Reprinted from APPLIED OPTICS, Vol. 17, page 3859, December 15, 1978
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Identification of the optically absorbing component in urban aerosols

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Received 29 August 1978.
0003-6935/78/1215-3859$0.50/0.
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Aerosol particles may play a significant role in modifying the local and global climate, and therefore it is important to study the optical properties of these suspended particulates. The over-all effect of aerosol particles in heating or cooling the earth's surface depends critically on the relative magnitude of their scattering and absorption coefficients.[1,2] In the past the effects of aerosols were thought to be due almost entirely to their scattering properties, but more recently it has been realized that the absorptivity of these particles is large. Therefore, much more attention has been given to the imaginary index of refraction in heat balance calculations as well as in visibility degradation.[3,4] To model the effects of fossil fuel combustion on climate and visibility, it is important to establish the nature of these absorbing species. In this Letter we will describe the application of Raman spectroscopy and an optical attenuation technique to show that the high optical absorptivity of urban particulates and particles produced directly from various combustion sources is due to graphitic carbon, one component of combustion-produced soot which also contains a complex mixture of organics.

Raman spectroscopy is a highly selective method of analysis, which, until recently, has not been applied to the characterization of air pollution particulates.[5-7] The technique can often be used to make unambiguous identifications since different chemical species have characteristic vibrational modes and therefore characteristic Raman spectra. The Raman spectroscopy apparatus uses a Coherent Radiation argon ion laser producing 1 W of power at 514 nm. The laser beam is focused by a 75-mm focal length cylindrical lens to a spot 0.06 mm × 2 mm on the sample surface via a small mirror, and the backscattered radiation is collected and imaged by an $f/1$ lens onto the slit of a 1-m Jarrell Ashe double monochromator equipped with two 1180-grooves/mm gratings blazed at 5000 Å. The output of the spectrometer is detected by an FW130 photomultiplier cooled to −20°C and used in a photon-counting mode. The pulses, after appropriate shaping, are counted and displayed on a multichannel analyzer. A computer-controlled grating drive made by RKB, Inc., allows a given spectral region to be scanned many times and added to the memory of the multichannel analyzer, greatly improving the SNR. In order to minimize heating effects, the highly absorbing samples used in these experiments are rotated at 1800 rpm by a motor, which increases the area illuminated by the laser beam by a large factor with almost no loss in signal level. The focal spot of the laser is located approximately 5 mm below the axis of rotation so that the effective illuminated area is an annulus of 5-mm radius and 2-mm width, resulting in the low power density of ~1 W/cm^2.

The Raman spectra between 920 cm^{-1} and 1950 cm^{-1} of ambient, automobile exhaust, and diesel exhaust particulates are compared with the spectra of activated carbon and polycrystalline graphite in Fig. 1. It is evident that the spectra of activated carbon, diesel exhaust, automobile exhaust, and the ambient sample are very similar, with the positions of the two Raman modes coincident to within ±10 cm^{-1}, the estimated experimental error. The ambient sample was collected as part of the RAPS program in St. Louis, Missouri; however, the same Raman modes are also evident in every urban sample studied, including samples collected in Buffalo, New York, and Berkeley, Fremont, and Anaheim, California. Koenig *et al.*[9] have studied the Raman spectrum of activated carbon and have identified the modes near 1600 cm^{-1} and 1350 cm^{-1} as being due to phonons propagating within graphitic planes. The close correspondence of the spectra in Fig. 1 indicates the presence of physical structures similar to activated carbon in both source and ambient samples. These graphitic species are formed directly in combustion, and throughout the text we shall use the term graphitic soot to describe them.

Urban and combustion source particulates collected on various filter media have a gray or black appearance. The graphitic species identified by Raman spectroscopy are the most likely candidate for explaining this coloration. To test this hypothesis, we have developed an optical attenuation technique to measure quantitatively various properties of the absorbing species. The optical attenuation apparatus compares the transmission of a 633-nm He–Ne laser beam through a loaded filter relative to that of a blank filter (Fig. 2). The loaded filters are placed in the beam with the loaded side toward the laser: after multiple scattering through the filter substrate, the light is collected by an $f/1$ lens and focused on a photomultiplier tube. The data presented in this paper were obtained from particles collected on Millipore or quartz