Marine Chemistry, 44 (1993) 167–187
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Coulometric total carbon dioxide analysis for marine studies: maximizing the performance of an automated gas extraction system and coulometric detector

K.M. Johnson[a], K.D. Wills[a], D.B. Butler[b], W.K. Johnson[c], C.S. Wong[c]
[a]*Oceanographic and Atmospheric Sciences Division, Department of Applied Science, Brookhaven National Laboratory, Upton, NY 11973, USA*
[b]*Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882, USA*
[c]*Department of Fisheries and Oceans, Institute of Ocean Sciences, 9860 West Saanich Road, Sidney, B.C. V8L 4B2, Canada*

(Received January 15, 1993; revision accepted June 7, 1993)

Abstract

A global survey of the distribution of dissolved CO_2 taking advantage of sampling opportunities provided by the World Ocean Circulation Experiment: World Hydrographic Program (WOCE-WHP) is being carried out through 1995. Goals include the measurement of oceanic inorganic carbon transport and the development of a data base from which future fossil-fuel CO_2 build-up can be monitored. The analytical method selected for total carbon dioxide (C_T) is gas extraction of acidified seawater with coulometric titration of the acid formed by the resultant carbon dioxide and monoethanolamine. To combine high accuracy and precision (± 1.5 μmol/kg for $C_T \geq 2000$ μmol/kg) with a high rate of analysis, we have modified an automated single-parameter system. Following prototype development between 1987 and 1990, an instrument emerged with the acronym SOMMA standing for single-operator multiparameter metabolic analyzer. Improved functional and operating procedures have integrated electronic calibration, CO_2 gas calibration, and sample analysis with automated pressure, temperature, and conductivity (salinity) sensing into a single convenient transportable package.

1. Introduction

The dynamic head-space or gas extraction method (Ioffe and Vitenberg, 1982) with coulometric detection of the resultant CO_2 (Huffman, 1977; Johnson et al. 1985) is the ship-board method chosen for the global oceanic inorganic carbon survey to be made in conjunction with the World Ocean Circulation Experiment–World Hydrographic program (WOCE–WHP) and the Joint Global Ocean Flux Study (JGOES) programs (see US JGOFS News 1(4): 1–2, 1990; Dickson and Goyet, 1991). Although total carbon dioxide (C_T) is not an official WOCE parameter, a coordinated effort will be made on WOCE cruises through 1995 to measure the spatial and temporal changes in C_T to estimate the transport of inorganic carbon in a manner analogous to oceanic heat transport (Bryden and Hall, 1980; Roemmich and Wunsch, 1985; Brewer et al., 1989), and to provide a data base for the subsequent estimation of anthropogenic carbon dioxide increases in the oceans. The consensus analytical goal is 0.05% for accuracy and precision, or $\pm 1.0\,\mu$mol/kg for sea water with a C_T of $\geq 2000\,\mu$mol/kg. Additionally, automated instrumentation is required for the thousands of real time analyses needed for the data set. An automated analyzer called UG-I described by Johnson et al. (1987) which is still in use with minor modifications (Robinson and Williams, 1991) is adapted to meet these requirements. Following the construction of four evolving prototypes between 1987 and 1990 at the Equipment Development Laboratory (EDL) at the University of Rhode Island's Graduate School of Oceanography in Narragansett, RI (02882), five instruments were funded in 1990 by the US Department of Energy (DOE) for distribution to DOE investigators involved in the WOCE survey (Johnson and Wallace, 1992). Subsequently, five additional instruments were built independently of the DOE in 1991. The acronym SOMMA standing for single-operator multiparameter metabolic analyzer is used for these instruments. In this paper, functional changes and improved calibration techniques incorporated into the instruments and their ship-board performance are described.

2. Materials and methods

2.1 An improved automated dynamic head-space analyzer

Unless otherwise indicated the SOMMA suppliers and component parts are identical with the UG-I system. A schematic diagram and a description of operation is given in Fig. 1. Briefly, operations controlled by a computer (*PC*) cause a sample from a thermostatted bottle to fill a thermostatted pipette through pinch valves (*PV*) 2,3, and 4 until it overflows into a reservoir and immerses a pair of wire electrodes to signal the PC that the pipette is full. The PC reads the pipette temperature, and the causes the contents to be pneumatically discharged into the stripper through PV 4. Following acidification, the resultant CO_2 is dried and titrated coulometrically. After the titration, the spent sample is drained through PV 9, salinity is determined, and the C_T concentration in μmol/kg is calculated from sample density and the "to deliver" volume of the sample pipette. The glassware (stripper, condenser, adapter, sample bath and reservoir) are from Gerhardt Finkenbeiner Inc. (Waltham, MA 02154). The chasis is produced using a computer-assisted-design (CAD) program controlling a milling machine at Plastics Plus Inc. (Cumberland, RI 02864), and assembly is completed at the EDL. Carbon dioxide is detected on the Model 5011 coulometer manufactured by UIC Inc. (Joliet, IL 60434) using a side arm type cell (Johnson et al., 1985) and UIC reagents. The conductance cell is the SBE 4 from Sea-Bird Electronics, Inc. (Bellevue, WA 98005).

The SOMMA chasis design (Johnson and Wallace, 1992) renders most components visible and accessible, and integrates diverse functions (sample handling, calibration, control, thermostatting, and extraction) into a format which allows the operator to observe execution. The chassis is made of three clear 2× 2 foot × 1/2 inch thick polycarbonate plates arranged to form a quad (four sectors) with grooves cut into the floor of the base plate to hold the two cross partition plates. The plumbing is located at floor level in the four interconnecting sectors (I–IV) formed by the cross partitions. The four sectors encompass eight vertical mounting surfaces, and channels cut in the walls support and protect the coolant lines used for thermostatting. Sectors I, II and IV are faced with 3 inch high stainless steel panels covered with removable floors to form three 3 × 12 inch wells. The panel faces are drilled to receive the gas service regulation valves. The plumbing emerges from the floors to connect with the components (valves, glassware, etc.). The glassware is protected with a "face guard" of stainless steel rod which does not limit access to the glassware. Each sector is given a dedicated function. Proceeding clockwise from the left-front sector (I); sector I houses the sample bath; sector II, the gas calibration system; sector III, the computer interfaces and control relays; sector IV, the process glassware. The chassis sits on a wooden base, and a reinforced removable and reusable shipping crate fits over the top of the chassis. The instrument is shipped intact.

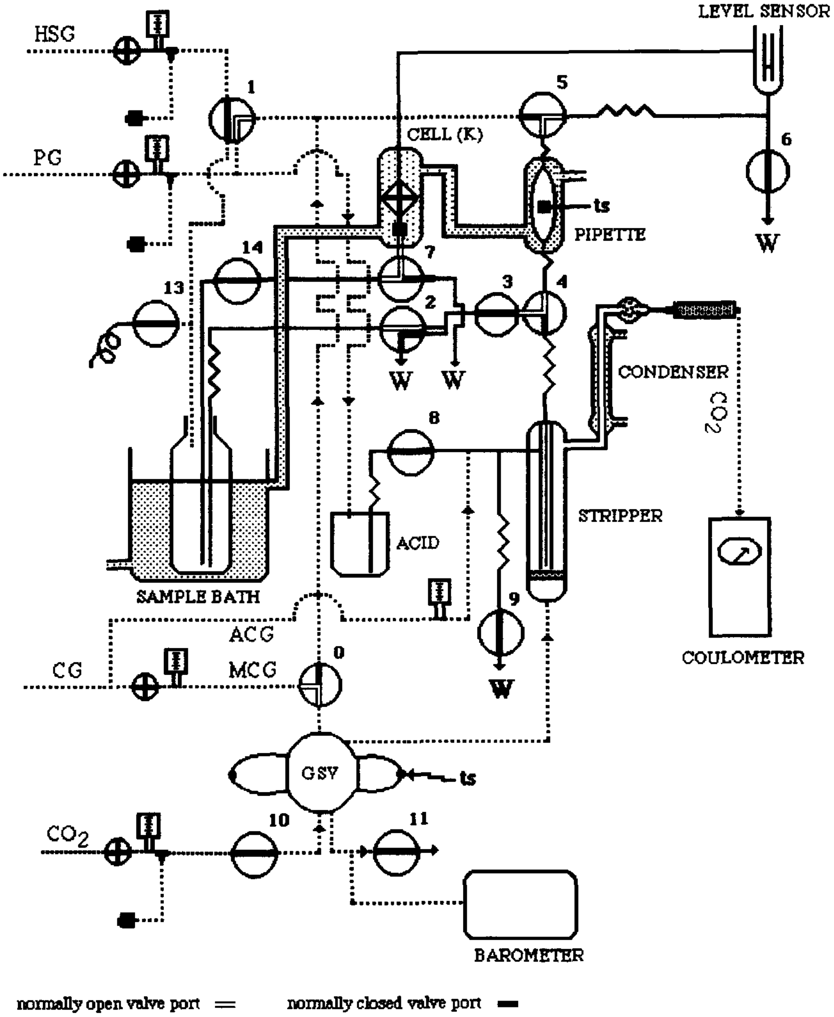

Fig. 1. A schematic diagram for the automated coulometric determination of C_T by continuous gas extraction and coulometric titration of the resultant CO_2 modified from system UG-I (Johnson et al., 1987) and now given the acronym Somma. Glassware changes since 1987 include a thermostatted pipette and a stripper which is supplied with two carrier gas streams – one entering at the top [Auxiliary (ACG)] to purge the stripper central inlet/outlet tube while the second [Main (MCG)] enters at the bottom to purge the main chamber. Gas lines are shown by dotted lines, while liquid lines are solid. Abbreviations: auxiliary carrier gas = *ACG*; carrier gas = *CG*; conductance cell = *K*; gas sample valve = *GSV*; head-space gas = *HSG*; main carrier gas = *MCG*; pneumatic gas = *PG*; temperature sensor = *ts*; waste = *W*.

2.2 Computer control and interfacing

The Somma works with IBM compatible computers having at least five expansion ports. Ports for two RS232 serial, an IEEE, a 24 line Digital Input/Output (*I/O*), an Analog to Digital (*A/D*), and a counter board are required for the coulometer (serial port 1), barometer (serial port 2), Digital Multimeter, solid state control relays, and sensors for temperature (T) and conductance (K), respectively. Solenoid valves are controlled by 5 VDC from the *I/O* board to 16 relays mounted on the module board in sector III. For the gas sample valve (GSV), the solid state relay activates a 115 VAC double-pole double-throw (DPDT) relay (PN 275-220, Radio Shack Corp.) wired to the electric actuator of the GSV (E68UWP, VICI Corp. Houston, TX

77255). Switching the DPDT relay switches the valve to either, "load" or "inject ".

The model AD500 *A/D* and the model DG24 Digital *I/O* boards are from Real Time Devices, Inc. (Box 906, State College, PA 16804). The module board (type PB-16, PN 21F856) and the solid state relays (type OAC5A, PN 21F872) are from Newark Electronics. The counter board (PCL-720) is from JDR Micro Devices, San Jose, CA. For safety, the module board is surrounded by a removable plastic shield. The *A/D* board supports 8 channels. Channels 1–6 are reserved for temperature sensors, while 7 and 8 support in-house "conductivity" type sensors (liquid level sensor, Fig. 1). The temperature sensors (model LM34CH, National Semiconductor, Santa Clara, CA 95051) with a voltage output of 10 mV/°F are calibrated against thermistors certified to 0.01°C (PN CSP60BT103M, Thermometrics, Edison, NJ 08817) with a certified mercury thermometer as a secondary standard. The voltages output between 0 and 35°C are regressed against temperature, and the calibration coefficients are entered into the SOMMA software. Temperature sensors monitor the pipette, the gas sample loops, and the coulometer cell. The level sensor (Fig. 1) is a pair of 1 mm diameter monel wires separated by 0.5 to 1.0 cm at the distal ends connected to the *A/D* board. The barometer is the model 216B-101 Digiquartz Transducer (Paroscientific, Inc. Redmond, WA 98052) calibrated for pressures between 11.5 and 16.0 psia. It is protected from over pressures ($\geq$ 19 psia) with an in-line pressure relief valve (PN 577T1-M-5) from Circle Seal Controls (Brunswick Corp., Anaheim, CA 92803), and powered from the PB-16 board (5 VDC). Minor modifications are made to the *A/D* and the relay module mounting (PB-16) boards. Details regarding the board modifications, sensors and appropriate software can be had by contacting K.W. At sea, the coulometer, volt meter, computer, and the SOMMA chassis are supplied with power through an uninterruptable power supply (UPS) with battery back-up.

2.3 Independent electronic calibration of the coulometer electronics

The coulometer measures the quantity of electrical charge passing through an electrolytic cell during a coulometric titration using charge to count (C–C) conversion circuitry consisting of a precision resistor and a voltage to frequency converter (VFC). The C–C circuitry generates electrical pulses (counts) at a rate directly proportional to the rate of charge passage. Charge (electrical current) passing through the titration cell and resistor generates a voltage across the resistor according to Ohm's law:

$$V = IR \tag{1}$$

where V is the voltage, I the current in amperes, R the resistance in ohms, and V is linearly proportional to I. In electronic calibration, the coulometric cell is replaced with an external precision four-lead resistor certified to 6 significant

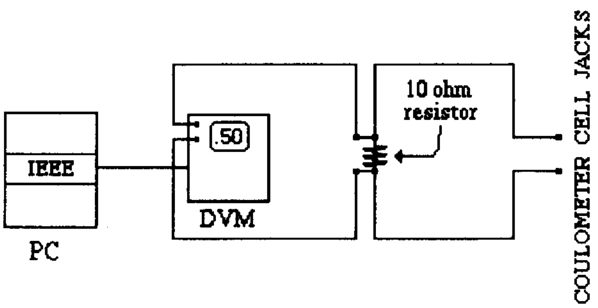

Fig. 2. A schematic showing the configuration for the components used to check the calibration of the coulometer's voltage to frequency converter. Abbreviations: digital volt meter = *DVM*; interface card = *IEEE*; computer = *PC*.

figures (PN VHP4, Vishay, Malvern, PA 19355) connected with the coulometer titration current (I) as in Fig. 2. After warming the coulometer [counts mode (0)] and DVM for at least 1 h, V across the external resistor is measured with a model 8840A DVM (John Fluke Mfg. Co., Inc., Everett, WA 98206) or equivalent at 50 mA (high) and 2 mA (low) titration currents for a fixed time (300 s). Voltage is read twice/s through an IEEE board (PN PC488A, BC Microsystem Inc., Sunnyvale, CA 94086). The instantaneous and integrated or average current (I_{avg}) is computed from Ohm's law until the final reading of the coulometer display at 300 s. The latter is the observed number of counts ($\sum$ Counts') at I_{avg}. This procedure is repeated for the low current (using the %T adjustment on the coulometer to lower the titration current). Alternatively, the low current selection switch inside the coulometer can be used to set the low current. The VFC is factory-calibrated to output 10,000 pulses (counts)/s at a titration current of 200 mA. From calibration and the relationships:

1 Ampere = 1 Coulomb of charge/s and
1 Faraday (F) = 96489 Coulomb/mol

then:

200 mA = 0.2 Ampere or 0.200 Coulomb/s
10,000 counts/s = 0.200 Coulomb/s
(10,000 counts = 0.200 Coulomb)

The theoretical number of counts ($\sum$ counts) for I_{avg} over 300 s is:

$$\sum \text{counts} = (I_{avg}/0.2)\ (10{,}000)\ (300) \qquad (2)$$

The slope and intercept calculated from the ratio of theoretical to observed counts at the two current levels are the electronic calibration coefficients.

2.4 Description of the CO_2 calibration hardware and operation

The gas (CO_2) calibration procedure for continuous gas extraction-coulometry is described by Goyet and Dickson (1991). Referring to Fig. 1, the SOMMA calibration hardware, located upstream of the stripper, consists of an 8 port Gas Sampling Valve (GSV) with two sample loops connected to a source of pure CO_2 through isolation valve (IV) 10. The vent side of the GSV is plumbed to a barometer and the latter is protected form over pressures by a pressure relief valve. The normally closed IV 11 retards air infiltration between calibrations, and isolates the barometer during the pressure reading. The carrier and calibration gas services merge in the GSV so that the calibration gas follows the same route to the coulometer as the CO_2 extracted from sea water. The mass (mol) of CO_2 contained in the loop is the loop volume (V) divided by the molar volume of CO_2 [$V(CO_2)$]. The latter is calculated iteratively from an equation of state using the instantaneous barometric pressure (P), loop temperature (T), and the first virial coefficient $B(T)$ for pure CO_2:

$$V(CO_2) = RT/P(1 + B(T)/V(CO_2)) \qquad (3)$$

The ratio of the calculated to determined masses is the gas calibration factor (CALFAC) used to correct the sample titrations for the small departure from 100% theoretical. The value of P is measured to ±0.1 mbar and T to ±0.05°C. Nominal loop volumes differ by at least 0.5 ml so that their carbon content encompasses the C_T range in sea water samples, and calibration factors determined from them should differ by $\leq 0.1\%$. The volume of the loops is determined gravimetrically with deionized water by the method of Wilke et al. (1993). The method includes the internal valve port volumes, and eliminates the effect of loop distortion during installation. Expansion due to temperature is calculated as in Johnson et al. (1987). The gas sampling valves used are factory-cleaned, -combusted, -installed, and -leak-checked. The internal spring tension of the retaining nut for the valve rotor is set at 80 instead of the standard 40 psi to prevent cross-talk between sample loops, and the polyimide (P) type rotor is used. The calculation above (Eq. 3) for mass of CO_2 at the measured temperature and pressure corrects a mistake in Johnson et al. (1987) where the mass was calculated for STP.

2.5 The analytical gases

The four SOMMA gas services, function and gas purities are summarized below:

Calibration gas	$CO_2 \geq 99.995\%$	System calibration
Headspace gas (HSG)	CO_2 in H_2 (330–1000 ppm)	Pneumatic loading of pipette
Pneumatic gas (PG)	N_2 (UHP, 99.999%)	Pneumatic addition to stripper
Carrier gas (CG)	N_2 (UHP, 99.999%)	Transport analyte (CO_2)

Regulators with steel diaphragms are used for all gases except the HSG. The PG and CG are normally from the same gas-cylinder connected to the common side of a union tee connector with one leg to the PG and the other to the CG service. Gases connect to the left side of the SOMMA chassis by means of 1/8 inch stainless Swagelok bulkhead fittings (SS-200-61, Crawford Fitting Co., Solon, OH 44139) and exit from the right side. Gas flow is regulated by takeoffs from quick-connect (QM2-B1-200, Crawford Fitting Co.) taps connected to a flow meter and the panel-mounted metering valves. The Gas Service nylon tubing is color-coded (green = CG; yellow = PG; blue = HSG), but the calibration gas survice tubing is acid-cleaned stainless steel (chromatographic grade). Gas flow rates in ml/min are; CG = 125; ACG = 50; HSG ≈ 200; PG ≈ 200; CO_2 = 150. The carrier and pneumatic gases are scrubbed with ascarite (A.H. Thomas Scientific, Swedesboro, NJ 08085), magnesium perchlorate ($MgClO_4$) (hereafter called dehydrite), and activated silica gel (ORBO-53, Supelco, Inc., Bellefonte, PA 16823) in that order. A particle filter (NUPRO SS-2F Series, Nupro Co., Willoughby, OH 44094) is installed downstream of the CG scrubber and the calibration gas cylinder to remove matter which could score the GSV surfaces.

2.6 Determination of the blank and low blanks

To determine the system blank (traces of CO_2 in the carrier gas, diffusion of CO_2 into the cell or contamination from the cell frit and stopper), the coulometer display is zeroed. When the display is positive again, it is rezeroed, and readings are taken every minute thereafter for 10 min. If the blank exceeds 250 counts in 10 min (≈ 0.005 μmol/min), it is redetermined. After use, the cell is cleaned by rinsing with deionized water or acetone, filling the side arm with solvent and passing it through the frit under gravity or vacuum. The cell is dried overnight at 50–55°C. The platinum cathode, stirrer, silver anode, teflon inlet line, cap vent, and cell cap are washed with distilled water and oven dried. The components connecting the stripper to the coulometer are kept in the drying oven when not in use. The seal between the cell cap (whether rubber or teflon) should be air tight, and the cell vent should not be extended above the surface of the cell cap so that liquids can not condense in vent tubing and drip back into the cell.

2.7 The determination and the checking of the "to deliver" volume of the SOMMA pipette

The "to deliver" volume (TDV) of the SOMMA pipette is determined gravimetrically with milli-Q deionized water degassed by sparging with helium for ≥ 30 min. Helium is also used for the headspace gas. The thermostatted sample pipette is filled from 300–500 ml bottles thermally equilibrated with the pipette, and then its contents are discharged into preweighed 50 ml serum bottles (PN 223745, Wheaton, Millville, NJ 08332) which are reweighed on a model R300S (Sartorius, Göttingen, Germany) or equivalent balance. The apparent weight (g) of water collected (W_{air}) is corrected to the mass in vacuo (M_{vac}) from:

$$M_{vac} = W_{air} + W_{air}(0.0012/d - 0.0012/80) \quad (4)$$

where 0.0012 is the sea level density of air at 1 atm, d is the density of the calibration fluid at the pipette temperature and sample salinity, and 8.0 is the density of the stainless steel weights. The "to deliver" volume of the pipette (TDV) is:

$$\mathrm{TDV} = M_{\mathrm{vac}}/d \tag{5}$$

Calibrations should be carried out at or very near the analytical temperature. In recent work the analytical temperature (bath and pipette) is 15.0 ± 1.0°C. At sea, the filled serum bottles are crimp-sealed with a high quality butyl rubber stopper (PN 2048-11800, Bellco Glass Inc., Vineland, NJ 08360), 20 mm aluminium seal (PN 2048-00150, Bellco Glass Inc.), crimper (PN 224303, Wheaton), stored, and reweighed on shore.

2.7 Software, program scaling (counts mode) and end point algorithm

The SOMMA software is written in GWBASIC Version 3.20 (Microsoft Corp., Redmond, WA 98052). It is driven from an options menu appearing on the PC monitor. There are integrated options (calibration procedures, blank determination, sample analysis, etc.) and subsets of the integrated options (filling and emptying the pipette, draining the stripper, adding acid, etc). At startup, readiness is determined by exercising the appropriate subset options from the menu, and the system file parameters (TDV, gas loop volumes, calibration temperatures, etc.) are checked or revised (input) from the menu.

Titrations are done with the coulometer in the counts mode. From the factory calibration (frequency = 10^5 counts/s at 200 mA), and the Faraday a scaling factor of 4.82445×10^3 counts/μmol is derived. The end point algorithm is set up so that the duration of any titration can not be < 9 nor > 20 min. During the titration the minute-to-minute increment is calculated (μmol/min), displayed and compared to the blank (μmol/min). If the increment is less than or equal to the blank, an end point event is recorded, and a titration is considered complete after four (4) end point events. If < 9 min, additional reading(s) will be made until 9 minutes elapse. After 20 min without an endpoint, the titration is terminated and the calculations are completed, but a warning message is printed before the program branches back to the menu. The algorithm gives the time of the titration (T_{T}), the time of significant current flow (T_I) where significant flow is defined as ≥ 2000 counts/min, and corrects the titration for the blank and electronic calibration (Slope and intercept) to give μmols titrated ($C_{\mu\mathrm{mol}}$):

$$C_{\mu\mathrm{mol}} = [\{\mathrm{Counts}/4824.45 - (\mathrm{Blank} \cdot T_{\mathrm{T}})\} - (\mathrm{Intercept} \cdot T_I)]/\mathrm{Slope} \tag{6}$$

2.8 Sampling, sources and calculations

Unless otherwise noted, samples are immediately poisoned with $HgCl_2$ according to Dickson and Goyet (1991). Aboard ship, 300 ml precombusted (450°C for 24 h) BOD bottles are filled from Niskin bottles. Before analysis, the samples are kept in darkness until thermally equilibrated to the pipette temperature. Samples in this work originate from the Canadian Survey Ship CSS *Parizeau* (cruise 90-01, coastal Pacific to the Alaska Gyre, May 1990), WOCE Leg A9 aboard the FS *Meteor* (cruise M15/3, Victoria, Brazil to Pointe Noire, Congo, February–March 1991), WOCE Legs P6E, P6M, and P6W aboard the R/V *Knorr* (Valparaiso, Chile to Sydney, Australia, May–July, 1992). Certified Reference Materials (CRM) supplied by Andrew Dickson of the Scripps Institution of Oceanography (see Dickson and Goyet, 1991) were also analyzed. The CRM are filtered sterile salt solutions or sea waters spiked with Na_2CO_3 analyzed for C_{T} by vacuum-extraction/Manometry in the laboratory of C.D. Keeling at Scripps.

The sample total carbon dioxide concentration (C_{T}) in μmol/kg is calculated from $C_{\mu\mathrm{mol}}$ (Eq. 6) and:

$$C_{\mathrm{t}} = C_{\mu\mathrm{mol}}(\mathrm{CALFAC})(1000/\mathrm{TD}V_{\mathrm{C}} \cdot p) \tag{7}$$

Table 1
The mean electronic calibration parameters (slope and intercept) determined for a Model 5011 Coulometer (SN CBC-9011-V) manufactured by UIC Corporation. The heaving n refers to the number of different days the coulometer was calibrated during the time period. At least two calibrations were made each day

Period	n	Slope (mean)	s.d.	r.s.d (%)	Intercept (mean) (μmol/min)
Jun 91[a]	7	0.99588	0.00010	0.011	−0.00262
Sep 91[b]	7	0.99548	0.00040	0.040	−0.00136
Nov 91	Factory recalibration				
Jan 92[a]	6	0.99946	0.00033	0.030	+0.00017
Apr–Jul 92[c]	8	0.99961	0.00010	0.010	+0.00036
Nov 92[a]	1	0.99970	0.00000	0.000	−0.00088
Jan 93[d]	12	0.99961	0.00006	0.006	−0.00055

[a] Calibrations at the Brookhaven National Laboratory.
[b] Calibrations on board the F/S *Meteor* (FRG) on Cruise M18.
[c] Calibrations on board the R/V *Knorr* (Woods Hole Oceanographic Institution) on Cruise P6.
[d] Calibrations on board the F/S *Meteor* on Cruise M22.

where CALFAC is the gas calibration factor, $\mathrm{TD}V_\mathrm{C}$ is the "to deliver" volume of the pipette in ml corrected for the thermal expansion of glass (Johnson et al., 1987; Dickson and Goyet, 1991), p is the density of sea water in kg/l from the equation of state (Millero and Poisson, 1981). For samples analyzed after the addition of $HgCl_2$, Eq. (7) is multiplied by 1.0002 or 1.0004 depending on the volume of the mercuric chloride solution added (Dickson and Goyet, 1991). Precision for a set of analyzed samples is expressed as the square root of the pooled variance (S_p^2) calculated according to Youden (1951):

$$S_\mathrm{p}^2 = \frac{\sum_{i=1}^{K}\left\{\sum_{j=1}^{n_i}(x_{ij}-\bar{x}_j)^2\left[\left(\sum_{j=1}^{n_i}(x_{ij}-\bar{x}_j)^2\Big/n_i\right)\right]\right\}}{\sum_{i=1}^{K} n_i - K} \tag{8}$$

where K is the number of samples in a set with more than one replicate and n_i is the total number of replicates for K samples.

3. Results

The SOMMA system differs from the UG-I system by having in a single chassis electronic calibration, completely automated gas calibration, a head-space gas service, independent gas service controls with built-in flow meter, a conductance cell, a redesigned stripper with two inlets for the carrier gas, a barometer, multiple temperature sensors, thermostatted pipette, and a built-in sample bath with the coolant lines integrated into the chassis walls. Commercially available components are used wherever possible to replace custom-made electronic components and glassware. It is somewhat faster than the UG-1 system because the rinsing and sample preparation steps have been speeded up by incorporating an extra solenoid (PV 2, Fig. 1) into the SOMMA, and because the data needed (temperature, pressure, salinity) for the C_T analysis is no longer input by the operator which also reduces operator error. However, the thru-put of both instruments is limited by the time required for the coulometric titration (normally, four samples per hour).

Table 1 gives electronic calibration data for a model 5011 coulometer (S/N CBC-9011-V) between its purchase in June of 1991 and January 1993. Originally this coulometer was poorly calibrated at the factory (slope = 0.995+), but after factory recalibration both the slope (0.999+) and intercept approached the theoretical values of 1.0 and 0.0, respectively. The voltage to frequency converter (VFC) response has

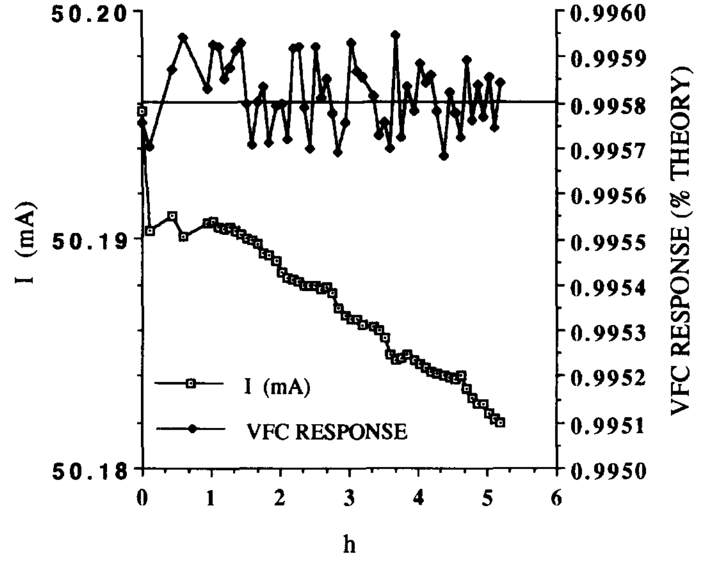

Fig. 3. The measured response (slope) of a Model 5011 Coulometer's voltage to frequency converter at a titration current (I) of approximately 50 mA over 6 h of continuous current flow. The titration current is computed from the voltage across a certified resistor of 10.0098 ohm and ohm's law. Each point is integrated over 300 s, and except for the first hour there are approximately 12 measurements/h. Abbreviations: *VFC* = voltage to frequency converter.

remained stable since recalibration despite shipping and service at sea. In Fig. 3, data from an experiment designed to test the effect of heating on the response of the VFC are given for the coulometer in Table 1 prior to its recalibration. In this case, the coulometer was caused to titrate continuously for 6 h at 50 mA with frequent calibrations. These data show a small drift in the titration current source, but no drift in the VFC response which varies around the mean slope (0.9958) for the entire period.

The rationale behind the head-space gas service is illustrated in Table 2. Data from the *Parizeau* cruise 90-01 are summarized by comparing same-bottle replicate differences ($n_2 - n_1$) against depth. The head-space gas is 400 ppm CO_2 in N_2. Some arbitrary definitions are used to group the data (e.g. 1–100 m represents the euphotic zone), but Table 2 shows that the 2nd replicate gives progressively lower results with increasing depth, and at depths > 300 m an almost complete predominance of negative differences with increasing imprecision. Apparent precision boundary lines materialized at 300

Table 2

A summary of the distribution by sample depth of the sign difference and magnitude of the difference between replicates one (n_1) and two (n_2), and the frequency of differences with an imprecision of $\geq$ 0.05% from automated coulometric determinations of C_T during Cruise 90-01 aboard the CSS *Parizeau*. A plus (+) difference indicates $n_2 > n_1$, a negative (−) difference indicates the reverse, and an equal sign (=) indicates no change

Depth class (m)	No. K	Diff. ($n_2 - n_1$)			Mean diff. (μmol/kg)	% negative	Imprecision$\geq$ 0.05% no.	%
		+	−	=				
0–100	47	17	26	4	−0.4	55.3	10	21.3
125–300	39	11	28	0	−0.9	71.8	8	20.5
400–2000	48	4	45	0	−2.0	93.8	26	54.2
2500–4000	20	4	16	0	−1.0	80.0	2	10.0
Totals	154	35	115	4	−1.1	74.7	46	29.9

Table 3
The effect of analytical temperature on the repeatability of automated coulometric determinations of C_T from duplicate samples (1210 m, 50 : 00.0 N, 145 : 00.0 W) analyzed at different pipette temperatures on 21 May 1990 aboard the CSS *Parizeau*. The in-situ water temperature of the samples is 2.49°C and the salinity is 34.483. Two replicates (n_1 and n_2) are analyzed per bottle, and the difference in μmol/kg is $n_2 - n_1$. The calibrated pipette volume at 25°C was 29.5955 ml

I.D. no.	Pipette T °C	(C_T) n_1	(C_T) n_2	$n_2 - n_1$	Mean (μmol/kg)	n	Mean (temp) (μmol/kg)	Diff.[a]
5	8.2	2380.2	2379.0	−1.2	2379.6	4	2379.2 (8.2)	0.0
8	8.2	2380.8	2377.0	−3.8	2378.9	—	—	—
16	10.0	2378.6	2377.3	−1.3	2378.0	2	2378.0 (10.0)	−1.2
4	15.0	2380.4	2378.9	−1.5	2379.6	2	2379.6 (15.0)	+ 0.4
10	20.0	2380.6	2377.7	−2.9	2379.2	2	2379.2 (20.0)	0.0
13	25.0	2380.8	2372.8	−8.0	2376.8	4	2378.0 (25.0)	−1.2
12	25.0	2382.1	2376.2	−5.9	2379.2	—	—	—
mean		2380.5	2377.0	−3.5	2378.8	14	2378.7	−0.5
± s.d.		1.0	2.1				2.4	
r.s.d. (%)		0.043	0.088				0.102	

[a] Difference between the mean (2379.2 μmol/kg) at 8.2°C and the mean at higher temperatures.

and 2000 m (better precision above and below). In depths between 400 and 2000 m, 93.8% of the samples show a negative difference and 54.2% exhibit an imprecision of ≥ 0.05%. These data suggest that CO_2 is probably lost to the sample bottle head-space during the 10–15 min required to titrate the first replicate due to differences between the in-situ conditions and the sample bottle head-space (partial pressure of CO_2 and temperature).

Table 3 gives some additional insight into precision. It shows the results of an experiment during Cruise 01–90 where replicate samples collected from a single depth (1210 m) with an in-situ temperature of 2.49°C are analyzed at pipette temperatures ranging from 8.2–25.0°C (2 replicates per bottle). The head-space gas remains 400 ppm CO_2 in N_2. The second replicate is characterized by a loss of CO_2 at all temperatures consistent with the results given in Table 2 except at 25°C where the decrease for the 2nd replicate is 3 to 4 fold greater than the average decrease (−2.0 μmol/kg) for depths between 300 and 2000 m given in Table 2. The agreement between the first replicates (precision, ±1.0 μmol/kg) over the wide temperature range meets the targeted goal, but the imprecision (±2.1 μmol/kg) for the 2nd replicates shows that they are affected by the disparity between in-situ and analytical conditions.

The results from Tables 2 and 3 led us to modify our strategy for the WOCE A9 leg in 1991. In this case, compressed air is the head-space gas for samples from ≤ 300 m, while 750 ppm CO_2 in N_2 is used for depths > 300 m. These data combined with the fact that very few certified reference material (CRM) were available ($n = 12$) for analysis on the A9 Cruise, caused us to fill up to 6 sample bottles from the deepest Niskin bottle at 18 stations as supplementary reference material (SRM). The SRM are poisoned, analyzed within 72 h, and evaluated for precision (hereafter called inter-bottle precision). The inter-bottle results are shown in Table 4 along with selected water mass criteria. The inter-bottle data (Table 4) are analyzed on different days with different cells and gas calibration factors so they afford a test of system repeatability (repeatability in this case means the agreement between independent analyses of samples from a single source in the same laboratory with the same method and instrument). Table 4 shows that under these conditions precision is generally ≤ 1.0 μmol/kg. For clarity, the individual C_T determinations and the means for samples having similar C_T concentrations are

Table 4
The inter-bottle precision of automated coulometric determinations of C_T and water mass parameters for the Supplementary Reference Materials (SRM) from 18 stations during Cruise M15 analyzed with a head-space gas of 750 ppm CO_2 in N_2 at a pipette temperature of 16.0°C and a calibrated "to deliver" volume of 28.7102 ml

Station	Press. DB	*T* CTD	*T* potential	*S*	Sigma[a]	Time[b] (h)	*n*[c]	C_T (mean) (μmol/kg)	s.d.	Cells[d] no.
165	3743	2.175	2.204	34.855	45.869	20.0	4	2199.15	0.64	1
178	3098	2.531	2.632	34.881	45.811	24.6	5	2192.29	0.90	2
181	3156	2.615	2.711	34.886	45.800	49.0	5	2189.86	0.67	3
187	4202	2.396	2.372	34.882	45.859	39.4	5	2210.29	0.36	2
190	4342	2.387	2.346	34.859	45.846	39.0	5	2208.66	0.68	3
193	4929	2.452	2.337	34.884	45.867	40.0	5	2210.70	0.79	3
196	5360	2.505	2.332	34.883	45.867	40.4	5	2211.36	1.06	3
199	5125	2.475	2.334	34.883	45.867	44.8	5	2211.18	1.16	3
202	4566	2.413	2.344	34.882	45.864	43.8	5	2211.12	0.62	3
206	5546	2.493	2.295	34.880	45.871	38.2	5	2211.21	0.38	3
212	5305	2.467	2.302	34.881	45.871	62.0	5	2216.75	0.46	4
214	5429	2.483	2.301	34.881	45.871	71.1	5	2216.02	0.86	4
217	2392	2.791	2.967	34.884	45.751	46.5	5	2192.33	1.20	3
221	3178	2.420	2.512	34.886	45.837	47.4	5	2207.05	0.60	3
225	2494	2.858	3.024	34.904	45.756	21.9	5	2191.28	0.37	2
226	5163	2.462	2.316	34.883	45.870	46.6	6	2224.37	1.13	3
229	4419	2.372	2.322	34.883	45.869	37.6	5	2227.71	1.46	2
232	3023	2.578	2.688	34.902	45.817	45.7	5	2211.67	1.25	4

[a] Density of sample when adiabatically brought to 4000 m (Sigma4).

[b] Time in hours required to analyze all of the sample replicate bottles.

[c] Number of bottles analyzed.

[d] Number of cells required to make the coulometric titrations of the sample replicates.

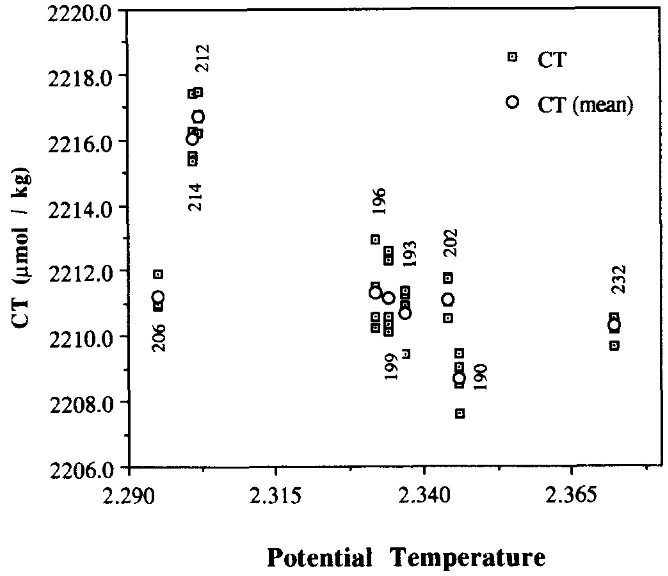

Fig. 4. The mean and replicate results of automated coulometric determinations of C_T for samples collected during Cruise M-15 with similar C_T concentrations plotted against potential temperature at 4000 m (see Table 4). ○ = sample means; ⊡ = replicate results.

Table 5
A summary of the precision of automated coulometric determinations of C_T made at sea between 1990 and 1992

Cruise	Depth(s) (m)	Type	K	n	mean C_T (μmol/kg)	Precision[d]	r.s.d. (%)
01–90[a]	0–100	Intra-bottle	47	2	2027.4	0.90	0.044
01–90	125–300	Intra-bottle	39	2	2202.6	1.10	0.049
01–90	400–2000	Intra-bottle	51	2	2353.9	2.00	0.084
01–90	> 2000	Intra-bottle	20	2	2348.4	1.10	0.046
01–90	All depths	Intra-bottle	154	2	2233.1	1.30	0.058
M15[b]	All depths	Intra-bottle	84	2	2153.5	0.71	0.033
M15	>2000	Inter-bottle	18	5	2208.2	0.83	0.038
P6[c]	All depths	Inter-bottle	147	2	2150.0	0.66	0.031

[a] Samples from May–June 90 aboard the CSS *Pariseau*.
[b] Samples from February–March 1991 aboard the FS *Meteor*.
[c] Samples from May–July 1992 aboard the RV *Knorr*.
[d] Precision = $\sum [n_1 - n_2]/K$ (Eq. 9) except for the M15 samples > 2000 m where S_p^2 is given.

plotted against potential temperature in Fig. 4. Fig. 4 and Table 4 (salinity, density, and potential temperature) indicates that samples 193, 196, and 199 probably originate from the same water mass. Samples 212 and 214 originate from a water mass which differs from the one above, while samples 232, 190, 202, and 206 can not be placed in either mass. If so, the mean and standard deviation for the three sample group (193, 196, and 199, $n = 15$) analyzed with 9 individual cells and gas calibration factors is 2211.10 ± 0.97 (0.044%), while for the second group (212, 213, $n = 10$) the corresponding results are 2216.34 ± 0.75 (0.034%).

For comparison, replicate analyses from the same bottle (intra-bottle precision) from 84 samples were made on the A9 leg in 1991. These data are shown in Table 5. For the 84 intra-bottle samples, the intra-bottle precision (s) is the mean absolute value of the difference between replicates 1 and 2:

$$s = \sum |(n_1 - n_2)|/k \qquad (9)$$

where $k = 84$. It is 0.71 μmol/kg. However, the mean difference ($n_2 - n_1$) is -0.46 μmol/kg. Although this difference is within 1.0 μmol/kg goal, it does indicate that the tendency towards lower second replicates observed during 1990 (Table 2) is reduced but not completely eliminated by adjusting the head-space gas concentrations.

The data associated with Table 4 reveal other aspects of SOMMA performance. Fig. 5 is a plot of the sample precisions (s.d., Table 4) vs. the cell-specific gas calibration factors used to correct the replicate titrations (Eq. 7). One cell (used to analyze replicates from samples 181 and 190 on 4 March) has a significantly different gas calibration factor (> 1.009) compared to the others, but Fig. 5 shows that the magnitude or the variance of the gas calibration factors associated with the replicate analyses are not correlated with their precision. This strongly suggests that gas calibration is an accurate and unbiased method. Another result which falls out of these data is shown in Fig. 6 where the individual replicate C_T determinations for each sample are plotted against the time elapsed between the first replicate and subsequent replicates. Fig. 6 shows that the inter-bottle samples remain stable during short term storage. This indicates that $HgCl_2$ addition has no adverse effect on analytical precision, and that the inter-bottle (multiple bottle replicates) precision is not significantly different from the intra-bottle precisions (multiple replicates one bottle) given in Tables 2 and 5. The mean difference between the last and first replicates for the 18 SRM is +0.78 μmol/kg indicating that if there is a trend during short term storage it is toward CO_2 production. For the SRM ($K = 18, n = 91$) the pooled standard deviation (S_p^2) is ± 0.83 μmol/kg. Because the

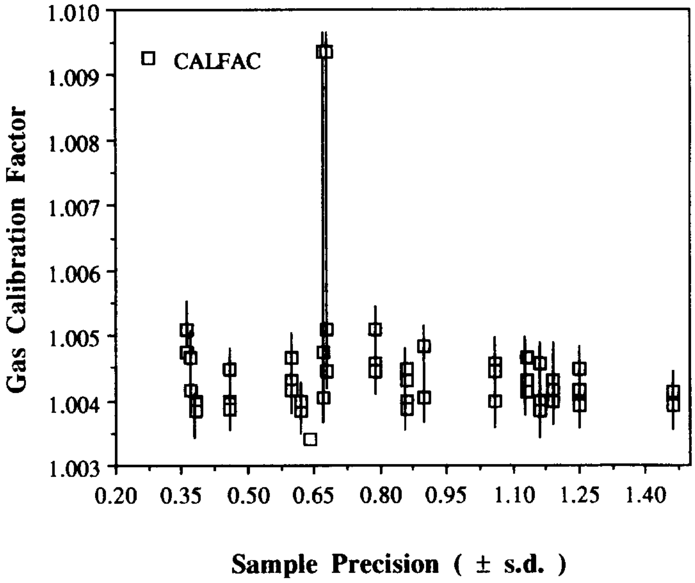

Fig. 5. The sample inter-bottle precisions (s.d.) given in Table 4 plotted against the individual gas calibration factors used to correct the replicate analyses (Eq. 7). For precision $n = 5$, and most replicate sets encompass three individual gas calibration factors. The solid lines connect the sample-specific gas calibration factors.

SRM analyses overlap the Somma-Coulometer system is actually stable longer than the time required to complete the replicates of a single sample. For example, the sum of the last-first differences between 1 March (sample 178) and 15 March (sample 214) is +2.07 μmol/kg ($n = 12$, mean = 0.17 μmol/kg) with positive and negative differences cancelling out. Combined with the few CRM analyses given below for the period, the SRM data show that it

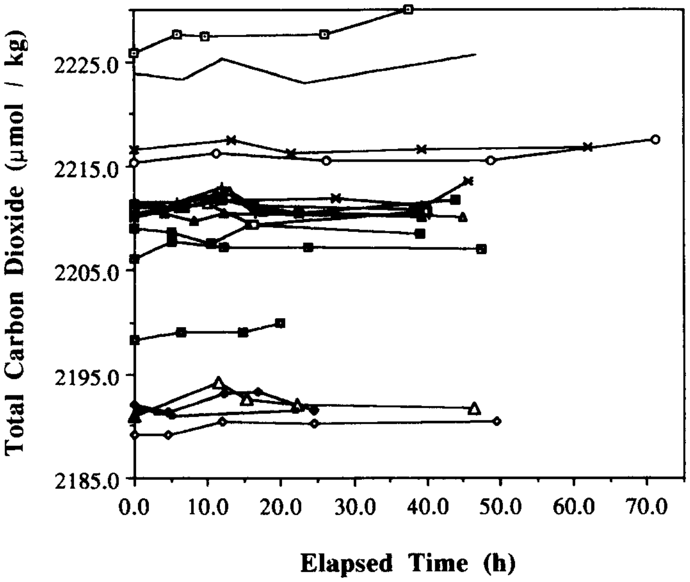

Fig. 6. The replicate automated coulometric determinations of C_T for the samples given in Table 4 plotted against the time elapsed (h) between the analysis of the first and the subsequent replicates.

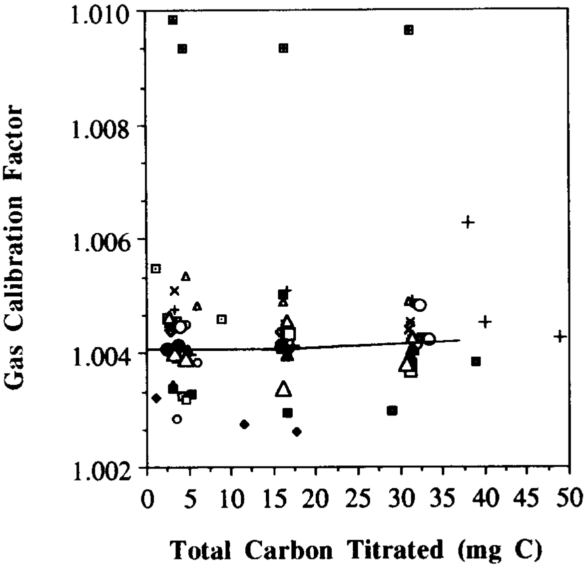

Fig. 7. The gas calibration factors ($n = 99$) determined for the automated SOMMA-Coulometer system during Cruise M-15 plotted against the amount of carbon titrated prior to gas calibration. The solid line connects the mean gas calibration factors at approximately 5, 15, and 30 mg C titrated.

is possible to deploy a repeatable analytical system.

Fig. 7 is a plot of the M15 gas calibration factors against the age of the cell where cell age is the total amount (mg C) of carbon titrated (TCT) since the initiation of current flow and the time of the gas calibration. During the M15 Cruise, the software caused automatic recalibration at TCT = 15 and 30 mg C. This accounts for the clumping of data points, and the straight line connects the mean gas calibration factor at these points. Fig. 7 indicates that there is daily variation in the gas calibration factors, but there is no evidence for a systematic drift in the cell response through 30 mg C. The mean gas calibration factor for Cruise M15 ($n = 99$) is 1.00444 or 99.557% of theoretical.

The equality between inter- and intra-bottle precision and the residual tendency to lower second replicates during the M15 Cruise led us to again alter our analytical strategy in 1992 for the three month P6 Cruise in the Pacific along the 30°C parallel. A head-space gas of compressed air is used for all samples, but precision is calculated from duplicate ($n = 2$) samples taken from the same Niskin bottle — normally double samples from the surface, middle, and bottom Niskin bottles. The double samples are assigned the letter, A, B, or C on a rotating basis so that during the analysis of the corresponding station profile the first water sample analyzed is one of the two letter A replicates. After analyzing 8–10 additional water samples (depending on the number of water samples in a profile), the second letter A replicate is analyzed, and following this a letter B replicate. After 8–10 additional water samples, the second letter B replicate followed by a letter C replicate, and when all of the remaining water samples are analyzed the final letter C replicate is analyzed. The precision calculated from Eq. (9) is 0.66 μmol/kg (Table 5).

With respect to accuracy, only 12 CRM were available to analyze over the 42 days of the M15 Cruise in 1991 (1 every 3 or 4 days). The mean C_T determined for the CRM during M15 is 1978.3 μmol/kg compared to the certified value of 1978.8 μmol/kg. Table 6, gives a larger data set encompassing 29 pipette "to deliver" volume determinations and 148 CRM analyses for the three legs of the P6 Cruise. Only two volume determinations survive from leg I, however, the 27 determinations from legs II and III show that the "to deliver" pipette volume declined by 0.045%. This is consistent with the small decline (0.07%) between legs I and III for the mean CRM concentrations determined for both high (2188.77 μmol/kg, batch 11) and low (1960.67 μmol/kg, batch 7) certified C_T concentrations. Sample salinity is the subject of Fig. 8 which is a plot of SOMMA salinity plotted against Salinometer salinity on the R/V *Knorr* during the P6 Cruise for samples between approximately 10 m and 4000 m. The regression equation for these data ($n = 36$) is $y = 0.9985(x) + 0.043$, $r = 0.997$.

4. Discussion

The SOMMA-Coulometer system evolved from

Table 6

(A) Comparison of the gravimetrically determined "to deliver" analytical pipette volume during Cruise P6 with the precruise calibrated "to deliver" volume

(B) Results of the automated coulometric determinations of C_T for Certified Reference Materials (CRM) using the precruise calibrated "to deliver" volume for the calculation of the C_T concentration (Eq. 7). For the CRM analyses, *n* is the number of individual bottles analyzed (single replicate per bottle)

Leg	Pipette *T* (°C)	*n*	r.s.d. (%)	Mean Volume (ml)		Diff.	Δ %
				determined	calibrated[a]		
(A) Gravimetric determination of the "to deliver" Somma pipette volume							
I	15.83	2	0.000	29.6813	29.6823	−0.001	−0.003
II	14.86	19	0.020	29.6770	29.6818	−0.004	−0.016
II	14.87	8	0.009	29.6685	29.6818	−0.013	−0.045
(B) Analyses of Certified Reference Materials							
				Mean (μmol/kg)			
				determined	certified		
I	15.83	20	0.061	1960.30	1960.67	−0.37	−0.018
I	15.83	24	0.030	2189.77	2188.77	+1.00	+0.045
II	14.86	35	0.040	1959.94	1960.67	−0.72	−0.037
II	14.86	31	0.041	2188.63	2188.77	−0.13	−0.006
III	14.87	15	0.044	1959.21	1960.67	−1.46	−0.074
III	14.87	23	0.046	2187.17	2188.77	−1.60	−0.073

[a] The precruise calibrated volume of the pipette at 19.95°C is 28.6833 ± 0.003 ml ($n = 8$). The calibrated volume shown in Part A above is the calibrated volume corrected to the pipette temperature as described in the Methods Section.

a desire by biologists and microbiologists to develop non-isotopic methods for measuring community respiration and production (Bender et al., 1987). Originally, only one or two custom instruments were envisioned. The current interest in global warming emphasizes the absolute measurements of the spatial distribution of dissolved inorganic carbon, and the large number of analyses needed resulted in a program to adapt the UG-I system for multiple copies of an automated, compact, transportable, precise, and accurate instrument which can be used with a minimum of formal training.

Under the rubric of calibration, electronic calibration is added, and gas calibration is now fully automated and integrated into the Somma chassis. The original 6 port gas sample valve is changed to an 8 port valve with temperature sensors and digital barometer added (Fig. 1). Electronic calibration provides an independent means of checking the coulometer calibration. The data shown in Table 1 and Fig. 3 (apart from the fact that the instrument tested was originally misscalibrated at the factory) indicate that the calibrated resistor in the coulometer's charge to count circuitry is not affected by heating under protracted use, and that the charge to count circuitry is unlikely to be a source of error if it is correctly calibrated at the factory or by our method. A two point procedure is used because the majority of the coulometric titration is carried out at the high (50 mA) and low (2 mA) currents. The coulometer does ramp from 50 to 2 mA, but intermediate levels are variable and short-lived so that calibration is carried out at commonest levels at continuous current flow. The calibration can not be made or extrapolated to periods where flow is erratic. These data (Fig. 5) are for a 50 mA current. The coulometer can titrate at currents up to 200 mA. While this is not recommended (e.g. resistive heating of the coulometer solution) our procedure could be used to check performance at other current levels.

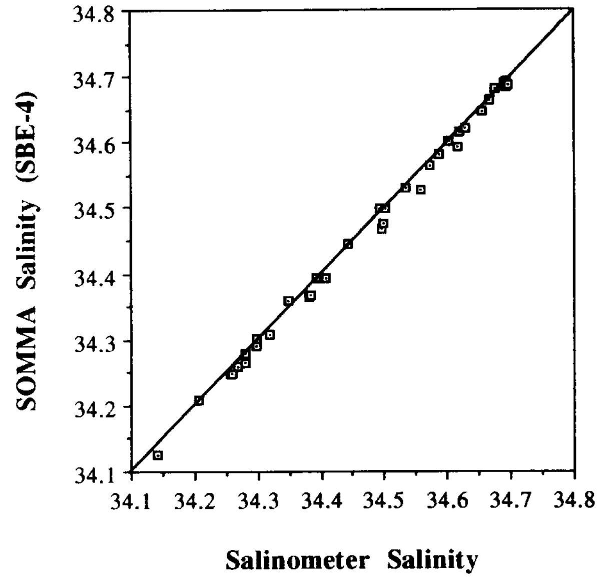

Fig. 8. Salinities ($n = 36$) determined on the automated SOMMA-Coulometer system during Cruise P6 plotted against the corresponding salinometer data. Results are for depths between 10 and 4000 m.

The two calibrations (electronic and gas) are related. Gas calibration without prior electronic calibration would yield a calibration factor (CALFAC) which includes an unknown error due to the departure of the VFC from the theoretical response. For example, the misscalibrated coulometer (Table 1, slope 0.9958) having a calibration factor of 1.004 (99.6% theoretical) when corrected for this departure (slope = 0.9958, Eq. 6) would give approximately 1.008 (99.2% theoretical) without correction [slope assumed to be 1.0, Eq. (6)]. Sample titrations corrected with the former calibration factor (VFC efficiency known) or the latter (VFC efficiency unknown) would give the same result. However, electronic calibration quantifies an error source (an analytical goal) and this knowledge brings system performance significantly closer to 100% of theoretical. From Table 1, the intercept correction before factory recalibration (5–12 counts/min) is similar to the blank correction (20–25 counts/min), and applying the intercept correction to periods when the titration increment is small would result in a large error (T_I is normally 3 to 4 minutes, while T_T varies between 9 and 15 min). Recalibration reduced the intercept correction to 1–2 counts/min, but for the reasons given above this correction is applied only for the period of continuous current flow (T_I). There is another rationale for electronic calibration. Gas calibration (this paper) and chemical calibration (Goyet and Hacker, 1992) data can not be compared unless the same coulometer is used for both sets of data or the coulometers are independently calibrated to correct for electronic differences between coulometers. This could be important for standardizing results from different investigators if the two methods of calibration continue in use.

Generally, gas calibration factors corrected for electronic calibration are commonly ca. 1.004 or 99.6% of theoretical. How this remaining error is partitioned is not known (whether a consequence of the photo-detector, coulometer solution composition, etc.), but its repeatability suggests it is real and not due to leaks or obvious causes. To our knowledge no one recovers 100% theoretical. Research would likely shed light on the matter, and many approaches are known to the authors and likely to the readers, however, the time and resources to research further are presently unavailable.

Adjustments and improvements are of necessity made by incorporating recent results into evolving standard operating procedures. This procedure was initiated at the Institute of Ocean Sciences (IOS) because they were an early SOMMA recipient. In Tables 2 and 3, factors affecting precision or repeatability are developed from Cruise 01–90 data. In Table 2 the replicate ($n = 2$) differences ($n_2 - n_1$) are expressed by the sign of the difference (+, −, or =). A sign is assigned to each pair even if the differences are insignificant, and the equal sign means identical results. A more or less equal mixture of signs is interpreted to mean random analytical error as in the depths between 1 and 100 m. Indeed, the distribution of the + and = differences are almost exclusively limited to depths ≤ 300 m. Below 300 m the differences are nearly always negative, and imprecision (differences $\geq 0.05\%$) increases dramatically. These data are interpreted to mean that CO_2 exchanged into the sample bottle head-space between the titration of the first and second replicates, and that this process is accelerated at depths where the pCO_2 is highest, or where the in-situ and analytical temperature difference is greatest. While pCO_2 data for the same samples is not available, many of the C_T measurements are from Ocean Station Papa (50 : 00 N × 145 : 00 W), or its vicinity. Previously (1973–1974) pCO_2 was calculated from C_T and alkalinity measurements at station Papa. When plotted against depth (Fig. 9), the earlier distribution of pCO_2 fits the current distribution of error in the C_T determinations with poorest precision in the region of highest pCO_2 and better precision at depths above 300 m or greater than 2500 m where pCO_2 decreases. The results in Table 3 show that sample warming can adversely affect the intra-bottle replicates. At depths below 2500 m warming may be as important a factor (pipette temperature varied between 8.8–11°C, in-situ water temperature between 1.5 and 1.9°C) as the partial pressure difference. In aggregate, Tables 2 and 3 suggest an oceanic water column analytical profile can be hypothesized in which higher temperatures and near saturation pCO_2 at the surface promotes good precision, followed by depths where increasing pCO_2 and decreasing temperature combine to promote sample vulnerability (exchange of CO_2 with the sample bottle head-space due to temperature and pCO_2 differentials), and finally a decreasing pCO_2 with somewhat lessened vulnerability. It is difficult to envision a scenario where both in-situ temperature and pCO_2 could be accounted for by continuous adjustments to temperature or the pCO_2 of the head-space gas. However, Table 3 shows that the first replicate is relatively insensitive to analytical conditions, and the precision under diverse analytical conditions is within the target goal of 0.05%. The second replicates are adversely affected by the disparity between analytical and in-situ conditions (0.09%).

In 1991, the water column was divided into two sections i.e., < and >300 m. Compressed air is the head-space gas for the former and 750 ppm CO_2 in N_2 for the latter, while the pipette temperature is constant at 16°C. The multiple bottle approach (inter-bottle) was tested with supplementary reference materials (SRM) from bottom waters and compared to the intra-bottle approach (replicates from the same bottle) with variable head-space gas. Both approaches are satisfactory (Table 5). The mean ($n = 84$) intra-bottle replicate difference from all depths using the two head-space gas concentrations is $-0.46\,\mu$mol/kg and the mean absolute value is $0.71\,\mu$mol/kg both within the target goal for precision (0.05%). The S_p^2 for the SRM is $\pm 0.83\,\mu$mol/kg. The SRM data (Table 4) plotted in Fig. 5 show that the daily or cell to cell variation in the gas calibration factors during M15 did not affect precision when these factors are used to correct the sample titrations (Eq. 7). Indeed, analyses of samples 181 and 190 on 4 March encompass a cell with a radically different gas calibration factor (1.009 or 99.2% of theoretical as opposed to the mean calibration factor of 1.0044 or of 99.6% theoretical), but even so the analytical precisions ±0.67 and $\pm 0.68\,\mu$mol/kg, respectively, of the samples analyzed with this cell are not adversely affected. The reason for the poor recovery on 4 March is not known. Together Fig. 5 and Table 4 demonstrate the validity of the gas calibration procedure. Furthermore, in Fig. 7 cell-specific gas calibration factors plotted against cell life show no change in response (more or less sensitive) as the total titrated CO_2–C reaches 30 mg. It takes at least 12 to 16 h of continuous titration to titrate this much carbon, and normally all of the samples from a depth profile can be titrated with the same cell. Currently, sample pipettes of approximately 20 ml are being installed on instruments so that the 30 mg C limit is not normally exceeded (see also Robinson and Williams, 1991). In the counts mode, blanks of < 25 counts/min ($0.005\,\mu$mol/min) are satisfactory. The data suggest (Figs. 5–7, Tables 4–6)

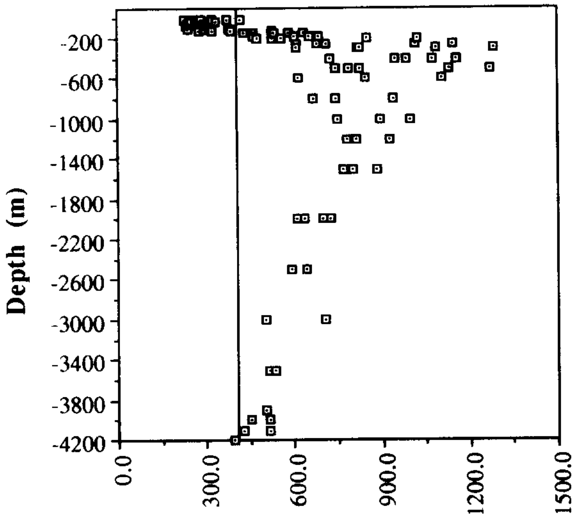

Fig. 9. A depth profile of pCO_2 calculated from pH and alkalinity at Ocean Station Papa (50 : 00 N × 145 : 00 W) during the years 1973 and 1974. The solid line at 400 ppm is the concentration of CO_2 in the head-space gas used in this work to determine the C_T of samples from the same location.

that the cell blank and gas calibration factor (response) are valid for the lifetime of the cell (daily), and that a stable system response when corrected for gas calibration is measured in weeks or months.

There is a notable exception to the procedures above. If a significant pause occurs between titrations (> 1.5 h), caution is advised because during inactivity the non-polarized silver electrode exerts no attraction on the AgI_2^- complex (Huffman, 1977), and the AgI_2^- complex may have time to diffuse through the cell frit and plate on the platinum electrode (cathode) during subsequent titrations which yield high results (this effect is regularly observed for cells left overnight and restarted the next day). Following long pauses, run replicate samples or a CRM for comparison with previous results. If the differences exceed $\pm 2\,\mu$mol/kg, change cells and inspect the platinum electrode. If necessary, clean it with 50% HNO_3, rinse, and dry.

The consistency of the cell response shown in Fig. 7 may be a benefit of keeping the silver anode positively polarized (running the samples in rapid progression) or of scrubbing the analytical stream of moisture and contaminates before the coulometric titration (Fig. 1; Johnson et al. 1987), or a combination. Cursory examination of sample data obtained subsequent to the M15 Cruise continues to indicate that cell response remains constant beyond 30 mg C titrated. There is another point to be stressed from Fig. 7. Note that the initial gas calibration factors reported are determined after several titration cycles (TCT $\geq$ 30 mg C). In practice, the blank 3.0 is determined followed by 1 or 2 replicates of a test seawater sample, and then two gas calibrations. The second is usually used for the sample corrections. If the second calibration is unsatisfactory (poor agreement between loops or mechanical failure), calibration continues until two successive calibrations give the same result (within $\leq$ 0.05%). Calibration factors obtained early in the cell cycle (< 3.0 mg C) may be biased by materials diffusing or driven out of the cell frit by current flow to give high recoveries (factors too low), or by insufficient purging of the CO_2 service so that the calibration gas is slightly diluted causing low recoveries (factors too high). Other means of calibration exist including the sodium carbonate solution procedure of Goyet and Hacker (1992). However, the advantages of gas calibration including ease of complete automation, availability and stability of pure CO_2, documentation (Dickson and Goyet, 1991), and satisfactory results (Table 6; Wilke et al., 1993) make it the choice for the SOMMA instruments. We have tested a fast electric actuator for the gas sample valve switching and a rotor made of Valcon E without success. The fast actuator does not function well at the 80 psi retaining nut spring tension (see Methods Section), and the Valcon E material interacts with CO_2 to a significant extent.

The evolving body of experience culminated in the one replicate per bottle procedure for the P6 Cruise in 1992. These data are given in Tables 5 and 6. The most conservative precision measurement, the mean absolute difference between bottles, is used. The system precision clearly improves with experience, and the system precision ($\pm 2s$) is $\leq 1.5\,\mu$mol/kg. Gravimetric measurements of the "to deliver" pipette volume shows that it decreased during the three months of the P6 Cruise and especially during the final leg. The decrease is, however, consistent with the CRM analyses. During periods of inactivity, the pipette is filled with deionized water to prevent fouling, but otherwise it is not cleaned. By the end of the cruise a noticeable build-up of a surface film at the top of the pipette occurred. This is proabaly a layer of grease introduced from the heavily greased CRM bottle stoppers which deposit a thin but visible surface layer of grease on the CRM samples. The decreasing "to deliver" volume suggests that grease may have displaced some volume, or that water adhering to the greasy pipette surface reduced its output. Nevertheless, the decrease is small ($\leq 0.05\%$, $13\,\mu$l) and it took two months to develop. The pipette is chemically cleaned only before and after the cruise (the glassware is completely disassembled). This is primarily due to the fear of introducing caustic solutions and inadvertently altering the behavior of the system while at sea. The gravimetric check procedure (Table 6) is used in lieu of cleaning.

The CRM data (Table 6) show that even aboard ship the coulometric-based system is able to reproduce the CRM results of the bench-mark static vacuum extraction/manometric technique. The true variance of the CRM is to our knowledge not known, and this raises the question of just how the CRM data is to be used to correct the sample results. No method is yet proposed Dickson and Goyet, 1991), but one is needed for the submission of data reports to the appropriate agencies. Table 6 does show that the errors between the determined and certified values are small, and that the precision and accuracy (except for leg III) is within the targeted ±0.05% goal.

The integration of a conductance cell for salinity into the SOMMA will be presented in detail elsewhere. Fig. 8 is, however, typical of the data obtained during the P6 Cruise. The salinity reading could not be taken until thermal equilibrium occurs between the cell and the sample, and the C_T and salinity determinations often required up to 20 min per sample. Recently, M22 Cruise, January 93, alterations to the hardware (addition of a heat exchanger) and the software provide a faster reading but with a small loss in accuracy as measured against the CTD salinity ($n = 236$, $y = 0.9963(x) + 0.165$, $r = 0.997$). To date, the vast majority of C_T determinations calculated using the SOMMA conductance cell salinity for density (Eq. 7) are within $\leq 0.1\,\mu$mol/kg of the C_T concentration computed from the corresponding salinometer salinity. On board salinity measurements have helped to detect erroneous information provided by samplers or malfunctioning Niskin bottles. The conductance cell and thermostatted housing can be retrofitted to existing instruments, or installed in other automated systems.

Attaining maximum performance blends past, present, and future efforts along four lines: (1) improving design and automation while producing a viable robust transportable production package; (2) developing and verifying calibration procedures for the coulometer electronics, sample pipette, gas sample loops, and overall system response; (3) developing operating procedures and determining their efficacy, accuracy and precision in field applications consistent with accepted norms (Dickson and Goyet, 1991); (4) adding additional analytical parameters as needed or desired. The targeted goals for the determination of C_T are 0.05% precision and accuracy for samples containing $2000\,\mu$mol/kg. These goals are demonstrably attainable (Tables 5, 6). The "to deliver" volume data (Table 6), CRM results (Table 6), and gas calibration data (Figs. 5 and 7, Table 6) show that system performance can be accurately monitored, and that corrections can probably be made for small errors in these parameters. The addition of pressure, temperature and conductance sensors to the SOMMA completes the automation of the C_T determination begun with the UG-1 system. Analytical head-space gas and temperature effects on the determination of C_T are minimized with the single replicate from each bottle procedure rather than adjustment of temperature or head-space gas concentration, and that single replicates from duplicate bottles at representative depths accurately estimates analytical precision. With experience, the importance of the head-space gas is somewhat diminished. However, should an error occur during the titration (e.g., computer fails to read the coulometer display or mechanical failure) a second replicate can be run from the same bottle with the expectation of reasonable results because the liquid phase remains in contact with a gas phase containing CO_2. Temperature effects are minimized by running the determinations at a cooler pipette temperature (ca. 15°C) after equilibrating the samples to the pipette temperature, and by calibrating the pipette at the analytical temperature. The SOMMA is transportable (units have been shipped intact around the world without damage except to the packing crates). However, improvements in software, operating manual, instrument robustness, and protection from electrical interference will be forthcoming. In this context, the opportunity to submit this paper for consideration is especially valued because it gives us a chance to bring the current work up to date, and identify future requirements.

Acknowledgements

We thank Frank Millero for the invitation to participate in the symposium and giving us the opportunity to submit this paper. We thank the officers and crews of the CSS *Parizeau*, F/S *Meteor*, and The R/V *Knorr*. Rick Wilke is acknowledged for the gravimetric pipette determinations following the P6 cruise and for his general assistance on and preparing for both the M15 and P6 cruises. Rick Wilke, Meridth Anderson, Craig Niell, David Hunter, and Victoria Coles are acknowledged for there assistance and skilled sampling work during the P6 Cruise. The critical support and assistance of Jim Sullivan and John King of the University of Rhode Island, Doug Wallace at BNL, and John Downing at Battelle are especially appreciated. The competence of machinist Gary Savoie at the EDL has also contributedly greatly to this work. Likewise the administrative efforts of Cathy Cipolla at the EDL. K.M.J. would also like to thank his German colleagues G. Siedler, J. Duinker, K. Kremling, and B. Schneider for making it possible to sail on the excellent German Research Vessels, and for providing the time and support to finish this work at the Institute für Meereskunde, Kiel, Germany. We thank Jürgen Holfort of the IMFK for the water mass calculations given in Table 4. This work was supported by NSF through Grant No. OCE-8911367 to J. McN. Sieburth and K.M.J., and by the Department of Energy through contract De-AC02-76CH000016.

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