DRI STANDARD OPERATING PROCEDURE

DRI Model 2001 Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples – Method IMPROVE_A

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1 INTRODUCTION

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 Model 2001 Thermal/Optical Carbon Analyzer; and
- Detail the concerns and procedures which will ensure a state-of-the-art carbon analysis measurement process.

This procedure will be followed by all analysts at the Environmental Analysis Facility (EAF) of the Division of Atmospheric Sciences (DAS) at the Desert Research Institute (DRI), Reno, Nevada, USA.

1.2 Measurement Principle

The operation of the DRI Model 2001 Thermal/Optical Carbon Analyzer is based on the preferential oxidation of organic and elemental carbon (OC and EC) compounds at different temperatures. Its function relies on the fact that organic compounds can be volatilized from the sample deposit in a non-oxidizing helium (He) atmosphere, while EC must be combusted with an oxidizer. The analyzer operates by: 1) liberating carbon compounds under different temperature and oxidation environments from a small sample punch taken from a quartz-fiber filter; 2) converting these compounds to carbon dioxide (CO_2) by passing the volatilized compounds through an oxidizer (heated manganese dioxide, MnO_2); 3) reducing CO_2 to methane (CH_4) by passing the flow through a methanator (hydrogen-enriched nickel catalyst); and 4) quantifying CH_4 equivalents with a flame ionization detector (FID).

The principal function of the optical (laser reflectance and transmittance) component of the analyzer is to correct for pyrolysis charring of OC compounds into EC. Without this correction, the OC fraction of the sample might be underestimated and the EC fraction might include some pyrolyzed OC. The correction for pyrolysis is made by continuously monitoring the filter reflectance and/or transmittance (via a He-neon 632.8 wavelength laser and a photo-detector) throughout an analysis cycle. The reflectance and transmittance, largely dominated by the presence of light absorbing EC, decrease as pyrolysis takes place and increase as light-absorbing carbon is liberated during the latter part of the analysis. By monitoring the reflectance and transmittance, the portion of the EC peak corresponding to pyrolyzed OC can be accurately assigned to the OC fraction. The correction for the charring conversion of OC to EC is essential for a less-biased measurement of carbon fractions (Johnson et al., 1981). The Thermal Optical Reflectance (TOR) and Thermal Optical Transmittance (TOT) charring corrections are not necessarily the same, owing to charring of organic vapors adsorbed within the quartz fiber filter (Chow et al., 2004; Chen et al., 2004). Charring by both reflectance and transmittance is reported in order to determine the differences in OC and EC.

Carbonate carbon can be determined by measuring the CO_2 evolved upon acidification of the sample punch before the normal carbon analysis procedure.

Seven temperature fractions, as well as the TOR and TOT charring correction, are individually quantified and reported when the IMPROVE_A (Chow et al., 1993, 2001, 2007) temperature protocol is applied. Values routinely reported include total OC, total EC, total carbon (TC, sum of total OC and total EC), and pyrolyzed carbon, monitored by both reflectance (OPR) and transmittance (OPT). Depending on the thermal/optical protocol applied for quantification, thermally-derived subfractions of OC and EC, and of carbonate carbon, are reported.

1.3 Measurement Interferences and Their Minimization

Precision of thermal/optical carbon analysis depends on the sample temperature in the analysis. Therefore, the correlation between sample temperature and thermocouple temperature should be established and calibrated semiannually so that the thermal protocol can truly reflect the sample temperature during the analysis (Chow et al., 2005). The thermocouple's position in relation to the sample, as well as the different heating properties of the thermocouple and the sample, govern the temperature offset. This relationship must be maintained for the temperature calibration to hold. The analyzer must not be used if the sample boat shifts position or becomes loose in its holder.

Carbonate carbon may bias carbon concentrations if it constitutes more than 5% of TC in the ambient or source sample. Carbonate carbon may be measured as either OC or EC depending on the chemical nature of the carbonates and their thermal decomposition temperatures. Acid pretreatment of filter samples can eliminate the carbonate interference (Novakov, 1981, 1982; Rosen et al., 1982). Carbonate carbon has been found at only a few IMPROVE monitoring sites, and the levels at these sites do not appreciably bias OC and EC concentrations (Chow and Watson, 2002).

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 darker sample. For samples which contain large fractions of resuspended soils, the split between OC and EC should be examined manually.

Some minerals, again predominantly in soil samples or soil-dominated samples, may affect the laser correction by temporarily changing color or changing the surface texture of the deposit residue. Unlike the effect described above, these changes are reversible and temperature-dependent.

Some colored organic compounds can affect the laser correction, causing increased reflectance or decreased transmittance as these compounds are removed. This effect is ascertained by examining the laser response during the organic portion of the analysis. The split between OC and EC should be examined manually if the effect is large.

The presence of certain elements (Na, K, V, Cr, Mn, Co, Ni, Cu, and Pb), existing either as contaminants on the filters (e.g., glass-fiber filters or borosilicate binders), or as part of the deposit material, has been shown to catalyze the removal of EC 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), if present in sufficient levels, can shift the FID baseline. To eliminate this effect, allow the sample punch to dry in the analyzer by passing carrier gases over it before starting the analysis.

1.4 Ranges and Typical Values of Measurements

Source-dominated or 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 in the field equipment. Deposits that are very black, such that the initial reflectance is close to zero, provide a less precise OC/EC split, because additional blackening due to OC charring is not quantified by the reflected light.

The carbon analyzer can effectively measure between 0.05 and 750 µg carbon/cm^2 for a typical punch size of 0.5 cm^2. The upper limit depends on the particular compounds on the filter and the temperatures at which they evolve. This upper limit may be extended by reducing the punch size or extending analysis times at lower temperature plateaus to avoid an over-range FID signal.

Typical carbon values range between 10 and 100 µg C/cm^2 for 24-hour ambient samples. The distribution between OC and EC depends on the particulate source types, ranging from negligible levels of EC (e.g., secondary sulfate) to 80% or more EC (e.g., diesel exhaust).

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

The lower quantifiable limits (LQLs) of thermal carbon methods depend on the variable carbon content of the field blank quartz-fiber filters, as well as the analysis method. For lower 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; DRI, 2004). All quartz-fiber filters originating from DRI are pre-inspected for defects such as pinholes or tears. They are then pre-fired for a minimum of four hours at 900 °C; 2% are acceptance-tested for blank levels before use in the IMPROVE network. Batches containing filters that fail to pass the preset acceptance levels (1.5 µg OC, 0.5 µg EC, and 2.0 µg TC per cm^2) are not used for sample collection. Average pre-fired blank levels are 0.15 ± 0.15 µg OC/cm^2, 0.00 ± 0.02 µg EC/cm^2, and 0.15 ± 0.15 µg TC/cm^2. Because pre-fired filters can adsorb organic vapors during shipping, storage, and exposure in the sampler, the analysis LQL on a particular set of filters depends on the number of field blanks analyzed and the variability in the results from those blanks. LQLs may vary between projects, depending on the sample and sample handling. To reduce the risk of contamination during shipping and storage, samples are vacuum-sealed and stored at < 4 °C. The vacuum sealing results in minimum air space surrounding the filter to ensure the blank levels are kept low.

The minimum detection limits (MDLs) represent the best sensitivity of the method and should always be less than or equal to the LQLs. The IMPROVE_A protocol is based on the analyses of approximately 1125 pre-fired laboratory blank quartz-fiber filters analyzed between January 2010 and December 2011 on 11 different analyzers. The MDL is defined as three times the standard deviation of their measured results. They are:

total OC	0.43 µg/cm^2	1.53 µg/filter
total EC	0.12 µg/cm^2	0.44 µg/filter
TC	0.49 µg/cm^2	1.72 µg/filter

Units of µg/filter are obtained using a deposit area of 3.53 cm^2, typical of 25 mm quartz-fiber filters. Acid-evolved carbonate levels in pre-fired quartz-fiber filters have been shown to be quite variable (0.0-1.0 µg/cm^2) over time. The reaction of ambient CO_2 with alkaline sites on the quartz fibers may be the cause of such variable blank levels. Acceptance testing for carbonate is only performed for special projects that require carbonate analysis.

The precision of carbon analysis has been reported to range from 2 – 4% (Johnson, 1981). For analysis of actual ambient and source filters, homogeneity of the deposit is most important for reproducible results. This can be demonstrated by the precision of CH_4 standard injection (by the Carle valve), which is always better than sample analysis. For homogeneous deposits containing > 5 $\mu g/cm^2$ (~10 times MDL) TC, precision is generally 10% or better; for inhomogeneous deposits replicates may differ by as much as 30%. The precision of carbonate concentrations is approximately ±10%.

The precision of the laser-dependent split between OC and EC fractions depends upon how rapidly the laser is increasing at the time of the split and whether or not the split falls in the middle of a large carbon peak. Typically, relative laser split times are reproducible within 10 seconds and deviations in calculated splits are < 5% of the total measured carbon. If the laser split is greater than 10 seconds and deviations are > 5%, the analysis is investigated for sample anomalies (e.g., inhomogeneous loading, low loading, etc.), instrument laser noise, or O_2 contamination.

The accuracy of TOR for TC, determined by analyzing a known amount of carbon, is between 2-6% (Rau, 1986). Precision of the OC/EC split is between 5% and 10%. This precision is also influenced by the filter loading and source type. Most of the uncertainty for low concentration samples is from the standard deviation of the field blanks or backup filters. Uncertainty is not determined by precision at low levels.

Since the MDL is always less than or equal to the LQL, and the LQL is included in the $\mu g/m^3$ uncertainty when the blank (or backup filter, if available) is subtracted, the MDL has no effect on the uncertainty of ambient concentrations. The MDL is most useful to match flow rates and sample duration with expected carbon levels when planning field studies or sampling networks.

1.6 Personnel Responsibilities

Before performing carbon analysis, all analysts in the laboratory should read and understand the entire Standard Operating Procedure (SOP), including routine system calibration, actual analysis, and immediate review of the data as it is produced, and how to correct system problems.

The responsibilities of the laboratory manager or supervisor are: to ensure that 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 of instruments; to verify an adequate quantity of supplies and gases are in stock to ensure 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 DAS is responsible for determining 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 periodically review and assess quality assurance and quality control data, 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 for IMPROVE_A Thermal Protocol for Carbon Analysis

The following terms are used in this document:

IMPROVE_A Thermal Protocol:	A thermal protocol used in carbon analyzers to quantify carbon fractions evolved at different temperature plateaus and atmospheres. The IMPROVE_A thermal protocol derives from the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal protocol initiated in 1987 (Chow et al., 2005, 2007).
Calibration Injection:	The injection of calibration gases, either CO_2 or CH_4, into the sample stream at the beginning and end of each work day to check instrument performance.
Calibration Peak:	The FID peak resulting from the automatic injection of methane calibration gas (CH_4/He) at the end of each analysis run for 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 per sample punch.
FID Split Time:	The time at which the laser split occurs plus the transit time required for thermally evolved carbon to travel from the sample punch to the FID.
Elemental Carbon (EC):	Carbon evolved from the filter punch in a 98% He/2% O_2 atmosphere at 580, 740, and 840 °C minus any pyrolyzed OC.
EC1:	Carbon evolved from the filter punch in a 98% He/2% O_2 atmosphere at 580 °C.
EC2:	Carbon evolved from the filter punch in a 98% He/2% O_2 atmosphere from 580 to 740 °C.
EC3:	Carbon evolved from the filter punch in a 98% He/2% O_2 atmosphere from 740 to 840 °C.

High Temperature OC: Carbon evolved from the filter punch in a He-only atmosphere at 280, 480, and 580 °C plus pyrolyzed organic carbon. This is OC minus the first OC peak (OC1).

High Temperature EC: Carbon evolved from the filter punch in a 98% He/2% O_2 atmosphere at 740 and 840 °C minus any pyrolyzed organic carbon present in these two peaks. This is EC minus the first EC peak (EC1).

Laser Split: The separation between OC and EC, which depends on the laser-measured reflectance and/or transmittance of the filter punch returning to its initial value. At this point all pyrolyzed OC has been removed and EC is beginning to evolve.

Lower Split Time: The time at which the laser-measured reflectance and/or transmittance of the filter punch reaches its initial value minus the precision of the laser signal (currently defined as 10 counts).

Organic Carbon (OC): Carbon evolved from the filter punch in a He-only (> 99.999%) atmosphere at 140, 280, 480 and 580 °C plus pyrolyzed organic carbon. This is the same as Volatile Organic Carbon (VOC) plus high-temperature OC.

OC1: Carbon evolved from the filter punch in a He-only (> 99.999%) atmosphere from ambient (~25 °C) to 140 °C.

OC2: Carbon evolved from the filter punch in a He-only (> 99.999%) atmosphere from 140 to 280 °C.

OC3: Carbon evolved from the filter punch in a He-only (> 99.999%) atmosphere from 280 to 480 °C.

OC4: Carbon evolved from the filter punch in a He-only (> 99.999%) atmosphere from 480 to 580 °C.

OP: The carbon evolved from the time that the carrier gas flow is changed from He to 98% He/2% O_2 at 580 °C to the time that the laser-measured filter reflectance (OPR) or transmittance (OPT) reaches its initial value. A negative sign is assigned if the laser split occurs before the introduction of O_2.

Pyrolysis: The conversion of OC compounds to EC due to thermal

	decomposition; this may be envisioned as "charring" during the organic portion of the analysis.
Regular Split Time:	The time at which the laser-measured reflectance and/or transmittance of the filter punch reaches its initial value.
Total Carbon (TC):	All carbon evolved from the filter punch between ambient and 840 °C under He and 98% He /2% O_2 atmospheres.
Upper Split Time:	The time at which the laser-measured reflectance and/or transmittance of the filter punch reaches its initial value plus the precision of the laser signal (currently defined as 10 counts).

1.8 Related Procedures

Standard Operating Procedures (SOPs), related carbon analysis activities, and other manuals that should be reviewed in conjunction with this document are:

DRI SOP #2-106	Pre-Firing of Quartz Filters for Carbon Analysis.
DRI SOP #2-111	Sample Shipping, Receiving and Chain-of-Custody
DRI SOP #4-118	Testing Oxygen Level in Helium Atmosphere of Carbon Analyzers

The DRI Model 2001 Thermal/Optical Carbon Analyzer Owner's Manual, revised 3/2004 (Atmoslytic, Calabasas, CA).

The DRI Model 2001 Thermal/Optical Carbon Analyzer Installation, Operation and Troubleshooting Manual, revised 12/2004 (Atmoslytic, Calabasas, CA).

2 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Instrumentation

2.1.1 Description

The components of the DRI Model 2001 Thermal/Optical Carbon Analyzer are depicted in Figures 2-1 through 2-3; the complete gas flow schematic is shown in Figure 2-4. Other details of the configuration of the DRI Model 2001 Thermal/Optical Carbon Analyzer are referred to in the owner's manual. 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 2-5.

In addition to the DRI Model 2001 Thermal/Optical Carbon Analyzer, which is connected to a Pentium compatible computer, the following items are needed for routine carbon analysis:

- Stainless steel punching tool: 5/16-inch diameter, 0.5 cm^2 nominal area for removing small sample punches from quartz filters. This punching tool must be kept clean and sharp. If the punching tool is resharpened, the punch area must be re-verified. Verification is performed by removing 10 punches from a 47-mm quartz-fiber filter (17.35 cm^2); then calculating the punch area [= 17.35 cm^2 x (initial filter weight minus the final weight after punches have been removed) / 10 times the initial filter weight)]. Further verification can be done by taking a precise measurement of the punching tool.

- Syringes: Hamilton Gas-Tight 1000 and 2500 µl syringes for calibration injections; 25 µl syringe for carbonate analysis and for analyzer calibration.

- Quartz filters: Pallflex® Tissuquartz, 2500 QAT-UP (Pall Life Sciences, Ann Arbor, MI) quartz-fiber filter or equivalent.

- Flat-tip tweezers.

- Flat glass plate.

- Logbook/notebook.

- Transparent tape.

- KIMTECH Pure* CL4 Critical Task Wipes and large KimWipes (EX-L).

- Small Styrofoam cooler or refrigerator.

- Blue ice (if using Styrofoam cooler).
- Butane or piezoelectric lighter.
- A copy of *DRICarb.exe* (the analysis program), *Carbon.par* (the analysis parameter file), and Microsoft Access to run *CarbonNetWork.mdb*

Figure 2-1. DRI Model 2001 Thermal/Optical Carbon Analyzer.

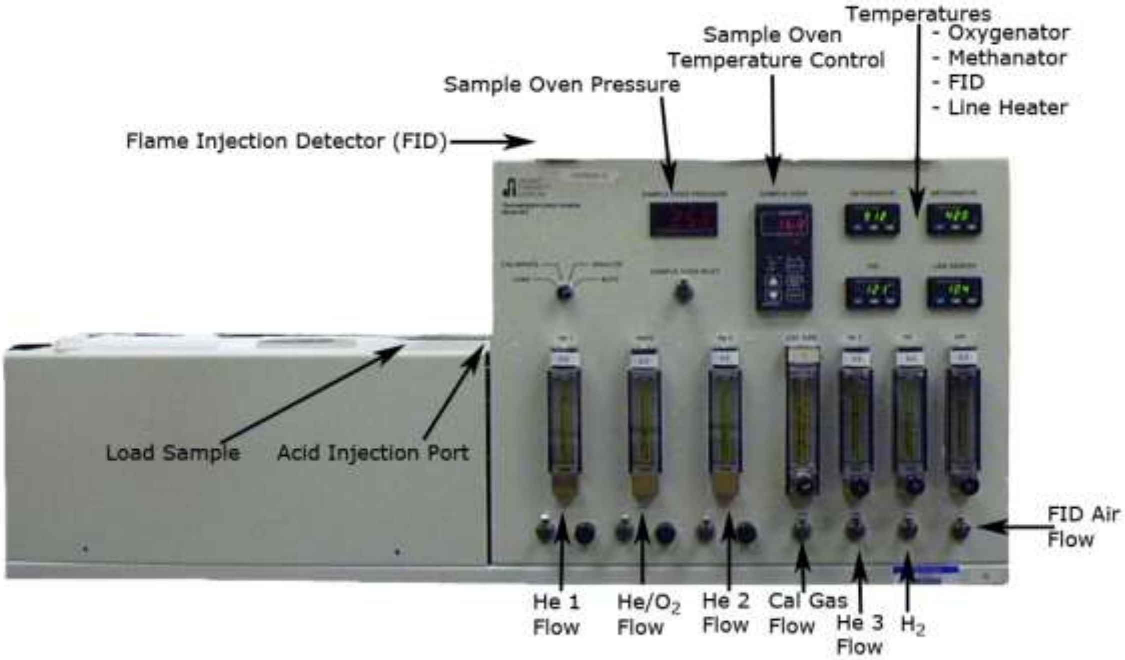


Figure 2-2. DRI Model 2001 Thermal/Optical Carbon Analyzer Schematic Diagram.

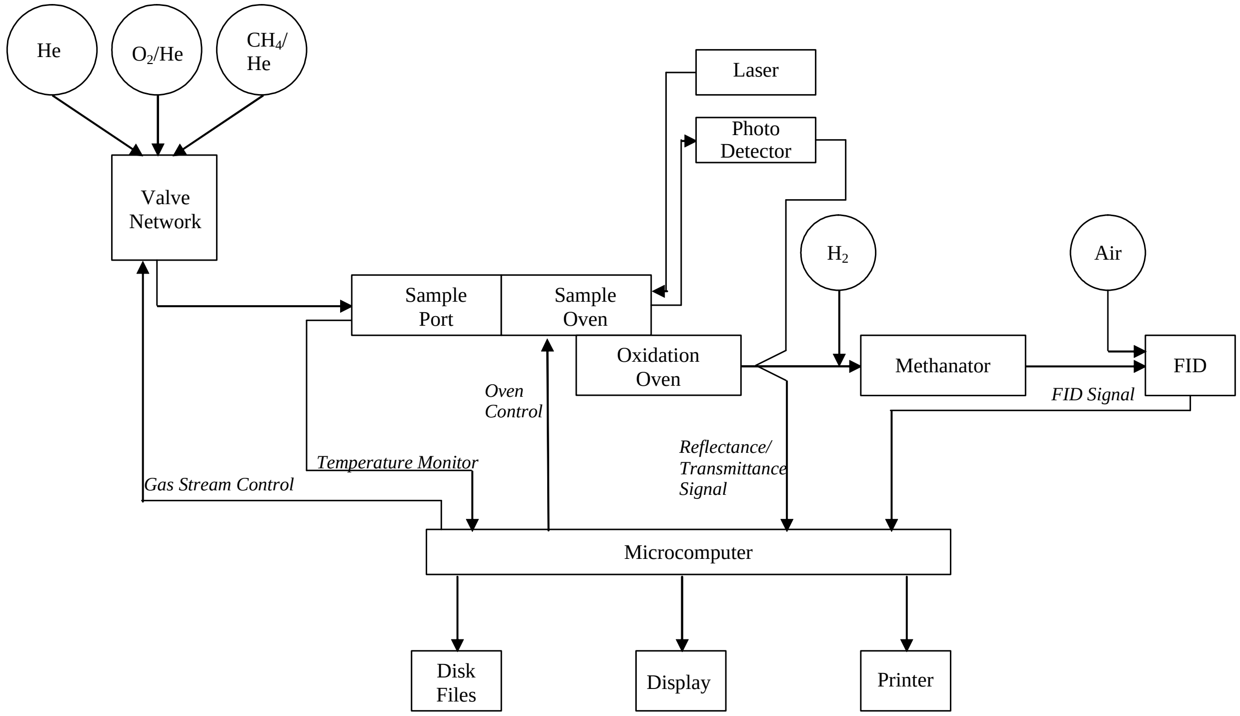
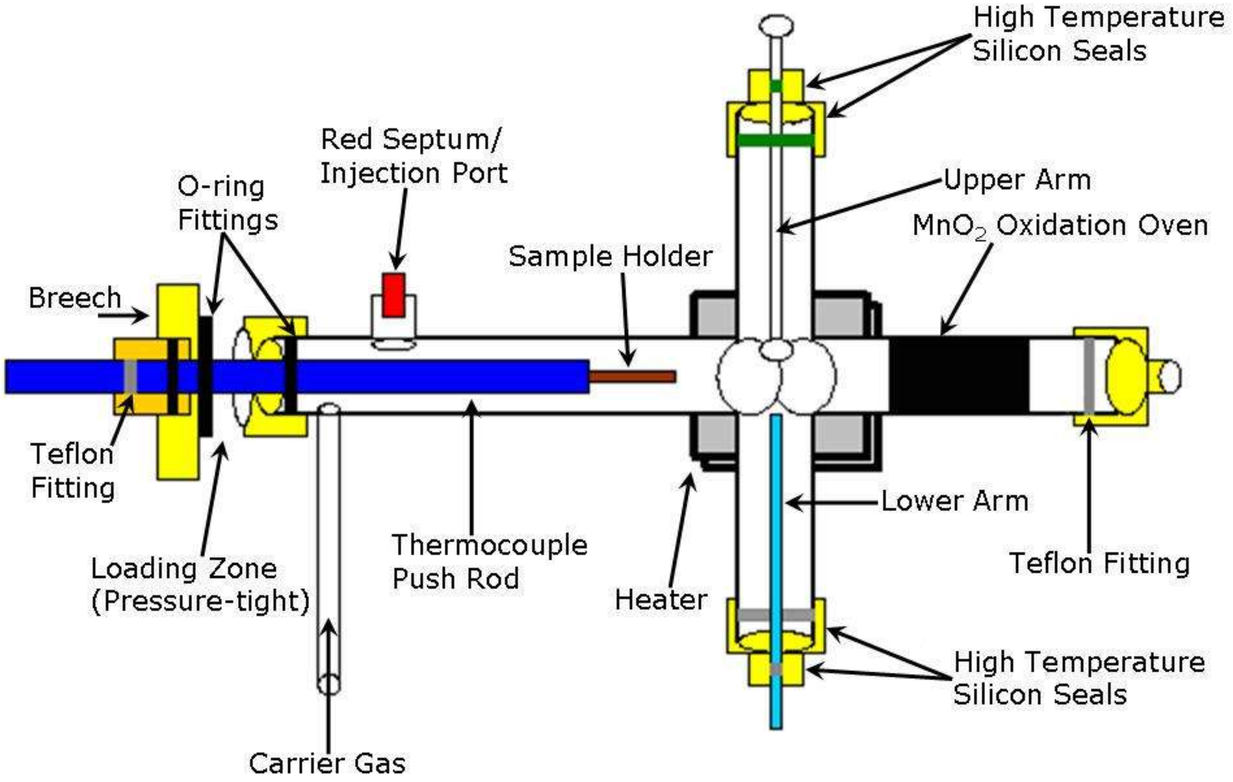


Figure 2-3. DRI Model 2001 Thermal/Optical Carbon Analyzer Sealing Diagram.



Note: In the breech, there is a Teflon-reducing ferrule to seal the pushrod thermocouple, plus two O-rings to seal the breech against the inlet (coupler) connector and one Teflon fitting (See the Model 2001 Owner's Manual for more details).

Figure 2-4. DRI Model 2001 Thermal/Optical Carbon Analyzer Gas Flow Schematic.

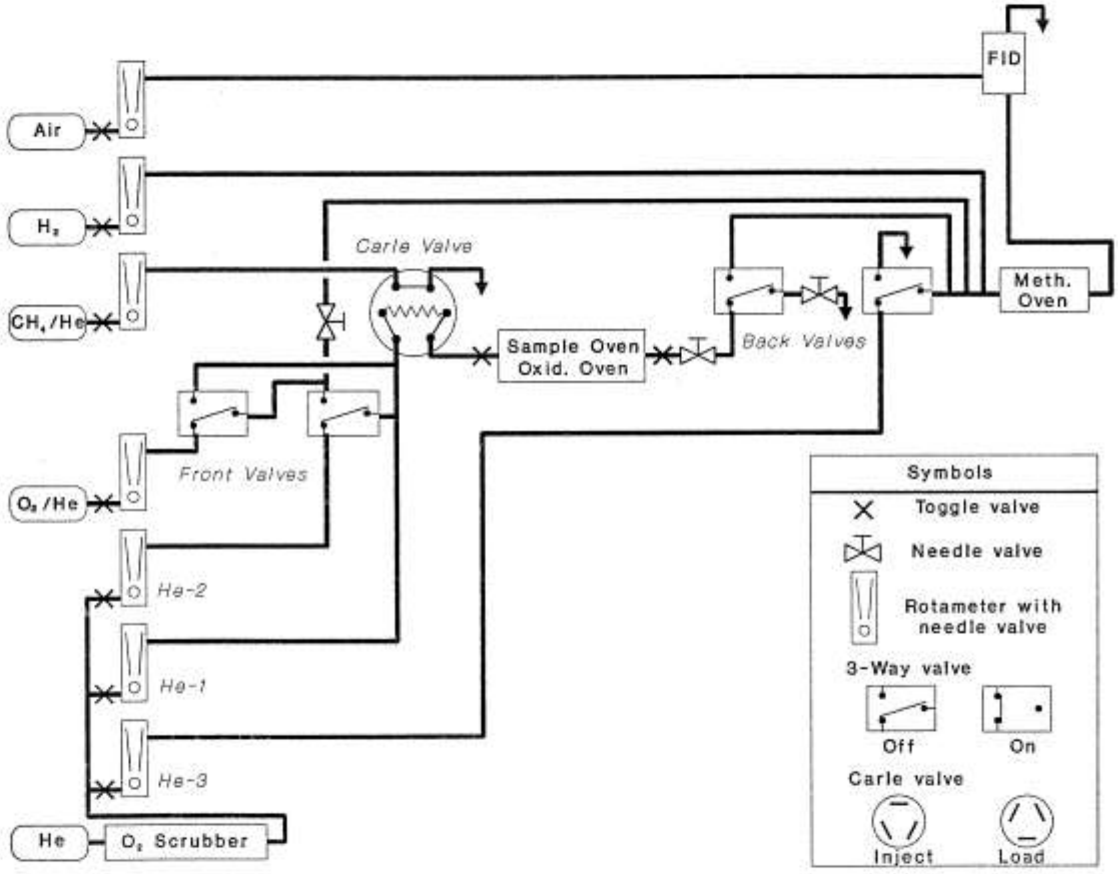
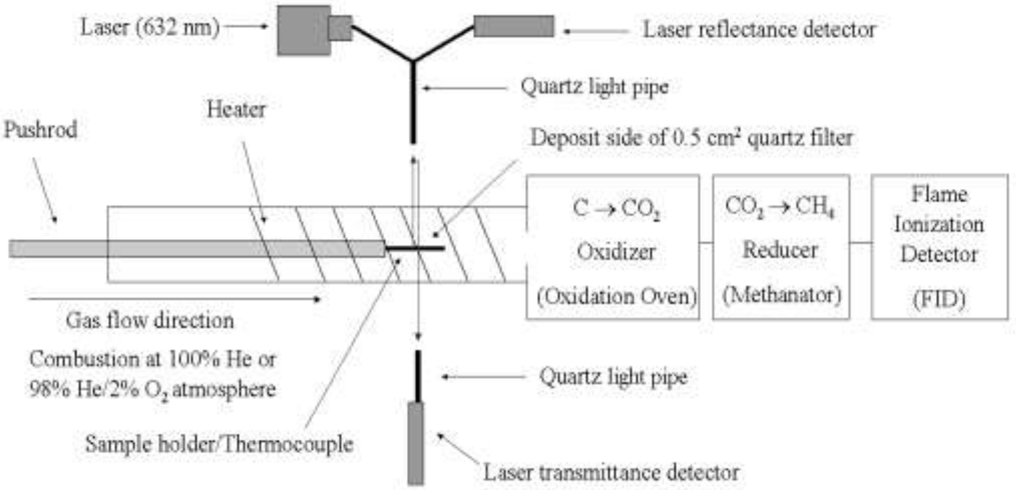


Figure 2-5. DRI Model 2001 Thermal/Optical Carbon Analyzer Combustion Oven.



2.1.2 Instrument Characterization

The DRI Model 2001 Thermal/Optical Carbon Analyzer is program-driven. Data is stored automatically to the hard drive via a PC-compatible computer processor board. Response times and signal lag times are built into the parameter file that is loaded when the analysis program begins. The program is driven by the thermal protocol. For example, when using the IMPROVE_A protocol, the program will advance to the next temperature or carrier gas mixture once the FID signal returns to its baseline; i.e., after a minimum of 150 seconds at one analysis condition. A maximum time limit (580 seconds) per analysis condition is also established to prevent a slight baseline drift from holding the analyzer in one condition indefinitely. For the Chemical Speciation Network (CSN, including the Speciation Trends Network [STN]) thermal protocol, the program advances from one specified temperature plateau to the next temperature or carrier gas mixture when the specified analysis time is reached. Both methods require at least one ~0.5 cm^2 punch per filter and do not require sample pre-treatment. The sample punch is destroyed by both methods.

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

- Verify sample oven pressure reading and specified flow range in the front-panel flow meters.
- DO NOT leave the room until the analysis begins.
- Check the graphical printout after each analysis run to ensure that the: 1) FID, 2) temperature, and 3) laser signals are behaving as expected (Section 4.2.1). Report any anomalies to the lab supervisor immediately.
- The quartz oven is susceptible to breakage. Care should be taken when handling and cleaning.
- Be careful that no fiber from the KIMTECH wipe is left on the sample punch, tweezers, and/or glass plate.

2.1.3 Maintenance

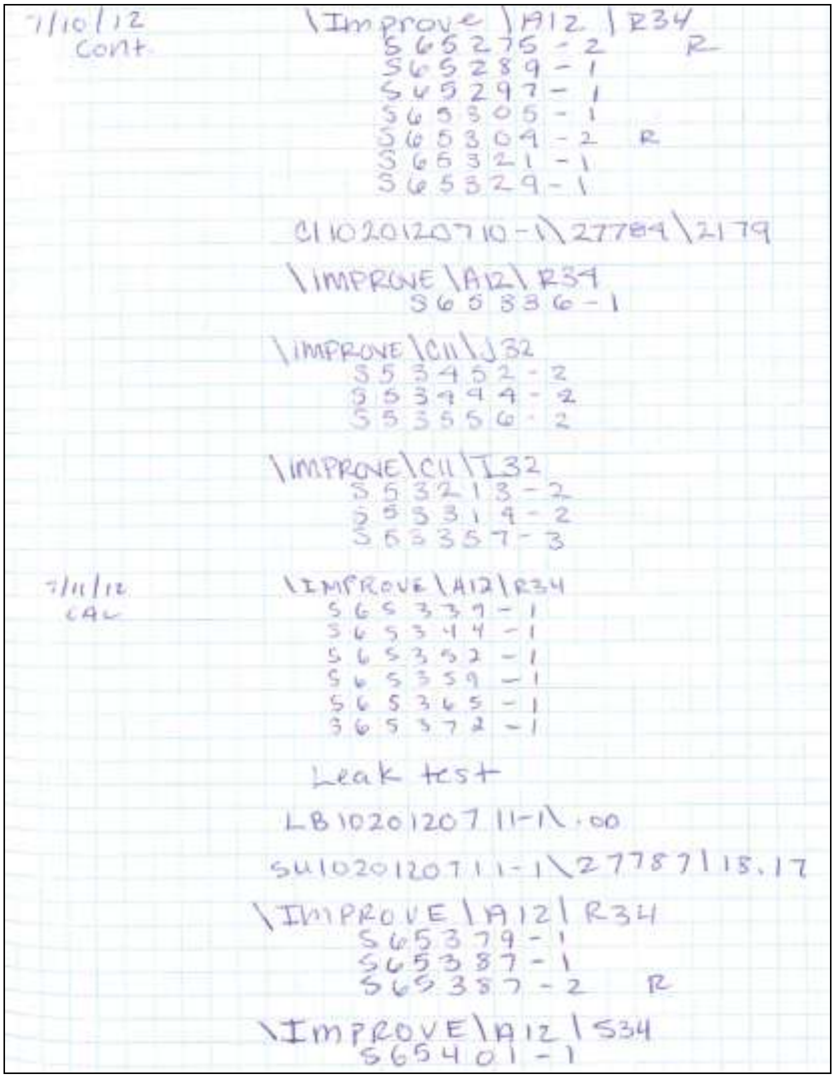
Regular maintenance for the analyzer involves daily checking of compressed gas supplies, cleaning the punching tool and tweezers between each sample with dry KIMTECH wipes, ensuring that the lab is clean, and backing up data files to disc on a daily basis (unless files are automatically backed up to server). Temperature calibrations for the six temperature plateaus (140, 280, 480, 580, 580, 740, and 840°C) need to be performed semiannually (see details in Section 3.3.3). Checks of laser adjustments and leaks are made at least monthly or on an as needed basis. The procedure for leak checks can be found in Section 4.1.2. Additional leak tests are performed with a He leak detector each time a part is replaced, or whenever the analyzer fails the leak check during the daily routine. The system should show no He leaks at the various connections of the quartz cross oven. Since He has high diffusivity, freedom from He leaks will safeguard against O_2 diffusion into the system. These O_2 levels are determined semi-annually using a gas chromatography/mass spectrometry (GC/MS) instrument on the analyzer. Quarterly levels are determined using an O_2 detector that is calibrated against the GC/MS. This is also used when a fresh He cylinder is installed to assure the quality of the gas supply and the condition of the O_2 scrubber. If the *cmdAutoCalibCheck* command is used for calibration, the condition of the catalysts will be indicated and appropriate action can be taken (such as catalyst replacement). All calibrations, repairs, and checks must be recorded in the Carbon Analyzer Logbook (Figure 2-6). Flow rates of all operating gases should be checked and adjusted (if needed) whenever a new quartz oven or methanator is installed or serviced. Additionally, a flow check and balance should be performed as well.

2.2 Spare Parts List

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

- Quartz furnace tube available from the manufacturer (Atmoslytic, Calabasas, CA).
- Quartz rods: 3 mm nominal diameter, optical quality (Atmoslytic, Calabasas, CA), polished for optical clarity with 104 mm (upper arm) and 119 mm (lower arm) lengths. The version of the carbon analyzer manufactured in 2001 uses a 98 mm rod for the upper arm. Measure the old rods for reference.
- Catalyst ovens: Watlow 15.24 cm length, 2.54 cm tube diameter element from the analyzer supplier.
- Quartz boats (Atmoslytic, Calabasas, CA).
- Quartz wool: For repacking the oxidation oven (Alltech Associates, #4033, Deerfield, IL).
- Thermocouple rods: 24.13 cm length by 0.32 cm outside diameter (OD), Type-K ground isolated with Inconel sheath (Omega, Part #TJ36-CAIN-18E-9.5, Stamford, CT). Remove 1 cm of the sheath with a file to obtain the longer tip needed in this application.
- FID flame tips: for Gow-Mac #12-800 FIDs (Gow-Mac, #132-117, Bethlehem, PA).

Figure 2-6. DRI Carbon Analysis Logbook Format.



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S53494-2
S53556-2

\IMPROVE\C11\I32
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S53357-3

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S65372-1

Leak test

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S65379-1
S65387-1
S65387-2 R

\IMPROVE\A12\S34
S65401-1

- Septa: Standard 0.32 cm or 0.64 cm cylindrical (Alltech Associates #6524, Deerfield, IL) for injection ports. Silicon septa 0.25 cm and 1.11 cm for oven seals (Alltech #15427 and #15429, Deerfield, IL).

- 1 ml gas tight syringe for gas injections.

- 25 µl syringes for liquid injections.

- Replacement needles for syringes (Alltech #7729-06, Deerfield, IL).

- Replacement oxygen/moisture trap (R&D Separations, Model OT3-2, Rancho Cordova, CA).

- Replacement hydrocarbon trap (R&D Separations, Model HT200-4, Rancho Cordova, CA).

- Replacement indicating oxygen trap (Chromatography Research Supplies, Model 202223, Louisville, KY).

- Viton O-rings: Size 013. Two needed for quartz oven tube inlet.

- Teflon ferrules: Parker or Swagelok style 0.64 cm front and back ferrule for the quartz oven tube outlet connections (Swagelock, T-400-SET, Solon, OH). Refer to instrument user manual for specific ferrule sizes.

- Teflon ferrules: 0.32 cm to 0.64 cm (Alltech Associates, #RF-400/200-T, Deerfield, IL), for the thermocouple rod at the inlet breech. Refer to instrument user manual for specific ferrule sizes (style varies by location on analyzer).

- High temperature silicone seals for quartz light rods and connector, prepared by Alltech Associates, #15427 and #15429, Deerfield, IL.

- Heating element for oven (Watlow, #VC401A06A-0000R [90° bend], Columbia, MO).

- Printer paper and toner cartridge.

- Computer CD for backup if not on server backup.

2.3 Reagents

2.3.1 Chemicals

The following chemicals should be reagent grade or better:

- Potassium hydrogen phthalate (KHP), for calibration (Fisher Scientific, cat #P-243, CAS 877-24-7, Fairlawn, NJ).

- Sucrose, for calibration use (EM Science, #SX1075-1, Gibbstown, NJ).

- Manganese dioxide (MnO_2), crystalline, as an oxidizer in the oxidation oven (Nurnberg Scientific, #C5162, Portland, OR; Aldrich Chemicals #24344-2, St. Louis, MO; or equivalent).

- Nickelous nitrate [$Ni(NO_3)_2 \cdot 6H_2O$], crystalline, used to prepare the nickel catalyst in the methanator (Fisher Scientific, cat #N62-5000, CAS 13478-00-70, Fairlawn, NJ).

- Chromosorb A, 20/30 mesh, used as a support for nickel catalyst in the methanator (from any chromatography supplier, such as Alltech cat #2-0165). Both nickelous nitrate and Chromosorb A are for preparing the reduction catalyst in the methanator.

- Hydrochloric acid (HCl), 0.4 molar solution, for use in cleaning punch and quartz ovens, and for use in carbonate analysis (Fisher Scientific, cat #A508-212, CAS 7647-01-0, Fairlawn, NJ).

- Hydrofluoric acid (HF), diluted to 15% may be used for removing the white deposits from devitrification (white deposits of SiO_2) on the quartz oven parts (Fisher Scientific, cat #A147-1LB, CAS 7664-39-3, Fairlawn, NJ). However, proper safety precautions must be followed when using HF and quartz oven parts may become brittle with repeated use.

- Nanopure water (used as described in Section 3.2.1).

2.3.2 Gases

The following gases should be ultra-high purity (UHP) grade or better:

- He for a carrier gas, regulated to 15-40 psi with a metal diaphragm regulator. The higher pressure is required due to the pressure drop across the Supelco oxygen scrubber.

- 5% CH_4 by volume in He for calibration injections and calibration peaks; regulated to 10 psi by a metal diaphragm regulator.

- 5% CO_2 by volume in He for calibration injections; regulated to 10 psi by a metal diaphragm regulator.

- 10% O_2 by volume in He as a carrier gas, regulated to 15 psi by a metal diaphragm regulator.

- Hydrogen for the FID flame, regulated to 15 psi with a metal diaphragm regulator.

- Hydrocarbon-free air to supply O_2 to the FID, regulated to 15 psi by a metal diaphragm regulator from a zero air generator.

- Compressed air for pneumatic activation, regulated to ~25 psi.

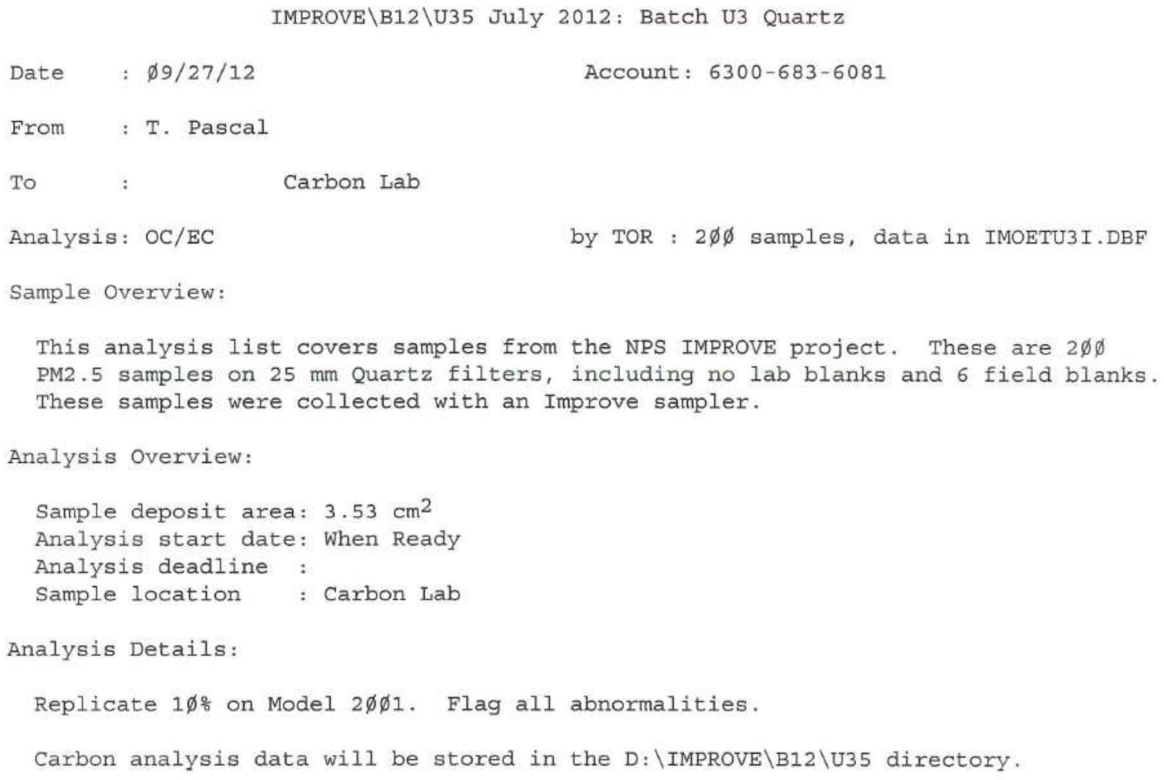
At least one backup cylinder per gas type should be kept on hand at all times. Depending on analysis volume, the 90% He/10% O_2 mixture are typically replaced every four to six weeks; H_2 and He are replaced once a week. All gases are replaced when the cylinder pressure drops below 500 psi (unless the cylinders are connected to an automatic change-over module). Check the O_2 scrubber and follow the manufacturer's recommendations for scheduling its replacement.

The flow settings on the flow meters (rotameters) are based on an input of 15 psi for He, 90% He/10% O_2, H_2, and FID air. The pneumatic drivers for the breech should have a pressure of ~25 psi to operate effectively (sealing the opening).

2.4 Forms, Paperwork, and Logbook

All samples are logged in upon receipt at the laboratory. A sample analysis list will be prepared by the laboratory supervisor or designated technician indicating which samples will be analyzed, plus any special instructions. As individual samples are analyzed, entries are made in the Carbon Analyzer Logbook, as shown in Figure 2-6. Figure 2-7 provides an example of the cover sheet of the sample analysis run list. Figure 2-8 provides an example of the Daily Analyzer Checklist that is completed at the start of each day in order to verify analyzer flow and FID response.

Figure 2-7. DRI Carbon Sample Analysis Run List.



IMPROVE\B12\U35 July 2012: Batch U3 Quartz

Date : 09/27/12 Account: 6300-683-6081

From : T. Pascal

To : Carbon Lab

Analysis: OC/EC by TOR : 200 samples, data in IMOETU3I.DBF

Sample Overview:

This analysis list covers samples from the NPS IMPROVE project. These are 200 PM2.5 samples on 25 mm Quartz filters, including no lab blanks and 6 field blanks. These samples were collected with an Improve sampler.

Analysis Overview:

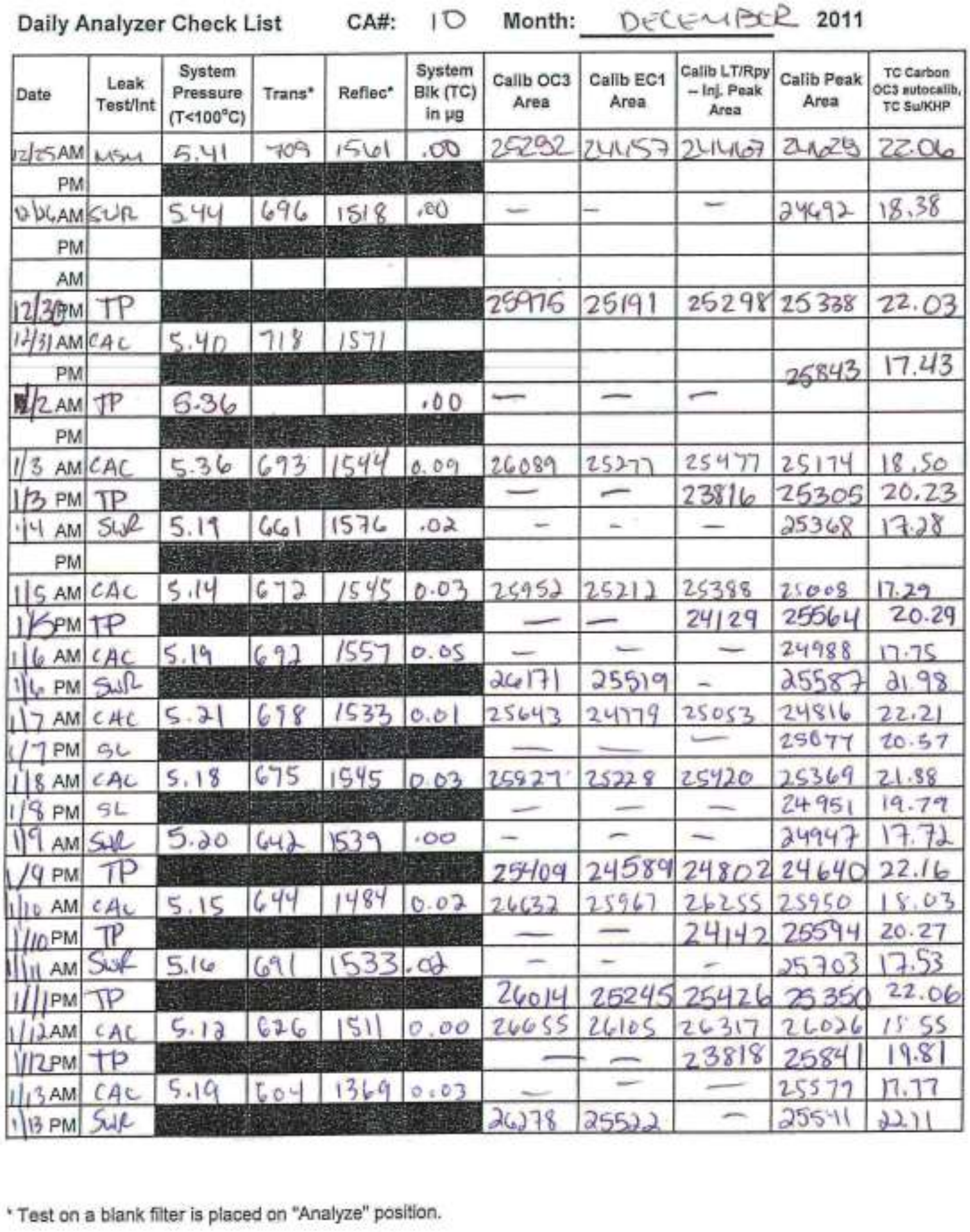
Sample deposit area: 3.53 cm^2
Analysis start date: When Ready
Analysis deadline :
Sample location : Carbon Lab

Analysis Details:

Replicate 10% on Model 2001. Flag all abnormalities.

Carbon analysis data will be stored in the D:\IMPROVE\B12\U35 directory.

Figure 2-8. DRI Carbon Daily Analyzer Checklist.



Daily Analyzer Check List CA#: 10 Month: DECEMBER 2011

Date	Leak Test/Int	System Pressure (T<100°C)	Trans*	Reflec*	System Blk (TC) in µg	Calib OC3 Area	Calib EC1 Area	Calib LT/Rpy – Inj. Peak Area	Calib Peak Area	TC Carbon OC3 autocalib, TC Su/KHP
12/25 AM	MSM	5.41	709	1561	.00	25292	24457	24467	24629	22.06
PM										
12/26 AM	SUR	5.44	696	1518	.00	–	–	–	24692	18.38
PM										
AM										
12/30 PM	TP					25976	25191	25298	25338	22.03
12/31 AM	CAC	5.40	718	1571						
PM									25843	17.43
1/2 AM	TP	5.36			.00	–	–	–		
PM										
1/3 AM	CAC	5.36	693	1544	0.09	26089	25277	25477	25174	18.50
1/3 PM	TP					–	–	23816	25305	20.23
1/4 AM	SUR	5.19	661	1576	.02	–	–	–	25368	17.28
PM										
1/5 AM	CAC	5.14	672	1545	0.03	25952	25212	25388	25008	17.29
1/5 PM	TP					–	–	24129	25564	20.29
1/6 AM	CAC	5.19	692	1557	0.05	–	–	–	24988	17.75
1/6 PM	SUR					26171	25519	-	25587	21.98
1/7 AM	CAC	5.21	698	1533	0.01	25643	24779	25053	24816	22.21
1/7 PM	SL					–	–	–	25077	20.57
1/8 AM	CAC	5.18	675	1545	0.03	25827	25228	25420	25369	21.88
1/8 PM	SL					–	–	–	24951	19.79
1/9 AM	SUR	5.20	642	1539	.00	–	–	–	24947	17.72
1/9 PM	TP					25409	24589	24802	24640	22.16
1/10 AM	CAC	5.15	644	1484	0.02	26632	25967	26255	25950	18.03
1/10 PM	TP					–	–	24142	25594	20.27
1/11 AM	SUR	5.16	691	1533	.02	–	–	–	25703	17.53
1/11 PM	TP					26014	25245	25426	25350	22.06
1/12 AM	CAC	5.12	626	1511	0.00	26655	26105	26317	26026	15.55
1/12 PM	TP					–	–	23818	25841	19.81
1/13 AM	CAC	5.19	604	1369	0.03	–	–	–	25577	17.77
1/13 PM	SUR					26278	25522	–	25541	22.11

* Test on a blank filter is placed on "Analyze" position.

3 CALIBRATION PROCEDURES AND STANDARDS

3.1 Types of Instrument Calibration

The calibration procedures for the carbon analyzers are of four types: 1) the end-of-run calibration peak; 2) the routine beginning and end-of-day calibration injections of He/CH_4 and He/CO_2 (or the auto calibration check using the *cmdAutoCalibCheck* command); 3) full instrument calibration, performed every six months, using KHP, sucrose, and the two calibration gases; and 4) temperature calibrations performed every six months using temperature-sensitive indicating liquids with different melting points. The routine calibration procedure type 1, end-of run calibration, is described in Section 4.2.1 while procedure type 2, routine beginning and end of day calibration, is described in Section 4.2.2.

3.1.1 End-of-Run Calibrations (Description)

The end-of-run calibration consists of a set quantity of He/CH_4 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 confirm that the analyzer is operating satisfactorily. Calibration peak area counts should be within an acceptable range (typically between 20,000 and 30,000 with minimal change between runs) for the specific analyzer. Check daily records to compare peak area counts and determine analyzer performance and stability. The end of run calibration procedure is described in Section 4.2.1.

3.1.2 Routine Calibrations (Description)

Routine calibrations must be performed at the beginning and end of each day, either manually or by using the automated routine calibration command (*cmdAutoCalibCheck*) in the *CarbonNetWork* database Command table. The routine calibration procedures are decribed in greater detail in Section 4.2.2

3.2 Full Calibration (Description)

Full instrument calibration, performed semiannually or after major maintenance or repairs, 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 5.0 to 20.0 µl of the 1800 ppm KHP and sucrose solutions and injecting 200 to 1000 µl of the CH_4 and CO_2 gases.

Four types of standards are used to calibrate the carbon analyzers: 5% nominal CH_4 in He, 5% nominal CO_2 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 CH_4 and CO_2 semiannually to establish the calibration curve of each analyzer.

3.2.1 Preparation, Ranges and Traceability of Standards

The calibration is done by injection of a known volume of the standard to yield a calibration curve of peak area ratio of injected carbon: CH_4 (internal standard) versus µg C injected (Internal Standard Calibration Method). For the best accuracy, the temperature and pressure at the time of analysis need to be taken into account. For a 100% CH_4 or CO_2 standard at 760 mm Hg at 20 °C, each microliter = 0.499 µg carbon. For a 5% standard, it will be 0.02495 µg C/µl at standard temperature and pressure (STP; 20 °C, 760 mm Hg). The Ideal Gas Law should be used to correct for the temperature and pressure of the laboratory.

$$\text{Acutal}\,\mu\text{g C per}\,\mu\text{L} = \left(\frac{\text{Pa}}{760}\right)\left(\frac{1}{(\text{T}+273.15)}\right)\left(\frac{1}{0.08206}\right)\times\%\text{ of cal gas}\times 12$$

where Pa is pressure in mmHg, T is ambient temperature.

The calibration gases are traceable to NIST standards. The calibration gases are assayed for exact concentrations by the gas supplier; the assay value is obtained from the tag on the cylinders and is typically determined by GC.

To prepare an 1800 ppm standard, 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 inside a desiccator. The weight of KHP used must be recorded. Dilute to volume with 0.4 ml concentrated hydrochloric acid (HCl) and 99.6 ml Nanopure water. 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:

$$Actual\ \mu g\, C\ per\ mL = \left(\frac{weight\ of\ KHP\, used\ in\ g}{vol\, of\ solution\ prep\, in\ ml}\right)\left(\frac{no\, of\ carbon\, in\ KHP\times 12}{MW\ of\ KHP}\right)$$

$$e.g. = \left(\frac{\text{weight of KHP used in g}}{100\text{ ml}}\right)\left(\frac{8\times 12}{204.23}\right)\left(\frac{10^6\ \mu\text{g}}{\text{g}}\right)$$

The nominal 1800 ppm carbon sucrose solution standard is prepared by transferring 0.428 g of sucrose into a glass 100 ml volumetric flask. Dilute to volume with acidified Nanopure water (see blank solution preparation instructions below). 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:

$$Actual\ \mu g\, C\ per\ mL = \left(\frac{weight\ of\ sucrose\, used\ in\ g}{vol\, of\ solution\ prep\, in\ ml} \right) \left(\frac{no\, of\ carbon\, in\ sucrose \times 12}{MW\ of\ sucrose} \right)$$

$$e.g. = \left(\frac{\text{weight of sucrose used in g}}{\text{100 ml}} \right) \left(\frac{12 \times 12}{342.31} \right) \left(\frac{10^6\ \mu\text{g}}{\text{g}} \right)$$

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

Only a limited set of 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 EC and carbonate compounds. Currently, KHP, sucrose, and the two calibration gases are used at DRI for calibration and system audit purposes.

3.2.2 Calculating Calibration Slope

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 TC, as no routine procedure exists to check the accuracy of the OC/EC split. An example of the worksheet is shown in Figure 3-1.

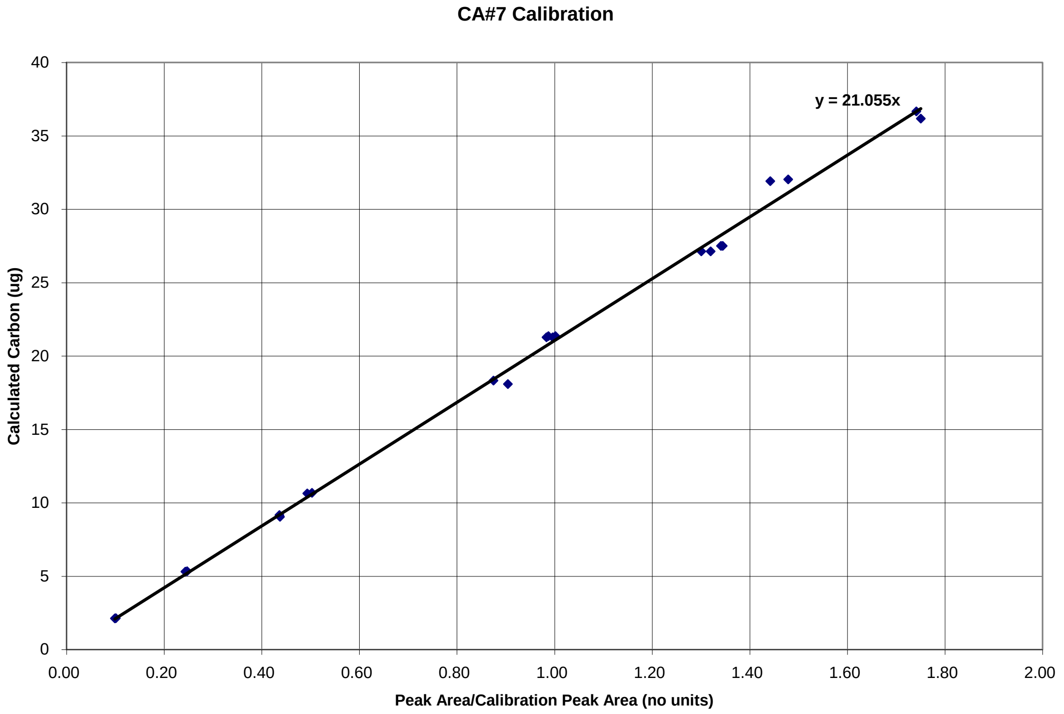
3.2.3 Typical Accuracy of Calibration Standards

The accuracy of the calibration standards is primarily limited by the accuracy of the calibration gas assays, the accuracy of the preparation of the KHP and sucrose solutions, and the technician’s injection technique. 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 3.1). Figure 3-2 shows an example of plotted calibration curves.

Figure 3-1. Example of Calibration Summary Worksheet Used to Determine Calibration Slope.

Cal Std	Run ID	Vol (µL)	Inject Peak Counts	Calib Peak Counts	Tech Initials	Peak vs µC	Area vs µC Label	Inject Peak/Calib Peak	Slope
CH4	MI0720110407-200	200	4506	24756	CDW	4.08	1.10	0.182	22.41
CH4	MI0720110407-500	500	11686	24914	CDW	10.20	1.15	0.469	21.74
CH4	MI0720110407-700	700	16162	25011	CDW	14.27	1.13	0.646	22.09
CH4	MI0720110407-1000	1000	22058	25063	CDW	20.39	1.08	0.88	23.17
CO2	cI0720110407-200	200	4381	24949	CDW	4.06	1.08	0.176	23.11
CO2	cI0720110407-500	500	10956	25027	CDW	10.14	1.08	0.438	23.17
CO2	cI0720110407-700	700	15421	24919	CDW	14.20	1.09	0.619	22.95
CO2	cI0720110407-1000	1000	22172	24823	CDW	20.29	1.09	0.893	22.71
SUC	SU0720110407_5	5	10529	24831	CDW	9.00	1.17	0.424	21.23
SUC	SU0720110407_10	10	21293	24743	CDW	18.00	1.18	0.861	20.92
SUC	SU0720110407_15	15	31159	24638	CDW	27.01	1.15	1.265	21.36
SUC	SU0720110407_15	15	31660	24747	CDW	27.01	1.17	1.279	21.11
SUC	SU0720110407_20	20	42388	24802	CDW	36.01	1.18	1.709	21.07
KHP	KHP0720110407_5	5	9674	24504	CDW	8.96	1.08	0.395	22.69
KHP	KHP0720110407_10	10	20449	24625	CDW	17.91	1.14	0.83	21.57
KHP	KHP0720110407_15	15	32170	24622	CDW	26.87	1.20	1.307	20.57
KHP	KHP0720110407_15	15	32345	24891	CDW	26.87	1.20	1.299	20.68
KHP	KHP0720110407_20	20	44640	24956	CDW	35.83	1.25	1.789	20.03

Figure 3-2. Example of a DRI Carbon Analyzer Calibration Curve.



3.2.4 Data Treatment for Calibration Data

- Calibration values are plotted as ratio of the integrated sample peak counts to the calibration peak counts vs. the actual calculated µg carbon (Figure 3-2). Obvious outliers are identified and rerun. Linear regression is performed on each set of calibration data (separate calculations for KHP, sucrose, CH_4/He, and CO_2/He). The slope (m) is calculated from:

$$\left(m = \frac{\sum (y_i x_i)}{\sum \left(x_i^{\,2}\right)} \right)$$

The standard deviation (s) is calculated by:

$$\sigma = \sqrt{\frac{1}{n-1} \frac{\sum (y_i - m x_i)^2}{\sum x_i^{\,2}}}$$

where:

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

and:

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

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

- The resulting slope is compared to previous calibration results. New values should be no more than 10% different than previous calibrations if no major analyzer changes have been made. If variation is > 10%, calibration must be redone to verify values.

- The new slope for each analyzer (derived from combined CH_4, KHP, and sucrose data) is placed into the *Carbon.par* file for each analyzer; this file contains analyzer parameters which are read into the Carbon program when it is first started. Therefore the *Carbon.par* file must be edited while the program is closed and the parameters will take affect when the program is restarted. The date and version number in the *Carbon.par* file is also updated.

- Calibration data and plots are retained electronically and in file folders stored with the raw analysis data.

3.2.5 Calculations

The conversion of integrated peak counts to µg 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:

$$peak\ \mu g\ C/punch = \frac{(integrated\ \ peak\ counts\ above\,baseline\ )x(\ calibratio\,n\ slope\ )}{(\ internal\ calibratio\,n\ n\ counts\ )}$$

For IMPROVE_A thermal protocol, the peaks reported are: four organic peaks (OC1, OC2, OC3, and OC4) corresponding to 140, 280, 480, and 580 °C in He atmosphere, respectively; three elemental carbon peaks (EC1, EC2, and EC3) corresponding to 580 °C after the introduction of O_2, 740, and 840 °C, respectively; and three pyrolyzed organic carbon peaks (Lower, Regular, and Upper Splits) by reflectance and transmittance, corresponding to the peaks after the introduction of O_2 and before the Lower Split Time, Regular Split Time, and the Upper Split Time, respectively, for the reflectance and transmittance optical charring correction (see Section 1.7 and Figure 4-4). The EC reported includes pyrolyzed carbon.

Carbon values per punch are converted to µg C/cm^2 by:

$$\mu g\,C/cm^2 = \frac{(\mu gC/punch)}{(puncharea)}$$

Finally, carbon values are converted to µg C/filter by:

$$\mu gC/filter = (\mu gC/cm^2)(filterdepositarea)$$

3.3 Instrument Calibration Instructions

3.3.1 Full Gas Calibration

- To perform the full calibration, select "Analysis" from the Main menu of the *DRICarb.exe* program Welcome screen.

- Choose "Calib" under the "Type" drop down menu. Project name, Batch #, and, Sub-batch # are not required. In the "Command table drop-down", select *cmdCalib-He* (for example). Fill out the Sample ID, Run #, and Tech Initials fields. The sample ID should be in the format, "MIxxYYYYMMDD_zzzz" (where "MI" is for CH_4 injection; use "CI" for CO_2 injection; xx is for the analyzer number and zzzz is the volume of gas injected). You can also select FID ID (typically FID_8) to determine the FID peak area and make comments and flag the analysis from this screen before the analysis starts.

- Select the atmosphere for calibration under the "Cal Gas" menu and select the proper "Carrier Gas". (He-only gas is recommended when doing full gas calibrations.) Verify the command table matches the options selected.

- Enter the technician initials in the "Tech initials" field.

- Choose "OK" to run the analysis, or "Exit" to leave the program. The analysis will start with the screen as shown in Figure 4-6. You will note that the top portion contains all the information in the Setup screen. The bottom half will display the thermogram when the run is initiated.

- Start a run by clicking on the Run command button. After the computer states "Please load gas syringe" flush the gas syringe with the calibration gas at least three times and then load it with the calibration gas. Time remaining until load will be stated, and then "Inject calibration gas". Inject the gas through the septum. Hold the plunger down with needle still inside septum for 10 seconds, or until peak appears.

- The CO_2 and CH_4 calibrations are run using the "Calibration" options from the main menu. The following volumes are injected:
  - 200 µl CO_2 & CH_4 gas (use 1000 µl calibrated gas-tight syringe)
  - 500 µl CO_2 & CH_4 gas (use 1000 µl calibrated gas-tight syringe)
  - 700 µl CO_2 & CH_4 gas (use 1000 µl calibrated gas-tight syringe)
  - 1000 µl CO_2 & CH_4 gas (use 1000 µl calibrated gas-tight syringe)

- Record these calibration values in the logbook as in Figure 2-6.

- The integrated peak counts are extracted manually from the tabular printouts and entered into the spreadsheet which is used to determine the final calibration.

3.3.2 Full Sucrose and KHP Calibrations

- To perform the full calibration, select “Analysis” from the Main menu of the *DRICarb.exe* program Welcome screen.

- Choose “Sample” under the “Type” drop down menu. Complete the information about the sample, including: Project Name, Batch #, and Sub-batch #. The Project name should be “SUKHPCAL”, the Batch # should be “MM” for the month; and the Sub-batch # should be “DD” for the date.

- A clean blank quartz punch is baked in the analyzer oven at 900 °C for 10 minutes using *cmdBakeOven* from the Command table.

- After baking the quartz punch, change to *cmdImproveA* under Command table.

- Perform system blank before running KHP or sucrose.

- Enter the Sample ID number or place your mouse cursor in the field. The sample ID should be in the format, “SUxxYYYYmmdd_zz” (where “SU” is for sucrose spiking; use “KHP” for KHP spiking; xx is the analyzer number and zz is the volume [05, 10, 15, or 20 µl]). You can also select FID ID (typically FID_8) to determine the FID peak area and make comments and flag the analysis from this screen before the analysis starts.

- Enter the Run #; the Punch area and Deposit area should be “1” for the filter being analyzed.

- Enter technician initials in the “Tech initials” field.

- After the punch has cooled to less than 50 °C, the KHP or sucrose solution (prepared as described in Section 3.2.1 and kept at room temperature) is injected onto the punch using a 25 µl syringe. The following volumes are used:

  - 5 µl KHP and sucrose solution
  - 10 µl KHP and sucrose solution
  - 15 µl KHP and sucrose solution (do twice)
  - 20 µl KHP and sucrose solution

  - no injection (as a system blank; see Section 4.1.6.1)
  - 20 µl acidified Nanopure water only (check of background level of Nanopure water)

- Flush the syringe at least three times with the calibration solution before taking up the volume for injection. Pump the syringe plunger to remove any trapped bubbles.

- Slowly spike the solution in the center of quartz punch and wash the syringe with Nanopure after use. If the solution is spiked too quickly it will bead up and run off the punch.

- Click “OK” on the analysis “Setup” screen. The boat will load to the calibration position.

- The computer will ask, “Would you like to proceed or would you like to delay analysis?” Enter the length of time in seconds you wish to delay the beginning of the analysis in the Delay box. This is used to purge dry a filter disc that has been deposited with an aliquot of KHP or sucrose standard solution, or when the sample is acidified for carbonate removal. In general, allow ~1.5 - 2 minutes of purge time for every µl of solution deposited (i.e., 5µl=600s, 10µl=900s, 15µl=1200s, and 20µl=1500s). Click “OK” and analysis will begin.

- 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 and the laser reflectance and transmittance signals. Select the *cmdImproveA* option from the analysis menu to start.

- The integrated peak counts for all seven temperature fractions for the sample and calibration peaks are recorded. The total peak is calculated by adding the peak area from OC1, OC2, OC3, and OC4, as well as EC1, EC2, and EC3. Pyrolysis counts are not included in the total.

3.3.3 Temperature Calibrations

Temperature calibrations are performed semiannually on all instruments to verify that the sample temperature is as accurate as possible.

3.3.3.1 Temperature Indicators

Since it is not possible to sense the temperature of the sample directly, materials were sought that: 1) could be placed where the sample would normally be located, and 2) would cause sharp reactions when known temperatures were achieved. Quick-drying temperature-indicating liquids of different melting points, Tempilaq° G (Tempil, Inc., South Plainfield, NJ, USA), were used as temperature indicators in muffle furnaces. A Tempilaq° G set contains long-chain hydrocarbons suspended in an organic solvent, which change their appearance at 44 specific temperatures spanning 80-1000 °C. The accuracy of Tempilaq° G is certified within ±1% of its designated temperature and is traceable to the National Institute of Standards and Technology (NIST). Tempilaq° G is bottled in liquid form and dries quickly to a dull, opaque film when applied to a surface. As the surface is heated to the designated temperature, the film liquefies and is accompanied by a change of appearance that can be optically monitored to determine sample temperature.

3.3.3.2 Analyzer Preparation

Preparation of the Model 2001 analyzer for temperature calibration includes the following:

- Change par file to 1 and 0 for slope intercept (par file must be edited with the program closed).
- Disconnect the back valve to prevent contaminating the system
- Replace existing MnO_2 oven with a clean backup oven (without a catalyst) to prevent contamination of the main oven. Install without connecting to the back valve.
- Connect an Erlenmeyer flask with ice in it where the oven connects to the back valve. This will help condense the organics when the Tempilaq is heated up.

3.3.3.3 Standard Preparation

Temperature calibration requires two pre-fired quartz-fiber filter (#2500 QAT-UP, Pall Life Sciences, Ann Arbor, MI) punches (0.5 cm^2 for DRI analyzer) and a clean matching-sized quartz disk (Continental Glass Engineering, Burbank, CA). Quartz-fiber filter punches are sliced in half (horizontally) with a filter-slicing device (Fung et al., 2004). A thin layer of Tempilaq° G (~25 µL) is uniformly applied to the glass and/or quartz disk surface with a 0.1 ml Eppendorf graduated Combitip (Brinkman Instruments Inc., Westbury, NY), and, before drying, is immediately covered with a sliced filter punch. For cost savings, a glass, instead of quartz, disk can prepared by a technician in the lab from a glass slide cover and used for Temiplaq° G at temperatures > 520 °C. Higher temperatures require the quartz disc to prevent melting. The disc sandwich (i.e., temperature standard) is then loaded on a sample holder for analysis. The mass of applied Tempilaq° G is determined gravimetrically to ensure its mass is ~10%.

3.3.3.4 Temperature Program

After insertion of the temperature standard into the analyzer, the temperature is slowly (2 °C/min) ramped across a 50 °C range containing the specified Tempilaq° G melting point. This slow ramping creates a quasi-equilibrium condition that allows the phase transition point to be resolved. Temperature indicators 121 through 510 are replicated three times and 704 and 816 are replicated twice. When the specified temperature is reached, the Tempilaqº G liquefies, causing a detectable change in reflectance and transmittance.

Figure 3-3 demonstrates the thermocouple temperature, reflectance, and transmittance as a function of thermal analysis time. In the example provided, the reflectance and transmittance remained relatively flat until the temperature approaches its specified value of 184 °C. Figure 3-4 compares the time series of reflectance, transmittance, and their respective first- and second-order derivatives. The second-order derivative (change in the slope) recorded the inflection point of reflectance or transmittance that provided the best indication of the attainment of the designated temperature. Thermocouple temperature at this critical point was recorded as "measured" temperature. The temperature deviation (ΔT) between the sample and the thermocouple temperatures is determined by comparing the rated Tempilaqº G temperature with this measured value (Chow et al., 2005).

In the Model 2001, the reflectance-based method generally gave a lower liquefying temperature than the transmittance-based method, within ±2 ºC. Given the uncertainty in the Tempilaqº G temperature rating of ±1%, calibrations based on the two optical methods were considered to be equivalent; therefore, their means were used. Among temperature indicators that achieve an adequate signal/noise ratio, temperature indicators of 121, 184, 253, 510, 704, and 816°C were chosen for IMPROVE_A protocol temperature calibration (Chow et al., 2005, 2007). Note, the 510 °C temperature experiences charring and therefore, transmittance results are variable.

Figure 3-3. Temperature ramping with a Tempilaqº G Temperature Indicator rated at 184 °C. Also shown are reflectance and transmittance of the temperature indicator (if available). The vertical dashed line indicates the achievement of the rated temperature.

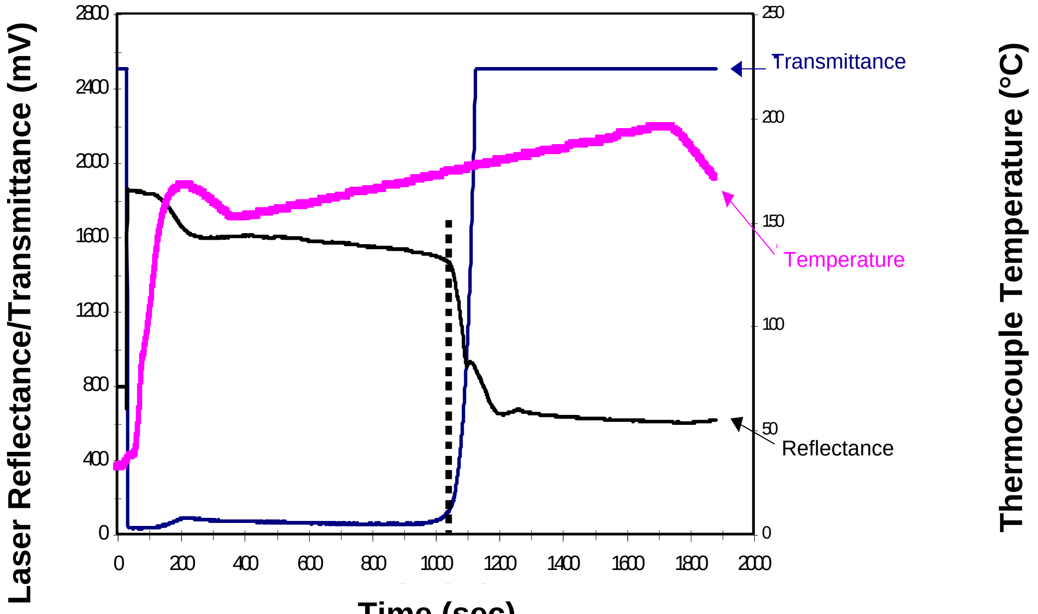
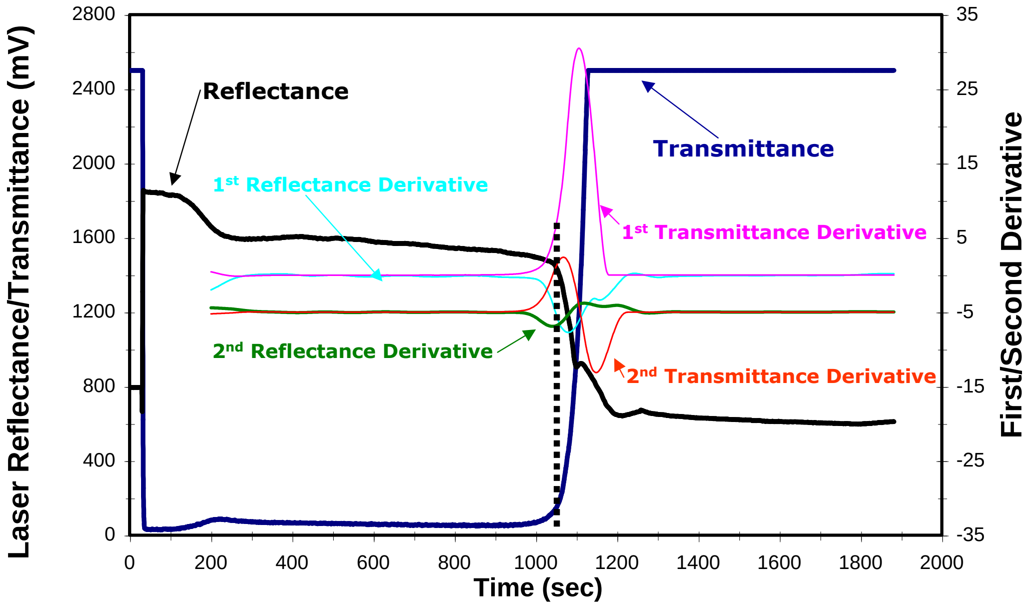


Figure 3-4. Reflectance and transmittance measurements and their first and second derivatives over time with a Tempilaqº G temperature indicator rated at 184 °C (Figure 3-3). The vertical dashed line indicates the achievement of the rated target temperature.



(Tempilaq's melting point 184 ± 2 ºC)

4 PROCEDURES

4.1 Routine Procedures

4.1.1 Analyzer Start-Up

When the analyzer is started up for the first time, or after an extended period of non-operation, it requires conditioning to reach a stable system background. At start-up, allow ~30 minutes to purge all the gases before activating any heating zones. Activate the FID and Line Heaters first by changing their controller setpoints to 120 °C and 105 °C, respectively. Activate the oxygenator and methanator ovens afterwards starting at setpoints of 120 °C then incrementing by 100 °C every 30 minutes until oxygenator and methanator are 912 °C and 420 °C, respectively. The heater setpoints can be changed from the controller in the front analyzer panel by holding the blue button while pressing the up or down buttons.

The following steps outline analyzer start-up:

- Check all gas cylinder pressures; cylinders with gas pressures less than 500 psi should be replaced before beginning the day's analysis.

- Check that all gas delivery pressures are correct:

Hydrogen (H_2)	15 psi
Helium(He)	15-40 psi (check label on regulator for current setting)
Compressed air	15 psi for FID, 25 psi for breech actuation
O_2/He mix	15 psi
CH_4/He mix	10 psi
CO_2/He mix	10 psi

- Check that the FID is lit by holding a pair of tweezers or glass plate over the FID exhaust stack and confirm presence of condensation. If the FID is not lit (as immediately after the H_2 or compressed air cylinders are changed), relight the flame by turning the H_2 rotameter to the upper limit (as posted on the flow meter) and holding a butane lighter or match over the FID stack. A soft pop indicates that the flame has been lighted. Verify that the flame remains lit by the tweezers test. Often the flame will not stay lit the first try, especially after the H_2 cylinder is changed and air gets into the gas lines. Return the rotameter to the operation setting after the flame is lit.

- 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 analyzers have not been affected.

- Turn on the computer monitor. Note: the computers are generally left on at all times; only the monitors are turned off when the analyzers are not in use.

- Confirm that the date and time on the computer are correct.

- Wipe the sample tweezers, flat glass plate, and punching tool with clean lint-free polyester wipe, taking care not to contact the cleaned surfaces with fingers or other dirty items. Check to make sure that no fibers are left on the surfaces after wiping.

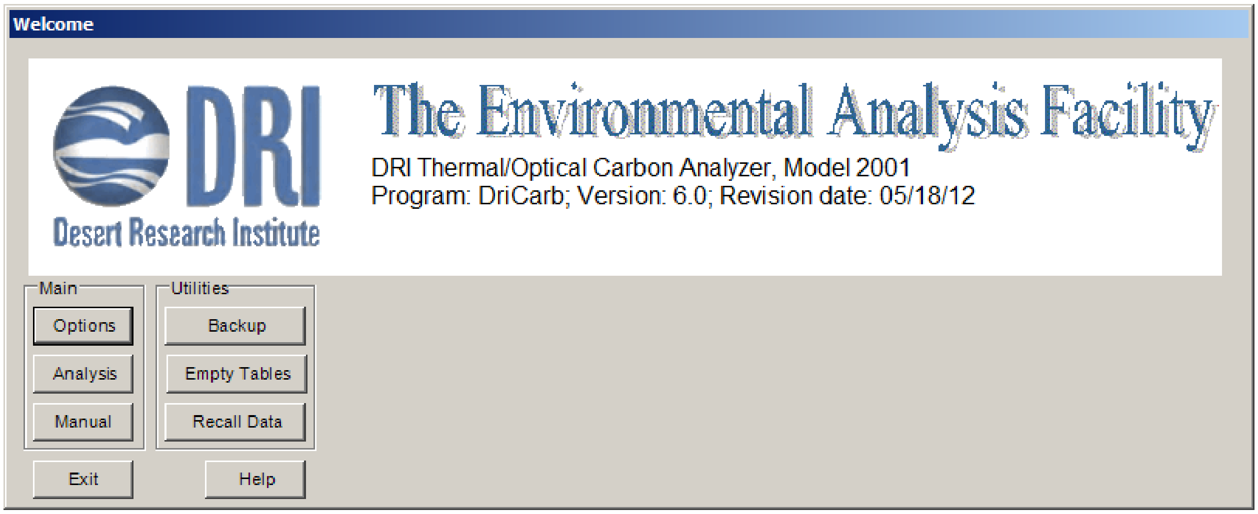
- Begin the daily entry in the Carbon Analyzer Logbook. Entries should follow the format in Figure 2-6.

- Make sure that the printer has enough paper for the day and that the toner cartridge is producing legible text and graphics.

- Go to C:\CarbonNet, then double click the *DRICarb.exe* program icon to begin the carbon program (or double click the *DRICarb.exe* shortcut on the computer desktop). The DRI welcome screen appears as depicted in Figure 4-1. Verify that the correct version of the software and database are being used. For normal analysis, the database should be "*CarbonNetWorkXX.mdb*", where *XX* is the analyzer number.

If for some reason the program freezes, allow the sample oven to cool to below 200 °C and then close the program and restart *DRICarb.exe*.

Figure 4-1. DRI Welcome Screen.



The Environmental Analysis Facility

DRI Thermal/Optical Carbon Analyzer, Model 2001
Program: DriCarb; Version: 6.0; Revision date: 05/18/12

NOTE: When using the carbon analysis software, clicking on the Exit button closes the program. Exiting in the midst of an analysis is not advisable, as the analyzer will revert to the default settings (see settings under Options\Manual); in such a case, a hot thermocouple will retract, possibly damaging the Teflon seal.

4.1.2 Leak Checks

Perform leak checks daily to detect leakage in the sample oven.

4.1.2.1 Manual Leak Check

- With the breech closed, flip the oven outlet toggle on the right side of the analyzer down (close) and let the sample oven pressure reach ~3 psi. Most systems are working in the ~2-2.5 psi range, but a leak is easier to detect when the pressure is at ~3 psi. Close the oven inlet toggle, on the front of the analyzer, and monitor changes in the sample oven pressure.

- A “leak free” condition is indicated by a steady pressure reading, or a decline of 0.01 psi or less per second (~0.01 ml/sec).

- Once the pressure stabilizes, flip the outlet oven toggle first and then the inlet oven toggle back up to the open position. Opening the inlet toggle first prevents over pressurization of the oven.

- If pressure fails to stabilize, locate the source of the leak with a He leak detector (Alltech, Deerfield, IL). Check the following components to determine the source of the leak:

  - All ferrules (especially the reducing ferrule), fittings and seals
  - Quartz oven
  - All tubing
  - Thermocouple
  - Breech O-ring.

- If the system still leaks, wipe all threads, replace ferrules and O-rings.
- Check the breech O-ring sits squarely in the groove and confirm that the line air pressure is sufficient (>25 psi) to close the breech.
- Refer to the carbon analyzer's *Troubleshooting Manual* for additional tips and procedures.

Once the system passes the leak test, make sure that the analyzer's multi-function knob (at the left of the front panel) is set at Auto in order to continue with routine analysis. Allow the system pressure to return to its original value and record this value on the Daily Analyzer Checklist shown in Figure 2-8. The pressure should be consistent with previous day's values.

4.1.3 Laboratory Blanks

Laboratory blanks are performed daily to check for system contamination and evaluate laser response. The following steps outline laboratory blanks analysis:

- Preload the analyzer with quartz fiber filter. Turn the analyzer multi-function knob to Load position, insert a new blank punch, turn the knob to Calibrate, then turn the knob back to Auto. Wait until the sample boat stops moving before turning the knob to another position. Perform bake oven (Section 4.1.4) to remove filter contaminants before proceeding. Punch from previous sample analysis that show no EC3 and no visible mineral deposit (filter coloration) can be reused without reloading and baking.
- Select "Analysis" from the Main welcome screen.
- Set Type to "Sample" and specifiy cmdAUTO_BLANK from the drop down menu in the "Command table" field. Fill the other fields with the following details.
  - Project Name: LABBLK
  - Batch: YYYYMM
  - Sub-batch: DD

  - Sample ID: LBxxYYYYMMDD

    where xx, YYYY, MM, and DD refers to analyzer number, year, month, and day, respectively.

- Enter 1 cm^2 as punch and deposit area. If additional laboratory blanks are run during the day, check for previous laboratory blanks and use a punch number one greater than the last.

- Void values and perform another laboratory blank if total carbon exceeds the 0.2 µg C/cm^2 limit. Perform bake procedure in between laboratory blank attempts until the system is clean (i.e., OC < 0.2 µg C/cm^2 and no EC).

- From the printed output, calculate the difference between the initial and final baseline values of reflectance (LR) and transmittance (LT). Difference >5% of initial indicates significant laser drift.

- Update the DRI Carbon Daily Analyzer Checklist (see Figure 2-8) using reflectance (LR initial), transmittance (LT initial), total carbon (TC), and calibration peak area (Cal peak area) from the printout.

- Values for reflectance should be between 1400 and 2000, transmittance should be between 800 and 1300, and consistent with previous days' values.

- Total carbon from laboratory blanks must be less than 0.2 µg C/filter.

- Calibration peak areas must be consistent to within 1000 mv-sec from previous days' values.

- Analyzers exceeding the limit for laser drift, reflectance, transmittance, total carbon, and calibration peak area after three laboratory blank runs must be taken offline for maintenance.

4.1.4 Oven Bake

Perform an oven bake when: 1) analyzer has been idle for more than 2 hours, 2) a new blank punch is loaded, 3) excessive contamination is detected after a laboratory blank analysis, or 4) persistent EC contamination is observed from samples. The oven bake can be performed manually or automatically.

4.1.4.1 Manual Oven Bake

Use the following procedure to perform a manual oven bake:

- Select “Manual” from the Main welcome screen. From the “Manual” screen, select “Control” on the drop-down menu list. (Note: analyzer must be in “Auto” mode for the manual control to work.) This will bring up the “Control” screen. Change the “Oven Temperature” field to “1000”. Change the “Sample Position” field to “Analyze”. Click “Go”. This will heat the oven to approximately 950 °C, depending on the instrument’s calibration. Exercise caution when working around hot surfaces of the analyzer. Continue until the FID returns to baseline.

- Repeat as necessary until the system is clean.

- System blanks (Section 4.1.6.1) are run after the oven bake.

- Stop bake after 15 minutes; set oven temperature to 5 °C

4.1.4.2 Automatic Oven Bake

Use the following procedures to perform an automatic oven bake:

- From the Main welcome screen, select “Analysis”.

- Set Type to “Sample” and select *cmdBakeMonitor* from the drop-down menu in the “Command table” field.

- Use Project Name “LABBLK”, Batch # “YYYYMM” for the year and month, and Sub-batch # “DD” for the day.

- The Sample ID should be in the format “BxxYYYYMMDD” where “xx” is the analyzer number and YYYY is the year (e.g. B0720050715 for analyzer number 7 on July 15, 2005,).

- Set the Run #, Punch area, and Deposit area fields to “1”. Click “OK”, then “Run”.

- System or laboratory blanks (Sections 4.1.6.1 and 4.1.6.2) are run after the oven bake.

- Monitor the graph of the FID response from printout or from the screen. Repeat the bake process when FID remains above the initial baseline levels.

4.1.5 OC/EC Analysis

Refer to the daily analysis run list (see Figure 2-7) for a list of samples to retrieve from the sample freezer. Transfer those samples into a Styrofoam cooler with blue ice, or place in the analysis room compact refrigerator.

Routine analysis procedure excludes carbonate measurements. For carbonate analysis, refer to Section 4.1.6.3, “Carbonate Analysis”.

Always perform the laboratory blanks procedure (Section 4.1.6.2) each day before beginning analysis to ensure a clean (<0.2 µg TC/cm^2) system. Run an oven bake (Section 4.1.4) when necessary.

4.1.5.1 Carbon Analysis Preparation

- Confirm the computer date and time.
- Verify sample oven pressure reading and specified flow ranges in the front-panel flow meters.
- Wipe the flat glass plate, tweezers, and punching tool thoroughly with a dry lint-free wipe.
- Remove the sample to be analyzed from the Styrofoam cooler or refrigerator in the order listed on the analysis run list.
- Record the filter ID in the analyzer log book (Figure 2-6).
- Open *DRICarb.exe* from the c:\CarbonNet folder or use the desktop “shortcut” to *DRICarb.exe*. Verify correct software version number on the Welcome screen.
- Select “Analysis” from the main welcome screen. This will open the Analysis window shown in Figure 4-2a and 4-2b.
- In the analysis setup form, enter “Sample” for the Type.
- Polarity should default to “Unipolar” and use FID_8 for greater FID sensitivity.
- Fill out the information about the sample, including: Project Name, Batch #, and Sub-batch #.
- Under “Command table” select the analysis protocol specified in the analysis run list. Most commonly used is *cmdImproveA* for the IMPROVE_A protocol.
- Enter the Sample ID number, or place your mouse cursor in the field and use a barcode scanner to read the barcode on the Petri dish.

- Enter the Run Number, Punch, and Deposit area of the filter being analyzed. These details are included in the analysis run list.

- Enter technician initials in the “Tech initials” field.

- Select any pre-analysis flags from the drop-down menu in the “Flags” field. A list of valid choices is presented on the screen.

- Select “OK” to complete entry of sample details. This prompts a graphical display window that shows details of the analysis. Select “Run” to begin. A visual and verbal prompt to load the filter for analysis appears after the analyzer has cooled to 50 °C.

4.1.5.2 Loading the Filter Punch

- Visually examine the filter and note any non-uniformity or unusual deposit. Remove it from the Petri slide or Petri dish with tweezers, handling the filter only by the edge. Place the filter on the glass plate and gently push down the punching tool to remove a sample punch. Rocking the punching tool slightly will ensure that the punch is completely severed. Try to remove the punch from the edge of the deposit to avoid wasting the filter, while trying to avoid areas of non-uniform deposits.

- Leaving the sample punch in the punching tool, place the punching tool on a clean lint-free wipe. Return the filter to the Petri slide or dish, being careful to handle only the filter with the tweezers.

- Click “OK” on the on the visual prompt to load the sample. The boat will immediately move to the load position.

- Use tweezers to remove any existing punch on the sample boat. Remove the punch from the punch tool and load new punch, deposit side up, into the boat.

- Click “OK” to complete sample loading. Another visual and verbal prompt, “Would you like to proceed or would you like to delay analysis?”, will appear. Enter any appropriate flags and click “Commit”. Check to make sure a 90-second delay is in the “delay” box. Click “OK” and analysis will begin.

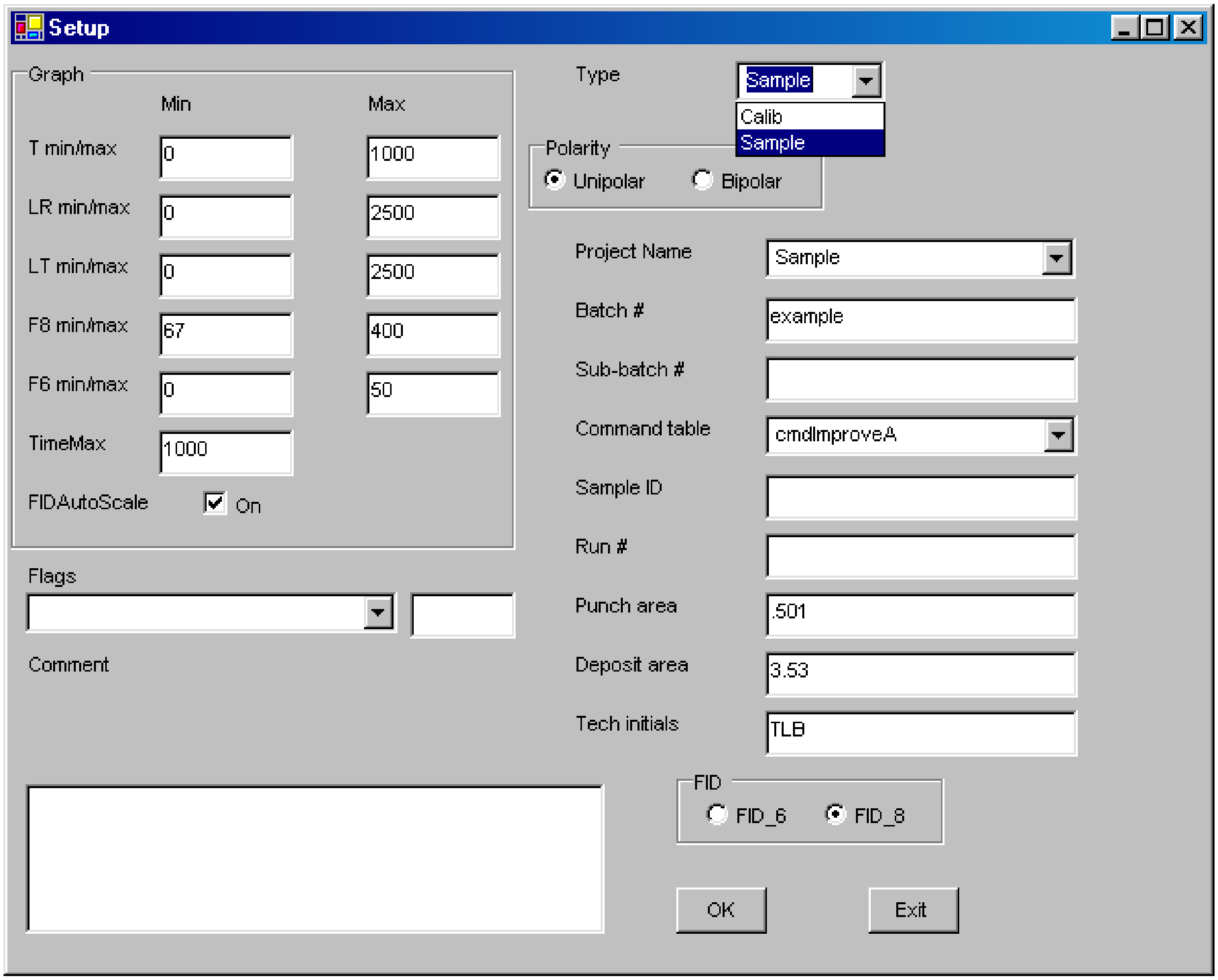
- Wipe the tweezers, flat glass plate, and punching tool with a clean lint-free wipe. Save the punch taken out of the analyzer and tape into that sample’s thermogram. Mark thermogram for any coloration that indicates minerals or unburnt material.

4.1.5.3 Post-Analysis

At the end of each analysis, data is saved to the database, split times are calculated, carbon peaks are integrated, and tabular and graphical printouts are produced. The sample boat will retract to the calibration position when it is sufficiently cooled by the fan (to < 100 °C) and will continue to cool until it reaches less than 50 °C.

- Examine the tabular printout (Figure 4-3) to confirm that the calibration peak counts are within specifications (typically >20,000 mV-sec and within acceptable range for specific analyzer, see Section 3.1.1).

Figure 4-2a. Setup Screen for the DRI Model 2001 Thermal/Optical Carbon Analysis Program.



Setup

Graph

	Min	Max
T min/max	0	1000
LR min/max	0	2500
LT min/max	0	2500
F8 min/max	67	400
F6 min/max	0	50
TimeMax	1000	

FIDAutoScale ☑ On

Flags

Comment

Type: Sample

Polarity: ● Unipolar ○ Bipolar

Project Name: Sample

Batch #: example

Sub-batch #:

Command table: cmdImproveA

Sample ID:

Run #:

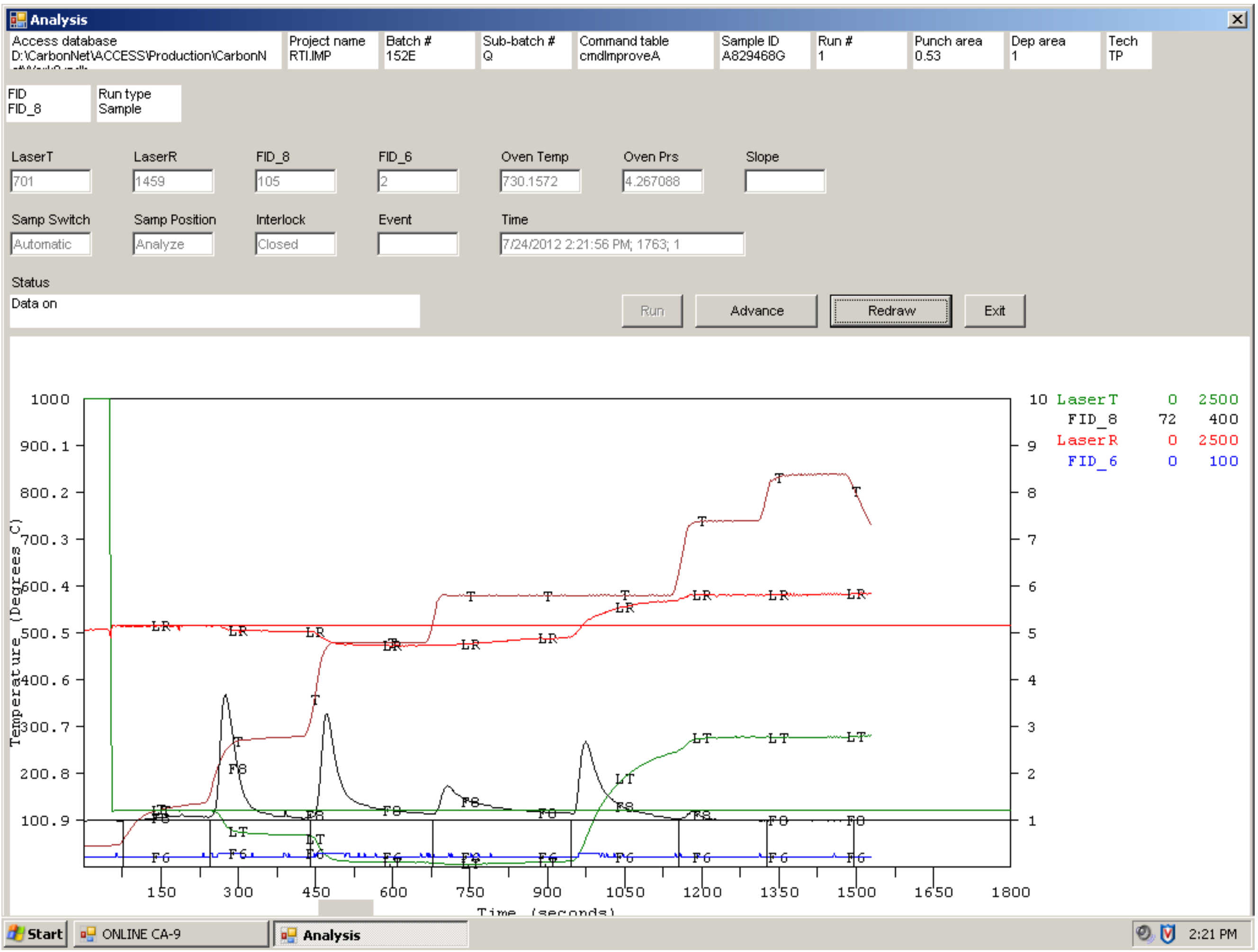
Punch area: .501

Deposit area: 3.53

Tech initials: TLB

FID: ○ FID_6 ● FID_8

Figure 4-2b. The Analysis Screen during Sample Analysis for DRI Model 2001 Thermal/Optical Carbon Analysis Program.



Access database D:\CarbonNet\ACCESS\Production\CarbonN
Project name RTI.IMP
Batch # 152E
Sub-batch # Q
Command table cmdImproveA
Sample ID A829468G
Run # 1
Punch area 0.53
Dep area 1
Tech TP

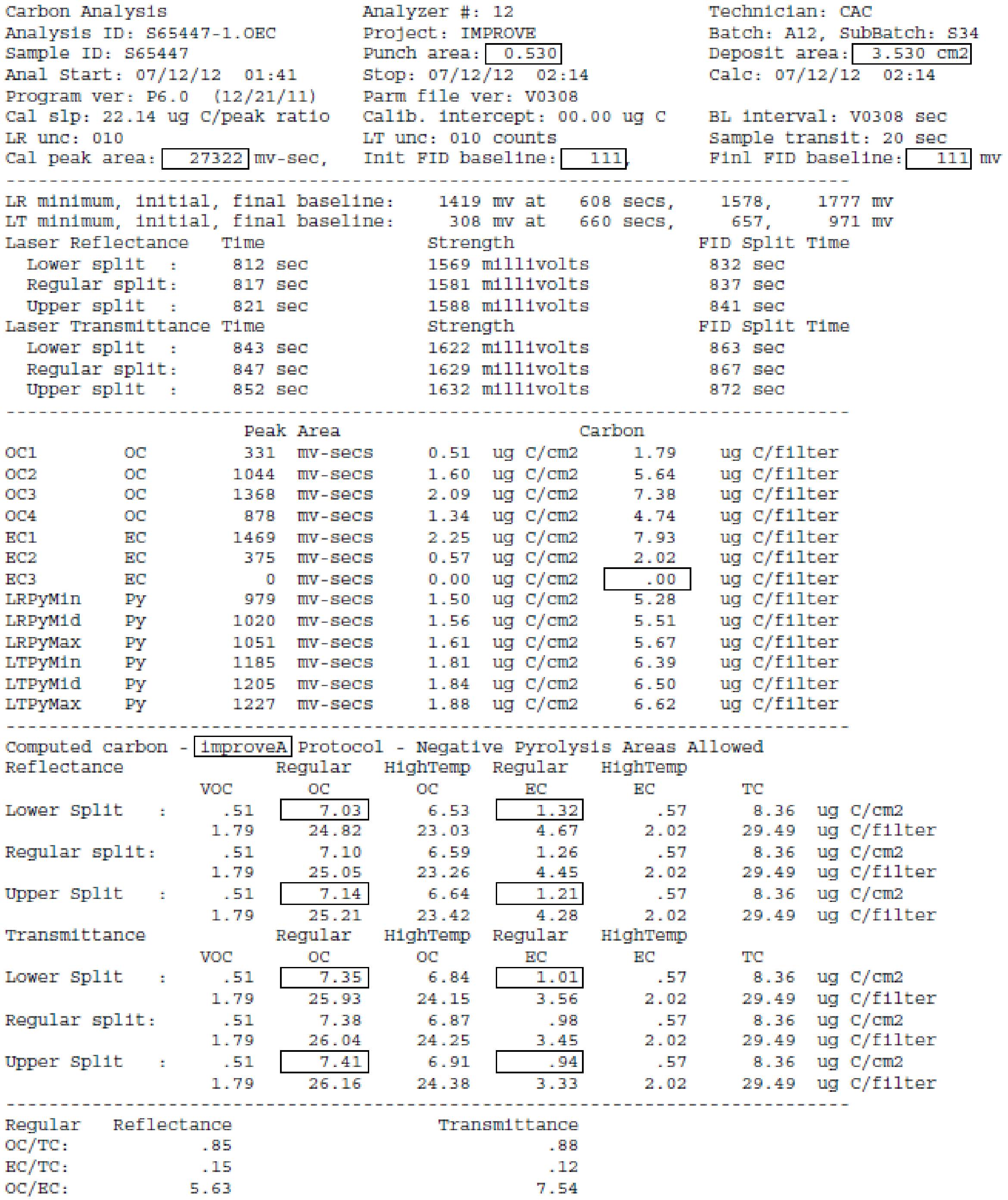
FID FID_8
Run type Sample

LaserT 701
LaserR 1459
FID_8 105
FID_6 2
Oven Temp 730.1572
Oven Prs 4.267088
Slope

Samp Switch Automatic
Samp Position Analyze
Interlock Closed
Event
Time 7/24/2012 2:21:56 PM; 1763; 1

Status
Data on

Figure 4-3. Tabular Printout from DRI Model 2001 Thermal/Optical Carbon Analysis Program.



```
Carbon Analysis                    Analyzer #: 12                     Technician: CAC
Analysis ID: S65447-1.OEC          Project: IMPROVE                   Batch: A12, SubBatch: S34
Sample ID: S65447                  Punch area: 0.530                  Deposit area: 3.530 cm2
Anal Start: 07/12/12  01:41        Stop: 07/12/12   02:14             Calc: 07/12/12   02:14
Program ver: P6.0  (12/21/11)      Parm file ver: V0308
Cal slp: 22.14 ug C/peak ratio     Calib. intercept: 00.00 ug C       BL interval: V0308 sec
LR unc: 010                        LT unc: 010 counts                 Sample transit: 20 sec
Cal peak area: 27322 mv-sec,       Init FID baseline: 111,            Finl FID baseline: 111 mv
-----------------------------------------------------------------------------
LR minimum, initial, final baseline:    1419 mv at   608 secs,    1578,    1777 mv
LT minimum, initial, final baseline:     308 mv at   660 secs,     657,     971 mv
Laser Reflectance   Time               Strength                  FID Split Time
  Lower split  :     812 sec           1569 millivolts            832 sec
  Regular split:     817 sec           1581 millivolts            837 sec
  Upper split  :     821 sec           1588 millivolts            841 sec
Laser Transmittance Time               Strength                  FID Split Time
  Lower split  :     843 sec           1622 millivolts            863 sec
  Regular split:     847 sec           1629 millivolts            867 sec
  Upper split  :     852 sec           1632 millivolts            872 sec
-----------------------------------------------------------------------------
                      Peak Area                      Carbon
OC1        OC          331  mv-secs     0.51  ug C/cm2     1.79    ug C/filter
OC2        OC         1044  mv-secs     1.60  ug C/cm2     5.64    ug C/filter
OC3        OC         1368  mv-secs     2.09  ug C/cm2     7.38    ug C/filter
OC4        OC          878  mv-secs     1.34  ug C/cm2     4.74    ug C/filter
EC1        EC         1469  mv-secs     2.25  ug C/cm2     7.93    ug C/filter
EC2        EC          375  mv-secs     0.57  ug C/cm2     2.02    ug C/filter
EC3        EC            0  mv-secs     0.00  ug C/cm2      .00    ug C/filter
LRPyMin    Py          979  mv-secs     1.50  ug C/cm2     5.28    ug C/filter
LRPyMid    Py         1020  mv-secs     1.56  ug C/cm2     5.51    ug C/filter
LRPyMax    Py         1051  mv-secs     1.61  ug C/cm2     5.67    ug C/filter
LTPyMin    Py         1185  mv-secs     1.81  ug C/cm2     6.39    ug C/filter
LTPyMid    Py         1205  mv-secs     1.84  ug C/cm2     6.50    ug C/filter
LTPyMax    Py         1227  mv-secs     1.88  ug C/cm2     6.62    ug C/filter
-----------------------------------------------------------------------------
Computed carbon - improveA Protocol - Negative Pyrolysis Areas Allowed
Reflectance               Regular   HighTemp  Regular   HighTemp
                 VOC        OC        OC        EC        EC        TC
Lower Split   :   .51      7.03      6.53      1.32       .57      8.36  ug C/cm2
                 1.79     24.82     23.03      4.67      2.02     29.49  ug C/filter
Regular split:    .51      7.10      6.59      1.26       .57      8.36  ug C/cm2
                 1.79     25.05     23.26      4.45      2.02     29.49  ug C/filter
Upper Split   :   .51      7.14      6.64      1.21       .57      8.36  ug C/cm2
                 1.79     25.21     23.42      4.28      2.02     29.49  ug C/filter
Transmittance             Regular   HighTemp  Regular   HighTemp
                 VOC        OC        OC        EC        EC        TC
Lower Split   :   .51      7.35      6.84      1.01       .57      8.36  ug C/cm2
                 1.79     25.93     24.15      3.56      2.02     29.49  ug C/filter
Regular split:    .51      7.38      6.87       .98       .57      8.36  ug C/cm2
                 1.79     26.04     24.25      3.45      2.02     29.49  ug C/filter
Upper Split   :   .51      7.41      6.91       .94       .57      8.36  ug C/cm2
                 1.79     26.16     24.38      3.33      2.02     29.49  ug C/filter
-----------------------------------------------------------------------------
Regular   Reflectance                  Transmittance
OC/TC:             .85                           .88
EC/TC:             .15                           .12
OC/EC:            5.63                          7.54
```

- Examine the thermogram (Figure 4-4) for proper laser response, temperature profiles, realistic carbon peaks, and the presence of the calibration peak at the end of the analysis.

- Examine the laser signal at the end of the run.

- If a problem is found, register it in the analyzer log book and run list, and notify the lab supervisor immediately.

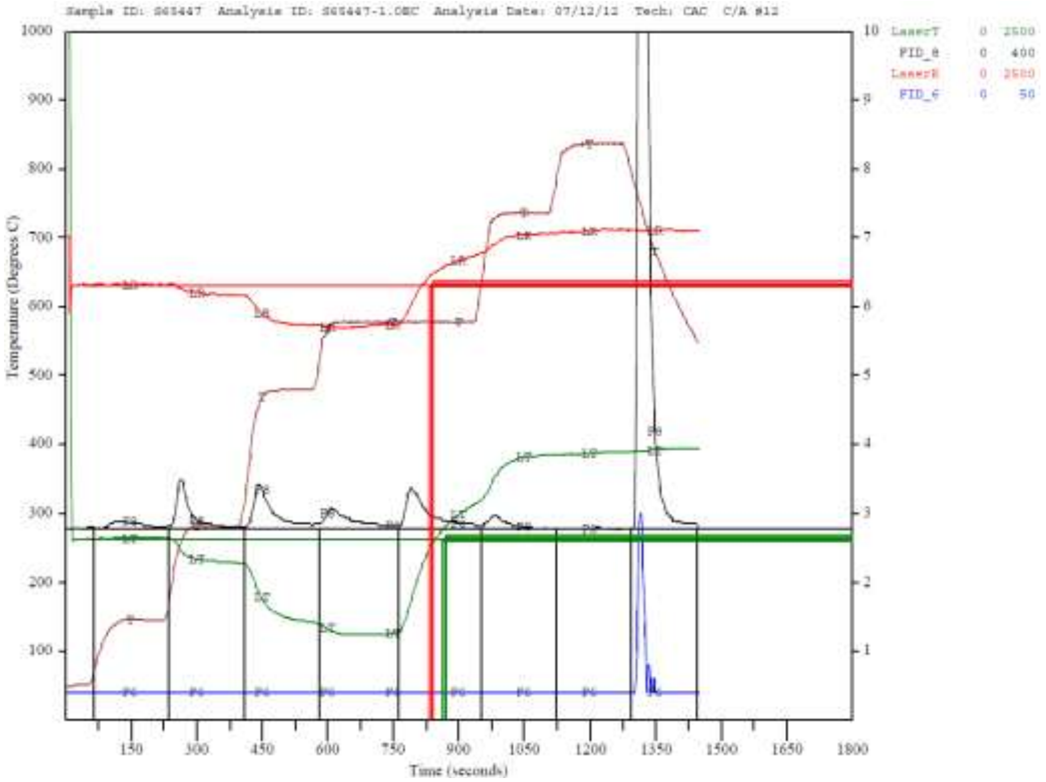
- Add any appropriate analysis flags to the post-analysis form that appears at the end of the run.

- Mark the analysis date on the sample analysis run list.

- Using clean tweezers, remove the punch from the boat and tape it to the thermogram with transparent tape, ensuring that the punch is deposit-side up.

Repeat the above steps for additional analysis runs.

Figure 4-4. Graphical output (thermogram) from the DRI Model 2001 Thermal/Optical Analysis Program.



4.1.6 Special Analyses

4.1.6.1 System Blanks

- Go through all the steps for a normal analysis, but remove the punch from the previous analysis. Proceed with the routine analysis.

- Use project name “SYSBLK”, Batch # “MM” for the month and Sub-batch # “DD” for the day. Punch area and Deposit area should be “1”.

- Calculated carbon concentrations from the system blank should not be more 0.2 µg carbon. Values greater than this warrant an additional system blank or oven bake.

4.1.6.2 Laboratory Blanks

- Go through all the steps for a normal analysis, but remove any filter and add the laboratory blank punch. Proceed with the routine analysis.

- Use project name “LABBLK”, Batch # “MM” for the month and Sub-batch # “DD” for the day. Punch area and Deposit area should be “1”.

- Use a Sample ID number “LBXXYYYYMMDD” derived from the analyzer # and the current date, where XX is the analyzer number (e.g., 07) and YYYY is the year, MM is the month, and DD is the day (e.g., LB0720120718 for July 18, 2012 for analyzer # 07). Enter the punch number as 1.

- Calculated carbon concentrations from the laboratory blank should not be more 0.2 µg carbon. Values greater than this warrant an additional system and laboratory blank or oven bake.

- If additional laboratory blanks are run during the day, check for previous laboratory blanks and use a punch number one greater than the last.

4.1.6.3 Carbonate Analysis

- Enter the Sample ID, Run #, Punch area, and Deposit area. Select *cmdImproveA_Carbonate* from the “Command table” drop-down field and start the analysis program.

- Follow the steps under Section 4.1.4 until the sample punch is loaded into the boat. Load sample and click “OK”. When asked if you want to delay or continue analysis, click “OK”. After 90 seconds the punch automatically centers under the acid injection port. The computer will prompt you to inject the hydrochloric acid (HCl), and then will state “Load syringe” and “XX seconds to acid injection”.

- Prior to acidification (approximately 90 seconds elapsed analysis time), flush the 25 µl syringe with 0.4 M HCl into a waste beaker.

- Inject 20 µl of 0.4 M HCl through the septum port to the sample, ensuring 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 Nanopure water to prevent corrosion of the syringe plunger.

- After analysis, the program will delay any further analysis for 900 seconds to allow the punch to dry.

- After the carbonate analysis is completed, a tabular summary and a copy of the graph will be printed (similar in format to Figures 4-3 and 4-4). Select *cmdImproveA* from the “Command table” drop-down field and click “OK”. Click “Run” on the analysis Setup screen. The program will automatically cycle into the normal OC/EC analysis, using the same Sample ID. Heat from the oxidation oven will dry the sample in this position (for approximately 15 minutes) without prematurely baking carbon from the sample; the sample temperature should not exceed 42 °C. When the punch is dry proceed with normal OC/EC analysis.

4.1.7 Analyzer Shut-Down

At the end of the day, shut down the analyzers using the following procedures:

- Leave the last analyzed punch in the boat with the boat positioned in the Calibrate position. This punch will be used as the laboratory blank the following morning.

- Perform end-of-the-day calibration gas injection routine, or use *cmdAutoCalibCheck* command, and record the calibration peak counts. Any values outside the expected ranges 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. Notify the lab supervisor.

- Leave the *DRICarb.exe* software open.

- If desired, He/O2, Cal Gas, and He-3 may be turned off with the toggle valves to conserve gases. However, all other gases should be left on as long as the oxygenator and methanator are heated.

- Place all of the day's printouts, including calibration data in a file folder labeled with the date and analyzer number. Place on the lab supervisor's desk for Level I validation (Section 6.4).

- Turn off the monitors. Leave the computers and analyzers on overnight unless the potential for power outages or power surges exists. Make a final check of the gas cylinder pressures to ensure that gas flow, especially the compressed air, will continue until someone will be available to check them again.

- Move the samples and blue ice in the Styrofoam cooler or refrigerator back into the sample storage freezer and verify that the freezer doors are completely closed.

- If the 25 or 50 µl syringe was used for carbonate analysis, thoroughly rinse the syringe with distilled water. Tightly cap all solutions and store in the refrigerator. Avoid freezing the solution to prevent crystallization.

- Lock the carbon analysis room.

4.2 Routine Instrument Calibrations

The calibration procedures for the carbon analyzers are of four types: 1) the end-of-run calibration peak; 2) the routine beginning and end-of-day calibration injections of He/CH_4 and He/CO_2 (or the auto calibration check using the *cmdAutoCalibCheck* command); 3) full instrument calibration, performed every six months, using KHP, sucrose, and the two calibration gases; and 4) temperature calibrations performed every six months using temperature-sensitive indicating liquids with different melting points. Calibration procedure 3, full instrument calibration is described in Sections 3.3.1 and 3.3.2 while calibration procedure 4, temperature calibration, is described in Section 3.3.3. The routine calibration procedures (1 and 2) are described in this section.

4.2.1 End-of-Run Calibrations (Description)

The end-of-run calibration consists of a set quantity of He/CH_4 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 confirm that the analyzer is operating satisfactorily.

Calibration peak area counts should be greater than 20,000 and within an acceptable range for the specific analyzer. Check daily records to compare and determine analyzer performance and stability.

4.2.2 Routine Calibrations (Description)

Routine calibrations must be performed at the beginning and end of each day, either manually or by using the automated routine calibration command (*cmdAutoCalibCheck*) in the *CarbonNetWork* database Command table.

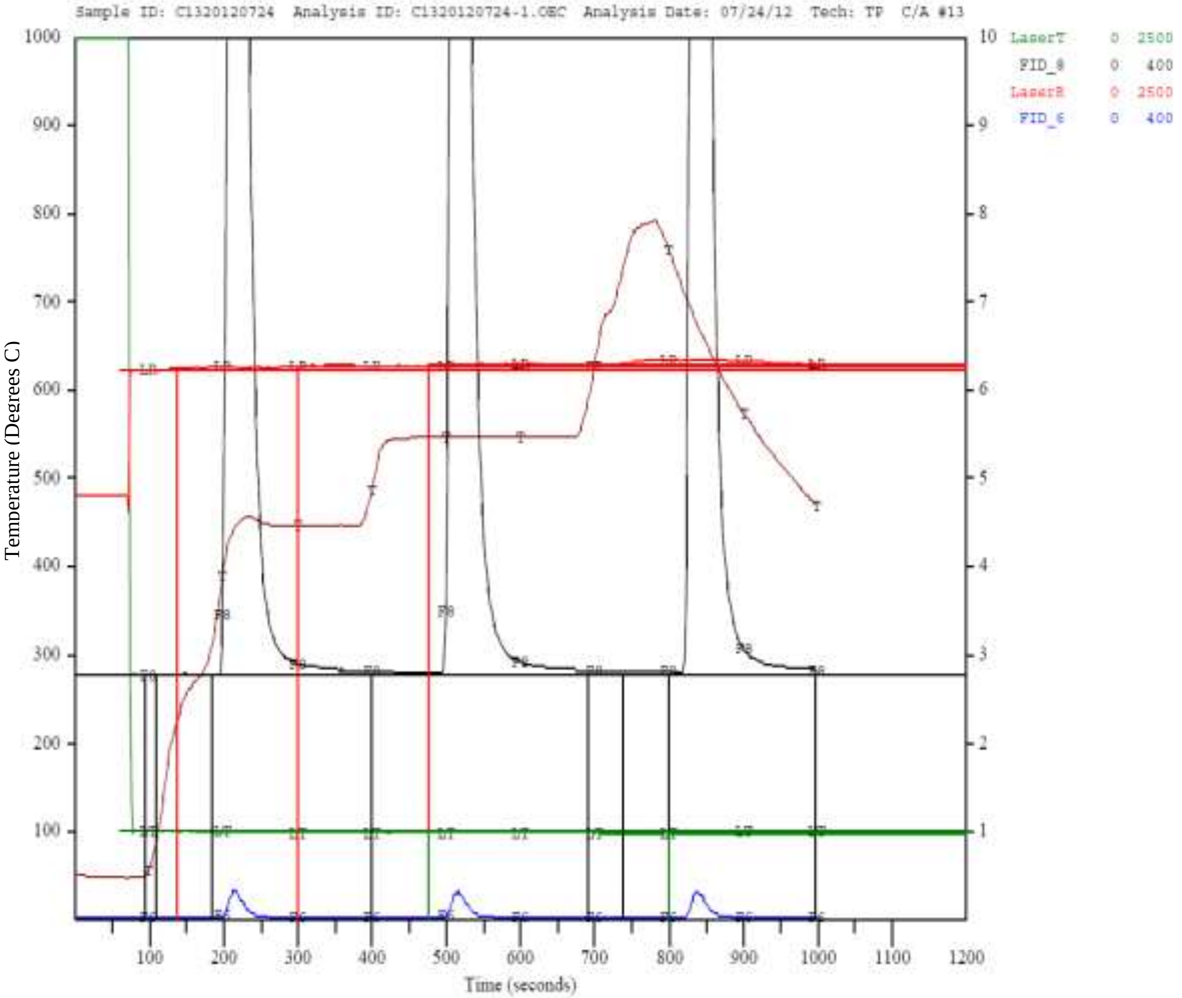
4.2.2.1 Automated Routine Calibration (Description and Instructions)

The automated calibration uses the Carle valve to inject the CH_4 standard once in a He-only atmosphere, once in a He/O_2 atmosphere, and finally, the normal calibration peak at the end of analysis. The three peaks should have similar areas if the catalysts are in good condition and the calibration factor holds (see Figure 4-5). Use the following steps to perform this automated calibration:

- From the *DRICarb.exe* Welcome screen, select “Analysis” from the “Main” submenu.
- Set Type to “Sample” and select *cmdAutoCalibCheck* from the drop-down menu in the “Command table” field.

The project name should be “CALIB”, Batch # should be “MM” for the month, Sub-batch # should be “DD” for the day, and the Sample ID should be in the format “CxxYYYYMMDD” where “xx” is the analyzer number (e.g. C0720050710 for analyzer number 7, run on July 10, 2005).

Figure 4-5. Calibration thermogram from the *cmdAutoCalibCheck* command of the DRI Model 2001 Thermal/Optical Carbon Analyzer.



- Set the Run # (“1” for first calibration of the day and “2” for second calibration of the day, etc.). Enter “1” in the Punch area, and Deposit area fields. Click on “OK” and then click “Run”.

- Review the thermogram and record these values in the logbook and on the Daily Analyzer Checklist as shown in Figure 2-8. The three calibration peak counts (OC3, EC1, LtPyMid) should be above 20,000 and within the acceptable range for the specific analyzer, and should be almost identical in area (and within 10% of the “Calibration Peak Area” value show on the tabular printouts). Check the average C value for the calibration gas against those posted on each carbon analyzer.

- Whenever the MnO_2 or Ni catalyst is replaced, an automated routine calibration should be run to confirm that the previous calibration curve holds.

4.2.2.2 Manual Routine Calibration (Instructions)

- From the *DRICarb.exe* Welcome screen, select “Analysis” from the “Main” submenu.

- Set Type to “Calib” and select *cmdCalib-HeO$_2$* (for example) from the drop-down menu in the “Command table” field. The setup screen is shown in Figure 4-6.

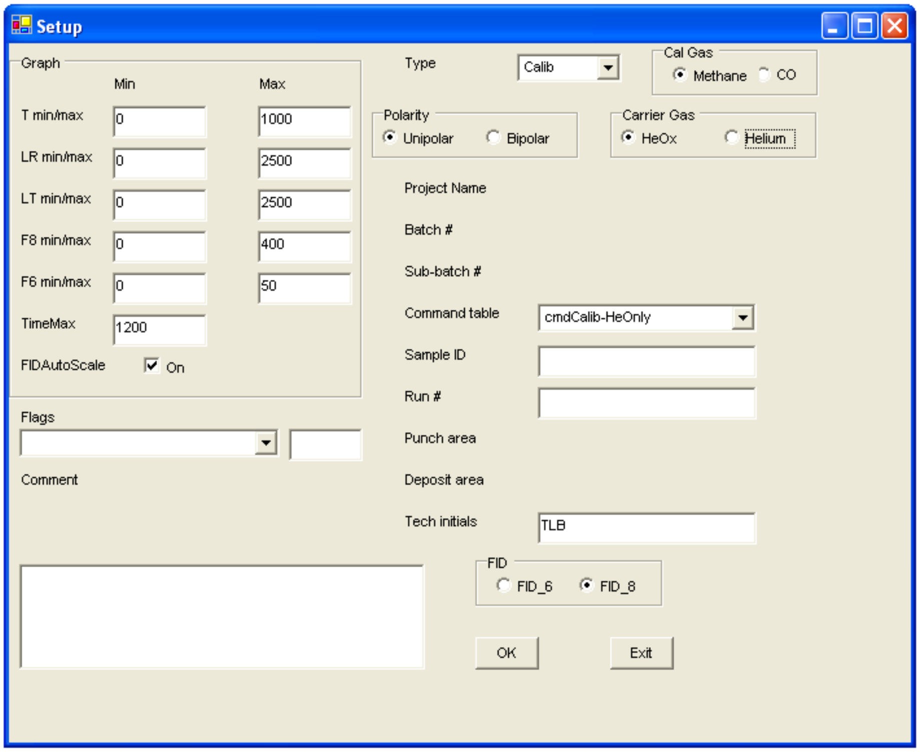
- Project name, Batch #, and, Sub-batch # are not required or available fields for entry. The sample ID should be in the format “MIXXYYYYMMDD” for CH_4 injection or “CIXXYYYYMMDD” for CO_2 injection where XX is the analyzer number (e.g. MI0720120710 for a CH_4 injection on analyzer number 07, run on July 10, 2012).

- Set the Run # (“1” for first calibration of the day and “2” for second calibration of the day, etc.). Click on “OK” and then click “Run”.

- Select the atmosphere for calibration under the “Cal Gas” (either CH_4 or CO_2) menu and select the proper “Carrier Gas” (either HeO_2 or He; HeO_2 for beginning of day and He only for end of day). These should be alternated with the calibration gas. Verify the command table matches the options selected.

- Choose “OK” to proceed with the analysis, or “Exit” to leave the program. The analysis will start with the following screen as shown in Figure 4-7. You will note that the top portion contains all the information in the analysis Setup screen. The bottom half will display the thermogram when the run is initiated.

Figure 4-6. Setup Screen for Manual Gas Calibration for the DRI Model 2001 Thermal/Optical Carbon Analysis Program.



Graph

	Min	Max
T min/max	0	1000
LR min/max	0	2500
LT min/max	0	2500
F8 min/max	0	400
F6 min/max	0	50
TimeMax	1200	

FIDAutoScale ☑ On

Flags

Comment

Type: Calib

Cal Gas: ● Methane ○ CO

Polarity: ● Unipolar ○ Bipolar

Carrier Gas: ● HeOx ○ Helium

Project Name

Batch #

Sub-batch #

Command table: cmdCalib-HeOnly

Sample ID

Run #

Punch area

Deposit area

Tech initials: TLB

FID: ○ FID_6 ● FID_8

- Start a run by clicking on “Run”. Note that standards are taken through the septum sampling port (typically orange in color) along the pressure regulated tubing of a size 10 cylinder. After the computer states, “Please load gas syringe”, follow the following gas injection procedure:
    - To load the syringe, open the main cylinder valve, secondary valves, and briefly (~2 seconds) the toggle valve (flip up) before inserting the syringe to draw the required gas volume. The toggle valve is opened briefly to purge out any air that may have been retained in the lines.
    - Insert the syringe into the sampling port and then pull the plunger until it is above the 1,000 µL mark. Pull the syringe off the sampling port and then push the needle to expel the contents. Repeat filling the syringe and expelling the content three times to ensure that residual air is eliminated. The fourth time, the contents of the syringe are expelled slowly until the plunger reaches the required volume.
    - The computer will then state, the “Time remaining until load - XX seconds” and then “Inject calibration gas”.

  - A 1,000 µL gas-tight syringe is loaded with the required standard volume within 2 minutes after setting the carbon analyzer for gas injection. [Note that routine checks require 1,000 µL while gas calibrations require multiple volumes of 200, 500, 700, and 1,000 µL.]
  - Insert the syringe into the injection port of the carbon analyzer and inject the gas when the analyzer prompts the user to do so by stating, "Inject calibration gas" or has "Inject" in the Event window. Hold the plunger down with the needle still inside the septum for 10 seconds or until a peak appears.
  - After injection, close the main and secondary valves of the gas cylinder to prevent gas leakage.
  - Return the syringe back to its drawer.

- Calibration gas injections should be in the following ranges for 1000 µl gas:

Manual Injection	**Lower Allowable Limit**	**Upper Allowable Limit**
CH_4	20.36 µg carbon [1 *]	22.50 µg carbon [1 *]
CO_2	20.28 µg carbon [2 *]	22.41 µg carbon [2 *]
Final Calibration Peak	20,000	--

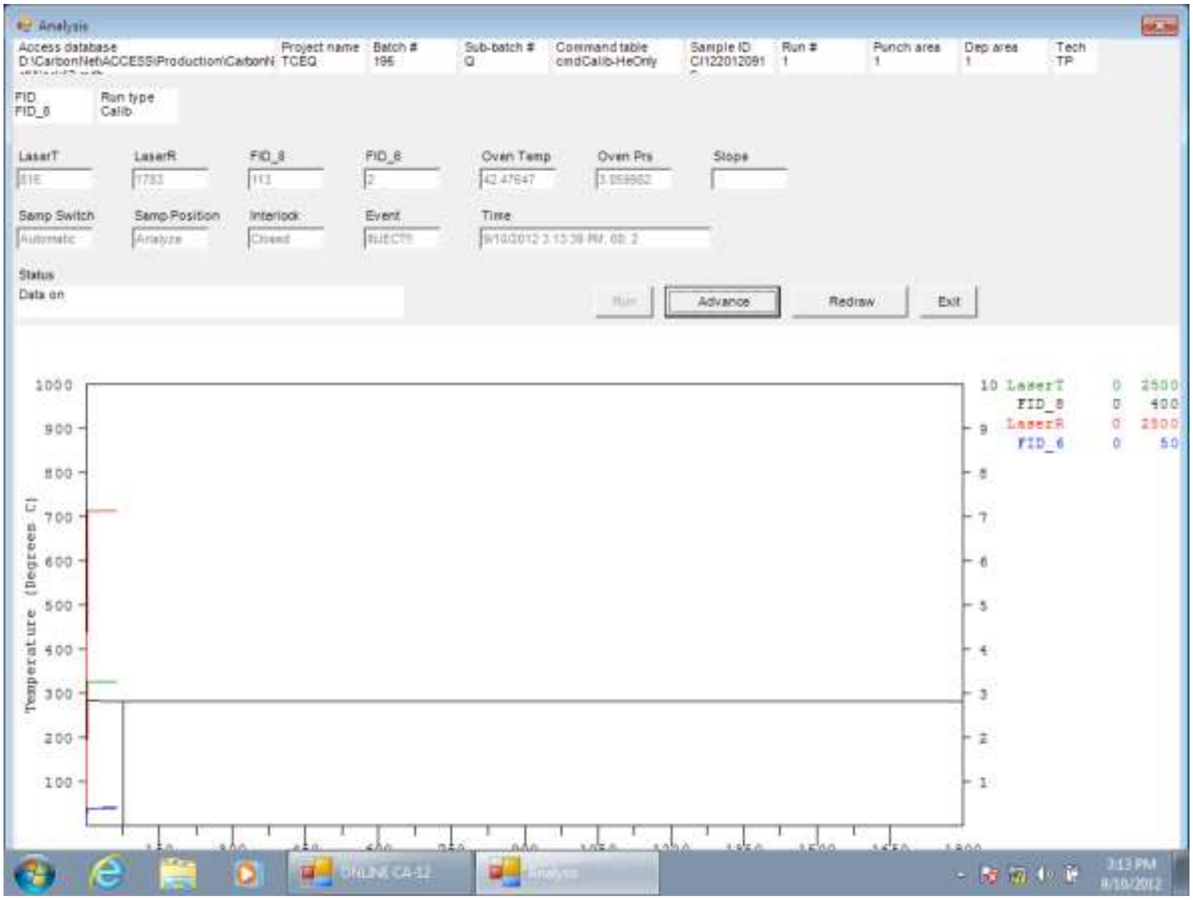
[1] Calculated in a real laboratory environment. For a 5.12% CH_4 standard at 646 mm Hg at 24 °C, actual mass of methane is 21.43 µg carbon.

[2] Calculated in a real laboratory environment. For a 5.10% CO_2 standard at 646 mm Hg at 24 °C, actual mass of carbon dioxide is 21.34 µg carbon.

* Lower Allowable Limit equals to 5% lower than the actual mass; Upper Allowable Limit equals to 5% higher than the actual mass. Limits should be adjusted according to the real laboratory environment.

- Note: Each time the MnO_2 or Ni catalyst is replaced, the instrument calibration should be checked to confirm that the previous calibration curve holds. A flow check and balance should always be performed after catalyst changes. Additional checks can be done by running a comparison sample (if available) or running two points from the six CH_4/He calibration volumes and two points from the six CO_2/He volumes used in the full calibration. The calibration peak area may also need to be checked for significant changes that would require a full calibration to calculate a new slope.

Figure 4-7. The Analysis Screen during Manual Gas Calibration for DRI Model 2001 Thermal/Optical Carbon Analysis Program.



Access database: D:\CarbonNet\ACCESS\Production\CarbonN
Project name: TCEQ
Batch #: 196
Sub-batch #: Q
Command table: cmdCalib-HeOnly
Sample ID: CI122012091
Run #: 1
Punch area: 1
Dep area: 1
Tech: TP
FID: FID_8
Run type: Calib
LaserT: 816
LaserR: 1783
FID_8: 113
FID_6: 2
Oven Temp: 42.47647
Oven Prs: 3.059982
Slope:
Samp Switch: Automatic
Samp Position: Analyze
Interlock: Closed
Event: INJECT
Time: 9/10/2012 3:13:39 PM; 60; 2
Status: Data on

4.3 Daily Operator Checklist

4.3.1 General

__ Check e-mail and notes on the board BEFORE starting analysis
__ Check all gas cylinders (> 200 psi)

4.3.2 Each Analyzer

__ Make sure a clean filter is on the sample boat (if the filter is an "m2" get a balnk punch from the box labeled "Blank Filters")
__ Leak test all analyzers
__ Record Transmittance and Reflectance on the Daily Check List
__ Run laboratory blank (total carbon [TC] should be < 0.2 μgC/cm^2). If TC is > 0.2 μg, use *cmdBakeMonitor* to bake oven, then repeat lab blank to check and see if TC is < 0.2 μg.
__ Run appropriate morning calibration for that day (SU, KHP, CO_2, Auto-calibration) using Table 4-1 and record the results on the Daily Check List
__ During the evening (~6 PM), perform a second calibration as indicated by Table 4-1and record the results on the Daily Check List

4.3.3 Routine Sample Analysis

__ Retrieve **correct** sample and **mark** the analyzer it will be run on and the analysis date on the runlist
__ Input **correct** parameters on the "Setup" page and **verify** entries
__ Punch a sample
__ Load sample on the boat
__ **Record** all information in the log book
__ Clean the tweezers, dish, and punch with Kimwipes
__ Put the filter sample back in the refrigerator
__ Get the printout and **verify** the report carefully after a run
__ Tape the analyzed punch to the thermogram printout
__ **Flag** the analysis if there is anything wrong
__ Repeat these steps for the next sample

4.3.4 Routine Precautions

- Keep all tools and working area clean
- Be careful not to contaminate filter samples (do not touch with bare hands)
- Double-check that you are running the correct sample on the correct analyzer
- Report any problem that cannot be solved to the supervisor

Table 4-1. Daily Calibration Schedule.

Daily Calibration Schedule

(Based on 24/7 operation)

	Sunday	**Monday**	**Tuesday**	**Wednesday**	**Thursday**	**Friday**	**Saturday**
Morning (Startup)	System Blank, Lab Blank, Autocalib	Lab Blank, Sucrose	Lab Blank, Autocalib, KHP	Lab Blank, Sucrose	Lab Blank, Autocalib, KHP	Lab Blank, Sucrose	Lab Blank, Autocalib
Evening	CO2 Injection	Autocalib	CO2 Injection	Autocalib	CO2 Injection	Autocalib	CO2 Injection

Note:
Sucrose and KHP- Total Carbon (TC) must be between 17.1-18.9 ug C/filter in order to pass.
System and Lab Blanks should be <0.2 µg C/cm^2

5 QUANTIFICATION

5.1 Measurement Calculations

Section 3.2.5 contains the equations used to determine measurement values.

5.2 Precision (Uncertainty) Calculations

Precision is determined from replicate measurements as the average fractional difference between original and replicate analysis concentrations. Concentration uncertainty is the fractional precision times sample concentration. If sample concentration times fractional precision is zero, then the detection limit is used as concentration uncertainty.

The precision calculation program for chemical analysis methods also allows for rejection of outliers and selection of concentration ranges for precision calculations. The uncertainty is calculated using the following formulas:

$$CV = \frac{\sum_{i=1}^{N} \frac{2 \times \left| c_i - c_{i,r} \right|}{c_i + c_{i,r}}}{N}$$

$$Unc_i = \sqrt{(CV \times c_i)^2 + (MDL/3)^2}$$

Where CV = coefficient of variance

N = number of samples

c_i = concentration of initial analysis

$c_{i,r}$ = concentration of sample “i” replicate analysis

MDL = minimum detection limit (3σ of laboratory blanks)

Unc = uncertainty

6 QUALITY CONTROL

6.1 Acceptance Testing

Acceptance runs for pre-fired quartz filters result in < 1.5 µg/cm^2 OC, < 0.5 µg/cm^2 EC, and < 2.0 µg/cm^2 TC for IMPROVE_A thermal protocol. Filters which exceed these levels must be re-fired or rejected. See DRI SOP #2-106, Pre-Firing of Quartz Filters Analysis for Carbon.

6.2 Performance Testing

System blanks are performed each Sunday and laboratory blanks at the beginning of each day to (see Table confirm the system is not introducing bias in the carbon results and to confirm 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.
- Sample boat contamination.
- Contamination of the carrier gas.
- Fibers left on the punch tool or on the flat glass plate during cleaning.
- Contamination from field operator.
- Contamination from normal use of analyzer.
- Maintenance/part replacement.

A temperature-dependent laser signal is potentially due to:

- Physical coupling of the push rod to the boat during the run.
- Boat movement due to loose boat holder.
- A quartz rod (laser light pipe) ready for replacement. As quartz is heated to high temperatures, devitrification (white deposits of SiO_2) occurs that leads to a decrease in the laser intensity. The end surface becomes frosty. The bottom light pipe also receives droppings of quartz particles from filter discs during analysis. Thus, the bottom light pipe will deteriorate faster than the upper light pipe. 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 4.2.1, 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. Only a limited set of primary standards (NIST-traceable) currently exist for carbon analysis. These do not include a range of organic compounds from low- to high-molecular weights, with varying degrees of susceptibility to pyrolysis, or EC and carbonate compounds. The *cmdAutoCalibCheck* command check allows the condition of the catalysts to be monitored and verified.

6.3 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 each group of ten is completed. The random analyzer for the replicate is identified using a chart created in Microsoft Excel (shown in Figure 6-1) using the random number generator, which results in replicate analysis on the same and different analyzers.

This practice provides a better indication of potential differences if samples are analyzed by different laboratories. The µg/cm^2 values for OC, EC and TC are compared with the original run. The values should meet the following criteria:

Range	**Criteria**
OC or TC < 10 µg/cm^2	< ±1.0 µg/cm^2
OC or TC $\geq$ 10 µg/cm^2	< 10 % of average of the 2 values
EC < 10 µg/cm^2	< ±2.0 µg/cm^2
EC $\geq$ 10 µg/cm^2	< 20 % of average of the 2 values

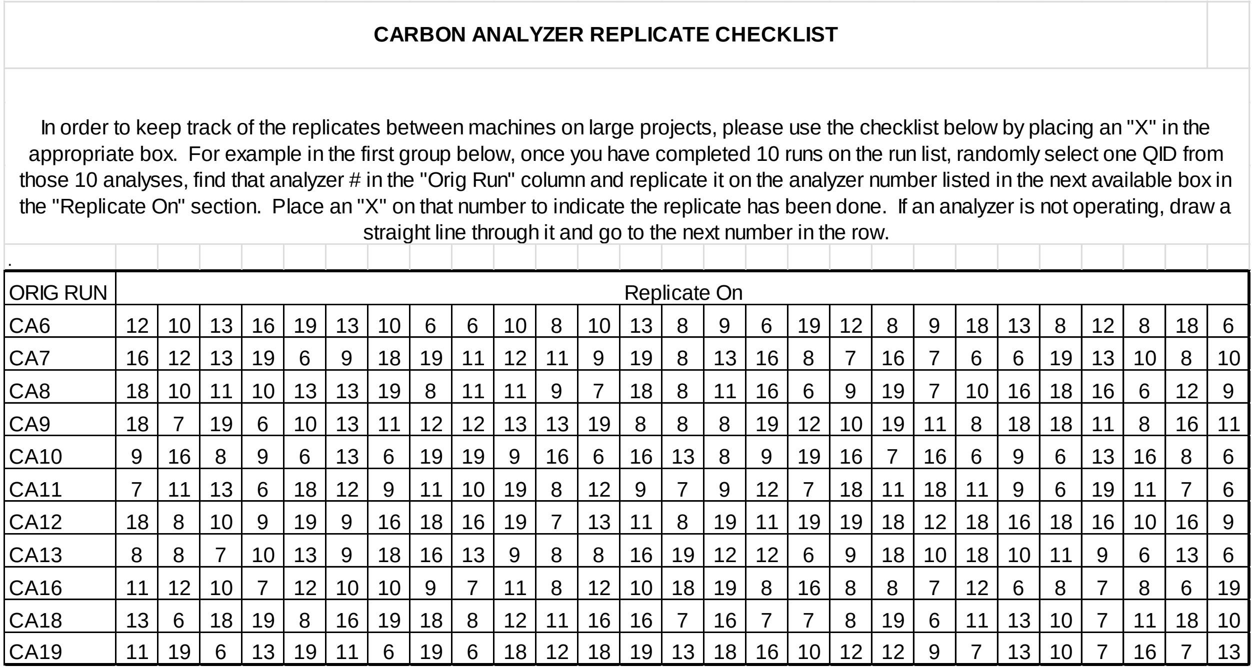
Notice that the criteria converge at 10 µg/cm^2. Replicates which do not meet the above criteria must be investigated for analyzer or sample anomalies. Analyzer anomalies include poor response (as reflected in the calibration peak areas) or poor laser signals affecting the splits between OC and EC. Typical sample anomalies include inhomogeneous deposits or contamination during analysis or from the field sampling location. Inconsistent replicates for which a reason cannot be found must be rerun again unless the filter condition will not allow an additional representative punch to be taken.

When samples are analyzed with an automated sample loader, the sample chamber tray will be set up such that the loader number six location will be a replicate of the first sample, the 12th location a standard spike of sucrose or KHP, and the 18th location a replicate of the sample in loader position.

6.4 Control Charts and Procedures≤

Control charts are updated at the beginning of each month. These charts include a month of calibration data and are posted in the carbon room until the end of the month, after which they are filed with the raw analysis results.

Figure 6-1. Example of carbon analyzer replicate checklist.



CARBON ANALYZER REPLICATE CHECKLIST

In order to keep track of the replicates between machines on large projects, please use the checklist below by placing an "X" in the appropriate box. For example in the first group below, once you have completed 10 runs on the run list, randomly select one QID from those 10 analyses, find that analyzer # in the "Orig Run" column and replicate it on the analyzer number listed in the next available box in the "Replicate On" section. Place an "X" on that number to indicate the replicate has been done. If an analyzer is not operating, draw a straight line through it and go to the next number in the row.

.

ORIG RUN	Replicate On																										
CA6	12	10	13	16	19	13	10	6	6	10	8	10	13	8	9	6	19	12	8	9	18	13	8	12	8	18	6
CA7	16	12	13	19	6	9	18	19	11	12	11	9	19	8	13	16	8	7	16	7	6	6	19	13	10	8	10
CA8	18	10	11	10	13	13	19	8	11	11	9	7	18	8	11	16	6	9	19	7	10	16	18	16	6	12	9
CA9	18	7	19	6	10	13	11	12	12	13	13	19	8	8	8	19	12	10	19	11	8	18	18	11	8	16	11
CA10	9	16	8	9	6	13	6	19	19	9	16	6	16	13	8	9	19	16	7	16	6	9	6	13	16	8	6
CA11	7	11	13	6	18	12	9	11	10	19	8	12	9	7	9	12	7	18	11	18	11	9	6	19	11	7	6
CA12	18	8	10	9	19	9	16	18	16	19	7	13	11	8	19	11	19	19	18	12	18	16	18	16	10	16	9
CA13	8	8	7	10	13	9	18	16	13	9	8	8	16	19	12	12	6	9	18	10	18	10	11	9	6	13	6
CA16	11	12	10	7	12	10	10	9	7	11	8	12	10	18	19	8	16	8	8	7	12	6	8	7	8	6	19
CA18	13	6	18	19	8	16	19	18	8	12	11	16	16	7	16	7	7	8	19	6	11	13	10	7	11	18	10
CA19	11	19	6	13	19	11	6	19	6	18	12	18	19	13	18	16	10	12	12	9	7	13	10	7	16	7	13

The control chart gives a plot of calibration peak counts as percent deviation from a historical mean versus date. Instances where the calibration peak area deviates by more than 10% from the historical mean must be investigated and the cause must be corrected. The historical mean covers results from the previous three months and is updated either quarterly, when the CH_4 calibration gas is changed, when the catalysts are renewed, or when extensive repairs are performed.

6.5 Data Validation

6.5.1 Analysis Flags

During Level 0 validation (see Section 6.4.2), 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 size, deposit area) are corrected.

Flags are applied to the Access file created from the analysis results (see Section 6.4.2). 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 unless a subcode is included which provides additional information (such as v3-“potential contamination”).

6.5.2 Daily Validation

Level 0 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 4-3):

- The filter ID is correct and Punch #.
- For calibration runs, the tabular and thermogram printouts are checked to make sure the catalysts are operating at required level.
- The analysis date and time is correct.
- The punch area is correct; errors in entry require that the calculated carbon concentrations be recalculated.
- 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 4.2.1).
- The initial and the final FID baseline readings are within three counts of each other; excessive FID baseline drift is a cause for re-analysis. NOTE: Some very heavily loaded filters will have an FID baseline drift greater than three counts no matter which carbon analyzer the sample is run on; typically a FID baseline drift greater than three counts signals either a problem with the sample (e.g., very light or very heavy loading) or with the carbon analyzer.

- 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, require re-analysis. Flags should be added to the data file print out as follows:
  - If Regular OC Reflectance split is greater than 5% note “RO” in comments field; If Transmittance split is greater than 5% note “TO” in comments field.
  - If Regular EC Reflectance split is greater than 20% note “RE” in comments field; If Transmittance split is greater than 5% note “TE” in comments field.
- Calculated carbon values for calibration injection runs are within 10% of the current mean value for the injected gas type on that analyzer.

Table 6-1. Common DRI Analysis Flags.

Validation Flag	Sub Flag	Description
b		Blank.
	b1	Field/dynamic blank.
	b2	Laboratory blank.
	b3	Distilled-deionized water blank.
	b4	Method blank.
	b5	Extract/solution blank.
	b6	Transport blank.
c		Analysis result reprocessed or recalculated.
	c1	XRF spectrum reprocessed using manually adjusted background.
	c2	XRF spectrum reprocessed using interactive deconvolution
d		Sample dropped.
f		Filter damaged or ripped.
	f1	Filter damaged, outside of analysis area.
	f2	Filter damaged, within analysis area.
	f3	Filter wrinkled.
	f4	Filter stuck to PetriSlide.
	f5	Teflon membrane separated from support ring.
	f6	Pinholes in filter.
g		Filter deposit damaged.
	g1	Deposit scratched or scraped, causing a thin line in the deposit.
	g2	Deposit smudged, causing a large area of deposit to be displaced.
	g3	Filter deposit side down in PetriSlide.
	g4	Part of deposit appears to have fallen off; particles on inside of PetriSlide.
	g5	Ungloved finger touched filter.
	g6	Gloved finger touched filter.

Table 6-1, continued.

Validation Flag	Sub Flag	Description
h		Filter holder assembly problem.
	h1	Deposit not centered.
	h2	Sampled on wrong side of filter.
	h4	Filter support grid upside down- deposit has widely spaced stripes or grid pattern.
	h5	Two filters in PetriSlide, analyzed top filter
i		Inhomogeneous sample deposit.
	i1	Evidence of impaction - deposit heavier in center of filter.
	i2	Random areas of darker or lighter deposit on filter.
	i3	Light colored deposit with dark specks.
	i4	Non-uniform deposit near edge - possible air leak.
m		Analysis results affected by matrix effect.
	m1	Organic/elemental carbon split undetermined due to an apparent color change of non-carbon particles during analysis; all measured carbon reported as organic.
	m2	Non-white (red) carbon punch after carbon analysis, indicative of mineral particles in deposit.
	m3	A non-typical, but valid, laser response was observed during TOR analysis. This phenomena may result in increased uncertainty of the organic/elemental carbon split. Total carbon measurements are likely unaffected.
	m4	FID drift quality control failure
	m5	Non-white (grey) carbon punch after carbon analysis
n		Foreign substance on sample.
	n1	Insects on deposit, removed before analysis.
	n2	Insects on deposit, not all removed.
	n3	Metallic particles observed on deposit.
	n4	Many particles on deposit much larger than cut point of inlet.
	n5	Fibers or fuzz on filter.
	n6	Oily-looking droplets on filter.
	n7	Shiny substance on filter.
	n8	Particles on back of filter.
	n9	Discoloration on deposit.
q		Standard.
	q1	Quality control standard.
	q2	Externally prepared quality control standard.
	q3	Second type of externally prepared quality control standard.
	q4	Calibration standard.

Table 6-1, continued.

Validation Flag	Sub Flag	Description
r		Replicate analysis.
	r1	First replicate analysis on the same analyzer.
	r2	Second replicate analysis on the same analyzer.
	r3	Third replicate analysis on the same analyzer.
	r4	Sample re-analysis.
	r5	Replicate on different analyzer.
	r6	Sample re-extraction and re-analysis.
	r7	Sample re-analyzed with same result, original value used.
s		Suspect analysis result.
v		Invalid (void) analysis result.
	v1	Quality control standard check exceeded ± 10% of specified concentration range.
	v2	Replicate analysis failed acceptable limit specified in SOP.
	v3	Potential contamination.
	v4	Concentration out of expected range.
	v5	Instrument error
	v6	Operator error
	v7	Software error
w		Wet Sample.
	w1	Deposit spotted from water drops.
y		Data normalized
	y1	XRF data normalized to a sulfate/sulfur ratio of three
	y2	Each species reported as a percentage of the measured species sum

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 4-4):

- 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 three millivolts of the initial FID baseline; excessive drift is cause for reanalysis.

- The laser reflectance signal during the first two minutes, prior to sample introduction to the "Analysis" position, appears near the bottom of the graph and shifts position once the sample is in the "Analysis" position. The transmittance signal will be out-of-scale until the sample is in the "Analysis" position.

- The laser signal should dip below the initial laser line until O_2 is introduced, at which point the signal should rise steeply. (For most samples, charring does occur). High temperature soot samples may not show this characteristic.

- 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 results in a decision that a sample should be reanalyzed, write "Rerun" in red on the printouts and prepare a re-analysis 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 analysis queue.

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

6.5.2.1 Validation of Final Data File

The following steps are followed to create an Excel or dbf file containing carbon data and to perform Level "I" validation on it:

- Each analyzer will have an Access database containing all of the raw carbon data.

- A query (manual or automated by connected server) is used to generate the project data in $\mu g/cm^2$ or µg/filter and a validation report is then generated from this query.

- The output of the Access query is saved or exported as an Excel file or database report for data validation and processing. The MS Excel file naming convention calls for a name in the following format:

  xxOETnnt.xls

where:

xx is the two-character project identifier
OET is organic/elemental carbon
nn is the two- or three-digit batch number (generally used to distinguish between different projects for the same client or between sampling quarters for an extended project)
t is the sample type based on sampler technology:

  A is agricultural burn emissions dilution sampler
  C is combination particle/gaseous sampler
  D is dichotomous sampler for $PM_{2.5}$, PM_{coarse}, and PM_{10}
  G is gaseous
  H is high-volume sampler
  I is IMPROVE/NPS sampler
  P is MiniVol Sampler
  Q is audit samples
  R is resuspension chamber
  S is sequential filter sampler (SFS)
  W is wet Deposition
  X is unknown
  Y is y-sampler (DRI source sampler)

- The final MS Excel or dbf file name is specified on the analysis list posted in the carbon room.

- Begin validation by matching the filters listed on the analysis list with the filters listed on the MS Excel or database printout. There must be at least one entry on the printout for every filter listed on the analysis list.

- Flag field and lab blanks while the list is being reviewed by placing "b1", "b2", "b3", or "b6" in the second column of the printout. Because the MS Excel or database 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 or misread by the scanner 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. Scan the deposit area column for incorrect entries. Circle the incorrect entries to ensure 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 appropriately.

- Scan for missing runs. The most common example is an error in the filter ID data entry. If a run is invalid, an entry for the first run must be inserted, flagged as invalid, and labeled with the reason it was invalid. All punches taken from the filters MUST be accounted for and documented in the file.

- Pull the analysis folders and go through the analysis summaries and thermograms one by one. Check for the conditions listed in Section 6.4.2

  - Reflectance and Transmittance Regular OC Lower Split and Upper Split are within 5% and Regular EC Lower Split and Upper Split are within 20%. 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. Comments should be added to the print out as follows:

    - If Regular OC Reflectance split is greater than 5% note “RO” in comments field; If Transmittance split is greater than 5% note “TO” in comments field.

    - If Regular EC Reflectance split is greater than 20% note “RE” in comments field; If Transmittance split is greater than 5% note “TE” in comments field.

  - Punch discoloration after analysis is complete (See Table 6-1 for m2 flag)

- Verify and resolve all circled items and 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 6.4) and are defined in Table 6-2.

  - If the temporary flag is not warranted, draw a line through the flag to indicate that 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 Table 6-1.

- Invalid samples without a definitive void flag must have an entry in the comments field to describe the reason that the sample is invalid.

- 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.

- Compare replicates against original run. The values should meet the following criteria:

Range	**Criteria**
OC or TC < 10 µg/cm^2	< ±1.0 µg/cm^2
OC or TC ≥ 10 µg/cm^2	< 10 % of average of the 2 values
EC < 10 µg/cm^2	< ±2.0 µg/cm^2
EC ≥ 10 µg/cm^2	< 20 % of average of the 2 values

- Check the OC/TC ratio. Typical rural samples should not be less than 0.65. Circle any possible outliers for further investigation.

- Scan for records where EC is greater than OC. These may require additional investigation, depending on loading and sample source. Circle records for further investigation.

- Scan blanks for OC being greater than 3.95 × deposit area and for EC greater than the deposit area. Rerun any unusually high blanks.

- Compare primary and secondary filters for validity. Secondary filters should have OC and EC measurements less than the corresponding primary filter. Typical rural secondary filters should have EC ≤ 3.8. OC should be less than or equal to 18. Circle any records that require further investigation.

- All operator-generated flags must be either converted to standard analysis flags (Table 6-1) 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.

Table 6-2. DRI Carbon Analysis Operator Temporary Data Validation 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
m2	Non-white sample punch after analysis
v	Invalid run
r	Replicate
b	Blank
i	Inhomogeneous
f	Filter media damaged
g	Sample deposit damaged
d	Sample dropped
n	Foreign substance on filter
w	Sample wet

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

- Finally, all comments, flags, insertions, and other changes made to the printout are entered into the MS Excel or database file. After all changes are made, generate a new printout. Label the new printout with the file name and printout date. Assemble a copy of the printout and the MS Excel or database file for further validation and reporting.

6.6 Summary of Quality Assurance/Quality Control Activities

Table 6-3 provides a summary of routine quality assurance/quality control (QA/QC) activities for the IMPROVE_A analysis of organic and elemental carbon, including frequencies and tolerances. See Table 4-1 for the daily calibration schedule.

Table 6-3. Summary of Quality Assurance/Quality Control Activities for IMPROVE_A Analysis of Carbon*

Requirement	Calibration Standard and Range	Calibration Frequency[b]	Acceptance Criteria	Corrective Action
Laboratory Blank Check	NA[a]	Beginning of analysis day.	<0.2 µg C/cm^2.	Check instrument and filter lots.
Leak Check	NA	Beginning of analysis day.	Oven pressure drops less than 0.52 mm Hg/s.	Locate leaks and fix.
Laser Performance Check	NA	Beginning of analysis day.	Transmittance >700 mV; Reflectance >1500 mV	Check laser and filter holder position.
Calibration Peak Area Check	NIST 5% CH_4/He gas standard; 20 µg C (Carle valve injection loop, 1000 µl).	Every analysis.	Counts >20,000 and 95-105% of average calibration peak area of the day.	Void analysis result and repeat analysis with second filter punch.
Auto-Calibration Check	NIST 5% CH_4/He gas standard; 20 µg C (Carle valve injection loop, 1000 µl).	Beginning of analysis day.	95-105% recovery and calibration peak area 90-110% of weekly average.	Troubleshoot and correct system before analyzing samples.
Manual Injection Calibration	NIST 5% CH_4/He or NIST 5% CO_2/He gas standards; 20 µg C (Certified gas-tight syringe, 1000 µl).	End of analysis day.	95-105% recovery and calibration peak area 90-110% of weekly average.	Troubleshoot and correct system before analyzing samples.

***** Assuming 24/7 Operation

Table 6-3, continued

Requirement	Calibration Standard and Range	Calibration Frequency[b]	Acceptance Criteria	Corrective Action
Sucrose Calibration Check	10µL of 1800 ppm C sucrose standard; 18 µg C.	Thrice per week (began March, 2009).	95-105% recovery and calibration peak area 90-110% of weekly average.	Troubleshoot and correct system before analyzing samples.
System Blank Check	NA	Once per week	<0.2 µg C/cm^2.	Check instrument and filter lots.
Multiple Point Calibrations	1800 ppm C Potassium hydrogen phthalate (KHP) and sucrose; NIST 5% CH_4/He, and NIST 5% CO_2/He gas standards; 9-36 µg C for KHP and sucrose; 2-30 µg C for CH_4 and CO_2.	Every six months or after major instrument repair.	All slopes ±5% of average.	Troubleshoot instrument and repeat calibration until results are within stated tolerances.
Sample Replicates (on the same or a different analyzer)	NA	Every 10 analyses.	±10% when OC and TC ≥10 µg C/cm^2 ±20% when EC ≥ 10µg C/cm^2 or <±1 µg/cm^2 when OC and TC <10 µg C/cm^2 <±2 µg/cm^2 when EC <10µg C/cm^2	Investigate instrument and sample anomalies and rerun replicate when difference is > ±10%.
Temperature Calibrations	Tempilaq® G (Tempil, Inc., South Plainfield, NJ, USA); Three replicates each of 121, 184, 253, 510, 704, and 816 °C.	Every six months, or whenever the thermocouple is replaced.	Linear relationship between thermocouple and Tempilaq® G values with R^2>0.99.	Troubleshoot instrument and repeat calibration until results are within stated tolerances.
Oxygen Level in Helium Atmosphere (using GC/MS)[c]	Certified gas-tight syringe; 0-100 ppmv.	Every six months, or whenever leak is detected.	Less than the certified amount of He cylinder.	Replace the He cylinder and/or O_2 scrubber.
Interlaboratory comparisons	NA	Once per year.	NA	Review and verify procedures.
External systems audits	NA	Once every two to three years.	NA	Take action to correct any deficiencies noted in audit report.

[a] NA: Not Applicable.

[b] Calibration performed by carbon analyst, except for interlaboratory comparisons and external systems audits, which are conducted by the U.S. Environmental Protection Agency (EPA) National Air and Radiation Environmental Laboratory (NAREL).

[c] Gas chromatography/mass spectrometer (Model 5975, Agilent Technology, Palo Alto, CA, USA).

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8 CHANGE DOCUMENTATION

9/27/2012 – made the following changes to document:

- Updated MDLs and added MDLs in units of µg/filter in Section 1.5
- Updated Section 1.8, adding reference to new SOP #4-118 on testing for O_2 in He atmosphere of carbon analyzer
- Reorganized sections on calibrations keeping full calibrations in Section 3 and moving more routine calibrations and checks into Section 4, Procedures
- Modified wording for volume injections under full gas calibration (Section 3.2.1)
- Added new Section 4.1.6.2 on laboratory blanks and renumbered section on carbonate analysis as 4.1.6.3
- Replaced Section 4.2, Abbreviated Procedures, with new Section 4.3, Daily Operator Checklist, with new Table 4-1, Daily Calibration Schedule
- Corrected equation for uncertainty in Section 5.2 by dividing MDL by 3 (as it is actually calculated)
- Added new Section 6.1 on Acceptance Testing and renumbered other sections
- Updated Table 6-1 on DRI analysis flags and deleted old Table 6-3
- In Sections 6.3 and 6.5.2.1 corrected criteria for EC $< 10\ \mu g/cm^2$ to $< \pm 2.0\ \mu g/cm^2$
- Added new Section 6.6 and new Table 6-3 on summary of QA/QC activities
- Added new Appendix B, Basic Troubleshooting Guide
- Updated figures with recent examples (i.e., Figures 2-6, 2-7, 2-8, 3-1, 3-2, 4-2b, 4-3, 4-4, 4-5, 4-7, & 6-1) and references
- Additional editorial, formatting, grammatical, and clarification changes throughout document

7/24/2008 – Made following changes to document:

- Revised cover page to include signature lines
- Updated Section 2 (Apparatus, Instrumentation, Reagents and Forms) with current information and forms
- Updated Figures 2-1 and 2-3 with more current and detailed information
- Renamed Quantification to Calibration and moved to Section 3
- Moved Temperature Calibration to Section 3
- Updated text and formulas in Section 3.1.3.1 under preparation of standards for clarification and accuracy.
- Updated Figure 3-4 with new worksheet and new volumes.
- Moved Procedures to Section 4 and updated to include additional details where needed
- Moved Quantification to Section 5; added precision calculations.
- Updated Quality Control (Section 6)
- Updated References as needed (Section 7)
- Added Section 8 (Change Documentation)
- Added Section 9 (Appendix A)

APPENDIX A: Abbreviations and Acronyms

°C	Degrees Celsius
µg/m^3	Micrograms per cubic meter
µl	Microliters
Cal Gas	Calibration Gas
Calibration Injection	The injection of calibration gases, either CO_2 or CH_4, into the sample stream at the beginning and end of each work day to check instrument performance.
Calibration Peak	The FID peak resulting from the automatic injection of methane calibration gas (CH_4/He) at the end of each analysis run for 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 per sample punch.
Chemicals Used:	

H_2	Hydrogen
HF	Hydrofluoric Acid
HCl	Hydrochloric Acid
He	Helium
CO_2	Carbon Dioxide
CH_4	Methane
O_2	Oxygen
Na	Sodium
SiO_2	Silicon Dioxide
K	Potassium
KHP	Potassium hydrogen pthalate
V	Vanadium
Cr	Chromium
Mn	Manganese
MnO_2	Manganese Dioxide
Co	Cobalt
Ni	Nickel
Cu	Copper
Pb	Lead

DRI	Desert Research Institute
EC	Elemental Carbon
EC1	Carbon evolved from the filter punch in a 98% He/2% O_2 atmosphere at 580 °C.
EC2	Carbon evolved from the filter punch in a 98% He/2% O_2 atmosphere from 580 to 740 °C.
EC3	Carbon evolved from the filter punch in a 98% He/2% O_2 atmosphere from 740 to 840 °C.
Elemental Carbon (EC)	Carbon evolved from the filter punch in a 98% He/2% O_2 atmosphere at 580, 740, and 840 °C minus any pyrolyzed OC.

FID	Flame Ionization Detector
FID Split Time	The time at which the laser split occurs plus the transit time required for thermally evolved carbon to travel from the sample punch to the FID.
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
High Temperature EC	Carbon evolved from the filter punch in a 98% He/2% O_2 atmosphere at 740 and 840 °C minus any pyrolyzed organic carbon present in these two peaks. This is EC minus the first EC peak (EC1).
High Temperature OC	Carbon evolved from the filter punch in a He-only atmosphere at 280, 480, and 580 °C plus pyrolyzed organic carbon. This is OC minus the first OC peak (OC1).
IMPROVE	Interagency Monitoring of PROtected Visual Environments
IMPROVE_A Thermal Protocol	A thermal protocol is used in carbon analyzers to quantify carbon fractions evolved at different temperature plateaus. The IMPROVE_A thermal protocol derives from the IMPROVE thermal protocol initiated in 1987 (Chow et al., 2005).
Laser Split	The separation between OC and EC, which depends on the laser-measured reflectance and/or transmittance of the filter punch returning to its initial value. At this point all pyrolyzed OC has been removed and EC is beginning to evolve.
Lower Split Time	The time at which the laser-measured reflectance and/or transmittance of the filter punch reaches its initial value minus the precision of the laser signal (currently defined as 10 counts).
LQL	Lower quantifiable limit
M	Mole
MDL	Minimum detection limit
NIST	National Institute of Science and Technology
OC	Organic Carbon
OC1	Carbon evolved from the filter punch in a He- only (>99.999%) atmosphere from ambient (~25 °C) to 140 °C.
OC2	Carbon evolved from the filter punch in a He- only (>99.999%) atmosphere from 140 to 280 °C.
OC3	Carbon evolved from the filter punch in a He- only (>99.999%) atmosphere from 280 to 480 °C.
OC4	Carbon evolved from the filter punch in a He- only (>99.999%) atmosphere from 480 to 580 °C.
OP	The carbon evolved from the time that the carrier gas flow is changed from He to 98% He/2% O_2 at 580 °C to the time that the laser- measured filter reflectance (OPR) or transmittance (OPT) reaches its initial value. A negative sign is assigned if the laser split occurs before the introduction of O_2.

OPR	Pyrolyzed carbon measured by reflectance
OPT	Pyrolyzed carbon measured by transmittance
Organic Carbon (OC)	Carbon evolved from the filter punch in a He- only (>99.999%) atmosphere at 140, 280, 480 and 580 °C plus pyrolyzed organic carbon. This is the same as Volatile Organic Carbon (VOC) plus high- temperature OC.
psi	Pounds per square inch
Pyrolysis	The conversion of OC compounds to EC due to thermal decomposition; this may be envisioned as "charring" during the organic portion of the analysis.
QA	Quality Assurance
QC	Quality Control
Regular Split Time	The time at which the laser-measured reflectance and/or transmittance of the filter punch reaches its initial value.
SiO_2	Silicon Dioxide
STN	Speciation Trends Network
TC	Total Carbon
TOR	Thermal/Optical Reflectance
TOT	Thermal/Optical Transmittance
Total Carbon (TC)	All carbon evolved from the filter punch between ambient and 840 °C under He and 98% He /2% O_2 atmospheres.
VOC	Volatile Organic Carbon
UHP	Ultra-High Purity
Upper Split Time	The time at which the laser-measured reflectance and/or transmittance of the filter punch reaches its initial value plus the precision of the laser signal (currently defined as 10 counts).
ΔT	Temperature Deviation

APPENDIX B: Basic Troubleshooting Guide

The following procedures describe fixes to address commonly observed issues during the operation of the Model 2001 thermal/optical carbon analyzer

B.1 Persistent Leaks

Failure to pass leak check (3.1.2) requires identifying the source of the leak using a helium leak detector. Procedures to address the leak depend on source. The following suggested procedures are based on the leak location:

- Reducing ferrule/thermocouple
  - Finger-tighten the nut that holds the reducing ferrule.
  - Retest for leaks. If tests show no leaks, resume analyzer operation. Persistent leak at this location requires reducing ferrule replacement. Consult installation/maintenance guide for instructions.
- Breech O-ring
  - Set the multi-function knob to the “Load” position.
  - Detach the orange breech O-ring. Clean the area around the breech where the O-ring sits.
  - Install new breech O-ring. Set the multi-function knob to “Analyze”. Test for leaks.
- Quartz oven outlet
  - Loosen the nut that connects the quartz oven to the stainless steel tubing.
  - Remove and replace the Teflon ferrules. Re-tighten the nut and check for leaks.

B.2 Laser Drift

- Set the multi-function knob to the “Load” position.
- Remove any punch on the sample boat. Test the snugness of the sample boat on the holder. Remove boat, pinch boat holder wire, re-install boat if still loose.
- Set the multi-function knob to “Analyze” position.

- Inspect the path of the laser beam through the quartz oven. Beam should pass through the center hole of the sample boat. Adjust the sample boat's horizontal alignment by loosening the screws holding the pushrod thermocouple.

- Place a blank punch on the boat, and perform a laboratory blank check (Section 4.1.3) to test laser drift levels. Consult the installation/maintenance manual if drift still exceeds 5% of initial laser value.

B.3 Calibration Peak Area Inconsistent from Previous Values

- Check for leaks.

- If leak-free, adjust gas flows to match calibrated values. Perform laboratory blanks (Section 4.1.3) or automated routine calibration (Section 4.2.2) to determine if the adjustment addressed the issue.

- A calibration peak that remains inconsistent after gas flow adjustment may require pressure balancing. To balance pressure, go to the “Manual” window from the Main Welcome screen,

    - Click “Control” to display temperature and valve controls. Change the Back valves to “Open”, Front valves to “Close”. Click “Go”.

    - Monitor oven pressure displayed on the front panel of the analyzer. Take note of the pressure once value has stabilized.

    - Change the Back valve to “Close”. Note any changes in system pressure. Adjust vent valve knob (right side panel of analyzer) until system pressure matches initial values.

    - Switch Back valve to “Open” and repeat process of adjusting vent valve until no noticeable pressure change is observed during valve switch process.

    - With the Back valve balanced, keep Back valve open and Front valve closed.

    - Set the front valve to open, but before clicking “Go”, observe the He/O_2 flow values. Notice if ball flow indicator bounced while front valves switched from close to open. A bouncing pressure ball indicates unbalanced pressures.

    - Carefully, and slowly adjust the He/O_2 valve on the right side panel to balance pressure. Rotate He/O_2 valve counterclockwise if ball was bouncing down, clockwise if bouncing up. Check if this has balanced the flow by changing the front valve to close and see if ball indicator bounced when front valve is switched to open.

- Run an additional laboratory blank to verify the correct calibration peak. If still inconsistent, replace the methanator.