Remote intelligent concentration measurement of gas dissolved in water

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Abstract. This thesis describes principle of remote gas detection via intelligent fiber optic sensing system. Introduction of fibre optic based systems, operating on the principle of optical spectroscopy allow remote intelligent sensing and concentration measurement of gasses dissolved in water on a great depth. Laser modulation spectroscopy is a suitable technique which can be applied to reduce the cost of water monitoring devices and provide accurate concentration measurements in water.

1. Introduction
The detection and concentration measurement of dissolved gases in a water medium are essential in natural gas deposit searches on a seafloor, environmental monitoring and providing safety within industrial facilities. Current methods being used suffer from complexity and slow response times. Optical methods are very promising and offer very high accuracy and possibility of real time measurement [1]. Among many existing spectroscopic methods only a few can be applied for practical use, because a majority of them are being used only as laboratory methods. The most appropriate methods for dissolved gas sensing are laser modulation spectroscopy and Raman spectroscopy. Raman spectroscopy is a well used technique for water measurements which uses Raman scattering spectra for detection and concentration estimation of measured matter, but it requires utilization of expensive components, such are powerful laser sources and sensitive spectrometers for weak signal detection and spectra analysis [2,3]. Modulation laser spectroscopy involves modulation of single-mode laser radiation at a frequency much less than the width of the measured absorption line. This modulated radiation is directed through a sample of a matter to be investigated and its intensity is measured with a photodetector. The concentration of a studied matter can be estimated according to the amplitude level of a second harmonic. Nevertheless, this technique is used merely for atmospheric measurements and needs more exploration to be applied in different areas such as measurements in water. Utilization of laser spectroscopy method for dissolved gas sensing should be completed according to conditions in which gas is measured e.g. very high pressure and low temperature what can theoretically make some influence on absorption lines width and their position in spectrum. Implementation of this method for deep-water measurement requires few utterly important fundamental and practical tasks to be solved. Firstly, water has very high absorption and scattering in near infrared region. According to this, optimal interaction between laser radiation and studied substance should be provided to ensure that gas absorption on discrete lines is higher than continuous absorption of water. Secondly, spectroscopic measurements make sense - only when actual absorption lines frequencies of dissolved gasses are
exactly known. Absorption frequencies of gasses such as methane in normal conditions may differ for
gasses dissolved in water on a great depth. Also there is an issue relating to how the laser radiation
would be brought deep under water where spectroscopic measurements are performed, considering
high attenuation of NIR radiation in water.

The presented work accesses the technique that is applied to ascertain the remote estimate of low
concentrations of gas dissolved in water at great depth. The features relating to the modulation laser
spectroscopy for spectral analysis in water medium with high attenuation are shown. This work also
describes fiber optic intelligent sensing system which has been developed for the purpose of remote
measurements in water. The main parts of the detection system are single mode fiber optic line,
tunable laser diode, optical sensor and transmitting/receiving components. The utilization feasibility of
laser modulation method with fiber optic based sensing system for the purpose of water analysis has
been appraised.

2. Remote measurement

Remote gas sensing and concentration measurements are mainly based on utilization of laser lidars [4]
and “open path” sensing systems [5], which bring the average concentration level of gases along the
laser beam propagation path. Usage of these systems in water conditions is not possible due to high
attenuation level of water medium. As an alternative to lidars and “open path” sensing systems for
concentration measurements of dissolved gasses, fiber optic gas sensing systems can be introduced.
These fiber optic systems can transfer signals on very long distances by fiber optic line with
reasonably low loses caused by actual loses in fiber. Furthermore, laser signal source and detection
equipment can be located elsewhere and will not be exposed to harmful conditions in water
environment, resulting in high reliability of the overall system. Such setup has been developed by
Sean J. Hurt and Robert A. Lamontagne [3]. It is intend for oceanic detection of methane in different
states including solid hydrate presented on an ocean floor. The system used for feasibility testing
consisted Nd:Yag Laser operating at 532 nm with a power of 35 mW at a repetition rate of 15 Hz and
a pulse width 3-5 ns. Radiation was delivered to dual parallel fiber design probe by multimode 600μm
fiber. After interaction with a studied sample, Raman scattered radiation was collected to second
600μm fiber and directed through notch filter (532 nm) to miniature spectrometer with a resolution of
approximately 150 cm⁻¹. Concentration was estimated using a PC according to obtained spectra from
miniature spectrometer. Another example fiber optic gas sensing system for atmospheric measurements
of methane is presented in the paper published by J. P. Carvalho’s at al [6]. Modulation laser
spectroscopy method was applied for interrogation in photonic crystal fiber sensor head which
includes a number of segments of hollow core photonic crystal fibre. These segments have a honey-
look periodic structure which surrounds a hollow core. The diameter of hollow core is approximately
16 μm. Numbers of PCF segments are connected through butt-couplings and this deliver equivalent
interaction pass length of much bigger optical sensors. Fiber sensing head has periodic openings to
allow the gas sample filling the core of segments where 90% of laser radiation is propagating. Laser
module and registration equipment are connected to the sensor head by means of regular single-mode
optical fibre. This system also has a reference cell filled with methane and it is used to lock the laser
frequency on the maximum of an absorption line. Both systems listed above feature utilization of
optical fibers to provide remote operation.

We are proposing to use a regular telecommunication fiber for our measuring system. However,
there are some restrictions on spectral area of possible spectroscopic measurements, defined by
transmission windows of an optical fibre. In Figure 1 diagram absorption of single mode optical
telecommunication fibre is shown.

Conventional single-mode optical telecommunication fibre has the lowest absorption of 0.19-0.21
dB/km in the spectral region of 1450-1650 nm and also at 1330 nm.

Absorption lines for different gases are presented in table 1 below. All these gasses can be
measured via optical fibre based systems if appropriate laser sources are being used.
3. Water absorption
The most transparent are visible and ultraviolet parts of water absorption spectrum. However, this absorption represents clean distillate water. Every natural water has organic absorption, which can exceed molecular depending on a water type. NIR Region is pretty transparent for biological organics and would not influence the incoming signal level [7]. There is a lack of precise data for absorption coefficients in NIR region. Nevertheless, general behavior of water absorption is presented on figure 2. We have also measured attenuation coefficient at 1.6448 μm that corresponds to strong methane absorption line. The attenuation coefficient was 5.55 cm⁻¹. According to this data, optical path for laser beam in sensor that is located at the place of measurement should be no longer than 10-15 mm, taking into account semiconductor lasers with power of 5-10 mW at 1.65 μm for methane detection.
4. Frequency modulation method

It is not possible to use classical absorption spectroscopy, because the power of laser radiation cannot be controlled at the end of an optical fiber. Frequency modulation method could be used as an alternative to classic absorption spectroscopy. This method allows tuning on a maximum of absorption line of measured gas by modulating laser frequency [8]. It will also exclude an influence of optical fibre and water to the signal. This will be possible to “scan” absorption line and estimate gas concentration, considering that the laser line width is much narrower than absorption line of the gas.

Concentration level of dissolved gas can be defined by equation

\[ \chi_2 / \chi_0 = 0.343 \alpha_0 C_{gas} \] (1)

\( \chi_2 \) - Amplitude of the second harmonic of frequency modulated optical signal after interaction with absorption medium;
\( \chi_0 \) - Amplitude of the full optical signal at the end of an optical fibre;
\( \alpha_0 \) - Gas absorption coefficient;
\( C_{gas} \) - Gas concentration.

According to equation (1) above, total standard uncertainty can be calculated by

\[ U_{\varepsilon}(C_{gas}) = \left[ U_A^2 + \left( \frac{\partial C_{gas}}{\partial \chi_0} \right)^2 \cdot U^2(\chi_0) + \left( \frac{\partial C_{gas}}{\partial \chi_2} \right)^2 \cdot U^2(\chi_2) + \left( \frac{\partial C_{gas}}{\partial \alpha_0} \right)^2 \cdot U^2(\alpha_0) \right]^{1/2} \] (2)

\( U_A \) - Type A uncertainty.
5. Structure scheme of an fibreoptic intelligent sensing system
Fiber optic sensing system is based on lasers with wavelengths that correspond to absorption lines of measured gas. According to this, NIR DFB semiconductor lasers with wide temperature wavelength tuning are preferable. The system also features frequency and power stabilization of the laser source. Measurement process might be permanent, as all transmitting/receiving components are located above water level. Only two optical fibres and optical sensor are submerged in water. The structure scheme of the fibreoptic intelligent sensing system is shown below in figure 3.

The length of fiber optic line between laser source and photo detector could exceed 1 km.

The measuring system can be equipped with any wireless or wired connection to integrate into any applications within a network environment.

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**Figure 3.** Structure scheme of the fibreoptic intelligent sensing system

Presented fiber optic system is intend for remote gas concentration measurement in water and it provides automatic control of an absorption line frequency of the measured gas which can change under different pressure and temperature conditions.

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