Title

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DISCLAIMER

THE RELATIONSHIP BETWEEN OPTICAL ATTENUATION AND BLACK CARBON CONCENTRATION FOR AMBIENT AND SOURCE PARTICLES*

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ABSTRACT

Light absorption provides the basis for a fast and nondestructive method for determining concentrations of black carbon (BC). The laser transmission technique measures the attenuation (ATN) of visible light as it passes through filter samples. We have measured [BC] and ATN simultaneously for a large number of solvent-extracted source and ambient particle samples, using temperature-programmed evolved gas analysis with continuous light attenuation measurement. For all data with ATN $\leq$ 200, ATN is directly proportional to [BC], with the proportionality constant = 25.4 $\pm$ 1.7 $cm^2\ \mu g^{-1}$. Because the relationship between ATN and [BC] does not depend on the origin of the carbonaceous particles, measurement of ATN alone can provide a good estimate of the black carbon concentration.

INTRODUCTION

Particulate material from ambient air and combustion sources usually appears black when it is collected on filters, due to the presence of light-absorbing graphitic or black carbon (BC)(ref.1). In the atmosphere, the light absorption due to these particles can degrade visibility (ref.2) and perturb the tropospheric radiation balance (refs.3,4).

Most methods for determination of black carbon (ref.5) rely on separation of organic carbon from black carbon by pyrolysis, oxidation, or solvent extraction before determination of BC as CO_2. These methods are destructive and often time consuming. In this paper we describe and calibrate a nondestructive and fast technique for [BC], the laser transmission method (LTM). This technique measures the attenuation of visible light (ATN) as it passes through a particulate sample on a filter.

In this study, we have measured [BC] and ATN simultaneously for a large group of source and ambient filter samples. The results have been used to calibrate the laser transmission method and provide a value for the specific attenuation, σ. σ is the value of ATN per unit mass of black carbon. It is

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important to note that the calibration method is independent of knowledge of the exact optical properties of black carbon.

SAMPLING

Samples of aerosol particles were collected on quartz-fiber filters that had been prefired at 800°C for 12 hours. Both high (40 SCFM) and low (10-20 SCFM) volume samplers were used. One-third of the samples were size segregated, with a particle cutoff of < 2 μm. Ambient samples were collected in Berkeley (two sites) and Los Angeles, California; Warren, Michigan (ref.5); Vienna, Austria; and Ljubljana, Yugoslavia. Some of the sampling sites were source influenced: one of the Berkeley sites was 100 m from a heavily travelled freeway; the sites in Austria and Yugoslavia were on the roofs of buildings in congested areas. Typical ambient sampling time was 24 hours.

A variety of combustion sources was 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 (ref.6). A small diesel bus was sampled 2 m from its exhaust pipe, while the bus idled in a vacant parking garage. 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.

ATTENUATION MEASUREMENTS

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

$$ATN = -100 \ln I/I_0 , \quad (1)$$

where I_0 and I are the transmitted light intensities for the blank and the loaded filter respectively. Rosen et al. (ref.1) and Yasa et al. (ref.7) have shown that the light attenuation is due to the presence of black carbon. If ATN has a linear dependence on [BC], then

$$[BC] = ATN/\sigma , \quad (2)$$

where σ is the specific attenuation for black carbon.

Attenuation was measured during the evolved gas analysis (EGA) procedure for determining [BC] (see next section) and also separately at room temperature by LTM. The two measurements of ATN agreed to within 3%. Measurement variability data (refs.8,9) for ATN measured during EGA are given in Table 1.

DETERMINATION OF BLACK CARBON

Temperature-programmed evolved gas analysis in oxygen (refs.10,11) with continuous light transmission measurement was used to identify and quantitate the black carbon. [BC] was determined from the area of the thermogram peak that

TABLE 1

Estimates of measurement variability (standard deviations)[a] and quantitation limits.

	ATN	[BC] µg cm^{-2}	n	k
Blanks, extracted, $\bar{x}_b \pm s_b$	-4±2	0.3±0.2	10	10
Replication of EGA and ATN only, s_t	5	0.3	16	6
Replication of extraction, EGA and ATN, s_x	7	0.6	42	13
Limits of detection $3s_b$, above blank	6	0.6	-	-
Limits of quantitation $10s_b$, above blank	20	2.0	-	-

[a] n = total number of determinations; k = number of different samples.

corresponds to the increase in light transmission during combustion. The black carbon peak is usually centered between 425 and 500°C. Thermograms of typical source and ambient samples are shown in Fig. 1. For source samples, the high temperature peak is always well resolved and can readily be used to determine black carbon concentration (Fig. 1a). Some ambient samples have distinct,

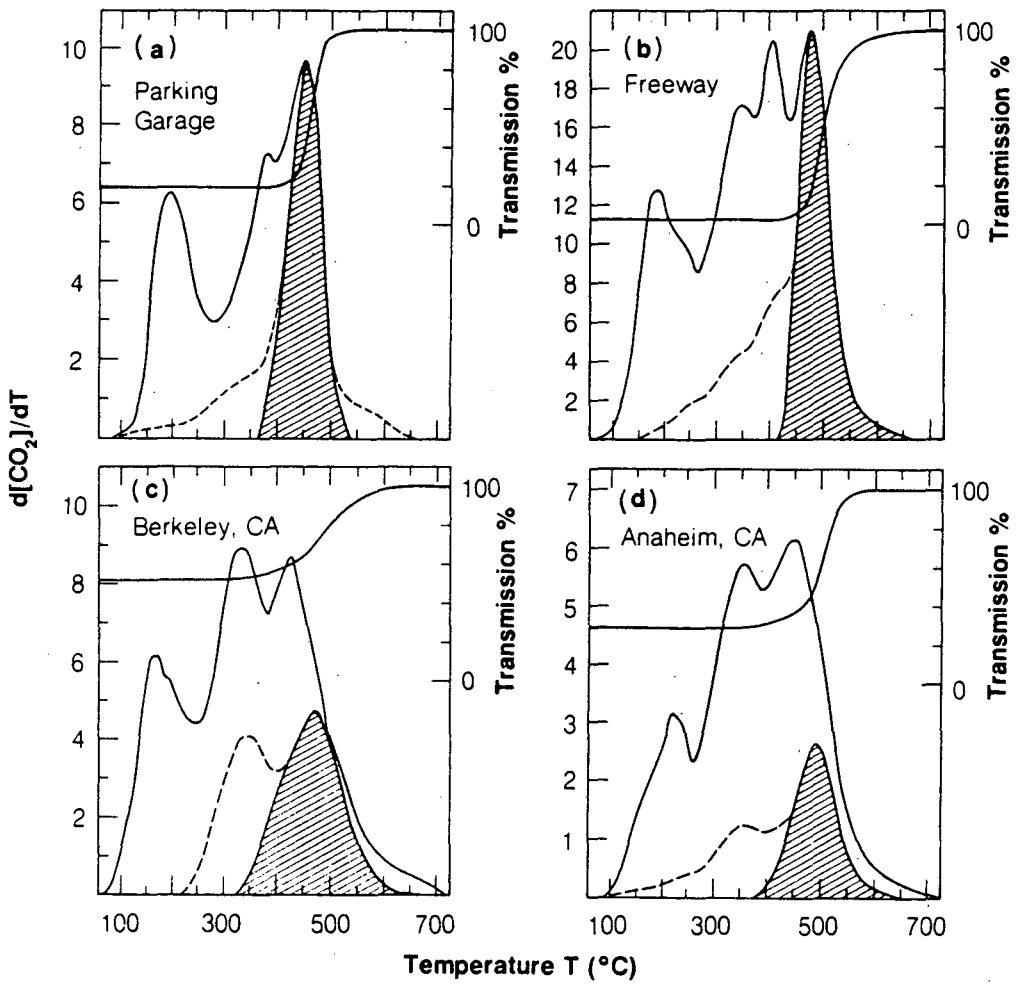

Fig. 1. Thermograms of source and ambient particles (solid line, untreated samples; dashed line, extracted filters). The shaded area is black carbon. Light transmission, in per cent, is given in the upper part of each section.

unambiguous black peaks, as illustrated by particulate matter collected near a major highway in Berkeley, California (Fig. 1b). Differentiation of black carbon from organic carbon in thermograms of some other ambient particulate samples is more difficult, as illustrated in Figs. 1c and d. Removal of soluble organic material by solvent extraction leads to thermograms in which isolation of the black peak is straightforward. This procedure removes most of the organic carbon; but it 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 that had been sequantially extracted by benzene and methanol-chloroform mixture (1:2,v:v) in soxhlet devices, in two 6-hr steps (ref.12).

Estimates of measurement variability and quantitation limits are given in Table 1. The limits of detection and quantitation for blank corrected samples are 0.6 and 2.0 μg BC cm^{-2}, respectively. This method of determination of BC was validated by an extensive 11-laboratory round-robin comparison (ref.5). Our results were indistinguishable from the mean values obtained in that study for three filter samples of ambient particulate matter from Warren, Michigan.

RELATIONSHIP BETWEEN ATN AND [BC]

ATN and [BC] data are presented in Fig. 2 for all source and ambient samples with ATN ≤ 200 and BC ≤ 8 μg cm^{-2}. For source particles, Fig. 2a, linear

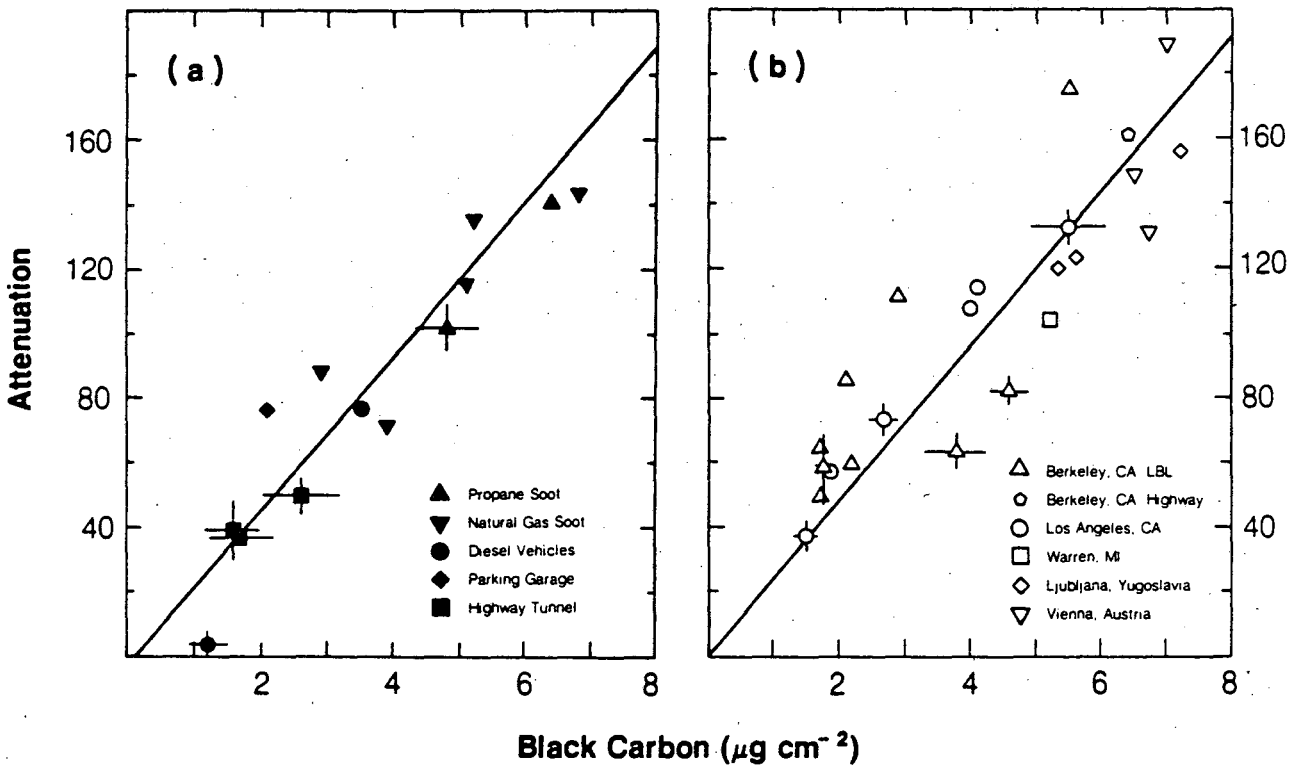

Fig. 2. The relationship between attenuation and black carbon concentration for ATN ≤ 200 and [BC] ≤ 8 μg cm^{-2}. Particles from a) sources and b) urban air.

regression gives ATN = (10.6 ± 16.6) + (24.1 ± 2.8)[BC], with r (the correlation coefficient) = 0.86. For ambient particles, Fig. 2b, ATN = (-0.8 ± 9.8) + (24.1 ± 2.3)[BC], with r = 0.89. It is clear from these results that, within experimental error, source and ambient particles follow the same relationship between ATN and [BC]. If we combine all data with ATN ≤ 200 and [BC] ≤ 8 μg cm^{-2},

$$ATN = (-1.6 \pm 8.7) + (25.4 \pm 1.7)[BC] \quad , \tag{3}$$

with r = 0.88. Since this intercept is indistinguishable from zero, the slope of equ. (3) is the specific attenuation, σ. Therefore [BC] can be predicted from equ. (2) with σ = 25 and a coefficient of variation for σ of 7%, when ATN ≤ 200. The expected error in [BC] ranges from 0.3 μg cm^{-2} at ATN = 50 to 0.6 μg cm^{-2} at ATN = 200, using s_σ from equ. (3) and s_{ATN} from Table 1. If we include all data, regardless of sample loading, a saturation effect is observed at high ATN (Fig. 3). This could be explained by a "light pipe" effect that was noticed during observation of heavily loaded filters by optical microscopy. If we assume that part of the incident light, αI_0, does not interact with the particle deposit, the light available for absorption by particles is reduced to $(1-\alpha)I_0$, where α is the fraction of the incident light that is conducted along the quartz fibers of the filter without interaction with the particle deposit. The transmitted light intensity is then, for Beer's Law absorption,

$$I = I_0(\alpha + (1-\alpha)\exp(-\sigma[BC])) \quad . \tag{4}$$

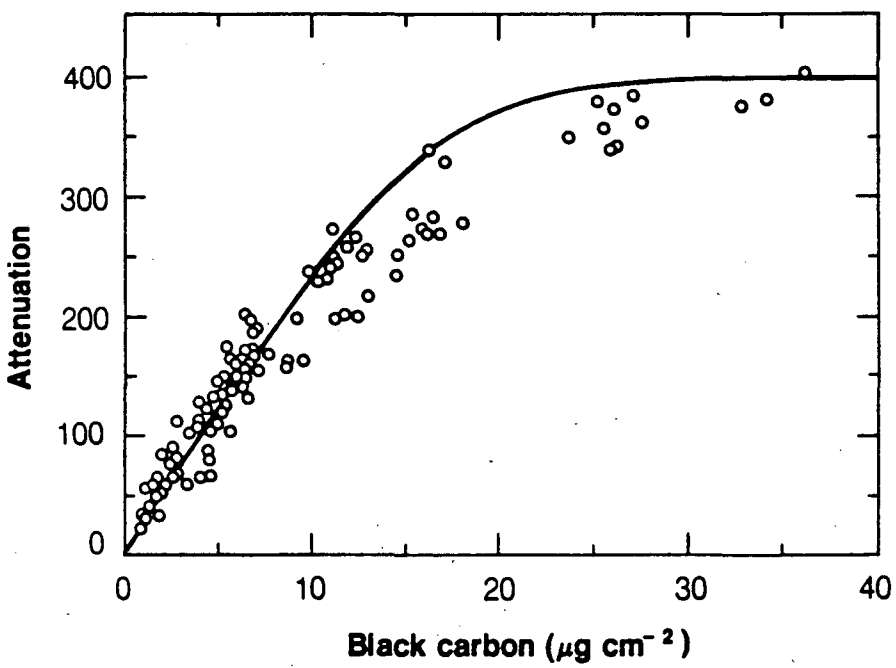

Fig. 3. The relationship between ATN and black carbon concentration for all data. The solid line gives σ = 23.9 ± 2.0 and α = 0.0172 in equ. (5).

Substitution of this expression for ATN in equ. (1) leads to equ. (5):

$$ATN = -100 \ln (\alpha + (1-\alpha)\exp(-\sigma[BC])) . \quad (5)$$

For all data this model gives $\alpha = 0.0172$ and $\sigma = 23.9 \pm 2.0$ and $r = 0.76$. The coefficient of variation of the specific attenuation is 8%. All data points were treated equally, as shown in Fig. 3, since the identity of the black particles does not influence the relationship between ATN and BC.

SUMMARY AND DISCUSSION

We have found that source and ambient carbonaceous particles from eight locations in the United States and Europe follow the same relationship between ATN and [BC]. Good predictions of [BC] can be made by using the simple ATN measurement as an alternative to solvent extraction and combustion EGA or other chemical methods, using equ. (2) and $\sigma = 25$. The ATN measurement is fast, nondestructive, cost effective, and will predict [BC] to within 10% for moderately loaded filter samples (ATN = 100); the useful range of the ATN measurement is 25-300 ATN units or 1-15 $\mu g\ cm^{-2}$ BC, using equ. (5) for ATN > 200.

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