An Overview of Applications of Photothermal Spectroscopy With Special Reference to Environmental Studies

G C Pandey* and Ajay Kumar
Research Centre, Indian Petrochemicals Corporation Limited, Baroda 391 346, India
E-mail: gepandey@wilnetonline.net

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Introduction

During last three decades photothermal (PT) based detections have received somewhat greater attention, though the basic principle of the technique [e.g., the photoacoustic (PA) effect] was known for more than a century. After a long gap, except a short spell in 1930s, a series of papers dealing with theoretical considerations, especially with the condensed phases, started appearing in late 1960s and the next three decades saw fairly fast developments both in instrumentation and applications. PA effect was extensively used both for chemical and physical analysis, especially in condensed phases, where conventional technique failed, e.g., in the analysis of highly absorbing materials. The technique essentially provides information on the thermal and absorption properties of a material or its components.

The advent of tunable lasers led to increased both sensitivity and application domain due to the availability of broader spectral range for analysis of the effect of photons on atoms and molecules, that was difficult in conventional emission and reflection based absorption spectroscopic techniques where structural characteristics are evaluated. For example, PA detection involves measurement of pressure fluctuations consequent upon non-radiative relaxation of molecules, whereas mirror effect based detection measures deflection of a probe beam as a result of change in refractive index of the medium caused by the heat transfer from the sample due to molecular relaxation. PT detection in general has given altogether a new direction to the absorption spectroscopy, trace detection, excitation transfer, and ultrasonic testing applications. Several reviews also appeared on these topics, especially for condensed phases, however, very little is available on the gas phase detection.

This paper presents an overview of various applications of PT based techniques, particularly those related to trace gas detection with special reference to lesser known areas like agriculture, environmental monitoring, etc. Potential of the technique as a tool for semiquantitative evaluation of environmental impact analysis (EIA) has also been discussed.

Principle

The PT detection is based on the principle of conversion of absorbed or incident light energy into heat energy through radiationless de-excitation process. When a sample is illuminated with a periodically chopped incident optical laser beam, a part of the energy absorbed by a sample is dissipated as heat through a nonradiative transition resulting either in a deflection of the probe beam due to change in refractive index of the medium or acoustic expansion (pressure) in the surrounding media.
at the frequency of the source intensity modulation which can be detected by a sensitive detector suitably located in the cell. The output signal is measured as a function of incident wavelength of the source which is displayed in the form of a plot. The PT based techniques could be used for analysing a variety of samples, irrespective of morphology or form, e.g., solids, liquids, vapours, powders, semi-liquids, etc. Several applications in basic sciences, material science, biology or medicine, and environmental science, etc., have been reported.

**Instrumentation**

Usually the experimental consists of (a) light source, (b) chopper (c) cell and detector, and (d) an output measuring system (Figure 2).

**Light Sources**

As already mentioned, the source of light is an important component of the measuring system and it depends upon the nature of samples to be analysed and also on analytical information required from the analyses. In principle, light sources, right from conventional UV to IR to highly specific and fixed wavelength lasers have been used. The availability of tunable, i.e., variable wavelength, laser sources have increased the potential of the technique considerably. Both continuous wave (CW) and pulsed lasers have been employed. A representative list of the different types of laser sources normally available that can be used for laser PT experiments are given in Table 1. The choice of a laser source will depend on the molecular absorption characteristics of a sample and the type of information desired from such analyses.

**Chopper**

Both, a mechanical chopper and an optoacoustic modulator have been used by different workers depending upon the application and the nature of a sample. Basically the chopping frequency provides information on the extent of the depth of a sample that can be probed by the technique.

**Cell and Detector**

Figures 3a and 3b show one of the configurations of a gas phase PA and mirage effect cells, respectively. In the case of PA, the cell (Figure 3a) consists of a closed, air-tight compartment for sample, with windows for incident light and a highly sensitive microphone, suitably located for measuring pressure variation within the cell. The configuration and dimensions of the cell are critical and decided on the basis of theoretical considerations. Mirage effect gas cell, on the other hand, does not require an air-tight cell and has the
Table 1—Some of the lasers commonly used for PT experiment

<table>
<thead>
<tr>
<th>Laser</th>
<th>Lasing wavelength (nm)</th>
<th>Region</th>
<th>Type</th>
<th>Power</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd:YAG</td>
<td>1064</td>
<td>NIR</td>
<td>Solid state (pulse and continuous wave)</td>
<td>100 mw-100 w</td>
</tr>
<tr>
<td>Second harmonic radiation</td>
<td>532</td>
<td>Visible</td>
<td>Solid state (Pulse)</td>
<td>360 mw-36.0 w</td>
</tr>
<tr>
<td>Third harmonic radiation</td>
<td>355</td>
<td>UV</td>
<td>Solid state (Pulse)</td>
<td>160 mw-15.0 w</td>
</tr>
<tr>
<td>Diode laser</td>
<td>532, 670</td>
<td>Green-visible/Red-visible</td>
<td>Solid state (continuous wave)</td>
<td>1 mw-5 mw/1 mw-10 mw</td>
</tr>
<tr>
<td></td>
<td>1064</td>
<td>NIR</td>
<td></td>
<td>10 mw-50 mw</td>
</tr>
<tr>
<td>Excimer (XeCl)</td>
<td>308</td>
<td>UV</td>
<td>Gas laser (Pulse)</td>
<td>160 mw-7 w</td>
</tr>
<tr>
<td>Excimer (KrF)</td>
<td>266</td>
<td>UV</td>
<td>Gas laser (Pulse)</td>
<td>280 mw-14 w</td>
</tr>
<tr>
<td>N2 laser</td>
<td>377.3</td>
<td>UV</td>
<td>Gas laser (Pulse)</td>
<td>10 mw-1.0 w</td>
</tr>
<tr>
<td>Ho-Ne laser</td>
<td>543.0, 632.8</td>
<td>Green-visible/Red-visible</td>
<td>Gas laser (continuous wave)</td>
<td>0.5-1.5 mw/0.5-35.0 mw</td>
</tr>
<tr>
<td>Ar2 laser</td>
<td>448, 514.5</td>
<td>Violet-visible/Green-visible</td>
<td>Gas laser (continuous wave)</td>
<td>10 mw-1 w/100 mw-10 w</td>
</tr>
<tr>
<td>CO2 laser (Tunable)</td>
<td>9000-11000</td>
<td>IR</td>
<td>Gas laser (continuous wave)</td>
<td>200 mw-50 kw</td>
</tr>
<tr>
<td>Dye laser (Tunable)</td>
<td>300-800</td>
<td>UV-visible</td>
<td>Liquid</td>
<td>0.1 mw-200 mw</td>
</tr>
<tr>
<td>T1-sapphire (Tunable)</td>
<td>695-950</td>
<td>Visible-NIR</td>
<td>Solid state (Pulse)</td>
<td>10 mw-2.5 w</td>
</tr>
</tbody>
</table>

flexibility to suit the requirements of a sample. The output from the detector is taken via a pre-amplifier to the lock in amplifier which detects both the phase and the amplitude (Figure 2).

Output

The signal generation and its detection can broadly be classified into two usual types. For laser based PT system, the main difference is in the use of laser, i.e., (i) the continuous wave (CW) laser with external modulation, or (ii) the pulsed laser. In the former, a sample is exposed to the modulated heating (laser) beam and the resultant heat, upon transfer into neighbourhood medium is measured as an electrical signal by the position sensor (mirage effect) or the microphone which is connected to the lock in amplifier or a correlator via an amplifier. The signal analysis is typically in frequency domain, and amplitude or phase of one or several Fourier components are measured. Filters are used to suppress noise, if needed. For the pulse laser, the beam is modulated at a very low duty cycles ($\text{eg} \ 10^5 \text{ Hz}$) but with high sensitivity of short duration and the detection is through box car averager in time domain and time gating can be used for noise reduction, i.e., it works as a frequency multiplexed probing with many Fourier components simultaneously.

The technique, though much more sensitive and probably the most effective for weakly absorbing samples, tends to fail for strongly absorbing materials, due to intense pulsed radiations, where well defined
modulation frequencies are needed for fixed thermal diffusion length (e.g., depth profiling, etc). The discussion will be restricted to CW lasers and give a brief overview of various applications, especially those related to the trace gas detection.

**Case Studies**

The technique essentially provides information on the photothermal and absorption characteristics of a sample or a component. The sensitivity of the measurement is directly influenced by the intensity of the source (heating) laser beam and thermo-optical properties of a sample and has been found to be better than that of conventional spectrometry by three to four orders of magnitude. The advantage of high signal to noise (S/N) ratio while retaining very good flexibility of the operation has made PT techniques the most effective for trace (gas) detection at the ppb or lower levels of concentration (Table 2).

The application areas of PT based detection for trace gas measurements have been reviewed and an overview of potential application areas of PT based detection system has been presented.

**Photodegradation Studies on Polymers**

In recent studies on photodegradation of polyethylene (PE), it was found that ethylene gas was released\(^1\). The amount of gas released was found to be characteristic of the type of PE, viz., high density polyethylene (HDPE), low density polyethylene (LDPE), produced by tubular (LDPE-T) or autoclave (LDPE-A) process, or linear low density polyethylene (LLDPE), a copolymer of PE and \(\alpha\)-olefin (e.g., butene-1, hexene-1 or octene-1). A detailed analysis was carried out to understand the mechanism of bond rupture, responsible for the release of ethylene\(^2\). Apart from the fundamental understanding, the unique conclusion of the study was that the concentration of ethylene gas released, under similar condition of photoexposure, was dependent upon the type of PE (Figure 4). The following trend was observed in different PEs in the concentration of ethylene gas released, viz., LDPE (T) > LDPE-A > LLDPE (C\(_x\)) > HDPE.

The above trend being reproducible has a potential application in fast identification of different PEs, which is a cumbersome and time taking process conventionally. Possibility of using the approach for recovery of monomer from waste PEs is another area, which still needs to be explored.

**Identification of Halogen in Air or Inert atmosphere**

Halogens like any other gas molecules have characteristic absorption spectrum. Laser PA has been used to study the absorption characteristics of pure halogens (i.e., Br, F).

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**Table 2**—Detection limits of some of the organic volatile compounds measured by the gas phase mirage setup

<table>
<thead>
<tr>
<th>Gas</th>
<th>Detection limit (ppb)</th>
<th>Gas</th>
<th>Detection limit (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_2)H(_4) (Ethylene)</td>
<td>0.25</td>
<td>C(_2)H(_5)Cl (Vinyl chloride)</td>
<td>45</td>
</tr>
<tr>
<td>C(_3)H(_5)Cl, H (Trichloroethylene)</td>
<td>2.5</td>
<td>SO(_2)</td>
<td>240</td>
</tr>
<tr>
<td>C(_4)H(_6) (Benzene)</td>
<td>12</td>
<td>NO(_2)</td>
<td>10</td>
</tr>
<tr>
<td>C(_5)H(_11) (Xylene)</td>
<td>20</td>
<td>NH(_3)</td>
<td>0.5</td>
</tr>
<tr>
<td>CFC-11/Freon-11</td>
<td>0.6</td>
<td>O(_3)</td>
<td>2.5</td>
</tr>
</tbody>
</table>

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Figure 3b—Schematic diagram of Mirage (effect) gas cell
or I$_2$, and in the presence of air or an inert atmosphere. The extent of band shift as a function of concentration has been attributed to the intermolecular collision in the gas, the extent of which was found to be different depending upon the number of components.

**Agricultural Applications**

Molecules like $C_2H_4$, $NH_3$, $O_3$, and $H_2O$ having vibrational absorption in the infrared region are well known to be released by plant kingdom during natural processes, e.g. during germination of seeds, ripening of fruits, or during the period of external stresses like the effect of acid rains on plants’ leaves or when a fruit is pricked externally. It may be mentioned here that though release of ethylene gas is rather well known/established, availability of methods to measure extremely low concentrations of $C_2H_4$ has invariably been a limiting factor. It is one of the major reasons why very little is known or reported on ethylene as a bio-indicator.

Effects of stimulants on the extent of germination of seeds of parasitic weed *Striga hermonitica* has recently been reported. The activity range of stimulants on seed germination was studied by PA technique and compared with conventional methods of per cent germination and also the concentration of $C_2H_4$ released, simultaneously. The per cent germination and ethylene release trends showed similar response supporting the fact further that release of ethylene can be used as a good bio-indication of germination of seeds (Figure 5). In another study, the same group used laser PA system for the detection of $C_2H_4$ emission of a single orchid flower after emasculation. Mirage effect spectroscopy has been used recently to measure the emission of ethylene gas during fruit ripening.

**Aerosols**

Aerosols are dispersions of particulate matter suspended in gas phase ranging in number density from single isolated particle to dense system (over $10^{12}$ cm$^{-3}$) and having characteristic dimensions from macroscopic (mm) down to the molecular levels. The chemistry and physics of such particles may differ from the original carrier gas or indeed even from the bulk condensed phase. The significance of studies of aerosols range from environmental science, meteorology, astronomy, combustion chemistry, surface science and optics which, in turn, lead to solutions to many problems of technological significance.

The absorption properties of aerosols are very important (e.g., laser propagation through atmosphere, solar heating and its effects on global temperature and, of late, particulate analysis) but the conventional transmission based measurements are limited due to light scattering which obscures light absorption and/or wing absorptions by background gases such as water vapour. For example, smog chamber studies invariably are limited to gaseous components only. PT based spectroscopy on the other hand allows particle specific absorption to be measured irrespective of their scattering or gaseous environment. The techniques may be used to measure the combined particle specific characteristics (i.e., signal that is of first order, free from the larger gaseous absorption contribution) and are sufficiently sensitive to characterize single micrometer-sized particle. Recently, Campillo and Lin, have reported a review on the topic covering various aspects of PT spectroscopy of aerosols with special emphasis on three very promising techniques, viz., PT interferometry, PT modulation of

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**Figure 4**—$C_2H_4$ references and sample spectra

**Figure 5**—Germination and ethylene gas production ($\Box$) and ethene (●) germination.
elastic scattering and photophoretic spectroscopy. The developments in this application area have been sudden and as a field of research, it is still in its infancy. Sensitivity limits are expected to approach to that of photon noise.

**Monitoring of Atmospheric Pollution**

Almost any atmospheric pollutant has a characteristic spectral fingerprint in the infra-red region (2-20 μ) and, hence, absorption IR spectroscopy has extensively been used for air pollution analysis. Spectroscopic techniques, based on interaction of laser radiation (high power, temporal and spatial coherences) with gaseous molecular species have attracted world wide attention. Despite the large amount of work reported on single pollutant species (present in a non-absorbing gas with a view to develop a library of relevant absorption cross-section), not much has been reported on PT based detection of gases in multicomponent mixtures, a situation nearer to the real time atmospheric system. The availability of relatively inexpensive tunable CO/CO lasers, and the recent developments in instrumentation have considerably increased the potential of PT based techniques for pollution monitoring in a multicomponent atmospheric system and in certain cases, such techniques have been found to be superior to the conventional techniques. Bicanic’s group in Holland and Sigrist’s group in Switzerland, in addition to a few others, possibly can be considered as the main pioneering groups who have extensively contributed towards the development of PA based instrumentation and their application in air pollution analysis. Recently, we, in association with Prof Boccar’s group in France, have also initiated similar studies using a newly developed compact gas phase mirage cell and used the instrumentation possibly for the first time for atmospheric pollution and other applications. The compact and portable system developed is advantageous as it is free from external turbulence and can be used for in situ and onsite measurements also.

**Acid Rains**

Acid rains are the results of dissolution of pollutant gases, acidic in nature (eg, SO₂, NO₂, etc), which produce dilute acids on dissolution in water (rain water). That is, the acidic gases if present in atmosphere not only affect the systems directly but also indirectly, e.g., plants, monuments, soil, etc. The impact of acid rains has extensively been reported in literature. Zimmering et al. have studied the effect of acid rains on the extent of ethylene gas released by leaf by measuring concentration of ethylene released by the plant simultaneously upon treatment of leaf with a very weak acid. The in situ study has opened up a new direction, i.e., evaluation of impact assessment on the ecosystem by PT based technique.

**Environmental Impact Analysis (EIA)**

EIA, as the name implies, does not require a direct measurement of the pollutant, instead, it is based on their effect on the ecosystem. The unusual capability of the gas phases’ mirage effect spectroscopy to measure selectively different pollutants and also measure/monitor (in situ) such low concentrations of ethylene gas released upon external stress created onto the plants has led us to conceive a novel application of the technique for semiquantitative evaluation of the impact of specific stress conditions, e.g., the effect of acid rains, specific pollutants, or pollutants in general, on the ecosystem. The evaluation of such stresses can be used as an indicator of the impact of such agents. A detailed study is in progress with a view to highlight the direct and novel application area.

**Conclusions**

The article is an attempt to present applications of the state of art of photothermal (PT) based techniques specially for trace gas measurement, their potential applications in different areas of research including environmental monitoring and environmental impact analysis (EIA).

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**References**