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APPLICATION OF THE OPTICAL ABSORPTION TECHNIQUE TO THE CHARACTERIZATION OF THE CARBONACEOUS COMPONENT OF AMBIENT AND SOURCE PARTICULATE SAMPLES †

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ABSTRACT

The optical absorption properties of some ambient and source particulate samples have been measured. These results suggest that the absorptivity is due to "graphitic" soot and that a major fraction of the ambient carbonaceous aerosol in the winter and summer episodes investigated is primary in origin.

ONE MAJOR UNCERTAINTY in the air pollution field is the extent to which the carbonaceous aerosol particle burden is due to secondary reactions or is of primary origin. Such a determination is clearly necessary for designing an effective control strategy; but due to the complex nature of the samples, it has been a difficult analytical problem to develop methods for discriminating between these two sources of carbon. One distinct feature of primary emissions, however, is that they appear to have a large "graphitic" soot component. This component offers an attractive tracer for primary emissions since it has some unique physical properties. These include a rather high oxidation threshold and a large and uniform absorptivity throughout the visible spectral region, which we suggest leads to the blackish or grayish appearance of ambient and source particulate samples. It should be emphasized that "graphitic" soot represents only one component of the primary carbonaceous aerosol particles, which, in general, also contain a large nonabsorbing and volatile organic fraction.

EXPERIMENTAL.

Particulate samples were collected simultaneously on 1.2-μm Millipore filters and on quartz fiber filters that had been prefired to remove all combustible carbon. The total carbon on the quartz fiber filters was determined by combustion in an oxygen atmosphere, followed by separation and measurement of the evolved CO_2 with a gas chromatograph/thermal conductivity detector system (1)*. After correction for differing flow rates, these values were then used to calculate the total carbon loadings on the corresponding Millipore filters. Optical attenuation measurements were made on the loaded Millipore filters by an apparatus incorporating a 1-mW He-Ne laser as a light source (λ = .6328 μm) and a photomultiplier as a detector. Essentially all of the light transmitted through the filter was collected and focused onto the photomultiplier by an f/1 lens, and compared with the average transmission through blank filters, which was assigned a value of 100%. This technique for measuring absorptivity is based on a principle similar to that of the opal glass technique developed by Lin et al. (2). The attenuation measured in the above fashion should be primarily due to absorption rather than scattering because most of the radiation scattered from abmient aerosol particles is in the forward direction and therefore should not contribute to the attenuation since it is collected by the small-f-number lens.

The particulate samples used in these experiments were (1) ambient samples collected in the winter in Berkeley, California (sampling times, from 15 min-4 hr; flow rate, ≈ 70 liters/min); (2) ambient samples collected in the summer in Anaheim, California (sampling time, 24 hr; flow rate, ≈ 7 liters/min); (3) tunnel samples collected in a storage room between two bores of the Caldecott Tunnel, on a major San Francisco Bay Area commuter route with a traffic flow of approximately 10^5 vehicles/day; (4) garage samples collected from the rear of an underground parking garage, in which the automobile traffic flow was approximately 35 vehicles/hr with an average stay of 1-2 hr; (5) diesel exhaust samples from a small air-cooled engine; (6) motor scooter exhaust samples from a two-stroke engine operating at a slow idle; and (7) soot samples generated by a very rich acetylene flame.

RESULTS.

The absorbing properties of ambient samples collected in Berkeley, California, in the winter and in Anaheim, California, in the summer can be compared with measurements made on various source particulate samples. In all cases a strong correlation between the carbon content and the absorptivity of the collected particulates is observed. This correlation, in combination with measurements of the wavelength dependence and temperature dependence of the absorptivity, suggests that the absorbing species is "graphitic" soot. A striking similarity is observed in the dependence of the absorptivity on the carbon content for the Berkeley and Anaheim particulate samples (Fig. 1a). This is true in spite of the fact that several of the Anaheim samples were taken under high oxidant conditions, which are expected to promote secondary production of aerosol particles. Also, the absorptivity per unit mass of carbon for these ambient samples is quite similar to that of various mobile source exhaust samples (Fig. 1b). These results may indicate that a large fraction of the carbonaceous aerosol particles in the summer and winter episodes investigated is primary in origin. Further studies are under way to test the generality of these results under a wide range of atmospheric conditions and for a variety of combustion sources.

Figures 1a and 1b show measurements of the attenuation vs. total carbon content of a number of ambient and mobile-source exhaust samples. There is a strong correlation between the carbon content and the attenuation. Since sulfur and nitrogen species in the form of common salts such as ammonium sulfate and ammonium nitrate are nonabsorbing in the visible region, and since there are no significant amounts of transition metals like Fe in these samples, we suggest that the absorption is due to the carbonaceous component of the aerosol particles.

It should be emphasized that the coverage of these samples is very light (≈ 1 monolayer or particles or less); and yet the absorptivity is quite high, implying that the refractive index of the

* Numbers in parentheses designate references at the end of the paper.

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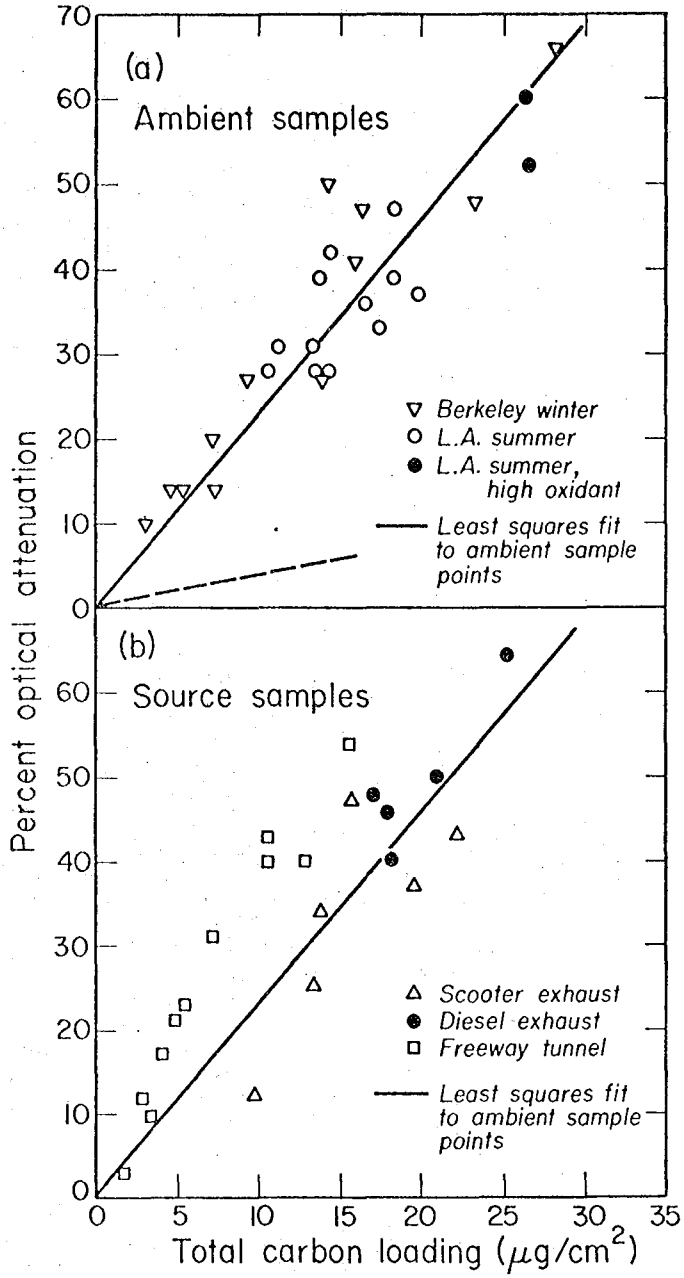

Figure 1. (a) Optical attenuation vs. total carbon loading for ambient samples collected in Berkeley, California, in the winter and in Anaheim, California, in the summer. The peak ozone levels for the daily summer samples ranged from 30 ppb to 270 ppb. The points designated by a solid circle have ozone levels ≥ 250 ppb. The dashed line corresponds to the theoretical prediction from a mass balance calculation using Pb as a tracer and assuming the dominant sources of primary particulate carbon are automobiles.

(b) Optical attenuation vs. total carbon loading for various mobile source samples.

absorbing species has a large imaginary part. The material most likely to be responsible for this absorption is "graphitic" soot, which has the requisite high imaginary index of refraction (n_I = .46) (3) and has been shown to be a major species in both ambient and source samples (4) (see data in Paper 187 which shows a direct correspondence between the absorptivity and the Raman intensity of the "graphitic" modes).

In order to gain a better understanding of the nature of these highly absorbing species, we have measured the wavelength and temperature dependence of the absorptivity for ambient, tunnel, and laboratory-generated soot samples (Figs. 2 and 3). The absorptivity shows a $1/\lambda$ wavelength dependence to within 20% over the visible spectral region (4500 Å - 7000 Å), as evidence the gray or black color of these samples. This result is consistent with the hypothesis that the absorption is due primarily to "graphitic" soot since it has been shown that the imaginary index of refraction of both acetylene and propane soot is essentially constant throughout the visible region (3). In fact it is difficult to find many organic species which meet this criterion: of the 13,000 organics listed in the 54th edition of the CRC Handbook, only 5 are gray or black in appearance.

The temperature dependence of the absorptivity was determined by measuring the absorptivity of particulates collected on quartz fiber filters before and after heat treatment at various temperatures. The heat treatment procedure consisted in heating the sample at the prescribed temperature for 30 min in air. The results of these measurements are plotted in Figure 3, which shows clearly that in all cases the absorbing species are stable in air until approximately 400°C, and then undergo what is presumably a rapid oxidation process to essentially disappear by 500°C. Note that this threshold is similar to that of polycrystalline graphite (5). The stability of the absorbing species at elevated temperatures again suggests that they are graphitic in structure, as most other organic species expected to be present in ambient and tunnel samples should oxidize or vaporize at significantly lower temperatures.

The characterization of the carbonaceous component of ambient aerosol particles in terms of primary and secondary species is crucial to the determination of any effective control strategy. In this respect the results shown in Figures 1a and 1b could have important implications. The similarity between the absorbing properties of the winter and summer ambient samples and the mobile source samples is quite striking and can be interpreted to indicate that a large fraction of ambient particulate carbon is primary in origin. It would seem quite fortuitous for secondary atmospheric processes to generate carbonaceous species which just happen to have similar absorbing properties as mobile source samples. It is also evident from the strong correlation between the absorptivity and carbon content that "graphitic" soot seems to constitute an approximately constant fraction of the total carbon content of the ambient samples even for oxidant levels exceeding 250 ppb (see Fig. 1a). This is expected from primary emissions, but not from secondary processes which would be expected to show more variability depending on atmospheric conditions (relative humidity, gas concentrations, oxidant level, etc.).

It has been suggested that most of the carbonaceous species in the Los Angeles Air Basin in the summer are of secondary origin, based on the concept of mass balance using Pb as a tracer (6,7). Most of the primary carbon is assumed to originate from mobile sources, while the contribution of other sources relative to the automobile is estimated from an emission inventory. The contribution of mobile sources is determined by assuming that such emissions are characterized by a C/Pb ratio of ∿ 1.7 (7). In the ambient samples, C/Pb ratios of the order of 10 are found, and the deviation from the automotive C/Pb ratio, after taking into account a small contribution from other sources, is attributed to the secondary production of organic carbon. Both the summer and winter episodes

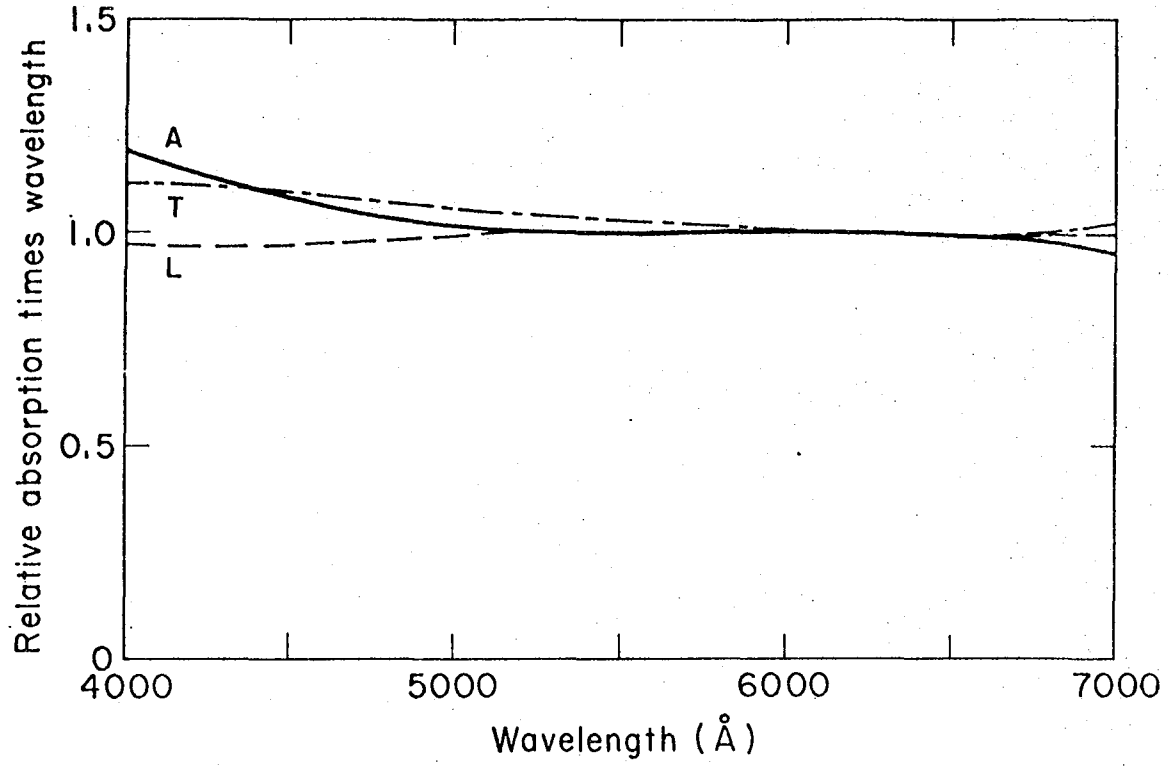

Figure 2. Plot of the product of absorptivity and wavelength vs. wavelength for A — ambient samples, T — tunnel samples, and L — laboratory-generated soot samples. Such a plot would be flat for a wavelength independent imaginary index of refraction.

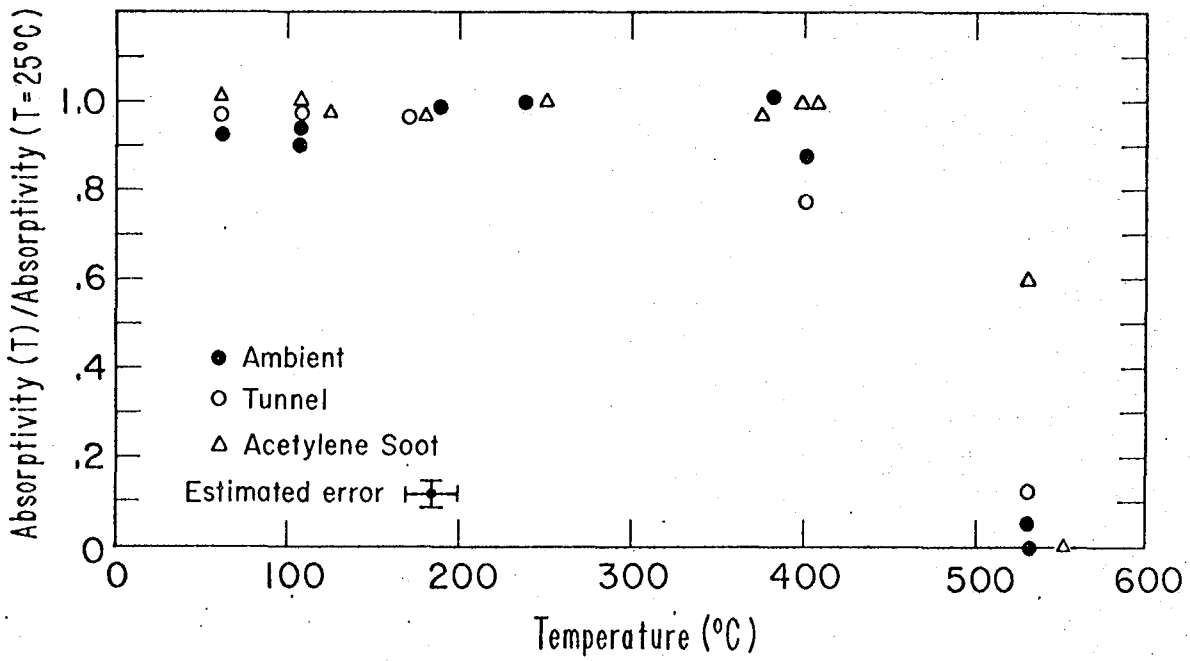

Figure 3. Plot of the ratio of the absorptivity of various samples after heat treatment at temperature T to the absorptivity at T = 25°C as a function of heat treatment temperature. The heat treatment procedure consisted in heating the sample in air for 1/2 hr at the prescribed temperature.

that we have investigated show a similar discrepancy (C/Pb in the ambient samples, ≈ 10, and C/Pb in the tunnel samples, ≈ 1). If we were to use the same analysis as above and further assume that black species ("graphitic" soot) are not produced in secondary processes, an approximate prediction of the absorptivity versus carbon content for our ambient samples would be given by dividing the slope of least squares fit of the tunnel points by 10. This is shown as a dashed line in Figure 1a and clearly does not agree with the ambient measurements. This disagreement may be due to the fact that sources other than automobiles make a major contribution to the carbon balance (e.g., diesels, home heating, aircraft, industry). It is also possible that there are some difficulties in using Pb as a tracer for mobile source emissions. For example, differences in the transport properties of lead and carbon could affect the C/Pb ratio. Also, we have found that the C/Pb ratio may depend markedly on driving conditions. Tunnel samples typically had a C/Pb ratio of ≈ 1 while parking garage samples taken under "start-stop" conditions had a C/Pb ratio of ≈ 8. This is quite reasonable since under these conditions we would expect the combustion process to be more incomplete and therefore produce more carbonaceous emissions.

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