STUDY ON THE WIDE RANGE APPLICABILITY OF PHOTOACOUSTIC SPECTROSCOPY

Ph.D. THESIS

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1. Introduction

In the last few decades the demand on sensitive, selective, fast and reliable gas monitoring systems in industry, biology and environmental applications is increasing. Infrared spectroscopy is a popular method because it does not need any consumables or chemicals, which reduces the maintenance costs and the need for supervision. Photoacoustic (PA) spectroscopy – a special version of infrared spectroscopy – is suitable for all gas detection areas. It fulfils the fast, automatic, long-term and stable operation requirements in industry, the high sensitivity requirement in biology or the needs of pollution or trace gas measurements in environmental applications.

The PA effect, discovered and described by Bell in 1880, basically implies the conversion of light into acoustic energy. However, due to the lack of an appropriate light source and the lack of a sensitive microphone, interest in the photoacoustic effect soon declined. By the end of the 1960s scientific interest increased once again due to the availability of laser sources, microphones as detection devices and improved signal processing developments.

2. Measurement methods

The basic theory behind photoacoustic detection is quite simple. Light absorbed by a sample (gas, liquid or solid sate material) will excite a fraction of the ground-state molecular population into higher energy levels. These excited states will subsequently relax through a combination of radiative or non-radiative pathways. The non-radiate relaxation results in local heat generation, and therefore an expansion in the irradiated region. The result is a transient pressure fluctuation in the case of pulsed excitation or a periodic pressure oscillation in the case of a modulated source which can be observed as an acoustic signal (sound wave) in the surrounding gas, and can be detected with a sensitive microphone. The intensity of the generated sound is proportional to the concentration of absorbing trace molecules.

The basic parts of a general photoacoustic system are the *(1) source of periodic radiation* (i.e., modulated continuous wave or pulsed) in the spectral region of interest, which illuminates the *(2) photoacoustic cell* containing the sample gas. Since the acoustic signal generation occurs in the cell a *(3) microphone* is attached to it. After amplification the signal of the microphone gets into a signal processing equipment for further analysis.

3. Objectives

From the beginning of its initial application, photoacoustic spectroscopy has undergone a tremendous development; however, it still has considerable development potential. One way is to find novel solutions for signal generation and signal detection. The measurement of gas mixtures is especially challenging, when individual components create significant PA signal at the excitation wavelength. Other possibilities for development of the PA spectroscopy are the application of new lasers as excitation sources or finding new application areas for existing systems. My thesis is focusing on these three above-mentioned areas of research.

1. Concerning the photoacoustic measurement of the concentration of carbon dioxide at 1431.4 nm wavelength **my aims** are:

- To investigate, how the molecular relaxation effect of carbon dioxide takes place at the 1430 nm wavelength.
- To develop a measuring and signal processing method, which can reduce the effect of molecular relaxation, thus the sensitivity of photoacoustic measurement of carbon dioxide concentration in nitrogen carrier gas can be maximized.
- To investigate the effect of molecular relaxation on the PA signal and its phase.
- To examine whether it is possible to build photoacoustic system for measurement of carbon dioxide concentration at the used wavelength (1431.4 nm) for practical applications.

2. The aims of measuring the products of alcoholic fermentation of young rice seedlings (submergence tolerant FR13A and submergence sensitive CT6241) with sensitive CO laser based photoacoustic trace gas detection technique are:

- To investigate the impact of different levels of oxygen shortage to the metabolism of rice plants.
- To compare the alcoholic fermentation of submergence-tolerant cultivar FR13A with a highly intolerant cultivar CT6241.
- To establish that oxygen level, that is required to inhibit alcoholic fermentation in both rice species.
- To determine the possible correlation between plants injury caused by the lack of oxygen and oxidative peroxidation, that takes place during alcoholic fermentation and re-exposure to air.

- To check the influence of illumination, since any resulting photosynthesis is likely to oxygenate the seedlings thus increasing the impact of the anaerobic gas supply on respiratory pathways.

3. The aims ozone concentration measurements with the photoacoustic method are:

- To design and construct a light source that illuminates in the UV spectral range, and is appropriate for photoacoustic measurement of ozone concentration.
- To compare the generation efficiency of the photoacoustic signal at low repetition rate and a quasicontinuous wave excitation technique.
- To demonstrate the practical applicability of the PA ozone measurements by filed tests.

4. In the case of the measurement of the optical absorption of aerosols with the photoacoustic method my aims are:

- To develop a three-wavelength photoacoustic system, that is able to measure optical absorption of aerosols at the UV, visible (green) and near infrared spectral range at the same time.
- To measure optical absorption coefficients of different aerosols (soot and mineral dust) at available wavelengths of the three-wavelength PA system.
- To demonstrate the field applicability of the multi-wavelength PA system.

4. New scientific results

1. An external cavity diode laser based photoacoustic set-up was built to investigate and eliminate the molecular relaxation effect of carbon dioxide at the wavelength of 1430 nm. The molecular relaxation effect can be

avoided by applying controlled wetting of the gas flow but as a side effect spectral overlapping of carbon monoxide and water vapor occurred. A successful method was developed for the elimination of the spectral overlapping of carbon monoxide and water vapor. With this method the minimum detectable concentration can be improved by an order of magnitude [1].

2. Alcoholic fermentation products, released from young rice seedlings into the gas flow were detected with CO laser-based photoacoustic trace gas detector, which is able to measure ethanol and acetaldehyde down to nl l^{-1} concentration range. It was proved that alcoholic fermentation began within 30 minutes after imposing an oxygen-free gas phase environment. Detailed comparison of the kinetics of ethanol, acetaldehyde and CO_2 releasing revealed no marked difference in anoxia and in re-exposure of air response between a submergence-tolerant (FR13A) and a more susceptible one (CT6241) [2, 6].

   During micro-aerobic treatment (notably 0.05 % O_2), and after re-aeration of rice seedlings acetaldehyde production is strongly enhanced while ethanol production was diminished. The effect was more pronounced in submergence-tolerant FR13A, and is linked to smaller level of peroxidation in lipid membranes as revealed by reports on slower ethane efflux. It was pointed out that lipid damage in a lower extent for FR13A is a result of diversion of more reactive oxygen species away from membrane attack by enhancing the production of less harmful H_2O_2, that serves as substrate in the conversation of ethanol to acetaldehyde [2, 6].

3. It was established that O_2 concentrations above 0.3 % are required in gas phase to inhibit alcoholic fermentation and to maintain normal aerobic

respiration in both rice genotypes. Furthermore, increasing the oxygen concentration of micro-aerobic treatment and illumination of the plants had very similar effects; both delayed the onset of fermentation and reduced its strength [2].

4. Three different types of excitation schemes were constructed for the photoacoustic measurement of ozone concentration. All of them based on the application of the fourth harmonic (266 nm) of Q-switched Nd:YAG lasers [3]. The measured ozone concentrations down to ppb level were compared for these three photoacoustic systems. The detection limit of the pulsed system was found not to be as low as was expected, due to large signal fluctuation arising from laser energy instability and optical saturation effect. Field tests of the modulated quasicontinuous wave system operating at few kHz repetition rate showed that it has a performance comparable to that of commercial ozone measuring instruments [4, 7].

5. A three-wavelength photoacoustic system was developed, based on a single laser source with nonlinear wavelength conversion [3]. This system was able to measure wavelength dependent optical absorption of aerosols. It was shown, that the presence of a strongly scattering aerosol fraction does not influence significantly the PA absorption measurement [5]. Field test showed that the multiwavelength PA system calibrated at laboratory was able to measure optical absorption of aerosols in the air under field conditions [11].

Publications and lectures related to the thesis

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