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Title NEW METHODS FOR CHARACTERIZING SOOT EMISSIONS FROM FIRES

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**Author** Rosen, H.

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### NEW METHODS FOR CHARACTERIZING SOOT EMISSIONS FROM FIRES\*

#### H. Rosen, A.D.A. Hansen, R.L. Dod, L.A. Gundel, and T. Novakov

Applied Science Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720

#### Abstract

Two new methods for characterizing soot emissions from fires will be described. One of these methods, the aethalometer, has the capability of measuring the absorbing component of soots (graphitic carbon) on a real-time basis. Such a capability is advantageous in aircraft studies of emission factors, aircraft studies of atmospheric aging and removal processes, and laboratory studies of time-dependent emissions from combustors. The other method, optical-thermal analysis, has the capability for unambiguous quantitation of both the graphitic and the various organic components of soot. Such separations are necessary for meaningful studies of the optical and chemical properties of soot and its emission factors.

#### Introduction

Soot emissions can be subdivided into two components: one component is black with a large optical absorption cross section and is known as graphitic or black carbon;

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the other component consists of a wide range of organics that are in general weakly absorbing in the solar spectral region. Since the optical properties of the soot depend on the relative proportions of each of these components, it is important to distinguish between them in nuclear winter scenarios. In this paper, two such methods will be described - one based on separation by optical absorption (aethalometer soot-meter), the other based on separation by thermal and chemical properties (optical-thermal analysis). The aethalometer has the capability of measuring the graphitic component and its associated optical absorption coefficient on a real-time basis. Recent measurements using the aethalometer in an aircraft to measure distributions of graphitic particles in the Arctic (1-min time resolution) and in a plume from a bio-mass burning (1-sec time resolution) in the Caribbean will be presented. Optical-thermal analysis has the capability of measuring both the graphitic and the organic components of the soot. Results of the relative contributions of each of these will be presented for various combustors.

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#### Aethalometer

Chemical techniques for the determination of the black carbon content of aerosol samples collected on filters are generally complex and time consuming<sup>1</sup>; in contrast, optical measurements are often simple and rapid. Here we describe an instrument that uses an optical technique to measure the concentration of aerosol black carbon in real time.<sup>2</sup> We have named the instrument the "aethalometer" from the Greek word " $\alpha\iota\theta\alpha\lambda\sigma\nu\nu$ ," "to blacken with soot." The aethalometer operates on the principle of continuous measuring of the attenuation of a beam of light transmitted through a filter while the particle-laden air is being drawn through it. At a constant airstream velocity, the rate of deposition of black carbon on the filter is proportional to its concentration in the aerosol and gives a corresponding rate of increase of optical attenuation. This method is a direct measure of the absorbing component of aerosol particles and is insensitive to their scattering properties. This has been shown directly in a photoacoustic study<sup>3</sup> and indirectly by noting that most of the aerosol mass responsible for scattering can be

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removed by solvent extraction or heat treatment procedures without appreciably affecting the optical transmission. Furthermore, a theoretical model has been developed that explains these observations.<sup>4</sup>

A block diagram of the instrument is shown in Fig. 1. A transparent mask with a 5-mm diameter hole covers the filter, which is usually prefired quartz fiber. The air stream is therefore drawn through only a small part of the filter, on which the particles are collected. The remainder of the filter is used as a reference for the optical measurement and as a blank for chemical analyses. The filter is uniformly illuminated by a stabilized incandescent (530 nm) lamp, and two optical fibers set into the filter support under the collecting and reference portions of the filter convey the transmitted light to a pair of matched photodetectors. The attenuation of the intensity I transmitted through the collecting part of the filter relative to the intensity  $I_0$  through the reference part is A = 100  $\ln(I_0/I)$  and is proportional to the surface concentration of black carbon. The detector outputs are coupled to a logarithmic ratiometer that produces a voltage proportional to the rate of deposition of black carbon on the filter. Since this rate may be slow, we use digital methods at discrete time intervals to perform the differentiation. Input via a 12-bit analog to digital converter gives a resolution of 0.025%, enabling us to detect an increase in optical attenuation of 0.075 units. This corresponds to the deposition of 3  $ng/cm^2$  of black carbon on the filter. The minimum resolving time  $t_{min}$  is the time necessary to collect this quantity  $Q_{\min}$  of black carbon from the air stream, whose velocity at the filter face is denoted v.

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If the concentration of black carbon in the aerosol is C, then  $t_{min} = Q_{min}/Cv$ . Using quartz fiber as the filtering medium, the aethalometer can operate at filtering velocities of up to 5 m/sec, giving a minimum resolving time of 6 sec for a black carbon concentration of 1  $\mu$ g/m<sup>3</sup>. A variable time base determines the actual interval over which the digitization and differentiation are performed. We may select longer time base periods to improve the accuracy of the concentration measurement at the expense of its



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Figure 1. Schematic of the aethalometer.

time resolution.

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To avoid the effects of optical saturation, a maximum loading  $Q_{max}$  of 8  $\mu$ g/cm<sup>2</sup> of black carbon on the filter is allowed before a filter change is required. At constant filtering velocity v and average aerosol black carbon concentration C, this occurs after a time  $t_{max} = Q_{max}/Cv$ . At maximum flow rate with C equal to 1  $\mu$ g/m<sup>3</sup>, this time is approximately 4-1/2 hr. In situations that do not require maximum time resolution or sensitivity, the time between filter changes may be extended by reducing the air-flow rate.

As illustrations of the real-time capability of the aethalometer, we present several vertical distributions of graphitic particles obtained at relatively low concentrations in the Arctic troposphere<sup>5,6</sup> (AGASP flights, organized by NOAA, March and April, 1983) and a horizontal profile of a plume from agricultural burning in the Bahamas.<sup>7</sup> Vertical profiles were obtained by dividing the atmosphere into altitude bins and determining the average aethalometer response in each of these bins over the particular time periods of interest. The bin size was chosen so that the errors due to the minimum detection limit of the aethalometer were small compared with the average aethalometer response in the figures are based on three times the minimum detectable limit of the aethalometer and correspond to a change in the transmission of the filter deposit of 0.075%. The error bars are different at different altitudes because they are inversely proportional to the volume of air sampled in a given altitude bin.

In Figs. 2 and 3, vertical profiles of graphitic carbon concentrations vs. altitude are shown for flights in the Norwegian Arctic. In Fig. 2, the graphitic carbon concentrations as a function of altitude are shown for a descent near Bear Island. Also shown for comparison are the average ground-level concentrations found at the NOAA-GMCC observatory near Barrow, Alaska, for April, 1982, and the annual average ground-level concentrations found in various urban areas in the United States. It is clear from this figure that the vertical profile has considerable structure with at least three layers located at

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Figure 2. Vertical profile of graphitic carbon concentrations expressed as nanograms per cubic meter on March 31, 1083, at - 74°N 25°E. Shown for comparison are the annual average ground-level graphitic carbon concentrations at various urban locations in the United States and the average April, 1082, ground-level values at the NOAA-GMCC observatory near Barrow, Alaska.

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Figure <sup>3</sup>a. Vertical profile of graphitic carbon concentrations expressed in nanograms per cubic meter on April 5, 1983, at  $-70^{\circ}N0^{\circ}E$ .

\_\_\_\_\_ 3b. Same as the above but with graphitic carbon concentrations expressed as a mixing ratio.

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approximately 1 km, 2.5 km, and 4.5 km, and what appears to be a very narrow layer at 1.7 km. The haze layers can have sharp boundaries with dramatic changes in concentration over distances less than 100 m. The concentrations within these layers are large, with the peak concentrations in the United States (Berkeley, Denver, Gaithersburg) and only about a factor of 2.5 lower than those in New York City. The concentrations in this band are about a factor of 10 higher than the  $0.15-\mu g/m^3$  April, 1981, ground-level concentrations at Barrow, Alaska. The flight profile also indicates a relatively clean region at low altitudes, which is consistent with the Barrow results and the limited ground-level measurements made in the Norwegian Arctic.

In Fig. 3, the graphitic carbon concentrations vs. altitude are shown for a descent above the Norwegian Sea. This profile is quite distinct from the one shown in Fig. 2: it has much less structure with only one sharp band at 3.75 km superimposed over an almost uniform haze layer, decreasing only slightly with altitude even close to the top of the troposphere. If this profile is plotted vs. the mixing ratio, as in Fig. 3b, it is essentially flat to the top of the troposphere with an intense band located at about 3.75 km. This profile could indicate significant transport at high altitudes above the planetary boundary layer. However, it may also be indicative of changes in the vertical distribution that have occurred after the air mass has reached the Arctic.

In Fig. 4, the output of the aethalometer is shown during a pass at 900 m altitude through a plume from agricultural burning obtained in a test flight of the P-3 in the Bahamas. The time base period was 4 sec, giving a horizontal resolution of approximately 500 m and a measurement accuracy of 5%. This profile, combined with a knowledge of the amount of fuel burned or the velocity field, could be used to determine the emission factor for graphitic particles from this burn.

#### **Optical-Thermal Analyses**

Soot particles contain not only a highly absorbing graphitic component but also a wide range of organics. It is important to separate these components because they have



Fig. 4. Aethalometer response during transit of a plume from agricultural burning over the Bahamas. The aethalometer timebase period of 4 seconds gives a horizontal resolution of approximately 500 m. significantly different optical effects and chemical reactivity.

Malissa<sup>8</sup> has reported a method of analysis for the carbonaceous component of atmospheric aerosol particulate material that involves measurement of the evolved gas during a temperature-programmed combustion in oxygen. We have extended this analysis by constructing an apparatus that simultaneously measures the optical transmission of the particulate matter collected on a filter.<sup>9</sup> Because the optical absorptivity of this material has been shown to be due to a graphitic component,<sup>10</sup> this combination of analytical techniques may provide a direct determination of the light-absorbing fraction of the sample.

A schematic representation of the apparatus used in our analysis of carbonaceous material is shown in Fig. 5. The particulate sample, collected on a prefired quartz filter, is placed in the quartz combustion tube so that its surface is perpendicular to the tube axis. The tube is supplied with purified oxygen and the excess oxygen escapes through an axial opening at the end of the tube. The remainder of the oxygen, together with gases produced during analysis, passes through a nondispersive infrared analyzer (MSA LIRA 202S) at a constant rate. Carbon may be evolved through volatilization, pyrolysis, oxidation, or decomposition. To ensure complete conversion of this carbon to  $CO_2$ , a section of the quartz tube, immediately outside the programmed furnace, is filled with a CuO catalyst, which is kept at a constant 900 °C by a second furnace. This is necessary, especially when the first furnace is at low temperatures where volatilization and incomplete combustion are the dominant processes occurring.

The actual measurement consists of monitoring the  $CO_2$  concentration as a function of the sample temperature. The result is a "thermogram," which is a plot of the  $CO_2$  concentration vs. temperature. The area under the thermogram is proportional to the carbon content of the sample. The carbon content is determined by calibrating with  $CO_2$  in oxygen. This calibration is crosschecked by analyzing samples of known carbon content.







The thermograms of ambient and source aerosol samples reveal distinct peaks or groups of peaks. One important component of the carbonaceous aerosol is the graphitic carbon, which is known to cause the black or grey coloration of ambient and source particulate samples. To determine which of the thermogram peaks corresponds to this graphitic carbon, we monitor the intensity of a He-Ne laser beam that passes through the filter, providing a simultaneous measurement of sample absorptivity and  $CO_2$  evolution. The light penetrating the filter is collected by a quartz light guide and filtered by a narrow band interference filter to minimize the effect of the glow of the furnaces. An examination of the  $CO_2$  and light intensity traces enables the identification of the thermogram peaks or peaks that correspond to the black carbon because they appear concurrently with the decrease in sample absorptivity.

The potential of this method (in the  $CO_2$  mode) is shown in Figs. 6-8, which illustrate the complete thermograms of several source samples and an ambient sample. The lower traces in each figure represent the CO<sub>2</sub> concentration, while the upper curves correspond to the light intensity of the laser light beam that reaches the detector during the temperature scan. Inspection of the thermogram shows that a sudden change in the light intensity occurs concomitantly with the evolution of a CO<sub>2</sub> peak. This demonstrates that the light-absorbing species in the sample are combustible and contain graphitic carbon. The carbonate peak in the ambient sample evolves at about 600 °C; and because carbonate is not light absorbing, it does not change the optical attenuation of the sample. In addition to black carbon and carbonate, the thermograms show several distinct groups of peaks at temperatures below approximately 400°C. These peaks correspond to various organics that do not appreciably affect the optical absorption measurement. It is apparent from these figures that the ratio of graphitic carbon t the organics can vary considerably from one source to the next and that the ratio will be highly dependent on combustion conditions. Such variations, which would strongly affect the optical properties of the carbonaceous particles, are important to understand in



Figure 6. Example of combustion thermograms of particulate material emitted from stationary sources. Dashed line is optical transmission.

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Figure 7. Example of combustion thermograms of particulate material emitted from mobile sources. Dashed line is optical transmission.

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order to reduce uncertainties in the source term in nuclear winter scenarios.

References

1. G.T. Wolff and R.L. Klimisch, eds., Particulate Carbon: Atmospheric Life Cycle, Plenum, New York, 1982, 411 pp.

2. A.D.A. Hansen, H. Rosen, and T. Novakov, Appl. Opt. 21, 3060 (1982).

3. Z. Yasa, N.M. Amer, H. Rosen, A.D.A. Hansen, and T. Novakov, Appl. Opt. 18, 2528 (1979).

4. H. Rosen and T. Novakov, Appl. Opt. 22, 1265 (1983).

5. H. Rosen and A.D.A. Hansen, Geophys. Res. Lett. 11, 461 (1984).

6. A.D.A. Hansen and H. Rosen, Geophys. Res. Lett. 11, 381 (1984).

7. A.D.A. Hansen, H. Rosen, and T. Novakov, Sci. Total Environ. 36, 191 (1984).

8. H. Malissa, H. Puxbaum, and E. Pell, Z. anal. Chem. 282, 109 (1976).

9. T. Novakov, Nature, Aim and Methods of Microchemistry, H. Malissa, M. Grasserbauer, and R. Belcher, eds., Springer-Verlag, Vienna, 1981, p. 141.

10. H. Rosen, A.D.A. Hansen, L. Gundel, and T. Novakov, Appl. Opt. 17, 3859 (1978).

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