Fosinopril sodium (Monopril) by ICP-MS. *Journal of Pharmaceutical and Biomedical Analysis* 13: 879–883.

Lewen N, Schenkenberger M, Raglione T and Mathew S (1997) The application of several atomic spectroscopy techniques in a pharmaceutical analytical research and development laboratory. *Spectroscopy* 12: 14–23.

Ma TS (1990) Organic elemental analysis. *Analytical Chemistry* 62: 78R–84R.

(1992) *Physician's Desk Reference*, 46th edn. Medical Economics Data, a division of Medical Economics Company. 1992.

Rousselet F and Thuillier F (1979) Atomic absorption spectrometric determination of metallic elements in pharmaceutical products. *Progress in Analytical Atomic Spectroscopy* 1: 353–372.

Schulman SG and Vincent WR (1984) Atomic spectroscopy (in pharmaceutical analysis). *Drugs Pharmaceutical Science* 11: 359–399.

Taylor A, Branch S, Crews HM and Halls DJ (1993) Atomic spectroscopy update – clinical and biological materials, foods and beverages. *Journal of Analytical Atomic Spectrometry* 8: 79R–149R.

United States Pharmacopeial Convention (1975). *The United States Pharmacopeia*, nineteenth revision.
http://www.searlehealthnet.com/pipeline.html
http://www.allp.com/drug _dev.html

Photoacoustic Spectroscopy, Applications

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ELECTRONIC SPECTROSCOPY/
VIBRATIONAL, ROTATIONAL &
RAMAN SPECTROSCOPIES
Applications

Introduction

In conventional absorption spectroscopy the measurement of absorption is transferred to a measurement of the radiation power transmitted through the sample. On the contrary, in photoacoustic spectroscopy, the absorbed power is determined directly via its heat and hence the sound produced in the sample. Photoacoustics, also known as optoacoustics, was pioneered by AG Bell, in 1880. The photoacoustic (PA) effect concerns the transformation of modulated or pulsed radiation energy, represented by photons, into sound. In general, two aspects have to be considered: first, the heat production in the sample by the absorption of radiation; and secondly, the resulting generation of acoustic waves. Closely related to the PA effect are photothermal (PT) phenomena which are caused by the original heating via absorption of radiation. While the PA effect is detected via acoustic sensors such as microphones, hydrophones or piezoelectric devices, the PT phenomena are sensed via the induced changes of the refractive index of the media by probe beam deflection, thermal lensing or, also, PT radiometry. Both PA and PT spectroscopy are widely used today in many applications. Experimental aspects are outlined in a separate article while this article discusses the main characteristics of this spectroscopic tool. The great potential is illustrated with examples from applications on solids, liquids and gases as well as in life sciences.

Spectroscopic applications

PA and PT phenomena are widely used for numerous non-spectroscopic applications such as the determination of thermal diffusivity, non-destructive testing of materials (in particular the probing of sub-surface defects) by thermal wave imaging, time-resolved studies of de-excitation processes or on biological photoreceptors, studies of phase transitions, etc. Here, only spectroscopic applications are considered that demonstrate the main characteristics and the potential of photoacoustic spectroscopy (PAS). In the following, illustrative examples are presented for solids, liquids, gases, biological and medical samples.

Studies on solids

A main advantage of PAS applied to solids is the fact that no elaborate sample preparation is required and unpolished sample surfaces pose no problems. Since the PA signal is proportional to the *absorbed* energy, even spectra of strongly scattering samples, e.g. powders, can easily be measured. However, it should be

mentioned that owing to the complex nature of the signal generation involving interstitial gas expansion, etc., PA studies on powders are usually only qualitative. Another advantage is the high sensitivity that is achieved because the PA detection is a null method for measuring absorption. Hence, absorbances as low as 10^{-7} can be detected. For modulated radiation a simple theoretical model has been developed which is based on the fact that the acoustic signal is due to a periodic heat flow from the solid to the surrounding gas, as the solid is cyclically heated by the absorption of the chopped light. Six different cases are distinguished, depending on the optical and thermal properties of the solid samples. This allows the unique feature of measuring totally opaque materials which is impossible by conventional transmission measurements. Hence PAS is technique to study weak bulk and surface absorption in crystals and semiconductors, to evaluate the level of absorbed energy in thin films, to measure the spectra of oxide films in metals, various powders, organic materials, etc. and also to investigate multi-layered samples.

An early example is shown in **Figure 1** for the insulator Cr_2O_3. Spectrum (A) depicts the normalized PA spectrum of Cr_2O_3 powder in the 200 to 1000 nm region. In comparison spectrum (B) shows an optical absorption spectrum obtained on a 4.4 μm thick bulk crystal, taken parallel and vertical to the crystal *c*-axis whereas spectrum (C) represents a diffuse reflection spectrum of Cr_2O_3 powder. The advantage of PAS is obvious in that the two crystal-field bands of the Cr^{3+} ion at 460 and 600 nm are almost as clearly resolved in the PA spectrum of the powder as they are in the crystal spectrum, and substantially better resolved than in the diffuse reflectance spectrum. It should be noted, however, that the theoretical description of the PA effect in strongly scattering media is not straightforward and quantitative data are therefore difficult to determine from such spectra.

Another example concerns adsorbates on the surfaces of solids. PAS is expected to be rather sensitive to surface adsorption, especially if the substrate is transparent or highly reflective in the wavelength region in which the adsorbate absorbs. Both sinusoidal modulation of the incident laser beam and pulsed lasers have been used for this purpose. An interesting version is the modulation of the laser beam polarization to suppress the background signal that originates from substrate absorption. A fraction of only 0.005 of a monolayer of ammonia (NH_3) adsorbed on a cold silver substrate in ultrahigh vacuum was detected. An example is shown in **Figure 2** where the PT signal is recorded as a function of time as ammonia is slowly admitted to the system and condenses
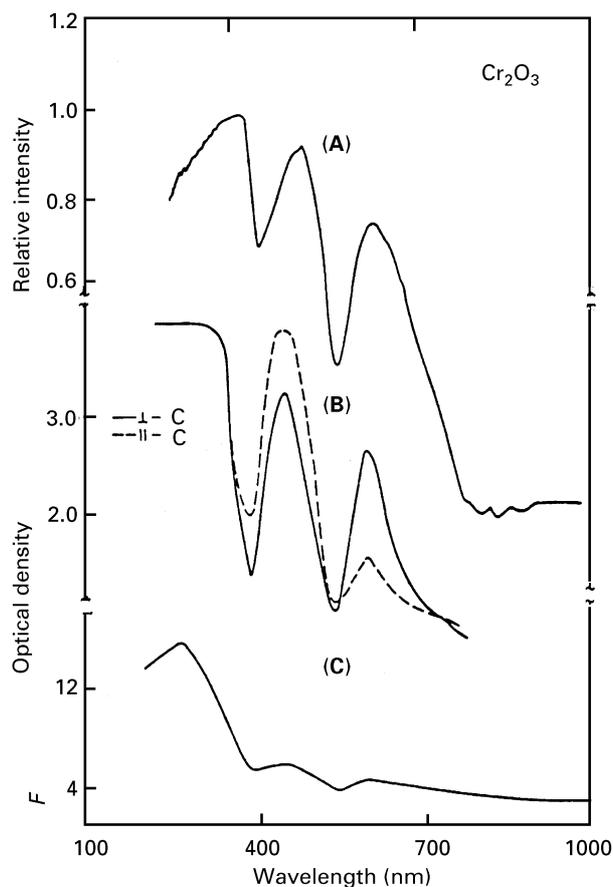

Figure 1 (A) Normalized PA spectrum of Cr_2O_3 powder, (B) optical transmission spectrum of a 4.4 μm thick Cr_2O_3 crystal, (C) diffuse reflectance spectrum of Cr_2O_3 powder. All spectra were taken at 300 K. Reproduced with permission of Academic Press from Rosencwaig A (1977). In: Pao Y-H (ed) *Optoacoustic Spectroscopy and Detection*. New York: Academic Press.

on the silver substrate. The signal of a microbalance as indicator of molecular coverage is monitored simultaneously. Later studies were aimed at investigating the kind of adsorption in more detail, e.g. to differentiate between chemisorption and physisorption, by combining the high spectral resolution and high sensitivity offered by pulsed laser PAS.

In other studies, the wide free spectral range offered by Fourier transform infrared (FTIR) spectroscopy combined with the step-scan methods has been increasingly applied in conjunction with PA detection for infrared spectral depth profiling of laminar and otherwise optically heterogeneous materials. IR spectra that are often unavailable by use of other techniques become accessible from samples that are strongly absorbing or even opaque, from strongly light-scattering samples and from samples in situ. The scheme is also applied as an analytical tool for chemical characterization and quantification, e.g. of
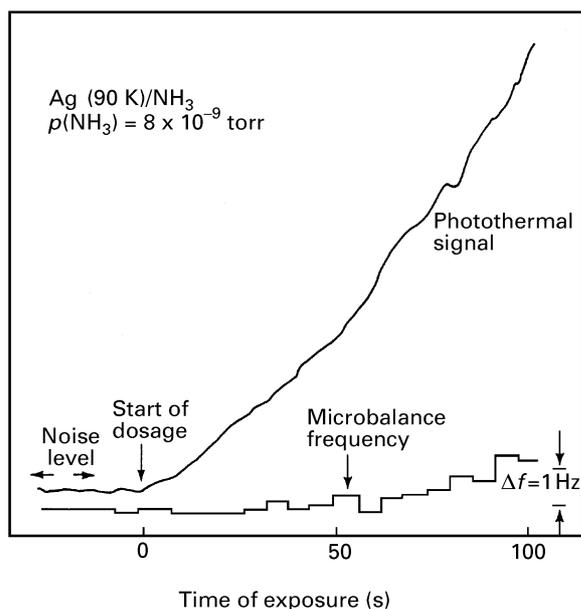
Figure 2 Photothermal signal and microbalance record versus exposure time as ammonia molecules are slowly adsorbed on a silver substrate. The maximum coverage is 0.8 monolayers, the ammonia partial pressure in the system is 8×10^{-9} torr. The noise level (left) indicates the signal from the clean substrate. Reproduced with permission of Elsevier from Coufal H, Trager F, Chuang T and Tam A (1984) *Surface Science* **145**: L504.

polychlorinated biphenyls (PCBs) in industrial waste management such as PCB contamination of soils.

Finally, the available spectral range for PA studies on solids has been extended to the X-ray region by using hard X-rays from synchrotron radiation. As an example, the X-ray absorption near Cu K-edge regions has been measured on copper (Cu), Cu alloys (brass) and Cu compounds (CuO, Cu_2O and $CuInSe_2$) with a PA detector and compared with the usual X-ray absorption (10 μm thick Cu and brass foils and < 50 μm thick powdered samples of CuO, Cu_2O and $CuInSe_2$ put on Scotch tape were used as specimens). It was found that the energy peak values derived from the PA spectra agree with those deduced from optical density spectra, suggesting that the heat production processes are also reflected in the absorption spectra. A more detailed insight is obtained by dividing the PAS data by the optical density data, i.e. by forming the ratios PAS:$\log(I_0/I_t)$, which are proportional to the heat production efficiency. In **Figure 3** these ratios are plotted for Cu, Cu_2O and $CuInSe_2$ versus the photon energy near the K-edge of Cu. The results clearly indicate differences between X-ray absorption and PA spectra and hence imply a spectral variation of the heat production efficiency. Obviously, the heat production process is also different in Cu_2O compared with the other Cu compounds.

Studies on liquids

Experimental and theoretical PA and PT studies on liquids comprise a wide absorption range from 'transparent' to opaque liquids.

For investigations on weakly absorbing media a flash-lamp-pumped dye laser with pulse energies of 1 mJ was used as excitation source and a submersed piezoelectric transducer for detecting the generated acoustic signals. The high sensitivity permits, e.g. the recording of the water spectrum in the visible range where accuracies of other techniques such as long-path absorption measurements are often limited. Another example concerns the study of weak overtones of the C–H stretch absorption band of hydrocarbons up to the 8th harmonic. In **Figure 4** the absorption band of the 6th harmonic at 607 nm of benzene dissolved in CCl_4 is plotted for different dilution ratios of benzene. With increasing dilution, the absorption peak is obviously blue-shifted and both the line width and the line asymmetry decrease. These and other results demonstrate that PAS permits the measurement of minimum absorption coefficients of 10^{-6} cm^{-1}, corresponding to absorbed laser pulse energies of only 1 nJ.

Another field of interest concerns analytical investigations on pollutants in liquids. Detection limits in the sub-ppb range were achieved by PAS, e.g. for carotene or cadmium in chloroform or for pyrene in heptane. More recently, pesticides in aqueous solutions have attracted interest. Different experimental arrangements with pulsed or CW pump lasers and various PA and PT lens detection schemes were used in these studies. Limits of detection are down to below 10^{-6} cm^{-1}, corresponding to ppb concentrations. An example is presented in **Figure 5** where the calibration curves for the detection of the dinitrophenol herbicide DNOC in aqueous solutions are compared with the untreated standard solution. The techniques used involved PT techniques, namely PT deflection spectroscopy (PDS, **Figure 5A**), thermal lensing (TL, **Figure 5B**), PT interferometric spectroscopy (PIS, **Figure 5C**), PAS (**Figure 5D**) and a conventional spectrophotometer (Cary 2400, **Figure 5E**). Obviously, the detection limit of the spectrophotometer in the low ppb (μg kg^{-1}) range is exceeded by the PA and PT methods. In particular, TL and PDS appear superior in the determination of environmental pollutants. It should be noted that both US and EU standards require detection limits of 0.1 μg L^{-1} for pesticides in drinking water.

On the other end of the scale are opaque or strongly absorbing liquids. PA spectroscopy offers the great advantage that absorption coefficients that are two to three orders of magnitude higher than is
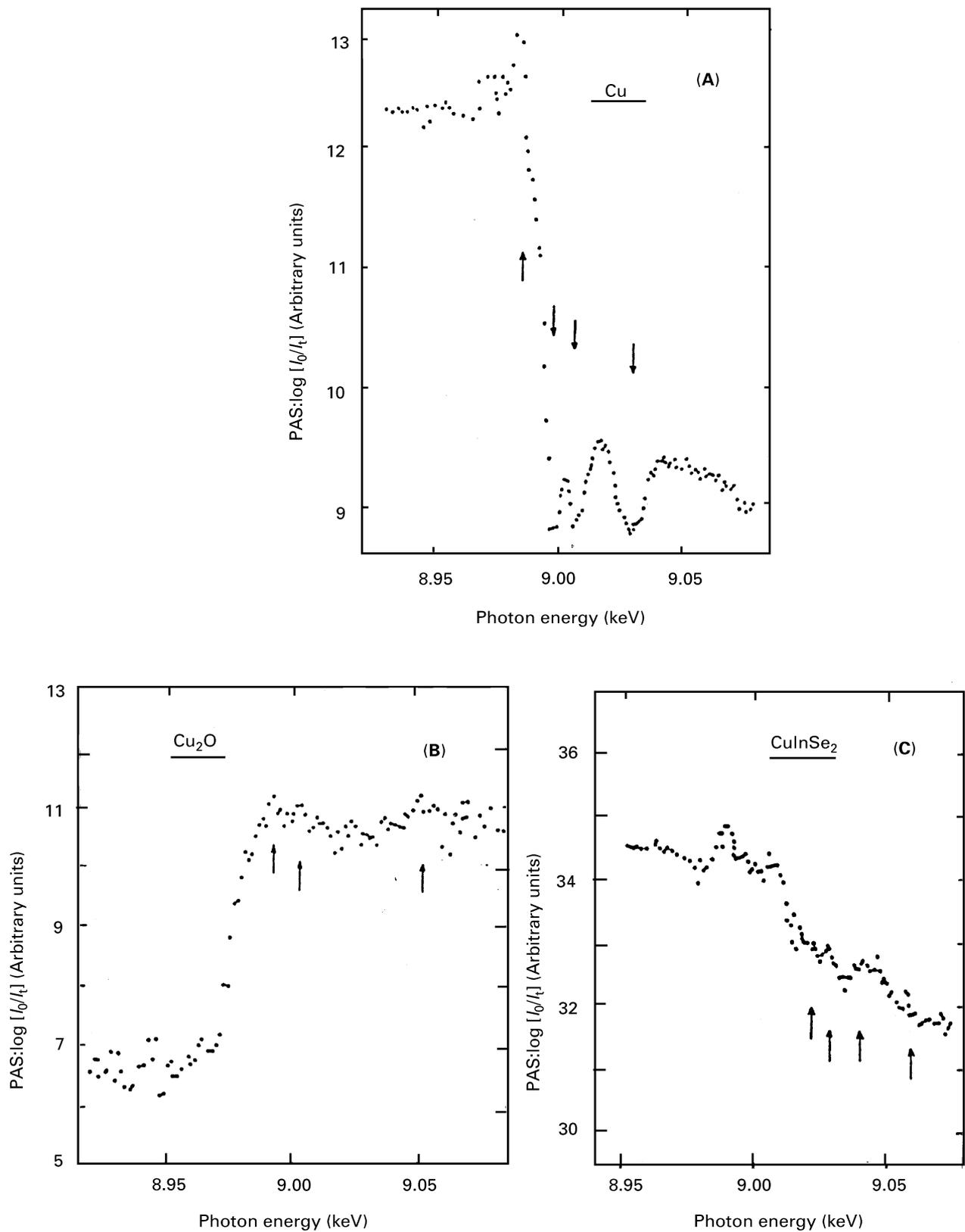
Figure 3 X-ray PA spectra normalized with optical transmission spectra (PAS : $\log I_0/I_t$), where I_0 and I_t denote the incident and transmitted intensity, respectively, at the K-edge region for different copper compounds. (A) Pure Cu, (B) Cu_2O and (C) $CuInSe_2$. Reproduced with permission of IGP AS, Trondheim, Norway from Toyoda T, Masujima T, Shiwaku H and Ando M (1995) *Proceedings of the 15th International Congress on Acoustics*, Vol I, 443.
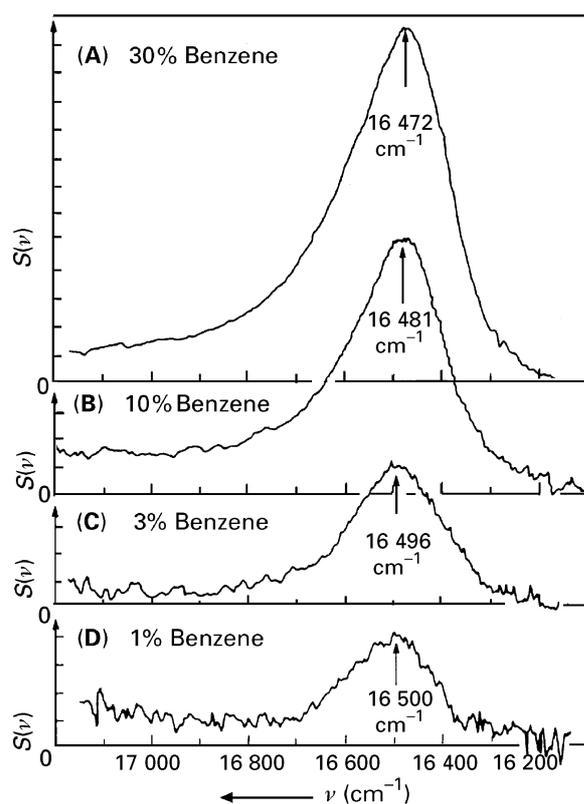
Figure 4 PA spectra of the 6th harmonic absorption of the C–H bond of benzene dissolved in carbon tetrachloride (CCl_4) in arbitrary linear units, as the volume dilution ratios indicate. The positions of the absorption peaks are given. Reproduced with permission of the Optical Society of America (OSA) from Tam AC, Patel C and Kerl R (1979) *Optics Letters* **4**: 81.

accessible by conventional transmission spectroscopy can be determined without difficulties. Various schemes have been proposed for this case including the optothermal window. As example, the *trans*-fatty acid (TFA) content of margarine was determined using a CO_2 laser and the optothermal window. Good agreement with alternative techniques such as FTIR, gas–liquid chromatography and thin-layer chromatography was obtained.

Studies on gases

Early PAS studies on gases had already demonstrated the high sensitivity that is achieved with a rather simple setup and have subsequently favoured further developments in trace gas monitoring. In comparison with conventional optical absorption measurements, PAS offers the following main advantages: (i) only short pathlengths are required which enables measurements at wavelengths outside of atmospheric transmission windows, (ii) the microphone as detector represents a simple room-temperature device with a wavelength-independent responsivity, (iii)
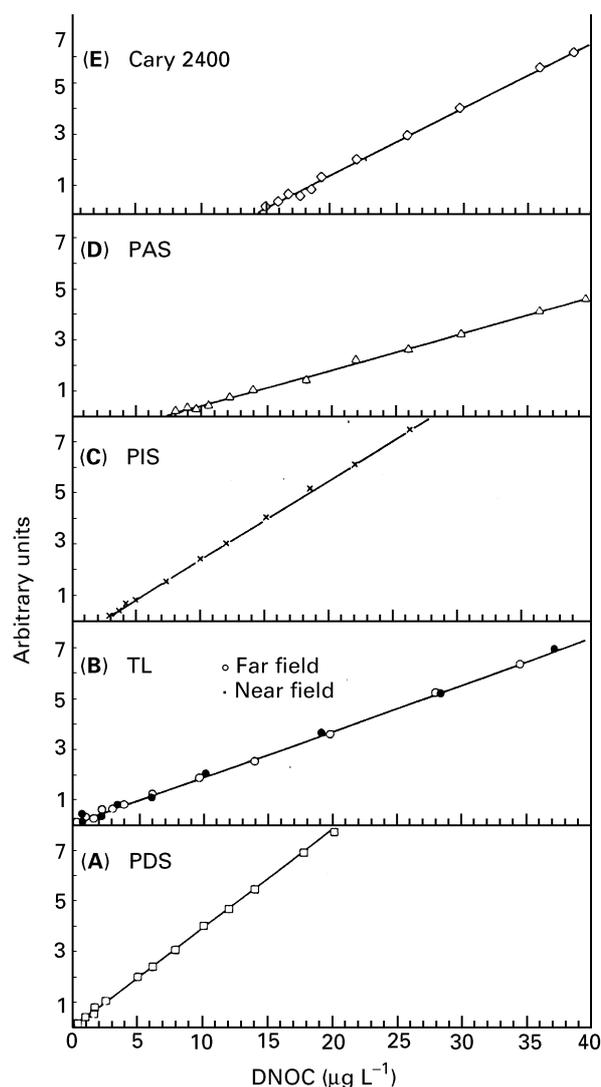
Figure 5 Calibration curves for the dinitrophenol herbicide DNOC in aqueous solution when using different techniques: (A) PDS: Photothermal deflection spectroscopy, (B) TL: thermal lensing, (C) PIS: Photothermal interferometric spectroscopy, (D) PAS: a photoacoustic spectroscopy, (E) a conventional spectrophotometer Cary 2400. Reproduced with permission of SPIE from Faubel W (1997) Detection of pollutants in liquids and gases. In: Mandelis A and Hess P (eds) *Life and Earth Sciences*. Progress in Photothermal and Photoacoustic Science and Technology, Vol III, Chapter 8. Bellingham: SPIE.

scattering effects are less important, and (iv) the dynamic range comprises at least five orders of magnitude. Measurements are generally performed with the gas either contained in or flowed through a specially designed PA cell. Typically, a minimum detectable absorption coefficient α_{min} of the order of 10^{-8} cm^{-1} atm^{-1}, corresponding to ppb (10^{-9}) concentrations, i.e. densities of μg m^{-3}, is achieved with laser-based setups. At the cost of dynamic range this limit can be lowered further to the <100 ppt range by

Table 1 List and detection limits of selected gas species monitored by laser PAS under interference-free conditions

Species	Type of laser	Spectral region (μM)	Detection limit [ppb]
Formic acid	Dye	220[a]	140
Sulfur dioxide	Dye	290–310[a]	0.12
Formaldehyde	Dye	303.6[a]	50
Nitrogen dioxide	Kr+	406.8[a]	2
Methane	DF	3.8	Few
Nitrous oxide	DF	3.8	Few
Carbon monoxide	$PbS_{1-x}Se_x$	4.6	40
Nitric oxide	CO–SFR	5.3	<0.1
Phosgene	CO	5.45	Few
Acetaldehyde	CO	5.66	3
Carbon disulfide	CO	6.48	0.01
Ethane	CO	6.7	1
Pentane	CO	6.8	0.1
Trimethyl amine	CO	6.93	10
Dimethyl sulfide	CO	6.95	3
Acetylene	CO	7.2	1
Hydrazines	CO_2	9–11	<10
Freons	CO_2	9–11	< 4
Explosives	CO_2	9–11	0.2–25
Ammonia	CO_2	9.22	0.4
Ethanol	CO_2	9.46	17
Ozone	CO_2	9.50	13
Methanol	CO_2	9.68	5
Ethylene	CO_2	10.53	0.3
Sulfur hexafluoride	CO_2	10.59	0.01
Vinyl chloride	CO_2	10.61	20

[a] In nm.

operating the PA cell intracavity. **Table 1** lists some gaseous compounds, laser sources used and (extracavity) detection limits achieved.

In practice, one usually deals with multicomponent samples. The analysis is done on the basis of the individual spectra and measurements performed at properly selected wavelengths to reduce absorption interferences. Apart from the PA signal amplitude the PA phase yields additional information for the analysis. A broad tuning range of the laser source and a narrow line width are advantageous for obtaining a high selectivity which is further enhanced for species with well structured spectra.

Most PA studies on trace gases have been devoted to laboratory investigations on collected air samples of different origin such as vehicle exhausts or industrial emissions. If the temporal evolution of the gas composition is of interest, the air is flowed continuously through the PA cell and the laser is switched repeatedly between appropriate wavelengths that are characteristic for the absorption of the gases to be recorded. In addition to laboratory analyses field studies yielding temporally and spatially resolved data on ambient trace gas concentrations and on their distributions are required to obtain a profound knowledge of atmospheric chemistry as well as of emission processes. Unlike lidar or long-path absorption measurements in the open atmosphere, PA schemes are not suited for remote studies but are applied to in situ measurements for the simultaneous monitoring of various compounds. Apart from non-laser based PA gas sensors only a few mobile laser PA systems have been operated so far. Examples include a balloon-borne system equipped with a spin-flip Raman CO laser PA spectrometer that was employed for recording stratospheric diurnal NO concentration profiles. Furthermore, a waveguide CO_2 laser PA system was applied successfully to in situ measurements at a power plant where the commonly used scheme for the reduction of the emission of nitric oxides (NO_x) by injection of ammonia (NH_3) into the combustion process was to be tested. This required a reliable, fast and selective monitoring of NH_3 down to the 1 ppm level under rough measurement conditions. Studies of this type at power-, incineration- or industrial-plants play a key role for the evaluation of the pollution, for the emission control and the testing of remedial strategies.

During the last few years a fully automated CO_2 laser PA spectrometer, which is installed in a trailer, has been developed and which is operated unattended for longer time periods. The computer control ensures a proper laser wavelength selection with a long-term frequency stability of 10^{-3} cm^{-1} for ~70 laser transitions between 9.2 and 10.8 μm using $^{12}C^{16}O_2$ or for ~65 transitions between 9.6 and 11.4 μm with a $^{13}C^{16}O_2$ laser tube. The resonant PA cell is connected to a gas flow system and the air to be analysed is pumped continuously through the cell at atmospheric pressure and with a flow rate of typically 0.5–1 L min^{-1}. The air is not pretreated by any means except for measurements in dusty environments where a micropore filter is inserted into the gas stream at the air inlet. The humidity and CO_2 monitor in the air stream allow independent measurements of water vapour and CO_2 concentrations for comparison. Furthermore, the trailer is equipped with meteorological devices for wind and solar irradiance measurements. Hitherto, we have applied this mobile system to industrial stack emission sensing and ambient air monitoring in urban and rural environments. The stack emission measurements demonstrated the good time resolution and the high selectivity that are achieved in multicomponent analyses. In certain cases it could even be differentiated between isomers, e.g. between o- and m-dichlorobenzene, among various

other compounds, mostly VOCs, at ppm concentration levels. The selectivity is determined by the compound to be measured, and the tuning characteristics and bandwidth of the laser source.

The air in urban environments often contains numerous pollutants with rather high and varying concentrations. More recently, the mobile system was used in a harsh and noisy environment at the exit of a freeway tunnel to record gases emitted by road traffic during one week. The polluted air, filtered by a Teflon dust filter with a porosity of 1 µm, was flowed continuously through the PA cell and the laser was tuned sequentially to wavelengths characteristic for ammonia (NH_3), ethylene (C_2H_4) and CO_2 absorption as well as to reference wavelengths with no

appreciable absorption by these compounds. Concentration profiles of these three species could thus be recorded almost simultaneously with a time resolution of 10 min. As **Figure 6** shows, the temporal concentration data are clearly correlated with the independently monitored CO concentration and the traffic density. Rather high concentrations are recorded, particularly for ammonia which are most probably caused by the majority of those cars that are equipped with catalytic converters. Based on the gas concentrations and the calculated air flow through the tunnel the corresponding emission factors (mass of an exhaust component per vehicle and kilometre) were determined. These factors are 15 mg km^{-1} for ammonia, 26 mg km^{-1} for ethylene,
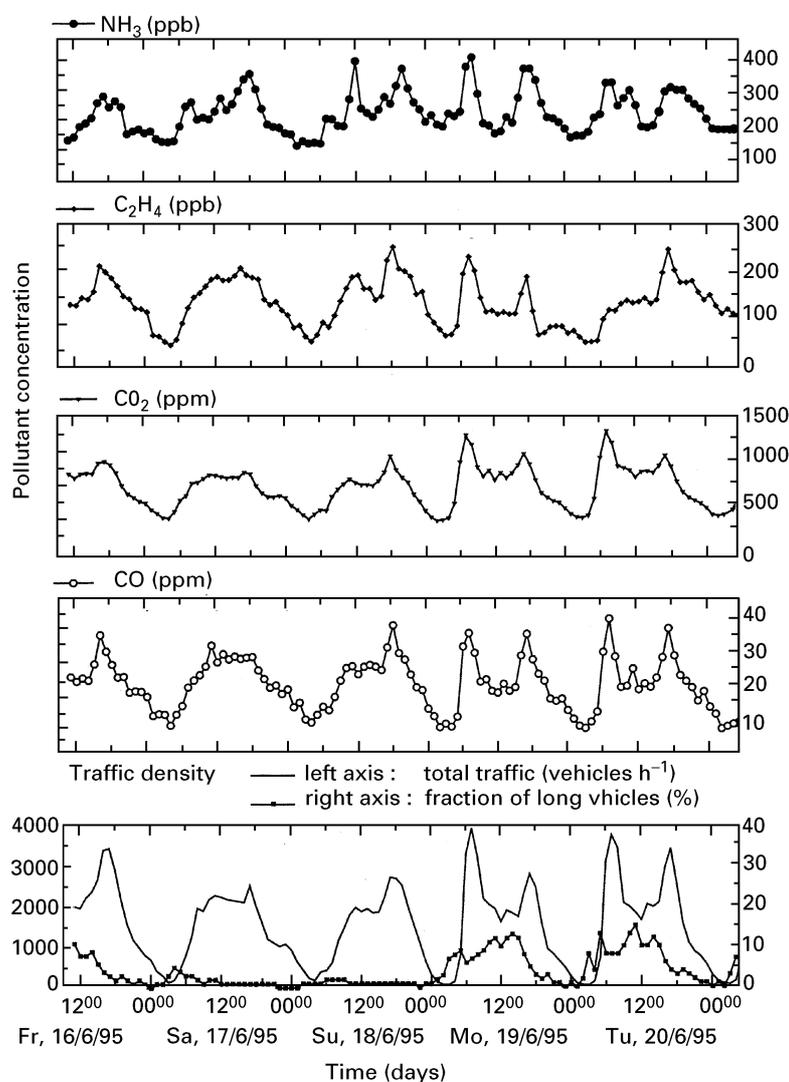

Figure 6 Temporal concentration profiles of four air pollutants during 5 days taken at the exit of a freeway tunnel. The NH_3, C_2H_4 and CO_2 were measured photoacoustically, CO was recorded with a commercial IR gas analyser. Total traffic density and fraction of long vehicles are recorded at the bottom. Reproduced with permission of the American Chemical Society from Moeckli M, Fierz M and Sigrist M (1996) *Environmental Science and Technology* **30:** 2864.
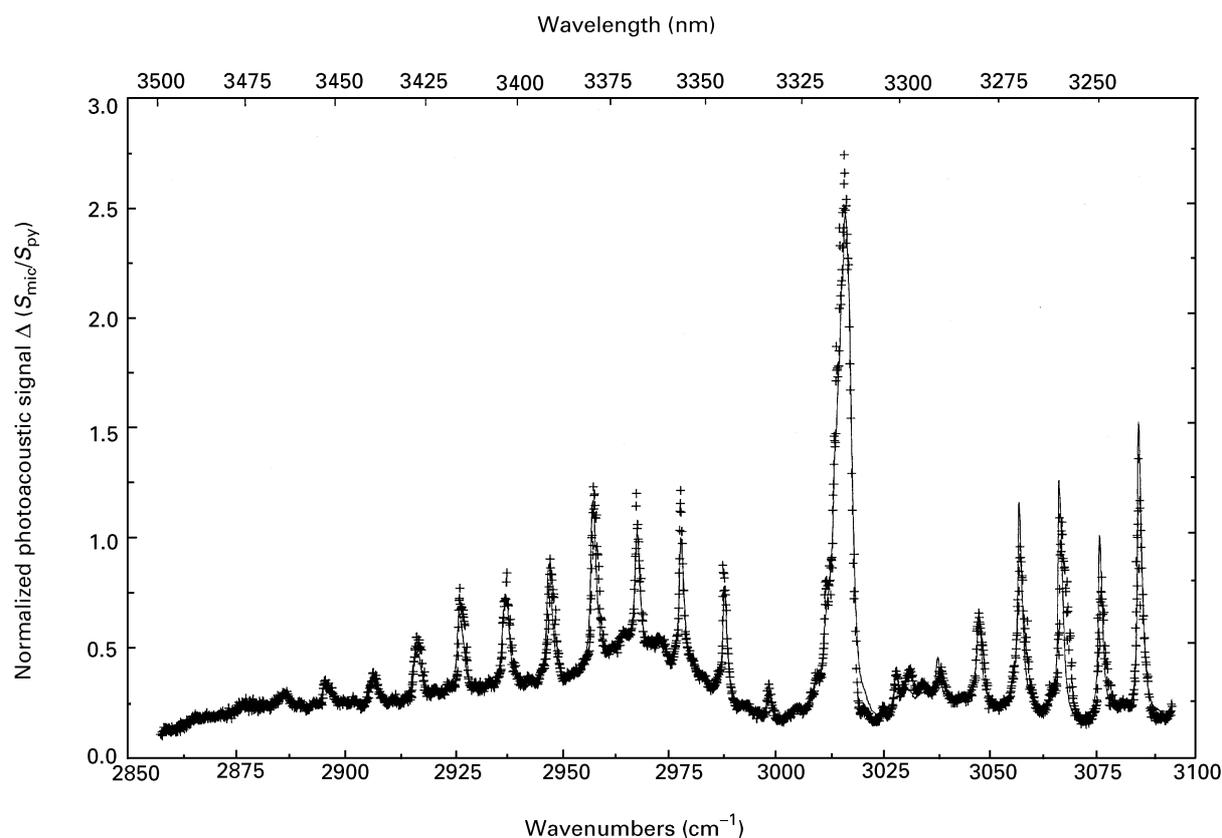
Figure 7 Spectrum of a gas mixture containing methane, methanol, ethanol, isopentane, benzene and toluene, all at ppm concentrations, buffered to 960 mbar total pressure with synthetic air (80% N_2, 20% O_2). The measured spectrum (+) was taken photoacoustically with a difference frequency laser spectrometer based on an optical parametric oscillator (OPO) with a line width of 0.2 cm^{-1}. Excellent agreement is obtained with the superimposed fitted spectrum (——) using the HITRAN database for methane and the previously recorded reference spectra for the other substances. Reproduced with permission of Elsevier from Bohren A and Sigrist M (1997) *Infrared Physics and Technology* **38**: 423.

5.2 g km^{-1} for CO and 201 g km^{-1} for CO_2. Such data are valuable for the estimation of the total annual emission of certain compounds from road traffic and their fractions of the total load in certain area.

Ambient monitoring in rural air requires detection schemes with very high sensitivity. So far, studies of PA sensing have concentrated on a few gases. An example concerns the in situ recording of ambient NH_3, H_2O vapour and CO_2 in a heath in the central Netherlands for several months in 1989. The mobile system was applied to measurements in a rural location in central Switzerland where H_2O vapour, CO_2, NH_3, O_3 and C_2H_4 were recorded simultaneously with a time resolution of 10 min by using nine carefully selected CO_2 laser transitions.

A key issue in analysing multicomponent samples is the detection selectivity, which is strongly influenced by the tuning characteristics and line width of the source as well as by the measuring conditions themselves (e.g. reduced gas pressure). Recent laser developments can enhance the performance substantially.

A continuously tunable narrowband high pressure CO_2 laser has, for example, enabled the analysis of a mixture of six CO_2 isotopes. In one study, presented in **Figure 7**, a mixture of six hydrocarbons at ppm concentrations has been analysed by an all-solid-state laser PA spectrometer.

Studies in life sciences

The inherent high light scattering and the often strongly varying depth structure render biological and medical samples rather difficult for investigations with conventional spectroscopic tools. As various researchers, however, have demonstrated, PA and PT techniques can successfully by applied to media such as skin tissue, blood or plants. *In vivo* studies were performed on human skin with specially designed PA cells that allowed the study on living skin by avoiding the noise induced by pulsating blood. In particular, the absorption of UV light by protein (α-keratin) and the application of sunscreens to protect skin from UV damage were studied spectroscopically by the PA
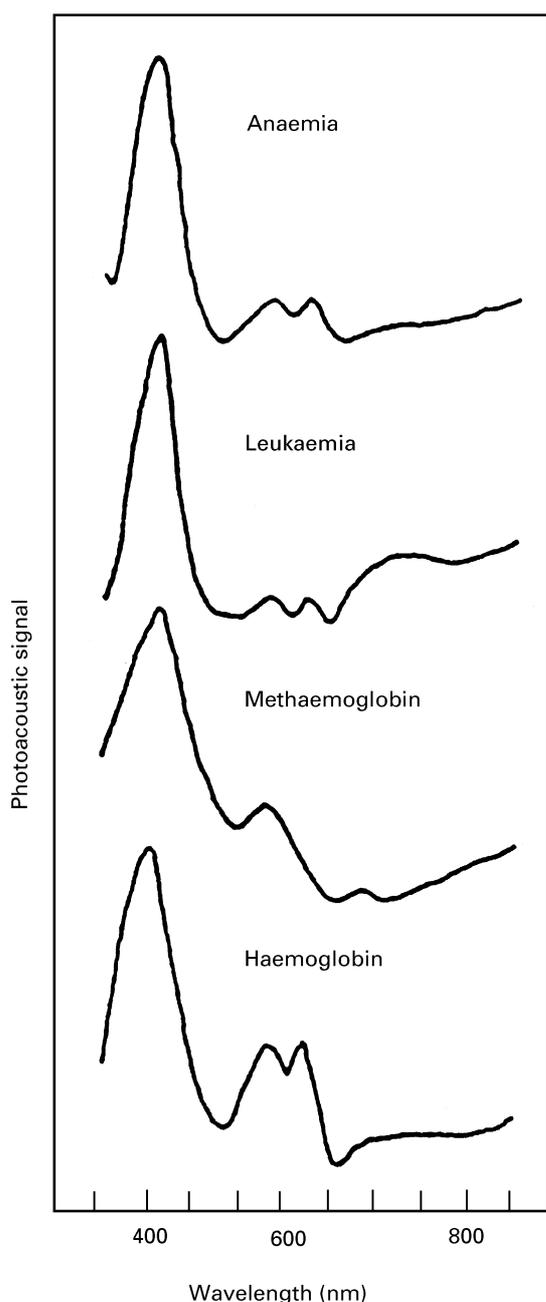
Figure 8 Photoacoustic spectra of haemoglobin and of the blood from anaemia, leukaemia and methaemoglobin patients. Reproduced with permission of Springer from Pan Q, Qui S, Zhang S, Zhang J and Zhu S (1987) Springer Series in Optical Sciences, Vol 58, 542.
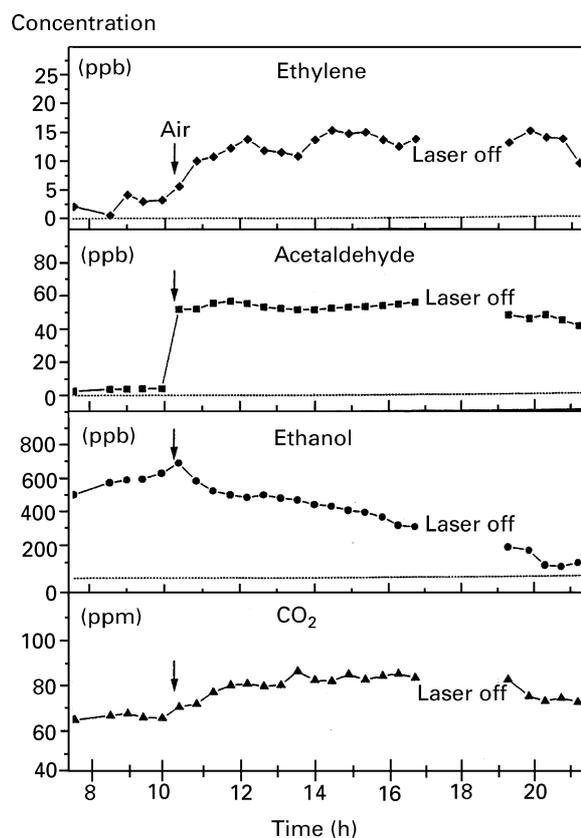

Figure 9 Temporal evolution of the emission of different gases (ethylene, acetaldehyde, ethanol and CO_2) from a cherry tomato subjected to a change from anaerobic to aerobic conditions at $t = 10.2$ h (indicated by the arrow). The emission of a reference fruit kept under aerobic conditions was subtracted to obtain the data in this figure. Reproduced with permission of SPIE from Harren F and Reuss J (1997). Applications in plant physiology, entomology, and microbiology; gas exchange measurements based upon spectral selectivity. In: Mandelis A and Hess P *Life and Earth Sciences*. Progress in Photothermal and Photoacoustic Science and Technology, Vol III, Chapter 4. Bellingham: SPIE.

technique. The dependence on the kind of sunscreen and the amount applied (in $\mu g\ cm^{-2}$) were investigated as well as the rate of penetration into the skin and the time of residence in different skin layers.

The ability of PAS to detect specific compounds present in a highly diffusive medium is a great advantage for spectroscopic studies on blood. The protein haemoglobin is responsible for the O_2–CO_2 exchange between blood and tissue. It exhibits three absorption bands, at 415, 540 and 580 nm, that are caused by the tetraporphyrin cycle bound to its amino acid skeleton. In **Figure 8** the typical haemoglobin spectrum is compared with blood spectra of patients suffering from anaemia, leukaemia and methaemoglobin. The deviations from normal blood are clearly visible and can complement other diagnostic results. The noncontact character of PA investigations and the fact that only minor sample amounts are required is another advantage that permits further studies on the same sample by alternative techniques.

It should be noted that no complicated preparation, treatment or any purification processes are required before measurements. This is advantageous

also for studies on living plants. Photosynthetic activities of plants and the influence of environmental stress have been investigated by various research groups. As example, a PA apparatus has been developed to measure the oxygen evolution rate directly at a single leaf of a living plant. Environmental factors such as the effects of water stress, temperature extremes, varying light flux and gaseous pollutants were studied in details. A study on plant physiology is presented in **Figure 9**. The measurements were performed with a CO-laser intracavity PA arrangement. To enhance the detection specificity selective trapping was applied by leading the incoming air stream over different temperature levels of a cold trap. In the experiment, three cherry tomatoes were kept under pure nitrogen in a cuvette for 10 h before switching back to an air flow. This re-exposure obviously caused significant changes of the production rates of the different compounds. This example demonstrates that the PA technique is well suited for the study of fast responses of plant tissues to changing ambient conditions.

Another area of interest where PA spectroscopy is a valuable tool concerns food science. Examples include the determination of the iron content in milk powder concentrate, moisture in instant skim milk powder, stem in ground pepper or the detection of adulterated powdered coffee. An example of a deliberate adulteration in spices concerns the contamination of ground red paprika spice by red lead (Pb_3O_4) which enhances the colour of paprika but also adds to its total weight. PA studies on ground sweet red paprika have demonstrated that PA spectroscopy can be recommended as a method for rapid and gross screening for Pb_3O_4 adulterant. The current limit of detection of 2% w/w) is, however, above the internationally adopted maximum permissible level and inferior to that of established techniques like atomic absorption spectroscopy (AAS) or inductively-coupled plasma spectroscopy (ICPS).

See also: **Environmental Applications of Electronic Spectroscopy; IR Spectrometers; Laser Applications in Electronic Spectroscopy; Photoacoustic Spectroscopy, Theory; Photoacoustic Spectroscopy, Applications; Photoacoustic Spectroscopy, Methods and Instrumentation; Surface Studies By IR Spectroscopy; Zeeman and Stark Methods in Spectroscopy, Applications.**

Further reading

Almond DP and Patel PM (1996) *Photothermal Science and Techniques.* London: Chapman & Hall.

Bialkowski SE (1996) *Photothermal Spectroscopy Methods for Chemical Analysis*, Chemical Analysis Series, Vol 134. New York: Wiley.

Bicanic D (ed.) (1998) Photoacoustic, Photothermal and related methods as problem solvers in agricultural and environmental sciences. Special Issue of *Instrumentation Science and Technology* **26** (2&3).

Hess P (ed) (1989) *Photoacoustic, Photothermal and Photochemical Processes in Gases.* Topics in Current Physics, Vol **46**. Berlin: Springer.

Hess P (ed) (1989) *Photoacoustic, Photothermal and Photochemical Processes at Surfaces and in Thin Films*, Topics in Current Physics, Vol. **47**. Berlin: Springer.

Mandelis A (ed) (1982) *Principles and Perspectives of Photothermal and Photoacoustic Phenomena*, Progress in Photothermal and Photoacoustic Science and Technology, Vol I. New York: Elsevier.

Mandelis A and Hess P (eds) (1997) *Life and Earth Sciences*, Progress in Photothermal and Photoacoustic Science and Technology, Vol III. Bellingham, Washington: SPIE.

Meyer PL and Sigrist MW (1990) Atmospheric pollution monitoring using CO_2-laser photoacoustic spectroscopy and other techniques. *Reviews of Scientific Instruments* **61**: 1779.

Pao Y-H (ed) (1977) *Optacoustics Spectroscopy and Detection.* New York: Academic Press.

Rosencwaig A (1978) Photoacoustic spectroscopy. In: *Advances in Electronics and Electron Physics*, Vol 46, Chapter 6.

Sell JA (ed.) (1989) *Photothermal Investigations of Solids and Liquids.* San Diego: Academic Press.

Sigrist MW (1986) Laser generation of acoustic waves in liquids and gases. *Journal of Applied Physics* 60: R83–R121.

Sigrist MW (1994) Air monitoring by laser photoacoustic spectroscopy. In: Sigrist MW (ed) *Air Monitoring by Spectroscopic Techniques*, Chemical Analysis Series, Vol 127, Chapter 4. New York: Wiley.

Tam AC (1983) Photoacoustics: spectroscopy and other applications. In: Kliger DS (ed) *Ultrasensitive Laser Spectroscopy*, Chapter 1. New York: Academic Press.

Tam AC (1986) Application of photoacoustic sensing techniques. *Reviews of Modern Physics* **58**: 381–431.

Zharov VP and Letokhov VS (1986) *Laser Optacoustics Spectroscopy*, Springer Series in Optical Sciences, Vol 37. Berlin: Springer.