TECHNIQUES FOR CHARACTERIZATION OF PARTICULATE MATTER:
NEUTRON ACTIVATION ANALYSIS, X-RAY PHOTOELECTRON
SPECTROSCOPY, SCANNING ELECTRON MICROSCOPY

Lester D. Hulett, John M. Dale, Juel F. Emery,
William S. Lyon, Jr., and William Fulkerson
Oak Ridge National Laboratory*
Post Office Box X
Oak Ridge, Tennessee 37830

In this paper, three techniques for particulate matter analysis will
be discussed: (1) neutron activation, which is a method that samples the
entire specimen, both surface and bulk; (2) electron spectroscopy for chem-
ical analysis (ESCA), which samples particle surfaces only, (3) scanning
electron microscopy (SEM), which reveals particle size and morphology, and
can be used to determine composition differences in individual particles.

The object of this discussion will be to demonstrate how these three tech-
niques can be combined to construct highly detailed characterizations of
particulate matter specimens. It will be shown that multielement analysis
can be quickly done by neutron activation and that surface analysis and
individual particle analysis obtained by ESCA and SEM, are very important
supplementary information.

Neutron Activation Analysis

This method involves the irradiation of the specimen of interest with
neutrons. The nuclear transmutations that result are followed by gamma
ray emission whose energies and intensities correspond to the elements

*The Oak Ridge National Laboratory is operated by the Union Carbide Cor-
poration under contract with the U. S. Energy Research and Development
Administration.

By acceptance of this article, the publisher or
recipient acknowledges the U. S. Government's
right to retain a non-exclusive, royalty-free
license to any copyrighted covering the
article.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
that were present and their concentrations. Table I illustrates the large number of elements that can be studied by this method. These data were taken from samples of fly ash collected in a study of the Allen Steam Plant operated by the Tennessee Valley Authority (1, 2, 3, 4). Concentrations of various elements, as a function of particle size, are listed. It is seen that the major elements are iron, aluminum, potassium and calcium. Magnesium, titanium, sodium and zinc occur in slightly lower concentrations. Other transition and lanthanide elements occur at trace levels.

Table I suggests that many elements concentrate on particle surfaces. It is seen that the concentrations of elements such as zinc, vanadium, chromium, barium and molybdenum are higher for particles of smaller size. For a given weight of specimen, specific surface areas are much higher for the smaller particles. Perhaps those elements that collect on particle surfaces do so by condensation from a vapor phase. We will discuss this further in the conclusions of this paper.

Electron Spectroscopy for Chemical Analysis

The photoelectric effect, which is the basis for many electronic devices, has been known for many years, but its application to chemical analysis has come about only recently. The ESCA technique utilizes soft x-rays, usually AlKα or MgKα, to photoeject electrons from core levels of atoms. The kinetic energies of the emerging electrons are related to their binding energies in a very simple manner:

\[ E_K = h\nu - E_B \]
\[ E_K = \text{kinetic energy of photoejected electron} \]
\[ E_B = \text{binding energy of photoejected electron} \]
\[ h\nu = \text{energy of soft x-ray photon} \]

Binding energies of core electrons are generally unique for individual elements. There are very few cases of interference. Spectra can be quickly interpreted. It should be emphasized, however, that the ESCA technique samples only the outer surface of particulate matter. Because the low energy photoelectrons have very small escape depths, only about 50 atomic layers of the outermost surface are sampled.

Figure 1 shows a surface analysis spectrum, taken by ESCA, of an air pollution specimen collected in Knoxville, TN. Lead, silicon, chlorine, sulfur, oxygen, nitrogen, and calcium are present. It is interesting to compare this spectrum with that of fly ash—lead, chlorine and nitrogen are not as highly concentrated on fly ash as for urban aerosols. With respect to these elements, fly ash has a much "cleaner" surface.

With respect to sulfur however, both fly ash and urban aerosols are extremely dirty. The case for fly ash is illustrated by the upper two spectra in Figure 2, which compare the intensity of sulfur photoelectrons from fly ash to pure \( K_2SO_4 \)—note that they are about the same. The total concentration of sulfur in this fly ash specimen was about 0.1%, however. This suggests that all the sulfur in the fly is concentrated on the surface. This argument will be further supported by the results of SEM studies to be presented in the next section.
Figure 2 illustrates another very useful aspect of photoelectron spectra, the chemical shift. If an element is in a chemical state for which its charge environment is appreciably different from the elemental state, its binding energy will be altered, which causes a small shift in the position of its peak in the photoelectron spectrum. For the case of sulfur, the oxidized forms, $SO_2$ and $SO_4^{2-}$, have larger binding energies (2 - 6 eV) because the oxygen atoms attract electrons away and induce positive charges on the sulfur atoms. Reduced forms of sulfur, such as sulfide, have lower binding energies because of the negative charge. The lower spectrum in Figure 2 shows that three forms of sulfur, $S^0$, $SO_3^-$ and $SO_4^{2-}$, are present in coal smoke particles.

Figure 3 is an illustration of how the ESCA chemical shift can be used to study sulfur adsorbed on metal oxides. The lower two spectra show that when CaO and MgO are treated with $SO_2$, most of the sulfur remains in the +4 valence state. The skewed sulfur peak for each oxide is due to the overlap of the peak from the +4 form with that of a smaller amount of +6 form. The upper two spectra are for $SO_2$ adsorbed on the transition metal oxides, $MnO_2$ and $Fe_2O_3$. Only one species of sulfur, +6, is present. In this experiment the oxides were exposed to $SO_2$ in the presence of air. One concludes that transition metal oxides accelerate air oxidation of $SO_2$ to $SO_4^{2-}$, whereas on alkaline earth oxides, the oxidation is much slower.

Figure 4 illustrates that one should be very cautious in comparing ESCA results with those of bulk chemical analysis. The as-received specimen of Hf was bright and apparently clean, but the photoelectron spectrum hardly
revealed any Hf peaks. Instead, tin, oxygen, nitrogen and carbon peaks predominated, showing that the Hf surface contained a rather thick coating of impurities. Coatings such as these can be removed, however, by the ion etching technique. This method employs bombardment with noble gas ion, usually argon or krypton, at 1-10 keV energy. The outer surface layers are ablated ("sputtered") away. The upper spectrum in Figure 4 shows the Hf peaks very clearly after the material that suppressed the Hf photoelectrons was removed. Figure 4 carries a very important message: solid surfaces are usually drastically different from their interiors. ESCA should therefore never be used in such things as "round robin" analyses that deal with bulk compositions. There is great value, however, in surface analysis data as supplementary information. This will be discussed in the Conclusions section.

The Scanning Electron Microscopy--X-Ray Fluorescence Method (SEM-XRF)

A major advantage of the scanning electron microscopy technique, as compared to the transmission microscopy method, is that thick specimens can be viewed directly, often with no preparation. The specimen surface is scanned by a finely focused beam of electrons. Simultaneously, another electron beam scans a cathode ray tube, synchronized with the beam scanning the specimen. The intensity of the beam striking the cathode ray tube is modulated according to the emission of secondary electrons from the specimen surface. Thus, in a point-by-point fashion, an image of the specimen is recreated on the cathode ray tube. In addition to secondary electrons, x-rays, from whatever elements are present in the specimen, are also induced by the electron beam. This provides a means of elemental analysis. Either
the entire field of view, or individual particles can be analyzed. The solid state Si(Li) detector is very convenient for measuring x-ray spectra. Spectra can usually be collected in five minutes or less.

The SEM-XRF method can be used to distinguish fly ash from other particulate matter pollution. The characteristic spherical shape and elemental composition is unique. The proportion of fly ash in the specimen must be 10% or greater, however, for easy detection. Figure 5 shows an agglomerate of fly ash particles, caught in a raindrop, that had fallen on a field collector. Figure 6 illustrates how individual particles, even different parts of individual particles, can be analyzed. The large, 10 µm particle was originally spherical. Ion etching on one side removed the outer surface and made it oblong shaped. The "hole-thru" area shows that the particle is hollow. Spectra of the outer surface and the interior of the particle (the etched side) are also shown. Note that sulfur, nickel and chromium, as well as other elements, are present on the outer surface, but their concentrations are extremely low in the interior. This observation is consistent with the findings by neutron activation and ESCA that some elements are concentrated on fly ash surfaces.

A "numbers discussion" is useful for establishing a perspective of the capabilities and limitations of the SEM-XRF method: consider a 1 µm particle, which has a volume of about $10^{-12}$ cm$^3$. By focusing the electron beam on this individual particle, its composition can be determined. All elements heavier than sodium can be detected at a level less than 1%. This means that the SEM-XRF method can measure all elements at a level of $5 \times 10^{-14}$ grams or less, provided they are concentrated in small particles. In most cases, of
course, the elements of interest are not concentrated in only a few parti-
cles; when they are, it is very difficult to find them. Nevertheless, there
are many instances when individual particle analysis is desirable, and the
SEM-XRF method is very useful for this.

**Summary and Conclusions**

By combining the three methods discussed above, one can construct a
rather complete characterization of particulate matter specimens. Neutron
activation analysis is capable of detecting trace elements at very low
levels; correlations of concentration changes with particle size provide
indications of those elements that tend to be surface concentrated. ESCA
results also show what elements tend to aggregate at particulate surfaces.
We have unequivocal proof that sulfur compounds collect on both urban aero-
sols and fly ash. ESCA also can be used to determine chemical species. The
SEM-XRF method is very useful for size, shape and composition determination.

Surface analyses and individual particle studies are very desirable
supplements to bulk analysis. In the case of sulfur, surface analysis may
prove to be the more meaningful for assessing pollution hazards. Particulate
matter, that remains as such through the weathering of the environment, must
necessarily be insoluble in water. Those elements concentrated at the sur-
faces of particles, such as sulfur, are more likely to be transferred to
plant and animal life than those buried in their interiors.

Another area of great interest in pollution research is the interaction
of gaseous and solid material in smoke and other emissions. The ESCA tech-
nique is very practical for studying problems of this type. Figure 3 shows,
for example, that certain metal oxides catalyze the conversion of $\text{SO}_2$ to $\text{SO}_4^{2-}$ while others do not. Our studies also tell us something about the history of fly ash formation: we can speculate that the particles probably condense as glassy droplets containing the major elements, Fe, Al, K, Ca, Mg, Ti and Na. At a later stage, when the gas is at a lower temperature, compounds of elements that tend to be more volatile, such as those of Mo, Ga, Cl, As, Sb, and S, condense on the particle surfaces.
Photoelectron Spectrum of Air Pollution Specimen (Taken from Work of W.J. Carter and T.A. Carlson).

Figure 1
Photoelectron Spectra of Sulfur on Various Substrates.

Figure 2
Photoelectron Spectra of Sulfur on Various Substrates.

Figure 3
Hafnium Corrosion Specimen.

Figure 4

Figure 6
FIGURE CAPTIONS

Figure 1  Photoelectron Spectrum of Air Particulate Specimen. These data furnished through the courtesy of William J. Carter and T. A. Carlson, Oak Ridge National Laboratory.

Figure 2  Photoelectron Spectra of Coal Smoke Particles, Steam Plant Fly Ash, and $K_2SO_4$ Standard

Figure 3  Photoelectron Spectra of Sulfur on Metal Oxides Exposed to $SO_2$

Figure 4  Photoelectron Spectrum of Hf Surface Before and After Ion Etching

Figure 5  Scanning Electron Photomicrograph of Fly Ash Particle Washed Out by Raindrop. Size of Larger Particles is about 5 $\mu$m.

Figure 6  Scanning Electron Microscope--X-Ray Fluorescence Study of Ion Etched Fly Ash Particle
REFERENCES


