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Operator's Manual

Single-Operator Multiparameter Metabolic Analyzer (SOMMA) for Total Carbon Dioxide (C_T) with Coulometric Detection

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INTRODUCTION 1

This manual contains the presently known information about using the SOMMA* (Single-Operator Multiparameter Metabolic Analyzer) -Coulometer system for total carbon dioxide (C_T) analysis of seawater samples. Being Version 1.0, it is preliminary and will be revised as new information is obtained from SOMMA users. We encourage users to share comments about the manual with us and to make suggestions for improving the procedures described herein. If you have suggestions, please contact Ken Johnson at Brookhaven National Laboratory (BNL). New information, revised pages, and changes to the manual will be distributed to recipients of Version 1.0 as they are developed.

As part of a U.S. Department of Energy (DOE) program to conduct a global survey of CO_2 in the ocean in conjunction with the World Ocean Circulation Experiment (WOCE) Hydrographic Program and Joint Global Ocean Flux Study, C_T measurements are being made with SOMMA systems by several U.S. and foreign laboratories. The purpose of the manual and future versions is to improve the accuracy and precision of seawater analysis through better documentation of methods and to facilitate communication of new operating procedures.

The concentrations of individual carbonate species ($CO_2^{*_{(aq)}}$, HCO_3^- , CO_3^{2-} , etc.) are not directly measurable in seawater. Consequently, C_T is used with other parameters to specify the system. An explanation of the carbonate/seawater system is contained in the *DOE Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water*. Typically, the equilibrium constants: K_0 , K_1 , K_2 , ..., are measured in the laboratory and used with field estimates of: $f(CO_2)$, C_T , total alkalinity, and pH to completely describe the system. Because the thermodynamics of acid-base pairs in seawater is not completely understood, at least three of these parameters are frequently measured, and the redundancy is used to check the accuracy of the various measurements. As the carbonate chemistry indicates, understanding C_T results

* Patent pending for the dynamic headspace process and custom glassware incorporated into the SOMMA chassis. The software is also copyrighted.

from SOMMA systems can be complex. We therefore recommend that you be completely familiar with the *DOE Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water* and references therein, and the Instruction Manual for Model 5011 or 5012 CO₂ Coulometer (UIC Corp.). The DOE Handbook can be obtained by writing Dr. Andrew Dickson, MPL-0902, Scripps Institution of Oceanography, 9500 Gilman Drive, La Jolla, California 92093-0902.

1.1 STRUCTURE OF THE MANUAL

The manual is written to meet the needs of SOMMA users with widely different experience. It is organized in four modular sections to facilitate quick access to specifics. For the experienced seawater analyst it is a reference source, for less experienced and first-time users, the manual is a step-by-step guide to setup, maintenance, repair, and routine SOMMA operations. General descriptions of the SOMMA and the analytical procedures are discussed in Section 2.0. Section 3.0 explains how to prepare the SOMMA for sample analysis, and seawater analysis procedures are given in Section 4.0. The sources of replacement parts, materials, and supplies are given in Appendix A. SOMMA temperature sensor calibration is discussed in Appendix B and flow meter calibration data are provided in Appendix C.

== OVERVIEW OF OPERATION 2

The SOMMA is a sea-going, computer-controlled automated dynamic headspace analyzer for the extraction of C_T from seawater. It is coupled to a coulometer for the coulometric detection of the extracted CO_2 . Figure 1 is a series of photographs of the SOMMA system. The current design of the headspace analyzer (Figure 2) is based on system UG - 1^(a). It features four independent gas services including a headspace gas (HSG) service, a water-jacketed pipette and sample bath, automatic temperature sensing, a built-in gas calibration system, and an auxiliary carrier gas (ACG) flow route. In addition, pipette rinsing capability and a protective plastic enclosure with coolant fluid conduits integrated into the enclosure have been added. The SOMMA comes with the electronic components and interface cables for IBM compatible PCs.

The dynamic headspace analyzer components are housed in an enclosure made of clear 1/2-in. thick polycarbonate plastic with its glassware visible and accessible. The plastic enclosure is mounted on a wooden base which can be anchored to ship benches by bolts or clamps. A removable and reusable shipping crate is furnished for transport.

2.1 C_T ANALYSIS

(Refer to Figure 2 while reading this section). The SOMMA dispenses and acidifies a known volume of seawater, strips the resultant CO_2 from solution, dries it, and delivers it to a coulometric detector. An analytical sequence begins by securing a sample bottle in a thermostatted bath and initiating the analysis from a PC keyboard and video menu. A HSG applied through pinch valve (PV) 1 pressurizes the sample bottle causing the sample to flow through PVs 2, 3, and 4 into the water-jacketed pipette. The overflow from the pipette empties into a reservoir until the electrodes located there are immersed. The latter action completes an electrical circuit sensed by the PC through an analog to digital (AD) interface and signals that the pipette is full. Next, the temperature of the pipette

— Abbreviations —

carrier gas, CG;
auxiliary carrier gas,
ACG; headspace
gas, HSG; pneu-
matic gas, PG;
waste, W; pinch
valve, PV; isolation
valve, IV; tempera-
ture sensor, ts.

^a Johnson, K. M., J. McN. Sieburth, P. J. leB. Williams and L. Brandstrom. 1987. Coulometric total carbon dioxide analysis for marine studies: Automation and calibration. Mar. Chem., 21:117-133.

Overview of Operation

Figure 1a SOMMA Coulometer System front view

Overview of Operation

Figure 1b - SOMMA Chemical Analysis System (continued)

Figure 1c. SOMMA Coulometer System--electronic detail

Figure 2. SOMMA Dynamic Headspace Analyzer Schematic

(ts) is read through the A/D interface and PVs 4 and 5 are simultaneously energized. This pressurizes the pipette with the pneumatic gas (PG) and connects the pipette fluid path to the stripper through the normally closed port of PV 4. The sample quickly drains into the stripper where it is acidified and degassed by the carrier gas (CG) which enters the stripper from both the ACG route and the main carrier gas (MCG) route. The analytical gas stream is dried by passage through a condenser, dehydrite, and silica gel before coulometric titration. After the titration is completed, PVs 4, 5, and 9 are energized causing the spent sample to drain through PV 9. To ready the SOMMA for the next replicate, a fresh aliquot of acid under pressure from the PG is injected into the stripper through PV 8, and the reservoir is drained under gravity through PV 6. The back pressure for draining the stripper is supplied by a restrictor located downstream from the stripper. Figure 2 schematically depicts the location of the on/off brass toggle and fine metering valves used to independently regulate each gas service. Table 1 provides a list of the valves used in the SOMMA. The PC and software determine the end point of the titration, make the necessary calculations, and save the data to disk.

2.2 GAS (CO₂) CALIBRATION OF THE SOMMA AND COULOMETER

The calibration hardware consists of an 8-port gas sampling valve (GSV) 12 with two calibrated sample loops connected to a source of pure CO₂ through isolation valve (IV) 10. The CG and calibration gas services merge in the GSV. Thus the calibration gas follows the same route to the coulometer as the CO₂ stripped from seawater. The contents of the sample loops are determined coulometrically after filling with pure CO₂. From the loop volume, instantaneous barometric pressure (P), and the loop temperature (T), the mass of CO₂ gas contained in each loop is calculated from the density of CO₂ at P and T. The average ratio of calculated to determined mass of CO₂ is the calibration factor used to correct the sample titrations. The normally closed IV 11 keeps air from infiltrating into the GSV when the system is not in use. The temperature of the sample loops is read by the PC through at least two and as many as four temperature sensors.

Number and Title	Function	Table 1. Valves for SOMMA Coulometer
Solenoid Isolation Valves (IV)		
0 carrier gas router ^(a)	routes CG to stripper or pipette	
1 pneumatic/headspace gas router ^(a)	routes PG to pipette and acid bottle, routes the HSG to sample bottle	
2 rinse manifold ^(b)	routes sample to waste during rinsing	
3 pipette guard ^(c)	controls entrance of the sample into pipette	
4 pipette inlet ^(b)	routes sample from pipette to stripper	
5 pipette outlet ^(b)	routes sample to reservoir or PG to pipette	
6 reservoir drain ^(d)	drains reservoir	
7 not used ^(d)		
8 acid router ^(e)	routes acid to stripper	
9 main drain ^(d)	drains the stripper	
Solenoid Isolation Valves (IV)		
10 CO ₂ inlet ^(f)	routes calibration gas to the GSV (12)	
11 CO ₂ vent ^(f)	vents calibration gas to the atmosphere	
13 headspace vent ^(f)	controls pressure of sample bottle headspace	
<hr/>		
^(a) 3-way multi-purpose pinch valve for 1/8-in. o.d. tubing		P/N 100P3MP 115-02B
^(b) 3-way multi-purpose pinch valve for 3/32-in. o.d. tubing		P/N 075P3MP 115-01B
^(c) 2-way normally closed pinch valve for 3/32-in. o.d. tubing		P/N 075P2NC 1150-1B
^(d) 2-way normally closed pinch valve for 1/4-in. o.d. tubing acid-resistant valve body version of this valve		P/N 100P2NC 115-05B P/N 100P2-S68
^(e) 2-way normally closed pinch valve for 1/8-in. o.d. tubing		P/N 100P2NC 115-02B
^(f) 2-way normally closed isolation valve for 1/4-in. - 28 fittings		P/N 100T2NC 115-62 TR/201

SYSTEM SET UP 3

This section contains an overview of the system components and detailed information on setting up and integrating those components. Software applications and conventions are also discussed as well as preparing the system for transit and storage.

- Abbreviations -

Normally closed, nc;
normally open, no;
bored-through, BT;
gas sampling valve,
GSV.

3.1 COMPONENTS

The primary components of the SOMMA-Coulometer system include the chassis, glassware, gas services, and electronic hardware. Each of these will be briefly introduced in the following paragraphs.

The chassis provides the framework within which the other components are arranged. Clear polycarbonate plates are used to partition four separate sectors on a floor mounted on a 3-in. frame. Within this frame, underneath the floor, the plumbing detail is neatly housed.

The major pieces of custom designed glassware include the stripper, the pipette, a condenser, which mates with the stripper outlet and contains a drip skirt to catch surface condensate, a drying tube adaptor, and a reservoir, which collects the overflow from the pipette.

There are four different gas services built into the SOMMA system: calibration gas, headspace gas (HSG), pneumatic gas (PG), and carrier gas (CG). The gas is used to calibrate the system, the HSG to move the sample fluid in the system, the PG to inject acid and sample into the stripper, and the CG to carry CO₂ to the coulometer cell.

The electronic hardware used with the SOMMA includes an IBM compatible computer (user supplied) interfaced with a keyboard, video monitor, and printer. When coupled with the SOMMA system, the computer interfaces with the coulometer, control relays, and sensors for temperature and conductivity. The

SOMMA comes with two interface boards, user manuals, two connecting cables, and a relay module board with 16 relays installed. The interface boards include a 24-line digital input/output (I/O) board (model DG24) and a 12-bit analog to digital board (model AD500).

3.2 SOMMA CHASSIS LAYOUT

The chassis (Figure 3) is made of three clear 2-ft x 2-ft x 2-ft x 10-mm 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 formed by the cross partitions. Sectors I, II, and IV are faced with 3-in.-high plastic or steel panels which are covered with removable top pieces (floors) to form three 3-in.-deep wells. The plumbing detail is protected by the flooring until it passes out of the wells and connects with the instrument components (valves, glassware, etc.). Each sector is given a dedicated function. Seen from the top down and proceeding clockwise from the left-front sector (I): Sector I houses the sample bath; Sector II houses the gas calibration system; Sector III contains the acid bottle, the control relays, module board, and computer connections; Sector IV contains the liquid level detector, pipette, stripper, and the gas scrubbing components. The forward facing wells of sectors I and IV are faced with a drilled stainless steel panel upon which are mounted four on/off brass toggle valves and five metering valves for gas service regulation. The locations of the toggle and metering valves are shown schematically in Figure 2. A rugged sea-going wooden case fits over the top of the chassis, and the instrument can be shipped fully assembled in this case.

3.3 GLASSWARE

The major pieces of custom-designed glassware are the stripper and the pipette. These items along with their associated solenoid valves are shown in Figure 4. The stripper is in fluid-flow communication with the pipette. The former has

Figure 3. Sector Diagram (Top View). Seen from the top, the components are housed in four (4) sectors numbered I to IV clockwise from the left front of the chassis.

System Set Up

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Figure 4. The Stripper-Pipette Assembly with Associated Solenoid Valves

inlets for the MCG line on the bottom and an ACG line on the top. The ACG enters through an arm of the central inlet tube to prevent CO_2 from sequestering in the central inlet tube and to ensure that acid added through a second arm of the central inlet tube is forced into the stripper. Also received in the central inlet tube of the stripper is the sample inlet tube through which the sample flows into the stripper. The teflon sample inlet tube is secured to the stripper in a fluid-tight manner with a bored-through (BT) nylon reducing union (1/4 in. to 1/16 in.). The 1/4-in. front ferrule is made of teflon. The terminal ends of the central inlet tube and the sample inlet tube are open and spaced 1 to 2 mm apart from the bottom of the stripper just above a coarse glass frit (ca. 50- μm pore size). Thus the outer surface of the sample inlet tube and the inner surface of the central inlet tube define an annular or ring-like passage through which the ACG, acid, and spent sample flow in different stages of the process. The pipette, nominal volume 27 - 29 mL, is water-jacketed for temperature control, and a well (indentation) on the back side of the pipette houses a temperature sensor connected to the PC through the A/D interface. The procedure for calibrating the "TO DELIVER" volume of the pipette is given in Section 4.2.3.

The three remaining glassware components are shown in Figure 5. A condenser (A) mates with the stripper outlet. A drip skirt to catch surface condensate empties into the system drain. The drying agent adapter (B) is installed on the exit side of the condenser. The reservoir (C) which collects the overflow from the pipette is shown with a pair of monel wire electrodes, the liquid level sensor, installed. The sensor is read through the A/D interface.

3.3.1 Cleaning the SOMMA Glassware

Before installation, the glassware was chemically cleaned in an oxidizing solution (10% NaOH with 3% KMnO_4 (W/V)), rinsed with an acidic Na_2SO_3 solution (3% with 150 mL conc. HCL 10 L^{-1}), and dried. Further cleaning after installation is problematical; however, the following recommendations and suggestions do apply:

System Set Up

A. Somma Condenser

B. Somma Drying Agent Adapter

C. Somma Reservoir

KEY:

§ = Standard Taper

S9201012.6

Figure 5. Glassware Components A) Condenser B) Drying Agent Adapter C) Reservoir. The condenser is shown with its drip skirt, the adapter packed with desiccant and the reservoir with a pair of electrodes for sensing the liquid level.

1. The drying agent adapter (B, Figure 5) should be washed with distilled water after use, and thoroughly dried before repacking and reinstallation. Additional detail concerning the adapter is given in the section dealing with gas purification and gas scrubbing (Section 3.4.2).
2. When not in use, the pipette should be filled with distilled water to kill fouling organisms, prevent salt build-up, and to keep its inner surface wetted.
3. The pipette is almost never removed from the system (it is shipped in place). No degradation in repeatability or change in delivery volume due to the accumulation of films or dirt on the inner surface has been documented. However, the DOE Handbook requires that C_T standard and sample bottles be sealed with greased stoppers, and some of this grease is bound to get to the pipette sooner or later. We therefore would like to suggest possible, untried, cleaning methods:
 - a. With the pipette installed, soak it for 1 to 2 h with an alcoholic KOH solution or a commercial preparation such as the Pierce (Rockford, IL61105) RBS or PCC-54 cleaning solutions mixed 1:1 with methanol. Rinse with distilled water.
 - b. Alternatively, the pipette could be dismantled and immersed in a cleaning bath as was done initially. Recalibrate after cleaning.

-CAUTION-

Do not spill any of the cleaning solutions on the plastic chassis as they will damage the finish. This caution also applies to the solenoid valves.

With the pipette in place, the automated sample routines can be used for the cleaning procedure (see Option 17, Section 3.8). As a minimum standard, we would suggest that the pipette be chemically cleaned prior to each WOCE cruise with recalibration after each cleaning. Do not spill any of the cleaning solutions on the plastic chassis as they will damage the finish. This caution also applies to the solenoid valves.

3.3.2 Installation and Removal of the SOMMA Glassware

The stripper (for cleaning or during pipette calibration) and the drying adapter are routinely removed from the chassis. The removal and installation of the adapter is self-explanatory, and the procedure for the removal and installation of the stripper is covered in the section on calibrating the pipette (see Section 4.2.3).

Removing the SOMMA pipette

If the pipette needs to be replaced or serviced, consult Figure 4 and do the following:

1. Completely loosen the 1/4-in. nylon nut securing the BT reducing union to the central inlet tube of the stripper (the stripper may now be removed, see Section 4.2.3 for details).
2. Loosen the screws which secure the pipette supporting brackets to the chassis wall, but leave the brackets attached. Tightening these screws causes the brackets to clamp the pipette securely.
3. Disconnect the pipette water-jacket outlet (upper) line from the temperature bath and raise it to a height or blow through it until the pipette jacket completely drains.
4. When the pipette jacket is empty, loosen the 3/8-in. nylon nuts on the jacket connections and disconnect the bath lines from the pipette.
5. Disconnect the pipette from the plumbing at the three unions shown in Figure 4, and pull the pinch valve tubing attached to the pipette away from the no and nc ports of PVs 4 and 5.
6. Carefully grip the pipette and slowly pull it straight toward you until it is clear of the supporting brackets and continue to pull it toward you until the reducing union and sample inlet tube are clear of the stripper (if the latter is still in place).

The pipette is installed in the reverse order. However, mate new pinch valve tubing sections or fittings to the pipette terminations before reinstallation. Likewise, the BT reducing union. Check calibration after reinstallation.

3.4 GAS SERVICES

There are four (4) different gas services built into the SOMMA system. The SOMMA gas services are:

Calibration Gas	pure CO ₂ 99.995 % ^a
Headspace Gas	CO ₂ in N ₂ (330 - 1000 ppm) ^a
Pneumatic Gas	N ₂ (UHP, 99.999) ^{a,b,c}
Carrier Gas	N ₂ (UHP, 99.999) ^{b,c}

- ^a Small cylinders of the gases may be used to save space. For example, Matheson cylinder sizes 2, 3, or the lecture bottle size for the calibration gas.
- ^b These gases must be CO₂-free because they flow into the coulometer cell.
- ^c Independently regulated lines from a single tank of gas could be used for both CG and PG functions.

The functions of these gases are described in Section 2.2 (shown in Figure 2).

Gases are connected to the left side of the SOMMA chassis by means of 1/8-in. Swagelok bulkhead fittings. The fittings are labeled with the gas service. Note the location of these inlets (see also Figure 6). Use connecting tubing through which atmospheric gases cannot diffuse. The most convenient tubing is nylon, but it must be protected from abrasion, cuts, etc. If stainless steel (SS) tubing is used, SS front and back ferrules must be used even though the bulkhead fittings on the chassis are brass. Check the SS connections periodically because they will loosen with vibration. Observe Swagelok's instructions for tightening the fittings, and do not overtighten.

The gases are regulated by means of toggle and needle valves on the engraved SS panels on the front of the chassis. Swagelok quick-connectors on the right side of the chassis, and a Porter flow meter mounted in Sector IV are used to monitor flow rates. These controls are depicted in Figure 6. Inspect the gas service panel and note their locations.

3.4.1 Gas Service Set Up and Operation

The following steps must be performed to ready the gas services for operation.

1. Clean the calibration gas tubing, CG tubing, and the GSV sample loops [the manufacturer (Valco) will specially clean the latter for a fee]. For SS, fill the tubing with 6 N HNO₃ and soak for 30 minutes. Rinse with copious quantities of distilled water, and thoroughly dry by passing dry

— NOTE —

Use approved CGA regulators, and provide a regulator with a steel diaphragm for the calibration and carrier gases.

— CAUTION —

Contaminants (Machine Oils, etc.) transported to the GSV and the sample loops make it virtually impossible to get the gas calibration operational.

System Set Up

S9201012.3

Figure 6. The Gas Service Controls. Seen from the top of the instrument, gases are connected to the bulkhead fittings on the left side of the instrument, quick connect-fittings on the right side allow the flow meter to be plumbed to gas services to check flow rates. Each gas is provided with a shutoff valve and a metering valve to regulate flow rates.

N₂ through the tubing for several hours. Nylon should be rinsed with distilled water or very dilute acid and thoroughly dried as above. Cleaning ensures that no liquid contaminants remain in the tubing connecting the CG and calibration gases to the SOMMA, and subsequently, the GSV.

2. Install CO₂ traps on the CG and PG tank(s). Use the two 12 x 3/8-in. o. d. glass tubes and the four (4) brass reducing unions provided. Fill the first half of the tubes with Ascarite (A. H. Thomas) or Malcosorb (Mallinkrodt), and the second half with Magnesium Perchlorate (MgClO₄) hereafter called dehydrite. Use phosphoric acid-cleaned glass wool to separate the reagents and to cap the tube ends. Replace the reagents when the Ascarite or Malcosorb become discolored to 50% of their length, or the coulometric blank increases. These traps remove the trace amounts of CO₂ in the CG or PG and the water formed from the reaction of CO₂ and the absorbent. Before connecting source gases and scrubbers to the SOMMA, experiment to determine the rate at which scrubber reagents are exhausted. Some source gases are "wetter" than others causing significant variation in the working life of the scrubbers.
3. Install a good particle filter (NUPRO SS-2F Series) between the CG scrubber and the SOMMA and between the CO₂ calibration gas source and the SOMMA to remove fine particulate matter which could score the GSV surfaces.
4. With the gas toggle valves on the front of the SOMMA instrument OFF (closed), connect the gas services (CO₂ calibration gas, HSG, PG, and CG) to the appropriate inlet fittings located in Sector II (Figures 3 and 6) of the SOMMA chassis. Ensure leak-tightness by leaving the toggle valves closed, and then shutting off the source gas cylinder. If the regulator pressure does not drop significantly in 60 minutes, the lines are tight. (Note: this check will have been done on the DOE instruments at BNL before shipping).
5. Set the flow rates of the calibration and PG in that order by opening the main tank valve and adjusting the regulator pressure to 10 psi (Note: if an in-line barometer is installed in the CO₂ line, set CO₂ regulator pressure no higher than 5 psi or in accordance with the barometer manufacturer's instructions). Mate the quick-connect stem to the appropriate quick-connect fitting located on the right side of the instrument (Figure 6), and connect the tube leading from the stem to the flow meter. Open (ON) the toggle valve on the front panel and set the flow rate with the needle valve.

-CAUTION -

When flow measurement is complete, remove the stem fitting from the quick-connect, otherwise gas will continue to flow through the quick-connect, and the SOMMA will not operate. Removing the stem seals the fitting and terminates flow.

System Set Up

— NOTE —

The flow meters are factory calibrated, but the calibration can be checked using a soap bubble meter.

— NOTE —

Do not turn off the MCG unless there is a check valve installed between the stripper and the GSV, or the stripper is completely dry.

- a. The calibration gas flow rate should be set to approximately 150 mL min^{-1} (setting 4.5 on the flow meter, see also Appendix C).
- b. The PG gas flow rate should be set to approximately 200 mL min^{-1} (setting 5.5 on the flow meter).

After the correct rate has been set, remove the stem from the quick-connect fitting. Leave the toggle valves open.

6. For the HSG, open the main tank valve and adjust the regulator pressure to 8 psi. Open the headspace toggle valve on the front panel and set flow to 5.0 on the flow meter. Flow can be fine tuned by adjusting it as the sample pipette fills. HSG flow should cause the pipette (ca. 27 ml) to fill in approximately 35 to 50 seconds (as the pipette fills the time elapsed is displayed on the video monitor to assist HSG adjustments).
7. The CG is divided into two branches, the MCG and ACG. Open the main cylinder valve. Adjust the regulator pressure to 8 psi. With the CG toggle OFF, connect the output line from the stripper to the flow meter. At this time the only gas flowing through the stripper is the ACG, adjust its flow rate with the appropriate needle valve to 50 mL min^{-1} , setting 2.0 on the flow meter. Open the CG toggle valve. Now both CG and ACG flow through the stripper. Set the combined flow to approximately 175 mL min^{-1} , setting 4.75 on the flow meter.
8. Connect the output line of the stripper to the coulometer cell. You are now ready to operate the SOMMA system.
9. When the analytical work has been completed you may turn the MCG down. The ACG will continue to flow through the stripper. Assuming gas-tight plumbing, the gas service toggle valves may be left ON (open). Do not turn off the MCG unless there is a check valve installed between the stripper and the GSV, or the stripper is completely dry.

3.4.2 Gas Purification and Scrubbing

Figure 7 shows the gas purification and scrubbing components of the SOMMA. In order, they are:

S9201012.7

Figure 7. Detail of the SOMMA Gas Scrubbing Components.

System Set Up

-CAUTION-

You cannot use the silica gel trap without the dehydrite moisture trap.

1. Condenser (removal of gross amounts of water vapor).
2. Perchlorate drying trap (removal of trace amounts of water vapor).
3. Port connector 1/8- to 1/16-in. (failure proof check valve).
4. Silica gel trap (removal of trace amounts of water vapor, acid gases, or acidic aerosols).

The reagents used with the components are listed in Appendix A.

The silica gel is a custom order. It should be ordered packed in unsealed tubes 4 x 1/4-in. (normally comes in sealed tubes of 6-mm o. d.). Use acid (H_2PO_3) treated glass wool when packing the drying tube adapter and sieve the Dehydrite through a 1-mm screen and discard the fines to prolong the operational life of the perchlorate trap.

Additional recommendations for these components include:

1. The top third of the standard taper (14/20) fitting of the drying tube adapter should be lightly greased with stop cock grease before insertion into the condenser.
2. Keep the condenser as cold as possible, but do not allow water vapor to freeze on the inner surface. The condenser temperature chosen will depend on temperature and humidity because at high humidity more water condenses on the outer surfaces of the cooling system. Set the refrigerated bath temperature between (0 - 8°C) to produce an acceptable amount of condensate. Insulate the condenser and feed lines.
3. Do not use check valves in the analytical tubing connecting the SOMMA to the coulometer cell. The reducing port connector (1/8- to 1/16-in.) shown in Figure 7 serves this purpose in the SOMMA system. This restrictor makes it difficult to displace air from the analytical line which prevents coulometer cell solution from backing up more than a few mm into the inlet tubing. The restrictor also provides back pressure which causes the stripper to drain when PV 9 (Figure 2) is opened. Do not remove.
4. The analytical tubing and components connecting the SOMMA to the cell should be kept absolutely dry (using semitransparent teflon tubing allows you to observe condensate). Before using, bake the hardware and tubing overnight at 55°C.

3.5 ACID REAGENT

The Dehydrite trap is installed each time the SOMMA - Coulometer system is started. The trap, loosely packed with Dehydrite flakes, has an operational lifetime in excess of 12 hours under conditions of constant use. An absolute useful life for the trap cannot be given because this depends on the CG flow rate, temperature of the condenser, etc. Ideally the trap should be left undisturbed until your analyses are finished. If the drying agent must be changed in the midst of an analytical series, equilibrium between the Dehydrite and the moist gas stream passing over it must be reestablished. Initial analyses following trap exchanges often show a departure from reference water (CRM) values until equilibrium is reestablished. If during a prolonged period of use (e.g., at sea), the lower half of the Dehydrite column becomes very wet (appearance of pudding) or very hard and new reagent is required; reanalyze a reference sample until you reproduce the correct value for the reference water (you may elect to run a couple of junk water replicates before analyzing the reference water). Because moisture seems to play a role in re-equilibration, water samples are recommended rather than gas calibration for checking system response after changing the Dehydrite reagent.

3.5.1 Handling the Acid Reagent

Make up phosphoric acid to 8.5% by volume, and sparge it for a least 30 minutes with CO₂-free N₂. To install, close the PG toggle valve on the SOMMA chassis. Disconnect the pressurized line from the acid bottle (shown in Figure 2) by loosening the 1/8-in. Ultra-Torr Union Connector. Separate the pressure line from the acid bottle, and remove the silicone rubber stopper. Fill the bottle with acid and restopper. Ensure that the transparent line connecting the acid bottle to the stripper is secure and seated in the nc port of PV 8 (you do not want to spill acid when you repressurize the acid bottle). Securely reconnect the pressure line, and open the PG toggle valve. Ensure that acid is injected into the stripper using Option 14 (PINCH VALVE FUNCTION CHECK) from the Options Menu given in Section 3.8. Figure 8 shows a simple scheme for measuring the volume of the acid injected into the stripper.

-NOTE-

Changing the
Perchlorate
(Dehydrite) reagent

- CAUTION -

The acid solution
will destroy the
plastic body of the
pinch and isolation
valves.

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S9201012.1

Figure 8. *The Determination of the Volume of Acid Injected into the Stripper. Acid inlet line is disconnected at the union, and a piece of tubing connected between the union and a 5 or 10 mL graduate. Using Option 14 (from the Options Menu and the procedure described in Section 3.3.1) the amount of acid injected can be determined or regulated.*

The amount of acid injected can be regulated through Option 14 and the software subroutine beginning at statement 13700 (see Table 2). Acid is injected by opening PV 8 (Figure 2) for a fraction of a second whereupon an aliquot of acid is injected into the stripper from the PG-pressurized acid bottle. The time step is normally 0.2 seconds which could be increased to regulate the volume of acid delivered (decreasing the time step will have no effect as opening and closing the valve consumes 0.2 seconds). The duration (0.2 seconds) of the time step is contained in statement 13770 as the variable DELAY, and the user may change the value of DELAY as required. Acid volume should be 2 ± 0.5 mL.

3.6 ELECTRONIC HARDWARE

In Figure 9, an IBM compatible computer (user - supplied) with Centronics RS232 serial, DG24, and AD500 interfaces is shown interfaced to a keyboard, video monitor, printer, coulometer [COM port 1 (p1)], control relays in Sector III, and sensors for temperature (T) and conductivity (K) in sectors II and IV. The circuitry for the PVs and GSVs is also shown. The PC sends 5 VDC signals to control relays. One side of the relays is connected to a 115 VAC source and the other side to a PV lead. The second PV lead is connected to AC neutral so that switching the relay energizes the PV from the 115 VAC source. The arrangement is different for the GSV because the control relay activates a double-pole double-throw (DPDT) relay. The latter is wired to the electric actuator of the GSV, and activating the DPDT relay causes the actuator to switch the GSV to one of two positions, "load" or "inject." The 115 VAC DPDT relay (#275 - 217) with mounting bracket (#275 - 220), Radio Shack Corporation, is securely attached to the floor of chassis Sector III.

The SOMMA comes with two (2) interface boards, user manuals, two (2) connecting cables, and a relay module board with 16 relays installed. The interface boards include a 24-line digital input/output (I/O) board (model DG24) and a 12-bit AD board (model AD500). Installation of the cards should be performed according to the instructions furnished with your PC.

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S9201012.2

Figure 9. The CPU Control Schematic

The relay module mounting board is in Sector III of the SOMMA chassis. For safety, the module board is surrounded by a removable plastic shield. Each relay module is separately fused with a 5-amp Littell pico fuse. These fuses are the small solid green solderless components (they look like a small resistor) just above each module relay. Note their location. They can be removed or replaced by hand.

One interface cable connects the DG24 board with the relay module mounting board, while the second connects the SOMMA sensors with the AD500 board. The latter provides for three (3) temperature sensors and one (1) "conductivity" (liquid level) sensor at the reservoir (Figure 5). The AD500 can, however, handle up to eight sensors. Both cables have a central connector so they can be disconnected without removing the end connectors from the SOMMA or PC. By convention, temperature sensor 1 (ts-1) is assigned to the pipette, and 2 and 3 (ts-2 and ts-3) to the GSV loops.

3.6.1 Interface Board Modifications

Minor modifications have been made to the DG24, AD500, and the relay module mounting boards (PB-16). Spare boards must be modified in order to work. On PB-16 a red jumper wire has been soldered between pin 49 on the edge connector and the positive (+) 5 VDC terminal located just above pin 49. Inspect the board and note the location of the jumper. Carefully note the positive (+) and negative (-) 5 VDC screw terminals just above pin 49 on the module board (horizontally oriented with respect to the edge connector). A 115 VAC source connected here would seriously damage your computer! Observe that the 115 VAC source for the PVs (Figure 9) is connected to the terminal labeled 1 on the module board (vertically oriented with respect to the edge connector). The 5 VDC terminals can be used to power devices requiring 5 VDC, e.g., the Paroscience barometer.

The DG24 board comes with three (3) blue chips installed at positions U5, U10, and U7. For compatibility with the relays, two (2) of these (positions U5 and U7) have been removed and replaced with two (2) driver chips (IC) (DM74LS245N) at positions A and B. Inspect the DG24 board and note their location. These chips

- WARNING -

Never connect a 115 VAC source to the +/-5 VDC terminal. A 115 VAC source connected here would seriously damage your computer.

-CAUTION-

When installing driver chips, observe CMOS handling precautions!

are easily obtained at a low cost. The DG24 board, no interrupt requests, has been configured to reside at HEX address \$200 in the PC.

The stock AD500 board does not have 5 VDC available on the edge connector to run the temperature sensors. A short jumper wire is used to bring 5 VDC from a point on the card to pin 21 of the edge connector. Note the location of the jumper on the back of the card, and duplicate on spare AD500 boards. The AD500 board, no interrupt requests, has been configured to reside at HEX address \$300 in the PC.

3.6.2 Electronic Hardware Installation

Perform the following steps when installing the electronic hardware.

1. Ensure that all of the SOMMA components are disconnected from the power source.
2. Install the DG24 and AD500 interface boards in your PC as described in the PC manual.
3. Remove the plastic shield covering the module mounting board in Sector III.
4. Connect the module mounting board to the DG24 board with the DG24 cable. Ensure that cable polarity is correct (arrow up) at the PC termination (they can be plugged in backwards!). The cable edge connector and the module board have been marked with large blue circles. Line the circles up for correct polarity.
5. Observing the polarity caution, connect the sensor cable to the AD500 board. Connect the liquid level sensor and temperature sensor leads to the sensor cable. For the temperature sensors, sensor 1 goes to the pipette (Sector IV), and sensors 2 and 3 are in the gas calibration system (Sector II).
6. Connect the printer and coulometer to the PC. The coulometer should be installed on serial port COM 1 (p1, Figure 9). Barometers or any other serial device should be installed on port COM 2 (p2).

7. Externally, set the 5011 coulometer "Mode" switch to 0 and the "Time Set" counter to 0.00. Consult the coulometer manual and set the coulometer serial port to 300 Baud without time printout.
8. Connect the GSV actuator and the Module Mounting Board power cords to a 115 VAC source. These can ONLY run on 115 VAC at either 50 or 60 Hz (a consideration aboard foreign research vessels).
9. Connect the remaining components to the appropriate power source. Aboard foreign vessels the coulometer and many computers (but not necessarily video monitors) can be run on 220 VAC at 50 Hz, or by transforming the 220 to 115 V.
10. Observe good electrical practice. Keep power cords bundled, plugged into a common source, and away from the sensor cables. We recommend that the coulometer be located at least 2 feet from the nearest PV and the Relay Module Board. This is because the photodiode on the coulometer is sensitive to the RF transmissions which may emanate from the PVs and Relays.

The SOMMA - Coulometer system is now electrically ready to run.

3.7 SOFTWARE

The software that enables the SOMMA system to perform its analytical functions was written in GWBASIC Version 3.20. It is designated SOMMA 1.0. Version 1.0 is written for an instrument having no built-in barometer and three (3) 0.1°C temperature sensors. Version 1.1 is written for instruments having a built-in barometer and 0.01°C temperature sensors. Contact BNL for Version 1.1. Using the software and an AT-compatible PC, an analyst can operate the gas service systems, perform calibrations and determine blanks, test main system functions, and automatically analyze a water sample. This section describes the SOMMA program, the options available from the menu, and frequently used variables and subroutines.

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-WARNING-

Running Option 4 will change the gas calibration factor (CALFAC) used by the software to calculate titrated $\mu\text{mol C}$.

Once the program has been loaded and the files initiated (described below), the Video Screen Options Menu allows the user easy access to the various options functions available. Those options are described below and discussed in detail in Section 3.8.

Option 1 initiates sample analysis and performs statistical routine.

Option 2 determines the blank for an unthermostatted cell.

Option 3 determines the blank for a thermostatted cell.

Option 4 runs the gas calibration subroutine.

Option 5 allows you to display or input different system file parameters.

Option 6 drains the stripper.

Option 7 fills the pipette.

Option 8 empties the pipette into the stripper.

Option 9 allows you to exit the program.

Option 10 allows you to view the current cell status and reset the TCT.

Option 11 performs a gravimetric calibration of the pipette output.

Option 12 performs electronic calibration (if applicable).

Option 13 purges the HSG line.

Option 14 allows you to check the function of individual PVs.

Option 15 pressurizes the pipette to check PV tightness.

Option 16 displays temperature sensor readings.

Option 17 rinses the pipette (for cleaning purposes).

Option 18 allows annotations to be made without terminating the program.

3.7.1 Software Conventions

Throughout this manual the following conventions are used when referring to commands, prompts, and on-screen text.

<u>Example</u>	<u>Description</u>
RELAY	UPPERCASE type represents what you will see on screen.
RETURN	SMALL CAPITALS indicate the names of keys on the keyboard.

CLASS/TITLE	RANGE (line nos.)	REMARKS	Table 2. Software Directory for the SOMMA Program
Main Routines			
Initialization	100-999	Initializes files, variables, DG24, AD500	
Menu option	1000-1500	Displays SOMMA options on monitor	
Principal Subroutines			
Blank, Option 3	2000-2999*	Thermostatted cell blank/stability check	
Blank, Option 2	3000-3999	Unthermostatted cell blank	
Calibrate coulometer	4000-5499*	Gas (CO ₂) calibration	
DOE Handbook calculations	5500-5999	Calculation of BT, density, and mass	
Parameter loading	6000-6519*	Input or change sequential file variables	
Initialize files	6520-6999*	Initialize sequential files on disk	
Analyze sample	7000-8099*	Analysis and sample statistics	
Recalibration	8500-8735	Controls automatic gas recalibrations	
Replicate handling	9000-9299	Sample replicate procedure	
System clear check	9500-9899	Ensures system is ready to operate	
Increment	9900-10299	Incremental computation of μ mol titrated	
Reset coulometer	10300-10499	Zero the coulometer display	
Read coulometer	10500-10999	Reads the coulometer display	
Relay activation	11500-11999	Controls status of relay modules 0-15	
Rinse	12000-12299	Rinses pipette prior to analysis	
Ready	12300-12399	Readies stripper for sample analysis	
Calibrate sample pipette	12500-13299	Pipette volume calibration	
Off	13300-13499	Sets all relay modules to status "off"	
Drain	13500-13699	Drains stripper	
Add acid	13700-13899	Injects acid into the stripper	
Empty pipette	14000-14199	Empties sample pipette into stripper	
Fill pipette	14500-14999	Fills the sample pipette	
Total carbon titrated	15500-15999	Logs carbon titrated	
End end point	16000-16999	Determines titration end point	
Density	17000-17499	Calculates density of water or seawater	
Reset total carbon titrated	17500-17999	Sets TCT to zero, controls recalibration	
End program	19000-19099	Terminates the program	
Pipette volume correction	20000-20099	Calculates pipette "to deliver" volume	
Remarks	25000-25599	Allows user to annotate hardcopy	
Module initialization	30000-30999	Initializes DG24 interface board	
Delay	35000-35999	Handles all time delays in program	
Temperature	40000-40999	Reads temperature sensor(s)	
Level sensor control (LSC)	45000-47999	Operates LSC(s) and AD500 board	
Clear screen and center	52000-52499	Clears video screen and centers cursor	

As you review the SOMMA software, you will note that certain variables, statements, and subroutines are frequently repeated. Some of the most important ones are discussed here. Table 2 contains a directory of the routines and subroutines used in the SOMMA program.

1. The variable RELAY. The relay module board in Sector III (Figure 2) has 16 relay modules (Figure 5) plugged into it. These modules are numbered 0 - 15. A number is assigned to each SOMMA valve, and this numbering scheme is given in Table 1 and shown in Figure 2. These numbers are on the valve bodies. In the software, an array called RELAY (15) is dimensioned, and Relay Assignment Status statements applicable to a particular relay (valve) contain the subscripted variable

RELAY (N)

where N is a number 0 - 15. Obviously, N corresponds to the particular valve (Figure 2) you wish to turn ON or OFF. Two additional conventions associated with the variable RELAY and Relay Assignment Status statements are

RELAY (N) = 0

RELAY (N) = 1

where: zero (0) means OFF and one (1) means ON. The Relay Assignment Status statements are executed through the DG24 board and they must always be followed by the statement

GOSUB 11500

where subroutine 11500 is the subroutine which controls the DG24 board and relays.

2. The variable DELAY. The argument of the variable always specifies a time delay in seconds. DELAY is used in conjunction with a timing subroutine built with the GWBASIC function called TIMER (where TIMER = seconds elapsed since midnight). There is a safeguard built into this subroutine for the condition where the variable TIMER is reset to zero (0) during the time delay (midnight). The variable DELAY is always followed by the subroutine call:

DELAY = 5 : GOSUB 35000

3. Temperature sensors. Three sensors are normally provided with the SOMMA. They are assigned the numbers 1 through 3. When a particular sensor is to be read, it is specified by setting the variable TSENSOR to one of these values and the subroutine call:

TSENSOR = 1 : GOSUB 40000

beginning at statement 40000. However, you can only read one sensor at a time, so you must specify the sensor to be read each time you call subroutine 40000. To read the three sensors at the same time the following are equivalent:

TSENSOR = 1 : GOSUB 40000

TSENSOR = 2 : GOSUB 40000

TSENSOR = 3 : GOSUB 40000

or

FOR Y = 1 TO 3

TSENSOR=Y

GOSUB 40000

NEXT Y

The temperature reading is returned as the variable TEMP, so be sure to save the sensor reading using a different variable name before reading the next temperature sensor, if and when, you modify the program (suggest TSN1, TSN2, TSN3, etc. because these variable names are not now used in the program).

4. Printing and Disk Storage. There is no spreadsheet incorporated into the SOMMA software. However, each LINE PRINT statement is also written to the A drive floppy disk so that, at the end of the day, the disk will contain an exact duplicate of the hardcopy (see Figure 10). Print statements usually take the form:

FOR DN = N TO NN

PRINT #DN

NEXT DN

where DN is a device number and N and NN include the range of devices to be written to. By convention DN#7 is the video screen, DN#8 is the line printer, and DN#9 is the floppy disk in drive A. For example, to print the variable DELAY to all three devices:

FOR DN = 7 TO 9

- WARNING-

If for any reason the program fails or the program must be terminated due to error, immediately press CONTROL BREAK.

PRINT 3DN, DELAY

NEXT DN

If for any reason the program fails or the program must be terminated due to error, immediately press

CONTROL BREAK

followed by the F10 function key. The latter will initiate

RUN 30000

The subroutine 30000 (see Table 2) restores the relay modules to the resting (OFF) status. When the difficulty has been repaired the program can be restarted by typing:

RUN

or activating the F2 function key.

3.8 INITIALIZING PROGRAM FILES

With plumbing, electrical, and coulometer connections completed, the program can be run. The program may be loaded from the hard or floppy disk drives of the computer in GWBASIC. If a floppy disk is used, remove it from the drive when the program is loaded. Because the screen, printer, and floppy disk drive are opened as files 7, 8, and 9, respectively, going from DOS to GWBASIC may have to be as follows:

GWBASIC /F:10

to allow GWBASIC to handle up to 10 files.

Loading and running the program initiates a series of prompts on the video monitor:

INSERT A FLOPPY DISK INTO DRIVE A: ENTER LTR Y
WHEN DONE

Insert a disk into drive A to receive your data. This should not be the program source floppy disk, and it must contain room for the data it will receive. The data will be stored by date. A typical file will appear in the Disk Directory as

03 - 18.DAT

where the first two digits represent the month, the second two digits the day of the month, and DAT is the file extension. You can view the data contained on the disk by returning to MS DOS and typing:

TYPE A:03 - 18.DAT

After inserting a disk into drive A, enter the letter Y from the keyboard, and the program will continue to execute with:

TO INITIALIZE A PARAMETER FILE TYPE YES - OTHERWISE

HIT RETURN

This is only run if you have never initialized the sequential files used by the program. Once it is run, do not run it again unless you change the program source disk (hard or floppy). If you type YES, then a series of prompts will ask you to initialize the files. For the first time through, initialize all of them. The sequential files created and used by the software are:

VOLUMES.INI	VSMLOOP, VLGLOOP, VP, TCAL, LPCALT
TCT.INI	current value of TCT
BLNK.INI	current value of the system blank, BLNKPMIN
GASCAL.INI	current gas calibration factor, CALFAC
SAL.INI	salinity of the water last in the pipette, PRESAL
ECAL.INI	electronic slope and intercept, ECALSLOPE, ECALINT
TEMPCAL.INI	sensor temperature coefficients, SLOPE, INTERCEPT

If you do NOT need to initialize a file, strike RETURN and the program will continue with

TOTAL CARBON TITRATED AT THIS TIME = (TCT)

TO ZERO THE TCT VARIABLE ENTER THE LTR R,
OTHERWISE RETURN

This prints the current value of the TCT contained in the file TCT.INI. If you are starting a new cell, enter the letter R from the keyboard to reset the variable TCT to zero (0). If you have restarted the program without changing the cell, hit RETURN to retain the current value of TCT. You can also change TCT from the options menu (see Option 10 described in this section). The program will display

THE CURRENT VALUE OF THE BLANK = (BLNKPMIN)
for a few seconds. This is just a reminder, and no action is necessary. The program will continue with a display of the Menu Options (p. 39) or the following:

ATTENTION THIS CELL HAS TITRATED OVER 15 mg C
GAS CALIB. IS AUTOMATIC AFTER 15 AND 30 mg C

ENTER 0 IF GAS CALIB. AT 15 mg C IS STILL REQUIRED
ENTER 1 IF GAS CALIB. WAS MADE AFTER 15 mg C TITRATED
ENTER 2 IF GAS CALIB. WAS MADE AFTER 30 mg C TRITRATED
ENTER 3 TO RESET TCT TO ZERO (0) IF REQUIRED
ENTER 4 TO CANCEL AUTOMATIC GAS RECALIB.

?

The software automatically repeats gas calibration after 15 and 30 mg C (TCT > 15 and 30) have been titrated. The initial calibration(s) will be run from the Options Menu shortly after starting the system, and the CALFAC (calibration factor) obtained will be saved and used for calculations. The data obtained during recalibration is printed out FYI and is not used in any calculations. If the program is interrupted and restarted, the options above will keep the software current with

respect to recalibration, or cancel them entirely. If you interrupt and restart the program with TCT < 15, program flow will skip directly to the Options Menu. You are now ready to select an option.

The Video Screen Options Menu

- 1 ANALYZE SAMPLE
- 2 DETERMINE BLANK (UNTHERMOSTATTED CELL)
- 3 DETERMINE BLANK (THERMOSTATTED CELL)
- 4 CO₂ GAS CALIBRATION
- 5 CHANGE OR INPUT SYSTEM FILE PARAMETERS
- 6 DRAIN STRIPPER
- 7 FILL PIPETTE
- 8 EMPTY PIPETTE CONTENTS INTO THE STRIPPER
- 9 EXIT PROGRAM
- 10 VIEW AND RESET TOTAL CARBON TITRATED (TCT)
- 11 PIPETTE CALIBRATION
- 12 ELECTRONIC CALIBRATION (IF APPLICABLE)
- 13 PURGE THE HEADSPACE GAS LINE
- 14 PINCH VALVE FUNCTION CHECK (INCL. ADD ACID)
- 15 PIPETTE PINCH VALVE TIGHTNESS CHECK
- 16 READ TEMPERATURE SENSORS
- 17 RINSE PIPETTE (EMPTY CONTENTS TO WASTE)
- 18 REMARKS

DESIRED OPTION NUMBER ?

These are the operations you can initiate from the keyboard by entering the appropriate number at the question mark prompt. Many are self-explanatory, additionally: Options 2 and 3 are used to determine the blank. When an unthermostatted cell is turned on, a significant rise in cell temperature occurs as

the residual CO_2 in the cell solution is titrated to the end point. The operating temperature varies with room temperature during subsequent sample analyses, but if the variation is small the cell temperature remains relatively constant after the initial startup. With Option 2 the blank is determined after the cell has come to its operating temperature, and the result ($\mu\text{mol min}^{-1}$) is automatically entered in the files to be used for subsequent analyses. If the cell is thermostatted the cell temperature remains constant after activation, and Option 3 can be used. With Option 3 the coulometer is read every 60 seconds and the increment or amount of carbon titrated (μmol) during the 60-second interval is displayed on the video monitor. These readings continue until the $\mathbf{M}$ key is struck whereupon the program returns to the menu. When the incremental readings are constant and satisfactory, the increment can be input as the blank ($\mu\text{mol min}^{-1}$) using Option 5 below (it will not be automatically input).

Option 5 allows you to display or input the following parameters into the disk files

- a. calibrated volume of the smaller gas sample loop as the variable VSMLOOP
- b. calibrated volume of the larger gas sample loop as the variable VLGLOOP
- c. calibrated volume of the pipette as the variable VP
- d. pipette calibration temperature ($^{\circ}\text{C}$) as the variable TCAL. Gas sample loop calibration temperature ($^{\circ}\text{C}$) as the variable LPCALT
- f. current system blank ($\mu\text{mol min}^{-1}$) as the variable BLNKPMIN
- g. current gas calibration factor as the variable CALFAC
- h. temperature sensor calibration coefficients as variables SLOPE and INTERCEPT

Once the sequential files have been initialized these variables are stored on disk and automatically read from the file into RAM each time the program is run. Some of them will almost never be changed e.g., TCAL, VP, LPCALT, etc., while others will be updated each time the applicable subroutine is run e.g., CALFAC and BLNKPMIN.

Option 10 allows you to view the current status of the cell. Exercising this option displays the variable TCT (mg C titrated). Reset it to 0 each time a new cell is installed. You can also control the automatic gas recalibration feature of the program or cancel them entirely. Follow the prompts.

Option 11 is used to collect the output of the pipette for gravimetric calibration (see Section 4.2.3). This option will also make the gravimetric calculations and buoyancy corrections required by the DOE Handbook.

Option 13 is used to purge the HSG gas line when the headspace gas is changed.

Option 14 checks the function of the individual pinch valves. It prompts the user for a valve number between 0 and 15. Inputting a number turns the corresponding valve ON and OFF ten times. While this is occurring, the movement of the valve plunger can be observed or adjusted. For PV 8, controlling acid (with acid bottle installed) injection to the stripper, the valve will be cycled only once each time the number 8 is input at the prompt. Repeat until you observe acid flowing into the stripper. The GSV (12) will be switched each time you strike RETURN.

Option 15 (with sample bottle in place) empties the stripper and fills the pipette with water. Then pipette inlet PVs 3 and 4 (Figure 2) are closed and PV 5 is opened for 60 seconds to pressurize the pipette with pneumatic gas (PG). In this configuration no water should flow from the pipette through any of the ports of PVs 3 or 4, and PG should not escape through the no port of PV 5 to the reservoir (no air bubbles entering the reservoir via the sample line). If water flows or PG escapes, then the valves are not sealing (insufficient plunger tension on the pinch valve tubing). Pinch valve tension can be increased by slowly turning the Allen screw on the rear of the valve from 1/4 to 2 full turns clockwise (seen from the rear) until the tubing seals, but do not overtighten and damage the valve. This adjustment can also be made for any other valve using Option 14 above. With use, PV tension will decrease, and decreased tension on PV 4 could affect the

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volume of water output by the pipette. If adjusting the Allen screw does not correct the problem, replace the PV.

Option 16 displays the temperature sensor readings in °C on the video monitor. The readings will be updated every 30 seconds until you hit the letter M on the keyboard. The latter action causes the sensors to be read one more time and returns the program to the Options Menu (Option 16 is a quick way of checking the function of the AD board and interface).

Option 17 (with sample bottle in place) fills and empties the pipette the number of times you specify when prompted (the number of rinse cycles should be consistent with the volume of the sample bottle). The contents of the pipette are discharged into the waste line. This is used for cleaning the pipette.

Option 18 allows an annotated record of analytical history to be written to the line printer and disk without having to terminate and restart the program. Three entries of 80 characters can be entered each time Option 18 is exercised. The date and time of the annotation are also recorded.

3.9 Preparation of SOMMA for Transit and Storage

The SOMMA chassis comes with a custom-made wooden shipping crate and base. The chassis may be left on its wooden base, but at sea, the wooden base is used to secure the chassis to laboratory benches. The remaining components, computer, printer, coulometer, etc should be rack-mounted at the user's discretion.

To ship the SOMMA chassis:

1. Secure the chassis to the wooden base with wood screws at the corners of the chassis. Secure all sector floor plates (small nonbreakable components, fittings, etc., can be stored under the floor plates).

2. Empty the acid bottle and sample bath. Store the reagent bottle, and spare tubing in the sample bath. Drain the sample bath and pipette jackets.
3. Install the protective shield^(a) in Sector IV (you may remove the stripper first, but if you do, tape the condenser to the brackets that hold stripper so that it won't flop around during shipping).
4. Loosen the brackets holding the pipette, but leave the pipette in place. Leaving the brackets tight could increase the possibility of shock damage.
5. Stuff foam between the glassware and the chassis walls and between the protective shield and the glassware.
6. Pull the pinch valve tubing free of the normally closed ports on PVs 0, 1, 2, 3, 5, 6, and 9 to avoid crimping during shipping or storage. When the acid bottle has been disconnected, pull the PV tubing from PV 8. Leave the tubing in place on PV 4 so as not to risk changing the calibrated "TO DELIVER" volume of the pipette.
7. Place all front panel toggle valves in the OFF position (handles down), and ensure that the vernier handles of needle valves will be cleared by the instrument cover. Disconnect the gas services and cap the gas service inlets.
8. With help from a friend, place the instrument cover over the chassis and secure the cover with the wood screws provided.

^(a) Newer units do not have a plastic shield, but are equipped with a permanent stainless steel "face guard" to protect the glassware components.

SYSTEM OPERATIONS 4

The primary function of the SOMMA - Coulometer System is to analyze discrete water samples for total carbon dioxide (C_T). Samples should be collected in accordance with the procedures given in the DOE Handbook.

When used with the SOMMA system, the coulometer is operated in the counts mode. This mode uses the coulometer voltage to frequency converter (VFC) output and constants supplied by the user, via the SOMMA software, to calculate $\mu\text{mol C}$ titrated.

4.1 COULOMETER CONSTANTS AND GENERAL RECOMMENDATIONS

There are scaling factors hard-wired into the coulometer for processing the raw data (pulses) coming from the VFC which may or may not be correct or current. In the SOMMA program all of the scaling is done in the software so that the scaling factors are known to, or changeable by, the user. For example, SOMMA uses a molecular weight of carbon of 12.01115 (98.892% ^{12}C and 1.108% ^{13}C), and a Faraday of 96489 Coulombs mol^{-1} . Additionally, more significant figures are lost with hard-wired scaling than with program scaling so program scaling increases sensitivity. Assumptions used in the SOMMA program are:

$$1 \text{ Ampere (amp)} = 1 \text{ Coulomb sec}^{-1}$$

$$1 \text{ Faraday (F)} = 96489 \text{ Coulomb mol}^{-1}$$

then:

$$200 \text{ ma} = 0.200 \text{ amp} = 0.200 \text{ Coulomb sec}^{-1}$$

The Coulometer is nominally calibrated to produce 10,000 counts sec^{-1} at a current of 200 ma

Computing mol sec^{-1} :

$$\frac{0.200 \text{ Coulombs sec}^{-1}}{96489 \text{ Coulombs mol}^{-1}} = 0.200/96489 = 2.07300 \times 10^{-6} \text{ mol sec}^{-1}$$

Computing counts mol⁻¹:

$$\frac{10000 \text{ counts sec}^{-1}}{2.07300 \times 10^{-6} \text{ mol sec}^{-1}} = 4.82445 \times 10^9 \text{ counts mol}^{-1}$$

Or:

$$4.82445 \times 10^3 \text{ counts } \mu\text{mol}^{-1}$$

Computing counts $\mu\text{g C}^{-1}$:

$$\frac{4.82445 \times 10^3}{12.01115} = 401.664 \text{ counts } \mu\text{g C}^{-1}$$

Recommendations for Sample Analysis

1. Use and calibrate the pipette at 20°C (preferably the same temperature). Keeping the pipette cool prevents the loss of CO₂, but it is permissible to have the pipette somewhat warmer than the coldest samples. Pipette temperatures 25°C will lead to rapid loss of CO₂. We usually store samples at or very near the pipette temperature, and let them come to thermal equilibrium before analysis.
2. As per the DOE Handbook, HgCl₂ must be immediately added to all samples upon collection.

4.2 SYSTEM STARTUP

It is recommended that the following sequence of procedures be completed (with the SOMMA program loaded) at the beginning of each day of SOMMA operations.

1. Check and reset gas services as necessary (see Section 3.4.1).
2. Ensure that the condenser is properly seated (gas-tight) on the stripper.
3. Renew the glass wool and perchlorate in the drying tube adapter. Reseat and ensure gas-tightness.
4. Install a fresh Silica Gel absorbent tube.
5. Attach dry CG line with hardware to the drying tubes, connect to the cell cap with Ultra-Torr union provided, and ensure gas-tightness at all connections.
6. Prepare the cell according to the Coulometer Instruction Manual.
7. Install the cell making sure that the cell cap is absolutely gas-tight (there are now several versions of caps available). For each installation, the platinum electrode should be located in the same position relative to the photodetector. We have had good results with the electrode positioned in the northwest quadrant (as seen from the top - upper left quadrant formed by imaginary vertical and horizontal lines intersecting at the center of the cell cap), and with the electrode as close to the photodetector without obstructing the light beam.
8. Adjust 100% T readout to 100 and turn the cell ON.
9. Run program, reset TCT (see Section 3.8), and use the Options Menu for the following steps.
10. Check function of the AD board by running Option 16 which reads the temperature sensors, and ensure the sensors are giving proper values compared to a mercury thermometer.
11. Operate PV 8 and add acid to the stripper using Option 14. Repeat until acid is observed flowing into the stripper. Immediately after checking PV 8, cycle GSV 12 several times to ensure that the rotor is seated.
12. With a sample bottle connected to the SOMMA, the liquid handling operations can be checked using Options 7 (Fill the Pipette), 8 (Empty Pipette), and 6 (Drain the Stripper) in that order. Correct malfunctions should they occur.
13. If necessary, annotate your record using Option 18.

14. Determine Blank using either Option 2 or Option 3 (see Section 3.8 for explanation).
15. Run two (2) replicates of a "junk" water sample (leftover CRM standard water from the previous day) using Option 1. Proceed if difference $1.5 \mu\text{mol}$.
16. Run gas calibration (Option 4) until a successful result is obtained (see Section 3.4.1).
17. Run samples in accordance with DOE Handbook starting with a CRM Standard water sample, and if satisfactory proceed to water samples (see Section 3.3).
18. At the end of the day, run a second CRM water standard.

4.2.1 Explanation of the Analysis Printout (Hardcopy)

The data diskette will contain the identical information as that on the analysis printout. In the example shown in Figure 10, a header supplies the ancillary data (pipette temperature, ANAL TEMP; salinity, SALNTY; the salinity of the previous sample, or water with which the pipette was filled, LAST SALNTY; sample density, SPL DENSITY; the "TO DELIVER" volume of the pipette corrected for temperature and salinity, PIPET VOL). Next, the headspace gas concentration and the volume correction factor (VCF) where:

$$\text{VCF} = 1000 / (\text{DENSITY} * \text{PIPET VOL})$$

and the duration of the rinse cycle are printed out. The system pauses to ensure that any CO_2 added by the rinse cycle or injection of acid to the stripper is titrated before analyzing the first replicate. The time course of the titration is shown followed by the results expressed as μmol titrated ($\mu\text{mols TITRT}$) at the endpoint (the output of the pipette) and as $\mu\text{mol kg}^{-1}$ (the final sample concentration) from:

$$\mu\text{mols TITRT} = \text{COULMTR} / 4824.45 - \text{BLNK} - (\text{IFLOW} * \text{ECALINT}) / \text{ECALSLOPE}$$

and:

$$\mu\text{MOL} / \text{KG (sample concentration)} = \mu\text{mols TITRT} * \text{GAS CAL'IB FACTOR} * \text{VCF}$$

where IFLOW is the duration (min.) of significant current flow (2000 counts min⁻¹). The spent sample is drained, and when more than one replicate is specified a fresh aliquot of acid is injected into the stripper. There is a short pause to clear the system before the second (third, etc.) replicate is analyzed. The routine terminates with a statistical analysis of the results.

4.2.2 End Point Algorithm

In the GWBASIC version of the program, the end point determination begins at statement 16000. The subroutine is set up so that the duration of the titration can not be less than 8 minutes nor more than 20 minutes. During the coulometric titration the coulometer is read every minute. The minute-to-minute increment in μmol titrated is calculated, displayed, and compared to the variable BLNKPMIN ($\mu\text{mol min}^{-1}$). If the increment is less than or equal to the variable BLNKPMIN, the variable TAIL is incremented by one (1). If the increment is zero, the variable SUCCRDNG is incremented by one (1). The endpoint is attained when

$$\text{TAIL} + \text{SUCCRDNG} = 4$$

Experience shows that this usually occurs between 9 and 13 minutes. If it occurs before 8 minutes, additional reading(s) will be made until 8 minutes have elapsed. After 20 minutes without an end point, the message:

END POINT ROUTINE TERMINATION AFTER 20 MIN. LIMIT

CAUTION

CALCULATED RESULTS NOT NECESSARILY VALID

will be displayed, but the calculations will be completed before the subroutine returns. An example of the end point printout is shown in Figure 10.

-NOTE-

The coulometer used was almost perfectly calibrated at the factory (ECALSLOPE - 1.000046 and ECALINT = 0.000415).

System Operations

ANALYSIS OF SAMPLE

THE CALIBRATED PIPETTE VOL = 28.7108 AT 20 DEG C
LAST SALNTY SALNTY AMAL TEMP SPL DENSITY PIPET VOL
34.9 34.9 10.02 1.026871 28.70801

THE HEADSPACE GAS = 351 PPM
THE VOLUME CORRECTION FACTOR = 33.92198
RINSING SEQUENCE START AT 06:37:45 END AT 06:39:31

FOR REPLICATE 1

SYSTEM CLEAR AND OPERATIONAL CHECK CALLED
AT 0 MIN. THE COUNTR = 75
AT 1 MIN. THE COUNTR = 2206
AT 2 MIN. THE COUNTR = 2260
AT 3 MIN. THE COUNTR = 2260
SYSTEM IS CLEAR OF CO2 AND OPERATIONAL -- CONTINUE

*** END POINT ROUTINE CALLED at 06:45:00 ***

AT 1 MIN. THE COUNTR = 20553 AT 27.7 C
TITRATION STARTING AT 1 MIN.
AT 2 MIN. THE COUNTR = 193801
AT 3 MIN. THE COUNTR = 292013
AT 4 MIN. THE COUNTR = 300445
AT 5 MIN. THE COUNTR = 301089
AT 6 MIN. THE COUNTR = 301121
AT 7 MIN. THE COUNTR = 301128
AT 8 MIN. THE COUNTR = 301128
AT 9 MIN. THE COUNTR = 301133
AT 10 MIN. THE COUNTR = 301133
AT 06:54:29 ZEROS = 2 BLKS = 2
ECAL SLOPE & INTERCEPT(4) MIN 1.000046 4.151985E-04

GAS CALIB FACTOR = 1.002843 (AGREEMENT = .3734662 Z)
BLNK(UMOL / MIN) AND TCT TITR(mg C) = 2.901885E-03 11.33577
uols TITRT. CORRECTED FOR BLNK. + ELEC. CALIB. 62.38455
2122.224 UMOL / KG

FOR REPLICATE 2

PAUSE BEFORE PROCEEDING TO ENSURE SYSTEM STABILITY
AT 1 MIN. THE COUNTR = 131
AT 2 MIN. THE COUNTR = 144
OK TO CONTINUE INCREMENT < BLNK

*** END POINT ROUTINE CALLED at 06:59:52 ***

AT 1 MIN. THE COUNTR = 19602
TITRATION STARTING AT 1 MIN.
AT 2 MIN. THE COUNTR = 192681
AT 3 MIN. THE COUNTR = 291594
AT 4 MIN. THE COUNTR = 300355
AT 5 MIN. THE COUNTR = 301070
AT 6 MIN. THE COUNTR = 301107
AT 7 MIN. THE COUNTR = 301107
AT 8 MIN. THE COUNTR = 301107
AT 9 MIN. THE COUNTR = 301107
AT 10 MIN. THE COUNTR = 301107
AT 07:09:21 ZEROS = 4 BLKS = 0
ECAL SLOPE & INTERCEPT(4) MIN 1.000046 4.151985E-04
GAS CALIB FACTOR = 1.002843 (AGREEMENT = .3734662 Z)
BLNK(UMOL / MIN) AND TCT TITR(mg C) = 2.901885E-03 12.08592
uols TITRT. CORRECTED FOR BLNK. + ELEC. CALIB. 62.37916
2122.04 UMOL / KG

THE SAMPLE STATISTICS

THE MEAN TCO2 = 2122.132 UMOL/KG FOR 2 REPLICATES
THE STD DEV = .1296478
THE STD ERR = 9.167481E-02
REL STD DEV = 6.109316E-03

Figure 10. A Hardcopy Analysis Printout

This algorithm also provides for departures from the theoretical response of the coulometer calibration resistor in the voltage to frequency circuit using the variables ECALSLOPE and ECALINT measured in the electronic calibration procedure. However, most instrument recipients will not routinely measure these coefficients (for DOE recipients, measurements were made at BNL and entered on the certification document). Assuming the electronic calibration procedure is not used, initializing the file ECAL.INI gives the variable ECALSLOPE the value of 1.0, and ECALINT the value of 0. In other words, no electronic deviation from theory is assumed, and the variable COULRDNG will not be altered when the electronic correction is applied. When and if the user adds electronic calibration, the coefficients will be written to the file ECAL.INI and applied, without software alterations, to correct COULRDNG.

4.2.3 Recommended Options

As noted above, it is recommended that Options 2 (or 3, as appropriate) and 4 be run prior to running a sample analysis. In addition, Option 11, Determining the TO DELIVER Volume of the SOMMA pipette, is recommended if conditions permit. These three options are detailed below.

Option 11. Determining the TO DELIVER Volume of the SOMMA Pipette

The volume output by the SOMMA pipette must be gravimetrically determined with great accuracy using a scale capable of weighing to 0.1 mg. Option 11 software performs the manual manipulations for determining volume, and calculates the TO DELIVER volume at temperature and salinity after correcting for buoyancy. The temperature of the water-jacketed pipette is adjustable with a thermostatted bath, but the calibration temperature should be at or near the actual measurement temperature and in no case should either temperature exceed 20°C. Distilled 18-mohm water in 300 or 500 mL bottles should be used as the calibration fluid. Degassing of the fluid can be done by sparging with He, and He may be used as the headspace gas during the calibration procedure.

Place a bottle of 18-mohm water in the sample bath in Sector I, connect it to the SOMMA pipette with the special stopper and clamp provided, and let it come to thermal equilibrium. Ready the following materials:

Aluminum foil pieces cut into 2-in. squares
60 mL serum bottles
stoppers
seals

Weigh 60 mL serum bottles with rubber stoppers, seals, and foil when at thermal equilibrium with the scale. Number them with a diamond pencil or felt pen for reference.

Consult Figure 3 and complete the following operations:

1. Remove the screws in Sector IV (Figure 2) securing the protective shield (if present) and flooring, and set these pieces aside.
2. Turn the three-way stopcock on the drain line until the drain line seals. Pull the drain pinch valve tubing from PV 9.
3. At the union connectors provided, disconnect the ACG, Acid, and Waste lines from the stripper. Do not spill acid on any of the solenoid valves. Wipe acid spills immediately.
4. Lift the condenser away from the stripper. It will be supported by its coolant lines.
5. Completely loosen the 1/16-in. nylon nut securing the sample inlet tube at the BT nylon union (this nut should be finger tight).
6. Remove the springs securing the stripper, and carefully pull the stripper away from its mounting brackets (Note: the carrier gas line connecting the GSV and the stripper usually has enough slack in it so that it need not be disconnected). As the stripper comes away from its brackets, the sample inlet tube will withdraw from the central inlet tube. Keep the stripper low with respect to the pipette, and continue to pull it toward you until the inlet tube is completely free. Set the stripper to one side.

7. Position the sample inlet tube so that it will discharge into a waste beaker. Put on a pair of disposable plastic gloves to avoid finger prints during the procedure. Select Option 11 from the Option Menu. The screen will clear and display:

CALCULATIONS OR CALIBRATION RUN ?

TYPE IN DESIRED OPTION CALC OR CALIB

If you type CALC, the buoyancy corrections for data inputted from the keyboard (follow the prompts for data inputs) will be made, but no physical manipulations will be done. Buoyancy corrections can be made for either pipette or gas loop calibration data. For CALC, the calibration temperature, tare weight, and the total weight in grams are needed. Typing CALIB will initiate the calibration procedure with the prompt:

THE CALIBRATION FLUID SALINITY ?

Inputting salinity (the PC automatically reads the pipette temperature) causes the prompt:

THE BOTTLE NO. ?

After this input, the pipette will be rinsed and filled with the calibration fluid (takes about 1.5 minutes). When this operation is complete the PC will BEEP and repeatedly display:

PLACE THE TEFLON SAMPLE INLET TUBE IN THE SERUM
BOTTLE NOW

At this point, tightly cover the mouth of the serum bottle with a preweighed foil square, dry the exterior surface of the sample inlet tube and insert it through the foil into the serum bottle. Place the serum bottle on the lower stripper bracket. Note that the pipette is now refilling. When the PC senses through the liquid level sensor that it is full, its contents will be injected into the serum bottle. When the monitor displays:

THE OUTPUT FROM THE PIPETTE HAS BEEN COLLECTED
tap the sample inlet tube and rub it on the foil cover to knock off surface droplets, and slowly withdraw it from the serum bottle. Crumple the foil, deposit it into the bottle and immediately stopper the bottle. Ideally, it should be reweighed at

this point. The prompts will continue with:

STRIKE RETURN (ENTER) TO RETURN TO THE MENU --
OTHERWISE

If you cannot weigh at this time, RETURN will get you back to the Menu. Seal and store the samples as described in the Checking procedure in Section 4.2.3.

ENTER TARE (EMPTY BOTTLE, STOPPER, FOIL) WEIGHT ?
followed by:

ENTER THE FILLED (TOTAL) BOTTLE WEIGHT ?

Inputting causes the PC to calculate the weight difference in air between the full (total) and empty (tare) serum bottle (W_{air}), and to correct the apparent weight to the mass in vacuo (M_{vac}) from:

$$M_{vac} = W_{air} + W_{air} (.0012 / d - .0012 / 8.0)$$

where .0012 is the density of air at 1 atm at sea level, d is the density of the calibration fluid at the pipette temperature, and 8.0 is the density of the brass weights in the scale. The "TO DELIVER" volume of the pipette (VP) at the calibrating fluid salinity and pipette temperature (TCAL) is:

$$VP = M_{vac} / d.$$

Consult the hardcopy for the results. By now the PC will have returned to the Menu, and you can repeat Option 11 for replicate determinations. The variables VP and TCAL are input through Option 5.

Reinstall the sample inlet tube, stripper, condenser, protective shield, and the Sector IV floor in that order. Ensure that all connections are tight, and that the drain pinch valve tubing is seated in PV 9 with the plastic three-way stopcock opened to the system drain.

Handling Serum Bottles at Sea

This procedure (Determination of the TO DELIVER Volume) requires an accurate (0.1 mg) weighing of serum bottles; however, this is rarely possible aboard ship. If serum bottles cannot be weighed when filled, they must be crimp sealed and stored until weighed on shore. This requires aluminum seals (20 mm) and a crimper. The seal should be included when the tare weight is determined. Checking provides a gravimetric record of the pipette performance during periods when the SOMMA is away from the laboratory, or when immediate weighing is otherwise inconvenient.

Option 2. Determining the Blank Following the Titration of Residual CO₂

The small system blank with the coulometric dynamic headspace method may be due to traces of CO₂ in the carrier gas, diffusion across or acid species leaching from the cell frit, and contamination from the cell stopper. Indeed, a small blank can be measured even if the coulometer cell is isolated. The system blank should not exceed 0.1 $\mu\text{g C min}^{-1}$, and is normally 0.05 $\mu\text{g C min}^{-1}$, which in the counts mode translates to approximately 200 counts 10 min⁻¹ or 0.004 $\mu\text{mol min}^{-1}$. With Option 2, the coulometer is zeroed, but the blank is not determined until the display is > 0, or until 5 minutes have elapsed. This ensures that the cell temperature is stable and the coulometer solution is exactly at the optical end point for the blank determination. A low blank is the normal condition and does not compromise the method. Experience shows that a low initial blank should not be changed or redetermined in that run. Occasionally, contamination of the cell solution (e.g., H₂S or other acid species from the stripper) will increase the blank. This can be remedied by waiting until the blank returns to normal (if the contamination is not too large) or changing cells.

Exercising Option 2 each time a new cell is installed from the Menu calls a subroutine beginning at statement 3000. There is a 10-minute delay option in the software to allow for the completion of the residual CO₂ titration (usual practice

is to exercise Option 2 and the delay after the solution turns blue following startup). The video display is:

BLK WILL BE DETERMINED AFTER A 10 MIN. DELAY IF D
IS ENTERED

If RETURN is struck, the blank determination will be immediate; however, with or without the 10-min. delay, a fresh aliquot of acid will be added to the stripper and the video screen will display:

BLANK DETERMINATION

THE DATE IS ----- THE TIME IS -----

BLNK PROCEDURE WAITING 75 SECONDS AFTER ACID ADDITION

Following the 75-second delay the coulometer is reset and the display shows:

LOOKING FOR THE END POINT BEFORE DETERMINING THE
BLANK

When a positive reading is acquired or 5 minutes elapses without incrementing the display shows:

STARTING BLANK MEASUREMENT

The coulometer is read and the video display is updated every minute for 10 minutes. If the count exceeds 200 after 10 minutes or 150 after 5 minutes, CO₂ from the large gas-sample loop will be injected into the cell and titrated, and the blank redetermined (the screen and hardcopy will be annotated when this occurs). If too high, a second shot of CO₂ will be injected, and the blank redetermined. If still too high, a fourth blank determination will be made, but without a prior injection of CO₂. After each blank determination, the result will be assigned to the variable BLNKPMIN ($\mu\text{mol min}^{-1}$) printed, and placed in the file BLNK.INI.

If after four (4) attempts the blank is still too high, the program will return to the Options Menu. The operator can choose to run another series of blanks, use the current blank contained in the file BLANK.INI, or change to a new cell.

Precautions and Procedures for a Low System Blank

The following recommendations assume that you are using a cell cap of rubber, and that the cell has a sidearm anode chamber:

1. The CO₂ trap installed on the CG source must be gas-tight, and the trapping reagent must be viable.
2. Use UHP (99.999%) grade N₂ for the PG and CG sources.
3. Ensure that the analytical plumbing is gas-tight and correctly installed with the Ultra-Torr nuts finger tight, and that the glass-to-glass fittings are lightly greased and securely seated.
4. Renew the analytical line silica gel trap daily. Install a silica gel trap in the CG line between the CO₂ trap and the SOMMA chassis.
5. After use, the main and anode cell chambers should be well rinsed with reagent grade acetone or distilled water. Fill the anode sidearm with acetone or distilled water and let it drain through the glass frit under gravity at room temperature for at least 6 h (overnight is better). Decant the remaining solution from the cell and dry it overnight at 55°C.
6. After use, thoroughly wash both sides of the rubber stopper, platinum electrode, stir bar, and the silver electrode with distilled water. Pass a stream of distilled water through the vent in the stopper and through the teflon input tube. Blow out the input tube and vent, and shake the cell assembly dry. Dry these components overnight at 55°C.
7. Before installing the rubber cell stopper, pass a dry pipe cleaner through the vent hole in the stopper, and ensure that the inner surfaces of the cell input tube are completely dry.
8. Use a very high grade phosphoric acid (ULTREX, J. T. Baker). Sparge the acid solution made from it with N₂.

-CAUTION-

Acetone is highly flammable!

Option 4. Gas Calibration

Option 4 from the Menu calls the gas calibration subroutine beginning at statement 4000. It is recommended that gas calibration be run after replenishment of the

coulometer cell solution. Two (2) stainless steel (SS) sample loops will be successively filled with pure CO₂, purged, and titrated. From the temperature of the loops (obtained through the AD board) the instantaneous barometric pressure, and the volume of the loops, the mass of CO₂ in μmol will be calculated (see DOE Handbook) and compared to the titrated result. The ratio:

$$\frac{\mu\text{mol calculated}}{\mu\text{mol titrated}}$$

is called the calibration factor (CALFAC). The loop calibration factors should agree to 0.10% or better. The mean of the two calibration factors is assigned to the variable CALFAC and written to the file GASCAL.INI. The variable CALFAC is used to correct the sample titrations for losses during gas extraction and titration. In the SOMMA, the calibration gas follows the same path as the CO₂ stripped from seawater samples, and CALFAC has been shown to be a valid correction for the sample titrations, i.e., sample and gas recoveries are closely coupled. However, experience suggests that the same convention adopted for the blank (BLNKPMIN) applies to CALFAC. Do not change CALFAC until you change the cell. Automatic recalibrations after 15 and 30 mg C have been titrated are built into the software, but the results are not used in subsequent calculations. They are saved for later reference. A CALFAC cannot be changed unless you initiate a calibration from the Menu or input a new value through Option 5 of the Menu.

Option 4 will display:

CO₂ GAS CALIBRATION

THE VOLUME OF THE SMALL LOOP IS — ML

THE VOLUME OF THE LARGER LOOP IS — ML

This gives you the current values VSMLOOP and VLGLOOP stored in the file VOLUMES.INI. There will be a system clear check before you are prompted:

BAROMETRIC PRESSURE IN MBAR ?

Valves opening and closing are audible as the loops are filled, purged, and titrated. The results and calculations will be displayed on the video monitor, printed, and written to disk. The above procedure including the prompt for barometric pressure will be repeated for the smaller sample loop. When the two loops have been analyzed, the message:

GAS CALIBRATION COMPLETED
CALFACTOR = _____ RUN AGREEMENT = ____ %

will display. The variable CALFAC will be input to file GASCAL.INI and used in subsequent calculations. If the loop disagreement is greater than 0.1 %, Option 4 can be run again.

There is a pause between the completion of the large loop run and the small loop run to ensure that the system is clear of CO₂ before loading the small loop. Normally, this pause takes between 1 and 2 minutes, but a maximum time of 6 minutes is allowed by the software. If the system does not stabilize in 6 minutes the following message will display:

WARNING SYSTEM UNSTABLE - BACK TO MENU

and the calibration routine will be terminated and the Menu displayed. The user will have to make a decision as to whether the problem is temporary, or whether the GSV has failed (loose rotor, leak, or scratched valve surface). To assist in this decision the user can exercise Option 14, cycle the GSV between "load" and "inject" several times, and then use Option 3 to observe the coulometer readings until the system stabilizes or until it is clear that there is a continuing problem which requires corrective action.

The software for gas calibration assumes that a stand-alone barometer is used. A program (SOMMA 1.1) does exit for users who incorporate the barometer into the SOMMA and interface it with their PC. Contact the BNL CO₂ Group for details.

4.3 ANALYZING A SAMPLE (Option 1)

With the System Start Up procedures taken care of and the necessary options run, the sample analysis routine can now be performed. The analysis begins by placing a sample bottle in the sample bath located in Sector I (see Figure 3) of the SOMMA chassis. The bottle is connected to the plumbing using the silicone stopper and a modified Millipore clamp. Option 1 from the Menu is exercised causing the screen to clear and display:

/////////THE SAMPLE ANALYSIS ROUTINE/////////

prompts asking for the sample identification:

ENTER THE WORD -- CRM -- FOR REFERENCE WATER

ENTER THE WORD -- TEST -- FOR JUNK OR TEST SAMPLE

OTHERWISE HIT RETURN

then prompts for additional identification depending on sample type:

SAMPLE ID ? (80 Characters)

or

THE CRM BOTTLE NUMBER ?

sample salinity:

SALINITY ?

headspace gas in ppm:

THE HEADSPACE GAS IN PPM ?

the number of replicates:

NO. OF REPLICATES ?

The screen clears and the analysis of the sample begins. This is signaled by the display:

RINSING SEQUENCE START AT (TIME)

The pipette and lines to the pipette will be automatically rinsed. The pipette will be double rinsed if the previously analyzed sample's salinity differs by more than 10% from the current salinity input above. This involves the variable PRESAL

which is stored in the file SAL.INI. When rinsing is finished the video display is:

RINSING SEQUENCE ENDED AT (TIME)

At this point, the stripper will be drained, acid injected into the stripper and the:

SYSTEM CLEAR AND OPERATION CHECK

called. Upon completion, the pipette will be filled, its contents injected into the stripper, acidified and the resultant CO_2 titrated. The endpoint will be determined using the end point algorithm. The result is corrected for CALFAC and the "TO DELIVER" pipette volume is corrected for temperature and salinity. From these data, the sample concentration in $\mu\text{mol kg}^{-1}$, is calculated, printed and saved. If two or more replicates are run, the last replicate will be followed by statistical analysis. When the analysis is finished, the status of TCT will be checked, and if indicated, a gas calibration run will be done before the program returns to the Menu.

4.4 SHUT DOWN

The recommended shut down procedure includes, but is not necessarily limited to the following steps:

1. Turn OFF the cell current, but leave the coulometer main power ON.
2. Remove the cell, and with the CG line still connected carefully remove the cell cap.
3. Wash and dry the cell and cell cap assembly as described in Section 4.2.3.
4. Disconnect the analytical line and hardware from the drying tube adapter assembly, and dry at 55°C . Wash and dry the drying tube adapter.
5. Remove the floppy disk from the A drive. The PC can be left ON, and the relay module board and GSV can be left connected to the mains.
6. Place a BOD bottle in the sample bath, connect it to the system, and fill the pipette with distilled water.

System Operations

7. Leave the condenser in place, but drain the stripper (if not already empty) and add a fresh aliquot of acid to the stripper with the MCG flowing (acid aerosols keep the inner surfaces of the condenser acidified).
8. The MCG flow can be turned down to conserve the gas supply. For prolonged shut downs the front toggle valves or cylinder regulators can be closed.
9. Collect and store hardcopy.

APPENDIX A SOURCES OF SUPPLIES

Pinch and Isolation Valves

To obtain the valves listed in Table 1, contact the supplier listed below.

Bio-Chem Valve Corporation
85 Fulton Street
Bconton, NJ 07005
Telephone (201) 263-3001 (ask for John Lawrence)

Glassware Components

To obtain the Glassware Components detailed in Section 3.3 contact:

Gerhardt Finkenbeiner, Inc.
33 Rumford Avenue
Waltham, MA 02154
Telephone (617) 899-3138 (ask for Don Sellars)
Fax (617) 647-4044

Electronic Hardware

Relay Modules

Additional Relay Modules, described in Section 3.4.1, can be purchased from Newark Electronics. These are expendable items, and spares should be purchased. Refer to Table 2 for part numbers.

Newark Electronics
500 Palaski Road
Chicago, IL 60624
Telephone (312) 785-5100

Computer Interface Boards

You can purchase additional Computer Interface Boards, described in Section 3.4.1, through Real Time Devices, Inc.

Real Time Devices, Inc.
P.O. Box 906
State College, PA 16804
Telephone (814) 234-8087

Questions concerning SOMMA electronics or purchasing additional supplies should be addressed to:

The BNL CO₂ Group
Attn: K. M. Johnson or D. Wallace
OASD, Building 318
Upton, NY 11973
Telephone
Fax (516) 282-2060

Gas Purification and Scrubbing Components

As described in Figure 7, the gas purification and scrubbing components of the SOMMA can be purchased through the following vendors.

Dehydrite (#C260-M61)

Thomas Scientific

Acid Treated Glass Wool

Supelco, Inc.
Bellefonte, PA 16823

Silica Gel

Activated Silica Gel, ORBO - 53 (#2-0265M). This item is a custom order. It should be ordered packed in unsealed tubes 4 x 1/4" (normally comes in sealed tubes of 6 mm o. d.). See Section 3.2.2 for further information.

Supelco, Inc.
Bellefonte, PA 16823

APPENDIX B THE SOMMA TEMPERATURE SENSOR AND CALIBRATION

The temperature sensors are semiconductor devices designed to produce a voltage linearly proportional to the temperature of the device. This voltage is measured by the AD board without additional circuitry. Two types of sensors are available. The first produces a voltage output of 10 mV /° C, and the second an output of 10 mV /° F. The Fahrenheit device has been chosen for SOMMA because it allows the use of a greater portion of the AD board's full scale voltage and increases the number of significant figures available for the measurement of temperature. By convention:

Temperature Sensor 1 is affixed to the pipette

Temperature Sensors 2 and 3 are affixed to the large and small gas sample loops, respectively.

The sensors are supplied by National Semiconductor (Model LM34CH) with the following specifications:

1. Operating range - 50°F to + 300 °F
2. Linearity 0.4°F over entire range
3. Untrimmed accuracy 0.8°F
4. Self-heating in still air 0.18°F
5. Long term stability 0.16°F

By calibrating the sensors and the digital output of the AD board against a certified thermometer, the accuracy of the measurement can be brought to 0.1°C. The sensors are calibrated in the following manner:

1. For stability, the sensors and the AD boards are burned in under power for 96 h prior to the calibration.
2. The sensors are mated with their AD channels prior to calibration, and once calibrated they should not be switched to another channel. If the cables or the AD board are replaced, the sensors must be recalibrated.

3. For minimum nonlinearity, the sensors are calibrated over a restricted temperature range (For SOMMA 10.0 - 30.0°C).
4. For elimination of self-heating errors, the sensors are calibrated in thermal contact with a heat conductive medium. The actual sensor case is hermetically sealed and can in theory be immersed. However, the wiring to the sensor is not adequately protected for immersion. The sensors can be calibrated by immersing them in a vessel of small aluminum pellets (1mm dia.). The vessel is placed in a water bath and allowed to come to thermal equilibrium with the bath. A certified thermometer provides the calibration temperature, and the A / D board gives a digital reading for that temperature. The SOMMA diskette also comes with a program entitled TEMPCAL. Use it to calibrate or check the calibration of your sensors.
5. The calibration regression equation for each sensor is computed from these data and:

$$\text{Temp} = \text{Slope (AD reading)} + \text{Intercept}$$

Each sensor will have its own regression coefficients. In the GW BASIC version of the SOMMA program the sensors are read and the calibration coefficients are stored in a subroutine beginning at statement 40000.

CAUTION. When in actual use in the SOMMA, the sensors must be thermally bonded to the object whose temperature is to be measured. Otherwise the self-heating error may become significant. The insulation of GSV well in Sector II is left to the discretion of the user.

APPENDIX C FLOW METER CALIBRATION DATA

FLOWMETER CALIBRATION DATA																				
CUSTOMER			CUSTOMER ORDER NUMBER				DATE													
							03-31-1989													
TUBE NUMBER: A-125-3					METERED FLUID: NITROGEN															
FLOAT MATERIAL: CARBOLOY BALL					METERING TEMPERATURE: 70°F															
FLOAT DENSITY: 15.00 G/CC					METERING PRESSURE: 14.7 PSIA															
CURVE NUMBER: CD-2570					METERING DENSITY:															
UNITS: CC/MIN					METERING VISCOSITY:															
MILLIMETER ELEVATION			FLOW		MILLIMETER ELEVATION			FLOW		MILLIMETER ELEVATION			FLOW							
65.0			----		253.44		40.0			----		120.50		15.0			----		34.40	
64.0			----		247.94		39.0			----		115.78		14.0			----		32.37	
63.0			----		242.42		38.0			----		111.14		13.0			----		30.39	
62.0			----		236.89		37.0			----		106.57		12.0			----		28.44	
61.0			----		231.35		36.0			----		102.10		11.0			----		26.52	
60.0			----		225.81		35.0			----		97.71		10.0			----		24.62	
59.0			----		220.27		34.0			----		93.43		9.0			----		22.72	
58.0			----		214.73		33.0			----		89.24		8.0			----		20.80	
57.0			----		209.20		32.0			----		85.16		7.0			----		18.85	
56.0			----		203.68		31.0			----		81.20		6.0			----		16.87	
55.0			----		198.18		30.0			----		77.35		5.0			----		14.84	
54.0			----		192.70		29.0			----		73.63								
53.0			----		187.25		28.0			----		70.03								
52.0			----		181.83		27.0			----		66.56								
51.0			----		176.44		26.0			----		63.22								
50.0			----		171.10		25.0			----		59.99								
49.0			----		165.80		24.0			----		56.90								
48.0			----		160.54		23.0			----		53.93								
47.0			----		155.34		22.0			----		51.09								
46.0			----		150.18		21.0			----		48.38								
45.0			----		145.08		20.0			----		45.79								
44.0			----		140.04		19.0			----		43.31								
43.0			----		135.06		18.0			----		40.34								
42.0			----		130.14		17.0			----		38.67								
41.0			----		125.29		16.0			----		36.50								

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