Simultaneous photoacoustic detection of multiple compounds based on orthogonal functions stimulation

Tomasz Starecki

Institute of Electronic Systems, Warsaw University of Technology
Nowowiejska 15/19, 00-665 Warsaw, Poland

Abstract. The paper presents a concept of photoacoustic measurements based on use of two different light wavelengths which intensities are modulated with sine waves of the same frequency but with phase difference of 90 degrees. Resultant photoacoustic signal is of the same frequency, but its amplitude and phase depends on the absorption at both wavelengths. Taking into consideration that sine and cosine are orthogonal functions, and having measured amplitude of the photoacoustic signal and its phase referred to the phase of the stimulating light modulation, it is possible to retrieve both components corresponding to sine and cosine modulation. As a result, the method can be applied to simultaneous detection of two compounds. An important advantage of the method is that it can be comfortably used with high Q-factor cells.

1 Introduction

Photoacoustic detection of multiple compounds can be done at least in a few ways. The simplest method is performing sequential measurements at selected wavelengths at which the compounds under detection would absorb (eg. [1]). The method has at least two disadvantages – the first is longer time of measurements (proportional to number of wavelengths at which the measurements are performed), the second is possibility of change in measurement conditions performed for consecutive wavelengths, especially if the equipment uses long averaging time in order to increase sensitivity. Both mentioned disadvantages can be eliminated if a method of simultaneous detection of multiple compounds is applied.

Probably the most common method of simultaneous photoacoustic detection is FTIR PAS, which produces a spectral characteristics of the investigated substance (eg. [2]). It should be noticed, however, that FTIR PAS method has also several drawbacks – the most important is sophisticated (and expensive) mechanical and optical components, which make the equipment more suitable for use in laboratory environment rather then for outdoor applications. Another disadvantage is requirement of using the PA cell that has wide acoustic bandwidth. This makes use of high Q-factor cells virtually impossible. If one takes also into account that optical output power per wavelength of FTIR PAS instruments is relatively low, it becomes quite obvious, that the method, although of great value in the case of qualitative analysis, is not of preferred choice when high sensitivity measurements (e.g. trace detection) are required.

Another method of photoacoustic detection of multiple compounds is based on simultaneous use of a few selected wavelengths which intensities are modulated with different frequencies (eg. [3]). Such an approach may be advantageous over FTIR in high sensitivity measurements if high power discrete wavelength light sources (e.g. lasers) are used, but application of high Q-factor cells in order to obtain further increase of sensitivity of such a setup is questionable, because if several different modulation frequencies are used, only one of them can be adjusted to the resonance frequency of the cell, which means that all the other modulation frequencies have to be shifted out of the resonance, which (in the case of high Q-factor cell) will result in much weaker acoustic amplification of corresponding components of the induced photoacoustic signal.

2 Description of the setup

2.1 Basic concept

According to the methods mentioned above it is not possible or it is difficult to efficiently use high Q-factor cells in simultaneous photoacoustic detection of multiple compounds, because of simultaneous use of a few different modulation frequencies. A way of overcoming the problem is to use a single modulation frequency adjusted to the resonance frequency of the cell. Traditional approach to photoacoustics is based on measurements of the amplitude of the acoustic signal produced by the light absorption while neglecting its phase (although there are some applications in which phase of the photoacoustic signal is also measured, eg. [4]). In such a case use of the same modulation frequency applied to more than one wavelength results in inducing corresponding number of photoacoustic signal components, all of the same frequency, which leads to ambiguous results as superimposed signal cannot be decomposed into corresponding components if the phase information is lost. Unambiguous distinction between the component signals can be implemented only if the components are orthogonal functions. In the case of a single modulation frequency this can be done by simultaneous sine and cosine modulation and measuring not only amplitude, but also phase (referred to the phase of the modulation signals) of the induced photoacoustic response.

2.2 Hardware description

An example of the setup that implements the described concept of orthogonal functions stimulation is presented at fig. 1. A generator produces two sine waves of the same frequency, but with the phase difference of 90 degrees. Taking into consideration that phase difference between the two signals should be of maximum stability (otherwise measurement errors will increase), a recommended method of producing the signals is direct digital synthesis (DDS), preferably based on a dual-DDS circuit (eg. AD

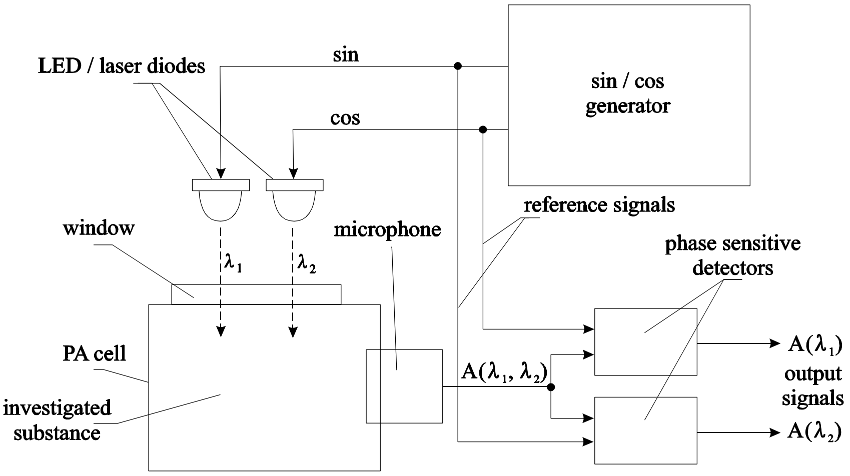
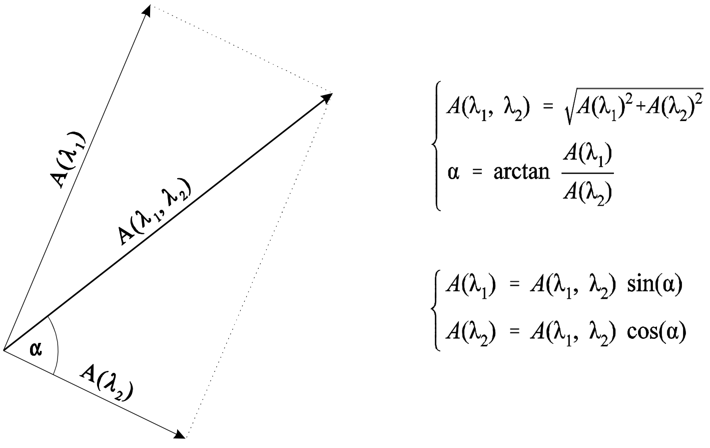


Fig. 1. Block diagram of a photoacoustic system based on orthogonal functions stimulation.

9958). The signals obtained from the generator are used to control intensity of two LED / laser diodes that emit wavelengths λ_1 and λ_2 selected according to the absorption spectra of the compounds to be detected. Both modulated light beams pass through the photoacoustic cell window and illuminate the investigated substance. Interaction of the light with the substance results in producing a photoacoustic signal. Every of the light beams produces separate component of the signal, and amplitude of the component depends in particular on the absorption of the corresponding light wavelength by the investigated substance. Taking into consideration that both photoacoustic signal components are of the same frequency (equal to the light intensity modulation frequency), the superimposed signal is also of the same frequency, but with its amplitude and phase depending on the amplitudes of both component signals (fig. 2). The photoacoustic signal from the PA cell can be then converted by means of a microphone into a voltage signal, and then fed to phase-sensitive detectors. The phase-sensitive detectors are referenced by the signals that are used for controlling intensity of the light sources. After calibration (adjustment of the phase shift) output signals of the phase-sensitive detectors are proportional to the corresponding photoacoustic signal components (which depends on the absorption of the corresponding wavelength λ_1 / λ_2 by the investigated substance). As first derivatives of sine/cosine functions are close to zero when the functions approach their maximum / minimum values, calibration of the phase-sensitive detectors should be performed not by looking for maximum output signal when the corresponding wavelength is active, but for minimum output signal with the other wavelength enabled (while the first one is switched off).



$$\begin{cases} A(\lambda_1, \lambda_2) = \sqrt{A(\lambda_1)^2 + A(\lambda_2)^2} \\ \alpha = \arctan \dfrac{A(\lambda_1)}{A(\lambda_2)} \end{cases}$$

$$\begin{cases} A(\lambda_1) = A(\lambda_1, \lambda_2)\,\sin(\alpha) \\ A(\lambda_2) = A(\lambda_1, \lambda_2)\,\cos(\alpha) \end{cases}$$

Fig. 2. Relationship between the superimposed photoacoustic signal and its components.

3 Conclusions and remarks

Single modulation frequency allows for use of the described method with high Q-factor cells, in particular in high sensitive simultaneous detection of two compounds. Proper calibration is a crucial factor in obtaining high accuracy, as especially at phase angles close to 0 and 90 degrees, any inaccuracy of the phase measurement (or phase instability) strongly affects final results (increasing errors). The described method is particularly suitable for ratiometric measurements, when relative concentration of two compounds is important. In such a case it is enough to measure only the phase of the photoacoustic signal. It should be noted that due to use of semiconductor light sources, the hardware can be easily miniaturized.

References

1. Z. Bozóki, J. Sneider, Z. Gingl, Á. Mohácsi, M. Szakáll, Z. Bor, G. Szabó, Meas. Sci. Techol. **10**, 999 (1999)
2. M.M. Farrow, R.K. Burnham, E.M. Eyring, Appl. Phys. Lett. **33** (8), 735 (1978)
3. J.-P. Besson, S. Shilt, L. Thévanaz, Spectrochim. Acta A **63**, 899 (2006)
4. S. Shilt, J.-P. Besson, L. Thévanaz, Appl. Phys. B **82**, 319 (2006)