

The main topic of the thesis is the detection of formaldehyde and ethane in trace amounts with a particular focus on the study of human lung exhaled air. The issue of biomarkers and the relationship of specific gases to their corresponding diseases is discussed. Conventional measurement techniques, primarily gas chromatography, are described.

Since the detection method used in the dissertation is laser absorption spectroscopy, it is discussed in detail. The very low concentrations of biomarkers in exhaled air (on the order of parts per billion) impose the need for ultra-sensitive measurement methods. The paper describes the most popular of these, such as wavelength-modulated spectroscopy, multi-pass spectroscopy, cavity ring-down spectroscopy and photoacoustic spectroscopy - including its variant using a quartz tuning fork.

The issue of absorption spectra of molecules is discussed, with particular emphasis on rotational-vibrational spectra in the infrared. The structure of formaldehyde and ethane molecules is presented, together with the characteristic absorption bands of the chemical groups comprising them. The literature discussing the oscillations of these molecules is also reviewed. Due to the fact of detecting biomarkers in the exhaled air from the lungs, an analysis of the spectra of other chemical compounds present in the breath in high concentrations (interferents) was carried out.

The thesis describes an experiment comparing the spectra of ethane and formaldehyde with data in the Hitran database. After positive verification, they were used to simulate the absorption of laser light by biomarkers and interferents. In order to find the optimum absorption line for direct breath testing, a computer program was written to analyse the spectrum at atmospheric and reduced pressure (that allowed separation of the absorption lines of biomarkers and interferents). The optimum wavelengths for detection of formaldehyde and ethane were determined - 3595.83 nm and 3336.80 nm, respectively. Simulation showed that it was necessary to reduce the pressure of the test gas - depending on the biomarker - to 0.01 atm (formaldehyde) and 0.1 atm (ethane).

From the previously described spectroscopy methods with increased sensitivity, multi-pass spectroscopy together with laser wavelength modulation was chosen - for reasons of stability. It was calculated that the multi-pass cell used must allow the optical path of the laser in the gas to be increased to a minimum of ten meters. As part of this dissertation, it was decided to construct a cell of its own, so general principles for their design are presented. A computer program to simulate Herriot cells in the Python language and made freely available under the GNU GPL is described. Using it, a multi-pass cell with an optical path of approximately 19 m was designed. It was prototyped in an open system (without the possibility to depressurize the test gas), which was used to verify the computer simulation with the real system. The developed cell proved to be very stable - for more than a year of use and multiple pressure changes inside it, it did not once require re-tuning.

A typical problem when working with multi-pass cells is the appearance of interference from so-called optical noise. They arise as a result of laser light interference inside the cell and lead to undesired modulation of the transmission spectrum of the optical system. The thesis presents a detailed analysis of a method for suppressing this unfavorable phenomenon by means of an additional (strictly selected for the multi-pass cell) modulation of the laser wavelength combined with signal averaging. The described method is not sensitive to the phase change of the interference (resulting, among other things, from the thermal expansion of the optical elements).

The dissertation describes in detail a system for the optical detection of trace amounts of formaldehyde in air. Detection of this gas, due to its specific properties, is problematic using conventional chromatographic methods. A literature review was conducted for the study of this compound in air using optical methods, in particular comparing the wavelengths used with the optimum wavelength found using computer simulation. These differed due to the inclusion of

interferents naturally occurring in human breath. Measurements of the power and wavelength of the laser used as a function of its current were presented - these showed the non-linearity of the light source. A vacuum system for the preparation of gas samples with different formaldehyde concentrations is described. Experimental results indicating the problem of formaldehyde deposition on the walls of the measuring device were presented. Measurements showed a sensitivity of about $1,8 \cdot 10^9$ formaldehyde molecules per cubic centimeter of air at a pressure of 0.01atm. This corresponds to a concentration of this gas of about 6.6 ppb.

The thesis also describes a system for the detection of ethane - the use of optical methods in the detection of this gas allows precise measurement in tens of seconds, which is not possible with gas chromatography. As in the case of formaldehyde, a literature review was performed on the detection of this biomarker. Due to the use of a lock-in meter and the nonlinearity of the laser, a measurement method using the fourth harmonic of the modulation frequency was developed and presented. An experiment was performed to test the sensitivity and linearity of the device. A measurement limit of 1 ppb was obtained (at 0.1 atm.). The linearity is good over three orders of magnitude (up to 1 ppm - higher concentrations were not measured). An Allan deviation plot was also drawn up to determine the precision of the measurement. In this way, it was determined that the optimum averaging time for ethane measurements is 20 s and a standard deviation of approximately 80 ppt is obtained.

In addition, the thesis describes the possibility of detecting four different gases present in breath with a single laser. Experiments were conducted to measure the concentration of ethane (3336.80 nm), methane (3334.37 nm), formaldehyde (3334.97 nm) and water vapour (3334.27 nm). Knowledge of the content of these substances in exhaled air can carry additional diagnostic information, and their measurement does not require another breath sample or additional optical elements.

An appendix to the dissertation describes prototypes of formaldehyde and ethane sensors for medical purposes. These devices allowed clinical trials to be carried out by directly measuring biomarkers in lung exhaled air by patients of the University Clinical Hospital in Warsaw. Automation of the measurement process and appropriate software allowed the devices to be operated independently by medical staff. Detection sensitivity was increased by building a new multi-pass cell with a longer optical path of approximately 40 meters.