Carbon speciation in airborne particulate matter with C (1s) NEXAFS spectroscopy

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Recent and current research activities on the chemical characterization of carbon in airborne carbonaceous particulate matter with near-edge X-ray absorption fine structure (NEXAFS) spectroscopy are reviewed. NEXAFS spectroscopy uses soft X-rays from synchrotron radiation facilities and allows for the bulk and surface speciation of particulates smaller than 2.5 micrometres (PM 2.5). This relatively novel technique is often superior to TEM-EELS and FTIR spectroscopy. In the extreme case, one single PM particle is sufficient for characterization. Liquids, extracts, solid core and surface functional groups can be quantified. Preliminary data on combustion derived PM such as diesel soot, wood smoke and tobacco smoke are compared with ambient samples.

Introduction

Soft X-ray spectroscopy using synchrotron radiation is increasingly used for probing light elements like carbon, oxygen and nitrogen in environmental samples. Carbon C (1s) NEXAFS spectroscopy is compared with the performance of related techniques like infrared (FTIR) and electron energy loss spectroscopy (EELS) and their conjugated spatially resolved derivates like transmission electron (TEM) and scanning transmission X-ray (STXM), and infrared spectro-microscopy. Raman,[1] X-ray photoelectron, nuclear magnetic resonance and electron spin resonance spectroscopy are also used, but will not be discussed in this review.

Synchrotron facilities are high intensity, high brilliance light and X-ray sources with photon energies ranging from infrared over ultraviolet to soft X-rays and hard X-rays. In soft X-ray spectroscopy, electrons from the highest occupied molecular orbital are excited to the lowest unoccupied molecular orbital.[2] The X-ray energy necessary for this is characteristic for the particular molecules or atoms and can often serve as a fingerprint for the molecular species. The K shell electron absorption edge of carbon is at around 285 eV. Photons of this energy range fall in the soft X-ray region and have a relatively short attenuation depth in solid materials.[2] This allows for surface sensitive studies, but also poses some technical challenges, which have been mastered more and more in the past 10 to 15 years. Stöhr's textbook[3] about NEXAFS spectroscopy features mostly carbon NEXAFS and provides a wealth of experimental and theoretical information on this topic, and it can actually be considered as the carbon NEXAFS reference book. A review on NEXAFS for environmental applications is given by Myneni.[4] Recent work by Ade, Jacobsen, Hitchcock and co-workers[5–7] features carbon NEXAFS and EELS as far as polymers and surface adsorbates are concerned. Cody *et al.* have made contributions to carbon NEXAFS spectroscopy with his work on coal.[8] Only few carbon NEXAFS data with respect to environmental applications are published. Lehman, Schäfer *et al.*[9] apply C(1s) NEXAFS for environmental studies on soils. Particulate matter can be very inhomogeneous, but carbon constitutes a major portion in the PM. This work will present results on soot,[10–13] kreosote and urban PM. Limitations, challenges, noteworthy breakthroughs and future potentials of NEXAFS for environmental analysis are discussed.

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Experimental

Solid carbonaceous samples, including various diesel soots, wood smoke, ambient particulate matter (PM), and liquids like diesel fuel and lubricant oil, were studied at NEXAFS beamlines at the Advanced Light Source (ALS) in Berkeley and the National Synchrotron Light Source (NSLS; Fig. 1) in Brookhaven National Laboratory. Some of the samples were
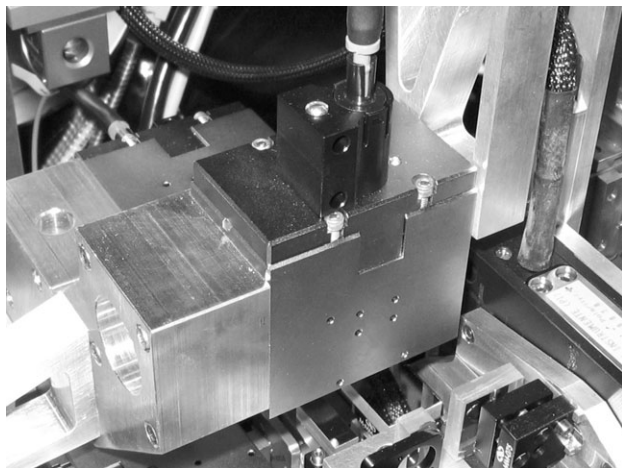
Fig. 1 STXM microscope at beamline X1A, Brookhaven National Laboratory. Courtesy Mirna Lerotic, SUNY.

subject to hot pressurized water extraction and were studied separately. Some results have been published already.[10–13]

Sample environment and preparation

NEXAFS beamlines operate at an ultrahigh vacuum of around 10^{-9} mbar.[4] This bears the danger that some volatiles may be pumped away from the sample before they can be detected. One major obstacle with carbon NEXAFS experiments is that beamline components are contaminated with carbonaceous adsorbates which leave a C(1s) signature in the spectra, but Schoell *et al.*[14] recently showed calibration and normalization routines which permit to acquire accurate C(1s) spectra. Some instruments operate at normal pressure but with a helium atmosphere in order to have only minimum parasitic absorption of X-ray photons. These can be particularly useful for environmental sciences, which can operate at normal pressure or even with liquids.[15–17]

Environmental samples collected on filters are difficult to measure because they have a very poor electric conductivity. Charging effects pose a problem then. Polycarbonate and cellulose filters are not very useful for C(1s) NEXAFS experiments because they contain carbon, which makes a significant and disturbing background signal, in particular on poorly loaded filters. However, a background subtraction is generally possible, in particular when the filter is heavily loaded with well conducting sample, and when an empty filter spectrum is recorded for reference.

A different approach is to immerse the loaded filter in a solvent like methanol and ultra-sonicate it to obtain a methanol-PM solution. A drop of this solution can be put on a clean gold surface. After evaporation of the solvent, a stain of PM sample remains, which can be measured directly in the UHV with sample current (SC) or electron yield (EY) detection mode. If plenty of material is available, then a pellet can be pressed and mounted on the sample holder. The lower the electric conductivity of the material, the thinner the pellet should be. In particular diesel soot yields high quality spectra with this route. If the amount of available sample is too low, the STXM microscopy may be the best choice. In the extreme case only one single PM particle is sufficient to obtain a high quality spectrum.

STXM is an X-ray transmission technique and requires very thin samples not to exceed one micron. STXM substrates other than TEM grids are ultrathin Si_3N or SiO windows. It is possible to enclose a sample between two such windows in a liquid or gaseous environment.[15–17] For the non-STXM C(1s) NEXAFS, no such thickness requirements exist. But information obtained from a sample significantly thicker than one micron will only represent the upper first micron thick shell in the sample. It is not advised to apply a gold coating, carbon coating or similar as usual in SEM sample preparation, because this causes additional photon absorption, on cost of the signal from the original sample.

Extracts from diesel soot, wood smoke and ambient PM, which in our case come in mixture with water, were dropped with a syringe on a clean gold foil. Evaporation of water occurred under ambient conditions.

The dried residuals and the original PM particles were also dissolved in acetone or methanol and dropped on the gold foil. Based on our current experience it seems that this is a good sample preparation technique because it requires only a very minute amount of sample without loss of data quality. This route permits densification of material from a poorly loaded $20 cm^2$ area filter to a richly loaded $10 mm^2$ area, or less. This is a densification by a factor of 200.

Radiation damage

Radiation damage in materials characterization does not always receive the consideration it deserves. Comparative studies with TEM-EELS and NEXAFS show that EELS is virtually blind to surface functional groups on diesel soot, for instance. The likely cause for the failure of EELS[11,18] is the high primary electron energy, which visibly causes damage on carbonaceous particles. From STXM studies on soot extracts we know that decarboxylation by radiolysis[19] causes depletion of the carboxyl peak and generation of a carbonate peak. This effect is observed at regular, non-STXM beamlines too, though to a much lesser extent. It is thus recommended to make always more than one scan of a spectrum. If the scans show a systematic change, this can almost always count as evidence for radiation damages. This is a way of to at least monitor the radiation damage.

Related techniques

EELS

Electron energy loss spectroscopy (EELS) has been widely used in analysis of carbonaceous materials, often in connection with electron microscopy. The EELS spectrum contains basically the same information like a NEXAFS spectrum and is representative for the sample volume that was passed by the primary electron beam. The information is hence bulk-sensitive. The wide availability of TEM equipped with EELS spectrometers make it a convenient tool.[20] Analysis can be carried out on selected particles, which is of interest for environmental scientists and astrophysicists who study cosmic matter.

A drawback of this technique is its limited applicability for carbon analysis. A recent comparative study on diesel soot with NEXAFS and EELS clearly demonstrated that NEXAFS could resolve typical surface functional groups and organic molecules in or on carbonaceous samples, which appear to be virtually absent in EELS spectra from the same samples.[11] The typically very high electron primary energy, rather than poor energy resolution of the electron spectrometer can be blamed for the blurred EELS C(1s) spectra. Primary energies range from 10 keV to sometimes higher than 50 keV. TEM operators report formation of bubbles on their samples under these harsh conditions. Surface functional groups barely survive this treatment or are gased off and cannot be detected anymore. In contrast, the EELS experiments by Francis and Hitchcock[21] are based on primary energies of 2.5 keV and yield brilliant spectra.

The ratio between the prime π peak at 285 eV and the σ peak at 292 eV is frequently used as a semi-quantitative measure for the degree of graphitization of the sample.[22] It appears that this ratio is not measurably affected by the high EELS primary energies.

IR

Infrared spectroscopy is widely used in the study of carbonaceous matter, including bio- and medical sciences, the study of battery electrodes, which contain carbon, and environmental sciences. Spectrometers come in many variations. Acquisition of spectra takes few minutes only. Spectra of countless reference compounds are well documented and supported by a wealth of theory, facilitating interpretation of spectra of complex materials like such that come in environmental sciences. Important stretching modes like from $C=O$, $C-OH$, COOH can be easily made out.

Use of IR generally requires infrared active species. Inactive molecules cannot be measured. The graphite $C=C$ peak can hardly be made out in IR. Water in samples can overlap with carbon-related peaks and require additional subtraction. The lack of strong infrared radiation sources poses a general problem on IR spectroscopy, but was partially overcome by the invention of Fourier-transform IR spectroscopy.

IR microscopes have been built for several years now. Their spatial resolution is in the range of several microns and of limited use for detailed study of fine particulate matter, but the toxic response of cells exposed to environmental hazards was studied with IR microscopy, for instance.[23] In general, many tasks for carbon speciation in environmental sciences can be solved with FTIR spectroscopy.

X-Ray Raman spectroscopy

The small penetration depth of soft X-rays puts a natural limit on the practical applicability of many carbon K shell NEXAFS experiments. Since C(1s) NEXAFS is at around 280–300 eV, the penetration depth is around 2.5 microns. This means that a STXM experiment with PM 2.5 is at a critical limit. PM 10 cannot be measured in full anymore. NEXAFS experiments not based on X-ray transmission can still be carried out, but the information depth is around 2.5 microns, too, for SC. Deeper regions of thicker samples cannot be probed.

X-Ray Raman spectroscopy provides a way out of this dilemma by using hard X-rays, which have significantly larger energy and penetration depth,[24] as carriers of the C(1s) inner shell signal. A realistic scenario is to use excitation energies of 10 keV and penetrate, hence probe, a carbon-rich sample of 1 cm thickness. The scattered intensity carries the C(1s) signal integrated over the entire sampled volume. This technique has not yet been used for the study of environmental samples, but was already applied on compounds containing lithium[25] and for a number of carbonaceous reference materials.[26] The drawback of this technique is that hard X-rays can impose a higher risk of radiation damages in the sample. Also, very specific instrumentation is necessary, such as a ultrahigh-resolution detector. This technique is not yet available for general synchrotron users. However, a special beamline for this technique is being planned at SSRL.

C (1s) NEXAFS spectroscopy with STXM

Combination of scanning technology with beam focusing techniques gave X-ray microscopy a strong boost for both hard and soft X-rays. As Cody[27] points out: "It is unlikely that we will ever have sufficient mass of organic (cosmic) matter from these sources to apply solid state NMR to solve their chemical structures", the amount of available sample may have significant impact on what kind of analytical techniques come to application. Since environmental and atmospheric scientists typically rely on limited amounts of sample on filters, spectromicroscopy techniques are necessary because focused beams allow direction of the radiation on single particles. Brandes et al.[28] have studied marine sinking particulate organic matter with STXM and identified four distinct phases, supporting a hypothesis that non-selective degradation dominates over par-
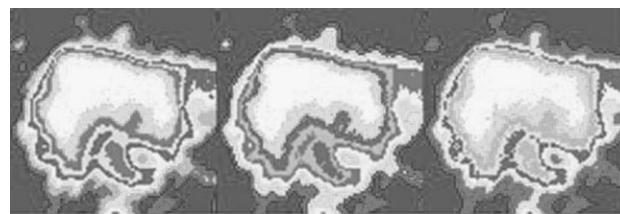

Fig. 2 Three STXM images of a black carbon particle for four components and up to ten clusters for principal component and cluster analysis. Courtesy J. Lehmann, Cornell University.

ticle re-mineralisation, and particle compositions are determined by near-surface processes. Botto et al.[29] used C(1s) STXM to spatially map the distribution of aliphatic and aromatic carbon in thin coal sections, allowing for rich detail information on the physical and chemical heterogeneity of maceral and sub-maceral domains and micro-fine mineral particles. Solomon et al.[30] have studied soil organic matter with C(1s) STXM and provide a detailed carbon-chemical analysis and discussion of their samples.[31] The black carbon particle discussed in ref. 31 is shown in Fig. 2. Prietzel et al.[32] used STXM for similar purposes like Solomon and Schäfer, but with respect to sulfur speciation and distribution (S(1s) STXM). Schäfer et al.[33] carried out time resolved in situ studies on clay minerals stabilized by dissolved in organic carbon in the STXM mode (C(1s)). Braun et al.[10] used C(1s) STXM to map diesel soot particle cores and extracted volatiles. Maria et al.[34] could distinguish with C(1s) STXM between surface and volume oxidation in carbonaceous PM (atmospheric aerosol samples). Many recent results are based on STXM image analysis, which add statistical significance to the data.[35]

Surface sensitive experiments

Lehmann et al.[31] used a typical thin section sample preparation technique to apply STXM surface sensitive and bulk sensitive on particles somewhat smaller than lateral 4 microns in size, a size range sufficient for meaningful quantitative analysis in STXM. Using highly complex state of the art mathematical algorithms (principal component and cluster analysis, and singular value decomposition), which is implemented in the beamline specific data analysis software allows for statistically robust high quality NEXAFS spectra for bulk and surface, for instance.

A different, non-microscopic approach allows separation of information on the molecular structure of fine carbonaceous PM from surface and bulk on a scale significantly smaller than accessible with STXM, by comparing SC spectra from EY spectra. With the penetration or attenuation depth of 280 eV X-ray photons in massive carbon around 1 micron, only an outer shell of 1 micron can be probed regardless whether the actual sample is thicker, unless X-ray Raman spectroscopy with hard X-rays is used. However, for PM2.5 samples this thickness criterion is satisfied per definition. When the SC detection mode is used, the obtained NEXAFS spectrum is basically representative of this single micron thick shell in this sample. For a homogeneous sample with two micron overall thickness, the entire sample can then be considered probed. Hence the SC spectrum is a bulk spectrum. Many NEXAFS beamlines have a multichannel electron energy analyzer, which permits to measure the EY as the detection signal. Since the mean free path of electrons in solid matter is only a few ångströms,[2] the EY spectra are representative to the upper few 1–5 ångströms in the sample, hence surface sensitive.

This effect is demonstrated in the SC and total EY C(1s) spectra of diesel soot particulates.[11] The SC spectrum reflects the graphitic nature of the solid soot core, but also exhibits signatures from surface functional groups. The EY spectrum shows a significantly stronger response of these groups, em-

phasizing the soot particle surface as the location of these groups. In addition do the EY spectra lack in the crystalline near order characteristics at higher energies, 290 eV and above, which are horizontal with EXAFS oscillations for graphite and for diesel soot, but different for EY spectra of the same material. However, the SC and EY spectra of soot extracts look very much alike because they are topologically homogeneous samples.

Photochemistry and radiolysis

Early photochemical reaction studies with C(1s) NEXAFS spectroscopy and STXM were carried out by Cody et al.[8] on vitrinite. They monitored gain and loss of organic functionality following time-incremental exposure to irradiation in air and observed formation of COOH groups through the photo-assisted attack of singlet oxygen.

Bioavailable diesel soot water extracts show photochemical decarboxylation during irradiation with soft X-rays.[19] The carboxyl peak, prevalent in virtually all diesel soot samples, decreases in intensity during irradiation, while a new carbonate peak is growing.[19] Exactly the same observation was made on alginic acid.[19] While such observations are normally referred to as "radiation damages", they can permit additional understanding of reaction scenarios that could be representative to chemical processes taking place in the atmosphere. Similar irradiation studies were recently made on amino acids.[36,37]

NEXAFS of diesel particulate matter

The Consortium for Fossil Fuel Sciences (CFFS) at the University of Kentucky (UK) has extensively studied diesel particulate matter (DPM) with C1(s) NEXAFS spectroscopy. The spectra of DPM show many similarities with such spectra from carbon black and ethylene soot, and all three spectra show strong similarities with graphite, evidence for the graphite-like character of soot (Fig. 3).

Particularly pronounced are the (a) C=C π bond peak at 285 eV which we refer to as the graphitic peak and its corresponding (b) σ bond peak at 291 eV. The larger the ratio of the peak heights of or area under aforementioned peaks, the more graphitic the material.[22] Graphite shows a very sharp exciton peak at 290.5 eV which can be found in DPM as well.[12,13] In addition to the graphitic character, soot contains surface functional groups, the carbon atoms of whose have X-ray transitions at energies throughout 284 to 292 eV. Easy
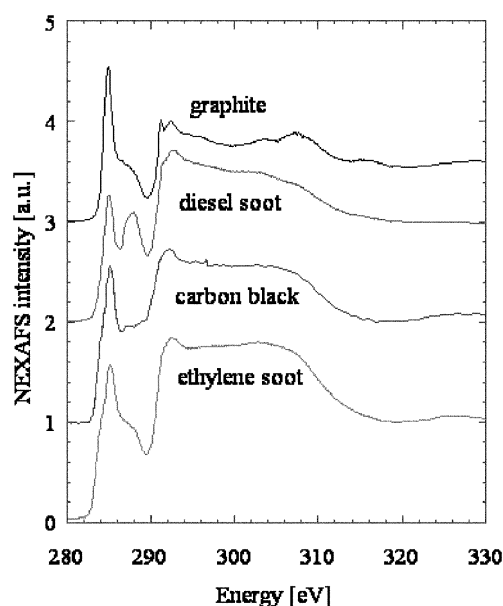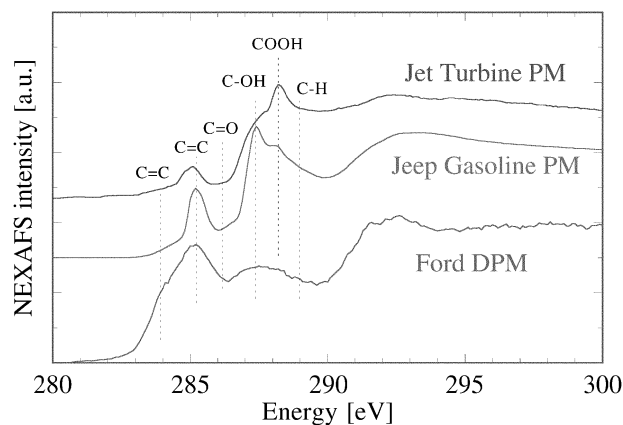
Fig. 4 C(1s) NEXAFS spectra of particulate matter from Ford diesel and Jeep gasoline vehicle, and a kerosene jet turbine.

to make out are C–OH, COOH and C–H resonances between 286 and 290 eV. DPM contains also benzo-quinone as evidenced from peaks and intensity shoulders at 284 eV (C=C) and 286 eV (C=O). Francis and Hitchcock[21] and Cody et al.[8] have assigned and compiled a number of C(1s) transitions which are essential for every carbon NEXAFS study.

Spectra of DPM from various sources

Spectra from different DPM sources such as from a Kubota 2-stroke test engine, a Ford diesel vehicle, NIST DPM standards SRM 1650 and NSRT 2975 (diesel forklift) show the aforementioned typical characteristics of DPM, but also differences in peak heights—indicative of differences in engines, engine conditions and probably different fuels.

However, none of the spectra from DPM samples looked similar to the NEXAFS spectrum of soot deposits from the muffler of a gasoline vehicle (Jeep Cherokee) and the exhaust from a helicopter kerosene turbine, as shown in Fig. 4. Jet PM has a dominant carboxyl peak, gasoline PM a strong C–OH peak, and DPM strong resonances from the solic graphite core and benzo-quinone groups (C=C and C=O).

Idle vs. load engine conditions

NEXAFS is sensitive enough to detect spectral differences in DPM depending on whether the engine was run under idle or under load conditions. These findings are supported by parallel investigation with X-ray scattering,[12,38] NMR spectroscopy,[39] and thermogravimetry.[12]

Soot from fuel with additives

NEXAFS spectra of DPM from diesel mixed with oxygenates have significantly more surface functional groups than reference fuel soot. Parallel toxicological tests on the extracts show that the oxygenated fuel forms DPM with higher genotoxicity.[40] Adding ferrocene to diesel fuel creates soot which lacks significantly in crystallinity, as can be seen from a very small graphitic peak at 285 eV, and from the absence of the exciton peak near 290 eV. These findings are confirmed by X-ray scattering.[41]

PM from biomass combustion

Spectra of PM from biomass combustion, such as woodsmoke or furnace deposits (kreosote) show an entirely different characteristic. These materials are less graphitic than the aforementioned DPM samples due to significantly smaller C=C peaks, but they have very pronounced carboxyl peaks and resonances from other surface functional groups. However, bioavailable
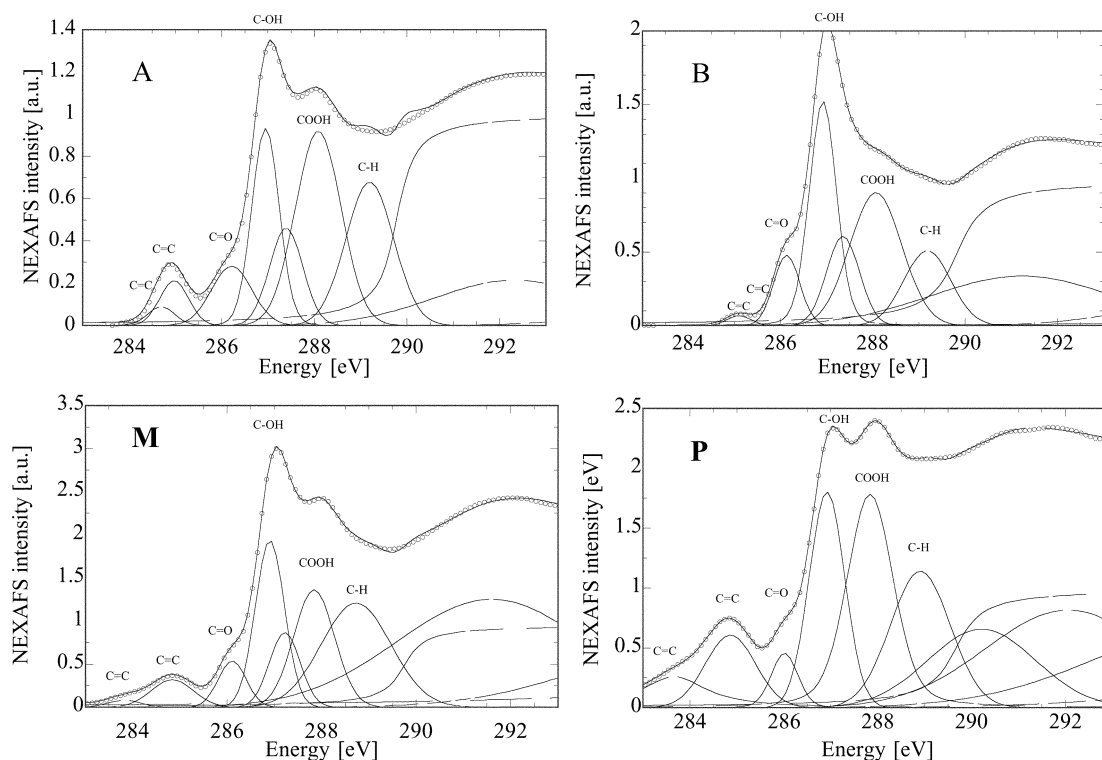
Fig. 3 Carbon K-edge NEXAFS spectra of graphite LS 25, diesel PM SRM 1650, carbon black N299 (after H. Ade), and ethylene soot.

Fig. 5 C(1s) NEXAFS spectra of woodsmoke deposits from four different fireplaces with different wood/biomass feedstock.

water extracts from woodsmoke and tobacco smoke taken at 25 °C show very strong peaks from polycyclic aromatic hydrocarbons at 285 eV.

Wood fire and furnace deposits

Fig. 5 shows the NEXAFS spectra of woodsmoke deposits (kreosote) from three different chimney fireplaces (A, M, P) and one wood burner (B). (A) Indoor masonry fireplace fed with urban wood (oak, fir, birch, cherry) broken in the 2003 Lexington ice storm. (B) Wood burner (Unical) for house central heating, with three year well dried beech wood in Eifel, Western Germany. (M) Chimney deposits from indoor wood stove with mostly beech, some fir dried longer than 2 years in Eifel. (P) Chimney deposits from indoor wood stove, mostly fir, some beech, dried not more than one year.

Spectra A, M and P show larger contributions from C=C bonds than spectrum B, which stems from a furnace with optimized combustion parameters that was fed with very dry wood. A, M, and P stem from fireplaces with mixed wood dried

less than 3 years. The C=C bonds in A, M, and P show also significant benzo-quinone signatures, while it is difficult to deconvolute this part of the spectrum in B. A and M look quite similar, with the major peaks coming from C–OH and COOH to almost equal partitions. Spectrum P however has a very large contribution from benzo-quinone and from carboxyl.

NEXAFS spectra from burnt biomass share common features, which vary depending on what feedstock was used and which combustion facility was used. Fig. 6 shows spectra of a woodsmoke and a tobacco smoke extract. The woodsmoke sample resembles striking similarity with spectrum B in Fig. 5, in particular the dominance of the C–OH peak. The broad peak at 287 and 288 eV in the tobacco smoke extract shows spectral similarities with spectrum P in Fig. 5 and can be interpreted as a double peak of similarly strong C–OH and COOH resonances. The ratio of COOH intensity over C–OH intensity plotted *versus* the years dried shows a linear decrease, suggesting that water content in the wood correlates with formation of COOH groups during combustion.
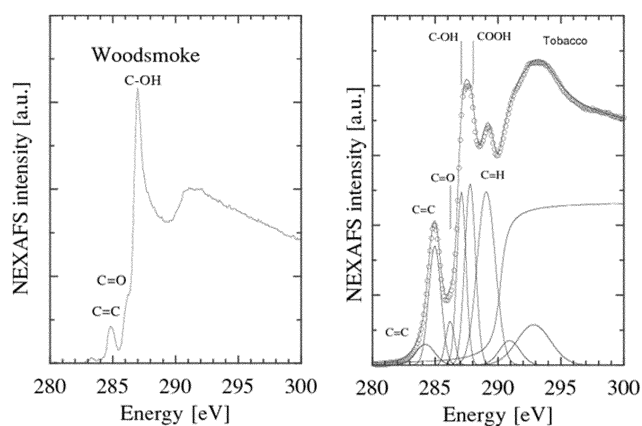

Fig. 6 C(1s) NEXAFS spectra of woodsmoke and tobacco smoke with proposed peak assignment.
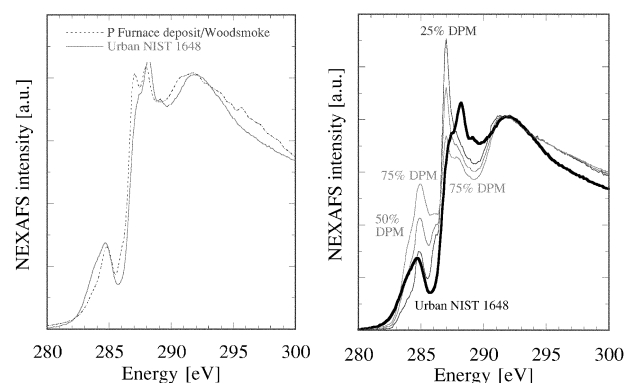

Fig. 7 Left: comparison of spectra from urban PM (SRM 1648) and woodsmoke deposit P. Right: urban PM spectrum and three linear combinations of DPM (SRM 1650) and sample P woodsmoke.
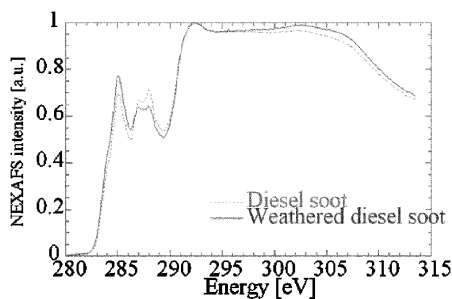
Fig. 8 Solid line: NEXAFS spectrum of weathered DPM from Ford. Dotted line: DPM spectrum before weathering.

Urban PM

Combustion source and fuel feedstock of the samples from aforementioned spectra were all relatively well known. One goal of applying NEXAFS spectroscopy is to carry out source apportionment of PM from ambient sampling, with very inhomogeneous samples and not much information on combustion sources available.

We have measured SRM 1648 Urban PM (a NIST standard collected in St. Louis) and PM 2.5 samples collected at a major road in Lexington. The C(1s) spectra of these ambient PM samples show no dominant C=C resonance at 285 eV, indicating that it is not a primarily graphitic material. For these two samples, DPM can be clearly ruled out as a major constituent. Instead, they have more spectral features in common with the previously discussed furnace deposits, in particular strong response at C–OH and COOH (Fig. 7, left). The right part in Fig. 7 shows the original SRM 1648 urban PM spectrum as well as three linear combinations of spectra from SRM 1650 DPM (25, 50, and 75%) with the spectrum from sample P, a furnace deposit. This is to simulate urban PM as a mixture of DPM and woodsmoke. Only the spectrum of the mixture with 25% DPM comes close to simulate urban SRM 1648 PM. Obviously, DPM is not a good representative for urban PM in this case. Instead, at least one other carboxyl-rich source (perhaps jet PM) is necessary to complement for the intensity at 288 eV.

The lack in DPM signature in these urban PM samples deserves more scrutiny because possible ageing and weathering of DPM was not taken into account in our considerations. However, in contrast to previous speculations, DPM becomes not less graphitic during weathering, but more graphitic. For instance, DPM from a Ford vehicle was exposed for 10 days to ambient humid and sunny environment, and its NEXAFS spectrum was compared with its non-weathered aliquot, as shown in Fig. 8. Obviously, upon weathering the C–OH and COOH resonances decrease, while the C=C resonances increase. The same effect is observed with oxidized and non-oxidized carbon nanotubes, for instance. Weathered DPM would hence appear even stronger in ambient urban PM, but still we see DPM as a minor contributor only.

Conclusions and outlook

C(1s) NEXAFS for environmental applications is still in its infancy but has a good potential to become a useful analytical technique for atmospheric and environmental scientists and combustion engineers, who need to address carbon relevant issues like global climate change or human health impact of PM. This concerns in particular soot, and similar combustion derived carbonaceous matter. The conjugated surface and bulk sensitivity of NEXAFS is superior to any of the aforementioned techniques and invaluable to researchers who have to tackle with a broad range of chemically and structurally complex carbonaceous PM. Extracts and solid residuals can be studied. Raman spectroscopy with hard X-rays provides an elegant way to yield C(1s) spectra from thick samples.[24–26] Radiation damages are less significant than in TEM-EELS but harder than in IR spectroscopy. Intense probe techniques like STXM bear the risk of considerable radiation damages and hence alteration of the sample, as previously observed,[19] but also the potential for atmospheric *in situ* studies.[17]

The deconvolution of spectra is not always unambiguous. For instance, the energy at which carbonyl is found can range over several eV, depending on its chemical environment.[5] A disadvantage is that NEXAFS studies require access to synchrotron facilities, but more and more such facilities are built and equipped for soft X-ray experiments.

Radiation damages might be useful for the simulation of weathering of PM, for instance. STXM, the microscopy variant of NEXAFS, lacks in resolution as far as the finest tail in size distribution of the ultra-fine PM is concerned. A potentially interesting near-future application of STXM will be the study of the interaction between PM and biological cells. Biological cells are large enough for STXM to give high resolution, better than the IR microscope in terms of spatial resolution, and better than TEM-EELS in terms of chemical sensitivity with respect to carbon. Biofilms[16] have already been studied with NEXAFS and STXM.[15] Several research groups have mastered the problems that result from bringing samples in aqueous environment into the STXM. Mechanisms that govern adverse health effects when humans are exposed to PM are more likely to be elucidated with such experiments. This review was about carbon NEXAFS spectroscopy. The same technique applies to oxygen as well. Another very important atom of interest for toxicological studies is nitrogen, but since its concentration in PM samples is very small, additional experimental efforts are necessary to carry out meaningful studies.

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