Cantilever Enhanced Photoacoustic with Laser and Other Sources

Jussi Raittila, Juho Uotila, Aleksi Helle, Juha Fonsen, Kari Roth, Henrik Kronholm, Arto Branders, Ismo Kauppinen, and Jyrki Kauppinen

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Gasera Ltd., Tykistökatu 4, 20520 Turku, Finland
The quest for greener and cleaner environment

The most important demands for gas analysis techniques

- Sensitivity
- Selectivity
- Hand-held size
Photoacoustic spectroscopy

- Photoacoustic effect was discovered in 1880 by Alexander Graham Bell
- This **theoretical potential has not been reached**, since conventional microphones have been used for sensing the pressure pulses
- Gasera's novel cantilever sensor technology allows the use of the full potential of the photoacoustic phenomena

Photoacoustic spectroscopy is based on the **absorption of light** leading to the **local warming** of the absorbing volume element. The subsequent expansion of the volume element generates a **pressure wave** proportional to the absorbed energy, which can be detected via a pressure detector.
Key inventions

- **Cantilever sensor**
  - Over 100 times greater physical movement can be achieved compared to conventional microphone membrane – cantilever has very low spring constant 1 N/m
  - Highly linear response

- **Optical readout system**
  - Contactless optical measurement based on laser interferometry
  - Measures cantilever displacements smaller than picometer ($10^{-12} \text{ m}$)
  - Extremely wide dynamic measurement range
PAS technology platforms

1. **LASER PAS**
   Reliable and cost effective gas analyzer products with down to ppb/ppt sensitivity in safety and industrial applications.

2. **FTIR PAS**
   Measures the full IR spectrum of the sample gas mixture and compares the result to library spectra of pure compounds. Enables sensitive and selective portable/hand-held gas analyzers for real-time simultaneous monitoring of over 50 gas compounds.

3. **NDIR PAS**
   Enables sensitive gas analyzer for multi-gas monitoring in industrial applications.

4. **DIFFERENTIAL PAS**
   Enables a small and cost effective single or dual gas sensor with extremely high sensitivity and selectivity for fast open path measurements with response time below 0.1 seconds. Highly suitable e.g. for gas flux measurements, breath diagnostics, and tail pipe measurements.
Current Product Lines

**F10 – Multigas Analyzer**
- Simultaneous monitoring of up to 9 gases
- Sub-ppm detection limits with 5 orders of magnitude dynamic range
- NDIR-PAS: Uses electrically pulsed IR source and 10 optical filters (no chopper)

**LP1 – Laser PAS Analyzer**
- Sub-ppb detection limits
- High selectivity
- Tunable laser spectroscopy combined with cantilever enhanced photoacoustics

**PA101**
- Lab FTIR accessory for gas analysis
- Automated gas exchange
- Closed loop headspace analysis from low volume

**PA301**
- Measures solid, semi-solid, and liquid samples
- 100 times faster compared to other alternatives
- Measures samples where conventional techniques fail
- Depth profiling
- FIR measurements
Powerful light sources for gas analysis

- NIR DFB laser offer typically power of 1mW-100mW depending on the wavelength
- Quantum cascade lasers typically provide 1mW – 100 mW power
- QCL allow the measurement in MIR wavelength range where the absorption lines are generally orders of magnitude higher than NIR lines
- OPO’s may provide up to 1 W power to 3um range where the hydrocarbons
- CW DFB QCL allows wavelength modulation over single lines
- ECQCL – allows measurement of spectrum in a wider wavelength area and true multicomponent analysis and enhanced selectivity
The advantages of cantilever enhanced photoacoustics

Cantilever based optical microphone ➔ Very high sensitivity!
High sensitivity with QCL

Formaldehyde

- Quantum cascade laser provides high light power to MID-IR range
- Formaldehyde sample of 2 ppm
- Continuous wave DFB-QCL source 47 mW (Alcatel Thales III-V lab) + Gasera PA201
- Detection limit (3 RMS): 623 ppt @ 28.5 seconds
- 30 spectral points, 0.951s/point

High sensitivity with QCL

Ammonia

- CW ECQCL from Daylight solutions
- Ammonia sample of 3.7 ppm
- DFB-QCL source (62 mW) + Gasera PA201
- Detection limit 240 ppt (0.9s) at 1065 cm\(^{-1}\)
- Resolution is 0.1 cm\(^{-1}\)
High sensitivity with OPO
Hydrogen cyanide

- OPO (optical parametric oscillator) is an IR-source providing high light power in MID-IR range and also at 3 μm range
- Measured at University of Helsinki
- Sample concentration: 17 ppb of HCN
- Continuous wave OPO (500mW) + Gasera PA201 (discrete sampling)
- Detection limit: 65 ppt @ 1 second

High sensitivity trace gas detection by cantilever-enhanced photoacoustic spectroscopy using a mid-infrared cw OPO, J. Peltola et al., Optic Express, submitted
High sensitivity with OPO Methane

- OPO from Cobolt AB
- Sample concentration: 10 ppm of CH4
- Pulsed OPO (100mW) + Gasera PA201 (discrete sampling)
- Detection limit: 3.3 ppb @ 1 second
- Demo at Gasera booth 555
The typical measurement setup

Typically 10 cm or less
The advantages of cantilever enhanced photoacoustics

Cantilever based optical microphone → Very high sensitivity!

Short optical path length → Wide linear dynamic range
Acetylene measurement in nitrogen

- Different acetylene concentrations were measured in nitrogen background.
- The detection limit of acetylene with 10 s integration time was 9 ppb (2 x RMS).
- The measurement was linear up to 10000 ppm and at 20000 ppm signal had decayed 6 %.
- Precision (1 x std) of the measurement results at 10 000 ppm was 0.3 % (28 ppm) and at 100 ppm concentration also 0.3 % (260 ppb).

Output data of the LP1 with different acetylene concentrations (0 ppm – 20 000 ppm) in nitrogen.

Dependence between the LP1 acetylene concentration reading and set concentration in logarithmic scale.
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Very high sensitivity!

Short optical path length
Wide linear dynamic range

Cantilever microphone allows use of low pressure
Improved selectivity with sensitivity maintained
Example of N2O measurement

Spectrum at ambient pressure

- Absorbance spectrum of N2O (350 ppb), CO2 (2.5 %), H2O (2 %), CO (200 ppm), and CH4 (200 ppm) mixture in the atmospheric pressure with 10 cm absorption path length.
Example of N2O measurement
Spectrum at 300 mbar pressure

Absorbance spectrum of N2O (350 ppb), CO2 (2.5 %), H2O (2 %), CO (200 ppm), and CH4 (200 ppm) mixture in the 300 mbar pressure with 10 cm absorption path length.
Measurement of N2O signal from car exhaust gas sample (petrol engine)

- Sample was taken into a syringe from the petrol engine tailpipe right after ignition and after short warm-up time.
- Laser spectrum of the sample indicate that there was 16 ppm of N2O in the first sample and 380 ppb after the motor was warmed up.
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Improved selectivity with sensitivity maintained

Photoacoustic signal is proportional to gas concentration
No gas = no signal, zero background and improved stability
Direct measurement in PAS vs. Transmission spectroscopy

In PAS only absorption is measured which makes the measurement very accurate and free of drift. This is the key factor for the unbeatable stability and reliability of the PAS method. In transmission spectroscopy the small decrease of the large signal is measured and therefore small changes in the background signal create large errors and drifts in the measurement result.
The advantages of cantilever enhanced photoacoustics

Cantilever based optical microphone

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Photoacoustic signal is proportional to gas concentration

- No gas = no signal, zero background and improved stability

- Minituarization
Towards minituarization

- Compact, rugged gas sensor providing orders of magnitude improvement in sensitivity (+ selectivity):
  - Volume < 5 cm³
  - Analysis response time ~ 100 ms
  - Min gas flow rate < 50 ml/min
  - Dynamic range > 10 000
  - Temperature range -30°C to +50°C
  - Cost €100

- Sensor will be applicable to a wide range of gases including: CO, CH₄, NH₃,…

- More info on FP7-MINIGAS website:
  - http://fp7minigas.openinno.net
Towards miniaturization

- The final realization body was made from aluminum
- Open path design with cell length of about 2 cm
- Photoacoustic cell was made with LTCC technique
- Contains two high power IR LEDS with TEC elements
- LEDs show high potential in MID-IR spectroscopy
  - Modulation frequency freely selectable
  - Unfortunately the power is still below 100 μW which limits considerably the use of them
Towards a hand-held instrument

- A hand-held instrument with a laser source
- Two microphone system in order cancel the effects of vibration
- ppb range sensitivity
- Superior selectivity

EU: MINIGAS, CUSTOM, Doyies
Thank you!

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See our other presentations:

Detection of Hidden Persons and Illegal Substances by an Array of Quantum Cascade Lasers and Cantilever Enhanced Photoacoustic Spectroscopy, **Tuesday, March 19, 2013, 04:15 PM, Room 117**

The Use of Photoacoustic Multi-Gas Analysis in Air Quality Monitoring Applications by Utilizing the Combination of a Tunable Laser Source and Filter Based NDIR Spectroscopy, **Monday, March 18, 2013, 09:35 AM, Room 119B**