PHOTOACOUSTIC GAS DETECTION METHOD FOR INDUSTRIAL, ENVIRONMENTAL MONITORING AND CLIMATE RESEARCH APPLICATIONS

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Outline of the presentation

- The photoacoustic effect
- How to build an optimized photoacoustic detection system?
- The basic equation of photoacoustics
- Comparison of the PA method with optical absorption spectroscopy based gas detection
- Application areas of the photoacoustic method
Photoacoustic signal generation

- The gas volume is illuminated by a modulated light which has its wavelength tuned to an absorption line of the targeted molecule.
- The absorbed radiation excites the molecules from their ground state to an excited state.
- Molecules relax non-radiatively back to the ground state while releasing the absorbed light energy.
- The absorbed and released energy generates temperature increase in the gas.
- By modulating the light at an acoustic frequency, the temperature variation becomes periodic.
- Periodic temperature change results in periodic pressure change which can be observed as acoustic signal that can be detected by a sensitive microphone.
Advantages of the PA method

- Direct, in-situ measurement in the gaseous phase
- High sensitivity
- Selectivity
- Wide dynamic range
- Fast response time
- Zero background measurement method (i.e. if there is no light absorption then PA signal is not generated)
Historical overview

- Photoacoustics (optoacoustics) is discovered by A.G. Bell in 1881
- PA signal can be generated not only in gases, but in liquids and solids too
- Any type of temporarily varying light source can generate PA signal: e.g. pulsed lasers
- Gives information not only about the optical but the thermal and acoustic properties of the studied sample too
- The method was booming in the sixties and seventies due to the application of CO and CO2 laser with record breaking sensitivities. However with these light sources automatically operated PA systems cannot be built.
- Our primary goal is to build fully automatically operable PA systems with extreme reliability.
Our basic photoacoustic set-up

[Diagram showing the set-up with labels: Photoacoustic cell, Microphone, Laser module, Laser controller, Signal analyser, Data processing, Gas inlet, Gas outlet, Computer]
Frequently asked questions

- **What is the so called „PA signal”?**
  The amplitude of the microphone signal variation at the frequency of laser modulation
  (Note: The phase of the PA signal can provide very important information too!)

- **What makes the PA method selective?**
  The laser, which is tuned to the absorption line of the targeted molecule
• **Are different components generate PA signal at different frequencies?**
  No, frequency is solely dictated by the laser modulation (matched to a acoustic resonance frequency of the detection cell)

• **Are PA measurements truly background free?**
  Almost, but absorption of light on the walls of the cell can generate PA signal at the frequency of laser modulation
How to build a PA system?

- Search for a strong absorption line of the targeted molecule with minimal spectral interference.
- Select an easy to handle laser to this wavelength, which emits in single mode and can be modulated or pulsed.
- Tune (and lock) the laser wavelength to the selected absorption line(s).
- Direct the light beam through the PA cell (by minimising the background PA signal)
• Build a proper gas sample conditioning system which ensures continuous gas flow through the PA cell
• Set the laser modulation frequency to the selected acoustic resonance frequency of the cell (and apply a method which follows possible changes in the resonance frequency)
• Apply a lock-in detection technique which filters the PA signal out from the wide band acoustic noise
• Calibrate the system with known concentrations (take into account possible molecular relaxation effects)
• Program it for long term automatic operation (by applying various self checking and correction algorithms with minimum execution time and maximum reliability)
The light source of our PA systems

- Single mode, room temperature operated, near-infrared DFB diode laser. Telecommunication type, fibre coupled.
- High reliability: lifetime of 10+ years
- Output power: 20-120 mW (depends on wavelength)
- Wavelength is tuned by changing the temperature of the laser (≈ 0.1 nm/°C)
- Modulated via its driving current
- Current has a slight wavelength tuning effect too (≈ 0.01 nm/mA)
- Can be amplitude or wavelength modulated
Frequently asked questions

- For which gases the PA method suits best?
  \( \text{H}_2\text{O}, \text{H}_2\text{S}, \text{NH}_3, \text{CO}_2, \text{CO}, \text{CH}_4, \text{HCl}, \text{HCN} \) etc.
- **Why?**
  They have characteristic absorption lines. Larger molecules have less-characteristic absorption lines.

- What is typical minimum detectable concentration with our diode laser based PA systems?
  0.1 ppm for \( \text{H}_2\text{O}, \text{H}_2\text{S} \); 100 ppm for \( \text{CO}_2, \text{CO} \).
- **Why?**
  Strongly asymmetric H-X bonds has strong overtone absorption bands in the near-infrared.
• **Can the PA method be used for multi-component analysis too?**  
  Yes, by sequentially tuning the laser wavelength to characteristic absorption features

• **Can light sources other than NIR diode lasers be applied in PA systems?**  
  Yes, e.g. QCL. However for practical applications price and long term reliability has to be considered.
• **What is wavelength modulation?**
The laser is not switched on and off (amplitude modulation), but the modulation amplitude is set to the smallest possible value, which just tunes $\lambda$ on and off the absorption line

• **What kind of advantages wavelength modulation can offer?**
More characteristic absorption lines, improved selectivity, suppressed background signal
• **Does the wavelength of diode lasers vary spontaneously?**
  Yes, after switching it on and also during long term operation (the so called ageing effect)
• **How long term spontaneous wavelength variations can be handled?**
  With pre-programmed, repeated wavelength checks using a strong absorption line either in the measured gas or in a calibration gas or in a reference PA cell
• How accurately the laser wavelength has to be set?

Depending on the application relative accuracy of $\frac{\Delta \lambda}{\lambda} = 5 \times 10^{-8}$ is required. We use a patented method for this.
The cell and the microphone of our PA systems

- Acoustic resonator which amplifies the generated acoustic signal at $\approx 4$ kHz
- Low Q ($\approx 20$) resonance, easy to handle (i.e. to track its variation due to e.g. gas composition)
- Special construction to suppress external noises
- A volume of a few cm$^3$ and consequently a response time of a few seconds
- Negligible light absorption in it, therefore another cell(s) can be excited with the outgoing light
- Very robust hearing aid microphone with negligible long-term variation in the sensitivity
Frequently asked questions

• **Why is it necessary to stabilize the temperature of the PA cell?**
  Because both the resonance frequency and the sensitivity of the cell depends on temperature

• **Which considerations one has to make when optimizing the cells temperature?**
  Cell sensitivity decreases with increasing T; response time improves with increasing T; chance of condensation decreases with increasing T
• **What influences the resonance frequency?**
  Cell temperature and gas composition (both via sound speed)

• **How to track resonance frequency variations?**
  We developed and patented a method in which the laser is driven by a multi-frequency excitation sequence and FFT analysis of the response of the microphone
The electronics of our PA systems

- Highly integrated
- Up to three lasers and five cells can be operated simultaneously
- Various self checking and self correction algorithms are implemented in it (i.e. wavelength correction, resonance frequency tracking, overload detection)
- Can be operated in standalone mode by storing the measurement results for months
- Various data transfer and communication protocols can be used
Frequently asked questions

- Why lock-in detection (or synchronised sampling plus FFT) has to be applied?
  Otherwise the useful PA signal is buried in wide-band acoustic noise
- What is the importance of overload detection?
  Overload can falsify the PA signal
The gas handling of our PA systems

- Sets the volumetric flow rate through the cell to 0.2-0.5 litre/minute. Flows above this rate generate excessive flow noise in the PA cell which can overload the system.
- Since the PA signal is pressure dependent, we prefer to ensure fixed (atmospheric) pressure in the cell.
- Usually, the gas handling determines the response time of the system.
- Low frequency pressure fluctuations can overload the system (a buffer volume has to be used).
The Basic Equation of Photoacoustics:

\[
PA = P \cdot M \cdot \left( C \cdot \alpha_0 \cdot c + A_b \right)
\]

- **PA**: the microphone signal (amplitude at the laser modulation frequency) [mV]
- **P**: the light power [mW]
- **M**: the microphone sensitivity [mV/Pa]
- **C**: „cell constant” i.e. the efficiency of acoustic signal generation by gas phase light absorption [Pa/cm\(^{-1}\)/mW]
- **\(\alpha_0\)**: the optical absorption coefficient of a gaseous component of unit concentration [cm\(^{-1}\)/(\(\mu\)mol/mol)]
- **c**: the concentration of a gas component [\(\mu\)mol/mol]
- **A\(_b\)**: efficiency of background signal generation e.g. by light absorption on the walls of the PA cell [Pa/mW]
Noise, sensitivity, MDC and MDOAC

- $\sigma$: measurement noise
- Its typical value is a few hundred nV (@ 1 second integration time)
- Inversely proportional to the square-root of the integration time

$$S = \frac{\Delta PA}{\Delta c} = P \cdot M \cdot C \cdot \alpha_0$$

$$MDC = \frac{3 \cdot \sigma}{S}$$

- $S$: sensitivity, MDC: minimum detectable concentration

$$MDOAC = \frac{3 \cdot \sigma}{S \cdot \alpha_0}$$

- MDOAC: minimum detectable optical absorption coefficient
Frequently Asked Questions

• **Is the PA equation indeed that simple?** Most of the cases yes, but the PA signal is mathematically a complex quantity (it has amplitude and phase)

• **How the phase of the PA signal is defined?** It is the delay of the PA signal relative to the laser modulation

• **Is the relation between concentration and PA signal always linear?** Sometimes not, especially at low concentration. (Primary because of the phase difference between the useful and the background signal)

• **What are the typical values for these quantities?** $M \approx 50 \text{ mV/Pa}$, $C \approx 2000 \text{ Pa/cm}^{-1}/\text{mW}$. $\text{MDOAC} \approx 5 \cdot 10^{-8} \text{ cm}^{-1}$

• **Based on the equations isn’t the PA an absolute method and thus no calibration is needed?** In principle yes, sensitivity can be estimated within 10%
Comparison of photoacoustic and optical absorption spectroscopy
Direct inter-comparison (at the Rice University Houston, 2001. Published in Applied Spectroscopy): the set-up
The result of inter-comparison at the Rice University: response time
Inter-comparison via ozone measurements: background noise

Measured $O_3$ concentration [ppb] vs. Time [hh:mm]
Inter-comparison via ozone measurements: field measurements

![Graph showing ozone concentration over time](attachment:image.png)
What we learnt from OA-PA inter-comparison:

- With laser power >5 mW, PA has a somewhat better measurement repeatability than that of OA
- PA systems can have shorter response time
- PA systems are far less sensitive to optical alignment
- PA systems are much less sensitive to contaminations of the windows of the cell or contaminants in the measured gas
Main application areas of our PA systems:

• \( \text{H}_2\text{S}, \text{CO}_2 \text{ and H}_2\text{O} \) concentration measurement for the oil and natural gas industry
• Gas permeability measurements of polymers
• Airborne measurement of atmospheric water vapour and total water
• Quantitative and qualitative analysis of combustion and atmospheric aerosol
Oil and Natural Gas Industry

By Hobré B.V. (The Netherlands) and Hobré Laser Technology (Hungary)
Typical Hobré-Hilase Applications

- $\text{H}_2\text{S}$ monitoring before and after scavenger dosing
- $\text{H}_2\text{S}$ in Crude Oil
- $\text{H}_2\text{S}$ levels in storage tanks
- $\text{H}_2\text{S}$ and $\text{H}_2\text{O}$ in Natural Gases and LPG's
- $\text{H}_2\text{S}$ and $\text{CO}_2$ in (amine) absorbers and Natural Gases
- $\text{H}_2\text{S}$ in production and test separators
- $\text{H}_2\text{S}$ in Refinery fuel and flare gases
- $\text{H}_2\text{O}$ and $\text{H}_2\text{S}$ in recycle gas
H₂S before and after sweetening
Dual Cell Hobré-Hilase
H$_2$S in Crude Oil Applications

**Custody Transfer**
- Safety during transport and storage

**Sulfide Stress Cracking**
- Pipeline and process equipment

**Separator Applications**
- Vapour pressure H$_2$S in gas phase

**Why using the Hobré-Hilase:**
- Measurement in liquid phase not possible,
- Stripping with carrier gas and measurement in gas phase,
- Dilution not required – 10 ppm H2S in liquid is approx. 500 ppm in gas phase,
- No interference from aromatics like with UV / less sensitivity to contamination,
- Low maintenance.
H$_2$S Levels In Storage Tanks

- The presence of H2S in fuels poses a dual danger through the storage and handling

- Fuel containing entrained H2S gas will release some of that gas throughout its storage

Factors:
- Quality H2S in liquid phase
- Time the fuel is stored
- Temperature of fuel oil

Measurement:
- H2S, CH4, C2H6
Refinery Applications

Recycle Gas in the Reformer
- Moisture and $\text{H}_2\text{S}$ are important for catalyst function

Hydrotreaters convert Sulphur to $\text{H}_2\text{S}$
- $\text{H}_2\text{S}$ removal from the gas, in most cases by amine treaters

Fuel Gas and Flare Gas
- Unique feature:
  Accurate at low level, but still able to follow upset in percent levels
  Independent to density variations
Natural Gas Applications

Concepts available:
- Optical detection, a single multi-pass measuring cuvette and scrubber which is used for background-matrix measurement (TDL/O)
- Photo acoustic detection, two measuring cuvettes in serie. One used on process gas and a second of reference gas coming from scrubber (TDL/PA)

**H2S at low ppm Levels**
The Hobré-Hilase does low ppm readings with repeatability of ± 0.3 ppm

**TDL/PA**
- No stream switching
- Low sample flow at levels as with tape analyser
- Multi-stream analysis possible with parallel flow paths
Hobré-Hilase with Scrubber

- Scrubber tube
- Tube with glass beads
- PA cell high range Inlet of process
- PA cell low range Outlet of process
Dual Cell Hobré-Hilase

For example, H₂S and H₂O
Atmospheric water vapour and total water measurements
Photoacoustics in the CARIBIC project

5 years,
> 30 flights,
Sensitivity: 0.2 – 0.5 ppm,
Response time: < 10 s
Measurement results (CARIBIC)

CARIBIC flight LH-158  Manila - Guangzhou 06 July 2006

Total water (vapor + cloud)

Water vapor

H$_2$O (ppmv)

Date / Time

2006.07.06 12:20 2006.07.06 12:50 2006.07.06 13:20
Qualitative and quantitative analysis of combustion and atmospheric aerosol
• Aerosol particles interact with light via scattering or absorption

• *Wavelength dependent absorption* is strongly influenced by the aerosol *chemical properties* (which in turn depends on the *source* of the aerosol particles and the generation mechanism)

• Although there are a few methods for optical absorption measurements, only PA is free from sampling and measurement errors (artifacts)

• Further studies are in progress to find unequivocal correlations between PA measurements and aerosol properties
Gas permeability measurements
DETECTION SYSTEM

Photoacoustic chamber

Mikrofon

Laser

Electronics

Mass Flow Controller

Diffusion cell

Sample

Gas of interest

\( \text{H}_2\text{O}, \text{H}_2\text{S}, \text{CH}_4, \text{CO}_2 \)
Advantages of the PA permeation method

- Continuous measurement with high sensitivity (due to the low sampling volume)
- Complies with the ISO standard 15106-2:2003
- Permeation at temperature up to 160°C and pressure up to 1000 bar can be measured
- Unlike with other methods, with PA the entire permeation process can be measured and thus a numerical fitting method to the entire curve can be applied (not only to the steady-state part)
- Improved accuracy of the permeation parameters, possibility to detect anomalous permeation (chemical reaction, spontaneous gas emission)
Representative results with Hilase-Perm

Amount of permeated methane (cm$^3$/m$^2$) vs. Time (hour)

- 1 mm
- 2 mm
- 4 mm
Representative results with Hilase-Perm

![Graph showing the amount of permeated CO2 (cm^3/m^2) over time (hour) at different temperatures (25 °C, 50 °C, 75 °C, 100 °C).]
Representative results with Hilase-Perm

\[ \ln P = \frac{1}{T} \]

- \( \text{H}_2\text{S} \)
- \( \text{CO}_2 \)
- \( \text{H}_2\text{O} \)
- \( \text{CH}_4 \)
Various sample geometries can be measured
Various sample geometries can be measured
Summary

• A carefully designed and operated PA system is a powerful tool in many applications

• A single PA system can be used as a combination of several analysers

• Outstanding advantage of the method is the capability of long term fully automatic operation
Thank you for your attention!