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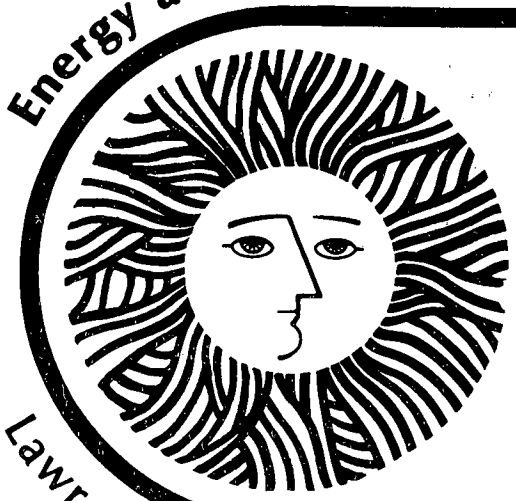

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A Photoacoustic Investigation of Urban Aerosol Particles

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DISCLAIMER

A PHOTOACOUSTIC INVESTIGATION OF URBAN AEROSOL PARTICLES

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The nature of the absorbing species in atmospheric aerosol particles has recently attracted considerable attention among atmospheric and environmental scientists. Recent studies using Raman spectroscopy and an optical attenuation technique[1] indicate that the absorbing species in urban particulates is "graphitic" carbon. We report here on the results of a photoacoustic investigation which gives an independent verification of this hypothesis.

Unlike conventional optical absorption techniques, photoacoustic spectroscopy measures the energy deposited in a sample due to absorption. Since questions have been raised whether the optical attenuation technique exclusively measures the absorbing rather than the scattering component of the aerosol, a comparison between photoacoustic and optical attenuation measurements made on the same aerosol sample should help resolve this ambiguity.

The photoacoustic measurements were made in an acoustically nonresonant detector with cylindrical geometry (Fig. 1). A Knowles microphone (Model BT-1759) was used, and the cell dimensions were 2.1 cm in diameter and 0.3 cm in length. The gas in the detector

cell was air at atmospheric pressure. A He-Ne laser operating at 632.8 nm with 0.5 mW of power was used as the light source, and the experiments were performed at a modulation frequency of 20 Hz. The aerosol particles, collected on 1.2-μ Millipore filter substrates, were mounted on a 1.5-mm-thick Pyrex backing with the particles facing the incident light beam. Experiments were also performed with the laser beam first incident on the filter substrate.

In the limit of low frequency light modulation ($\lesssim$ 100 Hz), it can be shown[2,3] that the photoacoustic signal is given by:

$$V(\omega) = \frac{\eta\gamma PW\mu_g\mu_{sb}G(\omega)}{2\sqrt{2}bTVK_{sb}}\,[1-\exp(-\alpha\ell)] \qquad (1)$$

where η - heat conversion efficiency

γ - specific heat ratio for air (C_p/C_v)

P - cell pressure

W - input power

μ_g - thermal diffusion length in air

μ_{sb} - thermal diffusion length in substrate

$G(\omega)$ - microphone response

b - dimensionless parameter taking into account the diffusion of heat from the sample to the Pyrex backing

T - temperature

V - cell volume

K_{sb} - thermal conductivity of substrate

α - absorption coefficient

ℓ - effective path length .

From Equ. (1) it follows that the photoacoustic signal saturates exponentially with increasing absorption to a value of

$$V_{sat}(\omega) = \frac{\eta\gamma PW\mu_g\mu_{sb}G(\omega)}{2\sqrt{2}bTVK_{sb}} . \qquad (2)$$

Hence the ratio of the signal from a given sample to a reference sample for which the signal is saturated yields

$$S_{ph} = V/V_{sat} = 1-\exp(-\alpha\ell) . \qquad (3)$$

This saturable behavior was observed for highly absorbing samples, and the sample which yielded the largest photoacoustic signal was used as the reference, V_{sat}. Note that such samples yield values of $\alpha\ell \geq 3$, as deduced from the optical attenuation measurements; hence the highest signal obtained from available samples is close to the actual saturation value.

The experimental setup for the optical attenuation measurements is described elsewhere.[1] In this technique the signal S_{op} is defined as 1-exp(-x). x is the optical attenuation of the sample and is given by -ln I/I_0, where I is the transmitted intensity of a loaded filter, and I_0 is the transmitted intensity of a blank filter.

In Fig. 2 we present a plot of the normalized photoacoustic signal S_{ph} vs. S_{op} for a wide range of ambient samples and samples collected directly from combustion sources. The samples include

urban particulates collected over a 24-hr period in Fremont and Anaheim, California; Denver, Colorado; and New York, New York; and particles collected in a highway tunnel and from an acetylene torch. The least squares fit of the experimental points yields a correlation coefficient r of 0.98 and a slope of 1.03, which would be expected if both techniques measure the same optical property of the aerosol particles. Since the photoacoustic signal is proportional to the heat generated by absorption, we conclude that the optical attenuation method measures the light absorbing component of the aerosol particles.

From a theoretical point of view, this result is somewhat surprising since aerosol particles have a large scattering coefficient, which would be expected to contribute to the optical attenuation measurement and not to the photoacoustic signal. However, careful examination of the experimental arrangment shows that the incident light interacts not only with the aerosol particles but also with the filter medium, which is almost a perfect diffuse reflector. In this circumstance, it is possible to show[4] that due to multiple reflections between the particles and the filter substrate, the optical attenuation measurement is insensitive to the scattering properties of the aerosol.

In conclusion, the results presented here, when combined with Raman scattering data[1] and thermal analysis[5] and solvent extraction results,[6] indicate that the optically absorbing component of urban aerosol particles is "graphitic" carbon. Extensions of this work are presently being carried out in our laboratories.

References

1. H. Rosen, A.D.A. Hansen, L. Gundel, and T. Novakov, "Identification of the optically absorbing component in urban aerosols," Appl. Opt. 17, 3859 (1978).

2. Over a frequency range of 5-100 Hz, the photoacoustic signal showed no variation, indicating that the sample was thermally thin. In this case, Equ. (1) follows from Equ. (21) of Ref. 3 in the limit of $\omega \rightarrow 0$ and after modification of their parameter b to take into account an additional boundary layer introduced by the Millipore filter.

3. A. Rosencwaig and A. Gersho, "Theory of photoacoustic effect with solids," J. Appl. Phys. 47, 64 (1976).

4. H. Rosen and T. Novakov, "Optical attenuation: a measurement of the absorbing properties of aerosol particles," in Atmospheric Aerosol Research Annual Report 1977-78, Lawrence Berkeley Laboratory Report LBL-8696, p. 54.

5. H. Rosen, A.D.A. Hansen, L. Gundel, and T. Novakov, "Identification of the graphitic carbon component of source and ambient particulates by Raman spectroscopy and an optical attenuation technique," Proceedings, Conference on Carbonaceous Particles in the Atmosphere, Lawrence Berkeley Laboratory, 1978 (in press).

6. R.E. Weiss, A.P. Waggoner, R.J. Charlson, D.L. Thorsell, J.S. Hall, and L.A. Riley, "Studies of the optical, physical, and chemical properties of light absorbing aerosols," Proceedings, Conference on Carbonaceous Particles in the Atmosphere, Lawrence Berkeley Laboratory, 1978 (in press).

Figure Captions

1. Experimental arrangement.

2. Plot of S_{ph} vs. S_{op} for various samples:

   ∇ - Fremont; ◻ - Anaheim; o - Denver

   Δ - New York City; ▩ - highway tunnel; ● - acetylene torch.

   The solid line is a least squares fit of the data.

Acknowledgments

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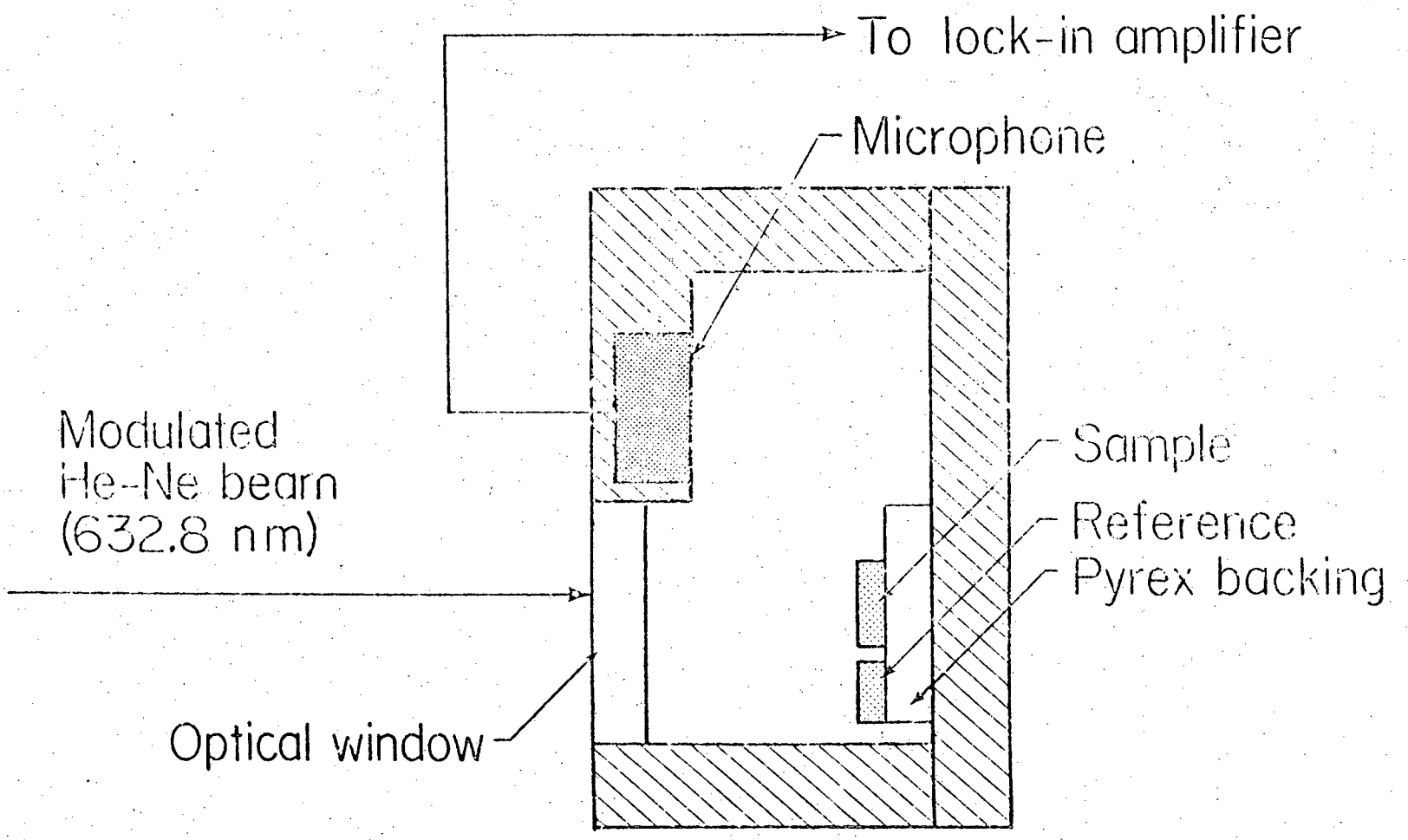

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Fig. (1)

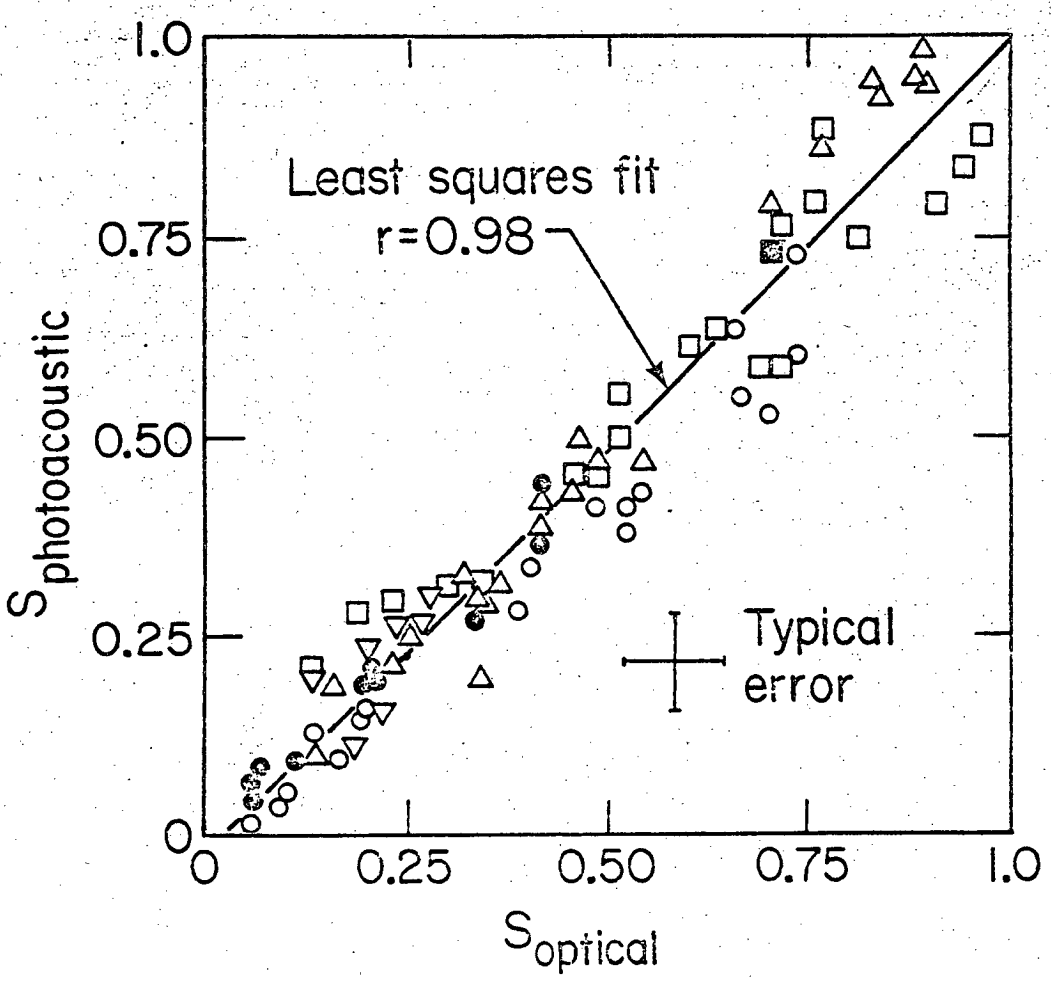
1.0
0.75
0.50
0.25
0
0
0.25
0.50
0.75
1.0
Least squares fit
r=0.98
Typical
error
S photoacoustic
S optical
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Fig. (2)

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