

Summary of Organic and Elemental Carbon/Black Carbon Analysis Methods and Intercomparisons

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Abstract

Many different thermal, optical, and thermal/optical carbon analysis methods for organic carbon (OC), elemental carbon (EC) or black carbon (BC) have been applied throughout the world to evaluate visibility and the Earth's radiation balance. Dozens of intermethod and interlaboratory comparison studies have been conducted. Several of these studies are catalogued and summarized here. BC or EC concentrations are found to differ by up to a factor of 7 among different methods; factor of 2 differences are common. Differences between methods are not consistent among comparison studies, with some methods showing higher BC for one set of samples and lower BC for other sets relative to a common benchmark. The absorption efficiency relating light absorption (b_{abs}) to EC that is derived from collocated optical and chemical measurements can vary by a factor of 10, depending on the collocated b_{abs} and EC measurement methods. Future intermethod and interlaboratory comparisons must include components that seek to understand the causes of these differences.

Keywords: Black carbon, elemental carbon, organic carbon, thermal/optical analysis, water-soluble organics, aerosol, light scattering/absorption efficiency.

1. Introduction

Elemental carbon (EC) and black carbon (BC) are operationally defined by the measurement method applied, although EC and BC are often used interchangeably. The objective of this paper is to: 1) summarize filter methods used to measure organic carbon (OC) and EC; 2) assemble interlaboratory and intermethod comparisons; and 3) identify knowledge gaps and research needs.

EC occurs as the mineral graphite or as diamond in its purest forms, but these structures of more than 0.1 micrograms (μg) are seldom found in ambient particulate matter (PM). Freshly emitted diesel soot consists of agglomerates of small spherical graphitic particles consistent in size from 20 to

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30 nanometers (nm). Even the soot from incomplete combustion contains non-carbon components and has a non-crystalline structure (Akhter et al., 1984, 1985). It has a large surface-to-volume ratio and reactive surfaces, so it attracts condensable materials (e.g., polycyclic aromatic hydrocarbon [PAH] gases) soon after emission into ambient air.

Of the major components of PM_{2.5} and PM₁₀, OC and EC are the most uncertain with respect to sampling and analysis (Huebert and Charlson, 2000; Jacobson et al., 2000; Turpin et al., 1994). Most EC and BC characterization involves collecting PM on filters and measuring either the carbon content on the filter or the attenuation of light reflected from or transmitted through the filter. Filter-based optical techniques include the British Smoke Shade method (Hill, 1936), the coefficient of haze (COH) (Hemeon et al., 1953), the integrating plate method (IPM) (Lin et al., 1973), the aethalometer (Hansen et al., 1984), and the particle soot absorption photometer (PSAP) (Bond et al., 1999). The scattering and absorption properties of particles distributed on top of and throughout a filter are not the same as they are in the atmosphere. Light absorption coefficients (b_{abs}) determined from these methods are often biased (Horvath, 1993).

It is generally agreed that EC is the major contributor to b_{abs} (e.g., Horvath, 1993; Watson, 2002). EC absorbs light due to conduction electrons associated with the graphitic structure. EC is, therefore, often referred to as BC. However, the specific mass absorption efficiency of EC has been estimated to range from 2 to 20 m²/g (Liousse et al., 1993). Particle light absorption depends on the wavelength (λ) of the incident light. Moosmüller (1998) reported that EC absorption efficiency varied as $\lambda^{-2.7}$ near Denver, CO, while Horvath et al. (1997) reported that absorption efficiency for aerosols in Santiago, Chile, varied as $\lambda^{-0.92}$. Kirchstetter et al. (2004) found that b_{abs} from engine exhaust varied as λ^{-1} whereas b_{abs} from biomass burning varied as λ^{-2} . Carbonaceous material from different sources (e.g., diesel versus wood burning) has different structures and compositions. A small quantity of carbonates (e.g., CaCO₃) is found in some fine particulate samples, but this is rarely comparable to the EC content (Chow and Watson, 2002; Cao et al., 2005). The remainder of the carbonaceous material is organic matter that is a complex mixture of hundreds of organic compounds covering a wide range of molecular forms and volatilities (Jacobson et al., 2000). Organic matter can be emitted directly from combustion sources with EC, or it can be formed in the atmosphere through condensation of low-volatility oxidation products of hydrocarbons (i.e., secondary organic aerosol [SOA]). Some components of OC may be weakly light-absorbing in the visible spectrum, but OC mainly influences direct radiative forcing through light-scattering or through mixing with EC to enhance the EC absorption efficiency (e.g., Fuller et al., 1999).

Particles change when they are extracted from the air onto a filter, on which most EC or BC measurements are made. The rate at which the material evaporates depends on how the filter is handled and stored between sampling and analysis. Quartz-fiber filters used for thermal carbon analysis absorb some organic vapors throughout their thickness; these vapors are often interpreted as OC by thermal methods and possibly as a portion of EC if the OC is charred.

Fuller et al. (1999) hypothesized that differences among estimates for soot extinction efficiencies are due to: 1) different wavelength dependencies; 2) deviations from spherical particles; 3) mischaracterization of the soot refractive index; 4) inaccurate densities; and 5) mixtures of graphitic material with other compounds. By applying radiative transfer models for non-spherical particles of non-homogeneous composition, Fuller et al. (1999) found that for the same quantity of EC, b_{abs} decreased rapidly for particles $>0.1 \mu\text{m}$, the particle size of most of the aged EC in the atmosphere. Up to 60% higher efficiencies were calculated for long chain aggregates relative to the same amount of EC in a sphere. Absorption efficiencies $>10 \text{ m}^2/\text{g}$ —exceeding $25 \text{ m}^2/\text{g}$ in some situations—were estimated for soot imbedded in a sulfate particle. Efficiency decreased as the EC fraction in the particle increased, implying that a lower EC concentration may yield a higher contribution per EC mass to light absorption under some circumstances. Efficiencies decreased by nearly 1 order of magnitude as an EC core at the center of a concentric sphere migrated through the sphere to its surface.

Martins et al. (1998) found similar results, with maximum soot absorption efficiencies approaching $30 \text{ m}^2/\text{g}$ when the carbon constituted 0.5% of the volume of a $0.5 \mu\text{m}$ diameter particle. Empirically derived soot extinction efficiencies are usually greater at non-urban than urban monitors (Horvath, 1993). This is consistent with an aged aerosol in which more of the fresh emissions become coated with condensed, absorbed, and adsorbed material. Horvath (1993, 1997) shows how light transmission through a filter varies depending on the filter loading, the presence or absence of light-scattering particles, and the location of particles within a filter. These results imply that constant conversion factors used to infer EC from b_{abs} , such as the $10 \text{ m}^2/\text{g}$ often used in visibility studies (Watson, 2002), are subject to large uncertainties.

OC and EC are measured directly by thermal evolution methods that quantify the amount of carbon that leaves the filter at different temperatures (Currie et al., 2002; Schmid et al., 2001). These methods use different combinations of temperature and analysis atmospheres to evaporate, pyrolyze, and combust the carbon-containing compounds on a filter sample, then detect the evolved carbon gases. The separation of OC from EC is ambiguous because some of the EC combusts in the presence of oxygen, and some of the OC chars (turns to EC) in an oxygen-deficient atmosphere. Light reflected from (Johnson et al., 1981; Huntzicker et al., 1982; Chow et al., 1993) or transmitted through (Turpin et al., 1990; Birch and Cary, 1996a, 1996b; Chow et al., 2001) the filter during the analysis is used to monitor and correct for this charring. Interlaboratory and intermethod comparisons (e.g., Chow et al., 2001; Countess, 1990; Currie et al., 2002; Schmid et al., 2001) show EC differences of a factor of 2 or more among thermal methods, depending on the protocol and type of sample. Analysis methods alone can account for the large differences in EC emission rates among inventories. In addition to OC and EC, carbon that evolves at several different temperatures has been found useful for source apportionment studies (Watson et al., 1994; Kim and Hopke, 2004).

2. Thermal Organic and Elemental Carbon Analysis Methods

Table 1 summarizes several of the thermal methods that have been applied to estimating total carbon (TC), OC, and EC. All of these produce OC and EC concentrations that are defined by the method rather than by an absolute standard. Many of these methods use a two-step temperature in which the carbon evolving below the temperature (~350 to 550 °C) is termed OC and the remaining carbon evolving at a higher temperature (~650 to 1100 °C) is termed EC. Between different methods, lower OC temperatures are used in an oxidizing atmosphere for which the combustion rate of EC is assumed to be low; higher OC temperatures are usually applied in a non-oxidizing atmosphere, with an oxidizer added at a time after which most of the OC is assumed to have left the sample. The evolved carbon is converted to carbon dioxide (CO₂), which can be detected directly or converted to methane (CH₄) for more sensitive detection.

As Table 1 shows, many of the methods employ thermal/optical reflectance (TOR) and/or thermal/optical transmission (TOT) to monitor the conversion of OC to EC as part of the analysis. Since EC is not volatile, it is released only by oxidation (typically in an oxygen [O₂] atmosphere at a temperature below 800°C) and is thereby separated from OC. Heating in an O₂-free environment, however, causes certain OC components to pyrolyze and form non-volatile, light-absorbing, "charred," material that can be mistaken for atmospheric EC. Light reflected from or transmitted through the sample monitors the darkening of the particle deposit on the filter due to OC charring. When O₂ is added to the analysis atmosphere (i.e., carrier gas) at a sufficiently high temperature (e.g., >350 °C), this black char combusts along with the original EC on the filter, and the filter becomes whiter. When the reflected or transmitted light attains its original intensity, the charred, or pyrolyzed, OC (POC) is considered to have been removed. All of the remaining carbon is associated with the EC that was originally on the filter. Therefore, a partitioning can be made by assigning carbon evolved before this split point to OC and after this point to EC. Johnson et al. (1981) and Yang and Yu (2002) pointed out that such partitioning assumes that: 1) charred OC evolves before the original EC in the thermal analysis, and 2) charred OC and original OC equally attenuate reflectance (R) and transmittance (T). Several of the thermal methods appear to be similar, but they contain subtle differences with respect to: 1) analysis atmospheres, 2) temperature ramping rates, 3) temperature plateaus, 4) residence time at each plateau, 5) optical pyrolysis monitoring configuration and wavelength, 6) standardization, 7) oxidation and reduction catalysts, 8) sample aliquot and size, 9) evolved carbon detection method, 10) carrier gas flow through or across the sample, 11) location of the temperature monitor relative to the sample, and 12) oven flushing conditions. These differences are not always well characterized or reported along with analysis results, but this information is critical to interpret variability in the results. For example, Chow et al. (2005a) demonstrate the influence of temperature calibration on TOR analysis for temperature-resolved carbon fractions. Chow et al. (2004) and Chen et al. (2004) discuss how TOR and TOT might determine different OC/EC splits for various types of samples.

Owing to differences in the form of EC and the methods that operationally separate OC from EC, there is no reason to expect a consistent relationship among samples measured in different laboratories. This is borne out by the summary of 40 different intermethod and interlaboratory comparisons studies in Table 2. These comparisons date from the early 1980s to the present and cover a wide range of samples, the thermal evolution methods described in Table 1, and types of sampled particles.

In some studies, several simulated and ambient samples were sent to different laboratories. These comparisons showed that TC was the same for well-calibrated instruments, but the OC/EC splits were different. Since EC usually constitutes the smallest fraction of TC, it shows the largest variation among laboratories (up to a factor of 7 as reported by Currie et al., 2002). Many of the methods agreed on EC from diesel exhaust or powdered graphite samples, but they often disagreed for ambient and biomass burning samples. Schmid et al. (2001) showed that biases were not consistent from sample to sample for paired measurements from several thermal/optical protocols. This demonstrated that differences depend on the samples analyzed as well as on the instruments and methods used for the analyses. Potential sample biases include: 1) non-uniform particle deposits on the filter; 2) particle deposits that are too light or too dark, which make R and T charring corrections uncertain; 3) organic vapor filter adsorption and its charring during heating; 4) catalytic and oxidation interactions between OC, EC, and non-carbonaceous material in the sampled particles; and 5) changes in optical properties of the particles during thermal evolution.

It is doubtful that future carbon comparisons will add much information to those already completed unless they include components that systematically quantify the effects of sample properties and the analysis variables cited above. This degree of systematization is lacking in most of the studies. While it is possible to observe differences, it is not possible to explain why.

As an example, Chow et al. (2004) examined charring of the filter backside and microscopic cross-sections of a filter punch at different parts of the temperature cycle during thermal analysis. It appeared that R was dominated by charring of OC that co-existed with EC in particles on the surface of the filter, while T was dominated by the charring of organic vapors distributed throughout the filter. When oxygen was added to the analysis atmosphere, the surface EC (original EC and charred OC) evolved before the charred OC that was distributed throughout the filter. Hence, T achieved its initial value later than R. Using a radiative transfer model, Chen et al. (2004) showed that this explanation is plausible, and that simultaneous R and T measurements can be used to estimate contributions to charring from the surface particulate OC and the charred vapors adsorbed throughout the filter.

Table 1. Summary of organic and elemental carbon thermal analysis protocols.

| Protocol | Carrier gas for OC | Carrier gas for EC | Temperature plateaus for OC (°C) | Residence time at each temperature for OC (s) | Temperature plateaus for EC (°C) | Residence time at each temperature for EC (s) | Optical charring correction | Converter and detector |
|--|--------------------|--|---------------------------------------|---|----------------------------------|---|--|---|
| IMPROVE ¹ | He | 98%He 2%O ₂ | 120,250,450, 550 | 150 – 580 ^a | 550,700,800 | 150 – 580 ^a | Reflectance | Methanator; FID/CH ₄ |
| TMO ² | He ^b | 98%He 2%O ₂ | 525 | 300 ^c | 750 | 180 | N/A | Methanator; FID/CH ₄ |
| OGI ³ | He ^d | 98%He 2%O ₂ | 600 | Varies ^a | 400, 500, 600 | 100,120,>200 | Reflectance | Methanator; FID/CH ₄ |
| NIOSH ⁴ 5040 | He | 98%He 2%O ₂ | 250,500,650, 850 | 60,60,60, 90 | 650,750,850, 940 | 30,30,30, >120 | Transmittance | Methanator; FID/CH ₄ |
| STN ^{5*} | He | 98%He 2%O ₂ | 310,480,615, 900 | 60,60,60, 90 | 600,675,750, 825,920 | 45,45,45, 45,120 | Transmittance | Methanator; FID/CH ₄ |
| HKGL ⁶ (Hong Kong) | He | 95%He 5%O ₂ | 350,550,850 | 70,70,110 | 550,600,700, 750,800,850 | 10,50,40, 30,30,70 | Transmittance | Methanator; FID/CH ₄ |
| HKUST-3 ⁷ (Hong Kong) | He | 99%He 1%O ₂ | 250,500,650, 850 | 150,150,150, 150 | 650,750,850, 890 | 150,150,150, 150 | Transmittance | Methanator; FID/CH ₄ |
| CalTech ⁸ (ACE-Asia) | He | 90%N ₂ 10%O ₂ | 310,450,575, 870 | 60,60,60, 90 | 550,625,700, 775,850,900 | 45,45,45, 45,45,120 | Transmittance | Methanator; FID/CH ₄ |
| MSC1 ⁹ (Canada) | He | 90%He 10%O ₂ | 250,450,550, 900 | 150,150,180, 90 | 550,700,800 | 240,210,150 | Transmittance | Methanator; FID/CH ₄ |
| RU/OGI ¹⁰ (Atlanta) | He | 90%He 10%O ₂ | Stepwise to 700 ^e | N/A | Stepwise to 850 | N/A | Transmittance | Methanator; FID/CH ₄ |
| LBL ¹¹ | O ₂ | O ₂ | Continuous (25 – 825) ^f | 10 °C per minute | Continuous (25 – 825) | 10 °C per minute | Transmittance | NDIR/CO ₂ |
| CNRS- CEA ¹² (France 2- Step) | O ₂ | O ₂ | 340 | 7200 | 1100 | ~600 ^a | Assume 10% of OC is charred; assume EC decompositio n rate of ~0.22% per min during OC analysis. | Coulometric titration/CO ₂ |
| U. Berne ¹³ (Switzerland 2-Step) | O ₂ | O ₂ | 650 ^c ,340 ^c | 60, 2520 | 650 | 1920 | N/A | NDIR/CO ₂ |
| BNL ¹⁴ | He | 90%He 10%O ₂ | 400 | 300 or 900 g | 700 | 300 or 900 ^g | N/A | NDIR/CO ₂ |
| GM ¹⁵ Research Laboratory | He ^h | Ambient air | 650 | ~100 ^a | 650 | ~120 ^a | N/A | NDIR/CO ₂ |
| VDI ¹⁶ 2465/1 (Germany) | N/A ⁱ | O ₂ | N/A | N/A | 200,650,200 | 60,420,120 | N/A | Coulometric titration/CO ₂ |
| VDI ¹⁷ 2465/2 (Germany) | He | 80%He 20%O ₂ | 80,350,620, 400 | 12,72,108, 18 | 300,700 ^j | 30,54 | N/A | Coulometric titration/CO ₂ |
| RCOP ¹⁸ (Japan) | N ₂ | 92%N ₂ 8%O ₂ | 450 | 600 ^k | 850 | 300 | N/A | Methanator; FID/CH ₄ |
| R&P 5400 ¹⁹ (continuous analyzer) | Ambient air | Ambient air | 340 | ~600 ^l | 750 | ~600 ^l | N/A | Low-volume IR CO ₂ Meter |

Table 1. (Continued)

- ^a Advance from one temperature to the next when a well-defined carbon peak has evolved.
- ^b Sample is acidified with 30 μ l of 0.02N hydrochloric acid (HCl) and preheated at 120 °C in contact with a bed of granulated manganese dioxide (MnO₂) in helium (He) for 180 s to remove volatile OC and carbonate. The sample remains in contact with MnO₂ throughout analysis.
- ^c Temperature change is accomplished by moving the sample from a lower-temperature oven to a higher-temperature oven.
- ^d Sample is preheated at 350°C in 98% He/2% oxygen (O₂) environment until all volatile OC is removed.
- ^e Cool to ~ 350 °C before the introduction of O₂ (Turpin et al., 1990).
- ^f The third of four carbon dioxide (CO₂) peaks evolving during thermal analysis is assigned to EC; this peak is usually accompanied by an increasing filter transmittance.
- ^g Residence times for loadings < 50 μ gC and > 50 μ gC per cm² are 300 s and 900 s each, respectively, for both 400 °C and 700 °C temperature stages.
- ^h Sample is preheated at 350 °C in ambient air for ~ 450 s to remove volatile OC.
- ⁱ OC on half a filter is extracted with 10 ml of a 50:50 volume %–mixture of toluene and 2-propanol for 24 hr, and the half-filter is dried in pure nitrogen (N₂) before thermal analysis. OC is estimated from the difference between TC and EC acquired from two separated filter halves.
- ^j The sample is cooled to 80 °C from 700 °C. Carbon evolved during cooling is also counted as EC.
- ^k Temperature changes are accomplished by moving the sample through an increasing temperature gradient in the oven.
- ^l The overall analysis time is adjustable but should not be > 30 min.

References

- 1 Interagency Monitoring of Protected Visual Environments, Chow et al., 1993, 2001, 2004
- 2 Thermal Magnesium Dioxide, Fung, 1990; Fung et al., 2002
- 3 Oregon Graduate Institute, Huntzicker et al., 1982
- 4 National Institute of Occupational Safety and Health, Birch, 1998; Birch and Cary, 1996a, 1996b; NIOSH 1996, 1999
- 5 Speciation Trends Network, Peterson and Richards, 2002
- 6 Hong Kong Governmental Laboratory, Sin et al., 2002; Chow et al., 2005b
- 7 Hong Kong University of Science and Technology, Yang and Yu, 2002; Yu et al., 2002
- 8 California Institute of Technology, Mader et al., 2001
- 9 Meteorological Service of Canada, Version I, Sharma et al., 2002
- 10 Rutgers University/Oregon Graduate Institute, Lim et al., 2003
- 11 Lawrence Berkeley Laboratory, Novakov, 1982; Ellis et al., 1984; Kirchstetter et al., 2001
- 12 Laboratoire des Sciences du Climat et de l'Environnement, Cachier et al., 1989a, 1989b
- 13 University of Berne, Switzerland, Lavanchy et al., 1999
- 14 Brookhaven National Laboratory, Tanner, 1982; Gaffney et al., 1984
- 15 General Motors Research Laboratory, Cadle et al., 1980, 1983
- 16 VDI, 1996
- 17 VDI, 1999
- 18 Radiation Center of Osaka Prefecture, Mizohata and Ito, 1985
- 19 Rupprecht and Patashnick, Rupprecht et al., 1995

Table 2. Summary of carbon intercomparison studies.

| Study/Period/Location/Type | Sampling and Analytical Method ^a | Summary of Major Findings |
|--|---|--|
| <p>A Comparison of Integrating Plate Method and Transmission Method (Sadler et al., 1981)</p> <ul style="list-style-type: none"> • Location: Five sampling sites in the western part of Washington state, from a highly congested site in a highway tunnel to a remote site on a western foothill of the Olympic Mountains. • Type: Rural ambient aerosol and urban traffic emission aerosol. | <ul style="list-style-type: none"> • This study compares absorption on three different sampling substrates (Nuclepore, Millipore, and quartz-fiber). <ul style="list-style-type: none"> - Integrating plate method (IPM) for measuring absorption coefficient through transmission. - Laser transmission method (LTM) for measuring absorption. This was the early development of PSAP. The LTM compared the transmission of a 633 nm He-Ne laser beam through a loaded Millipore filter relative to a blank filter to calculate the absorption caused by the particle deposit. - A total combustion/CO_2 evolution method on quartz-fiber filters for total carbon (TC) (Mueller et al., 1971). | <ul style="list-style-type: none"> • A total of 44 filters of each type were used in this comparison. The correlation coefficient between IPM and LTM measurements was 0.95, and the absorption coefficient determined by LTM was a factor of ~2.5 greater than that determined by the IPM. This difference was attributed to the filter material. • The correlation coefficient found between TC and IPM measurements for the urban data was 0.96. The absorption of urban aerosol was similar to that of a pure graphitic particle of 0.1 μm diameter and 0.66 imaginary refractive index. |
| <p>Colorado State University Aerosol Workshop (Bennett and Patty, 1982)</p> <ul style="list-style-type: none"> • Sample: Black carbon (BC) and white ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$ particles generated during the Colorado State University Aerosol Workshop. • Type: Artificial standard aerosol. | <ul style="list-style-type: none"> • Particles were deposited on the Teflon-membrane filter substrates at a flow rate of 16.7 L/min. The deposits were analyzed by: <ul style="list-style-type: none"> - IPM operated at 633 nm. - Photoacoustic detection (PAD) operated at 633 nm for measuring absorption coefficient based on absorptive and thermal properties of the sample. | <ul style="list-style-type: none"> • After a pure carbon deposit was analyzed by IPM and PAD, an overload of $(\text{NH}_4)_2\text{SO}_4$ was placed on top of the carbon, and the IPM and PAD measurements were repeated. The perturbation of salt to the IPM measurements was much larger (5 – 10 times) than expected, indicating that multiple scattering was apparently taking place within the samples. The perturbation to PAD measurements was much less. • IPM overestimated absorption when interfered with by scattering particles, but the opposite trend was found in PAD. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|--|---|---|
| <p>General Motors Intercomparison Study I (Cadle and Groblicki, 1982)</p> <ul style="list-style-type: none"> • Location: Three ambient sampling sites: Denver, CO, rural areas near Picas, SD, and Abbeville, LA. Source particulate samples were obtained from gasoline and diesel passenger cars run on a chassis dynamometer, and from residential fireplace wood combustion. • Type: Ambient and source emissions. | <p>Sampling and Analytical Method</p> <ul style="list-style-type: none"> • Samples were collected on a glass-fiber filter or a quartz-fiber filter. The analytical methods for EC included: <ul style="list-style-type: none"> - General Motors Research (GMR) thermal analysis protocol. OC removed from the sample by heating at 650 °C under He. - Solvent or Fluorinert FC-78 extraction for 8 hrs before thermal analysis. - Nitric acid (6N HNO₃) digestion for 24 hrs before thermal analysis. - Vacuum Stripping (1 torr, 180 °C or 350 °C) before thermal analysis. - IPM operated at 550 nm for measuring absorption. | <p>Summary of Major Findings</p> <ul style="list-style-type: none"> • Heating at 180 °C removed only 30% of the carbon compared to 62% at 350 °C in a vacuum. Heating in air at 350 °C removed even more carbon (67%). • Both 350 °C oxidation and 2 hr HNO₃ extraction removed 67-68% of the carbon compared to a maximum of 54% removal by the most effective solvent. Thus, a maximum of 14% of the organic matter was not extractable by solvent. • The amount of charring at 650 °C under He depended on the type of organic material present and percent of EC in the samples. Errors were small in automotive diesel particulate samples where charring is limited. The error can be large in samples susceptible to charring, such as wood burning. • The IPM absorption showed a good correlation with EC from thermal method ($r = 0.93$), resulting in an absorption efficiency of $\sim 10 \text{ m}^2/\text{g}$. |
| <p>General Motors Intercomparison Study II (Cadle et al., 1983)</p> <ul style="list-style-type: none"> • Location: One ambient sampling site near Luray, VA. Additional ambient samples were acquired at Warren, MI, during the winter and spring of 1981. Source particulate samples were obtained from diesel passenger cars run on a chassis dynamometer. Wood smoke was collected from a fireplace burning either softwood or hardwood. • Type: Ambient and source aerosol. | <p>Sampling and Analytical Method</p> <ul style="list-style-type: none"> • Samples were collected on quartz-fiber filters. The analytical methods for EC included: <ul style="list-style-type: none"> - GMR thermal analysis protocol. OC was removed from the sample by heating at 650 °C under He. Other heating temperatures were tested. - Three digestion methods were used to remove OC before thermal analysis. In one method, the filters were immersed in a 1.4 M H₂SO₄, 0.13 M K₂S₂O₈, 0.6%W/W AgNO₃ solution. In another method, the filters were immersed in a 1:1 solution of ethanol and 4N KOH for ~ 18 hrs. The third method consisted of immersion in a 30% H₂O₂ solution and irradiation with a 200W Xe-Hg arc lamp for 0.75 hr. | <p>Summary of Major Findings</p> <ul style="list-style-type: none"> • The absorption of organic vapor on glass- and quartz-fiber filters and silver-membrane filters may be a major problem. With some samples, the amount of carbon adsorbed by a backup filter was 30% of that on the front filter. • Thermal methods have the advantage of being rapid, but can cause charring of OC, even at 950 °C. The optimum thermal method varies with different samples. A two-step separation procedure employing heating at 350 °C in air followed by a 950 °C pyrolysis under He should be used for samples of unknown compositions. • The digestion methods investigated removed some EC and showed no advantage over the thermal methods. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|---|--|---|
| <p>Comparison of British Smoke Shade (BSS) with Elemental Carbon Concentration (Edwards et al., 1983)</p> <ul style="list-style-type: none"> • Location: Two aerosol sampling sites: the University of Washington campus provided a typical urban setting while a highway tunnel (U.S. 99) provided a high concentration of vehicle exhaust. • Type: Urban ambient fine aerosol and traffic emissions ($D_p < 1.6 \mu\text{m}$). | <ul style="list-style-type: none"> • Particles were collected on quartz-fiber and Nuclepore polycarbonate-membrane filters. • EEL reflectometer (OECD, 1964) for British Smoke Shade (BSS) measurement. • IPM operated at 500 nm. • OGI TOR (Johnson et al., 1981) protocol on quartz-fiber filters for EC. | <ul style="list-style-type: none"> • b_{abs} determined by reflectometer and IPM transmittance were well correlated to each other, but the slope varied with filter medium and face velocity of sampling. This was probably due to penetration of particles into the filters, causing them to be more reflective and transmit less light for a given aerosol loading than they would have if particles were retained on the surface. • The transmission of a sample on a fiber filter was always less than that for a Nuclepore filter, while the reflectance was either greater or less than that of the Nuclepore, likely due to multiple scattering effects. • The absorption efficiency of EC ranged from 7 – 12 m^2/g in this study. • A correction factor of 1.3 was applied to the BC calculated from BSS for a comparison with the EC. The data suggested that BSS might be used to estimate EC within about a factor of two. |
| <p>Allegheny Mountain Tunnel Study (Szkarlatt and Japar, 1983)</p> <ul style="list-style-type: none"> • Period: 7/14/1981 – 7/18/1981. • Location: Allegheny Mountain Tunnel on the Pennsylvania Turnpike. The tunnel is located in southwestern Pennsylvania with the closest population center being Somersett, 21 km to the west. • Type: Highway traffic emissions. | <ul style="list-style-type: none"> • High volume samplers (Misco Model 680, 5.5 μm size cutoff) were set up in the east portal of the eastbound tunnel. Particles were collected on glass-fiber and Teflon-membrane filters (4 – 7.5 hrs duration). The vehicle composition was monitored. • The organic-soluble fraction of the particulate emission was determined by 16 hr Soxhlet extractions of filter samples in 1:1 (v/v) mixtures of toluene/1-propanol. • The carbon content of extracted, nonextracted, and blank filters was determined by combustion (Spang Microanalytical Laboratory, Eagle Harbor, MI). • IPM operated at 500 nm. • Integrating nephelometer operated at 550 nm for particle scattering. • A He-Ne laser (632.8 nm) was used for total extinction measurements. | <ul style="list-style-type: none"> • The non-extractable carbon was assumed to be EC. Chemical analyses showed that: 1) 24% of the vehicle aerosol was extractable material, 2) 75% of the total mass was carbon, 3) 55% of the total mass was EC, and 4) the stoichiometry of extractable fraction of the diesel particle emissions was $\text{C}_x\text{H}_{1.7x}\text{N}_{0.05x}$. • The mass absorption efficiency of particulate emissions was estimated at $6.0 \pm 1.0 \text{ m}^2/\text{g}$ for diesel vehicles and at $6 \pm 24 \text{ m}^2/\text{g}$ for spark-ignition vehicles. • The measurement of mass fraction of EC in particulate emissions allowed the calculation of the mass absorption efficiency of EC, and it was determined to average $10.9 \pm 1.8 \text{ m}^2/\text{g}$ at 500 nm. • In terms of light extinction per km driven, diesel particle emissions were at least 1 order of magnitude more important than those of spark-ignition vehicles. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|---|---|--|
| <p>Ford Motor Company Dynamometer Study (Japar et al., 1984)</p> <ul style="list-style-type: none"> • Vehicles tested: A 1979 2.3 L Opal and a 1980 2.3 L Peugeot were tested. Both of them used diesel engines. • Driving cycle tested: Over a series of cruises between 20 mph and 60 mph, as well as over a portion of the Federal test procedure (FTP) driving cycle including cold start, hot stabilized, and hot start phases. • Type: Diesel emission fine PM. | <ul style="list-style-type: none"> • Samples were collected on Teflon-membrane and glass-fiber filters. Total particulate mass was determined by weighing Teflon filter. • The organic-soluble fraction of the particulate emission was determined by 20 hr Soxhlet extractions of Teflon filter samples in 1:1 (v/v) mixtures of toluene/1-propanol. • The quartz-fiber filters were analyzed for OC, EC, and TC by the OGI_TOR protocol (Johnson et al., 1981). | <ul style="list-style-type: none"> • The non-extractable mass can be assumed an upper limit to EC. The average ratio of EC to unextractable mass was 1.03 ± 0.06 for all filters. The regression gave a slope of 1.05 ± 0.04 when three outliers were excluded. • Outliers were attributed to dust components (Al, Si, Ca, Fe, S) in the non-extractable mass. • The ratio of OC to extractable mass was 0.7 ± 0.05. The regression gave a slope of 0.75. • The fraction of solvent extractable mass in total emission mass varied strongly (23 – 63%) with the vehicle operating conditions. |
| <p>Ford Photoacoustic Spectroscopy Validation (Adams et al., 1989)</p> <ul style="list-style-type: none"> • Period: 9/29/1986 – 11/10/1986. • Location: in a mobile office trailer located adjacent to Ford Motor Company's Scientific Research Laboratory in Dearborn, MI. • Type: Rural ambient PM₅. | <ul style="list-style-type: none"> • A high-volume sampler equipped with a 5 µm pre-separator was used to collect particles on quartz-fiber filters (5 – 6 hr duration), followed by TOT analysis. Samples were extracted overnight in a 50/50 (v/v) mixture of n-propanol and toluene. Thermal analysis included 250, 385, 580, and 680 °C in He and 600 and 750 °C in 2%O₂/98%He. The OC/EC split was determined by transmittance. • Photoacoustic instrument (Ford Motor Company) operated at 514.5 nm (30 sec average). | <ul style="list-style-type: none"> • A mass absorption efficiency (10 m²/g) was applied to obtain BC concentrations. Agreement between photoacoustic BC and thermal/optical EC were excellent ($r = 0.926$, slope = 1.10 ± 0.13, intercept = -0.1 ± 0.22 µg/m³). • The photoacoustic instrument showed a detection limit ~0.3 µgC/m³ (5 – 6 hr average). The instrument signal was sensitive to temperature and humidity, so frequent calibration was necessary as the ambient conditions changed. No influence from atmospheric light scattering species was observed. |
| <p>Southern California Air Quality Study I (SCAQSI) (Adams et al., 1990)</p> <ul style="list-style-type: none"> • Period: 6/19, 6/24-25, 7/13-15, 8/27-29, 9/2-3 in 1987 (ozone or PM₁₀ episode days). • Location: at Claremont, CA. • Type: Suburban ambient PM_{2.5}. | <ul style="list-style-type: none"> • A high-volume sampler equipped with a 5 µm pre-separator was used to collect particles on quartz-fiber filters (5 – 6 hr average) for OC, EC, and TC by TOT protocol. Samples were extracted overnight in a 50/50 (v/v) mixture of n-propanol and toluene. The thermal analysis included 250, 385, 580, and 680°C in He and 600 and 750°C in 2%O₂/98%He. The split of OC and EC was determined by transmittance. • Photoacoustic instrument (Ford Motor Company) operated at 514.5 nm (30 sec average). | <ul style="list-style-type: none"> • Correlation was good for the optical absorption measured photoacoustically with EC concentration determined by extraction/thermal analysis ($r = 0.945$). The EC mass absorption efficiency was estimated at 10.06 ± 0.56 m²/g at 514.5 nm. • The correlation between photoacoustic measurements and the thermal technique (no extraction) yielded greater uncertainty (10%). • This study confirmed that EC is the dominant source of aerosol optical absorption in the visible region. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|--|---|--|
| <p>Southern California Air Quality Study II (SCAQSI) (Turpin et al., 1990)</p> <ul style="list-style-type: none"> • Period: 6/19, 6/24-25, 7/13-15, 8/27-29, 9/2-3 in 1987 (ozone or PM₁₀ episode days). • Location: at Claremont, CA. • Type: Suburban ambient PM_{2.5}. | <ul style="list-style-type: none"> • OGI dual-filter/time-resolved thermal-optical carbon analyzer (80-min average followed by 40-min analysis). OC was evolved at 650 °C in a pure He atmosphere and EC was evolved at 750 °C in a 98%He/2%O₂ atmosphere. • Photoacoustic instrument (Ford Motor Company, 30 s average) operated at 514.5 nm. | <ul style="list-style-type: none"> • The comparison over the concurrent sampling periods indicated good agreements between OGI_EC and Ford absorption (b_{abs}). • When converting b_{abs} to BC concentration using an absorption efficiency of 10 m²/g, the two methods yielded a correlation coefficient of 0.905. The ratio of the mean Ford BC value to the mean OGI_EC value was 1.01, and a two-sided t-test showed no significant difference between Ford and OGI values at the 95% confidence level. |
| <p>Carbonaceous Species Methods Comparison Study I (CSMCS) (Cadle and Mulawa, 1990; Countess, 1990; Hering et al., 1990; Lawson and Hering, 1990)</p> <ul style="list-style-type: none"> • Period: 9 days from 8/12/1986 to 8/20/1986. • Location: at Citrus College in Glendora, CA, located in the northeastern portion of the Los Angeles Basin. • Type: Urban ambient fine PM (PM_{1,9} to PM_{2.5}, varied between groups). | <ul style="list-style-type: none"> • Ambient samples (4 – 12 hr average) were collected and analyzed for OC, EC, and TC by: <ul style="list-style-type: none"> – OGI TOR protocol (Johnson et al., 1981) with backup-filter correction. – Two-step (He and He/O₂) thermal evolution methods without optical charring correction: by U.S. EPA, Environmental Monitoring and Service, Inc. (EMSI), and GMR. – Optical absorption measurement for EC plus one-step combustion for TC by Air Industrial Hygiene Laboratory (AIHL). – Samples were analyzed for EC by oxidation in He over an MnO₂ catalyst (Thermal Manganese Dioxide Oxidation [TMO] method, 525 °C for OC and 850 °C for EC) (Fung, 1990). – Forward alpha scattering technique (FAST, Cahill et al., 1984) for TC by the University of California at Davis. This is a nuclear technique which does not distinguish between OC and EC. | <ul style="list-style-type: none"> • Consistently higher OC concentrations were reported by the AIHL undened quartz-fiber filter and the AeroVironment (AV; Monrovia, CA) denuded quartz-fiber filter. Lower OC was reported by the adsorption corrected quartz-fiber filter by OGI. The lowest OC were from University of Minnesota (UM) and GMR, both of which used impactors to collect particles. • The differences in OC were mostly attributed to sampling methods rather than to analytical methods, but much of the difference in EC was attributed to analytical methods. • The TC on Teflon-fiber filters determined by UCDFAST was consistently below (~ 64%) the mean of all other methods. • The adsorption of gaseous vapors onto quartz-fiber filters was a significant sampling artifact. For systems employing tandem filters, the TC found on the backup filters was 14% to 53% of the five-sampler mean for TC. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
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| <p>Carbonaceous Species Methods Comparison Study II (CSMCS) (Countess, 1990; Lawson and Hering, 1990)</p> <ul style="list-style-type: none"> • Period: 10 days in August, 1986. • Location: suburban Los Angeles, CA. • Type: Reference samples including suburban/urban ambient aerosol, gasoline/diesel source samples, wood smoke samples, a pure secondary organic carbon sample (generated from the photolysis of trimethylbenzene), and a blank (PM₁₀ or less). | <ul style="list-style-type: none"> • Quartz-fiber samples were analyzed for OC, EC, and TC by: <ul style="list-style-type: none"> - IMPROVE_TOR protocol. - OGI_TOR protocol. - Sunset TOT method (top temperature 700°C for OC). - Two-Step thermal methods: Global Geochemistry Corporation (GGC), U.S. EPA, EMSI, GMR, and Oregon Department of Environmental Quality (DEQ). - Pure oxygen/continuous ramping. - Optical absorption measurement plus one-step combustion (AIHL). - The samples were analyzed for EC by oxidation in He over an MnO₂ catalyst by TMO method (525 °C for OC and 850 °C for EC). | <ul style="list-style-type: none"> • All laboratories agreed well on TC analyses, with a pooled coefficient of variation for all reference samples of 9%. • The coefficient of variation for OC and EC were 25.8% and 52.3%, respectively. • The range of EC/TC ratios for the ambient PM₁₀ samples varied by a factor of three from a low of 0.1 (from U.S. EPA) to a high of 0.3 (from GGC) with a mean of 0.22. • Overall, U.S. EPA had the lowest average EC/TC ratio while the IMPROVE_TOR had the highest EC/TC ratio of 0.5. U.S. EPA's EC values might be low due to their methodology of switching carrier gases during operation (O₂ contamination). • Three of the four laboratories (except Sunset TOT) that attempted to correct for charring gave higher EC values than those without charring corrections. |
| <p>Carbonaceous Species Methods Comparison Study III (CSMCS) (Hansen and McMurry, 1990; McMurry and Hansen, 1990)</p> <ul style="list-style-type: none"> • Period: 10 days in August 1986. • Location: suburban Los Angeles, CA. • Type: suburban ambient aerosol (PM_{2.5}). | <ul style="list-style-type: none"> • Five-stage (2.5, 1.0, 0.6, 0.23, and 0.1 μm) impactors with aluminum foil substrates with quartz-fiber backup filter (University of Minnesota) (12-hr). • One-stage (0.1 μm) impactor with aluminum foil substrates with quartz-fiber backup filter (University of Minnesota) (12 hr). • Samples were analyzed for EC by oxidation in He over an MnO₂ catalyst by TMO method (525°C for OC and 850 °C for EC). • Aethalometer (University of California at Berkeley) (1 min). | <ul style="list-style-type: none"> • The aethalometer was calibrated against a chemical determination of EC by solvent extraction pretreatment followed by thermal evolved gas analysis (Gundel et al., 1984). • The results of the intercomparison yielded a slope (EC/BC) of 1.02 ± 0.04 and a correlation coefficient of r² = 0.973, within the limits of accuracy of actual determinations. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|--|---|--|
| <p>Carbonaceous Species Methods Comparison Study IV (CSMCS) (Hansen and Novakov, 1990)</p> <ul style="list-style-type: none"> • Period: 9 days from 8/12/1986 to 8/20/1986. • Location: at Citrus College in Glendora, CA, located in the northeastern portion of the Los Angeles Basin. • Type: Urban ambient total suspended particulate matter. | <ul style="list-style-type: none"> • Aethalometer (632 nm, minutely resolution) (6 hr) • IPM was used to calibrate the aethalometer. | <ul style="list-style-type: none"> • The 6-hr average BC concentration ranged from 1.1 to 6.5 $\mu\text{g}/\text{m}^3$, with the highest concentration for each day usually shown by the filter collected during period 0800-1400 Pacific Daylight Time (PDT). • Examination of minute-by-minute data showed definite events in which individual vehicles in an adjacent property emitted plumes contributing up to 5 $\mu\text{g}/\text{m}^3$. • The aethalometer filters were subsequently analyzed in the laboratory for BC by an IPM that had been calibrated against the solvent extraction/quantitative thermal analysis of EC. The comparison of these analyses confirmed the calibration of the aethalometer. |
| <p>DLR Research Center Aethalometer Intercomparison Study (Ruoss et al., 1992)</p> <ul style="list-style-type: none"> • Period: Winter 1990-1991. • Location: The field station of the Meteorological Institute at Garching, located about 20 km north of Munich, Germany. • Type: Artificial black (graphite) and white (salt) samples and ambient fine aerosols. | <ul style="list-style-type: none"> • Using DLR and Magee aethalometers (Magee Scientific Inc.), white light was emitted from a source on the downstream side of the filter. Light passing through the filter was detected by four photodiodes, two of them sensitive in the green range (550 nm) and two in the infrared range (950 nm). Two photodiodes measured the reference signals, and the other two detected the measuring signals. | <ul style="list-style-type: none"> • The response of the DLR aethalometer was critical to the ratio of the mass of absorbing and non-absorbing materials as compared with an optical absorption technique (Hänel, 1987; 1988). • During the field experiments, the measured soot concentration differed by ~ 50% on average between the DLR aethalometer and the Magee aethalometer. The results of the Magee aethalometer agreed with the absorption technique (Hänel, 1987; 1988) very well. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|---|---|---|
| <p>Comparison of Filter Absorption and Transmissometer Methods (Horvath, 1993)</p> <ul style="list-style-type: none"> • Samples: Pure carbon particles and transparent salt particles. • Type: Artificial black, white, and mixture fine aerosols ($D_p < 0.05 \mu\text{m}$). | <ul style="list-style-type: none"> • An aerosol consisting of pure carbon was produced by a spark discharge between carbon electrodes in an inert atmosphere. This aerosol was mixed with an aerosol consisting of particles produced by spraying a sugar solution from a constant output atomizer. Particles were collected by a cascade impactor. • Long-path transmissometers were used to measure extinction by pure carbon and sugar aerosols separately. • IPM for measuring absorption of particle deposit on Nuclepore filter. | <ul style="list-style-type: none"> • For pure carbon aerosol, when transmission of Nuclepore filter was between 0.4 and 0.95 (the filter has light- to medium-gray appearance), the light absorption coefficient measured with IPM was on the average 22% higher than the transmissometric measurements, assuming scattering is negligible. Agreements were obtained for transmission < 0.2. • Transparent particle deposit produced limited changes in IPM, but the change became significant if the sugar particle was replaced by latex particles. This is due to a stronger backscattering. • On a filter which already had carbon particles, an additional deposition of transparent particles onto it always decreased its transmission. Depositing sugar particles that had a scattering coefficient amounting to 50% of the absorption of the carbon particles caused a change in IPM of 14% on average. |
| <p>German Intercomparison Study I (Petzold and Niessner, 1995a)</p> <ul style="list-style-type: none"> • Locations: Long-term field studies were located at two sites of different pollution levels in Munich and Berlin, Germany, respectively. Additional short-term studies were conducted at two rural sites. • Type: Urban and rural PM_{10}. | <ul style="list-style-type: none"> • OC, EC, and TC were determined by the German VDI solvent extraction/thermal oxidation protocol. Volatile organic components were gasified in nitrogen (N_2) atmosphere at 500 °C. This method determined non-extractable carbon (NEC: only solvent extraction), non-volatilizable carbon (NVC: only thermal desorption), and apparent EC (AEC: thermal desorption and solvent extraction). • Aethalometer (AE-9, Magee Scientific) operated at 880 nm. • Black smoke method (Christolis et al., 1992). • Photoelectric aerosol sensor (PAS) (Niessner and Wilbring, 1989). | <ul style="list-style-type: none"> • The method yielded AEC fractions of TC from 9% to 30% at rural sites and from 18% to 53% at urban sites. The NEC fraction of TC was 68–78%. The EC-overestimation by removing OC only with solvent extraction was 35–135%. • Aethalometer BC showed a good correlation to AEC at all sites ($r = 0.81 - 0.97$) with AEC varying from $< 2 \mu\text{g}/\text{m}^3$ to $> 10 \mu\text{g}/\text{m}^3$. The regression slopes showed strong site dependence, indicating a variation of mass absorption efficiency of EC. • The black smoke method correlated well with NEC and AEC, but it was not possible to detect a mass concentration of $< 5 \mu\text{g}/\text{m}^3$. • The PAS was found to be much more sensitive to fresh soot than aged ambient EC. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|---|--|--|
| <p>German Intercomparison Study II (Pezzold and Niessner, 1995b)</p> <ul style="list-style-type: none"> • Period: 4/1992 – 4/1993. • Location: Two long-term field studies were located in Munich (Site 1: 4/1992 - 10/1992; Site 2: 11/1992 - 4/1993). Site 1 was in a residential district without industrial plants. Site 2 was at a traffic-impacted street crossing with a traffic volume of > 100,000 vehicles per day. Additional short-term studies were conducted at two rural sites. • Type: Urban and suburban ambient PM₁₀. | <ul style="list-style-type: none"> • A tandem filter design was used in this study. Sampling started at 7 a.m. daily (24 hr). • OC, EC, and TC were determined by the German VDI solvent extraction/thermal oxidation protocol. Volatile organic components were gasified in N₂ atmosphere at 500 °C. This method determined NEC, NVC, and AEC. • Aethalometer (AE-9, Magee Scientific) operated at 880 nm. • Smoke shade method (Christolis et al., 1992). • PAS, which makes use of photoelectron emission from particles when irradiated with UV light. | <ul style="list-style-type: none"> • The method yielded AEC fraction of TC between 40% and 50% and NEC fraction of TC between 75% and 78%. • Aethalometer BC and NEC yielded site-dependent mass absorption efficiencies (Site 1: 8.4 m²/g; Site 2: 13.7 m²/g) with respect to non-extractable carbon. • For the smoke shade method based on reflectometer, a detection limit of 4.2 µg/m³ with respect to EC was determined. Reliable NEC determination was not possible for NEC < 5 µg/m³. • The PAS showed complex dependences in its response to a given soot concentration on the age of aerosol. Hence, the PAS was found not to be a useful stand-alone technique for soot monitoring. But in combination with an EC measurement, the ratio of PAS signal to EC might allow an estimate of mobile source contribution to particulate carbon. |
| <p>Intercomparison of Black Carbon Measurement (Hitzenberger et al., 1996; 1999)</p> <ul style="list-style-type: none"> • Sample: Resuspended carbon black samples and ambient samples from a rural site (Bondville, IL). • Type: Artificial BC standards and rural ambient PM_{2.5} far away from source regions. | <ul style="list-style-type: none"> • The test aerosol was generated by nebulizing a suspension of carbon black (Elifex 124, Cabot Corp.) in a mixture of 80% ultrapure water and 20% analytic grade isopropanol and sampled by quartz-fiber and polycarbonate filters. Ambient samples acquired by micro-orifice uniform deposit impactor (MOUDI) and dichotomous samplers. • BC standards were analyzed by the pure O₂/2-step protocol (Cachier et al., 1989a, 1989b); ambient samples by the NIOSH 5040 protocol. • Integrating Sphere (IS) method (Hitzenberger et al., 1996). • Aethalometer (Magee Scientific) operated at 880 nm. | <ul style="list-style-type: none"> • b_{abs} measured through aethalometer and IS agreed well ($r = 0.943$; slope = 0.998; intercept = 0.001 m⁻¹). • For standards, the BC mass concentrations determined by aethalometer were only 30% of those from IS. When compared to the thermal method, the IS overestimated BC by 21%. The absorption efficiency (19 m²/g) for the aethalometer might be too high. • For ambient samples, BC determined by thermal/optical method and IS agreed within 5% of the 1:1 slope. • For ambient samples, a calibration factor of 6.8 m²/g yielded a slope of aethalometer vs. thermal/optical results of 0.99, very close to the expected 1:1 line, but there was a considerable offset. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|--|---|--|
| <p>IMPROVE Network EC/Absorption Comparison (Huffman, 1996)</p> <ul style="list-style-type: none"> • Period: 1988 – 1993. • Locations: Several rural sites (Pinnacles National Monument, CA; Bandelier National Monument, NM, etc.) • Type: Rural ambient PM_{2.5}. | <p>Sampling and Analytical Method</p> <ul style="list-style-type: none"> • Quartz-fiber filters were analyzed for OC, EC, and TC using the IMPROVE_TOR protocol. • Teflon-fiber filters were analyzed by laser IPM (LIPM) for b_{abs} at the University of California at Davis. | <p>Summary of Major Findings</p> <ul style="list-style-type: none"> • The ratio of b_{abs} to EC measured by IMPROVE_TOR consistently indicates an absorption efficiency that was twice the accepted value of 10 m²/g. Correlations between b_{abs} and TOR carbon fractions strongly suggest that the discrepancy was due to an underestimate of light-absorbing carbon rather than an overestimation of b_{abs} or due to a real, higher value of the absorption efficiency. • The potential errors in the current interpretation of TOR analysis included: 1) The pyrolysis correction based on optical reflectance monitoring; and 2) the carbon evolving between 450 and 550 °C in a pure He atmosphere, which was well-correlated with b_{abs} and appeared to be light absorbing as EC. |
| <p>Measurement of Haze and Visual Effects (MOHAVE) (Turpin et al., 1997)</p> <ul style="list-style-type: none"> • Period: 7/15/1992 – 8/30/1992. • Location: at Meadview, AZ, located 905 m above sea level on the western edge of Grand Canyon National Park, 95 km east of Las Vegas, NV, and 120 km northeast of the MOHAVE coal-fire power plant. • Type: Desert ambient PM_{2.5}. | <p>Sampling and Analytical Method</p> <ul style="list-style-type: none"> • Size-resolved PM was measured with MOUDIs by the University of Minnesota from 0700 to 1900 Pacific Standard Time (PST) using aluminum foil substrates and then analyzed by TMO method, in which samples were heated in He over an MnO₂ catalyst (525°C for OC and 850 °C for EC). • PM_{2.5} samples were collected by a standard IMPROVE four-module sampler and then analyzed by the IMPROVE TOR protocol. | <p>Summary of Major Findings</p> <ul style="list-style-type: none"> • Average MOUDI TC concentrations were 88% greater than IMPROVE TC, with 95% confidence limits, and the data were uncorrelated (n = 22). • OC on backup quartz-fiber filter was 50 ± 20% of the front filter loading. Subtracting the backup filter OC averaged over all sites caused Meadview OC concentrations to be underestimated by 60% on average. • The TMO reported an EC mass fraction of < 10% in TC while the IMPROVE_TOR reported an EC mass fraction of ~ 17% in TC. |
| <p>Southwestern Pennsylvania Air Pollution Health Effect Study (Allen et al., 1999)</p> <ul style="list-style-type: none"> • Period: Summer 1990, 11 weeks. • Location: at a school 2 km north of the center of Uniontown, PA, in a residential area. Uniontown is located in Fayette County, 60 km south-southwest of Pittsburgh, PA, and 90 km east of the Ohio River. • Type: Rural ambient PM_{2.5}. | <p>Sampling and Analytical Method</p> <ul style="list-style-type: none"> • Samples for OC and EC were collected (3 hr) using a parallel plate denuder/filter pack system. Quartz-fiber filters were analyzed by IMPROVE_TOR protocol. • Aethalometer (AE-9, Magee Scientific Inc.) operated at 880 nm. • Coefficient of Haze (COH; RAC 5000) operated at 400 nm. | <p>Summary of Major Findings</p> <ul style="list-style-type: none"> • Ten-min average aethalometer BC data were averaged into 3-hr values to match the 63 OC and EC samples. The two methods were found to be highly correlated (r² = 0.925). The regression equation is BC = (0.95 ± 0.4) EC – (0.2 ± 0.4). The range of EC was 0.6 – 9.4 µg/m³. • Collocated COH and aethalometer measurements were conducted in Philadelphia, PA, and showed comparable results. There was a linear relationship between the two measurements (r² = 0.98 with p-value < 0.001). |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|---|--|---|
| <p>NIOSH Interlaboratory Comparison Study (Birch, 1998)</p> <ul style="list-style-type: none"> Location: Source dominated samples were collected from four sites: at a construction site (where diesel-powered compressors were used) near downtown; at a diesel truck loading dock; in the bay of a fire engine house; and from wood smoke. Cigarette smoke was collected in the laboratory. Type: Various combustion source samples. | <ul style="list-style-type: none"> Quartz-fiber filter samples were analyzed for OC, EC, and TC by: <ul style="list-style-type: none"> NIOSH 5040_TOT protocols. TOR (similar to IMPROVE_TOR but the residence times were estimates based on scale shown in thermograms). C1: 800°C, 10 min in N₂ for OC; 800°C, 7 min in O₂ for EC. C2A: 200°C (2 min), 400°C (4 min), and 560°C (6 min) in N₂ for OC; 800°C (4.5 min) and 1200°C (2 min) in O₂ for EC. C2B, C3, C4: 200°C (2 min), 400°C (2 min), and 550°C (4 min) in N₂ for OC; 800°C (4.5 min) in O₂ for EC. C1-C4 detect carbon using coulometric methods. | <ul style="list-style-type: none"> Good agreement (relative standard deviation [RSD] < 15%) between the TC results were reported by all laboratories. Reasonable within-method agreement was found for EC results. For EC, all coulometric method results were positively biased relative to thermal/optical results. About 52% and 70% of the carbon found in sucrose and EDTA solutions, respectively, was quantified as EC by coulometric methods, while thermal/optical methods found < 3% of EC for these standards. The NIOSH 5040_TOT method reported only 2% of EC in cigarette smoke, while the coulometric method reported an average EC fraction of 40% in cigarette smoke. The coulometric method without charring correction overestimated EC due to inadequate removal of OC in the first part of the analysis. |
| <p>Northern Front Range Air Quality Study (NFRAQS) (Moosmüller et al., 1998)</p> <ul style="list-style-type: none"> Period: 12/17/1996 – 1/9/1997 Location: at Brighton, CO, located in a semi-rural environment about 30 km northeast of downtown Denver. Type: Suburban ambient PM_{2.5}. | <ul style="list-style-type: none"> Particles were acquired for 6- or 12-hr periods on: 1) quartz-fiber filters for OC, EC, and TC by the IMPROVE_TOR protocol; and 2) Teflon-membrane filters followed by light-transmission analysis (filter b_{abs}) using a Tobias TBX-10 Densitometer. Aethalometer (AE-10IM, Magee Scientific) (10-min average). Photoacoustic instrument (532 nm and 685 nm) (10-min average). | <ul style="list-style-type: none"> The aethalometer BC was well correlated with photoacoustic b_{abs} (r² = 0.87 – 0.92). The comparison resulted in an absorption efficiency for BC of ~ 5 m²/g at 685 nm and ~ 10 m²/g at 532 nm. The TOR EC also showed a good correlation with photoacoustic b_{abs} (r² = 0.85). Large variations occurred when the EC concentration was low. The comparison resulted in a absorption efficiency for EC of ~ 3.6 m²/g The correlation of photoacoustic b_{abs} and filter b_{abs} was fair (r² = 0.74). A correction method (Horvath, 1997) may be used to improve agreement. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|---|--|--|
| <p>Smoke, Clouds, and Radiation-Brazil (SCAR-B) Experiment (Reid et al., 1998; Martins et al., 1998)</p> <ul style="list-style-type: none"> • Period: 8/17/1995 – 9/20/1995. • Location: Samples were obtained from <i>in-situ</i> instrumentation or filters collected aboard the University of Washington Convair C-131A research aircraft flying over mountainous and Amazon forest regions of Brazil. • Type: Aloft fine aerosol dominated by smoke from biomass burning. | <ul style="list-style-type: none"> • Optical extinction cell (OEC), which is a 6.4 m long transmissometer operated at 538 nm. • IPM (Radiance Research), operated at 550 nm. • PSAP (Radiance Research) at 550 nm (1-min average) • Optical reflectance (OR) (Diffusion Systems), operated in a broadband visible mode to determine the absorption coefficient. • Pure O₂/2-Step thermal evolution (TE) method (Cachier et al., 1989a, 1989b). • Remote sensing (RS) techniques acquired measurements from satellite or Sun photometer combined with irradiance data to obtain estimates of the columnar-averaged, single-scattering albedo using SPCTRAL2 (Bird and Riordan, 1986) radiative transfer model. | <ul style="list-style-type: none"> • The IPM and OR methods produced data that scatter around 1:1 line; the mean residuals for IPM and OR were -3% and -0.5%, respectively. The uncertainties in IPM and OR methods were estimated at 40% and 17%, respectively. • There was a variance of 45% between the PSAP and the OR techniques. The uncertainty in PSAP was estimated ~±40%. This translated into uncertainties of ±0.05 in single scattering albedo for 1-min samples. • Combining of the scattering measurements from nephelometer, the OEC produced single scattering albedo for smoke particles that varied from 0.35 – 0.9. • The TE method produced data lying well below the 1:1 line with OEC ($r = 0.45$); the mean residual for TE was -49% relative to OEC, indicating systematic errors. The uncertainty of TE was estimated at 31%. BC in biomass burning aerosol was poorly correlated with b_{abs}. This might lead to biases in BC absorption efficiency estimates. • SPCTRAL2 model yielded single-scattering albedos slightly higher (by 0.01) than the columnar-averaged values derived from <i>in-situ</i> optical measurements on the aircraft. |
| <p>Free Troposphere Research Station Jungfraujoch (Lavanchy et al., 1999)</p> <ul style="list-style-type: none"> • Period: 7/1995 – 6/1997. • Location: at the Jungfraujoch high-alpine research station in Switzerland (3454 m above surface level). • Type: Free troposphere fine PM. | <ul style="list-style-type: none"> • Filter samples were analyzed by the Switzerland pure O₂/2-Step (340 and 650°C) TE protocol with flash heating. • Aethalometer (AE-10, Magee Scientific Inc.), operated at 880 nm (19 – 360 hr sampling duration). • PM₁₀ samples were acquired from a roadside location in Brene with heavy traffic and from a suburban site at Dübendorf. • Standards for OC were obtained by dissolution of starch, tri-sodium citrate 2-hydrate, glucose, and humic acid in pure water, and by pipetting a known volume of these standards onto quartz-fiber filters. EC standards were acquired by using flame soot 101 (Degussa) ultra-sonically suspended in pure water. | <ul style="list-style-type: none"> • The recovery of model organic compounds glucose and starch as OC was ~ 100% while charring was negligible. The recovery of humic acid as OC was 84% on average and artifact formation of EC due to charring was found to be 14%. • The correlation of the EC from TE method and BC from aethalometer was high ($r^2 = 0.91$), exhibiting an average absorption efficiency of $9.3 \pm 0.4 \text{ m}^2/\text{g}$. • Results confirmed that the aethalometer underestimates the true BC at remote sites when the manufacturer's calibration is used. • No significant seasonal cycle in absorption efficiency was found. Shorter term variability (days to weeks) was attributed to: 1) the EC/TC composition, and 2) a combination of the aethalometer filter temporal resolution and the fraction of air mass sampled. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|---|---|--|
| <p>Harvard/EPRI Intercomparison Study (Babich et al., 2000)</p> <ul style="list-style-type: none"> • Periods and Locations: <ul style="list-style-type: none"> - Riverside CA, 8/15/1997-9/20/1997 - Boston, MA, 9/10/1997-9/30/1997 - Chicago, IL, 10/10/1997-11/15/1997 - Dallas, TX, 12/5/1997-1/20/1998 - Phoenix, AZ, 12/10/1997-1/25/1998 - Bakersfield, CA, 2/10/1998-3/25/1998 - Philadelphia, PA, 8/1/1998-9/1/1998 - Bakersfield, CA, 1/8/1999-1/29/1999 • 2. Type: Urban ambient PM_{2.5}. | <ul style="list-style-type: none"> • Particles were collected on quartz-fiber filters (24-hr average) for OC, EC, and TC by the IMPROVE TOR protocol. • Aethalometer (AE-16U, Magee Scientific) at all cities except for Boston (5-min average). • Dual channel aethalometer (AE-20UV, Magee Scientific) operated at 325 nm and 880 nm (5-min average). | <ul style="list-style-type: none"> • For six cities combined, the EC measured by TOR and BC measured by aethalometer (880 nm) were highly correlated ($r^2 = 0.94$; 187 24-hr samples), but the BC values were consistently ~ 24% less than the EC across all six cities, using the aethalometer manufacturer's absorption efficiency (19.2 m²/g). • The ratios of BC and EC ranged from 0.62 to 0.81. The lowest ratio was obtained in Dallas, which had the smallest dynamic range of EC concentrations and minimum influence on the overall regression. |
| <p>Kyoto Intercomparison (Japan) (Tohno and Hitztenberger, 2000)</p> <ul style="list-style-type: none"> • Location: at Kyoto University, Uji campus, Kyoto, Japan. • Type: Urban ambient PM_{2.5}. | <ul style="list-style-type: none"> • R&P 5400 ambient carbon particulate monitor (ACPM) (0.14 - 2.5 μm) (1-hr average) • IS method (Hitztenberger et al., 1996). Atmospheric particles were collected on Nuclepore filters (3-hr average) downstream of a size-selective Anderson impactor. The exposed filters were dissolved in chloroform, then acetone, to produce liquid suspensions of the collected particles, and the blackness of the suspensions was determined in terms of BC content using the calibration curve of IS. | <ul style="list-style-type: none"> • Poor agreement was found for EC from ACPM and BC from IS. • BC mass fraction for particles less than 0.14 μm in diameter ranged from 0.5 to 0.7 in the measurements. Excluding particles below 0.14 μm from IS, the agreement between IS BC and ACPM EC improved. It was found that ACPM underestimated the real BC concentration without corrections. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|--|---|---|
| <p>Comparison of IMPROVE and NIOSH thermal evolution protocols for OC and EC (Chow et al., 2001)</p> <ul style="list-style-type: none"> • Period: Samples were acquired from a variety of sampling sites during 1997 – 1998. These included 41 ambient samples and 19 source samples. • Location: in CA; NV; CO; DC; VA; NC; TX; and Mexico. • Type: Urban (commercial, residential, and industrial), suburban agriculture, and rural ambient PM_{2.5}; resuspended dry lake soil and road dust; motor vehicle exhaust and chicken rotisserie cooking emissions. | <ul style="list-style-type: none"> • Pallflex quartz-fiber filter samples were analyzed for OC, EC, and TC by: <ul style="list-style-type: none"> – IMPROVE_TOR protocol. – NIOSH 5040_TOT protocol. | <ul style="list-style-type: none"> • The IMPROVE and NIOSH thermal evolution protocols were equivalent for TC sampled on quartz-fiber filters. • NIOSH_TOT EC was typically less than half of IMPROVE_TOR EC. The primary difference was the allocation of carbon evolving at the NIOSH high (850°C) temperature in He atmosphere to the OC rather than EC fraction. When this portion of NIOSH OC was added to NIOSH_TOT EC, the IMPROVE and NIOSH analyses were in good agreement. • The pyrolysis adjustment to the EC fraction was always higher for transmittance than reflectance regardless of the protocols used. The difference was most pronounced for very dark samples on which neither reflectance nor transmittance was able to accurately detect further blackening due to pyrolysis. |
| <p>Vehicle Emissions Research Laboratory (VERL) Dynamometer Study (Moosmüller et al, 2001b)</p> <ul style="list-style-type: none"> • Vehicles tested: 1996 Dodge Ram 2500 (29509 km), and 1999 Ford F250 SD (32401 km). • Driving cycle tested: Typical FTP driving cycle including cold start, hot stabilized, and hot start phases. • Type: Diesel emission PM_{2.5}. | <ul style="list-style-type: none"> • Time-integrated emissions were acquired on quartz-fiber filters followed by IMPROVE_TOR protocol for OC and EC analysis (1 – 10 min average). • TEOM (R&P 1105) (1-sec average). • Nephelometer (TSI DustTrak 8520) (1-sec average). • Aethalometer (Anderson RTAA-800) (1-sec average). • Photoacoustic Instrument (532 nm) (1-sec average). • Smoke Meter (DRI SM) (633 nm) (1-sec average). | <ul style="list-style-type: none"> • Aethalometer, photoacoustic, and smoke meter showed the best correlations with the IMPROVE TOR EC ($r^2 = 0.92$, 0.92, and 0.91, respectively). The aethalometer overestimated TOR EC by ~40%. Photoacoustic estimated an EC absorption efficiency of ~8.5 m²/g. • TEOM and nephelometer had better correlations with TC ($r^2 = 0.92$ and 0.84, respectively). • OC can be reasonably estimated by the difference between TEOM/nephelometer total mass measurements and EC can be estimated from aethalometer, photoacoustic, or smoke meter. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|--|---|---|
| <p>Carbon Conference International Aerosol Carbon Round-Robin Test (Schmid et al., 2001)</p> <ul style="list-style-type: none"> • Period: 11/7,8,10/1998 for 24-hr average sampling. • Location: Frankfurter Allee Street in the city of Berlin, Germany. The traffic volume is approximately 58,000 cars per day with a proportion of trucks of ~5%. • Type: Urban/traffic ambient PM₁₀. | <ul style="list-style-type: none"> • Particles were collected by a high-volume sampler (Digitel DHA80) with a PM₁₀ inlet and analyzed for OC, EC (or BC), and TC by various thermal protocols: <ul style="list-style-type: none"> - German VDI 2465 part 1 (solvent extraction, coulometry). - German VDI 2465 part 2 (thermal). - France CNRS-CEA two-step flash heating. - Thermal linear temperature method (20°C/min) in pure O₂. - TOT methods (various temperature programs). - IMPROVE_TOR protocol. - Shimadzu TOC 5000. - Elemental Analyzer CE 440; BC: optical transmissometry. - Modified IS method transmission mode. | <ul style="list-style-type: none"> • A good agreement was shown for the analysis of TC by all laboratories (7 and 9% interlaboratory RSD). • For EC, the within-laboratory RSD was ~5% and the interlaboratory RSD was 37% for the low load and 46% for the high load samples. • Thermal/optical methods obtained, on average, lower EC values than laboratories using only thermal methods, likely due to the charring correction. However, a relatively high RSD was found for the highest loaded sample with thermal/optical methods. • Agreements between thermal/optical methods (TOR/TOT) and methods that reduce charring (extraction, two-step flash method) were better. • Optical transmissometry and modified IS did not report exact BC since the sample was too dark. |
| <p>Soil BC Content Measurements (Schmid et al., 2001)</p> <ul style="list-style-type: none"> • Location: The eight Australian soils investigated originated from the surface horizons of Vertisols, Mollisols, Alfisols, and Oxisols. • Type: Sieved rural soil samples (coarse particles > 2 mm). | <ul style="list-style-type: none"> • The sieved soil samples were analyzed for BC using various methods: <ul style="list-style-type: none"> - Thermal oxidation method in which OC is removed at 375 °C for 24 hours, and EC is determined by C, N-elemental analysis using mass difference. - Additional acid extraction (with or without hydrofluoric acid [HF]) before thermal oxidation to remove OC. - Chemical oxidation with HNO₃ (65%) at 170 °C for 8 hrs to remove OC. EC is determined by GC/FID using benzene carboxylic acids as markers. | <ul style="list-style-type: none"> • Thermal oxidation resulted in BC concentrations exhibiting only small differences (41.8 – 58.7 g BC/kg) between samples compared to the other methods. When it was combined with extraction/hydrolysis as a pretreatment, measured values of BC were lower by factors of 8 – 10. • Pure chemical oxidation methods often resulted in higher BC concentrations (37.2 – 109.0 g BC/kg soil). Differences between samples were also larger. • BC concentrations generally decreased with increasing intensity of chemical attack. • BC measured for individual samples varied over 2 orders of magnitude (up to a factor of 571). |
| <p>Maryland Aerosol Research and Characterization (MARCH-Atlantic) Study (Chen et al., 2002)</p> <ul style="list-style-type: none"> • Period: 7/1999 – 7/2002 • Location: at Fort Meade Army base, near the middle of the Baltimore-Washington corridor. • Type: Suburban ambient PM_{2.5}. | <ul style="list-style-type: none"> • Samples were collected on quartz-fiber filters (24 hr). Tandem quartz/quartz and Teflon/quartz filter packs were employed. The quartz-fiber filters were analyzed for OC, EC, and TC by the IMPROVE_TOR protocol. • PSAP (Radiance Research) operated at 550 nm was deployed in 1/2001 for measuring absorption coefficient. (1 min). | <ul style="list-style-type: none"> • The backup quartz-fiber filters behind the quartz-fiber filters reported average OC 23 ± 12% of those on the front quartz-fiber filters. The backup quartz-fiber filters behind Teflon-membrane filters reported average OC 49 ± 19% of those on the front quartz-fiber filters. • The PSAP absorption coefficient showed a strong correlation with the IMPROVE_TOR EC ($r^2 = 0.87$). This comparison produced an EC absorption efficiency of 7.1 m²/g at 550 nm. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|---|---|---|
| <p>NIST Reference Material Study (Currie et al., 2002)</p> <ul style="list-style-type: none"> • Period: Bulk Standard Reference Material (SRM1649a) resulted from atmospheric sampling in 1976-1977. • Location: at Washington, DC, Navy Yard. • Type: Resuspended urban dust PM_{2.5}. | <ul style="list-style-type: none"> • The SRM were resuspended and sampled by quartz-fiber filters using URG filter packs and analyzed for carbon by various methods: <ul style="list-style-type: none"> - Aethalometer. - 375°C thermal oxidation method followed by flash/combustion/GC to determine residue EC. - Pure O₂/2-Step TE method (Cachier et al., 1989a, 1989b). - LBL pure O₂/continuous ramping. - NIOSH_TOT protocol with maximum temperatures of 900°C for both OC and EC. - IMPROVE_TOR protocol. - TOT protocol with linear temperature ramping. - Thermal kinetic oxidation/intercept method. - Thermal oxidation method with various acid pretreatments. - Pure chemical oxidation methods (no heating). - Isotope carbon (C¹⁴, C¹³) speciation for TC and EC. | <ul style="list-style-type: none"> • A good agreement was shown in the analysis of TC by all laboratories (<1 % variation in TC mass fraction). • The EC/TC ratios resulted from all analytical methods varied by about one order of magnitude (7% - 52%). Thermal method results cover the full range of EC/TC values, whereas results from pure chemical oxidation methods were restricted to the upper regions. • Particle loss may accompany chemical processing of very small samples. • The transmittance measurements for samples with EC > 10µg/cm² are unreliable due to saturation. • EC/TC ratios by TOR were higher than those by TOT. • From the isotope study, about 38% of the SRM particulate carbon was derived from modern carbon. The modern carbon fraction of EC ranged from 2.8 - 11.3%. Fossil fuel combustion generally produced a higher EC/TC ratio. |
| <p>Comparisons of IMPROVE_TOR and TMO Methods (Fung et al., 2002)</p> <ul style="list-style-type: none"> • Location: 60 samples from the U.S. IMPROVE Network, 16 from urban South Korea, 10 from Hong Kong, and 14 synthetic BC (or soot) samples. • Type: Urban (industrial and traffic) and rural ambient PM_{2.5}; reference BC samples (Cabot Monarch 120). | <ul style="list-style-type: none"> • Quartz-fiber filter samples were analyzed for OC, EC, and TC by: <ul style="list-style-type: none"> - IMPROVE_TOR protocol. - TMO method. | <ul style="list-style-type: none"> • TMO and IMPROVE protocols provided equivalent results of OC, EC, and TC values within ± 25% for a wide variety of samples. • EC biases were not consistent among different sample sets. EC levels were: 1) consistent for synthetic soot samples (no OC), 2) higher by TMO in heavily loaded Hong Kong urban samples, and 3) higher by IMPROVE_TOR for lightly loaded IMPROVE network and urban South Korea samples. • TMO method can effectively reduce charring in pure He environment. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|---|--|---|
| <p>Canada Black Carbon Study (Sharma et al., 2002)</p> <ul style="list-style-type: none"> • Period: Different time periods from 11/1998 to 8/2000 • Locations: Six sites across Canada: Alert (remote/continental); Egbert (rural); Downsview (suburban); Evans Avenue, Toronto (urban, roadside); Winchester (urban, school yard); and Palmerston (urban, school yard). • Type: Remote, rural, suburban, and urban ambient PM_{2.5}. | <ul style="list-style-type: none"> • Ambient PM_{2.5} sampler (averaging time from 12 hrs to 2 weeks). • Quartz-fiber filter samples were analyzed for OC, EC, and TC by IMPROVE_TOR, MSC1_TOT, and France CNRS-CEA 2-Step flash heating TE protocols. • Aethalometer (AE-11, Magee Scientific) (1-hr average). • PSAP (Radiance) (1-hr average). | <ul style="list-style-type: none"> • EC determined from MSC1_TOT and France TE protocols were similar with ~ 10% lower concentration from IMPROVE_TOR. • The aethalometer and PSAP BC agreed with each other but underestimated thermal EC by as much as 76% at all sites except for remote Alert, where all measurements agreed well. • The range of median site-specific absorption efficiency of EC for aethalometer and PSAP ranged from 6.4 - 28.3 m²/g and from 3.2 - 11.6 m²/g, respectively. • The highest absorption efficiency at the most remote site, Alert, was likely due to the more aged, internally mixed aerosols. |
| <p>Fresno Supersite Experiment (Watson and Chow, 2002)</p> <ul style="list-style-type: none"> • Time: 1/1/2000 - 12/16/2000 • Location: at the Fresno Supersite, CA (3425 North First Street), ~ 5.5 km north northeast of the downtown Fresno commercial district. • Type: Urban ambient PM_{2.5}. | <ul style="list-style-type: none"> • Single-channel RAAS-100 FRM (24-hr) • Six-channel RAAS-400 (with and without organic gas denuders) (24-hr) • Dual-channel sequential filter sampler (SFS) (24-hr) • Teflon-membrane filters were analyzed for b_{abs} using densitometer. • Quartz-fiber filter samples were analyzed for OC, EC, and TC by IMPROVE_TOR protocol. • R&P 5400 Ambient Carbon Particulate Monitor (1-hr average). • Single- and seven- wavelength aethalometer (AE-14U and AE-30S, Magee Scientific) (1-hr average). • PAS 2000 particle-bound polycyclic aromatic hydrocarbon (PAH) monitor (10-min average) | <ul style="list-style-type: none"> • Equivalence was found for PM_{2.5} mass, b_{abs}, TC, OC, and EC among RAAS-100 FRM, RAAS-400, and SFS samplers, and for front filter TC between denuded and non-denuded channels in the RAAS-400 samplers. • The average positive OC artifact was 1.62 ± 0.5 µg/m³ for the non-denuded Teflon/quartz channel and 1.12 ± 0.91 µg/m³ for the non-denuded quartz/quartz channel. With preceding denuders, the average negative artifact was 0.61 ± 0.5 µg/m³, ~ 9% of the front filter OC. • R&P 5400 TC was 40%-60% higher than filter carbon. • A high correlation (r>0.9) was found between b_{abs} and EC. The absorption coefficient ranged from 11.4 ± 0.7 to 12.0 ± 0.7 m²/g among FRM, RASS, and SFS. • Two aethalometer measurements showed a high correlation coefficient of 1, but an average of 0.11 µg/m³ less BC was measured by the seven-wavelength aethalometer for the 880 nm channel. • IMPROVE_TOR EC was consistently 20-25% higher than aethalometer BC. Particle-bound PAH were correlated with BC and EC, but not sufficiently to be considered predictable. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|---|---|--|
| <p>Big Bend Regional Aerosol and Visibility Observation Study (BRAVO) (Arnott et al., 2003)</p> <ul style="list-style-type: none"> • Period: 9/17/1999 – 10/17/1999 • Location: at Big Bend National Park near the Rio Grande River in South Texas. • Type: Rural ambient PM_{2.5}. | <ul style="list-style-type: none"> • Photoacoustic instrument operated at 532 nm (1-hr average). • Aethalometer (AE-16, Magee Scientific) (1-hr average). | <ul style="list-style-type: none"> • The aethalometer BC was weakly correlated with photoacoustic b_{abs} ($r^2 = 0.21 - 0.45$) at low ambient absorption coefficients ($< 2.1 \text{ Mm}^{-1}$). The comparison resulted in an absorption efficiency for BC of $8.4 - 9.9 \text{ m}^2/\text{g}$ at 532 nm. • The aethalometer BC data never went to zero, suggesting that a small fraction of its response was due to contamination by scattering aerosol. |
| <p>Southern Great Plains Intensive Operating Period (Arnott et al., 2003)</p> <ul style="list-style-type: none"> • Period: March and April 2000. • Location: at the Department of Energy Cloud and Radiation Testbed site in northern Oklahoma. • Type: Rural ambient PM_{2.5}. | <ul style="list-style-type: none"> • PSAP (Radiance) operated at 550 nm. • PSAP (Radiance) downstream of a humidifier operated at 550 nm. • Photoacoustic instrument downstream of a humidifier operated at 532 nm. • Humidified (i.e., 1 hr cycle for humidification) nephelometer (TSI Model 3563). | <ul style="list-style-type: none"> • The photoacoustic BC correlated well with the dry PSAP measurements ($r^2 = 0.96$), but the slope of the correlation was close to 1.61, meaning that PSAP might overestimate the absorption. • The photoacoustic BC showed weak dependence of light absorption on relative humidity (RH). • The humidified PSAP showed erroneously high light absorption as the RH increased. |
| <p>Atlanta Supersite Experiment (Lim et al., 2003)</p> <ul style="list-style-type: none"> • Period: 8/3/1999 – 9/1/1999 • Location: at the Atlanta Supersite, GA, (Jefferson Street), located in a mixed industrial-residential area ~4 km northwest of downtown Atlanta, GA. • Type: Urban ambient PM_{2.5}. | <ul style="list-style-type: none"> • Rutgers/OGI <i>in-situ</i> Thermal/Optical Carbon Analyzer (1-hr average every other hour). • R&P 5400 Ambient Carbon Particulate Monitor (1-hr average). • Aethalometer (Magee Scientific) (1-hr average) • PSAP (Radiance) (1-hr average) • Aerosol Dynamics Inc. (ADI) Flash Vaporization Carbon Analyzer (10-min cycle; flash temperature unknown) • MOUDI Impactor samples (12-hr average; analyzed by IMPROVE_TOR) • Integrated Filter Samples (Anderson RASS, Met One SASS, URG MASS, the FRM, R&P Speciation, BYU PC-BOSS, TVA PC-BOSS, ARA PCM, CIT PCM, and URG-VAPS) (24 hr). Filters were analyzed by IMPROVE TOR or TOT methods. | <ul style="list-style-type: none"> • The “inter-sampler precisions” with which semicontinuous particulate TC, OC, and EC were measured were 7%, 13%, and 26%, expressed as pooled coefficients of variations of 2, 3, and 4 instruments, respectively. • Correlations (r^2) between pairs of OC measurements were 74 - 97%. • OC and EC measured by R&P 5400 were 8% lower and 20% higher than RU/OGI OC and EC, respectively. • The best correlation for EC measurements was found between the PSAP and aethalometer ($R^2 = 0.97$), but PSAP measured only ~ 50% of aethalometer BC. • For time-integrated filter and MOUDI measurements, OC, EC, and TC had pooled coefficients of variation of 28%, 66%, and 25% (9 instruments), respectively. |

Table 2. (Continued)

| Study/Period/Location/Type | Sampling and Analytical Method | Summary of Major Findings |
|---|---|--|
| <p>Regional Visibility Experimental Assessment in the Lower Fraser Valley (REVEAL II) (Nejedlý et al., 2003)</p> <ul style="list-style-type: none"> • Period: 4/1994 – 6/1995. • Locations: Two sampling sites at the Abbotsford Airport in southern British Columbia, Canada, and near the Huntsman Marine Science Center at St. Andrews, New Brunswick, Canada. • Type: Rural ambient PM_{2.5}. | <p>Sampling and Analytical Method</p> <ul style="list-style-type: none"> • Ambient particles were collected by IMPROVE samplers Module A, B, and C, with an additional IMPROVE sampler Module A. • Particles were collected on quartz-fiber filters (24 hr) in the IMPROVE sampler Module C and then analyzed for OC, EC, and TC by the IMPROVE_TOR protocol. • Particles were collected on Teflon-membrane filters in the additional Model A and then analyzed by LIPM for BC at the University of Guelph. | <p>Summary of Major Findings</p> <ul style="list-style-type: none"> • A correction factor "R" for converting b_{abs} measured by LIPM to BC was empirically determined from values of absorption b_{abs}, concentration of EC, and BC mass absorption efficiency. • A polynomial fit of "R" as a function of areal concentration "s" yielded the new correction "R(s)". • The correction was retrospectively applied to the LIPM data and compared to the EC. The BC data derived from the LIPM measurements explained about 81% of the variability of the TOR EC. • The absolute value of the correction factor "R" at the two sites agreed for high filter loadings but differed by up to 50% in the case of the low filter loadings, highlighting the influences of aerosol composition. |
| <p>Reno Aerosol Optics Study (Sheridan et al., 2005)</p> <p>Period: 6/3/2002 – 6/28/2002. Location: at Reno, Nevada. Type: Kerosene soot (largely BC), white (NH₄)₂NO₃ aerosols, and mixtures thereof, as well as ambient PM_{2.5}.</p> | <p>Sampling and Analytical Method</p> <ul style="list-style-type: none"> • Cavity Ring-Down (CRD) Extinction (DRI, NASA, and Portland State University [PSU] CRD). • Classic extinction cell operated at 467, 530, and 660 nm. • Integrating nephelometers operated at 530 nm. • Photoacoustic instrument operated at 532 nm. • Aethalometer operated at 880 nm. • PSAP (Radiance) operated at 565 nm. • Multi-Angle Absorption Photometer (MAAP). | <p>Summary of Major Findings</p> <ul style="list-style-type: none"> • Photoacoustic absorption and absorption by the difference of extinction and scattering agreed with each other within about 10% for aerosols with scattering albedos ranging from ~0.3 – 1, yielding two quasi-equivalent primary standards for aerosol light absorption. • The CRD was capable of measuring atmospheric extinction down to below 1 Mm⁻¹. • Uncorrected filter-based absorption methods such as aethalometer and PSAP showed substantial systematic errors. • Filter-based methods corrected for scattering interference (e.g., MAAP) generally compared well (after empirical calibration) with primary standards such as the photoacoustic method. However, their dynamic range was limited. |

^a See Table 1 for detailed thermal/optical analysis protocols for most of the methods. Less commonly applied methods are summarized in the table to the extent that they could be interpreted from the intercomparison reports.

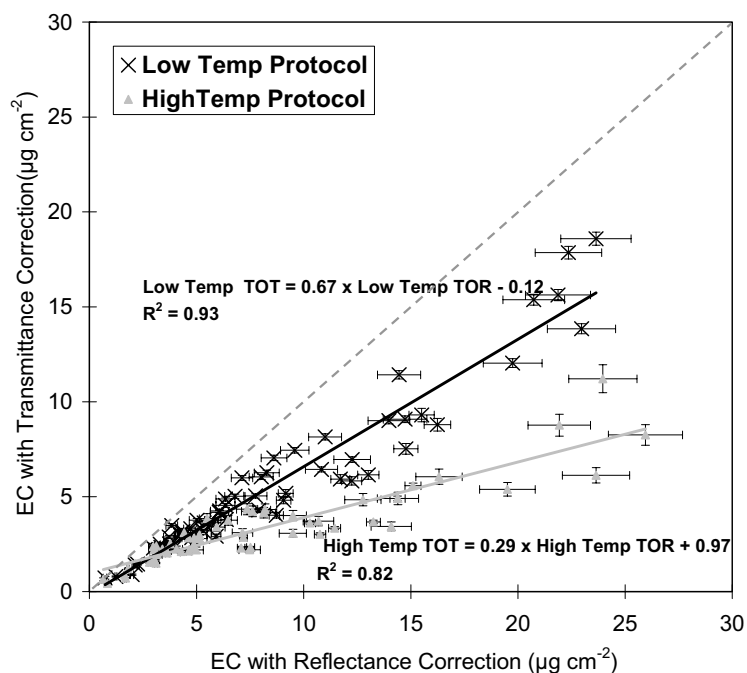


Figure 1. Comparison of EC derived from transmittance (TOT) and reflectance (TOR) charring corrections for low (IMPROVE in Table 1) and high (STN in Table 1) temperature protocols for 58 samples taken at the Fresno, California supersite from 08/23/2002 to 04/26/2003 (adapted from Chow et al., 2004). The dashed line indicates the 1:1 correspondence and the trend lines are derived from unweighted least squares fits.

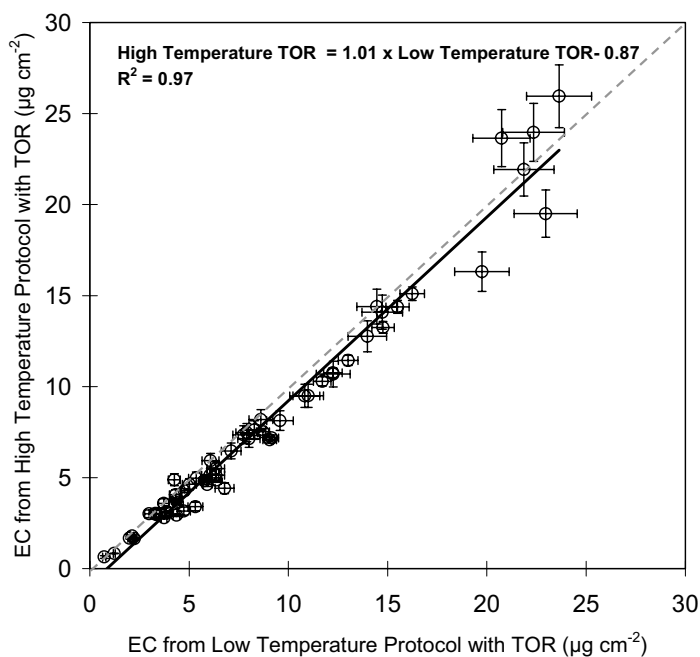


Figure 2. Comparison of Fresno supersite EC for the high and low temperature protocols with a TOR pyrolysis correction applied to both. The dashed line indicates the 1:1 correspondence (adapted from Chow et al., 2004).

Figure 1 shows how EC determined by TOT compared with EC by TOR for a high and low temperature analysis protocol. EC by TOT was lower than that by TOR in both cases, with the high temperature protocol yielding much lower EC values. Chow et al. (2004) hypothesized that much of the organic vapors adsorbed throughout the filter is desorbed at the 120 °C and 250 °C plateaus of the low temperature protocol, leaving less to char during the remainder of the analysis. The high initial temperature protocol begins analysis at 310 °C, and charring is immediately observed before volatilization is possible.

Figure 2 compares EC from the high temperature and low temperature protocols using the TOR correction. The values are in good agreement for this case. The correction is less sensitive to the temperature protocol than is the transmittance correction.

Carbonate carbon present with the OC and EC may interfere with the analysis if it decomposes during the analysis. For the high temperature protocol used in Figures 1 and 2, temperatures exceed 850 °C during the OC step, while for the low temperature protocol the temperature does not reach 800 °C until the EC step. Chow and Watson (2002) demonstrated that calcium carbonate is uncommon in many atmospheric samples and is not measured by thermal methods with temperatures <800 °C. Chow et al. (2001) showed that high temperatures (e.g., 800 °C) in the OC step may also oxidize EC via reactions with O₂-containing minerals in the sample (Fung, 1990; Fung et al., 2002).

While most air quality studies in the U.S. have measured OC and EC by thermal/optical methods, the two-temperature method of Cachier et al. (1989a, 1989b) is most widely used in global inventories and ambient studies. Owing to their widespread use, similarities and differences between the IMPROVE, STN, and CNRS-CEA protocols in Table 1 need special attention with respect to their comparability.

3. Optical Light Absorption Measurements

Also summarized in Table 2 are comparisons of thermal EC measurements with *in-situ* or filter-based optical BC measurements. A fundamental measurement of *in-situ* aerosol b_{abs} can be achieved by the photoacoustic instrument (Arnott et al., 1999; Moosmüller et al., 1997), which quantifies minute changes in the speed of sound in response to heating and cooling of PM by a modulated laser beam. It may be possible to relate EC or BC measurements to their absorption properties by collocating filter-based samplers with photoacoustic measurements.

Photoacoustic instruments have been used to measure BC in engine exhaust for more than two decades (Faxvog and Roessler, 1979; Killinger et al., 1980; Japar et al., 1982, 1984; Roessler, 1984), though it has only been recently that lasers have become adequately compact and powerful so that practical portable instruments can be fielded. The large dynamic range of the photoacoustic photometer allows it to measure b_{abs} over a wide range of BC concentrations in source and ambient samples (Moosmüller et al., 2001a, 2001b). For BC size distributions with mass median diameter < 0.3 μm, the BC mass absorption efficiency (b_{abs}/BC) is stable (Killinger et al., 1980). As explained

in the introduction, b_{abs} can be translated into a BC or EC concentration with an appropriate mass absorption efficiency. Consistent with other studies cited above, Table 2 shows that mass absorption efficiencies differ from study to study. These differences result from variability in the shape, density, material refractive index, and internal mixing of particles as well as inconsistencies in quantification EC by other methods.

A more common method of b_{abs} and BC (or EC) measurement is filter-based absorption using an aethalometer. The aethalometer measures optical aerosol absorption by quantifying the attenuation of light transmitted through a filter tape on which aerosol particles are collected (Hansen et al., 1984). Once the spot monitored on the filter tape exceeds a certain optical density, the aethalometer automatically advances the tape to a new spot. In this manner, the aethalometer can perform months of ambient monitoring without operator attention. The measured attenuation is reported as BC concentration after conversion with an empirically determined factor. The aethalometer also obtains its calibration by comparison with thermal EC measurements (Hansen et al., 1984; Hansen and Novakov, 1990). Arnott et al. (2005) suggested that a filter-loading correction is needed to account for the multiple scattering effects of filter material in the aethalometer. A 50% reduction occurs between when the filter is pristine and white after a filter change, and when it is dark right before a filter change. Time averaged aethalometer data tends to average out this variation if the source of BC is sufficiently steady. Otherwise, the aethalometer b_{abs} would not be linearly related to BC. This correction was not made in the earlier studies summarized in Table 2, and a wide range of b_{abs}/BC ratios is observed.

Similar to the aethalometer, the integrating plate method (IPM, Lin et al., 1973), measures the transmission of diffused light through a polycarbonate-membrane, Teflon-membrane, or quartz-fiber filter. Quartz-fiber filters have more internal scattering than the thin polycarbonate- or Teflon-membrane filters, and the transmittance is usually double that for a given deposit on the membrane filters. This method can be applied to 47 millimeter (mm) Teflon-membrane filters with a photographer's densitometer for filter transmission that is calibrated with photographers' neutral density filters (Wratten Kodak, Rochester, NY). Filter transmission is highly correlated with the aethalometer measurement and has been used as a surrogate for BC in several studies (e.g., Chow et al., 1997; Watson and Chow, 2002). Bond et al. (1999) note the importance of correcting for particle scattering when a mixed aerosol is sampled and measured by filter transmission as with the IPM.

4. Conclusions and Knowledge Gaps

This summary documents and compares many OC and EC measurement methods and the efforts made to determine the equivalence among them. OC and EC are operationally defined by these methods, but they are often not sufficiently documented to allow the methods to be repeated outside of the laboratory origin. In seeking to determine equivalence, samples have been prepared from organic chemicals, graphite, diesel exhaust, and wood smoke. Ambient samples have also been

circulated among laboratories or taken in parallel in a variety of environments. Measurements of particle absorption have been compared with thermal evolution and photoacoustic methods. The general conclusion is that different studies give different results for method comparisons, and that citation of a single comparison study is insufficient to establish comparability. More systematic comparisons are needed that hold most variables constant while varying only a few. These variables apply to the type of sample analyzed as well as to the analysis method.

Future comparison studies need to:

- Evaluate the sensitivity of OC and EC concentrations to variations in thermal evolution temperatures, pyrolysis corrections, analysis atmosphere compositions, presence or absence of oxidizing minerals and catalysts, vapor adsorption, and optical pyrolysis correction methods.
- Create reproducible and well characterized samples with homogeneous deposits of light, medium and heavy particle loadings that represent simple (e.g., graphite powder, organic compounds, carbon arc emission) and complex (diesel exhaust, wood smoke, mixtures with inorganic minerals and salts) situations that might be found in the environment.
- Implement the methods in Table 1 on a single instrument so that variables can be systematically changed for analysis of the prepared samples and selected ambient samples.
- Develop and apply methods to calibrate and audit temperatures, analysis atmospheres, and optical monitoring that can be applied to a variety of hardware to determine that analysis assumptions are met in practice.

Interpreting the data from comparisons that incorporate these features will provide the basis for determining why different methods give different results.

Acknowledgements

This work was jointly supported by the U.S. Environmental Protection Agency (EPA) STAR Grant No. RD-83108601-0, EPA Contract #R-82805701 for the Fresno Supersite, and California Air Resources Board Contract #04-307. The conclusions are those of the authors and do not necessarily reflect the views of the sponsoring agencies. Mention of commercially available products and supplies does not constitute an endorsement of these products and supplies. The authors wish to thank Eric Dieterle and Jo Gerrard of the Desert Research Institute for assembling and editing the manuscript.

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Received for review, March 31, 2005

Accepted, June 13, 2005