

## Tailored graphitized soot as reference material for EC/OC measurement validation

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**Abstract.** The lack of standard reference materials for calibrating, troubleshooting and intercomparing techniques that measure the composition 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 the combustion produced particles found in the atmosphere. The proposed soot reference material (SRM) uses EC as a basis substrate for surface coatings of organic compounds that are representative of the 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

Soot, also commonly referred to as black carbon (BC) is a ubiquitous substance, produced by incomplete combustion of fossil fuels, that contains a variable mixture of organic carbon (OC) and elemental carbon (EC). It is a long-term geochemical sink of carbon that is found not only in soil and water but 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 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 allergy-related diseases (Balbus et al., 2007).

In order to understand how soot impacts the environment, i.e. climate and health, accurate measurements must be made of the physical, chemical and optical properties. There are many unknowns related to these properties, especially with respect to their evolution with age and transformation by photochemical and aqueous processes. The lack of information on these properties is largely a result of the paucity of measurements over sufficiently broad scales in space and time. No single instrument has the capability of measuring all the properties of soot; hence various techniques are required to evaluate individual characteristics of these particles.



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In order to establish the accuracy and reliability of these different techniques, it is common practice to calibrate the sensors 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 method for calibration, they are the means of ensuring that reasonable comparisons can be made among different measurements of the same quantity. There are a number of challenges, however, to finding appropriate soot reference materials (SRMs). In this paper we focus on SRMs specifically for use with instruments that measure the elemental and organic (EC/OC) components of soot.

The mass of OC and EC in ambient particulate matter is typically measured by the thermal/optical analysis (TOA) technique. 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).

The standard procedure for calibrating the TOA is to prepare preconditioned filters with known organic material, like sucrose or potassium hydrogen phthalate (KHP) whose number of carbon molecules is precisely known. This provides an accurate procedure for relating the output of the analyzer of carbon dioxide or methane (depending on the TOA technique used) with the number of carbon molecules in the aerosol sample on the filter. This does not, however, test the fidelity of the technique for separating the EC from the OC since the carbon from these calibration materials contains no EC nor do they typically produce much charring.

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 alter the temperature at which complex/large organic compounds and EC evolve off the filter (Novakov and Corrigan, 1995; Boparai et al., 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).

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, if available. Comparing different TOA techniques with ambient or

atmospherically-relevant samples is difficult, however, 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 (with respect to OC/EC) SRM will reduce some of the uncertainties associated with the different thermal and thermal-optical techniques.

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 re-suspending 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 two standard protocols – the Interagency Monitoring of Protected Visual Environments (IMPROVE) and the Speciation Trends Network; National Institute of Occupational Safety and Health (STN-NIOSH; Chow et al., 1993; Birch and Cary, 1996; NIOSH, 1999) – even though the sum of the EC and OC agreed quite well, the measured fraction of OC differed by more than 60 % (Klouda et al., 2005). Due to the complexity of the NIST 8785 SRM, the source of the differences between the two techniques could not be resolved and it was concluded that the separation of EC and OC is method dependent with no way to assess which of the two protocols was providing the more accurate results.

The objective of the current work is to introduce the concept of a well characterized, laboratory-fabricated SRM for the express purpose of validating the methodology of thermal optical analyzers with respect to the accuracy of separating EC from OC. An approach is presented for the fabrication of SRM with precisely controlled mixtures of EC and OC that are representative of compounds found in the particles produced by combustion of fossil fuel. The utility of this approach is illustrated with an analysis of a number SRM samples using the TOA method.

## 2 Methodology

Chemical analysis of combustion particles 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 soot and relative concentration of organic precursor gases (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 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 a basic elemental carbon substrate and deposit organic compounds from these groups on it, compounds that are representative of the main classes of organics identified in the surface coverage of soots produced by fossil fuel burning, an approach suggested by Popovicheva et al. (2009).

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

Several kinds of technical carbon, commercially produced by pyrolysis of natural gas, were tested in our work as primary material for ECRM production. The ones eventually selected were the thermal soots TG-10 and TG-100 (Electrolyt 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  $3000^\circ\text{C}$  producing graphitized thermal soots (GTS) with surface areas of near 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 from this technique.

The main classes of non-polar organics that have been identified in diesel and aviation soot are alkanes and polycyclic aromatic hydrocarbons (PAHs) (Popovicheva et al., 2009). Polyethyleneglycol (PEG) is representative of the polymer polar compounds, and aromatic and aliphatic acids are related to polar materials. In our work representative organics were selected from each group of identified compounds: (1) octacosane,  $\text{C}_{28}\text{H}_{58}$ , for alkanes, (2) pyrene,  $\text{C}_{16}\text{H}_{10}$ , for PAHs, (3) 2,6-naphthalene dicarboxylic acid,  $\text{C}_{12}\text{H}_8\text{O}_4$ , 1,2,4-benzene tricarboxylic acid (trimellitic acid),  $\text{C}_9\text{H}_6\text{O}_6$ , and 1,3,5-benzenetricarboxylic acid (trimesic acid),  $\text{C}_9\text{H}_6\text{O}_6$ , for aromatic acids and (4) PEG Carbowax 600 (M 570–630)  $\text{OH}[-\text{C}_2\text{H}_4\text{O}-]_n\text{H}$  for polymer compounds. These choices take into account that the organic compounds deposited on the surface should be nonvolatile at normal temperatures and pressures and strongly bonded on the surface with a monolayer coverage stable up to  $200\text{--}250^\circ\text{C}$  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 from a given number concentration of the modifier. For this test GTS-6 was chosen as the basic EC substrate with

organic dyes acid orange  $\text{C}_{16}\text{H}_{11}\text{N}_2\text{O}_4\text{SN}$  (MW = 350) and acid anthraquinonic  $\text{C}_{16}\text{H}_9\text{N}_2\text{O}_7\text{SNa}$  (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  $110^\circ\text{C}$  for five hours.

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 dichloromethane.

A given modifier, in the amount proposed for modification, is mixed with the solvent and GTS 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 GTS 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 the evaporator then further extracted in an oven at a temperature  $10\text{--}20^\circ\text{C}$  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 organic matter (OM) that was deposited, and the estimated OC (using nominal OM) is listed for each sample. Samples with pyrene, octacosane and trimesic acid, deposited on GTS-6, were manufactured with the objective of producing GTS

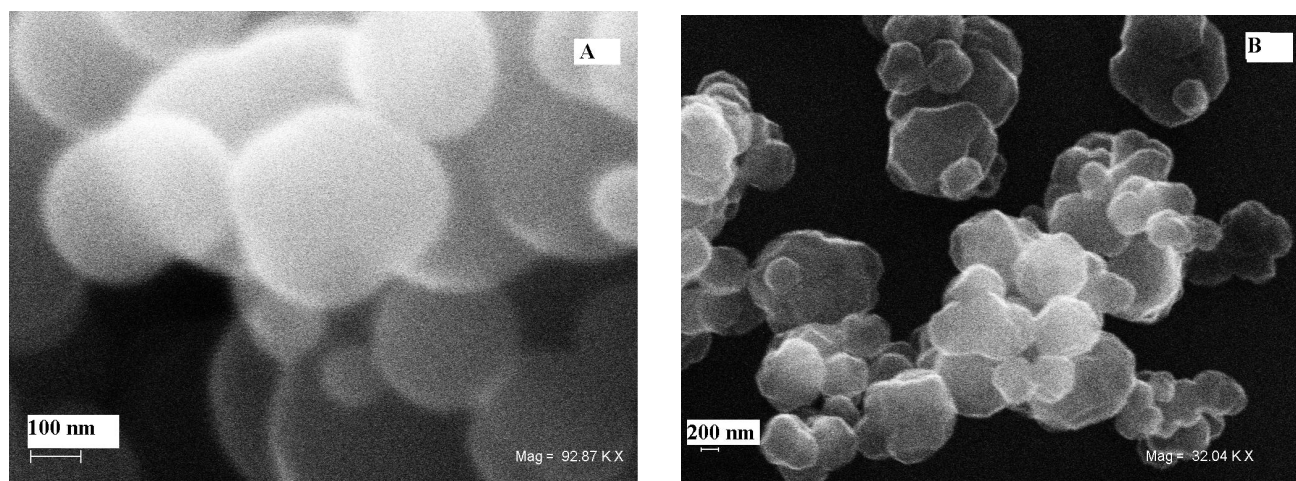
**Table 1.** Soot reference materials: EC basic and nominal organic matter (OM), organic carbon (OC), nominal and derived by the thermo/optical technique, wt%. Shaded cells indicate differences between the nominal and measured OC that are found to be outside the estimated uncertainty.

Sample #	EC basis	Type of organic coverage	OM nominal	OC nominal	OC measured
1	GTS 6	C <sub>16</sub> H <sub>10</sub>	0.32	0.304	0.06 ± 0.05
2	GTS 6	(Pyrene)	0.16	0.152	0.17 ± 0.07
3	GTS 6	C <sub>28</sub> H <sub>58</sub>	0.24	0.205	0.23 ± 0.08
4	GTS 6	(Octacosane)	0.12	0.102	0.14 ± 0.05
5	GTS 80	C <sub>16</sub> H <sub>10</sub>	1.0	0.94	0.95 ± 0.01
6	GTS 80	(Pyrene)	5	4.55	4.39 ± 0.44
7	GTS 80	C <sub>9</sub> H <sub>6</sub> O <sub>6</sub>	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 [–C <sub>2</sub> H <sub>4</sub> O–] <i>n</i> H (Carbowax 600 {M 570–630})	1.0	0.53	0.60 ± 0.11
10	GTS 80	C <sub>12</sub> H <sub>8</sub> O <sub>4</sub> (2,6 Naphthalene-dicarboxylic acid) “NDCA”	9.09	6.06	4.90 ± 0.50

slightly coated with organic compounds (0.1–0.3%). 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.

To demonstrate the quality of the applied graphitization procedure the selected materials have been characterized with respect to the elemental composition (carbon and oxygen content), the amount of impurities (ash) and quality of the surface (homogeneity). The morphology and the shape of soot particles deposited on a conductive silicone plate were determined by scanning electron microscopy (SEM) using a LEO 1430-vp (Karl Zeiss) with a spatial resolution of 5 nm. When coupled with X-ray Energy Dispersive Spectroscopy (XREDS) this analysis approach allowed the evaluation of soot elemental composition with a sensitivity of 0.3 wt%. The SEM measurements were accompanied by conventional bulk analysis that provides the average composition. Chemical elements with atomic numbers larger than 11 are determined by X-ray fluorescence spectroscopy (XFS) using a scanning vacuum crystal diffraction spectrometer SPECTROSCAN (40 kV) with the detection limit of 1 µg g<sup>-1</sup>. The volatile fraction (volatility) of technical carbons and GTS soot was roughly determined by weighing the sample before and after heating at 537 K for 30 min. The water soluble fraction (WSF) was obtained after washing in deionized water followed by filtration and evaporation.

The chemical and structural homogeneity of the fabricated material surface was analyzed by inverse gas chromatography (Rudzinski and Everett, 1992) using a Tsvet 100 chromatograph with a flame ionization detector and columns of 1 m × 2 mm i.d. Before the measurements the soot samples were baked in the nitrogen flow at 423 K for 10 h. Chemical compounds of different classes were used as probe molecules, such as *n*-alkanes, PAHs, and oxygen-containing hydrocarbons. The measurements were performed within a temperature range during which the time for a probe molecule to be adsorbed on the surface (retention time) was not influenced by the sample mass. The retention volumes per specific surface areas of GTS soots were determined. Gas chromatography was used to increase the accuracy of the SRM production with a given amount of OC on the surface. The chromatographic calibration was carried out based on the dependence of the residence time for a set of probe molecules of different polarity on the amount of OC deposited. Such a calibration allows the determination of the monolayer coverage and confirms the reproducibility of the production methodology. Additionally, the morphological and texture parameters of fabricated soots 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).

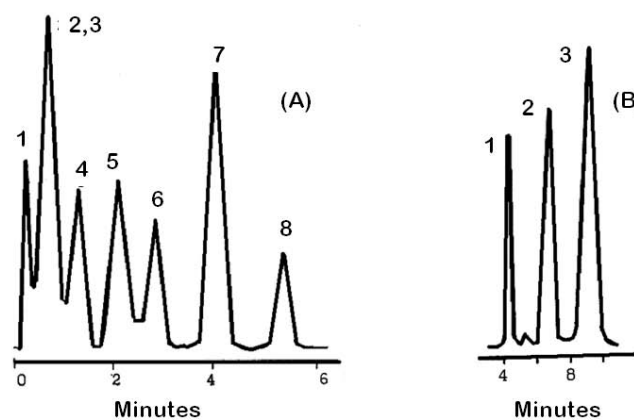


**Fig. 1.** Typical SEM image of (A) technical carbon (thermal soot) which was chosen for production of EC RM and (B) GTS-6 soot after graphitization of thermal soot.

### 3 Characterization of Elemental Carbon RM (ECRM)

Typical particles of thermal TG-100 soot are shown in Fig. 1a. The average diameter,  $D$ , of the primary particles is  $260 \pm 1.4$  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  $180 \pm 1.4$  nm and  $32 \pm 1.24$  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.

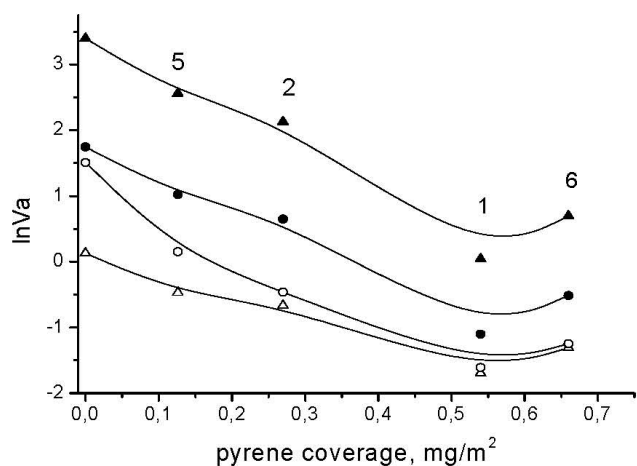
There are numerous studies in the literature demonstrating that the surface of graphitized soot is flat, chemically and geometrically homogeneous, and therefore inert and stable (Avgul and Kiselev, 1970; Kiselev and Yashin, 1969). Our examination of typical features of the interaction of probe molecules with the surfaces of GTS-6 and GTS-80 in the gas chromatograph validates these properties for fabricated SRMs. Figure 2a shows the chromatogram 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 chromatogram of complete separation of highly symmetric isomers on GTS-6 with 0.32 % pyrene (sample No. 1 of Table 1). Adamantane, with a more compact molecule structure, is eluted first followed by endo- trimethylenenorbornane (TMNB) which has



**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.

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  $\pi$ -electron system of benzene prevents this molecule from strong interaction with graphitized surfaces (see Fig. 3).



**Fig. 3.** Retention volume vs weight percent of pyrene deposited on GTS-6 and GTS-80 (samples are indicated with respect to Table 1. Probe molecules are used:  $\blacktriangle$  *n*-heptane,  $\triangle$  methylethylketon,  $\circ$  benzene,  $\bullet$  *n*-hexane.

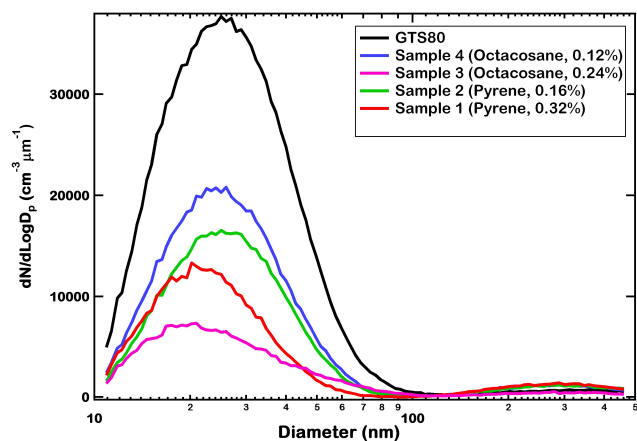
It is observed that increasing the pyrene coverage decreases the retention volumes. At  $0.54 \text{ mg m}^{-2}$  the minimum retention volume is seen to be related to the formation of a statistically dense pyrene monolayer (Kiselev et al., 1971). At higher coverages the interaction of probe molecules 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  $5.6 \pm 0.3$  and  $79 \pm 2 \text{ m}^2 \text{ g}^{-1}$  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 technical carbon reduces the oxygen content and water soluble fraction from 4.0 and 0.45 wt %, respectively, leading to a negligible amount of both oxygen and water in GTS-6 soot (within the measurement accuracy). The volatile fraction of technical carbon is determined to be 0.6 wt % before and .0032 wt % after treatment. Table 2 lists the content of mineral and metal impurities in TG-100 and GTS-80 obtained by XFS, 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

**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



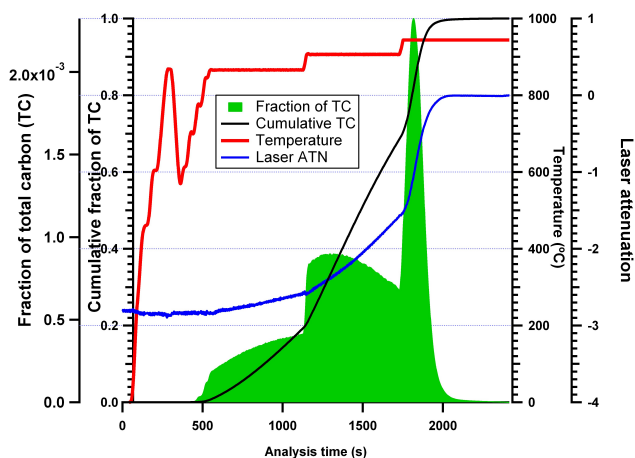
**Fig. 4.** These distributions show how the concentration of basic GTS-80 and GTS-80 soots with various organic coatings varies with size. Adding layers of material leads to an apparent shift in the distribution to smaller sizes but this is possibly due to changes in the shape of the particles that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

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 (1982) 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 cleanliness.

## 4 Evaluation of SRM properties

### 4.1 Size distributions

Samples of fabricated ECRMs and SRMs, always in powder form, were analyzed with a TSI Inc, scanning mobility particle sizer (SMPS) to evaluate the relative number 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 No. 4 and 3 (blue and pink curves) and with 0.16 % and 0.32 % of pyrene, Samples No. 2 and 1 (green and red curves). The relative concentrations are a



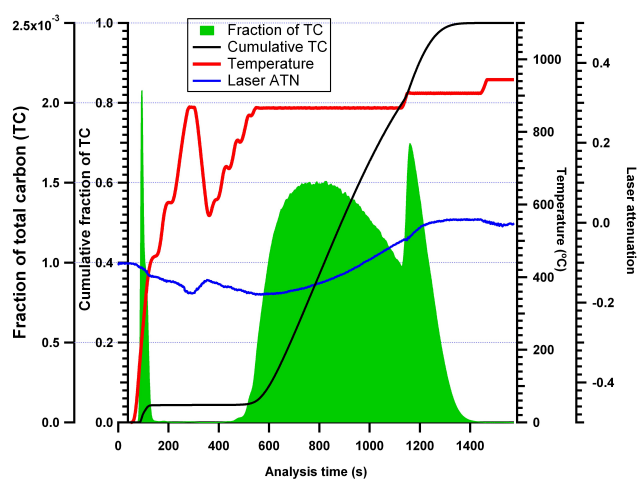
**Fig. 5.** This graph shows a typical time evolution of carbon that evolves from ECRM sample (GTS-6) during the thermal/optical process. The shaded green curve shows the fraction of total carbon (TC) that is released as the sample is heated. The cumulative percent of TC is shown in the black curve.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

function, not of the composition, but of the degree of dilution when dispersing a given sample with a nebulization system. 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 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 methodology for preparing the sample for analysis was as follows:

1. A clean Pallflex quartz filter was pre-fired and several segments were punched from this filter with dimensions of  $1.5 \times 1.0$  cm.
2. Each punch was weighed.



**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 No. 6).

3. The reference material, stored in a glass test tube, was gently mixed by shaking and then a small amount removed with a small spatula. The removed material just covered the surface of the spatula.
4. The material was transferred to the filter punches (at least two samples per filter) by gently tapping the spatula and spreading the material with the edge of the spatula over the center portion of the filter where the laser transmission is maximum.
5. The punch is weighed again to determine the sample weight.
6. The punch is placed in the analyzer and evaluated using the NIOSH protocol that is used in all Sunset Laboratory analysis.
7. After the analysis, the punch is weighed again to determine the weight of refractory materials.

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%) (Sample No. 6), 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, respectively. The TC is derived from the carbon dioxide ( $\text{CO}_2$ ) formed as the sample is heated and the carbon molecules are released and oxidized. The analysis is a two step process in which a sample is heated rapidly in a helium environment to release OC, then cooled and 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.

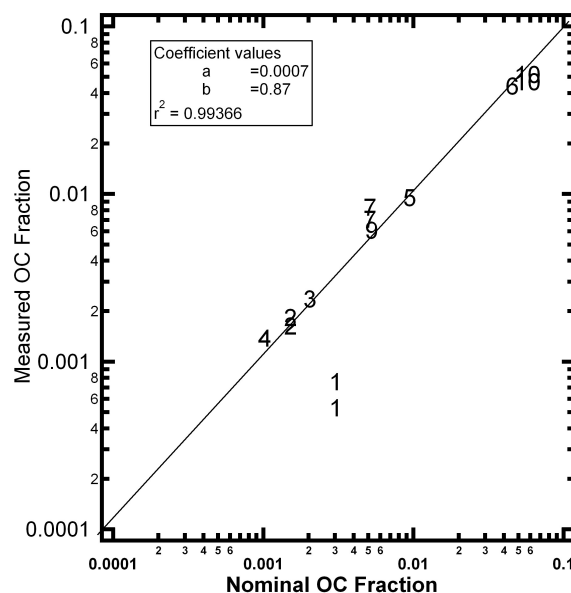
As seen in Fig. 5, since there is no OC on the ECRM there is no fractional TC appearing until 500 s when the temperature has exceeded 600 °C. In Fig. 6, however, the fractional TC is seen to momentarily increase at 50 seconds when the temperature reaches 100 °C then decreases as all of OC is removed by 150 s at 400 °C. Once again at 400 s and 600 °C, 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 0.065 % and 4.39 %, respectively. Analysis of the pure GTS showed very good precision, less than 5 % deviation amongst multiple samples.

The ten SRM samples listed in Table 1 were analyzed to compare the nominal OC mass deposited on EC basic 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. We especially pay attention to the SRMs with low OC, Samples No. 2, 3 and 4 that demonstrate the sensitivity of TOA techniques to low fractional amounts of OC. For one sample, Sample No. 1, 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 No. 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.

### 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



**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  $r^2$ .

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. The sample of GTS-80 that had been stored for more than six months at the Moscow University laboratory was sent back to Sunset Laboratories for reanalysis. The OC/TC ratio measured for the first GTS-80 sample was 0.0549 % and for the second sample it was 0.0575 %, compared to zero for nominal value for deposited organic matter. The good reproducibility of the water adsorption isotherm and very low volatility, just 0.03 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 very low OC for samples of GTS-6 and GTS-80, for both the original ones and those specially pre-treated before measurements (out-gassing at 350 °C). Therefore we may conclude that during the storage and transportation there are insignificant changes to the prepared samples due to absorption of ambient OC.

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 adsorbability, 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 No. 1 in Table 1 the mass loss was 0.08 %. For the sample No. 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 cm<sup>3</sup> g<sup>-1</sup>, 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 and validation 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 reference materials 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 SRM 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 soot is an excellent candidate as an SRM, for evaluating the sensitivity of thermal/optical analyzers with respect to the differentiation of OC from EC as a function of different organic coatings. The range of OC/TC ratios that we used in the initial tests would be a reasonable set of standards; however, all ten would not necessarily be needed as there does not seem to be any sensitivity to the type of OC. It is necessary to choose

a set of the smaller percentages of OC/TC to establish the sensitivity of a particular TOA methodology and as high a percentage as possible to look for non-linearities.

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