	No	B	50	NBS
CH-20-83(1)	8/23—28	11	1231.5	+2.7	0.22	19.2	10.5	Yes	B	50	NBS
CH-20-83(2)	8/23—28	9	1136.0	+1.3	0.11	13.4	3.5	No	B	50	NBS

[a] The average amount of carbon (mg) titrated prior to determination of the standard.
[b] The average age of the cell solution in hours.
[c] Presence or absence of the perma-pure gas drier (C_7, Fig. 1) in the system.
[d] A refers to the original cell supplied by Coulometrics, Inc., while B designates the modified cell shown in Fig. 1.
[e] $CaCO_3$ obtained from the National Bureau of Standards.

TABLE III

Summary of the precision of the coulometric TCO_2 determination for the periods and analytical conditions shown in Table II. Precision(s) were calculated by averaging the sample variances (s^2) and taking the square root of the means (SW, seawater; DW, distilled water)

Source	Type	Sampling[a]	Samples analyzed	Replicates (n)	Means					s.e.
					μg C	s^2	s	%CV	μmol l^{-1}	
CI-83-1	SW	B_1	9	3—4	1202.6	1.35	1.16	0.10	2089.6	1.2—1.4
CI-83-1	SW	B_2	4	3	1200.0	0.81	0.90	0.08	2085.1	0.9
GSO 1	SW	B_2	1	2	1023.2	0.40	0.63	0.06	1944.1	0.8
GSO 2	SW	B_2	19	3	989.4	0.45	0.67	0.07	1876.6	0.8
GSO 3[b]	SW	B_2, B_3	3	3	1093.3	0.51	0.71	0.07	2073.6	0.8
GSO 4	SW	B_2	8	3	798.0	0.57	0.75	0.10	1513.5	0.9
BBS 1	SW	B_4	17	3	1057.3	0.28	0.53	0.05	2007.2	0.5
BBS 2	SW	B_3, B_4	6	3	1066.3	0.50	0.71	0.07	2024.3	0.8
CII-20-83 (1)	SW	B_4	9	3	1083.5	0.35	0.59	0.06	2056.9	0.6
CII-20-83 (2)	SW	B_4	8	3	1075.7	0.52	0.72	0.07	2042.1	0.8
GSO(10/29-12/17)[c]	DW	B_3, B_1	13	3	11.6	0.13	0.36	3.15	20.2	0.4

[a] B_1 = sampling from Niskin bottle or distilled water reservoir directly into the detached sample pipet; B_2 = samples collected in 1-l teflon bottles and pumped into the sample pipet; B_3 = samples collected in 500-ml stoppered glass bottles and pumped into the sample pipet; B_4 = samples pumped from separate 125-ml glass O_2 bottles, with one bottle used to rinse the sample pipet and subsequent bottles used for a single replicate.

[b] Includes two oceanic samples which were preserved with $HgCl_2$.

[c] Analyses in 1982.

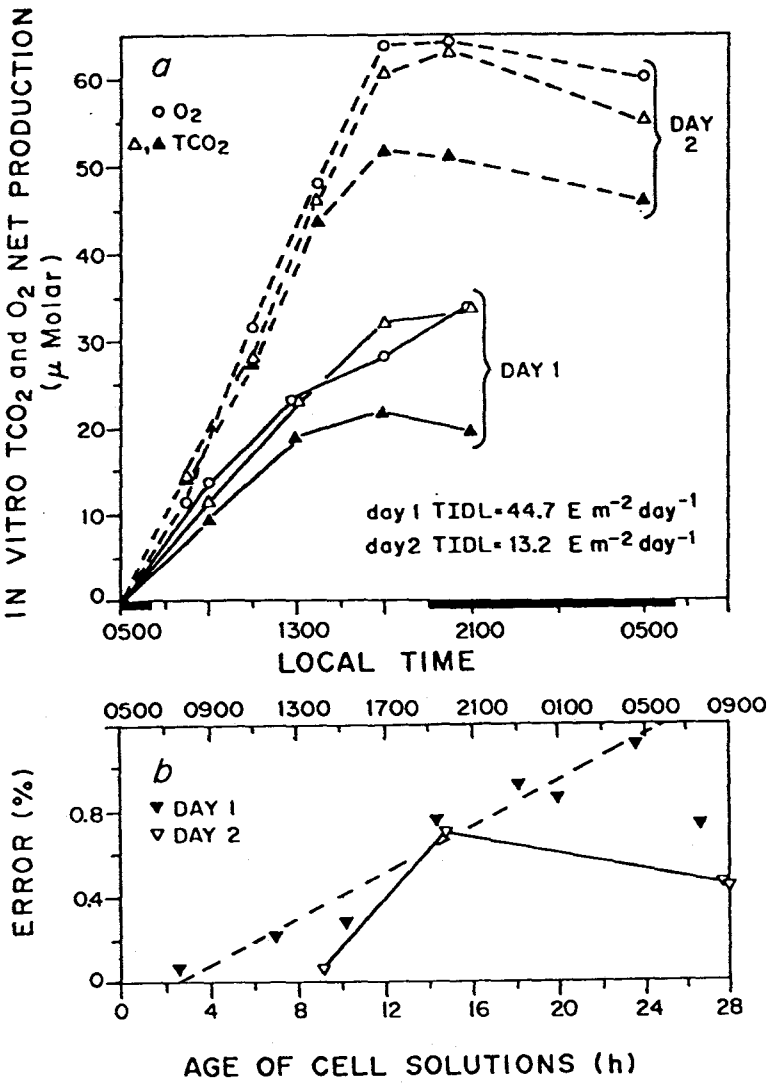

Fig. 5. The in vitro metabolism of seawater from two different MERL mesocosms in early April 1983. (a) Net production calculated from diel changes in O_2 (○) and coulometrically determined TCO_2 with (△) and without (▲) correction for error. Seawater was obtained from Tank 9 on day 1 (April 6) and Tank 5 on day 2 (April 8) and incubated under ambient light conditions in 125-ml O_2 bottles. Dark segments of the time axis denote dark periods, and total integrated daily light (TIDL) is given for the two days. (b) Positive errors (%) found from periodic analyses of accurately known weights of $CaCO_3$ during the experiments which were used to correct the TCO_2 results (▲, Fig. 5a).

TABLE V

An annotated summary of likely errors in the coulometric detection of TCO_2. Error descriptions are in italics, and combinations are possible

Error type	Descriptions and possible causes for errors in coulometric analysis of CO_2	Likely error
I	*Failure to quantitively extract CO_2 or scrub it without artifacts*: CO_2 leaks, CO_2 absorbing or desorbing from glassware, contamination from scrubber, etc.	Positive or negative
II	*Events, independent of CO_2 input, which cause the titration to begin or terminate erroneously*: by-products which absorb light, water droplets, gas bubbles, fading of indicator, electrical interferences, etc.	Positive or negative
III	*Current integrated incorrectly*: coulometer component or circuitry error due to failure, defect, or miscalibration	Positive or negative
IV	*Secondary reactions*: reaction by-products which react at the cathode and lower current efficiency	Positive

current is discussed by Lindberg (1978). Huffman (1977) also concluded that the photometric end point was the most sensitive and simplest for non-aqueous systems. To the advantages already mentioned can be added the formation of the AgI_2^- complex to prevent the migration of Ag^+ ions to the cathode and the solubility of the titration products in DMSO. Nevertheless, a positive systematic error developed with maturation of the cell solution (Figs. 4a and b).

Likely sources of error (designated types I—IV) have been summarized in Table V. Our data do not suggest type I errors such as leaks or losses of CO_2 (Tables I—III), but volatile organic acids in seawater or the oxidation of volatiles by H_2O_2 in the scrubber could interfere. Water vapor condensing and impinging on the cell acts as an acid by diluting the cell solution and raising $\%T$ so that base would be generated (positive error). Problems with the scrubber or interferences from the stripper should result in high blanks, and droplets should cause random rather than systematic errors. Although not observed, the gas drier appeared to improve both accuracy and precision (Tables I—III, and Fig. 4b) suggesting that there is some carry-over from the extractor—scrubber. So far, the only carry-over we have ruled out is Cl_2.

Type II errors cause the optical detector to misinterpret the titration bounds, but they are only significant near the equivalence point. Interference from gas bubbles is minimized by the positioning of the gas line in relation to the optics and by using moderate carrier gas flow rates so that $\%T$ remains stable in the absence of CO_2 additions to the cell. The coulometer

explanation for a type IV error. Eckfeldt and Schaffer (1965), however, found that the amount of silver recovered from the platinum electrode after titrations of acid with electrogenerated base could not account for their positive error. Likewise, silver recovered from the Coulometrics platinum electrode after extended use was also insignificant (E.W.D. Huffman, Jr., personal communication, 1983). We have found that the neutral anode solution becomes strongly alkaline after cell activation. White (1963, 1966) also refers to the slow evolution of alkali from the silver anode, but did not investigate further. It is not known whether the pH rise is associated with ethanolamine diffusing from the main chamber, the anodic oxidation of silver to the sparingly soluble and very alkaline argentous oxide (Ag_2O) (Amlie and Rüetschi, 1961), or other sources, but alkali may signal interfering side reactions. For example, CO_2 dissolved in the anode solution could, with the evolution of alkali, be converted to CO_3^{2-}. Carbonate ions, drawn to the anode during titrations, could diffuse through the frit during quiet periods and be converted back to CO_2 and titrated (error) upon the pH drop associated with the large influx of sample CO_2. Besides additional isolation of the cathode and anode, the literature recommends titration currents <100 mA, low current density, and an EMF below 90 V DC for acid—base coulometric titrations (Lingane, 1954; Streuli et al., 1964; Cotman et al., 1965; Haber et al., 1965). Figure 3c shows that, although this work is consistent with these recommendations, a type IV error of unknown origin probably occurred.

The biological data (Table IV and Fig. 5) will be discussed more fully elsewhere, but the analytical correspondence between in vitro and in situ O_2 and TCO_2 variation shows that the method is applicable to diverse studies of marine metabolism. Table IV, showing differences between coulometric and pH-alkalinity measurement of TCO_2 as well as previous work (Johnson et al., 1981), suggests that microbial metabolism could cause total alkalinity to differ from carbonate alkalinity by more than the borate alkalinity (Brewer and Goldman, 1976). Park (1965) has pointed out that such differences would be manifested as a discrepancy between TCO_2 measured directly and the indirect pH-alkalinity method. The in situ diel O_2 and TCO_2 variation (Table IV) is not as closely coupled as the in vitro data shown in Fig. 5a, but the low PQ with balanced metabolism (no significant net change in either CO_2 or O_2 over 24 h) in MERL Tank 5 repeats earlier results for the same mesocosm (Johnson et al., 1981). For productive waters in exchange with the benthos, coulometry promises to be simpler, more accurate, and easier to interpret than the classical pH-alkalinity method. At sea, the coulometer could resolve fundamental disputes concerning the oceanic carbonate system (Takahashi et al., 1976).

For calibration, $CaCO_3$ was used because Na_2CO_3 absorbs moisture in which CO_2 dissolves, probably as $NaHCO_3$ (D. Chipman, personal communication, 1983), so the CO_2 content of Na_2CO_3 standards increases with time. The availability of $CaCO_3$ with certified purity from the National

exceed another US $5 000. This introductory report demonstrates coulometry's potential for marine CO_2 studies including carbon metabolism, water mass movements, analytical calibration, and anthropogenic effects.

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REFERENCES

Amlie, R.F. and Rüetschi, P., 1961. Solubility and stability of silver oxides in alkaline electrolytes. J. Electrochem. Soc., 108:813—819.

Blom, L. and Edelhausen, L., 1955. Direct titration of carbon dioxide. Anal. Chim. Acta, 13:120—128.

Boniface, H.J. and Jenkins, R.H., 1971. The determination of carbon in steel by coulometric titration in partially aqueous medium. Analyst (London), 96:37—46.

Braid, P., Hunter, J.A., Massie, W.H.S., Nicholson, J.D. and Pearce, B.E., 1966. An examination of some of the factors affecting the determination of carbon dioxide by non-aqueous titrimetry. Analyst (London), 91:439—444.

Brewer, P.G. and Goldman, J.C., 1976. Alkalinity changes generated by phytoplankton growth. Limnol. Oceanogr., 21:108—117.

Buckley, B.A., 1983. Daily production and respiration. In: C.E. Lambert and C.A. Oviatt (Editors), Manual of Biological and Geochemical Techniques in Coastal Waters. MERL Series No. 1, University of Rhode Island, Narragansett, RI, pp. 19—21.

Burney, C.M., Johnson, K.M. and Sieburth, J. McN., 1981. Diel flux of dissolved carbohydrate in a salt marsh and a simulated estuarine ecosystem. Mar. Biol., 63:175—187.

Cotman, C., Shreiner, W., Hickey, J. and Williams, T., 1965. The coulometric titration of weak acids in non-aqueous media. Talanta, 12:17—19.

Eckfeldt, E.L. and Shaffer, E.W., Jr., 1965. Precise acid standardization by coulometric titration using simplified equipment. Anal. Chem., 37:1534—1540.

Fritz, J.S. and Gainer, F.E., 1968. Coulometric titration of acids in non-aqueous solvents. Talanta, 15:939—948.

White, D.C., 1966. Coulometric titration of carbon dioxide on the micro scale. Talanta, 13:1303—1311.

Williams, P.J. leB. and Jenkinson, N.W., 1982. A transportable microprocessor-controlled precise Winkler titration suitable for field station and shipboard use. Limnol. Oceanogr., 27:576—584.

Williams, P.J. leB., Heinemann, K.R., Marra, J. and Purdie, D.A., 1983. Comparison of ^{14}C and O_2 measurements of phytoplankton production in oligotrophic waters. Nature (London), 305:49—50.

Wong, C.S., 1970. Quantitative analysis of total carbon dioxide in seawater: a new extraction method. Deep-Sea Res., 17:9—17.