Carbon speciation of diesel exhaust and urban particulate matter NIST standard reference materials with C(1s) NEXAFS spectroscopy

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Abstract

The U.S. National Institute of Standards and Technology (NIST) provides a number of particulate matter (PM) standard reference materials (SRM) for use in environmental and toxicological methodology and research. We present here the first analysis with respect to the molecular structure of the carbon in three such NIST SRM samples, i.e. diesel engine exhaust soot from heavy duty equipment engines (SRM 1650), diesel soot from a forklift engine (SRM 2975), and urban PM collected in St. Louis Missouri (SRM 1648), with near-edge x-ray absorption fine structure (NEXAFS) spectroscopy. The NEXAFS spectra of the two diesel soot samples appear quite similar, while they differ significantly from the urban PM spectrum, in agreement with X-ray diffraction data published recently. Such comparison is made in terms of aromatic and aliphatic carbon species, as well as by a general comparison with graphitic materials. Both diesel soot SRM contain basic graphitic structures, but presence of exciton resonance and extended x-ray absorption fine structure oscillations in SRM 1650, and lack therof in SRM 2975 suggest that SRM 1650 is the more graphitic material. Presence of polycyclic aromatic hydrocarbons, which have a characteristic NEXAFS resonance at the same position like graphite, can obscure the graphitic character of soot, unless an extraction of the organic matter is made. Our NEXAFS data do not suggest that the urban PM sample SRM 1648 contains a substantial amount of graphite-like material.

1 Introduction

Airborne carbonaceous particulate matter, often referred to as “soot”, is known to cause adverse health effects [1] and is suspected to have an impact on global climate change [2]. Diesel exhaust particulate matter (DPM) is frequently believed to be a major constituent of airborne carbonaceous particulate matter in the environment. The U.S. National Institute of Standards and Technology (NIST) provides a number of particulate matter (PM) standard reference materials (SRM) for use in environmental and toxicological studies [3]. A recent “plea” expressed the need for larger amounts and more diverse types of diesel exhaust and urban PM samples, including SRMs [4,5], to provide a comprehensive assessment of health risks to NIST, numerous chemical analyses and toxicological studies. These samples have been analyzed for many elements, with one remarkable exception, and that is carbon. This is even more striking, since carbon is the dominant element in all of these SRMs. In the present work, three such NIST SRMs are studied with respect to the molecular structure of the carbon in the specimen. These are the two DPM materials SRM 1650 and SRM 2975, and urban PM SRM 1648.

A systematic chemical analysis and speciation of SRMs 1648 and 1650 of hazardous metals, sulphur and chlorine was recently conducted by our laboratory with X-ray absorption and particle induced X-ray spectroscopy [6]. SRM 1648 was subject to a similar extensive study by a research
team in Japan [7]. To some extent, SRMs can be meaningfully used as surrogates for other PM samples, such as SRM 1650 for representative diesel automobiles [8]. Possibly out of ignorance for the structural and molecular diversity that various solid carbon materials can have, or due to lack of access to sufficient amounts of DPM, industrial carbon black is frequently used as a surrogate for DPM, for instance. However, researchers have increasingly become aware of this discrepancy [9] and realize that the solid carbon itself (black carbon) can be highly complex in crystallographic structure, microstructure, and nanostructure. Little work was published in environmental, atmospheric and health science literature which addressed this issue. This is even more relevant since SRM 1650 and SRM 1648 contain as much as 98% or 70% carbon, respectively. The structure of DPM can significantly vary depending on fuel composition and engine operation conditions [10,11]. Differences in DPM and urban PM can be even more drastic [11,12], as we will see in the results of this paper.

Synchrotron-radiation based near-edge X-ray absorption fine structure (NEXAFS) spectroscopy has been used for the speciation of carbon in materials for almost 20 years [13], but has only been used to examine PM quite recently [14]. The spectra from NEXAFS experiments are quite similar to electron energy loss spectroscopy (EELS) data [15]. In NEXAFS spectroscopy, an electron is excited by an incident X-ray photon from the highest occupied molecular orbital to the lowest unoccupied molecular orbitals. A review for the carbon K-shell absorption, C(1s) NEXAFS is given in [16]. In EELS, inner shell absorption is used to probe elements. Often, transmission electron microscopes (TEM) come with an EELS spectrometer that allows for some rudimentary chemical analysis, including carbon. But only dedicated, non-TEM based EELS spectrometers have made significant contributions for carbon analyses so far. Worthwhile to mention are the works by A. Hitchcock and co-workers, see for instance [17], who provides an EELS spectra database for the scientific community. Similar databases for C(1s) NEXAFS spectra are provided by H. Ade [18] and C. Jacobsen [19] and co-workers, and can be found in the textbook by J. Stöhr [13].

More and more synchrotron beamlines allow for NEXAFS spectroscopy in a microscopy (Scanning Transmission X-ray Spectromicroscopy, STXM) mode with a spatial resolution better than 100 nanometer. Cody et al. made early, pioneering, use of STXM for carbon speciation in coal specimen [20,21]. More recently, STXM was used for the study of DPM [22] and for atmospheric aerosol particulates [23].

NEXAFS spectroscopy, like EELS, is entirely element specific. However, the molecular environment of the carbon atoms has a major influence on the electronic structure of the element, which for carbon can be probed with soft X-rays in the energy range from 280 to 400 eV. Spectra can serve virtually as molecular fingerprints. This work will present and discuss these fingerprints of three established PM standards.

2 Experimental Section

The SRM samples were purchased from NIST and had been stored in accordance with their regulations and specifications, which are available via the internet [24-26]. Commercially available natural graphite powder SL-25 (Superior Graphite) was used as a basic reference and energy axis calibration material.

According to the NIST certificates of analysis, SRM 1650 was obtained from the heat exchangers of a dilution tube facility after 200 engine hours of particulate accumulation from several direct-injection 4-cycle diesel engines. The organic compounds that contribute most to this sample are fluoranthene, pyrene, phenanthrene, and 9-fluorenone. SRM 2975 was obtained from the filtering system specifically designed for diesel powered forklifts. The organic compounds that contribute most to this sample are fluoranthene, pyrene, phenanthrene, and 9-fluorenone. Data for polycyclic aromatic hydrocarbon (PAH) compounds in SRM 1650 and 2975 provided in these analysis
certificates are rewritten for the convenience of the reader in Table 1. The urban PM SRM 1648 was collected over a 12 months period in the area of the city of St. Louis, Missouri.

Table 1: Concentrations in mg/kg of major PAH compounds in DPM SRMs as of NIST’s certificates of analysis [24-26].

<table>
<thead>
<tr>
<th></th>
<th>SRM 1650 [mg/kg]</th>
<th>SRM 2975 [mg/kg]</th>
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<tbody>
<tr>
<td>Phenanthrene</td>
<td>71 ±</td>
<td>17 ± 2.8</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>51 ± 4</td>
<td>26.6 ± 5.1</td>
</tr>
<tr>
<td>Pyrene</td>
<td>48 ± 4</td>
<td>0.9 ± 0.24</td>
</tr>
<tr>
<td>9-Fluorenone</td>
<td>33 ±</td>
<td>±</td>
</tr>
<tr>
<td>Chrysene</td>
<td>22 ±</td>
<td>4.56 ± 0.16</td>
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The percentage of extractable organic matter (EOM) is 2 % for SRM 2975 [5,27], and 17 % for NIST 1650 [5,27,28]. The surface O/C ratios as determined by XPS are 0.20 for SRM 2975, and 0.18 for SRM 1650 [27]. The specific surface area for SRM 2975 is 80 m²/g when not heated during outgassing, and 87 m²/g when heated during outgassing. For the SRM 1650, the values are 48 and 80 m²/g, respectively [27].

The graphite and PM samples were pressed into pellets of around 250 micron thickness (urban PM, 100 micron thickness only) and 25 mm square area and then mounted on a sample holder with sticky, electronically conducting carbon tape underneath. To avoid artefacts in the spectra, care was taken that the carbon tape was smaller than the sample, so that the sample completely covered the carbon tape and no carbon tape was hit by the x-ray beam.

Near-edge x-ray absorption fine structure spectra at the carbon K-shell absorption edge were recorded at beamline 9.3.2 at the Advanced Light Source in Berkeley, California. The X-ray energy was scanned from 260 eV to 320 eV in 0.1 eV steps, and from 320 to 400 eV in 2 eV steps, at an energy resolution of about 1/3,000. Three such scans were made for each sample, with a collection time of 500 msecs for every energy step, totaling about 68 minutes for data acquisition per sample. The spectra presented here were acquired by the more bulk sensitive target current detection technique, rather than by the electron yield technique, which is surface sensitive, or the photon yield technique, which has a sampling depth of few hundred nanometers [29]. For target current detection, the Auger electron yield is the process that forms the current [30]. Since Auger electrons are formed by the incident photons of the synchrotron at an attenuation length of around 1 micron in carbon at the absorption edge, we estimate 1 micron for massive and compact carbon at around 280 eV X-ray energies to be the sampling depth. Since DPM is a porous material, we can assume that PM2.5 can be probed bulk-sensitive with C(1s) NEXAFS spectroscopy.

The target current signals were divided by the incident beam intensity to account for photon losses during the operation of the synchrotron. The calibration of the energy axis was performed by using the graphite spectrum, which has a characteristically sharp π-transition at 285 eV.

3 Results

3.1 Graphite vs. Diesel soot

The C(1s) NEXAFS spectra of graphite and SRM 1650 are shown in Figure 1a and 1b. Figure 1b shows the actual relevant features we want to highlight in this work, but at first we will discuss the
general shape of the spectra. The spectra extend from 280 to 400 eV, with the NEXAFS features being between 285 and 295 eV. For a first qualitative comparison, we have normalized the spectra with respect to the intensity decay for high energies, which is frequently referred to as the EXAFS range (Extended X-ray Absorption Fine Structure), showing intensity oscillations due to local order in the material [13]. Both spectra were normalized so that they roughly overlap from 330 to 400 eV. The graphite spectrum shows EXAFS oscillations from 300 to 400 eV, indicative of graphitic crystalline order. These oscillations are most spectacular between 300 and 340 eV. The information contained in this part of the spectrum gives account on the crystalline structure and order of the specimen.
While EXAFS spectroscopy has been widely used in materials and environmental science with respect to many atoms, such as 3d metals, heavy metal, and rare earths, the technique is largely undeveloped for carbon and other low Z elements, whose primary absorption shells are covered by soft X-rays only.

The scope of this work is the NEXAFS range, which gives account of the molecular structure of the carbon atoms and their nearest neighbours. The discussion of the spectra will focus on peculiarities from 285 to 295 eV. While literature on carbon EXAFS is virtually non-existent, there is probably no other element than carbon which has been studied so extensively with NEXAFS spectroscopy [13].

Graphite has a prominent \( \pi \)-transition at 285 eV, owing to the unsaturated nature of the C=C bonding in the graphene sheets that form the graphite [31,32]. This is typically the strongest peak for graphite. Also, SRM 1650 has such a peak at 285, but at a lesser intensity. The next characteristic absorption of carbon atoms in graphite is at around 292 eV, due to a \( \sigma \)-transition, which, being closely located near the start of the EXAFS oscillations, is very sensitive to the local structure of the carbon atoms and their neighbours [13]. This peak is typically much broader than the \( \pi \)-transition peaks. Graphite has on the lower energy side from this broad peak a very sharp exciton peak at about 290.2 eV [32,33]; our data suggest that the exciton peak is more pronounced in well crystallized materials. With the normalization of both spectra made with respect to the high energy tail (range 300 eV – 400 eV) and the \( \sigma \)-peak at 292 eV, we can easily visualize the different degrees of graphitization in graphite and soot SRM 1650 by examining the transition at 285 eV: the intensity of this peak in SRM 1650 is as half as large as the intensity in commercial graphite SL-25.

Diesel soot is less crystalline than graphite, but has some crystalline properties. It is a noteworthy observation that even diesel soot shows tendencies to develop the exciton peak at 290.2 eV. For further analysis, we will look at Figure 1b, which shows both spectra magnified in the relevant energy range 280 – 320 eV. Also, the normalization is now changed so that the peaks for the \( \pi \)-transition at 285 eV quantitatively overlap. While the graphite spectrum is structureless from 287 – 289 eV, the diesel soot spectrum shows pronounced absorption features in this range. Not only one but several structures cause absorption in this range, viz., C-OH at 287 eV and C-OOH at 289 eV. We have adopted the peak assignments for the phenolic C-OH and the carboxylic C-OOH from published data [20,21,34,35].

3.2 Diesel particulate matter SRM 1650 vs. SRM 2975

With the basic features of the C(1s) NEXAFS spectra of graphite and soot discussed, we are now able to compare two closely related yet different diesel exhaust soot specimens. Figure 2a and 2b shows the NEXAFS-relevant spectral features of SRM 1650 and 2975 from 280 to 310 eV. The global behaviour of both materials is quite similar, viz. the pronounced C=C peaks at 285 eV, the rounded \( \sigma \)-peak at 292 eV, and in between, from 287 to 289 eV, the resonances from the surface functional groups attached to the soot, such as C-OH and C-OOH [20,21,34,35].
The forklift soot SRM 2975 appears to have more sub-structures than SRM 1650. At 284 eV and 286 eV, clear deviations can be seen from the ideal peak at this position in graphite. Although we found evidence for quinone structures in diesel soot SRM 1650, when compared with graphite, the presence of such quinone species is much more obvious for SRM 2975 due to the stronger intensity shoulder at 284 eV, which extends to more than 75% of the peak height of the central peak at 285 eV. The corresponding shoulder at 286 eV for the C=O structure can also be more clearly made out since it is at about the same height as the benzoquinone C=C resonance at 284 eV. The inset shows the peak at 285 eV overlaid for better comparison. Here the deviation of SRM 2975 from SRM 1650 due to benzo-quinones becomes even more striking. However, we recall that close inspection of the spectrum from SRM 1650 also revealed the presence of some benzoquinone, though to a lesser extent than does SRM 2975. The surface functional groups like hydroxyl at 287 eV and carboxyl at 288 eV also appear to be somewhat more abundant in SRM 2975 forklift soot, simply because they have slightly higher intensity in this energy range. We note that these two resonances appear more separated in SRM 2975 than in SRM 1650, i.e. due to the dip at 287.5 eV. Also, carboxyl has a stronger absorption in SRM 2975 than hydroxyl.

With respect to the higher energy features in the spectrum, SRM 1650 has somewhat more pronounced EXAFS oscillations than SRM 2975. In addition, SRM 1650 has a sharper exciton feature at 290.2 eV; this feature is missing in the spectrum from the forklift soot. We therefore believe that SRM 1650 is a more crystalline specimen than SRM 2975, probably with fewer but larger crystallites and hence with less defects and surface than specimen SRM 2975.

### 3.3 Diesel exhaust PM vs. urban PM

The C(1s) NEXAFS spectra of urban particulate matter and diesel exhaust soot differ significantly from each other. The carbon in urban PM has a small but obvious π-transition at 285 eV that is less than half the height of the corresponding σ-transition peak at 292 eV. In contrast, the transitions from surface functional groups at 287 eV and 288 eV, from hydroxyl and carboxyl, are pronounced. Neither the graphite nor the two diesel soot samples show such strong responses from these molecular species. Both peaks are sharper than the peaks at the same positions from the two diesel soot samples. Sharp absorption peaks are typical for so-called Rydberg transitions, which are normally observed for C-H species. Finally, we observe that the urban PM spectrum also has intensity at 284 and 286 eV, due to absorption from carbon atoms in a quinoid setting. We recall that C(1s) NEXAFS spectroscopy is specific to the carbon only, and hence ignores all other elements in the urban PM. Since the SRM 1648 was collected over a 12 months period in the area of the city of St. Louis, Missouri, many sources can contribute to this sample, including DPM. The weak absorption at 285 eV and the strong absorption at 287 – 289 eV suggest that DPM is not a major constituent in this urban PM sample. Insofar, the set of SRM 2975 and SRM 1650 NIST standard samples does not support a previous estimation that about 77% of anthropogenic PM2.5 are represented by DPM [36].
4 Discussion

The spectra of the two diesel soot SRMs exhibit some similarities with graphite and can be discussed in terms of graphitization of the carbon in the samples. The graphitic characteristic of DPM has been known for long time and is in line with many TEM observations and with X-ray diffraction [10,11]. The NEXAFS technique is powerful enough to distinguish not only between graphite and soot, but also between various types of soot, depending on their origin and history. We have made investigations on DPM with NEXAFS spectroscopy on soot from idle and load engine conditions, and from different fuels [10], and also from fuels doped with an iron-based catalyst [11]. Characteristic trends in the spectra were supported by parallel investigations with thermogravimetric analysis or X-ray scattering [10,11]. Hence, the differences in the spectra between SRM 1650 and SRM 2795 reflect differences in the molecular structure of the corresponding materials. The relative height of the NEXAFS absorption peaks or loss peaks in EELS at 285 eV and 292 eV provide semi-quantitative information for the degree of graphitization in carbon materials [15].

Since the forklift DPM spectrum has a relatively larger peak at 285 eV than the spectrum of SRM 1650, the forklift DPM appears more graphitic than that of SRM 1650. However, we should be aware that DPM contains polycyclic aromatic hydrocarbons (PAH) [5], which also have a strong absorption peak at 285 eV, and which can be mistaken as the resonance from the graphite-like carbon core, the solid part of DPM. This is particularly illustrative in the EELS spectra of pyrene and phenanthrene, Figure 4, which are reproduced from Hitchcock and coworkers’ database [17]. The small and clearly separated resonance peaks near 287 and 289 eV in these PAHs are possibly caused by splitting of $\pi$-molecular levels [37]. In this respect, phenanthrene appears more “graphitic” than pyrene. The DPM spectra have relatively higher absorption at these energies, which are likely caused by reaction products and residual oil and fuel. Figure 2 in ref. [38] shows the C(1s) NEXAFS spectra of DPM, one of its aqueous extracts, and the residual. The extract, which contained no visible black solid form of carbon, shows clear absorption at around 285 eV, which we assign to aromatic structures. The spectrum of the soot residual after extraction still shows X-ray absorption features at 287 and 288 eV, suggesting that the residual still contains a considerable amount of surface functional groups, or maybe even some residual oil and fuel, the NEXAFS spectra of which show strong absorption at 287 and 288 eV [22].
Not only from the chemical and structural, but also from an environmental and toxicological point of view, a distinction between solid soot core and adsorbed matter is relevant. Boland et al. [8] find that extracted SRM 1650 is phagocytosed, this is the ingestion of insoluble particles by a cell, to the same extent than native SRM 1650, demonstrating that phagocytosis is not caused by adsorbed organic compounds. In contrast to the phagocytosis in DPM, cytotoxicity is mainly induced by adsorbed organic compounds on the particles since extracted SRM 1650 is less cytotoxic than native SRM 1650, of the extracts of SRM 1650 [8].

We recall that our detection technique is not surface specific, but bulk sensitive. It is difficult to tell whether the surface functionalities are adsorbed between primary particles in the aggregates, or even within the graphene sheets that make up the primary particles spherules. The bonds at the boundary of the graphene sheets in the soot should be saturated, possibly by hydrogen. Internal oxygen of soot has been observed, and well designed experiments may shed some more light on whether species such as oxygen are present in the interiors of the primary particles [39,40], which may have a very complex, multiscale structure [41-44].

Nguyen and Ball find that in addition to the porous solid DPM core, even native organic extractable matter can absorb subsequently added organic materials such as PAHs [27]. STXM appears to be suitable to deeper investigate the leaching of EOM containing DPM: a simple experimental procedure using spatially resolved NEXAFS already showed that the solid carbon core of DPM appears more graphitic than the leached EOM, which shows NEXAFS features of residual oil or fuel, for instance [22]. Maria et al. [23] applied STXM on atmospheric aerosols and derived whether particles were subject to surface oxidation or volume oxidation. However, even without STXM, simple weathering studies are possible. Figure 8 in ref. [14] shows the NEXAFS spectra of original DPM and of slightly weathered DPM. The weathered diesel soot shows an increase of the peak at 285 eV and a relative decrease of the absorption features at 287 – 289 eV, suggesting that the weathered DPM sample has more graphitic features. Therefore, weathering of diesel soot PM would make the spectrum of urban PM look more graphitic, not less graphitic. However, since the urban PM sample SRM 1648 has not much such graphitic structures anyway, DPM appears to be not a dominant species in this particular sample.

Pineiro-Iglesias et al. [45] present X-ray diffractograms of diesel soot SRM 1650 and urban PM SRM 1648 and state, that the carbon rich SRM 1650 has a low degree of crystallinity and is in principal amorphous. This view is correct, provided the diffuse diffraction reflections of the carbon are compared with the sharp reflections from the mineral phases that occur particularly in the urban PM SRM 1648. However, many solid carbon species show broad Bragg reflexes which can basically be indexed by graphite peaks, and which can be quantitatively analyzed in terms of crystallite size and aromaticity, including diesel soot [10,46,47]. The term amorphous carbon is thus an oversimplification, whereas the term degree of crystallinity is a better suited expression, since soot structures can be considered intermediates between amorphous and crystalline carbon [48]. Analysis of peak profiles from X-ray diffraction is therefore a quite useful method and may find its ultimate challenge only where soot lacks entirely in graphite-like structures, such as when generated under extreme conditions. We have recently found such a case, when we mixed diesel fuel with ferrocene [11]. In that particular and extreme case, analysis of the carbon phase by profile analysis virtually failed.

Additional support for the suggestion that forklift DPM of the SRM 1650 is the more graphitic one might come from the presence of the exciton peak at 290.2 eV in the SRM 1650 soot, which results from the graphitic structure. SRM 2975 from the forklift does not yet show such exciton, and we thus believe SRM 2975 is the less graphitic soot. The authors are not aware of a systematic study on crystallite size, long range order and NEXAFS exciton peak at about 290 eV for the graphite, but a related study about diamond, which has an exciton peak at 288.9 eV, shows that this exciton peak evolves parallel with the degree of crystallinity in chemical vapor deposited diamond films, as measured by NEXAFS and X-ray diffraction [49]. And Agren at al. find in their theoretical study on polyacenes that an exciton is rapidly built up with the size of the aromatic ring system [37]. Further
indication of higher crystallinity in SRM 1650 is the lack of EXAFS oscillations in SRM 2975, while SRM 1650 has more pronounced EXAFS oscillations. Another indication that SRM 2975 is more graphitic than SRM 1650 comes from the internal surface areas of both samples. SRM 2975 has a slightly larger surface area than SRM 1650, and it is often the carbons with larger defect density, hence less crystallinity, that have the larger surface area [27].

Figure 4: EELS core excitation spectra of aromatic compounds C14H10 phenanthrene and C16H10 pyrene for reference. Spectra reproduced after data from Hitchcock et al. [17].

Müller et al [9] believe that industrial carbon black cannot be used as a meaningful surrogate for DPM in environmental and biological studies. Their opinion was based on the study of two samples. Although both samples, a true DPM sample from a vehicle, and a Degussa industrial carbon black, give rise to considerable differences in oxidative behavior and structural and spectroscopic properties, it can be said too that DPM is not a unique standard material per se. We have recently published data on soot from an ethylene/air flame [50] and find that its C(1s) NEXAFS spectra share some common features with the numerous DPM samples that we have studied in the past. Reference [50] also shows a spectrum of carbon black N299, reproduced after data from H. Ade, which, with the exception of absorption peaks between 285 and 290 eV, resembles features of DPM. On the other hand have we measured DPM samples obtained from fuel mixed with ferrocene as a catalyst, which entirely lacked graphitic or aromatic features [11] and did not fit the overall picture of DPM that we have obtained before. While it seems correct that carbon black is not a convincing surrogate for DPM, it is very likely also that the SRMs cannot serve as ultimate standards for environmental and toxicological studies. However, the SRMs were never developed for such studies, but rather for the evaluation of analytical methods [3,24-26]. This should hold in particular for urban PM, which comes not only from different sources, but has also been exposed to subsequent chemical reactions in the atmosphere. Hence the aforementioned need for a wider range of samples [4,5] appears justified.

Acknowledgements

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