

Quality assurance and quality control for thermal/optical analysis of aerosol samples for organic and elemental carbon

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Abstract Accurate, precise, and valid organic and elemental carbon (OC and EC, respectively) measurements require more effort than the routine analysis of ambient aerosol and source samples. This paper documents the quality assurance (QA) and quality control (QC) procedures that should be implemented to ensure consistency of OC and EC measurements. Prior to field sampling, the appropriate filter substrate must be selected and tested for sampling effectiveness. Unexposed filters are pre-fired to remove contaminants and acceptance tested. After sampling, filters must be stored in the laboratory in clean, labeled containers under refrigeration ($<4^{\circ}\text{C}$) to minimize loss of semi-volatile OC. QA activities include participation in laboratory accreditation programs, external system audits, and interlaboratory comparisons. For thermal/optical carbon analyses, periodic QC tests include calibration of the flame ionization detector with different types of carbon standards, thermogram inspection, replicate analyses, quantification of trace oxygen concentrations (<100 ppmv) in the helium

atmosphere, and calibration of the sample temperature sensor. These established QA/QC procedures are applicable to aerosol sampling and analysis for carbon and other chemical components.

Keywords Thermal/optical carbon analysis · IMPROVE_A protocol · Aerosol · Organic carbon · Elemental carbon · Pyrolysis · Quality assurance · Quality control

Introduction

Organic and elemental carbon (OC and EC, respectively) are important components of suspended particulate matter (PM), especially the respirable fraction with aerodynamic diameters (d_p) of less than $2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$). Excessive OC and EC concentrations can adversely affect human health [1–3], visibility [4, 5], climate [6–8], materials [9–11], and biotic systems [12–16]. Bioaerosols such as plant wax, insect parts, spores, pollens, fungi, and endotoxins can be important contributors to the OC fraction(s) [12–16]. The ultrafine-size ($d_p < 100$ nm) fraction also contains OC and EC [17, 18], and the fraction of PM carbon increases as particle size decreases [3]. OC and EC are measured in air quality monitoring networks and special studies using more than 20 variations on the evolved gas analysis (EGA) method [19]. These methods have been found to produce equivalent values for total carbon ($\text{TC} = \text{OC} + \text{EC}$), but dissimilar values for OC and EC.

Ambient air and source emission samples are collected onto a heat-resistant filter substrate and a portion of each filter is submitted to EGA for carbon determination. During heating under various temperatures and atmospheres, PM carbon in the sample volatilizes and combusts to carbon-containing gases that are oxidized to carbon dioxide (CO_2).

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The evolved CO₂ may be either directly determined by a non-dispersive infrared detector, or reduced to methane (CH₄) and determined by a flame ionization detector (FID) with lower detection limits. Since 1987, the Interagency Monitoring of Protected Visual Environments (IMPROVE) EGA method [20, 21] has been applied to (1) >300,000 samples (1987–2010) in the US non-urban IMPROVE network [22, 23], (2) >40,000 samples (2007–2010) in the US Chemical Speciation Network (CSN [24]), and (3) >150,000 other samples (1987–2010) from other ambient and source characterization studies. An example of an IMPROVE_A [21] thermogram is shown in Fig. 1.

When sample temperatures exceeded ~350 °C in an inert helium (He) atmosphere during EGA, Huntzicker et al. [25] noticed a visible darkening of the PM filter deposit, which was attributed to pyrolysis of OC to EC. To correct this artifact, a helium-neon (He-Ne) laser beam ($\lambda=632.8$ nm) was directed perpendicular to the PM deposit on the filter. The reflected light intensity decreased when the PM deposit pyrolyzed in the He atmosphere for OC analysis, but then increased when oxygen (O₂) was added to the He atmosphere for EC analysis, as shown in Fig. 1. Huntzicker et al. [25] reasoned that the carbon evolving after the reflected light intensity returned to its initial value equaled the EC in the PM deposit excluding the OC pyrolyzed during the analysis.

Turpin et al. [26] modified this thermal/optical reflectance (TOR) correction to a thermal/optical transmittance (TOT) correction to a thermal/optical transmittance

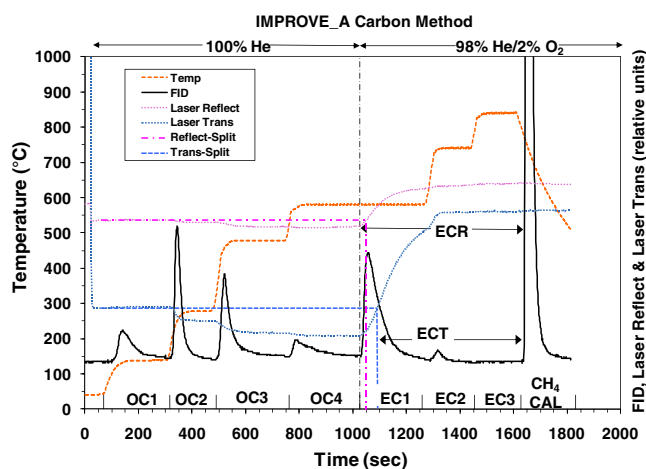


Fig. 1 Example of an IMPROVE_A thermal/optical reflectance and transmittance (TOR and TOT, respectively) thermogram. (Temperature-defined fractions are OC1–OC4, referring to organic carbon [OC] evolved from the filter punch in a pure He [$>99.999\%$] atmosphere at 140 °C, 280 °C, 480 °C, and 580 °C, respectively, and EC1–EC3, referring to elemental carbon [EC] evolved in a 98% He/2% O₂ atmosphere at 580 °C, 740 °C, and 840 °C, respectively.) The analysis temperature stays constant until each fraction is fully evolved; total analysis times are longer for more heavily loaded samples. Pyrolyzed OC (i.e., OP) is defined as the carbon measured after introduction of O₂ until reflectance (R) or transmittance (T) signals return to initial value at the commencement of analysis

(TOT) configuration in a continuous OC/EC monitor contemplating that the OC/EC split would be the same as that for TOR. The TOT method was subsequently incorporated into laboratory analyzers for PM filter samples [27–29]. This transmitted light signal is also shown in Fig. 1, but note that it returns to its initial value after the reflected light signal, thereby yielding a lower value for EC [30]. Chow et al. [31] and Chen et al. [32] attributed this phenomenon to charring of organic gases adsorbed by the quartz-fiber filter. The transmitted light is dominated by this charring within the filter, while the reflected light is dominated by charring of the sampled particles on the surface of the filter. Chow et al. [31] also found that the TOR OC/EC correction was insensitive to the temperature program, while the TOT correction resulted in varying EC values for different temperature programs.

The IMPROVE TOR and TOT protocols have been extensively characterized and compared to other methods [19–21, 33, 34]. However, the quality control (QC) measures and the results of their application over extended periods have not been previously documented. The goal of this paper is to outline these QC methods as applied to the IMPROVE_A carbon analysis protocol and report results achieved over several years of analysis. Procedures for sample chain-of-custody, including the preparation and handling of the filter substrate, as well as unification of data from the blank, sample, and replicate analyses, need to be followed prior to OC and EC analysis. Implementation of these QC tests ensures the reported ambient OC and EC concentrations have the specified accuracy, precision, and validity; such consistency allows the evaluation of long-term trends and the development of emission inventories. These QC procedures are appropriate for and applicable to other methods of aerosol sampling [35] and analysis [36] for carbon and other chemical components.

Filter preparation, receipt, and storage

After extensive evaluation, Pallflex QAT-UP quartz-fiber filters (Tissuquartz #2500QAT-UP; Pall Corporation, Putnam, CT, USA) are used for OC/EC sampling and analysis in the US long-term non-urban IMPROVE network and urban CSN following the IMPROVE_A_TOR protocol [21]. Quartz is the only material that is chemically stable and completely compatible with EGA methods [35, 36]. Quartz fibers tolerate temperatures as high as 1,000 °C without melting, assuring that all carbon is removed. The pure white color and diffuse transparency of the QAT-UP filters allow light to be reflected and transmitted, thereby permitting detection of OC pyrolysis during analysis by optical monitoring. The low flow

resistance of QAT-UP filters permits 22.8 L/min flow rates through 25 mm diameter filters. QAT-UP filters contain few contaminants (e.g., sodium chloride [NaCl] and/or trace metals) that can change the thermal evolution characteristics of collected carbon via catalytic reactions [37, 38]. Because quartz adsorbs organic vapors upon exposure to the atmosphere [31, 39–41], quartz-fiber backup filters and dynamic field blanks are used to quantify these artifacts [39, 41]. Quartz-fiber filters are brittle and may flake around the edges when loaded into a filter holder, and this flaking can negatively bias mass measurements. Gravimetric analysis is typically performed on parallel Teflon-membrane filters in most chemical speciation networks. The sampled portion of the quartz-fiber filter is not subject to mechanical stress and does not degrade during sampling.

Filter sampling effectiveness is periodically verified to assure that negligible fractions of the sampled particles pass through the filter. Sampling effectiveness is the fraction of particles removed by an inlet or filter as a function of size, and sampling efficiency is the fraction of mass removed by integrating the product of the sampling effectiveness and mass distribution functions [42, 43]. Sampling effectiveness for quartz-fiber filters has not been reported since Ellenbecker [44] showed an excess of 99% sampling efficiencies for 0.3 μm diameter dioctyl phthalate particles. Figure 2 illustrates the experimental setup used to test sampling effectiveness for a broader size range using neutralized submicron (40 nm geometric mean diameter) NaCl particles [35, 45–50], generated by atomizing a 3% aqueous solution. A differential mobility analyzer selects a monodisperse segment from this distribution, which is directed to the test filter. Particle number concentrations are measured alternatively through the test- and bypass-routes by a condensation particle

counter (Model 3010 CPC; TSI Inc, Shoreview, MN, USA). The second CPC (Model 5.403; Grimm Aerosol Technik, Ainring, Germany) is used to normalize aerosol concentration changes upstream of the test section. The testing flow rate of 22.8 L/min (i.e., 107 cm/s face velocity on 25 mm filters) correspond to the samplers used in long-term US networks (i.e., URG 3000N; Chapel Hill, NC, USA).

Filter sampling effectiveness is equal to one minus the ratio of the particle number for the test and bypass routes after normalization to the upstream CPC (Grimm 5.403) concentration. Figure 3 compares measured sampling effectiveness with theoretical sampling effectiveness for 25 mm QAT-UP quartz-fiber filters. Measurements were conducted with 0.025, 0.052, 0.101, 0.154, 0.192, and 0.309 μm NaCl particles. Diffusion is most efficient for particles smaller than $\sim 0.07 \mu\text{m}$; interception and impaction are effective for particles larger than $\sim 0.15 \mu\text{m}$. Particles in the size range of ~ 0.07 – $0.15 \mu\text{m}$ are too large for diffusion to be effective and too small for interception or impaction to be effective, yielding a most-penetrating size in the range of 0.07– $0.15 \mu\text{m}$. The measured sampling effectiveness of 99.87% for the 0.05– $0.10 \mu\text{m}$ size range exceeds the theoretical sampling effectiveness, probably due to conservative theoretical assumptions about the sizes and packing of the quartz fibers. When convolved with a typical mass size distribution, this sampling effectiveness would result in differences indistinguishable from a 100% sampling efficiency for the QAT-UP quartz-fiber filters.

Filters are pre-fired at $>900 \text{ }^\circ\text{C}$ for $>4 \text{ h}$ to remove adsorbed or residual carbon prior to carbon acceptance testing. Filter acceptance testing includes visual light inspection of every filter and carbon analysis of at least 2% of the filters in each 100-filter batch, after pre-firing to detect carbon contamination. Filters with visual flaws, pinholes, and discoloration are

Fig. 2 Experimental setup for filter sampling effectiveness measurement

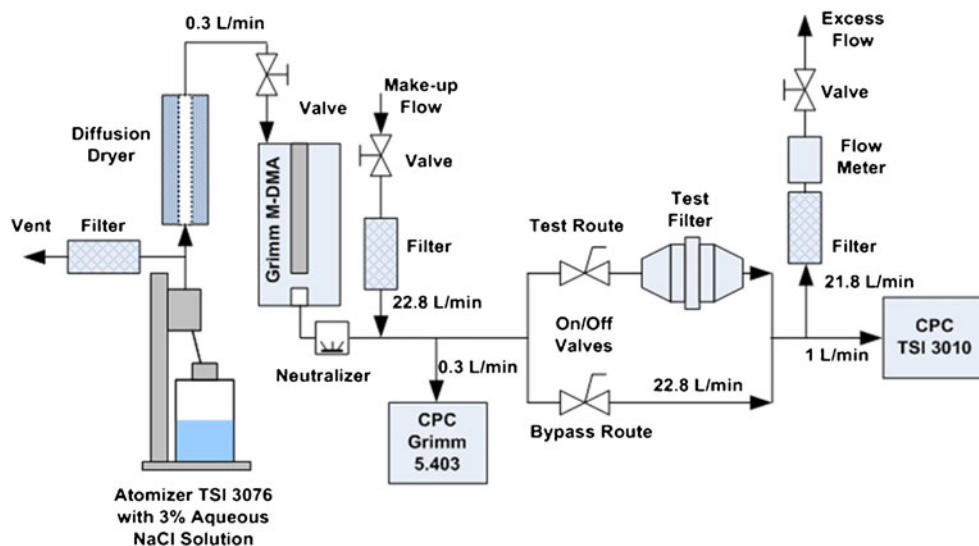
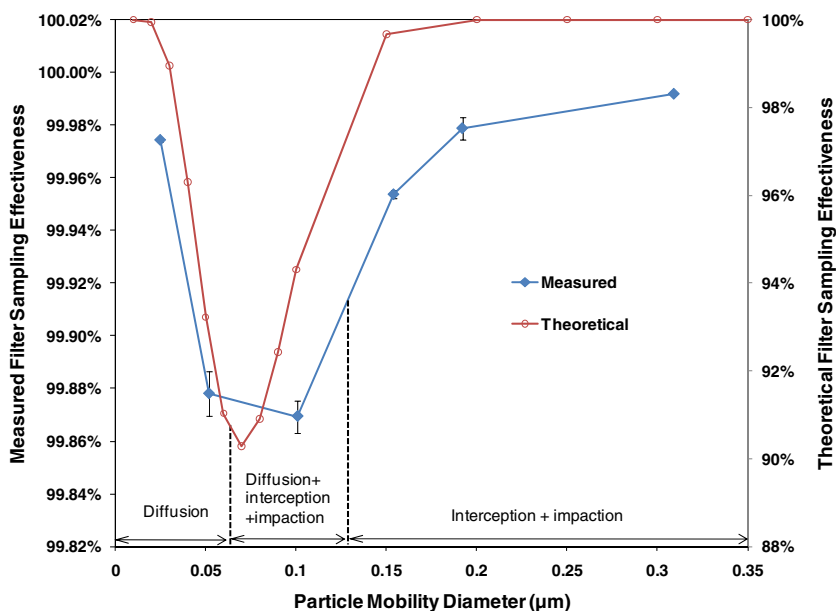


Fig. 3 Measured and theoretical sampling effectiveness for Pallflex QAT-UP 25 mm quartz-fiber filter. (The error bar indicates the standard deviation from three repeated measurements. Theoretical sampling effectiveness [84] assumes fiber diameter of 0.6 μm, packing density of 0.038 g/cm³, thickness of 0.432 mm, and face velocity of 107 cm/s.)

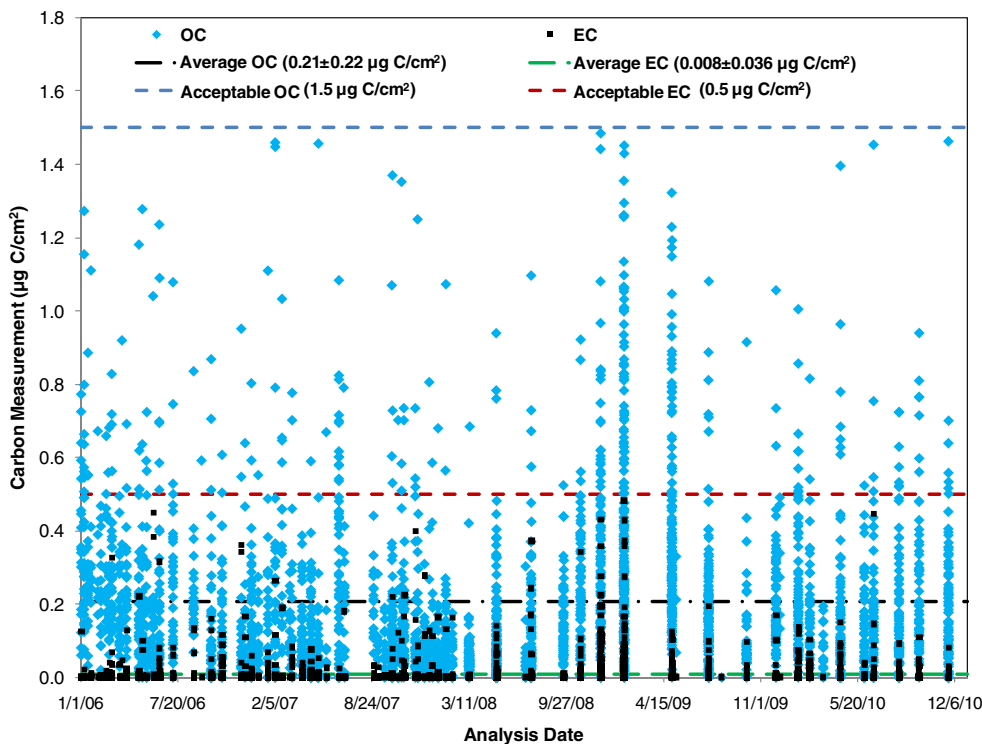


rejected. Batches corresponding to filters with blank carbon levels exceeding specified levels are re-fired or rejected. Figure 4 shows acceptance testing results for a 5-year period. Average laboratory blank filter concentrations from 2006 to 2010 were $0.21 \pm 0.22 \mu\text{g}/\text{cm}^2$ for OC and $0.008 \pm 0.036 \mu\text{g}/\text{cm}^2$ for EC; these levels are one to two orders of magnitude below the acceptance criterion ($<1.5 \mu\text{g}/\text{cm}^2$ for OC and $<0.5 \mu\text{g}/\text{cm}^2$ for EC).

After pre-firing, filters are stored under refrigeration in vacuum-sealed containers in aluminum (Al) foil-lined

boxes labeled by lot until loaded into labeled sampling cassettes that are shipped to and from the field. Samples returning from field sampling are removed from the cassettes, placed in ID-labeled Petri slides, and stored at $<4 \text{ }^\circ\text{C}$ both prior to and after laboratory analysis to minimize losses of semi-volatile organic aerosol. All filter transfer processes are performed in the laboratory with gloved hands and clean forceps beneath a laminar flow hood. Past studies have demonstrated that refrigeration is necessary to minimize negative (e.g., due to loss of volatile species) or positive

Fig. 4 OC and EC measurements for the QA/QC analysis of 3,400 pre-fired quartz-fiber filters (January 01, 2006 to December 6, 2010). Two filters are randomly selected from each batch of 100 quartz-fiber filters for acceptance testing



(e.g., due to organic gas adsorption) sampling artifacts [39, 41]. These artifacts have been reported in field and laboratory experiments [51] and during sample transport and storage [45, 52]. Chen [53] showed that leaving the quartz-fiber filter sample unrefrigerated at ambient room temperature ($\sim 25^\circ\text{C}$) for 3 days results in a 16% OC loss when compared to samples that were refrigerated immediately after sampling.

Sample analysis

IMPROVE_A TOR and TOT analyses are implemented on DRI Model 2001 thermal/optical carbon analyzers (Atmoslytic, Inc., Calabasas, CA, USA) to yield the thermogram illustrated in Fig. 1. Prior to analysis, an $\sim 0.5\text{ cm}^2$ punch is removed from each quartz-fiber filter, using a calibrated punch, and placed into the quartz sample boat. This boat has a 4.56-mm diameter hole to minimize interference with the optical signal and to allow carbon from both sides to be entrained in the carrier gas. As temperatures are ramped from ambient ($\sim 25^\circ\text{C}$) to a preset plateau (140°C to 840°C), carbonaceous material in the sample is volatilized, and pyrolyzed to gas-phase compounds that are converted to CO_2 as they pass through a manganese oxide (MnO_2) oxidizer at 912°C . The CO_2 is reduced to CH_4 as it passes through a granulated firebrick impregnated with a nickel catalyst at $\sim 420^\circ\text{C}$, and the CH_4 is then quantified by a FID. A 5-mW He-Ne laser ($\lambda = 632.8\text{ nm}$, red light) is directed perpendicular to the deposit side of the sample punch. Reflectance (R) and transmittance (T) are monitored at angles of 180° and 0° , respectively, with respect to the incident light throughout the analysis, as shown in Fig. 5. The laser signal is modulated with a chopper to separate R and T signals from stray light sources. The thermocouple extends under the sample boat so that it is as close to the

filter as possible. Even so, calibration is required for the thermocouple reading to equal the filter temperature [25].

A negative sign is assigned to pyrolyzed OC (i.e., optical pyrolysis (OP)) if the laser split occurs in the He atmosphere prior to the introduction of O_2 . This rarely occurs for the IMPROVE or IMPROVE_A temperature protocols, but it is common for other temperature protocols [28, 29] due to the incorrect presumption that carbonate carbon evolves at $\sim 850^\circ\text{C}$ in an inert analysis atmosphere, as real-world carbonate mixtures evolve across a wide range of temperatures [54–59]. Carbonate carbon typically accounts for $<5\%$ of mass in $\text{PM}_{2.5}$ samples [60], and its analysis is only required for special studies. To evaluate the potential for carbonate interference, an injection port on the Model 2001 analyzer allows $20\ \mu\text{L}$ of 0.4 M hydrochloric acid (HCl) solution to be injected with a micro-syringe onto the filter to react with carbonates; the CO_2 evolving from this reaction can be measured separately from other carbon fractions.

Performance tests and results

Table 1 summarizes QA and QC performance tests. Data validation involves thermogram inspection for each analysis, applying range checks to batches of data and investigating outliers, comparing replicate analysis differences to long-term averaged differences, and examining single- and daily-sample calibration performance tests. Validation flags that indicate filter appearance, filter damage, unusual deposits, excessive filter loading, and other anomalies observed during the analysis are entered into the database along with the carbon concentrations.

Multiple gas and solution standard calibration for OC is performed every 6 months or when indicated by failure of performance tests. Known amounts of reagent-grade crys-

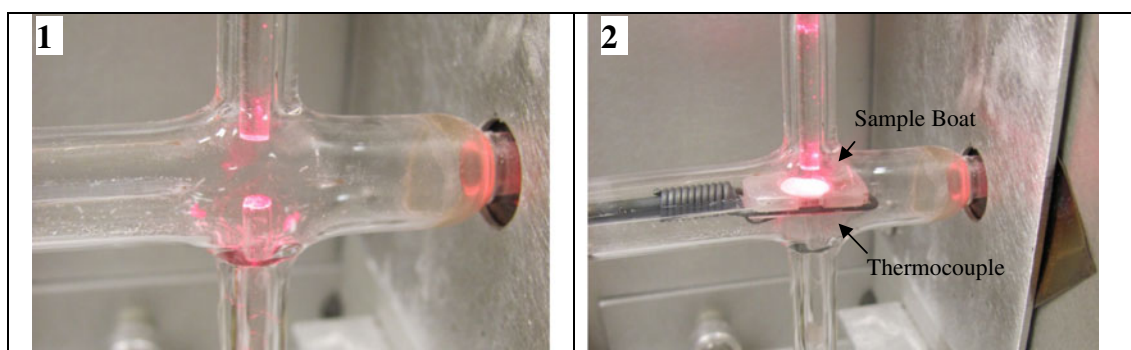


Fig. 5 Close-up of the DRI Model 2001 analysis zone and light pipes: (1) without and (2) with the sample boat and 0.5 cm^2 filter punch. The oven surrounds this area during normal operation. The 632.8 nm helium-neon laser light enters through the top light pipe, which also conducts the reflected light back to the detector. The bottom light pipe detects the transmitted light. Note that most of the light is reflected

back in the direction from which it came (angle of reflection opposite the angle of incidence) and that there is a small amount of light diffusion caused by the non-uniformity of the quartz sample surface. The orange glow to the right derives from the manganese oxide [MnO_2] oxidation oven and is similar to the radiation generated by the sample heating oven

Table 1 Quality assurance/quality control activities, frequencies, and tolerances for IMPROVE_A analysis of organic and elemental carbon (OC and EC, respectively)

Requirement	Calibration standard and range	Calibration frequency ^a	Acceptance criteria	Corrective action
System blank check	NA	Beginning of analysis day	$\leq 0.2 \mu\text{g C}/\text{cm}^2$	Check instrument and filter lots
Leak check	NA	Beginning of analysis day	Oven pressure drops less than 0.52 mm Hg/s	Locate leaks and fix
Laser performance check	NA	Beginning of analysis day	Transmittance >700 mV; reflectance >1,500 mV	Check laser and filter holder position
Calibration peak area check	NIST 5% CH ₄ /He gas standard; 20 $\mu\text{g C}$ (Carle valve injection loop, 1,000 μl)	Every analysis	Counts >20,000 and 95–105% of average calibration peak area of the day	Void analysis result and repeat analysis with second filter punch
Auto-calibration check	NIST 5% CH ₄ /He gas standard; 20 $\mu\text{g C}$ (Carle valve injection loop, 1,000 μl)	Beginning of analysis day	95–105% recovery and calibration peak area 90–110% of weekly average	Troubleshoot and correct system before analyzing samples
Manual injection calibration	NIST 5% CH ₄ /He or NIST 5% CO ₂ /He gas standards; 20 $\mu\text{g C}$ (certified gas-tight syringe, 1,000 μl)	End of analysis day	95–105% recovery and calibration peak area 90–110% of weekly average	Troubleshoot and correct system before analyzing samples
Sucrose calibration check	10 μL of 1,800 ppm C sucrose standard; 18 $\mu\text{g C}$	Thrice per week (began March 2009)	95–105% recovery and calibration peak area 90–110% of weekly average	Troubleshoot and correct system before analyzing samples
Multiple point calibrations	1,800 ppm C potassium hydrogen phthalate (KHP) and sucrose; NIST 5% CH ₄ /He, and NIST 5% CO ₂ /He gas standards; 9–36 $\mu\text{g C}$ for KHP and sucrose; 2–30 $\mu\text{g C}$ for CH ₄ and CO ₂	Every 6 months or after major instrument repair	All slopes $\pm 5\%$ of average	Troubleshoot instrument and repeat calibration until results are within stated tolerances
Sample replicates (on the same or a different analyzer)	NA	Every 10 analyses	$\pm 10\%$ when OC and TC $\geq 10 \mu\text{g C}/\text{cm}^2$; $\pm 20\%$ when EC $\geq 10 \mu\text{g C}/\text{cm}^2$ or $\leq 1 \mu\text{g C}/\text{cm}^2$ when OC and TC $< 10 \mu\text{g C}/\text{cm}^2$; $\leq 2 \mu\text{g C}/\text{cm}^2$ when EC $< 10 \mu\text{g C}/\text{cm}^2$	Investigate instrument and sample anomalies and rerun replicate when difference is $\geq \pm 10\%$
Temperature calibrations	Tempilac [®] G (Tempil, Inc., South Plainfield, NJ, USA); three replicates each of 121 °C, 184 °C, 253 °C, 510 °C, 704 °C, and 816 °C	Every 6 months, or whenever the thermocouple is replaced	Linear relationship between thermocouple and Tempilac [®] G values with $R^2 > 0.99$	Troubleshoot instrument and repeat calibration until results are within stated tolerances
Oxygen level in helium atmosphere (using GC/MS) ^b	Certified gas-tight syringe; 0–100 ppmv	Every 6 months, or whenever leak is detected	Less than the certified amount of He cylinder	Replace the He cylinder and/or O ₂ scrubber
Interlaboratory comparisons	NA	Once per year	NA	Review and verify procedures
External system audits	NA	Once every 2 to 3 years	NA	Take action to correct any deficiencies noted in audit report

NA not applicable

^a Calibration performed by carbon analyst, except for interlaboratory comparisons and external system audits, which are conducted by the US Environmental Protection Agency (EPA) National Air and Radiation Environmental Laboratory (NAREL)^b Gas chromatography/mass spectrometer (Model 5975, Agilent Technology, Palo Alto, CA, USA)

talline sucrose and potassium hydrogen phthalate (KHP; 99.95% to 100.05%), certified by the American Chemical Society (ACS), are analyzed to verify the OC fractions. A total of 18 different standards are used for each calibration. The FID response is normalized to a reference level of CH₄ in He that is injected at the end of each sample analysis. Performance tests of instrument calibration are conducted twice during daily operation, as well as at the end of each sample run.

Verification of calibration stability includes (1) daily autocalibration, system blanks, laser performance checks, and leak checks; and (2) two to four times weekly checks with sucrose, KHP, and/or CO₂ standards. An example of the analytic stability of sucrose QC checks is shown in Fig. 6. All measurements are within $\pm 10\%$ of actual TC. Instruments that do not attain QC tolerances ($\pm 5\%$) are taken offline immediately for troubleshooting. All intervening samples are re-analyzed if calibration changes of more than $\pm 5\%$ are found.

Minimum detection limits (MDLs) are determined by laboratory blanks, and lower quantifiable limits are determined by the variability of dynamic field blanks [51]. Analytical precisions for each batch of measurements are calculated from replicate analyses. Replicate analyses ($\geq 10\%$ of all samples) are performed on separate instruments. Figure 7 summarizes the results for the 3,460 replicate analyses for IMPROVE samples acquired during the past 5 years. Over 66% and 56% of OC and EC sample replicates, respectively, are within a $\pm 5\%$ range, demon-

strating the consistency among the 11 carbon analyzers and the homogeneity of particle deposits on the quartz-fiber filters. Higher deviations (in the 8–10% range) are found for EC than OC, partially due to the lower concentrations found for EC. Re-analyses are conducted on samples bracketed by these replicates when they fall outside of specified tolerances. These replicates are also used to calculate analysis precision, which is propagated to the final OC and EC concentrations [61].

The temperature of the thermocouple in Fig. 5 differs from that of the sample. Temperature calibrations [33] are conducted every 6 months, or whenever the thermocouple is replaced, using temperature-indicating materials (Tempilaq[®] G, Tempil, an ITW, Co., South Plainfield, NJ, USA). A Tempilaq[®] G set consists of chemicals that change their appearance at a specific temperature (rated temperature). A thin layer ($\sim 25 \mu\text{L}$) of Tempilaq[®] G is uniformly applied onto a glass or quartz disk surface and covered with a sliced quartz-fiber filter punch. When the specified temperature is reached, the appearance of the sample changes, as evidenced by R and T signals, and by which the deviation between measured (thermocouple) and sample temperatures can be determined. Triplicate tests are made at 121 °C, 184 °C, 253 °C, 510 °C, 704 °C, and 816 °C to obtain the calibration slope and intercept, which are then fed back into the temperature control program. This procedure ensures that each sample experiences a temperature plateau specified by the protocol. A significant change in calibration slope and intercept also triggers inspection for possible hardware deficiencies. Results

Fig. 6 Trends in the total carbon (TC) response from the analysis of a 10 μL sample of 1,800 ppm C sucrose standard (January 01, 2006 to December 31, 2010). Sucrose calibration checks were performed thrice weekly instead of every 6 months after March 2009. (Blue and red lines specify $\pm 5\%$ and 10% tolerance levels, respectively.)

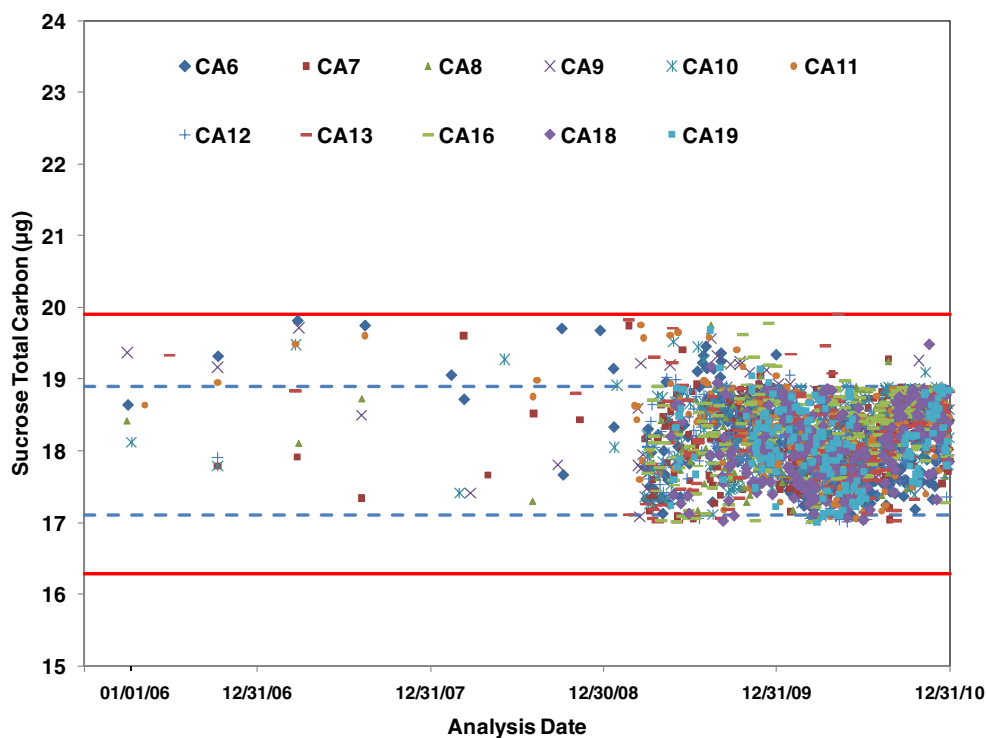
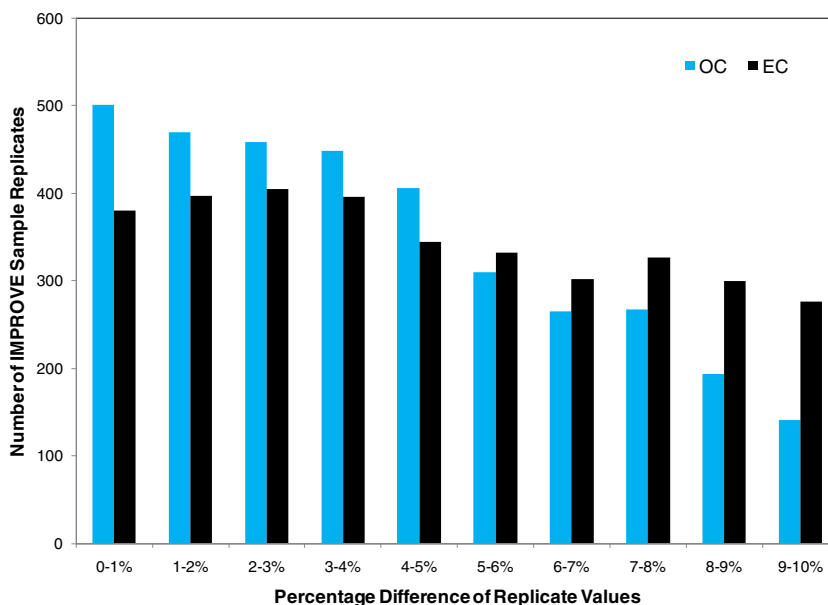


Fig. 7 Distributions of the 3,460 OC and EC replicate analyses of the IMPROVE filter samples collected between January 01, 2006 and December 31, 2010 using 11 DRI Model 2001 thermal/optical carbon analyzers (Atmoslytic, Inc., Calabasas, CA, USA). Additional replicates are analyzed if the acceptance criterion specified in Table 1 is exceeded

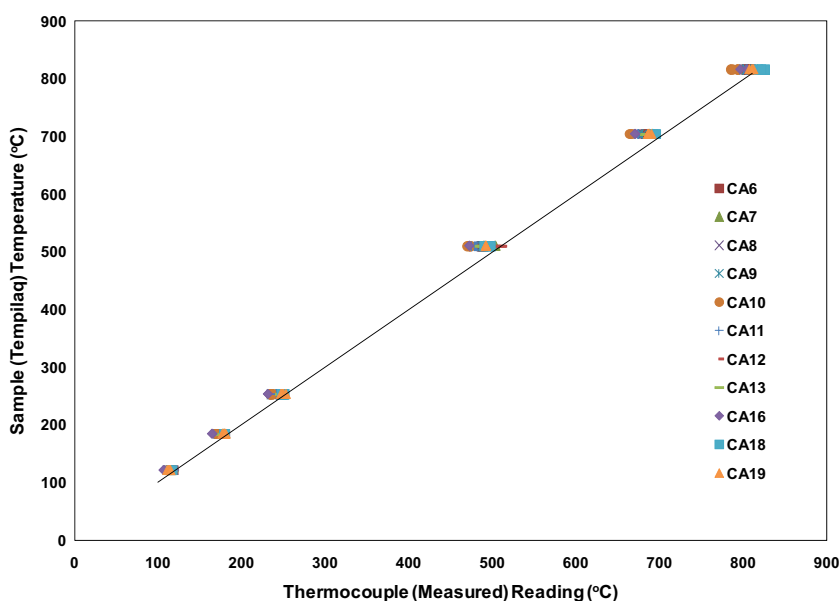


of a recent temperature calibration among the 11 DRI Model 2001 analyzers are shown in Fig. 8.

An external gas chromatograph/mass spectrometer (GC/MS; as shown in Fig. 9) is used to monitor traces of O₂ levels in the He atmosphere every 6 months. The presence of O₂ in the inert He analysis atmosphere may trigger EC or OP oxidation and bias the OC/EC split. The six-port Carle valve in “load” position directs the He carrier gas to the 1-mL sample loop. Computer-controlled actuation into the inject position transfers gases from the sample loop to the MS detector. The backpressure regulator in the vent maintains constant pressure through-

out the sample loop, sample lines, and carbon analyzer; minimizes pressure fluctuations during valve switching; and maintains steady-state conditions in the carbon analyzer. The Carle valve is switched between sample and inject position every 30 s, and the MS monitors the O₂⁺ ion (*m/z*=32). Peaks are integrated, and O₂ levels are calculated based on the linear correlation (*R*²=0.988) acquired from the O₂/He calibration standards (Scott Specialty Gas, Plumsteadville, PA, USA). Figure 10 shows the results of these tests, indicating that all O₂ levels are below 100 ppmv, which minimizes shifts in the thermal carbon fractions [21].

Fig. 8 Temperature calibration results for the 11 DRI Model 2001 analyzers. The thermocouple reading is related to the Tempilaq[®] G temperature by a calibration curve that is entered into the software that controls the temperature plateaus



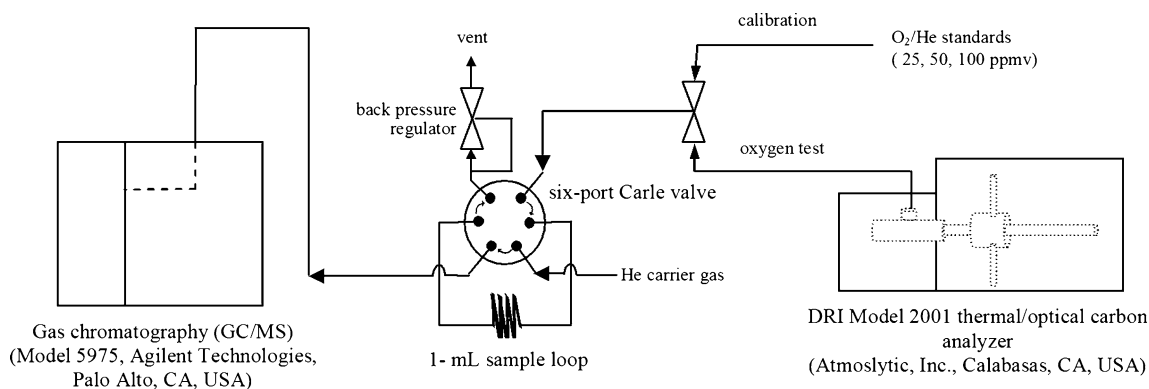


Fig. 9 Method to determine trace oxygen (O_2) levels in the inert helium (He) carrier gas

External audits and interlaboratory comparisons are also important QA components. The USA has a National Environmental Laboratory Accreditation Program [62] that requires laboratories to pass rigorous requirements for standard operating procedures, sample handling, and quality tests. The US Environmental Protection Agency (EPA) conducts on-site audits [63, 64] and interlaboratory comparisons using prepared and ambient samples [65–69]. External OC and EC method characterization and inter-comparison studies [3, 7, 21, 34, 39, 41, 52, 70–83] are also important QA components.

Summary and conclusions

To ensure accuracy, precision, and validity of the OC and EC measurements for ambient aerosol and source samples, a series of QA/QC activities and tests needs to be performed. Prior to field sampling, the appropriate filter substrate must be obtained, inspected, and tested

with respect to appearance and sampling effectiveness. Adsorbed organic vapors must be minimized by filter pre-firing (at >900 °C for >4 h) and acceptance testing prior to field sampling. Once in the laboratory, exposed filter samples must be stored in clean, labeled containers under refrigeration (<4 °C) to minimize loss of semi-volatile OC. Examples are given in this paper to document the methods and results from various QA/QC tests. QA activities include participation in laboratory accreditation programs, external system audits, and interlaboratory comparisons. In thermal/optical carbon analyses, periodic QC tests include full-scale calibration of the flame ionization detector with different types of carbon standards, thermogram inspection, replicate analyses, verification of trace O_2 concentrations (<100 ppmv) in the He analysis atmosphere, and calibration of the sample temperature sensor. These QA/QC tests assure the consistency of OC and EC measurements that allows for the evaluation of long-term trends and the development of emission inventories.

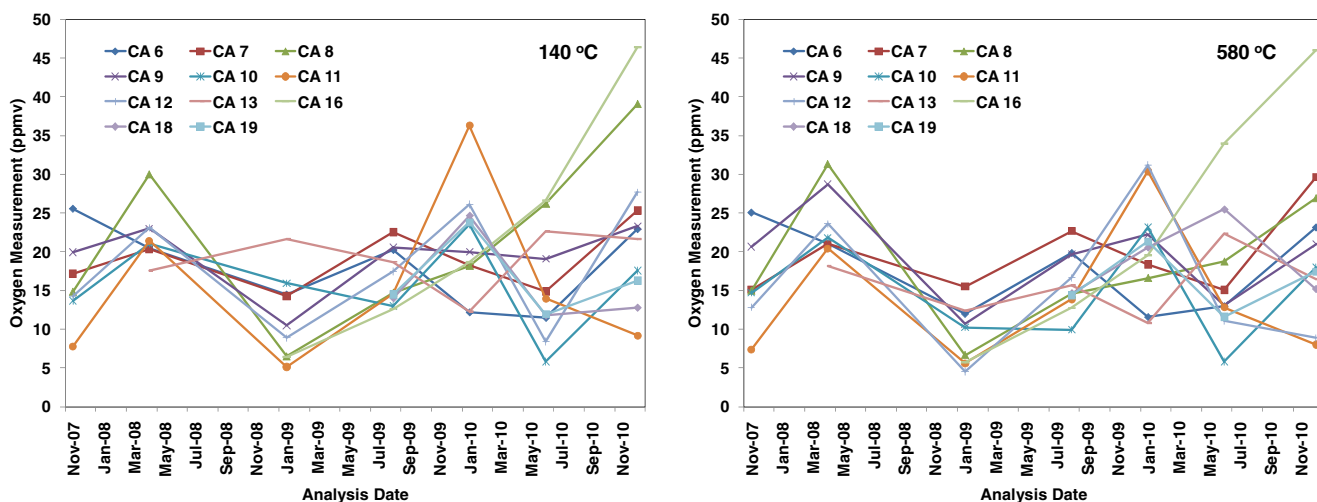


Fig. 10 DRI Model 2001 analyzer trace oxygen (O_2) levels in helium (He) carrier gas at 140 °C (OC1) and 580 °C (OC4) following the IMPROVE_A protocol [21], representing the temperatures at which oxidizing conditions are most sensitive to O_2

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