

DEVELOPMENT OF PHOTOACOUSTIC MEASUREMENT  
SYSTEMS AND THE DEMONSTRATION OF THEIR  
APPLICABILITY

Ph.D. THESIS

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## 1. Introduction

Due to the increasing technical development and the accompanying environmental pollution, recently, the need for gas detection methods and instruments is increasing. These requirements can only partly be satisfied, e.g. the requirements for instruments suitable for environmental field measurements are far higher than the performance of currently available measurement methods. Consequently, there is a possibility for the practical application of those measurement techniques that were previously used only in the laboratory (e.g. photoacoustic spectroscopy). The development of the photoacoustic method has been started in more directions: applications of new light sources, search for new application areas and development of automatic measuring systems.

My thesis is focused on the development of diode laser based photoacoustic systems for determining the concentration of vapor and gases. The Department of Optics and Quantum Electronics at the University of Szeged has more than ten years of experience in the development of lasers and their applications in material testing, biology and chemistry. Since the beginning emphasis has been put on the development of practically applicable systems, that are compact, automatic and operable under harsh industrial conditions.

## 2. Objectives

The aim of the presented work is the accomplishment of researches necessary for the development of diode laser based photoacoustic system for gas/vapor concentration measurement and the examination of the practical adaptability of

the developed systems. I present the results of experiments necessary for the development of two novel instruments and the further development of a third instrument. These instruments might solve important problems from environmental and industrial point of view.

My aim is the development of a new pressure dependant modulation procedure for a water vapor concentration measuring instrument, which improves the sensitivity of system in the typical pressure range of atmospheric research (200-1000 mbar), while maintaining the typical fast response and automatic function of the system, with previous modulation methods.

My next aim is the development of a photoacoustic equipment for continuous monitoring the water content of glycols used in the dehydration process of natural gas.

The third main aim is the development of a diode laser based photoacoustic ammonia monitoring system at ppb level for environmental application, which is suitable for the continuous measurement of air ammonia concentration.

### 3. Measurement methods

The photoacoustic effect is based on the conversion of light energy into sound energy by gas, liquid and solid. The basic theory of the photoacoustic effect in gases using infrared radiation is straightforward. When a gas absorbs the periodically modulated light, this will cause some of the molecules of the gas to be excited to a higher energy state. These molecules will subsequently relax back to the initial vibration state through a combination of radiative and non-radiative processes. For vibration excitation, the primary relaxation process is non-radiate vibration to translation energy transfer. This results in increased heat energy of

the gas molecules and therefore a temperature and pressure increase in the gas. If the irradiating light is modulated, the temperature and pressure is modulated as well. The modulated pressure will result in an acoustic wave, which can be detected with a sound measuring device, such as a microphone. The amplitude of this sound is proportional to the concentration of the light absorbing a component.

The photoacoustic system consists of four main parts: the *light-source* with the wavelength coinciding with the absorption line of the measurable component, a modulated outlet beam crosses over the *photoacoustic cell*, which contains the sample, in which it causes a periodic pressure change. The *detection unit* (lock-in, phase sensitive amplifier) evaluates the microphone signal, after a signal amplification done by a *microphone amplifier*.

#### 4. New scientific results

I have introduced a novel pressure dependant modulation procedure, which improves the sensitivity of a photoacoustic water vapor measuring system with approximately 20 % in the typical pressure range of the atmospheric research (200-1000 mbar), while maintaining the inherent fast response of the system. The measured minimum detectable water vapor concentration was found to be 300 ppb at 200 mbar pressure, and 188 ppb at 1000 mbar pressure, which is equal to the values demanded in the atmospheric researches. The simulated atmospheric test measurements proved that the developed modulation method has potential to be applied in typical tropospheric/lower stratospheric water vapor measurements [1, 6, 8].

I showed that the pressure dependence of sensitivity of the photoacoustic system is primarily determined by the pressure dependence of the microphone's sensitivity [1, 8].

I have designed and built a diffusion sampling unit, which I combined with gas phase photoacoustic system; this combined system is suitable for the measurement of water content of glycol [2, 4, 9].

I calibrated the photoacoustic water content measuring system onto low and high water contents in different glycol samples (mono-, di-, and tri-ethylene glycol). I found that the minimum detectable water concentration is dependent on the kind of the glycol, however it is independent of which phase of the dehydration process the glycol comes [2, 4, 9].

I developed an ammonia concentration measuring system with a detection limit of about 50 ppb. I proved with field measurements, that the instrument, calibrated in the laboratory, is suitable for measurement under field conditions [3, 7].

I have developed a dual wavelength measurement method, which proved to efficiently suppress cross-sensitivity to other atmospheric components (water vapor and carbon dioxide) [3, 7].

### ***Publication and lectutes related to this thesis***

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