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PHOTOACOUSTIC DETECTION OF CARBONACEOUS ATMOSPHERIC AEROSOLS

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ABSTRACT

The role of carbonaceous aerosols in the atmosphere as a risk factor in climatic changes and health effects and state-of-the-art monitoring processes are briefly presented here. In particular, development of a photoacoustic technique for measuring the concentration of carbonaceous particles is discussed. The photoacoustic measurement is based upon detection of pressure waves generated by localized time-dependent heating of air inside the photoacoustic chamber. Heating of air inside the chamber is due to absorption of visible laser radiation by carbon particles present inside the chamber. The laser radiation is chopped, and the resultant pressure signal produced by subsequent heating and cooling of the gas is monitored using a microphone. Sensitivity of this photoacoustic technique and its application in monitoring soot particles in the atmosphere is discussed.

INTRODUCTION

Absorption of solar radiation by atmospheric aerosols can be a major influence on climate and on the radiation budget determining the temperature of the Earth. The troposphere is the atmospheric region most directly affected by man's activities; airborne particulates have greatly increased due to the combustion of fossil fuels in industrialized countries. The structure and composition of these airborne particulates are extremely variable, depending on meteorological conditions, emission sources, and geographical locale.

Measurement of aerosol light-absorption coefficients are directly valuable for studies of atmospheric visibility, radiative transfer, and atmospheric heating rates, while determination of particulate concentrations are of direct value for source monitoring.

Experimental data on the absorption of solar radiation by aerosols have been obtained using 3 different methods:

1) airborne devices have been used to determine the radiative flux divergence in layers of the atmosphere which, on subtracting the calculated gaseous component, yields the aerosol absorption component (Roach, 1966; Robinson, 1966; Kondratyev *et al.*, 1974; Valero *et al.*, 1982). Careful instrumentation is necessary and long term averaging is required due to inhomogeneities in the surface albedo.

2) absorption analysis of filter-collected aerosol particle samples has been carried out (Fischer, 1973; Weiss *et al.*, 1979; Bennett *et al.*, 1981). There is, however, the possibility that the sample will be modified by collection, especially in the case of liquid or liquid coated particles.

3) absorption coefficients have been inferred from scattering properties of the aerosol (Eiden, 1971; Grams *et al.*, 1974). This requires detailed information on the scattering properties to carry out the required Mie calculations.

INTERACTION OF LIGHT WITH PARTICLES

Light extinction in a homogeneous medium is described by the Beer-Lambert Law.

$$I/I_0 = \exp(-\beta_{ex}L) \quad (1)$$

where I is the light intensity at a distance L into the medium, I_0 is the incident or initial intensity, and β_{ex} is the extinction coefficient for the medium at the specific frequency or frequencies of the incident light.

Extinction is due to absorption and scattering of the electromagnetic

energy. The extinction coefficient is the linear sum of the absorption (β_{ab}) and scattering (β_{sc}) coefficients.

$$\beta_{ex} = \beta_{ab} + \beta_{sc} \quad (2)$$

The extinction cross section (α_{ex}) of a particle is defined as the hypothetical area normal to the incident radiation that would geometrically intercept the total amount of radiation actually extinguished by the particle (Weast, 1980-81). The extinction coefficient of a monodisperse aerosol can be considered to be the product of the extinction cross section for individual elements (α_{ex}) of the medium and the number concentration, N , of those elements.

$$\beta_{ex} = N\alpha_{ex} \quad (3)$$

The amount of radiant power absorbed and scattered by the particle is given by,

$$P_{ex} = I_0\alpha_{ex} \quad (4)$$

where P_{ex} is the power absorbed and scattered from the incident beam of intensity I_0 . The extinction cross section of a particle is a linear summation of components due to absorption and scattering.

$$\alpha_{ex} = \alpha_{ab} + \alpha_{sc} \quad (5)$$

Photoacoustic techniques (Patel and Kerl, 1977; Faxvog and Roessler, 1979; Szkarlat and Japar, 1981; Roessler, 1984; Roessler and Faxvog, 1980; Terhune and Anderson, 1977; Bruce and Pinnick, 1977; Foot, 1979; Weast, 1980-81) offer a method of measuring absorption of light by aerosol particles directly. The basic theory behind photoacoustic detection is quite simple. Light absorbed by a sample will excite a fraction of the ground-state molecular population into higher energy levels. These excited energy states will subsequently relax through a combination of radiative and nonradiative pathways. The nonradiative component will ultimately generate heat in the localized region of the excitation light beam resulting, when the light intensity is modulated, in a pressure wave that propagates away from the source, or in the case of a small closed cell, a modulated pressure rise which may be detected by a sensitive microphone. A schematic of a typical photoacoustic apparatus for aerosol light absorption is illustrated in Fig. 1.

The spectrophone provides a means of continuous monitoring of ambient aerosol particulate concentrations that is far less time consuming than filter collection techniques. The time response of the spectrophone is on the order of seconds, with a detection capability of below 10^{-8} m^{-1} (Patel and Kerl, 1977).

Photoacoustic Detection of Carbonaceous Atmospheric Aerosols

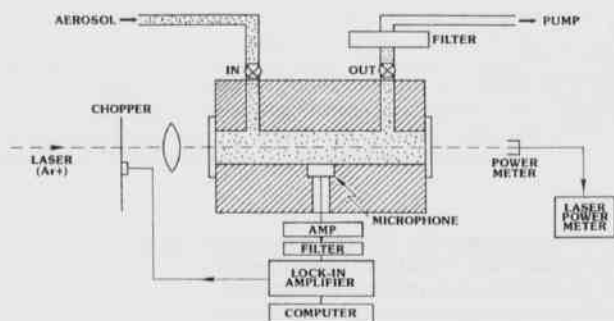


Figure 1. Schematic of photoacoustic measurement apparatus for aerosol light absorption studies.

The absorption and scattering cross sections, α_{ab} and α_{sc} , are defined in the same manner as the extinction cross section. When all scattering is negligible or has been subtracted from the extinction, Eq. (2) reduces to

$$I/I_0 = \exp(-\beta_{ab}L) \quad (6)$$

Normalizing β_{ab} to the mass concentration M of particles per volume V gives the specific absorption coefficient β_{ab}/M_v , where the specific mass $M_v = M/V$.

SCALING LAWS FOR PHOTOACOUSTIC SYSTEMS

The first important parameter is the responsivity R , of the system. It is a measure of the electrical signal produced by the microphone for a unit amount of power absorbed by the aerosol particulates. Convenient units for R are ($V/\text{watt} \cdot \text{m}^{-1}$).

For particle concentrations of interest, the microphone signals, S , of the photoacoustic system (Faxvog and Roessler, 1979) is therefore

$$S = R \cdot A_a \cdot M \cdot W_0 \quad (7)$$

where W_0 is the time-averaged incident power and R is the responsivity of the cell. M is the aerosol mass concentration, and A_a is the specific aerosol absorption coefficient.

The specific absorption coefficient A_a , is defined by

$$A_a = \beta_{ab}/M_v \quad (8)$$

System sensitivity is defined by the absorption coefficient

$$\beta_{ab} = \alpha_{ab} \cdot C \quad (9)$$

where α_{ab} is the absorption cross section of the species being measured, C is the fractional concentration of the absorbing species. In analyzing any photoacoustic method one must first develop a theoretical description of optimizing the optical and acoustic phenomena, then identify those factors which limit sensitivity of the device. In essence, the optimization is reduced to consideration of the following parameters:

- (a) maximizing the amount of laser energy absorbed by the gas or aerosol by either boosting the incident power or minimizing reflection losses.
- (b) minimizing the background signal by reducing absorption on those surfaces in direct contact with the sample gas or aerosol (i.e. windows, cell walls) and;
- (c) minimizing the effect of those loss mechanisms which one can control by appropriate system design.

ABSORPTION CHARACTERISTICS OF CARBON MIXTURES

For the purpose of this work we define 2 different ways in which soot might be included in atmospheric aerosols:

- 1) External mixture. The soot and non-soot aerosols exist in the atmosphere as distinct particles which are mixed without interacting. In this case the properties of the mixture are sums of the properties of the individual distributions.
- 2) Internal mixture. The soot is deposited as a shell on the outside of a solid non-soot particle or is the core of a particle with a sulfate solution shell.

The fact that soot as a core is more effective than soot as a shell in absorbing radiation is due to 2 effects. A solution sheath around the core acts to focus photons on the core, thus increasing its effective cross-section, whereas a particle with a soot shell has a greater tendency to reflect or refract photons than does a particle with a solution shell due to the larger real part of the index of refraction (Toon and Ackerman, 1981).

EXPERIMENTAL STUDY

Three spectrophones were tested for their sensitivity in making light absorption measurements: 1) a Burleigh Instruments, Inc. PAS-100 non-resonant spectrophone, (Fig. 2); 2) a laboratory built Helmholtz resonant spectrophone, (Fig. 3); and 3) a laboratory built longitudinal mode resonant spectrophone (Fig. 4). For 1 watt of average power from the

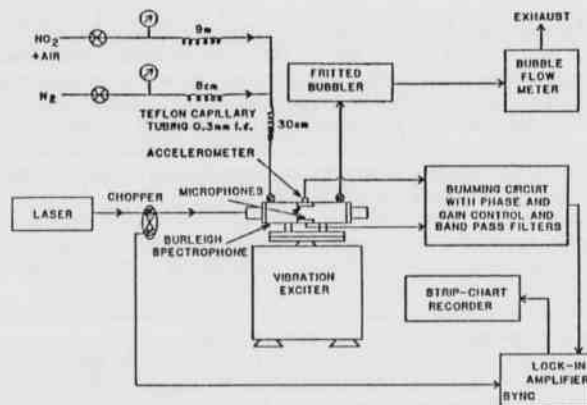


Figure 2. Experimental arrangement for making light absorption measurements and vibration measurements with the Burleigh spectrophone.

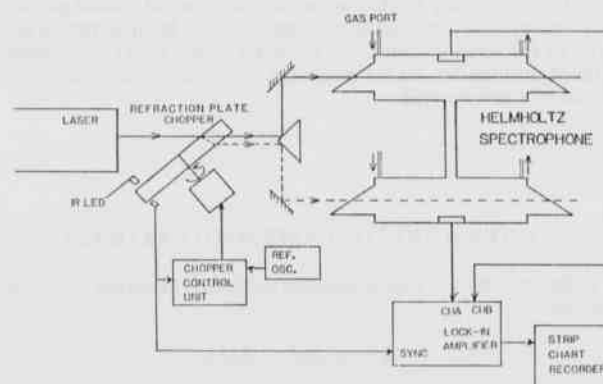


Figure 3. Experimental arrangement with the "Dual-Drive" Helmholtz resonant spectrophone using a slotted refraction plate chopper.

Duane Jackson

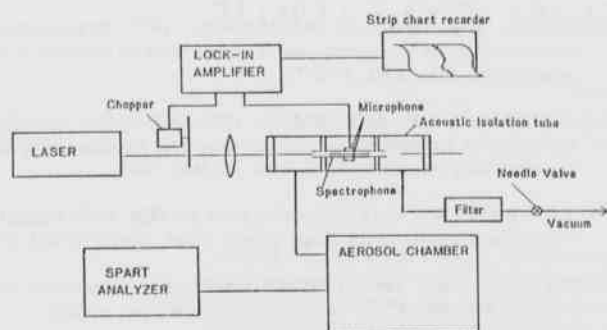


Figure 4. Experimental arrangement for measuring light absorption by aerosols.

488 nm line of an argon-ion chopped laser beam the sensitivities for the 3 spectrophones were $6.5 \times 10^{-6} \text{ m}^{-1}$, $2.5 \times 10^{-6} \text{ m}^{-1}$, and $3.0 \times 10^{-7} \text{ m}^{-1}$, respectively. The sensitivities are for a 1 second time constant on the lock-in amplifier and for a signal-to-noise ratio of one. The noise levels were measured under ambient laboratory conditions with no absorber in the spectrophone. Nitrogen dioxide, NO_2 , was used for calibrating the spectrophones because it exhibits strong absorption of visible light and because published absorption spectra and absorption coefficients were available from literature. The NO_2 concentration was monitored using the wet chemical reagent technique developed by Saltzman (1954). The longitudinally resonant spectrophone was found to provide the greatest sensitivity of the three. The first longitudinal resonance was at 814 Hz. A Radio Shack 270-092A electret condenser microphone was mounted at the longitudinal midpoint of the tube. This tube was housed inside an acoustic isolation chamber. The responsiveness of the longitudinally resonant spectrophone was about $120 \text{ mV ppm}^{-1} \text{ W}^{-1}$. The resulting sensitivity for NO_2 detection was about 0.7 ppb with 1 watt of chopped laser power and optimum noise conditions.

Photoacoustic measurements were made on aerosols of cigarette smoke, sodium chloride, and polystyrene latex spheres (PLS). Simultaneous measurements of the particle size distribution and the approximate number concentration were made using a Single Particle Aerodynamic Relaxation Time (SPART) analyzer (Mazumder *et al.*, 1979). Figure 5 shows a strip chart recording of the photoacoustic signal for cigarette smoke using the longitudinally resonant spectrophone. The

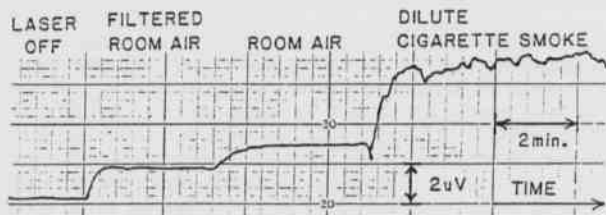


Figure 5. Strip chart record of measurements of the absorption of light by aerosols using a longitudinally resonant spectrophone.

count median aerodynamic diameter was about $0.6 \mu\text{m}$. Extrapolation of the signal down to the background noise level gave a detection limit of about 3×10^6 particles/ m^3 for 1 watt of average laser power. However, this corresponds to less than 1 particle in the illuminated volume at a time. The count median aerodynamic diameter for the NaCl particle was about $0.9 \mu\text{m}$. The photoacoustic signal for the NaCl particles was found to be about 3 orders of magnitude smaller than for the cigarette

smoke. A dependence on relative humidity was also observed. The detection limit for the PLS (diameter = $1.09 \mu\text{m}$) was estimated at about 5×10^8 particles/ m^3 . Some of this signal may have resulted from the high scattering intensity of the particles.

A detection limit for $1 \mu\text{m}$ carbon particles was calculated to be approximately $0.39 \mu\text{g}/\text{m}^3$. Measurements on cigarette smoke gave an extrapolated detection limit of $0.39 \mu\text{g}/\text{m}^3$. For NaCl and PLS the mass detection limit is $2.7 \text{ mg}/\text{m}^3$ and $.35 \text{ mg}/\text{m}^3$, respectively.

CONCLUSIONS

Future work will include the development of a prototype photoacoustic system for the simultaneous measurement of particle size, light absorption, and light scattering characteristics of carbon particulates on a single particle basis. The measurements will be performed in a cell having 3 functions: (1) suspending the test particle in an electrodynamic trap, (2) a photoacoustic cell to measure light absorption, and (3) a relaxation cell to measure aerodynamic diameter of the particle as well as light scattering intensity. Completion of this work will provide valuable insights into the spectral wavelength dependency, shape, and chemical composition of carbonaceous aerosols and their relationship in climate modification.

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