Title
AN INTERCOMPARISON OF THE INTEGRATING PLATE AND THE LASER TRANSMISSION METHODS FOR DETERMINATION OF AEROSOL ABSORPTION COEFFICIENTS

Permalink
https://escholarship.org/uc/item/83m4j98j

Author
Sadler, M.

Publication Date
2010-12-14
AN INTERCOMPARISON OF THE INTEGRATING PLATE AND THE LASER TRANSMISSION METHODS FOR DETERMINATION OF AEROSOL ABSORPTION COEFFICIENTS

M. Sadler, R.J. Charlson, H. Rosen, and T. Novakov

July 1980
AN INTERCOMPARISON OF THE INTEGRATING PLATE AND THE LASER TRANSMISSION METHODS FOR DETERMINATION OF AEROSOL ABSORPTION COEFFICIENTS

M. Sadler and R. J. Charlson
Department of Civil Engineering
University of Washington
Seattle, Washington 98195

and

H. Rosen and T. Novakov
Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Abstract

The absorption coefficients determined by the integrating plate method and the laser transmission method are found to be comparable and highly correlated. Furthermore, a high correlation is found between these absorption coefficients and the carbon content of the aerosol.
AN INTERCOMPARISON OF THE INTEGRATING PLATE AND THE LASER TRANSMISSION METHODS FOR DETERMINATION OF AEROSOL ABSORPTION COEFFICIENTS

M. Sadler and R. J. Charlson
Department of Civil Engineering
University of Washington
Seattle, Washington 98195

and

H. Rosen and T. Novakov
Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Recent studies of atmospheric aerosol particles indicate the presence of a large, optically absorbing component which can cause both visibility degradation and climatic effects. The nature of this absorbing species has been investigated in the past by solvent extraction, heat treatment, and wavelength dependence studies (Weiss et al., 1976; Rosen et al., 1977, 1980), which led to the conjecture that it could be a graphite-like material. More recently, the Raman scattering technique has been applied to identify this component in urban aerosols on a microscopic level as "graphitic" carbon (Rosen et al., 1978).

The fact that aerosol particles absorb light is evident from the usual grey or black appearance of filter samples collected from even rural locations. However, the absolute measurement of the component of extinction due to absorption, $\sigma_{ap}$, has posed significant challenges. Here we define the extinction coefficient, $\sigma_{ext}$, and its components with the Beer-Lambert law. For light of intensity $I$ passing through an atmospheric path of length $dx$:

$$\frac{dI}{I} = -\sigma_{ext} \ dx = -(\sigma_{scatter} + \sigma_{absorption}) \ dx$$
and

\[ \sigma_{\text{absorption}} = \sigma_{\text{absorption by particles}} + \sigma_{\text{absorption by gases}} = \sigma_{\text{ap}} + \sigma_{\text{ag}}. \]

Not only is the measurement of \( \sigma_{\text{ap}} \) difficult, it is also extremely hard to make aerosols of known absorption coefficient for testing, calibration, and validation of methods.

Historically, one of the earliest measurements was performed by Waldram (1945), who measured the total extinction and its scattering component, arriving at the absorption component by subtraction. He found a relatively large percentage of extinction to be caused by particle absorption, typically half in an industrial area of England. However, this result has often been discounted as being atypical and the assumption is usually that \( \sigma_{\text{ext}} \approx \sigma_{\text{scat}} \).

There are fundamentally two general approaches in use for assessing light absorption by particles. One family of methods aims at establishing the absorption coefficient in the atmosphere, \( \sigma_{\text{ap}} \); and the other set of methods determines the imaginary refractive index of the bulk material of which the particles are formed. These approaches can be connected via Mie calculations if size distribution and the distribution of absorbing material with size are known.

Besides the difference method of Waldram (1945), the integrating plate method (Lin et al., 1973; Weiss et al., 1979), the laser transmission method (Rosen et al., 1978), and the multipass transmissometer (Gerber, 1979) are examples of the first of these approaches; while the integrating sphere (Fisher, 1973), the Kubelka-Monk method (Lindberg and Laude, 1974), and inversion of angular scattering data have been used to estimate the imaginary
refractive index of the material of which the particles are formed.

Two of these methods (integrating plate and laser transmission) have been extensively used because of their practicality. This paper will compare the absorption coefficients determined by these two methods at a wide range of sites. Furthermore, these absorption coefficients will be correlated to the total carbon content of the aerosol. These measurements should provide an independent test of the strong correlation found by previous investigators (Hansen et al., 1979; Rosen et al., 1980) at urban locations, as well as to extend this type of observation to rural areas.

Methods

This study incorporated the use of three different sampling substrates (Nuclepore, 0.4 μm pore size; Millipore, 1.2 μm nominal pore size, type RATF; quartz fiber filters, Pallflex type, 2500 QA0) with the use of two different measurement techniques for light absorption. These three filter types were used as the after-filters of a single stage jet impactor (Marple, 1970), operating with a 50% cut point near 2 μ. This allows the evaluation of light absorption and carbon content of the long-lived accumulation mode particles while minimizing the confusing effects of biogenic carbon or of weakly absorbing dust of crustal origin.

Integrating Plate Method (IPM)

The integrating plate method (Lin et al., 1973; Weiss et al., 1979) is based on comparison of the transparency of a Nuclepore filter containing a small amount of aerosol with that of a clean filter. A path length x of air is passed through the filter, where x is the sample volume divided by
filter area. This technique requires that particles be located on the surface of the filter and that the deposit be optically thin ($\sigma_{ap} x << 1$). The particles and filter are placed against a plate of opal glass, removing the effects of most of the scattered light, so that the measured extinction is due mainly to absorption.

During aerosol sampling, the filters become darker and less transparent due to absorbing aerosol particles collected on them. The amount of light absorbed by particles on the filter can be calculated from the comparison of the transmitted light with and without particles on the filter using the Beer-Lambert relationship:

$$I/I_0 = \exp(-\sigma_{ap} x).$$

The original paper by Lin et al. (1973) describing the method reported its accuracy to be within a factor of two when using Nuclepore filters. However, more recent tests both with monodisperse laboratory aerosols (methylene blue), $0.8 \leq D_p \leq 2.8 \mu m$ and with long path transmissometers suggest an uncertainty of 20% or less for the value of $\sigma_{ap}$ (Weiss et al., 1979; Hall and Riley, 1979).

Laser Transmission Method (LTM)

The laser transmission method is an extension of the integrating plate technique to certain other filter media (millipore, quartz fiber, Teflon), which act as an efficient collection substrate as well as play the role of the opal glass as a diffuse scatterer. This method measures the absorbing component of aerosol particles and is apparently insensitive to its scattering properties. This had been demonstrated directly by a photoacoustic study (Yasa et al., 1979) and indirectly by noting that most of the mass
of the aerosol responsible for scattering can be removed by solvent extraction or heat treatment procedures without appreciably affecting the optical attenuation measurement (Rosen et al., 1978).

The laser transmission apparatus compares the transmission of a 633-nm He-Ne laser beam through a loaded filter relative to that of a blank filter. The loaded filters are placed in the beam with the loaded side towards the laser; after multiple scattering through the filter substrate, the light is collected by an f/l lens and focused on a photomultiplier tube. The absorption coefficient, $\sigma_{ap}$, is determined from the Beer-Lambert Law in a fashion similar to that outlined for the integrating plate method.

Carbon Analysis

The carbon loading on the quartz fiber filters is determined by a total combustion/$\text{CO}_2$ evolution method (Mueller et al., 1971). The filters are prefired overnight at 800 °C to remove all combustible carbon before sample collection. Periodic analysis of blanks typically yields about 0.5 µg C/cm$^2$.

Sampling Sites

Five sampling sites in the western part of Washington state were used in this study, from a highly congested site in a highway tunnel to a very remote site on a western foothill in the Olympic Mountains. By sampling such diverse aerosol conditions, the range of absorption coefficients of the air samples was more than three orders of magnitude, from $\sim 10^{-7}$ m$^{-1}$ to nearly $10^{-3}$ m$^{-1}$, with the total carbon concentration ranging from about 5 µg/m$^3$ (Mt. Octopus) to nearly 90 µg/m$^3$ (highway tunnel). The sites are shown in Figure 1.
Results

The results of these comparisons are shown graphically in Figures 2 and 3. In Figure 2, a plot of absorption coefficients is shown, as determined by the IPM using a Nuclepore substrate and the LTM using a Millipore substrate. Also shown in the figure are absorption coefficients determined at the University of Washington on quartz fiber filters. A total of 44 filters of each type was used in this comparison. The correlation coefficient between the two measurements is 0.95, with the absorption coefficient determined by the LTM being greater than the determined by the IPM by a factor of approximately 2.5.

Figure 3 presents the plot of the concentration of total carbon (µg/m³) versus the absorption coefficient from Nuclepore filters. The correlation found between these two variables was 0.90. Also shown in this figure is a value of $\sigma_{ap}$ for monodisperse graphite particles ($n_2 = 0.66$, $D_p = 0.1 \mu m$), estimated as a function of mass concentration from Faxfog and Roessler (1979).

Conclusions

Three points emerged as the main conclusions of this study. First, the light absorption coefficients determined by these two methods are comparable and highly correlated. The reason for the higher indicated absorption coefficient using the LTM could be due to several factors, including 1) penetration effects in the Millipore substrate, which could lead to enhanced absorption due to multiple scattering effects within the filter medium itself; 2) possible pile-up at the holes or loss of particles in the holes of the Nuclepore substrate; 3) differences in the collection efficiency of the two substrates. Studies are under way in both of our laboratories to assess the magnitude of these effects. It should be emphasized, however, that the differences found between these
two techniques are small in comparison with the large uncertainties reported in the literature for the magnitude of the absorbing component of aerosol particles. These differences are also small compared to the range of more than three orders of magnitude observed in the value of $\sigma_{ap}$.

Second, and at least as important, a high degree of correlation is found between the absorption coefficients, $\sigma_{ap}$, and the carbon loading with the ratio of $[C]/\sigma_{ap}$ being similar at the highway tunnel, the University of Washington, and Mt. Squak. This correlation has been observed in the past (Hansen et al., 1979; Rosen et al., 1980) in many urban locations and for various source emissions; but this work represents the first verification of this important result by an independent absorption technique. Both these results are quite independent of site and are correspondingly independent to a high degree of the concentrations of carbonaceous material or level of $\sigma_{ap}$. The higher value of $[C]/\sigma_{ap}$ for the remote sites on the Olympic peninsula may be an indication of a very small natural background of non-light-absorbing carbon compounds. Such a background evidently might have values of total carbon of the order one to a few $\mu g/m^3$. The results also indicate that light-absorbing aerosols are ubiquitous in the atmosphere, even in such remote locations as our coastal sites. The fact that the ratio of $[C]/\sigma_{ap}$ is nearly the same in rural areas as in an urban area might imply that the light-absorbing carbonaceous materials in our rural samples were derived from an urban source. This suggestion is of course highly tentative and requires further measurements for resolution.

Third, we include in Figure 3 a comparison of the observed C concentration/$\sigma_{ap}$ relationship to a calculation from the Mie formalism for pure graphite particles. Uncertainties of a factor of two or so exist in the imaginary refractive index for graphitic carbon, with 0.66 appearing as
a typical value (Roessler and Faxfog, 1980). This calculated relationship is close to the observed values, which is consistent with the suggestion of Novakov (1973) and Rosen et al. (1980) that soot (which contains a graphitic and an organic component) is a major fraction of the carbonaceous aerosol in urban areas.
References


Marple, V. (1970), Ph.D. disseration, University of Minnesota, Dept. of Mechanical Engineering.


Figure Captions

Figure 1. Sampling sites

Figure 2. Light absorption coefficient, $\sigma_{ap}(m^{-1})$, determined by the IPM on Nuclepore filters versus $\sigma_{ap}(m^{-1})$ determined on Millipore (X) and quartz (O) filters.

Figure 3. Light absorption coefficient, $\sigma_{ap}(m^{-1})$ determined by the IPM versus total carbon concentration in $\mu g/m^3$. For site notation, see Figure 1.
Figure 2
Figure 3
This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.