XPS ANALYSIS OF SOOT FOR CHEMICAL COMPOSITION, SURFACE CHEMISTRY AND CARBON CHEMICAL STATE

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Abstract

X-Ray photoelectron spectroscopy (XPS) is used for elemental speciation and surface chemistry characterization in soot aerosol samples. Survey scans provide elemental content. High-resolution scans over the C1s region identify the types of oxygen functional groups present on the surface in addition to the surface carbon hybridization (bonding state). These measures can provide unique signatures for source identification.

Introduction

A wide range of natural and anthropogenic sources emit organic gases and submicrometer aerosol particles to the atmosphere. Primary source emissions play a role in regulating atmospheric aerosol nucleation and oxidation events (Maria, Russell et al. 2004; Zhang, Suh et al. 2004) and also affect particle growth by condensation and the photochemical production of ozone and secondary organic aerosols (SOA) (Jang, Czoschke et al. 2002). Knowing how these processes evolve and the types and mass amounts of aerosol species they yield is essential for predicting the direct and indirect effects of atmospheric aerosol particles on the Earth's climate system and also for assessing the toxic effects that aerosols have on human health.

Here, surface atoms and carbon-oxygen bonding states in a wide variety of source emissions particles are identified and quantified using a traditional surface science tool – X-ray Photoelectron Spectroscopy (XPS). How soot surfaces generated from anthropogenic and biomass burning differ compositionally is an intriguing question that can be addressed with XPS studies. XPS analysis identified oxygen groups by bond type reflecting the occurrence and extent of soot surface oxidation. XPS also identified varying proportions of sp^2, sp^3, and fullerenic carbon entities present in soot from the different combustion emissions samples. Finally, a hypothesis about how the distribution and type of surface functional groups on soot might convolve in tandem with particle nanostructure is advanced.

Experimental

A total of seven aerosol particle samples were collected from anthropogenic combustion or biomass burning emissions sources and analyzed for surface chemistry using XPS. Unless noted otherwise, the aerosols were collected on pre-fired (550 ºC, 12 hr), high-volume quartz filters using the dilution sampling system (DSS) described by Hildemann et al. – a dilution ratio near 1:45 was typical for the source tests conducted with the DSS.

The emissions sources examined here include: (i) plant-, institutional-, and residential-scale oil boilers; (ii) jet aircraft; (iii) heavy-duty diesel (and bio-diesel) engine exhaust; and (iv) wildfire. Combined, the sectors to which the tested sources are assigned accounted for more than half of the direct fine PM emissions in the U.S. in 2002 (). Testing of the bio-diesel fuel in the heavy-duty vehicle was justified using this source's future potential impact on air quality as a basis. Further information about many of the sources being studied here was provided in Hays and Vander Wal ().

XPS method

Briefly, XPS is a surface science analytical tool for identifying elements and their bonding states. Monochromatic X-rays eject core shell electrons from elements, the kinetic energy of these electrons is resolved using an electron monochromator. The difference between the ejected electron energy and that of the incident X-ray (photon) is the binding energy of the electron, which is specific to the quantum shell as influenced by the local electron density and hence the element. Moreover, the binding energy, even of such a core-shell electron is subtly influenced by the valence shell bonding arrangement, namely the outer electron orbital hybridization and associated bonding to adjacent atoms. Therein XPS can also identify surface functional groups and elemental bonding states. In the work presented here, XPS is applied to source emissions aerosols.

XPS instrument and analysis.

XPS was performed on each sample using both a survey scan for elemental identification plus a (high resolution) scan for identification of carbon bonding states and oxygen functional groups. The percent of each element, determined by the survey scan was measured to +/- 0.1% was measured using a semi-quantitative program associated with the XPS software. The data was collected by a MatLab computer routine.

High resolution scans were run for carbon, with a minimum of 10 sweeps and 7 cycles. The resultant scan over the nominal C1s region was curve fit using Gauss-Lorenz peaks and a Shirley fit. Peak deconvolution was performed via the same MatLab program after setting the background parameters.

Results and Discussion

Elemental Identification

To provide an initial test of the hypothesis that soots from a wide variety of sources will carry different heteroelements reflecting the fuel origins, soots derived from plant-, institutional-, and residential-scale oil boilers, a jet aircraft engine, a heavy-duty diesel truck, and wildfire were examined. Figure 1 confirms distinct elemental surface compositions of the soots derived from these different combustion sources. Some soots produce a recognizable elemental fingerprint, consisting of a variety of heteroelements. Notably the lack of heteroelements is also an identifying marker in and of itself. For the oil-boiler soots examined thus far, the relative proportion of surface elements and the elemental signature may be sufficiently unique to serve as a marker for source identification.

Functional group surface chemistry

Complimentary to elemental identification is functional group surface chemistry. For carbonaceous materials, the primary functional groups are carboxylic, carbonyl and phenolic groups. These groups correspond to different degrees of oxidation of the carbon. As such, they may be introduced either during the combustion process or within the post-combustion exhaust. Lean combustion, such as generally occurs within a diesel engine leaves oxygen within the engine exhaust. Even so, hot CO_2 and H_2O as oxidants will also introduce these groups. Thus, the surface oxygen groups present an integrated record of the oxidation conditions to which the soot has been exposed. It should also be recognized that the number and possibly type of surface functional groups are convolved with the soot nanostructure. For example, a nanostructure that exposes more edge site carbon atoms will be better able to support carboxylic groups given steric considerations associated with this functionality.

In order to extract such information using XPS, a high-resolution scan over the C1s region is collected. This scan is then fit as previously described. By setting the oxygenated peak positions relative to the C1s peak, which is known via calibration, the fit allows for extraction of the relative intensities (concentrations) of the different oxygen functional groups. While not all samples possessed such marked differences, many did. The summary of this information is plotted in Fig. 2 where each row nominally corresponds to a representative C1s spectrum of soot from a given source. Each such row was obtained by averaging the corresponding integrated peak intensities for all samples from the particular source, followed by normalization to the summed intensities of all averaged peaks from that source. As illustrated, the relative amount and types of oxygen functional groups provides yet a second parameter by which the source of the soot may be identified for the soot sources presented here.

Carbon Chemical State

Just as the oxygen groups present a unique source signature for many soots, so to does the carbon sp2 and defective sp2 component. Although the precise nature of the defective component is not firm, still, the uniqueness of the graphitic and non-graphitic contributions to soots from different sources serves as a third signature by which the soot source may be identified. Figure 2 summarizes this information for the indicated samples. As seen, the main C1s peak has substantially different contributions from the nominal sp2 and defective components with most sources presenting distinguishable differences in both peak intensities and positions.

Conclusions

XPS provides three independent analytical signatures of carbonaceous aerosols that may be used to identify the soot source. First, it provides analytical measures of heteroelements. Secondly it provides identification of the surface oxygen functional groups, specifically hydroxyl, carbonyl and carboxylic groups. Third, resolution of the main C1s peak provides a measure of the relative fractions of sp2 versus defective carbon. Comparison of unknown soot samples against a sufficient database having been so analyzed would permit identification of the soot source. A prime benefit of such identification is the validation of pollution source models. Secondly, major sources may be unambiguously identified. Third, emission compliance can be aided. Fourth, legal interests may be served.

References

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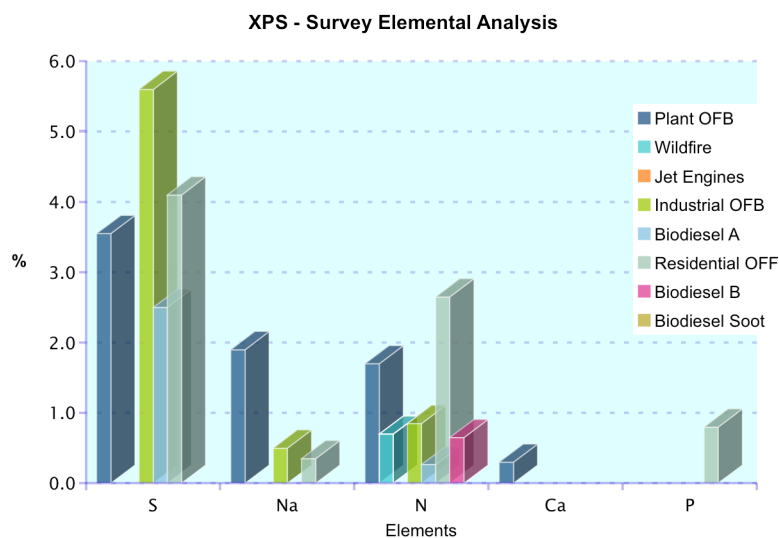
Figure 1. A bar graph summary of heteroelement contents of the studied soot samples. Upon examination, some examined soots contain a sufficient variety of elements (other than carbon) as to uniquely identify its origin among those studied.
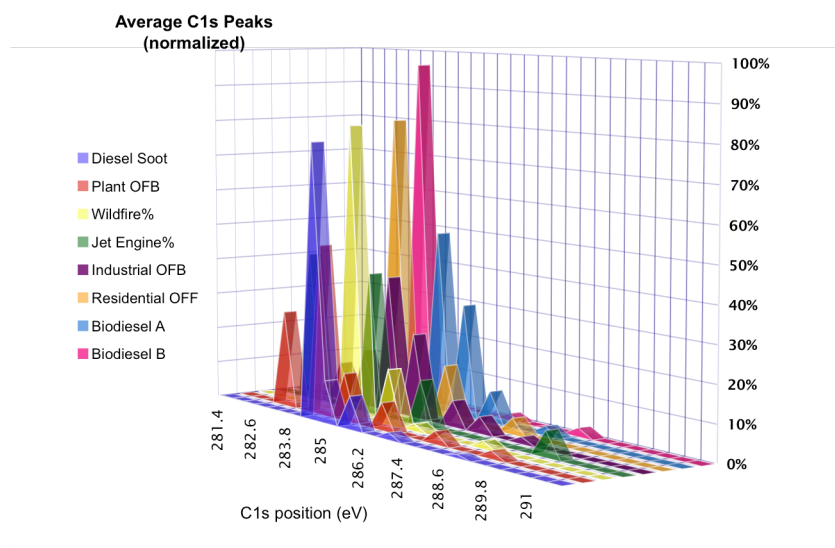
Figure 2. A stacked plot of individual C1s scans, normalized by the integrated intensities of each respective scan. Each row corresponds to a high-resolution survey scan over the nominal C1s core-shell region for a particular soot. The percentages of carbon atoms apportioned to different oxygen functional groups as well as the different carbon bonding states may be compared across the range of soot samples derived from the different indicated sources.