

Quantifying Hazardous Species in Particulate Matter Derived from Fossil-Fuel Combustion

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X-ray absorption fine structure (XAFS) spectroscopy at beamlines X18B and X19A was used to investigate and assess the hazards posed to human health from the presence of potentially toxic species in airborne particulate matter (PM) released during the combustion of fossil fuels. XAFS spectroscopy was combined with a leaching protocol and used to quantify the oxidation states of As and Cr in PM from coal combustion and the presence of Ni sulfides in PM from residual oil combustion. Such speciation information is needed in order to assess the potential bioavailability and health hazards posed by metals and other species in airborne PM.

In 1997 the U.S. Environmental Protection Agency (U.S. EPA) promulgated new regulations regarding exposure to fine airborne particulate matter, based on the results of several major epidemiological studies that demonstrated an association between the amount of fine particulate matter (PM) in the ambient atmosphere and various respiratory and cardiovascular health problems in humans. The new regulations propose keeping existing limits on emissions of particulate matter less than 10 μm in size (PM_{10}) and including new limits on finer PM, viz., the fraction less than 2.5 μm in size ($\text{PM}_{2.5}$). The additional regulations place increased emphasis on particle emissions from combustion processes that typically generate very fine particles (0.01 – 2.5 μm) in comparison to mechanical processes based on

comminution and fracture processes, which tend to generate coarser particles, usually greater than 2.5 μm in size. Major combustion processes thought to contribute significantly to ambient $\text{PM}_{2.5}$ include fossil-fuel (e.g. coal, residual oil) combustion for electrical power generation, biomass combustion (e.g. crop-clearing fires, forest fires, wood-stove combustion), and internal combustion engines powered by liquid (diesel, gasoline) fuels.

Although the link between the $\text{PM}_{2.5}$ content of the atmosphere and adverse health effects is well established, the actual mechanism of injury is still poorly understood and a multitude of different theories are being pursued. Another important research area is how to determine the relative proportions of different source contributions to the ambient $\text{PM}_{2.5}$ fraction.

Authors (left to right)
(top) Frank Huggins and Jerry Huffman
(bottom) Bill Linak and Andy Miller



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In this work, we used XAFS spectroscopy at beamlines X18B and X19A to investigate the speciation of hazardous metals in $PM_{2.5}$ derived from the combustion of coal and residual oil. Coal and residual oil samples were combusted in large laboratory-scale combustion units at the U.S. EPA's National Risk Management Research Laboratory, and two fractions of PM – a coarse $PM_{2.5+}$ fraction and a fine $PM_{2.5}$ fraction – were separated using a cyclone with a cut-point of 2.5 μm . The PM samples were then subjected to leaching in deionized water and hydrochloric acid, and both bulk samples and residues from the leaching experiments were investigated by XAFS spectroscopy. The combination of XAFS spectroscopy and leaching studies not only provides the means for quantifying the presence of various toxic species in PM samples, but can also provide important information regarding the solubility, and hence potential bioavailability, of such species. For coal combustion, the oxidation states of As and Cr in PM are important issues, whereas, for residual oil combustion, it is important to be able to establish the presence or absence of nickel sulfides. Our results show that the toxic species are distributed unequally among PM samples from different sources. For example, in coal PM, the toxic oxidation state of Cr, viz. Cr(VI), comprises between 10% and 40% of the total Cr in $PM_{2.5}$ derived from low-sulfur, lower-rank coals from the western United States. However, it is not usually detected (<5% of the total Cr) in $PM_{2.5}$ from the combustion of higher sulfur coals from the eastern United States. In PM from residual oil combustion, nickel sulfides were more prevalent in coarse $PM_{2.5+}$ than in fine $PM_{2.5}$ fractions (**Figure 1**). Similar information regarding the occurrence of individual hazardous species in PM samples collected for epidemiological or toxicological studies should be of significance for testing specific mechanisms of injury arising from exposure to PM.

The study summarized here is just one aspect of a large NSF-supported effort, involving groups at the Universities of Kentucky, Missouri and Utah in collaboration with groups at U.S. EPA, Ford Motor Company, EPRI, the Lovelace Respiratory Research Institute, etc., that is designed to provide detailed characterization of PM derived from combustion of fossil fuels in both stationary and mobile combustion processes.

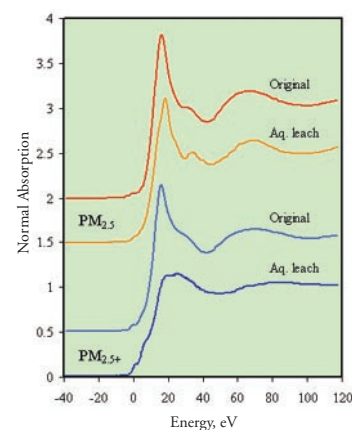


Figure 1. Ni XANES spectra for fine ($PM_{2.5}$) and coarse ($PM_{2.5+}$) particulate matter fractions from combustion of a low-sulfur No. 6 residual oil and for the residues obtained from them by aqueous leaching. The spectra are dominated by nickel sulfate in the original, as-received state, but, as a result of aqueous leaching, the Ni spectra have dramatically changed and indicate that the insoluble Ni is predominantly present as a nickel-bearing spinel in the $PM_{2.5}$ leaching residue and as a nickel sulfide in the coarse $PM_{2.5+}$ leaching residue. The zero-point of energy corresponds to 8333 eV.