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Characterization of Fine Particulate Matter Produced by Combustion of Residual Fuel Oil

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ABSTRACT

Combustion experiments were carried out on four different residual fuel oils in a 732-kW boiler. PM emission samples were separated aerodynamically by a cyclone into fractions that were nominally less than and greater than 2.5 μ m in diameter. However, examination of several of the samples by computer-controlled scanning electron microscopy (CCSEM) revealed that part of the PM_{2.5} fraction consists of carbonaceous cenospheres and vesicular particles that range up to 10 μ m in diameter. X-ray absorption fine structure (XAFS) spectroscopy data were obtained at the S, V, Ni, Fe,

IMPLICATIONS

Regulations on PM25 should be based on the best scientific data, particularly with regard to characterization. Although there are many analytical techniques for determining the elemental composition of PM25, information on molecular structure and microstructure is difficult to obtain. This paper presents the results of an investigation of the structure of $\mathrm{PM}_{\mathrm{2.5}}$ from combustion of residual oil using a variety of analytical techniques (XAFS spectroscopy, CCSEM, ¹³C NMR, inductively coupled plasma/ mass spectrometry [ICP/MS], and X-ray diffraction [XRD]). The results demonstrate that these techniques provide a rather complete analysis of the molecular structure of both the inorganic and organic components of PM25. Improved information is also obtained on particle size distributions, composition ranges, and morphologies. Since both health effects and source apportionment of PM25 are closely related to such parameters, this type of information should be valuable to regulatory authorities and industry.

Cu, Zn, and As K-edges and at the Pb L-edge. Deconvolution of the X-ray absorption near edge structure (XANES) region of the S spectra established that the dominant molecular forms of S present were sulfate (26-84% of total S) and thiophene (13-39% of total S). Sulfate was greater in the PM_{2.5} samples than in the PM_{2.5+} samples. Inorganic sulfides and elemental sulfur were present in lower percentages. The Ni XANES spectra from all of the samples agreed fairly well with that of NiSO₄, while most of the V spectra closely resembled that of vanadyl sulfate (VO \bullet SO₄ \bullet xH₂O). The other metals investigated (i.e., Fe, Cu, Zn, and Pb) also were present predominantly as sulfates. Arsenic was present as an arsenate (As⁺⁵). X-ray diffraction patterns of the PM_{2.5} fraction exhibit sharp lines due to sulfate compounds (Zn, V, Ni, Ca, etc.) superimposed on broad peaks due to amorphous carbons. All of the samples contain a significant organic component, with the loss on ignition (LOI) ranging from 64 to 87% for the PM_{2.5} fraction and from 88 to 97% for the PM_{2.5+} fraction. Based on ¹³C nuclear magnetic resonance (NMR) analysis, the carbon is predominantly condensed in graphitic structures. Aliphatic structure was detected in only one of seven samples examined.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) currently is considering new regulations for fine airborne particulate matter less than 2.5 μ m 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 $PM_{2.5}$, there has been relatively little research on its molecular structure and microstructure. Many scientists believe that both the effects on human health and the source apportionment of $PM_{2.5}$ are closely related to parameters such as particle size distributions and morphology and the valence and solubility of critical elements. It is therefore essential to identify and evaluate analytical methods that can provide such structural information.

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 (e.g., S, Cl, As, Cr, Hg, Ni, etc.) in coal, oil, fly ash, 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 and a number of additional analytical techniques were applied to a suite of residual oil fly ash (ROFA) samples separated aerodynamically into $PM_{2.5}$ and $PM_{2.5+}$ fractions. Briefly, the characterization data obtained included

- (1) XAFS analysis of the molecular structure of S, V, Ni, Fe, Cu, Zn, Pb, and As;
- (2) computer-controlled scanning electron microscopy (CCSEM) analysis of particle size, composition, and morphology;
- (3) ¹³C nuclear magnetic resonance (NMR) analysis of the molecular structure of carbon, the dominant element;
- (4) X-ray diffraction (XRD) identification of crystalline phases; and
- (5) inductively coupled plasma/mass spectrometry (ICP/MS) determination of metal concentrations.

COMBUSTION 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. Details on the construction and operation of this sampling system are available elsewhere.¹¹ The SASS cyclone produces 50 and 95% collection efficiencies at approximately 1.8 and 2.5 µm diameters, respectively. The resulting PM is collected on large (65-cm) Teflon (DuPont)coated glass fiber filters, transferred to sampling jars, and made available for analysis.

Four residual fuel oils were combusted, with sulfur contents ranging from 0.53 to 2.33 wt %. The ultimate analyses of these oils, together with the concentrations of the metals of interest for this paper, are given in Table 1. Table 2 contains the loss on ignition (LOI) and metal concentrations for the PM22.5 and PM2.5+ fractions. The metal analyses were performed using acid digestion and ICP/MS.¹⁰ Although burnout was fairly complete (>99.7%), the inorganic content of the oils was quite low (0.02-0.10 wt % ash), and the LOI results indicate that the dominant element of the ROFA is carbon (64-87 wt % for PM25 and 88-97 wt % for PM_{2 5-}). V is present at relatively large concentrations (~0.5-5 wt %); Ni, Fe, and Zn are present at moderate concentrations (~0.1-0.5 wt %); and several metals (Pb, As, Cr, Cu, Mn, Sb, and Cd) are present at concentrations that are rather low (~20-1000 ppm) but could still be significant for health considerations. The metals are typically more concentrated in the PM2.5 samples than in the $PM_{2.5+}$ samples by factors from ~3 to 6.

XAFS SPECTROSCOPY RESULTS

The samples were investigated by XAFS spectroscopy at the Stanford Synchrotron Radiation Laboratory (Menlo Park, CA) and the National Synchrotron Light Source at Brookhaven National Laboratory (Upton, Long Island, NY). 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 X-ray absorption near edge structure (XANES) regions of the spectra were analyzed by deconvolution, derivative, and comparative analysis methods, as discussed in earlier papers.¹⁻⁷ The results for the elements investigated to date are summarized below.

Sulfur

Typical S K-edge XANES spectra of ROFA $PM_{2.5}$ and $PM_{2.5+}$ samples are shown in Figure 1. 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 \rightarrow 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 the total S contained in different molecular forms.^{1,2}

The results of this analysis for the ROFA PM samples are summarized in Table 3. 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

	No. 5 Oil	Low Sulfur No. 6 Oil	Medium Sulfur No. 6 Oil	High Sulfur No. 6 Oil
		Ultimate A	nalysis, wt %	
Carbon	86.36	86.00	86.48	85.49
Hydrogen	10.82	11.29	10.98	10.36
Nitrogen	0.33	0.43	0.43	0.35
Sulfur	1.73	0.53	0.93	2.33
Oxygen*	0.34	1.24	0.67	0.92
Moisture	0.35	0.50	0.50	0.50
Ash	0.07	0.02	0.03	0.10
		Elemental /	Analysis, µg/g	
Arsenic	2	0.2	0.2	0.1
Beryllium	<1	< 0.3	< 0.3	< 0.3
Cadmium	0.1	0.50	0.60	0.60
Chromium	0.5	1.08	0.96	1.05
Copper	4	0.56	0.78	3.5
Iron	50	23	19	21
Lead	3	0.80	0.58	4.5
Mercury	-	0.06	0.12	0.10
Nickel	34	17	22	30
Selenium	< 2	< 0.1	< 0.1	< 0.1
Vanadium	180	35	70	220
Zinc	39	4.11	3.70	74



Figure 1. Typical deconvolution of S K-edge XANES spectra of ROFA $PM_{2.5}$ and $PM_{2.5+}$.

Note: * Determined by difference.

smaller particles. Additional components, including elemental S and inorganic sulfides, are present in lower percentages. The origin of the elemental S is not clear. 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.

Table 2. Metal concentrations and enrichment ratios of PM $_{25}$ and PM $_{25+}$ samples (µg/g).

	Low	Low Sulfur No. 6 Oil		Medium Sulfur No. 6 Oil		High Sulfur No. 6 Oil		No. 5 oil				
	2.5	2.5+	2.5/2.5+	2.5	2.5+	2.5/2.5+	2.5	2.5+	2.5/2.5+	2.5	2.5+	2.5/2.5+
Antimony	23.4	4.90	4.8	24.2	2.9	8.3	48.6	8.20	5.9	34.5	4.86	7.1
Arsenic	49.9	11.0	4.5	49.8	4.9	10	35.9	8.60	4.2	18.7	1.70	11
Beryllium	0.40	0.10	4.0	0.47	0.11	4.3	0.46	0.15	3.1	0.44	0.20	2.2
Cadmium	0.50	0.21	2.4	1.26	0.46	2.7	19.3	1.84	11	2.75	0.69	4.0
Chromium	32.6	27.5	1.2	44.7	46.9	1.0	60.2	41.3	1.5	60.5	33.3	1.8
Copper	123	33.8	3.6	159	36.8	4.3	1050	222	4.7	233	58.1	4.0
Iron	5100	1410	3.6	4460	1510	3.0	3850	2300	1.7	4220	1110	3.8
Lead	114	21.5	5.3	164	22.4	7.3	990	94.2	11	-	-	_
Magnesium	1450	428	3.4	1450	436	3.3	6190	2220	2.9	1770	101	18
Manganese	93.3	34.1	2.7	84.5	37.1	2.3	73.2	42.8	1.7	89.9	23.6	3.8
Nickel	4840	863	5.6	7470	1230	6.1	8020	2270	3.5	10600	2200	4.8
Vanadium	14700	4510	3.2	35300	7560	4.7	58900	19900	3.0	58600	13000	4.5
Zinc	1600	328	4.9	1840	422	4.4	21000	2740	7.7	2750	6530	0.4
LOI, mg/g	658	903	0.7	790	978	0.8	866	969	0.9	641	883	0.7

Vanadium

The molecular forms of the metals investigated in this study were identified by comparing the XANES spectra and the first derivative of the XANES spectra of the ROFA samples to those of standard compounds. The standard compound suite included most of the oxides, sulfates, and sulfides of each metal investigated.

Most of the V XANES and first derivative XANES spectra from both the $PM_{2.5}$ and $PM_{2.5+}$ fractions closely resemble the spectrum of vanadyl sulfate (VO•SO₄•xH₂O). This is brought out most clearly by the distinctive first derivative of the XANES spectrum, which exhibits 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 and also measured in this study. Typical V XANES and first derivative spectra from a $PM_{2.5}$ sample are shown in Figure 2. The spectra of several samples also indicate the presence of minor amounts of oxide, probably V_2O_5 .

Nickel

The Ni XANES and first derivative spectra from the PM samples (see Figure 3) were found to agree well with those of NiSO₄. For ease of comparison, the absorption scale for all spectra has been normalized to the same arbitrary unit of intensity. Similar XAFS results were obtained for Ni in an earlier investigation of ROFA⁵ by the authors. There is again evidence of a small amount of oxide (NiO) in one of the PM_{2.5} samples (low S No. 6), both in the first derivative spectrum and in the radial structure function obtained by Fourier analysis of the XAFS spectrum.

Iron

The Fe XANES and the first derivatives of the Fe XANES of the ROFA PM samples (see Figure 4) agree well with those of ferric sulfate, $Fe_2(SO_4)_{3'}$, indicating that it is the dominant iron compound in both the $PM_{2.5}$ and $PM_{2.5+}$ samples. This conclusion was reached by comparing the spectra for the ROFA PM samples with those of numerous iron-based



Figure 2. Distinctive V K-edge XANES (top) and first derivative spectra (bottom) for the ROFA $PM_{2,5}$ samples identify vanadyl sulfate (VOSO, •xH,O) as the dominant molecular form of vanadium.

standard compounds. One $PM_{2.5}$ sample (low S No. 6) contains a small amount of iron oxide, probably Fe_3O_4 .

Copper, Zinc, and Lead

Although fewer samples have been examined, and the data are of somewhat lower quality because of lower concentrations, it appears that sulfates are the dominant phases detected by the XANES spectra for these metals also. The phases tentatively identified are $CuSO_4 \bullet xH_2O$, $ZnSO_4$, and $PbSO_4$.

Table 3. XANES results for the percentages of the total sulfur contained in different molecular forms in ROFA PM samples.

Sample	PM Size (µm)	Sulfate	Thiophene	Elemental S	Inorganic Sulfide	Other Forms
No. 5 Oil	< 2.5	55	24	5	11	5
No. 5 Oil	> 2.5	32	37	8	19	4
Low S No. 6 Oil	< 2.5	84	14	-	-	2
Low S No. 6 Oil	> 2.5	58	34	6	-	2
Med. S No. 6 Oil	< 2.5	73	13	6	-	8
Med. S No. 6 Oil	> 2.5	55	35	6	-	3
High S No. 6 Oil	< 2.5	54	29	5	11	1
High S No. 6 Oil	> 2.5	26	39	9	26	_

Arsenic

The As XANES spectra establish that the arsenic is present as an arsenate (As^{+5}) but do not identify the specific phase. A discussion of the identification of arsenic valence states from XANES spectra can be found in refs 3 and 4.

CCSEM DATA

The principles of CCSEM have been summarized in numerous previous papers. Briefly, as the electron beam is rastered across the sample, the back-scattered electron intensity is measured and compared to a preset discriminator level to detect particles. When a particle is detected, the stepping density of the electron beam is increased by a factor of 256 and the cross-sectional area, maximum and minimum diameters, and energy dispersive X-ray (EDX) spectrum of the particle are measured. Details of the measurement procedure are summarized elsewhere.13-15 With a well-prepared sample, it is possible to measure the size and approximate composition of about 1000 particles in several hours. In the current studies, the CCSEM examination was carried out on PM samples dispersed on nucleopore filters, prepared as discussed elsewhere.13 For the current PM



Figure 3. Ni XANES and first derivative spectra for the ROFA $PM_{2.5}$ indicate that the dominant Ni phase is NiSO₄. The spectra are normalized to unit step height for easy comparison.

samples, C was by far the dominant element detected in the EDX spectra, while S was detected in most particles at concentrations of ~1–10%. Since EDX collection times were only 5 sec per particle, V, Ni, and other metals were detected only as minor components of selected particles.

Some preliminary CCSEM data for two ROFA PM25 samples are shown in Table 4 and Figure 5. The data are considered to be preliminary, because preparation of satisfactory SEM specimens for these samples has proven to be difficult, and we are still refining our procedures. Consequently, the current data, while informative, should be considered qualitative in nature. Table 4 indicates the three major classes of particles identified and the average composition of those classes based on the EDX spectra. Better information can be obtained regarding particle composition by the use of binary and ternary composition diagrams, 13 such as the C-S diagram for the medium S No. 6 PM_{2.5} sample shown in Figure 5a. This diagram includes all particles for which C + S was greater than 80%. It illustrates that the carbon-rich char particles contain a range of S concentrations, from 0 to approximately 20%, with peaks in the 0-2% and the 6-10% ranges. The particle size distribution for all of the particles analyzed for the low S No. 6 $PM_{2.5}$ sample is shown in Figure 5b. It is seen that a significant percentage of the particles classified aerodynamically as $PM_{2.5}$ by the cyclone separator are in fact greater than 2.5 μ m in diameter. Many of these appear to be cenospherical, vesicular carbon particles, such as those shown in Figure 6. The arrows in Figure 6 indicate inorganic particles rich in V and S, some of which also contain Ca, Al, and Si. These particles presumably consist primarily of vanadyl sulfate. It is worth noting that this type of configuration, small particle transition metal phases on a highly porous carbon support, could act as a good catalyst for chemical reactions. This type of microstructure is frequently observed in the ROFA $PM_{2.5}$.

NMR DATA

There has been extensive use of ¹³C NMR in examining the molecular structure of carbon in a wide range of materials. It is perhaps the best method of measuring the relative percentages of aromatic and aliphatic carbon in organic materials and can provide detailed information on the extended carbon skeletal structure and bonding groups.





Figure 4. Fe XANES and first derivative spectra indicate that $Fe_2(SO_4)_3$ is the dominant Fe

compound in ROFA PM25. The spectra are normalized to unit step height for easy comparison.

Detailed discussion of the methodology involved in such analyses is given elsewhere. 16 Four of the PM $_{2.5}$ and three of the PM $_{2.5+}$ ROFA samples were examined by $^{13}\mathrm{C}$ NMR. Cross-polarization experiments suggested that the proton

taken in the step-scan mode using 0.04° steps and 30-sec collection time at each step. The data were analyzed using a Jade software package and the Joint Commision of Power Diffraction Standards (JCPDS) data files.

Table 4. CCS	EM results for two	PM ₂₅ samples.	Composition	in atomic %
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Medium S #6 PM ₂₅ -	- 689 particles.					
Classes	Number	Number %	C	S	AI	Si
C/S Rich	423	61.4	83	10	1	1
C Rich	222	32.0	94	2	1	1
Al/Si Rich	35	5.3	59	2	11	26
Others	9	1.3				
Low S #6 PM, 522	2 particles.					
Classes	Number	Number %	C	S	AI	Si
0.00 0: 1						••
C/S Rich	310	58.4	82	11	1	1
C/S Rich C Rich	310 177	58.4 36.7	82 94	11 1	1 2	1 0
C/S Rich C Rich Al/Si Rich	310 177 20	58.4 36.7 3.6	82 94 60	11 1 4	1 2 12	1 0 21

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 PM_{2.5} sample derived from combustion of the high S No. 6 oil. The ¹³C NMR spectra were then acquired by using block decay with a pulse repetition rate of 10 sec and accumulating between 17,000 and 25,000 scans. Six of the seven samples examined exhibited spectra essentially identical to that shown in Figure 7 for the low S No. 6 oil PM_{25} sample. These spectra indicate that the carbon in these samples is predominantly condensed in graphitic structures. Second moment (line width) measurements are uniform at ~75 ppm (full width at half height [FW/HH]) for all six of the samples. However, the second moment for the high S No. 6 PM_{2.5} sample indicates a much narrower aromatic band (peak at ~120 ppm, FW/HH = 45 ppm), and the spectrum clearly shows the presence of aliphatic structure (peak at ~20ppm).

XRD DATA

The XRD experiments were carried out using a Wide Angle X-Ray Diffracto-meter (Rigaku Model D/Max) employing CuK α radiation (λ = 1.5418 Å). The data were



Figure 5a. CCSEM C-S distribution for medium S No. 6 PM_{2.5}.



Figure 5b. CCSEM particle size distribution for low S No. 6 PM_{2.5}.

Typical X-ray diffractograms are shown in Figure 8 for the PM_{25} from the No. 5 oil and the PM_{25} and PM_{25+} from the high S No. 6 oil. The diffractograms consist of sharp lines superposed on two broad peaks at $2\theta = 26^{\circ}$ and 44°. The broad peaks are due to amorphous carbon.¹⁷ The sharp lines are due to inorganic compounds and have been identified as sulfates and sulfites of Zn, V, Ni, Pb, Fe, Ca, and Cu. The identified compounds are $CaSO_4$, Zn₄SO₄(OH)₆•5H₂O, Zn(SO₃)2.5H₂O, VOSO₄, NiSO₄•6H₂O, PbS_2O_3 , $Fe_3(SO_4)_4 \bullet 14H_2O$, $ZnSO_4 \bullet xH_2O$, $Ca(SO_4) \bullet 2H_2O$, and Cu₂SO₄. Qualitatively, the intensities of the lines are largest for samples obtained from the high S No. 6 oil and for the PM_{2.5} fraction of No. 5 oil (BL5FH). This is understandable, since the high sulfur content would tend to produce higher levels of the sulfates. Generally, PM₂₅ fractions tend to have higher concentrations of the sulfates as compared to the PM_{2.5+} fractions, as illustrated by the comparison of the diffractograms for the PM_{2.5} and PM_{2.5+} fractions from high S No. 6 oil in Figure 8. For the PM_{25} fraction from the No. 5 oil, the intensities of the lines are the largest of all the samples, but only weak lines due to CaSO₄ are observed for the PM_{2.5+} fraction. A more complete summary of all the XRD data has been given elsewhere.18

SUMMARY AND CONCLUSIONS

The structure of $PM_{2.5}$ and $PM_{2.5+}$ from the combustion of several residual fuel oils in a commercial boiler has



Figure 6. Highly vesicular carbon rich char particles. The arrows point to inorganic particles on the particle surfaces, rich in V and S.



Figure 7. ¹³C NMR spectra of $PM_{2.5}$ from ROFA. Only the low S No. 6 $PM_{2.5}$ sample shows any aliphatic structure (top spectrum).



Figure 8. Typical X-ray diffractograms of PM_{2.5} and PM_{2.5+} samples from ROFA.

been characterized by a range of analytical techniques. XAFS spectroscopy was used to investigate the molecular structure of S, a number of metals (V, Ni, Fe, Zn, Cu, and Pb), and As. Deconvolution of the S XANES spectra revealed that the dominant molecular forms of S observed were 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. Sulfates were identified by XAFS as the dominant metal compounds (VOSO₄•xH₂O, NiSO₄, Fe₂(SO₄)₃, etc.). Arsenic was present as an arsenate (As⁺⁵). XRD also identified a number of metal sulfates and sulfites, including CaSO₄. CCSEM measurement of the particle size distributions of two PM_{2.5} samples established that a

 μ m) metal sulfate particles. This structure is similar to that of a supported catalyst and suggests that such particles might play a role in the formation of radicals in the lung. Based on ¹³C NMR, the carbon in the PM was predominantly graphitic or soot-like in structure, with only one sample exhibiting an aliphatic component. The current study is part of a more general investigation of petroleum-derived PM_{2.5}. Future work, in addition to further characterization of the current samples, will

significant percentage of particles exceeded $2.5 \mu m$ in diameter. Many of these were vesicular, cenospherical

carbon char particles. The surfaces of these highly po-

rous carbon particles were decorated with small (~1-3

include characterization of diesel emissions and PM

samples collected on filters from the ambient atmosphere in appropriate locations.

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