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## FY 1983 Annual Report
## ATMOSPHERIC AEROSOL RESEARCH

September 1984

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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# ATMOSPHERIC AEROSOL RESEARCH FY 1983

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Prepared for the U.S. Department of Energy under Contract No. DE-AC03-76SF00098

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# Role of Graphitic Carbon Particles in Radiative Transfer in the Arctic Haze*

*H. Rosen, A.D.A. Hansen, and T. Novakov*

Aerosol particles can change the radiation balance of the earth, leading to a cooling or heating effect with the magnitude and sign of the temperature change largely dependent on aerosol optical properties, aerosol concentrations, and the albedo of the underlying surface.[1] A purely scattering aerosol will reflect energy that would normally be absorbed by the earth-atmosphere system back into space, leading to a cooling effect. Conversely, an absorbing component in the aerosol can lead to a heating of the earth-atmosphere system if the reflectivity of the underlying surface is sufficiently high. Most studies of the effects of aerosols on atmospheric radiative transfer on a global scale have assumed a dominantly scattering aerosol with only a small absorbing component, since this appears to be a good representation of naturally occurring aerosols.

Analysis of the optical properties of aerosols in urban locations, however, indicates that the absorbing component can be substantial, because of large concentrations in the aerosols of combustion-generated graphitic carbon particles. These particles have been identified on a molecular level by Raman spectroscopy.[2-4] If they can be transported on a global scale, then significant aerosol absorption should be observable, even in remote locations such as the Arctic. This was confirmed in previous papers,[5,6] where we reported finding substantial concentrations of graphitic carbon particles at ground level in the western Arctic.

## ACCOMPLISHMENTS DURING FY 1983

If the large concentrations of graphitic particles found at Arctic ground-level stations also occur throughout the area's troposphere, they could have a significant impact on the Arctic radiation balance and climate.[7,8] During March and April, 1983, a series of flights, organized by the National Oceanic and Atmospheric Administration (NOAA), explored the vertical and horizontal distributions of the Arctic haze. One of the instruments on these flights was an aethalometer,[9] a soot meter developed at Lawrence Berkeley Laboratory and described in detail elsewhere in this annual report by Hansen *et al.* The aethalometer is capable of determining graphitic carbon concentrations in real time, using the calibration developed by Gundel *et al.*,[10] also described in this annual report.

The data from the flights have not yet been fully analyzed, but preliminary analysis of one flight in the Norwegian Arctic has been completed. This flight, northerly from Bodo, Norway, over Bear Island to northern Spitzbergen and back, took place on the morning of March 31, 1983. Data were taken during a slow descent from 7 km to 0.1 km at 74°N, 25°E. The graphitic carbon concentrations as a function of altitude are shown in Fig. 1. Also shown for comparison are the average ground-level concentrations found in Barrow for April, 1982, and the 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 approximately 1 km, 2.5 km, and 4.5 km. The concentrations within these layers are large, with the peak concentrations at 1 km only about a factor of 2.5 lower than those in New York City and a factor of 10 higher than ground-level concentrations measured at Barrow, Alaska (0.15 $\mu g/m^3$ in April, 1982). The flight profile also indicates a relatively clean region at low altitudes, which is consistent with the Barrow results at ground level and the limited ground-level measurements we've made in the Norwegian Arctic.

Recent modeling studies of the possible effects of the Arctic haze on the radiation budget of the Arctic indicate rather substantial changes in the heat balance if the optical depth due to absorption is sufficiently large.[7,8] One can calculate this optical depth from the results shown in Fig. 1 for various models of the Arctic aerosol. In these models, it is important to distinguish between graphitic particles mixed internally or externally with the other nonabsorbing components. Such differences, as shown by Ackerman and Toon,[11] can lead to significant changes in aerosol absorption. We will consider three examples:

*This work was supported by the Director, Office of Energy Research, Carbon Dioxide Research Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

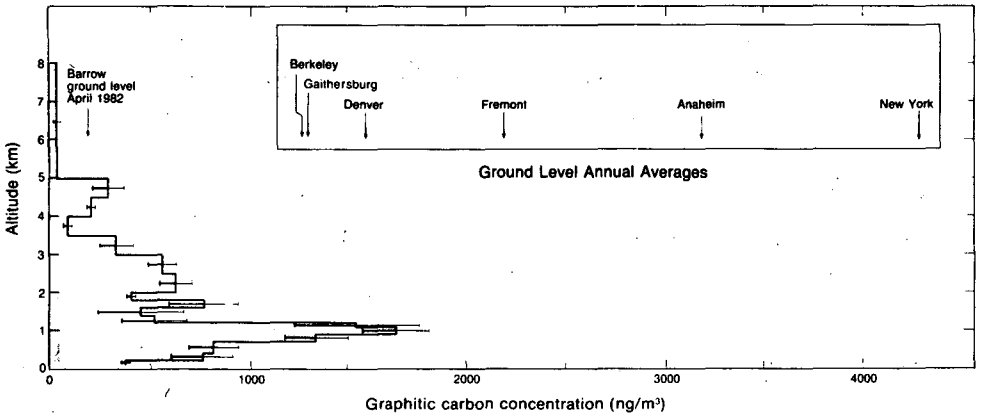


**Figure 1.** Graphitic carbon concentrations vs. altitude on March 31, 1983, at ~74°N 25°E expressed as nanograms per cubic meter. Shown for comparison are the annual average ground-level concentrations at various urban locations in the United States and the average ground-level values at the NOAA-GMCC observatory near Barrow, Alaska, for April 1982. (XBL 8312-4319A)

(1) Graphitic carbon particles internally mixed with all the major submicron aerosol components (i.e., sulfates, organics).

(2) Graphitic carbon particles internally mixed with only submicron organic aerosol components.

(3) Graphitic carbon particles externally mixed with the other aerosol components.

Of these three, the first two are the most likely combinations. For these, we treat the particles as homogeneous spheres and mix in the various components by volume mixing of dielectric constants.[12] In these calculations, the indices of refraction of graphitic carbon were chosen to be 1.94–0.66 $i$,[11] with a density of 1.5, and the index of refraction of the nonabsorbing components was taken to be 1.5. The relative concentrations of graphitic carbon, sulfates, and organic carbon are obtained from ground-level measurements in April at Barrow, Alaska, where detailed chemical analysis of the submicron aerosol has been completed. The particle size distribution for the submicron aerosol is assumed to be lognormal with $r_{gv} = 0.2\ \mu$ and $\sigma_g = 2$, which are obtained from Whitby[13] for the urban aerosol and are consistent with the results of Heintzenberg[14] for the Arctic aerosol. For the first two examples, Mie calculations yield absorption cross sections of 19 $m^2$ and 12 $m^2$ per gram of graphitic carbon, respectively. For the external mixture, we use the photoacoustic measurements of Roessler and Faxvog[15] and Szkarlat and Japar,[16] who obtain the average value of 8.3 $m^2/g$ at 0.5 $\mu$.

For these three examples, the optical depths due to absorption are respectively 0.052, 0.033, and 0.023. These optical depths are large enough to produce significant changes in the radiation balance over a highly reflecting surface.[7,8] This is illustrated by the calculations of Porch and MacCracken[7] and of Cess,[8] who have modeled the Arctic aerosol for an absorption optical depth of 0.021 (which is close to our minimum estimate), cloud-free conditions, a zenith angle of 72°, and a surface albedo of 0.8. For these parameters, they obtain a change in the noontime solar radiation balance at the top of the troposphere of about 20 $W/m^2$. When averaged over the day for March 15 at 70°N, the surface-atmosphere energy absorption would increase by about 7 $W/m^2$.[7,8] These changes are substantial: they would correspond to an increase in the energy absorbed by the earth-atmosphere system of approximately 5% of the incident solar flux at the top of the troposphere. Correspondingly larger changes would be expected for the internally mixed aerosol models.

## PLANNED ACTIVITIES FOR FY 1984

These first estimates of the effects of graphitic carbon on the Arctic radiation balance are based on the flight profile shown in Fig. 1, which is obviously only over a small geographical region and in a narrow time frame. Similar vertical and horizontal profiles in other areas of the Arctic will be analyzed during FY 1984. The data analyzed so far represent about 2% of the flight time over the Arctic. These data will be compared to a wide range of meteorological variables (wind speed, wind direction, relative humidity) and physical parameters such as scattering coefficients, condensation nuclei counts, and net flux measurements. These comparisons should help to improve our understanding of the sources and optical properties of the Arctic haze.

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# Carbon-Oxygen Ratios in Ambient Particulate Matter*


*W.H. Benner, L.A. Gundel, and T. Novakov*


The partial oxidation of gaseous hydrocarbons observed in smog chamber studies[1] has been correlated with aerosol formation. Such gas-to-particle conversion in the troposphere is thought to contribute to haze formation. In general, the partial oxidation of gaseous hydrocarbons produces compounds that have carbonyl and acid functional groups. These groups reduce the vapor pressure of the precursor hydrocarbon and cause the gas-to-particle conversion. Our recent development[2,3] of a method sensitive enough to quantitate oxygen on filter samples or in extracts of filter samples of ambient particulate matter is directed toward understanding these reactions and their importance in haze formation. This article summarizes our initial determination of C/O ratios in the organic fraction of ambient particulate matter.


This work was supported by the Director, Office of Energy Research, Office of Health and Environmental Research, Physical and Technological Research Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 and by the National Science Foundation under Contract No. ATM 82-10343.


## ACCOMPLISHMENTS DURING FY 1983

A high-volume sampler (~1100 lpm, 400 $cm^2$ filter) collected 24-hour samples of ambient or source particulate matter on prefired (775°C) quartz-fiber filters. A Soxhlet extractor was used to extract sequentially portions of each filter sample in benzene and then methanol-chloroform (1:2 vol/vol). Dessication of the samples over $P_2O_5$ for 24 hours pre-

cluded interference from adsorbed water vapor. The corrected pyrolyzable oxygen concentration ($O_{pc}/cm^2$) was calculated for each sample by subtracting the oxygen present in a sample as $NO_3^-$ and $SO_4^=$ from the pyrolyzable oxygen concentration ($O_p/cm^2$); i.e., $O_{pc} = [O_p] - [O_{NO_3^-}] - [O_{SO_4^=}]$ blank value. Concentrations of $NO_3^-$ and $SO_4^=$ were determined by ion chromatography.

Ambient samples collected in Berkeley were analyzed before extraction. Figure 1 shows that C and $O_{pc}$ correlate strongly and that the C/O ratio ≈ 1 (atomic ratio ≈ 1.3). Since particulate C is a major component of ambient particulate matter, constituting 4–40% of the total suspended particulate mass,[4] it can be inferred that oxygen is also a major component. Comparison of the plot of $O_p$ vs. C to the plot of $O_{pc}$ vs. C shows that oxygen in $NO_3^-$ and $SO_4^=$ makes up about 18% of the total $O_p$. Because oxygen-containing substances other than organics could be present in these samples, one cannot deduce the C/O ratio in the organic fraction from the data in Fig. 1. The major inorganic oxygen species are taken into account ($NO_3^-$ and $SO_4^=$ are quantitated, carbonate is minimal in Berkeley samples, and silica and alumina are not detected), but OH groups on silica and oxygen attached to the black carbon could prejudice the conclusions.

The C/O ratio in the organic fraction was determined in two ways. First, the set of samples reported in Fig. 1 was reanalyzed after solvent extraction, and the extractable $O_{pc}$ and extractable C values were calculated. Figure 2 shows that these

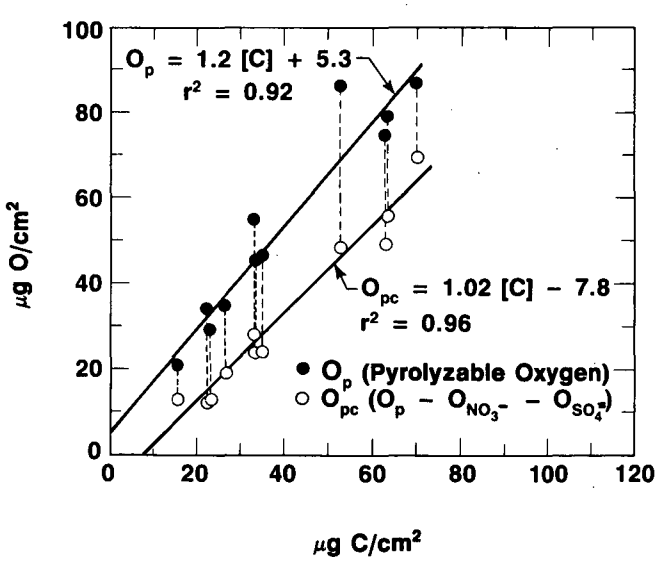


**Figure 1.** The determination of oxygen on filter samples of Berkeley ambient particulate matter. Filters analyzed before extraction. (XBL 838-2991A)

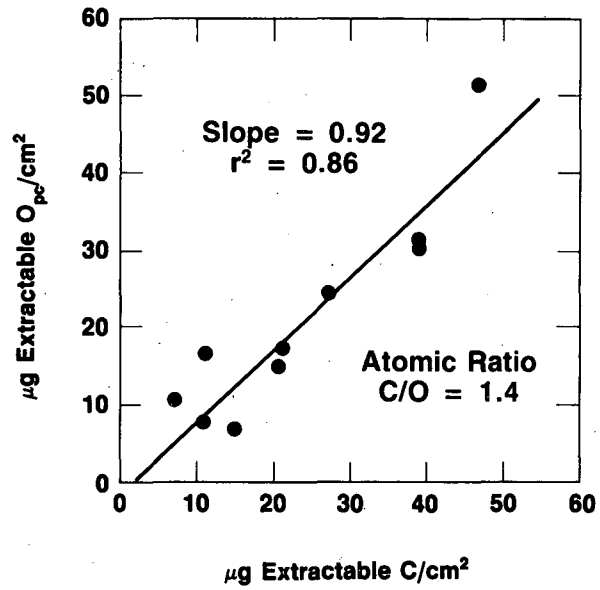


**Figure 2.** Determination of oxygen on filter samples of Berkeley ambient particulate matter. Filters analyzed before and after extraction and C and $O_{pc}$ lost by extraction calculated. (XBL 838-2935A)

two values correlate strongly ($r^2$ = 0.86). Extraction removes the soluble organic material; and unless insoluble oxygen-containing particles are lost during the extraction procedure, these data suggest that the soluble organic fraction of the ambient particulate matter is highly oxygenated, having an atomic C/O ≈ 1.4.

The analysis of the Berkeley samples before and after extraction is presented in another way in Fig. 3, where $O_{pc}$ on an extracted filter is plotted vs. $O_{pc}$ on the same filter before extraction. Figure 3 shows that as much as 40% of the $O_{pc}$ on a filter sample is insoluble. As long as none of this insoluble material is

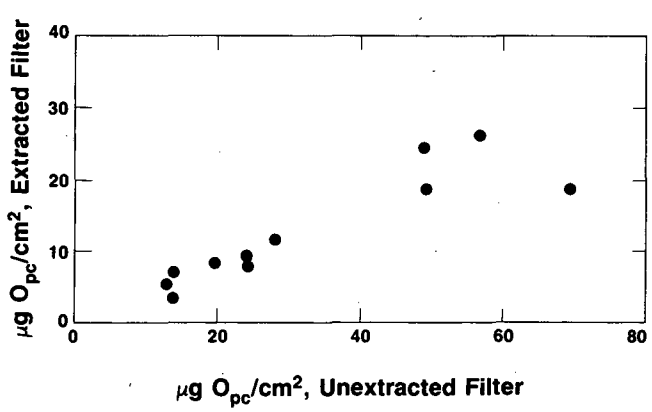


**Figure 3.** Determination of oxygen on filter samples of Berkeley ambient particulate matter. (XBL 838-2916A)

physically lost from a filter during extraction, the extractable C/extractable $O_{pc}$ ratio of ~ 1.4 is a correct value.

To exclude the possibility that insoluble particulate oxygen was lost during extraction and thus prejudiced the calculated C/O ratios, a second set of samples was extracted and the filtered extracts analyzed for C and $O_{pc}$. Several filter samples of aged ambient particulate matter were collected in Riverside, California. Two samples that represent ambient particulate matter enriched with fresh vehicular emissions were collected downwind and immediately adjacent to a freeway in Berkeley, California. Another two filter samples were collected in the exhaust duct of a freeway tunnel and represent a composite of vehicle sources. An additional sample was collected in an enclosed parking garage dominated by diesel bus traffic. The solvent extracts of each sample were filtered through 0.5-$\mu$m Fluoropore filters to remove any particles and filter fibers dislodged from the filter during extraction. The extracts were then concentrated by evaporation under $N_2$ at room temperature, and, finally, the concentrate was analyzed after evaporation onto a piece of quartz-fiber filter.

**Table 1.** Analysis of solvent extracts of ambient particulate matter.

| Sample | C/O (atom) |
|---|---|
| *Ambient* | |
| Riverside, CA, 16–17 June 1981 | 2.1 |
| Riverside, CA, 17 June 1981 | 2.3 |
| Riverside, CA, 16 June 1981[a] | 1.6 |
| Riverside, CA, 16–17 June 1981[a] | 1.7 |
| *Source-enriched ambient* | |
| Berkeley, CA, 30 August 1979 | 2.3 |
| Berkeley, CA, 29 August 1979 | 2.9 |
| *Source* | |
| Highway tunnel, 9 Feb. 1983, #5 | 6.4 |
| Highway tunnel, 9 Feb. 1983, #6 | 5.4 |
| Diesel bus, 12 Nov. 1978, #1 | 7.2 |

[a]Particulate diameter $\leq$ 1.5 $\mu$m.

Table 1 presents the $C/O_{pc}$ ratios found in these extracts. The organic fraction of size-segregated samples (particles having a diameter of less than 1.5 $\mu$m) of aged ambient particulate matter were the most oxygenated (atomic C/O $\approx$ 1.6), and fresh source samples were the least oxygenated (atomic C/O $\approx$ 6). Ambient samples from Riverside and Berkeley showed nearly similar atomic C/O ratios of about 2.3, even though the Berkeley samples were enriched in source particulate matter. The data in Table 1 suggest that the aging of particles is associated with a decrease in C/O, i.e., an increase in oxygenation. The $C/O_{pc}$ ratios determined from the analysis of filtered extracts and from the analysis of filters before and after extraction are not greatly different. But since these two procedures were performed on separate sets of samples, only the general conclusion that the organic fraction in age samples is highly oxygenated can be drawn.

## PLANNED ACTIVITIES FOR FY 1984

The data base for oxygen content of ambient particulate matter will be expanded so that the influence of meteorology, aging, and source emissions on the composition of the ambient aerosol can be evaluated.

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# The Relationship Between Optical Attenuation and Black Carbon for Urban, Arctic, and Source Carbonaceous Particles*

*L.A. Gundel, R.L. Dod, A.F. Berry, H. Rosen, and T. Novakov*

Particulate material from ambient air and combustion sources usually appears black when collected on filters, because of the presence of light-absorbing graphitic or black carbon (BC).[1] In the atmosphere, light absorption by these particles can degrade visibility[2] and perturb the tropospheric radiation balance.[3,4] These effects are especially important in the Arctic haze, where significant amounts of black carbon have been found.[5] In this article, we describe a nondestructive and fast technique for measuring black-carbon concentration — the laser transmission method. This technique measures the attenuation of visible light (ATN) as it passes through a particulate sample on a filter.

The results of this study, as reported here, have been used to calibrate the laser transmission method and to provide a value for the specific attenuation, $\sigma$, which is the value of ATN per unit mass of black carbon. It is important to note that the calibration method is independent of knowledge of the exact optical properties of black carbon. Earlier work in this project[6] focused on particulate matter collected in urban locations and from combustion sources. Here we include studies of black carbon in the Arctic haze.

## ACCOMPLISHMENTS DURING FY 1983

Samples of aerosol particles were collected on quartz-fiber filters that had been prefired at 800°C for 12 hours. Both high-volume (40 standard cubic feet per minute and low-volume (10–20 SCFM) samplers were used. One-third of the samples were size-segregated, with a particle cutoff of less than 2 $\mu$m. Ambient samples were collected in Berkeley (two sites) and Los Angeles, California; Warren, Michigan[6]; Vienna, Austria; and Ljubljana, Yugoslavia. Typical ambient sampling time was 24 hours.

A variety of combustion sources were sampled. A natural gas boiler (input of 290,000 Btu $hr^{-1}$) was sampled in its chimney. Propane soot was collected during an extensive intercomparison study.[7] A small diesel bus idling in a vacant parking garage was sampled 2 m from its exhaust pipe. Other samples, representing an average motor-vehicle population, were collected in the exhaust vents of the uphill bore of a highway tunnel and in a parking garage. The Arctic haze was sampled at Point Barrow, Alaska, using size-segregated (<2.5 $\mu$m) high-volume sampling at 40 SCFM for 1-week periods throughout the winter and spring of 1982–83.

The laser transmission method (LTM) measures the attenuation of visible light as it passes through the filter. ATN is defined as

$$\mathrm{ATN} = -100 \ln I/I_0 , \qquad (1)$$

where $I_O$ and $I$ are the transmitted light intensities for the blank and the loaded filter respectively. Rosen *et al.*[1] and Yasa *et al.*[8] have shown that the light attenuation is due to the presence of black carbon. If ATN has a linear dependence on [BC], the concentration of black carbon, then

$$[\mathrm{BC}] = \mathrm{ATN}/\sigma , \qquad (2)$$

where $\sigma$ is the specific attenuation for black carbon.

Attenuation was measured during the evolved gas analysis (EGA) procedure for determining [BC] and separately at room temperature by LTM. The two measurements of ATN agreed to within 3%. The limits of detection and quantitation for ATN are 6 and 20, respectively.

Temperature-programmed evolved gas analysis in oxygen[9] with continuous light transmission measurement was used to identify and quantify the black carbon. A thermogram of Arctic particles is shown in Fig. 1. [BC] was determined from the area of the thermogram peak that corresponds to the increase in light transmission during combustion. This carbon peak is usually centered between 425° and 500°C. Removal of soluble organic material by solvent extraction leads to thermograms in which isolation of this peak is straightforward. This procedure removes most of the organic carbon but leaves black carbon nearly unchanged, as shown by an average decrease in ATN for extracted samples of only 7%, for more than 100 samples. In this study, all BC determinations were performed on samples sequentially extracted by benzene and a methanol-chloroform mixture (1:2,v:v) in Soxhlet devices, in two 6-hour steps.[10] The limits of detection and

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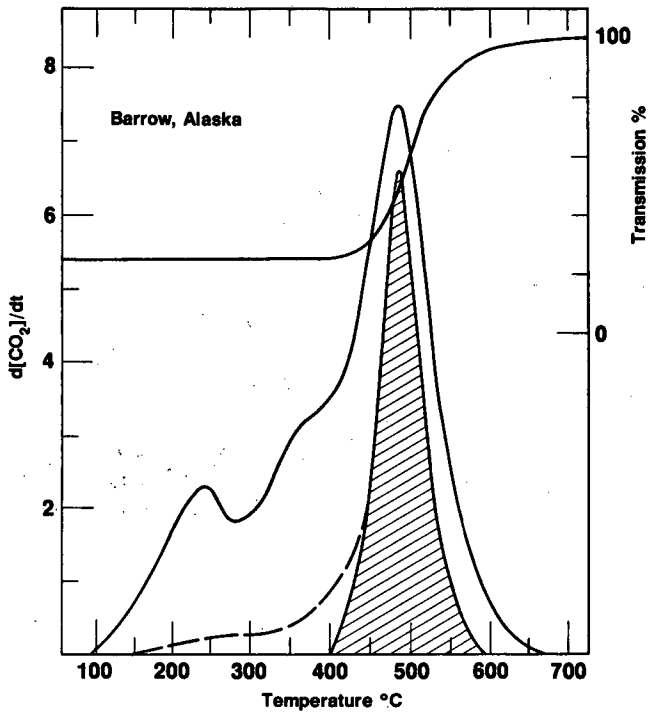


**Figure 1.** Thermogram of carbonaceous particles collected in the Arctic. Light transmission is shown by the *S*-shaped curve. The shaded area represents black carbon.
(XBL 8312-6902)

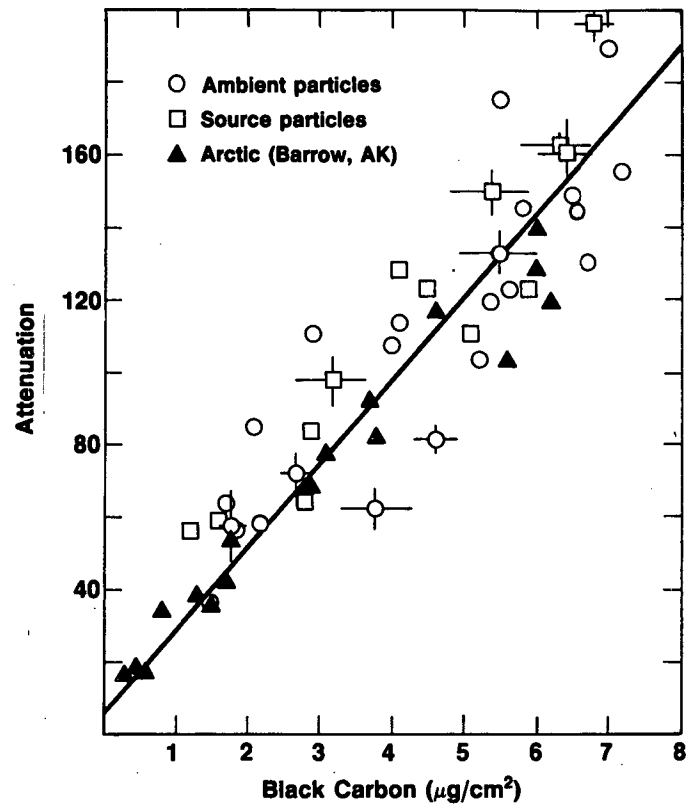


**Figure 2.** The relationship between attenuation and black carbon concentration for all data with ATN < 200 and BC < 8 $\mu$g cm$^{-2}$. (XBL 838-540)

quantitation for blank corrected samples are 0.6 and 2.0 $\mu$g BC cm$^{-2}$, respectively.

ATN and [BC] data are presented in Fig. 2 for all combustion-source, urban-air, and Arctic samples with ATN $\leqslant$ 200 and BC = 8 $\mu$g cm$^{-2}$. Within experimental error, all carbonaceous particles appear to follow the same relationship between ATN and [BC], regardless of their origin. If we combine all data with ATN $\leqslant$ 200 and [BC] $\leqslant$ 8 $\mu$g cm$^{-2}$,

$$\mathrm{ATN} = (7.2 \pm 5.7) + (23.1 \pm 1.2)[\mathrm{BC}], \quad (3)$$

with $r$ = 0.93, where $r$ is the correlation coefficient. [BC] can be predicted from Eq. (3) with an expected random error of 0.3 $\mu$g cm$^{-2}$ at ATN = 50, and 0.6 $\mu$g cm$^{-2}$ at ATN = 200, using the observed variances in [BC] and ATN. If the intercept of Eq. (3) is indistinguishable from zero, the slope of Eq. (3) is the specific attenuation, $\sigma$. If the non-zero intercept is real, it may indicate that $\sigma$ is dependent on [BC] at low concentrations.

All data, regardless of sampling loading, can be fit to the equation:

$$\mathrm{ATN} = -100 \ln [(1\ \alpha)e^{-\alpha[\mathrm{BC}]} - \alpha],$$

which reflects the observation that a small fraction, $\alpha$ (~0.02), of the incident light is conducted along the quartz fibers without interaction with the particle deposit. Using this equation, we find that the specific attenuation is 23.9 ± 2.0 for all data, with $\alpha$ = 0.017 and $r$ = 0.76.

## PLANNED ACTIVITIES FOR FY 1984

We plan to investigate the dependence of the specific attenuation on [BC] at low concentrations, while calibrating the real-time ATN instrument for [BC]. We will also investigate the influence of particle size and composition on the specific attenuation.

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# Primary Peroxides from Hydrocarbon Flames

*P.M. McKinney, W.H. Benner, and T. Novakov*

Hydrogen peroxide is an important oxidant for the aqueous-phase conversion of sulfur dioxide to sulfate in the atmosphere.[1,2] It has been assumed that this $H_2O_2$ originates from secondary photochemical reactions in the atmosphere; however, we have uncovered evidence that combustion is also a source of $H_2O_2$, as well as other, unknown peroxides.

## ACCOMPLISHMENTS DURING FY 1983

Figure 1 shows the experimental setup, in which combustion is carried out in the bottom of a Pyrex chimney 4 inches in diameter and 40 inches long. The chimney and all Teflon and glass lines to the impinger are heated to prevent condensation. Water-soluble combustion products are collected by drawing approximately one-third of the air that flows through the chimney (6 liters per minute total) through a 1-micron Teflon filter and then through one or more impingers, which contain 20.0 mL of water. The soluble anions were quantitated by ion chromatography.

In a typical experiment, 0.05 mole of propane or butane, or 0.15 mole of natural gas, is burned under optional conditions, e.g., an intermittent flame, a diffusion flame, or a flame in which the fuel was premixed with air. Sulfate, nitrate, and sulfite were quantitated before and after the addition of micromolar concentrations of sulfite. Samples were analyzed for peroxide by a titrimetric procedure using potassium iodide.[3] The limit of detection of this method was approximately $1 \times 10^{-5}$ *M* oxidant.

Peroxide was detected in samples collected during the intermittent combustion of propane and butane but not during the similar combustion of natural gas (Fig. 2). Diffusion and premixed flames from the three fuels produced no detectable peroxides in the impinger water. The addition of sulfite to

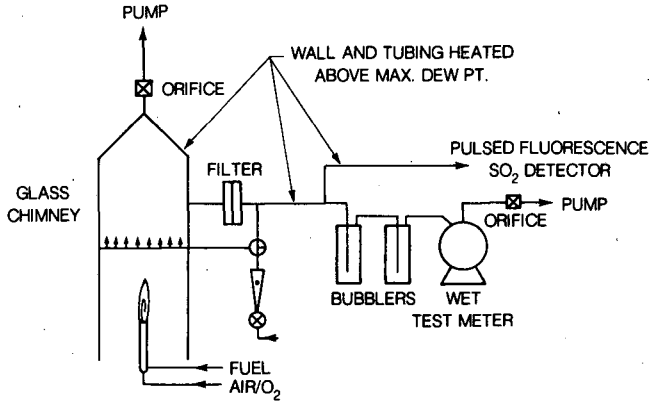


**Figure 1.** Apparatus for sampling primary oxidants. (XBL 834-173)

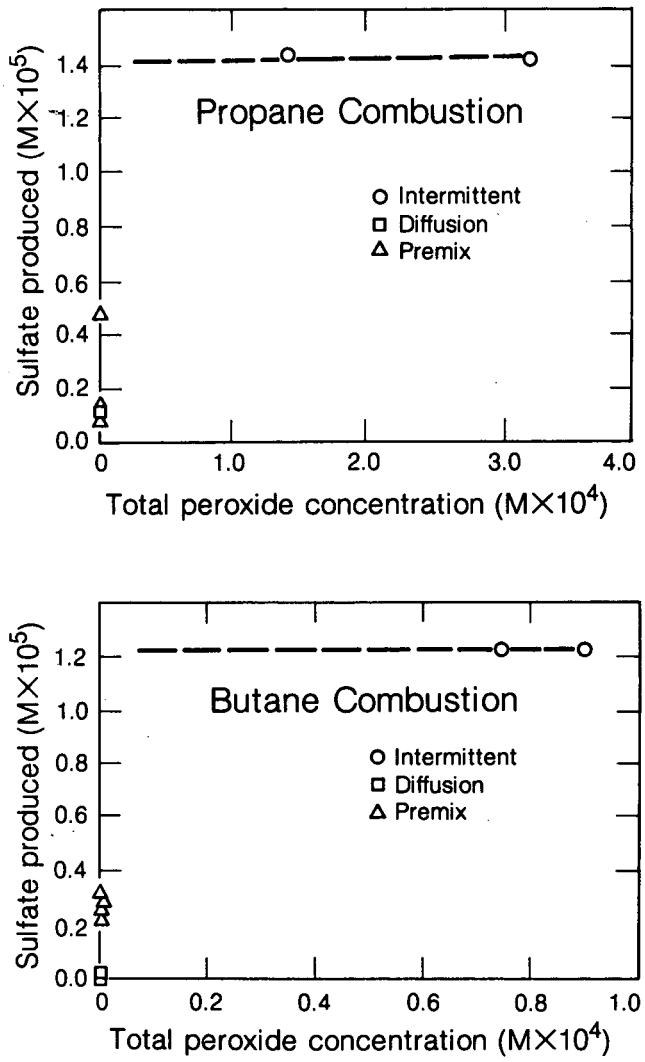


**Figure 2.** Sulfate produced vs. total peroxides.
(XBL 841-8319)

each sample resulted in sulfate formation in all but two samples, but sulfite oxidation was observed in at least one sample of each flame type. For the intermittent propane and butane samples, 14 $\mu$m and 12 $\mu$m sulfite were oxidized, respectively. Samples from the intermittent combustion of natural gas and from diffusion and premixed flames of the three fuels showed less oxidation of the added sulfite. A butane diffusion flame and an intermittent natural gas flame produced the least amount of sulfate. By modifying the sampling technique, combustion water was collected in an ice-cooled condenser. Oxidant concentrations as high as 0.02 *M* were observed in samples of intermittent propane flames.

Catalase, which selectively decomposes $H_2O_2$, was added to buffered impinger samples before peroxide analysis. These additions showed that more than 80% of the peroxide formed during the combustion of propane, and that 100% of the peroxide from butane was $H_2O_2$.

These simple experiments point out a fact apparently overlooked by many atmospheric chemists. Combustion can be a source of sulfite oxidants. This implies that primary oxidants could play an important role in the oxidation of $SO_2$ in fogs and clouds, thus helping to form acidic precipitation.

The importance of this finding depends on the amount of oxidant released by combustion sources. Table 1 presents the results of several filtered exhaust samples collected from three vehicles. Impinger water samples were analyzed before and after the addition of sulfite. All samples showed sulfite oxidation. Even before sulfite addition, a considerable fraction of the total aqueous sulfur was present as $SO_4^=$ (third column, Table 1). Because the production of primary sulfate during combustion

**Table 1.** Oxidation of exhaust $SO_2$ in impinger water.[a]

| Source vehicle | ppm S(IV) | ppm S(VI) | $\frac{S(IV)}{S(IV)+S(VI)}$ | Time (min) | ppm $SO_4^{2-}$ in exhaust |
|---|---|---|---|---|---|
| Alfa 1 | 0.31 | 0.073 | 0.19 | 10 | 0.067 |
| Alfa 2 | 2.43 | 0.81 | 0.25 | 15 | 0.40 |
| Alfa 3 | 3.20 | 1.20 | 0.27 | 15 | 0.67 |
| Audi | 3.36 | 1.21 | 0.26 | 10 | 0.92 |
| Truck[b] | 0.40 | 0.13 | 0.24 | 15 | 0.13 |

[a]ppm $SO_2$ oxidized in exhaust = $\frac{\text{ppm S(VI)} \times 20(\text{mL } H_2O)}{2.5 \times \text{time(min)} \times \text{flow(L/min)}}$.

[b]Catalytic converter.

is small (99% of sulfur emissions are $SO_2$) and because primary sulfate would not have passed through the filter, it can be argued that the detected $SO_4^=$ came from the oxidation of $SO_2$ in the impinger water. (The $SO_2$ came from sulfur in the fuel). These results suggest that vehicles can be a source of primary oxidants.

## PLANNED ACTIVITIES FOR FY 1984

We plan to further characterize combustion products and study the products of other fuels.

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# Non-Ammonium Reduced Nitrogen Species in Atmospheric Aerosol Particles*


*R.L. Dod, L.A. Gundel, W.H. Benner, and T. Novakov*


Particulate nitrogenous air pollutants have traditionally been considered to be limited largely to inorganic compounds containing ammonium and nitrate ions. This view was challenged about 10 years ago by results from the then-new technique of x-ray photoelectron spectroscopy (ESCA), which indicated that as much as half of the ambient particulate nitrogen could exist in forms more reduced than ammonium.[1] This nitrogen was later postulated to consist of amines, amides, and heterocyclic compounds and was given the collective name $N_x$.[2] Further indication of the existence of $N_x$ in ambient particles has been found with total nitrogen combustion analysis, which often indicates more nitrogen than does wet chemical analysis for $NH_4^+$.[3] However, no direct method reported can identify or quantitate the $N_x$ constituents.

We have developed an $NO_x$ thermal evolved gas analysis (EGA) system that differentiates among nitrogenous species based on volatility and thermal stability in an oxygen atmosphere.[4] EGA, in conjunction with ESCA and ion chromatography, has been applied to the analysis of ambient aerosol particulate samples collected by filtration to confirm the existence of $N_x$ and to identify characteristics that provide information regarding final speciation.


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## ACCOMPLISHMENTS DURING FY 1983

ESCA analysis of atmospheric particles has been described elsewhere.[5,6] The method analyzes for elemental composition as well as the oxidation states of those elements. Quantitation is achieved by comparing analyte photoelectron peak intensities to those for one or more independently determined species within the sample. The sample must be in vacuum, and its surface is analyzed to the escape depth of the photoelectrons (~ 20 angstroms). We have previously determined that ambient aerosol particles are usually resistant to vacuum degradation and have similar surface and bulk compositions. Concentrations of nitrogenous species were determined from ESCA spectra by reference to sulfur in the samples, which was independently determined by x-ray fluorescence and/or combustion analysis. Deconvolution of the reduced nitrogen peak was based on the peak position and on the form of the ammonium nitrogen peak in $(NH_4)_2SO_4$. All photoelectron spectra were taken with an AEI ES200 spectrometer modified by installation of a position-sensitive detector (Surface Science Laboratories Model 239G).

Evolved gas analysis ($CO_2$ and $SO_2$) has been used by Malissa, Puxbaum, and Pell to investigate collected aerosol particulate matter.[7] We have adapted this analytical technique to analysis of particles collected on quartz-fiber filters and have extended it to include visible light attenuation and evolved $NO_x$. Our system, shown in Fig. 1, uses an NDIR $CO_2$ detector (MSA LIRA 202S) and a chemi-

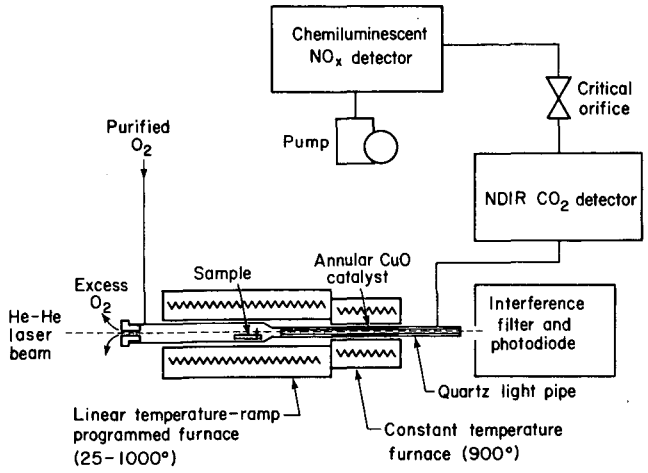


**Figure 1.** Schematic diagram of apparatus for thermal evolved gas analysis. (XBL 838-3111)

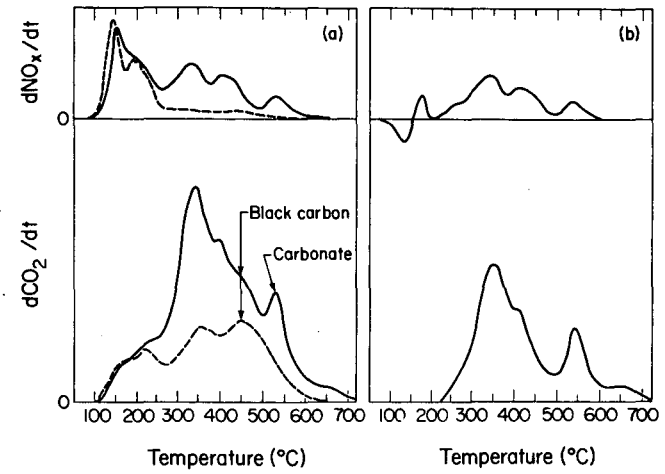


**Figure 2.** Evolved $CO_2$ and $NO_x$ thermograms for ambient particles from Riverside, California, 17 June 1981. (a) Thermograms for total particle sample (solid lines) and small-particle (<1.5 μm) sample (dashed lines) collected in parallel. (b) Thermograms of large particles determined by difference between total-sample and small-particle thermograms. (XBL 838-3114)

luminescent $NO_x$ detector (ThermoElectron 14D/E) in series to determine analyte concentrations in a single low-volume gas stream. Detection limits of less than 1 ppm for $CO_2$ and less than 0.01 ppm for $NO_x$ in the gas stream mean that, with a flow rate of 200–250 mL/min, the sample sizes required for quantitation with typical ambient particle samples are about 10 μg carbon and less than 1 μg nitrogen.

It has been shown that inorganic nitrogen ions in ambient aerosol particle samples can be identified from their ESCA spectra and can be further speciated to compounds with EGA.[4] We have shown that $N_x$ can often be quantified by EGA[8] and have found that it is linked to organic material evolved during thermal analysis at temperatures above 250–300°C.

Investigation of a series of filter samples collected during a severe photochemical air pollution episode in Riverside, California, in June, 1981, gives further clues as to the composition of $N_x$. High-volume samplers were operated in parallel on top of a trailer on the University of California campus. One sampler collected total particulates; the particles collected on the second sampler were restricted to less than 1.5 μm by a size-segregating inlet and an impactor. Flow rates were equalized so that the only difference was in the particle sizes collected.

For each sample pair, substantially more nitrogen (and carbon) was present in the total-particulate sample than in the small-particle sample. Thermograms of a sample pair are shown in Fig. 2(a). When the large-particle contribution is determined by subtracting the fine-particle thermogram from that of total particulates [Fig. 2(b)], it becomes obvious that there is an apparent similarity of form between the $CO_2$ and $NO_x$ thermograms of the large particles. This observation can be interpreted as an indication of chemical linkage between large-particle carbon and nitrogen. Such linkage could be caused by common existence in primary particles, by accretion of carbonaceous or nitrogenous species on large particles, or by some heterogeneous conversion of gaseous species on the surface of the particles. Although large and small particles may be different chemically, it seems unlikely that adsorption or conversion processes would be limited primarily to the large particles, which have a relative surface area less than that of the small particles.

## PLANNED ACTIVITIES FOR FY 1984

Evidence that, at least under some circumstances, $N_x$ is found primarily as a bulk component of the large aerosol particles suggests that further size-segregated sampling should be carried out. We intend to collect such segregated aerosol samples under a variety of atmospheric conditions. Analysis of these samples will be by the methods described above, with selected samples to be further analyzed by Fourier-transform infrared spectroscopy (FT-IR) for possible identification of at least some of the $N_x$ species.

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# Microencapsulation and Collection of Liquid-, Solid-, and Two-Phase Aerosols*

*R.J. Otto*

Work was started on the development of an advanced method for individual microparticle mass spectrometry based on the electrostatic accelerator of charged aerosol particles in the size range from 0.01 to 10 $\mu$m. An important first step in the research is the development of a collection method that will allow for the subsequent charging and acceleration of the aerosol particles. To this end, microencapsulation of the aerosol particles is being investigated as a new technique for preserving the physical and chemical properties of the particles for off-line analysis.

Microencapsulation has been used to fix cigarette smoke particles for size-distribution studies using electron microscopy.[1,2] Cigarette smoke is primarily a liquid-phase aerosol, and the normal procedure of collecting the particles on a Nuclepore filter for electron microscopy results only in the evaporation of the liquid phase, leaving a coating of tar on the filter and no visible particles in the micrographs. The mixing of gas-phase methyl-2-cyanoacrylate monomer (MCA, Eastman 910 adhesive) into a collection chamber containing smoke results in rapid condensation of the monomer on the smoke particles. The monomer then polymerizes and encapsulates the spherical liquid particles, which can then be filtered and will survive in the vacuum of an electron microscope. The polymeric reaction for MCA is an anionic initiated addition reaction catalyzed by water or hydroxyl groups.[3] The reaction is sufficiently rapid at 70°C that the particles can be collected immediately after mixing with the monomer. The term "encapsulation" implies the existence of a shell surrounding a liquid or solid core of material, which would be preferred. There is evidence, however, that true encapsulation does not occur with MCA, but rather that liquid particles are solidified by a polymer matrix, because of the solubility of the MCA monomer in the liquid phase.[1]

Aerosol microencapsulation can be broken down into three nearly sequential steps: mixing of the gas-phase monomer into the aerosol, condensation of the monomer on the aerosol surface, and polymerization of the monomer. Microencapsulation technology is being used for the controlled release of pesticides and drugs[4]; and although there are a large number of polymers used for this purpose, most of the work in this area has been with liquid suspensions. However, a number of these same polymers could be modified for encapsulation of aerosols. Control of the aerosol encapsulation

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process can be accomplished by selection of the polymerization reaction, by choice of initiator, and by control of the net rate of diffusion of the monomer to the surface of the aerosol, thereby controlling the amount of monomer deposited on the surface of the particle. Since temperature, pressure, and relative humidity affect the physical state of the aerosol, they would ideally be held constant during encapsulation.

Microencapsulation offers several advantages for use in preserving individual particles for off-line analysis. It effectively "freezes" both liquid-, solid-, and two-phase particles at the time of collection, preserving the particles' size distribution and isolating them from further chemical reactions with external reactants. It provides a uniform surface composition for all particles, which should result in uniform collection efficiency for particles of the same aerodynamic size but different chemical composition. Encapsulated hydrated aerosol particles will tend to be spherical, which should be the optimum shape for both their nonpreferential collection and acceleration. The ability to preserve the elemental composition of the liquid phase in the vacuum of the accelerator is also a distinct advantage. Another advantage is that the surface of the encapsulated particles could be modified to enhance their conductivity. The velocity of spherical conducting particles that have been electrostatically accelerated is proportional to the square root of the net charge on the particle. Since net charge is a function of particle radius, in-flight mass or size measurement can be achieved through measurement of the accelerated particles' velocity. Extremely thin high-purity gold or carbon coatings, similar to those used for scanning electron microscopy, could be applied to the encapsulated particles to make them uniformly conducting.

## ACCOMPLISHMENTS DURING FY 1983

A collection method is being sought that will preserve both the physical and the chemical properties of the aerosol to be analyzed. To date, cigarette smoke and an aerosol of deionized water have been successfully microencapsulated with MCA using the batch method suggested by Holmberg.[1] The particle size distributions for these two aerosols was determined by scanning electron microscopy. Particle sizes ranged from 0.1 to 1.0 $\mu$m, consistent with previously reported size distributions.[1] Experiments are being done to optimize the amount of monomer used for encapsulation to ensure that it is not altering the size distribution of the aerosol. A less soluble monomer — isobutyl-2-cyanoacrylate — has also been successfully used as an alternative. Further work needs to be done on the optimum monomer partial pressure for encapsulation, the optimum temperature for polymerization, and the thickness of the polymer coating. A continuous-flow encapsulation process was also tested.

Collection by encapsulation is only the first step toward mass spectrometry of aerosol particles; the next is electrostatic acceleration. Graphitic carbon fibers are being studied for use as a collection and charging surface in the high-voltage end of the accelerator. Experiments have therefore been started to determine the relative collection efficiency of encapsulated cigarette smoke on a single fiber. The fiber was placed directly ahead of a Nuclepore filter, and the relative number of particles in each size bin, on the fiber, and on the filter was determined. In addition, the absolute collection efficiency for 0.30 and 2.00 $\mu$m polystyrene latex spheres (PSL) was determined. The predicted efficiency for the 0.30 and 2.0 $\mu$m particles on the 7-$\mu$m diameter fiber at a flow velocity were 0.20% and 22% respectively; the experimental values were 0.15% and 0.31% respectively. The minimum collection efficiency was expected to be at 0.30 $\mu$m for the sampling conditions. The collection efficiency for both the PSL and the encapsulated particles above and below the minimum were lower than expected by a factor of 10 to 100.

## PLANNED ACTIVITIES FOR FY 1984

Further work on the relative and absolute collection efficiency of encapsulated particles as a function of particle size and chemical composition is planned. A monodisperse encapsulated microparticle generator needs to be built for this work. Microencapsulation of micrometer- and submicrometer-size aerosol particles with a polymer coating is a potentially useful technique for resolving some of the key issues in atmospheric aerosol science today. Both liquid and solid aerosol particles can be effectively frozen in their physical and chemical state at the time of encapsulation, preserving them for further analysis. However, microencapsulation of atmospheric aerosol particles is a relatively new and unexplored technique. Research into a few key aspects of microencapsulation should reveal its potential for a number of significant applications to hydrated and liquid-phase aerosols. Work on one or more of the following areas is planned to explore the usefulness of microencapsulation for: (1) preserving the physical and chemical characteristics of liquid and hydrated aerosols, fog, and cloud particles; (2) investigating the degree to which solid aerosol particles are hydrated; (3) determining the degree of internal

or external mixing of multicomponent aerosols; and (4) studying the physical and chemical heterogeneity of aerosol particles in a given size range.

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# The Aethalometer — An Instrument for the Real-Time Measurement of Optical Absorption by Aerosol Particles*†


*A.D.A. Hansen, H. Rosen, and T. Novakov*


Aerosol particles emitted from combustion sources contain many different carbonaceous compounds and structures. One of these components is carbon in a microcrystalline graphitic form,[1] which, because of its strong optical absorption, is called "black carbon." This material can only be produced by incomplete combustion: no secondary mechanisms for its production from airborne precursors are known. Since it is also inert to transformation in the atmosphere, it makes a good tracer for combustion emissions. Chemical techniques[2] for determining the black carbon content of aerosol samples collected on filters are generally complex and time consuming. In contrast, optical measurements are often simple and rapid. Because most ambient aerosols do not contain large amounts of other absorbing, noncarbonaceous particulate material, a measurement of optical absorption of the filter deposit corresponds very closely to the black carbon determination. These methods and results are discussed in detail by Gundel *et al.*[3] Here we describe an instrument that uses an optical technique to measure the concentration of aerosol black carbon in real time. We have named the instrument the *aethalometer*, from the Greek word "αιθαλουν," "to blacken with soot."

## ACCOMPLISHMENTS DURING FY 1983

The aethalometer continuously measures the attenuation of a beam of light transmitted through a filter through which particle-laden air is being drawn.[4] 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. Measurement of this attenuation constitutes the basis of the method. The aerosol particles are retained on the filter and are available for subsequent analysis by other physical and chemical means. Some of these results are used for calibration of the instrument.

The optics and electronics can detect an increase in optical attenuation of 0.00075 units of optical density, corresponding 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 minimum quantity, $Q_{min}$, of black carbon from the air stream, whose velocity at the filter face is denoted $v$. 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 seconds for a black carbon concentration of 1 $\mu$g/m$^3$. A variable time base determines the actual interval over which the digitization and differentiation are performed. We may select longer base periods to improve the accuracy of the concentration measurement at the expense of its time resolution.

To avoid the effects of optical saturation, a maximum loading $Q_{max}$ of 8 $\mu$g/cm$^2$ of black carbon on


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the filter is allowed before a filter change is required. At constant filtering velocity $v$ and average aerosol black concentration $C$, this occurs after a time $t_{max} = Q_{max}/Cv$. At maximum flow rate with $C$ equal to 1 $\mu g/m^3$, this time is approximately 4.5 hours. 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.

The aethalometer is calibrated by performing quantitative chemical analysis for black carbon[3] on the quartz-fiber filter. The result is compared to the integral of the real-time output to give the calibration factor. This factor may be used for routine work; when the greatest accuracy is required, we chemically analyze each individual filter.

In previous ground-level studies[5] of the black carbon content of ambient aerosols, the aethalometer showed the time-dependent behavior of black carbon concentration. This time-resolution capability can be used to determine the spatial distribution of the aerosol. As part of the National Oceanic and Atmospheric Administration's "AGASP" project, the aethalometer was operated on board an aircraft flying over the Arctic in March and April, 1983. Figure 1 shows the output during a test flight when passing at 900 m altitude through a plume from agricultural burning. The time-base period was 4 seconds, giving a horizontal resolution of approximately 500 m and a measurement accuracy of approximately 5% of peak. Figure 2 shows the output during a descent profile from 6000 m altitude to sea level in the Norwegian Arctic. A 1-minute time-base period was used, and we obtained a vertical distribution of aerosol black carbon with a resolution of approximately 200 m.

In summary, we have developed and refined an instrument that is capable of yielding a highly sensitive measurement of the concentration of aerosol black carbon in *real time.* This measurement may be directly calibrated by chemical analysis and may be interpreted in terms of an aerosol absorption coefficient. The instrument has sufficient sensitivity to perform this measurement in remote locations with a time resolution of minutes, and within seconds in plumes. Its capabilities suggest applications in many

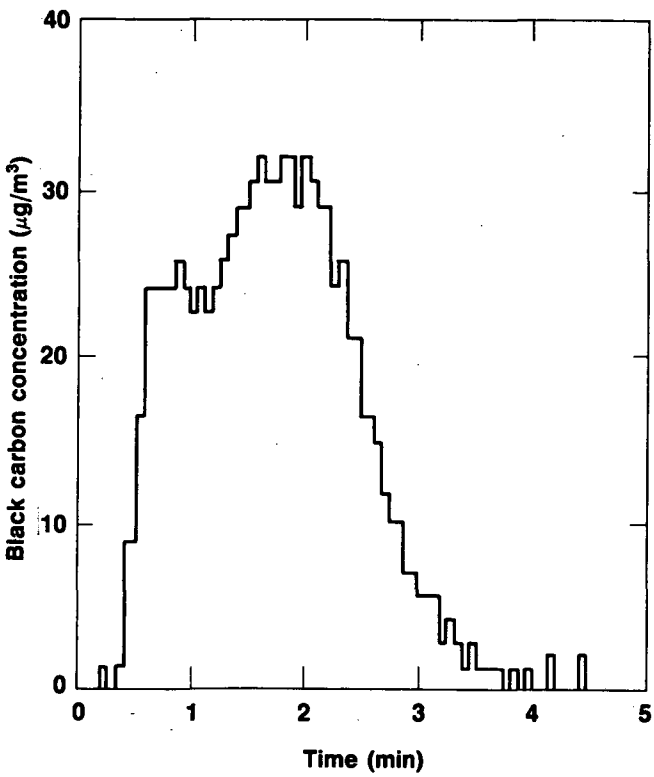


**Figure 1.** Aethalometer response during transit of a plume from agricultural burning over the Bahamas. The aethalometer time-base period of 4 seconds gives a horizontal resolution of approximately 500 m. (XBL 838-3120A)

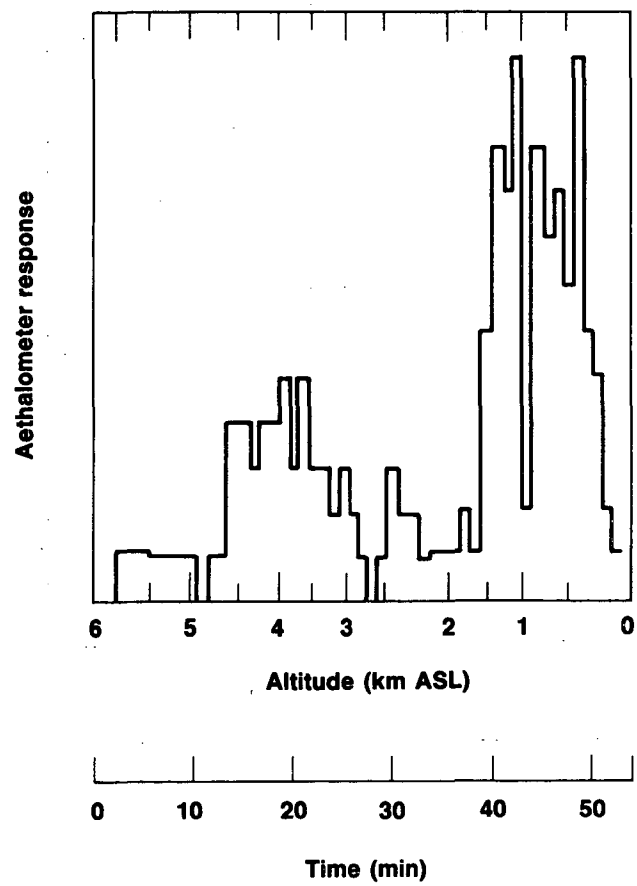


**Figure 2.** Aethalometer response during descent profile near Spitzbergen. A separate record of flow rate vs. altitude is also kept, which must be factored into these data to yield the aerosol black carbon concentration. The aethalometer time-base period is 1 min. (XBL 838-3118)

areas of atmospheric science as well as in combustion research.

## PLANNED ACTIVITIES FOR FY 1984

The AGASP flight program demonstrated the considerable value of an instrument that can measure, in real time, aerosol black carbon concentrations as a direct indication of combustion emissions in a particular air mass. Work is in progress to reduce the large data set generated during the AGASP program and to correlate the results with measurement of other aerosol and meteorological parameters. The aethalometer as flown was a modification of the original prototype. We are using the experience gained in this flight program to design the next version; the objective is to improve the instrument's sensitivity (and hence its time resolution), while reducing its size, weight, and power requirements.

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