

Perspective

A SCITECHNOL JOURNAL

Position Effects of Acoustic Micro Resonator in Quartz Enhanced Photo Acoustic Spectroscopy

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Received date: 11 February, 2022, Manuscript No. RJOP-22-60752;

Editor assigned date: 14 February, 2022, PreQC No. RJOP-22-60752 (PQ);

Reviewed date: 25 February, 2022, QC No. RJOP-22-60752;

Revised date: 07 March, 2022, Manuscript No. RJOP-22-60752 (R);

Published date: 14 March, 2022, DOI: 10.4172/Rjop.1000039

Description

The development of quartz-enhanced photo acoustic sensors for the sensitive and selective quantification of molecular trace gas species with resolved spectroscopic features is reported. The basis of the QEPAS technique, the technology available to support this field in terms of key components, such as light sources and quartz-tuning forks and the recent developments in detection methods and performance limitations will be discussed. Furthermore, different experimental QEPAS methods such as on beam and off beam QEPAS, quartz-enhanced evanescent wave photo acoustic detection, modulation-cancellation approach and mid-IR single mode fibercoupled sensor systems will be reviewed and analyzed. A QEPAS sensor operating in the THz range, employing a custom-made quartztuning fork and a quantum cascade laser will be also described. Finally, we evaluated data reported during the past decade and draw relevant and useful conclusions from this analysis. The detection and measurement of trace gas concentrations is important for both the understanding and monitoring of a wide variety of applications, such as environmental monitoring, industrial process control analysis, combustion processes, detection of toxic and flammable gases, as well as explosives. For example, trace gas sensors capable of high sensitivity and selectivity are required in atmospheric science for the monitoring of different trace gas species including greenhouse gases and ozone, and in breath diagnostics, nitric oxide, ethane, ammonia and numerous other biomarkers. Quantitative and qualitative gas sensors can be categorized into four general groups: analytical sensors, electrochemical, semiconductor sensors and laser optical absorption sensors. The sensor classification is primarily based on the physical mechanism that is used.

Analytical Techniques

Analytical techniques do not offer real-time response, tend to be costly, invasive and occupying a large spatial footprint. Electrochemical gas sensors can be relatively specific to individual gas, have usable resolutions of less than one part per million of gas concentration, and operate with very small amounts of current, making them well suited for portable, battery powered instruments. However, they experience hysteresis and are influenced by water humidity. Moreover, one important characteristic of electrochemical sensors is their slow time response: when first powered up, the sensor may take several minutes to settle to its final output value and when exposed to a mid-scale step in gas concentration, the sensor may take tens of seconds to reach 90% of its final output value. Techniques based on laser absorption spectroscopy trace gas sensing, compared to other techniques, are considerably faster with response times suffer from minimal drift, offer high gas specificity, capable of part-perquadrillion detection sensitivity and permit real time in-situ measurements. The principle of molecular absorption is based on the transitions that an electromagnetic wave causes in a chemical species. If a molecule is irradiated by infrared light, it is excited to a rotationalvibrational energy level manifold. Absorption lines are specific for each chemical species. To-date LAS has been developed mostly in the spectral region 12 µm, which covers a substantial spectral range of fundamental transitions in the so called molecular finger-print region. Further extension into the vibrational overtone, electronic and rotational spectral range is also feasible. The detection sensitivity of spectroscopic sensor systems that employ semiconductor lasers as a light source is limited by the available optical power, especially when dispersive elements and multi-detector arrays are used to analyze the light transmitted through the gas sample. In the near-IR spectral range optical parameter oscillators or conventional diode laser are typically the light source of choice. Two main QCL configurations are used distributed feedback QCLs having a Bragg reflector built on top of waveguide, which forces the QCL to operate in single axial mode operation. QCLs are tuned by keeping the device operating temperature fixed and changing the current or vice versa, keeping the current fixed and changing the temperature an external cavity QCL, in which the quantum cascade device is the laser gain medium and mirrors are arranged in a configuration external to the laser to create an optical cavity. By replacing one of the external cavity mirrors with a high quality diffraction grating, it is possible to tune the QCL emission wavelength over 15% of its central value.

Photo Acoustic Spectroscopy

This technique is also based on an optical absorption process, such as CRDS, ICOS and CEAS, but differs in the physical phenomenon used for the detection of the absorption signal. When light at a specific wavelength is absorbed by the gas sample, the excited molecules will subsequently relax to the ground state either through emission of photons or by means of non-radioactive processes. These processes produce localized heating in the gas, which in turn results in an increase of the local pressure. If the incident light intensity is modulated, the generation of thermal energy in the sample will also be periodic and a pressure wave a sound wave will be produced having the same frequency of the light modulation. The PAS signal can be amplified by tuning the modulation frequency to one of the acoustic resonances of the gas sample cell. The key advantage of this technique is that no optical detector is required and the resulting sound waves can be detected by a commercial hearing aid microphone. Continuouswave single-mode diode lasers and optical parameter oscillators in the near-IR and QCLs in the mid-IR have been successfully applied in PAS. Compact photo acoustic gas sensors based on broadband IR sources have been reported. Resonant PAS cells and optical fiber amplifiers have been developed to enhance the PAS detection sensitivity. The three main noise sources are noise caused by the radiation that is incident upon the walls of the PAS absorption cell, non-selective absorption of the gas cell window and external acoustic



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noise. In order to improve the signal-to-noise ratio, different designs for PAS cells have been proposed and implemented including a resonant cell with acoustic buffers, windowless and a differential cell. A differential cell includes two acoustic resonators equipped with microphones having the same responsively at the resonance frequency of the cell. Since the laser light excites only one of the two resonators, the difference between the two signals removes noise components that are coherent in both resonators. Quartz-enhanced photo acoustic spectroscopy is an alternative approach to photo acoustic detection of trace gas utilizing a quartz tuning fork as a sharply resonant acoustic transducer to detect weak photo acoustic excitation and allowing the use of extremely small volumes.