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Project Summary

Photoacoustic Detection of Particulate Carbon

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A photoacoustic technique for mass monitoring of carbonaceous aerosols deposited on filter substrates has been developed. A photoacoustic cell has been designed and calibrated using laboratory generated elemental carbon standards. The nature of the photoacoustic response is examined at several modulation frequencies using these calibration standards, and the physical principles necessary for an adequate interpretation of the experimental results is presented in detail. Practical considerations concerning ambient carbon monitoring are outlined; in particular, the perturbation due to the presence of scattering particles is examined, and limited experimental quantification of this perturbation is reported.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Photoacoustic detection has been successfully used in the past as a means of measuring levels of pollutant gases in the atmosphere. The same principle has been used to construct a sensitive real time photoacoustic soot monitor which measures levels of suspended carbon particles within an acoustically resonant photoacoustic cell. Other types of chemical species present in the atmosphere in particulate form are typically analyzed by the x-ray fluorescence of ambient particulate samples which have been deposited on various filter substrates by dichotomous samplers. Unfortunately, the atomic weight of carbon is too low to allow quantitative results from this very sensitive nondestructive technique. As a consequence, a great deal of data exists, from both past and on-going studies, in the form of ambient particulate samples deposited on filter membranes and for which no information on elemental carbon is available. Soot represents a significant fraction of any ambient particulate sample, either rural or urban, and this fraction is certain to increase as our oil supplies diminish and more and more demand is placed on "less clean" energy sources. Since particulate carbon has been related to adverse health effects, possible climatic perturbations and visibility degradation, it is important to establish a procedure by which accurate elemental carbon levels in the atmosphere can be obtained so that appropriate control strategies can be implemented.

Perhaps the most common nondestructive method of elemental carbon detection for samples collected on filter substrates is the integrating plate method (IPM). Although this technique is very simple and economical, experience in our laboratory has indicated that IPM is seriously affected by the presence of nonabsorbing scattering particles such as ammonium sulfate. The photoacoustic technique we have developed is much less effected by scat-

tering particles and is also nondestructive, simple, and economical. Even if scattering particles were not present in ambient samples, photoacoustic detection (PAD) would still be much more preferable than IPM. The limit of detection of IPM lies far above that of PAD for the following reason: IPM involves a difference of transmission measurements on filters before and after loading. If the light source – detection system stability is, for example, 1%, then one could not hope to make an IPM measurement on a sample which is 1% attenuating with an accuracy of any better than + 100%. The photoacoustic signal, on the other hand, is linearly dependent on the light source intensity so that a 1% fluctuation in intensity produces a 1% fluctuation in accuracy of any better than ± 100%. The photoacoustic signal, on the other hand, is linearly dependent on the light source intensity so that a 1% fluctuation in intensity produces a 1% fluctuation in photoacoustic signal. Indeed, examples of photoacoustic measurements on samples with attenuations of 10^{-4}-10^{-5} abound in the literature. It is clear, then, that the use of PAD will lead to decreased sample collection times and make possible more accurate measurements in clean air environments.

The photoacoustic effect in solids is a fascinating subject in its own right. As is evident from our data on pure carbon calibration standards, the very highly absorbing (and hence very thin) carbon samples prepared for this study illustrate a structure in the photoacoustic signal due to thermal wave interference. Since ambient samples are typically in the form of very thin deposits, it is essential to have a firm understanding of these phenomena if experimental data obtained by PAD is to be accurately interpreted. For example, thermal wave interference (and the resulting structure in the photoacoustic signal) is highly dependent upon the type of filter substrate used; therefore, it is necessary to make separate calibrations for each type of filter material.

Results

The physical principles underlying the production of the acoustic signal generated within the photoacoustic cell are outlined in detail. The equation for the photoacoustic signal (in one dimension) is established via the traditional boundary value approach and by a less vigorous, but more illustrative, approach which better illustrates the physics of the photoacoustic effect. Additional computations are also included which account for the added photoacoustic signal due to light reflected from the filter surface (this effect has been ignored in the past). An analysis of the IPM technique is included as well as a discussion of the decrease in transmission observed when the particles are sandwiched between the filter and the opal glass.

In order to make it possible to obtain measurements on ambient elemental carbon, a set of accurately weighed and evenly deposited elemental carbon calibration standards were prepared using Teflon filters. From IPM measurements on these pure soot calibration filters, we determine the absorptance $A = (1 - T)$ where T is the fraction of incident radiation transmitted by the carbon particles contained on a filter, and the optical thickness $\beta l = -\ln(T)$ where β is the absorption coefficient and l is the thickness of the sample. Figure 1 shows both a plot of absorptance *vs* loading and a plot of βl *vs* loading. Our measured photoacoustic signals for the same calibration filters used for Figure 1 are shown in Figure 2. A comparison of the photoacoustic with the absorptance data suggests (a) that the photoacoustic signal does not saturate with loading as quickly as does the absorptance, and (b) that there is more scatter in the photoacoustic data than in the absorptance data. We should mention that if the same filter is repetitively inserted and sampled, the photoacoustical signal for each measurement agrees to within 3%; the error associated with the loading measurements is contained within the scatter present in the data shown in Figure 1. It appears that the major source of the scatter in the photoacoustic data stems from the Teflon filters which were not thermally thick at 100 Hz. Different filters allow variable amounts of thermal energy to be transmitted to the gas from behind the filters. The interesting fact that the photoacoustic signal does not saturate as the carbon samples become opaque can be explained by considering the interference of thermal waves generated within the very thin carbon samples. Apparently, the thermal waves reflecting from the sample filter backing are shifted in phase by 180° so that the thermal waves at the sample-gas boundary interfere destructively for the thinner samples and interfere more and more

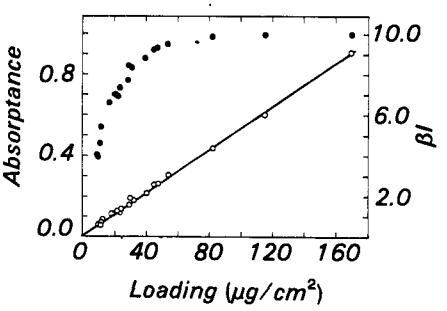

Figure 1. Plots of absorptance vs *loading and optical thickness βl* vs *loading.*

increases, thus causing the photoacoustic signal to continue to rise instead of reaching saturation as the absorptance approaches unity.

Conclusions

Photoacoustic detection appears to be a powerful technique for ambient carbon monitoring. The thermal wave mechanism associated with the production of the acoustic signal introduces additional structure not present when using the optical transmission IPM method. Although, at first glance, this additional structure may appear to be a complication, it is possible that the information provided by this structure will prove useful. It appears that the photoacoustic technique is much less perturbed by the presence of scattering particles than is the IPM method; however, the effect is significant for both methods in the range of loadings expected for ambient samples. The photoacoustic technique seems to provide a better estimate of the true carbon mass present in ambient samples than does the IPM method. Ultimately, the effect of scattering particles must be theoreti-

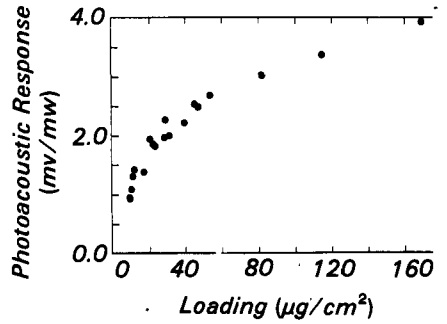

Figure 2. Plot of photoacoustic response vs *loading for a 100 Hz chopping frequency.*

cally and experimentally quantified so that accurate carbon levels may be deduced.

Recommendations

The photoacoustic technique promises to be an extremely accurate method for determining the absorbing component of atmospheric aerosols. More work is needed to adequately establish the role of scattering particles in relation to particle size, etc. In the future, more accurate photoacoustic results will be available if suitable attention is given to quality control of the filter substrates. It would be exceedingly attractive to fully automate a photoacoustic system (possibly with a capability for simultaneous IPM measurements) which could be put into routine operation.

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***W. A. McClenny** is the EPA Project Officer (see below).*
The complete report, entitled "Photoacoustic Detection of Particulate Carbon," (Order No. PB 81-245 425; Cost: $8.00, subject to change) will be available only from:
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