X-ray Absorption Fine Structure (XAFS) Spectroscopic Characterization of Emissions from Combustion of Fossil Fuels

Frank E. HUGGINS* and Gerald P. HUFFMAN*

*University of Kentucky 111 S. J. Sam Whalen Building,
533 South Limestone Street, Lexington, KY 40506-0043 USA
E-mail : fhuggins@engr.uky.edu

The application of XAFS spectroscopy is described for the determination of the speciation of sulfur and various hazardous or key metals in both coarse ($>2.5\,\mu$m) and fine ($<2.5\,\mu$m) fractions of particulate matter (PM) emitted in three different fossil-fuel combustion processes. The three processes consisted of (i) combustion of residual oil, (ii) combustion of various eastern and western U.S. coals, and (iii) combustion of diesel fuel formulations in an engine. Sulfur was found to exist in mainly sulfate forms in the emissions from all three processes, although minor to significant fractions of the sulfur were also present as thiophenic sulfur, elemental sulfur, and various other sulfur forms, depending on the fossil fuel, the combustion conditions, and the particle size of the collected fraction. Combustion of residual oil tended to form metal sulfates predominantly, although the coarse fractions ($PM_{2.5+}$) also contained minor amounts of sulfides of Fe, Cu and Ni, while the fine fractions ($PM_{2.5}$) contained oxides instead of sulfides as their minor components. Due to the presence of aluminosilicates in the coal, metal species in coal emissions were more complex. Chromium was present entirely as Cr^{3+} in both fine and coarse PM from combustion of eastern U.S. coals, but significant fractions of the chromium were present as more toxic and carcinogenic $Cr(VI)$ species in fine and coarse PM from combustion of western U.S. coals. In contrast, arsenic was present entirely as arsenate (AsO_4^{3-}) species in all coal PM samples (and residual oil PM samples), regardless of origin. No evidence was found for the more toxic As(III) oxidation state in any sample. The zinc speciation in PM samples from combustion of coal samples was also found to vary with geographic origin of the coal. Zinc in PM samples from eastern U.S. coals was present mostly as Zn ferrite ($ZnFe_2O_4$), while the Zn speciation in PM from western U.S. coals was more complex. The XANES signatures of Zn in PM from both residual oil and diesel combustion processes were quite different from those of PM from coal combustion and suggestive of anhydrous zinc sulfate.

Comparison was also made of sulfur and zinc XANES spectra for PM collected on filters from the ambient atmosphere with those from the fossil fuel combustion processes. Significant differences were observed in both sulfur and zinc speciation.

Key Words : Element Speciation, XAFS spectroscopy, Airborne fine particulate matter, Fossil fuel combustion

1. Introduction:

There is currently much interest in the gases and particulate matter that avoid capture by environmental control devices and are emitted to the atmosphere during combustion of fossil fuels. Such emissions may arise from either stationary (e.g. oil or coal-based electricity generating plants) or mobile combustion sources (e.g. diesel or petroleum-based vehicle engines). They are believed to contribute significantly to the generation of fine ambient particulate matter in the atmosphere, which has been demonstrated to have adverse effects on human health, especially with respect to pulmonary and cardiovascular functions [1]. The U.S. Environmental Protection Agency (EPA) has therefore established limits on the occurrence in the atmosphere of ambient particulate matter (PM) less than $10\,\mu$m in size (PM_{10}) and has recently proposed additional limits on finer particle sizes that are less than $2.5\,\mu$m in

size ($PM_{2.5}$) [2,3]. Consequently, it is important to characterize emissions from combustion sources thoroughly in order to assess the importance of their contributions to ambient particulate matter and to determine the chemical transformations that such emissions undergo in the atmosphere resulting in the formation of ambient particulate matter.

Ambient particulate matter is a complex, heterogeneous material that exhibits significant variations with geographic location, meteorology, time-of-day, season of the year, and particle size [1,4-7]. The major contributions to the composition of ambient particulate matter are sulfur in the form of sulfate, nitrogen as nitrate or ammonia, carbon in both elemental and organic forms, and various minor inorganic species [1,4,5]. Its composition reflects both natural and anthropogenic source contributions that may be local or global in origin. Major sources are believed to include

combustion of fossil fuels, biomass combustion, agricultural and geological dusts, salts from sea spray, and road dusts from vehicular traffic. Since fracture and other clastic processes of soils and geological materials rarely produce particles less than 10 μm in size, it is likely that combustion processes, which are capable of producing extremely fine particles, will contribute proportionately more to the finest ambient particulate matter [1]. Hence, emissions from combustion processes are now under much greater scrutiny as a result of the U.S. EPA's decision to promulgate legislation on the finer PM$_{2.5}$ fraction of ambient particulate matter [2,3].

As part of programs designed to provide a better characterization of fine particulate matter, we have begun to examine key elements in materials collected from combustion sources and from the ambient atmosphere with XAFS spectroscopy [8-11]. Our objectives in this work are to compare and contrast the occurrence of sulfur and key metals, especially those designated in the 1990 Clean Air Act Amendments (USA) as hazardous air pollutants (HAPs) [12], in primary sources of particulate matter from combustion of fossil fuels. In this paper, we report on the occurrences of such elements in size-classified samples of fly ash from combustion of residual oil and coal in small-scale combustion facilities and in samples of fine particulate matter from combustion of diesel fuel in automotive engines, in addition to those in samples of ambient particulate matter (PM$_{2.5}$) collected on Teflon filters.

2. Experimental:

(a) Collection of Samples:

a. Residual Oil Fly-Ash:

Samples of residual oil fly-ash (ROFA) were supplied to us from the U.S. EPA's National Risk Management Research Laboratory (NRMRL), Research Triangle Park, North Carolina. The samples were collected by means of a cyclone collection device that separated the fly ash into coarse (cyclone, >2.5 μm, PM$_{2.5+}$) and fine (filter, <2.5 μm, PM$_{2.5}$) fractions after combustion of the residual oil in a 732 kW, three-pass fire tube boiler with relatively short residence times, which produced PM rich in unburned char (~60-90% carbon) [13]. An additional PM$_{2.5}$ sample was produced in a refractory-lined combustor with higher temperatures and longer residence times that are more characteristic of large oil-fired utility boilers, and contained essentially no unburned carbon [14]. These two systems represent extremes of the range of practical conditions under which fuel oils are burned. Four residual fuel oils, with sulfur contents ranging from 0.53 to 2.33 wt.% and ash contents from 0.02 to 0.1 wt.% were burned. These oils are identified in the tables and figures as low sulfur no. 6 (LS6), medium sulfur no. 6 (MS6), high sulfur no. 6 (HS6), and baseline no. 5 (BL5).

In addition, two cyclone ROFA PM$_{2.5+}$ samples were leached in high-purity water for 24 hours at room temperature to remove the soluble sulfates from these samples. Such leaching generated aqueous-insoluble residues from these cyclone samples for analysis by XAFS and other techniques. The chemical composition of these leached fractions were analyzed by a combination of X-ray fluorescence (solids) and ICP-MS (solutions).

b. Coal Fly-Ash:

Samples of fly-ash from coal combustion were prepared in combustion experiments conducted at EPA NRMRL using a down-fired, refractory-lined laboratory combustor rated at 50 kW. The samples were generated by combustion of three high-volatile bituminous coals from the eastern U.S., *viz.*, Ohio, Pennsylvania (Pittsburgh #8), and Western Kentucky, and four coals of differing ranks from the western U.S., viz., Utah (bituminous), Wyoming (Powder River Basin, subbituminous), North Dakota (lignite), and Montana (lignite). A cyclone apparatus separated the fly-ash particles into coarse (PM$_{2.5+}$) and fine (PM$_{2.5}$) fractions. For the Montana coal, an ultrafine fraction (<0.1 μm) was also separated. A more detailed description of the combustion apparatus and sampling procedure, as well as extensive chemical and size distribution analysis, is given elsewhere [13,14]

c. Diesel Particulate Matter:

Diesel particulate samples from two main sources have been examined: (i) samples from the exhaust stack of a heavy-duty diesel truck while it was driven over 190 miles at an average speed of 60 mph [9]; and (ii) samples from a laboratory-based engine (Kubota model Z482B) under idle and load conditions, while running on different fuel formulations [15]. In the former case, the samples of exhaust particulate matter were collected on quartz or teflon filters using a dilution sampler after exhaust gases from the engine had been sent through a 2.5 μm cyclone separator. In the latter case, bulk diesel particulate samples were collected by a Graseby-Anderson high volume sampler designed for collecting particulate matter less than 10 μm in size.

d. Ambient Particulate Matter

Ambient particulate matter was collected on the roof of a building on the campus of the University of Kentucky, Lexington, KY, using a Rupprecht & Patashnick Partisol Model 2000-FRM sampling apparatus. This sampler processes approximately 1.0 m^{3}h^{-1} of ambient air and collects PM$_{2.5}$ samples on 48 mm diameter teflon filters. Samples for analysis by XAFS spectroscopy were typically collected over a 4-day period.

(b) XAFS Spectroscopy and Other Measurements:

a. XAFS Spectroscopy:

XAFS spectroscopy was carried out at either beamlines X-18B and X-19A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, Long Island, NY, or at beamline IV-3 of the Stanford Synchrotron Radiation Laborator (SSRL), Stanford University, Palo Alto, CA. Similar XAFS techniques were used at both facilities. For metals less than about 1000 ppm in abundance, the absorption spectrum was collected in fluorescence geometry using a multi-element germanium detector [16]. This detector is gated electronically to enhance the collection of X-rays fluoresced by the element of interest and minimize background X-ray absorption. The spectral signal noise ratio was further enhanced using Soller slits and (Z-1) filters [17], where appropriate. Multiple scanning, providing a total counting time per point of up to 30 secs, was used for metals of the lowest concentrations. For metals of higher concentration, e.g. Fe in coal fly ash and V and Ni in ROFA, a Lytle detector (SSRL) or a PIPS detector (NSLS) was sufficient to acquire high quality spectra in fluorescence geometry [18]. Sulfur XAFS spectra were collected only at beamline X-19A of NSLS using a PIPS detector and a helium-filled sample chamber. A number of standard samples of the different elements of interest were also examined in the course of this investigation. Such standard compounds, diluted to between 2 and 5 wt% of the absorbing element in SOMAR mix and pelletized, were typically measured in fluorescence geometry and, if possible, also in absorption geometry using ionization detectors. For low atomic number elements, such as S and V, only the fluorescence

spectra of the standards were of adequate quality.

XAFS spectra were collected from 100 eV below the absorption edge of interest to as much as 1000 eV above the edge using a rotating double-crystal monochromator. Typically, three spectral regions were defined: (i) the pre-edge region below the edge, which was scanned coarsely at 2 eV/step merely to define the pre-edge slope; (ii) the X-ray absorption near-edge structure (XANES) region from about 20 eV below the absorption edge to as much as 50 eV above the edge, over which the step-size was reduced to between 0.1 eV/step for sulfur and 0.3 eV/step for Pb, and (iii) the extended X-ray absorption fine structure (EXAFS) region, from about 50 eV to as much as 1000 eV above the edge, which was scanned in reciprocal space units of typically 0.05 Å^{-1}/step. Data collected in the three regions were combined to give the overall XAFS spectrum. Energy calibration was achieved by measuring the spectrum of the appropriate metallic foil in absorption and then defining the zero-point of the energy scale for the element of interest as the first major peak in the derivative of the XAFS spectrum obtained for the metal foil. The zero-points of energy for the sulfur and arsenic XAFS spectra were defined by the positions of the major peaks in the spectra of elemental sulfur and As_2O_3, respectively. Where possible, such calibration spectra were collected simultaneously in an absorption experiment behind the fluorescence experiment. For low-Z elements (S-Cr), collection of the spectra of the primary standards had to be interspersed periodically between scans of the particulate matter samples.

Analysis of the XAFS spectra was carried out in the usual fashion that is well described in the literature [19-21]. First, the energy scale of the XAFS spectrum is calibrated with respect to the zero-point defined in the spectrum of the primary standard. The pre-edge slope is then removed from the spectrum and the resulting spectrum normalized to unit edge-step, that is, the rise in absorption at the edge. The spectrum is then divided into two separate regions: the X-ray absorption near-edge structure (XANES) region, typically from -40 eV to 120 eV, that includes the edge itself and the fine structure associated with the edge, and the extended X-ray absorption fine structure (EXAFS) region that consists of the oscillatory structure that diminishes in intensity away from the edge. For the EXAFS region, the structure above the edge is isolated from the edge itself, but the absorption variation remains normalized to the edge-step (chi units). The energy scale of this chi spectrum is then converted from eV to k-space units (k units or Å^{-1}) and the absorption is weighted according to standard practice by k^3 [19-21]. The oscillatory structure becomes periodic in k-space and, by means of the application of a Fourier transform to the k^3-weighted spectrum, it is converted to a radial structure function (RSF), which is basically a one-dimensional representation of the local structure around the absorbing atom.

The XANES region is generally used as a fingerprint of how the element occurs in the material of interest and it reflects largely the chemical bonding involving the atoms or ions of the element of interest. It is especially sensitive to the oxidation state of the element in question. The EXAFS region and corresponding RSF spectrum reflect more the local structure, that is the position, number and type of atoms that surround the atoms of the element of interest. Generally, the simpler and more symmetric the local structure, the richer and more extensive is the structure in the RSF.

In the case of mixtures of two or more species involving the element of interest, the analysis of the XAFS data becomes more complicated, but various least-squares methods of analysis and

other data reduction procedures can resolve and separate specific components. However, the efficacy and appropriateness of such procedures vary from element to element.

b. Other Methods:

The XAFS work described herein is but part of major characterization efforts designed to characterize more completely PM from fossil-fuel sources. In addition to XAFS spectroscopy, the samples or fractions of the samples are being characterized by chemical analysis methods (XRF, ICP-MS, PIXE), by other spectroscopic methods (EPR, ^{13}C NMR), by X-ray diffraction, by GC-MS techniques, and by ^{34}S isotopic methods. Some results of these studies have been given elsewhere [8-11,13,14,22,23] and will not be repeated here, except where needed to supplement the XAFS results.

3. Results and Discussion:

(a) Compositional Comparison:

Results from the XAFS spectroscopic methods will be discussed on an element-by-element basis to facilitate comparison of the data for the different types of PM samples. However, it is important also to have an awareness of the typical range of composition exhibited by the different sample types, and such compositional data for sulfur and several heavy metals in the different types of PM investigated in this study are presented in Table 1.

It is clear that PMs from different fossil-fuel sources have quite distinct compositions. The coal PM samples have much lower carbon contents than the ROFA or diesel PM samples, although the relative amount of particulate matter from coal combustion is typically much greater than that from either of the other sources because of the much higher content of ash-forming inorganics present in the solid fuel compared to the two liquid fuels. Sulfur contents for the different particulate matter samples (Table 1) are comparable, although significant variation may be encountered, particularly for coal PM, depending on the actual ash constituents. However, the relative proportions of metals are quite different for the three types. Whereas the ROFA PM is dominated by V, Ni, Zn and Fe, only Fe is significant in the coal PM (although several elements not listed, e.g. Si, Al, Ca, and K, may be of higher or of similar concentration to that of Fe in coal PM) and the diesel PM is very low in most metals, with the exception of Zn and Fe. In addition, coal PM contains some elements, e.g. As, that are not at all significant in PM from the other two fuels.

(b) XAFS Results:

a. Sulfur:

Sulfur is a major element in all fossil-fuel PM samples and it is also one of the key components in ambient PM samples [1] and in atmospheric chemistry [24]. Sulfur XAFS is especially useful because of the large range in energy exhibited by the major peaks of sulfur forms of different oxidation states. As described in detail elsewhere [25-28], the peak position of different sulfur forms varies from -2.5 eV for metallic sulfides (sulfur formally as S^{2-}) to 10.2 eV for ionic sulfates (sulfur formally as S^{6+}), relative to the peak arising from elemental sulfur that occurs by definition at 0.0 eV. Various least-squares fitting methods have been developed [25,26,28] to extract quantitative information on sulfur forms in fossil fuels and similar procedures have also been applied to sulfur XANES spectra of fly-ash and particulate matter [8,11]. Examples of the fitted sulfur XANES spectra are given in Figure 1 for PM from different types of fossil fuels and the results of the

Table 1 : Comparison of Compositions exhibited by Particulate Matter
from Different Sources of Fossil Fuel Combustion

	ROFA PM*	Coal PM*	Diesel Exhaust PM+
C, wt% (LOI)	65 – 95%	1.7 – 15.7%	**
S, wt%	0.5 – 2.4%	<0.05 – 1.2%	0.02 – 0.1%
V, ppm	4,500 – 60,000	85 – 360	<dl
Cr	<dl	18 – 150	15 - 75
Fe	1,100 – 5,500	4,000 – 120,000	110 - 250
Ni	800 – 11,000	30 – 150	10 - 40
Cu	<50 – 1,050	45 – 105	5 - 125
Zn	300 – 21,000	32 – 750	50 - 1350
As	<dl	45 – 500	<dl
Pb	<20 – 1,000	6 – 95	8 - 20

*This study, see also Refs. [8,13,14].
+Personal communication, (J. D. Robertson et al., 2001)
**Not determined, but anticipated to be >98%.

least-squares fitting is summarized in Table 2 for each type of PM. As Table 2 indicates, the sulfur forms in PM samples from different sources are somewhat similar in that they consist mainly of sulfate forms, but the minor components appear to show some systematic differences from source to source. Thiophenic sulfur, which derives from the presence of aromatic organic sulfur forms in the original fossil fuel, is present in most PM samples in minor amounts. Its presence is related to incomplete combustion of the carbonaceous components in the fuels. In addition to sulfate and thiophene, other sulfur forms may be present in lesser amounts depending on the source of the PM. Additional minor sulfur forms identified in ROFA PM include metal sulfides and elemental sulfur, which are significant when residual oil is burnt under lean conditions. Elemental sulfur is also often observed as a minor constituent of coal PM. Furthermore, the presence of sulfite (SO_3^{2-}) has been noted in the PM samples from western US coals [11] and may be characteristic of high calcium coals. As has been reported previously [29], the presence of bisulfate (HSO_4^-) in diesel PM samples is sometimes observed as a prominent shoulder on the low-energy side of the sulfate peak (Figure 1c). However, it is difficult to distinguish this sulfur form from sulfone, which can also occur in PM samples from diesel engines [9], and the data listed in Table 2c are undifferentiated with respect to these two sulfur forms.

For both ROFA and coal combustion, thiophenic sulfur and other reduced sulfur forms (elemental sulfur, metal sulfide) are significantly more abundant in the coarser $PM_{2.5+}$ fractions than in the corresponding $PM_{2.5}$ fraction. This observation is interpreted to imply that the carbonaceous particulate matter in these PM samples are residual particles formed directly from incompletely combusted carbon-rich particles of coal or droplets of oil, and are not formed by condensation of vaporous organic species.

Most recently, we have started to examine leached ROFA PM samples with XAFS spectroscopy in order to establish which elements can be readily leached from the PM by aqueous solutions. The sulfur XANES spectrum of one ROFA PM sample is shown in Figure 2, along with the spectrum of the corresponding unleached PM sample. Such spectra clearly show that the sulfates present in the ROFA PM samples are almost completely soluble in H_2O, whereas the other sulfur forms present in the sample (thiophene, elemental sulfur, metal sulfides) are insoluble. As shown further below, XAFS spectra of metals in such leached samples provide unmistakable proof of the presence of specific metal sulfides, such as nickel sulfides, in the ROFA $PM_{2.5+}$ samples and raise some interesting questions about sulfur chemistry in the transition between primary sources of PM and the ambient PM

we encounter.

b. Metals:

Metals in fine PM are of interest because of their possible adverse effects on human health and their use for source
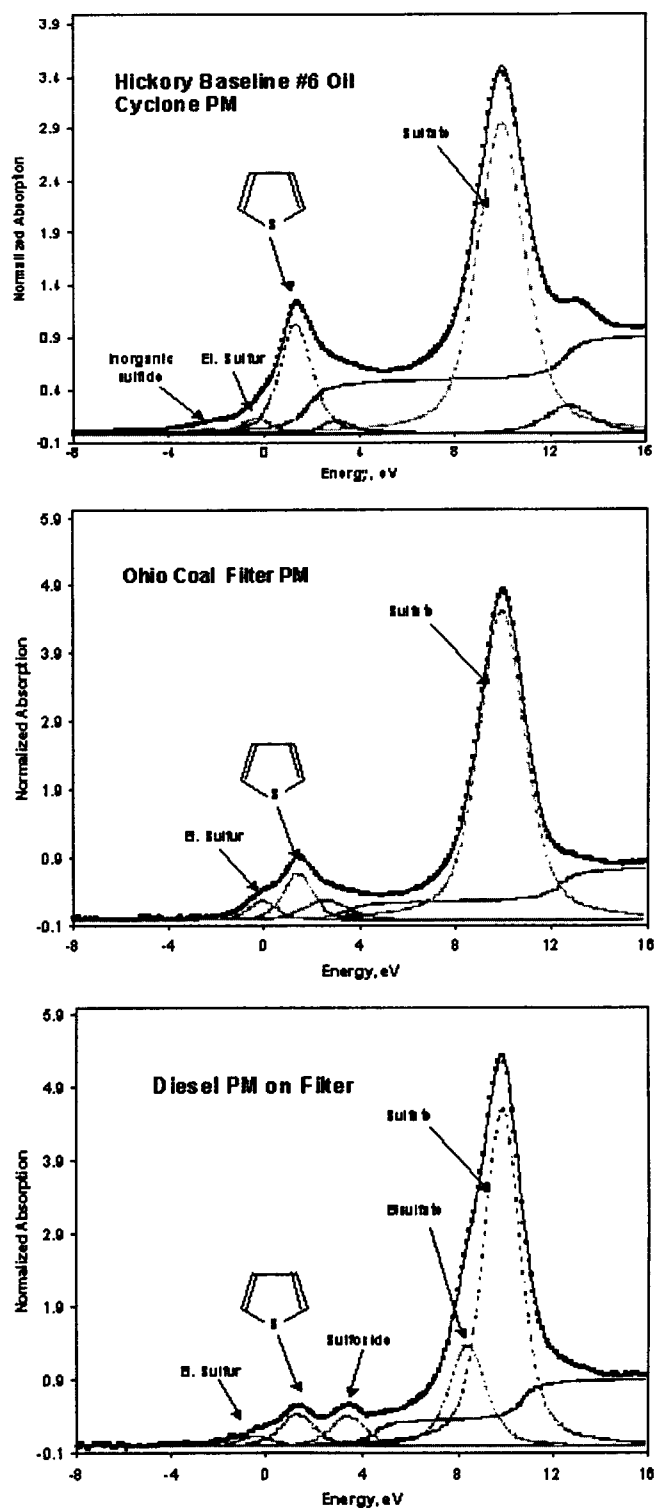

Figure 1 : Three examples of least-squares fitted sulfur XANES spectra from different types of PM samples: top: spectrum from coarse $PM_{2.5+}$ fraction from residual oil combustion; center: spectrum from fine $PM_{2.5}$ fraction from bituminous coal combustion; bottom: spectrum from $PM_{2.5}$ collected on a filter from diesel exhaust of truck.

Table 2a : Summary of Results from Least-Squares Analysis of S XANES Spectra of Particulate Matter Samples from Residual Oil Combustion.

PM Sample	% of Total Sulfur present in Different Forms				
	Sulfate	Thiophene	Elem. S	Sulfide[+]	Other**
No. 5 PM$_{2.5}$	55	24	5	11	5
No. 5 PM$_{2.5+}$	32	37	8	19	4
Low S No. 6 PM$_{2.5}$	84	14	0	0	2
Low S No. 6 PM$_{2.5+}$	58	34	6	0	2
Med. S No. 6 PM$_{2.5}$	73	13	6	0	8
Med. S No. 6 PM$_{2.5+}$	55	35	6	0	3
High S No. 6 PM$_{2.5}$	54	29	5	11	1
High S No. 6 PM$_{2.5+}$	26	39	9	26	0
High S No. 6 PM$_{2.5}$ (filter)*	100	0	0	0	0
Hickory No. 6 PM$_{2.5}$	94	6	0	0	0
Hickory No. 6 PM$_{2.5+}$	56	28	4	12	0

*Sample captures on filter from refractory furnace
**Minor amounts of sulfoxide and/or sulfone
+Metal or inorganic sulfide.

Table 2b : Summary of Results from Least-Squares Analysis of S XANES Spectra of Particulate Matter Samples from Coal Combustion.

PM Sample	% of Total Sulfur present in Different Forms				
	Sulfate	Sulfite	Thiophene	Elem. S	Other*
Eastern Coals:					
W. Kentucky PM$_{2.5}$	94	0	6	0	0
W. Kentucky PM$_{2.5+}$	82	0	15	0	3 sulfox.
Pittsburgh #8 PM$_{2.5}$	96	0	4	0	0
Pittsburgh #8 PM$_{2.5+}$	87	0	10	3	0
Ohio PM$_{2.5}$	87	2	11	0	0
Ohio PM$_{2.5+}$	66	0	28	6	0
Western Coals:					
N. Dakota PM$_{2.5}$	84	3	11	2	0
N. Dakota PM$_{2.5+}$	76	4	14	0	7 pyrrh.
Wyodak PRB PM$_{2.5}$	99	0	1	0	0
Wyodak PRB PM$_{2.5+}$	95	2	0	3	0
Montana UF	93	0	7	0	0
Montana PM$_{2.5}$	100	0	0	0	0
Montana PM$_{2.5+}$	89	10	1	0	0
Utah PM$_{2.5}$	86	0	14	0	0
Utah PM$_{2.5+}$	82	0	18	0	0

*Sulfox. – sulfoxide; pyrrh. – pyrrhotite, Fe$_{1-x}$S.

Table 2c : Summary of Results from Least-Squares Analysis of S XANES Spectra of Particulate Matter Samples from Exhausts of Diesel Test Engines

PM Sample	% of Total Sulfur present in Different Forms				
	Sulfate	Bisulfate and/or sulfone	Sulfoxide	Thiophene	Elem. S
Truck Exhaust:					
Diesel Filter PM1	90	7	0	3	<1
Diesel Filter PM2	86	8	0	6	<1
Diesel B2 9/99	98	2	0	0	<1
Diesel C2 9/99	84	11	0	5	<1
Utah Test Engine:					
No Additive, at idle	67	9	1	16	6
No Additive, at load	64	18	0	13	5
Mixture #5, at idle	67	17	1	10	6
Mixture #5, at load	74	8	1	13	3
DEC Additive, at idle	55	22	1	13	8
DEC Additive at load	55	21	0	17	7

DEC – Diethyl carbonate, (C$_2$H$_5$O)$_2$CO

pportionment. As suggested by a recent Canadian study [30], metals in fine PM appear to be implicated with adverse health effects. One proposed theory is that iron and other transition metals promote the formation of reactive oxygen radical species that impair lung function [31,32]; however, such metals must be bioavailable [32,33]. Therefore, it is important to speciate the occurrence of metals in fine PM. Furthermore, the spectral signatures of certain metals may be useful for source apportionment studies. It is well known that chemical composition can be used as a means to

apportion sources to ambient PM [34-37]. In this study, a unique suite and sequence of metallic components of varying concentrations characterizes each source of fossil-fuel based PM (Table 1). PM from residual oil combustion is characterized by decreasing concentrations of first series transition metals and certain HAPs elements approximately in the order [8,14]:

V>Ni, Fe, Zn, >Cu, Pb Mn>Cr, As.

In contrast, for PM from combustion of US coals, the corresponding trend is [14,38]:

Fe>>Ti>Mn, >V, Cr, Zn>Ni, Cu, As, Pb>Co>Se.

While for the diesel PM samples from Utah, the trend was found to be [39]:

Zn, Fe>>Cu, Cr, Ni>Pb>>As.

Similar trends, and incorporating actual chemical concentration data for most elements, are used as input in chemical mass balance receptor models [34-37] that apportion elemental concentrations in ambient PM to specific sources. By including individual elemental XAFS spectral signatures in such modeling, it may be possible to add a further dimension to such models. Here we present data for some of the elements in these different materials and assess the uniqueness of the spectral data for possible source apportionment applications.

Zinc: Zinc is one element that exists in all three fossil-fuel based PMs in sufficient quantities for analysis by XAFS spectroscopy. Furthermore, it illustrates most of the different aspects of the technique that can be brought to bear on the problem of speciating elements in complex materials like PM. Figure 3 illustrates the different zinc XANES spectra and the corresponding RSFs recorded for coal-derived PM samples. As can be seen, PM from eastern U.S. coals (Pittsburgh #8 and W. Kentucky samples) have very similar and characteristic zinc XANES spectra. The triple-pronged main peak can be identified readily as arising from a spinel phase of composition close to ZnFe$_2$O$_4$. In addition, the RSFs consist of two main peaks at 1.60 and 3.25 Å (phase shift uncorrected),
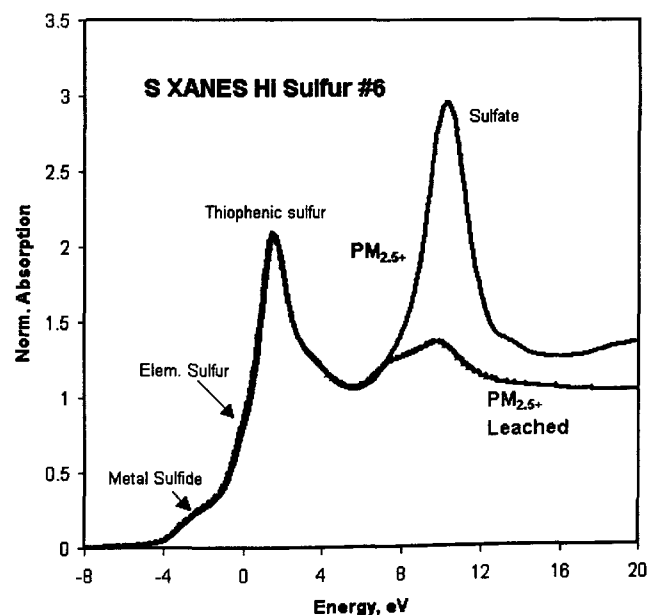

Figure 2 : Sulfur K-edge XANES spectra showing difference in sulfur forms before and after aqueous leaching of high-sulfur No. 6 ROFA PM$_{2.5+}$ sample.

which are again consistent with the zinc in the spinel structure.

The spectral data for zinc in PM from western U.S. coals (Utah and Montana samples) are somewhat different; in particular, the second peak at 3.25 Å in the RSFs is not nearly so prominent, if present at all. The Zn XANES spectra from these samples exhibit more variation than those from the eastern coal PM and suggest that the zinc speciation in the western coal PM is more complex and based on a mixture of phases, but which include only minor $ZnFe_2O_4$ at most. Quite different Zn XANES spectra were observed for the Montana $PM_{2.5}$, $PM_{2.5+}$, and ultrafine samples, which would appear to indicate that the zinc speciation varies significantly with particle size. However, whether such differences are due just to compositional differences or also reflect different formation mechanisms for the Zn species in the different size ranges remains to be established.

As shown in Figure 4, the XANES spectra of zinc in ROFA PM and diesel PM samples are different from those of coal PM and have been interpreted as being dominated by zinc sulfate [8,10,40]. The small variations in the spectra of these PM samples may indicate the presence of additional minor forms of zinc; however, species such as ZnS or zinc ferrite do not appear to be present in significant quantities [10,40]. Alternatively, the variation

in the zinc XANES spectra might be accounted for by differences in the hydrated nature of the zinc sulfate or possibly due to the zinc being incorporated in the crystal structure of a more abundant sulfate (e.g. $NiSO_4.xH_2O$ in the case of the ROFA PM).

Vanadium: Vanadium is usually the most abundant metal in PM from combustion of residual oil. It is of much lower concentration in coal-based PM and insignificantly low in diesel PM. Consequently, vanadium is only likely to be of concern with respect to health issues in PM arising from residual oil combustion. Again, speciation is important, because the major health concerns regarding vanadium focus on the toxicity of soluble vanadate compounds [41].

In our preliminary XAFS studies on vanadium in ROFA PM [8], similarities were noted between the vanadium XANES spectra of the PM samples and that of vanadyl sulfate $(VOSO_4.xH_2O)$, indicating that it is the major vanadium component. However, there are certain XANES features that needed to be examined in more detail, specifically a large pre-edge peak related to the dipole-forbidden $(1s \rightarrow 3d)$ transition at about 4-5 eV and the region inclusive of and above the K absorption edge. The PM samples in this study exhibit pre-edge peaks in the range 4.75 ± 0.35 eV in comparison with 4.6 eV found for vanadyl sulfate, which is consistent with the reported values for other V(IV) complexes [42,43]. The main features of the pre-edge peak (i.e. intensity and width) and its position for PM samples vary with respect to that of vanadyl sulfate. Such variation in width and position of pre-
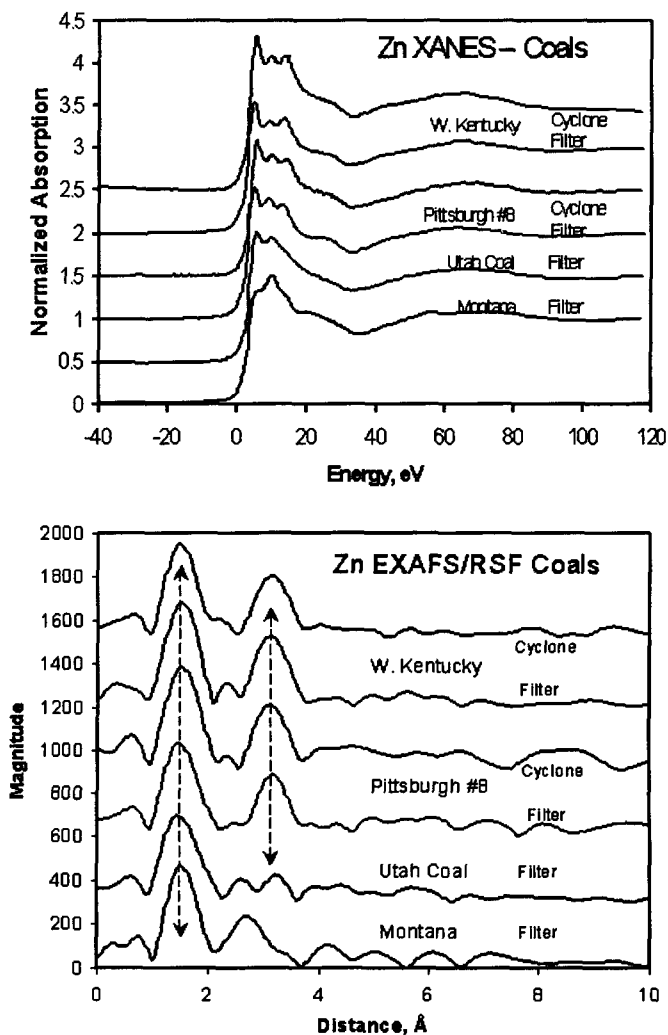

Figure 3 : Zn XAFS data for selected coal-derived PM samples: top: Zn XANES spectra; bottom: EXAFS/RSF spectra.
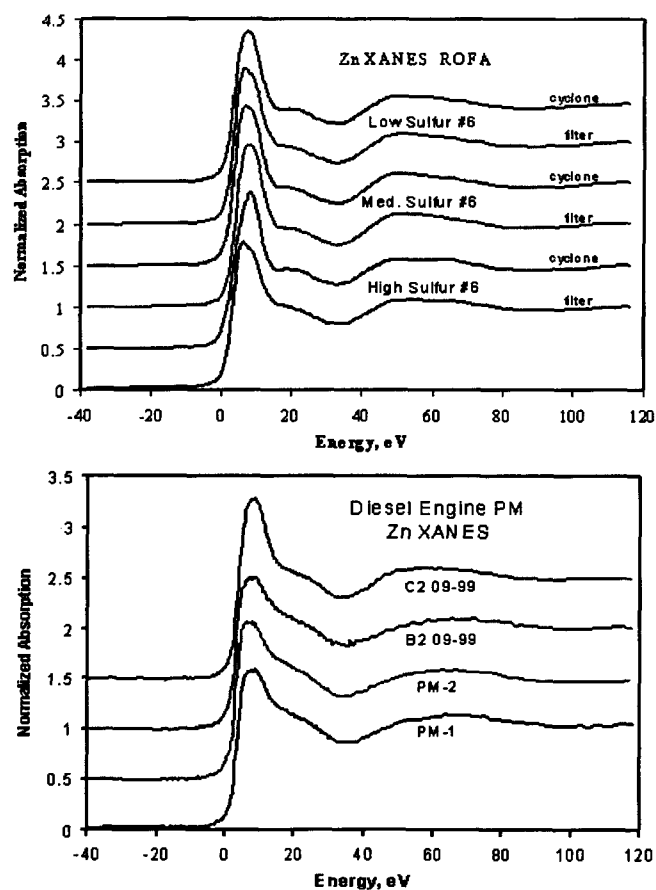

Figure 4 : Zn XANES spectra of selected PM samples: top: from residual oil combustion sources; bottom: from the exhaust of diesel truck engines.

Table 3 : Summary of results from least-squares fitting of Ni XANES and
EXAFS data

ROFA PM Sample	%Ni in sample in the form of					
	Ni sulfate		Ni subsulfide		Ni ferrite	
	XANES	EXAFS	XANES	EXAFS	XANES	EXAFS
HS6₂.₅	95	96			5	4
MS6₂.₅	96	93			4	7
LS6₂.₅	70	76			30	24
HS6₂.₅₊	83	87	17	13		
MS6₂.₅₊	84	90	16	10		
LS6₂.₅₊	80	89	20	11		

edge peaks can be explained by geometrical distortions within the vanadium-ligand polyhedron [43]. Such features are under active investigation and will be discussed in detail in the paper in preparation [40]. It does not appear that any vanadium sulfide is formed, in contrast to what has been observed for less electropositive metals (Fe, Ni, Cu) and it is suspected that one or more vanadium oxides may be present; however, this remains to be demonstrated.

Nickel: Nickel is an important component in ROFA PM, in which it is generally the second most abundant metal, but its occurrences in coal and diesel PM are much lower. Furthermore, there is much concern [41,44,45] about possible formation in ROFA PM of nickel subsulfides (Ni_xS_y, where x > y), which are reported to be carcinogenic [45]. At first inspection [8], the Ni K-edge XAFS spectra of the ROFA PM samples indicated that $NiSO_4.xH_2O$ is the major form of Ni present in the ROFA PM samples, in agreement with earlier investigations [46,47]. However, it was also observed that there were weak additional absorption features that could not be accounted for by nickel sulfate alone, for example, a small shoulder in the range 0-10 eV in most $PM_{2.5+}$ samples and a broad peak at about 35 eV in some $PM_{2.5}$ samples. Further analysis has enabled us to attribute such features to nickel sulfide and $NiFe_2O_4$, respectively. As discussed in detail elsewhere [10,40], the XANES and EXAFS regions of the Ni XAFS spectra of various ROFA PM samples have been analyzed independently by least-squares fitting to linear combinations of the spectra of various model compounds. The results of the two fitting approaches agree well (Table 3). $NiSO_4.xH_2O$ was indeed found to be the dominant nickel form, present in all of the ROFA PM samples. $NiFe_2O_4$ was found to be the second most common phase observed in the $PM_{2.5}$ samples; but it occurred only in a significant amount in the low-sulfur No. 6 oil $PM_{2.5}$ sample generated by combustion of the lowest sulfur fuel oil. A small amount (10-20%) of the Ni in the $PM_{2.5+}$ samples appears to be present as a nickel subsulfide, which as noted above, can be toxic and carcinogenic. Among the three nickel sulfides (i.e. NiS, NiS_2 and Ni_3S_2) included in the least-squares fitting as possible secondary sulfide phases, it was Ni_3S_2 that gave the lowest sum-of-squares residual factor with an energy shift of only about 1 eV. Such a result suggests that Ni_3S_2 is the most likely nickel sulfide present in the $PM_{2.5+}$ samples of the three candidate nickel sulfide standards considered.

Figure 5 shows a comparison of Ni K-edge XANES spectra of high sulfur No. 6 oil $PM_{2.5+}$ sample before and after leaching, with that of the corresponding $PM_{2.5}$ sample. The comparison clearly shows that the leached residue of the $PM_{2.5+}$ is mostly nickel sulfide. This simple chemical test readily confirms the presence of nickel subsulfide that was inferred from the least-squares refinements. The presence of nickel subsulfide was not observed in

previous studies [46,47] of commercial ROFA PM and this difference suggests strongly that the short residencetime conditions under which the experiments were run in the experimental furnace are largely responsible for the presence of nickel subsulfide. Hence, to ensure that such potentially harmful species are not formed in commercial operation, it is essential that the combustion be as complete as possible.

Chromium: In contrast to vanadium and nickel, chromium is of more concern in PM generated by coal combustion than in PM from residual oil or diesel combustion. In part, this is because of the higher concentration of chromium in coal PM and in part because the toxic and carcinogenic oxidation state of chromium, Cr(VI), has been observed previously in coal-based fly-ash [48,49]. Figure 6 shows the chromium XANES obtained for coal-based PM samples investigated in this study. It can be seen that the pre-edge peak at about 4 eV, the intensity of which is a measure of the fraction of chromium as Cr(VI), is enhanced to a small degree for some of the PM samples. In order to estimate the fraction of Cr(VI) in these samples, the same least-squares method of fitting the pre-edge peak [49] that was developed for quantifying the Cr(VI) contents of coal-based fly-ash was applied to the spectra of the coal-based PM samples. The results of such fitting are summarized in Table 4.

It can be seen from Figure 6 and Table 4 that the PM samples with measurable amounts of Cr(VI) derive exclusively from western U.S. coals. No Cr(VI) was detected in any of the PM samples from eastern U.S. coals. As the PM samples were prepared under similar conditions, this difference clearly indicates that there is a significant difference in the chemical behavior of chromium in the two types of ash. It is well known that coals from the western regions of the U.S. are generally much richer in calcium and contain it in different forms (i.e. carboxyl-bound Ca) than their eastern counterparts. It is therefore conceivable that there is interaction between Cr and Ca that results in the formation
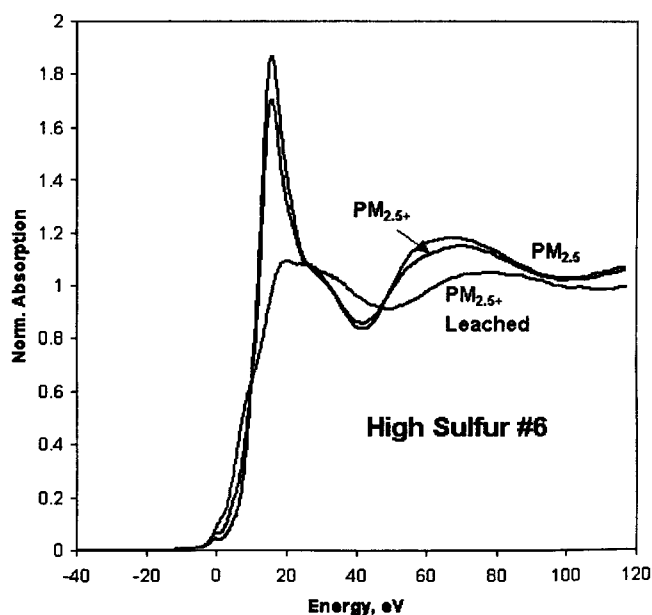

Figure 5 : Nickel XANES spectra of the high sulfur No. 6 ROFA $PM_{2.5}$ and $PM_{2.5+}$ samples and of the same $PM_{2.5+}$ sample after aqueous leaching.

Table 4 : Speciation Results for Cr and As in Coal-derived PM

Sample	Chromium		Arsenic	
	Cr(III)	Cr(VI)	As(III)	As(V)
W. Kentucky PM₂.₅	>97	<3	<10	>90
W. Kentucky PM₂.₅₊	>97	<3	<10	>90
Pittsburgh #8 PM₂.₅	>97	<3	<10	>90
Pittsburgh #8 PM₂.₅₊	>97	<3	<10	>90
Ohio PM₂.₅	>97	<3	<10	>90
Ohio PM₂.₅₊	nd	nd	<10	>90
N. Dakota PM₂.₅	94	6	<10	>90
N. Dakota PM₂.₅₊	nd	nd	<10	>90
Wyoming PRB PM₂.₅	(80)	(20)	<10	>90
Wyoming PRB PM₂.₅₊	79 (89)	21 (11)	<10	>90
Montana UF	>97	<3	<10	>90
Montana PM₂.₅	74	26	<10	>90
Montana PM₂.₅₊	84	16	<10	>90
Utah PM₂.₅	91 (91)	9 (9)	<10	>90
Utah PM₂.₅₊	(95)	(5)	<10	>90

nd – not determined. Values in parentheses obtained at NSLS X-19A.
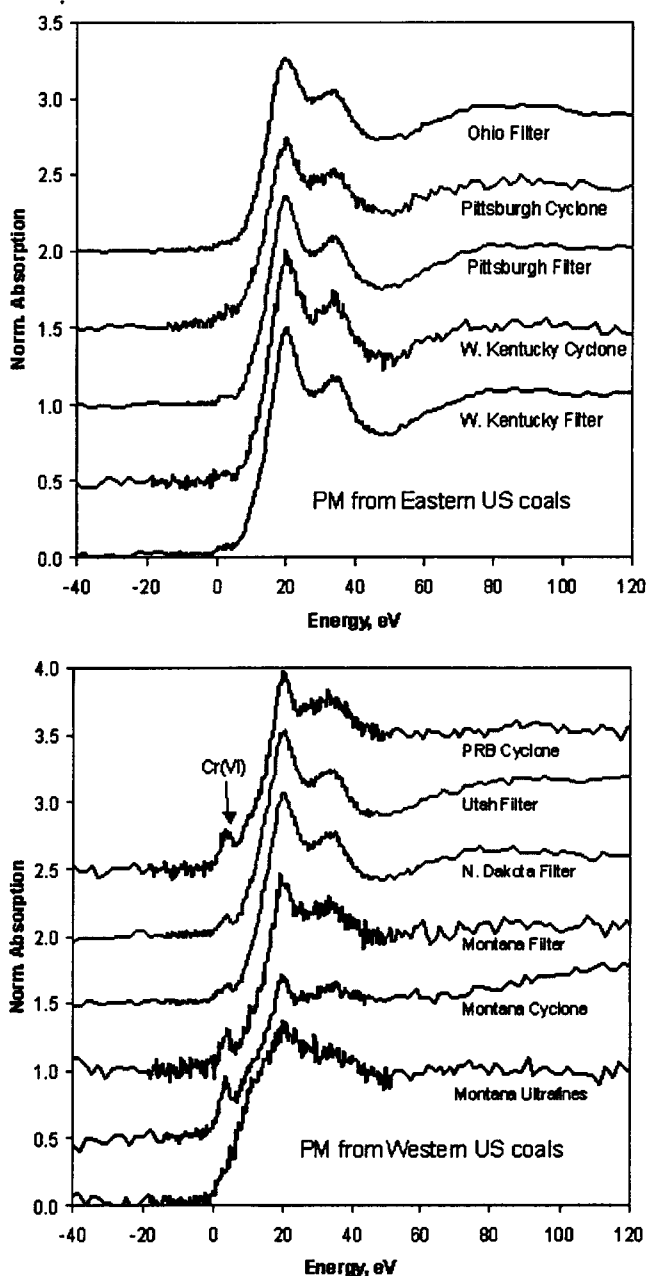
Figure 6 : Chromium XANES spectra for selected coal PM samples: top: PM from eastern U.S. coals; bottom: PM from western U.S. coals. Note the occurrence of small peak due to Cr(VI) in the PM from western U.S. coals.

of a stable calcium chromate species. Whether such interaction is also a function of the speciation of Cr in these coals remains to be established.

Arsenic: Arsenic is only considered to be of significance in PM from coal combustion as its presence in residual oil and diesel-based PM is below detection (Table 1). Nevertheless, arsenic in ROFA PM can be detected by XAFS spectroscopy (Figure 7) and the data are of sufficient quality in certain cases to extract a reasonable RSF (Figure 7b). The As XANES and RSF spectra from coal PM are very similar to those from the ROFA PM (Figure 8). As indicated by the principal XANES peaks at approximately 3.5-4.0 eV and RSF peaks at 1.25-1.30 Å (phase-shift uncorrected), all of the arsenic appears to be present as arsenate (AsO_4^{3-}) complexes in both types of PM (Table 4). Furthermore, there appears to be little difference between the occurrences of arsenic in the coarse and fine fractions, except as noted previously in concentration. Consequently, although the As XAFS data indicate that As^{3+}, the most toxic oxidation state of As [50], is not detectable in these primary combustion sources of PM, the As XAFS signatures appear not to be very useful for source apportionment purposes. However, as noticed previously
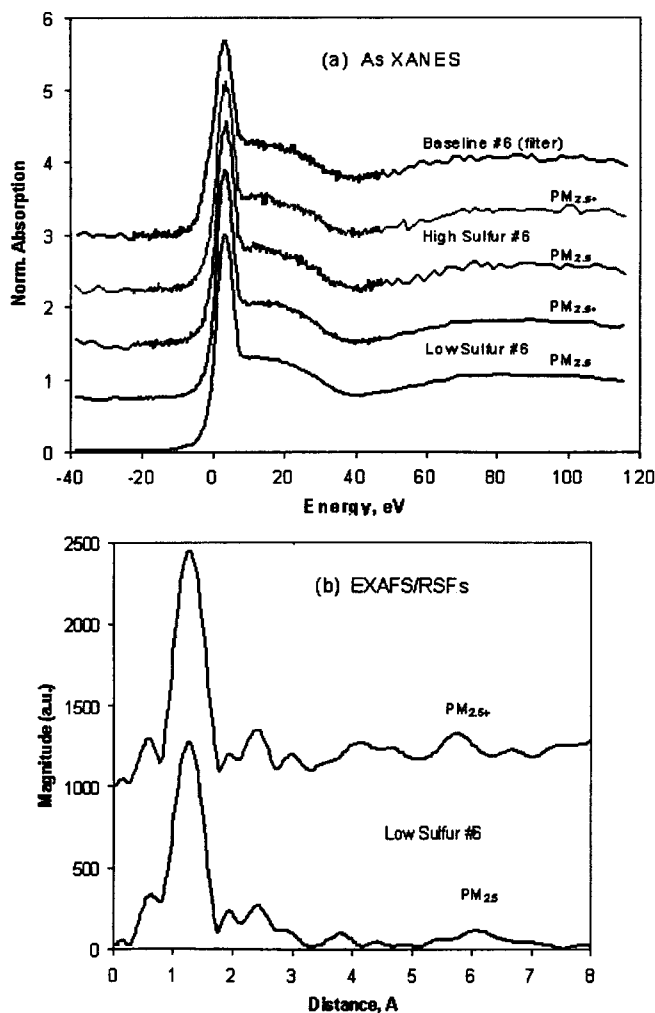

Figure 7 : As XAFS data for selected ROFA-derived PM samples: top: As XANES spectra; bottom: EXAFS/RSF spectra. Positions of major peaks in both plots clearly indicate that As is present entirely as As^{5+} in arsenate complexes.

for bulk fly-ash [51], there are some quite subtle differences in the As XANES spectra between PM from eastern and western U.S. coals that may yet have value for discrimination purposes.

Iron: Iron is not generally thought of as a hazardous element, but recent work [31-33] has suggested that biosoluble iron derived from PM may have a deleterious effect on human health by catalyzing the formation of reactive oxygen species within the lungs. Furthermore, iron is one of the more common metals in many sources of PM, particularly from coal combustion (Table 1). A number of XAFS spectra of iron in PM samples from fossil-fuel combustion sources have been obtained and some preliminary XAFS data on iron in ROFA PM have been presented previously [8,10]. However, for coal-based PM especially, the information obtained by XAFS spectroscopy is neither as specific nor as reliable as that obtained from ^{57}Fe Mössbauer spectroscopy and data from this latter technique, when it becomes available, will no doubt supersede the results obtained from XAFS data. One advan-

tage that XAFS spectroscopy does have over Mössbauer spectroscopy is that it is sensitive to much lower concentrations of iron. Hence, for diesel exhaust PM and certain ROFA PM samples, in which the concentrations of iron are less than about 0.25 wt%, Fe XAFS spectroscopy is the only technique that is viable.

Preliminary analysis [8,10] of iron XAFS spectra of ROFA PM indicated that iron is present as predominantly ferric sulfates, minor oxide species, and, in $PM_{2.5+}$ samples [10], some minor iron sulfide (pyrrhotite, $Fe_{1-x}S$). However, that may need to be revised in view of the response of the ROFA samples to aqueous leaching. Unlike nickel, in which virtually all of the Ni-O (sulfate) species were dissolved by water (Figure 5), a significant fraction of the iron remains bound to oxygen in the residue after aqueous leaching of the $PM_{2.5+}$ samples (Figure 9). This suggests that a more significant fraction of the iron may be present in insoluble iron oxide or oxyhydroxide forms. In addition, there are many varieties of iron sulfates [52] and more evidence is needed to define which iron sulfate is dominant in order to model the XAFS data most precisely.

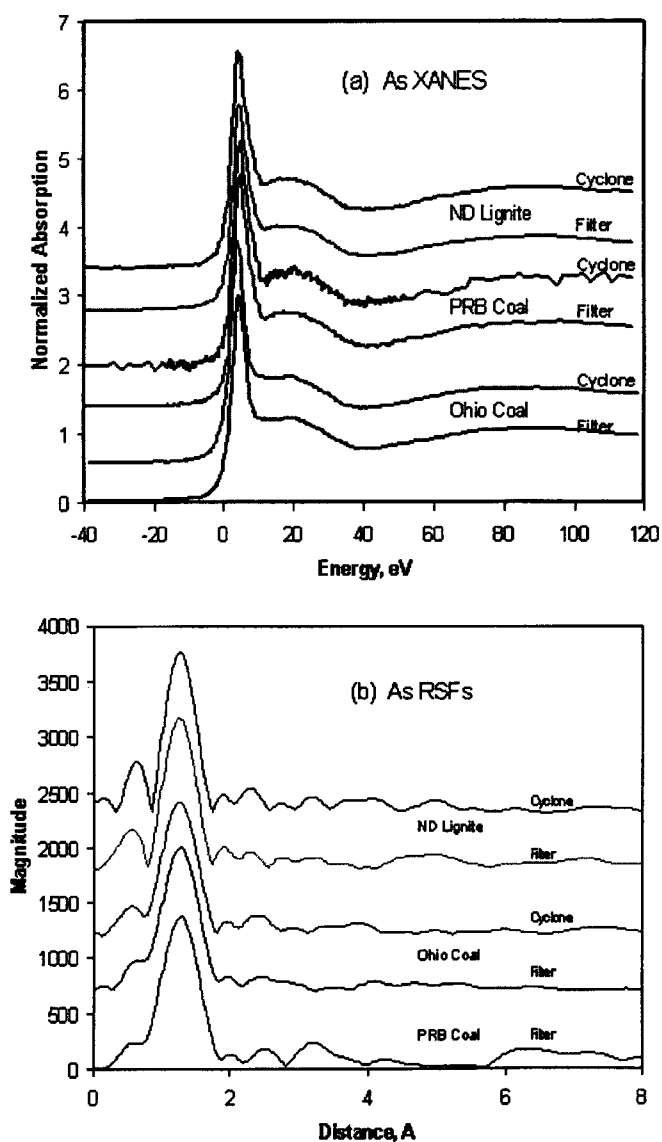*Other Metals:* A number of other elements have been exam-

Figure 8 : As XAFS data for selected coal-derived PM samples: top: As XANES spectra; bottom: EXAFS/RSF spectra. Positions of major peaks in both plots clearly indicate that As is present entirely as As^{5+} in arsenate complexes.
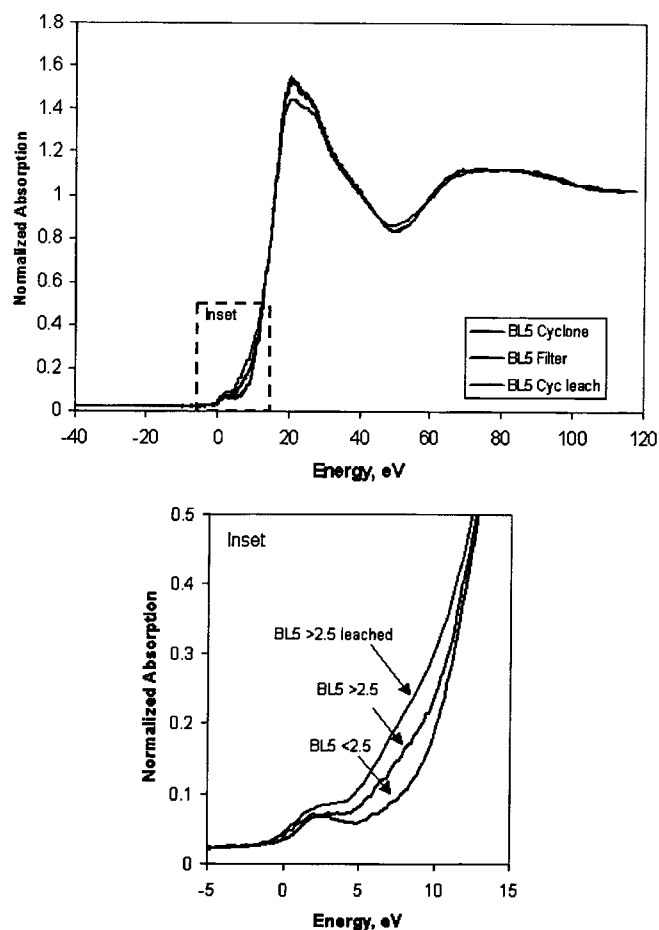
Figure 9 : Iron XANES spectra showing differences between ROFA PM Baseline #5 filter (PM<2.5) and cyclone (PM>2.5) samples and between before and after aqueous leaching of the cyclone (PM>2.5) sample. Inset shows region of maximum difference between spectra and indicates the presence of iron sulfide in the leached and unleached cyclone (PM>2.5) samples.

ined cursorily in various suites of PM samples using XAFS spectroscopy. Preliminary results for Pb and Cu in ROFA PM have been discussed elsewhere [8,10,40].

c. Ambient PM

We have recently started to examine the occurrence of sulfur and some of the key metallic elements in ambient $PM_{2.5}$ samples collected in a FRM sampler on the roof of a building in Lexington, KY. We found that quite good XAFS spectra can be obtained after 4 days of sampling; in that time, a reasonably complete and uniform layer of particulate matter has accumulated on the filter that is amenable to measurement by XAFS spectroscopy. Our intention is to compare and contrast the occurrences of sulfur and metals found in ambient air with those inferred above for primary sources of $PM_{2.5}$. In this way, we can assess the usefulness of XAFS spectroscopy as a fingerprinting method for source apportionment as well as using the technique as a means to identify directly potentially hazardous occurrences of metals in ambient $PM_{2.5}$.

Figure 10 shows the least squares fitted sulfur XANES data for an ambient filter sample. This spectrum should be compared with the corresponding sulfur XANES spectra for the three primary
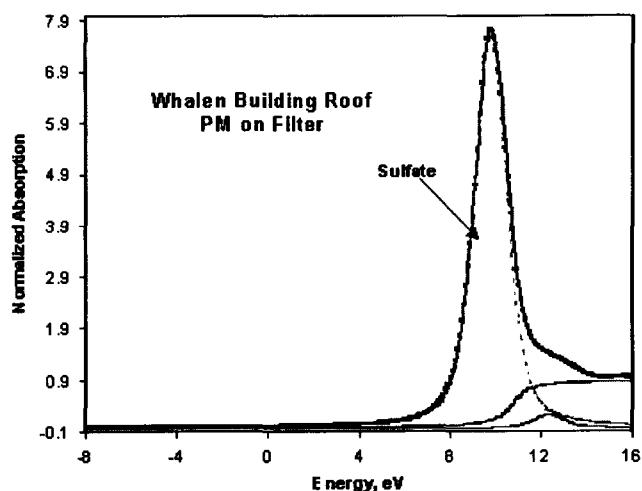

Figure 10 : Sulfur XANES spectrum of ambient $PM_{2.5}$ collected in FRM sampler from the roof of the Whalen Building, Lexington, KY.
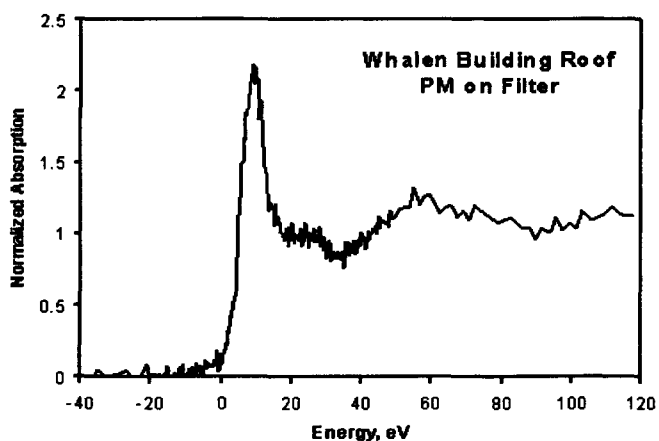

Figure 11 : Zinc XANES spectrum of ambient $PM_{2.5}$ collected in FRM sampler from the roof of the Whalen Building, Lexington, KY.

sources of $PM_{2.5}$ shown in Figure 1. As can be seen from this comparison, the sulfur XANES spectrum of the ambient air $PM_{2.5}$ sample differs from the other PM samples by exhibiting only a single peak in its sulfur XANES spectrum. This peak arises from sulfate occurrences of sulfur. There is no evidence for any thiophenic and other reduced forms of sulfur in the ambient $PM_{2.5}$ sample that are so common in the $PM_{2.5}$ samples we have examined from the primary fossil-fuel combustion processes. Owing to their lack of solubility in water (see Figure 2, and related discussion), it might be expected that the reduced forms of sulfur would be the ones that persist once they are incorporated in the fine particulate matter in the atmosphere, while the sulfate species would be removed by dissolution in meteoric water. However, that does not appear to be the case. Rather, it would appear that a secondary sulfate is being formed in the atmosphere either as a result of a chemical reaction between SO_x molecules or sulfate anions (SO_4^{2-}) and a basic gas (e.g. ammonia, NH_3) or as components come in contact with the filter. Furthermore, the lack of a thiophenic signature in the ambient $PM_{2.5}$ may also imply that the carbonaceous forms (i.e. elemental carbon, organic carbon) present in ambient particulate matter have their origin elsewhere than in primary emissions from fossil-fuel combustion. Clearly, these observations resulting from sulfur XAFS studies have important ramifications and further work is planned to explore this direction in more detail.

Figure 11 shows the zinc XANES spectrum for a sample of $PM_{2.5}$ collected in the FRM sampler. As was seen for sulfur, the spectral signatures of zinc in the $PM_{2.5}$ from primary fossil-fuel sources (Figures 3 and 4) are rather different from that of the $PM_{2.5}$ collected on the ambient filter. In particular, the spectra of zinc in coal PM are very different. Based on previous work with zinc standards [29], it appears likely that the spectrum of the ambient $PM_{2.5}$ represents hydrated zinc sulfate $(ZnSO_4.7H_2O)$, as this zinc standard comes closest to exhibiting the same spectrum as that of the $PM_{2.5}$ sample. However, there are similarities between the Zn XANES spectra from the ROFA PM and those of diesel exhaust PM and it is conceivable that the spectra of these samples may also derive from zinc sulfate, as sulfates would appear to be the most likely zinc phases formed in such systems. For these primary PM materials, however, the zinc sulfate would be anhydrous or at least less hydrated and this may account for the difference in appearance of their spectra when compared with that of the secondary PM. Further work, both on the variation of zinc sulfate with composition (waters of hydration) and on the effect of aqueous leaching of these PM materials, needs to be carried out. However, it would appear safe to conclude that, during the 4-day period when the ambient sample was collected, the zinc in the air in Lexington did not derive significantly from coal combustion, unless a mechanism can be found for how insoluble zinc ferrite can be converted to zinc sulfate in the atmosphere.

4. Conclusions:

In this investigation, we have demonstrated the utility of XAFS spectroscopies for delineation of the oxidation states and speciation of key elements in both primary and secondary sources of particulate matter. There is clearly a lot of work that yet needs to be done to complete such studies and to follow up on the important implications from the data collected so far in this study. Our important findings include:

• Demonstration that sulfur in primary $PM_{2.5}$ from three major fossil-fuel combustion processes (residual oil combustion, coal

combustion and diesel engine combustion) can exist in a variety of minor forms in addition to sulfate.

- The presence of thiophenic sulfur appears related to the amount of unburnt carbon in the primary PM sample.
- Other minor sulfur forms may be diagnostic for a specific combustion process. For example, the presence of sulfite in PM may be indicative of combustion of western US coals and the presence of bisulfate or sulfone may be indicative of diesel-derived PM.
- Most metals are present in ROFA-derived and diesel-derived PM as sulfates; however, iron is an exception and may exist largely as oxide or oxyhydroxide forms.
- Coarse ROFA PM ($PM_{2.5+}$) appears to contain metal sulfides of Ni, Fe and Cu, but such sulfides are largely absent from fine ROFA PM ($PM_{2.5}$). However, their presence may be related to the combustion under which the residual oil was combusted.
- A certain fraction of nickel in ROFA $PM_{2.5+}$ samples was found as nickel subsulfide, a reputed carcinogenic compound of nickel. Again, this may be largely due to the conditions under which the residual oil was combusted.
- PM samples from combustion of western US coals contain up to 30% of their Cr in the hexavalent oxidation state; Cr(VI) is not significant in PM from eastern US bituminous coals. Hexavalent Cr is both toxic and carcinogenic.
- Arsenic in all PM samples so far examined, regardless of source, exists as arsenate, in which the oxidation state is As (V). No evidence has been found for the presence of the more toxic As(III) oxidation state.
- XAFS experiments can be performed with reasonable success on Teflon filters used in FRM ambient air monitoring devices, as long as the sample is collected over a four-day or longer period.
- Sulfur in ambient $PM_{2.5}$ samples appears to exist almost entirely as sulfate.
- Zinc in ambient $PM_{2.5}$ exists as fully hydrated zinc sulfate (ZnS $O_4.7H_2O$); in contrast, anhydrous or only partially hydrated zinc sulfates may be present in ROFA and diesel-derived $PM_{2.5}$.
- Neither the sulfur nor the zinc XAFS data suggest the presence of a significant direct contribution from coal combustion in ambient $PM_{2.5}$ samples collected in Lexington, KY.

ACKNOWLEDGEMENTS

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