Combining XAFS Spectroscopy and Leaching Behavior for the Speciation of Critical Elements in Fine Particulate Matter

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Introduction: In this work, XAFS spectroscopy is being used to examine the form of occurrence (speciation) of sulfur and a number of metals in PM samples collected from primary combustion sources and from ambient air. The objectives are two-fold: to identify possible hazardous forms of critical elements of concern to human health and to provide information that can be used for source apportionment. To augment XAFS investigation of elements in PM samples, leaching studies were performed on various PM samples to provide suites of samples that enable the components of each element to be identified more definitively.

Methods and Materials: Samples of fly-ash were collected during combustion experiments using residual oil or coal in large-scale experimental furnaces at the EPA. The fly-ash samples were separated by a cyclone into a coarse fraction (PM > 2.5 µm, PM2.5+) and a fine fraction (PM < 2.5 µm, PM2.5). These fractions were subjected to leachings in pentane, distilled water, and 1N hydrochloric acid. The leaching residues, as well as the original PM sample, were examined by fluorescent XAFS at the S, V, Cr, Fe, Ni, Cu, Zn, As, and Pb absorption edges.

Results: Ni XANES spectra are shown for leached PM samples of residual oil fly-ash (ROFA) in Figure 1. The XANES spectra exhibit significant variation as a result of leaching and result in better identification of the different forms of Ni present in these materials. For the ROFA PM samples, the most important effect is that aqueous and acid leaching removes the dominant metal sulfate species, revealing much more clearly minor oxide and sulfide forms. Pentane leaching was rather ineffective. For nickel, the minor forms were readily identified as nickel ferrite, NiFe₂O₄, and a nickel sulfide. Using the three forms of nickel in these materials, the Ni XANES spectra were then fit by a least-squares procedure to quantify the forms of nickel in the ROFA PM samples. Similar procedures were applied with varying degrees of success for each of the other critical elements. It was found that most metals in ROFA PM samples are present predominantly in sulfate forms. Another important observation is that the minor sulfide forms of the elements tend to be more prevalent in coarse PM2.5+ than in finer PM2.5 fractions, whereas the minor oxide forms show the reverse relationship.

Conclusions: The combination of leaching and XAFS spectroscopy provides more information than either technique alone regarding the speciation of elements in PM samples derived from residual oil combustion and other combustion sources. Information obtained from these investigations should enable a better assessment to be made of the health risks posed by PM samples and should also make source apportionment methods for establishing the relative contributions of primary sources of PM to ambient PM more precise.

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Figure 1: Ni XANES spectra of fine PM2.5 (left) and coarse PM2.5+ (right) obtained from combustion of Baseline No. 5 (BL5) residual oil. The spectra of the BL5 samples and the pentane leached samples are dominated by nickel sulfate, whereas the spectra of the aqueous leached and acid leached fractions for the fine PM are dominated by nickel ferrite, NiFe₂O₄, (left) and those for the coarse PM are dominated by nickel sulfide (right).