

Laser Spectroscopy for Trace Matter Detection in Air

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Abstract: The article describes implementation of absorption spectroscopy methods for construction of trace compounds sensors in air. Multipass spectroscopy with laser wavelength modulation as well as cavity ring down spectroscopy was applied. High detection limits and good selectivity sensors of nitrogen oxide, dioxide, carbonyl sulphide, ethane, ammonia, methane, carbon oxide, acetone and water vapour were elaborated. The sensors were used in experiments about security and environmental monitoring, human breath analysis as well as for the geophysical research.

1 INTRODUCTION

Highly sensitive and quick response measurements of trace compounds in gases are of large importance for various fields, from the industrial ones, to agriculture, environmental monitoring, medical applications and different scientific research. There is a variety of gas sensing techniques that are useful for this purpose. Nevertheless, there is still a need to look for a low-cost, sensitive and an accurate technique which leads to use of small, affordable, easy-to-use equipment. Application of optical methods e.g. laser absorption spectroscopy provides opportunity for fast, selective and sensitive detection of certain gaseous compounds. Progress in optoelectronic technologies opens new capabilities of trace matter detection in gases. In this paper we present our achievements about application of laser absorption spectroscopy for trace gases detection in air for medical, environmental and atmospheric physics applications.

2 EXPERIMENTAL

Sensitive detection of trace compounds in gaseous matter requires ultrasensitive approaches. One of them is the multipass spectroscopy (MUPASS) applied together with wavelength modulation spectroscopy (WMS). The scheme of our experimental setup exploiting this method is presented in Figure 1. Its operation idea was

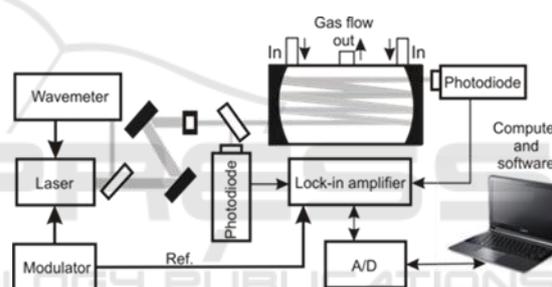


Figure 1: MUPASS with WMS setup.

described in details in the publications (Wojtas, 2012, Stacewicz, 2012).

In this approach we use semiconductor laser which is precisely tuned to characteristic strong absorption line of the investigated compound. The beam is sent to multipass cell filed with the air sample. Due to multiple reflection the effective light path in the sample reaches tens of meters. Laser wavelength is also swiped across the absorption line by a modulator. That causes AM modulation of the output beam. AM signal from the photodiode is demodulated with lock-in amplifier driven by the reference signal from the modulator.

Cavity ring down spectroscopy system (CRDS - Figure 2) exploits the experimental cell in the form of optical resonator (cavity) built with mirrors of very high reflectivity (O'Keefe, 1988, Berden, 2009). The measurement of absorption coefficient of the sample contained inside consists in the resonator testing using pulsed of AM-modulated laser radiation.

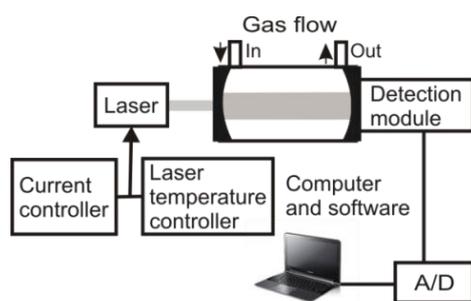


Figure 2: Simplified CRDS setup.

Photon lifetime in the cavity (τ_A) or the phase shift (φ_{nA}) between the relevant harmonics of input and output signals is determined in this way (Romanini, 1997, Ye, 1997). Such phase shift φ_{nA} occurs due to energy storage in the resonator. For n -th harmonic it fulfils the relation:

$$tg(\varphi_{nA}) = 2\pi f \tau_A \quad (1)$$

where f denotes the modulation frequency. Then the cavity parameters (τ_0 and φ_{n0}) are determined for the case when the resonator is filled with a reference gas (without the absorber). The absorber concentration is calculated using the formulas:

$$N = \frac{1}{\sigma} \left(\frac{1}{\tau_A} - \frac{1}{\tau_0} \right) = \frac{2\pi f}{\sigma} [ctg(\varphi_{nA}) - ctg(\varphi_{n0})] \quad (2)$$

where c denotes the light speed and σ is the absorption cross section.

In our system (Figure 2) the output signal from the cavity was registered by a detection module and analysed with A/D converter and PC. Special software allowed either the lifetimes determination (τ_A and τ_0) or the lock-in signal processing (φ_{nA} and φ_{n0} measurement). The absorption coefficients below 10^{-9} cm^{-1} were observed.

Such simple CRDS setup with blue- violet diode laser allows monitoring of nitrogen dioxide in atmosphere (Holc 2010). The detection limit below 1ppb was achieved. We used it for environmental investigation and for explosive material detection (Bielecki, 2012).

Detection of NO_2 does not require any special spectrum analysis due to broad absorption band of this molecule. Moreover, in atmosphere usually there is no any other compound that could interfere the NO_2 results in blue – violet range.

The situation is different in the case of infrared measurements. Especially the optical analysis of human breath in this range requires careful spectrum

investigation since more than 3000 compounds were already recognized in the air exhaled from the lungs. An excess of several compounds (called biomarkers) is related to certain diseases.

Breath analysis methods have been intensively developed recently. This activity is motivated by the great potential of the disease diagnosis at early state or therapy monitoring. Such medical investigation is simple, painless, no-stressful and non-invasive (Buszewski, 2013). It makes these methods useful for screening. Application of the optical methods provides opportunity for fast and sensitive detection of certain compounds in breath. Continuous progress in optoelectronics leads to construction of desktop systems.

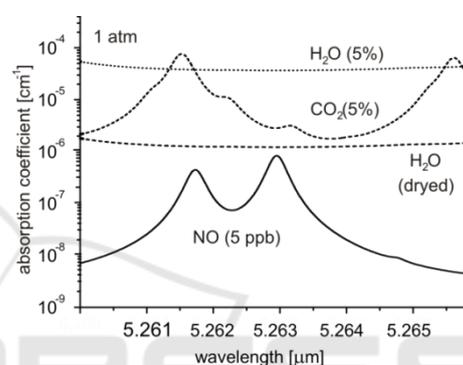


Figure 3: Absorption spectra of NO and its main interferences in breath at normal pressure.

The large number of compounds in breath causes that their absorption spectra might overlap a fingerprint of a certain biomarker and disturbs the measurement. Therefore the art of wavelength and circumstances selection for the optical detection consists in interference minimization. In Figure 3 an example for nitrogen oxide is presented (Rothman *et al* 2013). The spectra of main air constituents (N_2 and O_2) usually do not interfere, but the carbon oxide absorption lines are screened by CO_2 and H_2O (up to ~5% both in a breath), which are characterized by broad absorption bands. The situation cannot be improved by drying of the sample with special absorbers reducing the humidity. However the diminishing of the sample pressure to about 0.1 atm (Figure 4) is an approach that can efficiently reduce such disturbance. Due to that the pressure broadening is reduced about 10 times, but the absorption coefficient at the line peak is preserved. Therefore the backgrounds of H_2O and CO_2 are lowered about two orders of magnitude. Additional dehumidification of the sample leads to further reduction of H_2O interference.

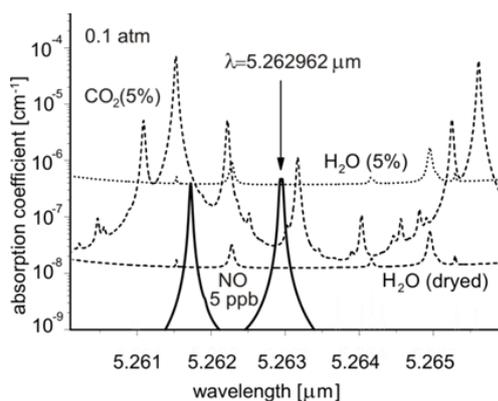


Figure 4: Absorption spectra of NO and main interferents at pressure of 0.1 atm.

In other cases the interferents, which might reach relatively high concentrations in breath, should also be taken into account. Carbon oxide, methane, ammonia and formaldehyde are worth to mention.

Sensitive and selective measurement of nitrogen oxide concentration requires using a single mode laser tuned to the peak of selected absorption line (5.262962 μm). In order to achieve precision better than 3% the wavelength stability should be about 10^{-6} μm . In our experiments single-mode quantum cascade laser developed by Alpes Lasers SA or the diode lasers from Toptica was used.

In such circumstances, NO concentration of 5 ppb might be detected. The integration time was about 1 min. Subsequent reduction of H₂O concentration (usually by a factor of 30) using Nafion membrane dehumidifier (Perma Pure Product, <http://www.permapure.com>) provides the opportunity to measure nitrogen oxide concentration with precision of 0.2 ppb, i.e. to monitor this compound in breath of healthy man.

3 RESULTS

Using the methods described above the sensors of several biomarkers were elaborated. The compounds, which were in scope of our interest, are the biomarkers of various important diseases. Application of special conditions, i.e. the dehumidification and the pressure reduction to 0.1 atm, was necessary only for NO (5.262962 μm) and C₂H₆ (3.3481590 μm). The detection of other compounds i.e. NO₂ (0.41 μm), OCS (4.8777716 μm), NH₃ (1.5270409 μm), CH₄ (2.2536598 μm), CO (2.3337197 μm) and acetone (0,266 μm) was performed at normal pressures. For the biomarkers characterized by the high morbid level (i.e. relatively

high absorption coefficient – ammonia, methane and carbon oxide) the use of MUPASS/WMS techniques was sufficient. Other compounds were detected with CRDS approach.

For majority of the cases the detection limit of the sensors was much better than the morbid level. That allows looking with optimism for future opportunity of the optical breath analysis application in medicine. Continuous progress in optoelectronics would lead to construction of cheap, easy to maintain desktop systems useful for screening.

Only for acetone the detection was not successful in spite of the application of the most sensitive approach (CRDS). Poor reflection coefficient of the mirrors that are available at 0.266 μm is the main problem here.

4 BREATH ANALYSER

Basing on the achievements about trace gas detection a breath analyser was constructed. Its scheme is presented in Figure 5. The analyser consists of sampling unit and gas sample preparation unit, the detection unit and data analysers.

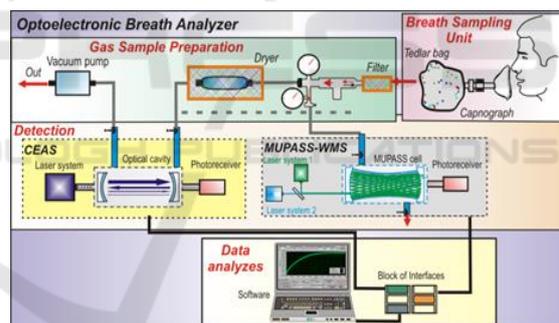


Figure 5: Scheme of the gas analyser.

Proper breath analysis requires that the exhaled air sample is prepared with the air following from the alveoli. The remaining air originating from upper respiratory tract does not undergo the gas exchange and can be a source of interferences during the biomarker testing. The separation of a gas sample for the biomarker investigation is possible by a monitoring of carbon dioxide contains in the exhaled air, since the air from lower respiratory ways is characterized by high CO₂ concentration.

The sampling unit consists of face mask which allows patient to breath with artificial air from a container (Szabra, 2017). The system of the carbon dioxide recording (capnograph) determines the proper breath phase and selects the air sample using

microprocessor controlled valves. The sample is directed either to optical detection system (when the *on-line* biomarker detection takes place) or to tedlar bags. In this case the sample is stored in the bag and then transported to the sample preparation and the optical detection unit (*off-line*).

The air sample (either from the face mask or from the tedlar bag) is directed to the sample preparation unit. Here it might be dehumidified with Nafion membranes and prepared under reduced pressure (if necessary) before sending to the optical detection unit. Finally the result of measurement is elaborated by data analyzer.

Proper operating of the breath analyzer was checked during the medical investigation (Szabra, 2017). For example the patients with chronic obstructive airway disease were examined. The samples of their breath were collected in *off-line* way about 2 hours before the optical treating. A huge exceed of NO concentration above the morbid level was stated in each case.

5 H₂O SENSORS

Optical detection is also suitable for sensitive humidity monitoring. Such measurements are widely used in various fields, from the technological ones to geophysical research. Water vapour is the most important greenhouse gas in atmosphere that absorbs the energy irradiated from the Earth surface. It is involved in climate feedback loop that includes complicated interactions between water vapour, clouds, atmospheric circulations, convection and radiation.

Water is a substance poorly mixed in the atmosphere. Quantity of H₂O molecules exceeds the value of about 10^{17} cm⁻³ at low altitudes, but it decreases below 10^{12} cm⁻³ at the altitude of 40 km (Figure 6). However local H₂O concentration in air might change even by the orders of magnitude in neighbouring regions on scales of hundred meters or less, e.g. due to turbulent mixing at tropopause, at the cloud edges or between the air parcels of different history. Therefore in-situ (airborne) measurements of absolute number of H₂O molecules per unit air volume are of great significance in atmospheric physics for studies of climate variations and trends, as well as for theoretical models testing.

In our optical hygrometer a single mode 20 mW cw diode laser (Toptica, DL 100) tunable within 1.390 – 1.395 μm range was used as the light source. CRDS approach was applied for H₂O absorption coefficient determination. Open path optical

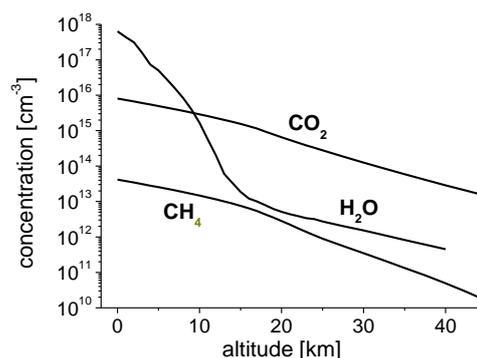


Figure 6: H₂O, CO₂ and CH₄ concentration in atmosphere at various altitudes.

resonator (Figure 7) was used in order to eliminate a disturbance of the results by water molecules adsorbed or desorbed from the resonator walls. That solution is especially important for the hygrometer designated for airborne investigation, working at the circumstances strongly changing with altitude. Numerical studies of history of a molecule starting from the upper or the bottom resonator wall and tending to the laser beam region was performed. It shows that for both laminar and turbulent gas flow the probability that the desorbed molecule reaches the laser beam region is negligible.

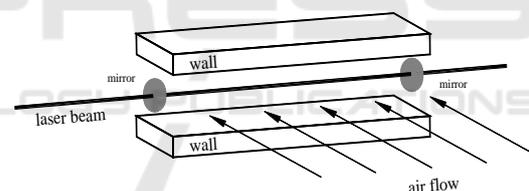


Figure 7: Scheme of open space optical cavity. Walls were 6 cm wide and 3 cm distant; air flow was perpendicular to the laser beam.

Spectrum analysis presented in Figure 8 shows that 1.3925335 μm H₂O line is the most suitable for this purpose (Rothman, 2012). Value of the cross section ($\sim 4.6 \cdot 10^{-20}$ cm⁻³) dominates about 3 orders of magnitude over that one of methane and more than 8 orders of magnitude over that one of carbon dioxide. That ensures, the absorption measurement of water vapour is not interfered by CO₂ and CH₄.

Shape of H₂O absorption line depends on air pressure, temperature and humidity. These parameters must be measured simultaneously with the water vapour absorption coefficient and – (according to eq. 2) used for the cross section correction. That procedure is especially important for airborne application. The pressure dependences are strongest (Figure 9), while the temperature

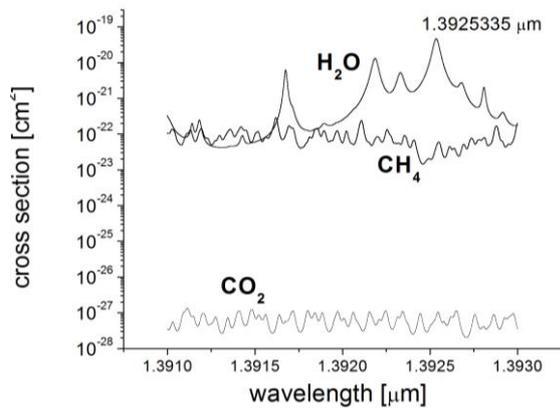


Figure 8. Absorption cross section of H₂O, CO₂ and CH₄ at normal conditions.

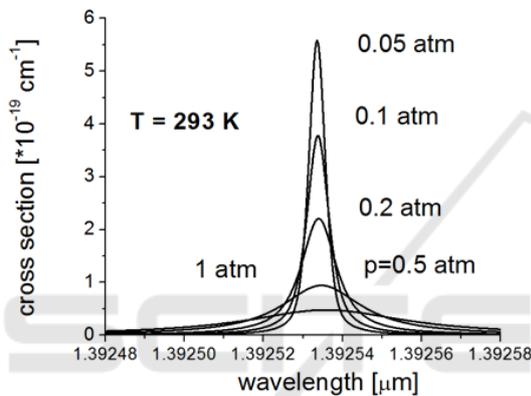


Figure 9: Shapes of 1.3925355 μm line at various air pressure.

influence is softer within the values occurring in atmosphere. The influence of the humidity (called self-broadening) becomes important at water vapour concentration higher than $5 \cdot 10^{16} \text{ cm}^{-3}$.

Our optical hygrometer was tested in a climatic chamber under controlled air temperature, pressure and humidity. Figure 10 presents result of registration of 1.3925335 μm water vapour line at 0.001 mbar and water concentration $(8.6 \pm 1.4) \cdot 10^{11} \text{ cm}^{-3}$. Continuous line corresponds to theoretical shape of Doppler broadened absorption line that should occur in such circumstances.

Large spread of the experimental points probably occurs due to insufficient stability of wavelength control system and due to pure signal to noise level at such low H₂O concentration, so the line profile was reproduced very approximately. Nevertheless one can assume that the detection limit of this optical hygrometer (defined as three times the standard deviation) was about $1.1 \cdot 10^{12} \text{ cm}^{-3}$, which corresponds to mean water vapour concentration at the altitudes above 30 km (Figure 6).

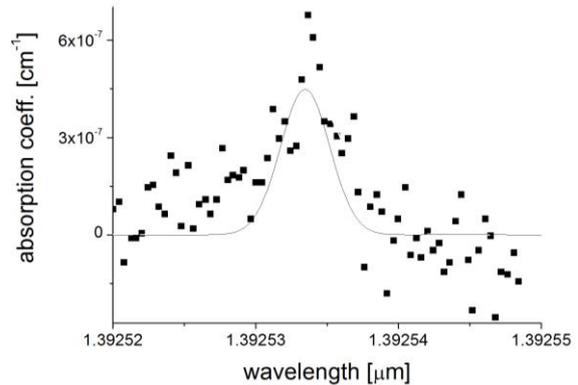


Figure 10: 1.3925335 μm line registered at 0.01 mbar and H₂O concentration of $8.6 \cdot 10^{11} \text{ cm}^{-3}$.

Elaboration of the optical hygrometer working at 6 μm wavelength is in progress. As far as the absorption cross section in this spectral range is about 20 times larger than near 1.4 μm , a much better detection limit can be expected.

Another optical hygrometer based on simple absorption measurement on 30 cm path was also built. It was characterized by short reaction time ($< 10^{-2} \text{ s}$). This construction is designated for monitoring of strong water vapour gradients at low altitudes.

6 CONCLUSION

Laser absorption spectroscopy of high resolution is a sensitive tool for trace gas detection. Due to application of modern optoelectronic solutions building of new apparatus is possible. These devices might be relatively cheap, small size and weight as well as low energy consuming. That provides opportunity to introduce cheap gas sensors on market together with novel methods which are useful for industry, non-invasive medicine diagnosis (screening), as well as for environmental and natural sciences research.

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