Characterization of Ambient Particulate Matter Using Electron Microscopy and Raman Spectroscopy Techniques

Gary S. Casuccio
RJ Lee Group, Inc., 350 Hochberg Road, Monroeville, PA 15146
E-mail: gcasuccio@rjlg.com, Telephone: (724) 387-1818; Fax: (724) 733-1799

Steven F. Schlaegle
RJ Lee Group, Inc., 350 Hochberg Road, Monroeville, PA 15146
E-mail: sschlaegle@rjlg.com, Telephone: (724) 387-1843; Fax: (724) 733-1799

Traci L. Lersch
RJ Lee Group, Inc., 350 Hochberg Road, Monroeville, PA 15146
E-mail: tlersch@rjlg.com. Telephone: (724) 387-1843; Fax: (724) 733-1799

Robinson P. Khosah
Advance Technology Systems, Inc., 639 Alpha Drive – RIDC Park, Pittsburgh, PA 15238
E-mail: rkhosah@atsengineers.com; Telephone: (412) 967-1900; Fax: (412) 927-1911

Allen L. Robinson
Carnegie Mellon University, Scaife Hall, 5000 Forbes Ave., Pittsburgh, PA 15213
E-mail: alr@andrew,cmu.edu; Telephone: (412) 268-3657; Fax: (412) 268-3348

Patrick J. Treado
ChemIcon, Inc., 7301 Penn Avenue, Pittsburgh, PA 15208
E-mail: treado@chemimage.com; Telephone: (412) 241-7335; Fax: (412) 241-7311

Donald V. Martello
National Energy Technology Laboratory, U.S. Department of Energy
626 Cochran Mill Road, P.O. Box 10940. M/S 94-212, Pittsburgh, PA 15236
E-mail: donald.martello@netl.doe.gov; Telephone: (412) 386-5948; Fax: (412) 386-5920

Summary

The Department of Energy - National Energy Technology Laboratory (DOE-NETL) is conducting studies to better understand the composition of ambient particulate matter with the goal of improving the current knowledge on the relationship between anthropogenic emission sources and ambient concentrations. As part of the overall DOE-NETL effort, electron microscopy and Raman spectroscopy techniques are being employed to provide detailed information on individual particle characteristics. Work conducted to date has focused on spherical alumino-silicate (SAS) particles, carbon and sulfur-bearing species. SAS particles are of interest because they are a by-product of coal combustion and can be used as a tracer for coal-fired power plant emissions. Carbon particles are being investigated to provide additional information on elemental and organic components associated with $PM_{2.5}$ and PM_{10}. Sulfur-

bearing particles are being characterized to provide additional insight on sulfur species and to investigate potential relationships to other particle species such as SAS.

Scanning electron microscopy (SEM), computer controlled scanning electron microscopy (CCSEM), and transmission electron microscopy (TEM) are being utilized as the primary analytical tools. SEM is used to provide detailed information on morphological and elemental characteristics through manual examination of individual particles. CCSEM permits large numbers of individual particles to be analyzed in a time efficient manner. Through the analysis of statistically significant numbers of particles, CCSEM is capable of providing a quantitative microscopic analysis and produces data that can be compared to a sample's bulk characteristics while retaining its microscopic properties. TEM is used to examine the ultra-fine particle component (<1μm) and to provide additional insight on carbonaceous and sulfur species.

Samples for SEM, CCSEM and TEM analyses are being collected at the DOE-NETL ambient air monitoring research sampling station, the Holbrook and Lawrenceville monitoring sites, and the CMU ambient air monitoring supersite. $PM_{2.5}$ samples collected at the DOE-NETL sampling station are being used to assist the NETL in-house research effort. (Martello, et. al., 2001) $PM_{2.5}$ samples are being collected at Holbrook and Lawrenceville as part of the DOE Upper Ohio River Valley Project (UORVP). (NETL Research Plan) The UORVP samples are being used to provide information on particle characteristics in rural (Holbrook) and urban (Lawrenceville) areas. $PM_{2.5}$ and PM_{10} samples are being obtained from the CMU supersite located near Carnegie Mellon University to complement the overall CMU program. All samples are being collected on polycarbonate (PC) filters or palladium coated PC filters using speciation samplers or mini-vol samplers at flow rates of approximately 6 l/min. Samples collected in this manner typically have particle loadings that are ideally suited for the SEM/CCSEM/TEM analysis.

Results obtained to date indicate that the SEM/CCSEM/TEM analysis approach can be used to provide a wealth of information on ambient particle characteristics. For example, analysis of samples collected as part of the NETL in-house research effort showed that CCSEM results for sulfur and carbon particles were in close agreement to results obtained using bulk analytical methods. (Martello, et. al., 2001) This is of significance because it illustrates that CCSEM can be used to provide quantitative data that can be compared directly to bulk analytical results. The NETL in-house research effort has also demonstrated the value of using of morphological information, obtained through manual SEM examination to distinguish SAS from crustal particles, and to provide for further discrimination on carbon species (e.g., carbon chain agglomerates and biological particles). Morphological information of this nature can be of great value in identifying specific source impact on ambient air quality, and it can only be provided through microscopic analysis.

Initial analyses of the Holbrook and Lawrenceville samples have focused on the similarities and differences related to SAS and carbon particles observed on samples collected at the rural and urban locations. The preliminary results indicate that the SAS particles account for a small amount (~0.05 to 0.1%) of the ambient concentration, and that the SAS concentrations are similar at the rural and urban sites suggesting a regional impact from coal-fired power plants. Additional samples are being analyzed to confirm these findings. Evaluation of carbon component has been performed using TEM to provide greater resolution on the elemental carbon component through the characterization of carbon chain agglomerates. Preliminary results show significantly higher concentrations of at the carbon chain agglomerates at the urban site. Carbon chain agglomerates may prove to be a key species because they can be used as a tracer for vehicular emissions.

The microscopy analyses of ambient $PM_{2.5}$ and PM_{10} collected from the CMU site has focused on the carbonaceous component to further resolve the organic and elemental carbon fractions. The initial SEM examination has indicated that biological particles consisting primarily of plant material can be easily distinguished based on the unique morphological characteristics. Future efforts are geared towards quantifying the concentrations of organic particulate matter using CCSEM techniques. The elemental carbon fraction of the samples appeared to be comprised mainly of fine carbon chain agglomerate particles the are best resolved using TEM techniques. The contribution of the carbon chain agglomerate particles compared well with the bulk elemental results. SAS and iron-rich particle spheres are also currently being investigated.

Examination of the $PM_{2.5}$ and PM_{10} samples using SEM, CCSEM and TEM analytical methods has already provided a wealth of information on individual ambient particle characteristics. However, one of the limitations associated with the SEM is that it does not have the ability to provide information on molecular structure. For example, the SEM can detect sulfur particles, but it does not have the ability to directly determine whether a sulfur particle is ammonium sulfate. The TEM, using selected area electron diffraction (SAED) analysis, can be used to provide on the molecular structure of crystalline particles. Work performed thus far has shown the potential to the TEM to identify ammonium sulfate particles. However, use of the TEM for this purpose is both time consuming and tedious. Thus, TEM SAED analysis cannot be used as a routine analytical tool for large numbers of particles.

Since a component of the overall objectives of the DOE-NETL program is to provide detailed characterization of the organic components on the fine particulate matter and to provide insight into the formation and atmospheric chemistry of secondary $PM_{2.5}$ formed from reaction of sulfur, nitrogen and ammonia, complementary microscopy analysis techniques must be employed to augment the electron microscopy techniques. Raman chemical imaging, which combines the molecular analysis capabilities of Raman spectroscopy and the visual power of an optical microscope, provides a potential solution for obtaining molecular information on individual organic and inorganic particles. Funded through the DOE STTR program, RJ Lee Group and ChemIcon are investigating the potential of a combined Raman/SEM (RSEM) microscope to provide information on the size, morphology, elemental and molecular composition, and molecular structure of fine particulate matter.

References

U.S. Department of Energy National Energy Technology Laboratory, Five Year Research Plan on Fine Particulate Matter in the Atmosphere, FY2001-FY2005.

Martello, D. V., Anderson, Anderson, R. R., White, C. M., Casuccio, G. S., Schlaegle, S. F., “Quantitative Scanning Electron Microscopy Methods to Characterize Ambient Air PM 2.5,” *ACS Fuel Chemistry Division Preprints*, **2001**, *46(2)*, 606-608.