Photoacoustic Spectroscopy: New Uses for an Old Technique

Photoacoustic spectroscopy, a 94-year-old technique that has been in disuse for 92 of those years, may prove to be one of the most important spectroscopic innovations of the 1970's. It is a surprisingly simple method that permits absorption spectroscopy to be used on an exceptionally wide variety of materials, including solids, semisolids, powders, gels, adsorbed films, and living tissue. Only one investigator has currently been performing photoacoustic spectroscopy on solids, but it is a certainty that the technique will be studied in other laboratories in the very near future. And once photoacoustic spectrometers are commercially available, they seem quite likely to have an impact on many scientific disciplines.

Photoacoustic spectroscopy was discovered independently by John Tyndall, Wilhelm C. Roentgen, and Alexander Graham Bell in 1881. They observed that intermittent light focused on a closed cell containing a gas produces pressure fluctuations in the gas as the absorbed light is converted to kinetic energy. These fluctuations were detected as an audible sound with a hearing tube. Bell also enclosed solids and liquids in the cell and obtained similar results. He observed that "the loudest sounds are produced from substances in a loose, porous, spongy condition" and from those "that have the darkest or most absorbent colors." Liquids, however, produce only very faint sounds. Bell postulated that the intermittent light produced a cyclic desorption and readsorption of gases from the surface of the solids and that this effect produced the pressure fluctuations, but this hypothesis has subsequently been proved wrong.

Limited Commercial Use

Photoacoustic spectroscopy has subsequently been used, to a modest extent, for analysis of gases. In typical commercial instruments, the wavelength of the incident light is varied through the region of interest with a conventional monochromator. Generally, a rotating disk with one or more holes in it is used to make the light intermittent. A sensitive microphone within the cell responds to fluctuations in pressure so that the intensity of the sound can be plotted as a function of wavelength to produce a spectrum similar to that obtained in conventional absorption spectroscopy. But such spectrometers offer little advantage over conventional gas absorption spectroscopy.

Recently, however, Lloyd B. Kreuzer and C. Kumar N. Patel of Bell Laboratories, Murray Hill, New Jersey, demonstrated that the use of a tunable laser as the light source in such systems increases the sensitivity by several orders of magnitude. Incorporation of the laser should thus make the technique very useful for many applications, such as the detection of trace quantities of air pollutants. In fact, a prototype commercial gas photoacoustic spectrometer incorporating a laser was demonstrated at the recent Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy by Yoh-Han Pao and his associates at Case Western Reserve University.

No one, however, seems to have followed up on Bell's work with solids until about 3 years ago, when Allan Rosencwaig of Bell Laboratories began experimenting with the method. He summarized those experiments at the Pittsburgh conference, and the enthusiastic reception of his results suggests that the techniques he has developed should soon find many applications.

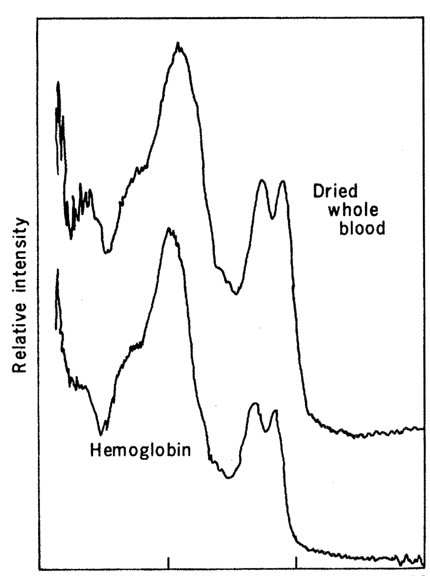

Fig. 1. Photoacoustic spectrum of a dried smear of whole blood and a conventional spectrum of hemoglobin. [Source: Allan Rosencwaig]

Rosencwaig used a conventional light source and readily available components to assemble his spectrometer but introduced a specially designed cell. The instrument is thus similar to gas photoacoustic spectrometers. But Rosencwaig has shown that light absorbed by the solid is converted, partly or completely, into heat by nonradiative processes within the solid. The periodic flow of this heat from the solid to the surrounding gas creates the pressure fluctuations in the gas, which are detected by the microphone within the cell. If the absorbed light energy is dissipated primarily by nonradiative processes, as is the case with most substances, the photoacoustic spectrum is comparable to an optical absorption spectrum. The acoustic response does not depend on reflected or transmitted light, and thus is not dependent on the physical state of the sample. The technique does not work well with materials that are highly reflective; but, by the same token, the response is not affected by light scattering, one of the most serious problems associated with conventional spectroscopy of solids.

Many Potential Applications

The number of potential applications of photoacoustic spectroscopy seems almost limitless, and Rosencwaig has been able to investigate a few of them. He and his colleagues have performed preliminary experiments applicable in several different disciplines, but perhaps the most impressive results were obtained with materials of biological origin.

Rosencwaig has shown, for example, that the ultraviolet and visible spectrum of hemoglobin can be obtained directly from dried smears of whole blood by photoacoustic spectroscopy. A similar spectrum cannot readily be obtained by conventional spectroscopy because of strong light scattering by protein and lipid components of whole blood and by red blood cells. The quality of the spectrum (Fig. 1), he contends, is comparable to that obtained with hemoglobin that has been extracted from the blood. Similar results have been obtained with dried solids containing several other hemoproteins, including both soluble ones such as cytochrome c and insoluble or membrane-bound ones such as cytochrome P-450. Absorbing substances (including some drugs) can also be identified in dried urine samples.

Plant material can also be screened. For example, a photoacoustic spectrum of an intact green leaf shows all the optical characteristics of leaf chloroplasts, including the Soret band at 420 nanometers, the carotenoid band structure between 450 and 550 nanometers, and the chlorophyll band between 600 and 700 nanometers. Most important, Rosencwaig contends, it can also be used to observe and monitor secondary metabolites that are of interest for their potential as pharmaceuticals.

Rosencwaig and Stan S. Hall of Rutgers University have shown that photoacoustic spectroscopy can be used to estimate the amount of certain of these metabolites in different species of air-dried marine algae. Conventional techniques, in contrast, necessitate a rather extensive extraction procedure before spectra can be obtained. Rosencwaig and Hall thus suggest that photoacoustic spectroscopy can reduce the amount of material required for screening of such substances (since extraction procedures generally require more material) and that it can greatly reduce the time required for the identification of plant species that deserve further study.

Monitor Bacterial Growth

Photoacoustic spectroscopy can also be used, Rosencwaig has shown, to monitor the growth of bacteria in culture or on surfaces, and possibly to identify the bacteria. It is also possible to study animal and human tissues. Rosencwaig and Angelo A. Lamolo of Bell Laboratories have examined the interaction of guinea pig epidermis and tetrachlorosalicylanilide, an effective antibacterial agent that unfortunately also causes photosensitivity and other skin problems. They have used the technique to obtain the first spectrum of the agent bound within the epidermis and suggest that such spectra may yield information about the photosensitization mechanism. Rosencwaig has also designed an open-ended photoacoustic cell that can be placed against skin, and elsewhere, to perform spectroscopy on living tissue or on objects too large for a conventional cell. He suggests that use of such a cell might make it possible to diagnose many diseases of the skin.

Other potential applications might be found in the study of inorganic materials. By plotting the acoustic response against the energy of the incident light, for example, it is possible to observe both direct and indirect band transitions for semiconductors. Figure 2, for instance, shows typical results obtained with three direct-band semiconductors, all in amorphous powder form. The transition energies obtained from the spectra, Rosencwaig says, agree quite well with values obtained by other methods. Photoacoustic spectroscopy, he adds, should be particularly useful for studies of the new classes of organic and glassy semiconductors and metallic systems, many of which are often in powder or other amorphous form. It would also eliminate the high-vacuum equipment and ultraclean surfaces that are required for conventional reflection spectroscopy.

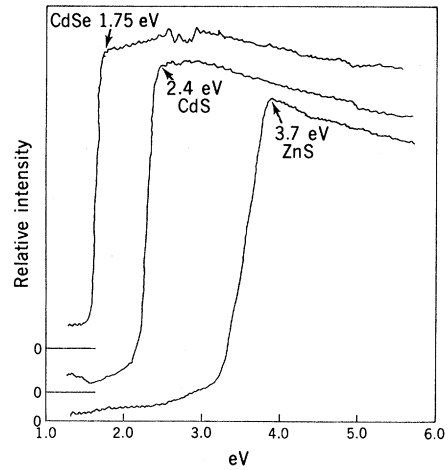

Fig. 2. Photoacoustic spectra of three direct-band semiconductors. [Source: Allan Rosencwaig]

Another type of material for which the technique may be useful is the one-dimensional metallic system. Rosencwaig, together with A. P. Ginsberg and J. W. Koepke of Bell Laboratories, has obtained the first spectrum in the ultraviolet and visible regions of the linear chain, one-dimensional conductor $K_2Ir_2(CO)_4Cl_5$, which is available only as an amorphous powder. The spectrum indicates that the delocalized conduction band of this compound is a strong, broad, infrared band that drops off in the visible region, and that localized iridium ion transitions dominate the ultraviolet region. Such data, which is difficult to obtain by conventional spectroscopy, is important in understanding the electronic structure of these materials, a subject of considerable interest and controversy.

Rosencwaig has also shown that photoacoustic spectroscopy might prove useful in the study of materials adsorbed or chemisorbed to the surface of other substances. Such studies can be performed at nearly any wavelength provided that the substrate either does not absorb or is highly reflecting at that wavelength. One possible application is in thin-layer chromatography, in which mixtures are separated into their constituent compounds on flat plates that are generally coated with silica gel or aluminum oxide. Unless the separated compounds can be made visible by reagent chemistry, their identification is a tedious and often impossible task.

Spectrum from TLC Plates

Conventional spectroscopy is essentially useless because of the opacity and light scattering of the adsorbent. But Rosencwaig and Hall have shown that photoacoustic spectra can be obtained directly from the plates, even when the compound to be examined is present in only a monolayer on the surface of the adsorbent. Rosencwaig and Harold Schonhorn of Bell Laboratories have shown that monolayers of adsorbed and chemisorbed materials can be detected and identified on other substrates. They thus suggest that the technique would be useful for the study of organic compounds and inorganic oxides deposited on metals, semiconductors, and polymers for the purpose of passivation.

And finally, since photoacoustic spectroscopy is sensitive to nonradiative de-excitation of molecules, it should have unique capabilities in the study of fluorescent materials and photosensitive solids. Rosencwaig thus suggests that it may prove quite valuable in the study of photoinduced changes in plastics, polymers, and pigments.

The potential of photoacoustic spectroscopy has barely been tapped, and the number of other possible applications seems very large. Investigations of such applications have so far been limited by the fact that Rosencwaig apparently possesses the only photoacoustic spectrometer designed for use on solids, but other investigators are assembling their own instruments with his assistance. Several instrument companies are interested in commercial production of the spectrometers, and it seems likely that other laboratories will be able to obtain them soon, so that the full potential can be explored.

—Thomas H. Maugh II