Suitability of NEXAFS spectroscopy for molecular speciation of soot surface organic functional groups

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ABSTRACT

With respect to the importance that surface functional groups may alter the sorptive properties of soot, it was explicitly stated in (1) that near edge X-ray absorption spectroscopy would not distinguish soot carbon and surface organic material. This statement is not correct.

Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy has been very helpful for the molecular speciation of carbonaceous inorganic and organic materials and compounds, including soot. The technique is based on electron transitions from the atomic core levels and therefore element specific. Moreover, the molecular environment of the probed atom is reflected in NEXAFS spectra, so that organic molecules may show fingerprint-type spectra, which can be modeled with molecular orbital theory. The spectral assignment of prominent surface functional groups is not unambiguous in every
case, but the merit of NEXAFS for speciation of aromatics and aliphatics like C=C, quinones, hydroxyl, carboxyl, carbonyl and many more, has been recognized.

NEXAFS theory and applications, particularly for light elements like C, O, and N, are given by Stöhr (2) and reviews on NEXAFS of organic molecules in the environment and for soot are provided in (3,4). The physical principles of NEXAFS are similar to electron energy loss spectroscopy (EELS). An overwhelming number of EELS and NEXAFS spectra of organic molecules can be found in databases (5). Insofar, NEXAFS and EELS can distinguish a wide range of organic molecules. The authors of (1) may have been misled by a remark that appeared in (6): “The presence of polycyclic aromatic hydrocarbons, which have a characteristic NEXAFS resonance at the same position as graphite, can obscure the graphitic character of soot, unless an extraction of the organic matter is made.” That remark was supposed to aid a fair assessment of the merits of NEXAFS, and not to invalidate the technique.

C(1s) NEXAFS spectroscopy for the speciation of airborne particulate matter (PM) has been employed with the goal of source assignment. While soot, such as diesel exhaust (DE) and wood smoke (WS), are chemically and structurally heterogeneous and subject to reaction in ambient environment, progress with NEXAFS allowed quantitative source assignment for DE and WS in ambient PM (7), and to develop a model for the weathering of soot (8).

Whereas these recent works are based on the relative heights of the C=C NEXAFS resonances at 285 eV, the issue of soluble organic matter (SOM) adsorbed on the solid carbon matrix has also been addressed. The first such work (9) involved separation of the graphitic core in DP from SOM by simple leaching and subsequent scanning transmission X-ray spectromicroscopy (STXM, (10)), where the graphitic matrix was distinguished from SOM. STXM is a NEXAFS method with high spatial resolution, use of which was pioneered by Cody et al. for the speciation of organics in coal (11). Maria et al. distinguished surface oxidation from bulk oxidation in PM, based on quantitative analysis of NEXAFS spectra in STXM (12). Also in soil science, STXM is increasingly being used for carbon speciation (13).
The surface and bulk sensitivity of NEXAFS detection modes for graphite and soot from ethylene and diesel was treated in (14,15). In order to study DP extracts and residuals separately, SOM was extracted with hot pressurized water so as to not infer additional organic signatures in the spectra (16). Because SOM can be prone to atmospheric photochemical reaction, extracts were subjected to radiation damage experiments in the STXM, along with kinetic reaction analysis for carbonyl and carbonate as distinguished by NEXAFS (17).

The developers of EELS and NEXAFS have been very considerate about potential effects of radiation damage, particularly to organic specimen (18,19), but NEXAFS is less critical to radiation than, for example, EELS in the transmission electron microscope (20), where virtually no surface functional groups could be detected.

In view of this brief record, it is obvious that NEXAFS spectroscopy can distinguish soot carbon and surface organic material.

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