Chemistry Lab CookBook
V 210.0

Instrument:

    Balances, GC's, ICP, Titrino, CHNS, Coulometer, IC

Documentation Available:

    All documents apply - see specific instrument cookbooks for specifics

Chem Lab, version v210.0

1. Instruments

Gas Chromatographs:

Both the GC3 and NGA chromatographs need to have directories set up for the leg. Go to File Manager and open the HPChem directory. Go to the GC3 or NGA directory. In both the Data, Method, and Sequence directories, create a Leg 1XX directory. Copy the method files (cal, drn, etc.) of the last method used from the previous Leg in the Methods directory. Then go to the HP Configuration Editor and select Path. To the usual data, method, and sequence path, add the Leg directory. For example, the data directory path for the GC3 on Leg 164 will read C:HPCHEM\GC3\DATA\LEG164, and the method directory path for the GC3 will read C:\HPCHEM\GC3\METHODS\LEG164. Save the new configuration.

Start GC3 and NGA from Chemstation. For GC3, go to Methods Menu and load the last method used; for example, GC3_167.M (in the subdirectory Leg 167), save it as GC3_168.mth. It will automatically be saved in the Leg 168 directory. Use that new method to recalibrate GC3.

For the NGA, proceed as above, but remember to edit the TCD method to change the second method name. For example, save the TCD167.M as TCD168.M, edit FID167.M and save it as FID168.M. Use these methods to recalibrate the NGA. Create a standard (STD) subdirectory in the Sample Info window. This is where the standards info will be stored.

NGA and GC3 Calibration Standards and Levels:

GC3 usually has at least four calibration points for ethane and ethylene (C2 and C2=), propane and propylene (C3 and C3=), and seven for methane (C1). NGA has as many as 8 levels for methane. Samples with high hydrocarbon levels (greater than C3) are injected in the NGA, so there are more calibration standards for this apparatus. In addition to the gases calibrated in the GC3, these gases are calibrated: IC4, NC4, IC5, NC5, IC6, NC6, and NC7.

The gas standards are listed as separate levels as such:

Std A	Level 1	(C1 = 19.9 ppm)
Std B	Level 2	(C1 = 1040 ppm)
Std C	Level 3	(C1 = 10,100 ppm)
Std D	Level 4	(C1 = 200,000 ppm)
Std 30%	Level 5	(C1 = 300,000 ppm)
Std 50%	Level 6	(C1 = 500,000 ppm)
Std 70%	Level 7	(C1 = 700,000 ppm)
Std 100	Level 8	(C1 = 100 ppm)

If there is the possibility of H_2S gas at a site or sites, some standards with various levels of H_2S will need to be calibrated and added to the method.

GC3 Calibration:

To recalibrate the GC, run 3 or 4 injections of a standard and print out the results. From the best three runs, select one run to be replaced by the actual calibration values and use the other two for

averaging. In the Data Analysis view load the signal that will be replaced, integrate it, then select "Calibrate/Recalibrate...". Select "Replace" in the Recalibrate field and make sure to select the correct level (ie. 1 through 7). Continue by loading the next run and selecting "Average" in the Recalibrate field. Do this once again with the final run. Continue with the other calibration levels in the same manner. All of the gases can be run at one time since the results are stored in memory.

NGA Calibration:
The NGA calibration is very much like the GC3 calibration. The main difference is that calibrations must be run for both detectors (the TCD and the FID). Proceed with the FID calibration on the NGA in the identical manner as the GC3 calibration, making sure to choose the "FID2B" signal when loading the signal. Proceed as above, replacing the signal then averaging until all the levels are calibrated. Once the FID is finished, repeat the above using the "TCD1A" signal from each run.

Dionex Ion Chromatograph:
Preparation of Eluents:
Eluent A is prepared by adding 20 ml of AS4 (hanging by the Dionex) to DI water in a 2000 ml flask. Fill flask to 2000 ml fill line. Place a filter (stored next to nanopure container) into the filter apparatus. Connect the vacuum pump (stored in the space to the left and below the Dionex, on the floor) to the apparatus. The filter apparatus can only hold 1000 ml at a time.
Eluent B is prepared by adding 2.6 ml MSA methane-sulfonic acid (stored in the Chem Lab acid locker) to DI water in a 2000 ml flask. Fill to 2000 ml fill line with nanopure water. Filter as described above.
Filtered water is prepared by pouring nanopure water through the filter apparatus, as described above.
Preparation of Standards:
IAPSO Seawater is used to prepare dilutions to be run as standards. Use the Hamilton Dilutor to prepare the dilutions. Calibration for anion analysis uses dilutions of 0% , 10%, 20%, 40%, 60%, 80%, and 100% of the IAPSO seawater. The calibration for cation analysis uses 0%, 20%, 40%, 60%, 80%, 100% and 120% dilutions of the IAPSO seawater.

Preparation of Samples:
The Hamilton Dilutor is used to prepare a 1:200 sample. It may be necessary to prime the Dilutor to clear any bubbles in the lines. Choose Program #1 for a 1:200 dilution. Pushing the button on the hand-held sampler will cause 5000 &l of filtered DI water to be taken into the left syringe. Wipe any water from the probe tip with a kim-wipe and insert the tip into the interstitial water in the plastic tube. Pushing the button for a second time aspirates (draws in) 50 &l of sample. Place the probe tip into the scintillation vial. The third push aspirates the 2 syringes (5050 &l total) into the vial. A fourth push fills the left syringe with 4950 &l of DI water. The fifth and final press will dispense the 4950 &l of DI water into the vial, resulting in a 1:200 dilution of sample. Repeat the above process with the remaining IW samples. Fill a 1.5 ml small glass vials with the standard, using a disposable transfer bulb-type pipette. Insert a septum

into the top and secure to the vial.

Setting up the Dionex run:
DIP Switches should be set as follows:
SW1   5 up
SW2   1-2 up; 3-8 down
SW3   1-3, 6 up; 4-5, 7-8 down
SW4   on
SW5   3 for cation, 2 for anion
Switch Nitrogen On and check that pressure at the cylinder regulator is between 90-110 psi. Turn System Power on and set Control System button to Local. Make sure the eluent and rinse bottles are full. Turn the N_2 switch on and regulate the pressure to 5-7 psi. Turn the Elu A/B-Rinse switch to Rinse. Open the bleed screw and turn on the pump. Leave the bleed screw open for about 30 seconds. The flow rates can be changed now, if needed. Cation runs require a flow rate of 165 or so, and the anion run should flow at about 74. Close the screw and let equilibrate for 10 minutes. Let the column rinse for 30 minutes or until the &S value is as low as possible. The pump pressure during a cation run should be about 1600-1700 psi (1700-1720, Leg 162) and the anion run should be about 1400-1600 psi (1320-1420, Leg 162).
Cell conductivities during the anion run should read about 1 &S for rinse water and 16 to 19 &S for Elu A. Cell conductivities during the cation run should read about 0.01 &S for rinse water and 0.1 &S for Elu B. Set the High-Limit switch to 2400 psi, the Low-Limit to Low On, the Range set to 30 &S, Pump switch On, Control to Relay, Sample to Load (always), and Offset to Off. The machine is ready to start.

Preparation of the Schedule and Method:
Load an old schedule and rename it as either ANxxx.SCH or CATxxx.SCH (xxx equals site). Name the data file CATxxx or Anxxx. From schedule to schedule, change the sample descriptions to state the current samples and the data field to state the current site. The injection volume, injections/vial, dilutions, and Int. Std. will remain the same.

Setting up the Software
Loading the Method:
First, load an old method and resave it as a new method, ie. load AN162.MET and resave it as AN164.MET. Exit the Method section back to the main menu. Under File open "Run AI-450 Accessory Programs...", them open "3500 Edit". The sample vials are "B" vials, and calibration vials are "A" vials. B01 is always a blank (BLANK), filled with DI water. Schedule two injections as BLANK. Next, run one injection of B01 as Autocal1R ("R" for replace, "A" for average). The next injection is B01 as Autocal1A. The six standards (vials A01-A06) are run next as Autocal2R, Autocal2A, Autocal3R, Autocal3A, etc, until ending with Autocal7A. There should be 15 lines in the schedule now. Run 2 injections of B01. The 17th injection should be A06, the 100% dilution of the IAPSO standard. Name this "28.9", the peak height of sulfate. The next vial to be injected should be the first sample, B02. Name it by the core, type and section. The A06 standard should be run about every 8 samples. Finish the run with 2 injections

of A06, then 2 B01 blanks. Save this schedule. To start the run select Start in the Run Menu of the Run window. During the calibration stage, check the calibration curve. The curve should be as close to 0.999 as possible. If individual points on the curve are obviously far off, these can be manually corrected. Go to the main Dionex menu and select Method. Load the appropriate method (Anxxx or CATxxx) and select Detector 1. Select Components, then select the component name that has the errant point. Select the individual level and replace the Area and Height average values with the values selected from the calibration run. Make sure and write down the old values in case the new values make a worse calibration curve. Once the values are replaced, exit the menu and save the new method. Check the Calplot again and note the new value of the calibration curve. Correction can be made up until the point that the unknown samples are run. Check the differences between peak heights for individual sulfates and chlorides. There shouldn't be more than a 2% difference or the injection should be rerun.

If there is a system crash or the batch crashes, go to File under Batch and "Build Batch Schedule". This goes to the Data File Selector. Find the data files needed from the numbers on the bad runs (ex. *.D19, *.D20, etc.). The schedule can be rebuilt with these numbers.

When the run is finished Close the Run window, turn relay to local, switch Low-Limit off, switch from Elu A to Rinse, open bleed valve (watch the pressure drop to zero), and prime for 5 minutes. Close the bleed valve, watch the pressure increase and switch to Low-Limit on once stable. Rinse for 1 hour, then shut off.

If the eluents need to be refilled during a run wait until the very beginning or end of the run to refill the bottle. Switch the N_2 off, open the pressurized bottle, fill it, close the bottle and switch the pressure back on.

Recalculating in Excel 5.0:
Select AI-450 Batch and open File: View Schedule. Open the appropriate file. Select the samples that are to be reprocessed (for example, skip the autocalibration standards and blanks). After selecting them, save the data and return to the Batch menu. Go to Option: Processing Options. Make sure the numbers to be reprocessed are listed. In Output options, clear all fields. In Update options, select only re-store data. Click OK and proceed to Export Options. Select Create Export option. Give the filename as C:\EXCEL\DXEXPORT\CA*SITE* or ..\AN*SITE*. This will create a .CVS file, readable in Excel. In Fields, select only Sample Name and Concentration. Return to the Batch menu and at Controls, select Start. When the Batch program is finished, close the application and open Excel 5.0. In Excel, open Dxexport and select CSV files. Open the file that was just made in the Dionex Batch program. Select all the number fields and decrease the decimal with the Decimal button. Abbreviate the chemical name to save space, ie. sodium becomes Na, Magnesium becomes Mg, etc. Now insert a blank column between B and C, C and D, etc (there will be 2 data rows and 2 average rows for anions and 4 data rows and 4 average rows for cations). The column next to each chemical data column should be named as the chemical average, as in "Na avg". After inserting the new columns for averages, the initial "average" cell can be selected with the "function" button. Select "average", then "finish". Delete the "number1, number2" from the description and enter; this gives an average value. Now select the average cell and the empty cell below it. With the cursor go to the lower right corner of the two selected cells and click and hold on the corner. Dragging the corner all the way

to the bottom of the averaged cells will repeat the averaging function for the entire column. Repeat for the other averaged columns. When saving the finished data sheet, select the "Microsoft Excel Workbook" choice, as that is the .XLS listing.

AA:

RockEval:
Running blanks:
Make sure the gases are turned on. Turn on RockEval. Using the "send" key, select the following:
INITIALIZATION = Y (SEND)
CLEAR RESULTS = Y (SEND)
DATE = Y (SEND)
TABLE RECAP = N (SEND)
LOG RECAP = N (SEND)
S3 ANALYSIS = Y (SEND)
CYCLE = select CYCLE1 (SEND)
CONTINUOUS = N (SEND)
TYPE = select BLANK (SEND)
PYROGRAM = Y (SEND)
CHART DRIVE = 1 (SEND)
SCALE = 1/32 (SEND)
OTHER STD = N (SEND)
SAMPLES DATA = N (SEND)
START = START
When the display reads "AWAITING SAMPLE", hit "START". Continue until the printout gives a C3 reading of 1500 or less. C1 and C2 should both be under 20.

Running the RockEval:
Weigh the samples with a 100 mg weight on the tare. The first standard should weigh *exactly* 100 mg, and the remaining samples should weigh as close to 100 mg as possible. The crucibles should be added to the boat from right to left, numerically increasing from right to left. Add crucibles to the boat with forceps.
Position of crucibles:
#1 and #2 are left empty (due to the bubble meter)
#3   Standard (55000)
#4   Blank (empty crucible)
#5   Check (55000)
#6+   Samples
Twenty crucibles can be run at a time.

Adding data to the RockEval:

At the "_**ROCK-EVAL**_" prompt, hit the SEND key until "CONTINUOUS?" comes up. Select CLEAR to erase, then SEND for "yes".
"LAST SAMPLE = " > requires the total of all samples and checks (not including standard and blank).
"TYPE OF RUN = " > CLEAR to erase, then hit the STANDARD button, then SEND.
"STD QTY = 100.0" > CLEAR, then enter the real value, then SEND.
"PYROGRAM = YES" > Continue to SEND until "OTHER STD?" comes up. CLEAR the screen, then SEND for "yes".
Enter the theoretical values:
"S2 = 08,62" (SEND)
"S3 01," (SEND)
"TMAX = 419" (SEND)
"S4 = 21,4" (SEND)
"SAMPLES DATA?" CLEAR, then SEND.
01 DEPTH = Sample number
01 QTY = Sample weight (SEND)
01 TOC = 2.86* (SEND)   (* for 55000)
02 DEPTH = > Continue in this manner until the final sample.
#2 will be the next unknown.
        If there is a mistake, hit RECALL to recheck data. RECALL, then START.

Carlo Erba CHNS:
Preparation of samples:
Setup requires two tweezers, one curved forceps, curved-head spatula, v-head spatula and metal block for holding tin capsules. Chemical supplies include V_2O_5, Sulfanilamide, Estuarine sample, tin capsules and crushed carbonate samples. Tare the Cahn balance with tin capsules on both sides. Measure between 5.500 and 6.999 mg of the crushed carbonate sample in a capsule. Pour a heaping v-head spoonful of V_2O_5 into the capsule. Remove capsule with tweezers, fold open end over flat, fold corners over, fold entire capsule in half, then squeeze capsule into a compressed box. Place box into autosampler tray. Continue until samples are finished. The first samples (5 if the column is new, 1 for subsequent runs) should be conditioners (capsules containing V_2O_5 and a small amount of sulfanilamide), then 3 samples of sulfanilamide (increasing in weight; ex. .5 mg, 1.0 mg, 1.5 mg) and V_2O_5, followed by 2 blanks (V_2O_5 only), then 2 Estuarine samples (to check CNS ratios). Unknown samples are run after the Estuarine samples. Run an Estuarine sample after every 8-10 unknowns. Finish with a final Estuarine.
        The Estuarine sample has %C of Ç1.65, %N of Ç0.18, and %S of Ç0.96. If the %C starts to fall below 1.63 it is time to replace the column.

Replacing the Column:
Cool off column to 200%C in standby position, filament off. Shut off the helium. Unscrew the autosampler from the top of the column. Remove nut from bottom of the column. Pull out old column and discard.

To make a new column:
1. Place parafilm at the bottom of a new glass column.
2. Pack 3 to 4 cm of glass wool in bottom of column.
3. Pour no more than 10 cm of Cu wire above glass wool. Pack firmly.
4. Add 2 cm of quartz wool.
5. At 5 to 6 cm of WO_3 (Tungsten Oxide)above the glass wool. Pack firmly.
6. Add 1 cm of glass wool.
7. Cut a nickel foil insert to the inner diameter and press it into the column until no light can be seen between it and the glass wool beneath it.

Insert the column into the CHNS. Place the O-rings (wider side towards inside of column) on column. Secure the bottom of the column with the large nut. Place the autosampler back on top of the column and secure.

Checking for leaks in the column:
After installing a new column, turn the helium on (valve panel behind CHNS, above left) and turn the "M" Carrier knob until the gauge reads 100 kPa. Cap the exhaust port behind the middle removable panel. When stable, turn the "M" Carrier knob fully CCW (several turns) and start the timer for 3 minutes. If the pressure falls more than 15 kPa, there is a leak. If there is a leak, try reinstalling the column, making sure the o-rings are seated properly and check for leaks again. This usually solves the problem.

Checking the flow:
Take the furnace off standby. It should be at 1000%C while checking the flow. If the bubble meter is used to check the flow, fill the it with Snoop. Otherwise, use the digital flowmeter, changing the settings for each gas checked (M carrier gas/Vent-M = He; R carrier gas/Vent-R = Air; O_2/O_2-Vent = O_2). Attach the flowmeter to the "VENT-M" nozzle. The flowmeter should read Ç82.0 units/min. If it is necessary to adjust this, turn the "M" carrier knob until the desired results are found. It is not necessary to adjust the flows of the "R" carrier gas or O_2 gas, but the measurements should be checked at the beginning of the leg. The flow rates should be 38 units/min for "R" carrier gas (air) and 28 units/min for O_2 gas. If the flow does need to be corrected, untape the needle valves at the base of the machine, adjust the flow, then re-tape the valves shut.

Checking for leaks in the Autosampler:
Slider out - A rubber disc and brass fitting are needed to seal the autosampler assembly, and are stored with the supplies under the CNS. Take the column out, replace the o-ring with the rubber disc to seal off the combustion hole and seal off the right side of the autosampler (opposite the carrier vent, ie. the purge vent) with the brass fitting. Bring the M carrier pressure to 150 kPa for 2 minutes to equalize, then back off the pressure. It can lose up to 15 kPa over 3 minutes. If the pressure holds for 3 minutes, test with the slider in.

Slider in - On the back of the autosampler, switch the blue tubing; #1 will go into #2 and #2 into #1. Put the air on to push the slider forward. Proceed as in the above description, bringing the carrier to 150 kPa, backing off pressure and seeing if it holds for 3 minutes.

If the pressure drops too much, the autosampler needs to be rebuilt. The slides should be polished and the teflon sampling replaced (per instructions in the instructional manual). After reassembly, the autosampler needs to be cycled for at least 3 hours to let the sampling slide "set". Set the switches as follows:
Cycle from 70 or 80 to 01; start from 15 to 02; stop from 65 to 05. The buttons "oxy inj" and "no peak stop" should be depressed. Press "start man" to begin the cycling. After 3 hours, disassemble the autosampler, clean the parts with ethanol, reassemble and leak check.

Running the Samples:
Go to C:\EAGER200\EAGER. To set up directories and leg number, access the menu, top left square. Select File Organizer. Make two directories, C:\EAGER200\METHODS \LEGxxx and C:\EAGER200\DATA\LEGxxx. Get out of File Organizer. Load an old method. Open the sample table and change directory at top of page (ex. c:\EAGER200 \DATA\LEG162 changed from LEG161). Go the "Sample Table" at the main menu. Numbers 1-5 should be named "Conditioner" (if the column is new, run 5 conditioners; otherwise, run only 1 conditioner), Type is "By-Pass". The first filename should begin A*site*number, example: A9801, A9802, etc. Forty-six samples should end with A98046. The next three samples should be the sulfanilamides of Type "Standard" with Standard Type "Sulfanilam". Weights should be given. The three sulfanilamides should increase from about 0.5 mg to 2.0 mg. The next two should be blanks, the first Type "By-Pass" and the second Type "Blank". Next, run two Estuarines, Type "Unk.". Weights are given for these and all other unknowns. The "F1" key brings up the main menu - save the new sample table here. Print out the sample table. After placing the carousel on the autosampler manually advance it CW from 0 to 1. Make sure the furnace is off standby and the filament is on. Make sure the correct Method is loaded. Make sure the purge valve (on top of the apparatus) is on (up). Go to Monitor Detector and start. If there is a problem, hit "Stop", not "Abort".

If a peak is quite wide, there may be a leak. See p. 92 in the Eager 200 manual for help.

If a peak is misidentified, ie. the carbon peak is identified as hydrogen, stop the run. Go to Component Table in the Main Menu. Change the bad retention times here (use an old printout for correct retention times). Go to Report Parameter and change from Printer to Video. Go to Recalculation and Reset for Recalculation. ESC through the component tables. Go to Recalculation, choose which samples to recalculate and Confirm. Hit Enter to switch through the chromatographs. Before the run is restarted, reset Report Parameter from Video to Printer. Go to Monitor Detector and Start Analysis again.

To stop the run or at the end of the run put the furnace on standby and the filament off. Quit Monitor Detection. Check the K-factors and peaks to make sure they are correct. K-factors for carbon should average around 0.134 to 0.145, and retention times for N, C, H, and S should be around 65, 90, 240, and 445 (take these values from the sulfanilamide results). Go to Recalculation, then Report Summary. Insert all the unknown samples to Group 1 and the

Estuarines to Group 2. Print all groups. Use Average, Std. Deviation, % Rel. S. D., and Variance. Add the %C, %N, and %S results to the CARBsite.WK1 worksheet.

Electronic Scales:
Cahn Calibration:
(Note: the electronic scales can only be calibrated in port call. Due to the motion of the ship at sea, calibrations will not be as accurate once the ship has left port)

The Coulometrics program runs on two PowerPC computers simultaneously (MC67, the Coulometrics PC and MC71, the Cahn PC). Open the Balance program on MC71. Make sure MC67 is connected and is shown on the desktop. If MC67 is not on the desktop, restart both computers and select MC67 from the Chooser on MC71. The data path will be "MC67:Coulometrics". If the programs still do not work, remove the "datapath.ini" file to the trash, restart both computers and reconnect from Chooser.

Remove the two hanging trays and clean the inside area with a damp paper towel. Clean the trays with a soft-bristled paint brush. Hang the trays back in the scale. Press the Tare button on the Cahn once, after the trays are stationary. Place a 200 mg weight on Side A. Press Cal on the Cahn, then remove the 200 mg weight from Side A. Make sure the interface is set up to count by statistics, Precision is 0.01, and Confidence = 99.50. Press the Calibration button and follow the instructions. The Cahn balance will be set up for a 10 mg and a 100 mg calibration:

10 mg Calibration:
Select Function "Calibrate" and execute with no weight on the tray. When the count is finished, continue on with weights of 1, 2, 5, 7, and 10 mg. Enter the values of the weights as 0.0 mg, 1.0 mg, 2.0 mg, etc. After the 10 mg weight is finished, select "SAVE Calibration" and give the calibration a name, such as "Calib164_10".
Leg 166: slope = 0.99749, intercept = 0.0017, and RMS = 0.00004.
Leg 168: slope = 0.99845, intercept = 0.0107, and RMS = 0.00006.
Leg 170: slope = 0.99488, intercept = 0.0390, and RMS = 0.00068.
Leg 172: slope = 0.99879, intercept = 0.0082, and RMS = 0.00006.
Leg 174: slope = 0.9936, and intercept = -0.0247.
Leg 174: slope = 1.0009, and intercept = 0.0018 (new weigh program).
Continue on to the 100 mg calibration.

100 mg Calibration:
The calibration can continue from the 10 mg calibration. Continue adding the 20, 50, and 100 mg weights in the manner described above. The minimum weights to be used are 0, 5, 10, 20, 50, and 100 mg. Save the calibration to a file such as "Calib164_100".
Leg 166: slope = 0.99994, intercept = -0.0073, and RMS = 0.00009.
Leg 168: slope = 0.99949, intercept = 0.0055, and RMS = 0.00004.
Leg 170: slope =1.00019, intercept = 0.0019, and RMS = 0.00005.
Leg 172: slope =1.00128, intercept = -0.0050, and RMS = 0.00007.
Leg 174: slope =0.9990, and intercept = -0.0466 (new weigh program).
Leg 175: slope =0.9999, and intercept = -0.0046.

Scientech Calibration:
Open the Scientech/Cahn v148 alias on the Mac. Select function "NB-A2000 Set Zero & Gain". This screen should have values of 10/1024 and 100000 Hz. Make sure Precision is set to 0.05 and "calibrate by stats" is selected. The interface type should be "NB-A2000 Analog Board". Adjust the Zero value, trying to get the actual zero (third number set) to as close to zero as possible, around 0.00x. Put a 20 gram weight on both the unknown and known sides and adjust the gain, trying to get the actual zero (third number set) to as close to zero as possible, around 0.00x. Switch back to the zero adjustment and remove both 20 gram weights. Continue adjusting the zero and gain until the actual zero is close to 0.X. This may take 6 sets of adjustments or more.

   Leg 164: zero = -0.030, gain = 1.0145.
   Leg 166: zero = -0.025, gain = 1.0140.
   Leg 172: zero = -0.027, gain = 1.0140.

When finished, hit "done". Hit "done" on the second "set" screen. The second "set" screen (Set Sample Count and Rate) should have values of 12/4096 and 50000 Hz. More details on this start-up are in the Leg 161 tech notes. Next, go to Function "Reset Tare". Make sure the slope = 1.0 and intercept = 0. Go to Function "Calibrate" and execute. Calibrate for weights 0.0 g, 0.1 g, 0.2 g, 0.5 g, 1 g, 2 g, 5 g, 10 g, and 20 g. Keep the weight on the unknown side. Hit "Stop and Calibrate" when finished. Put the calibration file in an appropriate folder, ie. "calib164". Select function "Load Calibration" and execute. Do this again, only cancel from the menu screen (bug in the system). The slope and intercept should change from 1.000 and 0.0 to new numbers.

   Leg 164: slope = 0.11120 and intercept = -0.0015
   Leg 166: slope = 0.10094 and intercept = -0.00004
   Leg 168: slope = 0.10101 and intercept = -0.0019
   Leg 170: slope = 0.10101 and intercept = -0.0019 (no change)
   Leg 172: slope = 0.10100 and intercept = -0.0007
   Leg 174: slope = 0.10100 and intercept = -0.0007 (no change)
   Leg 175: slope = 0.10100 and intercept = -0.0007 (no change)

Place a 2 g weight on the unknown side and weigh. The given weight should be within 0.00 places.

Spectrophotometer:

Alkalinity:
Preparation of standards for calibration:
To prepare alkalinity solutions for alkalinity calibration, use 0.1M Na_2CO_3 + 0.7M KCl. To make the 0.1M Na_2CO_3 solution: Dissolve 10.6 g Na_2CO_3 into 1000 ml DI H_2O.
To make the 0.7M KCl solution: Dissolve 52 g KCl into 1000 ml DI H_2O.

Borax ratios (20 and 40 mM):

20 mM Na$_2$CO$_3$ Solution: Pipet 10 ml of 0.1M Na$_2$CO$_3$ into 90 ml of 0.7M KCl.

40 mM Na$_2$CO$_3$ Solution: Pipet 20 ml of 0.1M Na$_2$CO$_3$ into 80 ml of 0.7M KCl.

These solutions must be kept in the refrigerator.

Buffer Calibration:

Do the buffer calibration first. Use pH solutions of 4.01, 7.41 and 10.0, stored with the gas standards. Pipette 5 ml of solution into the glass container and let it sit with the stirrer running for five minutes. Turn the stirrer off and let stand 2 more minutes, then take reading #1 on the alkalinity program. Continue on with the other 2 solutions in the same manner. When finished, hit calculate. The slope should be around -60.

Leg 164 buffer values: pH 4.01 = 191.18; pH 7.41 = -7.28; pH 10.00 = -167.40; slope = -59.79
Leg 166 buffer values: pH 4.01 = 184.17; pH 7.41 = -11.22; pH 10.00 = -168.83; slope = -58.86
Leg 168 buffer values: pH 4.01 = 183.21; pH 7.00 = 8.31; pH 10.00 = -173.50 ; slope = -59.55
(with Orion 4.01 and Fisher 7.0 and 10.0 buffers)
Leg 170 buffer values: pH 4.01 = 183.39; pH 7.00 = 8.52; pH 10.00 = -174.95; slope = -59.82
(with Orion 4.01 and Fisher 7.0 and 10.0 buffers)
Leg 172 buffer values: pH 4.01 = 176.49; pH 7.00 = 8.89; pH 10.00 = -178.08; slope = -59.19
(with Orion 4.01 and Fisher 7.0 and 10.0 buffers)
Leg 174 buffer values: pH 4.01 = 186.35; pH 7.00 = 9.38; pH 10.00 = -168.52; slope = -59.24
(with Orion 4.01 and Fisher 7.0 and 10.0 buffers)
Leg 175 buffer values: pH 4.01 = 179.97; pH 7.41 = -18.88; pH 10.00 = -175.26; slope = -59.26
(with Orion 4.01, Fisher 7.41 mix, and Fisher 10.0 buffers)

Determining Borax Ratio:

Select "Determine Borax Ratio" on the screen. Run the three standards (IAPSO 2.325 mM, 20 mM and 40 mM Na$_2$CO$_3$) at least 3 times apiece, or until the readings are consistent. The accepted values should be within 5% of the standard values: 2.21 to 2.44 mM for IAPSO 2.325, 19 to 21 for 20 mM, and 38 to 42 for 40 mM. Take an average of good results and use them in the "borax ratio" box in "Change Parameters".

Leg 164 results: IAPSO, 2.435; 20 mM, 19.598; 40 mM, 38.848
Leg 166 results: IAPSO, 2.371; 20 mM, 19.801; 40 mM, 39.688
Leg 168 results: IAPSO, 2.563; 20 mM, 19.666; 40 mM, 39.362
Leg 170 results: IAPSO, 2.544; 20 mM, 19.659; 40 mM, 39.352; 100 mM, 95.845 (3 ml)
Leg 170 results: IAPSO, 2.474; 20 mM, 19.919; 40 mM, 39.438; 100 mM, 96.766 (5 ml)
Leg 172 results: IAPSO, 2.606; 20 mM, 20.302; 40 mM, 39.909
Leg 174 results: IAPSO, 2.510; 20 mM, 19.961; 40 mM, 40.551
Leg 175 results: IAPSO, 2.555; 20 mM, 19.993; 40 mM, 39.526

Running the Alkalinity Program:

If the scientists would like to take the alkalinity data home with them on diskette, make sure to run the ALKP batch program instead of ALK. This saves the data in DAT files in the

ALKDATA directory. Normally one starts the Alkalinity program by moving to the C:\665 directory and typing ALK. Set the Brinkmann 605 pH-Meter on Measure, not Standby. The water bath should be on and steady at 25.0% C. Either 3 or 5 ml of sample from the IW (depending on how much IW is available) is pipetted into the glass container attached to Brinkmann water bath and the 665 Dosimat stirrer. Make sure the stirring bar is rotating. At the main screen choose "RUN A SAMPLE" to begin the process. Insert the glass probe in the solution with the sensor hole facing forward. The probe must have the rubber stopper unplugged when operating. When prompted place the titrator tip in the solution making sure the titrator is not dumping the 0.1M HCl into the sensor hole. When the process is finished write the amount of HCl dispensed (shown on the Dosimat display and at the end of the printout) on the IWPA tube along with the sample size used (3 or 5 ml), melt the tube end and place it in the sample box. Write the pH and Corrected Alkalinity on the IW sheet.

If the alkalinity starts to exceed the range the parameter is set for, the corresponding theoretical value must be changed in the Basic program. To do this, exit the main menu, press any key and the "ALK.BAS" program should be present. Hit "F2" to bring up programs and select "s244EnterBorax". Change the borax value to the new theoretical (not averaged) value and save the program. Return to the main menu by using "F5".

Borax Ratio Numbers:

If the alkalinity reading approaches 15, change parameters (at Alk Main Menu) to Borax Ratio 20 and set High Alkalinity rates. If the ratio gets closer to 30 change to Borax Ratio 40.

Required Maintenance:
Make sure the probe is filled with 3M KCl solution and the reservoir is filled with IAPSO.

Hamilton Dilutor:

Programs for different dilutions are pre-installed into the dilutor memory. They are:

#1	100%, 1:200	#4	40%, 1:500	#7	120%, 1:167
#2	80%, 1:250	#5	20%, 1:1000	#11	Lithium standards (AA)
#3	60%, 1:333	#6	10%, 1:2000		

These programs are listed on the left side of the main apparatus. When making new dilution programs never save them as #1-7; always save new programs as #12 and higher.

Coulometer:

Set up of Coulometer Apparatus:
Fill the sample scrubber (glass unit at left rear) 2/3 full with $AgNO_3$. The air scrubber (glass unit at left front) is filled 1/3 full (12 ml) with KOH. Air is hooked to the air scrubber. This bubbles through the KOH, removing CO_2. The air continues to the adaptor tube above the acid tube. Attach an empty vial to the base of the glass condenser to close the system. An air-line is inserted into the $AgNO_3$ in the rear scrubber. This air bubbles up through the solution and continues on through an air-line at the top of the scrubber to the cell. A line is attached from the 2N HCl bottle to the middle connection on the condenser.

All parts of the cell (the electrodes, air lines, etc) must be completely dry. Approximately 0.5 cm of granular potassium iodide (KI) is poured into the smaller chamber. Place the spinner bar in the cathode (large) side of the cell. Approximately 100 ml of cathode solution (big bottle) is poured into this side of the cell.   Fill the smaller chamber with anode solution (small bottle) to level with the cathode solution. Insert the platinum (curly) electrode and gas inlet tube (from the $AgNO_3$ scrubber) through the plug into cathode solution. Place silver electrode through its plug into the anode solution. Plug the electrodes into the coulometer. Switch on the unit at this time, but not the cell. Rotate the cell until maximum transmittance is seen. Adjust to 100% with the dial. Switch cell on.   Titration begins - the solutions should go from yellow to blue. Cell current goes from 200 to 0. Transmittance goes from 100% to 29%. Run a $CaCO_3$ standard next. When the carbonate is run the values generated on the Epson should be between 99% and 101% of $CaCO_3$.

Running the Carbonate Samples:
Carbonate samples (CARB) are retrieved from the core lab, the sample bags opened and placed in the freeze dryers for at least 12 hours. Write the time the freeze drying began on a yellow sticky on the container. The samples are crushed in a jade bowl after 12 hours. The label from the bag is placed on a 16 ml plastic-capped sample bottle. Pour the crushed sample into the bottle when finished. Samples are weighed on the Cahn balance into 10.000-10.999 mg amounts. Place a small square of weighing paper on the "known" side of the scale. A small holder of weighing paper (squared-U shape: _) is placed on the "unknown" side. Tare the balance, then add some of the sample to the unknown side until the correct weight in achieved. The sample is poured into the glass coulometer tubes. Once the coulometer is set up, place the tube on the apparatus and secure with an elastic band. When the run is finished, the acidic sample solution needs to be dumped out in the acid fume hood, the vials scrubbed and rinsed with DI water and dried for several hours in the oven.

Cleanup of Coulometer:
If the air-lines get dirty remove them, rinse them with DI water and blow them out with air. The $AgNO_3$ line needs to be whacked on the trash can to clear out the accumulated muck. Pour the cathode and anode solutions, the silver nitrate and KOH solution down the acid trap. If the Pt electrode is really corroded, let it set in nitric acid until clean. Rinse both sides of the cell thoroughly, then fill the small side with DI water and let it soak through the frit. Repeat several times until clean, then dry in the oven.

Solutions used with the Coulometer:
Air Scrubber/KOH Solution: 90 g KOH in 200 ml DI water
Sample Scrubber/$AgNO_3$ Soln: 3 g $AgNO_3$ in 100 ml DI water
Acid Dispenser/2N HCl Solution: 165ml HCl and 835 ml DI water (1000 ml total)

Manual recalculation:
If the coulometer hangs, the value can be manually recalculated. Divide the finished amount of

counts by the weight of the sample, then divide by ten. Multiply the value by 8.33 and the final number is the % CaCO$_3$.

Example: 1240 counts / 10.40 mg sample = 119.23; 119.23 / 10 = 11.92;
11.92 x 8.33 = 99.32% CaCO$_3$.

If large amounts of dolomite are in the samples, it may be necessary to change the acid solution from 2N to 3N (248 ml of 12.1N HCl to 752 ml DI water).

Using the Epson:
Prior to the coulometrics program on the Mac, an Epson computer was used to run the coulometer. If this should ever be re-used as a back-up, here are the proper settings:

Analysis=C (for carbon)
Factor=1
# of readings= 10
Blank= 0
Units: 2 (for mg)

Enter sample ID (# on tube) and sample weight (to 3 digits, ex: 10.513). Press "r" when ready to run. After the Epson clickity-clacks twice, raise HCl dispensette and inject acid to into the tube. After the readings have been taken enter the data into the spreadsheet.

Barnstead Water Filters:

Maintenance of Barnstead water filters:
The water filters are relatively maintenance-free. There are two disposable filters that need to be removed on a regular basis. The main water feed line, along the aft wall, has two canisters that hold the filters. Turn the power off on the NANOpure system, the ROpure system and the Barnstead system (the switch is on top of the STB assembly). Close the water valve on the feed line. Place a bucket under either canister (the STB canister can be removed from the holder) and twist off the lower section. Discard the old filter and install a new filter. Repeat with the other canister. Once finished, turn on the water, power up all the systems, and check for leaks.

The NANOpure system should provide DI water at 18.0 to 18.3 M3-cm. If the reading falls below 16.0 M3-cm, the cartridges in the NANOpure system (or possibly the ROpure) may need replacement. The NANOpure takes a D0809 cartridge in the left rear, a D0835 in the right rear, and two D5027 cartridges in the front. The ROpure system uses a D6318 cartridge in the rear and a D63112 cartridge in the left front. The right front canister is left empty.

When installing the rear cartridges (the D0809 and D0835) make sure the front D5027 cartridges are NOT installed. The D0835 cartridge should be installed first, with the other three canisters empty, and flushed several times. Then install the D0809 cartridge and flush it several times. After both rear cartridges are properly flushed install the carbon cartridges in the front canisters and flush several liters of water through the system. The system value should return to +18.0 M3-cm.

The 0.2 &m final filter, located at the water outlet on the NANOpure, should be replaced when there is a significant drop in the fill rate to the DI water storage tank.

On occasion the Replace Prefilter LED will come on. Remove the top of the ROpure and move switch #2 to the opposite position. This will reset the clock that is used for the prefilter.

Hydrogen Generators:
Changing drierite:
The alternate generator will be switched on-line while changing drierite. Turn on the idle generator and allow the pressure to build up to 40 psi. Once the pressure is at 40, open the shutoff valve, then open the valve on the distribution block (on the shelf above the generators, to the right). After a few minutes, close the valve on the distribution block to the second generator, then close the shutoff valve on the second generator (the unit with the exhausted drierite). Turn the power off, then SLOWLY crack the nut at the distribution block to release pressure from the generator. Once the pressure has dropped to 0 psi, the drierite cartridge can be removed and refilled.

If the "Generating" light turns off shortly after the unit is activated and the Output Pressure gauge shows no increase, the cell has probably dried out. Unplug the hydrogen generator and remove the cover. Slowly unscrew the cap from the cell inside (the cap is similar to the clear plastic cap on the drierite cell). Once the gas escapes the cap can be screwed on again. Plug in the unit and switch on the generator. The cell should began to bubble and the Output Pressure gauge should show a register of gas pressure. Once the proper operation has been verified, shut off the machine and unplug it before reinstalling the cover. Then turn the unit back on and procede with switching the two generators.

2. Supplies and Set-up

Carver Presses:

The squeezer assembly is set up with the rubber disk with a hole in the center placed under the stainless steel plate (with hole). This unit is placed onto the base. The outer casing is now placed on the base. The screen is put on top of the SS plate. A filter (see filter prep) is placed on the screen. Scrape the sides and top from the IW sample and place it on top of the filter. If the sample is very mushy two filters may be needed. Place the teflon disk on top of the sample and the rubber disk on top of the teflon disk. The piston is inserted into the whole assembly. Place the squeezer into the press. Make sure that the switches are up, the lever is to the right and the dial gauge is all the way CCW. Move the dial to about 5000 psi. Press both buttons at the same time until the press squeezes a drop of water from the apparatus (this will not necessarily happen at 5000 psi, though - soft sediment will yield water at much lower pressures and very hard sediments may require increasing the pressure to 20,000 psi before water appears). Stop and place a syringe with 0.45& filter cartridge into the syringe hole. Press the two buttons again until the psi needle passes the dial gauge and a click is heard. The press should squeeze automatically now. Once the appropriate amount of IW sample is extracted move the dial gauge all the way CCW and *slowly* move the lever to the left, relieving the pressure and dropping the press. Remove base assembly from the squeezer, manually press the squeezecake and remaining pieces from the squeezer and clean up. The squeezecake will be labeled IWSx and bagged. Any part that touches the sample or IW (syringe and needle, filter screen, outer casing, base and SS plate) needs to be rinsed with DI water and dried in the oven.

Salinity:

Check the calibration by taking a reading for DI water (=00%) and IAPSO (=35%) on the refractometer (stored in drawer across from solvent hood). The refractometer can be hand-calibrated by turning the set-screw (under the protective putty) on its bottom. Take a few drops from the IW sample to check IW salinity and record on the IW sheet.

IW Filter Prep:

Soak Whatman #1 filter papers in DI water, then dry in the oven. Store in a plastic bag for use in the squeezer.

IW Plastic Tubes:

Cut 1/2" PE Tubing (MATMAN # LS0151) into 4-6 inch sections using the tubing cutter stored beside the furnace. Wash the cut tubing in water, then oven-dry. Store in plastic bags when finished.

Acid Bath:

Fill the Nalgene acid bath with 18 liters of Barnstead water. Place the bath in the hood and pour in 2 liters of reagent grade HCl. This will give a 10% acid solution.

Water Filters for NANOpure system:

Turn off power on the ROpure Barnstead system (top left), ROpure ST system, and NANOpure system. Turn the water inlet valve off. Place the filter assembly in a bucket and unscrew the bottom filter container. Switch out the old filter with a new filter and screw the bottom container onto the assembly. Do this with the second filter system also. Turn the water valve back on. Turn all switches back on.

Solutions for Titrations:

Ammonium:

Alkaline Solution: Dissolve 7.5 g tri-sodium citrate and 0.4 g sodium hydroxide in 500 ml DI water. Refrigerate.

Silica:

Ammonia Molybdate Solution: Dissolve 4 g of ammonium paramolybdate in ~300 ml DI water in a 500 ml volumetric flask. Add 12 ml conc. HCl (12N), mix and make up the volume to 500 ml with DI water. Store in a dark bottle.

Metol Sulfite Solution: Dissolve 6 g anhydrous sodium sulfite in a 500 ml volumetric flask. Add 10 g Metol and then DI water to make the volume 500 ml. The solution should be filtered through a Whatman #1 filter and stored in a dark glass bottle and refrigerated.

Phosphate:

Ammonium Molybdate Solution: Dissolve 2 g ammonium molybdate in 1000 ml DI water. Store in a plastic bottle.

Sulfuric Acid Solution: Dilute 10 ml concentrated H_2SO_4 (specific gravity 1.82 g/cm^3) to 1000 ml with DI water.

3. Computer Programs

JANUS:

Sample Codes:

HS   Standard Sam Code; glass vial
IW   Standard Sam Code; plastic culture tube, 5 ml
IWGx   Chem Code; scientist sample in glass vial
IWPx   Chem Code; scientist sample in plastic tube
IWPA   Chem Code; acidified sample from Alk. test, in plastic tube
IWSx   Chem Code; scientist sample, squeezecake
IWT   Chem Code; IW trimmings, in bag
IWP   Chem Code; remaining water, returned to ODP in plastic tube

4. Lab Routine

Pre-Site (Port Call/Transit):
Calibrate GC3
Calibrate NGA
      FID
      TCD
Calibrate pH/Alkalinity
      Make buffer for pH
      20, 40 mM Na_2CO_3
Calibrate Cahn Balance
      10 mg calib.
      100 mg calib.
Calibrate Scientech
      zero and gain
      20 gm calib.
Lab Preparation
      Wash filters
      poly tubes
      ampules
      set up squeezers
      supplies
      IW/HS boxes
      acid bath
      freeze dryer
      make reagents for: Cl titration
                            Si analysis
                            NH_4 analysis
                            PO_4 analysis

      IAPSO Seawater

On-Site:
Set up spreadsheets
       IW
       HS

Running GC3 and NGA
       injecting
       reintegration (manual, split peak, etc)
       recalibration
       light FID, TCD on-off

Running Dionex
       Sample and standard dilution
       preparation of eluents
       setup of cation run and anion run
       setup of cation schedule and anion schedule
       switch from anion column to cation column
       adjusting calibration
       reprocessing of data
       installing new columns, guard columns and conditioning (both AS4 and CS12)
       installing (or regenerating) a suppressor
       recognize bad runs

Chloride Titration
       Make reagents
       titrate
       calculation

Si, NH_4, and PO_4 Analysis
       reagents
       procedure - spectrophotometer
       calculation

Coulometer
       Make chemicals
       setup system
       run
       manual recalculate (if necessary)
       clean system and electrode
       recording of data

CNS
       make column

change column
column leak check
autosampler leak check
setup of all flows:
  He (M and R), O_2, Air, Purge

run
shut off
data to Carb Results
eager 200 software:
  k-factor
  sample table
  change report parameters
  change component table
  reintegrate chromatogram
  recalculation option, including reset and recalculate (how and when to use it)

AA Spectrometer
  make sample dilutions for Li and Sr
  set up system including:
    installing burner
    installing lamp
    set wavelength and slit width
    set up gas flow
    using software to set up parameters for run
    aligning burner
    aligning lamp
    lighting flame (both air/acetylene and N_2O/acetylene)
    optimizing the flame
  calibrating the instrument
  running samples
  shut off
  cleaning burner

Sending Data to JANUS
  HS (and VAC)
  IW
  CARB
  RE

Daily to Weekly Maintenance:
  Hydrogen Generator
    keep tank filled with water
    change drierite

switch to other generator
Air and Gas system
     change drierite (incl. black container)
     bleed jun-air pump, refill with oil
     change gas bottle, <400 psi
     change drierite near gas bottle rack
DI Water system
     don't let it run dry!
     change pre-filter if conductivity falls below 16.0
     change ro-pure filters if light comes on; reset ro-pure inside unit
     change ro-pure pre-filters (2) if rusty
Titrators
     change drierite if pink

End of Leg Maintenance:
     fill Carver press reservoirs (all three)
     change drierite in all that need it (H-G, air, gas, titrators)
     change DI bag in H-G
     new gas bottles
     defrost freeze drier and change oil in the vacuum pump
     change pre-filters (2) for ro-pure and air filter on nano unit

Pressure Gauge settings:

Air Pressure (after the Alltech Drierite Cylinders and Charcoal): 60 psi
Gauge from 3-way valve to Alltech Drierite Cylinder: L 60-62 psi, R 72 psi
Hydrogen Generators (either): 40 psi

GC2:	Hydrogen	40 psi	GC3:	Hydrogen	22 psi	Column Head
	Air	38-40 psi		Air	45 psi	Pressure Gauge: 0 psi
	Helium	80 psi		Helium	90 psi	
NGA:	Hydrogen	20 psi	Air to valves:	100+ psi	
	Air	40-42 psi	Column Head Pressure Gauge: 24 psi		
	Helium	90-92 psi			

RockEval:	Hydrogen	39-40 psi	Air to coulometer:	40-42 psi
	Air	60 psi		
	Helium	55-60 psi		

CNS:	Air	60 psi	Carrier M	~80
	Oxygen	30 psi	Carrier R	~80
	Helium	22 psi	Oxygen	~88
			Air	~358

Switch Settings:

Lauda bath: Both switches on, temp dial on 25C.

pH meter: Dial 1 at 1.2, dial 2 at 20, dial 3 at 0.9, Pt100 and U/mV both depressed.

Carver presses: "Dart" dial set between 8-9, all switches up.

Coulometer: Time set 00.5, mode 2, run/latch up, count/time up.

CNS: Left Furnace 100, Rt Furnace 30, Oven 080, Fil Temp 190, Signal gain up.
        Cycle 70, Sample Start 15, Sample Stop 65, Oxy Inj Stop 75, Peak Enable Start 07.
        Manual Exclusion, all up; Recorder up, Recorder Attenuation 1.

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