

**DRI STANDARD OPERATING PROCEDURE**

**Thermal/Optical Reflectance Carbon Analysis  
of Aerosol Filter Samples**

**DRI SOP #2-204.6  
Revised June, 2000**

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Title: Thermal/Optical Reflectance Carbon  
Analysis of Aerosol Filter Samples

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## 1.0 GENERAL DISCUSSION

### 1.1 Purpose of Procedure

This standard operating procedure is intended to:

- provide a basic understanding of the principles of carbon analysis and carbon analyzer operation;
- describe routine determination of organic, elemental, and carbonate carbon from ambient and source filter samples using the DRI thermal/optical reflectance carbon analyzer;
- detail the concerns and procedures that will insure a state-of-the-art carbon analysis measurement process.

This procedure will be followed by all analysts at the Environmental Analysis Facility of the Division of Atmospheric Sciences at the Desert Research Institute.

### 1.2 Measurement Principle

The DRI thermal/optical carbon analyzer is based on the preferential oxidation of organic carbon (OC) and elemental carbon (EC) compounds at different temperatures. It relies on the fact that organic compounds can be volatilized from the sample deposit in a helium (He) atmosphere at low temperatures, while elemental carbon is not oxidized and removed. The analyzer operates by: 1) liberating carbon compounds under different temperature and oxidation environments from a small sample punch (normally 0.536 cm<sup>2</sup>) taken from a quartz fiber filter; 2) converting these compounds to carbon dioxide (CO<sub>2</sub>) by passing the volatilized compounds through an oxidizer (heated manganese dioxide, MnO<sub>2</sub>); 3) reduction of CO<sub>2</sub> to methane (CH<sub>4</sub>) by passing the flow through a methanator (hydrogen-enriched nickel catalyst); and 4) quantification of CH<sub>4</sub> equivalents by a flame ionization detector (FID).

The principal function of the optical (laser reflectance) component of the analyzer is correction for pyrolysis of organic carbon compounds to elemental carbon. Without this correction, the organic carbon fraction of the sample would be underestimated and the elemental carbon fraction would be overestimated by including some pyrolyzed organic carbon. The correction for pyrolysis is made by continuously monitoring the filter reflectance (via a helium-neon laser and a photodetector) throughout an analysis cycle. This reflectance, largely dominated by the presence of light absorbing elemental carbon, decreases as pyrolysis takes place and increases as light absorbing carbon is liberated during the latter part of the analysis. By monitoring the reflectance, the portion of the elemental carbon peak corresponding to pyrolyzed organic carbon can be accurately assigned to the organic fraction. The correction for pyrolytic conversion of organic to elemental carbon is essential for an unbiased measurement of both carbon fractions, as discussed in Johnson et al. (1981).

Carbonate carbon can be determined by measuring the CO<sub>2</sub> evolved upon acidification of the sample punch before the normal carbon analysis procedure.

Seven temperature fractions as well as the pyrolysis correction are individually determined and can be reported. Values routinely reported include total organic carbon, organic carbon evolved at temperatures greater than 120°C (high-temperature organic carbon), total elemental carbon, elemental carbon evolved at temperatures greater than 550°C (high-temperature elemental carbon), total carbon, and carbonate.

### 1.3 Measurement Interferences and Their Minimization

- Carbonate carbon presents significant interference in carbon analysis if it constitutes more than 5% of total carbon in the ambient or source sample, as it is measured as both organic and elemental carbon during thermal/optical carbon analysis. Acid pretreatment of the filter samples can eliminate the carbonate interference.
- The presence of certain minerals in some soils can affect the laser correction for pyrolysis. These minerals change color as the sample punch is heated, generally resulting in a sample which is darker. For samples which contain large fractions of resuspended soils, the split between organic and elemental carbon should be examined manually.
- Some minerals, again predominantly in soil samples or soil dominated samples, may affect the laser reflectance by temporarily changing color or changing the surface texture of the deposit residue. Unlike the effect described above, these changes are reversible and highly temperature dependent.
- Some colored organic compounds can affect the laser correction causing increased reflectance as these compounds are removed. This effect is readily ascertained by examining the laser response during the organic portion of the analysis. The split between organic and elemental carbon should be examined manually if the effect is large.
- The presence of certain elements (Na, K, Pb, Mn, V, Cu, Ni, Co, and Cr), existing either as contaminants on the filters (e.g., glass fiber filters) or as part of the deposit material, has been shown to catalyze the removal of elemental carbon at lower temperatures (Lin and Friedlander, 1988). Such catalysis would affect the distribution of carbon peaks during the analysis.
- Water vapor, either contained in the deposit or remaining after acidification of the sample punch, can shift the FID baseline. Allowing the sample punch to dry in the analyzer by passing carrier gases over it will eliminate this effect.

### 1.4 Ranges and Typical Values of Measurements

A wide range of aerosol concentrations can be measured with this method, the limiting factor being the concentration of the carbon compounds on a µg/filter basis. Heavily polluted environments, which would normally have carbon concentrations above the working range of the

carbon analyzer, may be sampled and analyzed within the range of the carbon analyzer by increasing the filter deposit area or by decreasing the sampling flow rate and/or sampling time.

The carbon analyzer can effectively measure between 0.05 and 750  $\mu\text{g carbon/cm}^2$ . The upper range is somewhat arbitrary, depending on the particular compounds on the filter and the temperatures at which they evolve. This upper range may be extended by taking special precautions, such as reducing the punch size or by special temperature programming, to avoid an over-range FID signal.

Typical carbon values range between 10 and 100  $\mu\text{g carbon/cm}^2$  for ambient samples. The distribution between organic and elemental carbon depends on the particulate source types, and range from no elemental carbon (e.g., hot gasoline exhaust) to 80% or more elemental carbon (e.g., woodsmoke and diesel exhaust).

### 1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

The lower quantifiable limits (LQLs) of carbon combustion methods depend upon the variable carbon content of the blank quartz filters as well as the analysis method. For better LQLs, the unexposed filters should be pre-fired in an oven at high temperatures for several hours to remove any residual carbon contamination (Fung, 1986; Huntzicker, 1986; Rau, 1986). All quartz filters originating from DRI are pre-fired for a minimum of four hours at 900°C and are acceptance-tested for blank levels before use. Any filters that fail to pass the preset acceptance levels (1.5  $\mu\text{g/cm}^2$  organic carbon, 0.5  $\mu\text{g}$  elemental carbon, and 2.0  $\mu\text{g}$  total carbon) are discarded and not used for sample collection. Average pre-fired blank levels are  $0.41 \pm 0.2$   $\mu\text{g organic carbon/cm}^2$ ,  $0.03 \pm 0.2$   $\mu\text{g elemental carbon/cm}^2$ , and  $0.44 \pm 0.2$   $\mu\text{g total carbon/cm}^2$ . Because even pre-fired filters can absorb organic vapors during shipping and storage, the LQL of analysis on a particular set filters depends on the number of field blanks analyzed and the variability in the results from those blanks.

The minimum detection limit (MDL) of the DRI carbon analyzers based on the analyses of 693 individual quartz-fiber filters and defined as three times the standard deviation of their measured results. They are:

total organic carbon	0.82 $\mu\text{g/cm}^2$
high-temperature organic carbon	0.81 $\mu\text{g/cm}^2$
total elemental carbon	0.19 $\mu\text{g/cm}^2$
high-temperature elemental carbon	0.12 $\mu\text{g/cm}^2$
total carbon	0.93 $\mu\text{g/cm}^2$

Acid-evolved carbonate levels in pre-fired quartz filters have been shown to be quite variable (0.0-1.0  $\mu\text{g/cm}^2$ ) over time. The reaction of ambient  $\text{CO}_2$  with alkaline sites on the quartz fibers may be the cause of such variable blank levels. Acceptance testing for carbonate is not routinely performed at DRI, as carbonate analysis is performed only upon special request by the client.

The precision of this analysis has been reported to range from 2 to 4% (Johnson, 1981). For analysis of actual ambient and source filters, homogeneity of the deposit is most important for

reproducible results. For homogeneous deposits containing >10 µg/filter of total carbon, precision is generally 5% or less; for inhomogeneous deposits replicates may deviate by as much as 30%. The precision of carbonate analysis results is approximately 10%.

The precision of the laser-dependent split between organic and elemental carbon fractions depends upon how rapidly the laser is increasing at the time of the split and whether the split falls in the middle of a large carbon peak or not. Typically, relative laser split times are reproducible within 10 seconds and deviations in calculated splits are less than 5% of the total measured carbon.

The accuracy of the thermal/optical reflectance method for total carbon determined by analyzing a known amount of carbon is between 2 to 6% (Rau, 1986). Accuracy of the organic/elemental carbon split is between 5 and 10%.

## 1.6 Personnel Responsibilities

All analysts in the laboratory should read and understand the entire standard operating procedure prior to performing carbon analysis, which includes routine system calibration, actual analysis, and immediate review of the data as it is produced to correct system problems.

It is the responsibility of the laboratory manager or supervisor to ensure the carbon analyses procedures are properly followed, to examine and document all replicate, standard, and blank performance test data, to designate samples for reanalysis, to arrange for maintenance and repair, to maintain the supplies and gases necessary to insure uninterrupted analysis, and to deliver the analysis results in database format to the project manager within the specified time period.

The quality assurance (QA) officer of DRI's Division of Atmospheric Sciences is responsible to determine the extent and methods of quality assurance to be applied to each project, to estimate the level of effort involved in this quality assurance, to update this procedure periodically, and to ascertain that these tasks are budgeted and carried out as part of the performance on each contract.

## 1.7 Definitions

The following terms are used in this document:

**Calibration Injection:** The injection of calibration gases (methane in helium [CH<sub>4</sub>/He] or carbon dioxide in helium [CO<sub>2</sub>/He]) into the sample stream to check instrument performance.

**Calibration Peak:** The FID peak resulting from the automatic injection of methane calibration gas (CH<sub>4</sub>/He) at the end of each analysis run (each sample). All integrated peak areas are divided by the calibration peak area and multiplied by an instrument-specific calibration factor to obtain µg carbon.

FID Split Time:	The time at which the laser split occurs plus the time required for carbon compounds to travel from the sample punch to the FID.
High Temperature Elemental Carbon:	Carbon evolved from the filter punch in an oxygen/helium (O <sub>2</sub> /He) atmosphere at 700 and 800°C minus any pyrolyzed organic carbon present in these two peaks.
High Temperature Organic Carbon:	Carbon evolved from the filter punch in a He-only atmosphere at 250, 450, and 550°C plus pyrolyzed organic carbon. This is the same as regular OC without the first organic carbon peak (VOC).
Laser Split:	The demarcation between organic and elemental carbon, at which the laser-measured reflectance of the filter punch reaches its initial value. At this point all pyrolyzed organic carbon has been removed and original elemental carbon is beginning to evolve.
Lower Split Time:	The time at which the laser-measured reflectance of the filter punch reaches its initial value minus the precision of the laser signal (currently defined as 10 counts).
Pyrolysis:	The conversion of organic carbon compounds to elemental carbon due to incomplete combustion/oxidation; may be envisioned as "charring" during the organic portion of the analysis.
Pyrolyzed Carbon:	The carbon evolved from the time that the carrier gas flow is changed from He to He/O <sub>2</sub> at 550°C to the time that the laser-measured filter reflectance reaches its initial value.
Regular Elemental Carbon (EC):	Carbon evolved from the filter punch in a helium/ oxygen (He/O <sub>2</sub> ) atmosphere at 550, 700, and 800°C minus pyrolyzed organic carbon.
Regular Organic Carbon (OC):	Carbon evolved from the filter punch in a He atmosphere at 120, 250, 450, and 550°C plus pyrolyzed organic carbon. This is the same as VOC plus high temperature OC.
Regular Split Time:	The time at which the laser-measured reflectance of the filter punch reaches its initial value.
Total Carbon (TC):	All carbon evolved from the filter punch between ambient and 800°C under He and O <sub>2</sub> /He atmospheres.
Upper Split Time:	The time at which the laser-measured reflectance of the filter punch reaches its initial value plus the precision of the laser signal (currently defined as 10 counts).

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Volatile Organic  
Carbon (VOC): Organic carbon evolved from the filter punch in a He-only atmosphere between ambient and 120°C (the first organic carbon peak).

## 1.8 Related Procedures

SOP's related to carbon analysis activities and other manuals which should be reviewed in conjunction with this document are:

- DRI SOP #6-001.1 Shipping and Mailing Procedures.
- DRI SOP #6-009.1 Field and Laboratory Safety Procedures.
- DRI SOP #4-001.1 Creation, Revision, Distribution, and Archiving of Standard Operating Procedures.
- DRI SOP #2-106.3 Pre-Firing of Quartz Filters for Carbon Analysis

The DRI Carbon Analyzer Model 3000 Owner's Manual, revised 6/90.

The DRI Carbon Analyzer Model 3000 Maintenance and Troubleshooting Manual, revised 7/94.

## 2.0 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

### 2.1 Apparatus and Instrumentation

#### 2.1.1 Description

The components of the DRI thermal/optical carbon analyzer are depicted in Figures 2-1 and 2-2; the complete gas flow schematic is shown in Figure 2-3. The programmable combustion oven is the heart of the carbon analyzer and includes loading, combustion, and oxidation zones in a single quartz "oven" as depicted in Figure 2-4.

In addition to the DRI thermal/optical analyzer connected to a Pentium compatible computer, the following items are needed for routine carbon analysis:

- Stainless steel punching tool: 0.516 cm<sup>2</sup> area for removing small sample punches from quartz filters. This punching tool must be kept clean and sharp. If the punching tool is sharpened, the punch area must be reverified.

Title: Thermal/Optical Reflectance Carbon  
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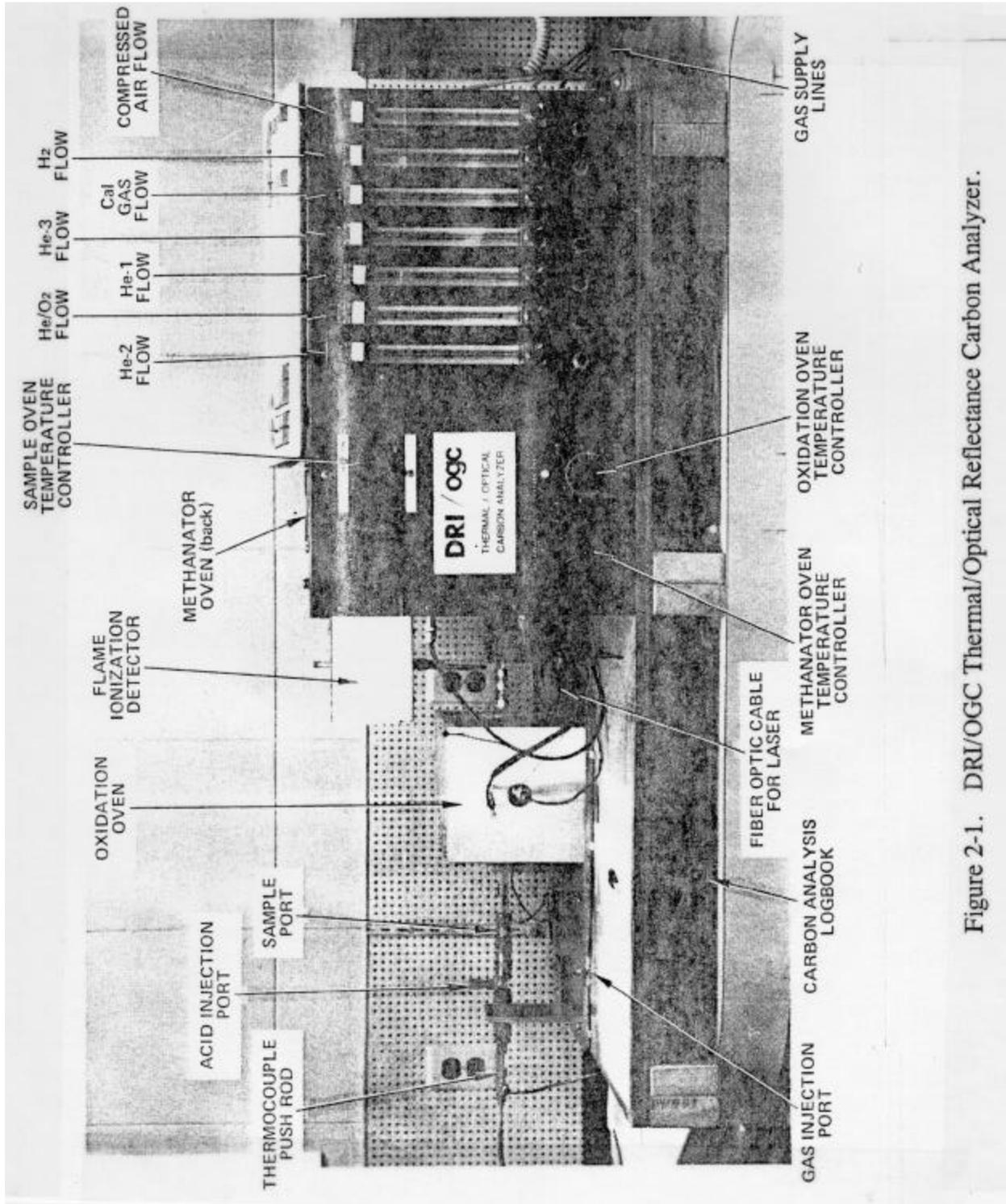


Figure 2-1. DRI/OGC Thermal/Optical Reflectance Carbon Analyzer.

Title: Thermal/Optical Reflectance Carbon  
Analysis of Aerosol Filter Samples

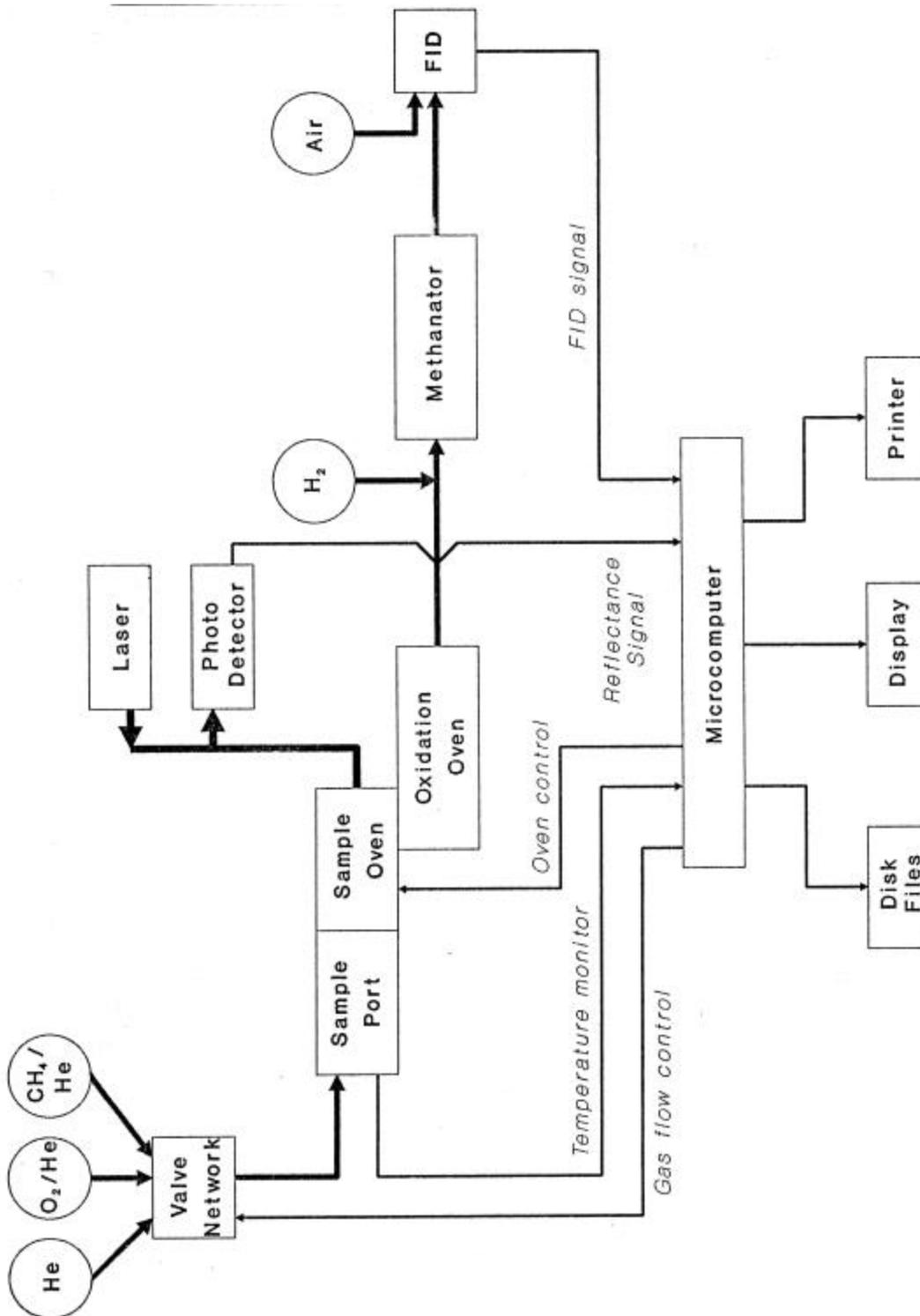


Figure 2-2. DRI/OGC Thermal/Optical Reflectance Carbon Analyzer Block Diagram.

Title: Thermal/Optical Reflectance Carbon  
 Analysis of Aerosol Filter Samples

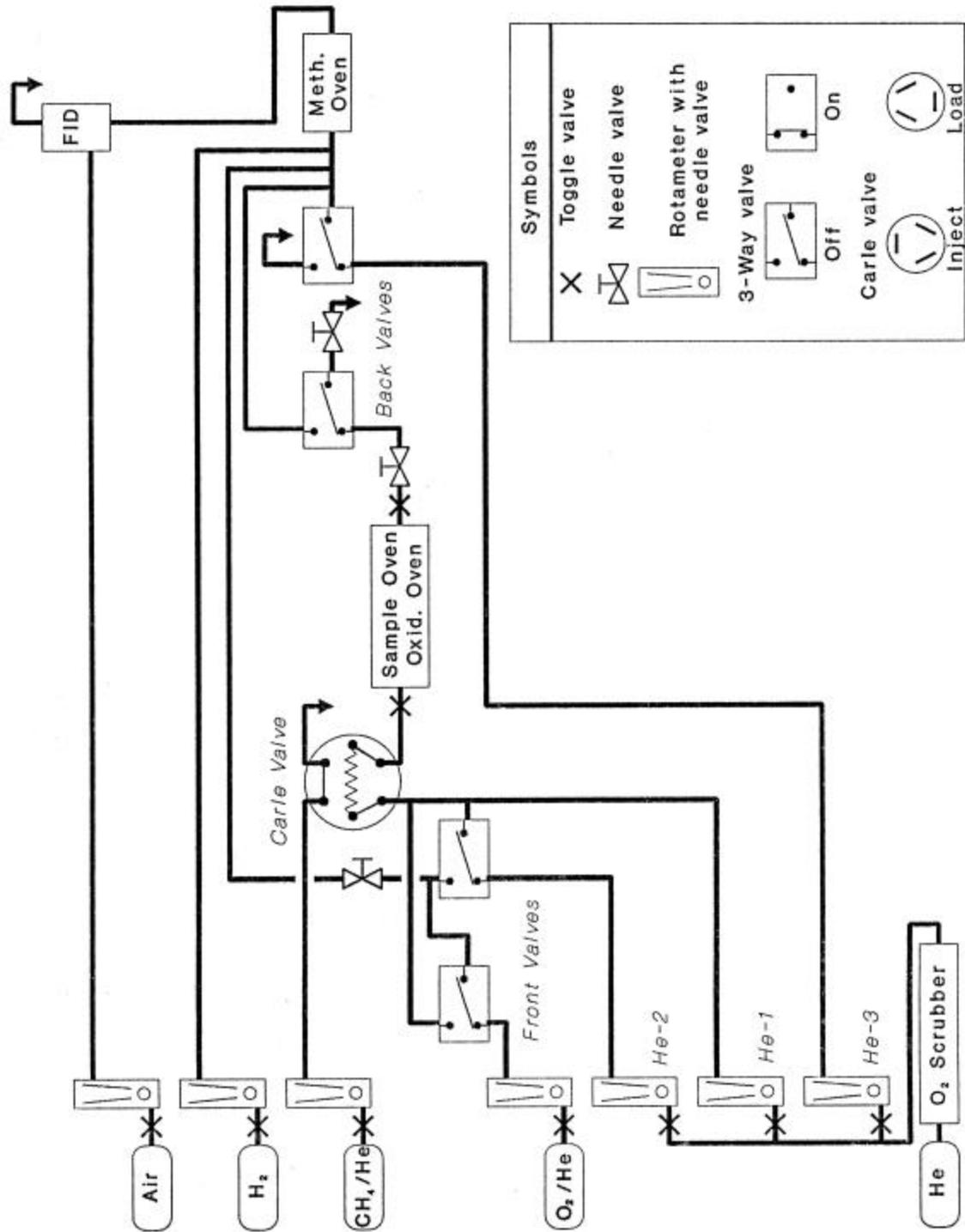


Figure 2-3. DRI/OGC Thermal Optical Reflectance Carbon Analyzer Flow Schematic.

Title: Thermal/Optical Reflectance Carbon  
Analysis of Aerosol Filter Samples

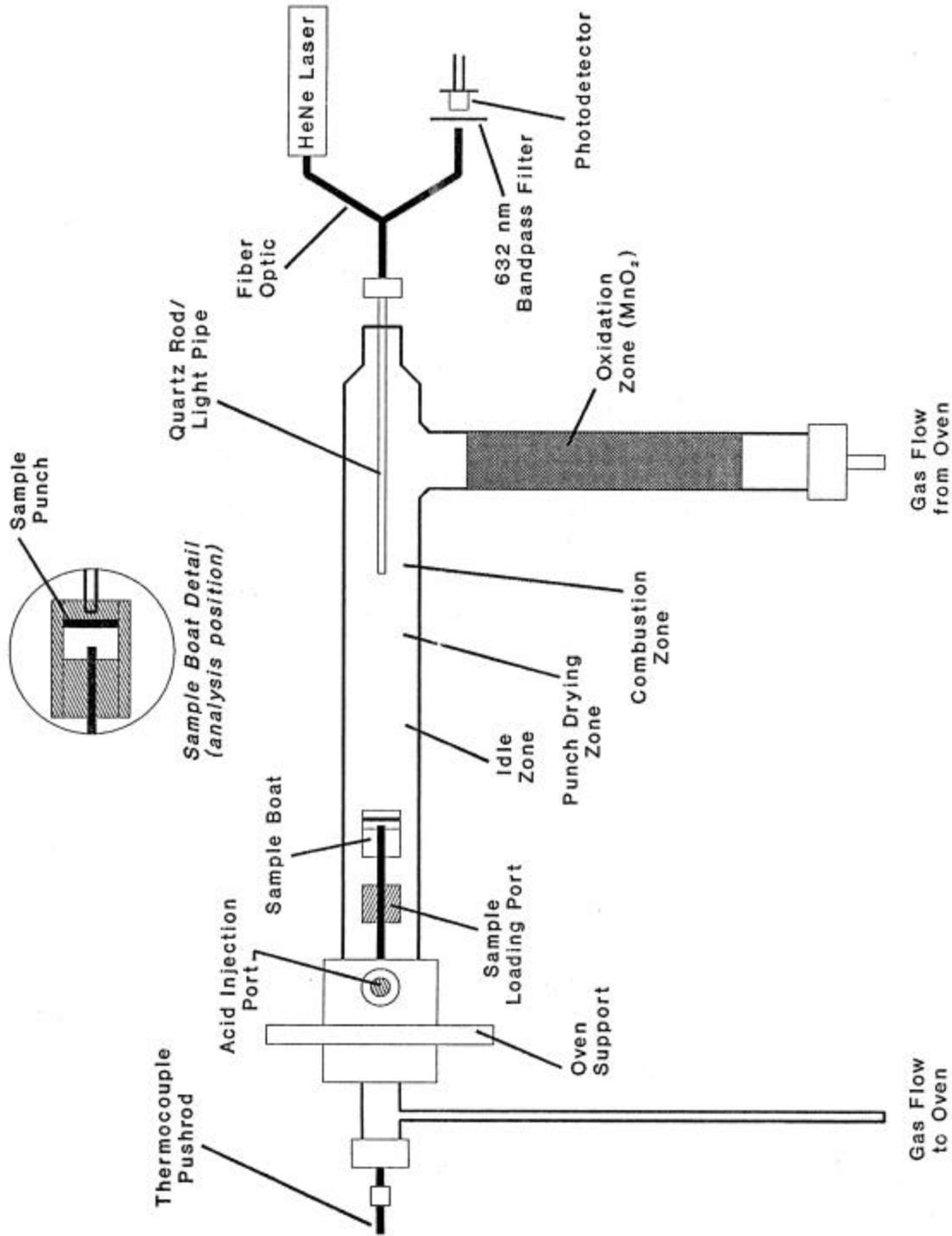


Figure 2-4. DRI/OGC Thermal/Optical Reflectance Carbon Analyzer Combustion Oven.

- Syringes: Hamilton gas-tight 1000 and 2500 ml syringes for calibration injections; 25 ml syringe for carbonate analysis and for analyzer calibration.
- Quartz filters: Pallflex 2500 QAT-UP or equivalent.
- Tweezers.
- Glass petri dish.
- Logbook/notebook.
- Transparent tape.
- Kimwipes.
- Small cooler.
- Blue ice.
- Butane lighter to light the FID.
- Small adjustable wrench.
- A copy of CARBON.EXE (the analysis program), version 4.0 or later, and CARBON.DAT (the analysis parameter file), version 4.0 or later.

### 2.1.2 Instrument Characterization

The DRI carbon analyzer is program-driven and data is stored automatically to disk via an Pentium compatible computer. Response times and signal lag times are built into the parameter file which is loaded when the analysis program begins. The program is event driven; that is, when the FID signal returns to its baseline after a minimum of 80 seconds at one analysis condition, the program will advance to the next temperature or carrier gas mixture. A maximum time limit per analysis condition is also established to prevent a slight baseline drift from holding the analyzer in one condition indefinitely. This method requires no sample pretreatment, requires between 15 and 70 minutes of analysis time per sample, requires at least one 0.516 cm<sup>2</sup> punch per filter, and destroys the sample punch.

Operator concerns for correct routine operation of the instrument include the following (refer to section 4 for more details):

- Insure that the sample port is tight after loading a sample punch.
- Remember to push the sample in when the computer tone sounds (Section 4.3); DO NOT leave the room until the analysis begins.

- Insure that the thermocouple is physically decoupled from the sample boat after pushing in the sample to prevent oven temperature from influencing the laser reflectance signal.
- Check the graphical printout after each analysis run to insure that the FID, temperature, and laser signals are behaving as expected (Section 4.3). Report any anomalies to the lab supervisor immediately.
- The quartz oven is susceptible to breakage, especially at the sample port. Care should be taken to avoid exerting tangential pressure on the oven when manipulating the sample port fitting.

### 2.1.3 Maintenance

Regular maintenance for the analyzer involves daily checking of compressed gas supplies, cleaning the punching tool and tweezers between each sample with dry KimWipes (Kimberly-Clark Corporation), and backing up data files on a daily basis. Checks of laser adjustments (physical and electrical) are made at least monthly; analyzer calibrations are performed every six months. All calibrations and repairs must be recorded in the log book. Additionally, all repairs must be recorded in the maintenance log book.

Refer to the maintenance and troubleshooting guide for additional information.

### 2.1.4 Spare Parts

The following spare parts must be kept on hand to insure minimal interruptions in carbon analysis:

- Quartz rods: 3 mm nominal diameter, Homosil optical quality rod, (GM Associates, Oakland), cut to 9-<sup>3</sup>/<sub>4</sub>" lengths and polished on both ends using a lap polisher.
- Quartz ovens: specially built ovens by Adams & Chittenden Scientific Glass, 1414 Fourth St., Berkley, CA 94710, voice: (510) 524-9551, fax: (510) 524-955, contact person: Tom Adams. Or by Glasstech, La Plata, MD, voice: (301) 392-0723, contact person: Mike Trembly.
- Quartz boats: made at DRI from scraps of broken ovens.
- Thermocouple rods: 12" length by 1/8" OD, type K ground isolated with 316 stainless steel sheaths (Omega, Part # TJ36-CAIN-18U-18).
- FID flame tips: for Gow-Mac #12-800 FIDs (Gow-Mac, #132-117). Gow-Mac Instrument Co., P.O. Box 25444, Lehigh Valley, PA 18002-5444, voice: (610) 954-9000, fax: (610) 954-0599.
- Septa: 1/4" and 1/8", for injection ports.

- 
- Replacement needles for syringes.
  - Replacement oxygen/moisture trap (R&D Separations, Model OT3-2).
  - Replacement hydrocarbon trap (R&D Separations, Model HT200-4).
  - Replacement indicating oxygen trap (Chromatography Research Supplies, Model 202223).
  - Stainless steel wire: for forming "ears" to hold the sample boat in position and for wrapping the "ears" onto the thermocouple push rod (Rocky Mountain Orthodontics, #RMO E-19, 0.914 mm).
  - Quartz wool: for repacking the oxidation oven (Alltech Associates, #4033).
  - Teflon ferrules: Parker or Swagelok style, 1/2" ID, for the sample port fitting.
  - Teflon ferrules: 1/2" OD by 1/8" ID, for the thermocouple rod at the back of the oven.
  - Heating element for oven: custom made 650 W coiled heater (Marchi-Norman Associates #SDH175). Marchi-Norman Associates, Inc., 630 Price Ave., Redwood City, CA 94063, voice: (415) 364-3411, fax: (415) 364-4138.
  - FID battery: 300 VDC (EverReady #495).
  - Printer paper.
  - Printer toner cartridge.
  - Computer super disks, LS-120.

## 2.2 Reagents

The following chemicals should be reagent grade or better:

- Potassium hydrogen phthalate (KHP), for calibration use (Fisher, #P-243).
- Sucrose, for calibration use (EM Science, #SX1075-1).
- Manganese dioxide ( $\text{MnO}_2$ ), crystalline, as an oxidizer in the oxygen oven (Nurnberg Scientific, #C5162).
- Nickelous Nitrate [ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], crystalline, used as a reducer in the methanator (Fisher Scientific, cat # N62-500, CAS 13478-00-7).

- 
- Chromosorb 60/80 mesh, used as a support for nickel catalyst in methanator (Supelco, catalog # 2-0165).
  - Hydrochloric acid (HCl), 0.4 molar solution, for use in cleaning punch and quartz ovens, and for use in carbonate analysis.
  - Distilled deionized water (DDW): total carbon background should be 6 ppm or less (determined as described in Section 5.1).

### 2.3 Gases

The following compressed gases should be industrial grade or better:

- Helium for a carrier gas, regulated to 15-20 psi with a metal diaphragm regulator. The higher pressure is required due to the pressure drop across the oxygen/moisture and hydrocarbon traps.

The laboratory supervisor will determine the minimum delivery pressure necessary for proper helium flows.

- 5% methane by volume in helium for calibration injections and calibration peaks; regulated to 10 psi by a metal diaphragm regulator, NIST traceable.
- 5% carbon dioxide by volume in helium for calibration injections; regulated to 10 psi by a metal diaphragm regulator, NIST traceable.
- 10% oxygen by volume in helium as a carrier gas, regulated to 10 psi by a metal diaphragm regulator.

In addition, the following gases are required:

- Hydrogen for the FID flame, regulated to 17 psi with a metal diaphragm regulator.
- Compressed air to supply oxygen to the FID, regulated to 10 psi by a metal diaphragm regulator

At least one backup cylinder per gas type should be kept on hand at all times. The calibration gases typically last for one year. The hydrogen, helium, and O<sub>2</sub>/He mixture are typically replaced every four to six weeks. The compressed air is replaced every 4 to 5 days. All gases are replaced when the cylinder pressure drops below 500 psi.

### 2.4 Forms and Paperwork

All samples are logged into a receiving book and into a computerized database login file upon receipt at the laboratory. Refer to Figure 2-5 for the format of this logbook. A sample analysis

list will be prepared by the laboratory supervisor indicating which samples will be analyzed and any special instructions.

As individual samples are analyzed, entries are made in the "Carbon Analyzer Logbook", as shown in Figure 2-6. As each analysis run is completed, the sample analysis list is marked with the date and analyzer number, as shown in Figure 2-7.

Title: Thermal/Optical Reflectance Carbon  
 Analysis of Aerosol Filter Samples

PROJECT	DATE RECD	BY	DUE DATE	SAMPLE ID	# SAMPLES ANALYSED	COMMENTS
IMPROVE ↓	030289 ↓	LCP ↓	7/89 ↓	Lot U ↓	481 NPS 14 NESC.	TOR ↓ 25 mm Q
IMPROVE ↓	040789 ↓	LCP ↓	9/89 ↓	Lot W ↓	470 NPS 27 NESC.	TOR ↓ 25 mm Q
SJVAQS	041889	LCP	7/89	4 <sup>th</sup> Quarter: assorted	353	XRF 47 mm T
IMPROVE ↓	042589 ↓	LCP ↓	9/89 ↓	Lot X ↓	492 NPS 18 NESC.	TOR ↓ 25 mm Q
AAAS	050389	LCP	5/31/89	89-114 - 89121	8	AC 8X10 GF

Figure 2-5. DRI Air Analysis Logbook Format.

12/27/95 MSM

1. BAKE OVEN
2. CHANGED AIR (2200)
3. LEAK TEST

C11227-1/19.9/23828

/BYSBLK

SB1227-1

/ZIRKEL.95/BATCH07

G66Q252-1  
 G66Q258-1  
 G66Q259-1  
 H96Q182-1  
 H96Q183-1  
 H96Q195-1 PUNCH FELL OUT DURING RUN  
 H96Q196-1  
 H96Q197-1  
 H96Q198-1  
 H96Q199-1  
 H96Q201-1

M11227-1/20.2/23693

12/28/95 MSM

1. BAKE OVEN
2. LEAK TEST

M11228-1/20.4/23798

/ZIRKEL.95/BATCH07

H96Q205-1  
 H96Q206-1  
 H96Q135-2 R FOR #2  
 J04Q332-1

/SEPULVEDA.95/BATCH03

SFTQ008-1  
 SFTQ010-1  
 SFTQ013-1  
 SFTQ014-1  
 SFTQ016-1  
 SFTQ021-1

Figure 2-6. DRI Carbon Analyzer Logbook Format.

Title: Thermal/Optical Reflectance Carbon  
 Analysis of Aerosol Filter Samples

IMPROVE: Batch P3 Quartz

Date : 07/15/94  
 From : F.Divita  
 To : J.Chow  
       C.Frazier  
       B.Hinsvark  
       Carbon Lab

Analysis: OC/EC by TOR : 300 samples, data in IMOETP3I.DBF

Sample Overview:

This analysis list covers samples from the NPS IMPROVE project. These are 300 PM2.5 samples on 25 mm Quartz filters, including no lab blanks and 3 field blanks. These samples were collected with an IMPROVE sampler.

Analysis Overview:

Sample deposit area: 3.8 cm<sup>2</sup>  
 Analysis start date: After Lot03  
 Analysis deadline : 6/16/94  
 Sample location : Back freezer

Analysis Details:

Carbon analysis data will be stored in the D:\IMPROVE\LOTP3 directory.

Filter	Description	OC/EC
 P59916	GRCA1#4#594C1P	Y _____
 P59917	GRCA1#4#594C1S	Y _____
 P59918	GRCA1#4#594C2P	Y _____
 P59920	OKEF1#4#594C1P	Y _____
 P59922	OKEF1#4#594C2P	Y _____
 P59924	MEVE1#4#594C1P	Y _____
 P59926	MEVE1#4#594C2P	Y _____
 P59927	MEVE1#4#594C2S	Y _____
 P59928	LAVO1#4#594C1P	Y _____
 P59930	LAVO1#4#594C2P	Y _____

Figure 2-7. Example DRI Carbon Analysis List.

### 3.0 CALIBRATION STANDARDS

#### 3.1 Preparation, Ranges, and Traceability of Standards

Four standards are used in calibrating the carbon analyzers: 5% nominal CH<sub>4</sub> in He, 5% nominal CO<sub>2</sub> in He, KHP, and sucrose. Only the calibration gases are used on a daily basis as analyzer performance monitors. KHP and sucrose are used in conjunction with the two gases semiannually to establish the calibration curve of each analyzer.

The calibration gases are traceable to NIST standards. The gases are assayed for exact concentrations by the gas supplier to two decimal places. The assay value is obtained from the tag on the cylinders.

The KHP is dried at 110°C for two hours before dispensing. Transfer 0.3826 g of KHP into a glass 100 ml volumetric flask after the KHP has come to room temperature. Dilute to volume with 0.4 ml concentrated hydrochloric acid (HCl) and distilled deionized water (DDW). Mix the KHP thoroughly. Store this solution in a refrigerator until it is used for calibration purposes. This solution is good for 40 days. Label the flask with the chemical name, the date of preparation, the name of the chemist preparing the solution, and the exact concentration. The concentration, nominally 1800 ppm carbon, is calculated by :

$$\left( \frac{\text{Actual g KHP}}{100 \text{ ml}} \right) \left( \frac{96 \text{ Carbon}}{204.23 \text{ g KHP}} \right) \left( \frac{10^{-3} \text{ ml}}{\text{ml}} \right) \left( \frac{10^6 \text{ mg}}{\text{g}} \right) = \frac{\text{mg Carbon}}{\text{ml solution}}$$

The nominal 1800 ppm sucrose solution is prepared by transferring 0.428 g of sucrose into a glass 100 ml volumetric flask. Dilute to volume with DDW. Mix the sucrose thoroughly. Store this solution in a refrigerator until it is used for calibration purposes. This solution is good for 40 days. Label the flask with the chemical name, the date of preparation, the name of the chemist preparing the solution, and the exact concentration. The concentration is calculated by:

$$\left( \frac{\text{Actual g Sucrose}}{100 \text{ ml}} \right) \left( \frac{144 \text{ Carbon}}{342.31 \text{ g Sucrose}} \right) \left( \frac{10^{-3} \text{ ml}}{\text{ml}} \right) \left( \frac{10^6 \text{ mg}}{\text{g}} \right) = \frac{\text{mg Carbon}}{\text{ml solution}}$$

To prepare a blank solution, add 0.4 ml of concentrated HCl to a glass 100 ml volumetric flask and dilute to volume with DDW. This acidified DDW is made fresh each time a 1800 ppm KHP stock solution is prepared.

No primary standards (NIST-traceable) currently exist for carbon analysis. Ideally, such standards should include a range of organic compounds from low to high molecular weights and with varying degrees of susceptibility to pyrolysis, as well as elemental carbon and carbonate compounds. Currently, KHP, sucrose, and the two calibration gases are used at DRI for calibration and system audit purposes.

### 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 <sub>2</sub> /He mix	--	10 psi
CH <sub>4</sub> /He mix	--	10 psi
CO <sub>2</sub> /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<sub>2</sub> 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<sub>2</sub> 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 system and wait at least two minutes to insure all calibration gas has progressed through the system.

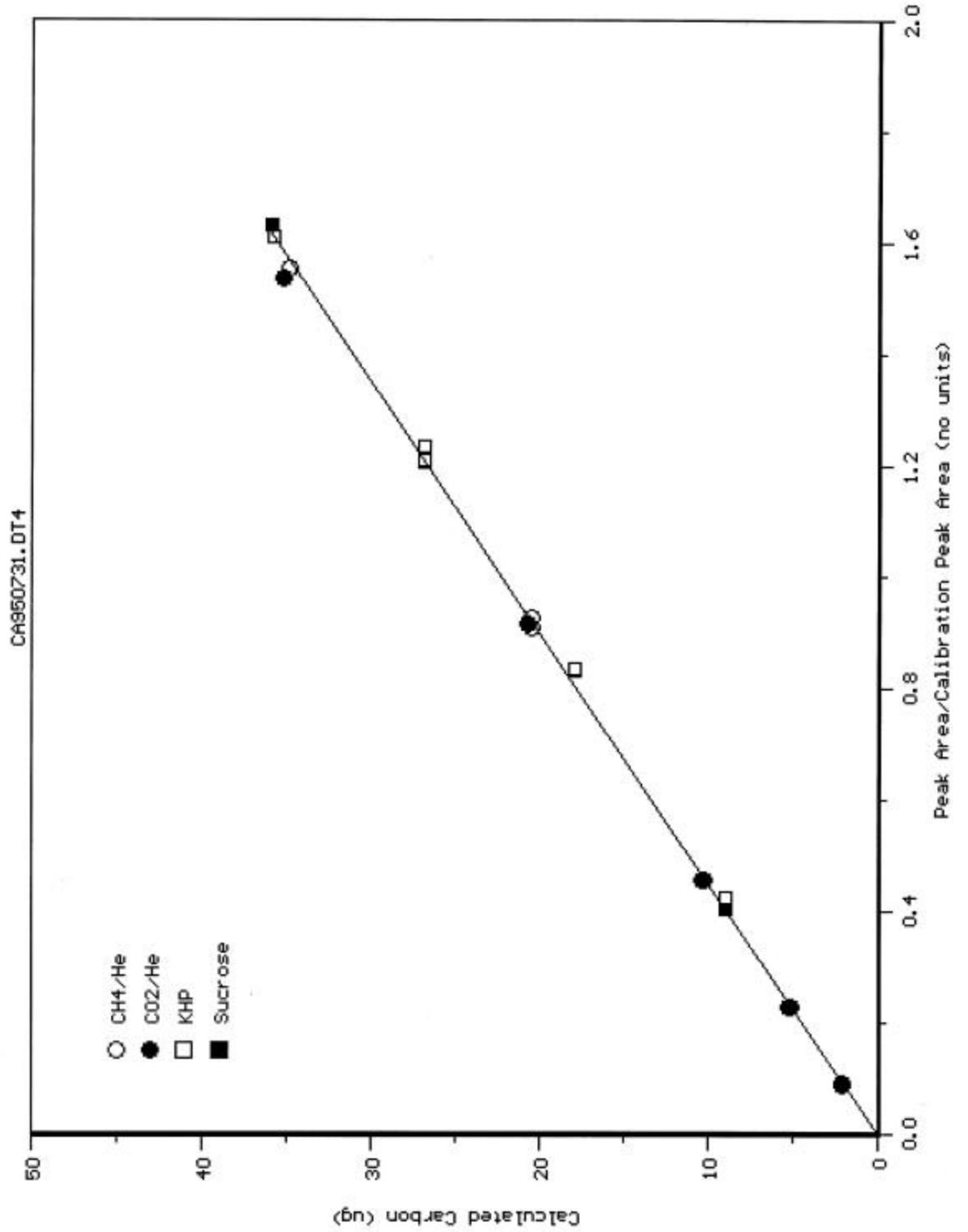


Figure 2.1

- 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<sub>2</sub> carrier gas (option 2). Select either CO<sub>2</sub> or CH<sub>4</sub> 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.

```
+-----+
| Current Directory: D:\CALIB |
+-----+

Program option : Calibration Injection           Technician: KGG
-----

Data file name  : MI1211-1.CAL

Carrier gas     : O2/He

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

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

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

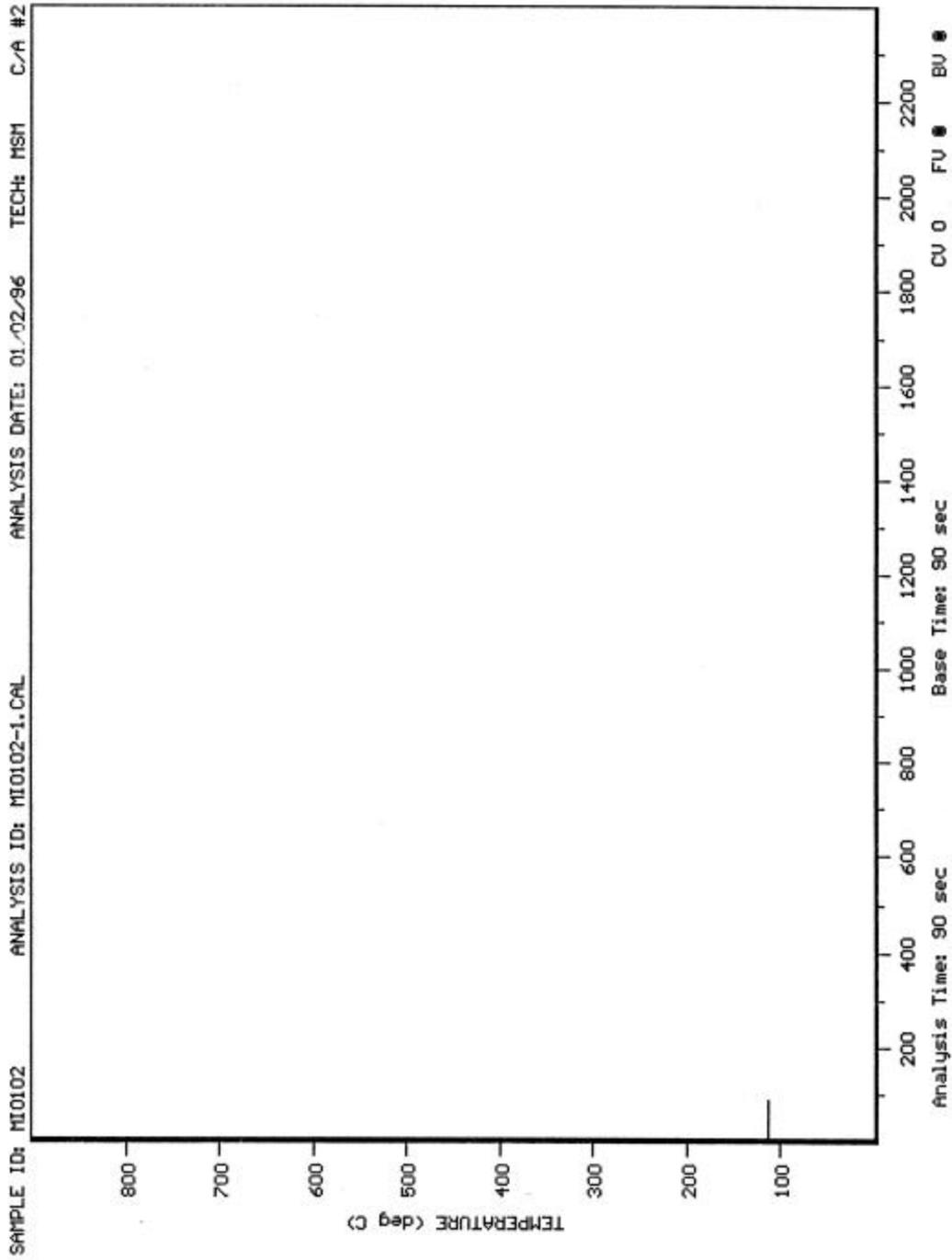


Figure 4-4. DRI Carbon Program Screen at 90 Seconds.

```

                                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 #1          : Peak Area          Carbon
                  : 21508 counts      20.16 ug C/injection
-----
*****
Calculated Carbon:
    20.2 ug C/injection

```

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

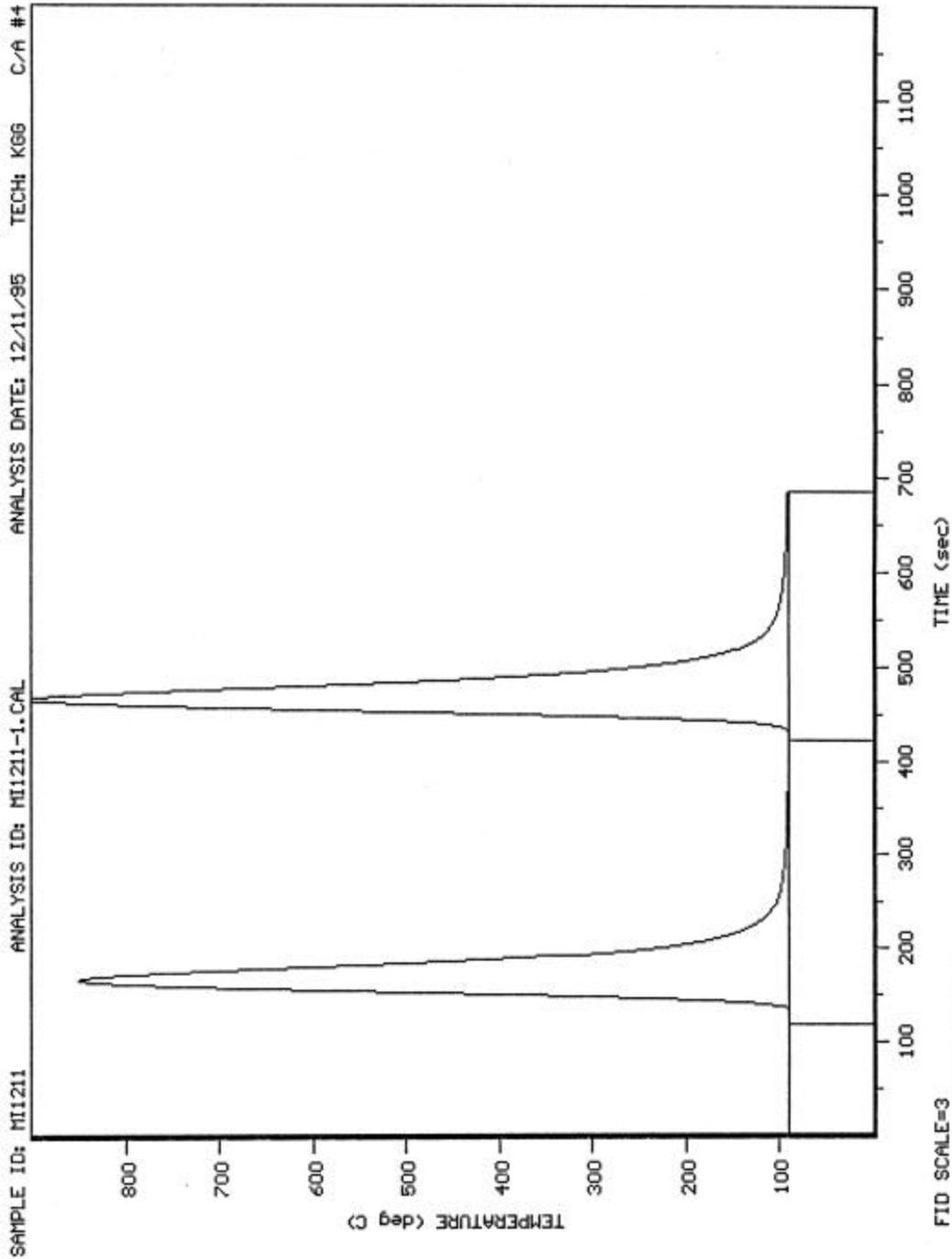


Figure 4-6. DRI Carbon Program Thermogram Printout, Calibration Run.

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<sub>2</sub> atmosphere.
  4. Repeat the calibration using the other calibration gas under a He/O<sub>2</sub> 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<sup>2</sup>) 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 cm<sup>2</sup>**

Filter deposit : **17.3 cm<sup>2</sup>**

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<sup>2</sup> and a 1.0 cm<sup>2</sup> 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

  *****
                                Regular          High Temp          Regular          High Temp
                                VOC           OC             OC             EC             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.

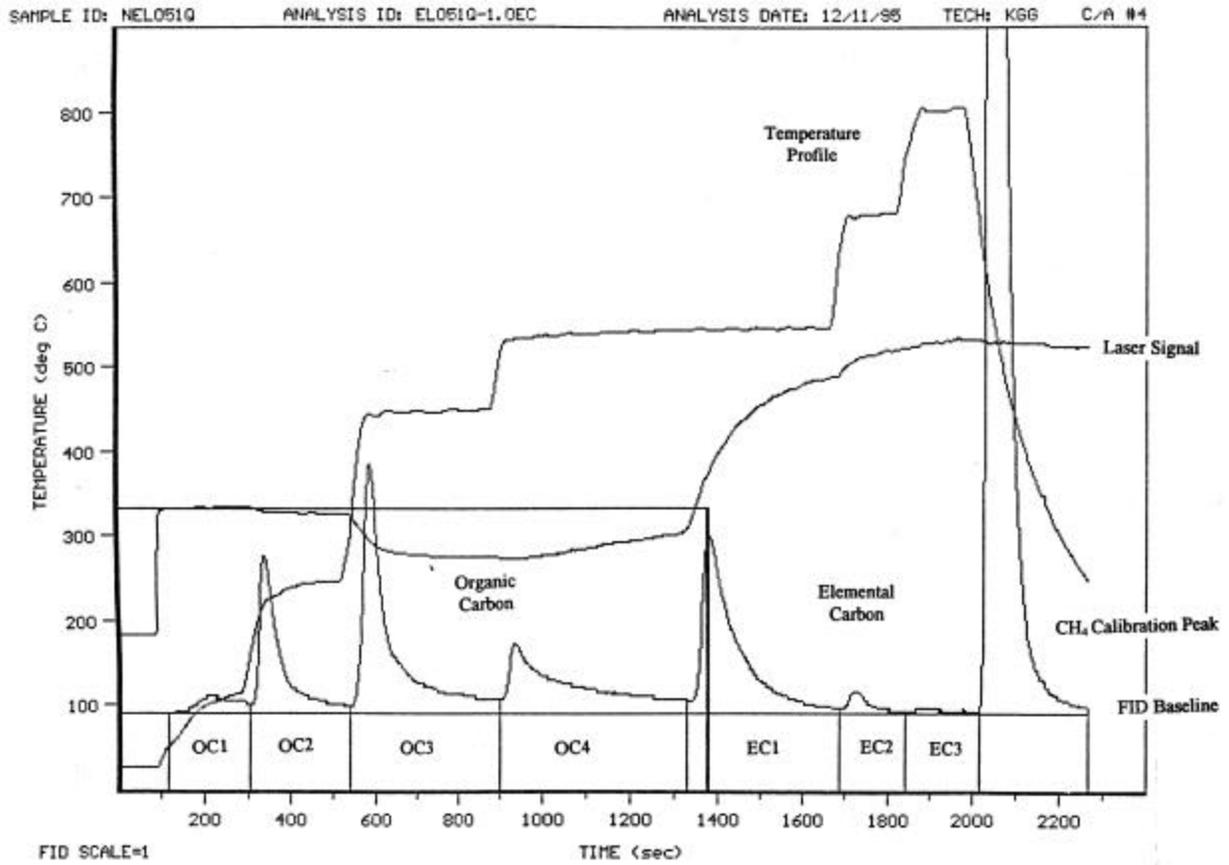


Figure 4-10. DRI Carbon Program Thermogram Printout, OC/EC Run.

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.

Title: Thermal/Optical Reflectance Carbon  
 Analysis of Aerosol Filter Samples

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	OC1 (ug/l)	OC2 (ug/l)	OC3 (ug/l)	OC4 (ug/l)	POC (ug/l)	EC1 (ug/l)	EC2 (ug/l)	EC3 (ug/l)	Deposit Area	Tech
EL051Q-1.0RC	NEL051Q	-99.00	10.84	56.29	112.12	72.80	18.34	100.82	8.07	1.77	17.30	MSM
EL052Q-1.0RC	NEL052Q	-99.00	10.42	52.03	109.02	75.73	26.44	118.83	7.43	0.37	17.30	MSM
ELR03Q-1.0RC	NELR03Q	-99.00	32.14	39.50	54.43	47.17	44.24	57.21	23.09	2.25	17.30	MSM
ELR04Q-1.0RC	NELR04Q	-99.00	28.12	42.13	57.22	47.65	52.74	61.60	20.42	2.45	17.30	MSM
ELR15Q-1.0RC	NELR15Q	-99.00	22.25	30.11	48.74	27.84	17.84	36.66	13.31	0.00	17.30	MSM
ELR16Q-1.0RC	NELR16Q	-99.00	23.65	36.28	49.66	32.09	25.49	47.77	14.15	0.18	17.30	MSM
OLF15Q-1.0RC	OLF15Q	-99.00	106.45	201.63	382.75	294.97	248.26	769.83	21.07	7.00	17.30	MSM
OLF16Q-1.0RC	OLF16Q	-99.00	82.42	179.69	333.19	257.24	211.95	680.76	22.26	7.05	17.30	MSM
OLF43Q-1.0RC	OLF43Q	-99.00	30.11	94.55	172.90	131.19	48.64	262.26	22.13	3.84	17.30	MSM
OLF44Q-1.0RC	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<sub>2</sub> 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<sub>2</sub> 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 than 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<sub>4</sub>/He and CO<sub>2</sub>/He, and instrument calibration using KHP, sucrose, and the two calibration gases.

The end-of-run calibration consists of a set quantity of CH<sub>4</sub>/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 pre-fired quartz punches with various amounts of the 1800 ppm KHP and sucrose solutions (Section 3.1) and injecting various volumes of the CO<sub>2</sub> and CH<sub>4</sub> 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 option from the main menu is selected and started. The integrated peak counts for all seven temperature fractions for the sample peak and the calibration peak are recorded.

The CO<sub>2</sub> and CH<sub>4</sub> calibrations are run using the calibration options from the main menu. The following volumes are injected:

- 100 ml CO<sub>2</sub> or CH<sub>4</sub> gas (use 1000 ml syringe)
- 250 ml CO<sub>2</sub> or CH<sub>4</sub> gas (use 1000 ml syringe)
- 500 ml CO<sub>2</sub> or CH<sub>4</sub> gas (use 1000 ml syringe)
- 1000 ml CO<sub>2</sub> or CH<sub>4</sub> gas (do once with 1000 ml syringe and once with 2500 ml syringe)
- 2000 ml CO<sub>2</sub> or CH<sub>4</sub> gas (do with 2500 ml syringe)

Again, the integrated peak counts are extracted manually from the tabular printouts.

Calibration values are plotted as actual µg carbon vs. the ratio of the integrated sample peak counts to the calibration peak counts (Figure 3-1). Obvious outliers are identified and rerun. Linear regression is performed on each set of calibration data (separate calculations for KHP, sucrose, CH<sub>4</sub>/He, and CO<sub>2</sub>/He). The calibration slope derived from the CO<sub>2</sub> injections typically has a slightly different slope and does not fit as well. The slope (m) is calculated from:

$$\left( m = \frac{\sum (y_i x_i)}{\sum (x_i)} \right)$$

and the standard deviation (s) is calculated by:

$$s = \sqrt{\frac{1}{n-1} \frac{\sum (y_i - mx_i)^2}{\sum x_i^2}}$$

where:

$$x_i = \frac{(\text{injected carbon peak area})}{(\text{calibration peak area})}$$

and:

$$y_i = \text{calculated carbon in spiked filter or manual injection (}\mu\text{g)}$$

Note that this is a special form of the regression formula, which insures that the curve passes through the origin.

The resulting slope is compared to previous calibration results. New values should be no more than  $\pm 10\%$  different than previous calibrations if no major analyzer changes have been made.

The new slope for each analyzer (derived from combined CH<sub>4</sub>, KHP, and sucrose data) is placed into the CARBON.DAT file for each analyzer; this file contains analyzer parameters which are read into the Carbon program when it is first started. The date and version number in the CARBON.DAT file is also updated.

Calibration data and plots are retained in file folders in the file cabinet with raw analysis data.

## 5.2 Calculations

The conversion of integrated peak counts to  $\mu\text{g}$  of carbon for each peak in the thermogram is performed by the computer at the end of the analysis program. For reference purposes, the calculation is:

$$\text{peak } \mu\text{g C/punch} = \frac{(\text{Integrated peak counts above baseline})(\text{calibration slope})}{(\text{Internal calibration counts})}$$

The peaks reported are: four organic peaks (OC1, OC2, OC3, and OC4) corresponding to 120, 250, 450, and 550°C, respectively; three elemental carbon peaks (EC1, EC2, and EC3) corresponding to 550°C after the introduction of O<sub>2</sub>, 700, and 800°C, respectively; and three pyrolyzed organic carbon peaks (Lower, Regular, and Upper Splits) corresponding to the peaks after the introduction of O<sub>2</sub> and before the Lower Split Time, Regular Split Time, and the Upper Split Time, respectively (see Section 1.7 and Figures 4-9 and 4-10).

Carbon values per punch are converted to  $\mu\text{g C/cm}^2$  by:

$$\mu\text{g C/cm}^2 = \frac{(\mu\text{g C/punch})}{(\text{punch area})}$$

Finally, carbon values are converted to  $\mu\text{g C/filter}$  by:

$$\mu\text{g C/filter} = (\mu\text{g C/cm}^2)(\text{filter deposit area})$$

## 6.0 QUALITY CONTROL

### 6.1 Performance Testing

System blanks are performed at the beginning of each week to insure the system is not introducing bias in the carbon results and to insure that the laser signal is not temperature dependent. Contamination is potentially due to:

- Operator practices, such as improper cleaning of tweezers and punch.
- Teflon particles on the push rod getting into the heated zone of the quartz oven.
- The sample boat contamination.
- The carrier gases contamination.

A temperature-dependent laser signal is potentially due to:

- Physical coupling of the push rod to the boat during the run.
- A quartz rod (laser light pipe) ready for replacement. Microscopic cracks in the quartz rod will increase internal reflectance of the laser light; as the number of these cracks multiply, the effect of temperature on these cracks, and thus on the reflectance, becomes an interference in the laser signal.

As described in Section 5.1, the calibration peak at the end of each analysis run serves as a regular standard; the integrated area under the calibration peak serves as a measure of analyzer performance. In addition, the daily injections of two calibration gases further serve as standards. Primary standards in the form of NIST-traceable spiked filter punches do not exist.

### 6.2 Reproducibility Testing

Replicates of analyzed samples are performed at the rate of one per group of ten samples. The replicate is selected randomly and run immediately after a group of ten is completed. The  $\mu\text{g}/\text{cm}^2$  values for OC, EC, and TC are compared with the original run. The values should fall into the following criteria:

Range	Criteria
$< 10 \mu\text{g}/\text{cm}^2$	$< \pm 1.0 \mu\text{g}/\text{cm}^2$
$> 10 \mu\text{g}/\text{cm}^2$	$< 10\%$ of average of the 2 values

Notice that the criteria converge at  $10 \mu\text{g}/\text{cm}^2$ . Replicates which do not fall within the above criteria must be investigated for analyzer or sample anomalies. Analyzer anomalies include poor response (as reflected in the calibration peak areas) or poor laser signals affecting the splits

between OC and EC. Typical sample anomalies include inhomogeneous deposits or contamination during analysis. Inconsistent replicates for which a reason cannot be found must be rerun again.

### 6.3 Analysis Flags

During Level I validation (see Section 6.4), unusual conditions of the deposit or analysis problems are noted on the analysis printouts. Errors in pre-analysis data entry (e.g., in filter ID, punch area, deposit area) are corrected.

Flags are applied to the dBase file created from the analysis results ASCII file (see Section 6.4). The analysis flags commonly used are presented in Table 6-1. Note that all results flagged with "v" must include a description of the reason for invalidating the sample in the remarks field.

### 6.4 Data Validation and Feedback

#### 6.4.1 Daily Validation

Level I validation is performed by manually checking the tabular and thermogram printouts the day after the analysis is performed. The laboratory supervisor or a designated technician is responsible for checking the data. The following items are checked on the tabular data (Figure 6-1):

- The filter ID is correct.
- For calibration injection runs, the carrier gas type is He/O<sub>2</sub> in the morning and He only in the afternoon, and the injection gas type is reversed between morning and afternoon injections.
- The analysis date is correct.
- The punch area is correct; errors in entry require that the calculated carbon concentrations be recalculated by hand.
- The deposit area is correct; errors in entry require that the calculated carbon concentrations be recalculated by hand.
- The calibration peak area is in the correct range (Section 4.1).
- The initial and final FID baseline are within 3 counts of each other; excessive FID baseline drift is cause for reanalyses. NOTE: Some very heavily loaded filters will have an FID baseline drift greater than 3 counts no matter which carbon analyzer the sample is run on, but typically a FID baseline drift greater than 3 counts signals either a problem with the run or with the carbon analyzer.

CARBON ANALYSIS RESULTS

Analyzer #4

Technician: KGG

Analysis ID : EL051Q-1.OEC  
 Sample ID : NELO51Q  
 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	10.84 ug C/filter
OC Peak #2 :	1848 counts	56.29 ug C/filter
OC Peak #3 :	3681 counts	112.12 ug C/filter
OC Peak #4 :	2390 counts	72.80 ug C/filter
Lower pyro'd OC :	533 counts	16.23 ug C/filter
Reg. pyro'd OC :	602 counts	18.34 ug C/filter
Upper pyro'd OC :	673 counts	20.50 ug C/filter
EC Peak #1 :	3310 counts	100.82 ug C/filter
EC Peak #2 :	265 counts	8.07 ug C/filter
EC Peak #3 :	58 counts	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 6-1. Example Level I Validated Tabular Printout.

**Table 6-1****Common DRI Analysis Flags**

---

Flag	Description
b1	Field blank
b2	Lab blank
b6	Transport blank
f1	Filter damaged outside of analysis area
f2	Filter damaged inside analysis area
i2	Inhomogeneous filter deposit - random areas of darker or lighter deposit
g4	Deposit falling off (usually occurs on heavily loaded samples)
i4	Abnormal deposit area, possible air leakage during sampling
m2	Non-white sample punch after analysis
r1	Replicate on same analyzer
r5	Replicate on different analyzer
v	Sample void

- 
- The lower laser split time and the upper laser split time are within 10 seconds of each other. If the times differ by more than 10 seconds, check that the lower split OC and upper split OC differ by no more than 5%. OC values which differ by more than 5%, unless due to a small change in laser signal resulting from an extremely clean or very dark sample, requires reanalysis.
  - Calculated carbon values for calibration injection runs are within 10% of the current mean value for the injected gas type on that analyzer.
  - Acceptance runs for prefired quartz filters result in  $< 1.5 \mu\text{g}/\text{cm}^2$  OC,  $< 0.5 \mu\text{g}/\text{cm}^2$  EC, and  $< 2.0 \mu\text{g}/\text{cm}^2$  TC. Filters which exceed these levels must be refired.

Items which are found to be okay are underlined in red. Items which have problems are circled in red.

The thermograms are checked for the following (Figure 6-2):

- The initial FID baseline is flat, indicating that the analyzer has been thoroughly purged before analysis began.
- The final FID baseline prior to the calibration peak is within 3 counts of the calculated FID baseline; excessive drift is cause for reanalysis.
- The laser signal during the first 90 seconds appears near the bottom of the graph (no reflectance); an excessively high initial laser is an indication that the internal reflectance of the quartz rod is too high, either due to too many internal cracks or a complete fracture of the rod. High initial laser signals should result in a physical inspection of the analyzer.
- The initial laser line drawn on the thermogram matches the laser signal immediately after the rod is pushed in. A laser line which is too low is an indication that the sample was not pushed into the oven in time; a laser signal which exceeds the calculated initial laser signal is a symptom of physical coupling between the sample boat and the push rod, although some automobile emission samples also show this characteristic; a spike or a number of jumps in the laser signal indicates that the operator had difficulty in decoupling the boat from the push rod. All of these problems are grounds for reanalysis if severe.
- The laser signal should dip below the initial laser line until oxygen is introduced at  $550^\circ\text{C}$ , at which the signal should rise steeply.
- The laser signal at the end of the analysis is flat; if the laser signal dips as the oven begins to cool, the boat is physically coupled to the push rod and the laser signal during the rest of the analysis is suspect.

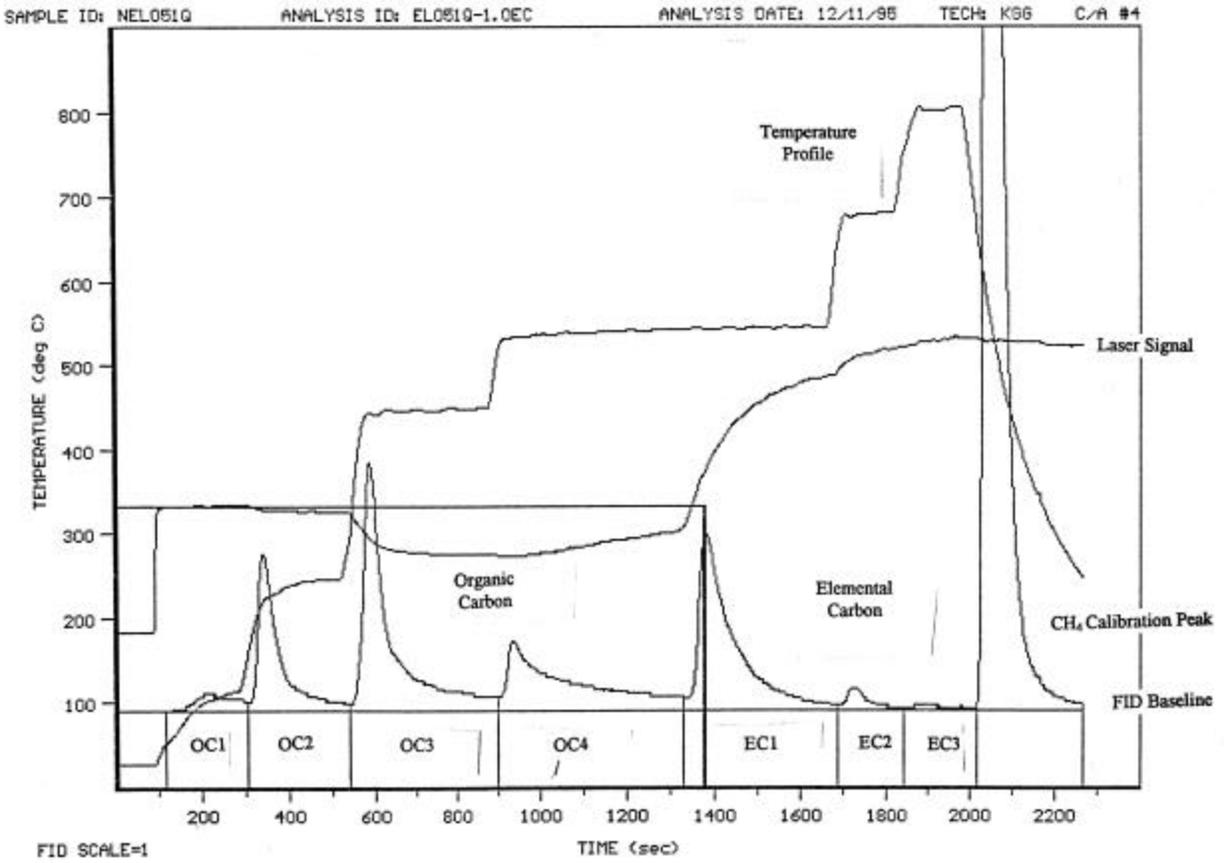


Figure 6-2. Example Level I Validated Thermogram Printout.

- The temperature readings reflect stable and smooth temperatures at each level and quick transitions between levels.

Problems or deviations from normal should be circled in red. If the sample punch taped to the thermogram is not white, it is also circled.

If examination of the tabular and thermogram printouts result in a decision that a sample should be reanalyzed, write "Rerun" in red on the printouts and prepare a reanalysis list. This list should be posted immediately after the validation is complete, and those samples should be rerun as soon as they can be conveniently fit into the current day's analyses.

Evidence of persistent analyzer problems must be resolved, either by physically examining the analyzer or reviewing the problems with the analyzer operator.

#### 6.4.2 Validation of Final Data File

The following steps are followed to create a dBase file containing carbon data and to perform Level "I" validation on it:

- Obtain copies of the latest version of the summary file from the directory corresponding to the desired project. These files are called **CPEAKS.n**, where n is the carbon analyzer number. These files may be either copied from the backup files or copied directly from the carbon analyzer computers. The latter method is recommended, as it guarantees that the summary files retrieved are the latest versions. These files are updated at the end of each analytical run, so the latest version is necessary to insure that all of the analyses are included.
- Copy the files to the working directory:

The ASCII **CPEAKS.n** file is reformatted, sorted, and placed into a dBase III file by the following:

**INPCARBN <Return>**

The **INPCARBN** program will prompt the user for an output file name. The dBASE file naming convention calls for a name in the following format:

xxOETnnt.DBF

where:

xx is the 2 character project identifier

OET stands for organic/elemental carbon

---

nn	is the 2 digit batch number (generally used to distinguish between different projects for the same client or between sampling quarters for an extended project)
t	stands for the sample type based on sampler technology:
A	Agricultural burn emissions dilution sampler
C	Combination particle/gaseous sampler
D	Dichot (both PM <sub>2.5</sub> and PM <sub>10</sub> )
G	Gaseous
H	High-volume sampler
I	IMPROVE/NPS sampler
P	Portable Survey Sampler
Q	Audit samples
R	Resuspension chamber
S	Sequential filter sampler (SFS)
W	Wet Deposition
X	Unknown
Y	Y-sampler (DRI source sampler)

The final dBase file name is specified in the analysis list posted in the carbon room.

After the **INPCARBN** program produces the dBase output file, the program will alert the operator that it is ready to print the contents of that file. Although the **INPCARBN** program is capable of printing the carbon data file, it is recommended that *Microsoft Excel* be used to print the file. If the file is opened in *Excel*, the uncertainty columns deleted, and the page setup set to landscape mode and fit to one page wide by many pages long, a good printout will be produced on a laserjet printer. If you must use the **INPCARBN** program to print the carbon data file, a wide carriage dot matrix printer is recommended.

After the printout is produced, immediately label the top of the printout with the file name and printout date. This can also be accomplished by using a labeling header in *Excel*.

Begin validation by matching the filters listed on the analysis list with the filters listed on the dBase printout. There must be at least one entry on the printout for every filter listed on the analysis list.

Flag field and lab blanks as the list is reviewed by placing "b1", "b2", or "b6" in the second column of the printout. Because the dBase printout is sorted by ID number, replicates and reruns will be grouped together.

Indicate missing data by writing the missing filter ID in the margin with an arrow drawn to the appropriate place of insertion. Scan the printout for unusual IDs which may have been mistyped during analysis. Generally these will appear at the beginning or end of the printout due to the sorting process. Make sure that all samples listed on a rerun list appear on the printout.

Resolve all missing data. If a large amount of data is missing because of analysis in the incorrect subdirectory, it is generally easier to retrieve the summary file from that incorrect subdirectory, trim the unnecessary data from that file using a word processor, combine the remaining data with the **CPEAKS.n** file, and rerun the **INPCARBN** program. If only a few data points are missing, it is generally not too much trouble to simply write the correct values from the daily folders on the printout and add those values manually to the dBase files at the same time the flags and other corrections are made.

Scan the deposit area column for incorrect entries. Circle the incorrect entries to insure that corrected values replace those currently in the database.

Scan the filter IDs for multiple entries of ID numbers. Under normal conditions, the only times multiple entries should occur are reruns and replicates. All multiple entries must be flagged to indicate the reason for their existence.

Scan for missing runs. The most common example is the first run being aborted or lost for some reason, and the only entry in the dBase file is the second run. An entry for the first run must be inserted, flagged as invalid, and labeled as to the reason it was invalid. All punches taken from the filters **MUST** be accounted for.

Scan the OC and EC columns looking for unusually high or low values. At this time make sure that the field blanks and/or lab blanks are all close to one another. Circle any possible outliers for further investigation.

Finally, pull the analysis folders and go through the analysis summaries and thermograms one by one. At this time, resolve all circled items and all missing flags. Determine if analyses flagged by the operator are legitimate. These flags are determined by the operator at the end of the analysis run (Section 4.2 and Figure 4-11); these flags are defined in Table 6-2. If the temporary flag is not warranted, draw a line through the flag to indicate it should be removed. If the sample should be rerun, add it to a rerun list. If the analysis has some anomaly but still appears to be legitimate, either flag or add notes to the comments field as appropriate. Analysis flags are defined in Section 6.3. All samples flagged as invalid must have an entry in the comments field to describe the reason that the sample is invalid. Common notes and comments are presented in Table 6-3.

All operator-generated flags must be either converted to standard analysis flags or removed. The flags in Table 6-2 are temporary flags only and are not recognized as legitimate analysis flags at DRI.

After all thermograms have been reviewed and all possible reruns have been identified, post the rerun list in the carbon room and have the reruns done as soon as possible.

Review the data from the reruns, looking for inconsistencies. Insure that the reasons for the rerun have been addressed. Mark the printout with the new values for manual insertion into the dBase file. Previous runs must be flagged as invalid or the reruns flagged as replicates.

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Finally, all comments, flags, insertions, and other changes made to the printout are entered into the dBase file. After all changes are made, generate a new printout. Label the new printout with the file name and printout date. Forward a copy of the printout and the dBase file on disk to the person putting the final report together.

#### 6.4.3 Use of the CARBVAL Program to Assist in Data Validation

A *Microsoft FoxPro* program named CARBVAL exists which will greatly assist in the validation process. When you use the CARBVAL program, you must specify if you are validating a data file which contains IMPROVE data or not. There are several validation steps that the CARBVAL program performs which are specific to IMPROVE.

The CARBVAL program will perform the following validations:

1. Identify records where the deposit area (deparea) is not equal to the deposit area entered by the user.
2. Identify records with duplicate runids.
3. Identify records before/after which contain gaps in runid sequence
4. Identify filters with more than one original run.
5. Identify records where elemental carbon concentration is greater than organic carbon concentration.
6. Identify blank filters where organic carbon concentration is greater than 3.95\*deparea
7. Identify blank filters where elemental carbon concentration is greater than deparea
8. Identify records where organic carbon concentration divided by the total carbon concentration is less than specified value (default is 0.75).
9. Identify voided samples that do not have a value in the comments column.
10. Identify replicate records incorrectly classified as 'r1' or 'r5'.
11. Identify samples where a 'm2' flag was not present in both the original and replicate runs.
12. Identify replicate runs where 'octc', 'ectc', or 'tctc' values are not within 10% or the deparea (in µg/filter) of original run.
13. IMPROVE only: Identify records where filter channel value is not equal to 'C'.
14. IMPROVE only: Identify records where filter type is not primary or secondary.
15. IMPROVE only: Identify secondary filters where 'ectc' value > 3.8 or 'octc' > 18.

16. IMPROVE only: Identify secondary filters where 'ctc' or 'ctc' values are > corresponding primary filter values.

17. IMPROVE only: Identify records where 'samdate' or 'week' values are empty.

18. IMPROVE only: Identify records with incorrect values in the 'day' field.

To use the CARBVAL program, first start *Microsoft FoxPro*. Then type 'DO CARBVAL' from the command window. The program will start and ask you for a file name. The program will then ask you a series of questions:

- the name of file used to store validation results,
- the deposit area of filter in square centimeters,
- the expected number of filters,
- and the octc/tctc ratio threshold (default = 0.75).

After the above values are entered, the CARBVAL program will begin validating the selected file. If the preliminary checks are satisfactory, the program will also ask you if you want to remove the carbon technicians validation flags and if you want to replace the 'r' replicate flag with the appropriate 'r1' or 'r5' validation flag. When the program is finished, it will allow you to browse the problem records on screen and will also print them.

It is recommended that you run the CARBVAL program as a first check after you have put the carbon data file together and then run it again as necessary, but certainly run it again when the final database is assembled. This will serve as a final check on the database.

**Table 6-2****DRI Carbon Analysis Temporary Flags**

Flag	Description
EI	Error in sample ID
EA	Error in sample deposit area
ST	Suspect temperature profile
SF	Suspect FID signal
SL	Suspect laser signal
Mi	Miscellaneous problem
v	Invalid run
r	replicate
b	blank
i	inhomogeneous filter deposit
f	filter media damaged
g	sample deposit damaged
d	sample dropped
n	foreign substance on filter deposit
w	sample wet

**Table 6-3****DRI Carbon Analysis Validation Comments**

Comments	Description
"Anomalous laser"	Despite good initial laser, laser signal drifted above initial laser signal before dropping (typical of auto emissions)
"Operator error"	Used with "v" flag; operator missed pushing boat in, pushed abort key, pushed manual advance key at an inappropriate time, etc.
"Analyzer malfunction"	Used with "v" flag; analyzer malfunction or problem beyond the control of the operator such as plugged FID, broken oven heater, etc.
"Poor replicate"	Replicate is outside the normal criteria, but no reason can be found for the discrepancy.
"Poor initial laser"	Used with "v" flag; severe coupling or boat not pushed in time for calculation of initial laser signal.
"Sample contaminated"	Used with "v" flag; rerun of sample yields lower values or different peaks. Typically used with blanks or reruns of replicates.
"Temperature problem"	Used with "v" flag, one or more of the temperature steps were not properly obtained. The most common example is the over-shooting of the first (120°C) temperature step.

## 7.0 REFERENCES

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