

CHARACTERIZATION OF AMBIENT CARBONACEOUS PARTICLES USING ELECTRON MICROSCOPY TECHNIQUES

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Introduction

The current understanding of the carbonaceous component associated with ambient particulate matter is limited. In most ambient speciation studies, carbon is determined through the thermal/optical evolution analysis of particulate matter collected on quartz fiber filters. Although organic carbon and elemental carbon are determined using the thermal/optical method, there is disagreement as to the accuracy of the results.¹ Furthermore, since organic carbon can originate from both combustion and naturally occurring sources, there is a need to obtain additional resolution on the organic fraction.

In an effort to improve the current understanding of the carbonaceous component associated with fine particulate matter, the U. S. Department of Energy (DOE), National Energy Technology Laboratory (NETL) is conducting studies that are designed to provide greater resolution on the carbonaceous component. As part of this effort, scanning electron microscopy (SEM), computer controlled scanning electron microscopy (CCSEM) and transmission electron microscopy (TEM) techniques are being employed to provide detailed information on individual carbon particle characteristics.

This paper outlines how electron microscopy methods are being used to complement the bulk carbon analysis methods. Information is provided to illustrate how morphology and individual particle chemistry data can be used to help speciate carbonaceous particulate matter.

Experimental Results

Electron microscopy is best performed on particles that are collected as a monolayer on a microscopically smooth filter substrate with minimal particle agglomeration. The polycarbonate (PC) membrane filter, because of its microscopically smooth surface, is a good substrate for the SEM, CCSEM and TEM analyses. Speciation samplers and "mini-vol" samplers are being used in the NETL studies to collect particles on PC filters at flow rates (~7 l/min) that typically produced samples that are well suited for electron microscopy analysis. Gravimetric analysis indicates that the PC filter sample concentrations ($\mu\text{g}/\text{m}^3$) are in close agreement to those collected on Teflon filters using the speciation sampler and also with samples collected with the FRM sampler.²

Preparation for the SEM and CCSEM analyses was performed by removing a wedge shape section (~1/8 the filter) of the filter and securing on a SEM stub using either double sided silver tape, conductive carbon tape or colloidal graphite in butanol ("DAG"). The samples were not coated with carbon or metals to permit examination of the particulate matter similar to the as-collected state. TEM preparation involved coating the sample with a thin layer of

carbon by evaporative deposition under vacuum and dissolving the PC filter in chloroform. This process leaves the particles attached to the thin carbon replica. Volatile particle species (e.g., secondary organic aerosols) may be removed during the TEM preparation.

SEM analyses were performed using the Personal SEM (Aspex Instruments) and JEOL 840 (Japan Electron Optics Laboratory) instruments. Each SEM was equipped with secondary and backscattered electron detectors coupled with an energy dispersive X-ray spectrometer (EDS) system capable of detecting elements with atomic number 6 (carbon) and greater.

The secondary electron (SE) detector yields an image that has excellent sharpness and depth of focus, which results in an image with a three-dimensional perspective. The backscattered electron (BE) detector provides an image that is dependent on the number of backscattered electrons generated when the electron beam interacts with the sample. This interaction results in intensity variations in which features consisting of higher atomic numbered elements appear brighter than features consisting of lighter elements. Thus, the contrasting brightness in a backscattered electron image is a function of composition that is not apparent in the secondary electron image. X-rays are also produced by the interaction of the electron beam and the specimen. The energy of the x-rays depends on the configuration of the electrons in the atoms of the material being examined; that is, it depends upon its elemental composition.

The secondary, backscattered and X-ray signals can be collected in synchronization with the position of the electron beam to provide highly detailed spatial and compositional information of microscopic features. With respect to characterization of carbonaceous particles, the SE and BE electron images combined with micro-chemical analysis provide a resolution that can not be obtained using the traditional bulk analytical techniques. This increased resolution is illustrated in Figure 1. In this figure, SE images and elemental spectra are provided for a carbon chain agglomerate feature and a biological (pollen) feature. The EDS spectrum indicates that the carbon chain agglomerate is composed primarily of carbon with a small amount of sulfur. The pollen is also composed primarily of carbon with small levels of potassium, sulfur and phosphorus. In general, biological material consisting of pollen and spores can be distinguished based on a distinct morphology and trace elements such as potassium and phosphorus.

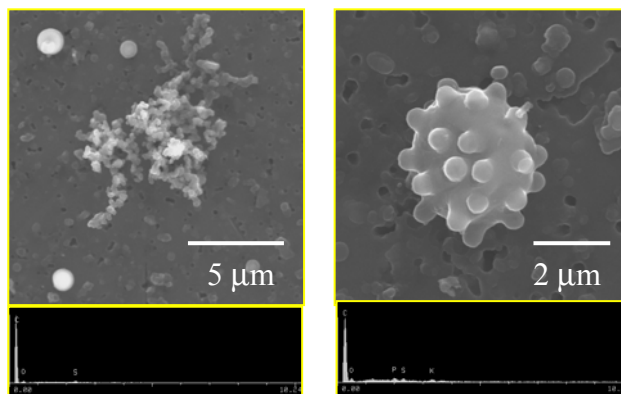


Figure 1. SE image and elemental spectra of a carbon chain agglomerate particle (left) and biological particle (right).

X-ray analysis of the particles at an accelerating voltage of 15kV produces an electron beam penetration on the order of 5 μm for

carbonaceous material. Thus, some of the carbon X-rays can be expected to originate from the PC filter substrate. In an effort to eliminate extraneous carbon X-rays generated from the filter matrix, the PC filters were coated with palladium prior to sample collection. Figure 2 provides SE images and elemental spectra of spherical alumino-silicate (SAS) particles. The image on the left is a SAS particle that was collected on a PC filter. The peak on the far left in the spectrum below the image is carbon. The image on the right is also a SAS particle. This particle was collected on a palladium coated PC filter. Note that carbon was not detected in this particle indicating that the carbon measured from the SAS particle on the left was generated from the filter matrix. The ability to effectively eliminate carbon X-rays from the filter matrix enables a better estimate on the carbon component.

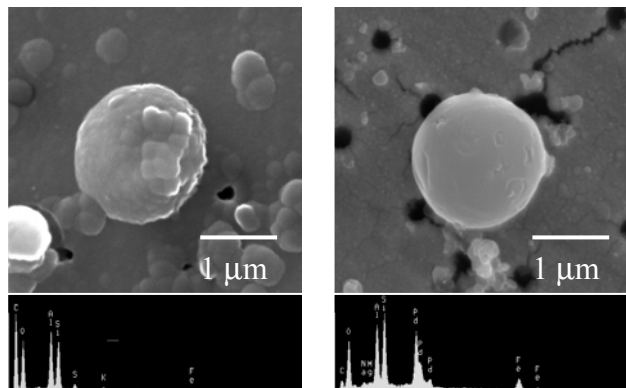


Figure 2. SE images and elemental spectra of SAS particles collected on a PC filter (left) and a palladium coated PC filter (right).

Although the manual SEM analysis can be used to provide a wealth of information on the characteristics of individual particles, quantitative data on particle concentrations and distributions is limited with this technique. This is due to the number of particles that can be analyzed effectively from the perspective of time and cost. CCSEM overcomes this limitation because it permits sufficient numbers of particles to be analyzed in an efficient manner ensuring representation of the particle population.³ With CCSEM, the size, shape (aspect ratio) and elemental composition associated with individual particles are measured and recorded in a totally automated fashion. A digital image can also be recorded for each particle (or a subset of particles) during the analysis. The CCSEM data can be summarized and reviewed off-line to potentially provide additional information based on the manual examination of the data.⁴ Thus, CCSEM analysis provides the ability to merge the strengths of a automated analysis with those obtained from a manual SEM analysis.

To evaluate whether the CCSEM carbon results were comparable to those obtained using other carbon analytical methods, an evaluation was performed on a set of seven samples. The CCSEM carbon data was obtained from samples collected on palladium coated PC filters. The CCSEM results were compared to carbon data collected using an Rupprecht & Patashnick (R&P) 5400 Ambient Carbon Particulate Monitor. Figure 3 provides a comparison of the CCSEM and R&P carbon results.

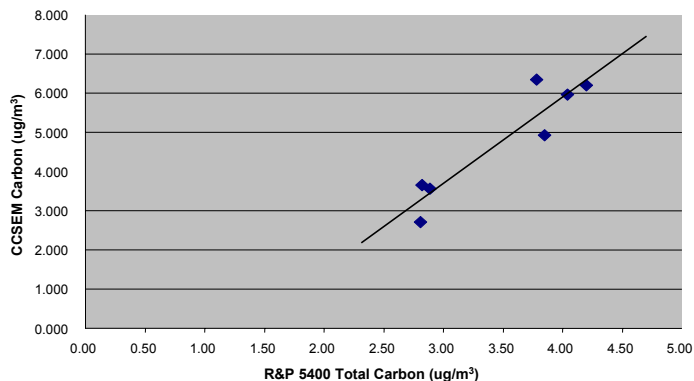


Figure 3. Comparison of CCSEM and R&P 5400 carbon data. ($\mu\text{g}/\text{m}^3$).

Results show fairly good agreement suggesting the CCSEM carbon data can be considered quantitative. Off-line review of the carbon particle images is currently being performed to further classify the carbon into subtypes consisting of pollen/spores, vegetative detritus, other biological, and soot/combustion products.

To provide additional information on the fine particle component, TEM analysis are also being employed. The TEM not only offers increased resolution for identification of submicron particles, it has the ability to provide information on molecular structure of crystalline structures through measurement of selected area electron diffraction analysis (SAED) patterns. Figure 4 provides a TEM image of $\text{PM}_{2.5}$ particles and an electron diffraction pattern of an ammonium sulfate particle.

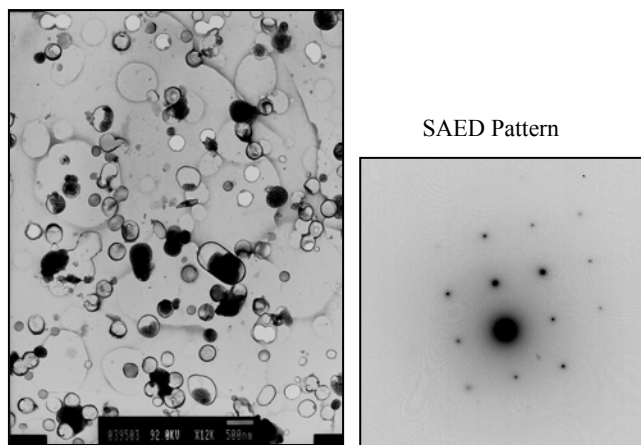


Figure 4. TEM micrograph and SAED pattern of an ammonium sulfate particle.

With respect to carbon, the TEM is being employed to provide additional resolution on carbon chain agglomerate (CCA) structures. The CCA features are a by-product of oil based fuels and thus can be used as an indicator of vehicular emissions. As part of this effort, the TEM carbon data is being compared to the elemental carbon results obtained using the thermal/optical evolution analysis method. The TEM analyses are being performed using JEOL 1200 and JEOL 2000 instruments. Each TEM is equipped with an energy dispersive X-ray spectrometer (EDS) system capable of detecting elements with atomic number 11 (sodium) and greater. The analysis protocol involves manual identification, counting, and measurement of the carbon chain agglomerates. The carbon chain agglomerates are

identified based on their unique morphological characteristics. The TEM data is used to estimate the mass of the carbon chain particles on the filter. This information is then compared directly to the elemental carbon data obtained using the thermal/optical method. Figure 5 provides TEM images of carbon chain agglomerate structures. Note the unique morphology associated with these particles.

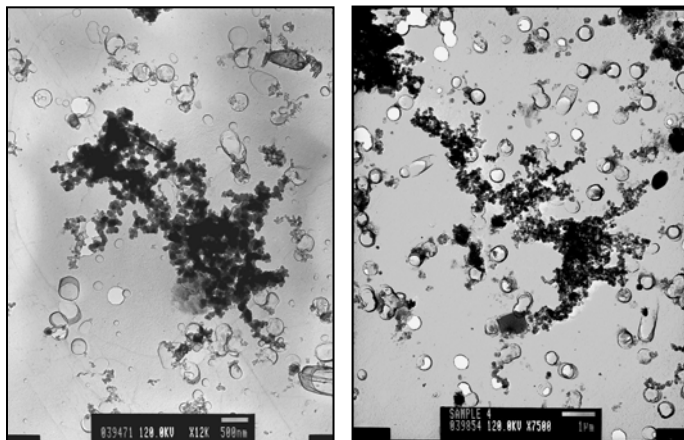


Figure 5. TEM images of carbon chain agglomerated particles.

Current efforts are focused on examining samples collected in a rural location (Holbrook, Greene County, PA) to samples collected in the Lawrenceville section of Pittsburgh, PA. Four 6-hour filter samples were collected at the Lawrenceville site and one 24-hour sample was collected in Holbrook over the same time period. Initial examination of the samples using TEM show higher concentrations of CCA on the Lawrenceville samples. This is illustrated in Figure 6.

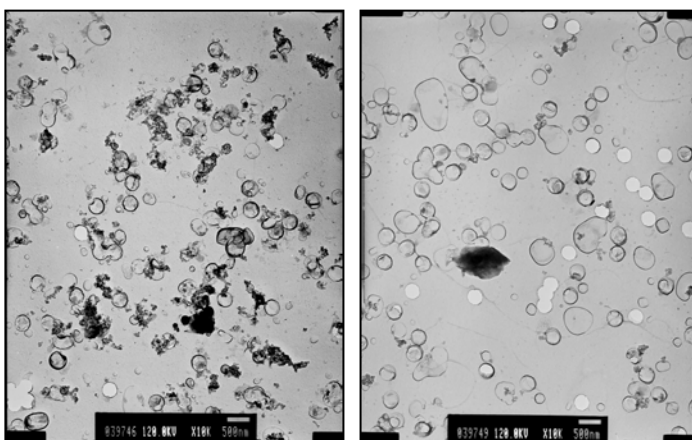


Figure 6. TEM image of samples collected in urban Lawrenceville (left) and rural Holbrook (right). The Lawrenceville sample contains a greater number of CCA particles.

TEM analysis for CCA particles was performed on the four samples collected over 6-hour periods at Lawrenceville on August 12, 1999. TEM CCA results varied from 6.2 percent (0000-0600 hours) to 28.6 percent (1800-2400 hours). The results from the Holbrook sample collected over a 24-hour period were significantly lower (3.8 percent). The TEM CCA values were compared to the elemental carbon (EC) results obtained from the analysis of samples collected on the same date using the thermal/optical technique. The

TEM CCA and thermal/optical EC results are summarized in Table 1. Comparison of the CCA and EC results shows fairly good agreement on four of the samples. A significant difference in the CCA and EC results was reported for the Lawrenceville, (18000-2400) sample. These results suggest that the EC component is composed of CCA. The results also indicate that there are significant differences between the urban and rural sites for CCA particles. Assuming that the majority of the CCA originate from vehicular emissions, the TEM results indicate that the impact from vehicular emissions was significantly higher at the urban site on this day.

Table 1. Comparison of TEM carbon chain agglomerate particles results and EC results for samples collected on August 12, 1999.

Location	Collection Time	TEM CCA Wt. %	EC Wt. %
Lawrenceville	0000-0600	6.2	10.1
Lawrenceville	0600-1200	27.1	20.0
Lawrenceville	1200-1800	14.5	11.1
Lawrenceville	1800-2400	28.6	10.5
Holbrook	0000-2400	3.8	3.4

Summary

SEM, CCSEM and TEM are capable of providing additional resolution on the ambient carbon component. Since bulk analysis methods indicate that approximately 1/3 of the total particle mass on ambient samples could be composed of carbon particles, there is both the interest and need to provide additional information on the characteristics and sources of this component. Effective utilization of electron microscopy techniques with bulk analytical methods offers the potential to provide greater insight on the concentrations and sources of organic and elemental carbon species.

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Disclaimer

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