Cantilever enhanced tunable diode laser photoacoustic spectroscopy in gas purity measurement – case study: acetylene in ethylene

Juho Uotila, Jussi Raittila, Ismo Kauppinen
¹Gasera Ltd., Tykistökatu 4, 20520 Turku, Finland

Pittcon 2012, Orlando
Photoacoustic technology with cantilever pressure sensor

- Photoacoustics is proved to be extremely sensitive technique in gas analysis – there is a long tradition of very sensitive measurements with gas lasers.
- Gasera is offering a choice for enhancing the microphone sensitivity by using an optical microphone with a cantilever pressure sensor.
- Cantilever is made out of silicon and has dimensions in the level of: length 5 mm, width 1.2 mm, thickness 10 µm.
- Because the cantilever has very low spring constant (1 N/m), it reacts to extremely low pressure variations.
- The cantilever movement is measured optically with a compact laser interferometer, which allows wide dynamic range for the measurement of movements from below 1 pm to over 10 µm.
Cantilever pressure sensor combined to laser sources

- The cantilever enhanced photoacoustic cell performs extremely well with laser sources.
- The best ever normalized noise equivalent absorption coefficient (NNEA) value $1.7 \times 10^{-10}$ cm$^{-1}$W/$\sqrt{\text{Hz}}$ for the photoacoustic cell was measured for cantilever enhanced cell by Koskinen et. al. This is more than ten times better than reported e.g. with tuning fork QEPAS $5.4 \times 10^{-9}$ cm$^{-1}$W/$\sqrt{\text{Hz}}$.
- In a test made by Lindley et. al. the three photoacoustic cells were compared by measuring the detection limit for acetylene:
  - a resonant cell containing a single microphone – 650 ppb,
  - a differential cell with dual microphone – 440 ppb,
  - a cantilever pressure sensor – 14 ppb.

LP1 photoacoustic gas analyzer

- Tunable laser photoacoustic spectroscopy with cantilever enhanced optical microphone
- Gas cell stabilized to 50° Celsius temperature
- Patented ultra-sensitive optical microphone based on a MEMS cantilever sensor coupled with a laser interferometer to measure microscopic movement of the cantilever sensor
- 19” 3U housing for both table stand and rack mount installation
- Built in PC computer with 5,7” color VGA display in the front
- User interface of setting the alarm levels for concentrations of gases under monitoring
- Data storage capacity of approx. 2 GB. Sufficient for more than a year of continuous monitoring of 2 gases with the shortest sampling interval.
- Transfer of measurement results to memory stick via USB or to PC via USB, Ethernet or serial ports.
- Three gas connections in the rear. The two incoming gas lines, sample and purge gas line, are equipped with filters for dust and small particles.
- Compensation of the fluctuations of temperature and pressure within the operational conditions
Measurement setup

- Optical microphone DSP unit
- TEC controller
- Laser driver
- Readout interferometer
- DFB diode laser
- Aspheric lens
- Photoacoustic cell: Length 100 mm, Diameter 4 mm
- Cantilever
- Beam dump
- Gas IN
- Gas OUT
- Balance cell
- Laser beam
Tunable diode laser spectroscopy with LP1

- Wavelength modulation
- Signal measured at the second harmonic frequency.
- No background signal.

Laser line

Gas absorption line

Laser current modulation signal

Photoacoustic signal

Frequency [Hz]

Time [a.u.]

Wavelength [μm]

Absorption coefficient [cm⁻¹]

1.5305 1.531 1.5315 1.532 1.5325

Fundamental frequency

2nd harmonic frequency
Acetylene impurity measurement

- It is essentially important to be able to measure impurities in gas manufacturing with a high precision.
- The measurement tasks can be challenging due to the high background of the bulk gas.
- An example of an important gas purity case is acetylene in ethylene.
- Ethylene is an important feedstock for the petrochemical industry.
- Because ethylene is used in the manufacture of a wide range of compounds, it has very stringent purity specifications.
- It is especially important for polymer grade ethylene as acetylene poisons polyethylene catalysts.
Acetylene absorption line selection

- Acetylene line at 1531.6 nm was used.
- The line has no cross interference with ambient atmospheric gases at the measurement pressure of 500 mbar.
- The second derivative spectra of acetylene and ethylene were measured indicating small interference.
- The second derivative phase locked wavelength spectra of 100 ppm of acetylene in ethylene, 100% ethylene, 10 ppm of acetylene in ethylene simulated from measured spectra, and simulated 100 ppm/500 mbar acetylene 2nd derivative of absorption coefficient from HITRAN.
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.
Acetylene measurement in ethylene

- Different acetylene concentrations were measured in ethylene background.
- The response to the ethylene concentration was as linear as with nitrogen background.
- Precision (1 x std) of the measurement results at 2000 ppm was 0.8 % (17 ppm) and at 100 ppm concentration 1 % (1 ppm) with 10 s integration time.

Output data of the LP1 with different acetylene concentrations (0 ppm – 2000 ppm) in nitrogen.

Dependence between the LP1 acetylene concentration reading and set concentration in logarithmic scale.
Acetylene measurement in ethylene

- Photoacoustic signal from different acetylene concentrations were measured in ethylene background.
- The detection limit of acetylene with 10 s integration time was 20 ppb (2 x RMS).
- The increase of the detection limit compared to nitrogen background is due to the photoacoustic signal decrease due to ethylene properties (heat conductivity, sound velocity, etc.).
Conclusions

- Cantilever enhanced photoacoustic detector is capable on measuring low ppb-level acetylene concentrations in nitrogen background and also in other background gases such as ethylene.
- Direct absorption measurement feature of photoacoustics, tunable diode laser wavelength modulation technique, and capability of using low pressures make the cantilever enhanced photoacoustics reliable and selective method for gas impurity analysis.
- Measurement of impurity gases other than acetylene is also possible, e.g. HCl, H2O, HF, H2S, etc.
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