

XAFS Spectroscopy and SEM Investigation of Fine Particulate Matter from Residual Fuel Oil Combustion

G. P. Huffman*, F. E. Huggins*, R. Huggins*, W. P. Linak†, C. A. Miller†, R. J. Pugmire# and H. L. C. Meuzelaar‡

*University of Kentucky, 533 S. Limestone St. - Rm. 111, Lexington, KY 40506

†U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Research Triangle Park, NC 27711

Dept. of Chemical and Fuels Engineering, University of Utah, Salt Lake City, Utah

Keywords: particulate matter, PM_{2.5}, XAFS, NMR, molecular structure, SEM, particle size distribution

Introduction

The EPA is currently considering new regulations for fine airborne particulate matter (PM) less than 2.5 microns in diameter (PM_{2.5}). Such regulations should be based on the best scientific data, particularly with regard to fine particle characterization. Although there are many analytical techniques for determining the elemental composition of PM_{2.5}, information on molecular speciation is much more difficult to obtain. Since the health effects of PM_{2.5} are closely related to speciation parameters such as valence, solubility and acidity, it is essential to identify and evaluate analytical methods that can accurately speciate the molecular structure of critical elements.

X-ray absorption fine structure (XAFS) spectroscopy is a synchrotron radiation - based technique that is uniquely well suited to characterization of the molecular structure of individual elements in complex materials. In previous research, we have used XAFS spectroscopy to determine the molecular forms of environmentally important elements (S, Cl, As, Cr, Hg, Ni, etc.) in coal, oil, flyash, and sorbents.⁽¹⁻⁷⁾ Our initial investigations of PM indicate that XAFS will also be a powerful tool in this area.^(8,9)

In the current work, XAFS spectroscopy was used to investigate several elements in a suite of residual oil flyash (ROFA) samples separated aerodynamically into fractions <2.5 (PM_{2.5}) and >2.5 microns (PM_{2.5+}) in diameter. The ROFA was generated by combustion of residual fuel oil at the EPA National Risk Management Laboratory.⁽¹⁰⁾ Complementary data were obtained using computer-controlled scanning electron microscopy (CCSEM), ¹³C NMR, GC/MS, and XRD. In the current paper, some examples of the XAFS, CCSEM, and NMR data are presented. The XRD data are discussed in a separate paper presented in this symposium by Seehra and Mannivanan.⁽¹¹⁾

Experimental Procedure

The combustion experiments were carried out in a North American three-pass fire tube package boiler, which is a practical, commercially available heavy fuel oil combustion unit. A detailed description of this boiler is given elsewhere.⁽¹⁰⁾ Samples were separated aerodynamically by a cyclone into PM_{2.5} and PM_{2.5+} fractions. The sampling system consists of a large dilution sampler capable of isokinetically sampling 0.28 m³/min (10 ft³/min) of flue gas using a Source Assessment Sampling System (SASS) cyclone. The SASS cyclone produces 50 and 95% collection efficiencies at approximately 1.8 and 2.5 micron diameter, respectively. The resulting PM is collected on large (65 cm) Teflon coated glass fiber filters, transferred to sampling jars, and made available for analysis.

Although burnout was fairly complete (>99.7%), the inorganic content of the oils was quite low (0.02-0.10 wt.% ash), and the dominant element of the ROFA is carbon. Loss on ignition (LOI) measurements indicates that the carbon content of the PM_{2.5} ranged from 64 to 87 wt.% and that of the PM_{2.5+} from 88 to 97 wt.%. S content of the PM samples was ~ 1 to several wt.%, while the V content ranged from 0.5 to 5.9 wt.%, and the Ni content from 0.08 to 0.8 wt.%. The metals are typically more concentrated in the PM_{2.5} samples than they are in the PM_{2.5+} samples by factors ~3 to 6.⁽¹⁰⁾

The samples were investigated by XAFS spectroscopy at the Stanford Synchrotron Radiation Laboratory (SSRL) and the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. All measurements were carried out in the fluorescent mode using either a Lytle detector or a multi-element Ge array detector, as described

elsewhere.⁽¹⁻⁴⁾ The XANES regions of the spectra were analyzed by deconvolution, derivative, and comparative analysis methods, as discussed in earlier papers.⁽¹⁻⁷⁾

Results and Discussion

CCSEM examination of the PM_{2.5} was carried out on samples dispersed on a nucleopore filter, prepared as discussed elsewhere.⁽¹²⁾ Since the particles were predominantly carbon rich, C was by far the dominant element detected in the energy dispersive x-ray (EDX) spectra. S, V and Ni were observed as minor components. Because the sample contained both a large particle component and a small particle component, quantitative particle size distributions have not yet been obtained. However, measurements of the spread of the PSD were obtained by examining fields containing primarily small particles at magnifications ~1000X and fields containing large particles at a magnification of 50X. Examples are shown in Figure 1. It is seen that the PSD of the small particle component peaks at 1-3 microns and that of the large particle component at 10-15 microns.

Typical S K-edge XANES spectra of ROFA PM_{2.5} and PM_{2.5+} samples are shown in Figure 2. The spectra are deconvoluted by a least squares computer analysis into a series of peaks (50% Lorentzian-50% Gaussian) and two rounded arctangent step functions, as discussed elsewhere.^(1,2) Most of the peaks represent 1s→3p transitions of photoelectrons excited from the K-shell by x-ray absorption. Both the position and relative intensity of these peaks vary significantly with the electronic state of the S atom, increasing with increasing valence. By using calibration data generated from mixtures of standard compounds, the peak area percentages can be translated into percentages of S contained in different molecular forms.^(1,2)

The results of this analysis for the ROFA PM samples are summarized in Table 1. For comparison, the results for the PM derived from combustion of a Pittsburgh No. 8 coal in the same boiler are also included. The dominant molecular forms of S observed are sulfate and thiophenic S. Sulfate was greater in the PM_{2.5} samples than in the PM_{2.5+} samples, reflecting the greater degree of carbon burnout for the smaller particles. Additional components, including elemental S and inorganic sulfides, are present in lower percentages. The origin of the elemental S is not clear at this time. The S in the PM_{2.5} of the ROFA from a high S residual oil burned in a second furnace where carbon burnout was much more complete was 100% sulfate. It is seen that both the PM_{2.5} and PM_{2.5+} from the Pittsburgh #8 coal are also predominantly sulfate.

Table 1. XANES results for the weight percentages of different S forms.

Sample	PM size	Sulfate	Thiophene	Elemental S	Inorganic sulfide	Other forms
Baseline # 5 oil	<2.5	55	24	5	11	5
Baseline # 5 oil	>2.5	32	37	8	19	4
Low S #6 oil	<2.5	84	14	--	--	2
Low S #6 oil	>2.5	58	34	6	--	2
Med. S #6 oil	<2.5	73	13	6	--	8
Med. S #6 oil	>2.5	55	35	6	--	3
High S #6 oil	<2.5	54	29	5	11	1
High S #6 oil	>2.5	26	39	9	26	--
Pitt. #8 coal	<2.5	95	5	--	--	--
Pitt. #8 coal	>2.5	85	14	--	--	1

Analysis of the XANES spectra from V and Ni in the ROFA PM samples indicates that they are present predominantly as sulfates. Most of the V XANES spectra closely resemble the spectrum of vanadyl sulfate (VO•SO₄•xH₂O). This is brought out clearly by the first derivative of the XANES spectra, which exhibited peaks in nearly identical positions and with similar intensities to the first derivative of the XANES spectrum of VO•SO₄•3H₂O reported by Wong et al.⁽¹²⁾ The Ni XANES and first derivative spectra from the PM samples agree well with that of NiSO₄, and with the Ni spectra observed in an earlier investigation of ROFA⁽⁴⁾ by the current authors. Similarly, the XANES and the

first derivative spectra of the other metals examined (Fe, Zn, Cu, Mn and Pb) also identify the principal components of these metals to be sulfates. However, secondary components are present in many of the metal XAFS spectra. In most cases, these secondary components appear to be oxides. The As XANES identify the arsenic as an arsenate (As^{+5}) but do not identify the specific phase.

NMR data

Seven of the samples were examined by ^{13}C NMR. Cross polarization experiments suggested that the proton content of the samples was very low and, hence, no useful data were obtained using this experimental technique. Proton spectra taken on several samples verified the very low H/C ratios for all but the high sulfur #6 $\text{PM}_{2.5}$ sample. The ^{13}C NMR spectra were then acquired using by using block decay with a pulse repetition rate of 10 s and accumulating between 17,000 and 25,000 scans. These resulting spectra are shown in Figure 3, where FL and CY denote filter ($\text{PM}_{2.5}$) and cyclone ($\text{PM}_{2.5+}$) samples, HS, MS and LS indicate high, medium and low sulfur #6 oil, and BL indicates baseline #5 oil. The spectra indicate that the carbon in the samples is predominantly condensed in graphitic-like structures. Second moment (line width) measurements are uniform at ~ 75 ppm (FW/HH) for six of the samples. However, the second moment of the high sulfur #6 $\text{PM}_{2.5}$ (FL-HS) sample indicates a much narrower aromatic band (45 ppm). In addition, this sample is unique in that aliphatic structure is clearly present in the spectrum.

Summary and Conclusions

XAFS spectroscopy, CCSEM and ^{13}C NMR data have been obtained from a series of $\text{PM}_{2.5}$ and $\text{PM}_{2.5+}$ samples produced by combustion of residual fuel oil in a commercial boiler. Analyses of the XANES spectra have been carried out for S and a number of metals in the PM. Deconvolution of the S XANES reveals that the dominant molecular forms of S observed are sulfate and thiophenic S. Sulfate was greater in $\text{PM}_{2.5}$ samples than in the $\text{PM}_{2.5+}$ samples, reflecting the greater degree of carbon burnout for the smaller particles. Sulfates are the dominant components of the metal spectra. CCSEM indicates that the aerodynamically separated $\text{PM}_{2.5}$ is bimodal in size, with a small particle component peaking at 1-3 microns and a large particle component peaking at 10-15 microns. The ^{13}C NMR indicated that the carbon in the PM was predominantly graphitic or soot-like in structure. However, one sample exhibited a much narrower aromatic band than the others and an aliphatic component.

Acknowledgement: Support of this research under U.S. Department of Energy (FE/NPTO) contract No. DE-AC26-99BC15220 is gratefully acknowledged. The XAFS experiments were conducted at the Stanford Synchrotron Radiation Laboratory and the National Synchrotron Light Source, which are also supported by the U.S. DOE.

References:

1. G.P. Huffman, S. Mitra, F.E. Huggins, N. Shah, S. Vaidya, and F. Lu, 1991, *Energy & Fuels*, **5**, 574-581.
2. M. Mehdi Taghiei, F.E. Huggins, N. Shah, and G.P. Huffman, 1992, *Energy & Fuels*, **6**, 293-300.
3. G.P. Huffman, F.E. Huggins, N. Shah, and J. Zhao, 1994, *Fuel Processing Technology*, **39**, 47-62.
4. F.E. Huggins and G.P. Huffman, 1996, *Int. J. Coal Geology*, **32**, 31-53.
5. K.C. Galbreath, C.J. Zygarić, D.L. Toman, F.E. Huggins and G.P. Huffman, 1998, *Energy & Fuels*, **12**(4), 818-822.
6. F.E. Huggins, M. Najih, and G.P. Huffman, 1999, *Fuel*, **78**, 233-242.
7. F.E. Huggins, G. P. Huffman, G. E. Dunham, and C. L. Senior, 1999, *Energy & Fuels*, **13**, 114-121.
8. F.E. Huggins, G.P. Huffman, and J. David Robertson, ACS, Div. Environ. Chem., Preprints, 1998, **38**(2).
9. F. E. Huggins and G. P. Huffman, 1999, *J. of Hazardous Materials*, in press.
10. C. A. Miller, W. P. Linak, C. King, and J. O. L. Wendt, 1998, *Combust. Sci. and Technol.*, **134**, 477-502.
11. M.S. Seehra and A. Mannivannan, this volume.
12. G. Huffman, A. Shah, N. Shah J. Zhao, F. Huggins, J. Helble, S. Srinivasachar, T. Peterson, J. Wendt, N. Gallagher, L. Bool, A. Sarofim, Proc. Eng. Fd. Conf., The Impact of Ash Deposition on Coal Fired Plants, Eds., J. Williamson and F. Wigley, 1994, pp. 409-423, Taylor & Francis, London.

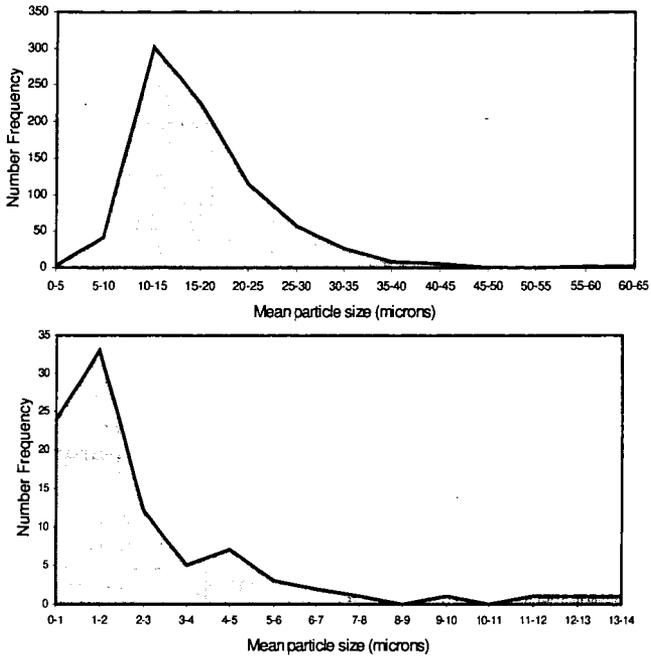


Figure 1. Particle size distributions for PM_{2.5} measured for a field of particles at a magnification of 50X and a second field at a magnification of 1000X.

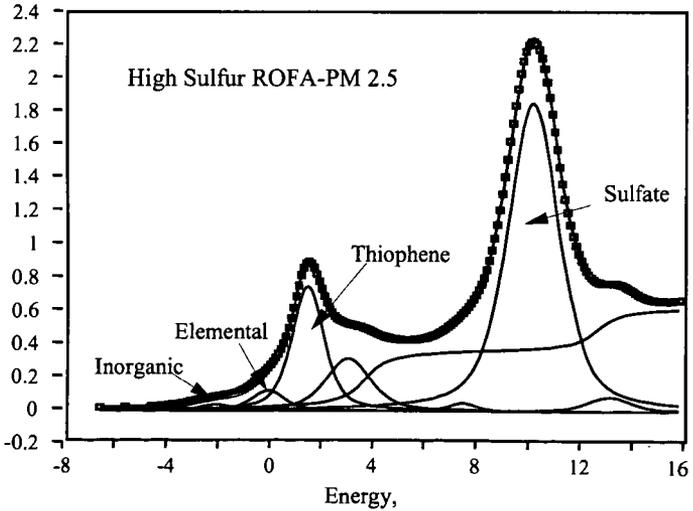


Figure 2. Typical least squares analysis of the S XANES of a ROFA PM_{2.5} sample.

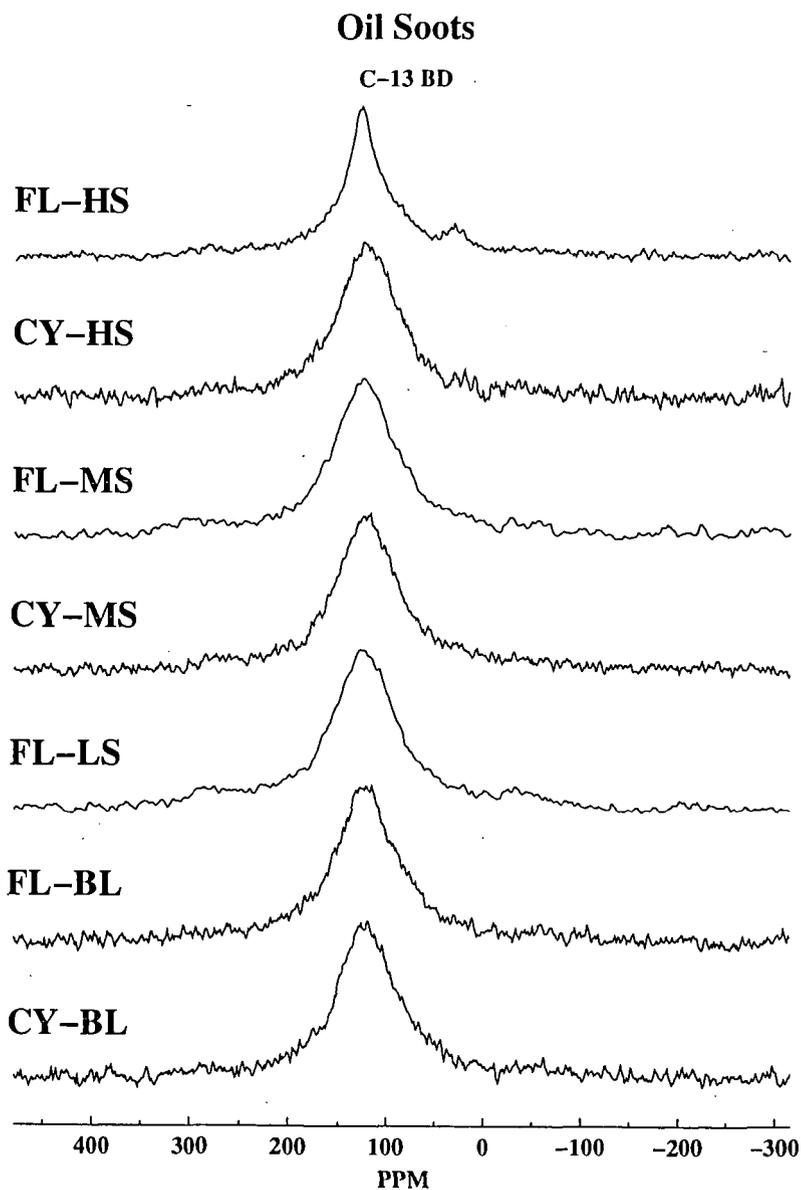


Figure 3. ^{13}C NMR Spectra of ROFA PM Samples.