1.5 A BRIEF HISTORY OF AEROSOL CARBON ANALYTICAL METHODS

Jeffrey S. Gaffney and Nancy A. Marley
Environmental Science Division
Argonne National Laboratory
Argonne, IL 60439-4843
630-252-5178
gaffney@anl.gov

1. INTRODUCTION

There has been significant interest in the role that carbonaceous aerosols play as radiatively important species in climate and visibility reduction, as potential toxic agents to human health in urban regions, and as surfaces that can catalyze atmospheric chemical reactions. These aerosols are a mixture of primary organic matter that is emitted from a number of sources, including mobile sources such as diesel engines, and secondary species formed from the tropospheric oxidation of primary organics from both anthropogenic and biogenic sources. Carbonaceous aerosols are therefore highly heterogeneous in nature and consist of complex mixtures of both semi-volatile and more refractory material. The semi-volatile material can consist of both primary and secondary organic matter and has been referred to generically as organic carbon in most analytical papers. The more refractory material has been referred to as elemental, sooty, graphitic or black carbon.

Carbonaceous aerosols have recently been identified as key aerosol species that could have significant impacts on the radiative balance of the atmosphere. We have previously presented a paper on the significance of megacities as major sources of carbonaceous aerosols and the roles that they can play in radiative forcing from both direct and indirect effects (*1*). Heavy diesel engine use in these megacities has been identified as a significant source of diesel soot, an important contributor to the carbonaceous aerosols levels in urban centers, and to the primary emission of this material into the atmosphere on regional and global scales.

We present here a brief review of some of the earliest work on carbonaceous aerosol characterization with particular attention given to the work before 1985. The methods used that have led to the common use of the terms, black carbon, elemental carbon, and graphitic carbon will be described, along with some of the past and current difficulties associated with the analytical characterization of this organic heterogeneous mixture. The early work on thermal evolution methods, optical absorption and spectroscopic characterization will be highlighted. In addition, the use of stable and radioisotopic measurements to aid in source determination will also be reviewed.

2. CARBON CHARACTERIZATION

An excellent review of the status of carbonaceous aerosol characterization methods and the atmospheric life cycle of particulate carbon, as it was understood in 1982, was written by Steve Cadle and Peter Groblicki at the General Motors Laboratories (*2).* Two general approaches were first used to determine carbonaceous aerosol composition: 1) a detailed analyses of the organic fractions by use of mass spectrometry (MS) or gas chromatography/mass spectrometry (GC/MS) or 2) a total-carbon analyses that yielded the total mass of carbonaceous aerosols. It was recognized early that the complexity of the carbonaceous aerosols made it a formidable task to routinely determine their complete molecular composition. Therefore, a third type of analytical approach evolved as a compromise between the detailed organic characterization and total carbon methods. This method separated the semi-volatile or the higher volatility carbon species by solvent extraction, measuring these as a class, followed by the measurement of the insoluble carbon fractions that remained (*2, 3*). The carbonaceous species that were efficiently extracted by organic solvents (e.g. benzene, carbon tetrachloride) became known as organic carbon. Since the carbonaceous fraction left behind was highly absorbing it became known as black carbon.

This hybrid approach was used by Dennis Schuetzle for the examination of organics in atmospheric aerosols in his thesis research (*4, 5*). Dr. Schuetzle continued this work using GC/MS methods to characterize the extracted fracitions for the source evaluation of polycyclic aromatic hydrocarbons (PAHs) from mobile sources. Daniel Grosjean, working in the Los Angeles and Riverside air basins, and a group in New York City led by Joan Daisey also used solvent extraction successfully to characterize both secondary organic and PAH components in urban aerosols (6, 7).

**Corresponding author address:* Jeffrey S. Gaffney, Environmental Research Division, 9700 South Cass Avenue, Argonne National Laboratory, Argonne, IL 60439-4843; e-mail: gaffney@anl.gov.

As the organic aerosol fractions were found to be correlated with the black carbon content in many urban areas, a group at Lawrence Berkeley National Laboratory (LBNL) made use of laser-Raman methods to characterize the carbonaceous aerosols (*8*). Noting that the black carbon had Raman bands similar to graphite, Rosen and Novakov used the term "graphitic" carbon to describe the material. Other optical measurements focused on the blackness of the carbonaceous aerosols by using optical transmission or optoacoustic methods to determine the mass of carbon emissions from diesel sources (*9-10*). The strong and relatively constant visible absorption of black carbon, along with the fact that there were no other major highly absorbing aerosol species in the visible range, led the LBNL group to develop the "aethalometer" for the continuous measurement of black carbon aerosols. The use of this instrument in the polar-regions demonstrated early on that the black carbon aerosols were transported long distances (*11, 12*). The LBNL group, led by Tica Novakov, had clearly identified black carbon or graphitic carbon, as they referred to it, as being important for its radiative effects as well as other important environmental impacts. Other key members of this research group included Hal Rosen, Tony Hansen, and Lara Gundel.

A modification of the third type of analytical approach to carbonaceous aerosol determination was also developed at this time. These methods used programmed sample heating as a means of selectively separating the more volatile organic species from the black carbon under a variety of pyrolysis conditions (*3, 12-16*). At this point, the more refractory black carbon material became known as elemental carbon in contrast to the more thermally labile organic carbon species. One of the issues with this approach was the potential for cross over effects due to organic carbonization, i.e. organic to elemental conversion during the thermal analysis. Therefore, the elemental or black carbon could be determined as organic carbon by early volatilization and the organic carbon could be charred in the process and reported as black carbon. This led to the combination of the thermal and optical methods by James Huntzicker at the Oregon Graduate Center. Using a thermo-optical approach, the "blackness" of the aerosol sample was monitored by optical transmission during the heating program to determine any changes in the refractory carbon content during analysis (*16*).

At about this time, research was also underway examining the effects of heating rates on the vaporization of thermally sensitive biological molecules by using mass spectroscopy. These studies observed that with faster heating rates vaporization would be favored over thermal cracking and charring of the organic compounds. This approach was shown to be effective in the development of a simple system for the efficient thermal separation of the organic and elemental carbon aerosol fractions. It was also demonstrated in this work and in subsequent research that the material was not in fact "graphitic" in nature in that it was capable of volatilization at about 700 C (*3, 20*). This work indicated that the heating rates, the temperature used for separation of organic and elemental (or black) carbon fractions, and the time the sample was maintained at the final temperature were all important if an empirical approach to using thermal aerosol characterization methods were to be successfully reproduced.

The initial sample volatilization was usually accomplished in an inert atmosphere such as helium followed by the use of a heated copper oxide tube to achieve complete catalytic oxidation of the evolved species to carbon dioxide. The second sample volatilization occurred in an oxygen atmosphere to achieve complete oxidation of the elemental or black carbon components. Most of the thermal analytical methods made use of gas chromatography with thermal conductivity detection to monitor the carbon dioxide that was evolved during the programmed sample heating process. In some cases, the carbon dioxide was monitored by the use of a non-dispersive infrared detector system. A more sensitive detection method was developed in Huntzicker's laboratory which made use of the conversion of the evolved carbon dioxide to methane followed by flame ionization detection (*16*).

It is interesting to note that these methodologies, initially developed in the 1970's and early 1980's, are now the current basis for a number of commercial instruments for the determination of organic and elemental carbon in atmospheric aerosols. There are still issues regarding the overall accuracy of these various approaches. Much of this uncertainty likely arises from the highly variable nature of the carbonaceous aerosols and the attempt to force their separation into the analytically defined classifications of organic and elemental carbon. Atmospheric carbonaceous aerosols are quite variable in composition and characteristics depending upon the sources and the "atmospheric ages" of the aerosols and therefore may not always easily fall into these analytically determined categories using empirical and method dependent categories.

3. ISOTOPIC CHARACTERIZATION

One of the authors (JSG) was involved in the determination of the source of black pulmonary pigment in human tissues during the late 1970s (*21*). This material was found in the bronchial and coronal lymph nodes of all individuals who had been autopsied and was at one time considered to be a pigment similar to melanin in the eye. However, further study indicated that the concentration of this material was dependent on the individual's exposure to combustion sources and was thought to be carbon soot particles deposited in the lymphatic systems after macrophages had ingested the particles as part of the bodies' cleansing mechanism. A procedure was developed for the separation of the black carbon from the surrounding tissue, and stable carbon isotopic analyses were used to help identify the material. In the process of these studies it was discovered that the high corn consumption in the North American diet acted to radio-label human tissue with high levels of ^{13}C when compared with the European diets (*22*).

Two primary biochemical pathways have been identified for the initial fixation of carbon dioxide into plants during photosynthesis. The first pathway, identified by Melvin Calvin and his colleague Benson, was called the C-3 pathway as three carbon dioxide molecules are fixed into the dicarboxylic acid formed by the process. Another more efficient biochemical pathway, which fixes four carbon dioxide molecules, was later identified by Hatch and Slack. The C-4 pathway is less discriminatory than the C-3 pathway towards the uptake of ^{13}C vs ^{12}C isotopes of atmospheric carbon dioxide and therefore leads to a smaller depletion relative to the stable isotopic ratio of atmospheric carbon dioxide.

The measurement of the stable isotopic ratios are compared to a standard (usually a limestone from the PeeDee Belemnite formation, PDB) that is considered to be 0. Thus, the isotopic ratio of atmospheric carbon dioxide is about 8 parts per thousand (^{o}/oo) less than the PDB standard and has a del value of -8. The plants which utilize the C-4 fixation have a $^{13}C/^{12}C$ ratio relative to PDB of approximately -12 ^{o}/oo while C-3 plants have a $^{13}C/^{12}C$ ratio relative to PDB of approximately -26 ^{o}/oo. Hence, corn that is a C-4 plant is nicely labeled in ^{13}C and this isotopic label is passed through the food change with some minor changes from the animal biochemistries. Thus, it was also found that this could be useful as a tool for identification of food adulteration such as soy/meat mixtures in corn fed beef (*23*).

The potential for the use of the radioisotope ^{14}C as well as the stable isotope ^{13}C as tracers for fossil carbon and C-3 or C-4 biogenic carbon was identified by a number of researchers in the late 1970s and early 1980s (*20, 25-29*). Two approaches were used for the determination of ^{14}C, one involved direct low-level counting using miniature gas proportional counters (*30*), and the other method, pioneered by Lloyd Currie at the then National Bureau of Standards, made use of high energy accelerator mass spectrometry (*31*).

This work led to the idea that both stable and radio-isotopes could be useful in the differentiation of many sources of carbon including aerosol sources (*20, 24*). Indeed measurements were made that clearly showed that the Arctic Haze identified in the late 1970s and early 1980s had a significant amount of biomass derived carbon based upon the isotopic signatures and ^{14}C content (*20*).

4. SOME FINAL REMARKS

This paper is primarily presented as a very brief review of some of the forefront research on carbonaceous aerosol characterization methods on which many of the current methods are based. These now include the use of multi-angle measurements to minimize scattering error in the determination of black carbon absorption, the application of other spectroscopic approaches including improvements in both optoacoustic or photoacoustic and photothermal methods as well as photoluminescence, and also the use of single particle aerosol mass spectrometry to measure both inorganic and organic aerosol species. There has been a great deal of literature that dates after this early research period, but it is important to reflect on some of the results that preceded the current work in order to keep the results in perspective.

Also, it is important to note that carbonaceous aerosols are dynamic. They can react and interact with gases and ultrafine aerosols as well as other condensable species and their surface and bulk properties are not fixed in time. Sources of carbonaceous aerosols include anthropogenic primary and secondary carbon sources, as well as biogenic primary and secondary sources. All of these sources can be important in different locations, etc. so one should not expect that all carbon aerosols will be similar in behavior either chemically, physically, or optically. That said, it is quite interesting that many of the carbonaceous aerosols have successfully been compared with the empirical approaches described here and have been found to be qualitatively similar and in some cases semi-quantitatively similar in certain scenarios (i.e urban centers in the eastern U.S). (20).

So it must be recognized that organic carbon, graphitic carbon, elemental carbon, and black carbon, etc. are descriptive terms originally defined by the early analytical methods used to characterize a heterogeneous material and not an indication of the existence of discrete molecular species. Much useful information can be learned about these species from these analytical methods, in particular, the identification of the "variability" of the carbonaceous aerosols in terms of their washout characteristics, surface chemistries, and optical properties as a function of their atmospheric lifetimes. We can also begin to attempt to parameterize their atmospheric behavior and chemical and physical transformations, recognizing that they are being treated as surrogate species in the atmospheric models.

4. ACKNOWLEDGEMENT

This work was supported by the US Dept. of Energy's Atmospheric Science Program. The authors wish to thank Mr. Rick Petty of the U.S. DOE for his continuing support and encouragement.

5. REFERENCES

1. Gaffney, J.S. and N.A. Marley, “Megacities as Sources of Black Carbon”, Sixth Conference on Atmospheric Chemistry: Air Quality in Megacities, 84th

National Meeting of the American Meteorological Society, Seattle, WA, paper J2.3 (2004), 6 pages in Combined Preprints CD-ROM volume.

2. Cadle, S.H. and P.J. Groblicki, In "Particulate Carbon: Atmospheric Life Cycle." Wolf, G.T. and R.L. Klimisch, Eds. Plenum Press, NY, 1982, pp. 89-108.

3. Tanner, R.L., J.S. Gaffney, and M.F. Phillips, "Determination of Organic and Elemental Carbon in Atmospheric Aerosol Samples by Thermal Evolution." *Anal. Chem.* **54** 1627-1630 (1982).

4. Schuetzle, D., "Computer controlled high resolution mass spectrometric analysis of air pollutants." A.L. Crittenden, Chemistry & R.J. Charlson, Civil Engineering advisors, University of Washington, Seattle, Ph.D. Thesis, 1972.

5. Schuetzle, D. Cronn, A.L. Crittendon, and R.J. Charlson, " Molecular composition of secondary aerosol and its possible origin." *Environ. Sci. Technol.* **9**, 838-845 (1975).

6. Grosjean, D. "Solvent extraction and organic carbon determination in atmospheric particulate matter: The organic extraction-organic carbon analyzer (OE/OCA) technique." *Anal. Chem.* **47**, 797-805, (1975).

7. Daisey, J. M., "Organic Compounds in Urban Aerosols." *Ann. N.Y. Acad. Sci.*, **338**, 50-69, (1980).

8. Rosen, H. , A.D.A. Hansen, L. Gundel, and T. Novakov, " Identification of the optically absorbing component in urban aerosols." *Appl. Opt.* **17**, 3859-3861 (1978).

9. Roessler, D.M. and F.R. Faxfog, F.R., "Optoacoustic measurement of optical absorption in acetylene smoke. *J. Opt.* Soc. Amer., **69**, 1699-1704 (1979).

10. Japar, S.M. and D.K. Killinger, " Photoacoustic and absorption spectrum of airborne carbon particulate using a tunable dye laser." *Chem. Phys. Lett.* **66**, 207-209 (1979).

11. Hansen, A., Rosen, H. and Novakov, T.. "The Aethalometer: an instrument for the real-time measurement of optical absorption by aerosol particles," *The Science of the Total Environment*, **36**, 191-196 (1984).

12. Rosen, H., T. Novakov, and B. Bodhaine, "Soot in the Arctic," *Atmospheric Environment*, **15**, 1371-1374 (1981).

13. Cadle, S.H., P.J. Groblicki, and D.P. Stroup, " Automated carbon analyzer for particulate samples. " *Anal.Chem.*, **52**, 2201-2208 (1980).

14. Ellis, E.C. and T. Novakov, Application of thermal analysis to the characterization of organic aerosol particles, *The Sci. of the Total Environ.* **23**, 227-238 (1982).

15. Puxbaum, H. " Thermal gas analyzer for the characterization of carbon and sulfur compounds in atmospheric particles. " Z. Anal. Chem. 298, 250-259 (1979).

16. Huntzicker, J.J., R.L. Johnson, J.J. Shah and R.A. Carey, "Analysis of organic and elemental carbon in ambient aerosols by a thermal-optical method." In Particulate Carbon: Atmospheric Life Cycle, G.T. Wolff and R.L. Klimisch, eds., New York, Plenum Press, 1982, p. 79-88.

17. Gaffney, J.S. R.C. Pierce, and L. Friedman, "Mass Spectrometer Study of Evaporation of α-Amino Acids." *J. Am. Chem. Soc.* **98** 4293-4298 (1977).

18. Gaffney, J.S. R.C. Pierce, and L. Friedman, "Ammonia Chemical Ionization of Some Free Amino Acids and Underivatized Peptides." *Int. J. Mass Spec. Ion Phys.* **25** 439-454 (1977).

19. Gaffney, J.S. and L. Friedman, "Studies on Rapid Heating of Thermally Fragile Molecules," Twenty-Fifth Annual Conference on Mass Spectrometry and Allied Topics, Washington, D.C., Abstract WD-6, 375 May 29-June 3, 1977.

20. Gaffney, J.S., R.L. Tanner, and M. Phillips, "Separating Carbonaceous Aerosol Source Terms Using Thermal Evolution, Carbon Isotopic Measurements, and C/N/S Determinations." *The Science of the Total Environment* **36** 53-60 (1984).

21. D.N. Slatkin, L. Friedman, A.P. Irsa, and J.S. Gaffney, "The $^{13}C/^{12}C$ Ratio in Black Pulmonary Pigment: A Mass Spectrometric Study." *Human Pathology* **9** 259-267 (1978).

22. Gaffney, J.S. A.P. Irsa, L. Friedman, and D.N. Slatkin, "Natural $^{13}C/^{12}C$ Ratio Variations in Human Populations." *Biomedical Mass Spectrometry* **5** 495-497 (1978).

23. Gaffney, J.S. A.P. Irsa, L. Friedman, and E. Emken, "$^{13}C/^{12}C$ Analysis of Vegetable Oils, Starches, Proteins, and Soy-Meat Mixtures." *J. Agr. Food Chem.* **27** 475-478 (1979).

24. R.L. Tanner and J.S. Gaffney, "Carbon Isotopes as Tracers of Biogenic and Fossil-Fuel Derived Carbon Transport in the Atmosphere." in *Fossil Fuels Utilization: Environmental Concerns* , edited by R. Markuszewski and B.D. Blaustein., American Chemical Society, Washington, D.C., *ACS Symposium Series* **No. 319**, pp. 267-276, 1986.

25. Currie, L.A., Kunen, S.M., Voorhees, K.J., Murphy, R.B., and Koch, W.F., "Analysis of Carbonaceous Particulates and Characterization of Their Sources by Low-level Radiocarbon Counting and Pyrolysis/Gas Chromatography/Mass Spectrometry," In: Proceedings of the Carbonaceous Particles in the Atmosphere, Lawrence Berkeley Laboratory, University of California, p. 36-48 (1978).

26. Currie, L.A., J. Noakes, and D. Breiter, In "Radiocarbon Dating", R. Berger and H.E. Suess, Eds. University of California Press, Berkeley, CA, 58-175, 1979.

27. Cooper, J.A., L.A. Currie, and G.A. Klouda, "Assessment of Contemporary Carbon Combustion Source Contributions to Urban Air Particulate Levels Using Carbon-14 Measurements", *Environ. Sci. Tech.*, **15**, 1045, (1981).

28. Gaffney, J.S., "Organic air pollutants: Setting priorities for long-term research needs. Report BNL 51605, UC-11 (1982).

29. Currie, L.A., G.A. Klouda and J.A. Cooper, "Mini-Radiocarbon Measurements, Chemical Selectivity and Impact of Man on Environmental Pollution and Climate", Radiocarbon, 22, 349-362 (1980).

30. Harbottle, G., F.V. Sayre, and R.W. Stoenner, "Carbon-14 Dating of Small Samples by Proportional Counting." *Science*, **206**, 683-685 (1979).

31. Currie, L.A., Klouda, G.A., and Voorhees, K.J., "Atmospheric Carbon: The Importance of Accelerator Mass Spectrometry," Nucl. Instrum. Methods Phys. Res. 233 (B5), pp. 371-379, (1984).