

Simple sample cell for examination of solids and liquids by photoacoustic spectroscopy

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sample and variation in scattering coefficients and molecular weights of the carotenoids. Larger errors might occur if the carotenoids have double-bond chains different from β -carotene, but these effects would be apparent in the RR spectrum in the 1525 cm^{-1} region. No such effects were observed in the samples used in this work.

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Simple Sample Cell for Examination of Solids and Liquids by Photoacoustic Spectroscopy

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A photoacoustic spectrometer assembled from available components with a sample cell utilizing an inexpensive microphone and integral preamplifier is described. The performance characteristics are given and representative spectra for several solids (SrTiO_3 , NiTiO_3 , FeTiO_3 , Eu_2O_3 , SmCl_3) and solutions (rose bengal, malachite green) are shown and discussed. Suggestions for improvement of spectrometer performance by utilizing dual channel operation and Hadamard transform techniques are included.

The photoacoustic effect has been used for many years to study relaxation phenomena in the gas phase (1-3). In 1973, Harshbarger and Robin (4) and Rosenzweig (5) published results of experiments investigating the optical properties of solids, which demonstrated the qualitative similarity between the solid photoacoustic absorption spectrum and the conventional solution optical absorption spectrum of certain samples. Recently Kirkbright and co-workers (6, 7) have described analytical applications of this phenomenon and reviews on photoacoustic spectroscopy (PAS) have appeared (8, 9).

The basic principles of the photoacoustic effect, as discussed in these papers as well as the theoretical treatment of Rosenzweig and Gersho (10) is as follows. The sample to be studied is placed in a sealed, gas-filled, cell of fixed volume containing a sensitive microphone as a detector. The sample is irradiated with high intensity, chopped, monochromatic light. Light absorbed by the sample is converted by radiationless processes to heat, which flows from the sample to a thin boundary layer of gas adjacent to the sample. This boundary layer expands and contracts at the chopping frequency and acts like a piston on the remainder of the gas in the cell. The periodic pressure wave set up by the acoustic piston is detected by the microphone yielding an electrical signal which can be processed further. Thus the detection of light absorption in PAS does not depend upon measuring

the reflected (or transmitted) light itself with optical detectors. This is especially advantageous for solid samples, since the condition of the solid and the nature of its surface is much less critical in PAS than in reflectance spectroscopy.

Previous publications on PAS of solids have given few experimental details concerning the construction of the cell or quantitative performance characteristics. We report here on the design of a photoacoustic spectrometer operating in the UV-visible region and its application to obtaining spectra of several semiconductor and solution samples. Additional areas of application and improvements in spectrometer design are also described.

EXPERIMENTAL

Instrumentation. A block diagram of the spectrometer is given in Figure 1. The light source is a Hanovia 2500-watt xenon short arc lamp housed in an Oriol Model LH-152N housing. The light beam is focused through an $f/1$ quartz lens on the monochromator entrance slit. The chopper uses a variable speed motor to produce chopping frequencies of 10 to 500 Hz. In the work presented here, the chopper was operated at either 12.6 or 18.8 Hz. The monochromator was a Jarrell-Ash Model 82-410 $1/4$ -meter $f/3.6$ unit using fixed slits of about 6 nm band-pass and equipped with gratings blazed for 300 and 600 nm. The system throughput averages 1.1 mW/cm^2 from 400-800 nm as measured with an EG & G Model 550 radiometer. An assembly drawing of the PAS cell is given in Figure 2. The cell was machined from Plexiglas. The stainless steel liner for the active cell volume was incorporated when light absorption and a resulting PAS background signal were found with the Plexiglas alone. The total cell volume is 2.8 cm^3 . The microphone used was a Knowles Laboratories Model BW-1789 microphone. This small, inexpensive, microphone had a very good performance, even at the low chopping frequencies employed here. Better results may be obtained with a more sensitive microphone, such as the B & K Model 4148 condenser microphone, and a cell based on this detector is currently being constructed. The signal from the microphone was amplified with the preamplifier whose circuit is given in Figure 3. This preamplifier was built directly into the PAS cell to decrease pickup and to prevent vibrations from any cable between preamp and microphone coupling to the microphone. Because of the high

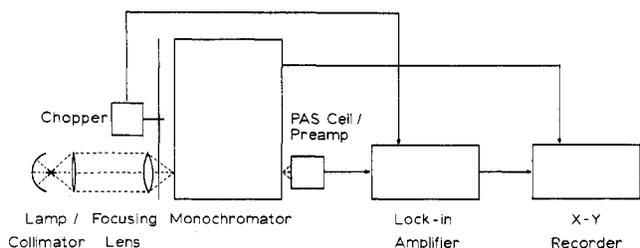


Figure 1. Block diagram of the single beam PAS system. See text for details

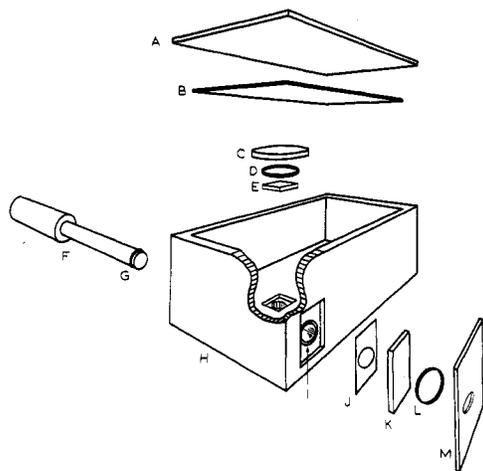


Figure 2. PAS cell construction detail. A, Cell lid (Plexiglas); B, follower, preamplifier circuit board; C, microphone part pressure seal (Plexiglas); D, rubber "O-ring" pressure seal; E, microphone; F, sample probe (aluminum); G, rubber "O-ring" pressure seal; H, cell housing (Plexiglas); I, sample chamber liner (stainless steel); J, Teflon pressure seal gasket; K, quartz window; L, rubber "O-ring" compression gasket; M, window assembly hold-down (aluminum)

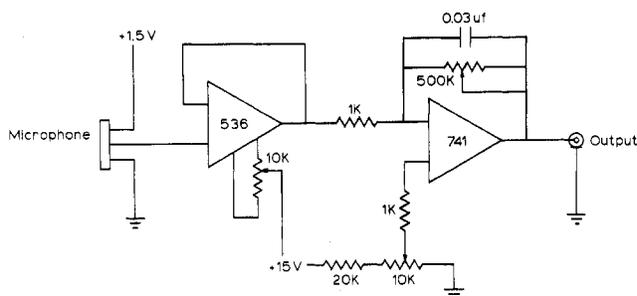


Figure 3. Schematic diagram of the PAS cell follower/preamplifier circuit. See text for details

output impedance of the microphone, a Signetics Type 536 FET operational amplifier was used in the preamp input in a follower configuration. A Type 741 IC operational amplifier, which provided an overall gain of about 200, was employed in the differential mode to compensate for the dc leakage of the microphone. The 0.08- μ f capacity in the feedback loop limits the noise band width. Both op amps were powered by batteries preconditioned with a bipolar voltage regulator to compensate for battery voltage drift. The microphone itself was biased with a 1.5-V battery. No regulation was required because of the extremely small (ca. 20 μ A) current drawn by the microphone.

The PAS cell was sealed with rubber O-rings at the sample holder and microphone outlet. The quartz window was sealed with a gasket made from Teflon tape. For solid samples, the sample was mounted on the probe with double stick Scotch tape and the cell positioned immediately adjacent to the exit slits of the monochromator. For solutions, the cell was turned so that the probe tip was horizontal and about 0.2 mL of solution placed in the well formed by the incompletely inserted probe. In this case the cell was placed immediately adjacent to and just below the exit slit of the monochromator and the emergent light beam

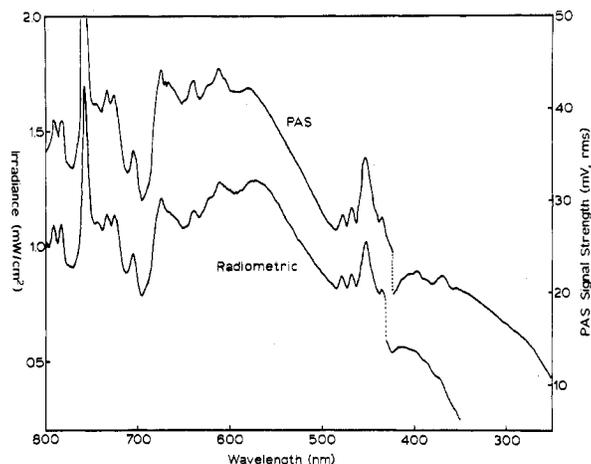


Figure 4. Comparison of the PAS spectrum of carbon black with the radiometrically determined system spectral distribution. The apparent discontinuity at approximately 425 nm is due to changing gratings. The grating used to the left was blazed for 600 nm, the grating to the right was blazed for 300 nm. The PAS signal strength includes the 46-dB gain of the cell preamplifier.

reflected into the cell with a planar front surface mirror. The preamplified acoustic signal was synchronously detected at the chopper frequency with a Princeton Applied Research Model HR-8 lock-in amplifier and recorded on a Hewlett-Packard Model 7005A X-Y recorder. The monochromator was scanned at either 25 or 10 nm/min depending upon the signal strength. Effective seismic noise isolation was achieved by mounting the chopper and lamp housing on rubber shock mounts and the PAS cell on a foam rubber pad. No attempt was made at complete acoustic isolation of the PAS cell. The Plexiglas PAS cell appeared less susceptible to acoustic interference than an earlier cell made totally of stainless steel (11).

Chemicals. The various organic dyes studied were of technical purity and used without further purification. Samarium chloride and europium oxide were purchased from Alfa Ventron Corp., (99.9% stated purity). The various titanates were prepared according to literature procedures (12).

RESULTS AND DISCUSSION

Spectrometer Performance. A comparison of the system power spectrum recorded with a radiometer and with the PAS cell containing a carbon black sample is shown in Figure 4. The radiometer trace extends only up to 400 nm because of the rapid fall-off in detector sensitivity below this wavelength.

The intensity axis of the carbon black spectrum is given in rms voltage after preamplification; the true microphone signal can be obtained by dividing these numbers by 200. The stated sensitivity of the Knowles microphone used in these experiments is approximately -55 dB re 1 volt per μ bar (i.e., 1.8 mV/ μ bar). The average signal level between 500 and 800 nm was 45 mV (i.e., a 0.225-mV microphone signal) which is equivalent to a synchronous pressure change of about 0.125 μ bar in our present cell configuration. Since carbon black probably approaches an ideal reference sample (i.e., total light absorption with no fluorescence) 0.125 μ bar will be the maximum average pressure change for any sample in this cell at these intensities.

The minimum signal level will ultimately be governed by the Brownian motion of the microphone membrane. In our system, however, the limiting factor is the noise in the preamplifier and lock-in amplifier. The coherent (in-phase) noise voltage of the present system is about 0.1 mV rms. This noise voltage is independent of the PAS signal level, and sets the limit of detectability (for S/N = 1) of the present system at 2.8×10^{-4} μ bar pressure change. The present system appears insensitive to external acoustic noise and careful mechanical decoupling of all moving components (chopper, lamp and power supply, cooling fans, etc.) from the sample

Table I. Effect of Source Intensity on Signal-to-Noise (S/N)^a

Filter absorbance	Relative intensity	S/N
0.0	100	120
0.1	79	100
0.2	63	88
0.5	32	44
1.0	10	11

^a Carbon black sample for wavelengths between 500 and 700 nm using 2500-W xenon lamp. Intensity of 100 corresponds to about 1.1 mW/cm².

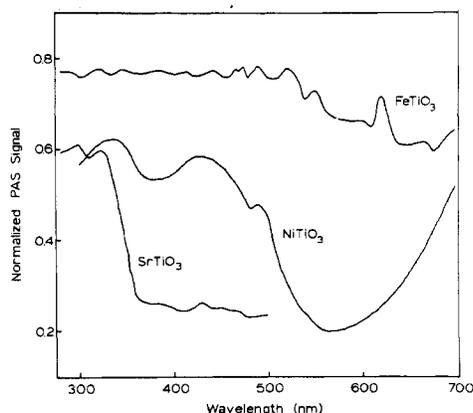


Figure 5. PAS spectra of several titanates. All spectra have been normalized to carbon black

cell reduced the seismic noise level below that of the preamplifier/lock-in amplifier electrical noise level.

Because the spectral distribution of the 2500-watt xenon lamp-monochromator system is not flat and the photoacoustic spectrum is a power spectrum, all spectra must be normalized by dividing the signal intensity at a given wave length to that of a carbon black sample at the same wave length. All of the spectra shown have been so normalized. The S/N ratio depends upon the source intensity. Typical results for carbon black using neutral density filters at the exit slit of the monochromator to decrease the power impinging of the sample are given in Table I. A direct proportionality between intensity and S/N is observed.

Semiconductor Materials. There has been much recent interest in the use of semiconductors as electrodes, especially in photoelectrochemical experiments. Of special interest in these studies is the magnitude of the semiconductor band gap energy (E_g) and information about the existence of surface states. PAS appears to be well suited to spectroscopic measurements designed to obtain such information, especially for polycrystalline and powdered samples. For example photoacoustic spectra for several titanates are shown in Figure 5. The spectrum of SrTiO₃ is characteristic of a direct band gap semiconductor and shows a sharp absorption corresponding to the band edge. The E_g value found here, 3.18 eV, is in good agreement with that given by Cardona (13), 3.2 eV. Both NiTiO₃ and FeTiO₃ show gradual slopes on the absorption curves which make estimation of E_g uncertain.

A comparison of the photoacoustic spectrum and diffuse reflectance spectrum of Eu₂O₃ is given in Figure 6; a similar comparison of SmCl₃·6H₂O powder is shown in Figure 7. The spectra are qualitatively the same with the photoacoustic spectrum shifted by about 8 nm toward shorter wavelengths. The differences in the reflectance and photoacoustic spectra probably can be attributed to errors in the wavelength calibration of the monochromators as well as differences in the normalization procedures and effects of scattered light. At

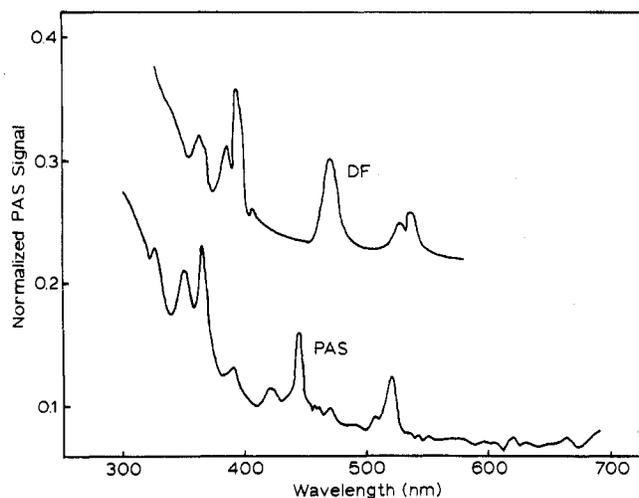


Figure 6. Comparison of the PAS spectrum of europium oxide normalized to carbon black and the diffuse reflectance (DF) spectrum (20)

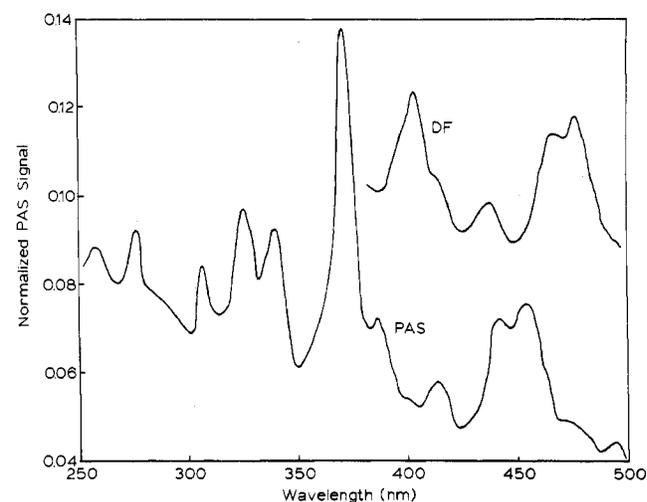


Figure 7. Comparison of the PAS spectrum of samarium(III) chloride hexahydrate normalized to carbon black and the diffuse reflectance (DF) spectrum (21)

shorter wavelengths, the Eu₂O₃ spectra show a continuous increase in absorption starting at about 500 nm (2.5 eV). This probably represents the absorption edge for band gap transitions. Similar effects have been observed in the spectra of other rare earth compounds.

Solution Spectra. Although PAS is especially useful for solid samples, its application to liquids and solutions is also of interest. It would be especially useful for optically opaque or turbid liquids (e.g. paints, dye baths) and for the examination of solid samples below a thin layer of liquid. A preliminary report of the solution photoacoustic spectrum of rhodamine B was given by Somoano and Gupta (14). The photoacoustic and optical absorption spectra of the dye malachite green (Figure 8) both have the same spectral features, supporting the use of PAS for examination of liquids. Furthermore, solid malachite green as examined by PAS also has a very similar spectrum, which suggests that the solid is characterized by transitions of isolated dye molecules or aggregates of small numbers of molecules, and that the band model of solids does not apply to this dye. This behavior can be contrasted with that of rose bengal (Figure 9). Here the solid exhibits a spectrum characteristic of a direct band gap semiconductor ($E_g = 1.8$ V). Semiconducting properties of rose bengal have indeed been reported (15). With respect to solutions of rose bengal, both the photoacoustic and optical spectra show two peaks. The difference in relative peak

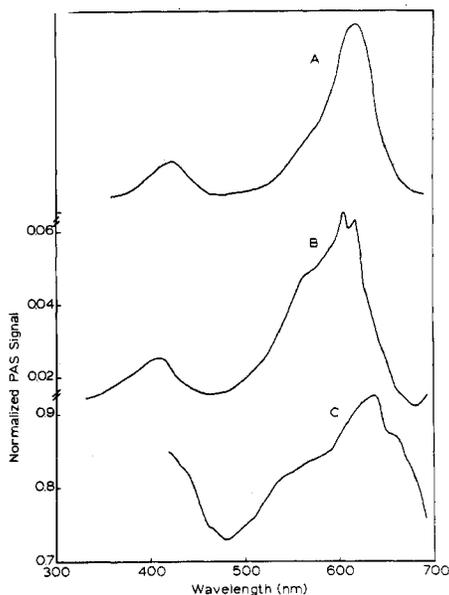


Figure 8. Malachite green spectra. A, optical absorption spectrum; B, PAS spectrum of Malachite Green water solution; C, PAS spectrum of the solid

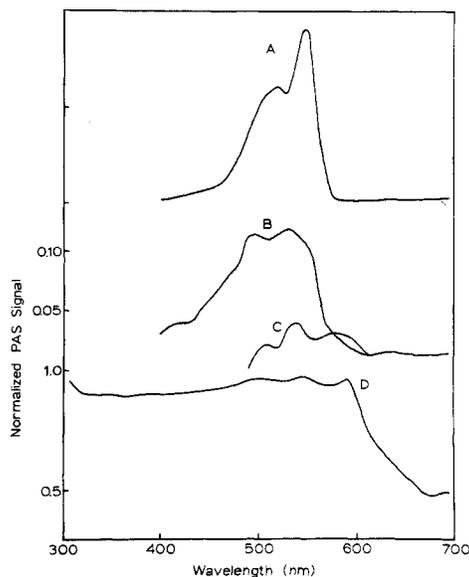


Figure 9. Rose bengal. A, optical absorption spectrum; B and C, PAS spectrum of aqueous solutions (concentration in C lower than that in B); D, PAS spectrum of solid

heights between the two spectra can be attributed to a larger amount of rose bengal dimer in the more concentrated solution used in PAS. Significant dimer formation has been reported for rose bengal solutions (16). PAS spectra at lower rose bengal concentrations show a variation in relative peak heights in the expected direction (Figure 9).

CONCLUSIONS

The results reported here confirm the usefulness of PAS to studies of solids and suggest that studies of liquids are also possible. Comparisons of solid and solution spectra will be especially informative. Since the photoacoustic response

depends upon both the optical (i.e., absorptivity) and thermal (i.e., conductivity) characteristics of the sample, quantitative studies will require a better understanding and theoretical treatment of the process.

Several instrumental improvements can be envisioned in the apparatus to obtain better sensitivity and make the measurements more convenient. Point-by-point normalization of the spectrum by comparison with the carbon black spectrum is tedious and suffers from errors associated with temporal changes in the spectral output of the lamp between measurement of sample and reference. A dual beam instrumental approach would overcome this problem. The simplest method involves using a beam splitter to feed a small portion of the light incident on the cell window to a reference detector such as a thermopile or radiometer. Analog division of the signals would give the desired signal. The photoacoustic response depends upon source intensity with the signal-to-noise ratio increasing with increasing intensity (Table I). Under these conditions the use of transform techniques, e.g., the Hadamard transform (17-19), appears useful. Since about 50% of the total useable light is transmitted to the sample with the Hadamard transform technique, the throughput advantage should allow greatly increased signal strengths while retaining reasonable resolution. The use of this technique will require digital data acquisition and decoding. However, in addition to the usual transform advantages of increased speed, sensitivity, and resolution, the digital data handling capabilities of ensemble averaging, digital filtering, and spectral response correction will be available.

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