STANDARD OPERATING PROCEDURE

DRI Model 2015 Multiwavelength Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples – Method IMPROVE_A

July 15, 2025

Prepared by:

Environmental Analysis Facility
Desert Research Institute
Division of Atmospheric Sciences
2215 Raggio Parkway
Reno, NV 89512

Prepared By: _____ **Date:** 7/15/2025

Reviewed By: _____ **Date:** 7/15/25

Approved By: _____ **Date:** 7/15/2025

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

Page

SAFETY

This section gives instructions to promote safe and proper handling of the DRI Model 2015 Multiwavelength Thermal/Optical Carbon Analyzer. General laboratory/facility safety guidelines should be followed in addition to the precautions specified here.

Laser Safety

The DRI Model 2015 Multiwavelength Thermal/Optical Carbon Analyzer is a Class I laser-based instrument. During normal operation, the laser light is enclosed, and operators will not be exposed to laser radiation. When servicing the analyzer involving unenclosed laser light, laser safety rules should be followed, including but not limited to the following precautions:

- **NEVER LOOK DIRECTLY INTO ANY LASER BEAM, REGARDLESS OF POWER.**
- Wear appropriate protective eyewear aligning the beam. **NEVER LOOK DIRECTLY INTO ANY LASER BEAM** even when wearing protective eyewear.
- Eliminate all reflective material from the vicinity of the beam paths.
- Never leave an unblocked invisible laser beam unattended.

Electrical Safety

- The instrument is set up to operate at 115VAC**. DO NOT PLUG THE ANALYZER DIRECTLY INTO POWER SOURCES > 125 VAC.**
- Never service electrical wiring/connections unless qualified and authorized.
- In case of emergency, turn off the analyzer power switch or the Emergency Power Off button in your laboratory.

Gas Safety

- Wear standard Personal Protective Equipment (PPE), including safety eye wear and a laboratory coat when using compressed gases.
- Properly secure gas cylinders.
- Properly install pressure regulators and set regulator pressures to prescribed levels. Do not over pressure the gas lines.

Hot Surface Safety

The analyzer contains a sample oven and an oxidation oven that can heat up to 850 ºC. Some of the solenoid valves may be warm/hot. The ovens are properly insulated. However, some surfaces may still be hot enough to cause burns. Use the following precautions for hot surface safety:

- Do not touch the sample oven, oxidation oven, the quartz cross and connected fittings, and solenoid valves with bare hands. If necessary, use a temperature probe to measure the temperature before servicing.
- Do not put flammable material on or close to the hot surfaces.

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 2015 Multiwavelength Thermal/Optical Carbon Analyzer; and
- Detail the concerns and procedures which will ensure a state-of-the-art carbon analysis process.

1.2 Measurement Principle

Thermal/optical carbon analysis is based on the preferential oxidation of OC and EC materials under different temperatures and atmospheres (Watson et al., 2005). 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. Figure 2-1 shows a schematic diagram of the analyzer. It operates by: 1) liberating carbon compounds under different temperature and oxidation environments from a small sample punch (~0.5 cm^2) taken from a quartz-fiber filter or other sample forms; 2) converting these compounds to carbon dioxide (CO_2) by passing the volatilized compounds through an oxidizer (e.g., heated manganese dioxide, MnO_2); 3) quantifying the CO_2 by a nondispersive infrared (NDIR) CO_2 detector (Chen et al., 2015; Chow et al., 2015).

Seven modulated diode lasers measure the reflectance (R) from, and transmittance (T) through, each filter sample at wavelengths from 405 to 980 nm (Chen et al., 2015; Chow et al., 2015). The 635 nm laser maintains the consistency with the DRI Model 2001, which uses a He-neon 632.8 nm wavelength laser 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 sample R and T throughout an analysis cycle. The R and T, largely dominated by the presence of light absorbing carbon, decrease as pyrolysis takes place and increase as light-absorbing carbon is liberated during the latter part of the analysis. By monitoring the R and T, 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 (Chen et al., 2004; Chow et al., 2004). Traditionally, charring is only monitored by one red laser. The multiwavelength R and T monitoring provides an opportunity to systematically study charring under different wavelengths and potentially improve the charring correction accuracy. Charring by both reflectance and transmittance for all seven lasers is reported.

The multiwavelength measurements allow estimation of light absorption by black carbon (BC) and brown carbon (BrC) as well as their absorbing properties (Andreae and Gelencser, 2006; Moosmüller et al., 2009). BC dominates the light absorption at red and near infrared wavelengths, while BrC absorbs strongly in the shorter wavelengths (<600 nm). In the DRI Model 2001, the 632.8 nm R measure of filter darkening, similar to that of British Smoke (Heal and Quincey, 2012), was used to further demonstrate a consistent EC trend when the Model 2001 replaced the earlier DRI/OGC analyzers (Chen et al., 2012; Chow et al., 1993). In Model 2015, R and T allow spectral light absorption properties for each sample to be estimated by taking the ratio of the initial R and T to the final R and T after the light absorbing carbon was removed, leaving a filter remnant that was usually white, like the unexposed filter. Using filter transfer standard characterized by a UV-VIS-NIR spectrophotometer (e.g., Lambda 35, Perkin Elmer, Waltham, MA), absolute spectral R, T, and absorption can be quantified (Chen et al., 2015; Chow et al., 2015). Using a simplified two-component model consisting of BC and BrC (Sandradewi et al., 2008), each with explicit absorption Ångström exponents, their contributions to spectral light absorption can be estimated. When mass- and wavelength- specific absorption efficiencies are measured or assumed, the optical BC and BrC mass can also be estimated (Chen et al., 2015).

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

When the IMPROVE_A protocol (Chen et al., 2015; Chow et al., 2007; 2011; 2015; 2018) is used, the values routinely reported include: 1) total carbon (TC, sum of total OC and total EC); 2) seven-wavelength total OC and total EC; 3) seven temperature fractions (i.e., OC1-4 and EC1-3); 4) pyrolyzed carbon, monitored by both reflectance (OPR) and transmittance (OPT) for each of the seven wavelengths; and 5) attenuation by reflectance and transmittance for each wavelength. Carbonate carbon is also reported when its analysis is specified by the analytical protocol.

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 on the thermocouple pushrod.

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; Novakov, 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 et al., 2001; 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 NDIR 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 or transmitted light.

The carbon analyzer can effectively measure between 0.1 and 4000 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 NDIR 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. 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 an air quality monitoring network such as the IMPROVE or CSN 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 data to determine the MDLs are based on the analyses of pre-fired laboratory blank quartz-fiber filters from the prior year, using a minimum of 100 filters and will be recalculated annually. The MDL is defined as three times the standard deviation of their measured results. The current MDLs are:

Total OC	0.09 µg/cm^2	0.33 µg/filter
Total EC	0.08 µg/cm^2	0.27 µg/filter
TC	0.13 µg/cm^2	0.45 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 µg/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 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 μg/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 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 (directly or by an automated protocol), or injection of sucrose or KHP onto a filter each day to check instrument performance.
Calibration Peak:	The peak of (NDIR CO_2 concentration × NDIR flow rate / 120) 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.

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.
Laser Split Time:	The time at which each laser split occurs plus the transit time required for thermally evolved carbon to travel from the sample punch to the NDIR. It has 14 values including seven for reflectance and seven for 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. OC has 14 values, corresponding to reflectance and transmittance pyrolysis corrections by each laser.
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. The Model 2015 reports OPR and OPT for each of the seven wavelengths.

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.

Transit Time: The time required for thermally evolved carbon to travel from the sample punch to the NDIR. It is approximated by the time between CH_4 injection through the light pipe near the filter punch and the detection of the CO_2 peak by the NDIR.

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 Multiwavelength Thermal/Optical Carbon Analyzer: Installation, Operation, and Service Manual revised 11/2015 (Desert Research Institute, Reno, NV).

2 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Instrumentation

2.1.1 Description

The components of the DRI Model 2015 Multiwavelength Thermal/Optical Carbon Analyzer are depicted in Figure 2-1 through 2-3. Other details of the configuration of the DRI Model 2015 are referred to the Installation, Operation, and Service Manual. The programmable combustion oven is the heart of the carbon analyzer and includes loading, combustion, and oxidation zones in a single quartz cross "oven" as depicted in Figure 2-3.

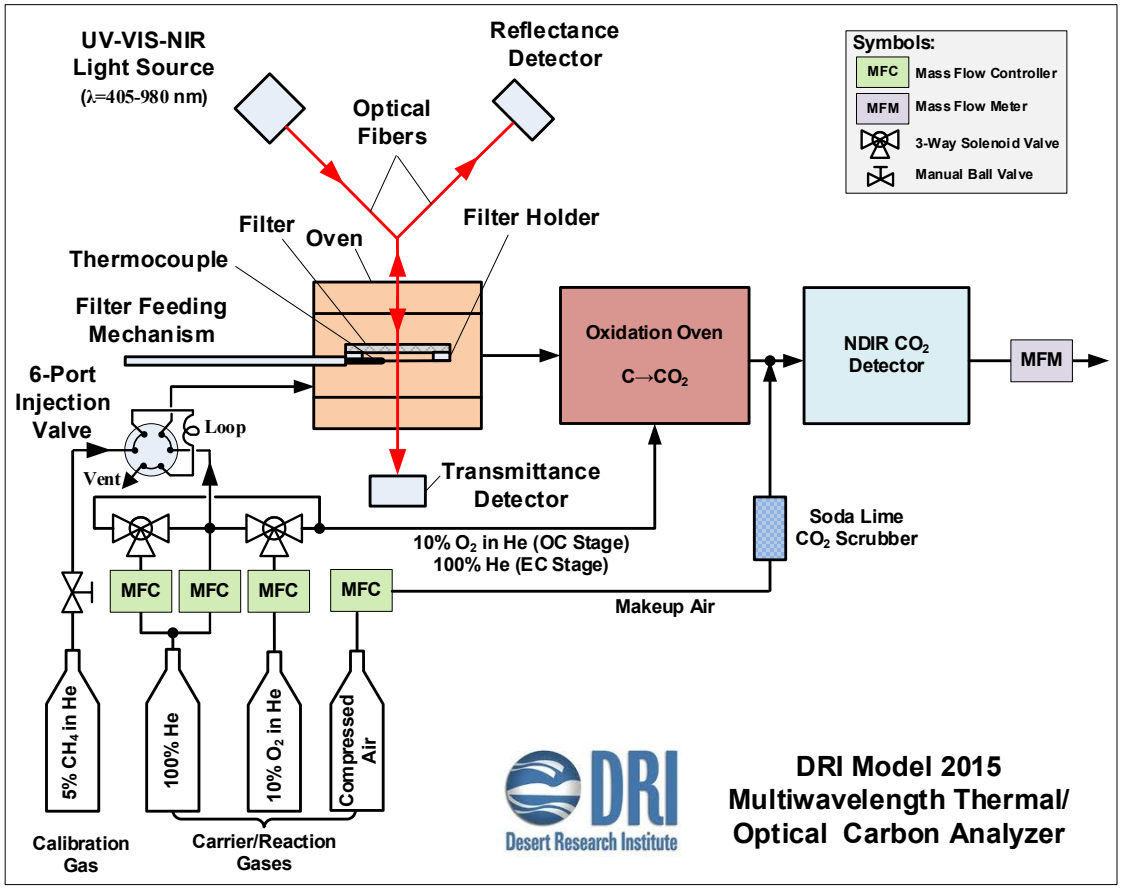


Figure 2-1. Schematic diagram of the DRI Model 2015 Multiwavelength Carbon Analyzer.

In addition to the DRI Model 2015 Multiwavelength Thermal/Optical Carbon Analyzer, which is connected to a 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).
- A copy of *Carbon2015* software (the analysis program) for instrument operation and Microsoft Word for documenting thermograms and data.

2.1.2 **Instrument Characterization**

The DRI Model 2015 Multiwavelength Thermal/Optical Carbon Analyzer is program-driven. Data is stored automatically to the hard drive via a PC-compatible computer processor board. The transit time is 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 NDIR signal returns to its baseline (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. This method requires at least one ~0.5 cm^2 punch per filter and does not require sample pre-treatment. The sample punch is destroyed after analysis.

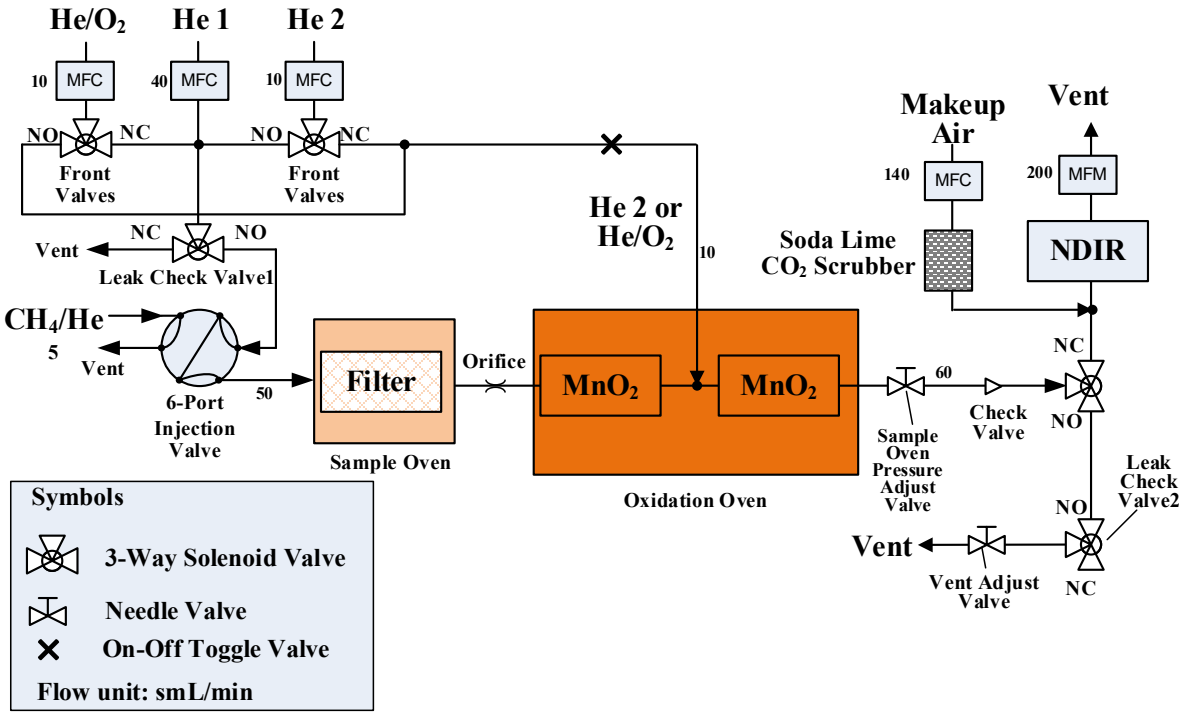


Figure 2-2. Flow diagram of DRI Model 2015 Multiwavelength Thermal/Optical Carbon Analyzer.

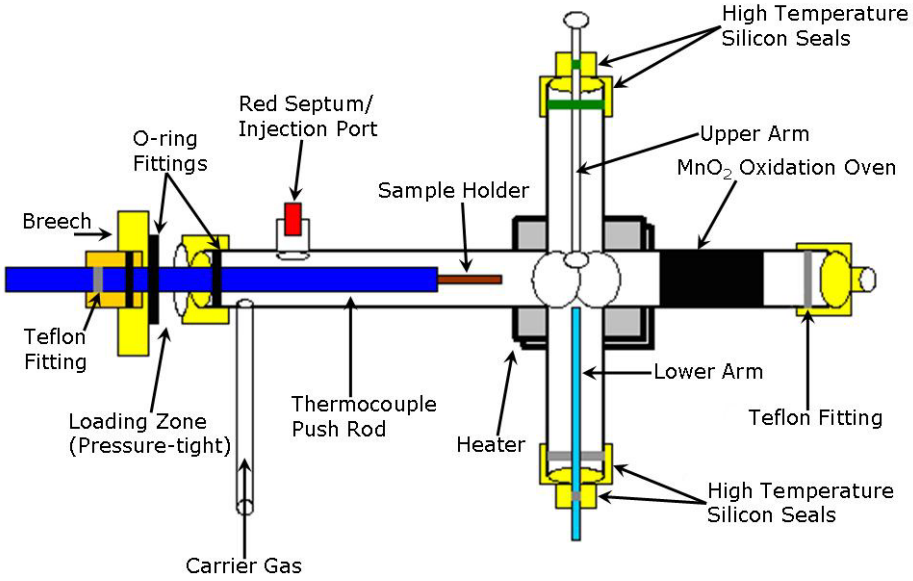


Figure 2-3. Schematic sealing diagram of the DRI Model 2015 Multiwavelength Thermal/Optical Carbon Analyzer.

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 2015 Manual for more details).

Correct routine operation of the instrument is confirmed by checking the following: (refer to Section 4 for more details):

- Verify sample oven pressure reading and specified flow range.
- DO NOT leave the room until the analysis begins.
- Check analysis status screens during and after each analysis run to ensure that the: 1) NDIR, 2) temperature, and 3) laser signals are responding as expected. Report any anomalies to the lab supervisor immediately.
- 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 3.5). Checks of laser adjustments and leaks are made on an as needed basis. The procedure for leak checks can be found in Section 4.1.1. 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. If the *AutoCalib* command is used for calibration, the condition of the oxidizer will be indicated and appropriate action can be taken (such as oxidizer replacement). All calibrations, repairs, and checks must be recorded in the Carbon Analyzer Logbook (Figure 2-4). Flow rates of all operating gases should be checked and adjusted (if needed) whenever a new quartz oven 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 Oven Cross (Wilmad-LabGlass, Vineland, NJ, Part No. DWGRECD82118).
- Quartz Light Pipes: 3 mm nominal diameter, optical quality, polished for optical clarity with 108 mm (upper arm; Part No. LP-108-DRI) and 119 mm (lower arm; Part No. LP-119-DRI) lengths (M.E. Taylor Engineering, Rockville, MD).
- Kanthal boat (Magee Scientific, Berkeley, CA Part No. DRI001009).
- Glass plate: 4” Dia.×1/4”thick, clear surface (available at any glass/quartz manufacturer).
- Push rod thermocouple: 24.13 cm length by 0.32 cm outside diameter (OD), Type-K ground isolated with Inconel sheath (George T. Hall Co, K23EMHZ-011(13/32)-00-18-T3012-2, Sparks, NV).

- Injection septa- Thermogreen, LB-1 cylindrical injection septa, 6mm x 9mm (Sigma-Aldrich, St. Louis, MO, SKU: 20668).
- High temperature silicon septa for oven seal, 11mm x 3mm– (Andwin Scientific, Schaumburg, IL, Part No. 606XLB-11).
- Oxidation oven replacement thermocouple (Omega, Part No. KMQXL-032G-6).
- Quartz wool: For repacking the oxidation oven (VWR, Radnor PA, Part No. 10184-986).
- Graphite ferrules, ¼" O.D. (Chromatography Research Supplies, Louisville, KY, Part No. 211400) for quartz oven tube outlet.
- Teflon ferrules for the thermocouple rod at the inlet breech (Chromatography Research Supplies, Louisville, KY, Part No. 214420).
- Teflon ferrules: Swagelok front and back ferrule for the quartz oven tube outlet connections (Swagelok, Solon, OH, Part No. T-400-SET).
- Teflon Ferrule Set, ½" (Swagelok, Solon, OH, Part No. T-810-SET) for quartz oven tube inlet.
- High Temperature Silicone O-rings: 9/16" ID; ¾ OD; 3/32" Width. Two needed for quartz oven tube inlet. (McMaster-Carr, Elmhurst, IL, Part No. 9396K26).
- Polyester Wipes for cleaning surfaces (VWR, Radnor, PA, Part No. AMDE003).
- 1 ml gas tight syringe for gas injections- (Hamilton Company, Reno, NV, Part No. 81330).
- 5 µl, 10 µl, 20 µl fixed-volume pipettes for liquid injections – (Eppendorf, Hamburg, Germany).
- Gas Syringe Replacement Needles (Hamilton Company, Reno, NV, Part No. 7779-01).
- Oxidation oven heater: 15.24 cm length, 2.54 cm tube diameter element from the analyzer supplier. (Watlow, Columbia, MO, Part No. VC401A06A-0000R [90° bend]).
- NDIR replacement (PP Systems, Amesbury, MA, Part No. AGA407).
- Flow meter (5-500 mL/min; e.g., Bios Defender 510; Mesa Labs, Butler, NJ) for flow calibration.
- Thermocouple Probe: Digi-Sense Type-K, Hi-Temp 25" L, .063" Diameter Probe, Mini Connector, Grounded, 3ft 24-Gauge. (Cole-Parmer Instrument Company, Vernon Hills, IL, Part No. FF-93631-21).
- OAKTON Temp-10 Type K Thermocouple Thermometer with Boot (Cole-Parmer Instrument Company, Vernon Hills, IL, Part No. EW-91427-10).
- NIST-Traceable Thermometer for thermocouple calibration: (Cole-Parmer Instrument Company, Vernon Hills, IL, Part No. FF-17002-10).

- Memory stick or external hard drive for data backup if not backed up to network.

2.3 Reagents

2.3.1 Chemicals

The following chemicals should be reagent grade or better:

- Custom Sucrose and KHP Solutions, 150 ppm and 1200 ppm, at 99.9% purity for calibration use (ERA Golden, CO www.eraqc.com)
- Oxidizer:
    - Manganese dioxide (MnO_2), crystalline, as an oxidizer in the oxidation oven (Sigma -Aldrich, St. Louis, MO, Part No. 243442) or
    - Part No. Carulite 110-TR (Carus, LaSalle, IL)
- Soda Lime ACS (4-8 mesh) indicator grade for carbon dioxide scrubber (VWR, Radnor, PA, Part No. JT3447-1)
- Nanopure water

2.3.2 Gases

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

- He for a carrier gas, regulated to 20-40 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.
- 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; He is replaced once a week or as needed depending on analysis volume. 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.

Detailed information on the mass flow controller settings can be found in the Manual. 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 2-4. Figure 2-5 provides an example of the cover sheet of the sample analysis run list. Figure 2-6 provides an example of the Daily Analyzer Check List that is completed at the start of each day in order to verify proper analyzer operation.

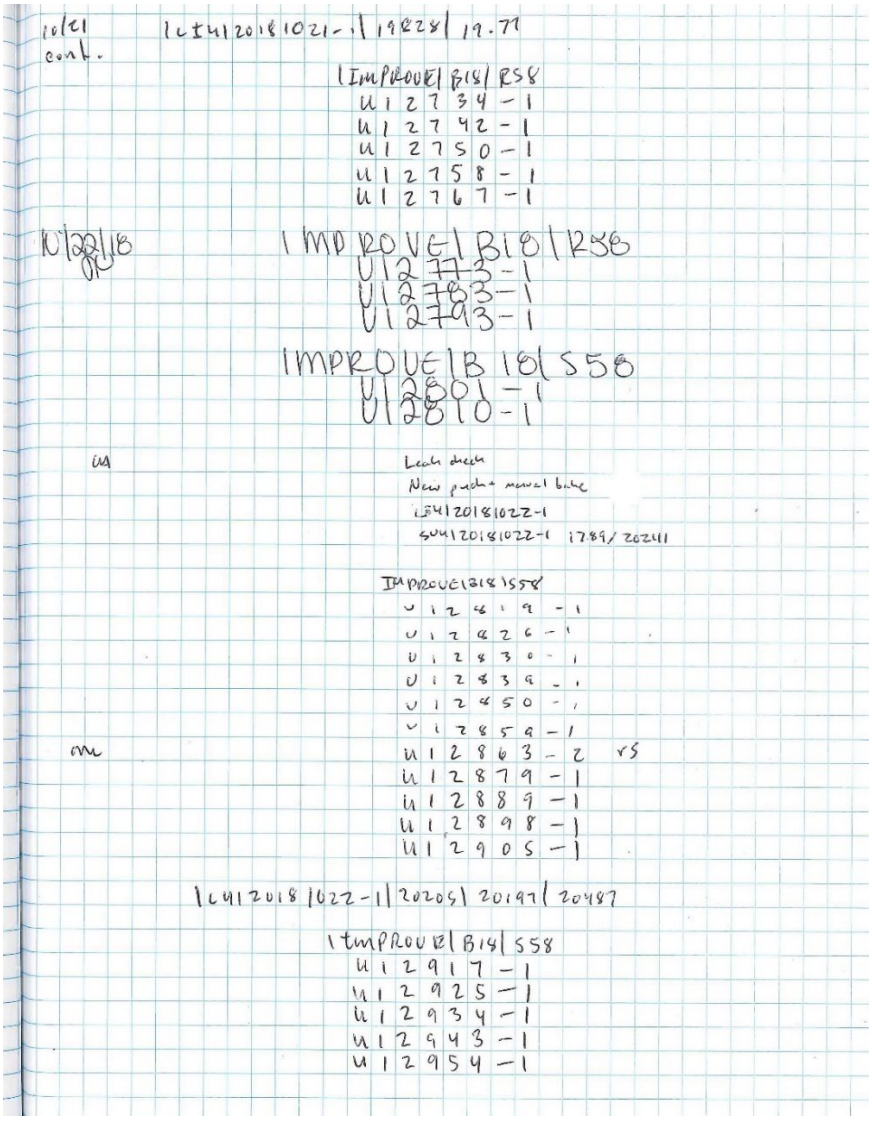
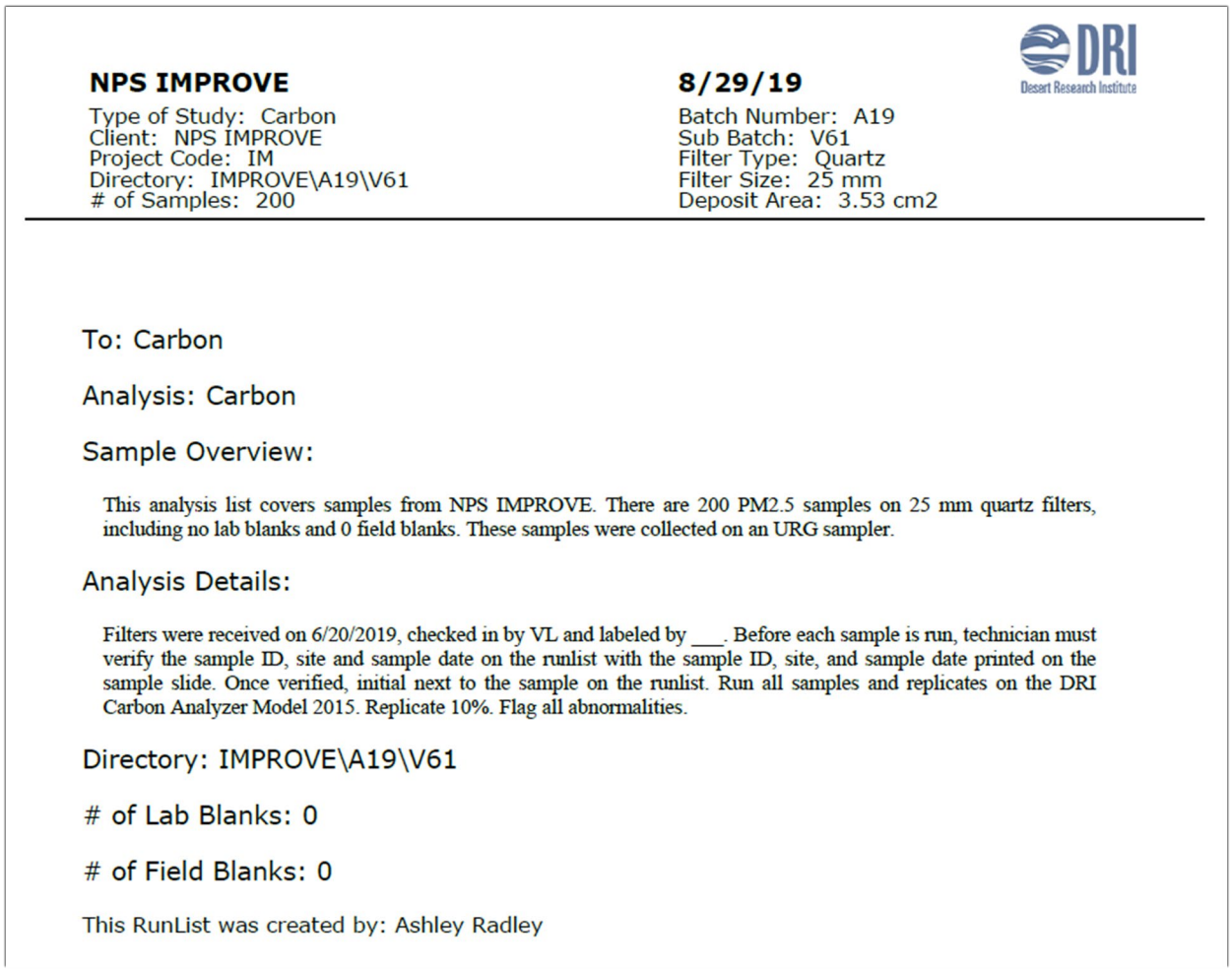


Figure 2-4. Example of carbon analysis logbook format.



NPS IMPROVE
Type of Study: Carbon
Client: NPS IMPROVE
Project Code: IM
Directory: IMPROVE\A19\V61
# of Samples: 200

8/29/19
Batch Number: A19
Sub Batch: V61
Filter Type: Quartz
Filter Size: 25 mm
Deposit Area: 3.53 cm2

To: Carbon

Analysis: Carbon

Sample Overview:

This analysis list covers samples from NPS IMPROVE. There are 200 PM2.5 samples on 25 mm quartz filters, including no lab blanks and 0 field blanks. These samples were collected on an URG sampler.

Analysis Details:

Filters were received on 6/20/2019, checked in by VL and labeled by ___. Before each sample is run, technician must verify the sample ID, site and sample date on the runlist with the sample ID, site, and sample date printed on the sample slide. Once verified, initial next to the sample on the runlist. Run all samples and replicates on the DRI Carbon Analyzer Model 2015. Replicate 10%. Flag all abnormalities.

Directory: IMPROVE\A19\V61

# of Lab Blanks: 0

# of Field Blanks: 0

This RunList was created by: Ashley Radley

Figure 2-5. Example of a DRI Carbon Sample Analysis Run List.

Daily Analyzer Check List CA#: 36 Date Range: 8/6/18 → 8/20/18 2018

				Lab Blank				Sys Blk	Auto Calibration				Injection			
Date	Leak Test-Tech Intitials	System Pressure (T<100°C)	Total Flow	Laser Trans Initial	Laser Reflec Initial	Total Carbon	Cal Peak Counts	Total Carbon	OC3 Peak Counts	EC1 Peak Counts	Cal Peak Counts	Max-Min	Suc TC	KHP TC	CO_2 TC	Cal Peak Counts
8/6 AM	CAL	5.6	194.5	180	291	.00	19893	–					17.80			20091
8/6 PM	CAL								19784	19744	19833	89				
8/7 AM	CA	5.6	194.5	195	279	.00	19805	–	19881	19820	19947	127		17.67		19748
8/7 PM	CAL														19.69	19827
8/8 AM	MF	5.6	194.5	201	281	.00	19934	–					17.54			19789
8/8 PM	TG								19752	19811	19900	148				
8/9 AM	CA	5.5	194.5	231	280	.00	19911	–	19805	19837	19937	138				
8/9 PM	KM														19.67	19674
8/10 AM	CA	5.4	193.58	174	280	.00	20133	–					17.84			20060
8/10 PM	TG								19794	19793	19898	104				
8/11 AM	KM	5.3	192.6	200	271	.00	19661	–	19589	19520	19862	342				
8/11 PM	TG													18.04	20.6	19617
8/12 AM	KM	5.5	193.5	200	281	.00	19823	.00	19905	19358	19709	357				
8/12 PM	CAL														20.32	19860
8/13 AM	CA	5.5	194.5	192	291	.01	20180	–					17.30			20004
8/13 PM	CAL								19740	19739	19963	224				
8/14 AM	CA	5.5	194.5	196	295	.00	19804	–	20015	19993	20067	74		18.03		20145
8/14 PM	CAL														20.61	19879
8/15 AM	CA	5.5	194.5	193	291	.00	19781	–					17.79			19588
8/15 PM	CAL								19851	19933	20065	154				
8/16 AM	JK	5.5	193.58	185	181	.00	20007	–	20080	20124	20270	190		17.72		20100
8/16 PM	KM														21.19	20180
8/17 AM	JK	5.4	193.5	190.4	283	.00	20026	–					17.71			20135
8/17 PM	VT								19978	19887	20109	231				
8/18 AM	KM	5.5	193.5	186	298	.00	19964	–	20016	19848	19968	118				
8/18 PM	VT													17.92	21.03	19990
8/19 AM	CAL	5.4	193.6	210	282	.00	19833	.00	19919	19841	19916	78				
8/19 PM	CA														20.65	19782
8/20 AM	KM	5.5	193.58	204	281	.00	19849	–					18.67			20077
8/20 PM	CAL								19891	19807	19923	116				

Figure 2-6. Example of daily analyzer check list.

3 CALIBRATION PROCEDURES AND STANDARDS

3.1 Types of Instrument Calibrations

The calibration procedures for the carbon analyzers are of four types: 1) the end-of-run internal calibration peak; 2) the routine beginning and end-of-day calibration injections of CH_4/He (or the auto calibration check using the *AutoCalib* protocol), CO_2/He, sucrose or KHP; 3) semi-annual performance check; 4) full instrument calibration, performed annually or after sample oven replacement, using KHP, sucrose, and the two calibration gases; and 5) temperature calibrations performed every six months or after pushrod thermocouple replacement using NIST-traceable thermocouple thermometers.

3.2 End-of-Run Internal Calibration

The end-of-run internal calibration consists of a set quantity of CH_4/He calibration gas which is automatically injected through the 6-port injection valve with a nominal 1000 µL loop by the carbon program. All NDIR readings during the analysis run are normalized to this peak to minimize the effects of oxidizer oxidation efficiency and NDIR performance change over time. The end-of-run internal 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 14,000-25,000) for the specific analyzer. Check daily records to compare peak area counts and determine analyzer performance and stability.

3.3 Daily Routine Calibration

The daily routine calibration schedule is listed in Table 3-1. If there is a period of non-operation, routine calibrations with gas standards must be performed prior to analysis as per the daily routine calibration schedule, either manually or by using the automated routine calibration *AutoCalib* protocol. Routine calibrations with sucrose or KHP are performed at the beginning of each day.

3.3.1 Automated Routine Gas Calibration

The automated calibration uses the 6-port injection valve to inject the CH_4 standard once in a He-only atmosphere, once in an O_2/He atmosphere, and finally, the normal calibration peak at the end of analysis. The three peaks should have similar areas if the oxidizer is in good condition and the calibration factor holds (see Figure 3-1). Use the following steps to perform this automated calibration:

- From the *Carbon2015* Software Selection screen, click the “Analyze Sample” button.
- Enter sample information details. Select the *AutoCalib* protocol. The project name should be “CALIB”, Batch # should be “YYYYmm” for the month, Sub-batch # should be “dd” for the day, and the Sample ID should be in the format “Cxx” where “xx” is the analyzer number (e.g. C22 for analyzer number 22). Look up Table 4-1 for suggested naming convention of different analysis types.

Table 3-1. Daily analyzer calibration schedule.

Daily Calibration Schedule

(Based on 24/7 operation)

	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
Morning (Startup)	Lab Blank, Autocalib* Sucrose/KHP	System Blank Lab Blank, Sucrose/KHP	Lab Blank, Autocalib*, Sucrose/KHP	Lab Blank, Sucrose/KHP	Lab Blank, Autocalib*, Sucrose/KHP	Lab Blank, Sucrose/KHP	Lab Blank, Autocalib* Sucrose/KHP
Evening	CO_2 Injection	Autocalib	CO_2 Injection	Autocalib	CO_2 Injection	Autocalib	CO_2 Injection

Note:
Sucrose and KHP- Total Carbon (TC) must be between 11-13 ug C/filter in order to pass. Sucrose and KHP calibration check will alternate daily
CO_2 is part of manual routine gas calibration check and criteria values are dependent on gas tank specifications.
System (performed once a week) and Lab Blanks (performed daily) should be <0.2 µg C/cm^2

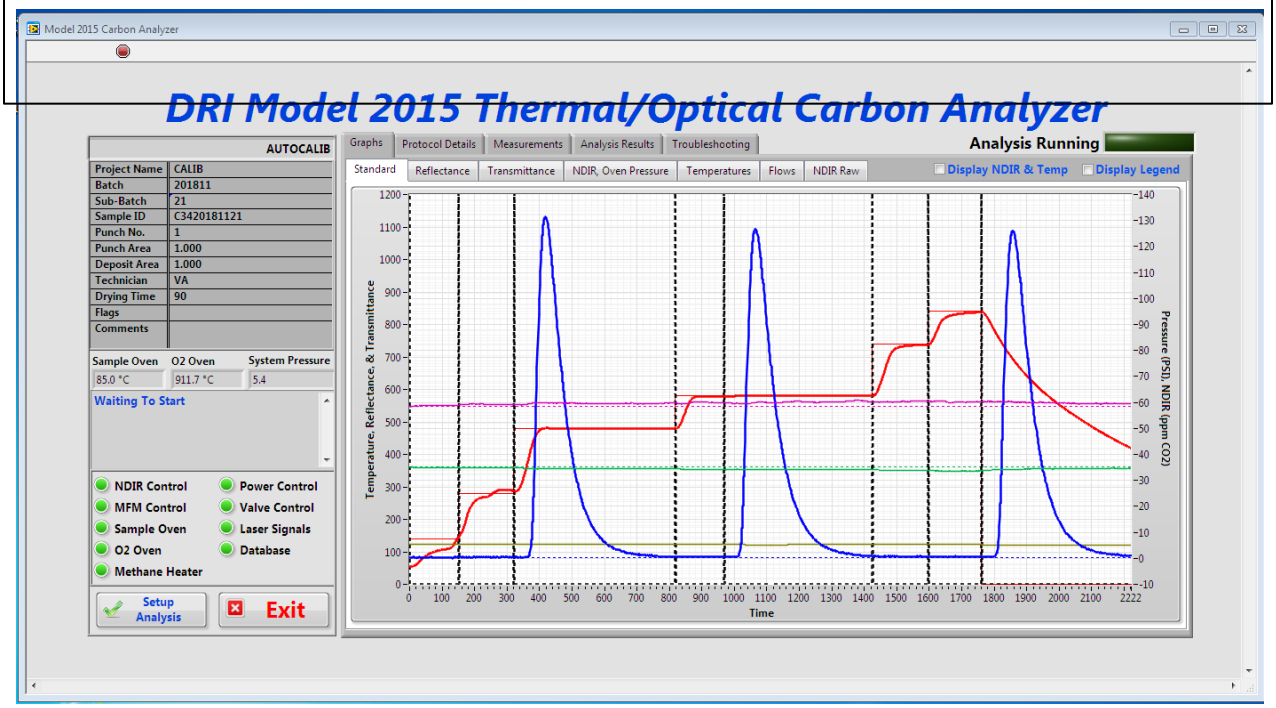


Figure 3-1. Calibration thermogram from the AutoCalib protocol.

- Set the Punch # (“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 the “Press to Continue” button to start the analysis.

- Review the thermogram and record these values in the logbook and on the Daily Analyzer Checklist as shown in Figure 2-6. The three calibration peak integrated counts (OC3, EC1, and CAL) should be within the acceptable range for the specific analyzer, and should be almost identical in area. Check the average C value for the calibration gas against those posted on each carbon analyzer.

3.3.2 Manual Routine Gas Calibration

- From the *Carbon2015* Software Selection screen, click the "Analyze Sample" button.
- Enter sample information details. Select the HeOnly protocol. The project name should be "CALIB", Batch # should be "YYYYmm" for the month, Sub-batch # should be "dd" for the day, and the sample ID should be in the format "MIxx" for CH_4 injection or "CIxx" for CO_2 injection where xx is the analyzer number (e.g. MI22 for a CH_4 injection on analyzer number 22). Look up Table 4-1 for suggested naming convention of different analysis types.
- Set the Punch # ("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 the "Press to Continue" button to start the analysis.
- Note that standards are taken through the septum sampling port along the pressure regulated tubing of a size 10 cylinder. 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 start zeroing the NDIR and acquiring the NDIR baseline.
    - 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. 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 (will vary based on tank specifications):

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] *

[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 oxidizer reactant is replaced, a full instrument calibration should be performed.

3.3.3 Routine Sucrose and KHP Calibration

- From the *Carbon2015* Software Selection screen, click the "Analyze Sample" button.
- Enter sample information details. Select the TC_Only (or IMPROVE_A) protocol. The project name should be "CALIB", Batch # should be "YYYYmm" for the year and month, Sub-batch # should be "dd" for the day, and the sample ID should be in the format "SUxx" for sucrose injection or "KHPxx" for KHP injection where xx is the analyzer number. Refer to Table 4-1. Detailed suggested metadata and protocols for analysis types. for suggested naming convention of different analysis types.
- Set the Punch # ("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. Set the drying time to 900 s. Click the "Press to Continue" button to start the analysis.
- The total carbon (TC) must be between 11-13 ug C/filter for 10 µl injection of 1200 ppm sucrose and KHP to pass.

3.4 Semiannual Performance Verification

After every six-month operation, the carbon analyzer performance will be verified using sucrose or KHP standards. Semiannual performance verification involves spiking pre-fired quartz punches with the following four standards:

- 10 µl of 150 ppm and 1200 ppm KHP or sucrose solution
- 20 µl of 150 ppm and 1200 ppm KHP or sucrose solution

In addition, the push rod thermocouple will be calibrated semiannually. Detailed calibration procedure follows the description in Section 3.5. Individual calibration point is repeated if the carbon/signal ratio (slope) for that calibration point is not within ± 10% of average ratio for all calibration points in the set. If the carbon regression slope differs from the original slope by more than 10%, troubleshoot the analyzer and a full carbon calibration may need be conducted to obtain a new slope.

3.5 Full Carbon Calibration

3.5.1 Full Carbon Calibration Description

The complete instrument carbon calibration, performed annually or after major maintenance or repairs, establishes the calibration slope used in converting the NDIR counts to µg of carbon, as explained in the next section. Instrument calibration involves spiking pre-fired quartz punches with 10.0 to 20.0 µl of the 150 ppm KHP and sucrose solutions, 5.0 to 20.0 µl of the 1200 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.

3.5.2 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 to CH_4 (internal standard) versus µg C injected. 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.

$$\text{Actual µg C per µL} = 0.499 \times \%\text{ of Cal Gas} \times \frac{P}{760} \times \frac{273.15+20}{273.15+T}$$

where P is the local pressure in mmHg and T is the local ambient temperature in ºC.

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

Sucrose and KHP standards can be purchased directly or prepared. To prepare a 1200 ppm standard, the KHP is dried at 110 °C for two hours before dispensing. Transfer 0.2553 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 1200 ppm carbon, is calculated by:

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

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

The nominal 1200 ppm carbon sucrose solution standard is prepared by transferring 0.2852 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:

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

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

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 1200 ppm KHP or sucrose 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. Liquid standards can be purchased from commercial vendors. For example, 150 & 1200 ppm sucrose and KHP standards can be purchased from ERA (Golden, Colorado) at www.eraqc.com, and gas standards can be purchased from Airgas at www.airgas.com.

3.5.3 Full CH_4 and CO_2 Gas Calibration Instructions

- To perform the full gas calibration, select “Analyze Samples” from the Software Selection Screen of the *Carbon2015* program.
- Select the HeOnly protocol in the Sample Info tab. The project name should be “CALIB”, Batch # should be “CARBON”, Sub-batch # should be “YYYYmmdd” for the year, month, and day. The sample ID should be in the format “MIxx_vvvv” for CH_4 injection or “CIxx_vvvv” for CO_2 injection where xx is the analyzer number and vvvv is the volume of gas injected). Look up Table 4-1 for suggested naming convention of different analysis types. You can also make comments and flag the analysis from this screen before the analysis starts.

- 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 2-4.
- The integrated peak and CH_4 end-of-run internal calibration peak counts are extracted manually from the tabular results document or the database, and entered into a spreadsheet which is used to determine the final calibration.

3.5.4 Full Sucrose and KHP Calibration Instructions

- Perform a system blank (without a blank filter punch) before running KHP or sucrose.
- A clean blank quartz punch is baked in the analyzer oven at 840 °C for 10 minutes using the *Bake* protocol.
- To perform the full calibration, select "Calibration Controls" from the Software Selection Screen of the *Carbon2015* program.
- Select the TC_Only (or IMPROVE_A) protocol in the Sample Info tab. The project name should be "CALIB", Batch # should be "CARBON", Sub-batch # should be "YYYYmmdd" for the year, month, and day. The sample ID should be in the format "SUxx_vv" for sucrose injection or "KHPxx_vv" for KHP injection where xx is the analyzer number and vv is the volume of gas injected). Look up Table 4-1 for suggested naming convention of different analysis types. You can also make comments and flag the analysis from this screen before the analysis starts.
- Enter the Punch #; the Punch area and Deposit area should be "1" for the filter being analyzed.
- Enter the length of time in seconds you wish to delay the beginning of the analysis. 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). 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 NDIR and the laser reflectance and transmittance signals.
- After the punch has cooled to less than 50°C, the sucrose or KHP solution (purchased or prepared as described in Section 3.4.2 and kept at room temperature) is injected onto the punch using a fixed volume pipette (5 µl, 10 µl, 15 µl, 20 µl) with disposable tips. The following volumes are used:

- 5 µl of 1200 ppm KHP and sucrose solution
- 10 µl of 150 ppm and 1200 ppm KHP and sucrose solution
- 20 µl of 150 ppm and 1200 ppm KHP and sucrose solution
- no injection (as a laboratory blank)

- Slowly spike the solution in the center of quartz punch using a fixed volume pipette with disposable pipette tips. If the solution is spiked too quickly it will bead up and run off the punch.
- Start the calibration run.
- The integrated peak counts for the sample and calibration peaks are recorded in the database.

3.5.5 **Calculating Calibration Slope**

Calibration values are entered in a worksheet as shown in Table 3-2, and are plotted as ratio of the integrated sample peak counts to the calibration peak counts (x) vs. the actual calculated µg carbon (y) (Figure 3-2). Obvious outliers (slope differs >±10% from average of the calibration set) are identified and rerun. Linear regression is performed on all calibration data in an Excel spreadsheet and the slope (m) is obtained from linear regression through the origin. This slope represents the response of the entire analyzer to generic carbon compounds and includes the efficiencies of the oxidation zones and the sensitivity of the NDIR. 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.

Note that

- A full oven replacement is done when the oxidizer is changed, which may cause a change the slope value.
- The new slope for each analyzer (derived from combined CH_4, KHP, and sucrose data) is placed into the *carbon calibration parameters tab of the calibration controls screen in the software* for each analyzer.
- Calibration data and plots are retained electronically in the calibration folder of each analyzer.

Table 3-2. Example of calibration summary worksheet used to determine calibration slope.

Cal Std	SAMPLE ID	Sample Vol (µL)	Injection Peak Counts	Calibration Peak Counts	Carbon in Std	Inject/Calib Peak	Slope
SU	SU2120190709_150_10	10	1628	20038	1.50	0.08	18.47
SU	SU2120190710_150_20	20	3329	20049	3.00	0.17	18.07
SU	SU2120190701_1200_5	5	6013	19655	6.00	0.31	19.62
SU	SU2120190711_1200_10	10	12596	20118	12.00	0.63	19.17
SU	SU2120190701_1200_20	20	24348	19785	24.01	1.23	19.51
KHP	KHP2120190701_150_10	10	1586	19595	1.50	0.08	18.52
KHP	KHP2120190701_150_20	20	3217	19753	3.00	0.16	18.41
KHP	KHP2120190702_1200_5	5	6337	19656	5.99	0.32	18.60
KHP	KHP2120190702_1200_10	10	12608	19722	11.99	0.64	18.75
KHP	KHP2120190702_1200_20	20	24945	19769	23.98	1.26	19.00
MI	MI2120190621_200	200	4143	19702	4.13	0.21	19.64
MI	MI2120190705_500	500	10996	19790	10.33	0.56	18.58
MI	MI2120190621_700	700	15177	19676	14.46	0.77	18.74
MI	MI2120190620_1000	1000	20734	19641	20.65	1.06	19.56
CI	CI2120190620_200	200	4345	19726	4.11	0.22	18.68
CI	CI2120190529_500	500	10816	19955	10.29	0.54	18.98
CI	CI2120190624_700	700	14983	19698	14.40	0.76	18.93
CI	CI2120190627_1000	1000	20978	19540	20.57	1.07	19.16

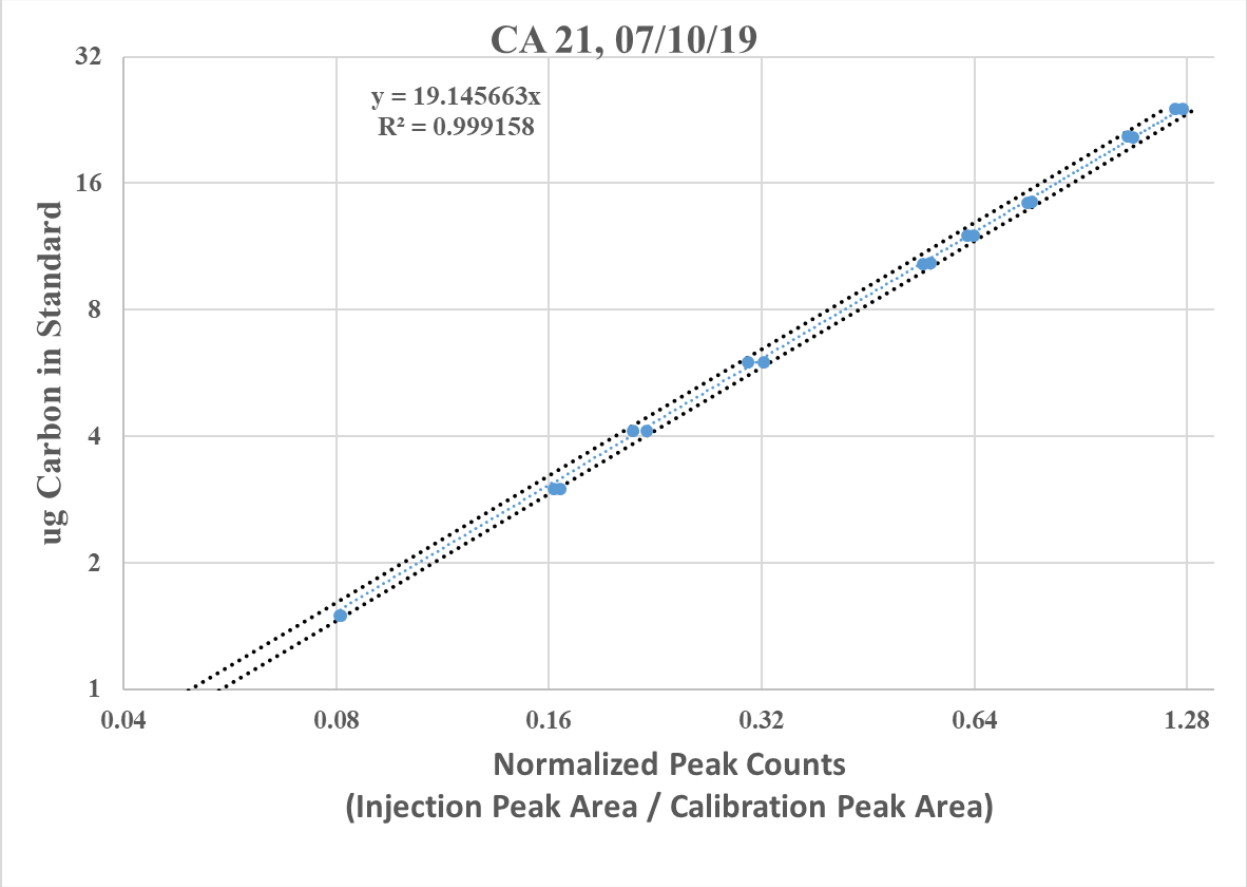


Figure 3-2. Example of a DRI carbon analyzer carbon calibration curve.

3.5.6 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 KHP and sucrose solutions, and the accuracy of the pipette and injection technique.

3.5.7 Carbon Calculation

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:

$$\mu g\ C\ per\ punch = \frac{\text{Integrated Peak Counts above Baseline} \times \text{Calibration Slope}}{\text{Internal Calibration Counts}}$$

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, 740, and 840 °C after the

introduction of O_2, respectively; OC and EC after pyrolyzed organic carbon corrections by reflectance and transmittance for each wavelength; and TC.

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

$$\mu g\ C/cm^2 = \frac{\mu g\ C/Punch}{Punch\ Area}$$

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

$$\mu g\ C/Filter = (\mu g\ C/cm^2) \times (Filter\ Deposition\ Area)$$

3.6 Temperature Calibration

Sample oven temperature calibration is typically done at least semiannually or when the thermocouple is replaced. A National Institute of Standards and Technology (NIST) traceable thermocouple is used for calibrating the sample oven temperature.

The sample oven temperature is calibrated with a NIST-traceable thermocouple following the procedure below:

1) Put a blank filter on the sample boat, and set the sample boat in ANALYZE position.
2) Remove the reflectance light rod on the top arm of the quartz cross oven.
3) Insert the NIST-traceable thermocouple probe through the top arm of the quartz cross oven, and make adjustments so that the thermocouple tip hovers directly above the punch.
4) Go to the Oven Calibration Screen (Figure 3-3), check the "Alter Calibration Values" box, and set the slope to 1 and the intercept to 0.
5) Set the sample oven temperature to a set point and record the pushrod thermocouple and NIST-traceable thermocouple readings when the temperature stabilizes, Suggested temperatures to be used for temperature calibration are: 60, 140, 280, 480, 580, 740, and 840 °C. These temperatures encompass the temperature steps used in the IMPROVE_A protocol.
6) Plot temperatures measured by the pushrod thermocouple (x) against that measured by the NIST-traceable thermocouple (y) (Figure 3-4). A linear regression is done separately for the lower temperatures and higher temperatures separated with a toggle point typically around 200-400 °C. The toggle point is set to be the temperature at which the two regressions are equal to one another or intersect. Input the two separate regressions and the toggle point into the Oven Calibration Screen.
7) Input the toggle point in the Oven Calibration tab (Figure 3-3) along with the high and low temperature regression slopes and intercepts, and click the "Save Config File" button.
8) Once the pushrod thermocouple calibration has been completed it is advised to run the Temperature Optimizer program to optimize the temperature ramping, which takes approximately 8 hours.

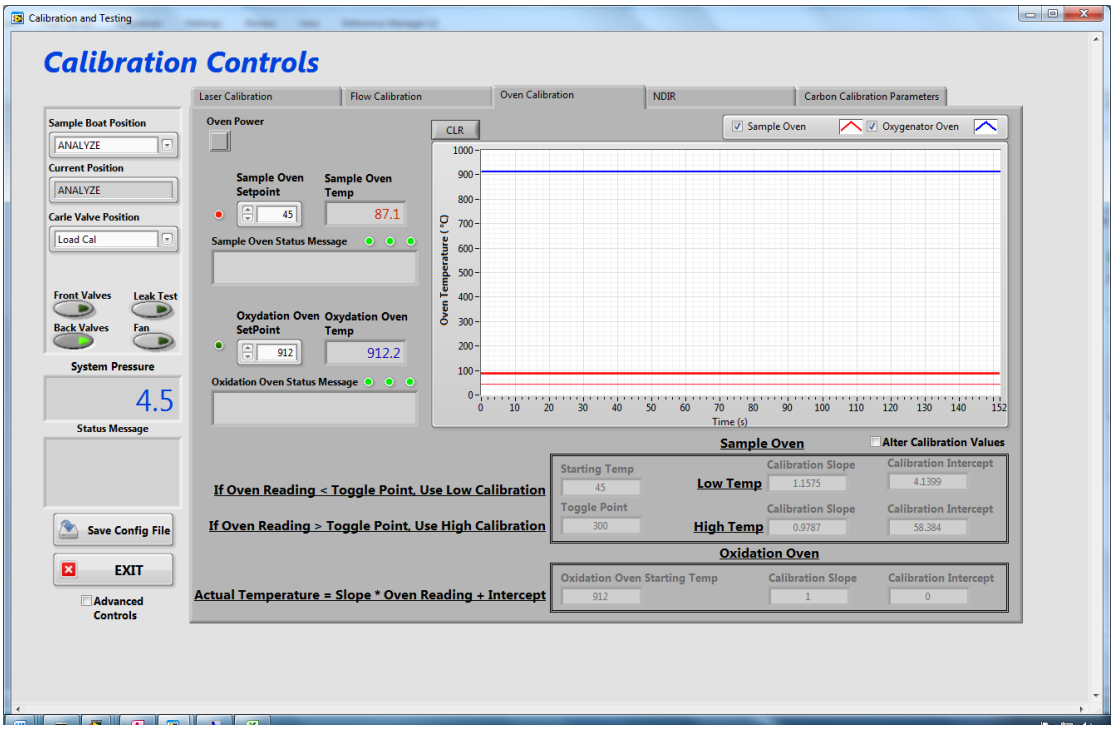


Figure 3-3. Calibration Controls, Oven Calibration.

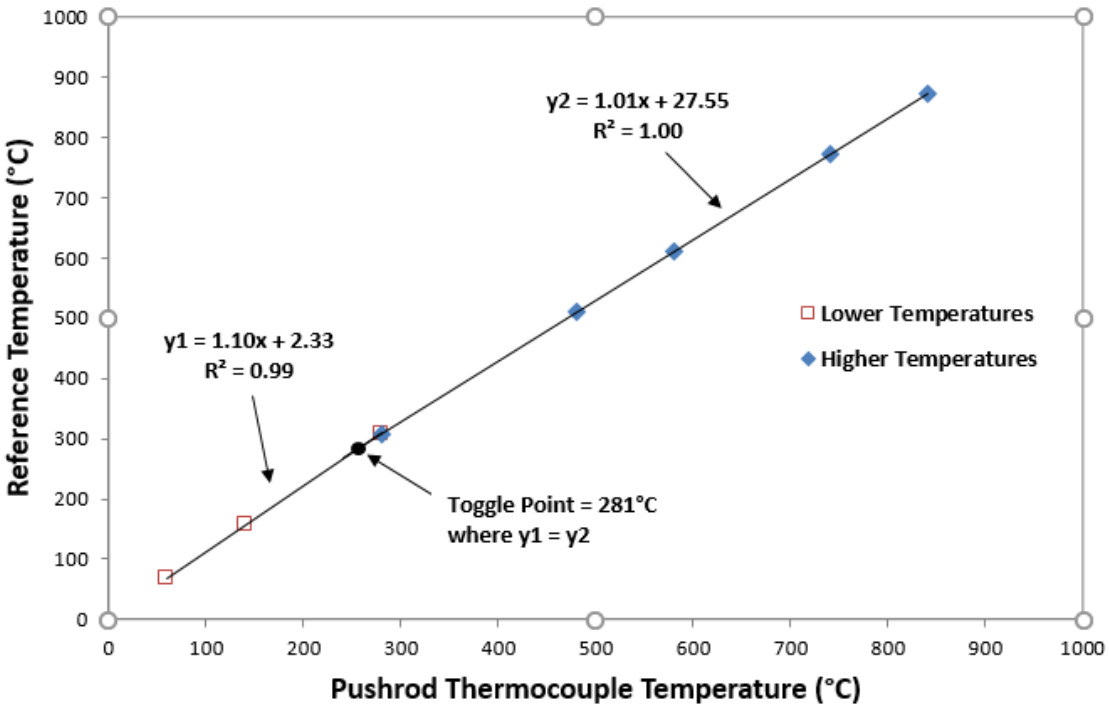


Figure 3-4. Example of temperature regression and toggle point determination.

4 ROUTINE PROCEDURES

4.1 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 oxidation oven afterwards starting at setpoint of 120 °C then incrementing by 100 °C every 30 minutes until oxidation oven is 850 °C. Always follow the ramping procedure to prevent breaking the oxidation reactor due to fast thermal expansion.

The following steps to start up the analyzer:

- Check all gas cylinder pressures; cylinders with gas pressures less than 500 psi should be replaced before beginning the day's analyses, unless the regulator is setup to automatically switch over to a backup gas cylinder.
- Check that all gas delivery pressures are correct.
- Mass flow controllers regulate all gases except the CH_4 and CO_2. See the Manual for more information.
- 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 2-4.
- Open the file *Carbon2015* program icon to begin the carbon analysis program (or double click the *Carbon2015* shortcut on the computer desktop). This opens the LabVIEW software and the Query Status screen (Figure 4-1a).
- When all components are “green” on the Query Status screen click “Continue” and the Software Selection Screen will appear (Figure 4-1b).

a) b)

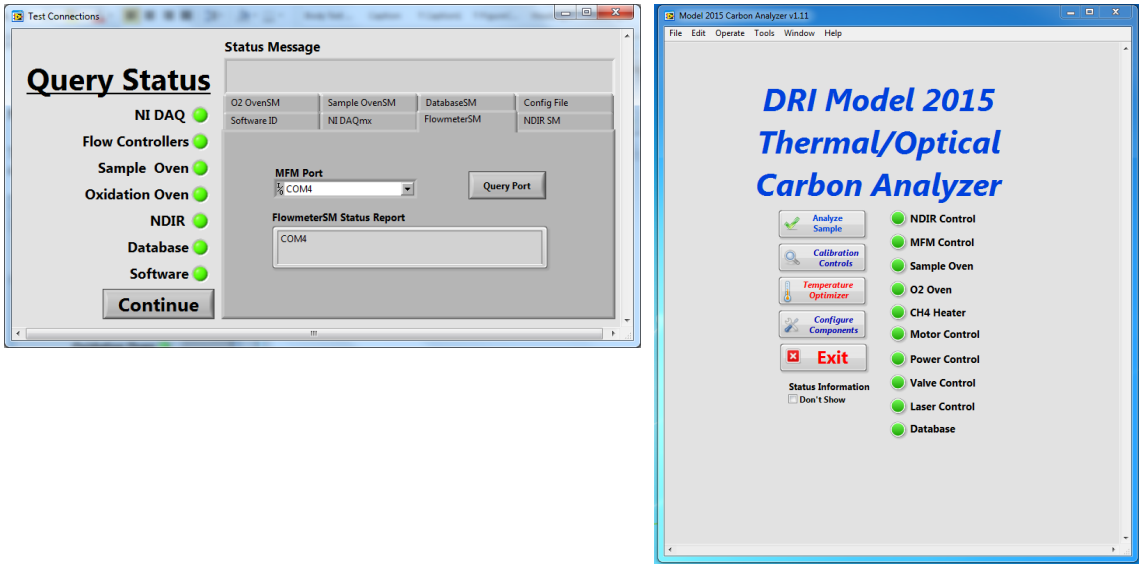


Figure 4-1. Carbon2015 software screens: a) Query Status; and b) Software Selection.

4.1.1 **Leak Checks**

Perform leak checks daily to detect leakage in the sample oven. The leak check valves are operated by the computer. To perform a leak check, use the following procedure:

- From the Software Selection window, click the “Calibration Controls” button.
- Set the He/O_2 flow to zero in the Flow Calibration tab (Figure 4-2), then turn off the on/off toggle valve on the line connected to the side arm of the quartz cross.
- In the Calibration Control window (Figure 4-2), toggle the back valve (from bright green to red color) to direct flow to the leak check valve.
- In the Calibration Controls window (Figure 4-2), toggle the leak check valve switch on. This seals the analysis region between the two leak check valves off from other components and the gas inlet.
- Observe the pressure reading. It will initially drop quickly and then stabilize in a minute. If it drops more than 0.1 psi per second after that, and does not stabilize, there is a leak in the system.
- Reverse the steps above to return to the normal flow configuration: toggle leak check valve OFF, back valve ON, He/O_2 toggle valve ON, and He/O_2 flow set to 10 sccm.
- Check for leaks using a sensitive helium leak detector or liquid leak detection solution (e.g., Snoop® Liquid Leak Detector).
- Likely leak areas are:

- The Teflon or graphite ferrules around the thermocouple push rod and the quartz oven inlet and outlet. A slight turn on the nut should cure the leak. If not, loosen the nut and use methanol to wipe the ferrule clean and retighten the nut. If the leak persists, the last resort is to replace the ferrule.
- The septum port. Replace septum if necessary.
- The top and bottom seals of the quartz oven cross. Make sure to check the light pipe positions related to the filter holder if tightening of the nuts is needed.
- The two nuts at the outlet of the oven cross. Slightly tighten the nuts or replace the ferrules if necessary. Be very careful not to overtighten causing the oven to break.
- If leak persists, the oven may have a crack. To check that, turn off the fan near the outlet of the oven, and use the leak detector to check if He is present near the oxidation oven outlet.

- 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.
- Once the system passes the leak test, allow the system pressure to return to its original value and record this value on the Daily Analyzer Checklist shown in Figure 2-6. The pressure should be consistent with previous day's values.

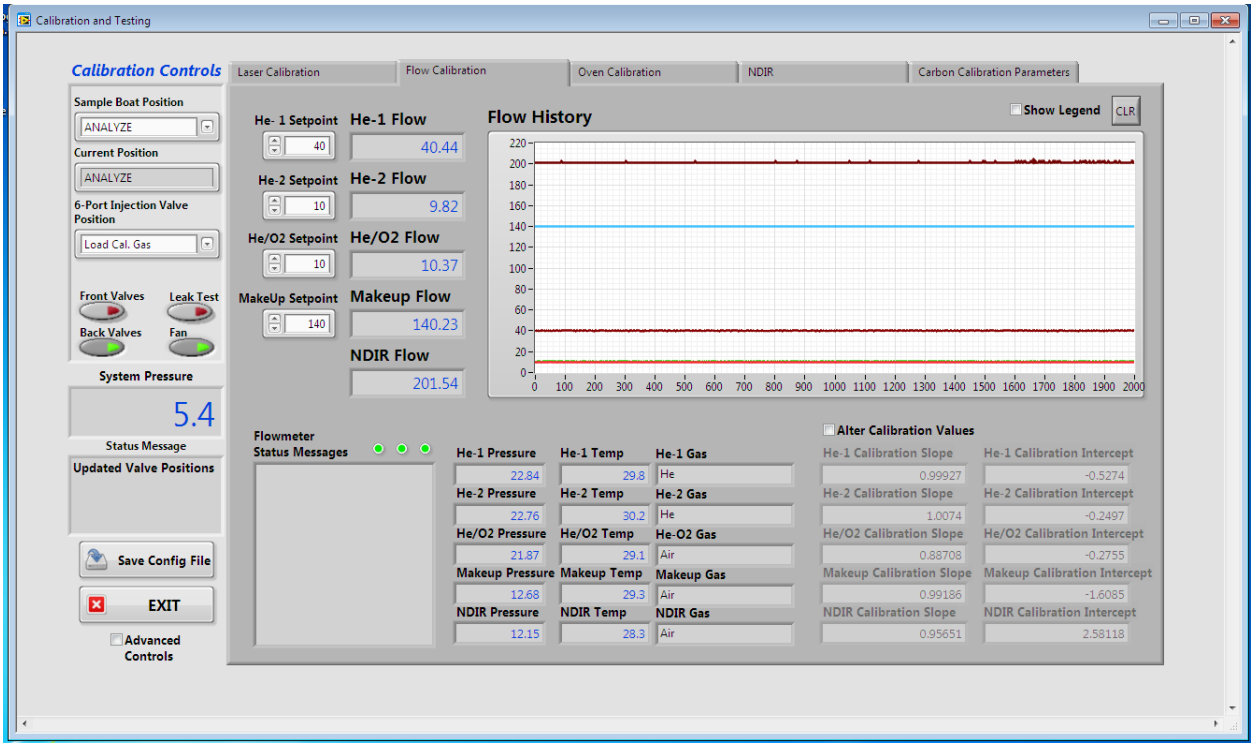


Figure 4-2. Calibration Controls - Flow Calibration.

4.1.2 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.

4.1.2.1 Manual Oven Bake

Use the following procedure to perform a manual oven bake:

- From the Software Selection window (Figure 4-1b), click the "Calibration Controls" button.
- Selected the Oven Calibration tab (Figure 3-3), and type in 840 in the Sample Oven Setpoint field and press enter. This will heat the oven to 840 ºC. Exercise caution when working around hot surfaces of the analyzer.
- Continue until the NDIR returns to baseline.
- Repeat as necessary until the system is clean.
- System or laboratory blanks are run after the oven bake.
- After bake is done, set sample oven setpoint to 5 ºC to cool the oven to the room temperature.

4.1.2.2 Automatic Oven Bake

Use the following procedure to perform an automatic oven bake:

From the Software Selection window (Figure 4-1b), click the "Analyze Sample" button. The Analyze Sample Screen (Figure 4-3) will appear.

Click the "Setup Analysis" button to bring up the Enter Sample Details screen (Figure 4-4).

- Select "Bake" analysis protocol.
- 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 "BAKExx" where "xx" is the analyzer number and YYYY is the year (e.g. Bake32 for analyzer number 32).
- Set the Punch #, Punch area, and Deposit area fields to "1". Click the "Press to Continue" button.
- System or laboratory blanks are run after the oven bake.
- Monitor the thermogram from results document or from the screen. Repeat the bake process when NDIR remains above the initial baseline levels.

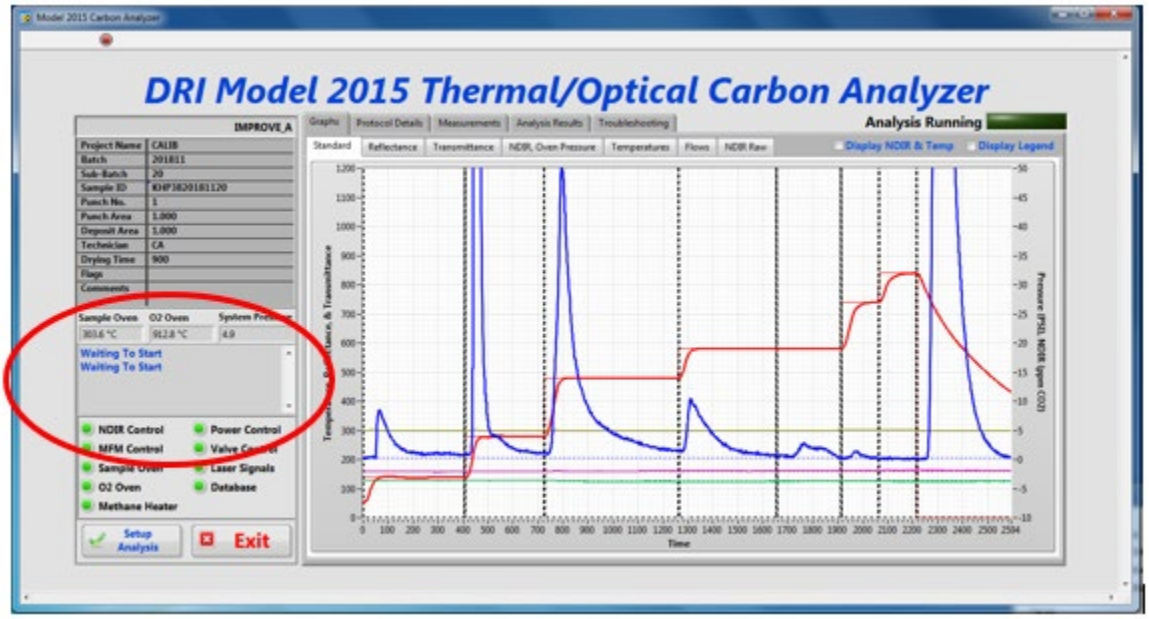


Figure 4-3. Analyze sample screen (waiting for next analysis).

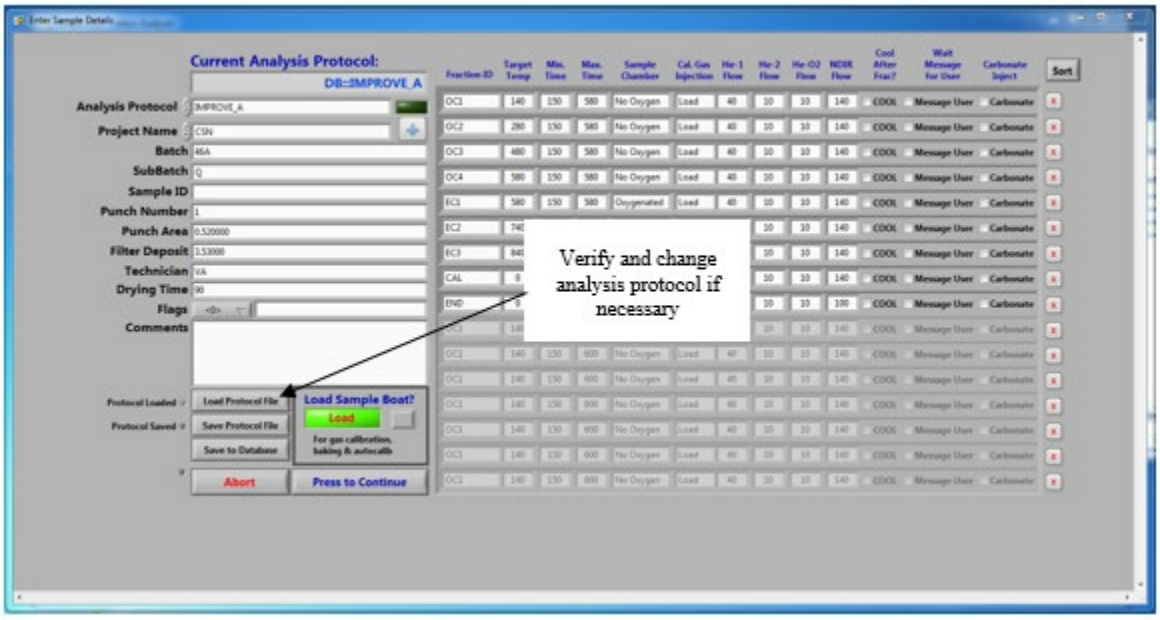


Figure 4-4. Enter Sample Details Screen.

4.1.3 **Laboratory Blanks**

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

- Run the "Bake" protocol following the procedure in Section 4.1.2.
- Run a laboratory blank using the TC_Only (or IMPROVE_A) protocol.
- Use the following for the sample details:
    - Project Name: LABBLK
    - Batch: YYYYmm
    - Sub-batch: dd
    - Sample ID: LBxx

    where xx, YYYY, mm, and dd refers to analyzer number, year, month, and day, respectively. Look up Table 4-1. Detailed suggested metadata and protocols for analysis types. for suggested naming convention of different analysis types.
- Enter 1 cm^2 for 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).
- Monitor the reflectance (LR) and transmittance (LT) of 635 nm laser. A difference >5% of initial indicates significant laser drift.
- Update the DRI Carbon Daily Analyzer Checklist (see Figure 2-6) using reflectance (LR initial), transmittance (LT initial), total carbon (TC), and calibration peak area (Cal peak area) from the results document.
- Values for reflectance and transmittance lasers should be consistent with previous values. The laser values should not have sudden changes at high temperature stages (EC1-EC3). A sudden drop of the laser signal indicates the photodiode is saturated due to oven glow. The laser or the light pipe may need adjustment.
- Total carbon from laboratory blanks must be less than 0.2 µg C/cm^2.
- Calibration peak areas should be consistent with typical values for that instrument unless major maintenance has taken place.
- Analyzers exceeding the typical limits for laser drift, reflectance, transmittance, total carbon, and calibration peak area must be taken offline for testing and maintenance.

4.1.4 **Daily Routine Startup Calibrations**

Each analyzer follows the daily routine morning startup calibration procedures listed in Table 3-1 to ensure performance. These include system and/or laboratory blanks, an automated CH_4 injections (*AutoCalib*), CO_2 injection, sucrose injection, and/or KHP injection. Detailed calibration procedure and described in Section 3.3.

4.2 OC/EC ANALYSIS

Refer to the daily analysis run list (see Figure 2-5) 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 4.2.5.2.

Always perform the analyzer start-up calibration outline in Section 4.1 each day before beginning analysis to ensure that the system is clean (<0.2 µg TC/cm^2), the optical signal and end-of-run internal calibration peaks are consistent, and carbon signals for standards are within specification.

4.2.1 Carbon Analysis Preparation

- Confirm the computer date and time.
- Verify sample oven pressure reading and specified flow ranges in the software.
- 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 2-4).

4.2.2 Software Setup Procedures

- Open the file *Carbon2015* program icon to begin the carbon analysis program (or double click the *Carbon2015* shortcut on the computer desktop). This opens the LabView software and the Query Status screen (Figure 4-1a).
- When all components are “green” on the Query Status screen click “Continue” and the main Software Selection screen will appear (Figure 4-1b).
- Click on “Analyze Sample” in the Software Selection screen and the Analyze Sample screen (Figure 4-3) will open.
- Click “Setup Analysis” button in the Analyze Sample screen to bring up the Enter Sample Details screen (Figure 4-4).
- Click on the folder icon in the upper right corner to select the analysis protocol. For a normal analysis or a blank, select “IMPROVE_A”, for gas injections select “HeOnly”, to clean the oven, select “Bake”, and to run an auto calibration, select “AutoCalib”.
- Enter the Sample ID number, or place the mouse cursor in the field and use a barcode scanner to read the barcode on the Petri dish.
- Fill out the information about the sample, including: Project Name, Batch #, Sub-batch#, 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.

- For a normal run, set the drying time to **90** seconds. For a 10 µL spiked filter (for sucrose and KHP), select 900 seconds.
- Under "Load Sample Boat", the default is on in order to have it automatically load once "Press to Continue" is clicked. Toggle this off if needed.
- Select any pre-analysis flags from the drop-down menu in the "Flags" field. A list of valid choices is presented on the screen.
- Once sample details have been completed and the analysis protocol has been selected, click "Press to Continue" which returns the user to the analysis screen shown in Figure 4-5. The status window will show the analysis initialization status.
- When the oven temperature is <50°C (as indicated in the status window) the push rod will retract the boat to the load/unload position and a prompt will appear stating, Press "OK to open Sample Chamber" as shown in Figure 4-6.

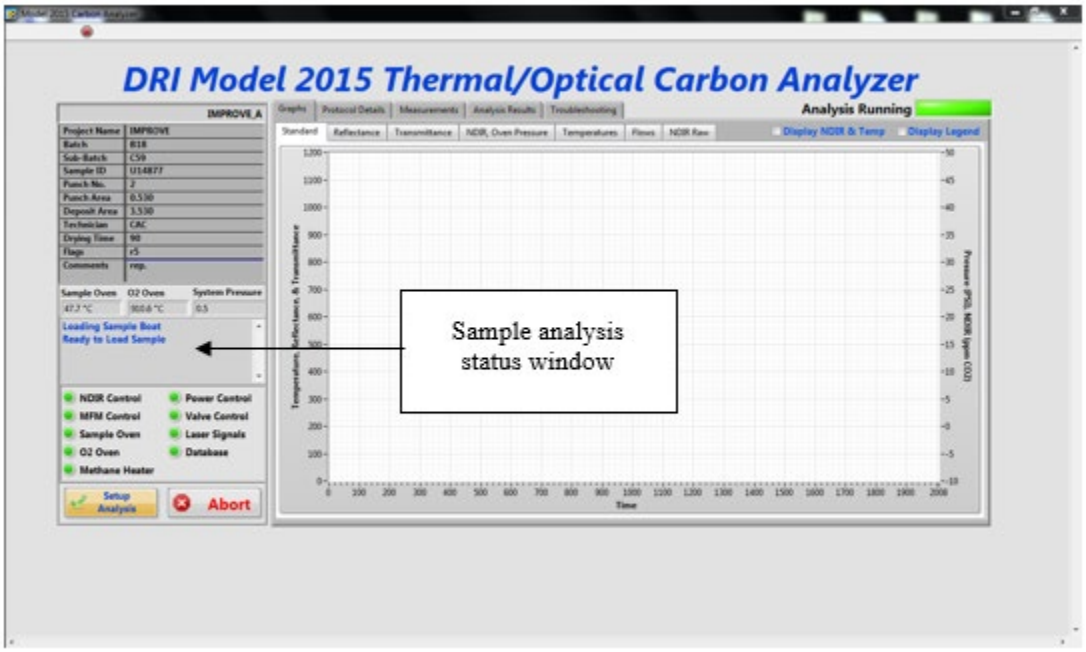


Figure 4-5. Sample analysis status screen

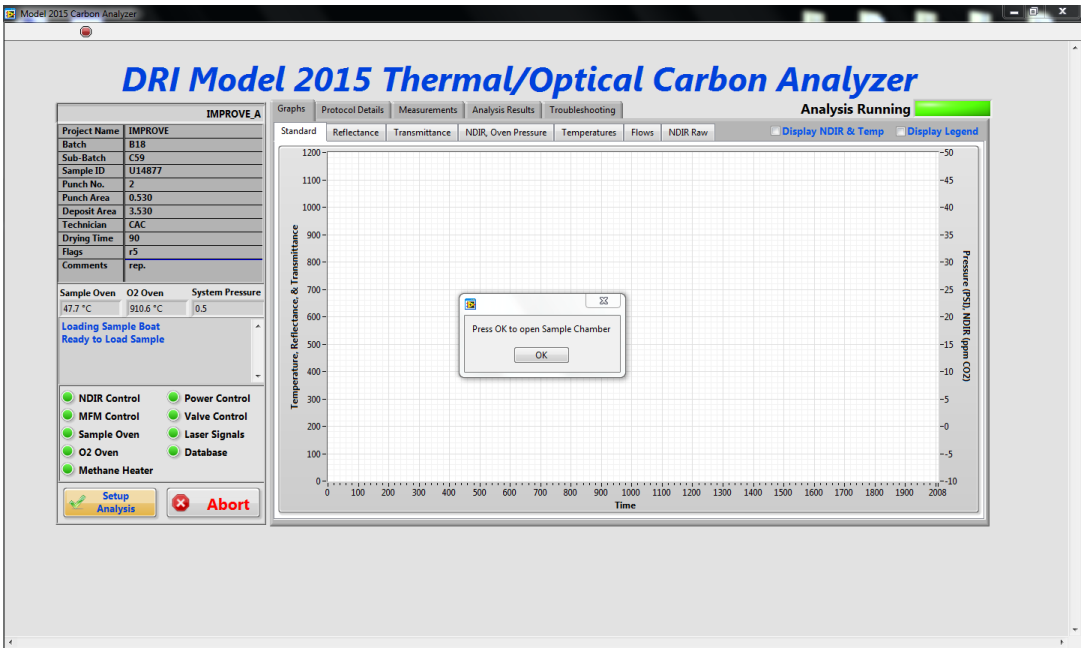


Figure 4-6. Sample analysis status screen with prompt to open the sample chamber.

4.2.3 OC/EC Analysis

- 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.
- Use tweezers to remove any existing punch from a previous analysis on the sample boat. Remove the new punch from the punch tool and load it into the boat, *deposit side up.*
- Click “OK” button in Figure 4-7 after loading the punch and the analysis will proceed.
- The status of the analysis can be monitored in the status window as indicated in Figure 4-5. The thermogram will appear in the Standard graphic window. Check from time to time during the run to verify if the temperature, optical, and carbon signals are normal. Pay special attention to see if any indicator in Figure 4.5 is red instead of green.
- Wipe the tweezers, flat glass plate, and punching tool with a clean lint-free wipe.

- When the analysis is complete, enter appropriate end-of-run flags and comments in the form shown in Figure 4-8 and click “Continue”.

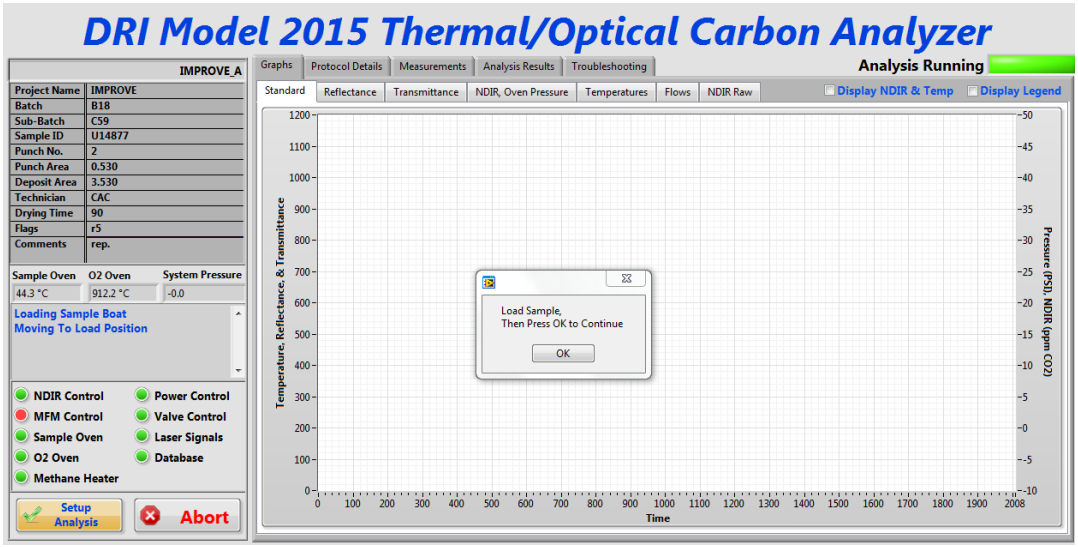


Figure 4-7. Sample analysis status screen with prompt to load the sample punch.

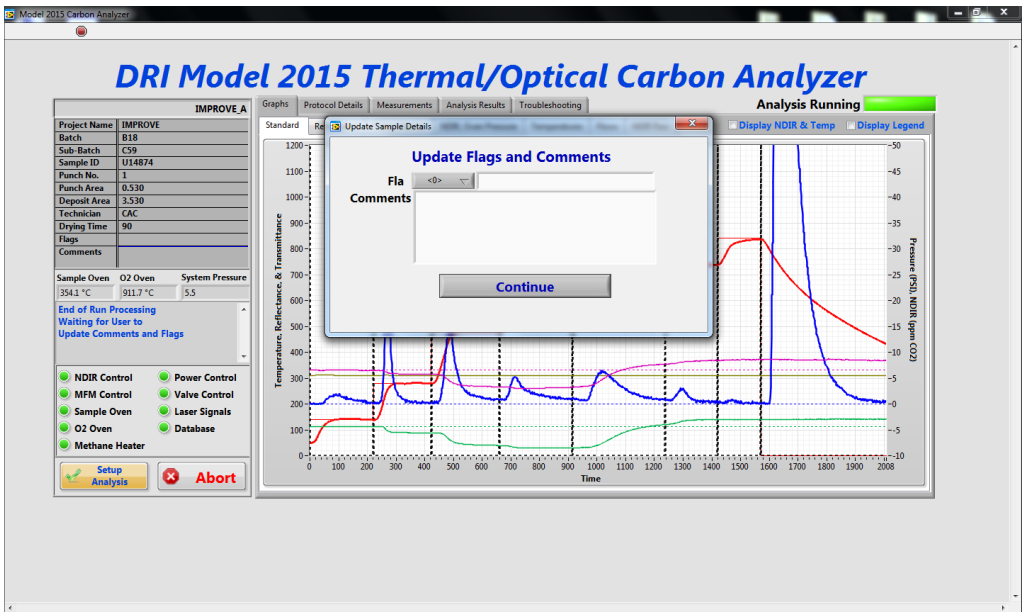


Figure 4-8. End of run form for entering post-analysis flags and comments.

4.2.4 **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 results documents 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. Take the following actions:

- Examine the tabular results document (Figure 4-9) to confirm that the sample details were entered correctly, instrument responses are correct, and the calibration peak counts are within specifications (Section 3.2).
- Examine the graphical thermogram document (Figure 4-10) to confirm that the NDIR, lasers, and sample oven temperature profile are normal. Pay special attention to NDIR baseline, reflectance and transmittance drift and signal level, sample oven temperature overshoot, and calibration peak value.
- Mark the analysis date and analyzer number 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. Mark thermogram for any coloration that indicates minerals or unburnt material.
- Repeat the above steps for additional analysis runs.

Run ID	2018102113064342	Analyzer ID	42	Carbon Fractions	NDIR Initial	O1TC	1.10046		
Protocol	IMPROVE_A	Start Time	13:06:49		0.0484670	O2TC	4.68126		
Project Name	IMPROVE	Date	10/21/2018	Units: µg C/filter	NDIR Final	O3TC	11.1027		
Batch	B18	Carbon Cal. Slope	18.9110		0.330000	O4TC	5.13349		
SubBatch	R58	Carbon Cal. Intercept	0.00000			E1TC	4.00190		
Sample ID	U12672	Gas Transit Time	14	Cal Peak	16240.4	E2TC	1.53251		
Punch Number	1	Pyrolysis Bandwidth	0.00000			E3TC	0.00000		
Punch Area	0.530000	Noise Precision	3.00000	OC635TRC	25.74	Sum OC	22.0179		
Filter Dep. Area	3.53000	Int. Method	Sum	EC635TRC	1.81	Sum EC	5.53441		
Technician	CA	Int. Threshold	0.720000			Total Carbon			
Drying Time	90	Software Version	2015Mar02	System Pressure	5.50791		27.5524		

Laser Transmittance									
635nm	OP635TTC	4.29	OC635TTC	26.31	EC635TTC	1.24	LT 1 Initial	249.77	LT 1 Final 269.67
405nm	OP405TTC	4.77	OC405TTC	26.79	EC405TTC	0.77	LT 2 Initial	55.51	LT 2 Final 71.81
445nm	OP445TTC	4.68	OC445TTC	26.70	EC445TTC	0.86	LT 3 Initial	316.03	LT 3 Final 384.50
532nm	OP532TTC	4.62	OC532TTC	26.64	EC532TTC	0.91	LT 4 Initial	259.50	LT 4 Final 293.25
780nm	OP780TTC	3.86	OC780TTC	25.88	EC780TTC	1.67	LT 5 Initial	326.21	LT 5 Final 353.14
808nm	OP808TTC	3.73	OC808TTC	25.75	EC808TTC	1.80	LT 6 Initial	281.32	LT 6 Final 305.69
980nm	OP980TTC	3.35	OC980TTC	25.37	EC980TTC	2.19	LT 7 Initial	64.22	LT 7 Final 70.51

Laser Reflectance									
635nm	OP635TRC	3.72	OC635TRC	25.74	EC635TRC	1.81	LR 1 Initial	359.27	LR 1 Final 360.85
405nm	OP405TRC	3.99	OC405TRC	26.00	EC405TRC	1.55	LR 2 Initial	82.41	LR 2 Final 90.44
445nm	OP445TRC	3.86	OC445TRC	25.87	EC445TRC	1.68	LR 3 Initial	423.40	LR 3 Final 459.37
532nm	OP532TRC	4.14	OC532TRC	26.16	EC532TRC	1.39	LR 4 Initial	447.91	LR 4 Final 457.00
780nm	OP780TRC	3.31	OC780TRC	25.33	EC780TRC	2.23	LR 5 Initial	452.92	LR 5 Final 468.70
808nm	OP808TRC	3.35	OC808TRC	25.37	EC808TRC	2.19	LR 6 Initial	476.89	LR 6 Final 493.94
980nm	OP980TRC	3.37	OC980TRC	25.39	EC980TRC	2.16	LR 7 Initial	398.32	LR 7 Final 417.26

Figure 4-9. Example of tabular data results document of sample analysis.

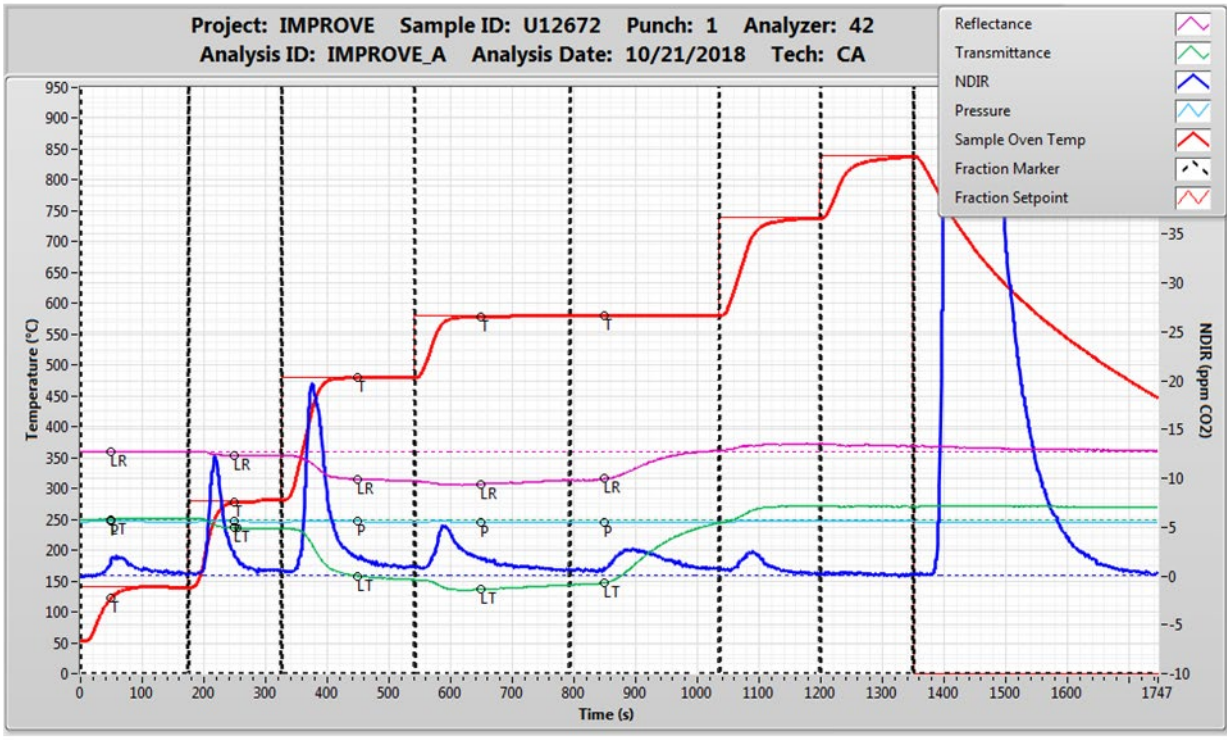


Figure 4-10. Example of graphical results document of sample analysis thermogram.

4.2.5 Special Analysis

4.2.5.1 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 # "YYYYmm" for the year and month and Sub-batch # "dd" for the day. The sample ID should be in the format "SBxx" where "xx" is the analyzer number (e.g. SB22 for analyzer number 22).
- Punch area and Deposit area should be "1".
- Calculated carbon concentrations from the system blank should not be more 0.2 µg carbon per cm^2. Values greater than this warrant an additional system blank or oven bake.

4.2.5.2 Carbonate Analysis

In the Enter Sample Details screen (Figure 4-4) enter the Sample ID, Punch #, Punch area, Deposit area, and other information. Select *IMPROVEA_Carbonate* analysis protocol.

- Follow the steps under Section 4.2.3 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 document with a tabular summary and a copy of the graph will be created (similar in format to Figure 4-9 and Figure 4-10). 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.

4.2.6 **Analyzer Shut-Down**

If analyzers are not in operation 24 hours a day, shut down the analyzers at the end of each day 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 *AutoCalib protocol*, and record the calibration peak counts following the schedule shown in Table 3-1. 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 *Carbon2015* software open.
- If desired, He/O_2 and CH_4 Cal Gas may be turned off with the toggle valves to conserve gases. However, all other gases should be left on as long as the oxidation oven is heated.
- 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.

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 blank 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 µg C/cm^2). If TC is > 0.2 µg, use the *Bake* protocol to bake oven, then repeat lab blank to check and see if TC is < 0.2 µg. Follow Table 4-1 for the suggested naming convention of different analysis types

__ Run appropriate morning calibration for that day (Sucrose, KHP, CO_2, Auto-calibration, System Blank) following the schedule in Table 3-1 and record the results on the Daily Check List.

__ During the evening (~6 PM), perform a second calibration as indicated by Table 3-1 and 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 run list

__ Input **correct** parameters on the sample details information form 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

__ Open the results document on the analyzer computer and **verify** it carefully after a run

__ Remove the analyzed punch from the analyzer and tape it to the logbook

__ **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. Detailed suggested metadata and protocols for analysis types.

Analysis Type	**Description of Purpose**	**Project Name**	**Batch**	**Sub-Batch**	**Sample ID**	**Protocol**
Laboratory Blank	Routine non-cleaning analysis of blank, clean, filter punch	LABBLK	YYYYmm	dd	LBxx	*TC_Only or IMPROVE_A*
System Blank	Non-cleaning filter-free analysis	SYSBLK	YYYYmm	dd	SBxx	*TC_Only or IMPROVE_A*
Cleaning Blank	Cleaning run to eliminate contamination issues	TESTBLK	YYYYmm	dd	TESTxx	*TC_Only or IMPROVE_A*
Oven Bake	Cleaning run to eliminate contamination issues	TESTBLK	YYYYmm	dd	BAKExx	*Bake*
Auto Calibration	Routine auto injection of internal standard	CALIB	YYYYmm	dd	Cxx	*Autocalib*
Carbon Injection (routine)	Routine carbon dioxide injection	CALIB	YYYYmm	dd	CIxx	*HeOnly*
Sucrose (routine)	Routine sucrose test	CALIB	YYYYmm	dd	SUxx	*TC_Only or IMPROVE_A*
KHP (routine)	Routine KHP test	CALIB	YYYYmm	dd	KHPxx	*TC_Only or IMPROVE_A*
Carbon Injection (calibration)	Carbon dioxide injection for carbon calibration	CALIB	CARBON	YYYYmmdd	CIxx_vvvv	*HeOnly*
Carbon Injection (calibration)	Methane injection for carbon calibration	CALIB	CARBON	YYYYmmdd	MIxx_vvvv	*HeOnly*
Sucrose (calibration)	Sucrose analysis for carbon calibration	CALIB	CARBON	YYYYmmdd	SUxx_vv	*TC_Only or IMPROVE_A*
KHP (calibration)	KHP analysis for carbon calibration	CALIB	CARBON	YYYYmmdd	KHPxx_vv	*TC_Only or IMPROVE_A*

5 QUANTIFICATION

5.1 Measurement Calculations

Section 3.4.7 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 minimum 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:

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

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

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 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 Monday and laboratory blanks at the beginning of each day (see Table 3-1) to 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 3.2, the calibration peak at the end of each analysis run serves as an internal standard; the integrated area under the calibration peak serves as a measure of analyzer performance. In addition, the daily injections of two calibration standards further serve as internal controls. 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 *AutoCalib* protocol allows the condition of the oxidizer 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. A random number generator is used to select the sample from each group of ten, and the replicate is run immediately after each group of ten is completed. The next available analyzer is used for the replicate run, 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 $\mu g/cm^2$ values for OC, EC and TC are compared with the original run. The values should meet the following criteria:

Range	**Criteria**
Avg of OC or TC < 10 $\mu g/cm^2$	< ±1.0 $\mu g/cm^2$
Avg of OC or TC ≥ 10 $\mu g/cm^2$	< 10 % of avg of the 2 values
Avg of EC < 10 $\mu g/cm^2$	< ±2.0 $\mu g/cm^2$
Avg of EC ≥ 10 $\mu g/cm^2$	< 20 % of avg of the 2 values

Notice that the criteria converge at 10 $\mu g/cm^2$. Replicates that do not meet the above criteria must be investigated for analyzer or sample anomalies. Analyzer anomalies include system leaks, poor NDIR response (as reflected in the calibration peak areas), poor laser signal response (affecting the splits between OC and EC), and oven ramping failure. 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.

6.4 Control Charts and Procedures

All analysis data is stored on an SQL Server database and is accessible to provide data for projects, calibration summaries, calibration trends, and maintenance information. The laboratory technicians and the laboratory supervisor closely monitor these reports to ensure QC criteria are being met or that corrective action is promptly taking place.

6.4.1 **Analysis Flags**

During Level 0 validation (see Section 6.4.2), analysis problems are noted in the database and errors in pre-analysis data entry (e.g., filter ID, punch size, deposit area) are corrected. Flags are also applied to the database (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 of the database unless a subcode is included which provides additional information (such as v3-“potential contamination”).

6.4.2 **Daily Validation**

Level 0 validation is performed by manually checking the tabular and thermogram documents 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 results document (Figure 4-9):

- All analysis runs have been successfully uploaded to the SQL Server database.
- The filter ID and Punch # are correct.
- Relevant flags for field blanks and replicates are present.
- For calibration runs, the tabular and thermogram documents are checked to make sure the values are within specified limits.
- The analysis date and time is correct.
- The punch and deposit areas are correct.
- The end-of-run internal calibration peak area is in the correct range (Section 3.2).
- Calculated carbon values for calibration runs are within the acceptable ranges for that analyzer.

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

Table 6-1. Common laboratory analysis flags.

Validation Flag	Sub Flag	Description
a		Sample received with punch removed
	a1	Sample received with one punch removed
	a2	Sample received with two punches removed
	a3	Sample received with three punches removed
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.
	d1	Dropped sample punch prior to analysis.
	d2	Dropped sample filter prior to analysis.
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.
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

Table 6-1 (continued). Common laboratory analysis flags.

Validation Flag	Sub Flag	Description
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 phenomenon may result in increased uncertainty of the organic/elemental carbon split. Total carbon measurements are likely unaffected.
	m4	NDIR 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.
o		Valid. Quality check(s) outside typical guidelines.
	o1	Valid. Multiple point calibration outside typical quality guidelines.
	o2	Valid. Calibration peak outside typical quality guidelines.
	o3	Valid. Auto calibration outside typical quality guidelines.
	o4	Valid. Manual injection outside typical quality guidelines.
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). Common laboratory analysis flags.

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.
t		Parameter changes which require reprocessing raw data.
	t1	Reprocessed, integration threshold changed.
	t2	Reprocessed, integration method changed.
	t3	Reprocessed, gas transit time changed.
	t4	Reprocessed, mass flow meter flow calibration(s) changed.
	t5	Reprocessed, laser calibration(s) changed.
	t6	Reprocessed, temperature calibration(s) changed.
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

The thermograms are checked for the following (Figure 4-10):

- The initial NDIR baseline is flat, indicating that the analyzer has been thoroughly purged before analysis began.
- The final NDIR baseline does not have excessive drift from the baseline.

- Unless the sample is very heavily or lightly loaded, 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 laser signal during OC4 stage should be nearly flat for most samples. If an analyzer shows consistent early split for samples and increasing laser signal during OC4 for sucrose runs, then the analyzer need be checked for laser stability and leak.
- 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.
- Relevant flags and/or comments for each detected issue are added to the database.

If examination of the tabular and thermogram documents results in a decision that a sample should be reanalyzed, then it should be marked in the database for reanalysis and a rerun list should be generated. This list should be posted 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.

6.4.3 **Validation of Final Data File**

The following steps are followed to perform Level I data validation and create an Excel file containing the final carbon data values:

- Raw data values are uploaded to the SQL Server database for each analysis run.
- This data is then available to lab personnel through a Microsoft Access interface (Figure 6-1). This interface is used to display data as well as the results of automated validation checks. It also creates the Excel reporting file containing sample data, concentrations, and measurement uncertainties. All of this is done by clicking the relevant buttons on the interface after inputting the desired sample subset in the boxes on the left-hand side.
- Begin validation by matching the filters listed on the analysis run list with the analyses uploaded to the database. There must be at least one analysis entry for every filter listed on the analysis run list. This can be done by running the *Check Missing Runs* query or inspecting the *Initial Analysis Report.*
- If any samples are missing, they could have either 1) failed to upload, or 2) are mislabeled so they are not showing up in the current sample set. If a handful in a row are missing, it is most likely due to a failed upload due to a server connection interruption.

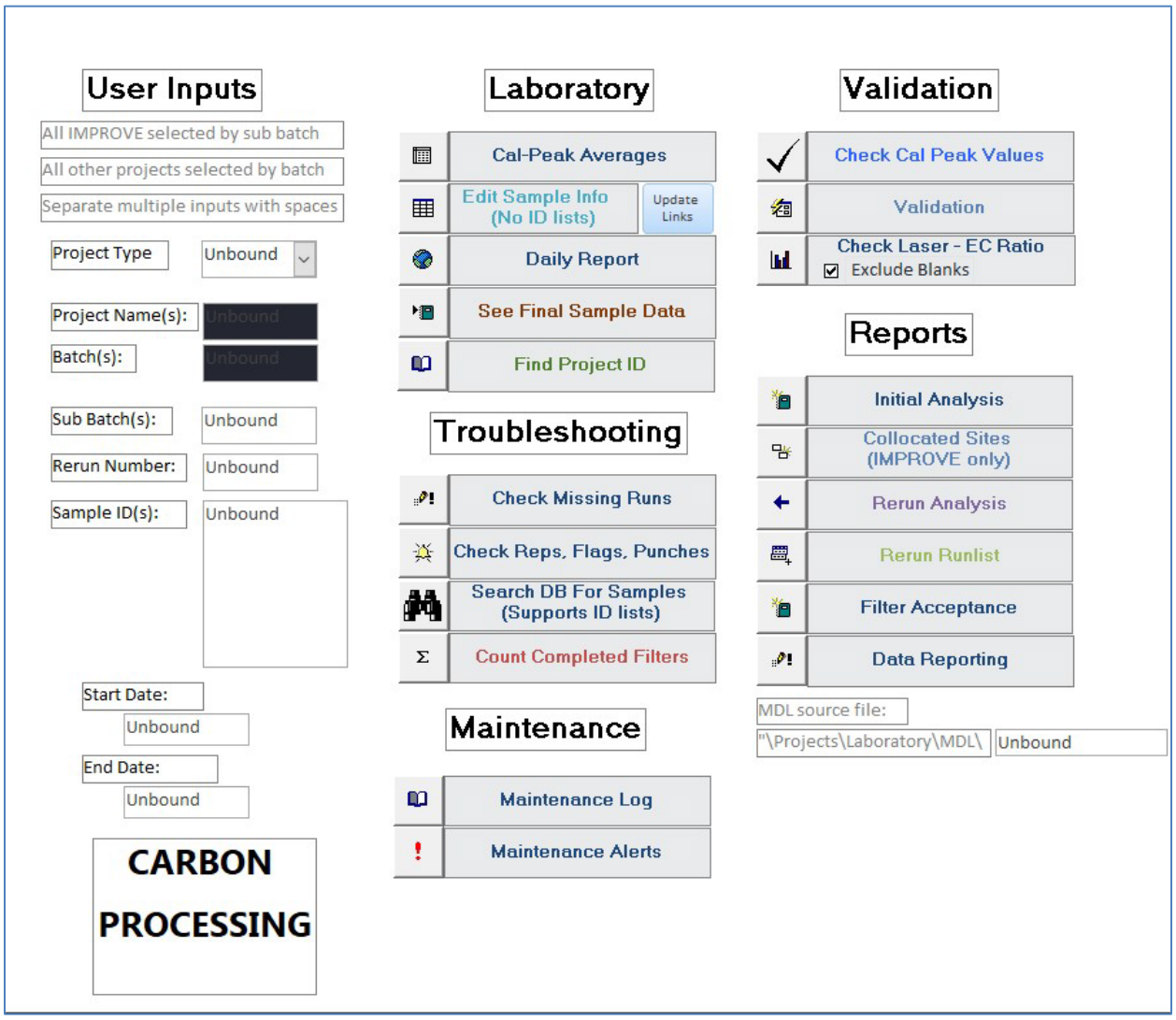


Figure 6-1. Microsoft Access interface for carbon data validation, analysis, and reporting.

- To determine the cause of missing samples, list the missing ID(s) in the *Sample ID(s)* box on the left of the interface. Several IDs must be separated by individual spaces. Then run the *Search DB For Samples* query. This will search the entire database (as opposed to the currently selected sample set) for the entered IDs. If the missing sample(s) appear, identify which field(s) are incorrect for each sample. This field can then be corrected using the *Edit Sample Info* query. IMPORTANT: if the project name is incorrect, the project ID must be changed, NOT the project name! Find the correct project ID using the *Find Project ID* query.

- If the missing samples do not appear, either the sample ID is incorrect, or they were not properly uploaded. To find incorrect sample IDs, look 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 results document, due to the sorting process. The analysis notebooks found at each analyzer may also give clues to where to find the sample. Check the analysis run list for the relevant Analyzer # and analysis date.
- A failed sample upload can occur due to an aborted run or a faulty server connection. Reupload or confirm a sample abort by inspecting the relevant analyzer's local database. If a punch was aborted, add a comment stating the reason to the next punch taken from the sample.
- Confirm all replicates are uploaded and that both replicates and field blanks are flagged correctly by running the *Check Reps, Flags, Punches* query. Any problem discovered can be corrected through use of the *Edit Sample Info* query and the missing sample procedures outlined previously. All punches taken from the filters MUST be accounted for and documented in the file.
- Verify the deposit and punch areas are correct by scanning the relevant columns in the *Edit Sample Info* query. The correct value can be found at the top of the analysis run list. This can be edited here as well, make sure any created reports are re-created after doing so as the concentration values will be affected.
- Check Cal Peak areas using the *Check Cal Peak Values* query. Add a comment for samples with Cal Peaks significantly higher or lower than the rest for each analyzer.
- Verify and resolve all operator comments and analysis flags.
  - Review analysis flags added to the database or analysis run list by the operator. 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.
- Print the *Initial Analysis Report* and (possibly) the *Collocated Sites Report* now that all samples have been checked.
- Open the *Validation Report* and review for suspicious sample data. Anything of interest can be written on the printed *Initial Analysis Report*.
- Run the *Check Laser - EC Ratio* query and inspect the resulting graph for unusual ratio values for the ratio of laser attenuation to EC. Anything of interest can be written on the printed *Initial Analysis Report*.
- Now that all useful information is on the printed *Initial Analysis Report,* review it for final determination of analyses to be voided and/or rerun.

- Scan the TC column 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.
- A comparison of replicates against original runs can be seen in the middle of the printed report. "O" symbols represent a failed comparison while "I" symbols represent a passed comparison. The values are based on the criteria in Section 6.3. Circle any "O"s for further investigation.
- Check the OC/TC ratio. 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.
- For the IMPROVE network, scan blanks for OC being greater than 3.95 × deposit area and for EC greater than the deposit area. Rerun any unusually high blanks.
- When applicable, 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 $\leq$ 3.8 μg/filter. OC should be less than or equal to 18 μg/filter. Circle any records that require further investigation. Check for visible loading, if necessary.
- Once all suspicious values have been noted, review the thermograms of each suspect sample to determine if it should be voided and/or reran. Reruns are labeled by placing a number (e.g., 1) representing the current rerun iteration in the *rerun number* column of the *Edit Sample Info* table.
- 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, confirm all reruns, flags, and comments have been entered into the database. Then print the *Rerun Runlist* and post it in the carbon room and have the reruns done as soon as possible.
- Review the data from the reruns, looking for inconsistencies and missing reruns (repeat validation up until this point on rerun data). This can be done using the *Rerun Analysis Report* in place of the *Initial Analysis Report.* Confirm that the reasons for the rerun have been addressed. Previous runs must be flagged as invalid, or the reruns flagged as replicates.
- Finally, confirm the number of completed samples matches the analysis run list by running the *Count Completed Filters* query. Then run the *Data Reporting* query to create an Excel file for reporting the sample data.

Table 6-2. Laboratory carbon analysis technician temporary data validation flags.

Flag	Description
	General Flags
v	Invalid run
r	Replicate
b	Blank
m	Punch discolored after analysis
i	Inhomogeneous deposit
f	Filter media damaged
g	Sample deposit damaged
d	Sample dropped
n	Foreign substance on filter
w	Sample wet
	Specific Flags
v5	Void due to instrument error
v3	Void due to potential contamination
v1	Does not compare with other replicates
r1	Replicate on same analyzer
r5	Replicate on different analyzer
b1	Field Blank
m2	Red punch discoloration after analysis
m5	Grey punch discoloration after analysis
d1	Dropped punch before analysis

6.5 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 3-1 for the daily calibration schedule.

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

QA/QC Activity	Calibration Standard and Range	Calibration Frequency	Acceptance Criteria	Corrective Action
System Blank Check	NA[a]	Once per week	<0.2 µg C	Check instrument.
Laboratory Blank Check	NA[a]	Beginning of analysis day	<0.2 µg C	Check instrument and filter punch and rebake
End-of-Run Internal Calibration Peak Area Check	NIST-traceable 5% CH_4/He gas standard; 20 µg C (6-port valve injection loop, 1000 µl)	Every analysis	Typical counts 14,000-25,000 and 90-110% of average calibration peak area of the previous day.[b]	Void analysis result; check flowrates, leak, and 6-port valve temperature; conduct an auto-calibration; and repeat analysis with second filter punch.
Auto-Calibration Check [e]	NIST-traceable 5% CH_4/He gas standard; 20 µg C (Carle valve injection loop, 1000 µl)	Alternating beginning or end of each analysis day [e]	Relative standard deviation of the three injection peaks <10%.[b]	Troubleshoot and correct system before analyzing samples.
Manual Gas Injection Calibration [e]	NIST-traceable 5% CO_2/He gas standards; 20 µg C (Certified gas-tight syringe, 1000 µl)	Maximum of four times a week [d,e]	<±5% of calculated standards based on individual tank specifications	Troubleshoot and correct system before analyzing samples.
Sucrose Calibration Check	10µL of 1200 ppm C sucrose standard; 12 µg C	Alternating days	11-13 µg C	Troubleshoot and correct system before analyzing samples.
Potassium Hydrogen Phthalate (KHP) Calibration Check	10µL of 1200 ppm C KHP standard; 12 µg C	Alternating days	11-13 µg C	Troubleshoot and correct system before analyzing samples.
Semiannual Performance Verification	10 µl of 150 ppm and 1200 ppm KHP or sucrose solution; 20 µl of 150 ppm and 1200 ppm KHP or sucrose solution	Every six months	The calibration slope is within ± 10% of previous slope.	Troubleshoot and conduct full carbon calibration if necessary.
Multiple Point Calibrations	150 ppm C Potassium Hydrogen Phthalate (KHP) and Sucrose; 1200 ppm C Potassium Hydrogen Phthalate (KHP) and Sucrose; NIST-traceable 5% CH4/He, and NIST-traceable 5% CO2/He gas standards; 1.5-24 µg C for KHP and Sucrose; 4-20 µg C for CH4 and CO2	Every 12 months or after major instrument repair	The carbon/signal ratio (slope) for each calibration point is within ± 10% of average ratio for all calibration points in the set.	Redo calibration for individual points with slopes differing by > ±10% from the average slope. If the overall slope differs from previous slope of the analyzer by >± 10%, verify if major maintenance has occurred. Troubleshoot instrument and repeat calibration if necessary.

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

QA/QC Activity	Calibration Standard and Range	Calibration Frequency	Acceptance Criteria	Corrective Action
Sample Replicates (on the same or a different analyzer)	NA	Every 10 analyses	<±10% of avg. of two values when avg of OC or TC ≥10 µg C/cm^2 <±20% of avg. of two values when avg of EC ≥ 10µg C/cm^2 or <±1 µg/cm^2 when avg of OC or TC <10 µg C/cm^2 <±2 µg/cm2 when avg of EC <10µg C/cm^2.	Investigate instrument and sample anomalies and rerun replicate.
Temperature Calibrations	NIST-traceable thermocouple	Every six months, or whenever the thermocouple is replaced	Linear relationship between analyzer and NIST-traceable thermocouple values with R^2>0.99.	Troubleshoot instrument and repeat calibration until results are within stated tolerances.
Oxygen Level in Helium Atmosphere (using LD8000[c])	25 ppm, 50 ppm, 75 ppm and 100 ppm certified gas standards	Every 12 months	< 100 ppm O_2	Replace the He cylinder and/or O_2 scrubber.

[a] NA: Not Applicable.
[b] Typical but not required calibration guidelines
[c] Trace impurity analyzer (Model LD8000, Rotronic Instruments Corporation, Inc, Hauppauge, NY, USA)
[d] Assuming operation on a 24 hour/7 day per week schedule
[e] Only applicable following periods of non-operation in laboratory

7 REFERENCES

Andreae, M.O.; Gelencser, A. (2006). Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols. *Atmos. Chem. Phys.*, 6:3131-3148.

Chen, L.-W.A.; Chow, J.C.; Watson, J.G.; Moosmüller, H.; Arnott, W.P. (2004). Modeling reflectance and transmittance of quartz-fiber filter samples containing elemental carbon particles: Implications for thermal/optical analysis. *J. Aerosol Sci.*, 35(6):765-780.

Chen, L.-W.A.; Chow, J.C.; Watson, J.G.; Schichtel, B.A. (2012). Consistency of long-term elemental carbon trends from thermal and optical measurements in the IMPROVE network. *Atmos. Meas. Tech.*, 5:2329-2338.

Chen, L.-W.A.; Chow, J.C.; Wang, X.L.; Robles, J.A.; Sumlin, B.J.; Lowenthal, D.H.; Watson, J.G. (2015). Multi-wavelength optical measurement to enhance thermal/optical analysis for carbonaceous aerosol. *Atmos. Meas. Tech.* ., 8:451-461.

Chow, J.C.; Watson, J.G.; Pritchett, L.C.; Pierson, W.R.; Frazier, C.A.; Purcell, R.G. (1993). The DRI Thermal/Optical Reflectance carbon analysis system: Description, evaluation and applications in U.S. air quality studies. *Atmos. Environ.*, 27A(8):1185-1201.

Chow, J.C.; Watson, J.G.; Crow, D.; Lowenthal, D.H.; Merrifield, T.M. (2001). Comparison of IMPROVE and NIOSH carbon measurements. *Aerosol Sci. Technol.*, 34(1):23-34.

Chow, J.C.; Watson, J.G. (2002). $PM_{2.5}$ carbonate concentrations at regionally representative Interagency Monitoring of Protected Visual Environment sites. *J. Geophys. Res.*, 107(D21):ICC 6-1-ICC 6-9.

Chow, J.C.; Watson, J.G.; Chen, L.-W.A.; Arnott, W.P.; Moosmüller, H.; Fung, K.K. (2004). Equivalence of elemental carbon by Thermal/Optical Reflectance and Transmittance with different temperature protocols. *Environ. Sci. Technol.*, 38(16):4414-4422.

Chow, J.C.; Watson, J.G.; Chen, L.-W.A.; Paredes-Miranda, G.; Chang, M.-C.O.; Trimble, D.L.; Fung, K.K.; Zhang, H.; Yu, J.Z. (2005). Refining temperature measures in thermal/optical carbon analysis. *Atmos. Chem. Phys.*, 5(4):2961-2972.

Chow, J.C.; Watson, J.G.; Chen, L.-W.A.; Chang, M.-C.O.; Robinson, N.F.; Trimble, D.L.; Kohl, S.D. (2007). The IMPROVE_A temperature protocol for thermal/optical carbon analysis: Maintaining consistency with a long-term database. *J. Air Waste Manage. Assoc.*, 57(9):1014-1023.

Chow, J.C.; Watson, J.G.; Robles, J.; Wang, X.L.; Chen, L.-W.A.; Trimble, D.L.; Kohl, S.D.; Tropp, R.J.; Fung, K.K. (2011). Quality assurance and quality control for thermal/optical analysis of aerosol samples for organic and elemental carbon. *Anal. Bioanal. Chem.*, 401(10):3141-3152.

Chow, J.C.; Wang, X.L.; Sumlin, B.J.; Gronstal, S.B.; Chen, L.-W.A.; Trimble, D.L.; Kohl, S.D.; Mayorga, S.R.; Riggio, G.M.; Hurbain, P.R.; Johnson, M.; Zimmermann, R.; Watson, J.G. (2015). Optical calibration and equivalence of a multiwavelength thermal/optical carbon analyzer. *AAQR*, 15(4):1145-1159.

Chow, J.C., Watson, J.G., Green, M.C., Wang, X.L., Chen, L.-W.A., Trimble, D.L., Cropper, P.M., Kohl, S.D., Gronstal, S.B., (2018). Separation of brown carbon from black carbon for IMPROVE and CSN $PM_{2.5}$ samples. Journal of the Air & Waste Management Association, 68, 494-510.

Heal, M.R.; Quincey, P.G. (2012). The relationship between black carbon concentration and black smoke: A more general approach. *Atmos. Environ.*, 54:538-544.

Johnson, R.L. (1981). Development and evaluation of a thermal/optical method for the analysis of carbonaceous aerosol. Oregon Graduate Center.

Johnson, R.L.; Shah, J.J.; Cary, R.A.; Huntzicker, J.J. (1981). An automated thermal-optical method for the analysis of carbonaceous aerosol. In *Atmospheric Aerosol: Source/Air Quality Relationships*, Macias, E. S., Hopke, P. K., Eds.; American Chemical Society: Washington, DC, 223-233

Lin, C.I.; Friedlander, S.K. (1988). Soot oxidation in fibrous filters. 2. Effects of temperature, oxygen partial pressure, and sodium additives. *Langmuir*, 4(4):898-903.

Moosmüller, H.; Chakrabarty, R.K.; Arnott, W.P. (2009). Aerosol light absorption and its measurement: A review. *J. Quant. Spectrosc. Radiat. Transfer*, 110:844-878.

Novakov, T. (1981). Microchemical characterization of aerosols. In *Nature, Air and Methods of Microchemistry*, Malissa, H., Grasserbauer, M., Belcher, R., Eds.; Springer-Verlag, Wein: Graz, Austria, 141-165

Novakov, T. (1982). Soot in the atmosphere. In *Particulate Carbon: Atmospheric Life Cycle*, Wolff, G. T., Klimisch, R. L., Eds.; Plenum Press: New York, NY, 19-41

Rau, J.A. (1986). Residential wood combustion aerosol characterization as a function of size and source apportionment using chemical mass balance modeling. Oregon Graduate Center.

Rosen, H.; Hansen, A.D.A.; Dod, R.L.; Gundel, L.A.; Novakov, T. (1982). Graphitic carbon in urban environments and the Arctic. In *Particulate Carbon: Atmospheric Life Cycle*, Wolff, G. T., Klimisch, R. L., Eds.; Plenum Press: New York, NY, 273-294

Sandradewi, J.; Prevot, A.S.H.; Szidat, S.; Perron, N.; Alfarra, M.R.; Lanz, V.A.; Weingartner, E.; Baltensperger, U. (2008). Using aerosol light absorption measurements for the quantitative determination of wood burning and traffic emission contributions to particulate matter. *Environ. Sci. Technol.*, 42(9):3316-3323.

Watson, J.G.; Chow, J.C.; Chen, L.-W.A. (2005). Summary of organic and elemental carbon/black carbon analysis methods and intercomparisons. *AAQR*, 5(1):65-102.

8 CHANGE DOCUMENTATION

3/4/2015: New SOP 2-226r0
1/25/2016: Updated MDL based on 280 blank samples ran on #21
8/20/2018: Added alternate text to all images to make them 508 compliant, replaced Figures 3-1 and 4-10 with figures with labeled axis
11/21/2018:
- Added reference (Chow et al., 2018)
- Grammatical edits
- Updated page numbers on Table of Contents, List of Figures, List of Tables
- Deleted Tempilaq procedures, text and figures; updated with NIST-traceable thermocouple procedures
- Updated parts list
- Removed laser split information
- Removed reference to O_2 detector
- Updated Quality Control requirements and guidelines for Model 2015 analysis (summarized in Table 6.3)
- Updated figures and charts with current images
- Updated daily calibration schedule to include KHP on Saturdays
- Added information on purchasing sucrose and KHP standards in lieu of preparing them in the laboratory
- Updated flags table (added a, t, and o flag group)
- Made all new images 508 compliant

12/31/2019:
- Updated Table 3.2, Figure 3.2 with more current images
- Updated low point carbon calibration standards
- Updated daily calibration schedule to reflect continuous operation vs non-continuous operations
- Grammatical edits
- Updated quality control Table 6.3 wording
- Updated page numbers on Table of Contents, List of Figures, List of Tables
- Updated headers

2/9/2021:
- Updated Section 1.5 to include current MDL values using 2020 data, explanation of how MDL values are calculated, and how frequently MDL values should be updated
- Updated quality control Table 6.3 wording
- Updated oxygen analyzer instrument in quality control Table 6.3
- Added additional oxidation agent manufacturer

10/1/2021:
- Added a section for safety precautions
- Generalized MnO_2 to oxidizer
- Added semiannual performance verification and changed the full maintenance (oven replacement) frequency from semiannual to annual or as needed
- Updated Section 6 “Quality Control” to reflect updated data validation/processing software.

12/13/2021 r7:
- Updated MDL based on 1089 lab blanks (all ran during 2021 on all analyzers).
- Removed printing thermogram from QA procedure; QA is now done on digital version.

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 NDIR peak resulting from the automatic injection of CO_2 calibration gas 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:

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

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.
NDIR	NonDispersive Infra-Red Detector
NDIR 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 NDIR.
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.
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
ΔT	Temperature Deviation

APPENDIX B: Basic Troubleshooting Guide

The following procedures describe fixes to address commonly observed issues during the operation of the Model 2015 Multiwavelength Carbon Analyzer

B.1 Persistent Leaks

Failure to pass leak check (Section 4.1.1) 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
  - In the Calibration Control screen (Figure 4-2), set the sample boat position to “Load”.
  - Detach the orange breech O-ring. Clean the area around the breech where the O-ring sits.
  - Install new breech O-ring. Set the sample boat position 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 sample boat position to the “Load” position.
- Remove any punch on the sample boat. Test that the boat is tightly coupled to the thermocouple pushrod. Tighten boat screw if it loose.
- Set the sample boat position 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.

- Check that the boat is tightly coupled to the thermocouple pushrod.
- Tighten boat screw if loose.
- If leak-free, check if the flow rates of all gases are correct. Measure and adjust the CH_4 flow to be ~10 mL/min.
- Use a thermocouple to measure the temperature of the 6-port injection valve to make sure the temperature is close to 50 ºC. Make sure the temperature sensor is tightly secured on the 6-port injection valve.
- Run an automated routine calibration (Section 3.3.1) to determine if the three CH_4 injections are comparable.
- Manually inject 1000 µL CH_4 and compare with the auto injection by the 6-port injection valve. If the manual injection results larger peak area than the auto injection, it's likely that there is a leak in connections around 6-port injection valve, or the temperature of the valve heater is too high.