

Application of Multiple Line Integrated Spectroscopy on CO Concentration Measurement

P. Komada¹, S. Cieszczyk¹

¹*Institute of Electronics and Information Technology, Lublin University of Technology,
Nadbystrzycka St. 38A, 20-618 Lublin, Poland
p.komada@pollub.pl*

Abstract—The paper presents possibility of application multiple of integrated spectroscopy for measuring CO concentration in a gas mixture. Sensors that are based on the method discussed can be applied in analyses of gas mixtures inside a power boiler or products of biomass gasification process. The principles of the method has been presented, however the main attention was paid to proper selection of the wavelength range and thus optoelectronic components. It would limit influence of disturbance factors and on the other hand, enable higher dynamic range of the CO analyser. Both simulation and laboratory tests that were presented in the paper would enable to build CO analyser that could operate in industrial conditions at acceptable measurement uncertainty.

Index Terms—Absorption, infrared spectra, spectroscopy, power plant.

I. INTRODUCTION

Optoelectronic sensors are commonly used in various everyday applications, especially in technology. For the sake of their response time, high selectivity, resistance to harsh weather conditions as well as long operating time, optoelectronic sensors tends to supersede conventional catalytic and electrochemical sensors [1]–[3]. One of significant field of application is power engineering, where they are applied both for controlling of fuel mixture composition and flue gas monitoring. Such sensors can be also applied for measurement of atmosphere composition inside a power boiler [3]–[7] so as e.g. to estimate the threat of low-oxygen corrosion [8].

The operation of the vast majority of optoelectronic sensors is based on absorption spectroscopy, thus it utilizes measurement of light transmission within a particular wavelength range. Nowadays, most of the interest has been focused on the sensors that operate within spectral ranges that are applied in optical fibre communication [3], [7]. It is commonly known that within the considered wavelength ranges, most of the measured substances reveal comparatively weak light absorption, yet their application seems to be promising taking their both attractive price and

quality into consideration. However, special measurement techniques have to be applied when weak absorption lines are utilized.

II. PRINCIPLES OF ABSORPTION SPECTROSCOPY

The dependence of a medium transmission on the concentration of the given substance is expressed by the Lambert-Beer law

$$\frac{I}{I_0} = e^{-\sum_i S_i g(\nu) p x_i L}, \quad (1)$$

where I_0 , I – intensity of the incident and the passing radiation, respectively; S_i – spectral line intensity for the i -th factor ($\text{cm}^{-2} \text{atm}^{-1}$), $g(\nu)$ – spectral line profile function, p – total pressure (atm), x_i – mole fraction of the i -th fraction, L – measurement path length (cm). For the given substance S_i and $g(\nu)$ depends both on pressure and temperature as well as the qualitative composition of the gas mixture measured. It can lead to measurement errors, especially in the case of non-homogeneous media.

Radiation absorption analysis for a given substance can be done for a single absorption line (dispersive methods) or for wide spectrum (non-dispersive methods) [2], [6]. Absorption measurement for the frequency corresponded to the maximum absorption line can be done by applying directly the Lambert-Beer law. Thus, a light source of very stable frequency ought to be applied for a slight deviation from the central frequency results in considerable errors. The more important problem could be due to limited sensitivity of narrowband methods, especially if a relatively weak absorption line is analysed [6]. In the case of wide-spectrum measurements, the most important problem is an influence of the other components for which the absorption spectra overlaps the spectrum range analysed.

An interesting method is the multiple line integrated spectroscopy (MLIS) [9], [10], which seems to be a compromise among classic approaches of absorption spectroscopy measurements.

III. INTEGRATED LINE SPECTROSCOPY

Measurements that are based on multiple line integrated

spectroscopy consist of two stages.

First, a calibration curve needs to be determined, which is essential in determination of the given substance concentration. For the integrated line spectroscopy the magnitude to be measured is the area under a few absorption lines.

Such an approach can lead to sensitivity increase comparing to the classic integration method (analysis of a single spectrum line) by increasing the ratio of the effective signal to noise. What is more, it maintains the sensitivity of the dispersive methods (for the proper wavelength range) as well as immunity to the other components of the mixture.

IV. GAS MIXTURE SPECTRA

A selection of the analysed wavelengths in spectroscopic measurements is depended on a few factors, such as absorption spectrum of the given gas, optoelectronic elements availability of the desired spectral characteristics as well as absorption spectra of each gas in the mixture. Measurement selectivity requires that within the wavelengths analysed, the other substances should have no absorption lines or of negligible amplitudes [3], [4], [11].

Taking into consideration measurements of a combustion process, an analysis of absorption spectra of the gases in a mixture depends mainly on chemical composition of the fuels [11]. Biomass co-combustion with coal leads to generation of many gaseous products, which are absent when only pure coal is burned. Another difference is generally higher contents of CO, CO₂ and water vapour for biomass co-combustion [5], [11].

The main CO absorption lines are present within the spectral range of 4,5 μm – 5,5 μm . As it was mentioned in the introduction, the sensor development is focused mainly on near-infrared range (around 1,5 μm), that is commonly used in optoelectronic telecommunication.

In the neighbourhood of $\lambda = 1/\nu = 1,5 \mu\text{m}$ CO has the second overtone of its absorption spectrum (known as the 3 ν band). The spectrum consists of two branches that are marked as P and R for the wavelength ranges corresponding to longer and shorter wavelength range, respectively. When greater measurement resolution is required (as it does in the case of multiple line integrated spectroscopy), single absorption lines (rotational lines) are considered. The R branch contains 22 rotational lines [12] marked as R0...R21, and lower numbers correspond to higher wavelengths. A fraction of R branch of carbon monoxide 3 ν spectrum – neighbourhood of the strongest line within the range discussed is presented in Fig. 1 for $L = 10 \text{ m}$ and $T = 273 \text{ K}$. For the spectra lines within the wavelength range considered are four order of magnitudes weaker than that of the main band, their utilisation requires longer optical paths as well as a special measurement technique.

When concentration of CO inside a power boiler is measured around $\lambda = 1,5 \mu\text{m}$, it is possible to consider only water vapour and carbon monoxide. Both gases have a significant percentage in the gas mixture. Moreover they have significant absorption lines within the wavelength range discussed. The resultant absorption spectrum for H₂O, CO₂ and CO mixture is presented in Fig. 1, if CO₂

concentration is ten times weaker than that of CO for the same measurement path.

As it can be observed in Fig. 1, absorption of the distorting gases seems to be comparatively low. For the case of a single absorption line and low CO concentrations it can lead to significant errors. The influence of CO₂ concentration on the CO concentration measurements by the differential method is presented in Fig. 2 for selected spectral lines. When CO concentration varies, the sensor output signal S does not have constant value for the given CO concentration. It proves the presence of absorption lines influence of the other (distorting) substances on the output signal of the sensor.

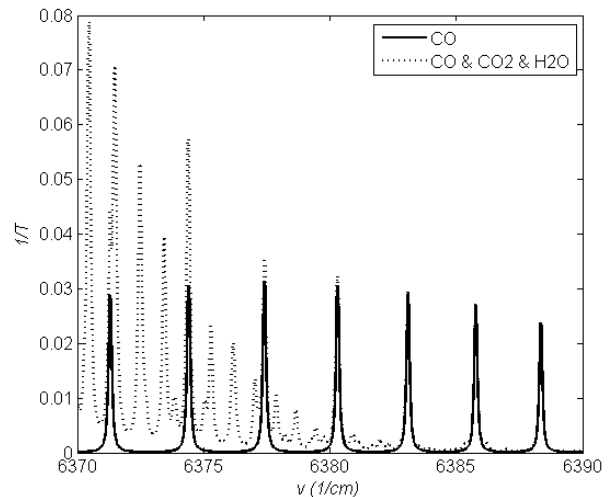


Fig. 1. Absorption spectra of CO, CO₂ and H₂O at $L = 10 \text{ m}$, $[\text{CO}] = 1 \%$, $[\text{CO}_2] = [\text{H}_2\text{O}] = 10 \%$, $T = 273 \text{ K}$.

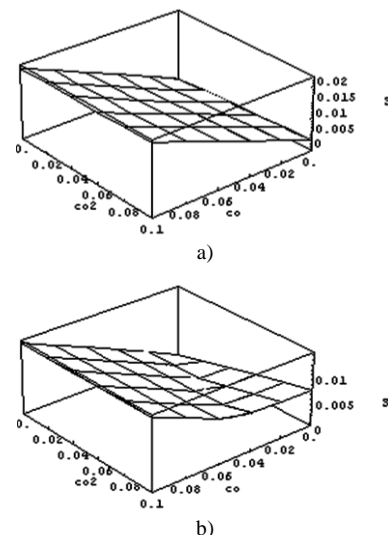


Fig. 2. Dependence of CO₂ concentration on CO concentration analyser signal S at: a) R7, b) R5.

V. SIMULATION RESEARCH

In order to check possibility of application of multiple line integrated spectroscopy for CO (concentration) measurements in a mixture that is a typical atmosphere of the inside of power boiler a number of simulations have been performed using the HITRAN database.

Numerical simulations have been made taking the following assumptions: temperature of the gas mixture:

$T = 273$ K, total pressure $p = 1$ atm, measurement path length $L = 10$ m, the gas mixture is consisted of CO of variable concentration within the range 0 % – 2 %, CO₂ and H₂O with 0 % concentration, when calibration curve had been estimated and 10 % while examining the influence of the mentioned gases as well as air. Composition of the gas mixture reflects conditions that can be found in power boilers.

It was arbitrary assumed the wavelength range of 6370–6390 cm⁻¹ (Fig. 1) was considered during the simulations, which includes seven absorption lines of CO, from R6 to R11. These lines are the strongest within 3 ν band that enables obtaining the output signal of relatively high amplitude.

For the CO absorption lines interfere with lines of the distorting gases, also weaker absorption lines have been taken into account (R5, R11) that are free from the interferences. The sensor calibration curve is a converse of the relationship to be estimated; hence it is the CO concentration dependence on sensor's signal level - W .

The calibration curve obtained is presented in Fig. 3, additionally with characteristics only for R7 line. It is worth noting that the difference between signals' dynamics for the both cases is significant and it points out an advantage of the multiple line analysis.

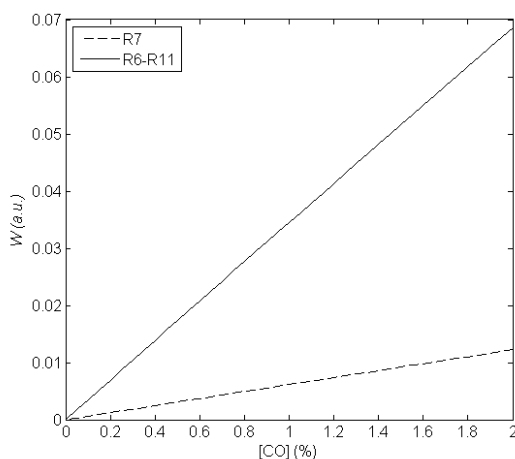


Fig. 3. Dependence output signal W on CO concentration for multiple line integrated spectroscopy method obtained as a result of numerical simulations (R6-R11), and after determining of absorbance of R7 line in 3 ν band of carbon monoxide (R7).

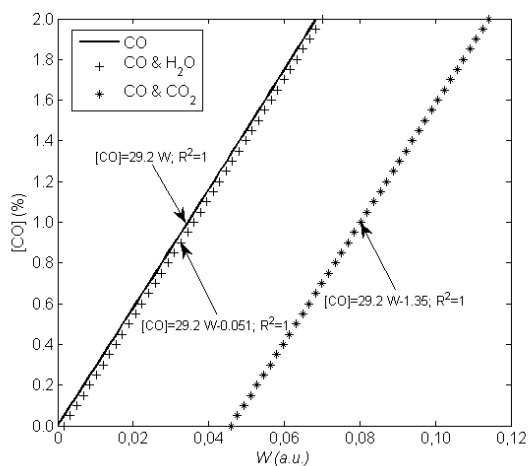


Fig. 4. Influence of water vapour presence and carbon monoxide on the calibration curve shown in Fig. 3.

Dependence of the output signal W on CO concentration is linear (within the considered wavelength range) and passes through the origin of the co-ordinate system. The slope of a straight line equals to 0.0343.

Influence of water vapour presence in the mixture as well as carbon monoxide is shown in Fig. 4. The calibration curve, that was obtained for a mixture containing 10 % of H₂O is shifted towards higher amplitudes of the signal W by $1.75 \cdot 10^{-3}$. It means that when water vapour is present in power boiler atmosphere with comparable concentration, the analyser would overestimate CO concentration by 0.051 % of content.

Similarly, it is in the case of carbon dioxide. It is worth noting that CO concentrations would be higher by 1.35 % of content. In the both cases, the influence of the distorting gases is evident; however performance of such a sensing device is acceptable in industrial measurements.

VI. LABORATORY RESEARCH

Satisfactory results of the simulations have impelled to laboratory tests. The tests have been done in the laboratory stand depicted in Fig. 5 that consisted of the following parts: absorption cell of 1 m length and of 1 dm³ volume, equipped with 8 mm CaF₂ windows; tunable laser by Sacher Lasertechnik; PIN G8370-1 photodiode by Hamamatsu; DAQ2000 - data acquisition board by IOTech.



Fig. 5. Laboratory stage for CO concentration measurements by multiple line integrated spectroscopy.

The FWHM of the light was 5 MHz (about 0.04 pm). The laser was tuned continuously within the range of 1500 nm – 1590 nm, with possibility of precise tuning of 0.7 nm by a voltage-driven, piezoelectric actuator. For this reason, the whole wavelength range of 6370 cm⁻¹ – 6390 cm⁻¹ was examined in a number of stages. The tuning unit of the laser was controlled with 0.5 Hz triangle wave.

The Hamamatsu photodiode has its maximum sensitivity that is equal to 0.95 A/W at 1550 nm. In the mentioned above wavelength range, the photodiode spectral response can be considered as constant. The photodiode output signal was amplified and then recorded at sampling rate of 1 kS/s and 16-bit resolution.

The absorption cell was filled with a mixture of atmospheric air and carbon monoxide. For the measurement path length was 1 m and CO concentration was as high as 20 % it made the product of concentrations and path length comparable to the previously simulated conditions. An example CO absorption spectrum, which was recorded during a series of experiments, is presented in Fig. 6.

On the ground of the results obtained, calibration curve has been determined with least squares method, according to $[CO] = 8.505 \cdot 10^{-3} W_s$ at $R^2 = 0.9688$ and shown in Fig. 7. It

was taken into account, that the curve must cross the origin of co-ordinate system because if there is no CO, absorption line height is equal to 0.

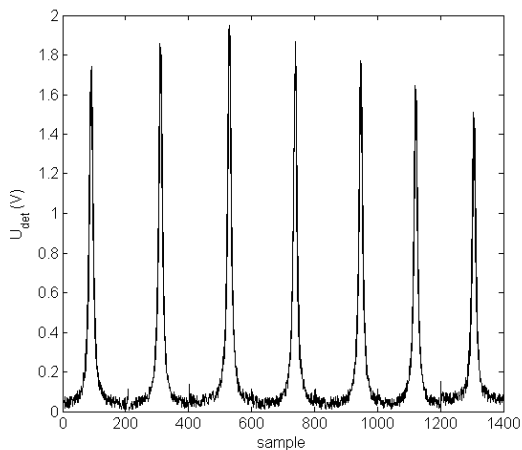


Fig. 6. An example CO spectrum recorded during experiments.

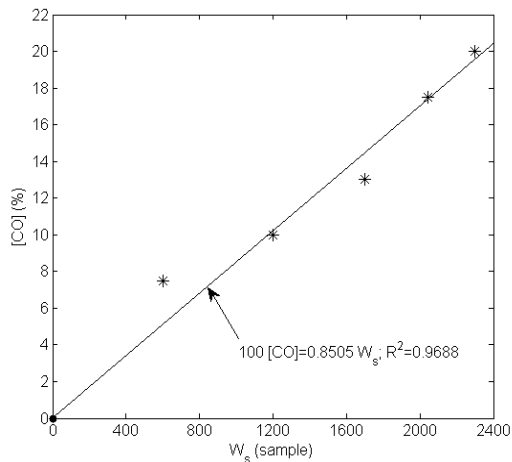


Fig. 7. The calibration curve obtained during the experiments.

The calibration curve was applied in CO content estimation in the gas mixture in the next test series, which were performed in the same conditions as the one described previously. Comparison results of the real CO concentrations in the gas mixture and CO concentrations calculated by multiple line integrated spectroscopy are presented in Table I.

TABLE I. COMPARISON OF REAL CO CONCENTRATIONS WITH SIMULATED RESULTS OBTAINED BY MLIS METHOD.

[CO]		δ (%)
real	MLIS	
4,0	4,2	5,00%
8,0	7,5	-6,25%
12,0	11,0	-8,33%
16,0	17,0	6,25%
20,0	21,5	7,50%
24,0	22,0	-8,33%

VII. CONCLUSIONS

Application of optoelectronic components designed for telecommunication purposes for use in measurement technology is more and more observed. The wavelength range of telecommunication lasers corresponds to CO absorption lines, thus the basic condition of their potential usefulness for building CO analyser is fulfilled. The main

limitations of the classic CO concentration measurement methods have been described (the presence of disturbances and limited analyser sensitivity) thus, application of the multiple line integrated spectroscopy has been proposed within the spectral range of $6370 \text{ cm}^{-1} - 6390 \text{ cm}^{-1}$.

The simulations and laboratory tests have enabled to evaluate the possibility of application the method presented for CO measurement in conditions that are typical for power boilers. Influence of both water vapour and carbon dioxide on measurement accuracy has been discussed as well.

The results obtained have led to a conclusion that the arbitrary chosen spectral range containing part of 3 v band allows CO concentration measurements at acceptable in industry accuracy level. Even the presence of distorting gases in the gas mixture does not cause significant accuracy deterioration.

Application of multiple line integrated spectroscopy enables making of CO concentration sensor, that could be used in industry, e.g. for gas analysis inside a combustion chamber or products of biomass gasification processes.

REFERENCES

- [1] O. V. Osadchuk, D. P. Dudnyk, R. V. Krynochkin, W. Wojcik, A. Iskakova, "Mathematical model of radiation interaction with gas", in *Proc. of SPIE*, 2013.
- [2] W. Wójcik, S. Cięższyk, P. Kisała, P. Komada, "Pomiary widm procesów spalania z wykorzystaniem spektrometru FTIR", *Elektronika*, no. 6, pp. 230–231, 2008.
- [3] L. Lathdavong, Jie Shao, P. Kluczynski, S. Lundqvist, O. Axner, "Methodology for detection of carbon monoxide in hot, humid media by telecommunication distributed feedback laser-based tunable diode laser absorption spectrometry", *Appl. Opt.*, no. 50, pp. 2531–2550, 2011. [Online]. Available: <http://dx.doi.org/10.1364/AO.50.002531>
- [4] V. Ebert, T. Fernholz, C. Giesemann, H. Pitz, H. Teichert, J. Wolfrum, H. Jaritz, "Simultaneous Diode-Laser-Based In-situ-Detection of Multiple Species and Temperature in a Gas-fired Power-Plant", in *Proc. of 28th Int. Symposium on Combustion*, University of Edinburgh, Edinburgh, Scotland, 2000.
- [5] W. Wójcik, K. Gromaszek, A. Kotyra, T. Ławicki, "Pulverized coal combustion boiler efficient control", *Przegląd Elektrotechniczny*, no. 11b, pp. 316–319, 2012.
- [6] W. Wójcik, P. Komada, V. Firago, I. Manak, "Pomiar stężenia CO z wykorzystaniem metod TDLAS w bliskiej podczerwieni", *Przegląd Elektrotechniczny*, no. 3, pp. 238–240, 2008.
- [7] R. K. Hanson, J. B. Jeffries, Zhou Xin, Liu Xiang, Li Hejie, D. Mattison, A. Klingbeil, "Smart Sensors for Advanced Combustion Systems", GCEP Technical Report, 2005. [Online]. Available: http://gcep.stanford.edu/pdfs/QeJ5maLQQRugiSYMf3ATDA/2.6.3.hanson_06.pdf
- [8] H. Kruczek, "Przydatność pomiaru warstwy przyściennej do oceny stopnia zagrożenia korozją wysokotemperaturową (niskotlenową)", *Energetyka*, no. 7, pp. 419–427, 2002.
- [9] A. Karpf, G. N. Rao, "Enhanced sensitivity for the detection of trace gases using multiple line integrated absorption spectroscopy", *Appl. Opt.*, vol. 48, no. 27, pp. 5061–5066, Sept. 2009. [Online]. Available: <http://dx.doi.org/10.1364/AO.48.005061>
- [10] G. N. Rao, A. Karpf, "Extremely sensitive detection of NO₂ employing off-axis integrated cavity output spectroscopy coupled with multiple-line integrated absorption spectroscopy", *Appl. Opt.* vol. 50, pp. 1915–1924, 2011. [Online]. Available: <http://dx.doi.org/10.1364/AO.50.001915>
- [11] W. Wójcik, P. Komada, S. Cięższyk, I. Manak, T. Golec, "Optoelectronic CO Concentration Analyser – Wavelength Selection", *Elektronika ir Elektrotechnika (Electronics and Electrical Engineering)*, no. 1, pp. 5–8, 2004.
- [12] S. L. Gilbert, W. C. Swann, "Carbon Monoxide Absorption References for 1560 nm to 1630 nm Wavelength Calibration SRM 2514 (¹²C¹⁶O) and SRM 2515 (¹³C¹⁶O)", *National Institute of Standards and Technology Special Publication*, pp. 260–146, 2002.