# Basics of photoacoustics for gas and aerosol concentration measurements

# Introduction

Photoacoustic (PA) measurements can be categorised as:

1. Qualitative photoacoustics. It has two sub-categories:

- Origin and interpretation of PA spectra;
- Description of a PA system via system theory (based on the frequency dependent responses of its sub-components).

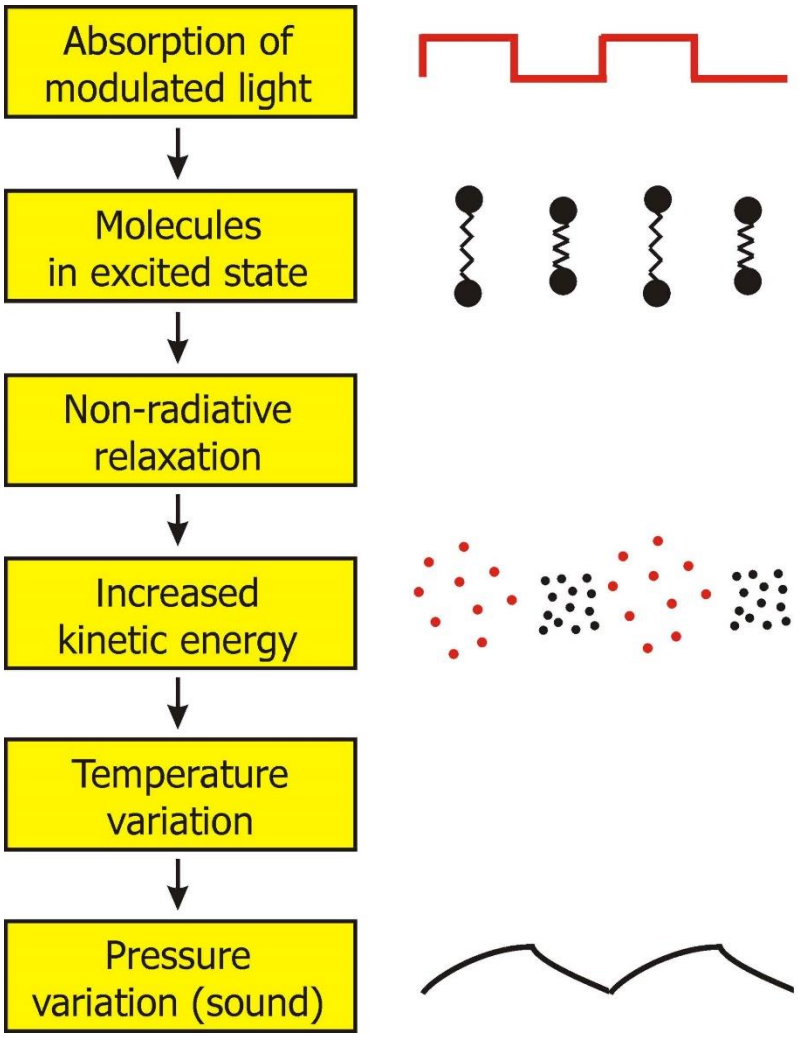
2. Semi-quantitative photoacoustics:

- Primary application is concentration measurement. (Proper calibration and the application of various self-checking and self-correcting algorithms are required).

3. Quantitative photoacoustics (not yet implemented):

- Working toward developing calibration-free PA systems.

# The mechanism of PA signal (PAS) generation




Laser wavelength is tuned to an absorption line of the analyte.

Modulation: absorbed light power varies in time.

Molecules are periodically excited to a state with higher energy.

Excited state relaxes to ground state, excess energy is converted to heat via molecular collision.

Temperature increase generates density and pressure increase.

Pressure variation propagates as sound, generates standing wave.

# The roles of the main components of the PA system: laser and PA cell

- **The laser:**
- It is tuned to an absorption line of the targeted molecule,
- It is modulated at an acoustic frequency corresponding to the resonance frequency of the PA cell.
- **The detection cell (supplemented with a gas handling system):**
- It is illuminated through by the laser with the help of optical windows fully transparent at the laser wavelength.
- It can be operated in a continuous gas flow.
- It amplifies the photoacoustically generated acoustic signal due to the coincidence between the frequencies of the laser modulation and the excited acoustic resonance.

# The roles of the main components of the PA system: electronics

- **The electronics:**

- It controls the laser wavelength and modulation parameters (for diode and quantum cascade lasers by adjusting the laser temperature and current).
- It detects and quantifies the PA signal corresponding to the microphone signal at the laser modulation frequency by using the lock-in detection technique.
- It executes various self-checking and self-correcting algorithms.
- It calculates the concentration of the targeted analyte with the help of pre-programmed calibration constants.

# The most important parameters of the components of a PA system

What are the most important parameters of the laser?

Power, wavelength, tuning range, emission linewidth, wavelength stability, the effect of modulation.

2. The detection cell. Most important parts?

Microphone, windows, central resonator.

3. The electronics. Most important sub-components?

Laser driver, microphone amplifier, signal processing unit (usually a lock-in detector).

4. The gas handling system. Most important parts?

Sampling inlet, flow control unit.

# Examples

Examples of successful application of the PA systems developed at the University of Szeged:

- $H_2S$, water vapour and $CO_2$ detection PA instruments for the oil and gas industry (implemented world-wide).
- PA instrument operated at a passenger aircraft for measuring water vapour and total water concentration in atmospheric air.
- Measurement of methane in exhaled air.
- Measurement of $NH_3$ emission from soil and by various agricultural activities.

# The most unique advantages of the PA method

- Photoacoustic signal is linearly proportional to the concentration over a wide range (5-6 orders of magnitude);
- Concentration measurement by photoacoustics is executed directly in the gaseous phase (no phase transition such as condensation, absorption or adsorption);
- With a proper light source (light power of at least 5 mW and tuneability to strong absorption lines) ppm, ppb, or even sub-ppb. concentrations are measurable;
- Volume of the PA cell is small (a few $cm^3$) making possible to measure with a response time less than a second;
- Simple system, robust construction, long term reliable and fully automatic operation.

# Number of measurable components

What determines the number of measurable components?

1. How wide the tuning range of the laser is,
2. How many molecules have at least one sufficiently strong absorption line in this tuning range.

Some lasers (e.g. mid-infrared CO or $CO_2$ lasers) have remarkably wide tuning range.

In principle all components which have absorption lines in the tuning range of the laser are measurable by the PA system.

In practice fewer components are measurable. Why?

- Absorption lines might be too weak;
- Spectral overlap between absorption lines can spoil the accuracy of the concentration measurements.

# Number of measurable components

The lasers we use (diode lasers and QCLs) have narrow tuning range.

As a consequence they can measure typically only one component.

In some cases the measured gas contains more than one component with strong absorption lines within the tuning range of our lasers. What is the problem with that?

These cases are typically characterised by strong spectral interference, which can be handled by careful optimisation of the operation of the PA system.

Examples of instruments which measure several components?

Mass spectrometer, FT-IR or gas-chromatography.

# The competitiveness of the PA method

PA instruments are routinely used in various applications:

1. Natural gas industry (Hobre Instruments BV sells more than 50 pieces of PA instruments yearly);
2. Medical diagnostics: measuring exhaled air;
3. Environmental-monitoring: Our PA instrument measures water vapour and total water concentration in the atmosphere operating on a passenger aircraft since 2004 throughout long distance flights (CARIBIC project).

What is common in all of these applications?

During the course of the measurement the physical and/or chemical properties of the measured gas varies (in some cases very rapidly and widely).

# The competitiveness of the PA method

Why is it surprising that in the most successful applications of the PA method the measured gas varies considerably?

Measurements under such conditions are not easy with the PA method. Why?

The actual value of the PA signal depends on the thermal and acoustic properties of the measured gas, so even when the measured concentration is constant, there can be considerable variations in the PA signal.

However, by applying carefully designed self-checking and self-correcting algorithms, the effects of these disturbances can be suppressed and the accuracy of the PA measurements can be ensured.

# Operating a PA instrument under varying measurement conditions

How is it possible to ensure the accuracy of PA concentration measurements under varying conditions?

Using self-checking and self-correcting algorithms.

In which sense these algorithms must be optimised?

- They must repeatedly adjust the operational parameters of the PA system to their optimum values;
- Their execution time should be as short as possible;
- They should work even when the gas physical or chemical parameters vary quickly.

Why the shortest possible execution time is important?

During their execution there is no concentration measurement.

# The principal equation of photoacoustics

$$PAS = P \cdot M \cdot (C \cdot \alpha_0 \cdot c + A_b)$$

*PAS*: the photoacoustic signal (in mV);

*P*: the laser light power (in mW);

*M*: the microphone sensitivity (in mV/Pa);

*C*: the PA cell constant (the efficiency of acoustic signal generation, in Pa/cm$^{-1}$/mW);

$\alpha_0$: the specific optical absorption coefficient of a gaseous component to be measured (in cm$^{-1}$/ppm);

*c*: the concentration of a gas component (in ppm);

$A_b$: efficiency of background signal generation (in Pa/mW).

# The photoacoustic signal (*PAS*)

$$PAS = P \cdot M \cdot (C \cdot \alpha_0 \cdot c + A_b)$$

There is one aspect of PA signal generation which is disregarded in this equation. What is that?

The laser modulation.

What is the more precise definition of the *PAS*, which takes into account the effect of modulation?

PAS is the amplitude of the microphone signal variation at the frequency, which is equal to the laser modulation frequency.

Furthermore, PAS has not only amplitude but phase too.

What is the physical meaning of the phase?

It corresponds to the time delay between modulation and *PAS*.

# The cell constant (*C*)

$$PAS = P \cdot M \cdot (C \cdot \alpha_0 \cdot c + A_b)$$

Based on its dimension ([*C*]= Pa/cm$^{-1}$/mW) what is the definition of *C*?

Amplitude of the acoustic wave within the PA cell generated by a laser having light power of 1mW and a gas sample having optical absorption of 1cm$^{-1}$. ($\alpha_0 \cdot c$=1 cm$^{-1}$.)

How one can achieve high value of the cell constant?

By setting the laser modulation frequency to be equal to a carefully selected acoustic resonance frequency of the PA cell.

(Note: not all the acoustic resonances can be excited with high efficiently by the PA signal generation method. See later.)

# The specific optical absorption coefficient ($\alpha_0$)

$$PAS = P \cdot M \cdot (C \cdot \alpha_0 \cdot c + A_b)$$

What do we know about $\alpha_0$?

It depends strongly on the measurement wavelength.

What is the wavelength of the strongest absorption lines?

They are in the mid-infrared (MIR) wavelength range.

In the near-infrared absorption lines are much weaker. Why?

They corresponds to optical transition to overtone vibrations.

Absorption is weak as these transitions are almost forbidden.

What makes NIR transitions not completely forbidden?

Slight nonlinearity in the potential curve of vibration.

# The specific optical absorption coefficient ($\alpha_0$)

Highly asymmetric molecular bonds result in stronger absorptions in the near-infrared. Examples?

$H_2O$, ammonia, methane, $H_2S$. General notation: X-H bonds.

But not: $CO_2$: very strong absorption in MIR, weak in NIR.

Besides large $\alpha_0$, what is the other requirement against the absorption line of the measured analyte?

It is better if the absorption line is narrow. Why?

It ensures better measurement selectivity. Why?

More characteristic lines, less overlap with other molecules, possibility of wavelength modulation. Examples?

$H_2O$, $NH_3$, $CH_4$, $H_2S$, NO, $NO_2$, $CO_2$ etc.

# The most important applications of the principal equation of PA

$$PAS = P \cdot M \cdot (C \cdot \alpha_0 \cdot c + A_b)$$

What is the semi-quantitative application of the equation?

Measuring *PAS* as a function of the concentration of the targeted analyte, calculating a calibration line from these data and using its parameters (slope and y-axis intercept) to determine *c* from measured *PAS*.

How this equation helps us to improve PA systems?

Shows the possibilities of increasing *PAS*. How to increase?

Increasing the light power, using more sensitive microphone, designing PA cell with higher cell constant, using a laser which can be tuned to an absorption line with high $\alpha_0$.

# Self-checking, self-correcting algorithms

$$PAS = P \cdot M \cdot (C \cdot \alpha_0 \cdot c + A_b)$$

What is the most important requirement against the calibration constants?

Remain constant over a long operation period (e.g. ½ year).

What is the use of these algorithms?

1. Keep the operational parameters at optimum values;
2. Detect variations of the calibration constants.

How to compensate for these variations?

1. Adjust the operational parameters to optimum value;
2. Complete recalibration whenever necessary.

# Algorithms for handling variations in the measurement conditions

What are the two most important physical parameters of a PA system that must be kept at optimum values continuously?

1. Laser modulation frequency;
2. Laser wavelength.

What are the basic requirements against these parameters?

1. Laser modulation frequency must be kept at the resonance frequency of the PA cell;
2. Laser wavelength must be kept at the top of the absorption line of the targeted molecule.

(There are special cases when the modulation frequency and the laser wavelength is optimised differently.)

# $A_b$: the background PA signal (BPAS)

Absorption of modulated light generates acoustic signal not only in the gaseous phase but in the solid phase too.

Accordingly, what are the sources of BPAS?

Absorption of the light by the windows or walls of the PA cell.

BPAS disturbs the PA measurements other way than noise.

What does this mean?

- Frequency of BPAS is equal to that of the PAS generated in the gaseous phase (that is why their separation is difficult);
- While noise typically occurs at all frequencies.

To which calibration quantity $A_b$ corresponds?

$A_b$ is the y-axis intercept of the calibration line.

# Handling the effects of the background PA signal (BPAS)

There are various methods to decrease BPAS:

1. Aligning the light path through the PA cell properly;
2. Using wavelength modulation instead of amplitude modulation (see later). How we can measure BPAS?

By using a gas that does not contain the measured analyte.

This is called as null-gas. How to generate null-gas?

1. One can use e.g. pure nitrogen;
2. From the original gas the analyte can be removed.

Usually the second method is preferable. Why?

Because this gas is much more similar to the gas the system will measure during its forthcoming application.

# The incompleteness of PEPS for analytical applications

The analytical performance of a PA system cannot be described with the help of the PA signal only. Why?

The noise of the measurement has equal importance. Why?

Noise determines the minimum detectable signal (MDS), that determines the minimum detectable concentration (MDC).

What is the correct definition of MDS and MDC?

- MDS: three times the noise;
- MDC: MDS divided by the slope of the calibration line.

MDC is too small to measure reliably. What is measurable?

1. Concentration that generates signal 10x higher then noise;
2. Concentration variation that equals to MDC.

# Optimising the components of a PA system

In principle various types of lasers, cells, microphones, windows, etc. can be used. What are the main restrictions?

1. The analytical performance should be the best;
2. Price must be kept as low as possible.

The light source is the most critical component. Why?

1. It affects many parameters in PEPS. Which ones?

$P$ and $\alpha_0$ (and $A_b$ as well).

2. The price of different lasers are hugely different.
3. Some lasers are easy to modulate, have very robust construction and long lifetime. (others are opposite).

Cells, microphones etc. can be varied (optimised) as well.

# Typical numerical values of the parameters of a PA system

Which are the roughly constant parameters of the PA systems?

1. The noise level (under typical conditions);
2. The cell constant i.e., the efficiency of PAS generation.

Numerical values for optimised PA systems:

1. Noise : ≈150 nV (with 1 second averaging time);
2. Cell constant ≈30 mV/cm$^{-1}$/mW. What does this mean?

This is the PAS in case of 1 mW light power and optical absorption coefficient of 1 cm$^{-1}$ of the measured component.

Why these two quantities are important?

The signal to noise ratio and the minimum detectable concentration depend on these quantities.

# Summary: basics of photoacoustics (test questions)

1. What are the three categories of PA measurements?
2. What are the main steps of PA signal generation?
3. What are the main components of a PA system?
4. What are the main advantages and limitations?
5. How the basic equation helps to develop PA systems?
6. What is the importance of the self-checking and self-correcting algorithms?
7. How null-gas is generated and used for what?
8. How background signal influences the PA measurements?
9. What are the typical numerical values characteristic to a PA system?

# Thank you for your attention!