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Tunable laser spectroscopy combined with novel photoacoustic technology for hand-held low-ppb gas analyzers in various applications

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Abstract

A versatile and modular technology suitable for several gas measurement applications requiring ppb level sensitivity and high selectivity in a hand-held size is presented. The proposed miniaturized cantilever enhanced photoacoustic detection scheme is combined with different types of NIR or MIR tunable laser sources. Several sources can be combined in the same miniaturized measurement cell and the sources are selected by the application requirements. The use of tunable laser sources provides the possibility to use high-resolution spectroscopy in order to achieve high selectivity in multi-gas analysis. The novel optical cantilever microphone provides high sensitivity in a miniaturized realization.

Key words: cantilever enhanced photoaocustics, hand-held, multi-gas analysis, widely tunable laser source, high selectivity.

Introduction

In the quest for cleaner and greener environment there is an obvious demand for improved gas analysis techniques. This demand emerges from the growing effect of global warming and the increase in the emissions of toxic gases from the industries and vehicles. A hand-held size multi-gas analyzer with ppb (parts per billion) level sensitivity would fulfill this need in several application fields such as homeland security, air quality, safety and asset management. Moreover, the existing technologies with compact size are not sensitive and selective at the same time. Therefore, new novel solutions should be sought after.

Research goals

Our aim is to develop a hand-held size and ppb level sensitivity multi-gas gas analysis technology platform, which can be configured into several different applications. Moreover this technology needs to answer to the most demanding request of being selective and sensitive at the same time. Also other requirements such as wide dynamic range, fast response time, lightweight, temperature and vibration stability, low power consumption, production cost and long maintenance period are considered.

Cantilever enhanced photoacoustics

Measurement setup based on optical infrared spectroscopy can be sensitive and selective at the same time and seems to be most promising in detecting simultaneously wide range of toxic industrial compounds (TIC) from the ambient air. Photoacoustic (PA) measurement principle has been selected due to the fact that sensitivity is almost not dependent on the optical path length and the analysis gas cell can be miniaturized without compromising sensitivity [1]. The sensitivity of the proposed technology platform is achieved partly by the use of patented silicon MEMS cantilever sensor (see Fig 1.) coupled with an optical interferometric readout system [1] and partly by the high optical power provided by tunable laser sources [2].

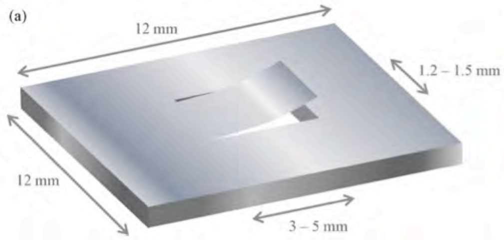

Fig. 1. The microfabrication process of the ultra-sensitive cantilever pressure sensors is based on silicon-on-insulator (SOI) wafer etching, in which the challenge is to control and minimize the residual stress related curving in thin (~ 5 µm) but large-area (few mm^2) components [3].

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Due to the use of cantilever sensor resonant PA cell is not required, and therefore, different light modulation frequencies can be used at the same time. Several laser sources can be connected to one miniaturized PA gas cell. The principle of a tunable laser based measurement setup is depicted in Fig. 2.

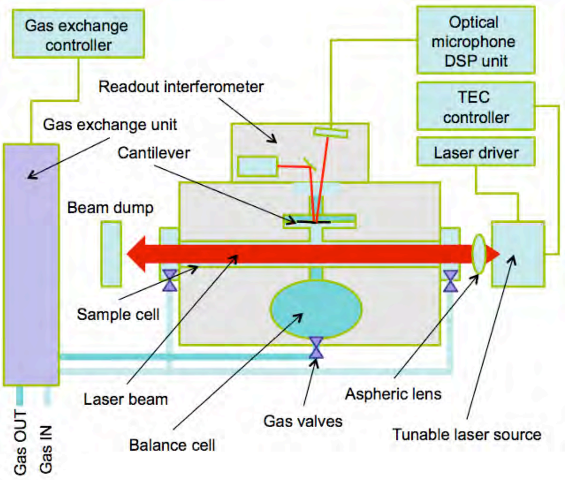

Fig. 2. The measurement principle of a tunable laser PAS system.

A comparison of the non-resonant mode cantilever cell against two other photoacoustic cells with capacitive microphones (a resonant photoacoustic cell and a differential Helmholtz resonance cell) was made by Lindley et al [4]. The cantilever enhanced cell proved to be about 100 times more sensitive than either of the two other cells. Koskinen et al have measured the best ever reported NNEA (1σ) value of 1.7×10^{-10} $cm^{-1}WHz^{-1/2}$ by using 30 mW DFB laser at 1572 nm for the detection of carbon dioxide [5]. Parkes et al demonstrated a modulation frequency divisional multiplexing (MFDM) with NIR (1534 nm – 1618 nm) DFB diode lasers using cantilever enhanced non-resonator cell [6]. The gases that they measured simultaneously were C_2H_2, CH_4, CO, and CO_2. The NNEA value that they received with CO_2 was 3.4×10^{-10} $cm^{-1}WHz^{-1/2}$ (3σ), which would correspond to 1.1×10^{-10} $cm^{-1}WHz^{-1/2}$ with 1σ noise.

Overcoming challenges

Disadvantages of the PA principle are known to be the sensitivity to external vibrations and that if the background gas matrix changes, relaxation processes and pathways can change, with a consequent alteration in the signal level [7]. Main concern in the robustness of the system is the tolerance of external vibration. Therefore, a dual cantilever sensor cell has been designed where summing the signals of the two cantilevers eliminates the acceleration noise signal. Two cantilevers are located in the opposite sides of the photoacoustic cell. Acceleration moves them to the same direction and photoacoustic signal to opposite directions. By subtracting the two cantilever signals the photoacoustic signal is doubled and acceleration noise signal is cancelled. This system, shown in Fig. 3., is capable on damping the acceleration noise in a wide frequency range by the factor of 100 – 500.

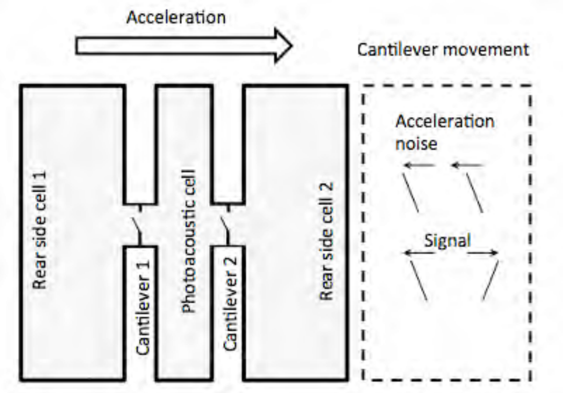

Fig. 3. The structure of the damping system for acceleration noise consisting of the two cantilevers.

A new spatial type readout interferometer design for the detection of the cantilever sensor displacement will enhance the stability so that the drifts e.g. due to temperature variations between their responses can be minimized. The resolution of the optical readout is below 1 picometer (10^{-12} m) with 1 second observation time. This is well below the cantilever movement due to the Brownian noise, and therefore, the readout system does not introduce additional noise as demonstrated in Fig. 4.

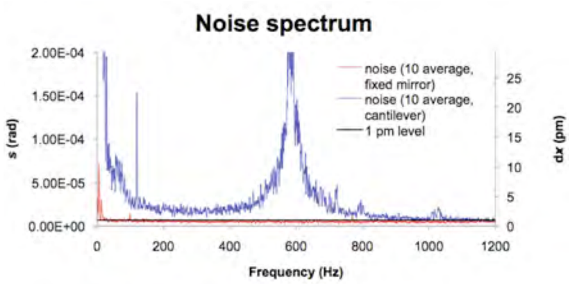

Fig. 4. The spatial readout interferometer was tested on a cantilever and a fixed mirror. The RMS noise from the fixed mirror was 0.47 pm with 1 s measurement time which is well below the Brownian noise of the cantilever sensor. The cantilever resonanace is clearly seen around 600 Hz.

Tunable laser sources

Possible light source for the photoacoustic gas measurement system are a broadband IR-source, LED source or a laser operating at continuous or pulsed mode. With lasers the selectivity and sensitivity can be enhanced compared to the broadband alternatives. Also amplitude and especially wavelength modulation can be easily performed without the need for mechanical choppers.

The versatility of the proposed technology platform originates from the fact that the system can be tailored to different applications by selecting appropriate laser sources. Almost complete coverage of the NIR and MIR infrared reqions can be found by different laser technologies as shown in Fig. 5.

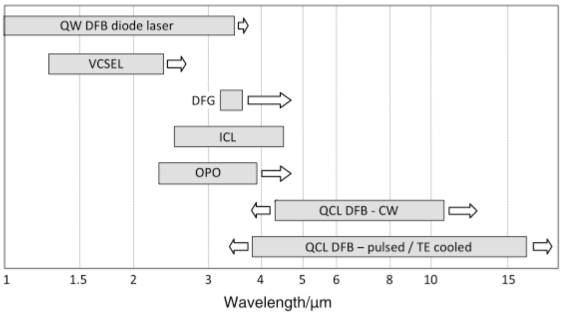

Fig. 5. Different laser technologies cover different wavelength regions in the infrared spectrum (CW: continuous wave, QW DFB: quantum well distributed feedback, DFG: difference frequency generation, ICL: interband cascade laser, OPO: optical parametric oscillator, QCL: quantum cascade laser) [7].

Among the laser technologies available, tunable DFB (Distributed FeedBack) semiconductor laser diodes as light sources in the Near-InfraRed (NIR, 0.8-2.5 µm) have shown a good potential. Compact, selective, sensitive and relatively low-cost trace gas analysis devices have been already demonstrated.

Fundamental mid-infrared (MIR) absorption lines are in the order of 100x stronger than the harmonics in NIR region. Therefore, MIR absorption spectroscopy will be more appropriate to the stringent sensitivity and selectivity requirements. Optical parametric oscillators (OPO) and Quantum Cascade Lasers (QCL) operate at the MIR range (3-12 µm) and provide wide tuning range. This makes them extremely attractive light sources for multi-gas analysis especially when combined with the cantilever enhanced photoacoutic detection scheme. These sources provide the potential to replace FTIR spectrometers for certain applications. Pulse mode operation allows low power consumption (in the order of few Watts), which is required for battery powered operation. In resent developments the tuning range has been extended to several 100 cm^{-1} and even over 1000 cm^{-1}. The linewidth is in the order of 1 cm^{-1} even in the pulsed mode operatation. This allows the use of similar chemometrics as used in FTIR spectroscopy and very good selectivity among the different measured components can be achieved. Wide linear dynamic range due to the short optical path length (few centimeters) in the photoacoustic detection ensure better starting point for the chemometric algorithms compared to FTIR systems where the optical path length is typically several meters and the response highly non-linear.

Uotila et al. have demonstrated measurements combining the cantilever enhanced photoacoustic detection with DFB-QCL (47 mW power) and EC-QCL source (64 mW power). Detection limit of 1.5 ppb for formaldehyde using DFB QCL source with 0.9 seconds measurement time was obtained and detection limit of 0.24 ppb for ammonia with 0.9 seconds measurement time using EC-QCL source was obtained [8]. The spectrum of the EC-QCL measurement is shown in Fig. 6.

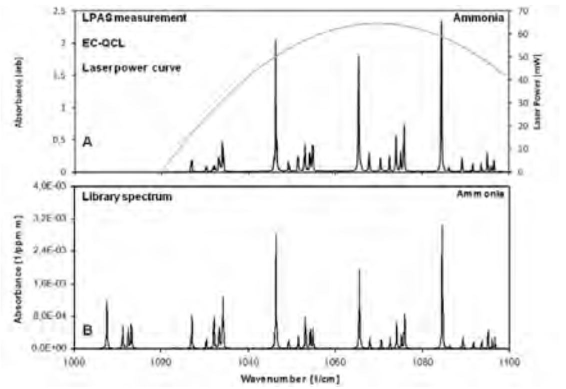

Fig. 6. Photoacoustic spectrum (3.7 ppm) and (PNNL) library spectrum of ammonia [8].

Among the technologies available, QCLs and OPOs have a potential for extreme compactness, long lifetime, high reliability and low cost. The aim in FP7 DOGGIES project is the development of a novel MIR source, which is based on multiplexing of an array of single-mode DFB QCLs through the extensive use of silicon Photonic Integrated Circuits (PIC) for the realization of a miniaturized tunable MIR laser source. The main advantages of the multiplexed single mode QCLs array device for optical spectroscopic systems are: emission in the MIR range (4-10 µm), highly compact, potentially low cost, widely tunable source directly usable with photoacoustic sensor systems to allow simultaneous selective measurement of several gas species in one instrument.

An example measurement of using cantilever enhanced photoacoustic detector combined with a compact tunable mid-infrared optical parametric oscillator (OPO) laser source is demonstrated in Fig 7. Target molecule in the demonstration was methane whose detection limit was determined to be 4 ppb in 1 second observation time. Other experiment with a high power OPO source demonstrates 160 ppt noise level for HCN measurement shown in Fig. 8.

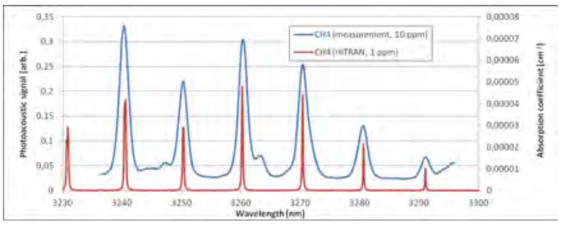

Fig. 7. Measured spectrum of 10 ppm methane in Nitrogen balance and simulated HITRAN spectrum for comparison. A compact OPO laser wavelength was scanned from 3236.45 nm to 3295.95 nm in 0.1 nm steps. Each step was measured 0.957 second.

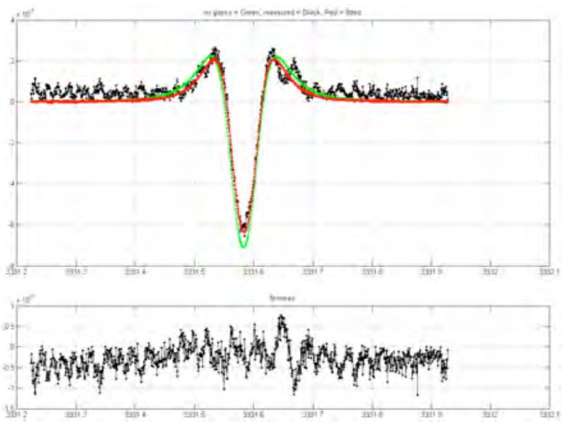

Fig. 8. demonstrates 160 ppt lower detection limit (1 s., S/N = 1) achieved by combining cantilever enhanced photoacoustic gas cell with an 0.5 W OPO source which was tuned over HCN transition at 3331.58 cm^{-1}. The sample concentration in the experiment was 17 ppb.

Hand-held multi-gas analyzer concept

The proposed hand-held multi-gas analyzer concept combines the latest development on both sides of the system utilizing widely tunble MIR range lasers combined with the cantilever enhanced photoacoustic detection. The maximum tuning range of single mode DFB QCLs achieved by changing the laser injection current is 5 - 10 cm^{-1}, which makes it difficult to scan far enough to allow simultaneous measurement of several gas species or to get the whole fingerprint of a complex molecule (> 4 atoms) with one DFB-QCL. One way to take advantage of the broadband gain of such QCLs is the use of an external cavity (EC) configuration to obtain a single mode operation at any wavelength within the laser gain profile. EC-QCLs are widely tunable and can achieve tuning range from 100 cm^{-1} even up to 1 200 cm^{-1}. Therefore a single widely tunable EC-QCL source can provide low ppb quantitative detection sensitivity for wide range of enviromental pollutants and TICs in a single instrument with only few seconds response time.

The concept is extremely versatile since the different applications can be covered by the selection of the laser source or sources. For example in air quality analysis volatile organic components such as Formaldehyde, Benzene, Toluene, Xylene and Acetaldehyde can be covered with EC-QCL tuning over the 1000 – 1200 cm^{-1} range and components such as NO_2 and H_2S could be covered with separate DFB-NIR lasers combined to the one single photoacoustic gas cell. High level of robustness is achieved due to the fact that the system has essentially no moving parts. Such a system can be packaged in a compact hand-held instrument size as illustrated in Fig. 8.

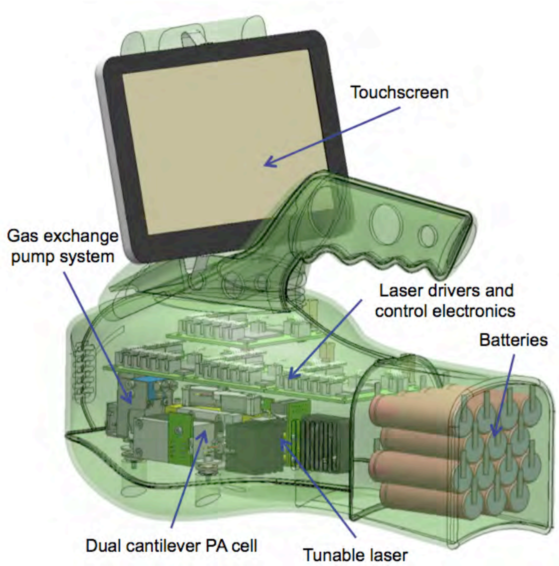

Fig. 8. Illustration of a possible realization of a hand-held multi-gas analyzer instrument with the proposed widely tunable laser photoacoustic spectroscopy concept.

Acknowledgements

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