

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

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An analysis protocol that combines X-ray absorption near-edge structure spectroscopy with selective leaching has been developed to examine hazardous species in size-segregated particulate matter (PM) samples derived from the combustion of fossil fuels. The protocol has been used to identify and determine quantitatively the amounts of three important toxic species in combustion-derived PM: viz., nickel sulfides in residual oil fly ash (ROFA) PM, and Cr(VI) and As(III) species in coal fly ash PM. Although it has been assumed that these toxic species might exist in PM derived from fossil-fuel combustion, the results presented here constitute the first direct determination of them in combustion-derived PM and their potential bioavailability. Detailed information on the presence of these toxic species in PM samples is of significant interest to epidemiological and toxicological studies of the health effects of both source and ambient PM. Additionally, information is obtained on insoluble forms that may be useful for source attribution and on the distribution of phases between size fractions that may be related to formation mechanisms of specific toxic species during combustion.

Introduction

Ever since the 1952 London “killer smog”, which resulted in thousands of premature deaths, smoke particles and sulfur dioxide have been implicated as a significant health risk for the general public (1). Consequently, regulations were enacted in many industrial countries limiting emissions of both ambient particulate matter (PM) less than 10 μm in size (PM_{10}) and SO_2 . More recently, in 1997, the U.S. Environmental Protection Agency (EPA) promulgated new standards on ambient concentrations of particulate matter smaller than 2.5 μm in aerodynamic diameter ($\text{PM}_{2.5}$) (2, 3). This action was taken because a number of epidemiological studies had demonstrated that the concentration of PM in ambient air correlated with human morbidity and mortality and that $\text{PM}_{2.5}$ exhibited a stronger correlation than PM_{10} (4–6). These new standards place increased emphasis on emissions from both stationary (e.g., coal and residual oil power generation) and mobile (e.g., diesel and other vehicular exhausts) fossil-fuel

combustion processes because combustion sources contribute increasingly to the formation of the smallest sized PM (7). Indeed, recent epidemiological findings (6, 8) have tended to implicate combustion processes as a source of toxicity in PM.

Despite these findings, it remains unclear (7, 9) what specific properties or chemical compounds in fine PM might give rise to the greatest health hazards. As a result, efforts to identify the underlying causes of adverse health effects of $\text{PM}_{2.5}$ have intensified in recent years. Samet et al. (9) point out that the relatively short time lag between changes in ambient PM levels and changes in the incidence of health effects argues in favor of an acute exposure–response relationship, such as an inflammatory mechanism of toxicity. The same authors (9) also point out that metallic compounds are prevalent in emissions from combustion processes, notably those in residual oil fly ash (ROFA), and that such compounds have been linked to adverse health effects in laboratory animals (10–12). Such testing indicates that a key factor contributing to adverse health impacts may be the amount of water-soluble (bioavailable) metals present in the PM. A recent Canadian epidemiological study (13) has shown that sulfate, iron, nickel, and zinc in ambient $\text{PM}_{2.5}$ appear to be more strongly associated with mortality than $\text{PM}_{2.5}$ mass. A factor-analysis study (14) of humans exposed to concentrated ambient particles has indicated that soluble components, notably a sulfate/Fe/Se factor, correlate with adverse effects in human lungs and blood. It has also been postulated (15–17) that iron and other transition metals could act as catalysts in the formation of reactive oxygen species that may be associated with the activation of many biochemical processes. Another possible factor in premature death from metals in $\text{PM}_{2.5}$ is disturbance of cardiac autonomic (heart-rate) function (18, 19; Margari et al. (20) were able to show a correlation between metal concentrations, specifically V and Pb, in inhaled fine PM and variation in cardiac autonomic function. Nickel is considered a significant health risk for emissions from oil-fired utilities and refinery operations because of its relatively high concentration in ROFA emissions and its possible emission in the form of crystalline nickel sulfide and subsulfides (Ni_{1-x}S , where $0.5 \geq x \geq 0$), which are both toxic and carcinogenic (21, 22). Similarly, Cr and As can be significant trace elements in coal fly ash, and it is well-known that Cr(VI) and As(III) present a significantly greater threat to human health than the other common valence states of the same elements, viz., Cr(III) and As(V) (23–28).

It is therefore imperative (29) to develop more quantitative methods of speciating elements in PM to correlate the presence of specific chemical species in $\text{PM}_{2.5}$ with adverse effects on the human body and to improve our understanding of their formation and reaction mechanisms. Direct determination of such species would aid epidemiological studies by providing unambiguous data on specific, potentially toxic, elemental forms. For example, the correlation between total Ni and health effects in a sample population is unlikely to be the same as the correlation with health effects of a minor, toxic species such as nickel sulfide.

In this paper, we document the application of X-ray absorption near-edge structure (XANES) spectroscopy and a simple leaching protocol to size-segregated samples for obtaining detailed information on how key elements occur in primary PM samples obtained from fossil-fuel combustion. By leaching PM samples in aqueous and acidic (1 N HCl) solutions, a systematic sample variation is introduced that reveals minor phases of an element and thereby provides

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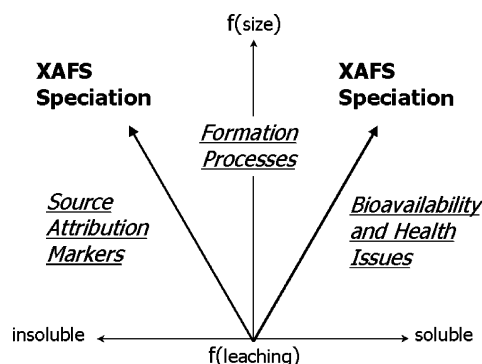


FIGURE 1. Application diagram for determination of elemental speciation by XAFS spectroscopy as a function of particle size and leaching behavior.

useful end points for the analysis of multicomponent XANES spectra, which are derived from X-ray absorption fine structure (XAFS) spectra. Furthermore, for PM studies, aqueous leaching reveals those phases that are soluble in water and therefore potentially bioavailable, whereas phases that are insoluble in acid are likely to be of most use for source apportionment issues (Figure 1). In addition, the data on size-segregated samples provide insight into how certain elemental species may have formed during the combustion process (Figure 1). We demonstrate the power of this combined XANES and leaching protocol by presenting quantitative data for nickel-containing sulfides in ROFA PM samples and for As(III) and Cr(VI) species in coal-derived PM samples.

Experimental Section

Particulate matter samples were prepared from combustion of residual oils and coals at the U.S. EPA's National Risk Management Research Laboratory. Four different residual oils were combusted in a commercial, 732 kW, three-pass, fire-tube boiler with relatively short residence times, which produced PM rich in unburned char (~60–98% carbon) (30–32). Three high-sulfur eastern bituminous coals and four low-sulfur western coals of various ranks were combusted in a smaller 50 kW down-fired refractory-lined combustor. In this combustion unit, the resulting coal PM had carbon contents of less than 16%. The combustion experiments, sampling procedures, and elemental analyses of these PM samples have been described in detail in earlier papers (30–32). The fine fly ash from the combustion experiments was sampled upstream of any particle removal system and separated by a cyclone apparatus with a 2.5 μm cut point into fine and coarse fractions with mean particle-size diameters <2.5 μm (PM_{2.5}) and >2.5 μm (PM_{2.5+}), respectively.

Both the coarse PM_{2.5+} and fine PM_{2.5} fractions from three of the four residual oils, viz., low sulfur no. 6 (LS6), high sulfur no. 6 (HS6), and baseline no. 5 (BL5), and those from two of the seven coals, viz., Pittsburgh bituminous coal from the eastern U.S. and Montana subbituminous coal from the western U.S., were leached. In the case of the LS6 and HS6 ROFA PM samples, aqueous leaching using deionized water was done as part of an ion chromatography (IC) procedure for determination of anions in PM. The PM fractions for the other ROFA sample (BL5) and those for both coal PM samples were subjected to leaching in both aqueous (deionized water) and 1 N HCl acid solutions. Typically, small samples (250–400 mg) of the PM fractions were exposed to 50 mL solutions for times up to 1 h with intermittent agitation (slow swirling of the beaker by hand). The solids were removed from the leachate solutions by filtration using Whatman no. 42 filters.

XAFS spectroscopy was performed on the solid residues of the leaching experiments as well as on the original

unleached PM_{2.5} or PM_{2.5+} samples at the Stanford Synchrotron Radiation Laboratory (SSRL) at Stanford University, California, or at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, New York. The XAFS experiments were made in fluorescence detection mode using either a Lytle (33) or a multi-element Ge array (34) detector, depending on the concentration of the element in the PM sample. Except for sulfur, Soller slits and a 6 μ (Z-1) filter (35) were also employed to increase the signal-to-noise ratio. Typically, three to six separate scans were made and averaged to provide a single spectrum with an improved signal/noise ratio. The PM samples were irradiated in the X-ray beam in the form of powders in thin polypropylene bags. The X-ray beam was monochromatized using either a Si(220) or a Si(111) double-crystal monochromator, which was typically detuned to between 30% and 70% of the maximum intensity, depending on the element of interest, to suppress higher harmonics. Primary calibration standards used in this study were elemental sulfur, nickel metal foil, chromium metal foil, and arsenic trioxide (As₂O₃) for S (at 2472 eV), Ni (at 8333 eV), Cr (at 5989 eV), and As (at 11867 eV), respectively. For the two metal foils, the zero points of energy in the XANES spectra were defined by the first major peak in the first-derivative spectra; for S and As, the white-line peak positions in the XANES spectra of elemental sulfur and As₂O₃ were used to define the zero points of energy. For Ni and As, the calibration spectra were normally recorded in transmission simultaneously with the recording of the fluorescence XAFS spectra of the element in the PM samples, whereas the calibration spectra for S and Cr were obtained in separate runs.

The XAFS spectra were analyzed in the usual manner (36–38). The spectra of a given element were first calibrated with respect to the appropriate calibration standard and then subdivided into separate XANES and extended X-ray absorption fine structure (EXAFS) spectral regions by means of normalization to the absorption edge step and subtraction of the pre-edge background. At the low concentrations of the toxic species prevalent in some of the samples, particularly the coal-derived fractions (30, 31), the XANES spectra were found to be more useful than the EXAFS spectra for detailed analyses. XANES spectra of the leached ROFA residues sometimes revealed the presence of an individual minor species of a given element, whose presence was not always evident in the spectra of the original unleached ROFA PM samples. Such a spectrum rather than the spectrum of a standard might then be used as input for the linear combination method of least-squares fitting of unknown XANES spectra. As discussed below, this alternative was adopted for inclusion of nickel sulfide in the least-squares fitting of nickel XANES spectra.

For sulfur, the least-squares procedure consisted of fitting Lorentzian–Gaussian peaks representing s–p transitions (white lines) for specific sulfur forms and a double arctangent function representing the edge step to the continuum for unoxidized and oxidized sulfur forms to the sulfur XANES spectrum over the range –8 to +20 eV. This procedure is described in detail elsewhere (39, 40). For the metals, different least-squares fitting procedures were used. In the case of As and Cr, the white-line or pre-edge peaks were fit according to procedures developed specifically for the estimation of the different oxidation states of As (41) and Cr (42) from such features. For Ni, least-squares fitting was based on the linear combination of XANES spectra of up to three standard spectra adjusted and weighted to give the best fit to the unknown spectrum, using the procedure in the WinXAS program for XAFS data analysis (43). The least-squares fitting extended over the region from –10 to +50 eV. Such fitting gave results superior not only to the qualitative results (44) but also to preliminary results based on least-squares fitting to just two

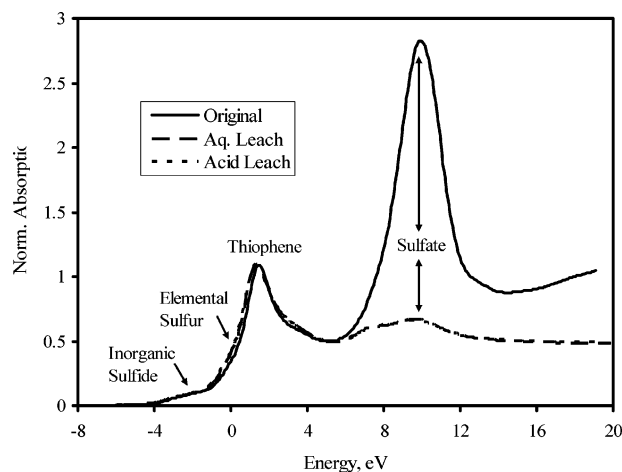


FIGURE 2. Sulfur XANES spectra for the original PM_{2.5} fraction and leached residues derived from combustion of the baseline no. 5 (BL5) residual oil. The spectra for the aqueous- and acid-leached residues overlap almost completely and appear as a single trace. Peaks due to different sulfur forms are indicated. The zero point of energy corresponds to 2472 eV.

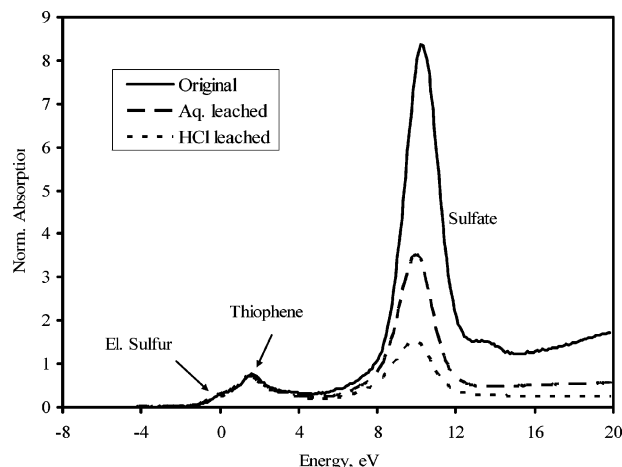


FIGURE 3. Sulfur XANES spectra for the original PM_{2.5} fraction and aqueous and acid (1 N HCl) leached residues derived from combustion of the Pittsburgh bituminous coal.

components (45) that were reported previously for some of these samples.

Results and Discussion

Determination of Bioavailable Sulfate. Sulfur speciation by XANES spectroscopy has revealed that sulfate is generally the dominant form of sulfur in both primary fossil-fuel and ambient PM samples (44–46). However, it is by no means the only form of sulfur in primary PM samples. As illustrated in Figure 2 for ROFA PM and in Figure 3 for coal PM, a number of other sulfur phases are observed including thiophenic forms, elemental sulfur, and, in the case of the ROFA PM, inorganic sulfide. The spectra in these figures are normalized to the thiophene component in order to accentuate the changes due to leaching. The sulfur forms present in leached and original PM samples were quantified by using a least-squares fitting procedure developed for quantitative determination of sulfur forms from sulfur XANES spectra (39, 40). We observe that aqueous and acid leaching removes almost all of the sulfate sulfur from the ROFA PM samples (Figure 2). However, up to 50% of the original sulfate remains in the coal-derived PM, even after acid leaching (Figure 3). This fraction of the sulfate in the coal-derived PM is not likely to be bioavailable and most likely represents alkaline-earth-

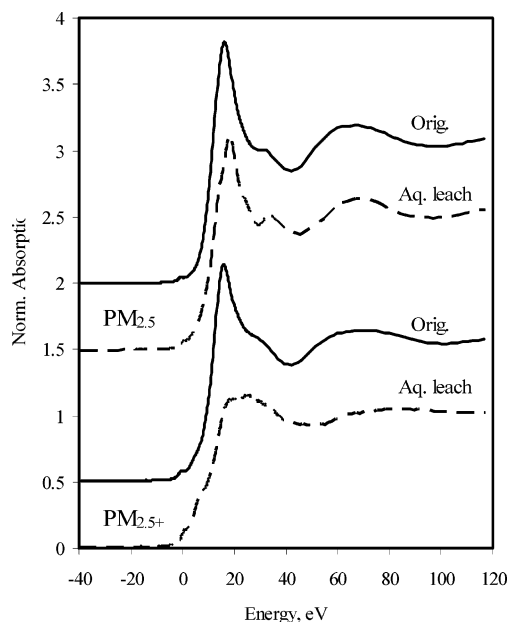


FIGURE 4. Nickel XANES spectra of original PM fractions and aqueous-leached residues derived from combustion of low-sulfur no. 6 (LS6) residual oil. The zero point of energy corresponds to 8333 eV.

metal (Ca, Sr, Ba) sulfates that are known to be sparingly soluble in aqueous and weak acid solutions. The other sulfur forms, thiophene, elemental sulfur, and inorganic sulfide, are largely unaffected by either leaching treatment. These results demonstrate that neither total sulfur nor total sulfate in a PM sample from combustion of coal or residual oil is an appropriate measure of bioavailable sulfate. However, the sulfate determined by ion chromatography normally involves aqueous leaching and therefore does appear to be a valid method of measuring bioavailable sulfate in PM samples.

Metal Speciation. The application of the combined XANES-leaching protocol to PM_{2.5} from combustion sources has led to the direct quantification of three significant toxic metal forms.

Nickel Sulfide in ROFA PM_{2.5}. Figure 4 shows the changes brought about in the Ni XANES spectra of the two LS6 ROFA size fractions before and after aqueous leaching. In the case of the fine PM_{2.5} fraction, the spectrum after aqueous leaching is closely similar to that of nickel ferrite (NiFe₂O₄) (47, 48), whereas for the coarse PM_{2.5+} fraction, a sulfide appears to be the dominant nickel phase in the aqueous-leached residue. In both cases, Ni in the form of NiSO₄·6H₂O has been removed by aqueous leaching to reveal these two minor Ni species. Fitting of the XANES spectra was therefore attempted on the basis of these three phases as input for simulation of the Ni XANES spectra of the leached and unleached ROFA PM samples using the procedure in WinXAS (43). However, it was soon realized that the least-squares fitting based on nickel sulfate, nickel ferrite, and nickel sulfide standard spectra was generally poor with a large residual for those spectra where the sulfide component was significant. The reason for this was that the spectra of the PM_{2.5+} residues after leaching did not closely resemble the spectrum of any of the standard sulfides (NiS, NiS₂, Ni₃S₂) available to us. Significant improvement in the fitting was found by substituting the spectrum of the leaching residue of one of the cyclone samples for the standard sulfide spectra, and these are the results summarized in Table 1. An example of a fitted spectrum and its components is given in Figure 5.

The data in Table 1 are unnormalized results from the WinXAS procedure and sum to within $\pm 5\%$ of 100%, with

TABLE 1. Distribution of Ni among Sulfide, Sulfate, and Oxide (Ferrite) Forms for ROFA PM Samples and Leaching Residues Obtained by Least-Squares Fitting of XANES Spectra

sample/residue	Ni content, $\mu\text{g/g}$	% Ni as			least-squares fit residual
		sulfate	sulfide	ferrite	
LS6 PM _{2.5} filter	4840	66	<	35	1.5
LS6 PM _{2.5} aq leach	nd	16	21	72	0.6
LS6 PM _{2.5+} cyclone	860	69	29	<	1.0
LS6 PM _{2.5+} aq leach	nd	<	>90	<	3.8
HS6 PM _{2.5} filter	8020	92	<	8	1.3
HS6 PM _{2.5} aq leach	nd	29	49	25	1.0
HS6 PM _{2.5+} cyclone	2270	73	23	<	1.7
HS6 PM _{2.5+} aq leach	nd	<	94	6	0.8
BL5 PM _{2.5} filter	8800	56	10	30	1.0
BL5 PM _{2.5} aq leach	4870	18	22	60	1.6
BL5 PM _{2.5} acid leach	3000	20	41	40	0.9
BL5 PM _{2.5+} cyclone	2600	54	43	<	1.9
BL5 PM _{2.5+} aq leach	1450		100 ^a		a
BL5 PM _{2.5+} acid leach	1250	6	89	5	0.5

^a Spectrum used as sulfide standard (see the text); < indicates phase not included in final fit—estimated not to exceed 5%.

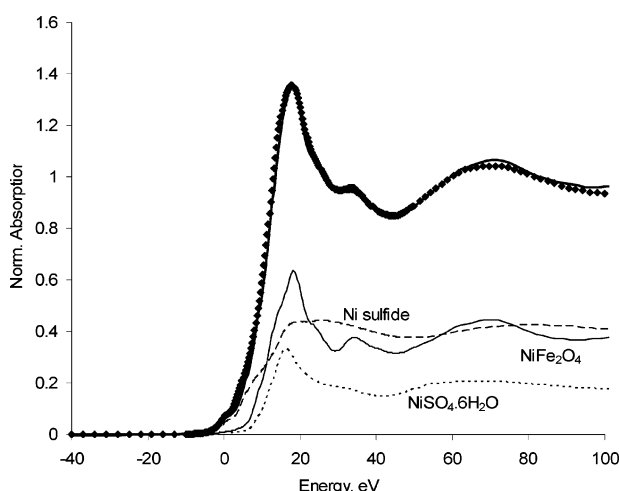


FIGURE 5. Example (acid-leached BL5 PM_{2.5} residue) of a least-squares-fitted Ni XANES spectrum. The XANES spectrum (tilted squares) is fit to a linear combination of the XANES spectrum of the three individual component spectra over the range from -10 to +50 eV. The spectrum used for the nickel sulfide was that for the aqueous-leached BL5 PM_{2.5} residue (see the text). The zero point of energy corresponds to 8333 eV.

residuals from the least-squares fitting in the range 0.55–1.95, for most samples. This agreement provides reasonable assurance that the three phases considered are indeed the three most important Ni-bearing phases in the PM samples. It also indicates that the errors in the determination of the individual Ni species are likely to be no more than $\pm 5\%$ for this combination of standard spectra.

It is clear, on the basis of the data in Table 1, that leaching reveals the presence of a minor but significant nickel-containing sulfide phase in these ROFA PM samples. However, it should be noted that these samples do contain much unburnt carbon, in the range 60–98% (30–32), and in this respect are quite different from PM samples collected from commercial electricity-generating plants, in which carbon burnout is much more complete. This difference is likely responsible for the lack of observation of Ni-containing sulfides in previous speciation analysis of residual oil fly ash and PM in other combustion systems (48). This observation emphasizes the importance that combustion conditions have on determining elemental speciation in the fly ash or PM.

One of the most important results to come out of the least-squares analysis is the observation that the minor nickel-containing sulfide and oxide (nickel ferrite) phases are predominantly found in the coarse and fine fractions, respectively. Although the sulfide is found in both fractions, it is always more abundant in the coarse fraction than in the fine fraction. Conversely, the ferrite phase is usually absent from the coarse fraction, but is the second-most abundant Ni phase after nickel sulfate in the fine PM_{2.5} fraction. On the basis of loss-on-ignition (LOI) data (30, 31), the PM_{2.5} fraction is always more completely burned out than the corresponding PM_{2.5+} fraction in the case of residual oil combustion. The combination of the short residence time and the incompleteness of the burnout must prevent the oxidation or decomposition of the nickel sulfide particles that are formed inside larger carbonaceous particles. In contrast, nickel sulfate is likely to have formed by condensation from the gas phase on the surfaces of uncombusted carbon-rich particles, regardless of size. Assuming that condensation will reflect the surface area of the particle, the observed higher concentration of Ni associated with the finer PM_{2.5} fraction can then be readily explained, since nickel sulfate is the major Ni phase in the system.

The association of the nickel ferrite phase with the PM_{2.5} fraction is more difficult to explain. Clearly, the fact that so little nickel ferrite is seen in the coarse fraction argues strongly against the indiscriminate process of volatilization–nucleation–condensation for the formation of this phase, since this process should result in the presence of nickel ferrite in all particles, in fashion similar to that of nickel sulfate. Hence, we hypothesize that, in very small char particles, initially formed metal sulfide phases undergo oxidation due to diffusion of oxygen into the char particle, resulting in the formation of oxide phases, such as nickel ferrite.

In their crystalline forms nickel sulfides, such as NiS, Ni₃S₂, and Ni₆S₅, are well-known to be toxic and carcinogenic (21, 22). However, as already noted, there are a number of significant differences between the Ni XANES spectra of the leached PM_{2.5+} fractions and those for NiS and Ni₃S₂ shown elsewhere (47, 48). It is therefore likely that the sulfide form is in fact a mixed nickel–iron sulfide since its oxidized counterpart in the leached PM_{2.5} fraction is predominantly nickel ferrite (NiFe₂O₄). According to Craig and Scott (49), the mixed sulfide (Fe,Ni)_{1-x}S is the most stable sulfide in the Ni–Fe–S system and the one most commonly formed at high temperature. Depending on its composition and the rate of cooling, this sulfide can remain as a single phase or can unmix and give rise to mixtures of the iron sulfide, pyrrhotite (Fe_{1-x}S), and various nickel sulfides.

Hexavalent Chromium in Coal PM. It has been recently shown (46) that PM from combustion of western U.S. low-sulfur coals contained significant fractions of chromium in the hexavalent oxidation state. In contrast, Cr(VI) was not detected in eastern U.S. high-sulfur bituminous coals. More recently, we have examined aqueous and leached fractions of PM from one eastern bituminous (Pittsburgh) and one western low-rank (Montana) coal. Whereas neither aqueous nor acid leaching produced any significant change to the Cr XANES spectra of the Pittsburgh coal PM, the Cr XANES spectra of the Montana coal were altered significantly by the leaching treatments (Figure 6). Using the analysis method developed previously (42), it was found that the Cr(VI) content of the original Montana coal PM_{2.5} fraction was reduced from 24% to 18% by aqueous leaching and to 0% by 1 N HCl treatment. In addition, as the Cr(VI) species and perhaps some Cr(III) species as well are increasingly leached, the Cr XANES spectrum of the residue approaches more closely the spectral profile of Cr(III) in the spinel, magnetite–chromite (50). The Montana coal PM_{2.5+} fraction showed similar behavior, except that it originally contained only 16% of the

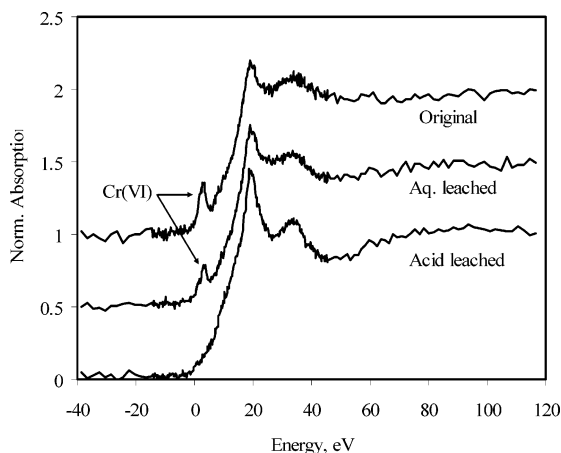


FIGURE 6. Chromium XANES spectra of the original PM_{2.5} fraction and aqueous and acid (1 N HCl) leached residues derived from combustion of the Montana coal. The zero point of energy corresponds to 5989 eV.

Cr as Cr(VI), which was reduced to 11% Cr(VI) in the aqueous residue and 0% in the acid residue.

The chromate species in the Montana coal PM fractions therefore consist of two components: one that is soluble in water and the other that dissolves only in 1 N HCl acid. For both size fractions, approximately 25–30% of the original Cr(VI) content is removed by aqueous leaching, leaving approximately 70–75% to be removed by acid leaching. However, for both the coarse and fine fractions, each of which contains only about 20 ppm Cr (45), the aqueous-soluble contents of Cr as Cr(VI) in the Montana coal PM amount to less than 2 ppm.

Estimation of As(III) in Coal-Derived PM. The toxicity of arsenic also depends strongly on its speciation, especially its oxidation state (26–28). In particular, the As(III) oxidation state is considered to be many times more toxic than the As(V) oxidation state (26). Therefore, it is important to be able to estimate the proportions of these two oxidation states, especially in the situation where As(III) is a small component in the presence of major As(V), to assess properly the threat to human health posed by arsenic. For the fine PM_{2.5} fraction derived from the Pittsburgh coal, significant changes are seen after acid leaching, including a significant increase in white-line peak width (Figure 7a). These differences are more obvious in the first-derivative spectra (Figure 7b), not only for the acid-leached sample, which exhibits two peaks, but also for the aqueous-leached sample, which exhibits minor, but obvious asymmetry. The positions of the major peaks at about 4.0 eV (41), as well as analysis of the EXAFS data regions for the original samples (46), confirm that the major form of arsenic is As(V) as arsenate and the asymmetry is to lower energy, indicating the presence of As(III). Although no asymmetry is apparent for the derivative XANES spectrum of the original fine PM_{2.5} sample, the corresponding spectrum of the original coarse PM_{2.5+} sample does exhibit slight asymmetry, approximately similar to that of the aqueous-leached PM_{2.5} sample, shown in Figure 7b. Further, the signal/noise ratio of the As XANES spectra diminishes significantly upon leaching, especially after the acidic treatment, indicating the removal of significant arsenic from the PM samples.

Least-squares peak fitting of the As XANES spectra (Figure 8) provides estimates of the relative amounts of the two arsenic oxidation states (Table 2). One-peak fits were also attempted for the samples, and in all cases except for the original PM_{2.5} sample, the sum of squares (χ^2) values were much greater than for the two-peak fits. For the original fine PM_{2.5} sample, χ^2 was higher for the one-peak fit, but only by a factor of 1.4, indicating there is little difference statistically

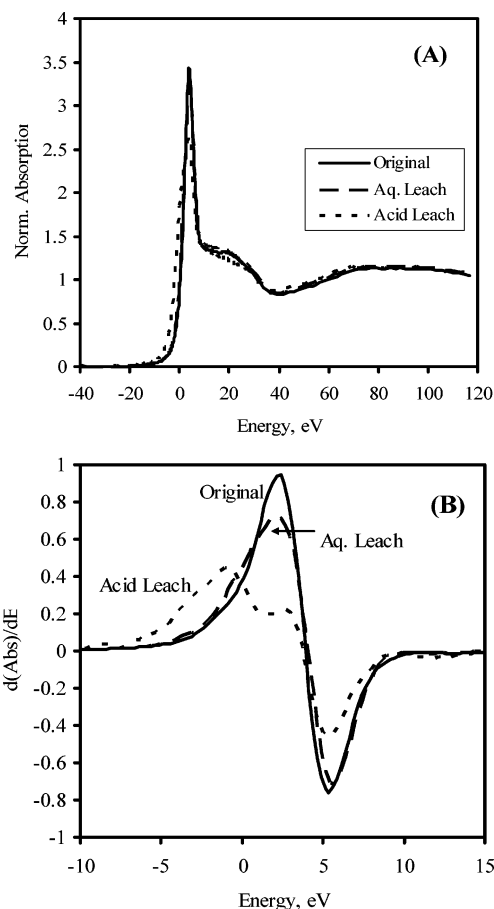


FIGURE 7. (A) Arsenic XANES spectra and (B) first-derivative XANES spectra of the original PM_{2.5} fraction and the aqueous and acid (1 N HCl) leached residues derived from combustion of the Pittsburgh bituminous coal. The zero point of energy corresponds to 11867 eV.

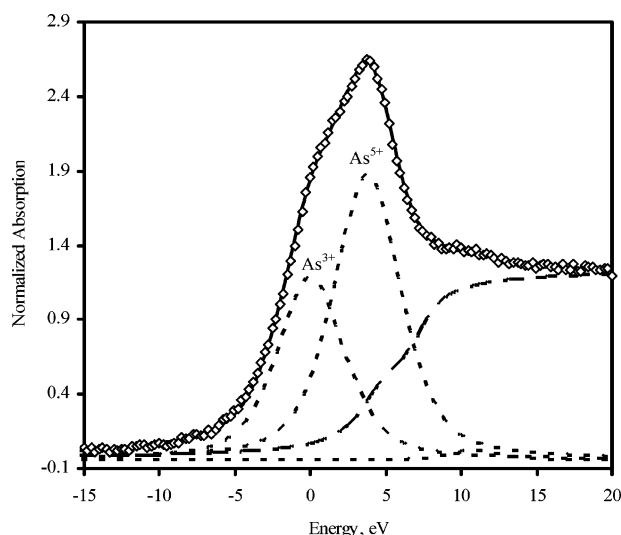


FIGURE 8. Example (acid-leached Pittsburgh coal PM_{2.5} residue) of least-squares peak-fitted arsenic XANES spectra. Data are shown as unfilled tilted square points, and the component peaks are indicated by dashed lines, the edge by long dashed lines, and the overall fit by the solid line. The zero point of energy corresponds to 11867 eV.

between the fits with 3% As and 0% As as As(III). In contrast, for the original coarse PM_{2.5+} sample, the corresponding factor for the one- and two-peak fits was 4.5, indicating that the two-peak fit is significantly better. From this analysis, we

TABLE 2. Estimated Percentages of Arsenic as As(III) and As(V) in Pittsburgh Coal PM Fractions and Leaching Residues Based on Peak Areas Derived from Least-Squares Fitting

sample	As content, μg/g	% As as		χ^2 ($\times 10^{-4}$)
		As(III) ^a	As(V) ^a	
original PM _{2.5}	310	3	97	2.4
PM _{2.5} after aq leach	n.d.	7	93	2.6
PM _{2.5} after acid leach	n.d.	39	61	2.8
original PM _{2.5+}	100	6	94	3.4
PM _{2.5+} after aq leach	n.d.	12	88	0.9
PM _{2.5+} after acid leach	n.d.	28	72	1.4

^a Estimated errors of determination $\pm 3\%$. nd = not determined.

may conclude that the uncertainty in the fitting is on the order of $\pm 3\%$ and that the presence of the As(III) in the original coarse PM_{2.5+} sample is statistically significant. The presence of significant As(III) in the leached residues confirms that the same species must occur in the original PM sample, albeit at a level close to the detection limit of $\sim 3\%$ As. This observation is important because even 3% of As as As(III) in the original PM may result in an approximate doubling (26) of the toxicity hazard posed by arsenic in the coal PM compared to the situation where all the arsenic is As(V). However, As(III) may not be so readily bioavailable as As(V) from this source in view of the observation that the As(III) species is more resistant to both aqueous and acid leaching.

Implications for PM_{2.5} Health Studies. The application of XANES spectroscopy to residues from simple leaching tests on PM fractions derived from the combustion of fossil fuels provides quantitative speciation of hazardous elemental species that are of significant concern for human health. This procedure enables us to identify and quantify the amounts of As(III) and Cr(VI) in PM from coal combustion and nickel sulfides in PM from combustion of residual oil. Furthermore, this combined XANES and leaching protocol also determines the potential "bioavailability" of such hazardous species. For example, the toxic Cr(VI) species in PM derived from combustion of western low-rank coals would appear to be more bioavailable than Cr(III) forms, while As(V) species are more readily dissolved than the much more toxic As(III) species in PM from the combustion of eastern bituminous coals. In the case of the ROFA PM, much nickel is readily bioavailable in the form of nickel sulfate, the major Ni component in these PM samples. In addition, a nickel-containing sulfide occurs as a minor Ni component in the coarse PM_{2.5+} fraction; however, this nickel form appears to be less readily bioavailable, as it is insoluble in both aqueous and acidic media. Furthermore, the identity of the Ni-containing sulfide in ROFA PM, on the basis of the XAFS data presented here, would appear to be more complex than those of the simple nickel sulfides considered previously in toxicological studies (22, 23).

Such speciation information relating to specific hazardous species in PM should be used to augment epidemiological and toxicological studies that would otherwise be based on elemental composition data alone. Information on the concentrations and bioavailability of specific hazardous species should make possible much clearer assessments of the underlying causes of adverse health effects caused by the inhalation of airborne PM. Similarly, speciation analysis provided by the combination of XANES spectroscopy and leaching should find application in source attribution studies. Clearly, those species identified as unleachable in acid, such as thiophenic sulfur or Cr(III) as magnetite—chromite, which are most likely to survive the transition from primary PM to ambient PM unchanged, should be of most significance for source attribution.

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