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THE CHARACTERIZATION OF SOLID SPECIMENS FROM ENVIRONMENTAL POLLUTION
STUDIES USING ELECTRON X-RAY AND NUCLEAR PHYSICS METHODS*

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ABSTRACT

This paper illustrates how the properties of environmental particulate matter can be better understood if a multitechnique examination is conducted. Some results for fly ash, using neutron activation analysis, scanning electron microscopy, photoelectron spectroscopy (ESCA), x-ray fluorescence and x-ray diffraction are described. The difference in composition between the surfaces and interiors of particles are discussed and the effects of water leaching on surface composition are shown. The propensity of natural iron oxide substrates to cover themselves with adsorbed material is illustrated; this may be an important factor in the transfer of pollutants on particulate matter surfaces. The final section describes how the element detection sensitivity can be predicted for an improved x-ray fluorescence system that uses monochromatic $\text{AgK}\alpha$ radiation for excitation.

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1. INTRODUCTION

Applied problems often require that solid specimens be examined and analyzed in many ways so that an overall characterization can be established. The type of data used to construct this characterization usually consists of the following: elemental analysis, chemical states of the elements, crystal forms of the compounds, particle sizes and shapes, and a determination of whether the elements of interest are segregated at the surfaces or distributed in the interiors of the particles. To gather all this information for the same specimen, one must use nondestructive methods. Electron, x-ray, and nuclear physics methods often fit this requirement very well. Elemental analysis is done by x-ray fluorescence and neutron activation. X-ray and electron diffraction provide crystal identification and compound analysis. Particle sizes and shapes are determined by scanning and transmission electron microscopy. Distributions of elements and compounds are determined by scanning electron microscopy and ESCA (Electron Spectroscopy for Chemical Analyses).

In this paper we shall present an example of how this multitechnique approach has been used to demonstrate that certain elements segregate at the surfaces of fly ash particles and other solids. We will show that the surfaces of solids found in the environment are usually totally different from the interiors in composition. We will demonstrate that sulfur can be easily washed from the surfaces of fly ash and transferred to the environment.

The neutron activation analysis, scanning electron microscopy, x-ray diffraction, and ESCA techniques that we use are somewhat standard, so no detailed explanation of these experimental methods is given. Our x-ray fluorescence method has some new features (monochromatic excitation source), however, so a discussion of its capabilities will be presented at the end of the paper.

2. SOME STUDIES OF THE NATURE OF PARTICULATE MATTER SURFACES IN THE ENVIRONMENT

Some of the fly ash specimens used for this study were collected at the Allen Steam Plant, operated by the Tennessee Valley Authority at Memphis, Tennessee. ORNL has done a mass balance study on this plant. The fly ash has been analyzed by spark source mass spectroscopy, atomic absorption, and microwave emission spectroscopy (1,2) as well as the methods discussed here. In this paper we will emphasize those techniques that provide surface information for an Allen Steam Plant specimen and two other specimens.

The Allen Steam Plant is equipped with electrostatic precipitators that remove most of the ash particles larger than one micrometer from the flue gas. Cascade impact collectors, that gather and sort specimens according to size, were placed at the precipitator inlet and outlet. Table I shows the results of activation analysis of some precipitator inlet specimens. Since tables are usually tedious to read, we attempted to give a graphical perspective to this one by listing the elements in order of decreasing concentration. Table I also indicates composition as a function of particle size. Note that certain elements, such as Mo, Cr, Zn, Ga, Sb, Sc, Nb, Mg, Ti, V, Ba, Cl, Mn, As, W, and Ta are higher in concentration for the specimens that have smaller particle sizes. This is strong evidence that these elements are segregated at particle surfaces.

We have done a large amount of study, using scanning electron microscopy and ESCA, on the adsorption of sulfur on particulate matter surfaces. We have demonstrated that a very large fraction of the total sulfur in fly ash is segregated at particle surfaces. Figure 1 shows a scanning electron photomicrograph of a fly ash particle that has been ion etched on the left side (Side A). The particle

was bombarded on this side with 8 keV argon ions. This caused an ablation of material on this side which left the interior exposed. Note the hole left after ion etching. This indicates that the particle was hollow. Surface material on the right-hand side of the particle was not ablated because it was shielded from the ion beam. When the electron beam of the scanning microscope was focused on the surface material on the right-hand side of the particle, the x-ray fluorescence spectrum in the lower part of Figure 1 was generated. Note that, in addition to the major elements such as Al, Si, K, Ca, and Fe, there is a large amount of sulfur, chromium and nickel. The beam was then focused on the ablated side of the particle to generate the spectrum in the upper part of Figure 1. The sulfur, chromium and nickel are not found, which shows that these elements were on the surface of the particle, but not in the interior.

Data taken by the ESCA technique also show (3) that sulfur segregates on fly ash particle surfaces and that its chemical state is sulfate. Lately we have expanded this work to study fly ash surfaces more completely. In addition to fly ash from the Allen Steam Plant (photoelectron spectrum in Figure 2), specimens from two other sources have been examined: Woods River Plant in St. Louis, Missouri; United States National Bureau of Standards (USNBS). Their photoelectron spectra are in Figures 3 and 4, respectively. We chose the Woods River specimens because they had been subjected to the Catox process which oxidizes SO_2 to SO_3 in the flue gas and facilitates sulfur removal. We chose the USNBS specimen because it has been studied extensively by many other laboratories. Each of the fly ash specimens was leached with distilled water. This simulates their contact with distilled water. The upper spectra of Figures 2, 3 and 4 show the before-leach compositions of the surfaces. The lower spectra show the after-leach compositions.

It is seen that the main effect of the leaching is to remove the sulfur from the surface. For two of the specimens the sulfur is completely removed from the surface. Note also that in all three cases the silicon peaks are enhanced by the washing process. The aluminum peaks were made more intense also, but not as much as silicon. This suggests that the sulfur was partially covering the silicon and aluminum "substrates". The binding energies measured for sulfur in all of the three sets of spectra show that its chemical form is sulfate, probably calcium sulfate. A standard spectrum of calcium sulfate matches very closely the sulfur and calcium peaks of Figures 2, 3 and 4. The leachings from each of the three fly ash specimens were freeze-dried and the residues examined by x-ray diffraction. The main crystal patterns found in all three residues was $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum).

The residues were also examined by x-ray induced x-ray fluorescence (see last section for details) to see if some of the heavy metals had also been removed from the fly ash surfaces. None was found. This is contradictory to practical experience in the field, for it is known that rain water run-off from fly ash piles is highly polluted with heavy metals. Perhaps the high pH of the washings in our experiments is an explanation for the discrepancy. In all three of our experiments the pH was high, ranging from 9.5 to 10.5. Heavy metal oxides are, of course, very insoluble in basic media. Run-off from fly ash piles is usually acidic. The residues from the freeze-dried washings are being examined by neutron activation analysis, but these results are not yet available.

The depth of sampling for fly ash specimens is 20-50 atomic layers. The very intense peaks of oxygen and carbon, shown in Figures 2, 3 and 4 are typical. They are presumably due to adsorbed oxygen, water, and hydrocarbons. The metallic elements of highest concentration are silicon, calcium, and aluminum. The surprising thing about fly ash photoelectron spectra is the low intensities of the

iron peaks. As seen in Table I, the bulk concentration is very high. The x-ray fluorescence spectrum of the USNBS fly ash in Figure 7 also shows iron to be high in concentration. One might conclude that the ESCA technique is insensitive to iron, but this is not true; the photoelectric cross section for iron is actually higher than any of the other elements that appear in Figures 2, 3 and 4. Therefore, we must conclude that the concentration of iron on the outer surfaces (10-50 atom layers deep) is very low.

We have observed this tendency of iron to "mask itself" many times. Figure 5 illustrates another example. The specimen in this case is powdered iron metal that has been taken from a foundry environment. The x-ray fluorescence spectrum shows a very high concentration of iron and smaller amounts of manganese, zinc, and lead. The photoelectron spectrum does not show the presence of iron, manganese, or zinc, however. The main elements on the surface are oxygen, carbon, silicon, lead and chlorine. Apparently iron compounds are very efficient "getters" such that they adsorb other materials on their surfaces very readily. Tamura (4) has shown that iron oxide on clay surfaces greatly enhances the capacity to adsorb cobalt. Recently, Wilson, Tamura and Hulet (5) have found that the presence of iron on Kaolinite surfaces increases the adsorption capacity for cadmium. This effect will be studied more extensively in future work.

3. A DISCUSSION OF THE CAPABILITIES OF X-RAY FLUORESCENCE FOR ANALYZING ENVIRONMENTAL SPECIMENS

In our laboratories we make extensive use of x-ray fluorescence for elemental analysis. The equipment that we use the most was designed at ORNL by Sparks and coworkers (6). For exciting the fluorescence, a silver x-ray source, made monochromatic by a pyrolytic graphite crystal, is used. The Bragg diffraction condition of the crystal is adjusted so that only the $\text{AgK}\alpha$ energy is passed. Brehmstrahlung and other background is greatly reduced, which allows very good peak-to-background conditions for the fluorescence peaks. The x-ray fluorescence radiation is detected by a Si(Li) detector. To evaluate the capabilities of this technique for environmental applications, we have chosen a specimen that is primarily organic, USNBS orchard leaves, and one that is primarily inorganic, the USNBS fly ash. Figures 6 and 7 show their spectra.

The sensitivity of the x-ray fluorescence method for a given element depends on the photoelectric cross section and fluorescence yield for that element, the detector sensitivity for the fluorescence radiation, and the magnitude of the spectrum background in the region in which the fluorescence peak occurs. In this discussion we will relate all of these factors to the x-ray fluorescence energy of the element in question and show that sensitivity for all the elements varies as a function of fluorescence energy in a regular and predictable manner.

In Figure 8 we have plotted schematically the x-ray fluorescence spectra of all known elements for the energy range of 0-25 keV. All elements have either a K, L or M x-ray fluorescence band in this energy range. The silver $\text{K}\alpha$ radiation (22.3 keV) is capable of exciting, with varying degrees of efficiency, K transitions for all elements lighter than rhodium. It is capable of exciting the L and M transitions of almost all other elements. For both the K and L transitions, the photoelectric cross sections and the fluorescence yield are very large for fluorescence energies above 10 keV. From Figures 6 and 7, however, we see that the background, due to Compton scattering, begins to be very large above about 15 keV. This means that the fluorescence energy region for which we have good sensitivity is restricted to 10-15 keV. From Figure 8 we see that this embraces the K-series for elements 32 to 39. For the L-series it embraces all elements between 81 and 97. By measuring the peak-to-background conditions from the spectra in Figures 6 and 7, we determine that the detectability limit for elements having either a K or L

transition in the 10-18 keV energy region is about 1 ppm for a spectrum accumulated over the length of time (one hour) for Figures 6 and 7. This sensitivity is indicated on the periodic table in Figure 9.

For elements with K or L transitions in the 5-10 keV region, the spectral background is favorable, but the cross sections and fluorescence yields steadily decrease with decreasing energy. Therefore, our sensitivity is only moderate for this energy region. By measuring peak-to-background conditions for the spectra of Figures 6 and 7, and consulting cross section tables, we have estimated the varying sensitivities entered for the elements 23 to 31 and 59 to 80 in Figure 9.

Below 5 keV the cross sections, fluorescence yields and background are very unsatisfactory. This sensitivity for the lower-Z elements can be improved if one uses an ^{55}Fe excitation source, which produces 5.8 keV x-rays. For titanium in organic matrices we have achieved a sensitivity of about 15 ppm. For the low-Z elements one should be very cautious in using x-ray fluorescence for quantitative analysis. Not only is the sensitivity rather poor, but escape depths are very small. It is well-known (7) that this gives rise to large errors due to particle variation.

For elements 42 through 69, which includes most of the rare earths, the ^{241}Am excitation source (60 keV gamma) is very effective. The K-series is excited. There is excellent resolution. We have this facility in our laboratory also. For mineral matrices we can achieve a detection sensitivity of about 50 ppm.

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FIGURE CAPTIONS

Figure 1. Scanning Electron Microscope and Electron-Induced X-Ray Fluorescence Spectra of an Ion Etched Fly Ash Particle.

Figure 2. Photoelectron Spectra of Fly Ash, Before and After Water Leach, from the Allen Steam Plant, Memphis, Tennessee.

Figure 3. Photoelectron Spectra of Fly Ash, Before and After Water Leach, from the Wood River Steam Plant, St. Louis, Missouri.

Figure 4. Photoelectron Spectra of United States National Bureau of Standards Fly Ash, Before and After Water Leach.

Figure 5. A Comparison of the Photoelectron Spectrum and X-Ray Fluorescence Spectrum of Metallic Iron Powder Taken from a Foundry Environment.

Figure 6. X-Ray Fluorescence Spectrum of the United States National Bureau of Standards Orchard Leaves Specimen, Excited by Monochromatic $\text{AgK}\alpha$ X-Rays.

Figure 7. X-Ray Fluorescence Spectrum of the United States National Bureau of Standards Fly Ash Specimen, Excited by Monochromatic $\text{AgK}\alpha$ X-Rays.

Figure 8. Schematic Diagram of the K, L and M X-Ray Fluorescence Spectra for Elements 11-104.

Figure 9. Approximate Detectability Limits for the X-Ray Fluorescence Technique, Using Monochromatic $\text{AgK}\alpha$ Radiation for Excitation.