3.2 Use of Standards

The calibration slopes derived from the two gases and the KHP- and sucrose-spiked filter punches are averaged together to yield a single calibration slope for a given analyzer. This slope represents the response of the entire analyzer to generic carbon compounds and includes the efficiencies of the oxidation and methanator zones and the sensitivity of the FID. Note that the current calibration procedure is based only on the total carbon; currently no routine procedure exists to check the accuracy of the OC/EC split.

3.3 Typical Accuracy of Calibration Standards

The accuracy of the calibration standards is primarily limited by the accuracy of the calibration gas assays and by the accuracy of the preparation of the KHP and sucrose solutions. The calibration slopes determined by these four compounds historically differ by less than 5% on a given analyzer if sufficient care is taken during the calibration procedure (Section 5.1). Refer to Figure 3-1 for an example of plotted calibration curves.

4.0 PROCEDURES

4.1 Analyzer Start-Up

The following steps outline analyzer start-up:

- Check all gas cylinders' pressures; cylinders with gas pressures less than 500 psi should be replaced before beginning the day's analysis. The cylinder pressure of new tanks should be recorded in **ALL** analyzer log books.

- Check that all gas delivery pressures are correct:

Hydrogen	--	17 psi
Helium	--	15 psi
Compressed air	--	10 psi
O_2/He mix	--	10 psi
CH_4/He mix	--	10 psi
CO_2/He mix	--	10 psi

- Check that the FID is lit by holding a pair of tweezers over the FID exhaust stack and watching for condensation. If the FID is not lit (as immediately after the hydrogen or compressed air cylinders are changed), relight the flame by turning the H_2 rotameter to "100" and holding a butane lighter or match over the FID stack. A light pop indicates that the flame is lit. Verify that the flame remains lit by the tweezers test. Often the flame will not stay lit the first time, especially after the hydrogen cylinder is changed and air gets into

the gas lines. If the FID is cold, allow at least 30 minutes at the high gas flow to pass before turning the H_2 rotameter to its correct setting.

- Check and readjust if necessary all gas flows at the analyzer. The correct readings are posted on each rotameter. Read through the center of the ball. If drastic adjustments are required on one analyzer, recheck that flows on the other three analyzers have not been affected.

- Double-click the **CARBON** shortcut to begin the carbon program.

- Insure that the sample port fitting is tight and that the thermocouple push rod is reasonably snug at the back fitting. If the push rod is loose, tighten the rear fitting NO MORE than 1/16 of a turn. Do not overtighten this fitting: a push rod that is too tight is difficult to operate smoothly, and will cause excessive wear of the Teflon ferrule.

- Perform a leak test on the system by flipping off the "From Oven" toggle valve. After the He-1 and He-2 rotameters settle to zero (if they don't reach zero in 2 minutes, see leak correction procedures below), flip off the "To Oven" toggle valve. This process pressurizes the oven and connecting tubing and then isolates the oven. After 30 seconds, flip on the "To Oven" toggle valve. If the He-1 rotameter float jumps more than 5 units, the system has an unacceptable leak. Correct the leak by checking the following items:

  - Check that the sample port fitting is tight.

  - Check that the push rod is snug.

  - If the system still leaks, disassemble the sample port fitting, wipe all threads and ferrules clean with a clean, dry Kimwipe, reassemble, and retry.

  - If the system continues to leak, check the integrity of the quartz oven and all tubing. Refer to the carbon analyzer troubleshooting manual for additional tips and procedures.

- When the system leak checks satisfactorily, select option 5 (manual mode) from the main menu of the Carbon program. This will result in the screen shown in Figure 4-2. While watching the He-1 and Cal Gas rotameters, select option 4 (toggle Carle valve). The He-1 rotameter should not change from zero, and the Cal Gas rotameter should momentarily dip down. While watching the same rotameters, select option 4 again. The He-1 rotameter should jump up momentarily and the Cal Gas reading should jump slightly. Behavior different than this indicates a leak in the calibration gas injection system which must be corrected before beginning any analyses. Refer to the carbon analyzer troubleshooting manual for additional information.

- Because calibration gas has been injected into the system by the above step, the system must be purged before continuing. Open the "From Oven" toggle valve to restore flow through the oven and wait at least two minutes to insure all calibration gas has progressed through the system.

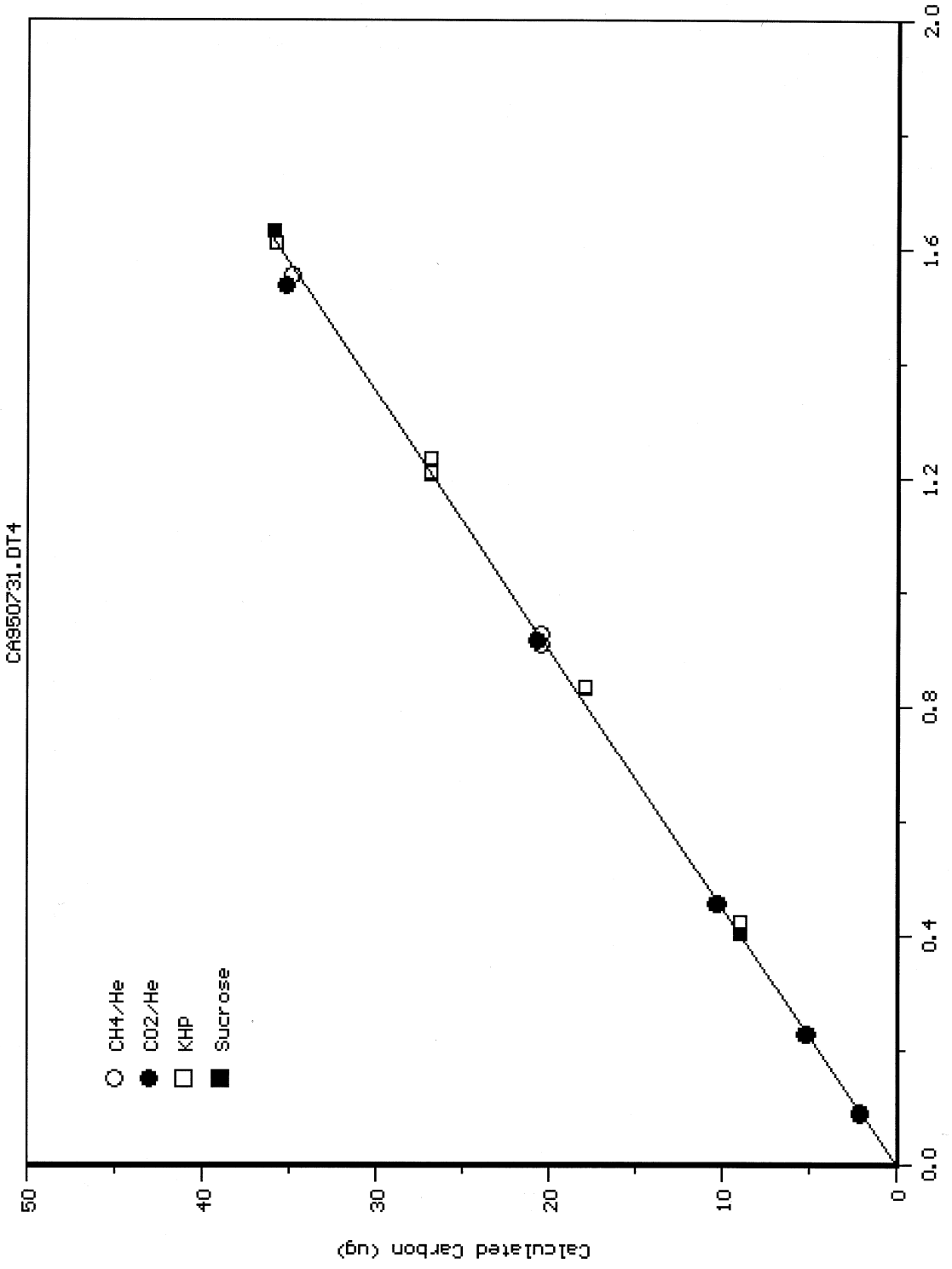

Figure 3-1. Example DRI Carbon Analyzer Calibration Curves.

- From the opening menu, select option 4; see Figure 4-1. After insuring that the thermocouple push rod is pushed into the combustion zone, type "Y" to begin baking the oven. The oven will be baked at 800°C for 10 minutes to insure that the system is clean before beginning analysis. This option is self-timed and will turn off the oven after 10 minutes has elapsed.

- Begin the daily entry in the carbon analyzer logbook. Entries should follow the format in Figure 2-6.

- Use the sample tweezers to remove a Kimwipe. Wipe the sample tweezers, petri dish, and punching tool with clean Kimwipes, taking care not to contact the cleaned surfaces with fingers or other dirty items.

- Insure that the printer has enough paper for the day and that the printer toner cartridge is producing legible printing.

```
+-------------------------------------------------------------------------------+
|                          ** CARBON ANALYSIS PROGRAM **                        |
|  (c)1988-1995, L.C.Pritchett                          Ver. P4.1  (11/21/95)   |
+-------------------------------------------------------------------------------+
                         +------------------------------+
                         | Current Directory: C:\SYSBLK |
                         +------------------------------+
Program options:

    1 ... OC/EC Analysis
    2 ... CO3 + OC/EC Analysis
    3 ... Calibration Injection

    4 ... Bake Oven
    5 ... Manual Mode

    6 ... Recall Previous Data

    7 ... Disk/Directory Functions
    8 ... End-of-Day Functions
    9 ... User Options

 <Esc>... Exit Program

Input option:
```

Figure 4-1. DRI Carbon Program Main Menu.

- Press **<Esc>** to return the Carbon program to the main menu. Select option 3 (calibration run) to begin the morning calibration injection. Note: the program will automatically change to the **\CALIB** subdirectory during the calibration run, and will return to the current subdirectory when the calibration run is done. Select He/O_2 carrier gas (option 2). Select either CO_2 or CH_4 calibration gas type as the same gas used the previous afternoon (check the analyzer logbook). For any given day, one gas will be used in the morning and the other in the afternoon. By using the same gas in the morning as was used the previous afternoon, the calibration gas used in the morning will be rotated on a regular schedule.

- The computer will create a sample ID based on the gas type, current date, and run number. This ID should be entered in the analyzer logbook (see Figures 4-3 and 2-6). Press **<N>** in response to the purge option to begin the calibration run.

- Insure that the printer is on-line.

- When the elapsed time reaches 60 seconds (Figure 4-4), flush the 1000 ml syringe with the appropriate calibration gas three times. A low pitch warning tone will sound at 84 seconds (the number of beeps corresponds to the carbon analyzer number). When the analysis start tone sounds at 90 seconds, inject 1000 ml of the calibration gas into the injection port before the oven. The rest of the analysis is automatic.

- If the calibration injection is late or missed, press **<Esc>** to abort the run. Restart the calibration run by selecting option 3 from the main menu.

- When the analysis is complete, a tabular and graphical printout similar to Figures 4-5 and 4-6 will be generated. From the tabular printout locate the calibration peak counts and the calculated µg C/filter. Record these values in the logbook as in Figure 2-6. The calibration peak counts should be above 20,000 counts. Check the µg C value for the calibration gas against those posted on each carbon analyzer.

```
Oven:  62 °C       Reflectance: 1.658 V      Transmission: NA         FID: 0.100
--------------------------------------------------------------------------------
Current settings:  Temperature : 5 °C
                   Front valves: Off   Back valves: Off   Carle valve: Inject
                   Fan         : Off   Pushrod    : Undef
--------------------------------------------------------------------------------

Manual control options:

    1 ... Set Oven Temperature

    2 ... Toggle Front Valves
    3 ... Toggle Back Valves
    4 ... Toggle Carle Valve

    5 ... Toggle Cooling Fan

    6 ... Move Pushrod

    7 ... Reset All

 <Esc>... Exit Option

Input option:
```

Figure 4-2. DRI Carbon Program Manual Control Menu.

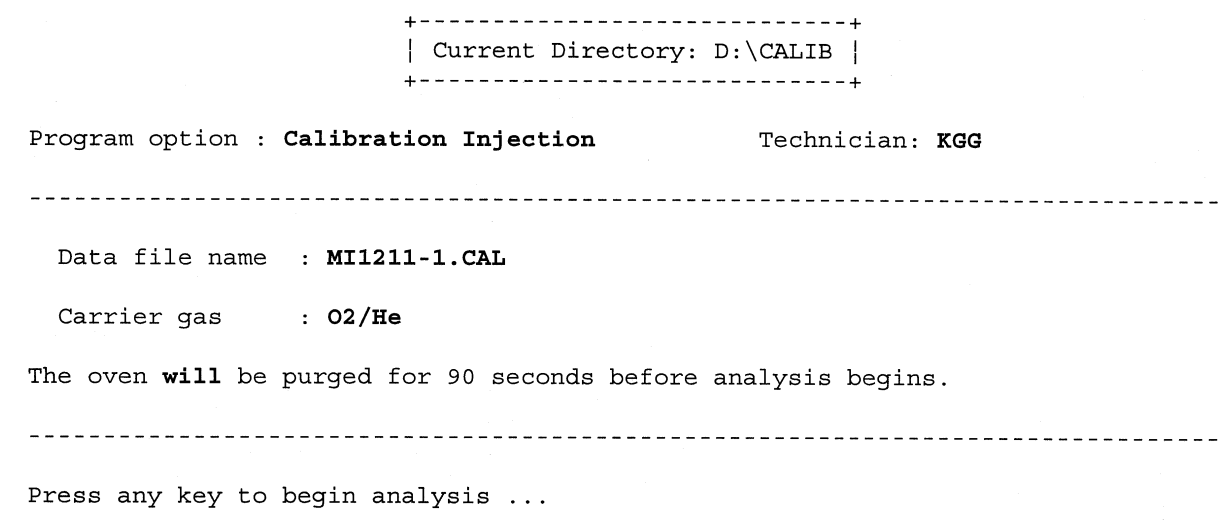

Figure 4-3. DRI Carbon Program Screen Before Starting Calibration Run.

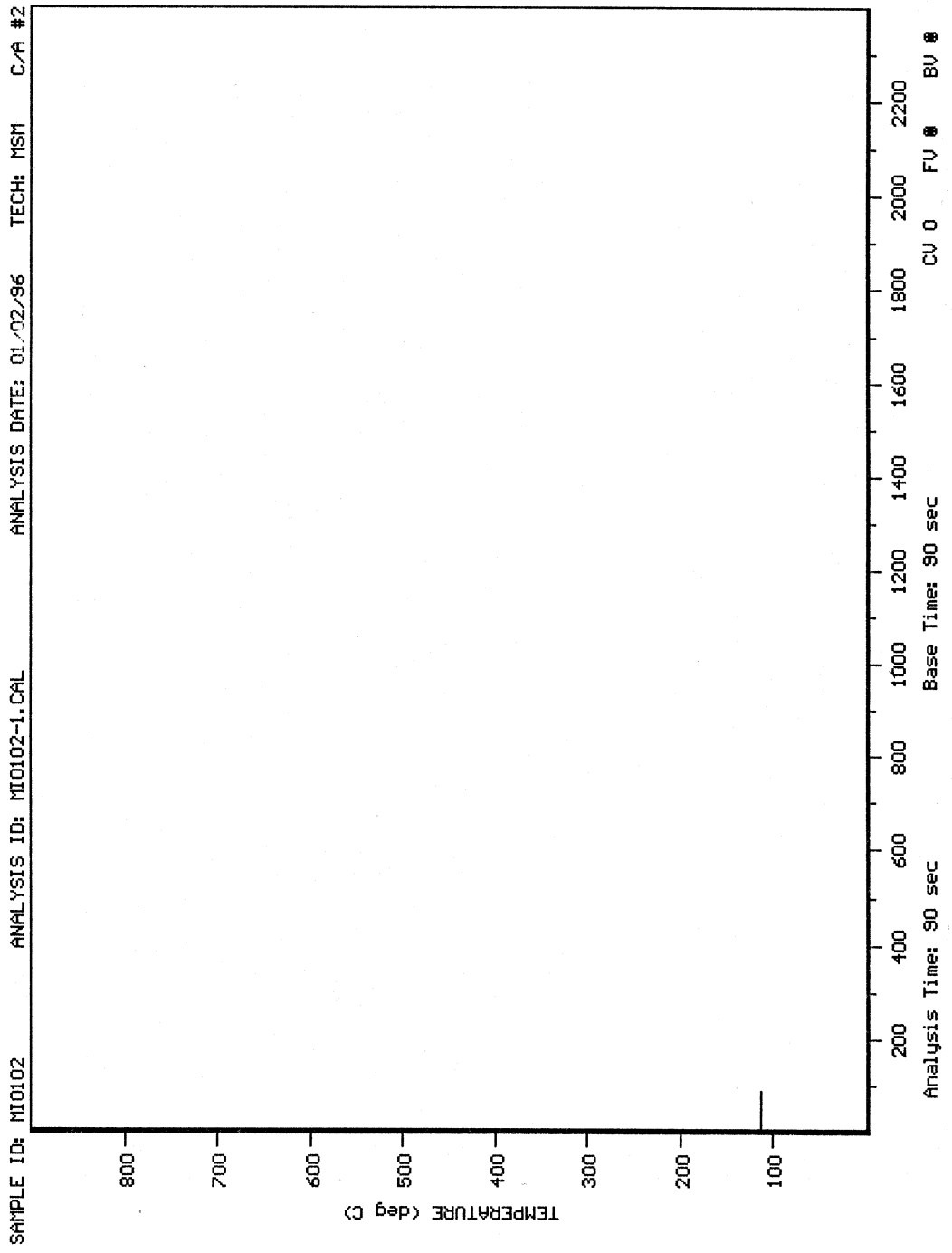

Figure 4-4. DRI Carbon Program Screen at 90 Seconds.

```
                              CARBON ANALYSIS RESULTS
Analyzer #4                                                    Technician: KGG
--------------------------------------------------------------------------------

Analysis ID     : MI1211-1.CAL
Sample ID       : MI1211
Carrier gas     : Oxygen/Helium mix

Analysis        : 12/11/95  09:33        Calculation      : 01/03/96  14:57
--------------------------------------------------------------------------------
Anal program ver: P4.1  (11/21/95)       Parm file ver    : D4.04  (11/21/95)
Calib. slope    : 22.25 ug C/peak ratio   Baseline time    :   90 sec
Calib. intercept:  0.00 ug C              Baseline window  :    1 counts
Reflectance unc.:    10 counts            Transmission unc.:   10 counts
Sample transit  :    28 sec               Calib. transit   :   45 sec
--------------------------------------------------------------------------------
Calibration peak area: 23736 counts
Initial FID baseline :   205 counts
--------------------------------------------------------------------------------
                      Peak Area                        Carbon
  Peak #1         : 21508 counts    20.16 ug C/injection

********************************************************************************

  Calculated Carbon:
       20.2 ug C/injection
```

Figure 4-5. DRI Carbon Program Tabular Printout, Calibration Run.

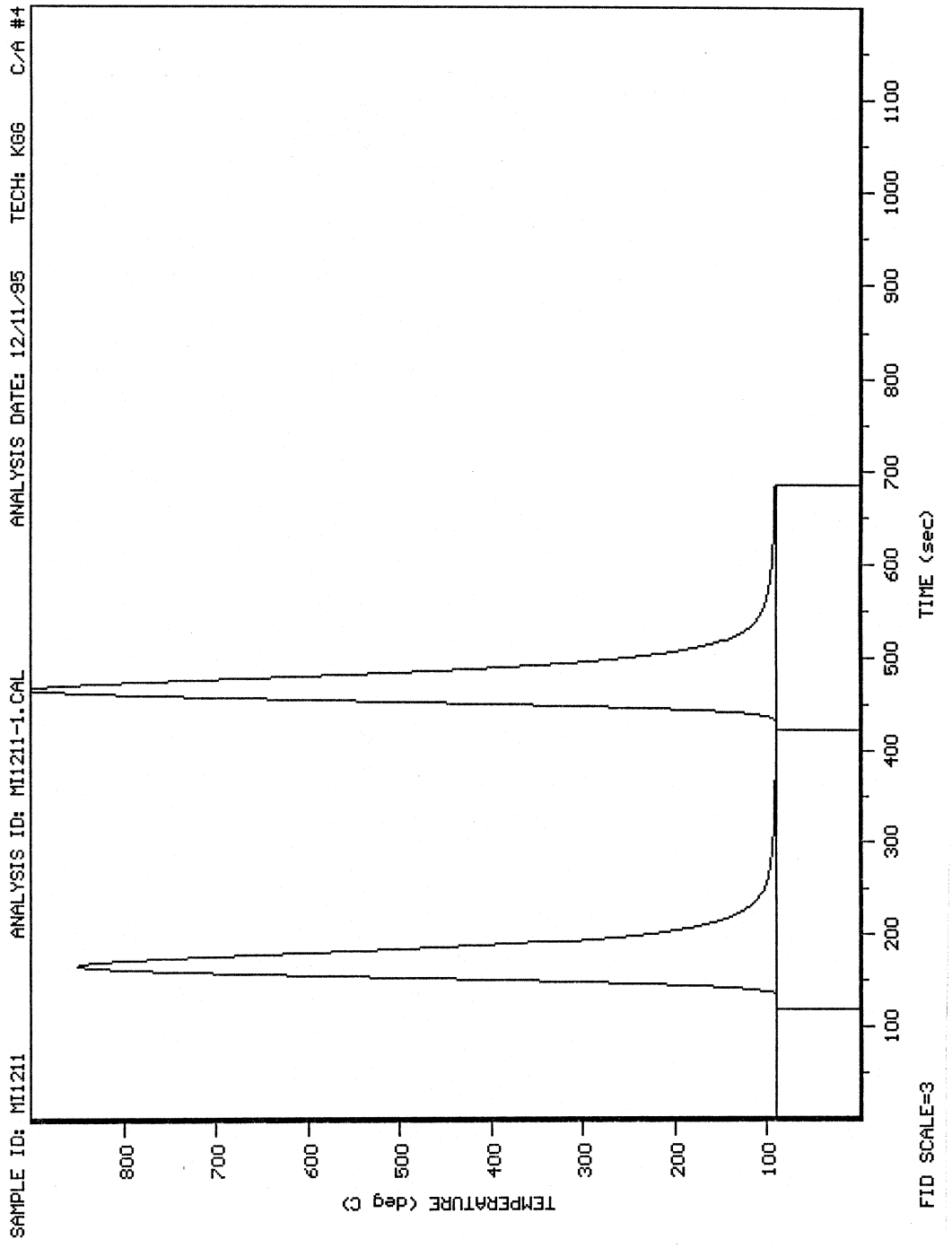

Figure 4-6. DRI Carbon Program Thermogram Printout, Calibration Run.

If the calibration result is unsatisfactory, follow the steps below until a satisfactory result is obtained:

1. Repeat the calibration using the same calibration gas under a He only atmosphere.

2. Perform a full "Leak Test" as described in Section 4.1 in order to determine if a gas leak exists. If this test fails, correct the problem and proceed to Step 3 (the most common problem is a poorly placed port fitting).

3. Repeat the calibration using the same calibration gas but under a He/O_2 atmosphere.

4. Repeat the calibration using the other calibration gas under a He/O_2 atmosphere.

5. If the calibration still does not pass and if possible, consult the laboratory manager for instructions.

- From the main menu of the Carbon program, select option 7 to change to the appropriate subdirectory for the samples to be analyzed. The new subdirectory name, if valid, will be displayed at the top on the screen.

- Based on the analysis list for the day, retrieve the samples to be analyzed from the sample freezer and place in a cooler with blue ice. Place the cooler in the instrument room.

4.2 Routine Operation

Routine analysis procedures depend on whether or not carbonate carbon will be determined before OC/EC analysis. The procedures are different for these two options.

4.2.1 Routine OC/EC Analysis

- Pull the push rod back to the idle zone of the quartz oven (approximately half way between the sample port and the heating element). Allow the boat/push rod to cool until the reading on the front of the analyzer reaches 50°C or less. Do not pull the boat into the sample loading zone when the boat is still hot as the heat will damage the Teflon ferrules of the sample port fitting.

- Insure that the petri dish, tweezers, and punching tool are thoroughly wiped clean with a dry KimWipe.

- Based on the analysis list, remove the sample to be analyzed from the sample cooler.

- Remove the filter from the PetriSlide or petri dish with tweezers, handling the filter only by the edge. Place the filter on the glass petri dish and remove a sample punch by pushing down gently on the punching tool. Rocking the punching tool slightly will insure that the punch is complete severed. Try to remove the punch from the edge of the deposit to avoid wasting the filter, but try to avoid areas of non-uniform deposits. Leaving the sample punch in the punching tool, place the punching tool on a clean Kimwipe. Return the filter to the PetriSlide or petri dish.

- Record the filter ID in the analyzer log book (Figure 2-6).

- After the boat has cooled to 50°C or less, loosen the sample port fitting carefully with a wrench. NOTE: avoid exerting any sideways pressure on the quartz oven. Try to confine the wrench pressure to only rotational torque. Loosen the front fitting before attempting the rear fitting. Slide the sample port fitting forward.

- Pull the boat back until it is centered in the sample port, taking care that the small stainless steel "ear" holding the boat to the push rod does not catch on the sample port opening and bend. If the "ear" does bend, carefully bend it back into position with tweezers or small clean pliers.

- Using the tweezers, push the bottom of the punch in the boat forward so that the top of the punch can be accessed. Remove the punch and place it on the top of the analyzer.

- Push the top of the sample punch with tweezers to rotate the punch within the punching tool. Remove the sample from the punching tool by grasping the bottom edge with the tweezers. Place the punch in the sample boat. Generally, the punch must be inserted sideways into the boat and then turned so the punch wedges itself facing forward. Push the punch forward until it is seated against the front of the slot in the boat.

- Push the push rod forward until the boat is located in the idle zone of the quartz oven (Figure 2-4). Slide the sample port fitting back until it is centered over the sample port and tighten firmly by hand. **DO NOT** tighten with a wrench. As before, avoid exerting any sideways pressure on the quartz oven.

- Select option 1 of the main menu of the Carbon program (Figure 4-1). Input the full sample ID. NOTE: the program will automatically place the computer into Caps Lock mode. After verifying the sample ID, enter the run number (1-9). The run number must correspond to the number of punches removed from the filter; for example, if the punch placed in the quartz boat is the third punch taken from the filter, the run number must be "3". Replicate runs are designated simply by the appropriate punch number (usually "2"). Note: the program creates a file name using the last six characters of the sample ID plus the run number; if the program finds another file with the same name, it will request that a new run number be input so the existing file will not be overwritten.

- Input the appropriate punch size (normally 0.536 cm^2) and filter deposit area (defined on the sample analysis list, Figure 2-7). Note that pressing **<Return>** is not necessary. Also note that if a mistake is made during input of analysis data pressing **<Esc>** will allow the option to be aborted and restarted.

- Enter any analysis flag options. A list of valid choices is presented on screen.

- Answer the purge question (Figure 4-7) by pressing **<Y>**. The sample oven must be purged with He for two minutes to remove all oxygen before the analysis begins. This question may be answered **<N>** if the run was aborted and is being restarted and the sample port was not opened.

- A data verification screen will appear (Figure 4-8). When all data is deemed correct, press any key except **<Esc>** to start the analysis program. If corrections are necessary, press **<Esc>** to clear the screen and return to the main menu.

- Using a small piece of clear tape, attach the previous sample punch to its thermogram, insuring that the deposit side is up.

- Wipe the tweezers, petri dish, and punching tool with clean Kimwipes.

- Replace the PetriSlide or petri dish containing the filter into the styrofoam cooler.

- The program will purge the oven with He for 90 seconds, after which data collection will begin. Readings are collected for 90 seconds to establish baselines. At 84 seconds, a warning tone will sound (the number of beeps corresponds to the analyzer number). At 90 seconds the analysis start tone will sound. At that time, push in the thermocouple/push rod until the stop is against the back fitting. While watching the punch, pull the push rod back 1-2 mm to physically decouple the push rod from the boat. If the boat slides back, immediately push the thermocouple back in and try again. The boat cannot be physically attached to the push rod during analysis, since the expansion of the thermocouple as the sample is heated will push the sample punch closer to the laser rod and cause erroneous laser signals.

- All physical adjustments must be made within 10 seconds: the laser baseline is calculated between 100 and 110 seconds analysis time. If the sample is not correctly positioned at the end of 10 seconds, press **<Esc>** to abort the program, pull the boat back to the idle zone, and restart the program. Decoupling the boat is most important for a meaningful laser signal.

```
+----------------------------------------+
| Current Directory: D:\MINTEK.94\BATCH09 |
+----------------------------------------+

Program option : OC/EC Analysis                    Technician: KGG

Enter full sample ID: NEL015Q Is this okay? Y

Enter run/punch number for this sample (1-9): 1

-------------------------------------------------------------------------------
Punch size options:

    1 ... 0.536 cm²
    2 ... 0.484 cm²
    3 ... 1     cm²
    4 ... other

Input option: 1

-------------------------------------------------------------------------------
Filter deposit area options:

    1 ...   1   cm²
    2 ...   3.8 cm²
    3 ...   6.4 cm²
    4 ...   8.3 cm²
    5 ...  13.8 cm²
    6 ...   7.1 cm²
    7 ... other

Input option: 7

-------------------------------------------------------------------------------
Analysis flag options:

    1 ... no problems
    2 ... blank filter (field blank, transport blank, etc.)
    3 ... sample dropped
    4 ... filter media damaged
    5 ... sample deposit damaged
    6 ... inhomogeneous sample deposit
    7 ... foreign substance(s) on deposit
    8 ... wet sample

Input option: 1

-------------------------------------------------------------------------------
Does the oven need to be purged? Y
```

Figure 4-7. DRI Carbon Program Before Starting Regular Analysis Run.

```
+----------------------------------------+
| Current Directory: D:\MINTEK.94\BATCH09 |
+----------------------------------------+

Program option : OC/EC Analysis                    Technician: KGG

-------------------------------------------------------------------------

Sample ID          : NEL051Q

  Data file name   : EL015Q-1.OEC

  Punch size       : 0.536 cm²

  Filter deposit   : 17.3 cm²

  Analysis flag    :

The oven will be purged for 90 seconds before analysis begins.

-------------------------------------------------------------------------

Press any key to begin analysis ...
```

Figure 4-8. DRI Carbon Program Data Entry Verification Screen.

- The program will proceed automatically from this point without further operator intervention. At the end of the program, data is saved to disk, split times are calculated, carbon peaks are integrated, and tabular and graphical printouts are produced. When the printer begins, the push rod may be pulled back to the idle zone to begin cooling.

- Examine the tabular printout (Figure 4-9) to insure the calibration peak counts are within specifications (see Section 4.1). Examine the thermogram (Figure 4-10) for proper laser response, temperature profiles, realistic carbon peaks, and the presence of the calibration peak at the end of the analysis (Section 6.5.1). Finally, examine the laser signal at the end of the run. Drooping of the laser signal as the temperature is dropping is an indication that the boat was coupled to the push rod and that the sample should be rerun. If all aspects of the analysis appears correct, select the appropriate analysis flag from the screen that appears at the end of the run (Figure 4-11). Also, mark the analysis date on the sample analysis list. If a problem is found, indicate the problem in the analyzer log book and rerun the sample.

- Repeat the above steps for additional sample runs.

4.2.2 System Blanks

System blanks are run at the beginning of each week. Follow the steps outlined in Section 4.2.1 with the following exceptions:

- Use option 7 from the main menu to change to the **\SYSBLK** subdirectory.

- Go through all the steps for a normal analysis, with the exception that the punch from the previous analysis is not removed. Open the sample port, pull the boat back into the loading zone, and without touching the existing punch push the boat forward into the idle zone, seal the sample port, and proceed with the analysis.

- Use an ID number derived from the current date: e.g., **SB0412** for April 12.

- Use a punch size of 1.0 cm^2 and a 1.0 cm^2 deposit area.

- Calculated carbon concentrations should not be more than 0.2 µg total carbon. Values greater than this warrant additional system blanks. Samples may not be analyzed until the system blank is < 0.2 µg total carbon.

4.2.3 Carbonate Analysis

- Follow the steps under Section 4.2.1 until the sample punch is loaded into the boat. Pull the boat BACK until the punch is centered under the acid injection port, taking care that the "ears" holding the boat to the push rod are not bent in the process.

CARBON ANALYSIS RESULTS

Analyzer #4 Technician: KGG

Analysis ID : EL051Q-1.OEC
Sample ID : NEL051Q
Punch area : 0.536 cm2
Deposit area : 17.30 cm2

Analysis : 12/11/95 10:23 Calculation : 01/03/96 15:11

Anal program ver: P4.1 (11/21/95) Parm file ver : D4.04 (11/21/95)
Calib. slope : 22.25 ug C/peak ratio Baseline time : 90 sec
Calib. intercept: 0.00 ug C Baseline window : 1 counts
Reflectance unc.: 10 counts Transmission unc.: 10 counts
Sample transit : 28 sec Calib. transit : 45 sec

Calibration peak area: 23577 counts
Initial FID baseline : 205 counts
Final FID baseline : 206 counts

	Reflect Split Time	Laser	FID Split Time
Lower split :	1348 sec	1661 counts	1376 sec
Regular split:	1350 sec	1678 counts	1378 sec
Upper split :	1352 sec	1694 counts	1380 sec

	Peak Area		Carbon
OC Peak #1 :	356 counts	0.63 ug C/cm2	10.84 ug C/filter
OC Peak #2 :	1848 counts	3.25 ug C/cm2	56.29 ug C/filter
OC Peak #3 :	3681 counts	6.48 ug C/cm2	112.12 ug C/filter
OC Peak #4 :	2390 counts	4.21 ug C/cm2	72.80 ug C/filter
Lower pyro'd OC :	533 counts	0.94 ug C/cm2	16.23 ug C/filter
Reg. pyro'd OC :	602 counts	1.06 ug C/cm2	18.34 ug C/filter
Upper pyro'd OC :	673 counts	1.18 ug C/cm2	20.50 ug C/filter
EC Peak #1 :	3310 counts	5.83 ug C/cm2	100.82 ug C/filter
EC Peak #2 :	265 counts	0.47 ug C/cm2	8.07 ug C/filter
EC Peak #3 :	58 counts	0.10 ug C/cm2	1.77 ug C/filter

	VOC	Regular OC	High Temp OC	Regular EC	High Temp EC	TC	
Lower split :	0.6	15.5	14.9	5.5	0.6	21.0	ug C/cm2
	10.8	268.3	257.4	94.4	9.8	362.7	ug C/filter
Regular split:	0.6	15.6	15.0	5.3	0.6	21.0	ug C/cm2
	10.8	270.4	259.5	92.3	9.8	362.7	ug C/filter
Upper split :	0.6	15.8	15.1	5.2	0.6	21.0	ug C/cm2
	10.8	272.6	261.7	90.2	9.8	362.7	ug C/filter

OC/TC: 0.75
EC/TC: 0.25
OC/EC: 2.93

Figure 4-9. DRI Carbon Program Tabular Printout, OC/EC Run.

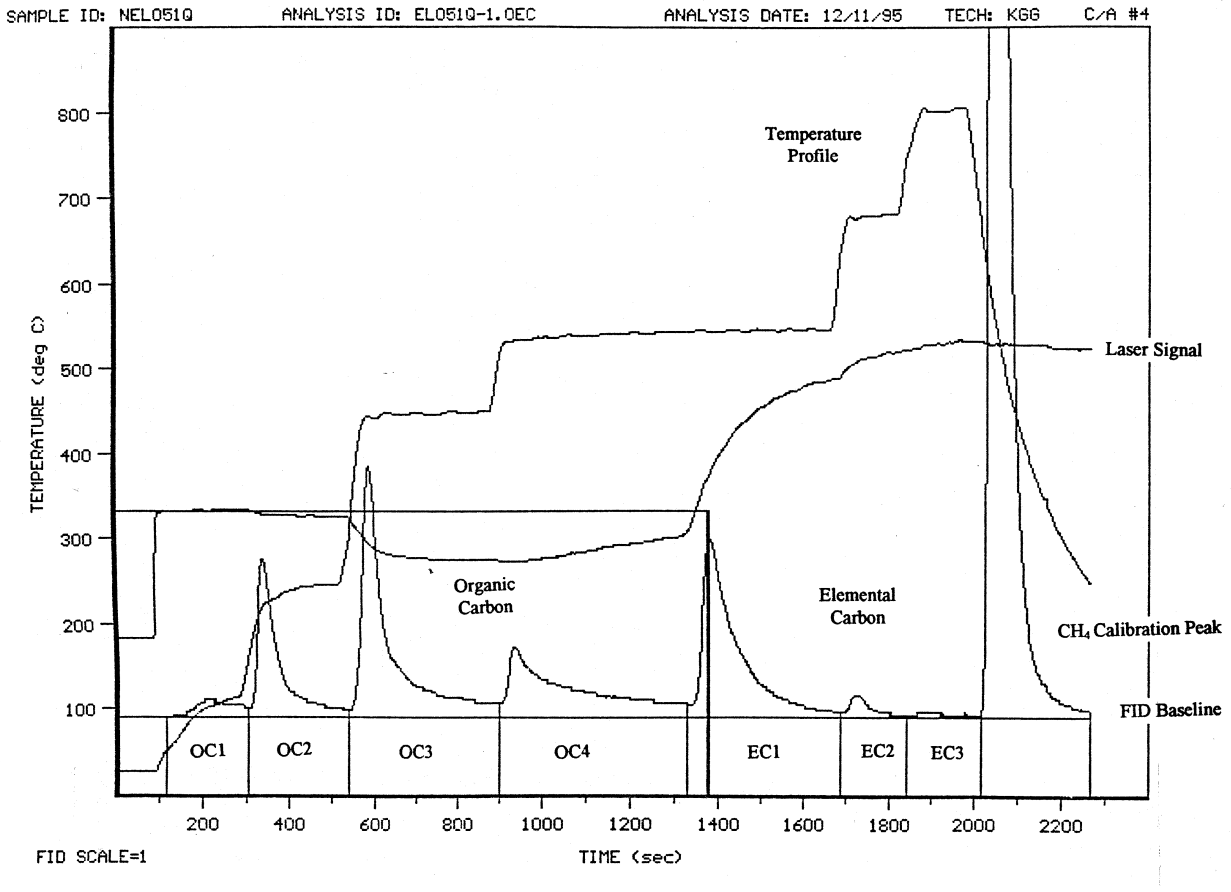

Figure 4-10. DRI Carbon Program Thermogram Printout, OC/EC Run.

```
Analysis validation values:

          Initial FID baseline :  23577 counts
          Final FID baseline   :    205 counts
          Calibration peak     :    206 counts

          Current analysis flag:
--------------------------------------------------------------------------------
Analysis flag options:

    1 ... No Problems
    2 ... Error in Sample ID
    3 ... Error in Deposit or Punch Area
    4 ... Temperature Suspect
    5 ... FID Suspect
    6 ... Laser Suspect
    7 ... Miscellaneous Problem
    8 ... Invalid

    9 ... Recall Thermogram for Review

 <Esc>... Exit Option (accept current flag)

Input option:
```

Figure 4-11. DRI Carbon Program Analysis Flags Menu.

- Select option 2 from the main menu (Figure 4-1). Enter the sample ID, run number, punch size, and filter size. Select the purge option and start the analysis program.

- At 60 seconds elapsed analysis time, flush the 25 ml syringe with 0.4 M hydrochloric acid (HCl) into a waste beaker. When the start tone sounds at 90 seconds elapsed time, eject 20 ml HCl onto the filter punch, insuring that the needle bevel is turned toward the punch and that the needle tip is touching the top of the punch.

- When the analysis is underway, flush the syringe with distilled water to prevent corrosion of the syringe plunger.

- After the carbonate analysis is completed, a tabular summary and a copy of the graph will be printed (similar in format to Figures 4-5 and 4-6). The program will automatically cycle into the normal OC/EC analysis, using the same sample ID. Push the sample boat into the punch drying area (about 1 cm from the first coil of the sample oven; see Figure 2-4). If the sample punch has tipped over during the carbonate analysis, open the sample port, reorient the punch, close the port, and proceed with drying the punch. Heat from the oxidation oven will dry the sample in this position without prematurely baking carbon from the sample; the sample temperature should not exceed 42°C. When the punch appears to be dry (wait at least 5 minutes), start the OC/EC analysis.

4.3 Analyzer Shut-Down

After the final sample for the day is analyzed, shut down the analyzers by:

- Leave the last analyzed punch in the boat with the boat positioned in the heating zone.

- Select option 3 to begin the calibration gas injection routine. Follow the injection procedures outlined in Section 4.1, with the exceptions that a He-only atmosphere is used during the afternoon check and the alternate calibration gas is used.

- When the analysis is completed, record the calibration peak counts and calculated injection calibration in the logbook. Any values outside the ranges defined in Section 4.1 should be investigated and rerun. Because low values from the end-of-day calibration could potentially invalidate the entire day's runs, any deviation from the accepted ranges must be noted and the cause identified.

- Select option 8 (End-of-Day Functions) from the main menu (Figure 4-1). A submenu will appear with options for daily summary printouts and automated backup of all new data files (Figure 4-12).

- Select option 1 from the submenu and follow all on-screen directions. A single page summary will be printed for each subdirectory (each project) containing samples analyzed during that day (Figure 4-13). The End-of-Day Functions submenu will reappear when the printing is done.

```
                +----------------------------------------+
                | Current Directory: D:\MINTEK.94\BATCH09 |
                +----------------------------------------+

Program option: End-of-Day Functions


Function options:

    1 ... Print Daily Summary Files
    2 ... Backup Raw Data Files

 <Esc>... Exit Option

Input option:
```

Figure 4-12. DRI Carbon Program End-of-Day Functions Menu.

DAILY CARBON ANALYSIS SUMMARY
****

Analyzer : #4
Analysis Date : 12/11/95
Directory : D:\MINTEK.94\BATCH09

Original Analyses : 10
Reruns/Replicates : 0

Analysis ID	Sample ID	Flag	CO3 (ug/f)	OC1 (ug/f)	OC2 (ug/f)	OC3 (ug/f)	OC4 (ug/f)	POC (ug/f)	EC1 (ug/f)	EC2 (ug/f)	EC3 (ug/f)	Deposit Area	Tech
EL051Q-1.OEC	NEL051Q		-99.00	10.84	56.29	112.12	72.80	18.34	100.82	8.07	1.77	17.30	KGG
EL052Q-1.OEC	NEL052Q		-99.00	10.42	52.03	109.02	75.73	26.44	118.83	7.43	0.37	17.30	MSM
ELR03Q-1.OEC	NELR03Q		-99.00	32.14	39.50	54.43	47.17	44.24	57.21	23.09	2.25	17.30	MSM
ELR04Q-1.OEC	NELR04Q		-99.00	28.12	42.13	57.22	47.65	52.74	61.60	20.42	2.45	17.30	MSM
ELR15Q-1.OEC	NELR15Q		-99.00	22.25	30.11	48.74	27.84	17.84	36.66	13.31	0.00	17.30	MSM
ELR16Q-1.OEC	NELR16Q		-99.00	23.65	36.28	49.66	32.09	25.49	47.77	14.15	0.18	17.30	MSM
OLF15Q-1.OEC	OLF15Q		-99.00	106.45	201.63	382.75	294.97	248.26	769.83	21.07	7.00	17.30	MSM
OLF16Q-1.OEC	OLF16Q		-99.00	82.42	179.69	333.19	257.24	211.95	680.76	22.26	7.05	17.30	MSM
OLF43Q-1.OEC	OLF43Q		-99.00	30.11	94.55	172.90	131.19	48.64	262.26	22.13	3.84	17.30	MSM
OLF44Q-1.OEC	OLF44Q		-99.00	26.94	70.64	153.11	118.14	30.43	184.84	24.20	5.83	17.30	MSM

Figure 4-13. DRI Carbon Program Daily Summary Printout.

- Select option 2 from the submenu and follow all on-screen directions. Pre-formatted LS-120 super disk must be available before this option is selected. The program will automatically copy to the floppy disk all files created or modified since the last backup in each subdirectory selected that day. Begin with the floppy disk used the previous day. If the floppy disk is filled, the program will prompt for a new formatted disk. When all files are copied to the floppy disks, the End-of-Day Functions submenu will reappear. Press **<Esc>** to return to the main menu.

- Label the floppy disks in the following format:

Analyzer# CARBON BACKUP startdate-enddate

For example, for a disk containing data files for analyses run on September 1, 2, and 3, the label would be written:

C/A# 1 CARBON BACKUP 09/1/00-09/1/00

- Place full disks in the storage boxes located in the laboratory supervisor's office. Leave partially filled disks (there should be no more than one per analyzer) in the "Active Floppies" box in the Carbon Laboratory.

- Press **<Esc>** to end the Carbon program. This is necessary because when the Carbon program ends, it sets the analyzer valves such that oxygen is flowing through the MnO_2 catalyst, allowing some regeneration of the catalyst overnight.

- Remove the printouts and attach them to a manila folder labeled with the date and analyzer number. Place on the lab supervisor's desk for Level I validation (Section 6.5).

- Leave the computers and analyzers on overnight unless the potential for power outages or surges exists. You may turn the monitors off or leave them on. **DO NOT** start a screensaver program. This will interfere with the nightly backup program.

- Make a final check of the gas cylinder pressures to insure that gas flow, especially the compressed air, will continue until someone will be available to check them again.

- Put the samples and blue ice in the sample cooler back into the sample storage freezer and lock the freezer.

- If the 25 ml syringe was used for carbonate analysis, thoroughly rinse the syringe with distilled water and tightly cap all solutions.

- Lock the carbon analysis room.

4.4 Abbreviated Operational Checklist

4.4.1 Start-Up:

- Check all gas cylinders' pressures and delivery pressures.
- Check that all FIDs are lit by holding a pair of tweezers over the FID exhaust stack and watching for condensation. Relight if necessary.
- Check and readjust if necessary all gas flows at the analyzer.
- Turn on the computer monitor.
- Insure that the date on the computer is current.
- Double-Click the **CARBON** icon to begin the carbon program.
- Insure that the sample port fitting is tight and that the thermocouple push rod is reasonably snug at the back fitting.
- Perform a leak test, involving isolating the oven and operating the Carle valve.
- Purge the system of calibration gas injected by the above step.
- From the opening menu, select option 4 to bake the oven for 10 minutes.
- Begin the daily entry in the carbon analyzer logbook.
- Wipe the sample tweezers, petri dishes, and punching tool with clean Kimwipes.
- Insure that the printers have enough paper for the day and that the toner cartridge is producing legible printing.
- Perform the morning calibration injection by selecting option 3 and He/O_2 carrier gas (option 1). When the analysis is complete, record the calibration peak counts and injection concentration. Insure that these values are within their proper ranges.
- Change to the appropriate subdirectory for the samples to be analyzed.
- Retrieve the samples to be analyzed from the sample freezer.

4.4.2 Routine OC/EC Analysis

- Pull the push rod back to the idle zone of the quartz oven and allow the boat/push rod to cool.

- Insure that the tweezers, petri dish, and punching tool are wiped clean.
- Based on the analysis list, remove the sample to be analyzed from the sample cooler.
- Remove a sample punch from the filter.
- Record the filter ID in the analyzer logbook, along with any comments on the condition of the deposit or any other conditions which might affect analysis results.
- After the boat has cooled to 50°C or less, remove the previously analyzed sample punch and load the current sample punch.
- Begin the analysis by selecting option 1 from the main menu of the Carbon program and inputting the sample ID, run number, punch size, and filter deposit area.
- Push the sample into the heated zone at 90 seconds, insuring that the boat is not physically coupled to the push rod.
- Using a small piece of clear tape, attach the previous sample punch to its thermogram, insuring that the deposit side is up.
- Clean the tweezers, petri dish, and punching tool.
- Replace the PetriSlide or petri dish containing the filter into the sample cooler.
- At the end of the analysis, the push rod should be pulled back to the idle zone to begin cooling.
- Examine the thermogram for proper laser response, temperature profiles, realistic carbon peaks, and the presence of the calibration peak at the end of the analysis. Examine the tabular printout to insure the calibration peak counts are within specifications (see Section 4.1). Finally, examine the laser signal at the end of the run. Rerun any deviants immediately. Indicate successful analyses on the sample analysis list.
- Repeat the above steps for additional samples.

4.4.3 System Blanks (run first each Monday):

- Change to the **SYSBLK** subdirectory.
- Go through all the steps for a normal analysis, with the exception that the punch from the previous analysis is not removed. Open the sample port, pull the boat back into the loading zone, and without touching the existing punch push the boat forward into the idle zone, seal the sample port, and proceed with the analysis.

- Use an ID number derived from the current date: e.g., **SB0412**.
- Calculated carbon concentrations should not be more that 0.2 µg carbon. Values greater than this warrant an additional system blank.

4.4.4 Carbonate Analysis:

- Follow the steps under Routine Analysis until the sample punch is loaded into the boat. Pull the boat BACK until the punch is centered under the acid injection port.
- Select option 2 from the main menu. Enter the sample ID, run number, punch size, and filter size. Select the purge option and start the analysis program.
- At 90 seconds elapsed time, eject 20 ml HCl onto the filter punch.
- Flush the syringe with distilled deionized water between samples.
- Continue the normal OC/EC analysis when the carbonate cycle is complete.

4.4.5 Analyzer Shut-Down:

- Leave the last analyzed punch in the boat with the boat positioned in the heating zone.
- Select option 3 to begin the calibration gas injection routine. Follow the injection procedures outlined in the Start Up section with the exception that a He only atmosphere is used.
- When the analysis is complete, record the calibration peak counts and calculated injection calibration in the logbook. Any values outside the ranges defined in Section 4.1 should be investigated and rerun.
- Print summaries of the day's analyses.
- Backup the day's data files.
- Remove the printouts and attach them to a manila folder labeled with the date and analyzer number. Place on the lab supervisor's desk.
- Turn off the computer monitors.
- Make a final check of the gas cylinder pressures.
- Put the samples and blue ice in the sample cooler back into the sample storage freezer and lock the freezer.
- If the 25 ml syringe was used for carbonate analysis, thoroughly rinse the syringe with distilled water and tightly cap all solutions.

- Lock the carbon analysis room.

5.0 QUANTIFICATION

5.1 Calibration procedures

The calibration procedures for the carbon analyzers are of three types: the end-of-run calibration peak, the manual calibration injections of CH_4/He and CO_2/He, and instrument calibration using KHP, sucrose, and the two calibration gases.

The end-of-run calibration consists of a set quantity of CH_4/He calibration gas which is automatically injected by the Carbon program. All FID readings during the analysis run are normalized to this peak to minimize the effects of FID performance and electronic drift over time. The end-of-run calibration occurs automatically at the end of each analysis run and requires no operator intervention. The integrated calibration peak counts should be checked by the operator immediately after each run to insure that the analyzer is operating satisfactorily.

The manual calibration injections are performed at the beginning and ending of each analysis day, and serve to verify proper analyzer performance. The procedure for manual injections are described in Section 4.1 and 4.3.

Instrument calibration, performed twice a year or when a new calibration gas cylinder is started, establishes the calibration slope used in converting counts to µg of carbon, as explained in the next section. Instrument calibration involves spiking prefired quartz punches with various amounts of the 1800 ppm KHP and sucrose solutions (Section 3.1) and injecting various volumes of the CO_2 and CH_4 gases.

A clean blank quartz punch is baked in the analyzer oven at 800°C for 10 minutes using option 4 from the main menu of the carbon program. After the punch has cooled to less than 50°C, the KHP or sucrose solution (prepared as described in Section 3.1) is injected onto the punch using a 20 ml syringe. The following volumes are used:

- 5 ml KHP or sucrose solution
- 10 ml KHP or sucrose solution
- 15 ml KHP or sucrose solution (do twice)
- 20 ml KHP or sucrose solution
- no injection (as a system blank; see Section 4.2.2)
- 20 ml acidified DDW only (check of background level of DDW)

The sample port is sealed and the spiked filter punch is pushed to 1 cm from the sample oven. In this position the punch will experience a temperature of 35 to 40°C due to the heat from the oxidation oven. Allow the punch to dry thoroughly; the punch will turn from translucent to opaque as it dries. The punch must be dry to avoid water vapor effects on the FID. The OC/EC analysis