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EFFECT OF THE GRAIN SIZE ON THE
PHOTOACOUSTIC SPECTROSCOPY OF POWDERED SAMPLES

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ABSTRACT

The dependence of the photoacoustic signal on the grain size of optically and thermally thick powdered samples is discussed. It is shown that as the grain size increases the photoacoustic signal decreases. This effect is interpreted as a consequence of an increase of scattered light as the size increases, resulting therefore in a decrease of the absorbed light.

The photoacoustic spectroscopy (PAS) of solids has demonstrated ^{1,2} to be an extremely useful tool for studying absorption spectra of crystalline, powdered and amorphous solids. Its theory was developed by Rosenwaig and Gersho ³ and has recently been used to determine the absolute value of the absorption coefficient. According to Rosenwaig and Gersho's (RG) theory³, the primary source of the acoustic signal arises from the periodic heat flow from the solid to the surrounding gas, as the solid is cyclically heated by the absorption of chopped light. The periodic flow of this heat into the gas cell produces pressure fluctuations in it and this is how the sound originates.

As pointed out in Ref.2, one of the main advantages of the photoacoustic spectroscopy is that it enables one to obtain optical absorption spectra on any type of solid or semisolid materials. This ability of the PAS has been attributed to the fact that only the absorbed light is converted into sound, which therefore allows one to calculate absolute optical absorption coefficients⁴. The scattered light, which presents such a serious problem when dealing with many solid materials by conventional spectroscopic techniques, should present no difficulties in photoacoustic spectroscopy^{2,3}. Although this affirmative regarding the role of scattered light is generally true, some caution should be exercised when dealing with photoacoustic spectroscopy of fine grains. Physically, this may be inferred by assuming, for sake of reasoning, that the sample consists of an assembly of spherical grains of diameter d . As the grain size increases the amount of light being scattered increases due, for instance, to Rayleigh scattering (We remember that the Rayleigh scattering cross-section varies with the square of the grain volume⁵). This in turn entails that one should expect the amount of light being absorbed to decrease. Since the strength of the acoustic signal in the photoacoustic cell is in close correspondence with the amount of light absorbed, one may then expect to observe a dependence of the acoustic signal on the grain size of powdered sample.

The main purpose of the present paper is to point at and demonstrate the dependence of the acoustic signal on the grain size of a sample in powder form. The sample material chosen to demonstrate the effect was graphite of various grain sizes. This choice was determined by the requirement that the sample be thermally thick for relatively small sample thicknesses as well as optically opaque. The grain sizes were selected using precision meshes with a diameter range of about 35 μm to 100 μm . The experimental apparatus consisted primarily of a 200 Watts tungsten filament lamp, a variable-speed light chopper, an air filled aluminum cell with a condenser microphone and low-noise preamplifier, and a lock-in amplifier. The sample cell enclosed a cylindrical chamber with a diameter of 1.0cm providing for a sample length, $l_s = 0.20\text{cm}$, and a gas column length, $l_g = 0.50\text{cm}$. The microphone was mounted in a side wall of the chamber. The light from the filament lamp, after passing through a monochromator, was selected to provide a 1.0 cm^2 square cross-section beam at 600 nm incident on the cell window.

Fig. 1 shows a plot of the photoacoustic signal relative to carbon black as a function of the sample grain size for a chopping frequency of 226 Hz. In all measurements care has been taken to keep the same sample length of 0.2cm. This ensured that the only varying parameter was the grain size d . The kind of behavior of the photoacoustic signal depicted in Fig. 1 can be explained by RG theory, provided one reinterprets their optical absorption coefficient β as being the total light extinction coefficient from an assembly of fine grains. Let the subscripts s and g designate physical parameters for the sample and gas, respectively, and define the following parameters: ω , the chopper angular frequency; k , the thermal conductivity (cal/cm sec $^\circ\text{C}$); C_p , the specific heat at constant pressure; ρ , the density (g/cm 3); $\alpha = k/\rho C_p$, the thermal diffusivity (cm 2 /sec); $a = (\omega/2\alpha)^{1/2}$, the thermal diffusion coefficient (cm $^{-1}$); $\mu = 1/a$, the thermal diffusion length (cm); γ , the ratio of the specific heats; P_0 and V_0 , the ambient pressure and volume, respectively; I_0 , the incident monochromatic light

flux (W/cm²). Then, for the case of optically and thermally thick samples, $\exp(-\beta l_s) \approx 0$ and $\exp(-\sigma_s l_s) \approx 0$ and assuming the RG theory to be valid, the complex amplitude Q of the harmonic pressure variation in the gas due to the photoacoustic effect is given by³

$$Q \approx - \frac{j \beta \mu_s^2}{2 a_g k_s} \cdot \frac{\gamma P_o I_o}{2\sqrt{2} \lambda_g T_o} \quad (1)$$

Now, as is well known from the theory of light extinction by fine particles⁵⁻⁸, the total loss in intensity of an incident beam of light, when traversing a system of solid grains, is given by a combination of absorption and scattering (generally denoted by turbidity). In particular, the theory of light scattering and extinction by assemblies of spherical particles larger than the wavelength is well established⁶⁻⁸. Hence, in the case of photoacoustic spectroscopy of powdered samples the absorption coefficient β ($I = I_o \exp(-\beta x)$) should be written as⁶⁻⁸

$$\beta = \beta_o + \tau \quad (2)$$

Where β_o is the intrinsic absorption coefficient due to the imaginary part of the refractive index, and τ is the turbidity which is strongly dependent on the shape and size of the grains. In general, the calculation of τ for arbitrary grain size and shape is quite involved. However, in the case of spherical grains with diameter (d), much larger than the wavelength, it can be shown that⁶⁻⁸ τ varies as d^{-1} . Since in the present case $d \gg \lambda$ Eq. (2) can be written as

$$\beta = \beta_o + \frac{C}{d} \quad (3)$$

Substituting Eq. (3) into Eq. (1) one can fit the photoacoustic signal data as

function of the grain size d . This is represented in Fig.1 by the solid curve. The fitting parameters obtained are $\beta_0 = 0.026$ (arbitrary units) and $c = 12.617$. The measurement data are displayed in Table I.

Summarizing, this paper reports on the effect of grain size on the PAS of optically and thermally thick powdered samples. It was shown that, as the grain size increases, the photoacoustic signal diminishes. Physically, this was explained in terms of the decrease in the total loss of intensity of monochromatic light (β), within the sample, due to an increase of scattered light as the grain size increases.

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FIGURE CAPTION

Figure 1. Experimentally determined photoacoustic signal as a function of the grain size diameter for powdered graphite. The solid curve represents the fit of Eqs. (1) and (3) to the data. The thermal parameters are those for graphite and air at 293⁰K and atmospheric pressure:

$$\rho_s = 2.22 \text{ g/cm}^3, k_s = 0.24 \text{ W/cm}^{-0}\text{K},$$

$$C_{ps} = 0.69 \text{ J/g}^0\text{K}, \rho_g = 1.195 \times 10^{-3} \text{ g/cm}^3,$$

$$k_g = 2.58 \times 10^{-4} \text{ W/cm}^0\text{K}, C_{pg} = 1.006 \text{ J/g}^0\text{K},$$

$$\gamma = 1.404 \text{ [Values taken from American Institute of Physics Handbook, 2nd].}$$

(Mc Graw - Hill New York, 1963)]:

TABLE CAPTION

TABLE I. Observed photoacoustic signal of graphite as a function of the grain size for a chopping frequency of 226 Hz with incident light of $\lambda=600\text{nm}$. The photoacoustic signal of a carbon black sample was 5.85 mV.

d (μm)	Photoacoustic signal (mV)	Photoacoustic Signal normalized to the carbonblack signal
37	2.15	0.37
44	1.80	0.31
74	1.16	0.20
88	0.95	0.16
105	0.86	0.15

Table I - Ghizoni et al

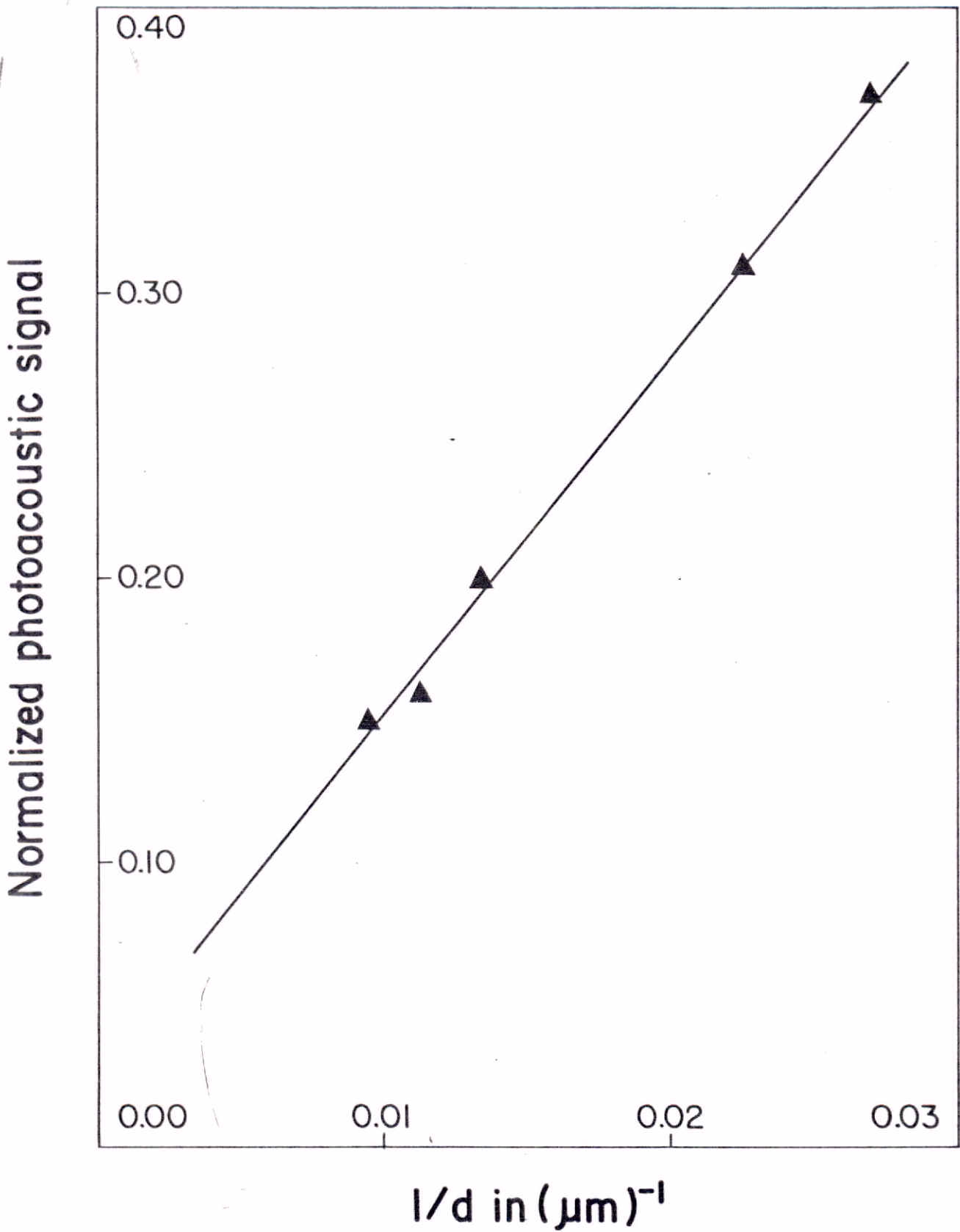


Fig. 1 - GHIZONI et al.