

# Light and sound—photoacoustic spectroscopy

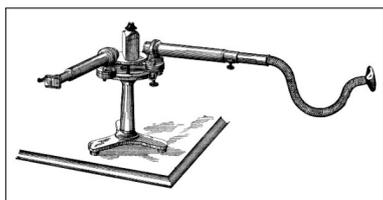
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## Introduction

Like many other spectroscopic techniques, which are today carried out with laser light sources, photoacoustic spectroscopy is much older than the development of the first laser in 1960. In 1881 A.G. Bell proposed a *spectrophone* (Figure 1) “for the purpose of examination of the absorption spectra of bodies in those portions of the spectrum that are invisible”.<sup>1</sup> This instru-



**Figure 1. The *spectrophone*, the first proposed application of photothermal spectrometry for absorption analysis, taken from a publication from the year 1881.**

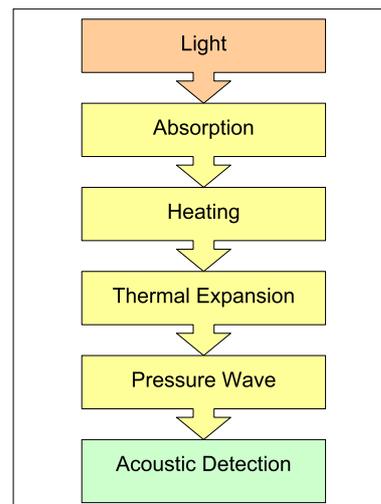
ment was based on his experiments for the transmission of sound without a cable connection. The field then lay largely dormant until the mid-1970s, when Allan Rosencwaig and Allen Gersho laid the theoretical basis for the photoacoustic effect in solids, the so-called R-G Theory.<sup>2</sup>

The basic principle of all photothermal (PT) techniques is the absorption of light in a sample with a subsequent change of its thermal state. This may be either a change of the temperature or other thermodynamical parameter of the sample related to the temperature. Measurement of either the temperature, pressure or density change that occurs due to optical absorption is ultimately the basis for all PT spectroscopic methods. PT analysis can be considered as an indirect absorption measurement as the measured quantity is not an optical signal. (It should be noted here that the classical absorption measurement is not a direct measurement either. Though the measurement value

in this case is an optical one, namely the transmitted light, the absorbed light quantity is derived from the difference of the incident and the transmitted energy.) The sample heating which produces the PT signal is correlated directly to the absorbed electromagnetic energy. In contrast to conventional transmission spectroscopy, neither scattered nor reflected light contributes to the signal. This makes PT spectroscopy particularly attractive for absorption measurements in gaseous, liquid and solid media containing scattering particles, and on solid boundaries.

The most straightforward detection scheme for a photoacoustic signal is the observation of the temperature change at the irradiated sample surface. If this observation is carried out by temperature transducers on the sample surface the technique is called thermometric detection. The more common technique is the detection of the emitted thermal radiation from the sample surface, which represents the temperature distribution within the sample. If the temperature rise in the absorbing sample volume occurs faster than this volume can expand a local pressure increase (wave) is the consequence. This pressure wave can be considered as a sound signal. PT absorption measurements based on the detection of this sound wave are named photoacoustic (PA) techniques. The basic steps of PA analysis are summarised in Figure 2. The means for the detection of a PA signal are multifarious: in a gaseous matrix a microphone may be employed, whereas pressure fluctuations in a solid or liquid sample can be probed by pressure sensitive elements like piezo transducers. Alternatively, the pressure fluctuations can be observed by optical methods.

Although a PT effect can be induced by any light source, lasers are the preferred excitation source nowadays for two reasons: (i) the PT signal, to a first approximation, is proportional to the temperature rise in the sample and thus proportional to the absorbed energy, i.e. the pulse energy, (ii) for many



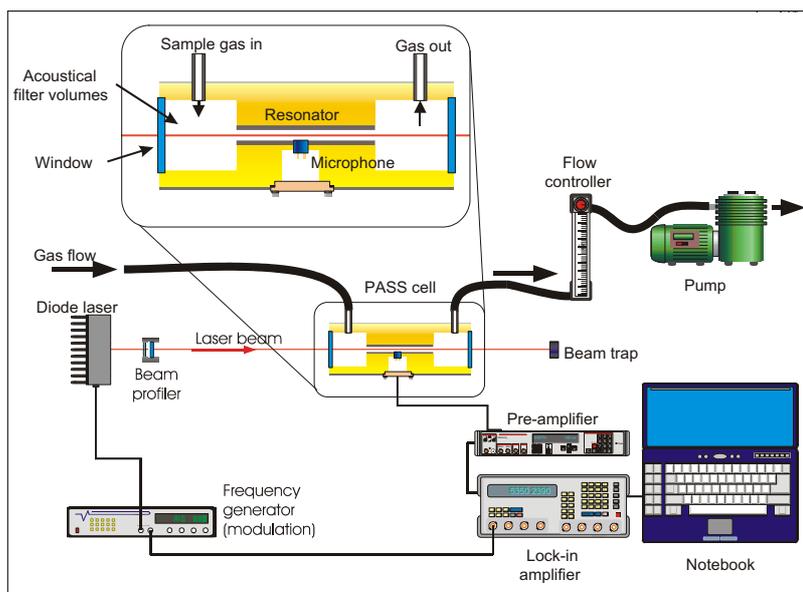
**Figure 2. Principle of a photoacoustic experiment.**

applications the selectivity of a PT analysis, as with any other absorption analysis, depends on the band-width of the excitation wavelength.

## Selected applications

### Quantification of soot particles in diesel engine exhaust gas

For analytical purposes, gas analysis is the oldest application of PA spectroscopy (PAS). The components of A.G. Bell's set-up can all also be found in today's PAS gas analysers. A modulated laser source, tuned to an absorption band of the analyte gas, replaces the sun as the light source (see Figure 3). Instead of the ear, a sensitive microphone detects the sound signal. The microphone signals are electronically amplified and detected by a lock-in amplifier. A lock-in amplifier is a frequency and phase-sensitive data recorder that picks up only signals with the same frequency as a reference signal. This type of data recorder can be used as an extremely narrow band-pass



**Figure 3. Experimental set of the PASS (photoacoustic soot sensor) system.**

filter. For PA spectroscopy with a modulated light source, the modulation frequency is taken as a reference signal, since the PA signal has exactly the same frequency as the excitation source.

The PA system presented here, named PASS (photoacoustic soot sensor), is optimised for the quantitative detection of soot particle mass in the exhaust gas of diesel engines, and serves as an example for a variety of similar PA gas sensors. The specific requirement for the soot detection was a detection limit below  $50 \mu\text{g m}^{-3}$  with a time resolution of 1 Hz. The insensitivity of PA spectroscopy to light-scattering particles in the probe volume compared to other techniques is especially favourable, as the exhaust gas stream may contain a high amount of liquid droplets, which can act as strong light-scatterers. For the excitation a diode laser with a wavelength of about 800 nm and an output power of 1 W was chosen. Soot, or black carbon, shows a wide absorption continuum over the whole visible and near infrared spectrum. To avoid cross-sensitivity with any potential trace gases in the exhaust gas stream, e.g. NO or water vapour, a limited wavelength range around 800 nm is used.

To increase the PA signal, resonance amplification of the acoustical wave is applied. The absorption of the modulated laser beam takes place in an acoustical resonator tube, through which the sample gas is sucked. Since the intensity of the generated pressure wave follows the modulation of the exciting laser, they both have the same frequency. Hence, the sound wave can be tuned to match the resonance frequency of the resonator by tuning the

modulation frequency of the laser. The resulting resonance amplification can reach values from 10 to more than 1000, depending on the design of the resonator. The optimum resonance amplification for a certain analytical application is not necessarily the highest, because higher resonance amplification, i.e. a higher resonance profile always corresponds to a more narrow profile shape. The resonance frequency depends both on the shape of the resonator and on the velocity of sound of the gas within the resonator. If this velocity changes, e.g. due to changing gas temperatures or humidity, a narrow profile leads to significantly reduced amplification, and, as a consequence, to signal fluctuations. As the conditions of the exhaust gas being investigated can change drastically over an experiment, a relatively low resonance amplification of around 20 was chosen. At each end of the resonator tube is a cylindrical buffer volume, which acts as an acoustical filter. Their length measures about half the length of the resonator. The destructive interferences in these buffers filter external noise with the resonance frequency of the laser. Noise sources with other frequencies are less relevant as they are not amplified, neither by the resonator nor by the lock-in amplifier.

A gas handling system completes the PASS system. It consists of an intake tube which fits to standard exhaust gas probes and leads directly into the PA cell. After the cell the gas is filtered to protect the mass flow controller. The gas is sucked through this system by a pump. After this pump the sampled gas can either be released or fed back into the exhaust gas stream, which is



**Figure 4. Photograph of the PASS (photoacoustic soot sensor) system.**

required for some exhaust gas probe systems. In order to prevent condensation of water vapour in the PA cell, it can be heated to  $50^\circ\text{C}$ . A picture of the complete PASS sensor, without the lock-in amplifier, is shown in Figure 4.

In Figure 5, the calibration of the PASS system is illustrated. The system is calibrated in soot mass per cubic metre. Reference analysis is carried out by sampling the soot on a filter followed by thermochemical carbon analysis. The calibration points labelled in red were measured with strongly varying  $\text{NO}_x$  concentrations, which are given on the graph. Clearly, no cross-sensitivity of the soot measurement to this gas, which is present in any exhaust gas, can be observed. A typical application of the PASS system is displayed in Figure 6. Here, the PASS was employed to analyse the soot mass concentration over a 30 min transient driving cycle. These test cycles at an engine test stand simulate a truck driven through a city, on a highway and on a motorway. They are used for engine development and type approval of new engines.

## PA analysis of highly concentrated textile dyes

The analysis of a highly concentrated textile dyestuff is used as a second example for demonstrating a specific advantage of PA absorption spectrometry over conventional transmission spectroscopy. The concentrations of these dyes are in the range of more than  $5 \text{ g L}^{-1}$ , resulting in absorption coefficients of  $10^3 \text{ cm}^{-1}$ . Changes in the concentrations are required to be monitored during the dyeing process. An additional problem is the continuously increasing contamination of the dye solution by fuzz from the textile. This combination of extremely high absorption and scattering particles in the dye solution makes a classical transmission spectroscopic analysis impossible. PA

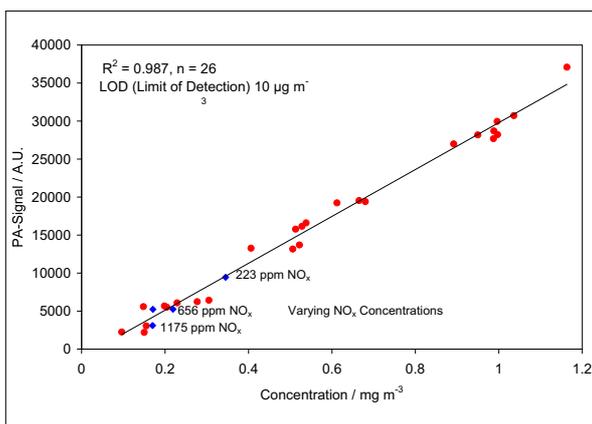


Figure 5. Calibration curve of the PASS system vs thermochemical analysis.

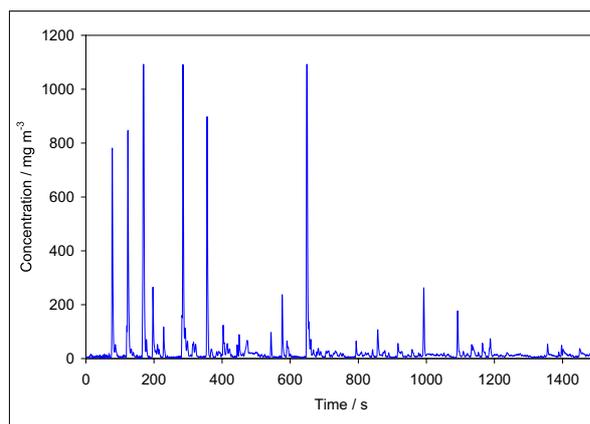


Figure 6. PASS signal of a driving cycle for diesel engine testing.

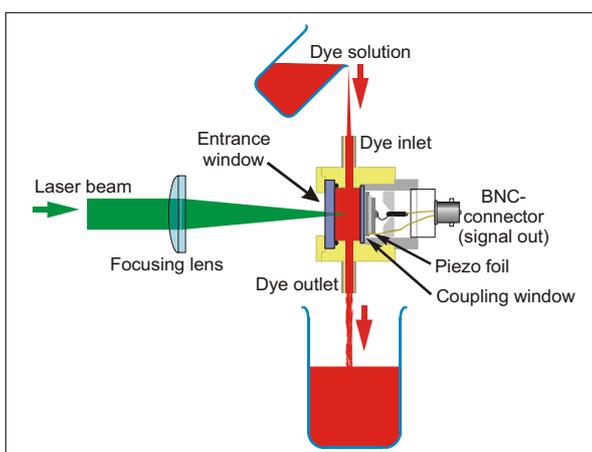


Figure 7. Design of the flow cuvette for the PA analysis of concentrated dyestuff.

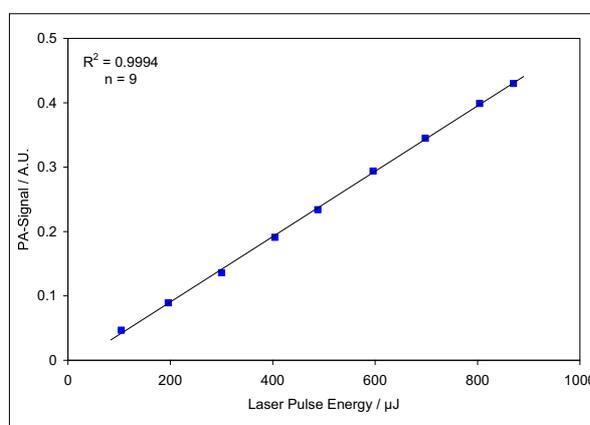


Figure 8. Dependence of the PA signal on the laser pulse energy.

spectroscopy is a viable approach to overcome the problems.

Instead of a modulated light source, in this case a pulsed laser is employed. To get spectral information about the dye solution this laser source has to be tuneable over the whole visible spectral range. Suitable laser systems are dye lasers, for instance, which are optically pumped either by an excimer laser or by a nitrogen laser. The latter is the more cost-effective and manageable, since no gas refilling is required. Running costs and maintenance are key considerations for a system meant for on-line routine application in an industrial environment. The fundamental experiments presented here were produced using a frequency doubled Nd:YAG laser, which was coupled into an optical fibre. This type of laser is not tuneable, but it is a real turn-key instrument and most conveniently applied. The laser wavelength is 532 nm, the pulse energy behind the optical fibre is 1 mJ with a pulse duration (FWHM) of 6 ns.

The laser beam is directed through an entrance window into a cylindrical flow cell (see Figure 7). This cell has a

diameter of 0.8 cm and a length of 1.0 cm, resulting in a cell volume of  $\approx 0.5 \text{ cm}^3$ . An inlet and outlet are installed at opposite sides of the cell. Thus, the sample flow passes through the cell perpendicular to the incident laser beam. The PA signal is detected by a hydrophone opposite to the laser input window. Hence, the laser impinges directly on the hydrophone, if there is no absorbing liquid in the cell. This layout was found to be advantageous for the case of strongly absorbing liquids, as the sound wave produced shows an approximately spherical propagation characteristic, while the sound wave produced in a low absorptive solution propagates in the form of a cylindrical wave. This kind of waveform with its axis of symmetry collinear with the laser beam is detected best perpendicular to the laser beam.

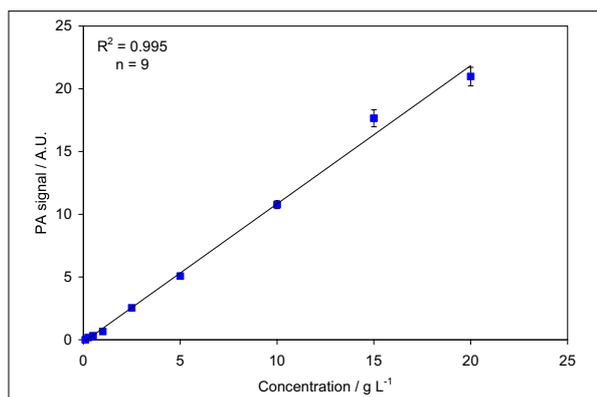
The hydrophone consists of a quartz front window (diameter 10 mm), which is coupled to the front contact of the piezo-active foil. Although there is no need to use an optically transparent material for the front surface, quartz was found to result in an opti-

um coupling efficiency of the sound signal to the piezo foil. This polyvinylidene fluoride (PVDF) foil has a thickness of 25  $\mu\text{m}$ . The second metallic contact is on the backside of the foil and directly connected to a BNC coupler. This whole hydrophone is encapsulated in a metal housing.

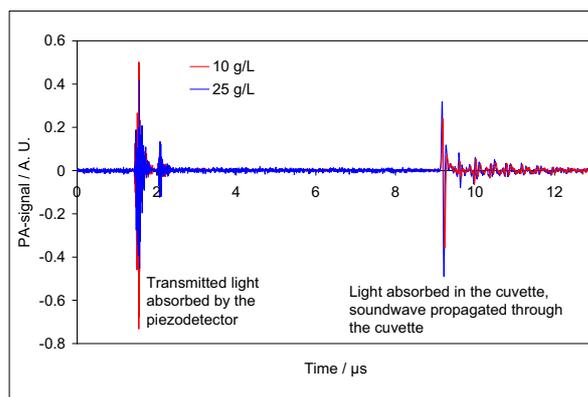
As mentioned above, the PA signal intensity depends on the laser pulse energy deposited in the sample. Figure 8 depicts this linear relation. A typical calibration graph of the described PA system for concentrated dyestuff is shown in Figure 9. This calibration is linear in a concentration range more than 10 times higher than achieved with conventional transmission spectrometry.

## Further aspects of PA analysis

The time-resolved PA signals as shown in Figure 10 contain additional information, which is not exploited in a bulk absorption analysis as described in the example above. The first signal in time is the signal generated by the



**Figure 9.** Calibration of the PA sensor system for textile dyestuff.



**Figure 10.** PA signal of two different concentrations of textile dyestuff in water.

light that is transmitted through the sample and impinges directly on the hydrophone. The second signal stems from the light absorbed in the sample liquid. Due to the high absorption in the sample the electromagnetic energy is deposited mostly directly on the front side of the cuvette. The pressure wave generated there propagates through the cuvette and is detected after a delay. This delay is the time ( $\sim 7 \mu\text{s}$ ) the sound needs to propagate the length of the cuvette (1 cm), (the

speed of sound in water  $\sim 1500 \text{ m s}^{-1}$ ). For a non-homogeneous sample a depth-resolved absorption measurement can be carried out in this way. Each delay corresponds to a certain depth in the sample. This simple example is included to give an idea of an interesting field of application or PA analysis. Of course, the design of such a sensor system would be different, for example, the hydrophone could be placed on the same side as the laser. However, the description of

depth resolved analysis by PA spectroscopy is beyond the scope of this short article.

## References

1. (a) A.G. Bell, *Phil. Mag.* **11**, 510 (1881).
2. A. Rosencwaig and A. Gersho, "Theory of the Photoacoustic Effect in Solids", *J. Appl. Phys.* **47**, 64–69 (1976).