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development of
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materials**

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Towards the development of standard reference materials for soot measurements – Part 1: Tailored graphitized soot

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Received: 24 March 2010 – Accepted: 28 March 2010 – Published: 15 April 2010

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

The lack of standard reference materials for calibrating, troubleshooting and intercomparing instruments that measure the properties of black carbon, commonly referred to as soot, has been a major obstacle that hinders improved understanding of how climate and health is impacted by this ubiquitous component of the atmosphere. A different approach is offered here as a means of constructing precisely controlled material with fractions of organic carbon (OC) on the surface of elemental carbon (EC) whose structure reflects that of combustion particles found in the atmosphere. The proposed soot reference material (SRM) uses elemental carbon as a basis substrate for surface coatings of organic compounds that are representative of main classes of organics identified in the coverage of soot produced by fossil fuel burning. A number of methods are used to demonstrate the quality and stability of the reference EC and SRM. Comparison of the nominal fraction of OC deposited on the EC substrate with the fraction measured with thermal/optical analysis (TOA) shows excellent agreement. Application of this type of reference material for evaluating the different methods of carbon analysis may help resolve differences that currently exist between comparable measurement techniques when trying to separate OC and EC from ambient samples.

1 Background

Soot¹ is a ubiquitous substance that is produced by incomplete combustion of fossil fuels and is a variable mixture of organic carbon (OC) and elemental carbon (EC). It is a long-term geochemical sink of carbon that is found in soil and water and is one of the most important particulate species in the atmosphere as a tracer for anthropogenic activity. Soot alters climate on a global scale and health on a local scale. As recently highlighted by Ramanathan and Carmichael (2008), in regions with large

¹Soot is sometimes referred to as black carbon (BC) but given that BC is also associated with only the light absorbing component of soot, throughout the remainder of this paper we will only refer to soot in the sense that it is a mixture of organic and elemental carbon (OC/EC).

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anthropogenic emissions, soot is currently the second strongest contributor to global warming after carbon dioxide. In urban areas soot particles are considered a dangerous pollutant with respect to human health and can cause or exacerbate respiratory, cardiovascular, and allergic diseases (Balbus, et al., 2007).

5 In order to understand how soot impacts the environment, i.e. climate and health, accurate measurements must be made of its physical, chemical and optical properties. There are large uncertainties related to these properties, especially with respect to their evolution with age and transformation by photochemical and aqueous processes. The uncertainties are largely a result of the paucity of measurements of the physical, chemical and optical properties of soot over sufficiently broad scales in space and time. No
10 single instrument has the capability of measuring all the properties of soot thus requiring various techniques to measure individual characteristics. Thermal/optical analysis (TOA) techniques are used to separately derive the mass concentration of OC and EC, other techniques can measure the ability of soot particles to form cloud droplets or ice crystal, i.e. cloud condensation nuclei (CCN) or ice nuclei (IN) and yet another
15 class of instruments is used to measure their optical properties, i.e. the absorption and scattering coefficients, B_{abs} and B_{scat} .

In order to establish the accuracy and reliability of a measurement system, it is common practice to calibrate the sensor with a material having the well characterized properties that are being measured by the instrument in question. These materials are referred to as reference standards and, in addition to providing a calibration for sensors,
20 are the means of ensuring that reasonable comparisons can be made among different measurements of the same quantity. Any differences are then attributed to variations in physical processes and not to instrumental issues. There are a number of challenges, however, to finding a soot reference material (SRM) for calibrating instrumentation.
25 Given that there are three categories of measurements to be made, i.e. OC/EC mass, CCN/IN concentration and $B_{\text{abs}}/B_{\text{scat}}$, a single SRM may not be appropriate or adequate for calibrating every instrument. Secondly, soot found in the atmosphere can be so chemically and physically complex that a single reference material may not be

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adequate for calibrating an instrument over the entire range of possible mixtures and shapes that could affect how an instrument responds. For example, instruments designed to measure the separate masses of EC and OC in an aerosol sample may be sensitive to the type of OC, not just its mass (Schauer et al., 2003). Likewise, some filter based instruments measuring the B_{abs} of aerosols must be corrected for artifacts introduced by the presence of certain types of light absorbing organics (Lack et al, 2008; Capa et al., 2008) and other adjustments must be made for biases introduced by light scattering of the particles on the filter (Bond et al., 1999). For either example, selected reference materials may provide an excellent calibration for a certain category of soot while leading to erroneous results when soot formed by another process is introduced to the instrument.

The mass of OC/EC in ambient particulate matter is typically measured by TOA. A punch from a filter sample is heated to high temperatures, either in an oxidizing atmosphere (most thermal techniques) or first in an inert atmosphere, followed by an oxidizing atmosphere. When OC associated with soot is heated some fraction of it chars into an EC-like, light-absorbing, refractory substance. TOA methods monitor either light transmission through or reflection from the sample punch to correct for the charred OC (Chow et al., 1993; Birch and Cary, 1996). Intercomparisons between the TOA methods have shown that the temperature protocol and the optical technique can make a difference in the measured EC content (Chow et al., 2001; Schmid et al., 2001; Schauer et al., 2003; Subramanian et al., 2006). The organic composition can also affect the measured EC, as not all organic matter chars (Schauer et al., 2003). Inorganic matter such as mineral oxides and salts found in biomass smoke (such as KCl) can also alter the temperature at which complex/large organic compounds and EC evolve off the filter (Novakov and Corrigan, 1995; Boparai, Lee, and Bond, 2008). This means that using a single cut-off temperature to determine OC/EC content may introduce uncertainties that are not easily quantified since changes in the rate at which charred OC and EC evolve affect the optically-determined OC/EC split (Subramanian et al., 2006).

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Build-up of refractory mineral oxides on the filters used in semi-continuous OC/EC analyzers can also affect the OC/EC split (Polidori et al., 2006). The effect of varying mineral oxide content on the thermal behavior of soot can be isolated and quantified with a “pure soot” material. Comparing different TOA techniques with ambient or atmospherically-relevant samples is difficult since the actual chemical composition – the fraction of OC/EC in the sample – is not known a priori. Mixtures of a known quantity of soot with known masses of different organic compounds or organic extracts of ambient particle mass can overcome this difficulty. Thus, a well-characterized OC/EC SRM would reduce some of the uncertainties associated with the different thermal and thermal-optical techniques.

The absorption coefficient of soot is measured with instruments that measure light transmitted through an aerosol loaded filter or by measuring the amount of heat radiated by aerosols that absorb light. In the former case two filters are used: a “clean” reference and one where aerosol particles are being accumulated. Light at a single wavelength illuminates both filters and the amount of attenuation by the aerosols is directly proportional to the absorption coefficient. No calibrations are made with reference materials given that they operate on first principles, i.e. Beer’s law that directly relates the absorption coefficient to the attenuation of the incident light, derived from the aerosol laden filter, to the incident light derived from the reference material. There are, however, numerous corrections that must be made to account for factors that alter this relationship, e.g. differences from filter to filter, contributions to the attenuation by light scattered from the particles on the filter, wavelength dependency of the absorption, and many others that lead to significant differences from instrument to instrument when measuring the same air sample (Bond et al., 1999; Cappa et al., 2008; Lack et al., 2008) A SRM is needed that can be routinely used to calibrate these instruments and determine the contribution of the different sources of interference on a routine basis.

The photoacoustic technique measures the pressure increase in a sample chamber caused by aerosols absorbing light and heating the surrounding air (Arnott et al.,

1999). This system is calibrated using a gas whose absorption cross section is well known, at the wavelength of the laser being used. Given that the absorption coefficient of aerosols is wavelength dependent, the photoacoustic technique is implemented with more than a single wavelength of light and at the longer wavelengths, i.e. in the near infrared, it is difficult to find gases that absorb at the desired wavelength; hence, in those cases the calibration is derived by estimating the absorption coefficient from the attenuation of the laser through a dense cloud of light absorbing particles, usually generated from a kerosene burner and measured with the power monitor of the laser (Arnott et al., 2000). This method has uncertainties associated with the abnormally high concentrations of particles required to produce a sufficiently large change in the laser signal on the detector and requires an assumption that the calibration remains linear down to the smaller values that are normally encountered with ambient aerosols. A SRM, whose light absorption cross section is well known, is needed to provide calibrations under such conditions.

A number of potential candidates for soot reference materials have been introduced in recent years (Yang and Yu, 2002; Chen et al., 2004; Klouda et al., 2005); however, none have been generally accepted as the standard by those who measure BC properties. For example, a filter-based NIST standard, reference material 8785, was specifically developed for calibrating TOA methods. This SRM is produced by resuspending Urban Dust (NIST standard 1649a) and filtering it with quartz fiber filters (Klouda et al., 2005). This approach is compelling because the chemical composition of the urban dust is very well characterized. When these filters were evaluated, however, with a number of standard methodologies – the Interagency Monitoring of Protected Visual Environments (IMPROVE) and Speciation Trends Network–National Institute of Occupational Safety and Health (STN–NIOSH) protocols (Chow et al., 1993; Birch and Cary, 1996; NIOSH, 1999) – although the sum of the EC and OC, agreed quite well, the measured fraction of OC, differed by more than 60% (Klouda, 2005). Due to the complexity of the NIST 8785 SRM, the source of the differences between the two techniques could not be resolved other than concluding that the separation of EC and OC

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is method dependent with no way to assess which of the two was providing the more accurate value.

An international steering committee, formed during the 1999 Geochemical Society meeting (Goldschmidt Conference), was charged with developing representative and accessible soot reference materials for the environmental sciences community. In May 2000 this committee issued preliminary recommendations for the properties of BC reference materials that included: (i) five matrices containing materials such as soot, charcoal, aerosol, soil, sediment and (ii) materials potentially creating soot during analysis, for use in detecting methodological artifacts such as humics, kerogens and coals. In addition, this committee recommended that these reference materials must be: (1) generally available, (2) homogeneous, (3) stable over a longer period of time, (4) inexpensive to obtain, and (5) representative of natural samples (EOS, 2003). Whereas the focus of the soot reference steering committee was mostly on the problem calibrating and testing instrumentation for measuring soot carbon mass content, there are similar problems associated with instrumentation for measuring the optical and cloud forming properties of BC yet no such material has been produced that fulfills the requirement for calibrating and testing instruments that any of the soot properties.

The objective of the current work is to introduce the concept of a well characterized, laboratory-fabricated SRM for the purpose of calibrating instruments that measure any soot property and that meets the criteria that was put forward by the international steering committee on black carbon. An approach is presented for the manufacture of SRM with precisely controlled mixtures of EC and OC that are representative of compounds found in the combustion of fossil fuel. The validation of this approach is shown with some examples of these SRM samples analyzed with one of the TOA methods.

2 Methodology

Chemical analysis of combustion soot found in the ambient atmosphere shows that it is EC mixed with varying amounts of OC whose thickness depends on the sources of combustion, age of the aerosol and relative concentration of organic precursor gases

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(Fernandez et al., 2003; Moteki et al., 2007). We assume that laboratory-fabricated soot is representative of ambient soot as long as its physical and chemical structure is similar; however, the complexity of organic species found in combustion particles may significantly restrict the utility of such an approach. To resolve this problem a simplification of the representation of organic components in atmospheric particles was suggested by McFiggans et al., (2005) who grouped organic aerosol species into a relatively small number of representative compounds. In our work we use EC as a basis substrate and deposit organic compounds which are representative of the main classes of organics identified in the surface coverage of soot produced by fossil fuel burning, an approach suggested by Popovicheva et al. (2009).

The basic carbon substrate, referred to herein as elemental carbon reference material (ECRM), may be produced using a graphitization procedure. The randomly ordered microstructure of technical carbon² undergoes graphitization at temperatures of $\approx 3000\text{ }^{\circ}\text{C}$ in an oxygen-free atmosphere (Avgul and Kiselev, 1970) and the normally amorphous carbon microstructure changes to well-organized crystallites of graphite platelets. Simultaneously, at this temperature, soot loses any inorganic or organic coverage, volatile oxygen-containing groups or mineral contaminations (ash).

Several kinds of technical carbon, commercially produced by natural combustion processes, were tested in our work as primary material for ECRM production. The ones eventually selected were the thermal soots TG-10 and TG-100, produced by pyrolysis of natural gas (Electrougly Ltd. and Uchta OPP) with surface areas of 10 and $98\text{ m}^2\text{ g}^{-1}$, respectively, because they could be easily graphitized and have distinct primary particle sizes. These were heated in an oven with nitrogen at $3000\text{ }^{\circ}\text{C}$ producing graphitized thermal soot (GTS) with surface areas of 6 and $80\text{ m}^2\text{ g}^{-1}$ (GTS-6 and GTS-80), respectively. The reproducibility of the GTS properties was evaluated using multiple samples generated with this technique.

The main classes of non-polar organics that have been identified in diesel and aviation soot are alkanes and polyaromatic hydrocarbons (PAHs). Polyethylenegluco

²Technical carbon is also known as thermal black.

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(PEG) may act as a representative of the polymer polar compounds, and aromatic and aliphatic acids are related to polar materials (Popovicheva et al., 2009). In our work representative organics were selected from each group of identified compounds: (1) octacosane, $C_{28}H_{58}$, for alkanes, (2) pyrene, $C_{16}H_{10}$, for PAHs, (3) 2,6-naphthalene dicarboxylic acid, $C_{12}H_8O_4$, 1,2,4- benzene tricarboxylic acid (trimellitic acid), $C_9H_6O_6$, and 1,3,5-benzenetricarboxylic acid (trimesic acid), $C_9H_6O_6$, for aromatic acids and (4) PEG Carbowa 600 (M 570–630) OH $[-C_2H_4O-]_nH$ for polymer compounds. These choices take into account that the organic compounds deposited on the surface should be non-volatile at normal temperatures and pressures and strongly bonded on the surface with a monolayer coverage stable up to 200–250 °C as required by the methodology for OC coverage (see below).

Synthetic soot was created by this method to estimate the amount of organic matter deposited from the solution of a given number concentration of the modifier. For this test GTS-6 was chosen as the basis EC substrate with organic dyes -acid orange $C_{16}H_{11}N_2O_4SN$ (MW=350) and acid anthraquinonic $C_{16}H_9N_2O_7SNa$ (M=372) as organic modifiers. Adsorption was performed from the aqueous solution of a given acid concentration. The concentration is controlled by measurements of the optical density of the aqueous solutions during adsorption and the process is assumed completed when the solution loses its color. The solution is removed and the soot residual is dried at 110 °C for 5 h.

The method of “forced adsorption” is used for producing coverage by deposition of a given organic species on the EC substrate (Vlasenko et al., 1997; Esteve et al., 2004). It is based on the techniques developed in adsorption science for the production of modified soot with “programmable properties”. The forced adsorption is generated from the organic solutions dependent on the nature of the modifier and its solubility in a given solvent. The concentration of the modifier is chosen to be less than its solubility in the solution. For adsorption of octacosane, *n*-hexane is used as a solvent while pyrene is deposited from benzene. For adsorption modification by trimesic acid, trimellitic acid and dicarboxylic acid, naphthalene dimethyl formamide, acetone and water solution of

ammonia are used, respectively. Carbowax is deposited from dichlormethane.

A given modifier, in the amount proposed for modification, is mixed with the solvent and the GTS substrate is then introduced into the prepared solution where the ratio of modifier to soot mass defines the thickness of the proposed coverage. The solution volume should be larger than the EC sample volume by 5–10%. The mixture of solvent with modifier and GTS is heated for 2–10 h and a homogeneous distribution of the modifier over the GTS surface is achieved by carefully mixing the solution with GTS in a rotor evaporator. The solvent is partially removed in a rotor evaporator then further extracted in an oven at a temperature 10–20 °C higher than the solvent boiling temperature. The final purification of fabricated samples takes place in an inert gas flow at high temperature determined by the thermal stability of the deposited organics. Experience indicates that a 1–3% variation in the coating can be expected.

Variation of the solution concentration allows the deposition of organic matter from sub-monolayer to multilayers, i.e. the production of up to 10% of an organic coverage, by weight percent, where the methodology proposed may provide the most stable, strongly bonded compounds on the surface. For this purpose the concentration of GTS soot in the solvent is varied from 5 to 50%. Reproducibility of results is proven by numerous repetitions of the laboratory soot production and characterization of its properties.

A list of GTS-based SRMs that have been created and tested is presented in Table 1. The nominal amount of OC that was deposited is given for each sample. Samples with pyrene, octacosane and trimestic acid, deposited on GTS-6, were manufactured with the objective of producing GTS slightly coated with organic compounds (0.1–0.3%). Initially creating an SRM with a very small coating of OC serves to demonstrate the sensitivity of techniques for measurements of the OC fraction in soot (Sect. 4). Larger amounts of pyrene and trimellitic acid (up to 5%), deposited on GTS-80 can be used for evaluating those techniques where the thickness of the OC coverage may play a role. A maximum organic coverage of 9% has thus far been deposited on GTS-80 using naphthalene dicarboxylic acid with higher percentages possible.

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the monolayer coverage and confirms the reproducibility of the production methodology. Additionally, the morphological and texture parameters of ambient and fabricated soot are determined using the nitrogen adsorption data. The surface area of fabricated samples was measured by a single point BET technique. To demonstrate the perfect rigid structure of GTS the cycle of water adsorption–desorption was also measured. Complete details of the morphological and texture analysis are presented in Popovicheva et al. (2008).

3 Characterization of Elemental Carbon RM (ECRM)

Typical particles of thermal T-900 soot are shown in Fig. 1a. The average diameter, D , of the primary particles is 260 ± 1.4 nm, evaluated from more than six hundred TEM images of thermal soot (Popovicheva et al., 2008). Graphitization of thermal soot significantly changes the shape and size of primary particles. Analysis of TEM images of GTS-6 and GTS-80 shows that the average diameters are 180 ± 1.4 nm and 32 ± 1.24 nm, respectively. Figure 1b illustrates a typical SEM image of GTS-6 soot particles and shows the polyhedron structure of primary particles that arises due to graphitization of soot under high temperature exposure.

There are numerous studies in the literature demonstrating that the surface of graphitized soot is flat, chemically and geometrically homogeneous and therefore inert and stable (Avgul and Kiselev, 1970; Kiselev and Yashin, 1969). Our examination of typical features of the interaction of probe molecules with the surfaces of GTS-6 and GTS-80 in the gas chromatograph validates these properties for fabricated SRMs. Figure 2a shows the chromatogramme for a number of probe molecules on GTS-6 which are highly symmetric. Together with the independence of the retention time from the amount of interacting probe molecules and the linear dependence of the retention volume on a number of atoms in a hydrocarbon probe molecule, these features indicate the homogeneous surface of fabricated ECRM. Similar features of homogeneous surfaces are demonstrated for SRMs with deposited organics. Figure 2b shows the

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chromatogramme of complete separation of highly symmetric isomers on GTS-6 with 0.32% pyrene (sample 1 of Table 1). Adamantane, with a more compact molecule structure, is eluted first followed by endo-trimethylenenorbornane (TMNB) which has a larger number of surface contacts. Exo-TMNB, which has the most planar structure, is finally eluted.

Homogeneous GTS is characterized by the strong disperse interaction with non-polar probe molecules. Modification of GTS, whenever there is a modifier, leads to a decrease of the interaction and therefore to a decrease of the retention volumes for probe molecules. Figure 3 shows the high retention volumes observed on GTS (zero pyrene coverage) preferably for GTS with *n*-alkanes (*n*-heptane and *n*-hexane). Because of very limited polar heterogeneities of the GTS surface, the interaction with polar methylethylketon is relatively small. Even a π -electron system of benzene prevents this molecule from strong interaction with graphitized surfacing (see Fig. 3). It is observed that increasing the pyrene coverage decreases the retention volumes. At 0.54 mg m⁻² the minimum retention volume is seen to be related to the formation of a statistically dense pyrene monolayer (Kiselev et al., 1971). At higher coverages the interaction of probe molecules is enhanced by the formation of a pyrene monolayer. Thus, this chromatographic calibration determines the monolayer coverage providing the quantitative analyses of deposited material and the reproducibility of the production methodology from a sub-monolayer up to a few monolayers.

The measured surface areas of GTS are 5.6 ± 0.3 and 79 ± 2 m² g⁻¹ for GTS-6 and GTS-80, respectively. The decrease of the surface area after graphitization leads also to the decrease by a factor of 1.5 of the mesopore volume for GTS-6 (Popovicheva et al., 2008). This nearly non-porous microstructure is a good prerequisite for the stable particle microstructure. The heat treatment of GTS reduces the oxygen content and water soluble fraction to 4 and 0.45 wt%, respectively, leading to a negligible amount of both in GTS-6 soot (within the measurement accuracy). The volatile fraction of GTS is determined to be 0.6 wt% before and just 3.2×10^{-2} wt% after treatment. Table 2 lists the content of mineral and metal impurities in TG-100 and GTS-80 obtained by XFS,

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demonstrating the negligible amount of any inorganic contaminations in graphitized soot.

Additional examination of the composition of the SRM may be made by reasonably assuming a high sensitivity of water molecule absorbability to oxygen-containing functionalities and water soluble compounds on the surface. Comparative analysis of water uptake on original thermal and fabricated GTS (Popovicheva et al., 2008) validates that thermal soot may be classified as hydrophobic soot due to water adsorption on some active sites (oxygen-containing functional groups of the surface organic and inorganic contaminations). In contrast, GTS shows negligible adsorption, so little that we could not estimate the number of active sites. It has been pointed out in Gregg, and Sing (1972) that when heating at 1300 K the functional groups, which are responsible for the water adsorption, are almost removed from the soot surface, together with the surface coverage. Thus, GTS should be classified as extremely hydrophobic soot with chemically homogeneous surface of high quality cleanness.

4 Evaluation of SRM properties

4.1 Size distributions

Samples of fabricated ECRMs and SRMs were analyzed with a TSI Inc, scanning mobility particle sizer (SMPS) to evaluate the relative concentration as a function of the mobility diameter. Figure 4 shows an example of the size distribution of uncoated GTS-80 particles (black curve), GTS-80 coated with 0.12% and 0.24% of octacosane, Samples 4 and 3 (blue and pink curves) and with 0.16% and 0.32% of pyrene, Samples 2 and 1 (green and red curves). The relative concentrations are a function of the degree of dilution when dispersing a given sample with a nebulization system and not on the composition. There is a slight decrease in the modal diameter as the relative fraction of organic material is increased. This is related to how the SMPS sorts particles by size, measuring the mobility rather than the geometric diameter of particles. Particles

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are removed from the sample volume of the SMPS based upon their electrical and mechanical mobility and their aerodynamic behavior in the moving airflow in the SMPS sample chamber. The motion of non-spherical particles in the airflow and electrical field are different than spherical particles under the same conditions (Zelenyuk and Imre, 2007) due to how non-spherical particle align themselves in the electrical field. The result is that those particles that have shape factors $\gg 1$, i.e. highly non-spherical, will have apparently larger mobility diameters than more symmetrical particles. This is apparent in Fig. 4 where the coating of OC on the SRM changes the more irregular shape of GTS to a smoother and more spherical form that has a subsequently smaller mobility diameter.

4.2 OC and EC content of the SRMs

The SRM samples listed in Table 1 were evaluated at Sunset Laboratories using TOA with Transmission (TOT) to measure the relative fraction of OC and EC. The samples were deposited on filters prepared with sufficient material to exceed the limit of qualification (Peralta et al., 2007) of approximately $17 \mu\text{g}$. The TOT technique, described in the background section, produces a thermogram of the carbon molecules that evolve as a function of temperature and is used to derive the fraction of OC and EC. Figures 5 and 6 show thermograms generated from uncoated GTS-6 and GTS-80 coated with pyrene (5% wt%), respectively. The abscissa of the graphs is time in seconds and the green, black, red and blue curves indicate the fraction of total carbon (TC), cumulative TC fraction, temperature and the amount of laser attenuation. TC is derived from the carbon dioxide measured as the sample is heated and the carbon molecules are released and oxidized to form CO_2 . The analysis is a two step process in which a sample is heated rapidly in a helium environment to release OC, cooled then heated more slowly with oxygen in order to release the carbon in EC. The laser light is transmitted through the sample and used to indicate when the light absorbing carbon (EC) has been totally removed. When the transmitted light reaches its maximum value and remains constant, this indicates that no EC remains.

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As seen in Fig. 5, since there is no OC on the ECRM there is no fractional TC appearing until 500 s when the temperature has exceeded 600 °C. In Fig. 6, however, the fractional TC is seen to momentarily increase at 50 s when the temperature reaches 100 ° then decreases as all of OC is removed by 150 seconds and at 400 °C. Once again at 400 s and 600 °, fractional TC is again seen to increase until all EC is completely removed by 1400 s. For the uncoated GTS-6 and coated GTS-80, the mass fraction of OC is found to be 0.01% and 4.39%, respectively. Multiple analysis of the pure GTS showed very good precision.

The ten SRM samples listed in Table 1 were analyzed to compare the nominal OC mass deposited on EC basis substrates to the OC derived by the Sunset Labs TOA. As shown in Table 1 seven of the ten samples demonstrated a very good correspondence between the nominal and measured OC, within the expected uncertainty in the measured OC fraction. For one sample, Sample1, the difference between the nominal and measured OC fraction is far outside the expected uncertainty. This sample was measured a number of times with the similar result that the OC fraction is significantly smaller than the nominal. The differences in nominal and measured in Samples 7 and 10 are only marginally outside of the estimated uncertainty. At this time the discrepancy in the first sample cannot be explained. The other two samples, although outside of the expected deviation are still in reasonably good agreement with the nominal values.

Figure 7 summarizes the comparisons between the nominal and measured soot reference materials listed in Table 1, where the numbers refer to the sample numbers tabulated in the Table. Multiple markers with the same sample number represent those filters that were analyzed more than once. As the regression analysis shows, the slope of the best-line is within 13% of one to one and an offset of only 0.0007. If the measurements from the first sample are removed, the slope of the best fit line becomes 0.95. The linearity ($r^2 = 0.993$) and almost 1:1 slope over almost two orders of magnitude suggests that, even though this is not an exhaustive evaluation, these soot reference materials provide a very good method for assessing the accuracy and sensitivity of the TOA technique for estimating EC and OC.

4.3 SRM stability

The property of particles to adsorb water vapor from a humid atmosphere and organic gases from polluted environments, given sufficient time, is of particular concern when working with soot that has a high surface area such as GTS-80. Therefore, any reference material that is prepared for instrument calibration may acquire either a water or an organic covering if stored for too long after it has been fabricated. The susceptibility of the GTS reference materials was tested by evaluating some samples of SRMs after six months of storage in a plastic box with a loosely fitted lid. Good reproducibility of the water adsorption isotherm and very low volatility, just 0.003 wt%, indicates the high level of chemical inertness of this material and hence, a good candidate for an SRM. Moreover, as a result of thermo/optical measurements of these stored samples we have obtained OC for samples of GTS-6 and GTS-80 very closed to nominal, for both the original ones and those specially pre-treated before measurements (outgasing at 350 °C). Therefore we may conclude that during the storage and transportation there are insignificant changes to the prepared samples.

An additional advantage of fabricated ECRM is that it can be thermally cleaned if necessary. The high thermal stability of graphitized soot guarantees negligible changes in the morphology and microstructure, in contrast to microporous particulates generated from combustion that are susceptible to contamination (Everett and Ward, 1986). Cycling the GTS-6 soot particles through high relative humidity (humidified to 98% RH and then dried to 0.5% RH) does not change the water solubility, unlike, for example, kerosene flame produced particles (Popovicheva et al., 2008).

Special attention has been focused on evaluating SRMs after long-time storage. The methodology of the stable strong bonding of deposited compounds on the surface, applied for reference material production, should guarantee a stable covering of GTS. In order to evaluate the quality of samples that had been stored in the plastic boxes during four months they were exposed to nitrogen at 150 °C for eight hours then weighed to analyze the loss of mass. For example, for the Sample 1 in Table 1 the mass loss was

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0.08%. For the Sample 5 the measurements of the retention volumes for three probe molecules were repeated after four months. The retention volume for benzene was changed from 93 to 95.8 cm³/g, a value that is well within the framework of the measurement accuracy of 5%. These results indicate negligible change in the composition of the SRM during long-time storage.

5 Summary

Calibration of instruments that measure the properties of black carbon (soot) is a major obstacle to our understanding of how this ubiquitous atmospheric particle is formed, evolves and impacts health and climate. The lack of a reference material whose properties are well characterized has hampered efforts by the atmospheric community to arrive at standard calibration techniques that allow evaluation of measurement methods and comparison of data sets taken at multiple locations over different periods of time. An SRM is proposed that consists of graphitized thermal soot coated with precise coverings of organic material with different molecular structures, similar to those found in the natural environment. A preliminary evaluation has been conducted of ten samples of this ECRM with organic matter from 0.102%–9.09%. The OC mass percent was measured with a Sunset Laboratory's EC/OC Thermal/Optical analyzer with a nearly one to one correspondence between the nominal and measured OC percent by weight. Evaluation of the long-term stability of the samples showed negligible change in the chemical or morphological properties after storage for four months. These results suggest that tailored graphitized thermal soot is an excellent candidate as an SRM, for evaluating the sensitivity of thermal/optical analyzers for separating OC from EC as a function of different organic coatings.

Part II of this work, currently being prepared for publication, evaluates these tailored materials for calibrating TOA methods and compares the performance of instruments that measure the optical and hygroscopic properties of soot.

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Acknowledgements. This work was funded by CRDF “First Step to Market” Program, Project 5059 “Production of Black Carbon Reference Material for applications in environmental monitoring”. The authors thank M. A. Timofeyev (Moscow State University) for SEM measurements.

References

- 5 Arnott, W. P., Moosmüller, H., and Rogers, C. F.: Photoacoustic spectrometer for measuring light absorption by aerosols: Instrument description, *Atmos. Env.*, 33, 2845–2852, 1999.
- Arnott, W. P., Moosmüller, H., and Walker, J.: Nitrogen dioxide and kerosene-flame soot calibration of photoacoustic instruments for measurement of light absorption by aerosols, *Rev. Scientific Instruments*, 71, 4545–4552, 2000.
- 10 Avgul, N. N. and Kiselev, A. V.: Physical Adsorption of Gases and Vapours on Graphitized Carbon Blacks, *Chemistry and Physics of Carbons*, edited by: Walker, P. L., 6, Dekker, New York, 1–124, 1970.
- Balbus, B. et al.: Meeting report: hazard assessment for nanoparticles - report from an interdisciplinary workshop, *Environ. Health Persp.*, 115, 1654–1657, 2007
- 15 Birch, M. E. and Cary, R. A.: Elemental Carbon-Based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust, *Aerosol Sci. Technol.* 25, 221–241, 1996.
- Bond, T. C., Anderson, T. L., and Cambell, D.: Calibration and intercomparison of filter-based measurements of visible light absorption by aerosols, *Aerosol Sci. Technol.*, 30, 582–600, 1999.
- 20 Boparai, P., Lee, J., and Bond, T. C.: Revisiting Thermal-Optical Analyses of Carbonaceous Aerosol Using a Physical Model, *Aerosol Sci. Tech.*, 42, 930–948, 2008.
- Cappa, C. D., et al. :Bias in filter-based aerosol light absorption measurements due to organic aerosol loading: Evidence from laboratory measurements, *Aerosol Sci. Tech.* 42, 1022–1032, 2008.
- 25 Chen, L.-W. A., Chow, J. C., Watson, J. G., Moosmüller, H., and Arnott, W. P.: Modeling Reflectance and Transmittance of Quartz-Fiber Filter Samples Containing Elemental Carbon Particles: Implications for Thermal/Optical Analysis, *J. Aerosol Sci.*, 35, 765–780, 2004.
- Chow, J. C., Watson, J. G., Crow, D., Lowenthal, D. H., and Merrifield, T.: Comparison of IMPROVE and NIOSH Carbon Measurements, *Aerosol Sci. Technol.* 34, 23–34, 2001.
- 30 Chow, J. C., Watson, J. G., Pritchett, L. C., Pierson, W. R., Frazier C. A., and Purcell, R. G.:

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The DRI Thermal Optical Reflectance Carbon Analysis System—Description, Evaluation and Applications in United-States Air-Quality Studies, *Atmos. Environ A-Gen.*, 27, 1185–1201, 1993.

EOS Meeting report: Final Recommendations for Reference Materials in Black Carbon Analysis, *Eos*, 84, 582–583, 2003.

Esteve, W., Budzinski, H., and Villenave, E.: Relative rate constants for the heterogeneous reactions of NO₂ and OH radicals with polycyclic aromatic hydrocarbons adsorbed on carbonaceous particles. Part 2: PAHs adsorbed on diesel particulate exhaust SRM 1650a, *Atmos. Environ.*, 38, 201–211, 2005.

Everett, D. H. and Ward, R. J.: A study of the effects of heat treatment on the physical properties of the carbon black Vulcan 3, *J. Chem. Soc., Faraday Trans.*, 1, 2915–2928, 1993.

Fernandes, M., Skjemstad, J., Johnson, B., Wells, J., and Brooks, P.: Characterization of carbonaceous combustion residues. I. Morphological, elemental and spectroscopic features, *Chemosphere*, 51, 785–795, 2003.

Kiselev, A. V. and Yashin, Ya, I.: *Gas-Adsorption Chromatography*, New York, Plenum Press, 289 pp., 1969.

Kiselev A. V., Kovaleva, N. V., Nikitin, Yu. S.: *Gas Chromatography on monolayers*, *J. Chromatograph.*, 58, 19–30, 1971.

Klouda, G. A., Filliben, J. J., Parish, H. J., Chow, J. C., Watson, J. G., and Cary R. A.: Reference Material 8785: Air Particulate Matter on Filter Media, *Aerosol Sci. Technol.* 39, 173–183, 2005.

Lack, D. A., et al.: Bias in filter-based aerosol light absorption measurements due to organic aerosol loading: Evidence from ambient measurements, *Aerosol Sci Tech.*, 42, 1033–1041, 2008.

Lee, H. M., Okuyama, K., Mizohata, A., Kim, T., and Koyama, H.: Fabrication of Reference Filter for Measurements of EC (Elemental Carbon) and OC (Organic Carbon) in Aerosol Particles, *Aerosol Sci. Tech.*, 41, 284–294, 2007.

McFiggans, G., Alfarra, M. R., Bower, K., Coe, H., Cubison, M., Topping, D., Williams, P., Desesari, S., Facchini, C., and Fuzzi, S.: Simplification of the representation of the organic component of atmospheric particulates *Faraday Discuss.*, 130, 2005.

Moteki, et al.: Evolution of mixing state of black carbon particles: Aircraft measurements over the western Pacific in March 2004, *Geophys. Res. Lett.*, 34, 4 pp, 2007.

National Institute of Occupational Safety and Health (NIOSH), Elemental Carbon (Diesel Partic-

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3, 1743–1773, 2010

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ulate): Method 5040, Issue 3 (Interim), NIOSH Manual of Analytical Methods, 4 Edn., DHHS (NIOSH) Publication No. 94-113, edited by: Cassinelli, M. E. and O'Connor, P. F., National Institute for Occupational Safety and Health, U.S. Department of Health and Human Services, Cincinnati, OH, 1999.

- 5 Novakov, T. and Corrigan, C. E.: Thermal Characterization of Biomass Smoke Particles, *Mikrochim Acta*, 119, 157–166, 1995.
- Peralta, O., Baumgardner, D., and Raga, G. B.: Spectrothermography of Carbonaceous particles, *J. Atmos. Chem.*, 57, 157–169, 2007.
- 10 Polidori, A., Turpin, B. J., Lim, H.-J., Cabada, J. C., Subramanian, R., Pandis, S. N., and Robinson, A. L.: Local and Regional Secondary Organic Aerosol, Insights from a Year of Semi-Continuous Carbon Measurements at Pittsburgh, *Aerosol Sci. Tech.*, 40, 861–872, 2006.
- Popovicheva, O. B., Persiantseva, N. M., Shonija, N. K., DeMott, P., Koehler, K., Petters, M., Kreidenweis, S., Tishkova, V., Demirdjian, B., and Suzanne, J.: Water interaction with hydrophobic and hydrophilic soot particles, *Phys. Chem. Chem. Phys.*, 10, 2332–2344, 2008.
- 15 Popovicheva, O. B., Kireeva, E. D., Shonija, N. K., and Khokhlova, T. D.: Water interaction with laboratory-simulated fossil fuel combustion particles, *J. Phys. Chem. A*, 113, 10503–10511, 2009.
- Ramanathan, V. and Carmichael, G.: Global and regional climate changes due to black carbon, *Nat. Geosci.*, 1, 221–227, 2008.
- 20 Rudzinski W. and Everett D. H.: Adsorption of Gases on Heterogeneous Surface, Academic Press, London, 578 pp, 1992.
- Schauer, J. J., Kleeman, M. J., Cass, G., and Simoneit, B.: Measurements of emissions from air pollution sources. 2. C1 through C30 organic compounds from medium duty diesel trucks, *Environ. Sci. Technol.*, 33, 1578–1587, 1999.
- 25 Schauer, J. J., Mader, B. T., Deminter, J. T., Heidemann, G., Bae, M. S., Seinfeld, J. H., Flagan, R. C., Cary, R. A., Smith, D., Huebert, B. J., Bertram, T., Howell, S., Kline, J. T., Quinn, P., Bates, T., Turpin, B., Lim, H. J., Yu, J. Z., Yang, H., and Keywood, M. D.: ACE-Asia Intercomparison of a Thermal-Optical Method for the Determination of Particle-Phase Organic and Elemental Carbon, *Environ. Sci. Technol.*, 37, 993–1001, 2003.
- 30 Schmid, H., Laskus, L., Abraham, H. J., Baltensperger, U., Lavanchy, V., Bizjak, M., Burba, P., Cachier, H., Crow, D., Chow, J., Gnauk, T., Even, A., ten Brink, H. M., Giesen, K. P., Hitznerberger, R., Hueglin, E., Maenhaut, W., Pio, C., Carvalho, A., Putaud, J. P., Toom-

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- Saunry, D., and Puxbaum, H.: Results of the “Carbon Conference” International Aerosol Carbon Round Robin Test Stage I, Atmos. Environ., 35, 2111–2121, 2001.
- Subramanian, R., Khlystov A. Y., and Robinson, A. L.: Effect of Peak Inert-Mode Temperature on Elemental Carbon Measured using Thermal-optical Analysis, Aerosol Sci. Tech., 40, 763–780, 2006.
- 5 Vlasenko, E. V., Gavrilova, T. B., and Daidakova, I. V.: Adsorption, Science & Technology, 15, 2–79, 1997.
- Yang, H. S. and Yu, J.: Uncertainties in Charring Correction in the Analysis of Elemental and Organic Carbon in Atmospheric Particles by Thermal/Optical Methods, Environ. Sci. Technol., 10 36, 5199–5124, 2002.
- Zelenyuk, A. and Imre, D.: On the Effect of Particle Alignment in the DMA, Aerosol Sci. Tech., 41, 112–124, 2007.

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Table 1. Soot reference materials: EC basis and organic carbon (OC), nominal and derived by the thermo/optical technique, wt%. Shaded cells indicate differences between the nominal and measured OC that are found to be outside the estimated uncertainty.

Sample #	EC basis	Type of organic coverage	OM nominal	OC nominal	OC measured
1	GTS 6	C₁₆H₁₀	0,32	0.304	0.06±0.05
2	GTS 6	(Pyrene)	0,16	0.152	0.17±0.07
3	GTS 6	C₂₈H₅₈	0,24	0.205	0.23±0.08
4	GTS 6	(Octacosane)	0,12	0.102	0.14±0.05
5	GTS 80	C₁₆H₁₀	1,0	0.94	0.95±0.01
6	GTS 80	(Pyrene)	5	4.55	4.39±0.44
7	GTS 80	C₉H₆O₆	1	0.51	0,77±0.14
8	GTS 80	(1,2,4-Benzenetricarboxylic acid)	4,88	2.57	2.64±0.25
9	GTS 80	OH [-C₂H₄O-]<i>n</i>H (Carbowax 600 {M 570-630})	1,0	0.53	0.60±0.11
10	GTS 80	C₁₂H₈O₄ (2,6 Naphthalene-dicarboxylic acid) “NDCA”	9,09	6.06	4.90±0.50

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Table 2. Content of mineral and metal impurities in thermal and graphitized soots, 10^{-3} ·wt%.

	Si	Al	Ca	Cu	B	Mn	Mg	Fe	V	Ti
TG-100	.5	.29	.72	.14	.35	.43	.36	1.24	.11	.17
GTS-80	0	.01	.61	0	.04	.11	.11	.13	0	0

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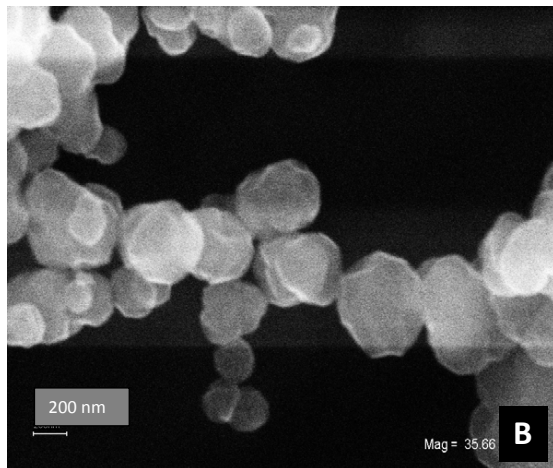
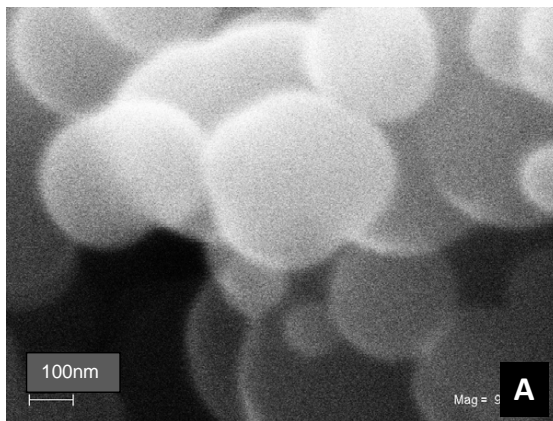


Fig. 1. SEM images of **(A)** technical carbon (thermal soot) which was chosen for production of EC RM and **(B)** GTS-6 soot after graphitization of thermal soot.

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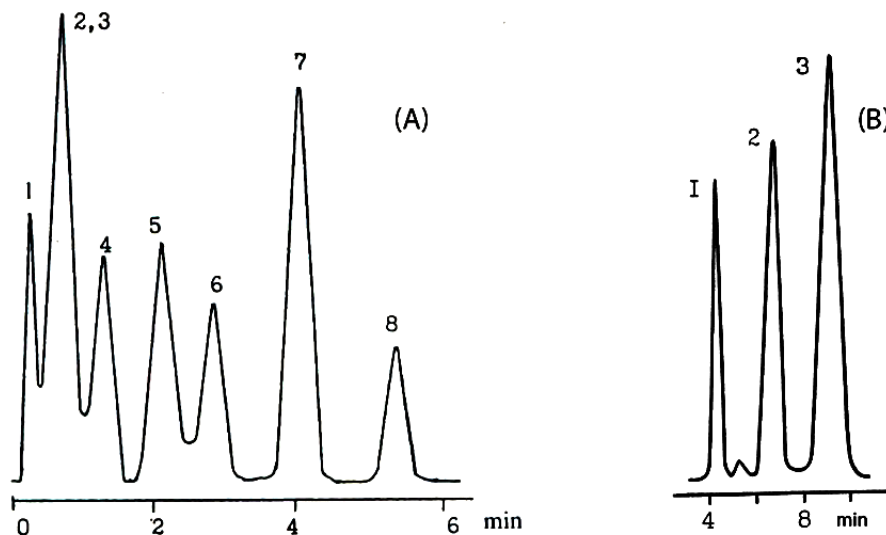


Fig. 2. Chromatograms on **(A)** GTS-6 for demonstration of high geometrical and chemical uniformity of the surface. The peaks correspond to (1) *n*-hexane, (2) adamantane, (3) *n*-heptane, (4) *n*-octane, (5) *n*-nonane, (6) indene, (7) tetralin, and (8) *n*-decane. **(B)** GTS-6 with 0,32% pyrene (Sample 1 in Table 1). The peaks correspond to (1) adamantane, (2) endo- and (3) exo-trimethylenenorbornane.

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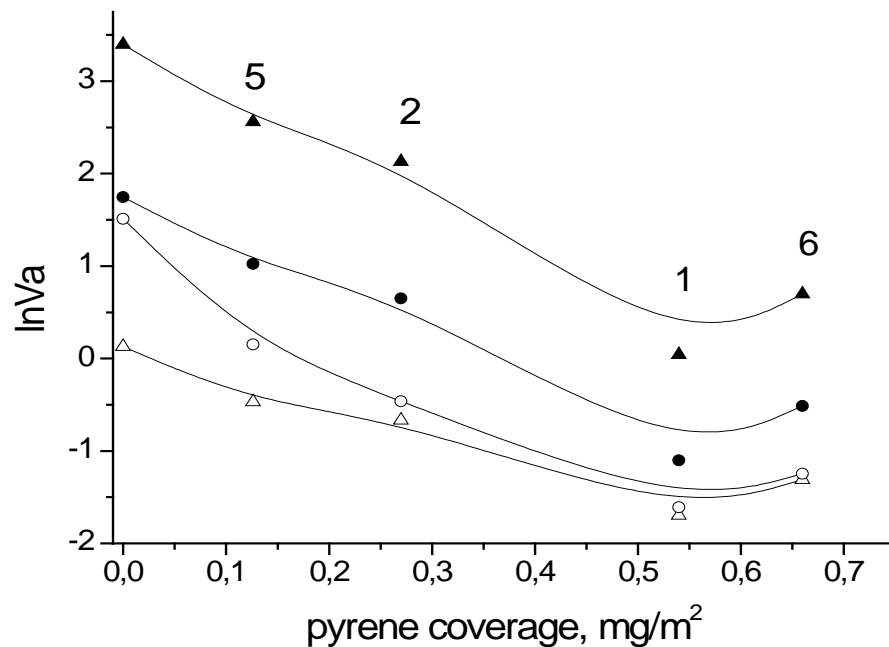


Fig. 3. Retention volume vs. weight percent of pyrene deposited on GTS-6 and GTS-80 (samples are indicated in respect to Table 1. Probe molecules are used: ▲) *n*-heptane, △) methyllethylketon, ○) benzene, ●) *n*-hexane.

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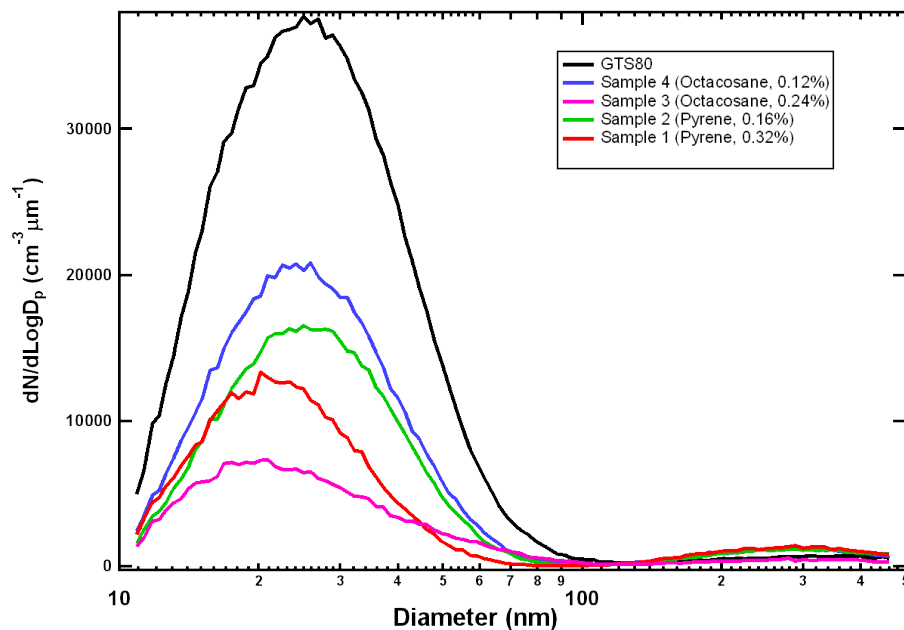


Fig. 4. These distributions show how GTS-80 and GTS-80 with various organic coatings vary with size. Adding layers of material leads to an apparent shift in the distribution to smaller sizes but this is due to changes in the diffusivity and shape of the particles that alter their behavior in the differential mobility analyzer.

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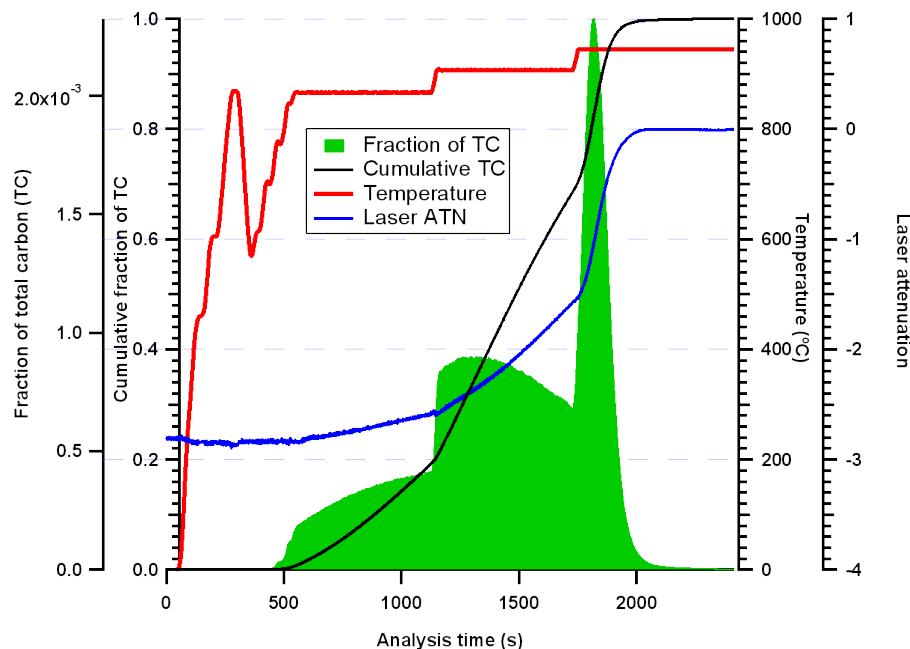


Fig. 5. This graph shows a typical time evolution of carbon that evolves from an ECRM sample (GTS-6) during the thermal/optical process. The shaded green curve shows the fraction of total carbon (TC) that is released as the sample is heated. The cumulative percent of TC is shown in the black curve. The temperature history is given in red and the attenuation of the laser transmitted through the sample filter is given in blue.

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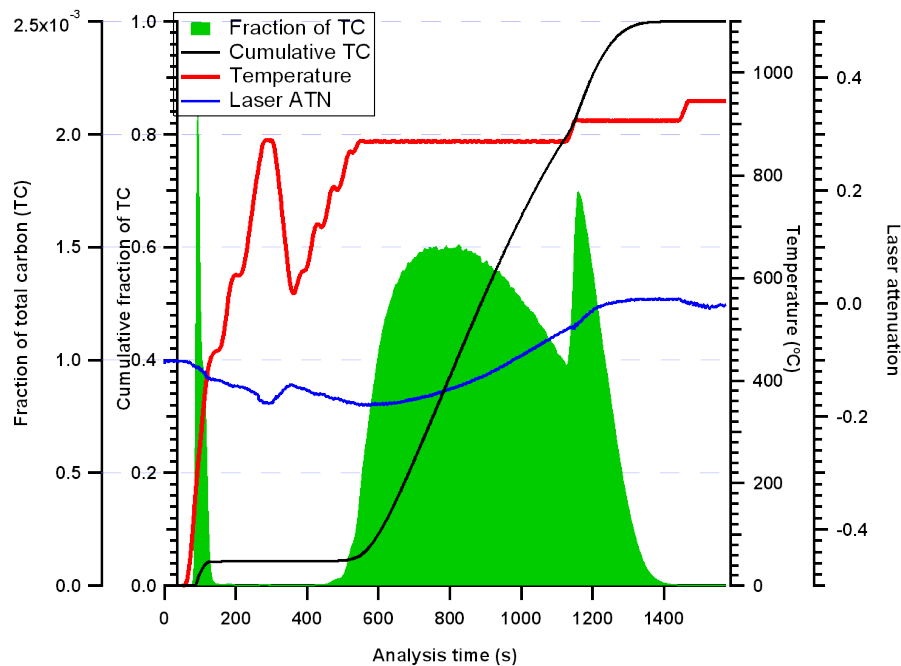


Fig. 6. This graph is the same as shown in Fig. 5 except the analysis is for GTS-80 covered with 5% of pyrene (Sample 6).

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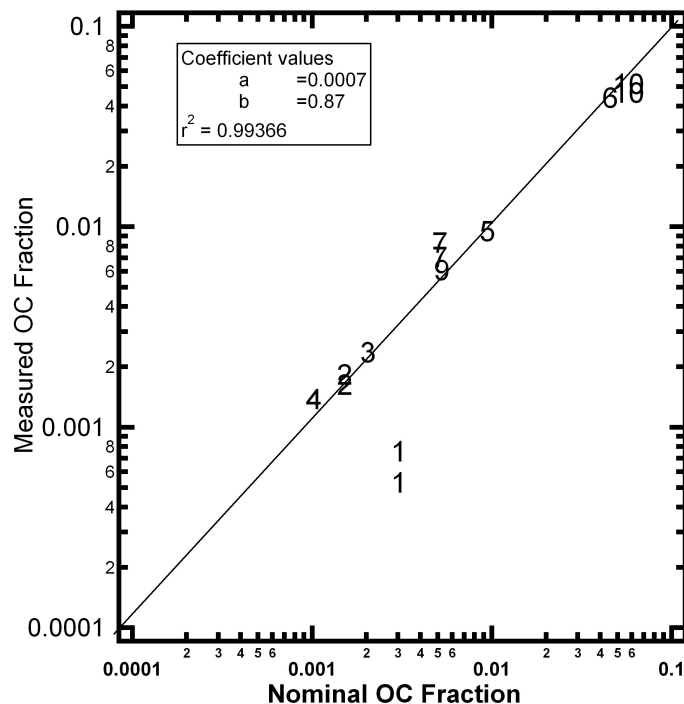


Fig. 7. The SRM samples that are listed in Table 1 were analyzed using the thermal/optical analysis (examples shown in Figs. 5 and 6) to derive the weight percent of OC for comparison with the nominal values. This graph shows the comparison where the numbers refer to the samples in Table 1. The coefficient values refer to the linear regression, $Y = a + bX$, where X and Y are the nominal and measured values, respectively. The correlation coefficient is given by r^2 .

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