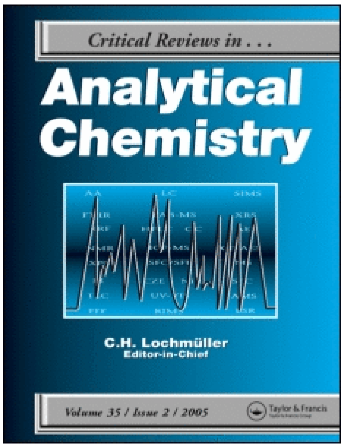


Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Analytical Aspects of Photoacoustic Spectroscopy

D. Betteridge; P. J. Meylor

To cite this Article Betteridge, D. and Meylor, P. J.(1984) 'Analytical Aspects of Photoacoustic Spectroscopy', Critical Reviews in Analytical Chemistry, 14: 4, 267 — 295

To link to this Article: DOI: 10.1080/10408348408542773

URL: http://dx.doi.org/10.1080/10408348408542773

ANALYTICAL ASPECTS OF PHOTOACOUSTIC SPECTROSCOPY*

Authors: **D. Betteridge**
P. J. Meylor
Department of Chemistry
University College of Swansea
Swansea, United Kingdom

TABLE OF CONTENTS

---

* *Editor's Footnote:* The editorial policy of this journal is to have each review refereed, with the referee's name prominently displayed. This review is a departure from the above-stated policy. The reason is that a difference of opinion- or perhaps interpretation-arose between authors and referee that, in my view, is controversial and represents honest stances by those involved. Not being one to avoid honest controversy, I have exercised an editor's perogative and gone forward with the printing of the review. Thus the authors' review, together with their opinions, is printed herein. Another aspect of this situation is that some of the material may now be somewhat dated, as the lapse of time between printing and writing is longer than usual.

I. INTRODUCTION

A. The Optoacoustic Effect

The optoacoustic effect arises when an absorbing species (solid, liquid, or gas) is irradiated with modulated electromagnetic radiation in an enclosed chamber. Pressure waves are set up and these can be detected with a sensitive microphone. Thus, an optical event is transformed into an acoustic signal.

If the sample under consideration is a gas, then when it is illuminated, a molecule in the gas will absorb a photon and go to an excited state. When this molecule collides with any other molecule in the gas, it may return to the ground state with a transfer of some of its energy to translation (thermal) energy, with consequent increase in the temperature of the gas. The modulation of the light source is then seen as modulation in the temperature of the gas.

In the case of a solid sample, if it absorbs any of the incident radiation, then some energy levels in the sample will be excited. These will de-excite, almost instantaneously at room temperature, by a non-radiative or heat-producing mechanism. Modulating the incident radiation will result in a periodic heat flow from the sample to the surrounding gas, thus producing a pressure change in the cell which is detected by the microphone.

The effect was first observed by Bell,[1] and an extract from a letter by him clearly describes the basic experiment and its versatility:[2]

> Metropolitan Hotel
> Rue Cambon, Paris
> Nov. 2, 1880.
>
> Dear Mr. Tainter, . . . I have devised a method of producing sounds by the action of an intermittent beam of light from substances that cannot be obtained in the shape of thin diaphragms or in the tubular form; indeed, the method is specially adapted to testing the generality of the phenomenon we have discovered, as it can be adapted to solids, liquids, and gases.
>
> Place the substance to be experimented with in a glass test-tube, connect a rubber tube with the mouth of the test-tube, placing the other end of the pipe to the ear. Then focus the intermittent beam upon the substance in the tube. I have tried a large number of substances in this way with great success, although it is extremely difficult to get a glimpse of the sun here, and when it does shine the intensity of the light is not to be compared with that to be obtained in Washington. I got splendid effects from crystals of bichromate of potash, crystals of sulphate of copper, and from tobacco-smoke. A whole cigar placed in the test-tube produced a very loud sound. I could not hear any thing from plain water; but when the water was discolored with ink a feeble sound was heard. I would suggest that you might repeat these experiments and extend the results . . . .

Soon after the initial discovery, there was a flurry of activity in the field, but interest was not sustained for long. Interest was revived in 1938 by the work of Veingerov,[3,4] followed up by Pfund[5] and Luft,[6] all of whom used the optoacoustic effect for nondispersive infrared gas analysis. This application was successful and resulted in several commercial gas analyzers.

The advent of lasers and sensitive microphones has led to an extensive reexamination of the technique over the last decade. Much of the theoretical and instrumental developments have been made by physicists, whose interest is primarily in the measurement of thermal characteristics. The analytical potentialities have been seen to lie in (1) sensitive, selective gas analysis, (2) the diversity of samples and the ease with which they may be presented to the apparatus, and (3) the possibility of nondestructive examination of layers of a sample. At the forefront of the analytical developments have been Kreutzer, Rosencwaig, and Kirkbright whose early review papers provide a good introduction to the technique.[7-9] In this review we seek to give an account of the history, practice, theory, and analytical applications of the technique. In accordance with modern practice, apart from the historical section, the term "photoacoustic spectroscopy" (PAS) will be used.

B. Discovery and Early History of the Optoacoustic Effect

The Optoacoustic Effect was discovered in 1880 by Alexander Graham Bell. He found[1] that by focusing an intermittent beam of radiation onto various materials in the form of thin discs, and placing his ear against these discs, he could hear "musical notes". This apparatus, which caused the production of sound by light, he termed a "Photophone". Although Bell obtained sounds from thin discs he could obtain no sounds from larger quantities of the material. He surmised that this was due to a surface effect and so placed a tube in contact with the illuminated surface of the material and the other end of the tube against his ear. He was thus able to hear sounds from quantities of the materials other than in the form of discs. These results were also summarized in a paper read to the French Academy by Breguet.[10]

Bell's next step from here was to obtain sounds from various materials[2] as described above. Bell, with M. Sumner Tainter, then studied the effect by enclosing the materials in a conical cavity in a piece of brass closed by a flat plate of glass. A brass tube leading into the cavity served as a connection with a hearing tube. This receiver was found to produce even louder sounds than before.

Bell next constructed an apparatus for comparing the magnitudes of the sounds produced from different materials. Light was shone on two similar lenses (A,B) which focused the light onto the chopping disc (C). The two samples were placed in holders (D,E) which were attached to the hearing tube by two equal lengths of flexible tubing. The sample holders (D,E) were placed on slides so that they could be moved along a scale. The beams of light passing through the chopping disc (C) were alternately cut off by the swinging of a pendulum (L), which thus produced alternately a sound from D and E. One of the sample holders was fixed in position while the other one was moved until the sounds obtained from D and E were of equal intensity. The relative positions of the sample holders were then noted. In this way, Bell compiled a table of results in which the materials were placed in order of magnitude.

Bell also constructed a dispersive instrument for use in the infrared region of the spectrum. He called this instrument a "Spectrophone". The eyepiece of a spectroscope was removed and replaced by an opaque diaphragm fitted with a slit behind which the sample was placed. The samples were placed at the focal point of the instrument and a listening tube placed at the end of the telescope.

Other scientists also carried out work on the phenomenon. Mercadier carried out experiments on what he termed "Radiophony".[11-13] He was in agreement with Bell in that he believed the phenomenon was due to a surface effect, but as well as using the sun as a source of radiation, he also carried out experiments using an electric lamp, a platinum spiral, and a gas burner.

Rayleigh,[14] using Bell's photophone, made a calculation which he used to try and prove that the phenomenon was due to the bending of the discs due to unequal heating.

Preece[15] repeated Bell's experiments using a similar apparatus and added some experiments of his own, but rather than rely on his ear to determine the magnitudes of the sounds he used a sonometer.[16] From his results, Preece stated that the phenomenon was due purely to an effect of radiant heat which occurred because of changes in volume in vapors and gases produced by the degradation and absorption of this heat in a confined space. In Rosencwaig's view he provided the first essentially correct theory.[17]

Roentgen carried out experiments on the sounds produced by the intermittent radiation of gases.[18,19] He found that ammonia gave a sound but not air, dry hydrogen, or oxygen. His explanation of the phenomenon was that it was caused by heating and expansion produced by absorption, and the subsequent cooling and contraction of the absorbing body.

Tyndall also studied the action of an intermittent beam of radiant heat upon gases and vapors.[20-22] A diagram of the apparatus used by Tyndall is shown in Figure 1. The source

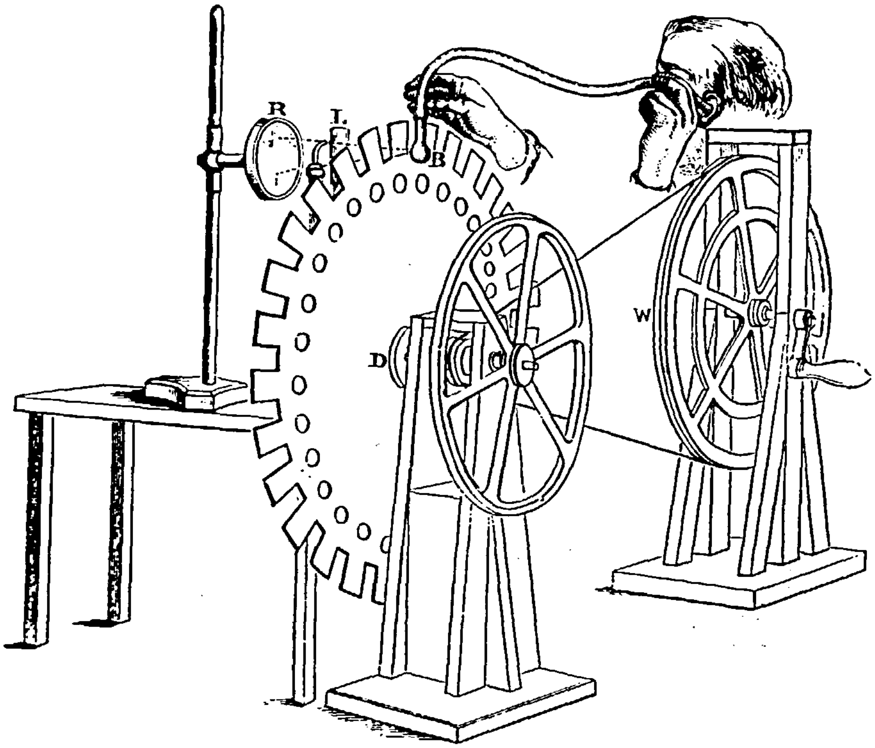


FIGURE 1. Tyndall's apparatus for demonstrating the optoacoustic effect. (From Tyndall, J., *Sound*, 6th ed., Longmans, Green, London, 1898.)

was a lime cylinder (L) heated by an oxy-hydrogen flame. The rays from this source fall onto a concave mirror (which focused the radiation onto the bulb (B) of a flask containing the gas or vapor. The bulb was connected with the ear by a piece of rubber tubing, ending in a tapering tube of boxwood or ivory. The intermittence of the radiation was caused by the rotation of a strong cardboard disc (D) which had 29 teeth and the corresponding interspaces at the circumference. The intermittence was sometimes produced by the series of equidistant circular holes shown in Figure 1. The chopping disc was rotated by the wheel (W), with which it was connected by a band. In the cases of gases lighter than air, the bulb (B) was inverted. Tyndall's results showed that some vapors and gases emitted sounds which were louder than other vapors or gases. In his book he produced two tables, one for vapors and one for gases, in which he placed the various vapors and gases in decreasing order of magnitude of sound.[22]

Thus, by 1881 the technique was established, a theory had been developed, and the qualitative and quantitative aspects of it were evident. However, in view of the limitations of the apparatus and contemporary theories of spectroscopy it is not too surprising that it was not taken up as a routine technique until 60 years later.

II. EXPERIMENTAL

A. General Considerations

A variety of photoacoustic spectrometers have been designed and built during the last decade, and several types are available commercially. They vary from the complex apparatus of Kreutzer,[7] which employs a computer-controlled, high-power gas laser as a source to single-beam spectrometers, not far removed from those of Bell and Tyndall.

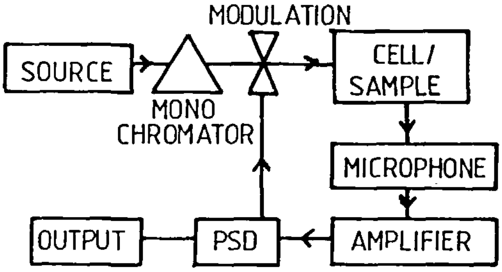


FIGURE 2. Block diagram of a single-beam photo-acoustic spectrometer.

Valuable descriptions of PA spectrometer construction have been given by Munroe and Reichard,[23] King,[24] Beadle,[25] and Davey;[26] here, we summarize some of the salient factors.

Almost any optoacoustic spectrometer will consist of a radiation source with suitable optics, a modulation unit (e.g., mechanical rotating sector), an optoacoustic cell with transducer/preamplifier, source compensation, a signal processing unit, and a data acquisition/display system (Figure 2). These requirements are discussed below in detail.

B. Source Compensation

This area will be considered first because it is the source compensation which will determine the type of optoacoustic spectrometer to be constructed, i.e., single-beam, double-beam, or "pseudo-double-beam".

The output power from a monochromatic light source usually varies significantly with both wavelength and time. Therefore, the optoacoustic signal will have to be normalized to allow for this variation. A single-beam recording optoacoustic spectrometer usually employs a microprocessor or similar device where a reference spectrum is stored digitally, and is divided into the sample spectrum either while the sample spectrum is being recorded or after it has been recorded.

A pseudo-double-beam spectrometer employs a thermopile or pyroelectric detector. A small percentage of monochromated radiation is split from the radiation before it reaches the optoacoustic cell. This small percentage of radiation is focused onto the detector (e.g., thermopile). The output voltage from this detector (after processing with a lock-in amplifier) is divided into the optoacoustic signal (after processing) with a radiometer and displayed on a chart recorder.

A double-beam optoacoustic spectrometer has two optoacoustic cells, one containing the sample under consideration and the other, a reference sample, e.g., carbon black. The output from each transducer is taken to two separate lock-in amplifiers before dividing the optoacoustic signal with the reference signal by means of a ratiometer. Again the resultant signal can be displayed on a chart recorder. Both optoacoustic cells and transducers have to be well matched to produce identical responses. The three types of optoacoustic spectrometers are shown schematically in Figures 2 and 3.

C. Radiation Source

The ideal optoacoustic radiation source would have a spectral resolution of 1 nm or less, an average output power of at least 100 mW, and be tunable from the vacuum UV to the far IR. Practical sources fall somewhat short of this ideal and are limited to either a laser or a lamp-monochromator combination.

Dye lasers give a high output power, excellent spectral resolution, and simplified optics but are expensive and there is the inconvenience of frequent dye changes. The output

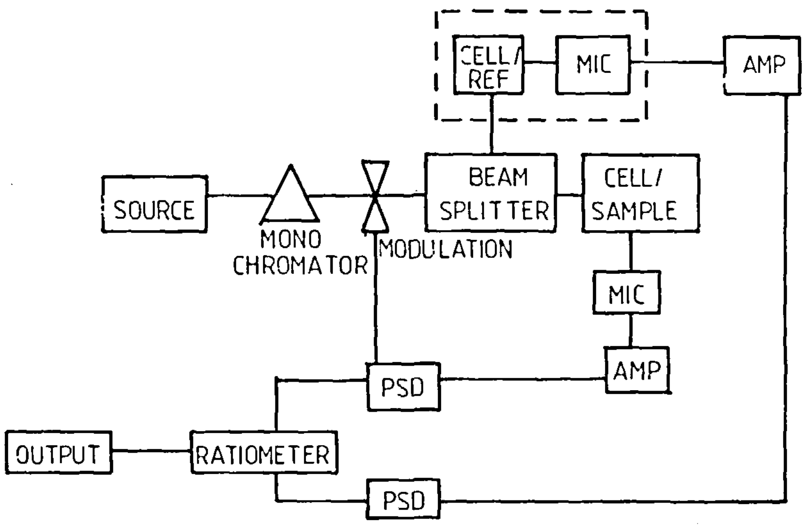


FIGURE 3. Block diagram of a double-beam photoacoustic spectrometer.

power of a dye laser varies greatly over the wavelength range of each dye and, for a CW (continuous wave) dye laser, manual source compensation can be extremely tedious. Although the built-in modulation of pulsed lasers eliminates the vibration and acoustic problems associated with mechanical choppers, they have a limited range of pulse repetition rate or frequency (about 120 Hz maximum), and since they are peak-power limited, output average power will vary directly with frequency. Gas lasers may also be employed, but the limited number of spectral lines and the problems associated with tuning them restrict their range of useful application.

A lamp-monochromator radiation source is one of the most widely used for recording optoacoustic spectrometers. Such a combination must be optimized to obtain sufficient output power together with a sufficiently narrow spectral band pass (resolution). One of the most commonly used lamps in optoacoustic spectroscopy is the xenon arc lamp which is normally used over the wavelength range 260 nm to 3.2 μm. If measurements are to be made at wavelengths corresponding to the line spectra of mercury or mercury-xenon arc lamps, then such lamps may be the best choice. It should be noted, however, that the relatively flat spectral characteristic of xenon lamps minimizes the dynamic range required of a source compensation system. Beadle[25] has found that a sealed quartz-halide lamp, such as is used in automobile headlights, gives performances on a par with xenon arc lamps, and without the ozone hazard associated with the latter.

Since the magnitude of the optoacoustic signal is proportional to the source intensity, then as powerful a lamp as possible should be used, e.g., 1000-W xenon arc lamp, although good quality spectra have been obtained with 300-W xenon lamps, and there is a commercially available optoacoustic spectrometer which uses such a lamp. Careful consideration is necessary in the selection of a xenon arc lamp because not only the power output is important but also the power density of lamp. This will be dependent on the efficiency of the optics of the lamp, e.g., a lamp employing a xenon bulb with an integral parabolic reflector will be more efficient than a xenon bulb fitted in a housing, where the housing has a spherical reflector placed behind the lamp. The focusing assembly of the lamp should provide an output converging beam whose solid angle (f/no.) matches the acceptance cone of the monochromator. The f/no. of a lens is given by the equation

$$f/\text{no.} = \frac{\text{focal length}}{\text{diameter}}$$

The power of the source and, hence, the intensity of the signal decreases with increasing wavelength, with the consequence that it is not possible to obtain good spectra in the fundamental region of the infrared with such a source. The lamp/optics assembly should allow the focused image of the lamp to be no larger than the dimensions of the monochromator entrance slit or radiation will be lost.

The monochromator should be chosen to have as high a throughput as possible, i.e., high dispersion (mm/nm) and low f/no., and high resolution. Grating monochromators should be used in preference to monochromators employing prisms because gratings provide constant angular dispersion over the entire region of radiation dispersed, constant bandwidth over the entire range of application with constant width exit slit, and there is no loss in intensity due to absorption by the optical material, as is the case with prisms. Gratings are also less affected by water vapor. For convenience, it is best to choose a monochromator which has quick interchangeable gratings and which requires as few gratings as possible over a given wavelength range.

Order sorting filters should always be used with grating monochromators to prevent overlapping spectral orders of diffraction from being transmitted to the optoacoustic cell.

D. Modulation

Some xenon arc lamps can be pulsed but this results in a shortening of the lamp lifetime and a decrease in the quality of spectra. The most common form of modulation is with a mechanical rotating sector. The sector should have a maximum number of apertures to reduce its rotational velocity and so reduce background noise. On the other hand, the apertures in the sector should be slightly larger than the image of incident radiation to ensure as much radiation as possible is allowed through. The sector has to be driven at constant speed to provide a constant reference signal which is fed into the phase-sensitive detector (PSD). The rotating sector must be chosen to provide a range of chopping frequencies compatible with those required for possible future applications (30 Hz and upwards) and the reference signal must be suitable for use with the PSD.

E. Optoacoustic Cell Design

The design of the optoacoustic cell is probably one of the most critical factors in the construction of an optoacoustic spectrometer because it is inside the cell that the optoacoustic signal is produced. The subject has been considered in great detail by Rosengren.[27]

Two main types of optoacoustic cells have been used. There are resonant and nonresonant cells. Sample cells may be made acoustically resonant such that their conversion gain will exhibit a peak at some desired frequency. At frequencies well below resonance, the conversion gain will be equal to that of a nonresonant cell of the same total volume.

There are two basic approaches to the design of acoustically resonant cells.[23] In a cavity resonance design,[28] one or more sample cell dimensions is chosen to be a half-wavelength ($\lambda/2$) at the desired modulation frequency (f). Since ($\lambda/2 = C/2f$ where C is the velocity of sound at atmospheric pressure (344 ms^{-1}), then for $f = 50$ Hz, for example, $\lambda/2 = 3.44$ m. Unless used at unusually high frequencies, the large dimensions and correspondingly large volume dictated by cavity resonance designs make them impractical for optoacoustic spectroscopy of solids.

A better approach is to utilize a cell consisting of a sample chamber and microphone chamber connected by a hollow tube.[23,26] The main disadvantage of resonant cells is that, for resonant operation, they are restricted to a single frequency.

A nonresonant cell design is far more versatile than a resonant design, e.g., it can be used in thickness measurements where a number of different chopping frequencies are required.

The material from which the cell is made is very important, not only because of any possible effect on the magnitude of the optoacoustic signal,[29] but it must be of a resilient material, inert to the samples being used, and easily machined. For most applications, the best material is probably stainless steel, although glass, brass, copper, aluminum, and nylon may also be used.

The signal in the cell, for solid samples, varies inversely with the gas volume in the cell. Therefore the gas volume should be minimized, although if the volume is minimized too much the acoustic signal produced at the sample suffers appreciable dissipation to the cell walls through thermoviscous damping effects before reaching the microphone.[26] To prevent this problem, all areas through which the acoustic pressure wave passes should be sufficiently large so as to permit passage of an acoustic pressure wave with minimal dissipation of the sound energy to the surrounding walls.

It is also necessary to ensure that energy is not lost to the window directly in front of the sample. The distance between the sample surface and the cell window, or some other cell boundary, should always be greater than the thermal diffusion length of the gas, since it is this boundary layer of gas that acts as the acoustic piston generating the signal in the cell. For air at room temperature and pressure, the thermal diffusion length is 0.02 cm at a chopping frequency of 100 Hz.[30] Taking this thermal diffusion length criterion into account and the need to minimize sound energy dissipation to the cell boundaries via the thermoviscous effect, one finds that a cell usable over a wide range of chopping frequencies will usually have a minimum distance between sample and window, and minimum passageway dimensions of 1 to 2 mm. A method of minimizing cell volume without the microphone dimensions interfering is with a side-arm-microphone holder arrangement.

In addition to being sample dependent, the conversion of radiant power to pressure in a sample cell is proportional to the ambient pressure in the cell and the thermal diffusivity of the coupling gas.[31,32] It is doubtful, however, that the advantages obtained by pressurizing the cell or by using helium,[31,33] for example, in place of air, are worthwhile in view of the resulting practical difficulties and inconvenience.

The cell must be insulated from external acoustic noise. Double glazing is most effective, and it may be advantageous to insulate the mountings of the spectrometer.

An important consideration in cell design is the microphone configuration, a variety of which can be used. Some people construct their own transducers for specific purposes but commercially available transducers are usually used. Of the many microphone types and sizes that are available commercially, the sensitivity and low frequency response required for optoacoustic spectroscopy use limit the choice to one of four varieties — the ½″ or 1″ diameter condenser microphone and the ½″ or 1″ electret condenser microphone. Electret microphones have the advantages of higher capacitance (less noise at low frequencies) and do not require a polarization voltage. Condenser microphones, on the other hand, are usually more sensitive.

Cylindrical microphones have been used[26] because they are easy to construct and have a large surface area, thus increasing their sensitivity. However, they do not usually have a flat frequency response over a large acoustic frequency range.

The microphone preamplifier should be placed as close as possible to the transducer so that the optoacoustic signal is amplified before it picks up any extraneous noise. A cell has been designed[34] so that the preamplifier is held between the sample chamber and an outer wall, a very short distance from the transducer. The power supplies available with transducers are usually battery operated to prevent mains pick-up although main power supplies have been specially constructed for the purpose.

F. Signal Processing

The processing of the optoacoustic signal is nearly always carried out with the aid of a lock-in amplifier which, as well as amplifying the input signal, also isolates the component of the input signal which is at the same frequency as the reference signal supplied by the modulation unit. This means that only the optoacoustic signal (plus any extraneous noise at that exact chopping frequency) is measured. Most lock-in amplifiers have a phase adjustment which varies the phase between the optoacoustic signal and reference signal, and, thus, function as phase-sensitive detectors. This is important for depth profiling measurements to be taken.[35,36]

G. Data Acquisition

The tasks of acquiring, storing, and displaying the data can be performed in many ways and is partly dependent on the type of optoacoustic spectrometer used. For a single-beam spectrometer, provision must generally be made to remove from the optoacoustic spectrum any spectral structure resulting from the lamp, monochromator, and optics of the system. This normalization can be done by digitizing the analog signal from the lock-in amplifier, and then performing a point-by-point normalization (i.e., division) with a previously recorded optoacoustic spectrum obtained with a black absorber. The sample and reference spectra can be recorded by, for example, a microprocessor[37] or a microprocessor-based transient recorder. Further computations could be carried out on a suitable computer by transferring the normalized spectra onto, for example, paper tape. The normalized spectra can also be output onto an X-Y or x-t recorder. The main advantages of a microprocessor-assisted single-beam optoacoustic spectrometer are that it allows the averaging of several spectra, thereby increasing the signal-to-noise ratio, storing and updating the reference and sample spectra, producing the difference between two sample spectra, and permanently storing the data on paper tape or magnetic tape. This then enables an extension of possible applications, e.g., depth profiling.[36] This, of course, is based on the assumption that the source output remains constant over the time interval that the reference and sample spectra are acquired. Any short-time fluctuations can be eliminated by recording slowly and/or with a time constant. Any long-term fluctuations are eliminated by updating reference and sample spectra.

In a double-beam spectrometer, normalization can be performed in analog real-time fashion by dividing the analog output from the lock-in amplifier processing the sample signal, with the output derived from a reference signal. The normalized spectrum can then be recorded on an X-Y or x-t recorder.

III. THEORY

A. General Considerations

There is broad agreement on the fundamental processes which account for the photoacoustic effect, but a divergence of views on how these may be expressed in mathematical form. The major factors are summarized in Figures 4A to 4C. For gases, the basic steps are the rhythmic absorption of optical energy and its subsequent conversion, by collision, to thermal energy. For solids, the thermal deactivation involves diffusion of the heat to the surface of the sample, and its transfer to the gas molecules in the cell. A useful concept is that of a layer of gas molecules adjacent to the sample surface acting as a piston as they are periodically heated and cooled. If the solid has two layers, it is assumed that the rate of thermal diffusion is such that the signal from the second layer lags behind that from the first. Thus there is a phase difference between the signal from two layers and by appropriate adjustment of the phase-sensitive detector, both signals may be detected separately. This is the basis of nondestructive depth profiling.

The simple models have limitations, both physical and mathematical.

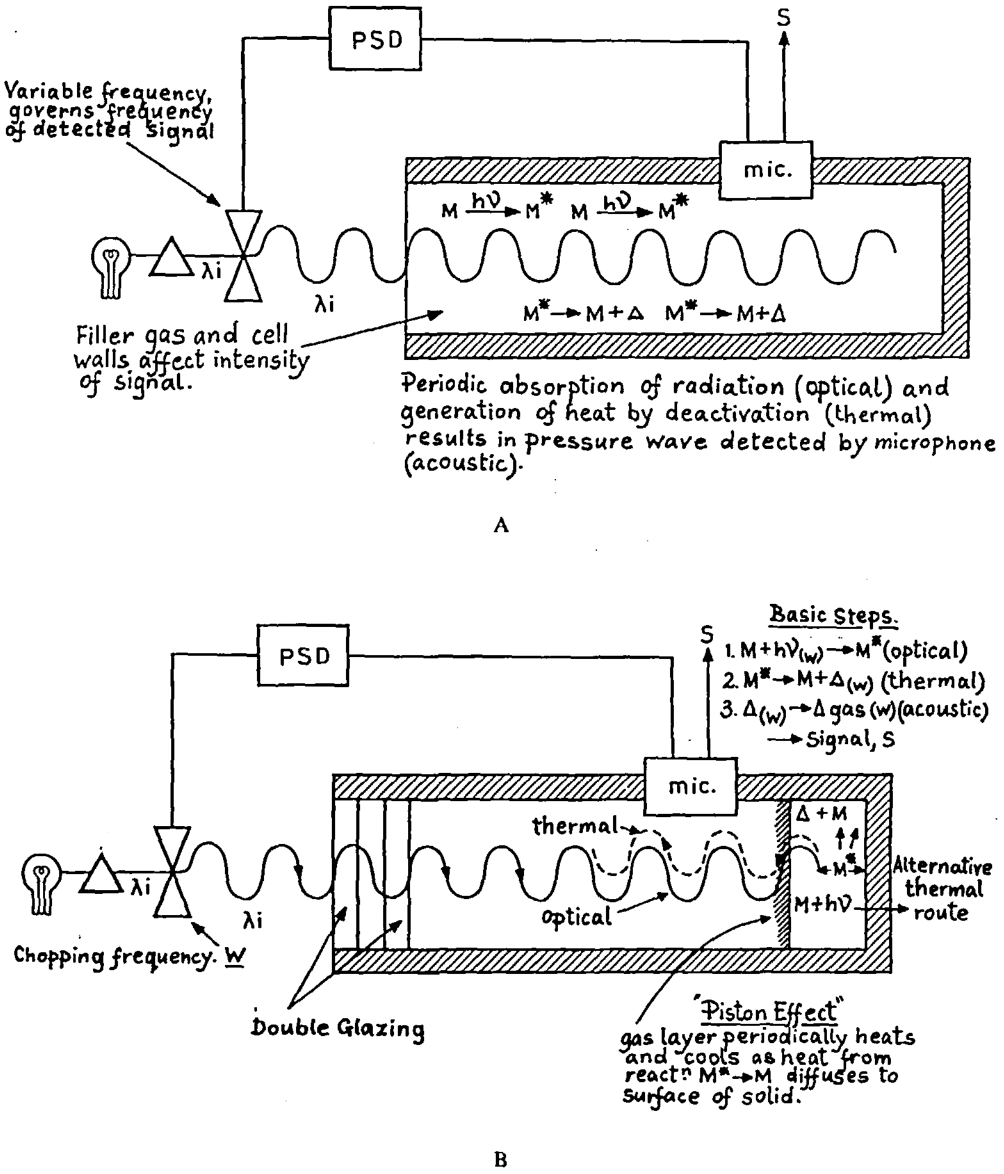


FIGURE 4. (A) Basic PAS model for gases, (B) basic PAS model for solid sample, (C) basic PAS model for two-layer solid samples.

On the physical side there are several possibilities for alternative thermal routes and deactivation processes. The filler gas, cell material, and sample backing are all capable of conducting heat from the sample, hence their thermal characteristics have to be taken into account. (This is not only a matter of theoretical concern, for it means that the matrix of the sample and its thickness will affect the intensity of the acoustic signal even if other parameters such as filler gas and cell material are fixed.) Deactivation steps by alternative optical processes may affect the signal, also. Usually the photoacoustic spectrum is identical with the optical absorption spectrum but Robin has shown that this is not always the case.[38]

On the mathematical side, the problem arises from the satisfactory combination of the

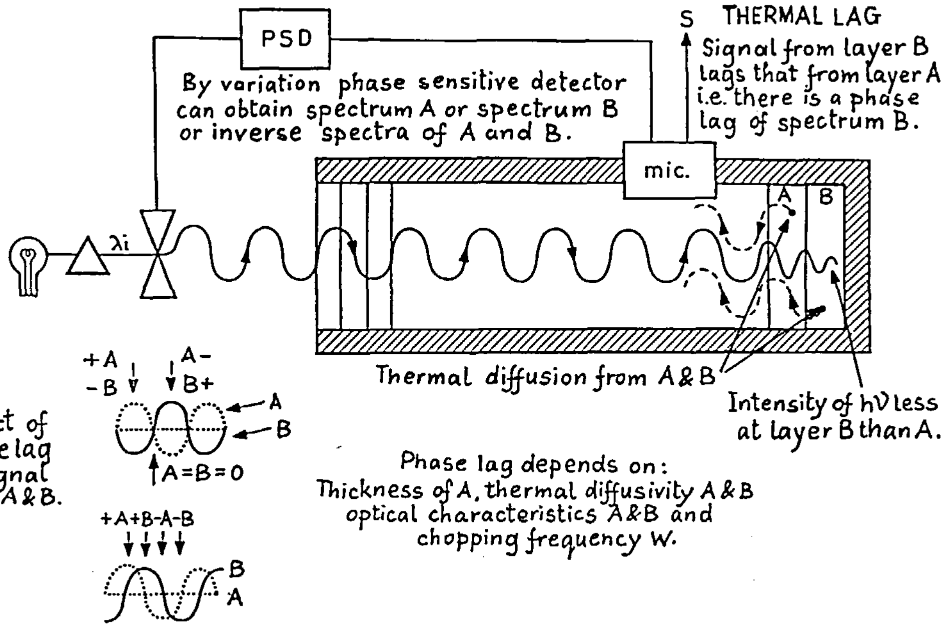


FIGURE 4C

numerous steps into a useful formulation. A common assumption is that the modulation is sinusoidal, rather than square wave. (Since the chopper is far from ideal, it is not an unreasonable assumption.) The physical steps can be described by well-known equations, mainly exponential, as for the optical absorption, or second order differential, as for the diffusion processes. If these various steps are combined into exact equations, the formidable problem arises of how to use them. One approach is to make simplifying assumptions so that they can be reduced to useful forms; another is to use dimensionless variables. Both approaches have severe limitations in practice.

Some authors have added further refinement to the physical model, e.g., taking into account the oscillation of the sample surface so that one has couplied "gas and solid pistons".

The bare bones of these approaches are indicated below, and the relationships between them are given so that the reader may more easily study the original papers. Discussion of the two-layer model is reserved to the section on applications.

B. Theory and the Photoacoustic Effect in Gases

There have been several attempts to describe the theory of the optoacoustic effect in gases. The first was by Gorelik who, in a thermodynamic approach, assumed an internal and a translational temperature and a relaxation equation between these quantities.[39] This approach was also followed in the surveys given by Cottrell and McCoubrey[40] and Read,[41] although the former approach was better suited to the investigation of the significance of certain assumptions. Delany[42] and Kaiser[43] used a reaction kinetic approach and balanced optical and collisional transfer.

Tripodi and Vincenti[44] described a gas-dynamic model for couplied vibrational and radiative nonequilibrium in carbon dioxide. Collisional rate equations were derived and a solution for the spectrophone (optoacoustic cell for gases) was presented, including expressions for the phase lag in the pressure signal that results from radiative excitation.

Bauer[45] presented a theory for a periodically driven as well as pulse-driven spectrophone for a gas with an arbitrary number of collisional excitation and de-excitation reactions, starting from reaction rate constants. An example of a three-level gas system was also given.

Kruzer[46] derived a theory of the spectrophone following, in part, Kaiser's[43] treatment. Rosengren introduced a new theoretical model for an optoacoustic gas concentration detector.[47] He derived expressions for the minimum detectable gas concentration and the laser power required to reach this sensitivity. Cannemeijer et al.[48] developed Delany's theory[42] for a one-step relaxation process and then went on to consider a two-step relaxation process.

The theory of a resonant sample chamber has been described by Dewey,[49] Rosengren and Max,[50] and Nodov.[51] Dewey derived scaling laws for both resonant and nonresonant acoustic systems which allowed the sensitivities and dynamic range of the optoacoustic method to be assessed for a particular application. Rosengren and Max postulated a theory for a resonant detector and derived an equation for the minimum detectable gas concentration, which was 10^{-4} parts per million for ammonia. Nodov introduced a new cell design and derived an equation for the pressure wave in this cell.

More recently, Bennett and Forman[52] have described the theory of an optoacoustic gas cell where they solved the equations which they used to compute the temperature and acoustic-stress profiles in the optoacoustic cell under steady-state conditions, applicable to a particular cell which they define. They gave several boundary conditions, cited the assumptions used to make the problem amenable to computation, and the conditions by which the intermediate range of frequencies were defined. They also provided an analysis by which, in general, the surface- and bulk-absorption coefficients of weakly absorbing materials can be separated. Bennett and Forman have also presented a much shorter version of this theory applicable to the measurement of just low absorption coefficients.[53]

Hunter discussed the theory of the photoacoustic effect when the technique is used as a sensitive detector for weak transitions or for species at low concentrations, and as a means of adding to the available data of molecular relaxation processes.[54] He derived expressions for the pressure wave at the transducer for the case where the whole cell was uniformly irradiated, and for the case of irradiation uniformly over a small cylinder, e.g., with a laser beam.

Farrow and Richton[55] studied theoretically and experimentally the response of a cylindrical photoacoustic cell when filled with an absorbing gas and irradiated by a laser beam passing along its axis, as a function of gas pressure and composition. The pressure on the cell microphone was calculated by solving numerically, for the experimental parameters of interest, the general heat-diffusion equation with a forcing function which was shown to depend upon both space and time for the realistic case of 50% modulation of the laser beam. The pressure equation used by Farrow and Richton was obtained from the earlier treatment of Kerr and Atwood.[56]

Wrobel and Vala[57] constructed a set of heat-flow equations governing the optoacoustic effect in gases and solved them under certain restrictions. The general solution was examined in detail for excitation into a vibrational level of the lowest triplet state. A method was presented for the extraction of lifetime and nonradiative yield parameters from the expected time-resolved pressure signal. Wrobel and Vala also presented a simplified two-state model and the general form of the expected pressure signal.

Colles et al. derived an expression for the gas pressure in an optoacoustic cell and showed that the amplitude of the acoustic wave was a function of the thermodynamic properties of the system.[58] The expression indicated that the pressure signal varied sinusoidally and the phase of the pressure signal lags the input beam.

Amer and co-workers have used the treatment of Kerr and Atwood[56] to show the dependence of the optoacoustic signal on pressure and buffer gases for a resonant[59] and nonresonant[32] cell design.

C. Theory of the Photoacoustic Effect in Solids

There are a number of elementary approaches which take into account the periodic absorption of light and the thermal dissipation of the absorbed energy.[35,60,61] Bennett and Forman,[62] Kerr,[63] and Afromowitz et al.[64] have investigated various aspects of the process, measured absorption coefficients, and derived theoretical models to account for their results. However, the two approaches we have found most useful have been those of Aamodt et al.[33,65] and Rosencwaig and Gersho.[17,30] In both the physical model is virtually the same and is that outlined above. Both agree on the importance of the piston effect of the gas layer adjacent to the surface of the sample. Rosencwaig and Gersho calculate, on the basis of the time-dependent part of their equation for the temperature variation at the surface of the sample, that the thickness of the "piston" is 2 $\pi\mu_g$ where μ_g is the thermal diffusion length. At 100 Hz, a typical chopping frequency, 2 $\pi\mu_g$, is approximately 0.1 cm. Aamodt et al.[33] consider the transfer of energy through the gas phase in detail employing a thermal transport equation derived earlier by Parker.[66] They argue that it is more complex than the diffusion process in solids since there are "thermal" nonpropogating and "acoustic" or propogating contributions to the temperature.

In both theories, the optical absorption steps and the thermal processes in the solid are considered in detail. Various assumptions have to be made about the latter, since the heat flow through the solid can take place in any direction, whereas the signal can only arise from a heat transfer across the sample-cell gas interface. Consequently, the model must provide for flow from the point of optical absorption to the surface of the sample. It is simplest to assume a thermally thick sample of reasonable dimensions so that the effects of the cell and sample holder acting as heat sinks can be ignored, and the sample can be considered as an infinite solid, which makes the solution of the diffusion equation more straightforward. However, a fully developed theory can take into account nonideal conditions and both these theories, especially that of Aamodt et al., consider the implications of sample thickness and diverse cell materials and filler gas in some detail.

The relevant equations of both theories are summarized and compared in Table 1. From the physicist's point of view there is an attraction to PAS in that the thermal diffusivity and thermal conductivity of the sample are related to the intensity of the acoustic signal. There is the possibility that the values of these constants may be determined much more easily by PAS than by conventional methods. To the analytical chemist, the dependence of the acoustic signal on the thermal characteristics of the sample is of some concern, since it implies matrix effects. It is possible to envisage, for example, spectra of different intensities arising from the same concentration of optically absorbing species in different samples of optically transparent matrices, e.g., a coloring agent in plastic films or wrappers where the color is the same but the plastics differ in composition. With powdered samples, the intensity of the signal varies with the particle size and mode of packing. In addition, the intensity of the signal varies with the thickness of the sample, the material of the cell,[29] and the nature of the cell filler gas,[65] so one must conclude that quantitative measurements require a lot of care on the part of the operator.

The optical absorption step is, by contrast, relatively straightforward, and results in an optical absorption spectrum, which is almost identical with that obtained by conventional absorbance or diffuse reflectance spectroscopy. Where the theories differ is in their approach to the solution of the equations. Aamodt and Murphy[65] use dimensionless variables to reduce the full equations to soluble forms. They have plotted a number of important parameters and made correct predictions about the effect of cell length and filler gases. The difficulty with the approach is that the parameters are presented in a form which obscures their physical basis. Thus it is difficult to gain a quantitative physical insight into the processes involved. Nevertheless, the relative importance of the various optical, thermal, and energy transfer steps is evident.

Table 1
PHOTOACOUSTIC EFFECT IN SOLIDS

Equations	Ref.
$Q = \frac{\gamma P_o \theta}{\sqrt{2}\,\ell_g a_g T_o}$ where $\theta = \frac{\beta I_o}{2K_s(\beta^2 - \sigma_s^2)}\left[\frac{(r-1)(b+1)e^{\sigma_s \ell} - (r+1)(b-1)e^{-\sigma_s \ell} + 2(b-r)e^{\beta \ell}}{(g+1)(b-1)e^{-\sigma_s \ell} - (g-1)(b-1)e^{-\sigma_s \ell}}\right]$	30
$S \propto \frac{-\alpha I_o D_o B(C_2 - 1 + DS_2)/k_g K_g}{2(C_2 - 1) + EXS_2(1 + BD\Gamma) + (D + B\Gamma)(EXC_2 + S_2)}$	33
$S(s) = H(s)\,\pi_i R_i$	65
$P_g \approx \frac{-j\,P_o\,\gamma I_o}{\omega\,\ell_g 2\rho_s C_{ps}}\left(\frac{\beta}{\sigma_g T_o (g+1)(r+1)} + \beta_T[1 - \exp(\beta \ell_s)]\right)$	67
$<p_g\ (t;\ \omega_o)> = \left\{\frac{P_o I_o \eta \beta}{2k_s T_o L}\right\} \mathrm{Re}\left[\left\{\frac{\exp(i[\omega_o t - \pi/4])}{\sqrt{2}a_g(1 + i\omega_o \tau)(\beta^2 - \sigma_s^2)}\right\} X \left\{\frac{(r-1)(b+1)\exp(\sigma_s \ell) - (r+1)(b-1)\exp(-\sigma_s \ell) + 2(b-\tau)\exp(-\beta \ell)}{(b+1)\exp(\sigma_s \ell) + (b-1)\exp(-\sigma_s \ell)}\right\}\right]$	68

Table 1A
RESPONSE TERMS USED BY AAMODT AND MURPHY[65]

Response	Condition	
R_{cl}	$\frac{\mu S\tau DS_1}{2\mu(S\tau)^{1/2}(1 - C_1C_2) - (b + D)[\mu(S_\tau)^{1/2}(C_1S_2 + S_1C_2) - bDS_1S_2}$	Thermal wave only
	$\frac{\mu(S\tau)^{1/2}(C_1 - C_2 - DS_2)}{2\mu(S\tau)^{1/2}(1 - C_1C_2) - (b + D)[\mu(S\tau)^{1/2}C_1S_2 + C_1C_2]\,bDS_1S_2}$	Acoustic wave only
	$\frac{1}{(S\alpha_s)^{1/2}\,C_{ps}}$	Thin layer
R_s	$\frac{1}{SC_{ps}}$	Thermally thick layer; uniform heating
	$\frac{\beta(\alpha_s)^{1/2}}{(S\alpha_s)^{1/2}[(S)^{1/2} + \beta(\alpha_s)^{1/2}]}$	Thermally thick layer; exponential heating
	ϵ	Thin sample
R_{sub}	1	Thermally thick sample
	$1 - (1 + m)Q_o$	Intermediate sample uniform heating
R_{pt}	$\sum_{ij} E_i/E_m V_{ij}(k - SI)^{-1}_{jm}$	Optical pumping of m th level only

Rosencwaig and Gersho[17,30] prefer to make reasonable physical assumptions and to simplify the equations thereby. The process leads to a number of different limiting cases for which relatively simple equations hold. The difficulty lies in recognizing when the assumptions no longer hold. Despite their limitations, both theories are extremely useful and provide great insight into the complexities of the photoacoustic effect.

McDonald and Wetsel, Jr.[67] have extended the theory of the optoacoustic effect to include the contribution of mechanical vibration of the sample. They have solved coupled equations for thermal and acoustic waves in both sample and gas, and shown that the pressure signal in the gas may be significantly affected by acoustic coupling in the sample. They also confirmed this extended theory by experiment. The results of the fully coupled treatment were shown to be accurately reproduced by an extension of the Rosencwaig piston model: the piston-like motion of the gas boundary layer adjoining the sample was superimposed on the mechanical vibration of the sample surface to give a composite piston displacement which then produces the pressure signal in the gas. The composite-piston model proves relatively simple algebraic results applicable to many cases of physical interest.

Recently, Mandelis et al.[68] extended Rosencwaig's optoacoustic model to include the relaxation time of the radiationless de-excitation process. The emphasis was on the effect of this quantity on the phase of the optoacoustic response.

I. Important Equations Related to the Optoacoustic Effect in Solids

The equations for the magnitude of the optoacoustic signal, obtained from the important theories on the optoacoustic effect in solids, are given in Table 1, the appropriate definitions for which are given in Tables 1A and 1B.

IV. APPLICATIONS

A. General

There is an increasing number of reported analytical applications. The rate of growth and areas of interest are indicated in Table 2, which summarizes in chronological order most of the papers published to date. Of most interest are gas analysis, the examination of materials which are difficult to examine by conventional absorption spectrophotometry, and the investigation of layered samples. These will be considered separately.

B. Gas Analysis

There have been a number of calculations which have shown that, in principle, PAS is an extremely sensitive technique for gas analysis. It should be possible to make determinations at the ppb level or below;[46] the limit of sensitivity is due to the Brownian noise of the microphone, i.e., 1 in 10.[13] In practice, sensitivities achieved so far do not represent significant improvements on standard methods of gas analysis. We have carried out experiments to determine the sensitivity limit for the measurement of nitrogen dioxide in air. With a 40-W argon ion laser as a source and a single-beam apparatus, with the laser power amount 0.5 W, it was possible to detect 20 ppm with a signal-to-noise ratio of 100. By extrapolation it was concluded that at higher powers it is possible to determine 6 ppb of NO_2 although the relationship between power and signal is nonlinear at power in excess of 1 W. This seems to be in line with the findings of other workers, who have determined nitric oxide,[69] sulfur dioxide,[70] ten pollutants,[71] or nitrogen dioxide.[72] Improvements could be made by application of refined data processing, a higher powered source, and a more sensitive microphone. However, given (1) the present cost of the high-powered laser, its limited number of wavelengths, and the difficulty of changing wavelengths and (2) the state-of-the-art with respect to microphones, it must be concluded that PAS does not have a clear advantage over conventional techniques. No

Table 1B
DEFINITION OF TERMS USED IN TABLE 1

Term	Rosencwaig and Gersho[30]	Aamodt et al.[33]	Aamodt and Murphy[65]	Mandelis et al.[68]	McDonald and Wetsel[67]
Magnitude of optoacoustic signal	Q	S	S	$\mid <P_g\,(t{:}\omega_o)> \mid$	P_g
Optical absorption coefficient	β		β	β	β
Incident flux	I_o	I_o		I_o	I_o
Thermal conductivity	K	K		K	k
Ambient pressure	P_o			P_o	P_o
Thermal diffusivity	$\propto$	$\propto$	$\propto$	$\propto$	$\propto$
Thermal diffusion coefficient of material	$a = \left(\frac{\omega}{2\propto}\right)^{1/2}$	k		a	σ
Ambient temperature	T_o			T_o	T_o
r	$\frac{(i-j)\beta}{2a_s}$			$\frac{(1-i)}{(\beta/2a_s)}$	$\frac{\beta}{\sigma_s}$
σ	$(i+j)a$			$(1+1)a_j$ and $a_j = \sqrt{\omega/2\alpha_j}$	Thermal diffusion coefficient
b	$\frac{K_b a_b}{K_s a_s}$		BQ_oq_o	$\frac{a_bK_b}{a_sK_s}$	
g	$\frac{K_g a_g}{K_s a_s}$			$\frac{a_gK_g}{a_sK_s}$	$\frac{k_g\sigma_g}{k_s\sigma_s}$

$\sqrt{-1}$	j	j		i	j
Chopping frequency	ω	ω		ω_0	ω
Volume coefficient of thermal expansion					β_T
Heat capacity of gas at constant pressure	C_{pg}	D_o	C_{pg}		C_p
V_{ij}			Nonradiative transition rate from j th to i th level		
D		$\frac{K_g k_g}{K_w k_w}$	$[k_g(k_w)(C_{pg}/C_{pw})]$	$\frac{a_g K_g}{a_w K_w}$	
Cell length		L	L	L	
Sample thickness	ℓ	ℓ	ℓ	ℓ	
Efficiency of radiationless de-excitation process				η	
Γ		$\frac{\epsilon + (1-\epsilon^2)S_4C_4}{1+(1-\epsilon^2)S_4^2}$			
ϵ		$\frac{K_s k_s}{K_b k_b}$	$[(k_s/k_h)(C_{ps}/C_{ph})]^{1/2}$		
E		$\frac{(2j)^{1/2}}{\gamma - 1}$			
S_2		$\sinh k_g L$	$\sinh [L(S/\propto g)^{1/2}]$		
S_4		$\sinh k_s$,			
X		$(\omega/2\propto g)^{1/2} L$			
C_2		$\cosh k_g L$	$\cosh [L(S/\propto g)^{1/2}]$		
C_4		$\cosh k_s \ell_s$			

Table 2
SUMMARY OF ANALYTICAL APPLICATIONS OF PAS

Application	Author	Ref.
Analysis of gas mixtures in I.R.	Veingerov	3
Measurement of atmospheric pollutants	Pfund	5
Vibrational relaxation measurements	Woodmansee and Decius	75
	Cannemeijer et al.	76
	Parker and Ritke	77
Measurement of absorptivities in gases	Kerr and Atwood	56
Measurement of gas concentrations	Kreuzer	46
Detection of atmospheric pollutants in I.R.	Dewey et al.	78
	Goldan and Goto	79
Detection of weakly absorbing gases	Kamm	80
Study of aldehyde photochemistry	De Groot et al.	81
Study of products of continuous pyrolysis of netromethane	Angus et al.	82
Study of molecular properties of gases	Webster	83
Analysis of solids	Harshbarger and Robin	84
	Rosencwaig	85
	Adams et al.	9
	King	24
	Munroe and Reichard	23
Determination of quantum yields in fluorescent solutions	Lahmann and Ludewig	86
Trace analysis in liquids	Lahmann et al.	87
Thermal diffusivity in OAS	Adams and Kirkbright	35
Water vapor absorptivity measurement	Shumate et al.	88
Forbidden transitions in unstable sulfur compounds	Dixon et al.	89
Detection of sulfur dioxide below parts-per-billion level	Kock and Lahmann	70
Gas chromatography detector	Kreuzer	120
Analysis of highly corrosive gases	Marinero and Stuke	90
Paper samples	Ferrell Jr. and Haven	91
Study of surface and surface-related effects	Kanstad and Nordal	92
Powdered samples	Monahan Jr. and Nolle	93
	Murphy and Aamodt	94
Investigation of transport properties of semiconductors	Ghizoni et al.	95
Determination of ultra trace cadmium	Oda et al.	96
Determination of mixtures in a liquid	Oda et al.	97
Depth profiling in a two-layer system	Betteridge et al.	36
Thickness measurements	Betteridge and Meyler	74
	Adams and Kirkbright	98
Study of T.L.C. plates	Rosencwaig and Hall	99
Biological systems	Maugh	100
	Rosencwaig	101
	Adams et al.	73
	Rosencwaig and Pines	102
Analysis of turbid solutions	Oda et al.	103
Photocolorimetry	Chance and Shand	104
Investigation of phase transitions	Siqueira et al.	105
Subsurface blow detection in metals	Thomas et al.	106
Measurements of diesel particulate emissions	Faxvog and Roessler	107
Study of the photochemical reaction of sensitizing dyes adsorbed on semiconductor powder	Iwasaki and Oda	108
Optoacoustic raman gain spectroscopy	Patel and Tamm	109
Far infrared optoacoustic spectroscopy	Walzer et al.	110
In situ studies of lobster shell carotenoprotein organization	Mackenthun et al.	111
Subsurface structures of solids by scanning photo-acoustic microscopy	Wong et al.	112

Table 2 (continued)
SUMMARY OF ANALYTICAL APPLICATIONS OF PAS

Application	Author	Ref.
Studies of electrode surface changes	Fujishima et al.	113
Fourier transform photoacoustic spectroscopy	Farrow et al.	114
Fourier transform infrared photoacoustic spectroscopy	Rockley	115
Simultaneous measurement of photoacoustic and fluorescence spectra	Kato and Sugitani	116
Raman photoacoustic spectroscopy	West and Birrett	117
Quantitative spectroscopy of micron-thick liquid films	Patel and Tam	118
Circular dichroism	Saxe et al.	119

doubt technical improvements will come about with consequent improvement of the sensitivity, but the basis of the assessment of PAS relative to conventional techniques will remain financial, since the technique does not yield any novel information.

C. Maintaining Sample Integrity

The same comment holds for the analysis of solids which are difficult to examine by standard absorptiometry. Such samples are semiconductors, polished oxides, biological materials, all of which are either difficult to dissolve, press into KBr discs, or change their properties during these conventional processes. The PA spectra of these compounds are usually very similar to the corresponding diffuse reflectance spectra. However, because the source is appreciably cheaper than a high-powered laser, the cost of instrumentation is, or could be, comparable with conventional uv-vis diffuse reflectance spectrophotometers. Opaque materials such as coal may also be examined by PAS.

D. Depth Profiling

Depth profiling is the one area where PAS can provide novel information, and in view of its importance this will now be discussed fully.

1. *Theory*

Two different approaches have been advocated. One, from Kirkbright's group, is based on the concept of phase lag. The other, due to Rosencwaig, depends on varying the frequency of modulation. Both approaches provide valuable insights.

a. Phase Dependence of PA Signal

It follows from Figure 4 that the magnitude of the PA signal is dependent upon the phase setting of the lock-in amplifier. In the extreme cases, the signal can be maximum positive, maximum negative, or zero if the phase lag is 0, 180, 90, or 270°, respectively. Thus, by altering the phase setting, one can easily obtain a conventional absorption spectrum, its inverse or no spectrum at all from the same sample! This is shown by the computer-drawn diagram in Figure 5.

Kirkbright et al. have argued that if the sample consists of a substrate covered by a thin surface layer it is possible to adjust the phase lag so that the spectrum of the surface layer is positive while that of the substrate is zero, and then to find another setting where the situation is reversed.[9,35,73] It is assumed that the surface layer transmits light, so that the substrate can absorb the incident radiation and that its thermal properties are such that the transfer of thermal energy from both layers to the cell filler gas is possible. One of the first examples was provided by the examination of a spinach leaf.[24] The surface layer was colorless and provided negligible signal at zero phase lag. At a phase lag of 90° the green color of the leaf was measurable. (In practice, there is an instrumental phase lag, β, so

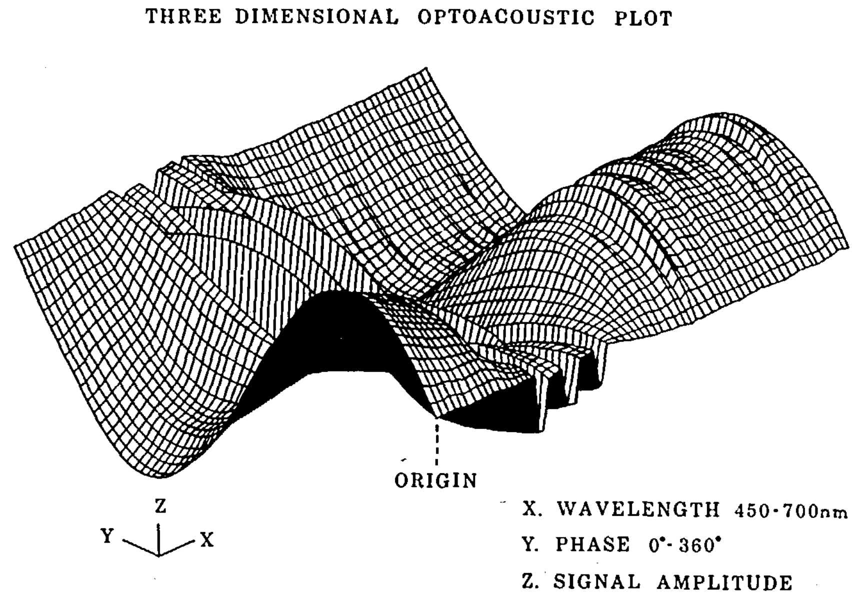


FIGURE 5. Computer-drawn diagram of PA spectra as a function of phase lag. X = wavelength, 450 to 700 nm; Y, phase 0 to 360°C; Z, signal amplitude.

strictly one should write 0 + β° and 90 + β°). A test of the theory is provided by comparison of the spectra obtained at various phase settings of a red transparent sheet of polymer placed on a green insulating tape, both of which are common materials in the lab. The results are shown in Figure 6 and compared with those calculated from the two spectra taken at phase lags of 0 and 90° (the in-phase and quadrature spectra). The calculations are based on the relationships:[36]

$$Y(\Delta\lambda_i,\Theta) = C_{\Delta\lambda_i} \cos(\Theta - \psi_{\Delta\lambda_i})$$

where $Y(\Delta\lambda_i,\Theta)$ is the magnitude of the optoacoustic signal at phase Θ over the ith wavelength and interval $\Delta\lambda_i$, λ is the wavelength, $C_{\Delta\lambda_i}$ is the signal maximum, and $\psi_{\Delta\lambda_i}$ is the phase angle at which $Y_{\Delta\lambda_i} = C_{\Delta\lambda_i}$

$$\psi_{\Delta\lambda_i} = \tan^{-1} \frac{Y(\Delta\lambda_i, 90°)}{Y(\Delta\lambda_i, 0°)}$$

and

$$C^2_{\Delta\lambda_i} = [Y(\Delta\lambda_i, 90°)]^2 + [Y(\Delta\lambda_i, 0°)^2]$$

From these it follows that if optoacoustic spectra are obtained at phase angles of 0 and 90° (the in-phase and quadrature spectra), the spectrum for any phase angle can be computed and that it is possible to plot ψ as a function of wavelength. The spectra at 270 and 45° correspond to the pure spectra of the red transparency and green tape, respectively, those at 90 and 225° to their inverse.

It is thus an established experimental fact that the spectra of successive layers of a sample may be obtained nondestructively, although there are some limitations. Because of the inversion of the spectra, it definitely helps to have a clear idea of the spectrum sought, and, in our experience, it is virtually impossible to distinguish clearly three colored layers.

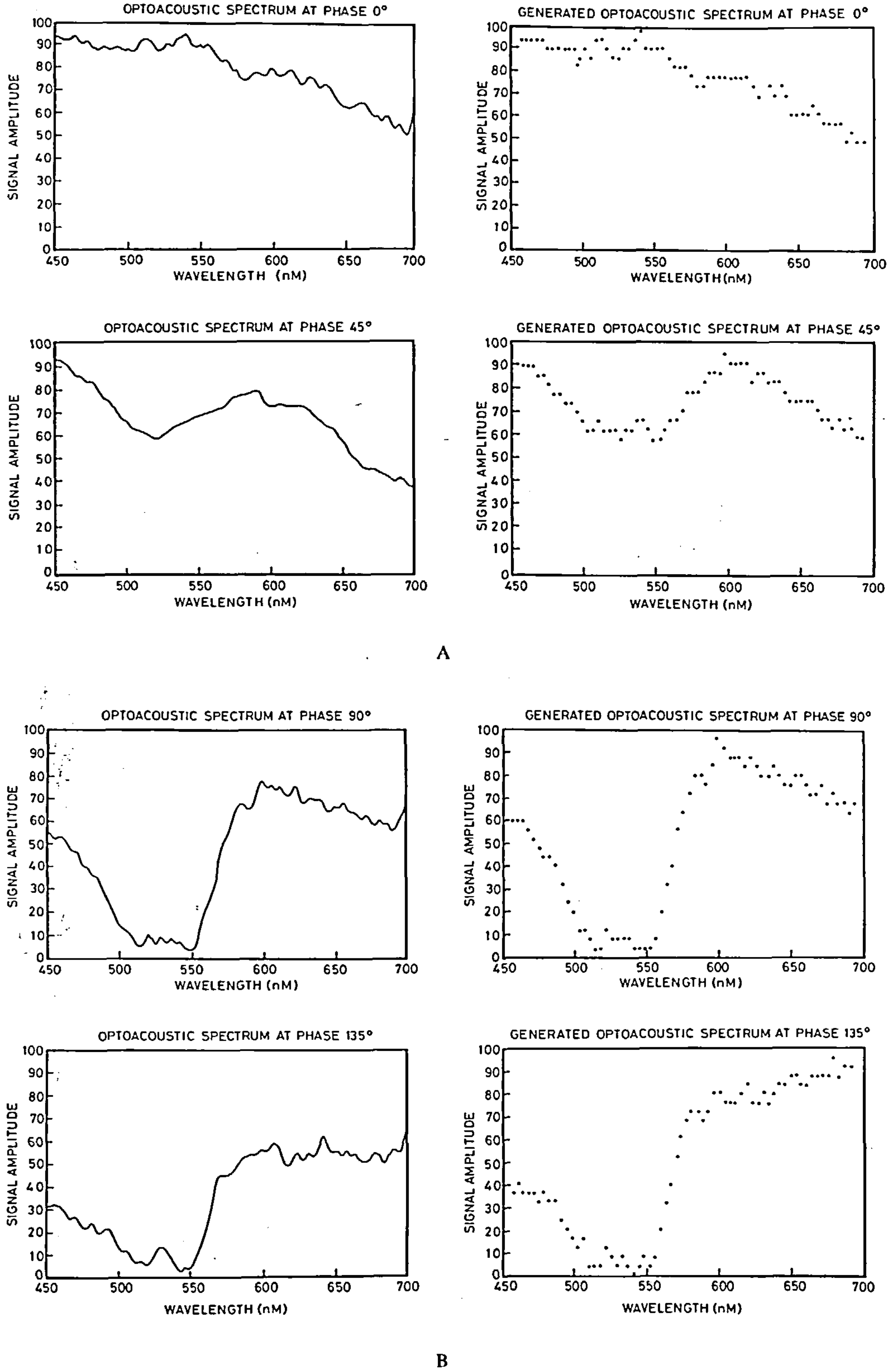
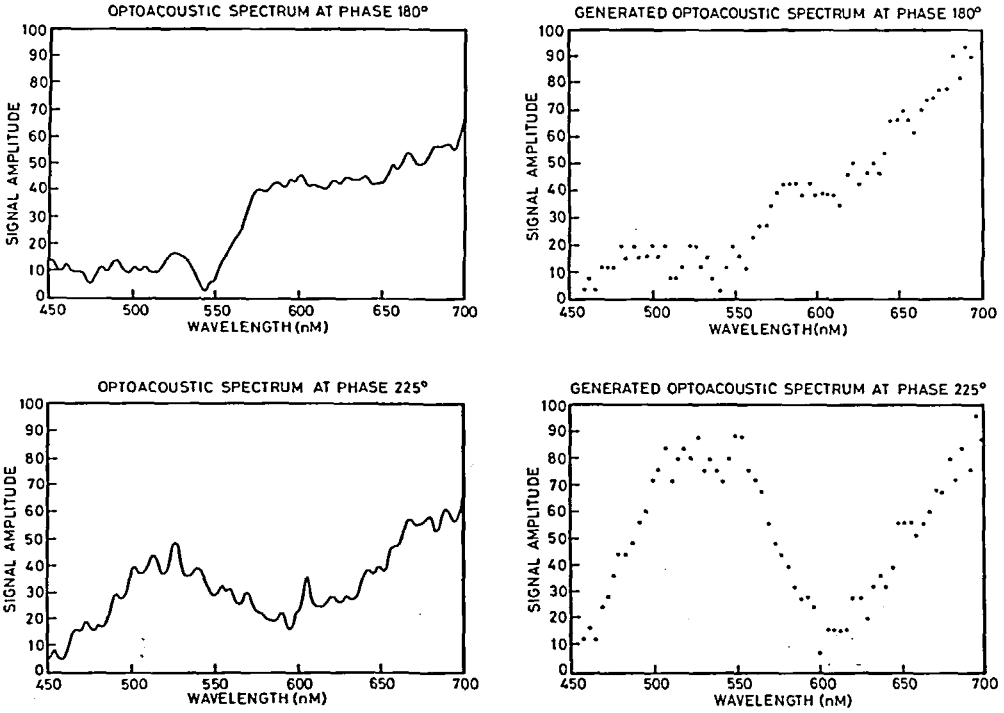


FIGURE 6. Photoacoustic spectra obtained at different phase angles for a red polymeric film on a green insulating tape. Solid spectra — experimental; dotted spectra — calculated.



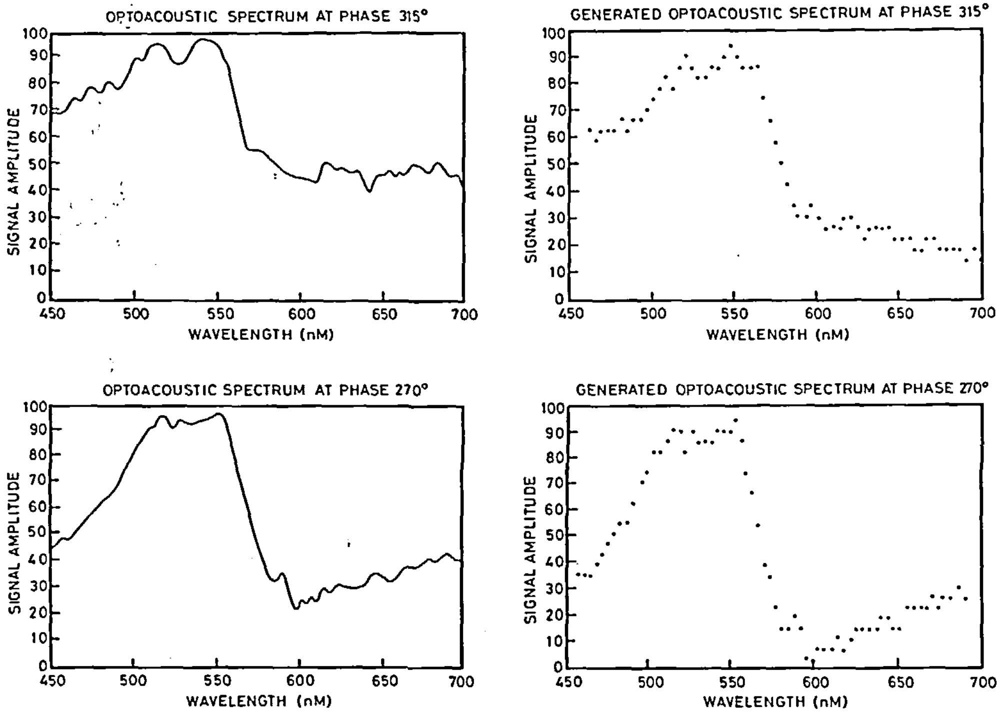
OPTOACOUSTIC SPECTRUM AT PHASE 180°

GENERATED OPTOACOUSTIC SPECTRUM AT PHASE 180°

OPTOACOUSTIC SPECTRUM AT PHASE 225°

GENERATED OPTOACOUSTIC SPECTRUM AT PHASE 225°

FIGURE 6C



OPTOACOUSTIC SPECTRUM AT PHASE 315°

GENERATED OPTOACOUSTIC SPECTRUM AT PHASE 315°

OPTOACOUSTIC SPECTRUM AT PHASE 270°

GENERATED OPTOACOUSTIC SPECTRUM AT PHASE 270°

FIGURE 6D

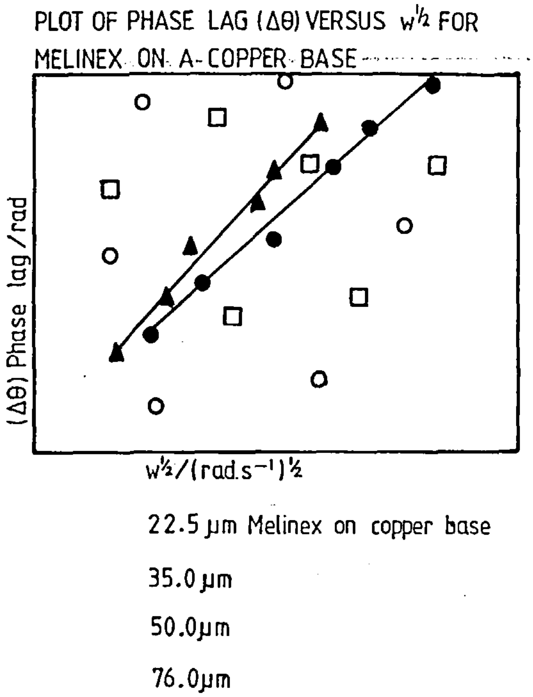


FIGURE 7. Plot of phase lag, $\Delta\theta$, vs. $\omega^{1/2}$ for melinex on a copper base. Thickness of melinex, µm: 0 22.5; 35.0; 0 50.0; 76.0.

There has been great interest in determining whether the method can be used to measure the thickness, d, of the surface film. Intuitively, one would deduce that the phase lag, $\Delta\lambda$, would be a function of d, the thermal diffusivity, α, of the surface layer, and the modulating frequency, ω. Adams and Kirkbright deduced a simple relationship,[9]

$$\Delta\Theta = d\,\frac{\omega}{2\alpha}^{\frac{1}{2}} + \beta$$

where β is a phase lag caused by instrumental characteristics. In deriving this equation, it was assumed that the surface layer, whose thickness was to be determined, could be taken as a semiinfinite solid. Nevertheless, it was shown to hold for thin films of polymer on a copper base. A reexamination[74] (Figure 7) of the system confirms that for thin films the relationship is applicable, but for thicker ones it is not. It appeared to hold for layers of carbon black deposited on a nickel-alumina-based catalyst (Figures 8 and 9).

These observations are rationalized by the theory of Mandelis, Teng, and Royce, who have studied in detail phase measurements in the PAS of solids. Their general equation (Table 1) simplifies to that given by Adams and Kirkbright, with $\beta = \frac{\pi}{4}$, for the case of a thermally thin, optically transparent film on an optically opaque substrate. If the film is appreciably thicker than the thermal diffusion length, then no contribution from the substrate is detectable. If the substrate has a lower optical absorption coefficient than the surface layer, an additional contribution will be made to the phase by the thermal diffusion times in the substrate. They conclude that phase data from PAS provides valuable insights into the properties of the system under study, but warn that because the data contain contributions from many sources that only in special limits of sample optical and

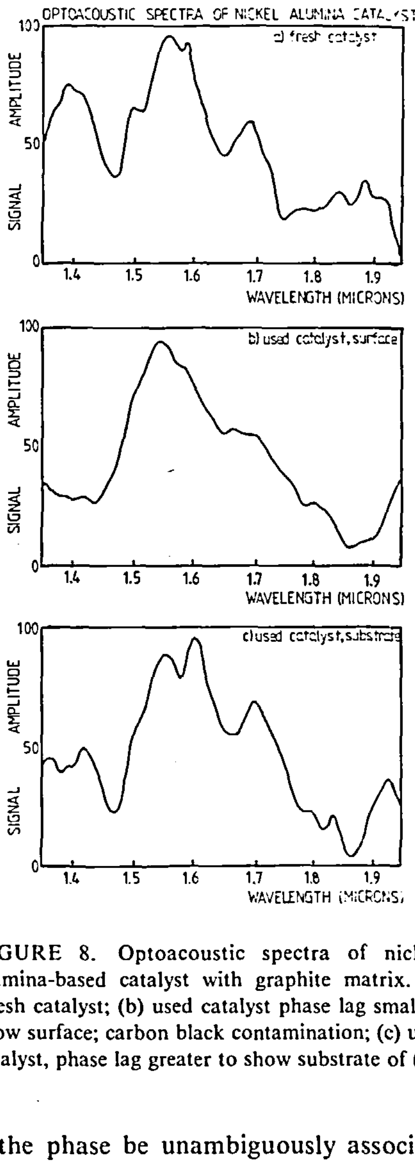


FIGURE 8. Optoacoustic spectra of nickel-alumina-based catalyst with graphite matrix. (a) Fresh catalyst; (b) used catalyst phase lag small to show surface; carbon black contamination; (c) used catalyst, phase lag greater to show substrate of (a).

thermal properties can the phase be unambiguously associated with one particular mechanism.

2. *Varying Modulation Frequency*

Rosencwaig's treatment of the photoacoustic signal from solids has led him to conclude that depth profiling can be achieved by variation of the modulation frequency.[16] The signal is a function of the thermal thickness μ_s and this varies as function of the modulating frequency as well as the thermal diffusivity of the material. It can be calculated that for the most favorable case (optically transparent surface layer on opaque backing material) the signal can be obtained from the first 0.1 μ at 10,000 to 100,000 Hz or from 10 to 100 μm at 20 Hz. Hence, by variation of the chopping frequency successive depths may be sampled.

This conclusion follows from the simplification of the basic equation for the PA signal. There are six limiting cases, and not all give rise to the possibility of depth profiling. These are shown in Figure 10. The division is based on the relative thickness of the thermal diffusion length, μ_s, compared with the thickness of the sample layer, ℓ, and the opti-

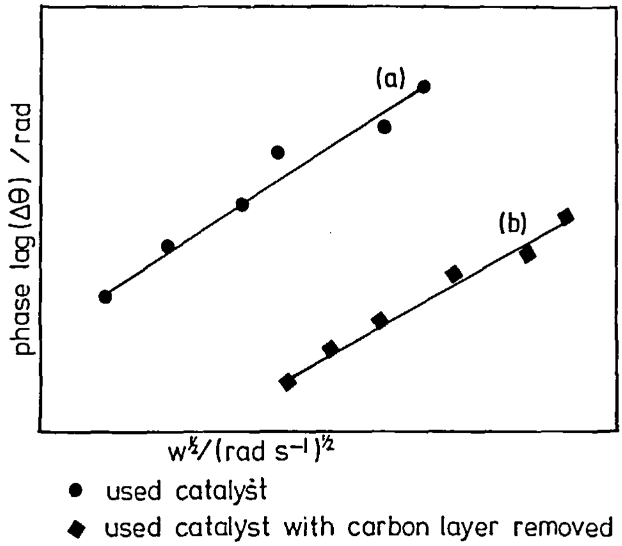


FIGURE 9. Plot of phase lag, $\Delta\theta$, vs. $\omega^{1/2}$ for nickel-alumina catalyst. (a) Used catalyst; (b) used catalyst with carbon layer removed.

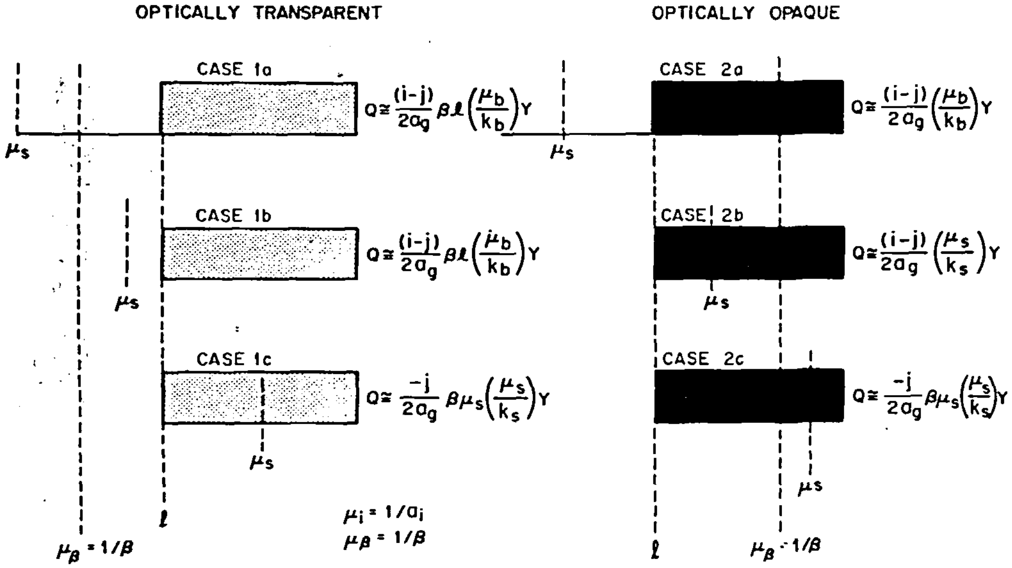


FIGURE 10. Schematic representation of special cases for the photoacoustic effect in solids.

cal absorption length $\mu_\alpha = 1/\alpha$. (It is assumed that $g < b$; $b \sim 1$, i.e., $k_g a_g < k_b a_b$; $k_b a_b \sim k_s a_s$.) Then the categories are

1. Optically transparent solids, $\mu_a > \ell$
   A. Thermally thin solid, $\mu_s >> \ell$; $\mu_s > \mu_a$
   B. Thermally thin solid, $\mu_s > \ell$; $\mu_s < \mu_a$
   C. Thermally thick solid, $\mu_s < \ell$; $\mu_s << \mu_a$

2. Optically opaque solid; $\mu\beta >> \ell$
   - A. Thermally thin solid, $\mu_s >> \ell$; $\mu_s >> \mu\alpha$
   - B. Thermally thick solid, $\mu_s > \ell$; $\mu_s > \mu_\alpha$
   - C. Thermally thick solid, $\mu_s < \ell$; $\mu_s << \mu_\alpha$

In all of the simplified equations Y is defined as $\gamma P_o I_o / 2\sqrt{2}\ell_g T_o$ which always appears in the expression for Q.

When the signal is proportional to $\alpha\ell$ (1A and 1B) or independent of α (2A and 2B) it has a dependence on ω^{-1} and when it is proportional to $\alpha\mu_s$ (1C and 2C) the dependence is on $\omega^{-3/2}$. It is to be noted that an optically opaque sample will give a photoacoustic signal provided $\alpha\mu_s < 1$. For thermally thin solids, the backing material contributes to the signal.

It is evident that whatever approach is used, a knowledge of both the thermal and optical characteristics of the sample will be advantageous, and that the scope for erroneous spectral interpretation is considerable.

V. CONCLUSIONS

An instrument manufacturer once defined the three stages of instrumentation development as: (1) a large expensive black box is built to be examined by a few research groups (it doesn't matter if it works, its novelty will ensure funding); (2) the results from stage 1 are sufficiently encouraging to make refined black boxes, for a larger number of research groups (these should work and should be cheaper); and (3) success demands a robust, reliable, cheap analytical instrument (it must work, and it has to be competitive). Stage 3 is the one which is toughest.

PAS has probably reached the second stage. There are several commercial spectrometers available and a number of laboratories are trying them out. Shall we see stage 3?

Fundamentally, PAS provides little that is new by way of information. Many who are sympathetic to new spectroscopic techniques have concluded that it is not worth the investment. In the infrared region, there is little doubt that ATR and FFT interferometry provide the same type of information as easily and with greater sensitivity and resolution. In the visible region there is more to be said in favor of PAS vs. diffuse reflectance, but it is a region of less general analytical significance than the infrared. Again, at present the capabilities for depth profiling have not been demonstrated convincingly or been shown to be superior to standard IR techniques.

It is always foolhardy to write off new methods before they have been fully developed, and in the case of PAS there is considerable scope for improvements in sources and microphones. In both cases this would give rise to better sensitivity. Since there is a lot of work going on in lasers and acoustic devices, it is probable that developments in these fields over the next few years will also affect PAS instrumentation. Similarly, work on data accumulation and processing offers scope for improvement. Indeed, a Fourier transform PA spectrometer has already been described.[115,116] A photoacoustic cell as an attachment to a Fourier transform infrared spectrometer has become commercially available as this review was being written. Early reports of this are favorable and indicate that good IR spectra are obtainable on samples such as coal and materials which suffer during the preparation of KBr discs. This seems a sensible combination, since it is easy to convert from the conventional to the PAS cell and the price of the latter is modest in comparison with the total outlay.

Whatever the state of instrumentation, it must remain true that the photoacoustic signal is dependant upon the nature of the sample matrix, its particular form, and the manner of its presentation to the incident radiation. These factors may limit its use in the long run.

ACKNOWLEDGMENT

We gratefully acknowledge the Studentship for P.J.M. provided by the Science Research Council in conjunction with British Gas.

REFERENCES

1. **Bell, A. G.,** *Proc. Am. Assoc. Adv. Sci.,* 29, 115 (1880).
2. **Bell, A. G.,** *Phil. Mag.,* 11, 510 (1881).
3. **Veingerov, M. L.,** *Compt. Rend. (U.R.S.S.),* 19, 687 (1938).
4. **Veingerov, M. L.,** *Compt. Rend. (U.R.S.S.),* 46, 182 (1945).
5. **Pfund, A. H.,** *Science,* 90, 326 (1939).
6. **Luft, K. F.,** *Z. Tech. Physik.,* 24, 97 (1943).
7. **Kreutzer, L. B.,** *Anal. Chem.,* 46, 241A (1974).
8. **Rosencwaig, A.,** *Anal. Chem.,* 47, 592A (1975).
9. **Adams, M. J., King, A. A., and Kirkbright, G. F.,** *Analyst,* 101, 73 (1976).
10. **Breguet, M. A.,** *Compt. Rend. (Paris),* No. 15, 79 (1880).
11. **Mercadier, M. E.,** *Phil. Mag.,* 11, 78 (1881).
12. **Mercadier, M. E.,** *Compt. Rend.,* 91, 929 (1880).
13. **Mercadier, M. E.,** *Compt. Rend.,* 91, 982 (1881).
14. **Rayleigh,** *Nature,* 23, 274 (1881).
15. **Preece, W. H.,** *Proc. R. Soc.,* 31, 506 (1881).
16. **Hughes, Prof.,** *Proc. R. Soc.,* 29, 56 (1880).
17. **Rosencwaig, A.,** *Optoacoustic Spectroscopy and Detection,* Pao, Y.-H., Ed., Academic Press, New York, 1977, chap. 8.
18. **Rontgen, W. C.,** *Phil. Mag.,* 11, 308 (1881).
19. **Rontgen, W. C.,** *Ann. Phys. Chem.,* 12, 155 (1881).
20. **Tyndall, J.,** *Proc. R. Soc.,* 31, 307 (1881); *Nature,* 23, 374 (1881); *Chem. News,* 43, 63 (1881).
21. **Tyndall, J.,** *Proc. R. Soc.,* 31, 478 (1881).
22. **Tyndall, J.,** *Sound,* 6th ed., Longmans, Green, London, 1898.
23. **Munroe, D. M. and Reichard, H. S.,** Applications Note 147, Princeton Applied Research Corp., N.J.
24. **King, A. A.,** Ph.D. thesis, University of London, 1976.
25. **Beadle, B. C.,** Ph.D. thesis, University of London, 1978.
26. **Dewey, C. F., Jr.,** *Optoacoustic Spectroscopy and Detection,* Pao, Y.-H., Academic Press, New York, 1977, chap. 3.
27. **Rosengren, L.-G.,** *Appl. Opt.,* 14, 1960 (1975).
28. **Dewey, C. F., Jr.,** *Opt. Eng.,* 13, 483 (1974).
29. **Betteridge, D., Hallam, H. E., and Meyler, P. J.,** *Z. Anal. Chem.,* 290, 353 (1978).
30. **Rosencwaig, A. and Gersho, A.,** *J. Appl. Phys.,* 47, 64 (1976).
31. **Eaton, H. E. and Stuart, J. D.,** *Analyst,* 53 (1977).
32. **Wake, D. R. and Amer, N. M.,** *Appl. Phys. Lett.,* 34, 379 (1979).
33. **Aamodt, L. C., Murphy, J. C., and Parker, J. G.,** *J. Appl. Phys.,* 48, 927 (1977).
34. **Blank, R. E. and Wakefield, T., II,** *Anal. Chem.,* 41, 50 (1979).
35. **Adams, M. J. and Kirkbright, G. F.,** *Analyst,* 102, 281 (1977).
36. **Betteridge, D., Lilley, T., and Meyler, P. J.,** *Z. Anal. Chem.,* 296, 28 (1979).
37. **Eaton, H. E. and Stuart, J. D.,** *Anal. Chem.,* 50, 587 (1978).
38. **Robin, M. B.,** *Optoacoustic Spectroscopy and Detection,* Pao, Y.-H., Ed., Academic Press, New York, 1977, chap. 7.
39. **Gorelik, G.,** *Dokl. Akad. Nauk. S.S.S.R.,* 54, 779 (1946).
40. **Cottrell, T. L. and McCoubrey, J. C.,** *Molecular Energy Transfer in Gases,* Butterworths, Reading, Mass., 1961.
41. **Read, A. W.,** *Adv. Molec. Relax. Proc.,* 1, 257 (1967).
42. **Delany, M. E.,** Ph.D. thesis, University of London, 1959.
43. **Kaiser, R.,** *Can. J. Phys.,* 37, 1499 (1959).
44. **Tripodi, R. and Vincenti, W. G.,** *J. Chem. Phys.,* 55, (1971).
45. **Bauer, H.-J.,** *J. Chem. Phys.,* 57, 3130 (1972).
46. **Kruzer, L. B.,** *J. Appl. Phys.,* 42, 2934 (1971).
47. **Rosengren, L.-G.,** *Inf. Phys.,* 13, 109 (1973).
48. **Cannemeijer, F., De Vasconcelos, M. H., and DeVries, A. E.,** *Physica,* 53, 77 (1971).
49. **Dewey, C. F., Jr.,** *Opt. Eng.,* 13, 483 (1974).

50. **Rosengren, L.-G. and Max, E.,** *Opt. Commun.,* 11, 422 (1974).
51. **Nodov, E.,** *App. Opt.,* 17, 1110 (1978).
52. **Bennett, H. S. and Forman, R. A.,** *J. Appl. Phys.,* 48, 1432 (1977).
53. **Bennett, H. S. and Forman, R. A.,** *App. Opt.,* 16, 2834 (1977).
54. **Hunter, T. F.,** *Lasers Chem. Proc. Conf.,* West, M. A., Ed., Elsevier, Amsterdam, 1978, 427.
55. **Farrow, L. A. and Richton, R. E.,** *J. Appl. Phys.,* 48, 4962 (1977).
56. **Kerr, E. L. and Atwood, J. G.,** *App. Ont.,* 7, 915 (1968).
57. **Wrobel, J. and Vala, M.,** *J. Molec. Struct.,* 47, 267 (1978).
58. **Colles, M. J., Geddes, N. R., and Mehdizadeh, E.,** *Contempt. Phys.,* 20, 11 (1979).
59. **Thomas, L. J., III, Kelly, M. J., and Amer, N. M.,** *Appl. Phys. Lett.,* 32, 736 (1978).
60. **Somoano, R. B.,** *Angew. Chem. Int. Ed.,* 17, 238 (1978).
61. **Adams, M. J., King, A. A., and Kirkbright, G. F.,** *Analyst,* 101, 73 (1976).
62. **Bennett, H. S. and Forman, R. A.,** *App. Opt.,* 14, 3031 (1975).
63. **Kerr, E. L.,** *App. Opt.,* 12, 2520 (1973).
64. **Afromowitz, M. A., Yeh, P.-A., and Yee, S.,** *J. Appl. Phys.,* 48, 209 (1977).
65. **Aamodt, L. C. and Murphy, J. C.,** *J. Appl. Phys.,* 49, 3036 (1978).
66. **Parker, J. G.,** *App. Opt.,* 12, 2974 (1973).
67. **McDonald, F. A. and Wetsel, G. C., Jr.,** *J. Appl. Phys.,* 49, 2313 (1978).
68. **Mandelis, A., Teng, Y. C., and Royce, B. S. H.,** *J. Appl. Phys.,* 50, 7138 (1979).
69. **Kreutzer, L. B. and Patel, C. K. N.,** *Science,* 123, 45 (1971).
70. **Koch, K. P. and Lahmann, W.,** *Appl. Phys. Lett.,* 32, 289 (1978).
71. **Kreutzer, L. B., Keynon, N. D., and Patel, C. K. N.,** *Science,* 177, 347 (1972).
72. **Claspy, P. C., Ha, C., and Pao, Y.-H.,** *App. Opt.,* 16, 2972 (1971).
73. **Adams, M. J., Beadle, B. C., King, A. A., and Kirkbright, G. F.,** *Analyst,* 101, 5531 (1976).
74. **Betteridge, D. and Meyler, P. J.,** *Z. Anal. Chem.,* 300, 337 (1980).
75. **Woodmansee, W. E. and Decius, J. C.,** *J. Chem. Phys.,* 36, 1831 (1962).
76. **Cannemeijer, F., De Vasconcelos, M. H., and De Vries, A. E.,** *Physica,* 53, 77 (1971).
77. **Parker, J. G. and Ritke, D. N.,** *J. Chem. Phys.,* 59, 3713 (1973).
78. **Dewey, C. F., Jr., Kamm, R. D., and Hackett, C. E.,** *Appl. Phys. Lett.,* 23, 633 (1973).
79. **Goldan, P. D. and Goto, K.,** *J. Appl. Phys.,* 45, 4350 (1974).
80. **Kamm, R. D.,** *J. Appl. Phys.,* 47, 3550 (1976).
81. **De Groot, M. S., Emeis, C. A., Hesselman, I. A. M., Drent, E., and Farenhorst, E.,** *Chem. Phys. Lett.,* 17, 332 (1972).
82. **Angus, A. M., Marinero, E. E., and Colles, M. J.,** *Nature,* 262, 681 (1976).
83. **Webster, C.,** *New Sci.,* 17 Feb., 383 (1977).
84. **Harshbarger, W. R. and Robin, M. B.,** *Acc. Chem. Res.,* 6, 329 (1973).
85. **Rosencwaig, A.,** *Phys. Today,* 28, 23 (1975).
86. **Lahmann, W. and Ludewig, H. J.,** *Chem. Phys. Lett.,* 45, 177 (1977).
87. **Lahmann, W., Ludewig, H. J., and Welling, H.,** *Anal. Chem.,* 49, 549 (1977).
88. **Shumate, M. S., Menzies, R. T., Margolis, J. S., and Rosengren, L.-G.,** *App. Opt.,* 15, 2480 (1976).
89. **Dixon, R. N., Haner, D. A., and Webster, C. R.,** *Chem. Phys.,* 22, 199 (1977).
90. **Marinero, E. E. and Stuke, M.,** *Rev. Sci. Instrum.,* 50, 241 (1979).
91. **Ferrell, W. G., Jr. and Haven, Y.,** *J. Appl. Phys.,* 48, 3984 (1977).
92. **Kanstad, S. O. and Nordal, P.-E.,** *Int. J. Quant. Chem.,* 12, 115 (1977).
93. **Monahan, E. M., Jr. and Nolle, A. W.,** *J. Appl. Phys.,* 48, 3519 (1977).
94. **Murphy, J. C. and Aamodt, L. C.,** *J. Appl. Phys.,* 48, 3502 (1977).
95. **Ghizoni, C. C., Siqueira, M. A. A., Vargas, H., and Miranda, L. C. M.,** *Appl. Phys. Lett.,* 32, 554 (1978).
96. **Oda, S., Sawada, T., and Kamada, H.,** *Anal. Chem.,* 50, 865 (1978).
97. **Oda, S., Sawada, T., Nomura, M., and Kamada, H.,** *Anal. Chem.,* 51, 686 (1979).
98. **Adams, M. J. and Kirkbright, G. F.,** *Analyst,* 102, 678 (1977).
99. **Rosencwaig, A. and Hall, S. S.,** *Anal. Chem.,* 47, 548 (1978).
100. **Maugh, T. M.,** *Science,* 188, 38 (1975).
101. **Rosencwaig, A.,** *Science,* 181, 657 (1973).
102. **Rosencwaig, A. and Pines, E.,** *Biochim. Biophys. Acta,* 493, 10 (1977).
103. **Oda, S., Sawada, T., Moriguchi, T., and Kamada, H.,** *Anal. Chem.,* 52, 650 (1980).
104. **Chance, R. R. and Shand, M. L.,** *J. Chem. Phys.,* 72, 948 (1980).
105. **Siqueira, M. A. A., Ghizoni, C. C., Vargas, J. I., Menzes, E. A., Vargas, H., and Miranda, L. C. M.,** *J. Appl. Phys.,* 51, 1403 (1980).
106. **Thomas, R. L., Pouch, J. J., Wong, Y. H., Favro, L. D., Kuo, P. K., and Rosencwaig, A.,** *J. Appl. Phys.,* 51, 1152 (1980).

107. **Faxvog, F. R. and Roessler, D. M.,** *J. Appl. Phys.,* 50, 7880 (1979).
108. **Iwasaki, T. and Oda, S.,** *J. Chem. Phys.,* 84, 1060 (1980).
109. **Patel, C. K. N. and Tam, A. C.,** *Appl. Phys. Lett.,* 34, 760 (1979).
110. **Walzer, K. Tacke, M., and Busse, G.,** *Inf. Phys.,* 19, 175 (1979).
111. **Mackenthun, M. L., Tom, R. D., and Moore, T. A.,** *Nature,* 278, 861 (1979).
112. **Wong, Y. H., Thomas, R. L., and Pouch, J. J.,** *Appl. Phys. Lett.,* 35, 368 (1979).
113. **Fujishima, A., Masuda, H., and Honda, K.,** *Chem. Lett.,* 9, 1063 (1979).
114. **Farrow, M. M., Burnham, R. K., and Eyring, E. M.,** *NATO Adv. Study Inst. Ser. Ser. C,* C50, 161 (1978).
115. **Rockley, M. G.,** *Chem. Phys. Lett.,* 68, 455 (1979).
116. **Kato, K. and Sugitani, Y.,** *Bull. Chem. Soc. Jpn.,* 52, 3733 (1979).
117. **West, G. A. and Barrett, J. J.,** *Opt. Lett.,* 4, 395 (1979).
118. **Patel, C. K. N. and Tam, A. C.,** *Appl. Phys. Lett.,* 36, 7 (1980).
119. **Saxe, J. D., Faulkner, T. R., and Richardson, F. S.,** *Chem. Phys. Lett.,* 68, 71 (1979).
120. **Kreutzer, L. B.,** *Anal. Chem.,* 50, 597A (1978).